Advanced Ceramics for Strategic Applications

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Lecture - 39
Sintering of Ceramics (Contd.)

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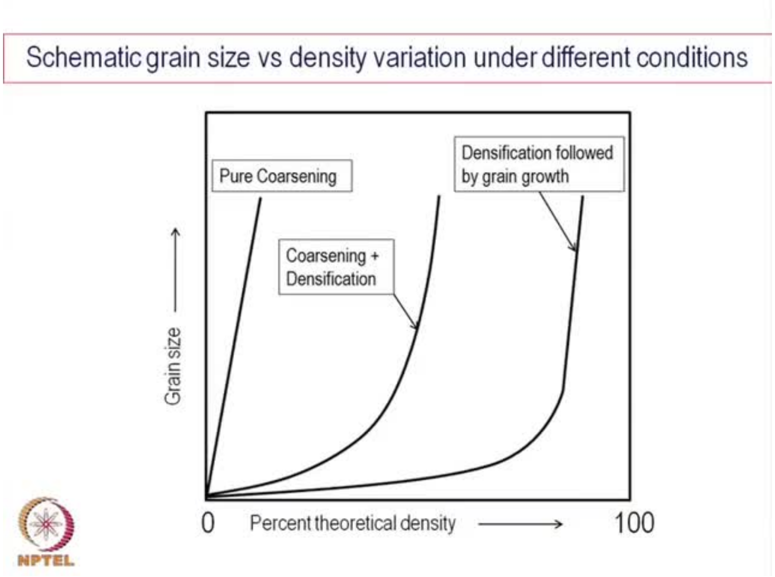

Schematic grain size vs density variation under different conditions

Today we are going to continue our discussion on sintering of ceramics. Earlier will have introduced the subject, we define what is sintering, what we expect out of sintering? And few kind of results or the effect of sintering on the material was discussed. We will continue more of the same discussion and go to other aspects of this particular phenomenon. This particular view graph was presented earlier, where we have plotted the grain size against percent theoretical density, because one of the basic effects of sintering is the increase of density from a porous material. We actually proceed towards a dense material and of course, the idea is to have the theoretical density 100 percent density.

All the pores must be removed, but it does not does not take place just like that. It is also associated with many other effects, one of them of course, the grain size. The starting particle size is finer and as we sinter or densified more and more the grain size also start increasing. However, it is not a uniform increase depending on the situation there maybe three different cases, which has been presented here. One is as we discussed earlier is the pure coarsening. Coarsening of the initial particles. So, there the grain size increases very fast without changing without much change in the theoretical density. So, if the initially the finite particle get coarsen by some process, we will discuss how exactly they can do.

Then the grain size increases quite fast without increasing the theoretical density. The other extreme is on this site, that is the densification initially proceeds without much change of the end size. Then towards the end very close to the theoretical density 100 percent theoretical density, there is a sudden change in grain size. So, this is densification followed by grain growth. So, initially densification takes place then the grain growth takes place. Here without densification the grain growth takes place. So, pure coarsening and this thing, this situation is somewhere in between this were both coarsening and densification proceeds more or less simultaneously.

So, depending on the experimental condition, depending on the starting sizes are starting size of the powders, their properties, there surface properties and so on such situations may arise. We have to understand, why it is taking place? Why this is happening and accordingly takes corrective measures. So, however necessary, so these are the two extreme case and this is somewhere intermediate and depending on the situation depending our goal we can control these properties or control this behavior to a large extent.

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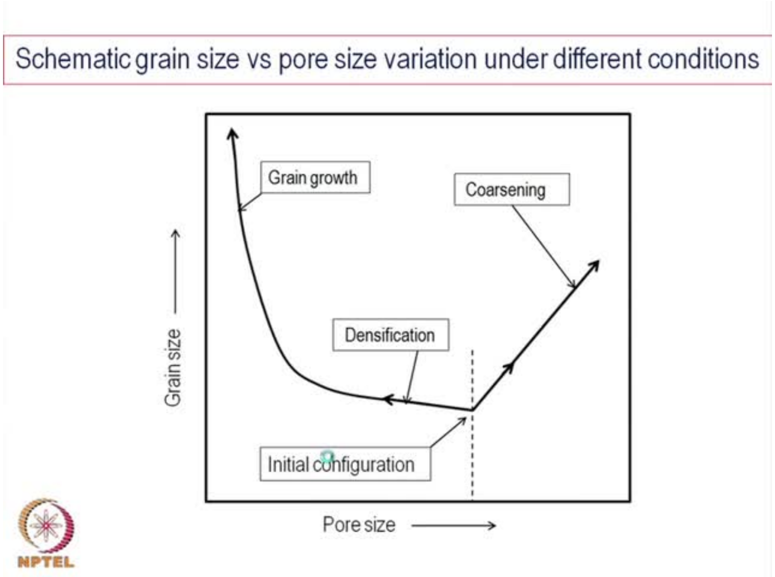

Schematic grain size vs pore size variation under different conditions

This is another situation or the phenomena can be described in the slightly different way here, we have plotted once again grain size versus pore size not the theoretical density, which ever plotted earlier. But here it is grain size again plotted on the vertical axis on the horizontal axis is the pore size because theoretical density increase of theoretical density is also a actual reduction of the pore size or pore volume. So, here this is our starting situation or starting condition, where this is the initial configuration where somewhere this is a pore size here and the grain size there.

So, initially when a compact is made particles are consolidated by some technique what will call the green compact before firing and that green compact as a green density. Also depending on that density the pore size will also there depending on the particle size. Then as we proceed the sintering the particles gets with each other and wants some grains. So, if the pore size is increasing, then this is a situation where the pore size is increasing and grain size is also increasing. From here we are increasing the grain size and the pore size is also increasing and this is what happens? There is a relationship between the coarsening of the particle earlier will have seen when the grain size sorry, we go to the earlier slight.

This is coarsening and that is what happens, this has been plotted in a slightly different way, not in the terms of theoretical density, but pore size. So, when coarsening takes place this happens. Pore size increases grain size also increases more or less in a linear fashion whereas, if there is a densification and then grain growth here, then the pore size actually reduces pore size do not increase. So, pore size because our purpose is not to increase the pore size in is actually decrease the pore size. So, by sintering our aim is our objective is to decrease pore size and has a result get densification and as we decrease more and more the pore size towards the end.

There will be a grain growth, so from this, this is not a preferred situation. This is not a preferred situation where pore size also increasing and there is a grain size is also increasing and which results from the particle course in initial particle coarsening, which is not a very desired situation whereas, more desirable situation is this one, where the pore size is increasing and consequently there is a densification. Then towards the end there is a grain growth and the pore size becomes finer and finer. So, you have a correlation between pore size and grain size as well as grain size and theoretical density, what we have discussed earlier. So, our objective is to avoid this coarsening, coarsening of the particles before it gets actually centre.

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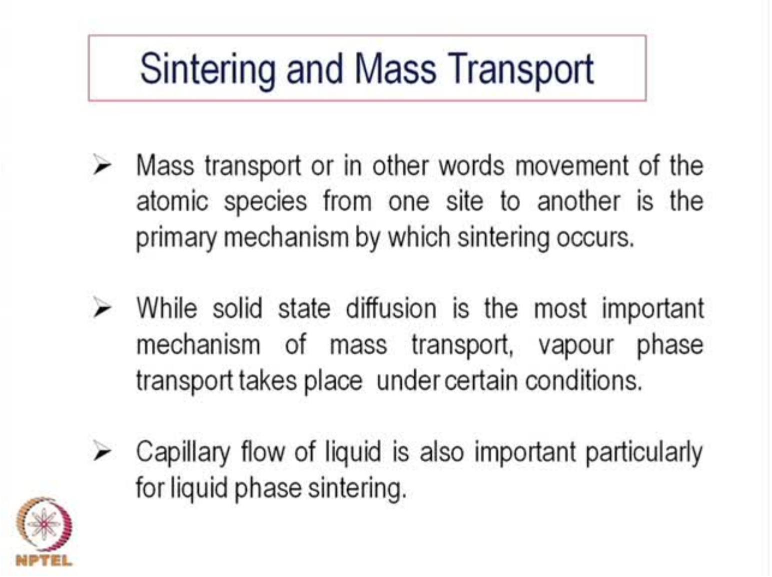

Sintering and Mass Transport

- Mass transport or in other words movement of the atomic species from one site to another is the primary mechanism by which sintering occurs.
- While solid state diffusion is the most important mechanism of mass transport, vapour phase transport takes place under certain conditions.
- Capillary flow of liquid is also important particularly for liquid phase sintering.

Well what is really happening when you are sintering a product or sintering a ceramic material? The main thing what is happening is a mass transport. Sintering is the result of a mass transport in an atomistic level. So, the mass transport and sintering has a very, very direct correlation and mass transport, or in other words the movement of the atomic species from one site to another is the primary mechanism by which the sintering occurs. So, sintering means actually there is mass transport at the atomistic level and a very micro level.

So, while solid state diffusion is the most important mechanism of mass transport well there are different mechanisms of mass transport or we might have discussed in other courses. In this course we have not discussed in detail what are the mechanism of mass transport. I am sure diffusion is known to everybody, so the solid-state diffusion is the most important mechanism of mass transport. However there are other mechanisms also, it is a vapour phase transport can also take place. That means the material is getting transported from one site to another through a vapour phase diffusion.

Of course, as we mention diffusion is one the very most common and important mechanism mass transport were the atom by atom movement is taking place in the structure, in the crystallographic structure or the assembly of atoms. The other possibility is the vapour phase, which means from the surface the materials gets evaporated to the vapour phase and then gets deposited somewhere. So, it may be within that material or it may be outside the material. So, it is kind of an evaporation, evaporation and condensation, one can say.

The condensation can take place at some other site of the same material or same piece of substance or the condensation can take place at a some other place on a other substrates, which is actually the phenomena takes place in thin film, thin film depositing by evaporation or physical hyper deposition. There is an another technique or mechanism by which mass transport can also take place. The capillary flow of liquid, in case of a liquid the because of the surface tension force and the capillary action the liquid can move from one place to the other and that also is a form of mass transport. So, capillary flow of liquid is also an important particular important particularly for liquid phase sintering. Earlier we have discussed the solid state sintering and liquid phase sintering.

So, if you in solid state sintering these are the two mechanisms, which are more important, diffusion mechanism of course, we will see later on that the diffusion mechanism also have different variants, different types of diffusion, different parts of diffusion are possible. In addition to diffusion in the solid state sintering or solid state mass transport you have evaporation and condensation whereas, in a liquid phase the liquid moves by normally by a capillary flow technique or viscous flow technique or viscous flow magnesium. So, will discuss those things also, what this particular slide means or conveys that. There is a strong or a very important correlation between sintering and mass transport in fact sintering is the result of mass transport at the atomistic level.

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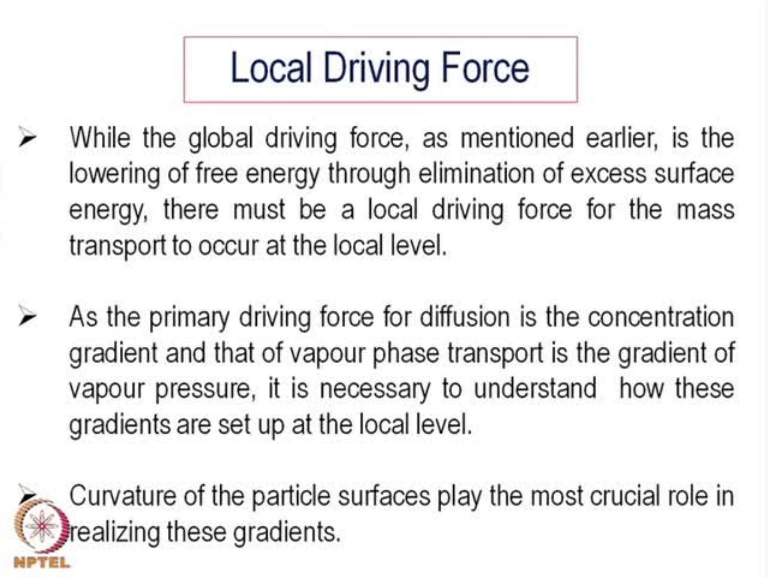

Local Driving Force

- While the global driving force, as mentioned earlier, is the lowering of free energy through elimination of excess surface energy, there must be a local driving force for the mass transport to occur at the local level.
- As the primary driving force for diffusion is the concentration gradient and that of vapour phase transport is the gradient of vapour pressure, it is necessary to understand how these gradients are set up at the local level.
- Curvature of the particle surfaces play the most crucial role in realizing these gradients.

Now, whenever there is a mass transport and the atomistic level, there must be a driving force. Why the mass or the material must move from one place to the another place or on the site? There has to be certain driving force, we have a earlier discussed that sintering takes place because of the, there is a global driving force that is because of the, that is the change of surface energy to the surface area changes and therefore, the additional energy due to the surface energy decreases. Therefore, there is driving force and the surface energy is the major change of surface energy is the major driving force in the overall or global level.

Also, we just now discussed that that surface energy change is actually realized by mass transport phenomena and so there a mass transport there will be again another driving, driving force at the atomistic level and that is we are called local driving force. Well the global driving force as mentioned earlier is the lowering of the free energy through elimination of the excess surface energy, there must be a local driving force for the mass transport to occur at the local level as a preliminary driving force for diffusion is the concentration gradient and that for the not preliminary primary, sorry as the primary driving force for the diffusion is the concentration gradient. That of the vapour phase, vapour phase transport is a gradient of the vapour pressure, it is necessary to understand, how this gradients are set up at the local level. So, because diffusion is basically requires a concentration gradient.

So, that is the fix first and second law says that until unless there is a concentration gradient diffusion cannot take place. We have, we are attaining that the diffusion is one of the primary cause or mechanisms by sintering takes place. So, there must be a concentration gradient setup at the local level or at the atomistic level or if you are talking about vapour phase transport, then there must be a difference in the vapour pressure at one at different sites.

So, that the vapours can move from one point to the other or the material can move from one point to the other. So, you have to understand, how this concentration gradients or vapour pressure gradients are getting realized at the local level at the atomistic level? In this context curvature of the particle surface play most important, important at the crucial role in realizing this gradients, because what by sintering what we mean, we have the way we have defined sintering is the agglomeration or the is the agglomeration of certain particles, which when heated or provided the activation energy by heating it to higher temperature.

They just with each other and forms a strong bond. So, there is no other in, we are not creating any concentration gradient by from outside. So, if there is a only some particles and just the conglomeration of these particles generates some amount of certain type of concentration gradient or the vapour pressure gradient. So, the reason is the curvature itself, the particles having different curvature different sizes of the particles will have a different curvatures and at different sites. They have a different nature of a curvature and it appears that this curvature itself plays the role, plays the most important or most crucial role in realizing these gradients. So, that is what we have to understand, how this curvature becomes so important in setting up this kind of vapour pressure gradient or even concentration gradients? So, that will be our discussion in the next few minutes.

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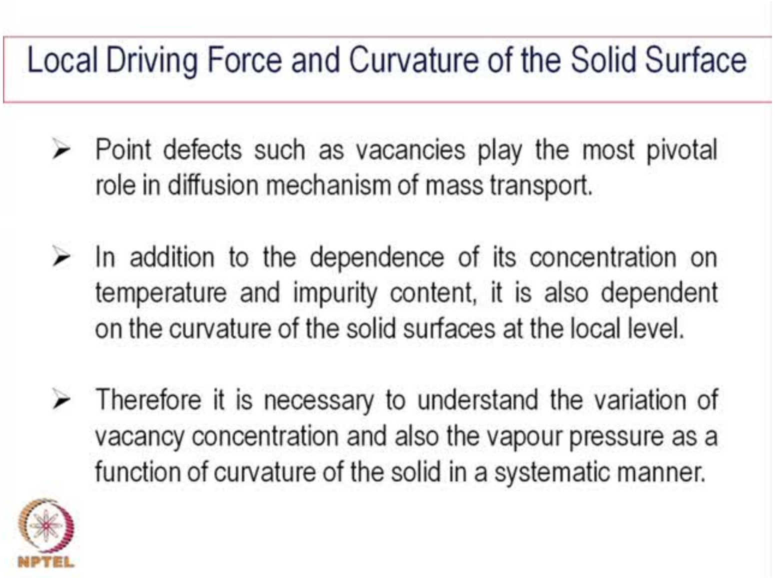

Local Driving Force and Curvature of the Solid Surface

- Point defects such as vacancies play the most pivotal role in diffusion mechanism of mass transport.
- In addition to the dependence of its concentration on temperature and impurity content, it is also dependent on the curvature of the solid surfaces at the local level.
- Therefore it is necessary to understand the variation of vacancy concentration and also the vapour pressure as a function of curvature of the solid in a systematic manner.

So, the local driving force and curvature of the solid surface that is what we like to discuss or understand point defects such as vacancy play the most pivotal role in diffusion mechanism of mass transport. Diffusion takes place or diffusion arises takes place in the in a solid primarily by point defects by the presence of point defects and vacancy is one of the more most important point defects, which causes material transport or mass transport in a material. So, there is a vacancy mechanism of diffusion. So, if the diffusion has to take place, can we expect a vacancy gradient? So, that is what is our objective now.

In addition to the dependents of its concentration on the temperature and impurity content, it is also dependent on the curvature of the solid surfaces at the local level. We know from our discussion of point defects, the point defects are created at a higher temperature because, we provide at higher temperature a activation energy is provided for the creation of this defects. These defects are thermodynamically thermodynamic species and creation of defects lowers the free energy of the system. Therefore, there is temperature dependence and an exponential temperature dependence.

So, defects are certainly created by increasing the temperature that is one way of introducing some defects. In addition, if you add impurities to that we have also seen in earlier lectures that by adding certain impurities of different valance one can also create vacancies by a because of the charge neutrality requirement. So, these are the two known parameters by which one can generate vacancies. However, in this case in currently what we are will look that the change of curvature also sets up a vacancy concentration.

So, the concentration of the vacancy is not same throughout the surface, if the there is a change in curvature of the surface the concentration also changes, particularly of the vacancies. Therefore, it is necessary to understand the variation of the vacancy concentration and also the vapour pressure contents. These are the two terms we are basically looking at; one is the vacancy concentration, how it changes to the curvature and other is the vapour pressure of the material is it a function of a curvature that is also is our interest.

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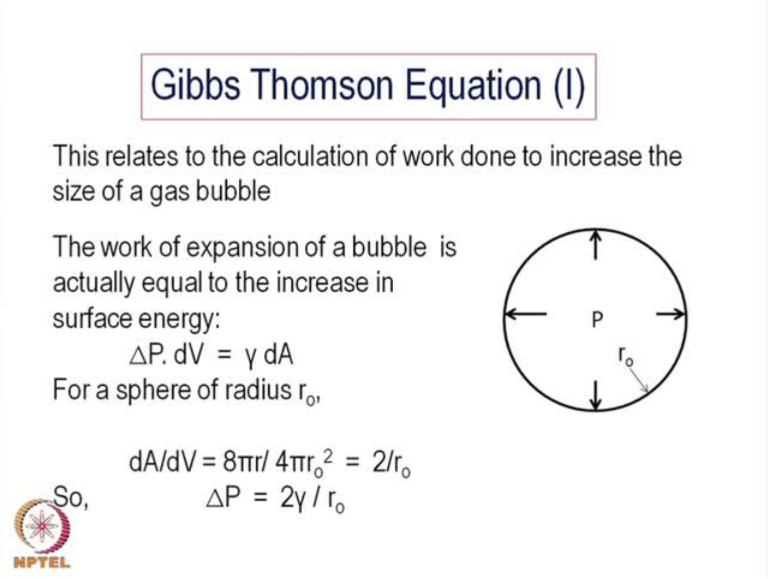

Gibbs Thomson Equation (I)

This relates to the calculation of work done to increase the size of a gas bubble

The work of expansion of a bubble is actually equal to the increase in surface energy:

$$\Delta P. dV = \gamma dA$$

For a sphere of radius r_o,

$$dA/dV = 8\pi r / 4\pi r_o^2 = 2/r_o$$

So, $\Delta P = 2\gamma / r_o$

Now, if you want to understand this, we have to look at a something slightly different from analogous situation where let us say this is what we call the Gibbs Thonson equation. T t actually relates the calculation of work done to increase the size of the gas bubble. In fact it is a basically how the gas bubbles are created? For example, soap bubbles or in it grows under certain situations, it collapses under certain situation. So, from that one can find out what will be the energy required and is there any difference between the energies of the two different surfaces having two different radius of curvature.

So, that is what we will see here. The work this is a gas bubble which is this is a surface of the gas bubble a film, basically a film which is trying to grow because there is a pressure. So there is a pressure generated because of the pressure generated it is giving a isostatic or isostatic pressure in all directions and the bubble is growing. This work, this pressure is creatingor making some work done. So, the work of expansion of the bubble is actually equal to the increase in the surface energy. So, the work done is against the surface tension forces. So, that must be equal the energy surface energy and the work done must be equated. So, in this form, if one can do the delta P is the difference in pressure and d V is the change in volume and gamma is the surface energy and d A is the change in area.

So, this is per unit area, so the change in area. So, this is the work doneby the surface energy term and this is the work done by the pressure difference, so that must be two be equated. For a sphere of radius r 0, if this is a sphere of radius r 0 d A d V equal to one can calculate from geometric that 8 pi r by 4 pi r r 0 square that should be r 0, that should be r 0 not r. r 0 square, so it will become 2 by r 0, 2 by r 0. So, d delta P will be equal 2 gamma by r 0. So, that is how from this equation. So, that is one relationship between the pressure required to increase or in put in equilibrium at at what size or what r 0 will be that will be determine by the surface energy term as well as the pressure term.

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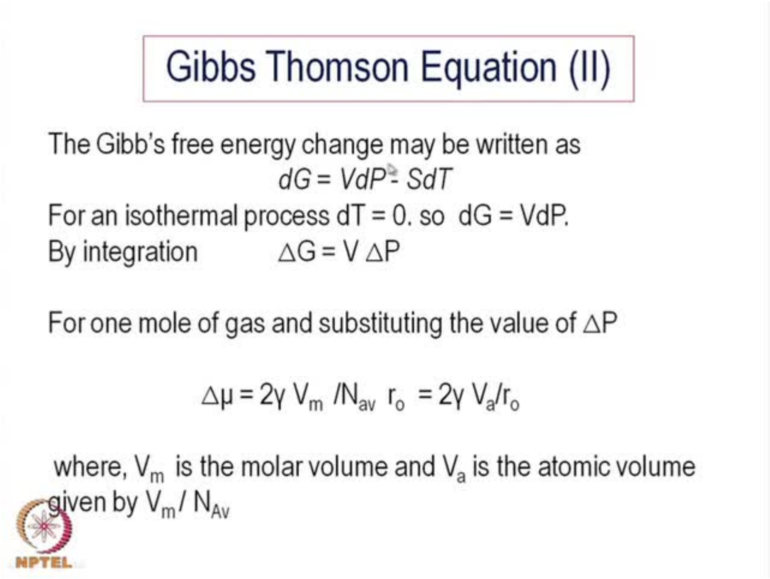

Gibbs Thomson Equation (II)

The Gibb's free energy change may be written as

$$dG = VdP - SdT$$

For an isothermal process $dT = 0$. so $dG = VdP$.

By integration $\Delta G = V \Delta P$

For one mole of gas and substituting the value of ΔP

$$\Delta\mu = 2\gamma V_m / N_{av}\ r_o = 2\gamma V_a / r_o$$

where, V_m is the molar volume and V_a is the atomic volume given by V_m / N_{Av}

To continue that, the Gibbs free energy change may be written as this is a very simple question or everybody knows d G is equal to V d P S d T, S is entropic term, T is the temperature, this is the pressure and this is the volume. So, the change in and Gibbs free energy is given by this. For an isothermal situation d T equal to 0, so d G will be equal to V d P and by integration one can find the delta G is actually V delta P. For 1 molecule 1 mole of gas and substituting the value of delta P, one gets delta mu.

Delta mu is the change in chemical potential, mu is here the chemical potential. So, one can get 2 gamma V m by a n a number into r 0 equal 2 gamma V a by r 0, while V m is the molar volume, V m is the molar volume, volume of one mole of gas, a one mole of material. V a is the atomic volume, so that it is given by V m by number V m by V n this becomes actually V a that is what has been substituted here. So, the delta mu term the change of chemical potential is actually related to the surface energy and of course, the atomic volume and the size of the sphere, size of the sphere of that gas bubble.

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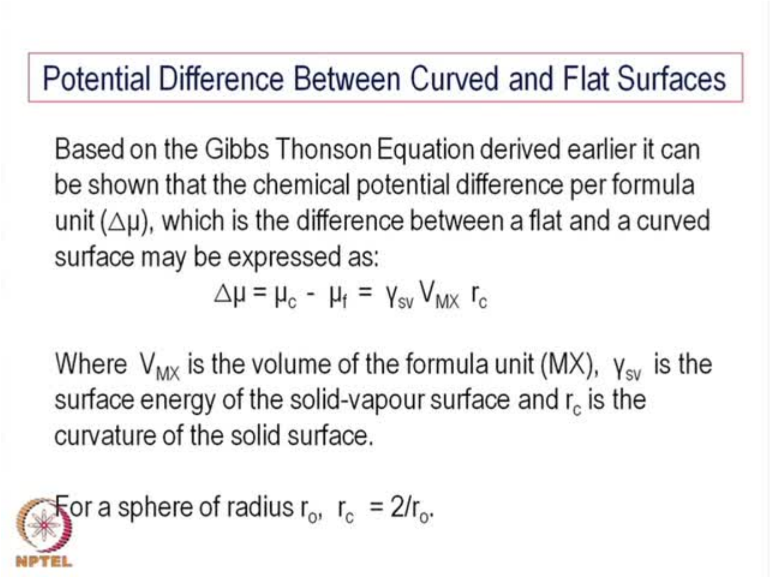

Potential Difference Between Curved and Flat Surfaces

Based on the Gibbs Thonson Equation derived earlier it can be shown that the chemical potential difference per formula unit ($\Delta\mu$), which is the difference between a flat and a curved surface may be expressed as:

$$\Delta\mu = \mu_c - \mu_f = \gamma_{sv} V_{MX} r_c$$

Where V_{MX} is the volume of the formula unit (MX), γ_{sv} is the surface energy of the solid-vapour surface and r_c is the curvature of the solid surface.

For a sphere of radius r_o, $r_c = 2/r_o$.

So, based on this Gibbs Thonson equation, which has been just derived, it can be shown that the chemical potential difference for formula unit that is what has been done earlier. The delta mu that is the chemical potential difference, which is the difference between a flat and a curved surface may be expressed as delta mu between a curved surface and a flat surface. So, this is mu c is that of a potential of a curved surface and mu f is of a flat surface. That gives the difference is delta mu equal to gamma S V now. S V solid to vapour the solid to vapour surface tension surface energy and then V M X and r c, r c is the radius of curvature not the radius of the sphere.

But it is termed radius of curvature and there is of course, a relationship between the radius radius of this sphere and that of the r c. So, r c is equal 2 by r 0 that is a again from the geometry one can find that. So, the there is a difference in potential between the curved surface and the flat surface and that can be expressed in terms of the surface energy between the volume and the within solid and vapour in this case. So, we are not talking about the gas bubble here we are actually talking about two surfaces, two surfaces of the solid two surface of a solid where, one is a curved surface. It may be concave, it maybe convex and another is a flat surface and that depends on the surface energy term between that solid and the vapour and the adjoining vapour. So, that we have introduced earlier also.

The gamma is V and V M X here we are talking about a material called or of the form M X, M in the metal X is another anion, so it maybe an oxide. So, it maybe a M O also. Whatever is the compound it is not an element now, we are talking about a compound. Compound of the form M X and this V X is the volume of the formula unit, one formula unit whatever the volume is. Then r c is the curvature of the solid surface, so from that Gibbs Thonson equation, we find out that there is a difference in potential chemical potential between these two surfaces. So, this is the relationship between the radius of curvature and the radius of the sphere.

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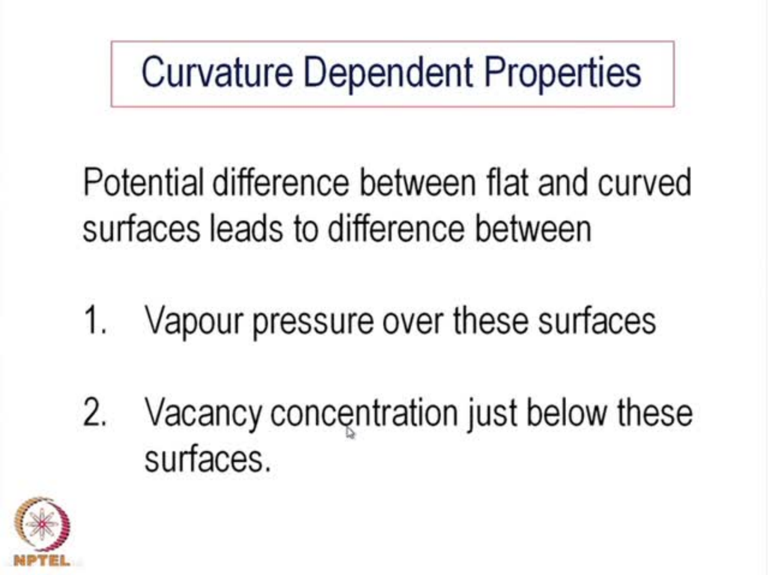

Curvature Dependent Properties

Potential difference between flat and curved surfaces leads to difference between

1. Vapour pressure over these surfaces
2. Vacancy concentration just below these surfaces.

Now, what are the different parameters, which depend on the curvature of the solid surface? These are the two most important parameters which depend on them the potential difference between flat and curved surfaces, lead to difference between these two parameters; one is the vapour pressure over these surfaces and the vacancy concentration just below these surfaces. So, if you have a a surface, a curved surface either a convex or concave that will have a different vapour pressure than the a flat surface, which can be taken as the reference.

So, between a flat surface and the curved surface, there is a chemical potential difference and that also leads to a vapour pressure difference and the vacancy concentration just below the surfaces. Also because on the surface there is the, we cannot consider a vacancy to be on the surface vacancies are within the solid a vacancy phase. In fact coming to the surface it gets an hailated. So, the vacancies just below the surface also changes, its concentration changes depending on whether it is in the flat surface or the curved surface.

So, these are the two most important observation from the earlier consideration that is the Gibbs thonson equation and consequently chemical potential. So, because there is a chemical potential difference between the curved and the flat surface, consequently there will be vapour pressure difference and also there will be vacancy difference vacancy concentration difference.

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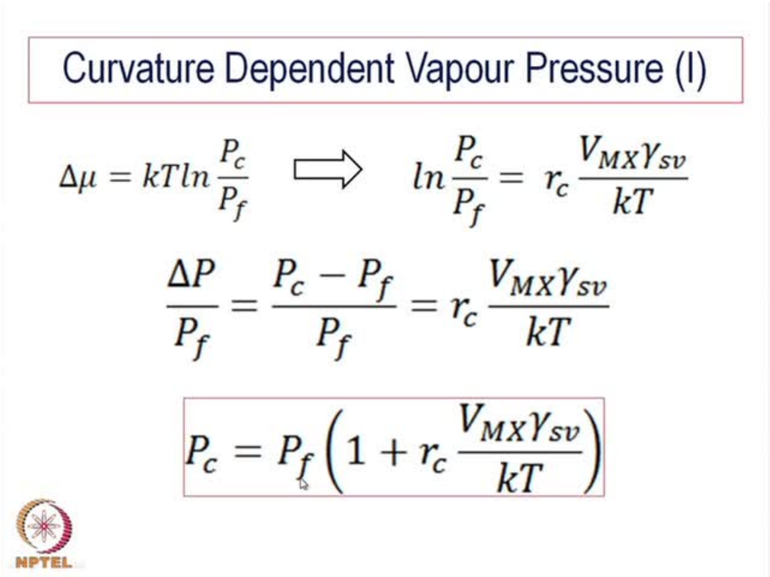

Curvature Dependent Vapour Pressure (I)

$$\Delta\mu = kT ln\frac{P_c}{P_f} \Rightarrow ln\frac{P_c}{P_f} = r_c\frac{V_{MX}\gamma_{sv}}{kT}$$

$$\frac{\Delta P}{P_f} = \frac{P_c - P_f}{P_f} = r_c\frac{V_{MX}\gamma_{sv}}{kT}$$

$$\boxed{P_c = P_f\left(1 + r_c\frac{V_{MX}\gamma_{sv}}{kT}\right)}$$

Now, we can do some calculations of course, these are not a very detailed calculations we are not able to present here, but some they are not completely empirical. But they have some mathematical basis we will see only the final results in most of the cases. So, the curvature dependent vapour pressure, we have seen we have seen that there is a pressure difference. But how much is the difference and what is its consequences, this is delta mu again and that can be related to either concentration difference or the partial pressure difference.

Here it is you can call it partial pressure or vapour pressure, so delta mu actually is k T. k is Boltzmann constant, T is the temperature and l n P c by P f. This case two partial pressures, one is on the curved surface another is on the flat surface, that is your reference, so that is delta mu. Then this gives to l n P c by p f equal to r c. Now, once in delta mu as been expressed earlier here delta mu is here. From this also we get that expression r c is equal to V M X gamma is V by k T gamma is P is again the surface energy solid to vapour surface energy.

Then this is also the volume of the one molecular unit one formula unit of M X and then r c is the radius of curvature and k T as usual the Boltzmann constant and the temperature. So, from this you can get delta P by P f delta P by P f, which is nothing but this P c minus P f by P f P c minus by P f is the delta P. Then, this becomes r c V M X a gamma s v k T. The same thing now this has come this has come because these has been expressed in this fashion because the difference is very small and so this can be approximated as this. Then from this equation P c becomes equal to P f 1 plus r c, this expression.

So, there is a relationship now that the partial pressure or the vapour pressure on the curved surface over the curved surface is equal to the vapour pressure and the flat surface multiplied by 1 plus this term. Of course, the r c is their r c is the radius of curvature. So, the radius of curvature comes into his expression and this is relationship between partial pressure of the curve surface and the partial pressure of the flat surface. So, if this becomes our equation or relating these two partial pressures or the vapour pressures.

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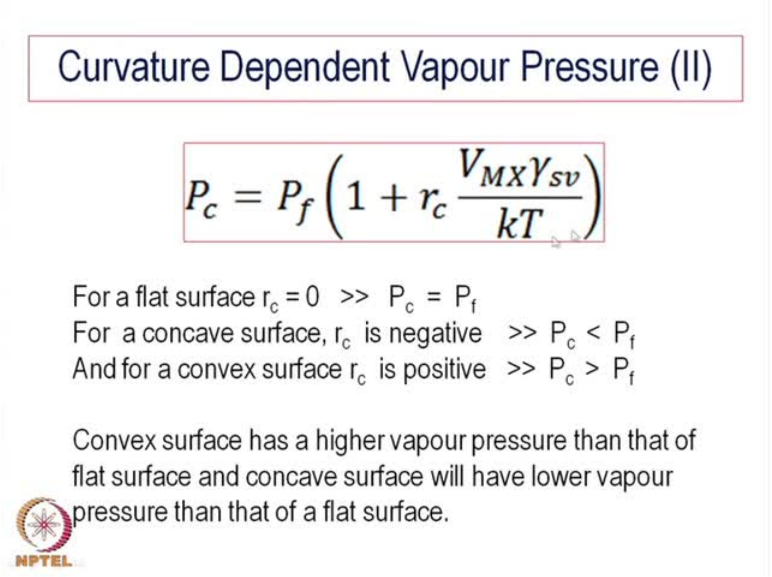

Curvature Dependent Vapour Pressure (II)

$$P_c = P_f\left(1 + r_c \frac{V_{MX}\gamma_{sv}}{kT}\right)$$

For a flat surface $r_c = 0$ >> $P_c = P_f$
For a concave surface, r_c is negative >> $P_c < P_f$
And for a convex surface r_c is positive >> $P_c > P_f$

Convex surface has a higher vapour pressure than that of flat surface and concave surface will have lower vapour pressure than that of a flat surface.

The same thing has been written here. Then we can have three different conditions quite obviously for a flat surface r c equal to 0 because the r equal to infinity. So, r c becomes 1 by infinity equal to 0 and that leads to these not greater than this leads to P c equal to P f. So, these two terms will be equal, so which is obvious on a flat surface P c will be equal to P f anywhere is in the equal to here. But the more important results are here for a concave surface P c is negative, so if this is negative this becomes total quantity becomes negative and then this quantity becomes less than 1.

So, this becomes less than 1 and therefore, P c the curved surface the vapour pressure on the curve over the curved surface is less than that of the flat surface. So, P c is less than P f on the other end for a convex surface r c is positive r c is positive. So, that leads to P c is greater than P f. So, on a convex surface the vapour pressure becomes larger than that on the flat surface whereas, on a convex concave surface this is smaller or lower than that of the flat surface. So, these are the two most important findings out of this analysis, what we have presented there.

So, convex surface either has a same thing is written here. Convex surface has a higher vapour pressure than that of the flat surface and the convex are concave surface will have a lower vapour pressure than that of the flat surface. So, without changing the temperature, without changing the concentration or the impurity content or the composition of the material just by changing the surface as a curvature of the particle, which we are trying to put together, so those particles will have a different vapour pressure at different points.

If is of course, a spherical surface you will be uniform everywhere, but we will see when agglomerate or a conglomeration of particles are made all the surfaces are not really of similar curvature. They have a different curvature at different points and different sites and the somewhere it is a positive somewhere it is negative and that actually makes the difference. That creates so called the local driving force, which we are talking about. The local driving force that is either the concentration difference of the vacancy or in this particular case here we have talking about the vapour pressure difference. So, the vapour pressures are automatically changes depending on the curvature. So, it is irrespective of temperature, irrespective of any composition.

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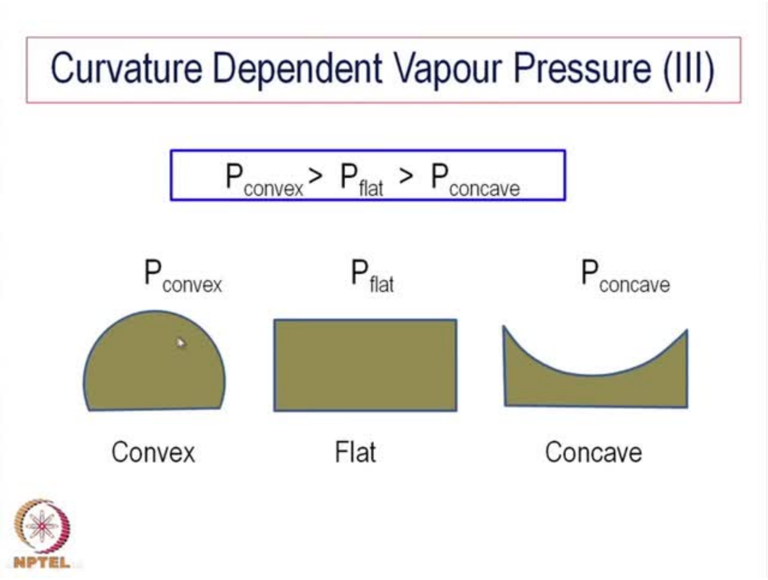

Curvature Dependent Vapour Pressure (III)

$P_{convex} > P_{flat} > P_{concave}$

This is what we have already discuss just a pictorial representation the curvature dependent vapour pressure, we have a flat surface we have a flat surface there. This is a convex surface, this is a convex surface and this is a flat surface, and this is a concave surface. So, these are the same composition kept at same temperature, but just because there radius of curvature are different, the vapour pressure will be different. So, the P convex, the vapour pressure on this surface. That means if you measure the vapour pressure just above this surface added in temperature will find some value.

That is more than what is the vapour pressure here on a flat surface, just above the flat surface. Incidentally you must know that whenever a material is kept in anywhere in in any environment, there is always an equilibrium. So, there will be always some vapour of that material solid vapour will try to equilibrate with the gas phase, whatever the gas phase is. Of course, this equilibrium becomes or the kinetically it becomes faster, when it there is a high-temperature and the evapouration rate is fast. If the evapouration rate is not fast course thermodynamically, it has to be an equilibrium, but the kinetically it may be a very sluggish or slow process.

Finally, if you have a concave surface like this that also have some vapour pressure here of the same material. So, m evapours of the same material will always be there depending on the temperature. Of course, but the temperature, then the gradient will be high because the evaporation rate will be very low. If the temperature is high, the evaporation rate will high and there will be always an equilibrium. So, that vapour pressure, the concave vapour pressure corresponding the concave surface is still lower than this. So, this is highest this is intermediate and this is the lowest. So that is the important observational or important conclusion were findings forever mathematical analysis we have done so far.

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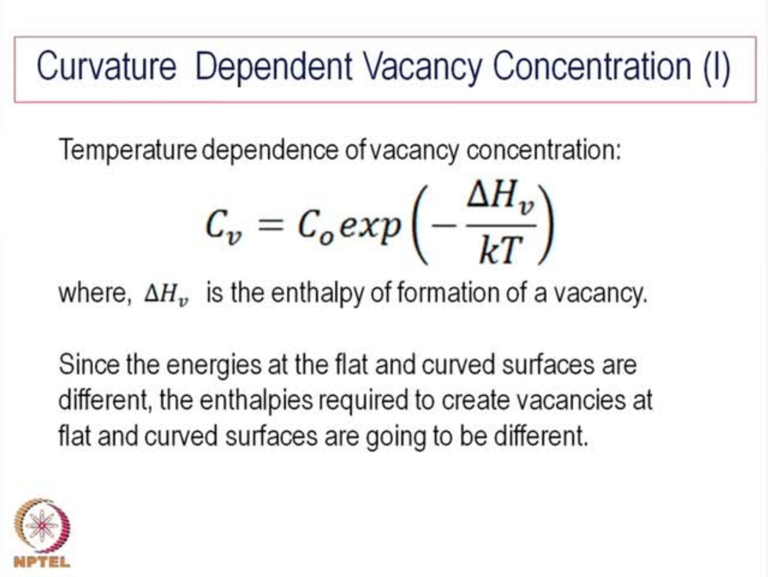

Curvature Dependent Vacancy Concentration (I)

Temperature dependence of vacancy concentration:

$$C_v = C_o exp\left(-\frac{\Delta H_v}{kT}\right)$$

where, ΔH_v is the enthalpy of formation of a vacancy.

Since the energies at the flat and curved surfaces are different, the enthalpies required to create vacancies at flat and curved surfaces are going to be different.

Next is we are talking about two terms or two driving forces, one was the vapour pressure or vapour phase transport other was solid state transport. Of course, all its solid state within the solid itself without involving the vapour phase. This is the curvature dependent vacancy concentration, we can also write some equation for that. But this is a different equation, this is just a temperature dependence of any vacancy concentration that was this, we discussed earlier when you are talking about the point defects, the creation of point defects, either the vacancies interstitials, Frenkel defect or the Schottky defects, right?

So, for each for creation of any such defects, we need an activation any activation energy here. This is the enthalpy; the enthalpy change delta v delta, H v is the enthalpy of formation of a defect. So, the enthalpy change is delta H v and that gives us the temperature dependent exponential temperature dependence. So, C 0 is a constant T exponential term exponential minus delta is by k T, this so called Arrhenius equation, the well known Arrhenius type of equation. Since, the energies at the flat and curved surfaces are different, that we have seen that the potential are different by delta mu. So, since they are different the enthalpies required to create vacancies at the flat and the curved surfaces are also going to be different.

So, the energies at different surfaces we have seen that energy are and that energy also leads to the vapour pressure difference for the same reason. Since, the energies are different at different surfaces or different in types of surfaces, the vacancy concentration just beneath it, because you need certain energy to create these vacancies. So, if the host material has different energies naturally, the available energies will be different and or we have to work against different energies or therefore, the concentrations of the vacancies just below that surface will also be different. This is in addition to the temperature effect.

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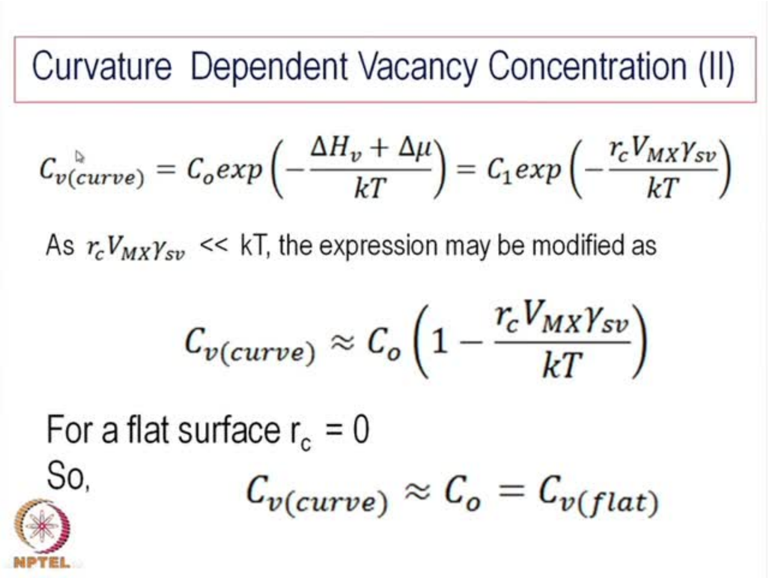

Curvature Dependent Vacancy Concentration (II)

$$C_{v(curve)} = C_o exp\left(-\frac{\Delta H_v + \Delta\mu}{kT}\right) = C_1 exp\left(-\frac{r_c V_{MX}\gamma_{sv}}{kT}\right)$$

As $r_c V_{MX}\gamma_{sv}$ << kT, the expression may be modified as

$$C_{v(curve)} \approx C_o\left(1 - \frac{r_c V_{MX}\gamma_{sv}}{kT}\right)$$

For a flat surface $r_c = 0$

So, $$C_{v(curve)} \approx C_o = C_{v(flat)}$$

So, this can be expressed in C v the vacancy concentration at the curved surface is equal to C 0 exponential minus. So, that was general term temperature dependent term lets on a flat surface and that plus the delta mu. The delta mu is the chemical potential difference, which we have discussed earlier. So, if that is added to that that will be the total activation energy needed for creation of the particular vacancy, this can be simplified as C 1. Another three exponential terms with delta mu again can be replaced by r c M X V M X gamma is V and then k T.

So, these are earlier we have seen. So, if as r c V M X and gamma is V. This term is much, much less than k T. This the numerator is much less than the denominator here. So, the expression may be modified as this exponential term can be changed to this kind of an expressionc curve C v curve that means at a curved surface and C 0 C 0. Actually, C is although a pre exponential term, but ultimately we will find that C 0 is actually the flat surface.

So, this is simplified exponential term is simplified into linear fashion and linear expression and then for a flat surface r c, that r c radius of curvature here which comes from the mu delta mu term r c equal to 0. If r c is equal to 0, this whole term becomes the 0. So, C v at a curved surface, that is the vacancy concentration over a curved or below a curved surface almost equal to C 0, which is nothing but the vacancy concentration at the flat surface, because for the flat surface. We have taken r c equal to 0. So, the C 0 becomes actually a flat surface vacancy concentration and that that is by definition r c is equal to 0.

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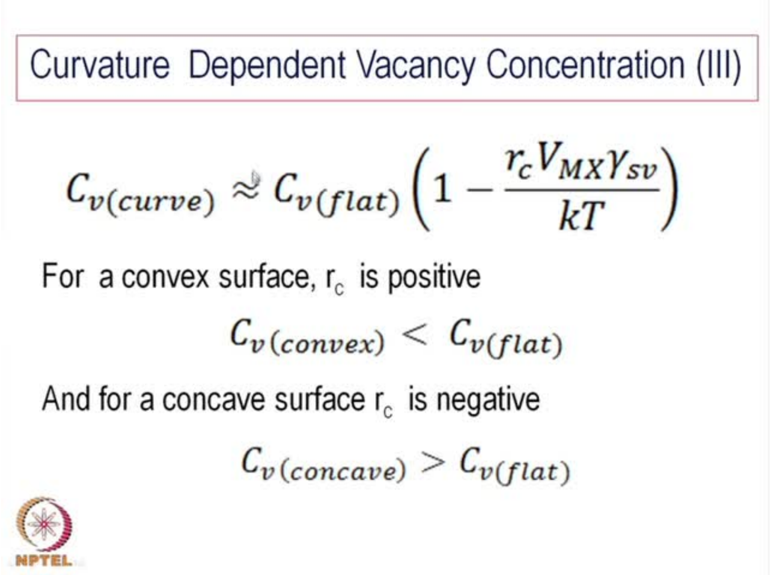

Curvature Dependent Vacancy Concentration (III)

$$C_{v(curve)} \approx C_{v(flat)}\left(1 - \frac{r_c V_{MX} \gamma_{sv}}{kT}\right)$$

For a convex surface, r_c is positive

$$C_{v\,(convex)} < C_{v(flat)}$$

And for a concave surface r_c is negative

$$C_{v\,(concave)} > C_{v(flat)}$$

Now, the similar fashion what we have seen, we have seen in case of vapour pressure the concentration of the vacancy over a curved surface or below a curve not over its a below curved surface is almost equal to C v flat C 0 C 0 has been replaced by this and 1 minus the same thing same expression r c V M X gamma is p by k T. Now, if this becomes the final expression for the concentration on a curved surface with respect to the flat surface. Then we will have two conditions, will have two conditions; one is r c positive as you have seen in the case of the vapour pressure r.

If r c is positive, then the concentration of sthe vacancy on the convex surface, this is true. For a convex surface is less than the concentration on a flat surface. So, if this is positive this becomes a negative term and that has once it is deducted from 1, it is actually less than 1. So, the concentration on the convex surface is less than that of the flat surface. Similarly, in a concave surface r c is negative. So, this becomes positive than negative its positive. So, C v the concentration on the concave surface becomes more than that of the flat surface.

So, that is another very important observation or another findings out of this analysis mathematical analysis, what we have little done here. So, ultimately our conclusions or the findings are that the concentration of below the convex surface is less than that of the flat surface. The concentration vacancy concentration below a concave surface is more than that of the flat surface and that is very, very significant and important for our purpose.

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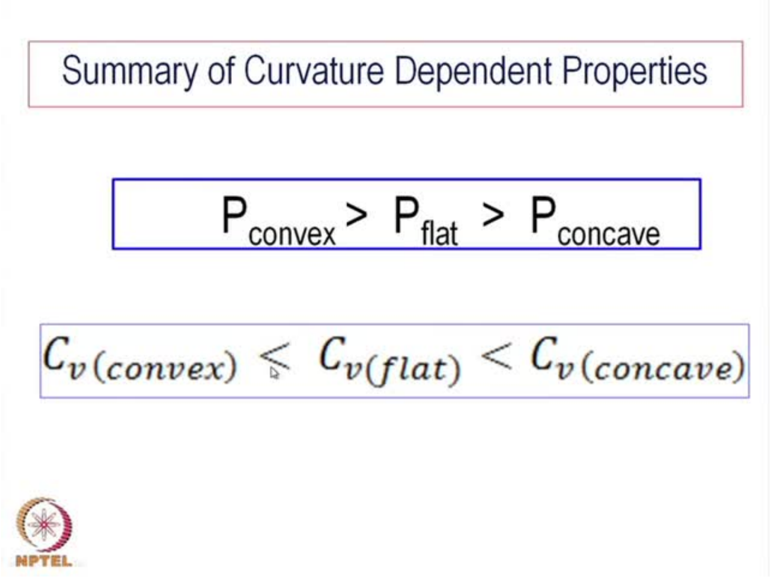

Summary of Curvature Dependent Properties

$$P_{convex} > P_{flat} > P_{concave}$$

$$C_{v(convex)} \leqslant C_{v(flat)} < C_{v(concave)}$$

So, finally, this is our conclusion summary of the curve curvature dependent properties, this is for the vapour pressure we have seen it earlier and this is for the concentration. Now as this is for the vacancy concentration, all right? This for the vacancy concentration and you can see the two things are in a reverse order here, the convex is more than the flat and the flat is also more than the concave. Here is the reverse, the convex vacancy concentration on the convex is less than the flat and is still less than the concave. So, the concave here is a concave is highest whereas, here convex is the highest, so there in two different, two different ways or in the order, in the order is difference. This is one kind of order this is another kind of order.

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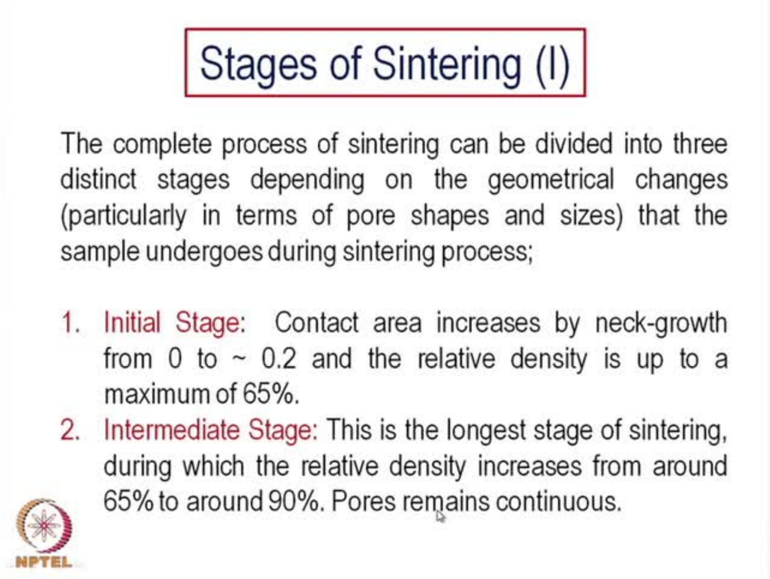

Stages of Sintering (I)

The complete process of sintering can be divided into three distinct stages depending on the geometrical changes (particularly in terms of pore shapes and sizes) that the sample undergoes during sintering process;

1. Initial Stage: Contact area increases by neck-growth from 0 to ~ 0.2 and the relative density is up to a maximum of 65%.
2. Intermediate Stage: This is the longest stage of sintering, during which the relative density increases from around 65% to around 90%. Pores remains continuous.

We will see later on how all these differences actually lead to mass transport and then to the sintering process, right. Before that let us have another consideration, so far as sintering is concerned. Sintering is a time-dependent phenomena, it is also dependent on temperature, is also dependent on time. So, both time and temperature are very, two very important parameters which controls the sintering process. And and also we know that by sintering actually there is a densification from a porous material, more dense material or a more sound material is prepared or formed by sintering.

So, the whole process of sintering has been subdivided into three different stages; the complete process of sintering can be divided into three distinct stages, depending on the geometrical changes particularly in terms of pore shape and size. That the sample undergoes during the sintering process. So, basically the during the sintering sample undergoes some geometrical changes particularly in terms of pores, size pore volume and distribution and so on and also the mechanical strength increases densification changes, densification increases and so on. So, whole process can be subdivided into three different stages depending on what extent of densification is taking place, how much time we have allowed and so on.

So, the first is what is called initial stage of sintering, here the contact area because we are talking again a congomauritian of some particles, so fine particles, so they there will be some contact area between the particles and it may be very small. To start with if we take a spherical particles or a uniform size spherical particles the contact area, theoretically it will be sign kind of point contact, but actually there will be some kind of finite contact area between the particles. So, the contact area increases by neck-growth will see what is really neck-growth, is actually the at the area of the contact we call it a neck.

Neck is formed between the two particles and this neck growth initially its obviously the area of the neck growth, initially it should be 0 theoretically and then as the sintering proceeds, this neck area increases. So, the initial sintering stage the by definition it has been empirically defined in this manner that it increases from 0 to 0.2, 1 being the final figure. So, 0 to 0.2 that means about 20 percent growth has taken place? So, far as the area of the contact area has concerned between the particles depends all the particles and the relative density is up to a maximum of 65 percent of the theoretical density. So, relatively density is about 65 percent. Then neck area has grown up to about 20 percent, so that is the find initially stage. We define it has an initial stage of sintering and then we have an intermediate stages.

This is the longest stage of sintering in timescale, during which the relative density increases from around 65 from this 65 to around 90 percent and the pore remains continuous, pore to start with is a continuous phase because you have only contacts, point contacts. So, the pores to start with are continuous and solids are also continuous, so it is a interpenetrating two different phases; the solid phase and the pore phase or the gaseous phases and 65 to 90 percent and the pore still remains continuous. So, that is the longest sintering stage or in in terms of time.

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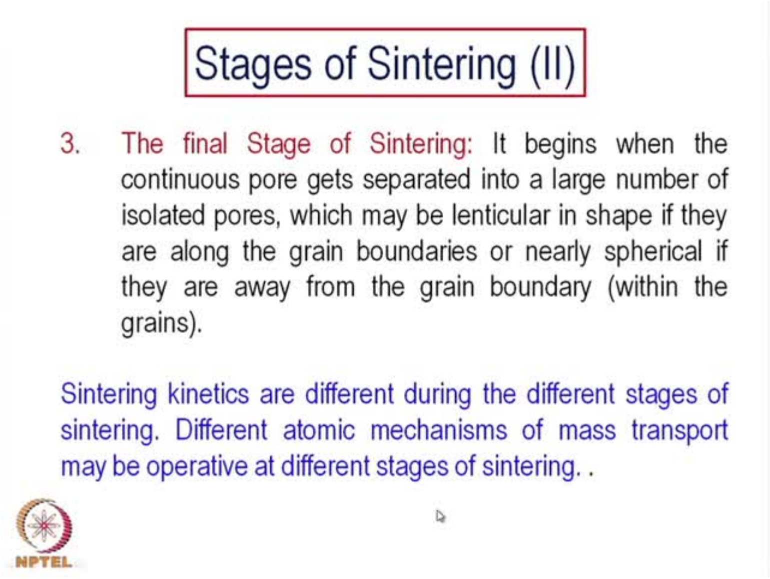

Stages of Sintering (II)

3. The final Stage of Sintering: It begins when the continuous pore gets separated into a large number of isolated pores, which may be lenticular in shape if they are along the grain boundaries or nearly spherical if they are away from the grain boundary (within the grains).

Sintering kinetics are different during the different stages of sintering. Different atomic mechanisms of mass transport may be operative at different stages of sintering. .

And this stage is call the final stage of sintering, it begin when the continuous pores get separated into a large number of isolated pores, towards the end when the pore volume decreases towards significantly because 90 percent densification has already taken place. Starting from 50, 50 to 60 percent, we have gone to about more than 90 percent, so only 10 percent of the pores is still remaining and they need not be most of the time they are not continuous, so they becomes isolated pores. Isolated pores which maybe lenticular in shape if they are along the grain boundaries or nearly spherical if they are away from the gain boundaries or within the grains, so they get isolated.

The continuous phase, the pore, pore is no longer a continuous phase, solid is remains continuous, but the pore is no longer continuous, they become isolated. There shapes of individual pores depend a on where exactly they are located? They may be located at the grain boundaries, at the contact area between the two grains or the two particles or they may come within the grains, within the grains and they are remaining became isolated. So, whichever is within the grains they like they tend to become spherical whereas, which we are within at the contact area of the grains or between the two grains or the grain boundaries, they will be little elongated in nature.

So, these are the three different stages depending on the extent of sintering extent of time spent for the sintering operation and the, and the growth of the grains as well as the reduction in the pore, pore volume. However, the final conclusion is like this the sintering kinetics are different during the different stages of sintering, the kinetics are different. Different atomic mechanisms of mass transport may be operative at different stages of sintering, so it is not necessarily that the same mass transport mechanism will be operative and their kinetics may also be different.

So, the overall the sintering is a very complex phenomena and many different processes do take place simultaneously. So, the mathematical analysis is certainly complex and we will take it up the further things, how exactly everything happens in a slight more details in the next class and we complete or we end this class here as the time is up. So.

Thank you, thank you for your attention.