Solid State Chemistry
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Lecture – 05
Review of Week 1 and Practice Problems

So, in the 5th lecture of week 1 which will be the last lecture of week 1; I will briefly review what we learnt in week 1 and then do a few practice questions ok. So, we have we have a Review of Week 1 and Practice Problems which will be the content of week 1 lecture 5.

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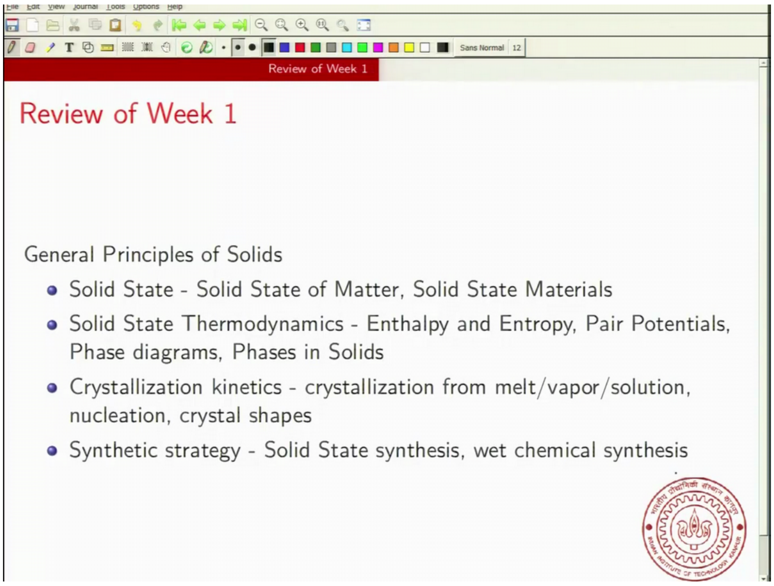

Review of Week 1

General Principles of Solids

- Solid State - Solid State of Matter, Solid State Materials
- Solid State Thermodynamics - Enthalpy and Entropy, Pair Potentials, Phase diagrams, Phases in Solids
- Crystallization kinetics - crystallization from melt/vapor/solution, nucleation, crystal shapes
- Synthetic strategy - Solid State synthesis, wet chemical synthesis

So, first let us review what we learnt in week 1; in week 1 we learnt the general principles of solids. And we started with learning about the solid state of matter and different solid state materials. Then we learnt some very general principles of solid state thermodynamics; how enthalpy and entropy affect the formation of the solid state. We learnt about interaction between atoms or molecules and we learnt about pair potentials very briefly everything. And then we learnt briefly about phase diagrams and we learnt the concept of different phases that can exist in a solid ok.

And then we moved to the kinetics of crystallization and again we saw this very quickly. We saw crystallization from melt, from vapor or from solution and we learnt about nucleation and we briefly saw what gives rise to different shapes of crystals. And then we in the last lecture that was lecture 4; we learnt about the general overall synthetic strategy where you have you can either have solid state synthesis or you can have wet chemical synthesis. And let me emphasize that throughout this week we have just given very short overview of each of these things.

We have not gone in depth in any of these ok; the idea is that you should be aware of these concepts and we are as I said we did not discuss this in great detail ok, but if you want you can learn for example, you can learn a lot about phase diagrams and issues of enthalpy and entropy from standard thermodynamics books. And you know you know we in this course; I will not discuss too much about all these ok, but at least I wanted to give you an overall idea.

Similarly, similarly we discussed very briefly solid state synthesis and wet chemical synthesis, but you know if you take any standard book on solid state chemistry; usually a whole chapter is dedicated to synthesis of solid state materials. And usually lot of different examples are given which showcase the different methods. And again I have not tried to do that; I have not even attempted to do that and rather I have left it to you to I have given you the overall principles. And if you are interested or if you need to learn more of these things you can learn them ok.

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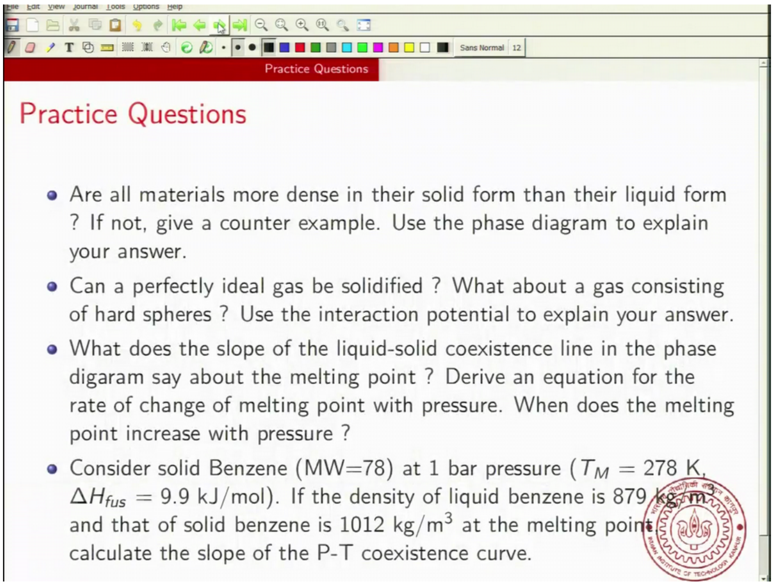

Practice Questions

- Are all materials more dense in their solid form than their liquid form ? If not, give a counter example. Use the phase diagram to explain your answer.
- Can a perfectly ideal gas be solidified ? What about a gas consisting of hard spheres ? Use the interaction potential to explain your answer.
- What does the slope of the liquid-solid coexistence line in the phase digaram say about the melting point ? Derive an equation for the rate of change of melting point with pressure. When does the melting point increase with pressure ?
- Consider solid Benzene (MW=78) at 1 bar pressure ($T_M = 278$ K, $\Delta H_{fus} = 9.9$ kJ/mol). If the density of liquid benzene is 879 kg/m^3 and that of solid benzene is 1012 kg/m^3 at the melting point, calculate the slope of the P-T coexistence curve.

So, now I will do a few practice questions. So, these are general questions that that help you think about the concepts that you have learnt and I will just give a few just four questions here ok. So, the first question is; are all materials more dense in their solid form than their liquid form? If not give a counter example and use the phase diagram to explain your answer ok. So, the; so the basic question is if you take any material then is it more dense when it is in a solid than in a liquid ok; is that always the case that is usually the case, but is that always the case if not give a counter example.

And I also said that you can use a phase diagram to explain your answer and this as this will actually be related to the third question ok. The second question is can a perfectly ideal gas be solidified and what about a gas containing consisting of hard spheres? And then I said use the interaction potential to explain your answer.

The third question is what does the slope of the liquid solid coexistence line in the phase diagrams say about the melting point ok. And derive an equation for the rate of change of melting point with pressure what when does the melting point increase with pressure? The next question and the last question in this in this set of practice problems is this is actually a numerical question where we take solid benzene whose molecular weight is given and it is that 1 bar pressure. The enthalpy of fusion is given and its density of liquid benzene and solid benzene are given at the melting point and you are asked to calculate the slope of the P T coexistence curve.

So let us answer this question. So, the first question are more materials are all materials more dense in their solid form than their liquid form ok.

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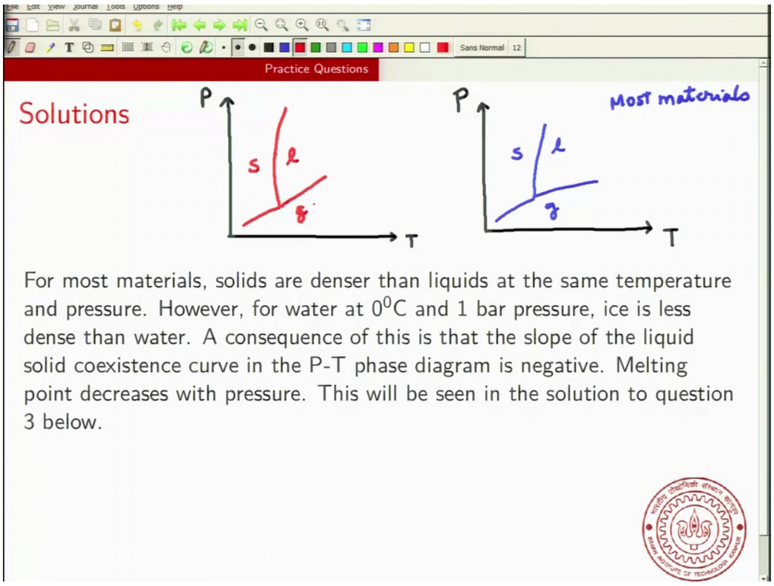

Solutions

For most materials, solids are denser than liquids at the same temperature and pressure. However, for water at 0^0C and 1 bar pressure, ice is less dense than water. A consequence of this is that the slope of the liquid solid coexistence curve in the P-T phase diagram is negative. Melting point decreases with pressure. This will be seen in the solution to question 3 below.

The answer is usually for most materials solids are denser than liquids at the same temperature and pressure; however, for water at 0 degree centigrade and 1 bar pressure ice is less dense than water and you know that because ice floats on water. And consequence of this is that the slope of the liquid solid coexistence line in the P T diagram is negative ok.

So, melting point decreases as you increase the pressure and we will see this in the solution to question 3. So, so what I basically wanted to say is that if you look at the pressure versus temperature phase diagram ah; for most materials you will see that it has, it looks something like this. So, so this is a solid, this is a liquid, this is a gas ok.

Now, for this is for most materials and what I mean is that this line; this line is has a positive slope ok, but for water for water the phase diagram looks a little different. So, it looks like this and then this line actually goes like this; eventually it comes back ok. So, and (Refer Time: 07:00); so the solid liquid. So, the coexistence line of solid and liquid actually has a negative slope. So, so right here right at the melting point the slope is negative alright.

Now, the next question have to do with can a perfectly ideal gas be solidified and question is what about a gas consisting of hard spheres and use the interaction potential to explain your answer.

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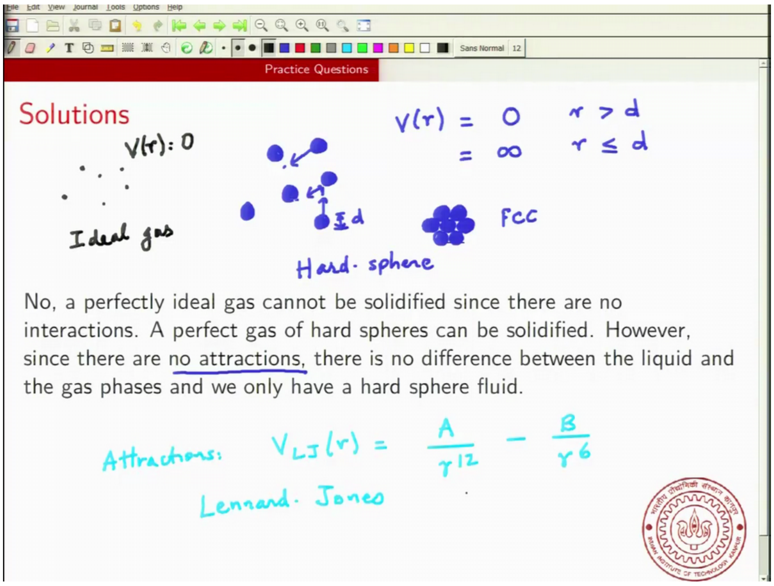

Solutions

$V(r): 0$

Ideal gas

$V(r) = 0 \quad r > d$

$= \infty \quad r \leq d$

$\leq d$

FCC

Hard-sphere

No, a perfectly ideal gas cannot be solidified since there are no interactions. A perfect gas of hard spheres can be solidified. However, since there are no attractions, there is no difference between the liquid and the gas phases and we only have a hard sphere fluid.

Attractions: $V_{LJ}(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$

Lennard-Jones

So the answer is that if you take a perfectly ideal gas, you it cannot be solidified since there are no interactions. Since there are no interactions the particles it does not even make sense to talk about the size of particles ok, but so we just think of particles or point particles and there is this is ideal gas ok. So the so the particles have no size since there are no interactions you can they can go right through one another; one particle does not even see the other particles and it is never possible to completely solidify it.

Now, suppose you take a gas full of hard spheres ok. So, hard spheres are let me show them in this blue color. Now emphasizing that they are to emphasize that they are hard I am showing them as rounded balls; so if you had a gas of hard spheres ok. Now and let us say let us say the size of each of the each of the gas is the same of all the particles are the same. And now what will happen is that this gas does not see the other particle it; it keeps. So, so for example, if one particle is moving this way it does not see this particle ok. So, long as it does not it does not hit it ok, but now if this hits this other particle then it bounces off.

So, if it hits a particle then it bounces off and so the particles actually if they it is unlike particles which attract each other ok. So, its unlike particles which attract each other when they are far apart ok; these particles have no attractive forces they only have the repulsive forces. So, so what we said if you remember the pair correlation function we said that your V of r; the pair correlation pair interaction function not the correlation function.

So, the pair interaction function V of r is equal to 0 if r is greater than d which is the hard sphere diameter; which is a diameter of these spheres. And V equal to infinity if r is less than equal to d ok; its infinity means you cannot crush them, they are hard ok. And in this case it turns out that if you pack them and you can see this I mean you just take a bunch of balls and you push them closer and closer to each other; then you will find that eventually they arranged into an ordered pattern ok.

So, when it is sufficiently dense these will; these will pack into a closed pack pattern ok. I will just they will they will closely pack into essentially an FCC crystal the close packed crystal or an FCC crystal. So, when the density of this hard sphere gas is very low ok; then it will form an FCC crystal ok. What is interesting is that since there is no attractive interaction; since there are no attractions ok, there is no difference between the liquid and the gas phase and we only have a hard sphere fluid.

So, there is; so whether you call this a gas or a liquid this phase where they where it will you have a hard sphere crystal where everything is perfectly order. And then you have a hard sphere fluid where the particles are going around randomly ok. You do not have anything you do not have a solid to a liquid to a gas you just have a solid to a fluid in this case and that is a consequence of the fact that there are no attractions.

So, this V of r does not have any attractive term ok. So, the counter the example of V of r with attractions; so attractions one example is the V Lennard Jones, the Lennard Jones of r ok. So, that has a; A over r to the 12 minus B over r to the 6. So, so there is a term that is attractive; so this second part leads to an attractive interaction ok. So, so attractions are there in something like a Lennard Jones and again I want to emphasize that hard sphere ideal gas ideal gas and Lennard Jones are all are all models ok. So, these are sort of idealized models of real atoms or molecules.

So, an ideal gas the particles do not interact at all V of r is 0; for a hard sphere gas V of r is only repulsive, it is either 0 or infinity it is never negative there is no attractive term. And for a Lennard Jones potential your V of r has both an attractive part and they have both a repulsive part and an attractive part ok.

So, next question let us go to the next question what is the slope of the liquid solid coexistence line in the phase diagram say about the melting point? And derive an equation for the rate of change of melting point with pressure. When does the melting point increase with pressure ok?

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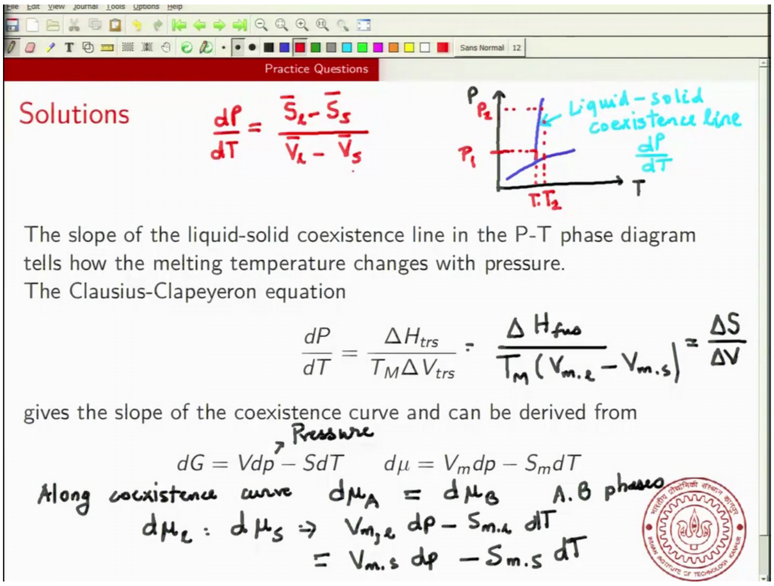

Practice Questions

Solutions

$$\frac{dP}{dT} = \frac{\bar{S}_l - \bar{S}_s}{\bar{V}_l - \bar{V}_s}$$

The slope of the liquid-solid coexistence line in the P-T phase diagram tells how the melting temperature changes with pressure.
The Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_{trs}}{T_M \Delta V_{trs}} = \frac{\Delta H_{fus}}{T_M (V_{m,l} - V_{m,s})} = \frac{\Delta S}{\Delta V}$$

gives the slope of the coexistence curve and can be derived from

$$dG = V\overset{\text{Pressure}}{dp} - SdT \qquad d\mu = V_m dp - S_m dT$$

Along coexistence curve $d\mu_A = d\mu_B$ A.B phases

$$d\mu_l = d\mu_s \Rightarrow V_{m,l}\, dp - S_{m,l}\, dT = V_{m,s}\, dp - S_{m,s}\, dT$$

So, let us quickly see this ok. So, the answer is that and what we are really talking about here is this if you look at this P T; PT phase diagram and you look at any typical materials. So, we are looking at this particular line, this is the liquid solid coexistence line. So, what it means is that along this line if you are at this pressure and temperature; if you are at a pressure and temperature that falls on this line then the liquid and the solid phase will coexist ok.

Now, the question is what is the slope of the coexistence line? So, what we are asking is what is dP by dT along this line ok. So, what is dP by dT along this line ok? So, along this line this line has a certain slope and what is that slope ok. And what this tells us is this actually tells us how the melting point changes with pressure ok. So, why we say that is that if you are; if you ask what is the melting point of the liquid at this pressure at let us say P 1; the melting point is equal to T 1; at P 2 the melting point is equal to T 2 ok.

So, so the slope of this line tells you how the melting point changes as you change the pressure ok. So, and this is given by you can rewrite this relation called the Clausius Clapeyron equation; you might have seen it in your thermodynamics classes. This tells you how this tells you the slope of this coexistence line dT by dP and you can derive that this is delta H; delta H is the change in enthalpy of this transformation from solid to liquid ok, divided by the melting temperature tm times the change in volume of this transformation ok.

And this transformation you can you can just write this as equal to delta H fusion ok; this is the enthalpy of fusion divided by T m times; now this delta V is the volume of liquid minus volume of solid. So, I will just write it as a molar volume of the liquid minus molar volume of the solid ok. So, this is exactly this equation; so the molar volume of the liquid is usually more than that of the solid solid is more dense ok. And you can see from here that in case the solid is less dense than the liquid then this line will be sloped the other way ok. Then the slope of this line will be negative; so it will move in this direction ok; so ok.

And you can derive this relation very easily from this fundamental relation that the change in Gibbs free energy is V times dp minus S times dT. And it should it should be have been a little imprecise this P is same as the pressure the seam same as same as the pressure ok. And if you divide this by the number of number of atoms or molecules number of molecules ok; then the molar you get the molar Gibbs free energy which is nothing, but the chemical potential. So, the d mu can be written an V divided by number of; number of molecules gives you the molar volume dP and S divided by number of molecules gives you the molar entropy times dT.

Now, if you go if you go from one point on the coexistence curve to another point on the coexistence curve ok; then, so ok. Now along the coexistence curve the d mu of phase A should be equal to d mu of phase B ok. So, A and B are two A and B are two phases; so, so if you want to be if you want to be more, if you want to be in this particular case. So, the d mu of the liquid should be equal to d mu of the solid ok.

And so this implies that V m of the liquid times dP minus S m of the liquid times dT ok. This should be equal to V m of the solid times dP minus molar entropy of the solid times dT ok. And you can rearrange this equality equal; you can rearrange this equality to get to get the Clausius Clapeyeron equation ok.

So, when you rearrange this you will first get dP by dT is delta S divided by delta V ok. And then and then you can write the delta S as delta H fusion divided by T m. So, we use we can we will first get delta S divided by delta V this end delta refers to the transformation. So, you can easily derive this Clausius Clapeyeron equation ok. And this is a very useful equation because it tells you the slope of the coexistence curve.

Now, what you notice is that if you take a liquid in a solid ok; so, let me write it here. So, we will just write dP by dT is equal to let me let me write this explicitly. So, let me write S liquid minus S solid and this is a molar and mole and I will put a bar just to indicate molar. So, the molar enthalpy a molar entropy of liquid minus molar entropy of solid divided by the molar volume of the liquid minus molar volume of the solid ok. You can use for molar quantities you can either use a bar or you can use an m. So, in this case I used an m subscript here I am just using a bar.

So, so usually the liquid has a greater entropy than a solid ok. So, the numerator is positive and usually the liquid has a greater molar volume than a solid. So, the denominator is also positive and so the line thus this coexistence line has a positive slope ok.

Now in rare cases like water the density of water is actually greater than that of ice floats on water. So, ice has a smaller molar volume. So, V L for ice is less than V S which is a molar entropy molar volume of ice is actually is greater than that of water ok. So, ice occupies more volume than water and what; that means, is that this denominator becomes negative. And if the denominator becomes negative then this whole quantity dP by dT becomes negative and the coexistence lines has a negative slope ok.

So, so this is a very simple example of how you can understand lot of physical phenomena using this phase diagrams ok. Now let us go to the last question ok; so last question is a numerical question. So, we consider solid benzene molecular weight 78 at 1 bar pressure; melting temperature is 278 K enthalpy of fusion is 9.9 kilo joule per mole.

If the density of liquid benzene is 879 kilogram per meter cube and that of solid benzene is 1012 kilogram per meter cube at the melting point ok; calculate the slope of the P T coexistence curve. And I should I should emphasize this is the slope at the melting point ok. So, again this is a straightforward use of the Clausius Clapeyeron equation; so we can directly go to the solution ok.

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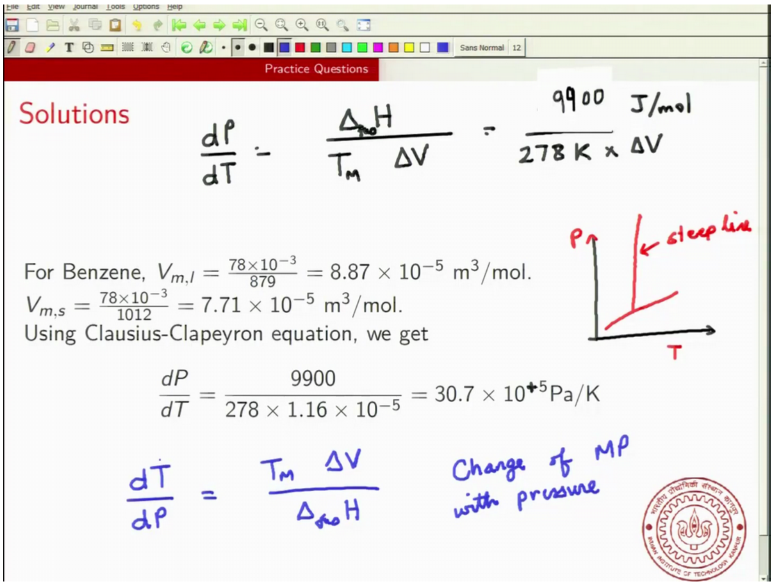

Solutions

$$\frac{dP}{dT} = \frac{\Delta_{fus} H}{T_M \ \Delta V} = \frac{9900 \ \text{J/mol}}{278 \ \text{K} \times \Delta V}$$

For Benzene, $V_{m,l} = \frac{78\times10^{-3}}{879} = 8.87 \times 10^{-5}$ m^3/mol.
$V_{m,s} = \frac{78\times10^{-3}}{1012} = 7.71 \times 10^{-5}$ m^3/mol.
Using Clausius-Clapeyron equation, we get

$$\frac{dP}{dT} = \frac{9900}{278 \times 1.16 \times 10^{-5}} = 30.7 \times 10^{+5} \text{Pa/K}$$

$$\frac{dT}{dP} = \frac{T_M \ \Delta V}{\Delta_{fus} H}$$

Change of MP with pressure

So, we recall the I will just write down the Clausius Clapeyeron equation which is dP by dT is equal to delta H; delta heat of enthalpy of fusion times H divided by the melting temperature times delta V ok.

So, so delta H is already given ok. So, delta H was 9.9 kilo joule per mole ok. So, that is and the melting temperature is also given melting temperature was 278 Kelvin and all you need is to calculate this delta V ok. So, to calculate delta V you need the molar volume of the liquid and the molar volume of the solid.

So, the molar volume of the liquid you can calculate because you can take the molar mass that is 78 divided by the divided by the density that is divided by the density that was given as 879 kilogram per meter cube ok. And this 10 raised to minus 3 is to convert grams to kilograms.

So, the molar mass in grams is 78 into 10 raised to minus 3 in kilograms is 78 into 10 raised to minus 3 kilograms. You divide that by the density ok; you will get the molar volume ok. So, then the molar volume comes out to 8.87 into 10 raised to 5; 10 raised to minus 5 meter cube per mole. Similarly the molar volume of solid benzene there all you have to do is to replace this 879 by 1012 and you get 7.71 into 10 raised to minus 5 meter cube per mole.

And now if you put this in the Clausius Clapeyeron equation ok; then you will get an answer of 30 into 10 raised to minus 5 Pascal per Kelvin 30 into 10 raised to plus 5 actually 10 raised to plus 5 plus 5 Pascal per Kelvin. Now, so you can calculate the slope of the coexistence curve; what is interesting is that if you want to change the melting point by 1 Kelvin ok; then you have to change the pressure by 10 raised to 10 raised to 5 Pascal ok. And that is the reason why if you look at if you look at most phase diagrams ok; the solid solid liquid coexistence line is very steep; it is actually very steep ok.

So, the slope of the solid liquid this is a very steep line ok. Because if you want to just change the melting temperature by a little bit; this is if you just want to change the melting temperature by a little bit you have to change the pressure a lot. Incidentally, I should I should emphasize that if I write this equation backwards if I write this equation upside down ok; then I will get the if I write dT by dP is equal to T m; delta V by delta fusion H ok. This tells you how the melting temperature changes with pressure ok. And this is only you know; so this basically tells you how the melting temperature changes as you change the pressure ok.

So, this gives you change of melting point with pressure ok. And now in the case of in the case of water to ice you can see that as you increase the pressure; the melting point actually decreases. So, usually when you increase the pressure of a solid it is harder to melt it ok. But in the case of ice if you increase the pressure; it is actually easier to melt it ok.

So, in most solids when you increase the pressure it is harder to melt, but in the case of ice when you increase the pressure it is easier to melt. And this is something that you have seen in several experiments ok; you might have done in high school or you might have played with a block of ice. And you might have seen that when you apply pressure it melts and when you release a pressure it sometimes freezes back ok.

So, I hope I have been able to give you some flavor of the basic principles and thermodynamics of solids ok. I have not put any questions from the topics like nucleation or the synthesis part ok. These are descriptive topics and you know you will have some of those questions also in your assignment in your first problem set ok. So, so with this I will conclude week 1 of this course.

Thank you.