



So, it is often not considered and when we talk about the internal energy, we again have to talk about we need to understand about three things. So, when you talk about internal energy, I will sort of introduce it in a slightly different way. So, if you think of internal energy of some gas. So, what are the water gas. So, essentially, we all know about the kinetic theory of gases. So, the gas molecules are there.

So, gas molecules move so there is kinetic energy, but this in this kinetic energy is internal kinetic energy. then what next? Next is the interaction between the molecules. Of course, in ideal gases there is consider it is considered that there is no interaction between the molecules but in real gases we have interaction between the molecules. And more importantly if you go to liquid the condensed phases gas is a non condensed phase.

If you go to the condensed phases like liquid or solid this interaction between the molecules is very, very important. one such example of interaction we have already talked in the context of discussing the water phase diagram is the hydrogen bonding. it is the inter molecular interaction due to the polar interaction or the polar nature of the permanent dipole of the molecules. So, essentially the interaction of the molecules leads to the internal potential energy.

And probably most of you know that the most common form of this in inter molecular interaction is the induced dipole induced dipole type interaction which is loosely referred to as Van Der Waals interaction and the third form of internal energy is intra molecular interaction. So, all the interaction that takes place inside a molecule. So, essentially, we have the bonds and then the molecules around the bond can undergo some rotation or the individual atoms can undergo some rotation or there can be vibration etcetera.

So, the third major component of internal energy is rotation, vibration etcetera. Okay. So, this is interesting but very simple. So, internal energy again comprises of internal kinetic energy, internal potential energy and energy associated with rotation vibration etcetera. but let us quickly first finish off the discussion on the external energy. So, which is known to all of us therefore I will no drag it at all I should have discussed it formally before I moved on to internal energy.

But it is it is fine. So, external energy, so, kinetic energy is the energy associated with the motion of an object and we know that kinetic energy is equal to half  $mv^2$  where  $m$  is the mass and  $v$  is the velocity. So, of course an object which is under motion possesses kinetic energy but an object that is static does not have any kinetic energy. The potential energy nothing much to discuss.

So, essentially potential energy is the energy possessed by a system because of the force exerted on its mass by means of body forces. So, the easiest example of body force is of course the gravitational force, but the second example of body force is the electromagnetic forces, if any. So, the most common form of the potential energy is  $mgh$ .

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**Internal Energy (U)**

It is a macroscopic concept that takes into account all molecular, atomic and sub-atomic energies.

→ Internal Energy cannot be measured directly, but can be estimated from other state variables like Pressure, Temp, Volume, composition etc.

Internal Energy → Internal Kinetic Energy – Dominant in Gases.  
 → Internal Potential Energy → Dominant in Condensed phase (Liquid, Solid)  
 → Rotation/Vibration → Mono-atomic gases  $\approx 0$

|               |                            |   |
|---------------|----------------------------|---|
| Gas           | Liquid                     | Internal K.E. = $K_B T$                                       |
| Internal K.E. | Internal Potential Energy. | Average translational K.E. of molecules = $\frac{3}{2} K_B T$ |
|               |                            | $T = \text{Abs temp. in Kelvin}$                              |

Then coming back to the internal energies, we already had a discussion. So now we know. So, internal energy its essentially a macroscopic concept or macroscopic concept that takes into account all molecular atomic and sub-atomic energies. and we have already talked about it. So, essentially the internal energy you can see that it comprises of internal kinetic energy internal potential energy and energy associated with rotation and vibration.

You need to understand that internal energy cannot be measured directly. This is something important to realize but can estimated from other state variables like pressure, temperature, volume, composition etcetera. So, you need to also understand. So, we now know that there can

be. So, as we have already discussed that different forms of internal energy. So, we have internal kinetic energy we have internal potential energy associated with vibration and rotation. now there can be lot of very interesting discussions around these things.

So, now if we talk or ask you that we have a gas and a vapor and a liquid. do you have both the systems have internal energy the answer to this is yes both the systems have internal energy. but the interesting part is for a gaseous system. So, these are some agreeing to the fact that we already know that what are the different components of internal energy? And the different components of internal energy are essentially internal kinetic energy.

So, I am coming to the functional form of internal kinetic energy which is due to the motion of the molecules. Then you have internal potential energy which is due to the interaction between the molecules and then you have the rotation and vibration which is intra molecular interaction. So, agreeing to the fact that internal energy comprises of internal potential energy or internal kinetic energy internal potential energy and energy associated with rotation vibration etcetera.

Now I have a simple question. So, suppose we have a gas and we have a liquid. So, first thing to understand is both of them possess internal energy. But what is interesting to note is that in a gas the major part of the internal energy will be the internal kinetic energy. In contrast, in a liquid or in a solid the major part of internal energy the kinetic energy will almost be zero because in a solid or a liquid the molecules do not are not in a position to roam around freely.

So, therefore the internal kinetic energy of the molecules is almost negligible. So, whatever you have the internal energy is due to the very strong interaction of the molecules or is due to the interaction or inter molecular interaction which is the internal potential energy. So, you can also now distinguish a liquid and a solid or a liquid or a gas based on its internal energy components.

So, what exactly defines whether something is a liquid or a solid both are condensed phases in a solid what you need to understand is the intermolecular interaction or the internal potential energy is even stronger than a liquid. liquid is strong enough therefore liquid has some volume, but its shape can deform. And in a gas for example in an ideal gas you know that there is actually

no internal potential energy because ideal gas law assumes that the molecules are volume less particles and there is no interaction between them.

The third component rotation and vibration are more attributed to the material property because you see in order to have rotation or vibration within a molecule or atom within a molecule you essentially need to have multiple atoms. You need to have a bond around which vibration or rotation can take place. So, if you have mono atomic material like mono atomic gases any way the rotation and vibration is going to be zero it is not present.

In case, you if you have a diatomic gas or polyatomic molecules compounds. So, it can be elements polyatomic elements or compounds there are possibility and there is actually some rotation and vibration associated with it. But remember the for mono atomic gases for example or mono atomic molecules because there is no axis to rotate or vibrate there are no bonds around which a second molecule can rotate and vibrate with respect to the first molecule.

This component is going to be zero this is an important realization because I will tell you how exactly we define what exactly is an ideal gas. Many of you know but a gas that obeys ideal gas law is not the definition the ideal gas is defined in certain way and as a consequence of that it obeys the ideal gas law. So, this component is absent for monoatomic gas. So, internal kinetic energy is dominant I guess all of you can understand it in gases and this is dominant in condensed phases.

So, which is liquid and solid, okay, so this is how it goes and probably we also need to just touch upon that internal kinetic energy, the average value of internal kinetic energy is  $k_B T$ . the average internal kinetic energy, average translational kinetic energy of molecules or gas molecules is  $k_B T$  where  $T$  is the absolute temperature and  $k_B$  is the Boltzmann constant. So, you can. So, we all know that as we increase temperature gas pressure increases.

So, why, the answer to that is written here because what happens is, we all know that the translational kind we understand now that the translational kinetic energy of the molecules actually increases or in other words the molecule starts to move faster. Now what exactly is gas

pressure? gas pressure is nothing but manifestation of the number of collisions the molecules are undergoing. But here also there is a catch. remember gas pressure is not or gas pressure is not due to all collisions the molecules are undergoing.

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Average Translational K.E of Molecules (Gas) =  $k_B T$

Distribution of KE → Evaporation happens is due to this distribution

With increase in Temp → Gas Pressure Increases.

As  $T \uparrow$ , Internal K.E. of the molecules increase.

Gas Pressure is a manifestation of Collision of the molecules with the Wall.

Critical Point

Above Critical Point We can not Liquify a gas, whatever be the amount of Pressure we apply.

As we increase  $T \uparrow$ , KE increases, or the capability of molecule to zoom around/move around increases.  $T > T_{critical} \rightarrow$  KE becomes so high, that Int PE can never match it!

The phase diagram shows pressure (p) on the vertical axis and temperature (T) on the horizontal axis. It features three curves: solid-liquid (S-L), liquid-vapor (L-V), and solid-vapor (S-V). The critical temperature  $T_{cr}$  is indicated at the end of the L-V curve.

So, gas pressure we all know. So, let us just have a quick discussion on this. So, average translational kinetic energy of molecules particularly gas molecules are  $k_B T$ . Please do remember that this is average translational kinetic energy. all molecules of a gas or a liquid or any system does not have the same amount of kinetic energy. some have higher some have lower. in fact this is the reason there is always a distribution of internal energy of the molecules.

Particularly the kinetic energy of the molecule. there is always a distribution. and the biggest example of this distribution is the phenomena of evaporation and condensation. in fact, when a molecule from the liquid phase evaporates to the vapour phase; which are the molecules that actually evaporate? The molecules that actually have higher amount of kinetic energy or higher amount of energy can overcome the interaction of the molecules, the cohesive interaction of the molecules in the solid phase and go to the liquid phase.

So, unless there is a distribution of the kinetic energy of the molecules if all molecules are at the same energy level. the probability of evaporation will almost be zero. So, there please remember this is average translational kinetic energy this is not the kinetic energy of each molecule. So,

there is always a distribution of kinetic energy. And, one I always prefer to give it like that evaporation happens again something I will leave this for your heat transfer professor to teach evaporation what exactly is evaporation is due to this distribution.

Now, coming back to the point that with increase in temperature, gas pressure increases. So, what exactly is happening? What happens is with increase in temperature, the kinetic energy rather the internal kinetic energy of the molecules increases. And what is gas pressure? Gas pressure is a manifestation of the collision of the molecules but remember it is not all collisions, collisions of the molecules with the wall.

So, gas pressure is a manifestation of collision of the molecules with the wall. So, as the kinetic energy of the molecules increase the frequency of this collisions or a greater number of molecules collide with the wall and which manifests in increasing the gas pressure that that is as simple as that. So, these are all related to internal kinetic energy this is a molecular level picture. but in classical thermodynamics we treat kinetic energy we lump all these different interactions into internal energy which is treated as a macroscopic entity.

So, the other important concept that is also related to these different forms of internal kinetic energy is what we have already talked in the context of the phase diagram and that is essentially the critical point. So, we all have talked about. So, let us draw a regular one not water. So, this class I guess is knowledgeable enough to understand that this phase diagram does not represent that of a water.

So what happens is? what is critical point? above critical point you cannot liquefy see many times I actually write in very simple English, what I narrate there is no point in talking about some symbols and this and that as long as you understand the basic concept that is the most important thing. So, above critical point we cannot liquefy a gas whatever be the amount of pressure we apply. So, why this thing happens. now what exactly is liquefaction.

So, essentially, we know that if we compress a gas, if we apply pressure then we can liquefy. So, what is the main difference between a liquid and a gas? this is the main difference between

liquid. And a gas for a gas that is dominated by internal kinetic energy that means that the potential energy, internal potential energy is almost zero that means the molecules do not interact or mean free path is infinity and in a liquid the kinetic energy is almost zero because mean free path is zero the molecules cannot move freely.

So, what is the process of liquefaction it is very simple. So, you take some amount of gas you apply pressure. So, when you are applying pressure you are essentially reducing the volume or in other words now you are physically confining large number of gas molecules into a very, very small amount of space. So, as the molecules are now forced to come close to each other it is expected that there might be interaction between these molecules and if these molecules. So, this interaction can happen because of their polarity or the induced dipole or whatever.

So, essential idea is that it is like a large number of children playing around here and there you bring them artificially to the school on the first day and then try to make them friends that is exactly what is liquefaction. So, you apply lot of pressure. So, the volume now is reduced and within this limited volume you have all these gas molecules. So, it is expected that these gas molecules will start interacting with each other and once they start interacting with each other the molecules cannot escape freely here and there.

So, again their mean free path has now gone to zero and therefore it has actually transformed from a vapor phase to a or a gas phase to A liquid phase this is what happens. Now what opposes? So, what are the opposing forces? So, in favor of liquefaction is the internal potential energy, opposing the liquid fraction or which wants the material or object to remain in the gaseous state is the kinetic energy.

So, because of kinetic energy the molecules want to move around, and because of the potential energy now you want the molecules to stay together now it turns out as we have already seen that the internal kinetic energy is a function of temperature. its  $k_B T$ . In contrast internal potential energy is not a function of temperature. So, it is actually a function of separation distance if you are talking about Van Der Waals interaction the strength of this interaction is one by  $R$  to the power 6.

So, if the molecules are very close to each other, they can interact, and it is not a function of temperature. So, what happens is if you keep on increasing the temperature and you still keep on compressing as you increase the temperature the kinetic energy of the molecules increases. Or that means in other terms that as you increase the temperature, increases or they are the ability that the capability of the molecules to roam around or move around increases. in contrast your potential energy internal potential energy is not a function of temperature.

So, despite increasing temperature that its strength remains constant, so, critical point is actually that temperature above which the kinetic energy becomes so high that potential energy can never match up to it. So, for a  $T$  greater than  $T$  critical the kinetic energy becomes so high internal kinetic energy becomes so high that potential energy can never match its value. and therefore, liquefaction can never happen.

This is actually the significance of the critical point that is the reason why above critical point is very simple way of looking into it. this is the reason above which above critical point whatever pressure you apply you can never liquefy a gas. So, I think this is a good point to stop and next class. So, we now have completed ten lectures in this component of energy balance. So, that means that we are ending 8th week now.

And from the next class we are in a good position now to talk about the first law of thermodynamics and quickly move on to estimation of physical parameters, Thank you very much.