Material and Energy Balance Computations
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Lecture-43
Estimation of Physical Parameters-II

Welcome back and we started our discussion on estimation of physical parameters and in the previous class we talked about the specific heat capacity of gases C p and C v.

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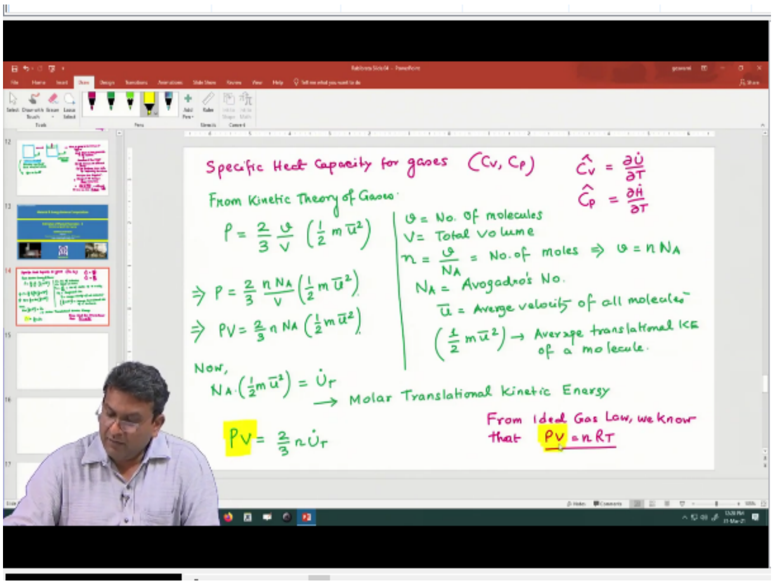

Specific Heat Capacity for gases (C_v, C_p)

$\hat{C_v} = \frac{\partial \dot{U}}{\partial T}$

$\hat{C_p} = \frac{\partial \dot{H}}{\partial T}$

From Kinetic Theory of Gases:

$$P = \frac{2}{3}\frac{\vartheta}{V}\left(\frac{1}{2}m\bar{u}^2\right)$$

ϑ = No. of molecules

V = Total volume

$n = \frac{\vartheta}{N_A}$ = No. of moles $\Rightarrow \vartheta = nN_A$

N_A = Avogadro's No.

$\bar{u}$ = Averge velocity of all molecules

$\left(\frac{1}{2}m\bar{u}^2\right) \rightarrow$ Average translational KE of a molecule.

$$\Rightarrow P = \frac{2}{3}\frac{nN_A}{V}\left(\frac{1}{2}m\bar{u}^2\right)$$

$$\Rightarrow PV = \frac{2}{3}nN_A\left(\frac{1}{2}m\bar{u}^2\right)$$

Now,

$$N_A\cdot\left(\frac{1}{2}m\bar{u}^2\right) = \dot{U}_T$$

$\rightarrow$ Molar Translational Kinetic Energy

$$PV = \frac{2}{3}n\dot{U}_T$$

From Ideal Gas Law, we know that $PV = nRT$

So, now we understand what exactly C v and C p means. So, we all know that it is specific heat under constant volume and constant pressure, but more importantly C_v cap or C_v dot as you can say specific molar heat at constant volume or the rate of interchange of internal energy with temperature. C_v can actually be estimated for an ideal gas from the first principle from essentially the kinetic theory of gases. And therefore many of you know that the value of C_v is 1.5R under certain conditions but I think it is a good idea to know from where you get it. And, you get it from first principle. From kinetic theory of gases, what we have p is pressure of course, v is the number of molecules, V is the total volume and $n = v/N_A$ is the number of moles where of course, N_A is Avogadro's number. u bar is the average velocity of all molecules. Therefore, $(½)m\ \bar{u}^2$ is the average translational kinetic energy of a molecule. For a single molecule why are we using the word average because it is based on the average mean velocity. So, from here what we get is v equal, from here what we get is $v= nN_A$ and therefore this equation you can write as $p = (2/3)(nN_A/V)\{ (½)m\ \bar{u}^2 \}$ or $PV = (2/3)(nN_A)\{ (½)m\ \bar{u}^2 \}$. Now what we can write is $N_A(½)m\ \bar{u}^2 = U_T$ dot which is the molar translational kinetic energy. So, this is for one molecule and you multiply that with the Avogadro's number, so you get the molar translational kinetic energy and if you substitute that in the equation we get PV= 2/3 n U'_T. On the other hand, from ideal gas law we know that PV= nRT.

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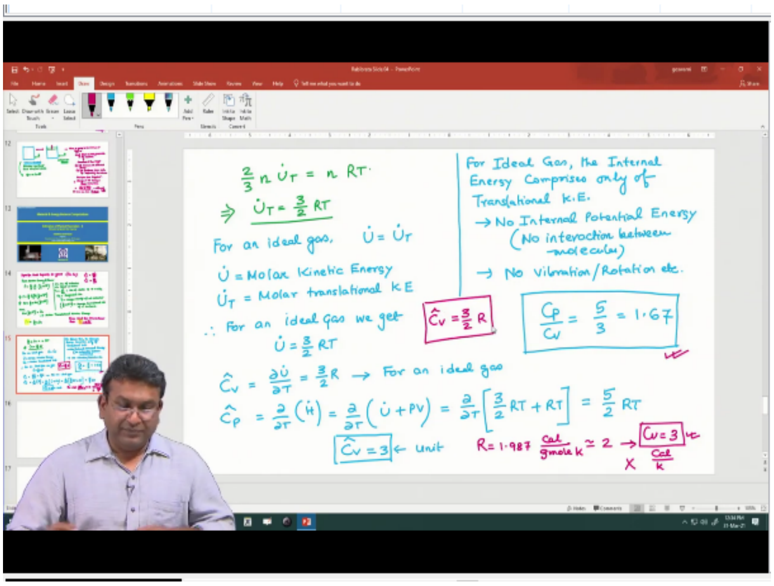

$\frac{2}{3} n \dot{U}_T = n RT$

$\Rightarrow \dot{U}_T = \frac{3}{2} RT$

For an ideal gas, $\dot{U} = \dot{U}_T$

$\dot{U}$ = Molar Kinetic Energy

$\dot{U}_T$ = Molar translational K E

∴ For an ideal gas we get $\dot{U} = \frac{3}{2} RT$

$\boxed{\hat{C}_v = \frac{3}{2} R}$

$\hat{C}_v = \frac{\partial \dot{U}}{\partial T} = \frac{3}{2} R \rightarrow$ For an ideal gas

$\hat{C}_p = \frac{\partial}{\partial T}(\dot{H}) = \frac{\partial}{\partial T}(\dot{U} + PV) = \frac{\partial}{\partial T}\left[\frac{3}{2} RT + RT\right] = \frac{5}{2} RT$

$\boxed{\hat{C}_v = 3} \leftarrow$ unit

$R = 1.987 \frac{cal}{gmole\, K} \simeq 2 \rightarrow \boxed{C_v = 3}$ $\times \frac{cal}{K}$

For Ideal Gas, the Internal Energy Comprises only of Translational K.E.

→ No Internal Potential Energy (No interaction between molecules)

→ No Vibration/Rotation etc.

$\boxed{\frac{C_p}{C_v} = \frac{5}{3} = 1.67}$

So, what we get if we combine the expressions of PV from both the places, 2/3 n U'_T = nRT or U'_T= (3/2)RT. Now what is an ideal gas? If I ask you this question; most of you will give an answer that a gas that follows the ideal gas law is an ideal gas. Well that's fine but a more precise and specific answer particularly now that you understand the components of internal energy is that ideal gas is that gas; for ideal gas the internal energy comprises only of translational kinetic energy.

So, there is no internal potential energy, what does it mean? No interaction between molecules and no intramolecular interactions either. So, no vibration, rotation etcetera. So, in for an ideal gas one can say the internal energy as internal energy as internal energy entirely comprises of internal translational energy therefore what we have a translational kinetic energy for an ideal gas U'_T = U' where u dot is molar kinetic energy.

And let me repeat again U'_T is molar translational kinetic energy, therefore for an ideal gas what we get U'=(3/2)RT and Cv^ = $\partial U'/\partial T$= (3/2)R. And, mono atomic gases are actually closest to ideal gas because their molecules do not have multiple atoms. So, therefore there is no possibility for rotation and vibration that is something you may want to remember.

And what about C_p? so $C_p = \partial/\partial T\{H'\}=\partial/\partial T\{U'+PV\}= \partial/\partial T[(3/2)RT+RT] = (5/2)RT$. So, these are stuff you can calculate from the first principle. These are important things to remember. So, for all other gases other than mono atomic gases C v turns out to be greater than 1.5 R. So, also you may note that some people are writing that C v is 3. Now this is be careful because this comes with an unit, this comes with an unit in the sense that one of the values of R is 1.987 calories per gram mole Kelvin which one can approximate as 2.

Therefore C v is 1.5 into R, from here you get C v = 3, many people loosely use this but then please do remember that this is in calories per Kelvin or calories per Kelvin or whatever because be careful about it. Because when you say C v is 3 that is specific with a unit of R and that is only when R = 1.987 you use that value and approximate that as 2 you get this number 3.

Therefore, be careful about this however this C p by C v = 1.67 is independent of the value of R that you are taking. More I mean people like you should who understand everything should be more comfortable remembering that C v is 1.5 not this T, sorry C v is 1.5 R. That is a far better way of remembering things. So, I hope this one is clear.

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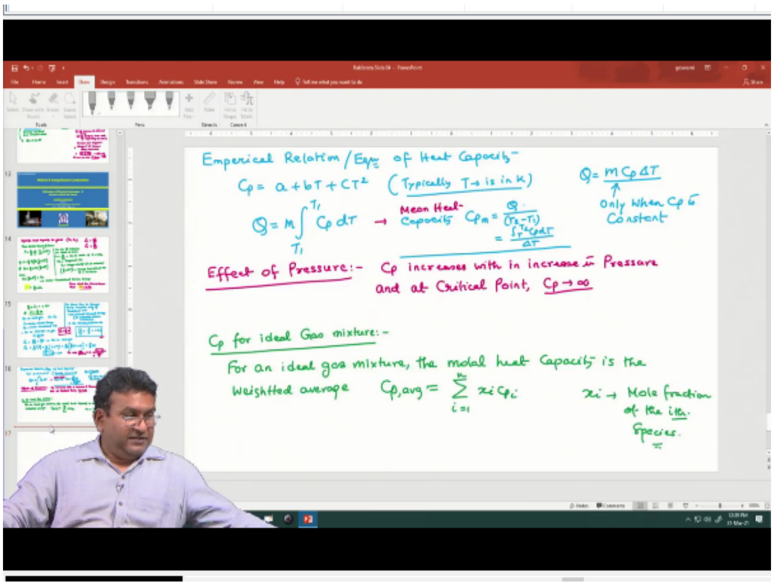

Emperical Relation / Eqn of Heat Capacity

$C_p = a + bT + CT^2$ (Typically T → is in K)

$Q = m\int_{T_1}^{T_1} C_p\,dT$ → Mean Heat Capacity $C_{pm} = \frac{Q}{(T_2-T_1)} = \frac{\int_{T_1}^{T_2} C_p dT}{\Delta T}$

$Q = mC_p\Delta T$ ↑ Only When C_p is Constant

Effect of Pressure:- C_p increases with in increase in Pressure and at Critical Point, $C_p \to \infty$

C_p for ideal Gas mixture:-

For an ideal gas mixture, the molal heat Capacity is the weighted average $C_{p,avg} = \sum_{i=1}^{n} x_i C_{p_i}$

x_i → Mole fraction of the ith. Species.

Now in addition you may also encounter empirical relation or equation of heat capacity which can be of the form like C p = a + b T + c T^2 and typically this is important to note that T is in Kelvin in most cases it is given like that. So, in this case you cannot really do a calculation of $mC_p\Delta T$ straight away. This is valid; this calculation you can do only when $Q= mC_p\Delta T$; only when C_p is constant.

So, in this case if you have a relation of C_p like this then in order to calculate Q you have to essentially do a integral from writing the expression of C_p into dT from T 1 to T 2 and be very careful often the problem will state that you are increasing the temperature from 30 degree centigrade to 70 degree centigrade or something like that but your relation is given in terms of Kelvin.

So, please do care that in that case the integral limits must be converted to Kelvin, otherwise you would not get the appropriate value. so be careful about that. Effect of pressure; so below atmospheric pressure the, it is negligible, above atmospheric pressure C_p increases C_p typically increases with increase in pressure and at critical point I do not know how many of you know this C_p becomes equal to infinity.

Why it happens maybe you can find it out or I will try to address this question in the live interaction session. Now, one can also find out the mean heat capacity if you have an empirical relation like this. So, one can calculate the mean heat capacity but please do remember that mean heat capacity is valid for the temperature range. So, one can find $C_{pm} = Q/(T_2-T_1)$.

The next thing that we should quickly talk about is the C p for ideal gas mixture. Now for an ideal gas mixture what we have the molal heat capacity is essentially the weighted average. So, what you get is $C_{p,avg} = \sum(i = 1 \text{ to } n)\, x_iC_{pi}$ where x_i is mole fraction of the i^{th} species. So, these are simple stuff.

But remember water is a system we repeatedly come back to, remember steam is not an ideal gas and therefore this values of C_p and C_v are not valid for steam. I don’t want to see this mistake in your assignments because many, many people make this mistake by taking steam staking steam as an ideal gas. Now next thing that comes up is the heat capacity of solids.

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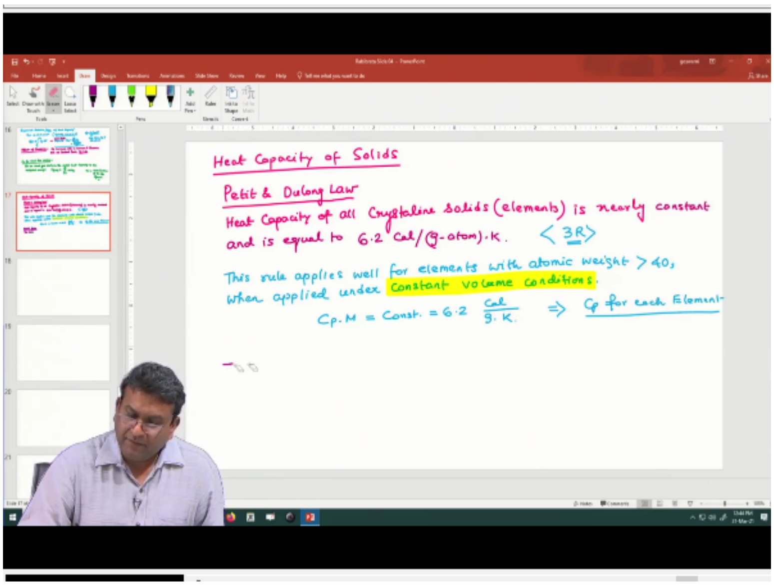

Heat Capacity of Solids

Petit & Dulong Law

Heat Capacity of all Crystaline solids (elements) is nearly constant and is equal to 6.2 Cal/(g-atom).K. < $\underline{3R}$ >

This rule applies well for elements with atomic weight > 40, when applied under constant volume conditions.

$$C_p \cdot M = \text{Const.} = 6.2 \frac{\text{Cal}}{\text{g.K.}} \Rightarrow \underline{C_p \text{ for each Element}}$$

So, we talked about heat capacity of gases. So, now essentially we are talking about heat capacity of solids and it is given by a very reasonable law it is known as the Petit and Dulong law. And, this part of the course is actually a hardcore of engineering nature where as I mentioned previously also we rely on the approach that something is better than nothing. So, we are more interested in having some sort of an approximation rather than having a very precise value.

So, what this law states is heat capacity of all crystalline solids elements I must mention is nearly equal, nearly not only equal, nearly constant right word, you don't have to remember or mug what is Petit Dulong law but you should know that something is nearly constant and is equal to 6.2 calories per gram atom Kelvin. So, this is how it goes. this rule. This let us write down, this rule applies well for elements with atomic weight greater than 40 when applied under constant volume conditions.

So, essentially what it gives is so C p if you are looking at the molar specific heat C p into m. So, what this gram atom means is you just multiply to the molecular weight is equal to constant equal to 6.2 calories per gram Kelvin. So, from here you can get an first estimate about the value of C_p. C_p for each element solid crystalline element you can calculate. Again the value 6.2 if you look at the unit it essentially is nothing but 3 R because I told that R has a value of 1.987 in calorie.

So, this is 3 R, so this is very interesting I mean you know you have noted that C_p is 1.5 R and this also the measurements are done under as it is written under constant volume condition. So, the specific heat for raising the temperature for a solid is higher than that of a gas and it is almost exactly double on a molar basis I hope this is clear to all of you. Next another similar but very useful rule is there which is known as the KOPP rule.

And let me again tell you that you are all interested in physics based courses and the way we have been learning this course is also based on physics and understanding phase diagram, critical point etcetera. According to that these are some semi empirical relations. So, you might get a little disheartened, but do not get discerned these are the engineering stuff you need to do if you are actually in a company or working with new materials.

So, you let us say come up with discover a new material or you find some material in your hand and you need to do some quick calculations, and you have nothing. So, these act as very, very good first approximations. So, what is KOPP rule? The KOPP rule is essentially an extension of Petit petit Dulong law it sort of you can say based on that the heat capacity or let me just use a fresh paper, run out of space in this page.

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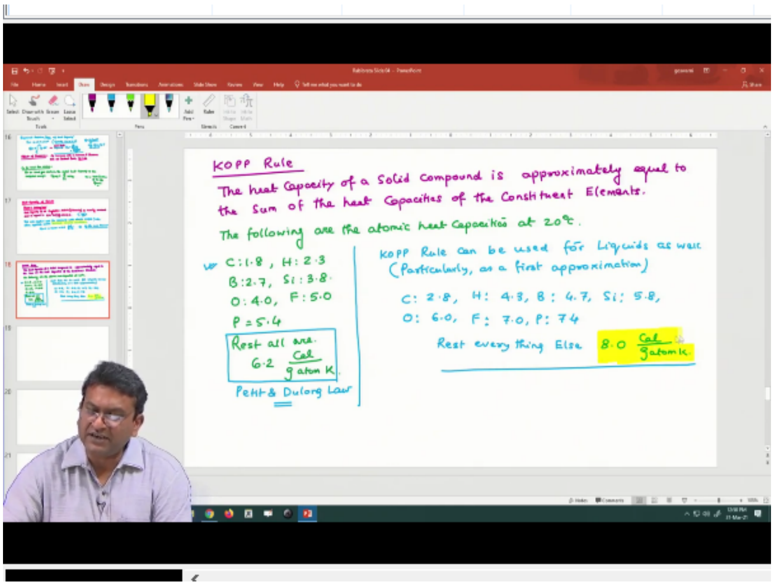

KOPP Rule

The heat Capacity of a Solid Compound is approximately equal to the Sum of the heat Capacities of the Constituent Elements.

The following are the atomic heat Capacities at 20°C.

C: 1.8, H: 2.3
B: 2.7, Si: 3.8
O: 4.0, F: 5.0
P = 5.4

Rest all are. 6.2 $\frac{Cal}{g\ atom\ K}$

Petit & Dulong Law

KOPP Rule can be used for Liquids as well (Particularly, as a first approximation)

C: 2.8, H: 4.3, B: 4.7, Si: 5.8,
O: 6.0, F: 7.0, P: 7.4

Rest every thing Else 8.0 $\frac{Cal}{g\ atom\ K}$

So, KOPP rule; it says the heat capacity of a solid compound is approximately equal to the sum of the heat capacities of the constituent elements and you already know the heat capacity of the constituent elements. So, you know and essentially either from Petite Dulong law or from ideal gas law. So, for example if you have a solid oxide, the heat capacity of the constituent element is that of the oxygen.

So, for here so not exactly like that do not take Cv equal to 1.5 R here are some numbers. So, the following are the atomic heat capacity I am really sorry I withdraw that statement I get corrected the following this particular slide is something you can take note of because this might be very useful in even in a close book examination I never asked to remember the values to the students but again it is important to note that for certain elements there are some unique values and for others everything is governed by Petit Dulong law.

So, here the values are C is 1.8, hydrogen its 2.3, boron is 2.7, silicon is 3.8, oxygen is 4.0, fluorine is 5.0, phosphorus is 5.4 and rest all are 6.2 calorie per gram atom Kelvin. So, there is no point for guessing where this, 6.2 calories from calories per gram atom Kelvin comes from, it comes from the Petit Dulong law and more importantly in the context of Petit Dulong law we talked that it works better for atomic weight greater than 40.

So, these are all elements with atomic weight lower than 40 and you have some specific these are empirical relations I don't remember or know that specific experiments can be done to determine definitely some experiment must have been done you do not bother about it. So, this is what is KOPP's rule. so, as I mentioned. So, firstly the heat capacity is a summation of all the constituent elements, the weighted sum of course and then primarily it is based on Petit Dulong law.

The other interesting footnote I would say or extension is KOPP rule can also be applied can be applied for liquids as well. And, what we have is particularly in absence as a first approximation and what we have again here are some numbers for liquids carbon is 2.8, hydrogen is 4.3. So, you can see these numbers are higher than that for solid, boron is 4.7, silicon is 5.8, oxygen is 6.0, yeah, fluorine is see I am just copying it from my notes. So, there is no point, no marks for guessing them correctly, fluorine is 7.0, phosphorous is 7.4, please also do not bother in certain cases I am using colon certain cases these.

So, let me maintain uniformity and let me make colons for all and rest everything else its 8.0 calories per gram atom Kelvin. So, again it is more like a Petit Dulong type of a relation. Petit Dulong relation is explicitly valid for solids therefore that 6.2 I did not mention about this 8 but what you can find out here that almost for liquid you have some similar relation like the Petit Dulong law which tells you that for most liquids the heat capacity on calories per gram atom Kelvin basis is constant it is equal to 8.0.

So, out of the 5 entities that we need for complete heat transfer calculation what we have mentioned in the previous class there are 3 specific heats and 2 latent heats, out of the 5, 3 we have some gas, so for gas we can calculate the C v for solids, solids and liquids we can calculate the C p or C v or whatever some specific heat.

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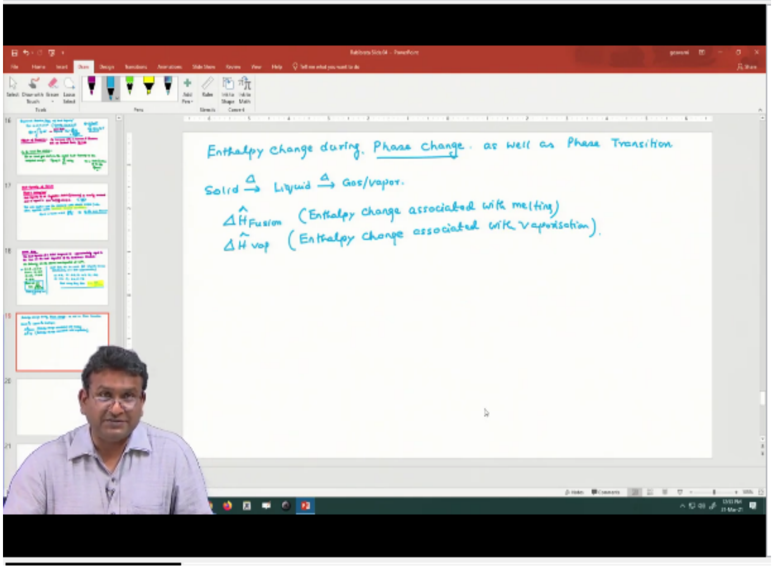

Enthalpy change during Phase Change as well as Phase Transition

$\text{Solid} \xrightarrow{\Delta} \text{Liquid} \xrightarrow{\Delta} \text{Gas/vapor}$.

$\Delta \hat{H}_{Fusion}$ (Enthalpy change associated with melting)

$\Delta \hat{H}_{vap}$ (Enthalpy change associated with vaporisation).

Now, what we are left with so the enthalpy change during phase change and also you must this is also a good point to highlight change as well as phase transition. So, phase change is easy so you have a solid, melt, it melts to liquid you heat further it becomes a vapour or a gas. So, you essentially have the latent heat of fusion that is the enthalpy associated with, enthalpy change associated with melting and we have delta H vapourisation which is the enthalpy change associated with vaporization. So, we are running out of time in this class; so I will stop here and pick up the discussion from here in the next class, thank you very much.