

Thermodynamics And Kinetics of Materials

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Lecture 5

Heat capacity relations in materials

In the previous lecture we have talked about introduced heat capacity and we have told that there are two types of heat capacity at constant volume and heat capacity at constant pressure. So C_v is heat capacity at constant volume, C_p is heat capacity at constant pressure, we have introduced the concept of enthalpy and then we told what is the, we ended here, what would be the C_p minus C_v or difference between heat capacity at constant pressure and heat capacity at constant volume for an ideal gas. So if we want to do that, so as we know if we recall C_p is $\frac{dH}{dT}$, H is enthalpy, $\frac{dH}{dT}$ at constant pressure and C_v is $\frac{dU}{dT}$ at constant volume. Now for ideal gas it becomes pretty easy because you have the equation of state, right, this is the equation of state. Now you know δW , this is reversible work obviously, is equal to minus $p dV$ and this is mechanical work and you also know from first law that dU equals δQ plus δW . Now since you know that you would also know δQ is the heat input is equal to dU plus $p dV$ because δW is minus $p dV$, it's a work done, all the system is positive and δW is minus $p dV$, this we already have found out.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \quad pV = nRT \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Equation of state

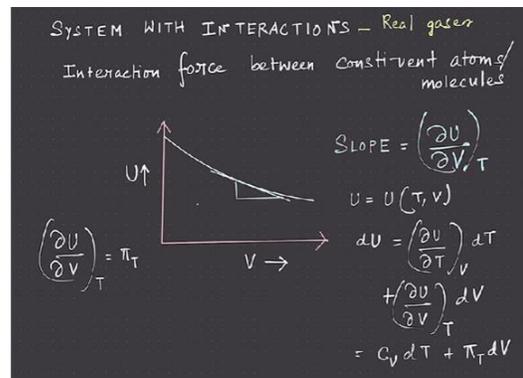
$$\delta W = -p dV \quad dU = \delta q + \delta W \quad d(pV) = p dV + V dp = d(nRT) = nR dT$$

$$\delta q_p = dH = C_p dT \quad \delta q = dU + p dV = C_v dT + p dV$$

$$C_p dT = C_v dT + nR dT$$

or, $C_p - C_v = nR$

Fix pressure and n
 $p dV = nR dT$



So δQ is dU plus $p dV$, dU is $C_v dT$ plus $p dV$, right, because as you see from this definition, from the definition here that dU is nothing but $C_v dT$ and you have $p dV$, right. Now you see δQ if I tell constant pressure that means p is constant, then I can write δQ is nothing but dH , basically it's like δQ is nothing but dH which is nothing but $C_p dT$. So dU is $C_v dT$ and δQ is $C_p dT$, so you can see now you have dT here, you have dT here and you have $C_p dT$ equals to $C_v dT$ plus $p dV$, now $p dV$ I have

changed to $nR dT$, you can easily see. So you have pV equals to nRT , you have $pV p dV$ plus $v dP$, from $p V$ you can write $p dV$ plus $v dP$ that is basically nothing but d of pV which is equals to $p dV$ plus $v dP$ which is equals to, now this dpV is $dnRT$, now if n is constant, if pressure is constant and n is also constant, that is the mole number is constant, then you have, you see R is anyway constant, it's universal gas constant and so you have $RT dn$, this $RT dn$ term will go to 0 because n is constant.

n - no. of moles of ideal gas

If the energy of an ideal gas is $\frac{3}{2}nRT$

What is its molar heat capacity $C_{v,m}$?

$C_v = C_{v,m} = \frac{C_v}{n}$

n is the total no. of moles of a substance

We denote $C_{v,m}$ as molar heat capacity at constant volume

$C_{p,m}$ as molar heat capacity at constant pressure

Specific heat - Heat capacity per unit mass

So $p dV$ plus $v dP$, now if pressure is constant then $v dP$ this term will go to 0, so you have $p dV$ which is equals to $nRT dT$, $p dV$ equals to $nRT dT$ and so you have substituted here, so you have got $C_p dT$, you have got $C_p dT$, $C_v dP$ and $nR dP$, now you can rearrange and you can write C_p minus C_v equals to nR , remember n is the number of moles of the ideal gas. However, when it comes to non-ideal gases or any other substance you will see that it becomes slightly more complex, in fact knowing the definition of entropy becomes very useful there or applying Maxwell relations that we will learn soon will be useful there, so I will come up to that but please remember that there is a difference in heat capacity at constant pressure and heat capacity at constant volume and for ideal gas that difference is equal to nR , right. Now remember we are talking about ideal gases but we know that the ideal gases have, there is no interaction force between the ideal gas molecules, right, that's the ideal gas atoms do not interact with each other, that is there is no force of interaction between them. However, for real gases you have interactions, right, between the constituent atoms that is there is a force of interaction between the constituent atoms or molecules. Now in such a case, in such a case U is also a function of V , see the problem is when you have no interactions then basically we can tell that in such a case the change in internal energy is only because of change in temperature, change in volume or basically pressure does not affect it but when it comes to, as you know, as you recall that U is an exact, du is an exact differential and du equals to, if I tell U is a function of T and V for example, if I tell U is a function of T and V we can write du equals to $\frac{\partial u}{\partial T} dT$ plus $\frac{\partial u}{\partial V} dV$, right, and this part, this one is your C_v , right, this is equal to your C_v , so basically you can write this is equal to $C_v dT$ and I will, and $\frac{\partial u}{\partial V} dV$ let me call it π , $\frac{\partial u}{\partial V} dV$ let us call it πT plus πT .

Specific heat c_p of water at room temperature and 1 atm. pressure is $\sim 4 \text{ J K}^{-1} \text{ g}^{-1}$.

Molar heat Capacity: $C_{p,m} = ?$

Water - H_2O

H atomic mass = 1 amu
O atomic mass = 16 amu

What is the relation between C_p and C_v ? $C_{p,m} - C_{v,m} = R$

Volumetric coefficient of thermal expansion α

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{K}^{-1}$$

Compressibility (β or K_T)

$$K_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{Isothermal compressibility}$$

Now as you can see that the change in energy is of, is really changing the pressure and that is the relation, that relation what you get is C_v at constant volume and if you use constant temperature you have something called $p_i T$ which is like pressure. Now in such a case this $p_i T$ basically becomes non-zero when you have interacting gases or real gases. In ideal gases $p_i T$ is zero because in ideal gases the interaction force between constant molecules or atoms is not there, so there is only kinetic energy, there is only temperature that is relevant and change in temperature and change in temperature causes change in internal energy of the ideal gas, however change in pressure, so change in volume does not, change in volume does not. Now if there is change in volume there is no change in internal energy. So if you now look at it, so if you look at the energy of an ideal gas which is $3/2 RT$ again so this is one thing that I have to tell, $3/2$ if I tell $3/2 RT$ this $3/2 RT$ what's the unit? This is something that R is joules per, R generally is given by joules per mole Kelvin.

So when I am talking about energy of an ideal gas we are already talking of energy per mole if I just write $3/2 RT$. So if I have to write the energy of an ideal gas containing N moles it will have to be $3/2 N RT$. So basically that's why there is something called molar heat capacity which is $C_{v,m}$ which is basically so here this has to be $3/2 N RT$ where N is the number of moles this is something that you have to understand this will consume of ideal gas. So molar heat capacity is per mole so it is C_v, M which is nothing but $C_v N$ where N is the number of moles of a substance. Now you see for a real gas as I told you U versus V also as a slope.

Specific heat c_p of water at room temperature and 1 atm. pressure is $\sim 4 \text{ J K}^{-1} \text{ g}^{-1}$.

Molar heat Capacity: $C_{p,m} = ?$

Water - H_2O

Atomic mass = 18 gm.

1 mole of H_2O - 18 gm of water

H atomic mass = 1 amu
O atomic mass = 16 amu

$4 \frac{\text{J}}{\text{K gm}} =$

$$C_p - C_v = \frac{\alpha^2 TV}{K_T}$$

For the general proof, we need to use Maxwell relations

Consider an ideal gas

$$PV = nRT$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{PV} = \frac{1}{T}$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{PV}$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = + \frac{nRT}{P^2 V} = \frac{1}{P}$$

$$\left(\frac{\partial V}{\partial P} \right)_T = -\frac{RT}{P^2}$$

$$\frac{\alpha^2 TV}{K_T} = \frac{V/T}{1/P} = \frac{PV}{T} = \frac{nR}{T}$$

Now what type of slope is it and why is this slope? So this is something that we have to understand. Now as you can see look at this equation let us look at this let us have a look at this equation first. You have du from your exact differential you got du equal to $C_v dt$ where C_v is the heat capacity constant volume plus $\pi T dU$ and πT and also you know dU equals to δQ minus $P dV$. If you compare you see πT is nothing but minus P which we can call as internal pressure πT is nothing but an internal pressure because minus PdV when we are doing what we were looking at? We were looking at something like this I have a piston here and then I had a volume and the volume was reducing so initially I have a volume here initial volume was like V and then it decreased by an amount of dV right there is a decrease in the amount by an amount dV and dV is negative and P is the external pressure so as a result you have to put a minus PdV because work done on the system is positive that is what is our convention according to our convention. Now πT if you see has a negative it is πT same as pressure but πT has a plus in front of it right it is negative it is basically πT has a sign opposite to that of the of P right so here P is the external pressure and πT is something like an internal pressure now you see what I told that since there is no interaction in ideal gas there is no interaction between molecules no interaction between molecules as a result πT equal to C however for real gases there is interaction between molecules now if that is so then you have this surface where U is plotted so you have U going up and temperature is increasing as you can see here and V is decreasing as you can see so as you can see now look at the slope now if it is U versus V if you look at the slope the slope increases as V decreases so as V is decreasing the slope is increasing or internal energy is increasing internal energy increases as the volume decreases that is for a real gas the interactions become more and more effective means the contribution from the interactions increases to the internal energy increases as you decrease the volume as you decrease the volume on the other hand as you increase temperature the increase temperature means with temperature you generally will see that there is a upward slope right so basically if you look at the slope that we are showing here you can see there is a downward slope now if I do U versus T it should be an upward slope right so if I look at say U versus T here this is your let me cross it with another color just to distinguish yeah so you can see if you have U this axis U along Y axis and T along X axis in general you will see the slope will be going

something like this right so you will go something like this so you will have a positive slope so from U so as V increases internal energy decreases so as you can see here.

$$C_{p,m} - C_{v,m} = \frac{nR}{n} = R$$

For solids and liquids,
 $C_p - C_v$ is small

$\frac{1 \text{ atm}}{10^5 \text{ Pa}} = 10^{-5} \text{ Pa}^{-1}$

$\kappa_T(\text{Al}) = 1.385 \times 10^{-11} \text{ Pa}^{-1}$
 $\alpha(\text{Al}) = 69.3 \times 10^{-6} \text{ K}^{-1}$

$T = 298 \text{ K}$ Room temperature
 $\frac{T}{V} = 10 \text{ cm}^3/\text{mol}$
 $= 10^{-5} \text{ m}^3/\text{mol}$

Heat capacity of solids
 Near room temperature, heat capacity of most solids is $3k_B$ per atom
 - Law of Dulong and Petit

Translational degrees of freedom - $\frac{3}{2} k_B T$ per atom
 Vibrational degrees of freedom - $\frac{3}{2} k_B T$ per atom

Energy per atom of solid = $\frac{3}{2} k_B T + \frac{3}{2} k_B T$
 From equipartition of energy = $3 k_B T$

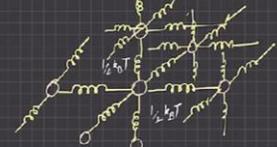
So what it can say here is that as from this curves or even from this surface you can tell that as T increases as T increases U increases there will be an increase in U right with the increase in temperature there will be an increase in U however as V increases U will go down and this is basically true for real gases or real systems with interactions right so width increase in temperature internal energy increases width increase in volume internal energy increases okay so another thing that you have to often you will see that we often refer to something called specific heat specific heat in general is defined as heat capacity per unit mass like heat capacity per gram per Kelvin or heat capacity per kg per Kelvin like that and molar heat capacity is per unit mole right it is $C_{v,m}$ for example is molar heat capacity at constant volume $C_{p,m}$ is molar heat capacity at constant pressure now as you know C_p minus C_v equals to nR where n is the number of moles so now molar heat capacity $C_{p,m}$ minus $C_{v,m}$ molar equals to R because R is joules so and it has a unit of joules per mole Kelvin we have things that you should understand so for example if I take this and if I tell heat capacity so if I tell specific heat of water at room temperature and one atmosphere pressure is 4 joules per kelvin per gram now if I tell you what will be its molar heat capacity what will you do you know you are talking of water, water molecule H_2O there are 2 H atoms there are 1 molecule of water there are 2 H atoms and 1 O atom and as you know H has an atomic mass of 1 atomic mass unit or you can convert it to grams then it becomes 1 gram and oxygen has 16 grams so basically the atomic mass of water in grams if I tell 18 grams now that means you have 18 grams as that of mass and you have gram here so you have a unit of 4 joules by kelvin gram now you are telling a gram and you want to convert it to mole so 1 mole of H_2O or water contains 18 is basically 18 grams of water so 1 gram is 1 by 18 so basically this will become 1 gram is basically 1 by 18 so 18 is 72 joules per kelvin right so basically because the molecular weight of water is 18 right it is so the molecular weight of water is 18 1 mole contains 18 grams of water and 18 grams equal to 1 mole therefore 1 gram equals to 1 by 18 moles and I am just instead of 1 gram I am putting 1 by 18 so 18 into 4 it becomes 18 into 4 which is 72 so 72 joules per kelvin per mole is the molar heat capacity of water right so

this is how from specific heat you can go to molar heat capacity now you know the relation between C_p and C_v when you have ideal gas that C_p molar minus C_v molar equals to R but what about all substances now see we will now define more measurable quantities.

So we already know about what are the measurable quantities T , P and then C_p and C_v you can obtain using calorimetry okay I will discuss maybe later some principle of calorimetry but that you have a standard sample based on the standard sample when you look at how much it is transferred and you can calculate C_p or C_v right you can use like bomb calorimetry and stuff now the point is C_p and C_v there is a difference R for ideal gas and but for in general what is the relation between C_p and C_v for say some any real gas or for solid or for liquid so in such cases we need to know some two more measurable quantities one measurable quantity which is of interest is volumetric coefficient of thermal expansion α right you often know about the linear coefficient of thermal expansion now what we are defining here is a thermal expansion coefficient that is volumetric so this is defined as how the volume of a material will change as temperature changes keeping pressure fixed so volume change as a function of temperature keeping pressure fixed and normalized with a volume itself volume in the body itself so it is $1/V \frac{\partial V}{\partial T}_P$ which is basically α right so $\frac{\partial V}{\partial T}_P$ so volume is like centimeter cube and this is like Kelvin but you have $1/V$ a normalization so it is like $1/\text{centimeter cube}$ so this becomes it has the unit of Kelvin inverse the unit is Kelvin inverse its temperature inverse basically so $1/V \frac{\partial V}{\partial T}_P$ now there is also something called compressibility or which is represent as β or κ_T so κ_T or β is basically changing volume with respect to changing pressure again normalized with the volume so this is called and remember temperature is kept constant here.

$1 \text{ atm.} = 101325 \text{ Pa}$
 $\alpha^2 TV = \frac{(69.3 \times 10^{-6})^2 \times 298 \times 10^{-5}}{1.885 \times 10^{-11}} \text{ J/mol-K}$
 $\approx 1 \text{ J/mol-K}$
 $C_p - C_v$ is small
 for solids and liquids
 $C_p \approx C_v$
 $H = U + PV$
 $H \sim U$
 for condensed systems - liquids & solids
 C as the heat capacity

Internal energy per mole of solid
 $U = 3k_B T N_A$
 N_A - Avogadro no.
 $C_{v,m} = \frac{\partial}{\partial T} (3k_B T N_A)$
 $= 3k_B N_A = 3R$ / mole
 EACH ATOM IS AN OSCILLATOR WITH SIX DEGREES OF FREEDOM



So it is called isothermal means it is a isothermal compressibility isothermal because temperature is kept constant compressibility and that is there is a negative sign here I will tell you why it becomes there should be a negative sign here because we are looking at compression right you are looking at compression and again as I told you that as you increase pressure volume decreases right so there is a obviously a negative sign that we

want to put in here so it becomes minus 1 by $V \frac{\partial V}{\partial p}_T$ now these are two more measurable quantities so we are basically finding out different measurable quantities that we can measure as like see thermodynamics in general deal with macroscopic quantities not molecular level quantities and in the macroscopic quantities that are measurable are more and more useful because there will be quantities such as energy for example which is not directly measured right but you can measure temperature you can measure pressure using a parameter temperature using a thermometer you can measure use calorimeters to measure heat capacities whether it is at constant pressure or at constant volume also you can measure the coefficient of thermal expansion and coefficient of compressibility now if you know how to measure all of these then you will see we will use Maxwell's relations later.

So I am not immediately going to give you the proof but what I am going to give you is a what I am going to do is I will state the relations $C_p - C_v = \alpha^2 T v \kappa_T$ or $\alpha^2 T v \beta$ now as you can see here α is your coefficient of thermal expansion κ_T is isothermal compressibility T is temperature v is volume volume is again measured think of an ideal gas again in your ideal gas you know $p v = nRT$ if you look at α in that case for this $p v = nRT$ equation state you will see α is nothing but $1/T$ it is inverse of the temperature for an ideal gas and κ_T is nothing but $1/p$ now if you look at that side the κ_T is nothing but minus 1 by $v \frac{\partial v}{\partial p}$ so you have $\alpha^2 T v$ so it is nRT by p^2 because v is there and $\frac{\partial v}{\partial p}$ is what you are looking at so you are writing v equals to nRT by p so there is a minus sign so minus and here there is a minus sign so it becomes plus right this is the plus and so then you get nothing but nRT is $p v$ $p v$ by p^2 is $1/p$ right so you get this value here and so you get if you substitute all of these here $\alpha^2 T v \kappa_T$ is nothing but PV/T because $1/T$ is nRT/PV is $1/T$ and there is a T and v/T goes out there is a v α^2 so there is a p^2 so v by T by $1/p$ which is $p v$ by T which is nothing but equal to right so you can see that this relationship definitely holds for ideal gas but this relationship holds good for any substance whether it is liquid water whether it is a solid ice whether it is for any material this relation holds and then you require to know the α you require to know the isothermal compressibility of the material and obviously for obvious reasons let me tell you what will be say for condensed phases what will be the isothermal compressibility how much is the isothermal compressibility if you know then you can see how much is the difference between C_p and C_v for solids and liquids and so on ok so that is the idea only thing I can tell you since β is small in general for solids and α is also actually small but let's think of aluminum for example if you see for aluminum it's aluminum solid you have ok it's $1/p$ so it's pascal inverse so for aluminum it is 1.

However, C_v decreases as temperature decreases and vanishes at $T=0\text{ K}$

Einstein Model Assumptions

- i) Solid - a lattice structure with N atoms

Each atom moves independently within the lattice in 3D - 3 degrees of freedom



- ii) No interactions with each other
- iii) All atoms vibrate at same frequency

Assumption ii is not correct

- Sound propagation through solid
- Heat propagates through solid

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 3 N k_B \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{(\exp(\theta_E/T) - 1)^2}$$

$$\theta_E = \frac{h\nu}{k_B}$$

h - Planck's constant
 $= 6.62607015 \times 10^{-34} \text{ J}\cdot\text{s}$

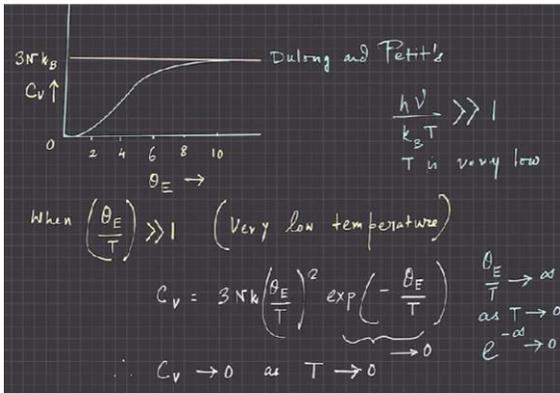
Remember $E = h\nu$ for a photon

385 into 10^{-1} Pascal inverse is your isothermal compressibility and α is 69.3 into 10^{-6} per Kelvin and let us take the temperature T equal to 298 Kelvin which is basically room temperature in fact it is Celsius and let's take the molar volume of aluminum let us assume at 298 Kelvin not assume means you can measure it you will find that it is approximately 10^{-5} meter cube per mole now in such a case if you add all of these so basically you get and one atmosphere as you know is 101325 Pascal's right 101325 Pascal's so if you evaluate this what you get is like 1 joule per mole Kelvin on the one hand you have that C_p minus C_v which is R which is like 8.314 joule per mole Kelvin on the other hand for solid aluminum C_p minus C_v is small right C_p minus C_v is small many a times we use this approximation of C_p is approximately here to C_v or we tell that the PV contribution is very small and we often use one type of heat capacity we use one type of heat capacity which is basically we substitute we neither use C_p nor C_v but we directly tell C_v for as the heat capacity means we tell that C_p minus C_v is small we can think of heat capacity at constant volume or at constant pressure many a times we take C_p heat capacity at constant pressure as the heat capacity of solids and so C is the heat capacity it can be either C_p or C_v because C_p minus C_v is small for solids and liquids so basically when you tell this what we tell is basically h equals to U plus PV and PV work for normal pressure conditions not very high pressure not like go exceed like 20 30 GP of pressure no then there will be a pressure induced a new type of equilibrium will be created where pressure dependence is coming but here in general for solids pv work is much smaller so h can be written as approximately the same as for this is again for condensed phases for condensed systems which include liquids and solids however as you can see that there is still some difference like C_p minus C_v is 1 joule per mole kelvin it's not really that small so right so but it is much much smaller if you compare two gases that's right now I give you some aside here this is something where this is a part of means in your soil state physics or thermal physics course or something like that you might have learned about it so this is about the heat capacity of solids right it was there it's too long and bit it's long I think you some of you might have read it so near room temperature which states that near room temperature room temperature is pretty high for physics in

for physics they deal with temperatures much much below room temperatures like they deal with temperatures which are close to like absolute zero so they look at temperatures which are like really really below the room temperature so as a result where quantum type quantum approximations become very very relevant this quantum nature becomes very very relevant you don't use maxwell goldsman statistics and stuff you will learn about it more in your solid state physics courses but here I'll give you an aside because from solid state physics or from the molecular interpretation of thermodynamics if you look at the molecular version of it or statistical mechanical version of it you will see that there you are considering atom atomic description and you are trying to basically find a bridge between this atomic description and the thermodynamic description macroscopic thermodynamic description now in such cases you will see that as you have previously we have defined energy internal energy right because we told the partition theorem and we told that all this gas molecules are colliding and there is this transition of energy and there is this $\frac{3}{2} k_B P$ right for each gas molecule they are basically they have in ideal gas in kinetic theory for example you have this liquid partition theorem $\frac{3}{2} k_B P$ on an average for a mono atomic ideal gas is going to be the energy contribution for a $\frac{3}{2} k_B P$ right now these are the translational degrees of freedom now you have solids for example the solids also vibrate right it's like solids you can think of like there are atoms that can occupy springs and the solid each atom is like an oscillator so it is oscillating there and it is vibrating and it can vibrate along x direction along y direction or z direction right so you can have like here also you can have 3 degrees of freedom right if the atom is vibrating oscillating this way or this way or this way now if you look at that then basically you have $\frac{3}{2} k_B P$ from the translational degrees of freedom and from the vibrational degrees you have $\frac{3}{2} k_B P$ so energy per atom of a solid we can write as $3 k_B P$ right now if you look at that energy is $3 k_B P$ per atom heat capacity is $\frac{du}{dt}$ right heat capacity is $\frac{du}{dt}$ so basically it is given as $3 k_B$ that is something that was observed by dulong and petit so for most solids means it includes whether it is copper whether it is lead whether it is aluminum it does not matter it is approximately going to be $3 k_B$ per atom that was what dulong and petit state right so basically internal energy as I told you per mole will now become $3 k_B T N_A$ where N_A is the number and $3 v$ for the molar heat capacity if I tell it is like $\frac{du}{dt}$ of $3 k_B T N_A$ which is basically $3 k_B N_A$ which is equal to $3 r$ right $3 r$ per mole right this molar heat capacity of any solid is like $3 r$ per mole $3 r$ right molar heat capacity is $3 r$ now as I told each atom is an oscillator with 6 degrees of freedom is something that we are telling that each atom is having a 6 degrees of freedom but there are two so if that is so on an average you know you can think of $\frac{1}{2} k_B T$ contribution for each degree of freedom so $\frac{1}{2} k_B T$ plus $\frac{1}{2} k_B T$ plus $\frac{1}{2} k_B T$ so total basically if you think of that with 6 degrees of freedom means translational as well vibrational and total it is $3 k_B$ right so that is how we are looking at it right these are atoms connected by states in all directions however it has been observed that the heat capacity continues to decrease as temperature decreases and heat capacity vanishes as T

equal to 0. So Einstein looked at it so basically Deulong and Petit's law can explain the high temperature heat capacity molar heat capacity of solids however as you go to lower temperatures it cannot explain anything Deulong and Petit's law does not even hold right it does not even hold as you go to lower and lower temperatures particularly you have to remember that it vanishes at T equal to 0 Kelvin it is quite low and then it grows and it goes to Deulong and Petit's regime which is the classical resistance. Now Einstein proposed a model where he considered a solid as a lattice structure this is obviously correct with an atom so it is like it can be of a simple cubic atom it can be physical cubic lattice it can be a body simple cubic lattice simple cubic lattice diagonal lattice whatever, but it is having a lattice structure with some same number of atoms.

Now each atom what Einstein again these are assumptions from Einstein's model these are assumptions. As you can see solid has a lattice structure which is correct right solid generally when you tell crystal structure of solid say a crystalline solid we tell what is a crystal structure it has a lattice and it has motif motif is nothing but atoms lattice plus motif equal to so a solid is always associated with an underlying lattice structure right which is periodic in nature right it has translation of the density etc etc and it has assumed such an lattice structure with m atoms and we are also telling or Einstein assumed that each atom moves independently within the lattice in three directions. So basically it is like a lattice gas so you have the lattice positions of the atoms and atoms themselves are moving independently that means if I have one atom here in the lattice say let us take a square length. Now this atom has all the six degrees of freedom and it is moving independently so this one is moving independently it does not care about these guys movement these atoms movement of these ones right so it does not care about whether this atom is moving this way or this way it does not matter it will be moving in a minute that was like and it has like and in 3D so it has basically if you think of in 3D and then if it's constraint we are talking about like three degrees of freedom and we are telling the next point which is like no interactions with each other there is no interaction between the atoms of a solid. Now that has a this is a problem this is not a really a tight dimension because then how come sound travel through solids sound if sound is travel through solids the sound wave has to move through some medium now how does it move through a medium it disturb some atoms that these atoms disturb the next ones and so on and so forth and that way the sound can travel through the solid.



Assumption ii is not correct

- Sound propagation through solid.
- Heat propagates through solid.

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk_B \left(\frac{\theta_E}{T} \right)^2 \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\left(\frac{\theta_E}{T}\right) - 1\right)^2}$$

$$\theta_E = \frac{h\nu}{k_B}$$

h - Planck's constant
 $= 6.62607015 \times 10^{-34} \text{ J}\cdot\text{Hz}^{-1}$

Remember $E = h\nu$ for a photon

Now if there is no interaction between atoms in solids then sound cannot travel so that it's a fallacy this assumption is not really correct no interactions with each other is a problematic assumption and there is also another assumption that all atoms vibrate the same frequency so this no interaction is one of the assumptions where we immediately can understand that that is not really true right even heat transfer the way it happens say for example you have a hot plate made of steel, steel is a solid and it's like it's a you can think of or say some iron plate iron solid iron plate and you are hitting say on the back the back side and but you are feeling the heat also on the top right otherwise cooking out many things are not possible. Now how is it possible that means heat also has to travel through the solid right so if there is no interaction how does it travel or sound also has to travel through the solid how does it travel if there is no interaction between atoms. So assumption two as you can see is not really correct sound propagation or heat propagation through solid does take place right now with all these assumptions Einstein devised on temperature called Einstein temperature again he looked at a different type of statistics I do not going to at least in this part of the lecture I am not going to go into the detail of these Einstein's derivations and all but once you go into some statistical mechanical interpretation we may again come back to it. So here what we are telling here that sound can propagate through solid heat can propagate through solid therefore assumption two which is basically atoms do not interact is not there right and now we have this thermodynamic definition $\Delta U / \Delta V$ and we define something called θ_E which is Einstein temperature which is equal to $h\nu / k_B$ where ν is the frequency of oscillation of these atoms and h is Planck's constant and k_B is Boltzmann's constant and then what we get we get an expression $3Nk_B$ so I am not going to derive the expression but I am telling that this is some expression that Einstein got θ_E / T whole square and θ_E is $h\nu / k_B$ so it is like $h\nu / k_B T$ whole square and here also this there is some exponential term and stuff what happens here is as θ_E / T here θ_E / T means $h\nu / k_B T$ when it is large obviously you can understand that T is very small or very low right as we go to very low temperatures θ_E / T is very very large then you can basically approximate this exponential θ_E / T minus one whole square as

exponential minus θ/T which tends to zero because T is very very low so this is T is very very small so this is like minus infinity θ/T minus infinity is zero so right so because θ is $h\nu/kB$ and T is very very small so this entire θ/T is approaching θ/T is approaching infinity as T tends to zero now if that is so e to the power minus infinity tends to zero right so as a result as you can see C_v tends to zero as T tends to zero now this is Einstein temperature as you can see this is your Deulong-Petit law free $n k p$ Deulong-Petit law and as you can see here as T tends to zero as T tends to zero this is zero approaching zero then it increases increases increases and then it merges with the Deulong-Petit at high temperatures high temperatures means here I am talking about room temperature as a high temperature so high temperature limit is as you can see here or the classical limit is θ/T less than one that means T is large right T is large so if T is large then you can approximate this as you will see that C_v this is something that you can prove also because you go to this expression T is very large so this becomes like small so it becomes like very very small here also it is small and here is a θ/T whole square and there is a θ/T if you expand and you neglect the terms you will basically get that θ/T whole square as θ/T whole square on here and here it cancels out and you will finally get this $3n k v$ so basically I leave the proof to you you can try this you can use this approximation and you will find that C_v in such case at high temperature limit becomes equal to $3r$ so you understand so θ/T less than one that means T becomes very very large if T becomes very very large you can show that this because if as you know e to the power x you can write the series and you can tell that okay if T is large x is small right which is θ/T right if T is large x is very small so you do not go to x square x cube and stuff so you have for example e to the power c which is equal to one here you look at this this can be like one plus θ/T plus θ/T whole square plus dot dot dot minus one one one goes off and you can tell that okay these terms are all neglected so you have in the denominator θ/T and here you have θ/T whole square and basically if you look at that so you will see this is θ/T and this is over this is whole square problem square so you get a θ/T whole square in the denominator θ/T whole square in the numerator and as a result these things cancel out and you get three $n k$ you can easily see that or three $n k$ where n is say Avogadro number if I take n as n_A then C_v is nothing but three which is two amperes so you recover do long and plate it as you go to high temperature you recover C_v tends to zero as t tends to zero as you go to low temperature for surface this is Einstein model now Peter Debye he proved down Einstein model again I will not go into all the detail I will not go into the Bose Einstein statistics and stuff but I will tell that Peter Debye used something very very important and you must have learnt you can solve some physics and that is the concept of phonons all that is vibrations so it is not like one single atom is oscillating independently of the other atom and stuff but it is basically a collective motion of the lattice which is propagating through the material it is like a

lattice vibrations that is happening collectively right so there are lots of animations of such a lattice such lattice vibrations you can see so how this lattice vibrations happen and lattice vibrations can be different modes but again unlike electromagnetic waves you cannot have like infinite number of modes and stuff right so basically you now introduce a concept called phonon which is nothing but lattice vibration and when there is a thermal excitation like there is a some some some heating different stuff you will start seeing that there is an excite this excitation passes through the entire lattice as in the form of lattice vibrations it is propagating through the material.

$$\epsilon = \hbar \omega$$

Energy of phonon

$$\hbar = \frac{h}{2\pi}$$

ω - angular frequency

$$\omega = v_s |\vec{q}|$$

\vec{q} - wave vector

$$n_E = \frac{1}{\exp(E/k_B T) - 1}$$

no of phonons in a state with energy E

Phonon do not have infinite modes of frequency
 N - primitive unit cells - N modes of phonon frequency

Maximum allowed phonon frequency or Debye frequency

$$\omega_D = \omega_{\max} = v_s \left(6\pi^2 \frac{N}{V} \right)^{1/3}$$

N/V is number density of atoms

Energy $U = \text{Phonon energy} \times \text{Avg no of phonons} \times \text{number of modes}$

$$\theta_D = \frac{\hbar \omega_{\max}}{k_B}$$

(Debye temperature)

So if you look at that you can define energy of one phonon as h cross ω where ω is the angular frequency which is the speed of sound effective speed of sound through the solid and this is the magnitude of the wave vector right that wave that is propagating now if you see that because you are having vibrations right oscillations and the number of phonons is given by the statistics I am not going to the detail of it but one thing to note is that phonons do not have infinite modes of frequencies the modes of frequency are limited to the lattice in which we are working right so it is basically related to the related to the number of atoms that are there arranged in the lattice right it is basically if you think of n primitive unit cells then you have n modes maximum n modes of phonon frequency and there is a maximum allowed frequency that Debye came up with again I am not going to the detailed proof of it but later when we go to a more deep into the molecular interpretation or the statistical interpretation of or the connect between statistical mechanics and phonon dynamics we may try to prove some of this but currently we are telling that there is a definitely a molecular connect and this molecular connect is what we are explaining and when we are trying to explain this remember C_v C_p all are macroscopically measurable quantities these are like macroscopic manifestations but all of these have an atomic or molecular origin and that is what I am talking about now if you look at Debye frequency this is the maximum allowed phonon frequency in a lattice right in a solid and that is given by ω_D which is related to v_s and it is also related to number density of atoms n is the number of atoms V is the volume right number density of atoms and there is a $6\pi^2$ squared and to the power $1/3$ power now if you see that the energy is phonon energy right times the average so phonon energy times average number of phonons times the number of modes because like Einstein where he assumed

that modes can be infinite here modes are basically if there are n lattice points or n primitive cells then there are only n phonon modes now you have $h \times \omega_{\max}$ by $k \times v$ as the Debye temperature you have a Debye frequency of ω_{\max} which is $v \times s$ into this thing and you have $h \times \omega$ is the energy so $h \times \omega$ by $k \times v$ is your Debye temperature now if you have that again after some manipulation actually Debye showed in a very different way but you can derive this expression in several ways by looking at again statistical and mechanical tools which we are not dealing with currently but I want to tell you that the connect that you get is u is equals to this $9 k_B T$ by θ_D^3 and 0 to θ_D by T^3 by x to the power $x - 1$ is 1 plus at high temperature x is small right at higher temperatures as you go to higher and higher temperatures x is basically θ_D by T so x becomes small right T increases so it becomes small so if x becomes small then you basically have x^3 by e^{x-1} now if you think of this you have x^3 by x because $1 + x - 1$ so x^3 by x is nothing but x^2 and you have p by θ_D^3 and there is a θ_D^3 by p^3 and then there is a one third so it becomes you recover again two long entities now c_v is equal to 3 and c_v is equal to 0 and at low temperature if you go to the low temperature you get θ_D by T tends to infinity right because as you go to low temperatures and this becomes x^3 by $x - 1$ to infinity becomes π^4 by 15 and then you have this expression of u and $\frac{du}{dt}$ is your c so you basically get $12 \pi^4$ by $5 n k_B T$ by θ_D^3 and if you plot C_v by $3 n k_B$ as a function of p by θ_D this is your Einstein curve but this is the more correct you can see the dotted lines is the more correct divider you please have a look at it and have a check at it means which one is the Einstein model and which one follows the divider you can have a plot you can plot it yourself and you can see remember there is one very interesting outcome of the long and purpose law at room temperature copper and lead both have the same heat capacity molar heat capacity of lead and copper are same which is $3R$ now if that is so how are they different they are different we know that they are different because the specific heats are different right because this is joule per mole kelvin which is $3R$ but as you can see here you can easily verify if you look at the atomic mass for example where it is there so this is 3.6 for copper lead is 207 so as you can see here $3R$ in one case it is $3R$ by 207 in another case right is joule per mole kelvin is this mole you are converting to gram so if you do that so molecular weight so or atomic weight so 207 is for lead right this is joules per gram kelvin and for copper it is $3R$ by 63 .

High temperature limit $\frac{\partial E}{T} \ll 1$
 (T is large) $C \approx 3Nk$
 $P_{int} = Nk$
 then, $C_V = 3R$

Model by Peter Debye

- Concept of phonons or lattice vibrations
- Not oscillations of single atom but collective motion of lattice propagating through the material

For real gases,

$$dT = \eta_{JT} dP$$

$$T_f - T_i = \eta_{JT} (P_f - P_i)$$

$$\left(\frac{\partial T}{\partial P}\right)_H = - \frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P}$$

Unit of η_{JT} is K/Pa

All real gases have an inversion point where η_{JT} will change sign
 Inversion temperature of $O_2 = 491C$

Below inversion temperature,
 $\eta_{JT} > 0$
 $dP < 0$
 $dT < 0$
 Cooling

Above inversion temperature
 $\eta_{JT} < 0$
 $dP < 0$
 $dT > 0$
 Warming

6 which is the copper is 2 per immediately you can see that this is much larger than this one so lead has lower specific heat than copper lead has lower specific heat okay now I go through another very interesting observation that again can be explained from first law and from the knowledge of C_P , C_V and enthalpy is that we will look at adiabatic flow through a valve and this becomes very very important for real gases because this is a joule terms of expansion is something that is used for refrigeration right it is this process a very interesting process I will come up with and that process is called isoenthalpic process isoenthalpic means we know about isovolume we know about isobaric we know about isothermal isoenthalpic means the enthalpy means the cell right so let us have a look at this adiabatic flow very quickly so if you look at the inlet and the outlet and this is a system and adiabatic means heat cannot be added to the system cannot be removed from the system and you have this valve here you are so you press some you press a gas here and then you just move a piston this way and you will see that the gas expands and while the real gas expands it causes cool it is something that we will show so the so real gases as I was telling cool upon expansion and this process is adiabatic that means the enthalpy or heat content does not change right and then you can define a joule terms of preparation which is eta JP which is del P del P at constant right now again H is a state function so DH is an exact differential so dH again can be written as delta H del H by del PT del H by del PP and there are this reciprocal so this is something that you can have a look at as I told you partial differentiation our knowledge of partial differentiation is very important when you understand to understand from the mix and reciprocal entities I think this is something that all of us know del X by del X Z equal to del Y del Z and this Euler chain rule is something quite interesting Z is a function of X and Y you can write and you can prove this del Y del X Z so del Y del X at fixed Z del X del Z at fixed Y del Z del Y at fixed X is all as you can see it's a chain rule now you see here del Z here there is a del Z del X del X del Y del Y and this is equal to minus 1 now if that is so you can use this identity or this Euler chain rule in many places please try to prove this this is something that's very important and you know about this so as you can see here I can I have taken H as a function of P and T it's like Z as function of X and Y then I use del H del PT del P del P H del T del HP and this becomes minus .

For ideal gases,

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = 0$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$H = U + PV$$

$$\left(\frac{\partial H}{\partial P} \right)_T = \left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T + V$$

$$= \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T - P \frac{nRT}{P^2} + V$$

$$= 0 - V + V = 0$$

$$\eta_{JT} = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_P} = 0$$

So you see here you have a $\left(\frac{\partial H}{\partial P} \right)_T$ and what is your ΔT it is $\left(\frac{\partial T}{\partial P} \right)_H$ so we can also use the reciprocal identity so if I have this so we can write $\left(\frac{\partial H}{\partial P} \right)_T = -1 / \left(\frac{\partial P}{\partial H} \right)_T$ now this becomes minus of $\left(\frac{\partial T}{\partial P} \right)_H$ $\left(\frac{\partial H}{\partial P} \right)_T$ so of dH equals to minus $\left(\frac{\partial T}{\partial P} \right)_H$ right $\left(\frac{\partial H}{\partial P} \right)_T$ which is C_P and here again there C_P PT so for isenthalpic process as you know $dH = 0$ right $dH = 0$ that is isenthalpic and you get $dH = -\eta_{JT} C_P \left(\frac{\partial T}{\partial P} \right)_H + C_P \left(\frac{\partial T}{\partial P} \right)_H$ and then because $dH = 0$ I can tell and C_P can cancel we get η_{JT} equals to $\left(\frac{\partial T}{\partial P} \right)_H$ constant right so we can see how we got the Joule-Thomson coefficient for isenthalpic process right and as I told you that you have a gas a real gas this is upstream so you move the piston this way you compress it completely now downstream you are essentially expanding it right you are just moving the piston away for right and the gas is allowed to expand so P_F is going in general or less than P_I right so $P_F < P_I$ and you have isothermal compression here and you have isothermal expansion here and if you look at that you have W_i which is basically you started with a volume V_I say for example the volume is V_I and it goes to 0 right we are compressing it so much that the volume goes to 0 so $\int P dV$ which is basically going to be $P_I V_I$ this is work done on the system minus $P dV$ so and W_p is minus $P_F V_F$ minus 0 which is minus $P_F V_F$ here so as you can see the change in energy here because it is adiabatic is ΔU change in term energy is $U_F - U_I$ which is $P_I V_I - P_F V_F$ here and if you know add in $U_F + P_F V_F$ is H_F and $U_I + P_I V_I$ is H_I so you can see that indeed the process is ISO important right so as I told for real gases ΔT the change in temperature is related to change in pressure right so there is a $\left(\frac{\partial T}{\partial P} \right)_H$ it is equal to $\eta_{JT} \left(\frac{\partial P}{\partial T} \right)_H$ right so and as I told you $\left(\frac{\partial T}{\partial P} \right)_H$ again from Euler-Chen rule you can say that $\left(\frac{\partial T}{\partial P} \right)_H$ is nothing but minus of $\left(\frac{\partial H}{\partial P} \right)_T$ and this is $\left(\frac{\partial H}{\partial P} \right)_T$ and the unit of this Kelvin per Pascal and all real gases have an inversion point where η_{JT} change is sign right so inversion a pressure for oxygen for is 491 degree Celsius so below inversion a pressure η_{JT} is equal to is greater than 0 now η_{JT} is greater than 0 dP if η_{JT} has to be greater than 0 as you can see which is $\left(\frac{\partial E}{\partial P} \right)_H$ since dP is less than 0 right dP is less than 0 dP

has to be less than 0 and you get what is called cool right if you have Joule-Thompson expansion below inversion temperature what you get is cool above inversion temperature your η_{JT} is itself negative now DP is less than 0 right DP is still less DP is always less than 0 that's what I we have told that PF is less than PI DP is less than 0 then DT has to be now greater than 0 now DT has to show above inversion temperature joule-thompson expansion causes warming and below inversion temperature where η_{JT} is greater than 0 since DP is less than 0 you will always get DT to be less than 0 right because η_{JT} remember the η_{JT} is what it is $\frac{\Delta T}{\Delta P} = \frac{\Delta T}{\Delta H}$ now if DP is negative ΔT has to be negative because η_{JT} has to be positive so below inversion temperature you will always see joule-thompson expansion causes cooling above inversion temperature it becomes the opposite it causes warming so for ideal gases if you see as we have already mentioned very quickly $PI = T \frac{dU}{dT} + P$ and if you see this $\frac{dH}{dP} = T \frac{dU}{dP} + V$ if you look at the proof here $\frac{dH}{dP} = T \frac{dU}{dP} + V$ plus $P \frac{dV}{dP} + V$ now you have $\frac{dU}{dV} = \frac{dV}{dP}$ this is from chain rate so this you are writing this minus $P \frac{dV}{dP} + V$ now $\frac{dU}{dV} = \frac{dV}{dP}$ is nothing but $\frac{dU}{dV} = \frac{dV}{dP}$ is nothing but V so minus V plus V becomes 0 and this guy $\frac{dU}{dV}$ itself is 0 so as a result η_{JT} for ideal gases is equal to 0 right so from next class onwards I will start with the reversible I will just tell one or two more important points of reversible adiabatic expansion then I will start with the second law right so we will start with the second law so you look at the reversible adiabatic expansion because we just want to know what is a we know the C_P minus C_D but what about C_P by C_D and this is why is it become why does it become useful so we will look at a reversible adiabatic expansion in the next class but remember this joule-thompson expansion coefficient η_{JT} for ideal gases is okay so if you have any questions please post those questions to us and we'll have a look at if you have any doubt we will try to we will try to get back to this emails and we'll get back to it.