Chemical Principles II
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Zero-th Law of Thermodynamics

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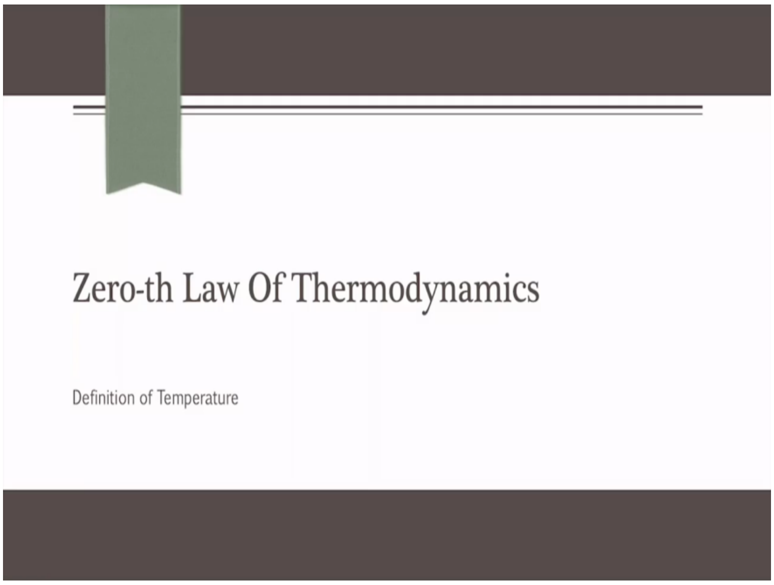

Now let us talk about zero-th law of thermodynamics, so in thermodynamics there are 4 laws zero-th law, 1st law, 2nd law and 3rd law of thermodynamics. And zero-th law is the one that comes at the end because that's why the name zero-th Law came, so first law to come out was the 2nd law of thermodynamics and then you know 1st and 3rd came and then finally zero-th Law came later on.

But this is so important because this gives the foundation of subsequent laws that it had to be put as one of the laws of thermodynamics and zero-th law gives us a definition of temperature.

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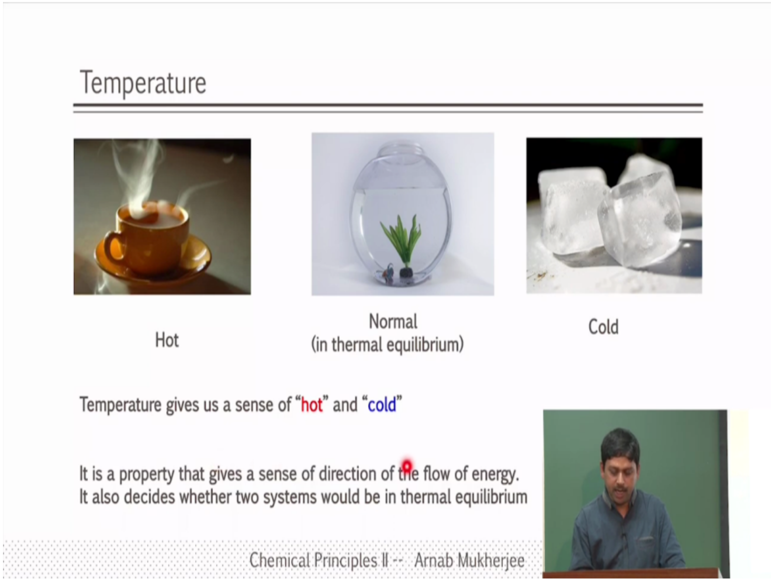

So what is temperature? Temperature when you talk about that, okay and the temperature of the room is very high. So you talk about that it is hot or cold? It gives us a sensation that one thing is hot or cold when you touch it, for example hot cup of tea we know by our sense itself that it is hot. When you touch an Ice we know that it is cold it is a sensation of feeling cold.

And then even for normal water we say that okay, it is normal. So temperature is something that is associated with a sense of hot and cold and you will see that it is a property that gives a sense of direction of the flow of energy, again governed by the laws of thermodynamics. And temperature also decides whether 2 systems will be in thermal equilibrium or not.

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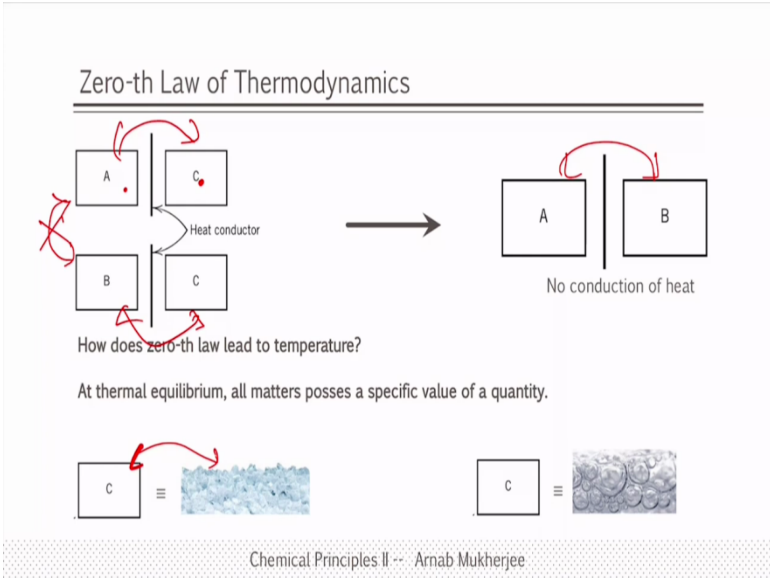

So what is the formal definition of zero-th law of thermodynamics? Zero-th law of thermodynamics says that if 2 quantities A and C, let us say A and C are in thermal equilibrium with each other and B and C are also in thermal equilibrium with each other than A and B without being in contact with each other will be in thermal equilibrium. It looks simple but it is a profound theory.

What it says is that, A and B are not connected with each other, you see it's not connected. Yet when we see that C is in equilibrium with both A and both B separately then A and B is also in thermal equilibrium with each other. So what is C? You can think of C as a thermometer. So basically you using C as a thermometer you measure A, a temperature of A.

And using C as a thermometer you measure the temperature of B and if they happen to be same then when A and B will have the same temperature. So the quantity when 2 things are in thermal equilibrium with each other like for example A and C and B and C, a particular quantity which is defined to be temperature is same irrespective of the nature of material you can put a liquid with the solid or gas with the liquid or irrespective of the nature of the matter.

Irrespective of the size of the system when 2 things are in contact with each other and if this is not an isolated system for example as I told you isolated system does not allow the transfer of energy. Then if the energy transfer is allowed than 2 systems in contact with each other we will actually come to finally in thermal equilibrium. Thermal equilibrium essentially will give rise to the quantity which is defined to be temperature to be constant within these 2.

So how does that zero-th Law lead to temperature? So at thermal equilibrium all matters posses a specific value of a particular quantity when 2 things are close together. For example let us say that C is a block of Ice, so that means when A is in contact with Ice A will have the same quantity, a particular quantity that we are talking about with this temperature as Ice.

When C is in contact, let's say C is a boiling water then C will be, when A is in contact with C then it will have the same temperature as that of a boiling water. So before we go further we are going to demonstrate to you that how particular you know quantity when it comes in equilibrium with other quantity will give rise the change in that property.

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So right now this particular Thermo meter which is like you can say that it is the C object that we are talking about. It has a certain amount of volume here and that volume gives, we have some gradation in that particular capillary and it shows that is the temperature is 27 degree centigrade approximately. Now we are going to put that in this particular water and let it equilibrate.

I can dip it like this, so initially thermometer was in contact with the atmosphere, so it had the same particular quantity that atmosphere had was there in the Thermo meter. Now we put that in this particular water which is slightly warmer than the room therefore there will be, since now this is serving as close system the Thermo meter, there will be a transfer of energy between the water and the Thermo meter which is going to change that particular quantity both in the Thermo meter and in the water.

However water is much larger in quantity therefore the water's temperature is not going to change and when it comes to equilibrium we are going to see the value of that and that the temperature turns out to be 50 degree. So right now if I touch it I feel it the same hotness as that of the bottle. So initially the temperature was 27 degree it has become 50 degree coming in contact with that. See here I am putting a metal tip in a liquid.

They are completely 2 different materials with material property. However in contact with each other, both of these particular 2 objects assume the same temperature. However if we talk about temperature, then we have to define it, see in Thermo meter we said that it is 27 degree initially and 50 degree later on. Now how do we say that how hot and how cold?

How do we define this particular value of 27 degree? How do we define that it has particular value of 50 degree? So in order to understand that we need to have a standard of measurement. We have to fix the value of hotness and coldness to certain quantity, once we do that then observing that quantity we will be able to observe the effect of temperature on those objects.

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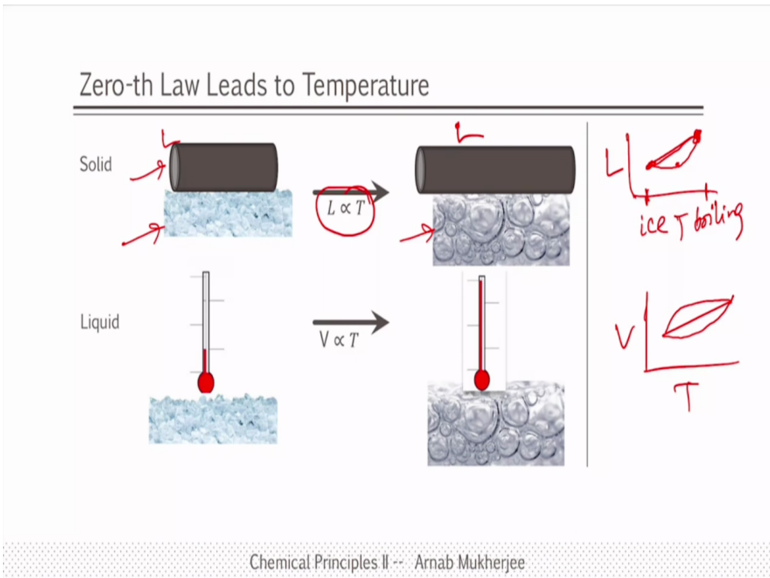

In order to measure the value of temperature one has to associate that with material property. So people knew that when you keep an object like a metal object in a cool room versus in a hot place, then the length of that metal is going to change. So for example the standards of measurement for one meter let's say a metal rod which is kept in a very you know isolated conditions such that, that size is called one meter.

Now if you take out that and put it somewhere else for example in this particular room, the length of that particular metal is going to change and therefore the value, the sense of length which you call as one meter is also going to change. So we need a standard for every measurement, right? So therefore looking at, so people knew that when this metal object will come in contact with different environment then this property is going to change.

For example let's say if you put this metal object on a block of Ice then by zero-th law of thermodynamics there will be a thermal equilibrium between the Ice and the rod in such a way that anything that will have the temperature of the Ice, the metal also will have the same temperature. Now let's say we associate the length of the metal, we calculate the length of the metal when it is in contact with the Ice.

And we put a value for that at the value of Ice, we calculate the length and then let us put the metal object on boiling water and we calculate the value for boiling water. There will be a difference and that difference will indicate that the temperature is increasing. So therefore the length is associated with or proportional to the temperature because we know that boiling water is hot, Ice is cold and at 2 different stages at equilibrium we will have a particular link associated with the metal object in these 2 different situations.

So now we are associating the length along with the temperature of the object. However this expansion of metal with temperature is very small. They do not you know the coefficient of thermal expansion is not very high. So therefore it is very difficult for a very small amount of change in temperature, it is very difficult to see or measure the change in the length of the metal.

So people have use liquids, liquid expand more than solids with temperature and we know that in Thermo meter what we have typically is that we have mercury.

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Here in this particular volume. And then there is a small capillary very thin and narrow tube through which the volume can expand. Now because of the smaller surface area of the capillary, the change in the length for a given amount of volume will be much larger and on top of that there is a prism to magnify what is there inside.

So this very small amount of expansion in liquid can be now measured or can be observed when you put in this particular setup of system to measure that. So basically our older thermometer is basically an expansion of liquid which is mercury.

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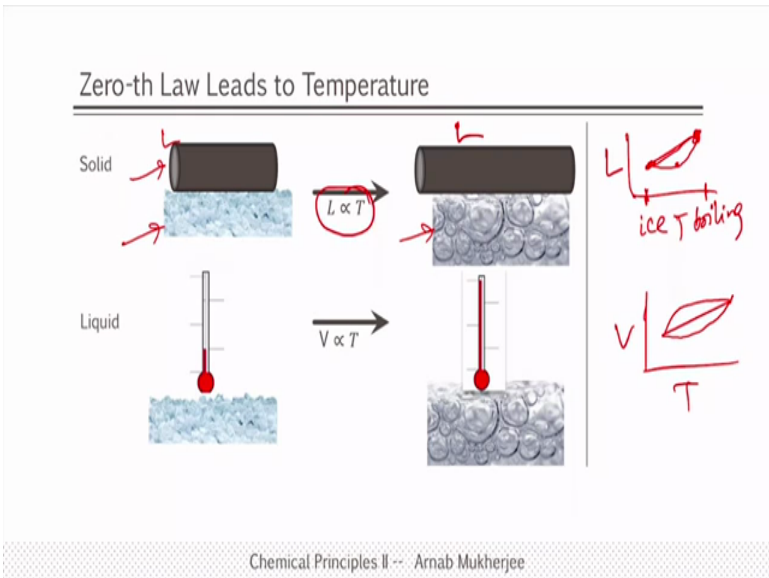

So therefore we can say that for a liquid now volume is going to increase with temperature. So we have not yet specified how it is going to increase. We have only taken 2 points, however there is an expansion of length with temperature can be linear or may not be linear. Let's say we take a 3rd point and it is here, then expansion will not be linear. Same case you know we can have with volume also. The expansion may be very different from the linear expansion.

Therefore all the intermediate temperature between Ice and the boiling water cannot be measured assuming that it will have a linear behavior. So we are going to show these demonstrations of both expansion of metal and expansion of liquids with temperature.

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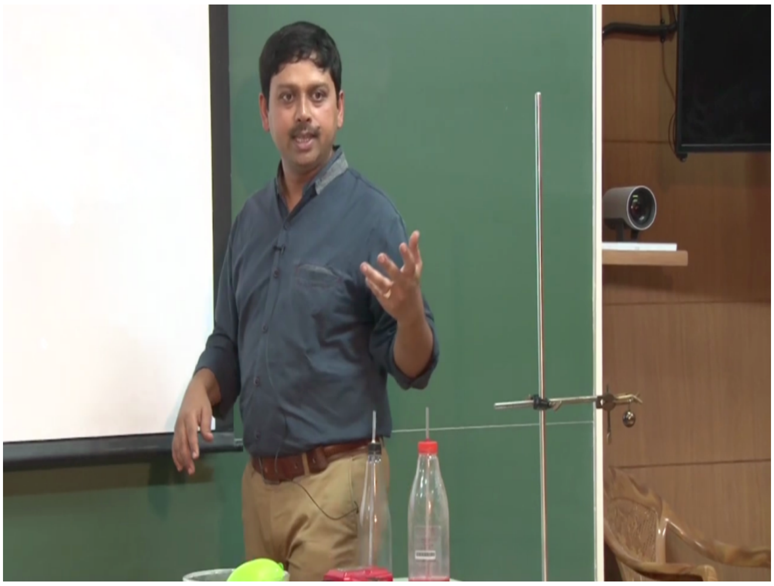

So the first thing that we are going to show you is that how heat changes the size of the metal or we can say volume or length of the metal, in this particular case we are going to show the volume, yes. So this is typically known as the Boyle's experiment where you know long back people used to see that this particular object, the ball can easily pass through this hole when it is, right now is in equilibrium with the surrounding and we know that surrounding temperature is right now 27 degree.

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Now we are going to heat up this particular ball.

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So what we are doing here is that? We are heating up the ball and we are hoping that the ball will still pass through this particular hole. So we will see whether it is passing through or not? Still passing through. Yes, so certainly it has expanded and therefore it cannot pass, so the metal object when you put heat on that expands, that people have observed.

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Now we are going to show you that how liquid expands with temperature. So this is a bottle it is in equilibrium with environment but you know that our body temperature is higher, right? Our body temperature is basically 37 degree Centigrade, so we are going to warm it up little more and we are going to put that over the bottle and the bottle is colored for you to see and there is a capillary inside that and you just holding that bottle.

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Do you see the increase in the level? So now the bottle was cold enough from the heat that is coming out from my hand is getting transfer to the bottle that is increasing the volume now you can see the volume going up because the surface area of the capillary is actually small therefore the change in the length is more and this same principle we are using in the thermometer.

So most of the materials actually not all the materials, most of the materials expand with heat and that expansion if we now relate to this particular temperature then it will give us an idea about the temperature itself. However as we discuss that liquid expands from you know when you put heat into that but then what liquid you will use? Will you use water or some other liquid?

So depending on the liquid also the amount of expansion is going to change.

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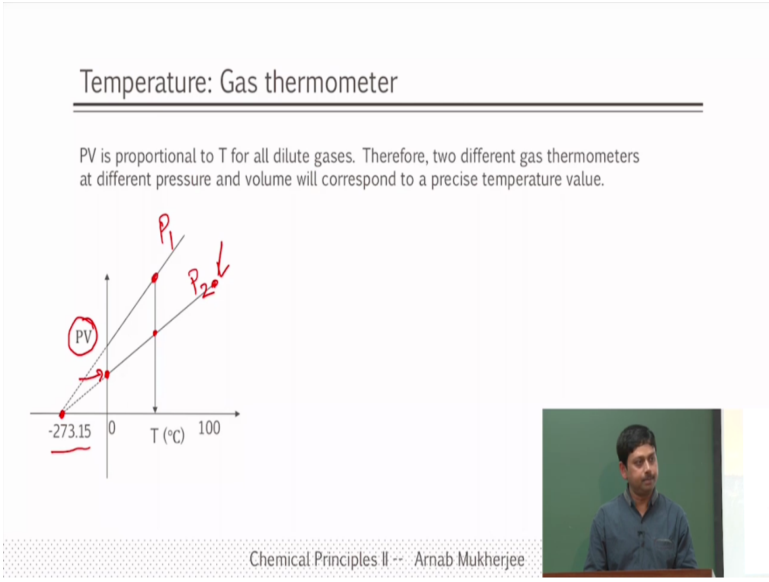

So therefore people have figured out that the gases expand much more easily and much larger quantity with temperature. So people have seen that when you calculate pressure into volume with temperature then for all dilute gases you get a linear behavior. So the PV if you calculate PV at different temperature for example if you can calculate PV at 2 different values.

One at when it is in contact with Ice, another when it is in contact with boiling water then one can draw a straight line between them, such that and another pressure also it is linear and at any given intermediate value of PV one can have a measure of the temperature and that is possible because we are talking about the gas, a very dilute gas and this dilute gas follow a linear behavior with respect to temperature.

So we are defining temperature by the amount of PV at 2 different values 0 degree and 100 degree by the way 0degree and 100 degree is defined based on the value of PV and these 2 lines are for 2 different pressures P1 and P2. At 2 different pressures is that both of them follow linear behavior for a dilute gas and when you extend that to even lower temperature, lower than the temperature of the Ice, then one can extend that to a value where PV will go to 0.

So we will see later on that it is not possible to go to this particular value, however that's why you put dotted line and that value corresponds to minus 273.15 degrees centigrade because it is possible for the gas to have any intermediate values, people have used dilute gas in the gas thermometer.

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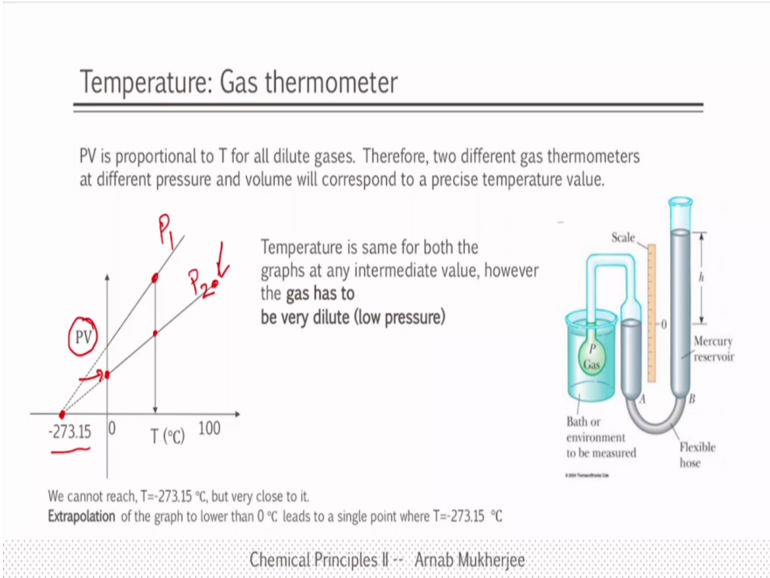

So this is the picture of gas thermometer where you have the gas in this particular cylinder and then you have mercury here. In this particular place, you have mercury. Now in order to keep the constant volume, the level of mercury should be at zero, at this place. Now let's say you put this particular system inside a beaker and if the temperature of the content of the beaker is higher then the gas would like to expand more.

However you put more mercury here in order to keep the level at zero. So therefore it is a constant volume process, where the volume of the gas is not changing. However it is balanced by pressure of the mercury. So therefore we can plot the height here, with temperature and it will increase.

So what is happening is that, this site is now proportional to the pressure, the pressure of the gas is now being balanced by the height of the mercury which is there. So therefore by looking at the height calculated from this particular value one can have a measure of temperature. So you see we are not measuring temperature directly, we are measuring temperature from properties of other materials.

So either volume of the gas or length of metal or volume of liquid. So by associating those things, now why the zero-th law is important because it gives us a sense that we can only calculate those quantities, we can only calculate the volume, we can only calculate the length, we can only calculate the material properties. So therefore zero-th law tells us that when those things are in contact with Ice, then it assumes the same temperature as that of Ice.

That's where it becomes very important to understand that, we can associate material properties with the quantity or temperature. So this is by our definition, so thermal equilibrium is the fact but then associating that thermal equilibrium to a value of temperature is our definition. So we define that when the temperature of Ice is 0 degree Centigrade, we define that temperature of boiling water is 100 degrees centigrade.

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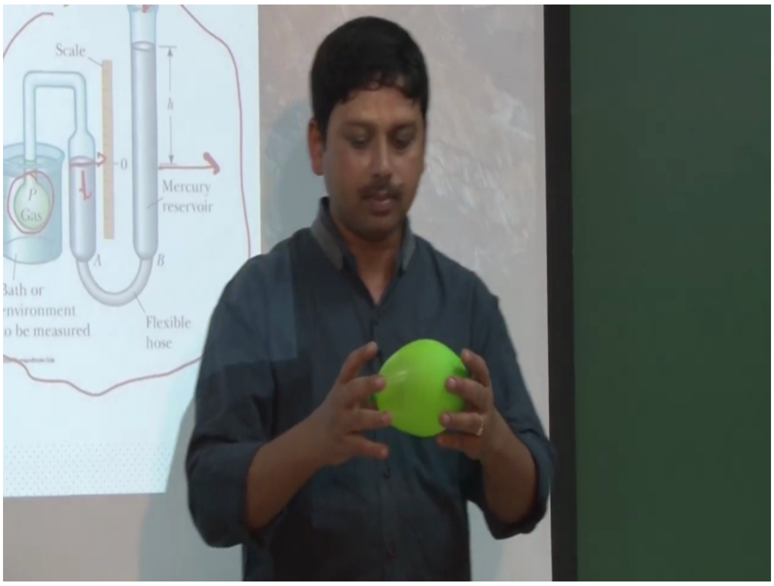

Okay, so we are going to show you the expansion of gas, a small experiment. So this is a balloon. Of course there is air inside that balloon and we are going to heat it up but heating a balloon is, we cannot heat it just by that heater that was there, balloon will burst. So right now you see that the balloon is passing through very easily, now we are going to warm up the gas inside that and for that we are going to use…

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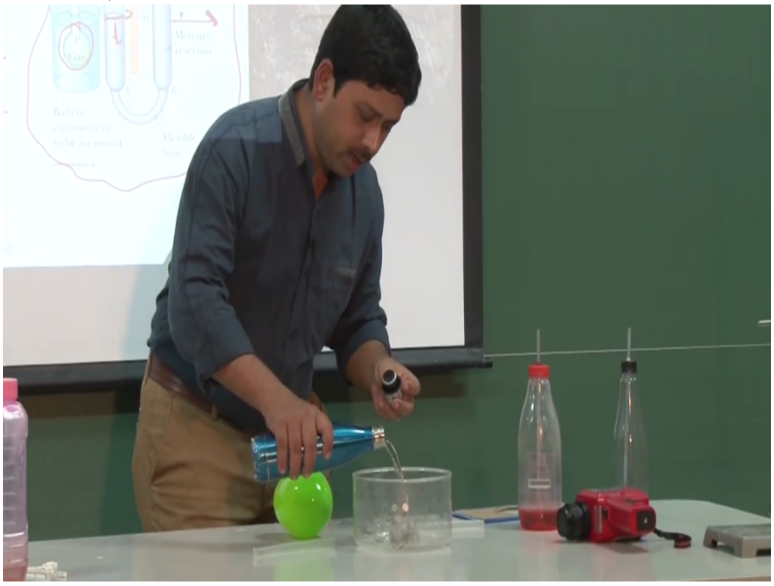

So we are pouring hot water, still not warm enough, okay. So it requires little bit more force. Okay we have to put it for a longer time in order for it to really expand. So all this material properties when they are in contact with other systems, then there will be a thermal equilibration and it will come to same value of temperature. So that's how we define the temperature.

We define the temperature by the fact that we say that, this object has same value of temperature as this object when they are together. So if something is in contact with Ice, we say that it has the same that quantity, temperature as that of the Ice. And that quantity or that temperature is 0 degree Centigrade. So if the zero-th Law would not be there, then we will not be able to define the temperature.

If thermal equilibration is not there irrespective of the material, then if I put a metal on top of Ice or if I put gas on top of Ice they would have different values of those quantities, if zero-th Law did not exist but zero-th Law says that irrespective of, whatever material it is, when it is in contact with the Ice, then it will have same value of temperature, whether it is a gas or a metal or a liquid it does not matter and that gave us temperature as a handle to calculate rest of the things.

You will see that in both 2nd law and 1st law the temperature is very important quantity because we will show that heat does not flow from low-temperature to high-temperature spontaneously. It only flows spontaneously from high to low, so without a definition of temperature we will not be able to discuss any of those quantities.

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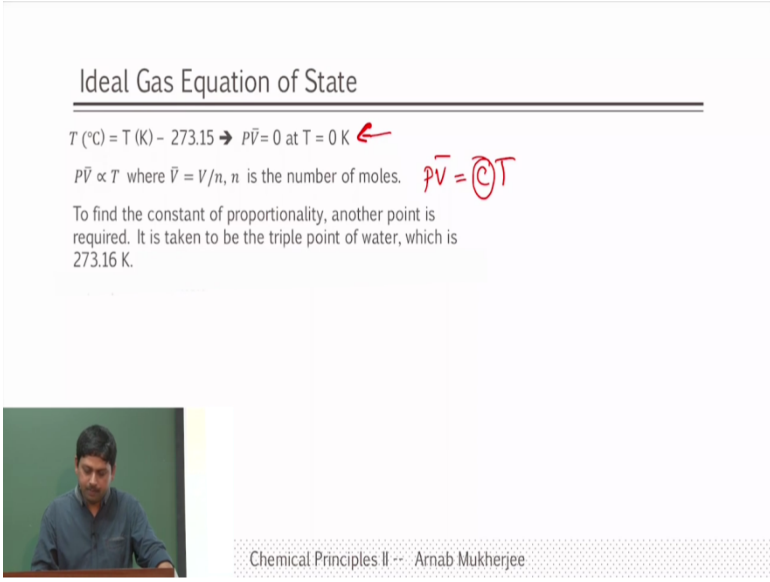

So now we showed that PV for a dilutive gas can be extended to value of zero at minus 273.15 degree centigrade as it is mentioned here and we also see that, PV with temperature is linear, so PV is proportional to T. So we can say that PV is basically CT because it is proportional to T temperature. So now, to find this particular constant of proportionality, we need another point because we already have one point, I'll show you that.

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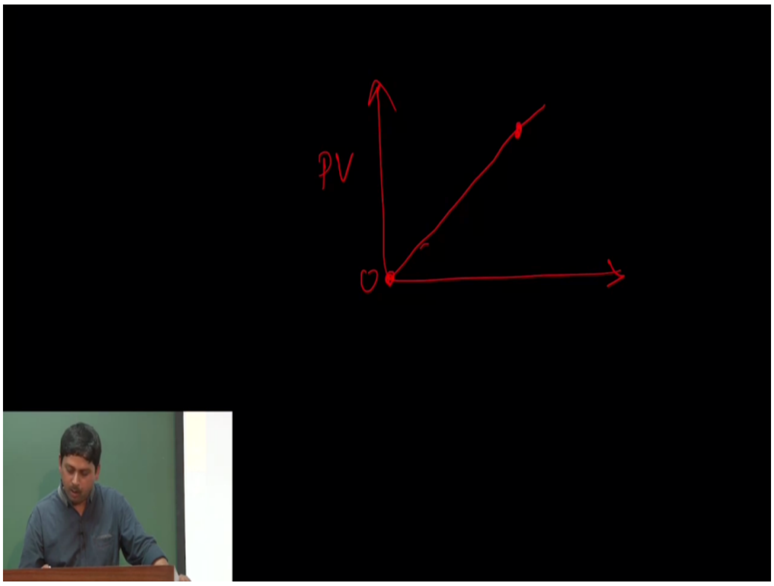

So we are measuring PV and we say that the value is zero at one value but in order to draw a straight line I need another value then only one can draw a straight line, right?

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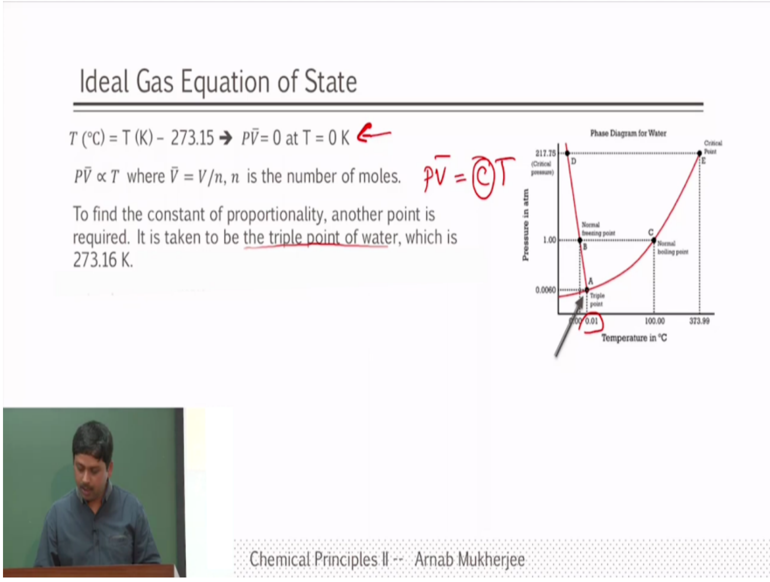

So this particular value is taken to be the triple point, the temperature of the triple point of water. Now what is triple point of water? I will just briefly mention that triple point of water is very specific, extremely specific state of a system where solid, liquid and vapor all 3 phases of water coexist and that point happens to be 0.01 degree Centigrade, 0.006 atmospheric pressure, so at that value all the 3 phases of water coexist.

And since it is very very extremely specific, then scientist always would like to measure it extreme specificity so that things will not change. Now let's say if object is in contact with that particular system in which all 3 phases of water coexist, then that value will be always fixed that 0.01 degree Centigrade. Now in order to have a universal scale, the Kelvin scale was introduced.

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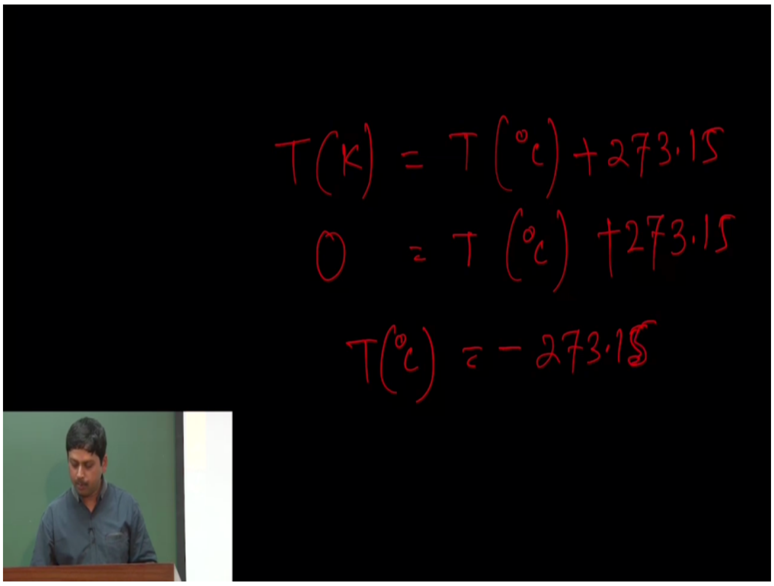

Which says that, temperature at Kelvin is, the temperature for degree centigrade plus 273.15. So at 0 Kelvin temperature at degree centigrade is minus 273.15, so this is the temperature, so this is minus 273.15 degree Centigrade, this particular temperature is called 0 Kelvin and you will see later that this is unachievable. So one cannot really attain 0 Kelvin temperatures.

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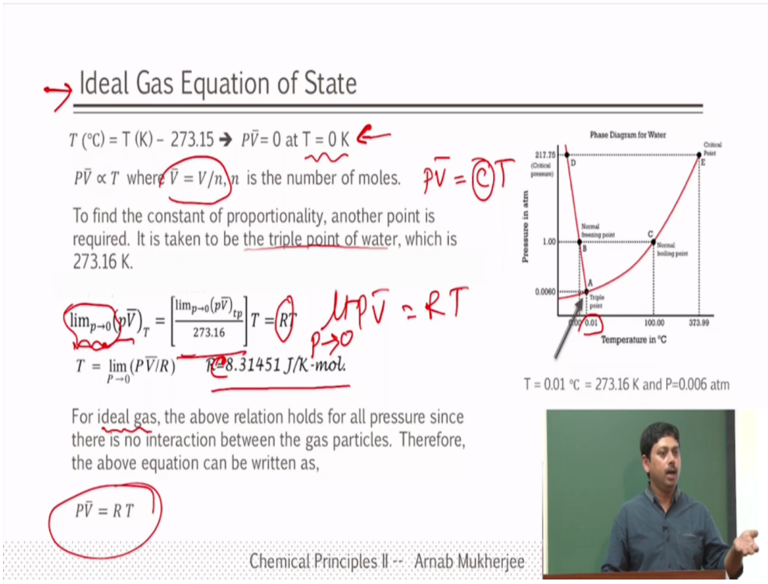

So now we have 2 points one point is, that zero Kelvin or PV is zero and another point is triple point of water. So we can now plot, so limit P tends to 0 indicates a very dilute gas, we are plotting PV is a molar volume V bar, V bar indicates molar volume as mentioned here. Now this is now CT, now C is, whatever the value of PV at triple point divided by 273.16.

So that at 273.16 if you multiply by 273.16, then we will get back this particular quantity. So this C is a ratio of these 2 quantities and it happens to be universal for all gases which is called universal gas constant R. So that's how we now have PV is equal to RT when we take any gas which is dilute. By dilute I mean the pressure is very less. So you see automatically from zero-th law of thermodynamics and from expansion of gas by taking dilute gases we arrived at the equation PV equal to RT.

And V here is molar volume and R has a value of 8.314 Joule per Kelvin mole. Now there is something called ideal gas, which has no interaction among the molecules, which is ideal therefore it's hypothetical system, in which we do not have to worry about dilute gases any more.

Since they don't have, molecules don't have interactions with each other, it does not matter whether pressure is low or not and in that case we don't have to put this particular condition of P tends to 0 and we get PV equal to RT and all of us know that what it means, right? PV equal to RT, that is an equation of ideal gas equation of state. So ideal gas equation of state basically can be an experimental observation by using the real gases at a dilute limit.

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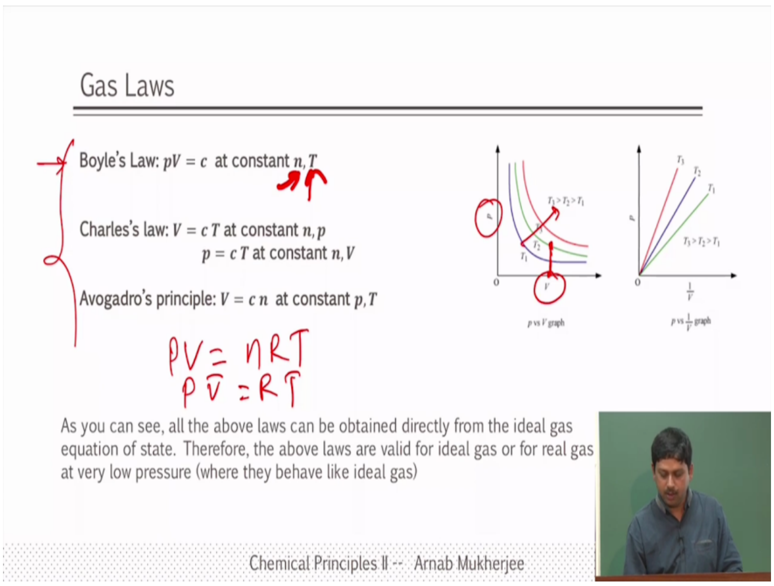

This ideal gas equation of state also can be observed from you know gas laws by Boyle which said that PV equal to constant at constant number of moles and temperature. Charles's law which says that volume is proportional to temperature at constant number of moles and pressure and then Avogadro's principle is that volume is proportional to number of moles.

Now if we put all that together then one can get this particular, again from all these 3 one can get PV equal to nRT or PV bar equal to RT. So you can see in this graph we have plotted P against V and they all form rectangular hyperbola because PV equal to constant and as the temperature is changing then the particular values of P at a particular value of V increases.

So for example at this value as the temperature increases this changes and similarly when you plot P as proportional to P against 1 by V then it is just a linear relation with this. Okay, so here we will stop.