Nanomaterials and their Properties
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Lecture – 09
Thermodynamics of Nanomaterials

This is the lecture number 9. So far, we have been discussing about surfaces and their properties. But, in today's lecture, I am going to take some different topics, mostly Thermodynamics.

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Discussion of surface energy and related aspect continue

Lattice parameter
Magic numbers
Vapour pressure

Recap..

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

But, before that let us recap, you know we have discussed about surface energy and related aspects, and mostly we have discussed about effect of surface energy on various aspects like lattice parameter, vapour pressure, even the you know curvature effect of curvature on the different aspects of surface energy. And then, we discussed about magic numbers which are very important.

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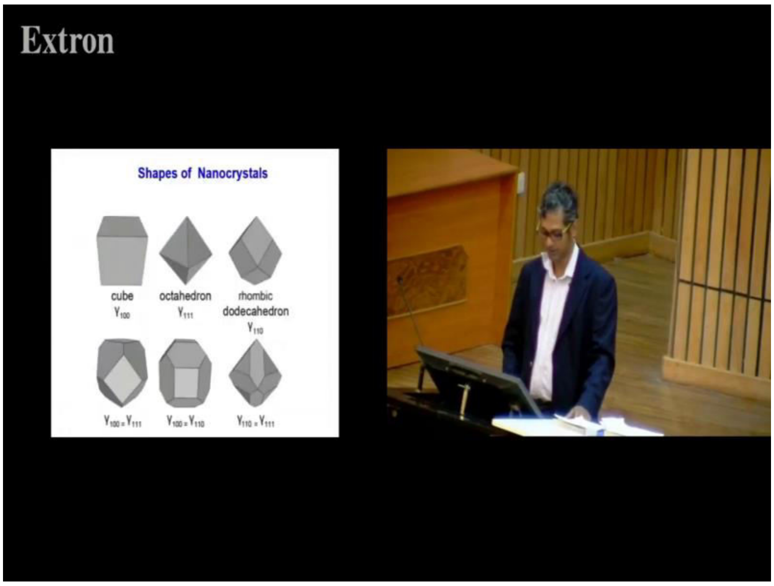

Shapes of Nanocrystals

And, finally, in the last lecture I discussed about shapes, ok. So, let us go into that little bit then before we come back.

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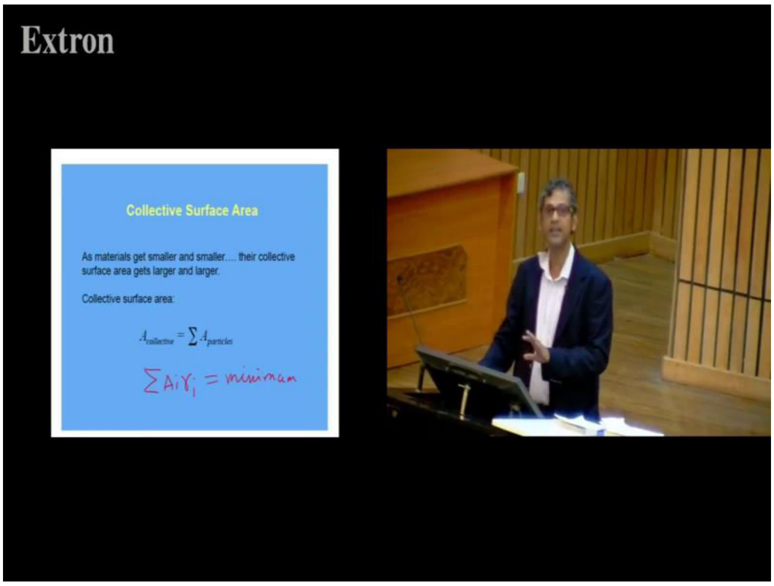

Collective Surface Area

As materials get smaller and smaller.... their collective surface area gets larger and larger.

Collective surface area:

$$A_{collective} = \sum A_{particles}$$

$$\sum A_i \gamma_i = \text{minimum}$$

And you know shapes are very important, and shapes are dictated by the minimization of the term called $\sum A_i \gamma_i$ ok $\sum A_i \gamma_i$. Or $A_i \gamma_i$ means addition of surface area multiplied by the surface or specific surface energy terms, ok. This should be minimum for any shape which is the equilibrium shape. And nanoparticles do show different kinds of shapes.

So, in order to justify that, this methodology is used. And that is something I discussed in the last lecture. As you know there are different kinds of shapes which is stabilized cube, octahedron, rhombic, dodecahedron or even some other shapes which are shown in the bottom of this slide. But, why do these shapes are actually found in different kinds of nanoparticle that is something which needs deliberation.

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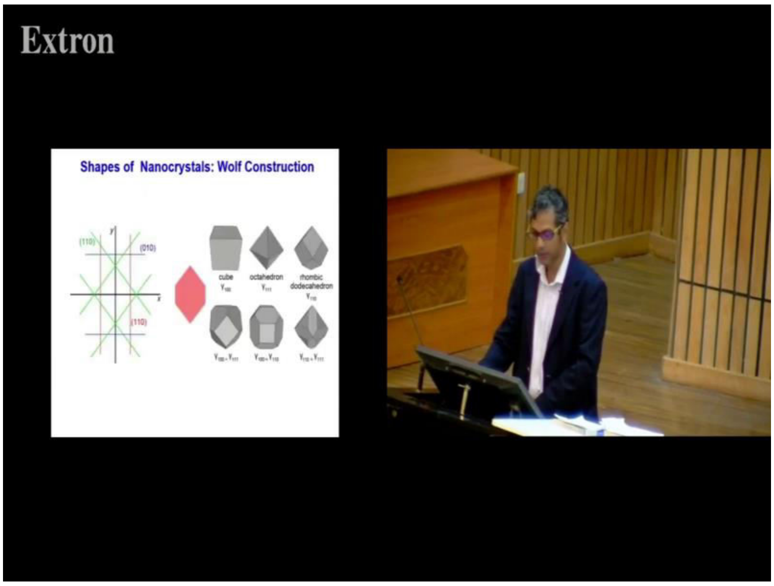

Shapes of Nanocrystals: Wolf Construction

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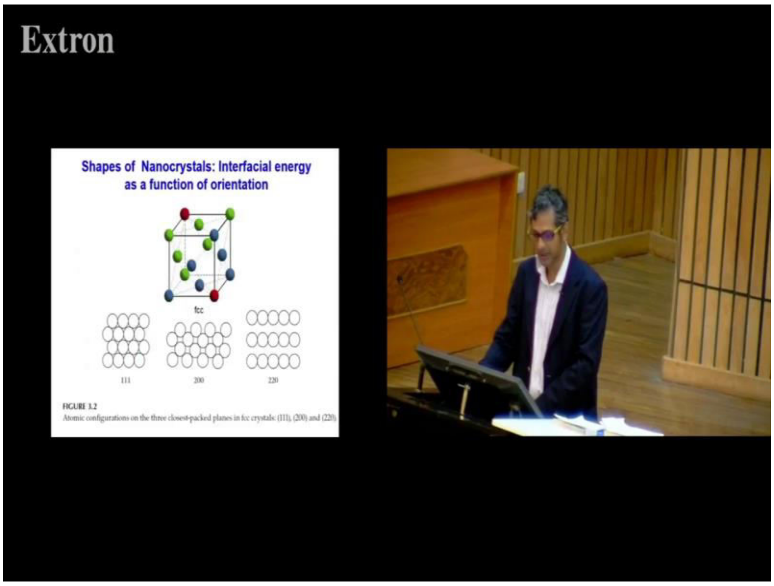

Shapes of Nanocrystals: Interfacial energy as a function of orientation

FIGURE 3.2
Atomic configurations on the three closest-packed planes in fcc crystals: (111), (200) and (220)

And to do that we have start discussing about the wulff constructions. And wulff constructions is basically considers the interfacial energy as a function of orientations.

And we have discussed about that. Interfacial energy of any FCC crystal for the sake of understanding are different on different planes like 111, 200 or 220 planes. That means, what? That means, we can plot interfacial energy as a function of orientation, like see it here, right.

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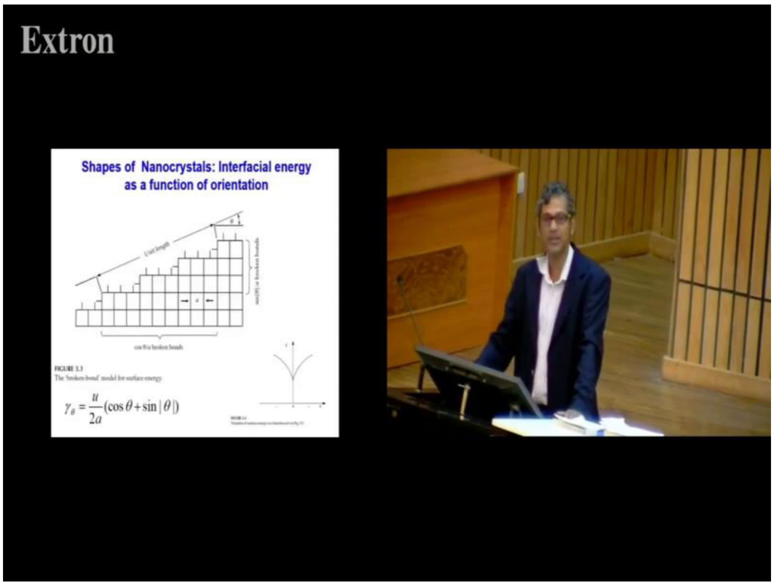

Shapes of Nanocrystals: Interfacial energy as a function of orientation

FIGURE 3.3
The 'broken-bond' model for surface energy

$$\gamma_\theta = \frac{u}{2a}(\cos\theta + \sin|\theta|)$$

And what is that? This is what is shown I showed, I am showing you again and again because, so that you do not forget. Interfacial energy in 2D will depends on theta by the function cos and sin, but, $cos\theta + \sin|\theta|$. Please remember that.

An interfacial energy do change as a function of theta, ok like this, right. And this is minimum is at a closest packed plane like 111 plane in FCC structure. As you go away from that the interfacial energy increases rapidly.

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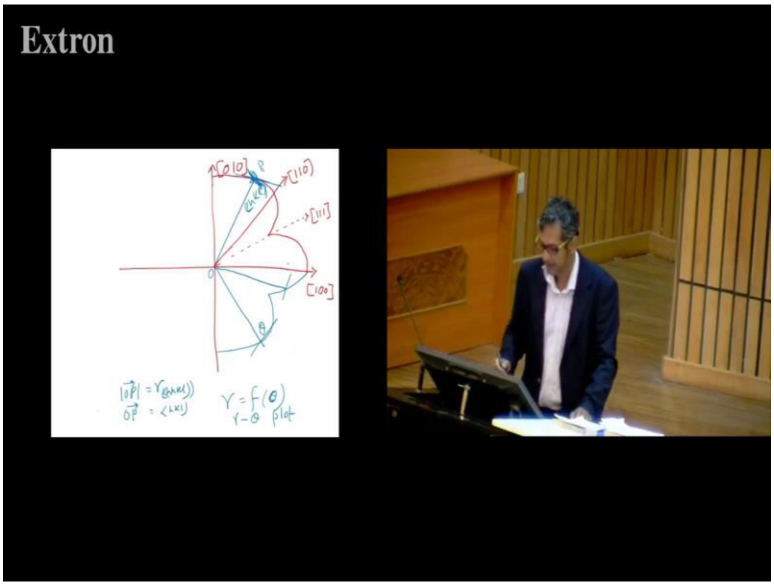

So, that means, what? that means, we can create an interfacial energy versus theta plot, ok. We can always create that. And I am going to do it for you before actually I move into other topics. So, you can draw x and y axis, ok, like this. And suppose x axis corresponding to 100 direction in a cubic crystal, y axis corresponding to, ok y axis corresponding to 011; sorry not 011, 010 plane of cubic crystal.

And cubic crystals directional planes are same. So, therefore, the 45^0 angle will be the direction 110 and that is nothing, but summation of these two directions. And perpendicular to these direction as I have said this is one 001 directions, ok. What is 001? This is z axis, this is y axis, this x axis, this is z axis. So, that means, 111 direction is basically summation of this and this vertical direction, and if you project that this will lie somewhere like this, correct.

So, now you can actually plot surface energy and it will be maximum here, then it will be less here, finally, it will be minimum here, ok, then again it will go to maximum here. This is one quadrant of that surface energy. So, you can do that for different quadrants, right. You can do that for different quadrants. It will be also like this, right. Similarly, on the other half.

Now, wulff construction tells you if this is the γ plot or γ as a function of theta plot. How do you know this theta? Because this angular relationship between these different planes are basically given by theta, right. That is what is a theta. Gamma plot, so it is called $\gamma - \theta$ plot, and properly known as a γ plot.

So, once you know this gamma plot for a particular crystal structure, it will vary dependent on crystal structure, depending on the material. Then you can generate the wulff construction by simply making, suppose this is a point on this gamma plot, you connect this point P to this direction, ok. And this is one of the <hkl> direction, suppose any odd hkl direction it will be between, obviously, 010 and 110 that is why it is lying there.

Now, this, if this is the odd direction like that, so and the value of the gamma, value of the surface energy is basically magnitude of this vector that is the value of gamma <hkl>, ok and direct vector is taking you telling you the <hkl> direction. Then, if you take a at this point if you take a 90^0 cut or basically take a normal, correct.

So, this normal is then can be used to create a shape inside it. So, suppose if I draw another vector like this and this is O cube and then I make another normal here. So, these normals can be made everywhere, ok, like this. So, I can create another normal here, right. So, go to the next slide, it will be clear. So, that is what is done.

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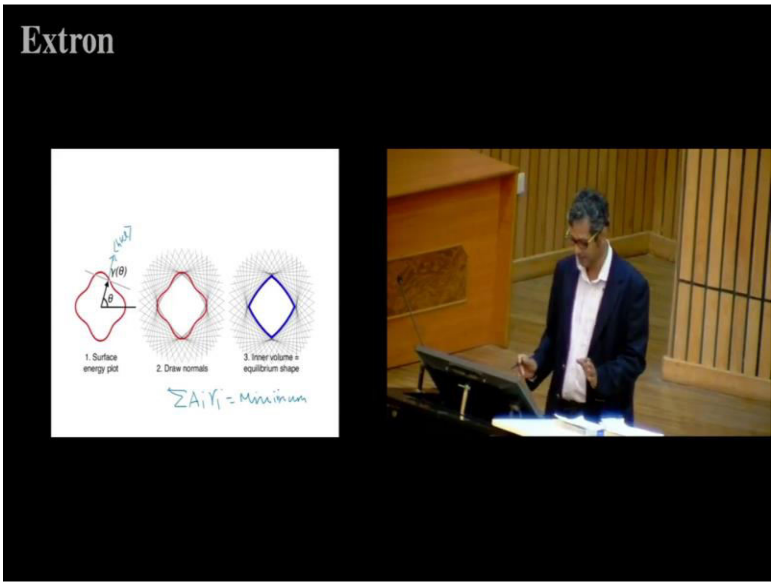

So, this is the vector and this is the $\gamma(\theta)$ at that angle theta, and this is must be at a particular direction <hkl>, and then I have, we have taken a normal to that at this point wherever this normal is intersecting the gamma. So, you can do this. And inside volume is or actually it is not volume, it's area is the equilibrium shape, correct. Please remember that this is the what is wolf construction. And this analyze this aspect what I discuss $\sum A_i \gamma_i$ minimum, right. That is what is this is true, ok.

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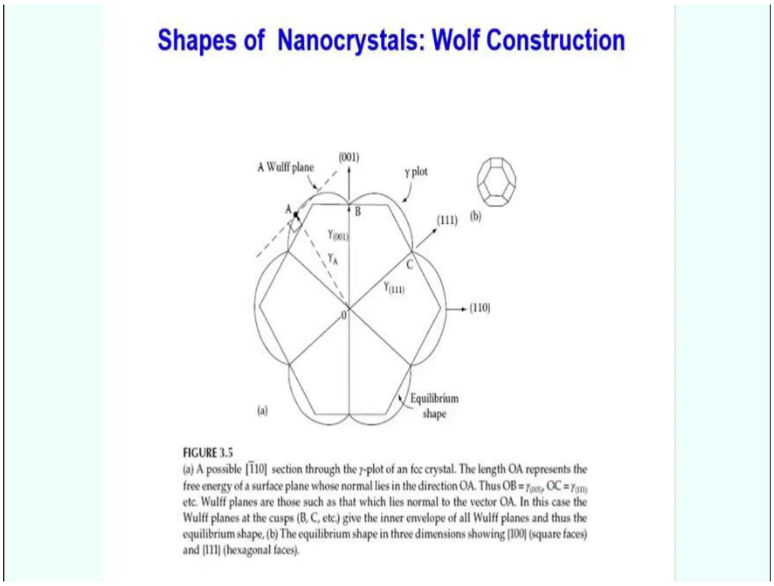

Shapes of Nanocrystals: Wolf Construction

FIGURE 3.5

(a) A possible [$\bar{1}$10] section through the γ-plot of an fcc crystal. The length OA represents the free energy of a surface plane whose normal lies in the direction OA. Thus OB = $\gamma_{(001)}$, OC = $\gamma_{(111)}$ etc. Wulff planes are those such as that which lies normal to the vector OA. In this case the Wulff planes at the cusps (B, C, etc.) give the inner envelope of all Wulff planes and thus the equilibrium shape, (b) The equilibrium shape in three dimensions showing {100} (square faces) and {111} (hexagonal faces).

So, now this is something I discussed in the last class. And then, one can generate different shapes. This is one sub shapes, this is a this 2D section of the cube octahedral shapes, this is the cube octahedral shapes generated, right. So, that is something which we discussed now.

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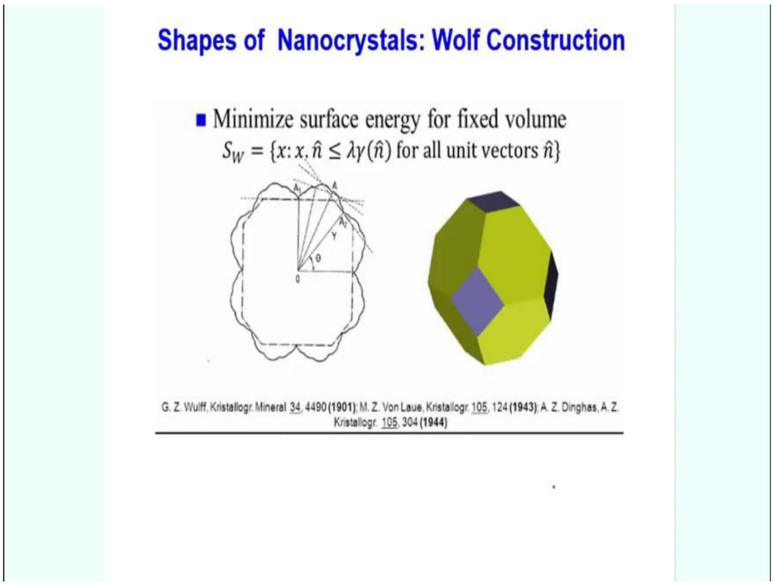

Shapes of Nanocrystals: Wolf Construction

- Minimize surface energy for fixed volume

$S_W = \{x: x.\hat{n} \leq \lambda\gamma(\hat{n})$ for all unit vectors $\hat{n}\}$

G. Z. Wulff, Kristallogr. Mineral 34, 4490 (1901); M. Z. Von Laue, Kristallogr. 105, 124 (1943); A. Z. Dinghas, A. Z. Kristallogr. 105, 304 (1944)

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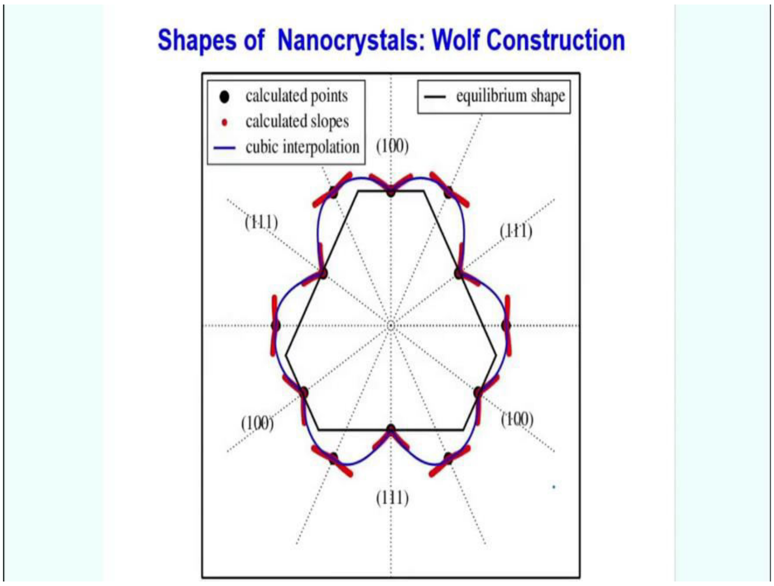

Shapes of Nanocrystals: Wolf Construction

Today, in this lecture I am going to deviate a little bit. We will come back to surface energy maybe sometime later, but we will talk about the thermodynamics.

You know thermodynamics talks about free energy, right. All of you should know that. Free energy is the basic functions of thermodynamics. And whenever you are trying to find some system to be at equilibrium, it is the minimization of free energy again. So, what is the free energy which you use in material science is the Gibbs free energy. We normally use Gibbs free energy in material science not as compared to the Wolfs Helmholtz free energy, ok.

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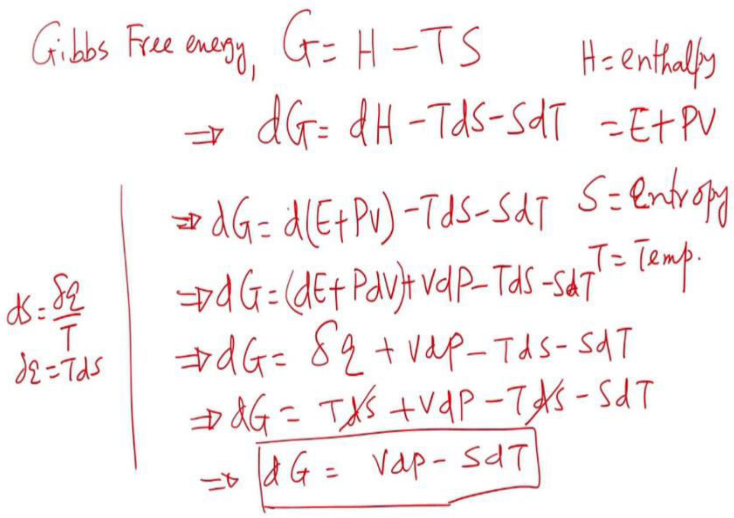

Gibbs Free energy, $G = H - TS$ $\quad H = \text{enthalpy}$

$$\Rightarrow dG = dH - TdS - SdT \quad = E + PV$$

$$\Rightarrow dG = d(E+PV) - TdS - SdT \quad S = \text{Entropy}$$

$$\Rightarrow dG = (dE + PdV) + VdP - TdS - SdT \quad T = \text{Temp.}$$

$$dS = \frac{\delta q}{T}, \quad \delta q = TdS$$

$$\Rightarrow dG = \delta q + VdP - TdS - SdT$$

$$\Rightarrow dG = T\cancel{dS} + VdP - T\cancel{dS} - SdT$$

$$\Rightarrow \boxed{dG = VdP - SdT}$$

So, Gibbs free energy is given by G and G is nothing, but H -T S, right. What is H? H is the enthalpy. What is T? T is the temperature. What is S? S is the entropy. You have studied this. If you have not studied this, then please go back study. I am not going to give a lecture on thermodynamics of the you know undergraduate troubles because this is a post graduate course. So, we have been we will be borrowing the concepts from there. But, I am going to discuss you very basic things.

So, G is the Gibbs free energy, ok. So, that is something let us write it up Gibbs free energy, ok. What is Gibbs free energy is? Gibbs, it is named after Gibbs, ok, Wulff W Gibbs; Gibbs free energy. It is free to use because do work. H is the enthalpy, ok and this H is given by internal energy plus PV term. S is the entropy and T is the temperature.

So, let us first do the first thing first. See if I take derivative total derivative dG, it is nothing, but dH-TdS-SdT, right. That is something everybody should know. So, now, that is the total differential of G, correct. Now, I can write down same thing dH = E + PV, right. d(E + P V)- TdS- SdT, we are not changing these two terms here.

So, or therefore, dG = dE + PdV + VdP - TdS - SdT, right. You can follow me, right. You can do these steps one by one. There is no problems in understanding that. That is nothing, but differentiation of P and V, that is PdV and VdP, right.

So, now, I just reorganize this. How do I reorganize that? Using first law and second law of thermodynamics. Let us first apply the first law of thermodynamics, ok. So, you know dE + PdV is what? I mean the first law of thermodynamic a constant pressure that is nothing, but heat, δq, right. You go back to your thermodynamics you will get that. That is plus VdP.

And why do you use different kind of delta here? Because this is a path variable not a state variable and then TdS - SdT, ok. So, now, this is understandable, right. This is the first law of thermodynamics dE + PdV is equal to δq that is the heat given by.

So, now, next step is what? Next step is this; this δq is according to second law of thermodynamics is TdS, right. If you define entropy that is what will come, ΔS or dS rather, dS equal to δq by T at equilibrium. You know that, right or you do not know. Well, let us do that, dS our definition is this. So, δq is TdS. So, I can write down TdS + VdP - T dS -SdT. So, finally, what do I get? dG is equal to TdS, TdS get cancelled VdP - SdT.

Now, you must be thinking why I am doing that, because this is the relationship we are going to use in next derivations of different kinds of things, that is why we have used this one. So, what are the derivations we are going to do? We are going to do how two things we are going to do here, if time permits today. One, how the curvature will affects the temperature, ok, other one is the pressure.

That is something we should know, ok. So, but this fundamental relationship dG = VdP - SdT will be used every now and then, that is what I thought I should derive and show you. So, that you do not forget, ok. Now, let us erase this part, ok. Let us erase this part and do the next thing, ok.

Well, before I do the next thing as you know I will keep this relationship on the top, the total differential of free energy, right. I am doing this because it gives me feeling of erasing a blackboard, although we are not using the black board. But it gives a very feeling as if that you are erasing the black board, although it is you are doing it on the computer screen. And it also gives you some time to think, right. Instructor gets some time to think also by erasing the board.

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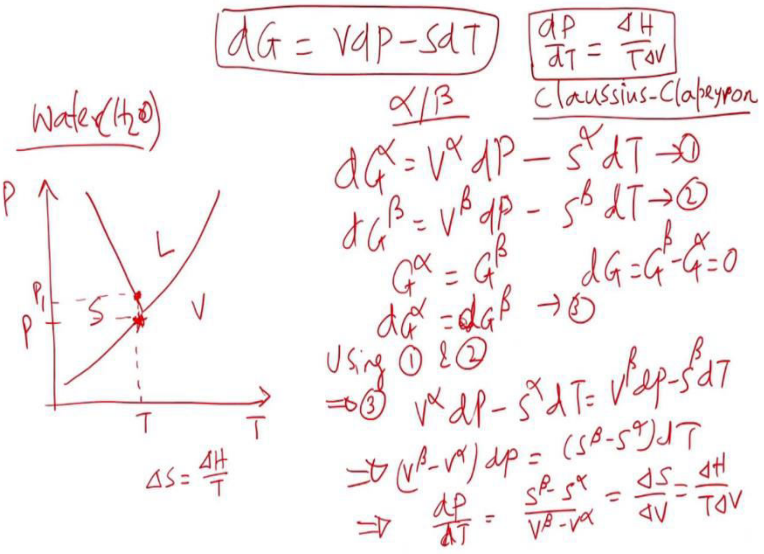

$$\boxed{dG = VdP - SdT}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

Claussius-Clapeyron

α/β

$$dG^\alpha = V^\alpha dP - S^\alpha dT \rightarrow ①$$

$$dG^\beta = V^\beta dP - S^\beta dT \rightarrow ②$$

$$G^\alpha = G^\beta \qquad dG = G^\beta - G^\alpha = 0$$

$$dG^\alpha = dG^\beta \rightarrow ③$$

Using ① & ②

$$\Rightarrow ③ \quad V^\alpha dP - S^\alpha dT = V^\beta dP - S^\beta dT$$

$$\Rightarrow (V^\beta - V^\alpha)\, dP = (S^\beta - S^\alpha)\, dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

So, what is the relationship we have going to keep it? Remember that total differential dG = VdP - SdT, and I am writing a different color, ok. So, you all of you know that phase diagrams actually are reflection of free energy minimization, ok. So, phases which are having minimize minimum free energy are basically form in a particular temperature or pressure conditions.

Let us first do the phase diagram of water, right. You know water, all of you water is nothing, but H_2O this can form three phases. Water as a liquid which you drink, water ice is solid which forms when you cool down in your refrigerator, and if you heat it up during making tea or coffee or whatever in the cooking you get vapour, the three phases presents, right.

So, water phase diagram is basically nothing, but source variation of temperature and pressure. You have to understand that. Why it is so? Because there is no composition variable, water is a pure component. And water is a peculiar phase diagram, correct. So, what is this? This is a solid, this is vapour, this is liquid. Solid is what? Ice. Liquid is what? Water, which you drink. Vapour is what? Which is forms into vapour, ok. Now, each of this line indicates certain kind of equilibrium between solid and liquid, liquid and vapour, and solid and vapour.

So, for the sake of understanding, let us consider very generic thing equilibrium between two phases alpha and beta. It can be further liquid and vapour or vapour and solid, ok. So, let us consider for generalization between two solids, two phases alpha and beta. So, we can use that relationship. I can write down $dG^{\alpha}= V^{\alpha}$dP -S^{α}dT, right. You can do that. And dG^{β}=V^{β}dP- S^{β}dT, right. You can understand that.

Well, you may be thinking why is that P and dT are remaining same. Well, that is obviously, at a particular temperature and pressure. This is temperature, this is pressure you can see the solid and vapour is stable or if you increase the pressure little bit here, this is P_1 your solid and liquid is stable, right this point. And this point solid and vapour is stable, ok. So, temperature and pressure are constant at this points. We are not changing that. Thus clarifies your point.

Now, at equilibrium, free energies must be equal. Why? but, at equilibrium dG that is nothing, but dG^{α}- dG^{β} (Refer Time: 18:37) is 0 because that is just minimized. So, condition of minimization is that the first derivative will be 0. So, that means, I can write down dG^{α}= dG^{β}. Now, you understand, right. Now, everything is clear, right, why I am doing this. You must have done it, but you know you forget sometimes that is why we have to redo it, so that you do not forget again.

So, I can write down then from the top these two, 1 and 2, using 1 and 2, 3 can be rewritten. 3, why it is can be written? Very simple V^{α}dP -S^{α}dT =V^{β}dP- S^{β}dT.

Now, once you reorganize, I will not do it. This will be (V^{β} -V^{α})dP is equal to (S^{β}-S^{α}) dT. So, I get what? What do I get? I get very simple thing that is why, $\frac{dP}{dT} = \frac{(S^{\beta}-S^{\alpha})}{(V^{\beta}-V^{\alpha})}$ that, right. Let me erase it. I like erasing. So, that is nothing, but $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$.

And as you know what is ΔS? ΔS is basically infiltration of change of delta is ΔS. So, ΔS is nothing but $\frac{\Delta H}{T}$, T is the at the melting temperature, evaporation temperatures, solidification temperature, whatever. So, that can be Tm, Tv. So, this is ΔH is heat of sublimation, heat of melting. So, I can write down then, $\frac{\Delta H}{T\Delta V}$.

So, these relationships, ok, let me write down at the top again. This relationship $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ is known as Clausius Clapeyron equation, ok. What is Clausius Clapeyron? Well, it tells you; Clapeyron equation. It tells you the change of temperature, if you apply pressure or vice versa. You know ice, if you apply pressure it melts down that is because volume change is negative, from ice to water, water has lower volume than the ice, that is why. So, that is the sign of $\frac{dP}{dT}$ is negative that is why this curve between solid and liquid has a negative slope.

Now, we understand why this has a negative slope. Obviously, ΔH is not negative. When ice melts it absorbs heats, ok. So, that is it. So, V, ΔV is basically negative when ice melts to water. So, when you apply pressure, melting temperature goes down. That is why if you take a chunk of ice put under your feet, apply pressure, it melts down very easily. That is something which you should remember that, correct. Now, this is, fine, ok.

What about solid liquid, solid vapour and liquid vapour curve? See, if you look at this curve they look like exponential. Let us do a little bit maths, so that you do not forget and I keep those two relationships everything else I erase, ok. I am doing these things for you know making your concepts clear, so that you do not forget when you come back to nano size. Something we need to know before in the bulk size before going to nano size, ok. So, we are considering going to consider any of these two equilibria or any of these two equilibria that is solid vapour, liquid vapour. Let us consider liquid and vapour, correct.

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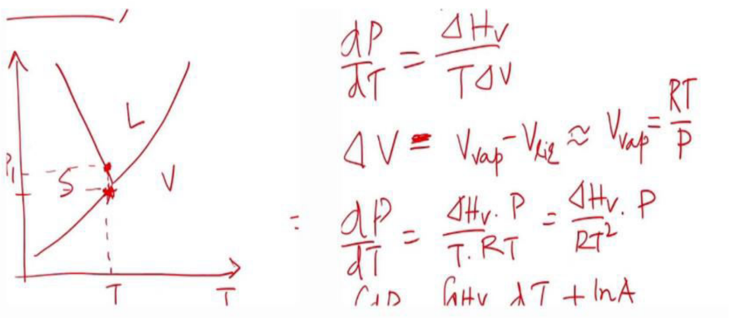

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta V}$$

$$\Delta V = V_{vap} - V_{liq} \approx V_{vap} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H_v \cdot P}{T \cdot RT} = \frac{\Delta H_v \cdot P}{RT^2}$$

$$+ \ln A$$

So, this relationship will remain constant, right. There also, $\frac{dP}{dT}$ if you are considering liquid to vapour transformation. This relationship will remain constant. It will not change, all right.

But, what is ΔV then? ΔV is equal to or is equal to not while, is equal to, right, $\Delta V = V_{vap} - V_{liq}$. Now, you tell me vapour has a very large volume as compared to liquid if masses are same. If I take one gm. of water, the space or the volume occupied by the vapour is much much larger than the that will depend on pressure obviously, and we are talking about one atmospheric pressure let us suppose. So, volume will be much larger, it depends on whatever volume you are using. It does not matter whether you are using a small volume or big volume, but volume will be larger.

So, we can always ignore the liquid volume or we can write down this equal to V_{vap}. And normally, vapour will follow what? Universal gas law. So, that means, for one mole I can write down PV = RT. So, $\Delta V = V_{vap} = \frac{RT}{P}$, correct. Now, plug in this into the equation. So, dP, so we are coming from here $\frac{dP}{dT}$ is nothing, but $\frac{\Delta H_v}{T\Delta V}$ and we are putting this. So, RT remain here, P goes up, so that means, $\frac{\Delta H_v P}{T \times \mathrm{RT}}$ You can do that. You can follow my steps, right. There is no problem.

What we have done? We have considered the vapour as a much larger volume than liquid. That is true for even solid to vapour transformation also. And, we converted this V_{vap} using the gas law, ok. So, this can be again written $\frac{dP}{P} = \frac{\Delta H_v dT}{\mathrm{RT}^2}$. So, now, if you integrate it on both sides, you will get a constant, right. Let us log write log of A because $\frac{dP}{dT}$ will come as a log. So, ln P = $\frac{\Delta H_v}{RT} + lnA$.

So, now if you consider P, $P = Aexp(-\frac{\Delta H_v}{RT})$. I think we should write ΔH_v here, ok. This is V, vapourization by RT, that is nothing, but exponential curve and that is what you see there. And in fact, both of them lie on the same exponential curve that is pretty understandable. So, our theory explains exactly what you see in actual in water vapour, water liquid vapour equilibria or solid vapour equilibria. So, we have explained now both the concepts, ok.

So, now, I again, so now, it is evident to you how these things are important. So, now, knowing these aspects we will go further. This is these are the two basic things you should have known. And I hope you know all of you know, but in case you have forgotten I am doing it. So, that it reminds you. And this simple maths are basically important. So, now, we do not require water phase diagram anymore. We can even erase that also. So, these three relationships we will keep for the water phase diagram.

See, I am doing it for pure, right, pure water. Why? Because many of these nano materials are pure component, pure copper, pure aluminium, ok. So, that is why I am doing it for pure, for that is a simple thing you understand, you do not forget. And now for alloys for the impure things we have to use different concept that we will come back later on, ok.

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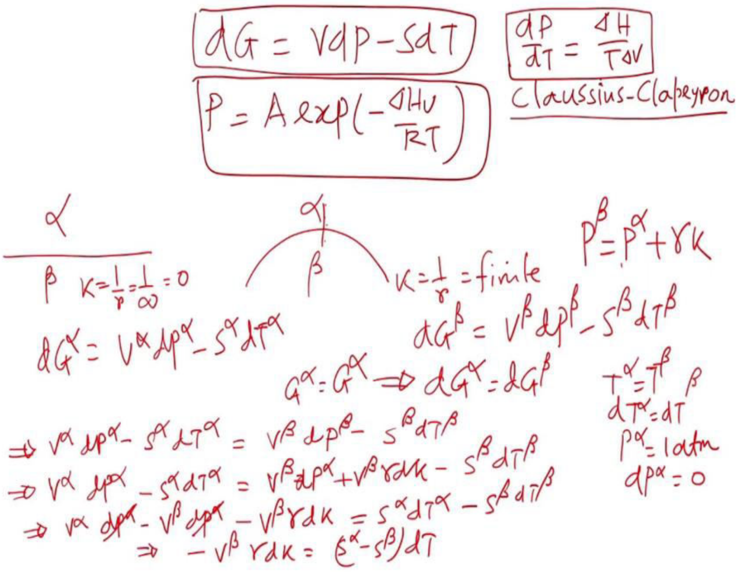

$$\boxed{dG = VdP - SdT}$$

$$\boxed{P = A\,exp\left(-\frac{\Delta H_v}{RT}\right)}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

Claussius-Clapeyron

$K = \frac{1}{r} = \frac{1}{\infty} = 0$

$K = \frac{1}{r} = \text{finite}$

$P^\beta = P^\alpha + \gamma K$

$dG^\alpha = V^\alpha dp^\alpha - S^\alpha dT^\alpha$

$dG^\beta = V^\beta dp^\beta - S^\beta dT^\beta$

$G^\alpha = G^\alpha \Rightarrow dG^\alpha = dG^\beta$

$T^\alpha = T^\beta$

$dT^\alpha = dT$

$p^\alpha = 1\,atm$

$dp^\alpha = 0$

$\Rightarrow V^\alpha dp^\alpha - S^\alpha dT^\alpha = V^\beta dp^\beta - S^\beta dT^\beta$

$\Rightarrow V^\alpha dp^\alpha - S^\alpha dT^\alpha = V^\beta dp^\alpha + V^\beta \gamma dK - S^\beta dT^\beta$

$\Rightarrow V^\alpha \cancel{dp^\alpha} - V^\beta \cancel{dp^\alpha} - V^\beta \gamma dK = S^\alpha dT^\alpha - S^\beta dT^\beta$

$\Rightarrow -V^\beta \gamma dK = (S^\alpha - S^\beta) dT$

So, let me just write this equation that is here $P = Aexp(-\frac{\Delta H_v}{RT})$. So, by these three things we can explain everything. Now, we go back to our nano things, ok. For the last 30 minutes we have been discussing this.

So, first thing is nano materials has a serious problem as per this curvature is concerned. They all are curved and very small. And surface to volume ratio is large. This we have been discussing again and again. So, how we can you know we are using some equations which we have not understood it, like what is the effect of curvature on the melting temperature or the pressure, right. So, let us do that.

So, as you know if I consider a flat surface, this is a flat surface, ok and we are considering equilibria between again alpha and beta phases, and flat is defined as curvature which is nothing but, $\frac{1}{r}$, which is nothing but 1 by infinity, which is nothing but 0, correct. We have defined curvature, right. So, a flat curvature is 0.

Now, I consider a concave surface, again alpha and beta, right. Here curvature is, $\frac{1}{r}$ and this is finite, this is not 0, this is finite, ok. So, as you see β and α there is a boundary and you know the case of soap bubble, right, the pressure inside the soap bubble is higher than the outside. And so, therefore, here P_β, that means, pressure inside the beta phase will be given by P_α plus some additional term because of this curvature, because of this curved surface.

What is that? That is nothing, but surface energy multiplied by kappa, surface energy between β and α and the κ. κ is the curvature that is $\frac{\gamma}{r}$, right. Obviously, there will be some constant sometime $\frac{2\gamma}{r}$, sometime $\frac{4\gamma}{r}$ depending on different geometries or sometime; so, let us forget about it. For simple thing this is S related to γ into κ and κ is related to r. This is understood, right.

So, now we are going to use this top equation here for alpha and beta. I am going to start from here. So, $dG^\alpha = V^\alpha dP^\alpha - S^\alpha dT^\alpha$, because we do not know what is the pressure and temperature of individual phase is same or not. So, we are using specific things for alpha and beta, correct. And here I write β. What is β? $dG^\beta = V^\beta dP^\beta - S^\beta dT^\beta$, right. It is clear to you. Nothing, but equations where which we are doing, ok.

And, again these two phases are equilibrium, so equilibrium says what? $G^\alpha = G^\beta$, my hand is going to G already right, that is obvious. And that is can be written again $dG^\alpha = dG^\beta$, so, let us plug in these two, right.

So, $V^\alpha dP^\alpha - S^\alpha dT^\alpha$, ok. I am expanding this $dG^\alpha = V^\beta dP^\beta - S^\beta dT^\beta$, right. Am I clear, ok. So, then $V^\alpha dP^\alpha - S^\alpha dT^\alpha$. So, what will be dP^β? dP^β=$dP^\alpha + \gamma d\kappa$, right. $\gamma$is constant, γ we always assume constant.

So, we are differentiating this thing P; $dP^\beta = dP^\alpha + \gamma d\kappa$. So, that is you just multiplied by V^β, where $V^\beta$is there, that is what it is. You have to do yourself otherwise you know steps will be very large $S^{\beta} dT^{\beta}$, right. So, I am going to do it now very simple. So, dP^{α}- V^{β} dP^{α}- V^{β} $\gamma d\kappa$ = $S^{\alpha} dT^{\alpha}$ S^{α}it will this side transfer $S^{\beta} dT^{\beta}$.

So, as you know this is a continuum. And this concave thing is very convex maybe it is not concave, this convex thing is a curved surface. So, temperature must be continuous it has to be, temperature cannot deform between these two. If I consider draw a line like this, ok temperature of a soap bubble outside inside. Does it differ? No, it does not, right. So, therefore, T^{α} = T^{β} = T. So, therefore, dT^{α}, dT^{β}, dT is equal to 0. There is no change. And you can always assume also one more thing for simplicity P^{α} =1 atmosphere. So, $dP^{\alpha} = 0$, right, ok.

So, dP^{α} = 0, correct. So, it is become $-V^{\beta}$ $\gamma d\kappa$ = (S^{α}- S^{β}) dT, correct, right, ok. I think there is some mistake, this should be this, it is not 0, but they are same. So, now, let me erase the some part, otherwise I cannot complete it. As I said I am going to use it as a board.

It is very nice, right, sometimes you should do it. So, that you write on your notebook you do not listen. If only listening on your things you may not write anything, but this forces you to write because I am using the same thing, same slide again and again.

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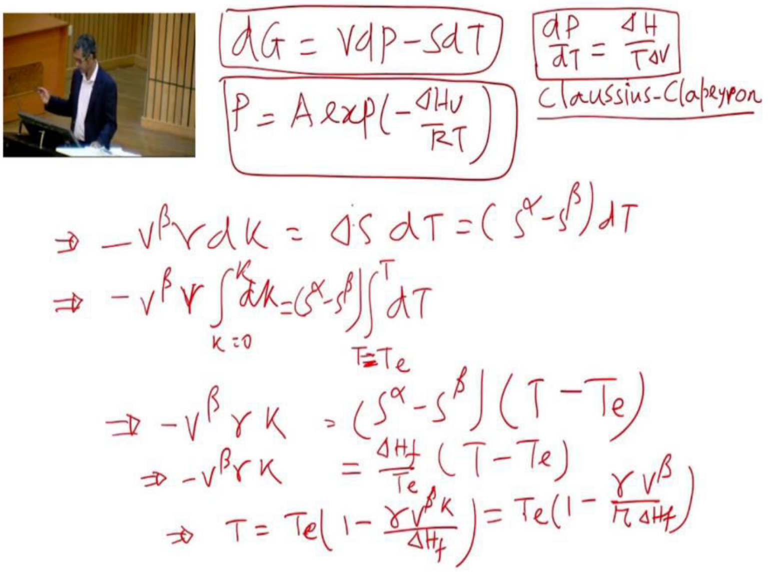

$$\boxed{dG = VdP - SdT}$$

$$\boxed{P = A\exp\left(-\frac{\Delta H_v}{RT}\right)}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

Claussius-Clapeyron

$$\Rightarrow -V^{\beta}\gamma d\kappa = \Delta S\, dT = (S^{\alpha}-S^{\beta})dT$$

$$\Rightarrow -V^{\beta}\gamma\int_{\kappa=0}^{\kappa} d\kappa = (S^{\alpha}-S^{\beta})\int_{T=T_e}^{T} dT$$

$$\Rightarrow -V^{\beta}\gamma\kappa = (S^{\alpha}-S^{\beta})(T-T_e)$$

$$\Rightarrow -V^{\beta}\gamma\kappa = \frac{\Delta H_f}{T_e}(T-T_e)$$

$$\Rightarrow T = T_e\left(1-\frac{\gamma V^{\beta}\kappa}{\Delta H_f}\right) = T_e\left(1-\frac{\gamma V^{\beta}}{r\Delta H_f}\right)$$

So, what I do? I then modify this equation is $-V^{\beta}$ $\gamma d\kappa$ = ΔS dT or that is nothing, but (S^{α}- S^{β}) dT. Now, integrate, what you integrate? $-V^{\beta}$ $\gamma \int_{\kappa=0}^{\kappa} d\kappa$, κ will be 0 for flat surface to any kappa of kappa that is equal to $(S^{\alpha}$- $S^{\beta})\int_{T=T_e}^{T}$ dT and T for flat surface is the equilibrium temperature; that means, that is what is without any curvature effect.

So, that is called equilibrium temperature. You can also define other way, but that is nothing the term which is not dependent on equilibrium temperature that is equal to T, right. So, when you have a finite curvature, ok. So, I can erase everything here now, fine.

So, I can write down this $-V^{\beta}\ \gamma\kappa$ is equal to $(S^{\alpha}$- $S^{\beta}) \times (T - T_e)$, right. So, finally, if you do the maths clearly, what you get? You get and that is can be written even this way also $-V^{\beta}\ \gamma\kappa$, this is nothing, but ΔS. And ΔS is what? ΔS I have already done, right.

That is $\frac{\Delta H_f}{T_e}$. Yes, we are using T_e, T_e is what is the equilibrium temperature for the flat surface, that is what it is. So, this gives me $T = T_e(1 - \frac{V^{\beta}\gamma\kappa}{\Delta H_f})$. So, that is it. So, if you have a curved surface and this temperature is reduced by this effect.

Now, if you look at this I can expand this term, that is where the nano crystalline effect will come $T = T_e(1 - \frac{V^{\beta}\gamma}{\text{r}\Delta H_f})$ is constant, that is a mole of volume beta phase. γ is surface energy, and this is r remember that, ok. It will create problem for you whenever you see later on.

So, let us not use this r, use this, right. ΔH_f is also constant. So, as you decrease r, the temperature or melting temperature is going to go down drastically below. Why? Because the r is decreasing, r is becoming smaller. So, this factor is increasing this will be always less than 1, because this is 1, ok, but this factor will decrease, ok, sorry increase as r decreases and therefore, 1 minus this factor will decrease and this is multiplied by T_e

So, if you consider equilibrium temperature melting temperature of water, basically ice to water is 0^0 Kelvin, 0^0 Celsius, 273 Kelvin that is equal to T_e, and you have the gamma, and you have ice particle of suppose 10 nanometers. You know the volume of water, molar volume of water, you know the heat diffusion, so you can basically calculate what is the melting temperature of ice particle of 10 nanometer diameter, correct or radius whatever. So, this is something which you should know very well. That is what we have been using it. And this is true for the pure components.

Now, for the time whatever I have, let us quickly get into the other thing. What is that? The effect of curvature on the vapour pressure, right, ok. Do not tell me too much mathematics. Sometimes we need to know, in this my lecture there will be a lot of mathematics that is why the problems will be defined and solved in your face-to-face research, ok. So, what are the effect of curvature on vapour pressure? That is the effect of curvature on temperature, effect of κ on vapour pressure. This we have done, but we are showing you mathematically, ok. I can use this equation, right or no.

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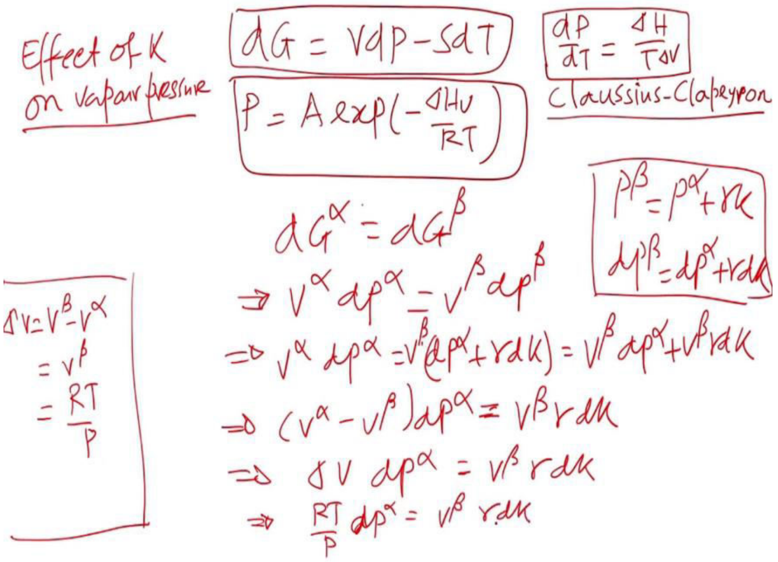

Well, obviously, $dG^{\alpha} = dG^{\beta}$ let us do it quickly. But, we will come back if you do not understand again. And what you can do? We can write down this very easily, right. We are ignoring SdT term here. Why? That is because temperature is constant. So, dT is 0, right. Here pressure is changing, vapour pressure is changing.

You are keeping a material at a constant temperature and asking yourself whether it will vaporize or not, that will depends on the curvature, that is what you are going to see it or the size. So, therefore, ΔT is constant 0, ok, T is constant. That is why SdT term vanishes, we do not need to use it. Am I clear, yes.

So, now as you have already looked at it P^{β}=$P^{\alpha} + \gamma d\kappa$ and therefore, dP^{β}=$dP^{\alpha} + \gamma d\kappa$. So, we can write down this $V^{\alpha}dP^{\alpha} = V^{\beta}dP^{\beta}$. So, $V^{\alpha}dP^{\alpha} = V^{\beta}(dP^{\alpha} + \gamma d\kappa\ )$ that is nothing, but $V^{\beta}dP^{\beta} = V^{\beta}(dP^{\alpha} + \gamma d\kappa\ )$, you must be thinking you are doing the same thing, no, well, see the difference. So, I write down $(V^{\alpha} - V^{\beta})\ dP^{\alpha} = V^{\beta}\gamma d\kappa$, right. So, that is nothing, but $\Delta V dP^{\alpha} = V^{\beta}\gamma d\kappa$.

Now, what is ΔV? Let us do the math this side, ok. So, ΔV = $(V^{\beta} - V^{\alpha})$ that is nothing, but V^{β}, right, that is nothing, but $\frac{RT}{P}$ for 1 mole. So, you can write down that. For the sake of generalization, let us remove all α, β things, that is no longer needed. Because; why do not longer needed? Because we are finally, deriving equations on which everything is related to phases. So, what do you get? If you solve this equation, what you get?

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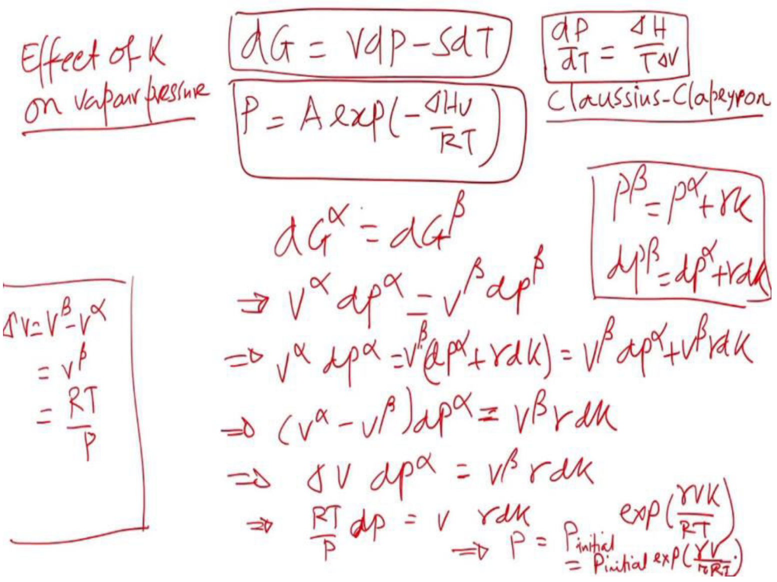

Effect of κ on vapour pressure

$$\boxed{dG = VdP - SdT}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

Claussius-Clapeyron

$$\boxed{P = A\exp\left(-\frac{\Delta H_v}{RT}\right)}$$

$$\boxed{\begin{aligned} P^{\beta} &= P^{\alpha} + \gamma\kappa \\ dP^{\beta} &= dP^{\alpha} + \gamma d\kappa \end{aligned}}$$

$$dG^{\alpha} = dG^{\beta}$$

$$\Rightarrow V^{\alpha} dP^{\alpha} = V^{\beta} dP^{\beta}$$

$$\Rightarrow V^{\alpha} dP^{\alpha} = V^{\beta}(dP^{\alpha} + \gamma d\kappa) = V^{\beta} dP^{\alpha} + V^{\beta}\gamma d\kappa$$

$$\Rightarrow (V^{\alpha} - V^{\beta}) dP^{\alpha} = V^{\beta}\gamma d\kappa$$

$$\Rightarrow \delta V\, dP^{\alpha} = V^{\beta}\gamma d\kappa$$

$$\Rightarrow \frac{RT}{P} dP = V\gamma d\kappa \Rightarrow P = P_{initial}\exp\left(\frac{\gamma V\kappa}{RT}\right) = P_{initial}\exp\left(\frac{\gamma V}{rRT}\right)$$

$$\begin{aligned} \Delta V &= V^{\beta} - V^{\alpha} \\ &= V^{\beta} \\ &= \frac{RT}{P} \end{aligned}$$

Well, I will write down the final equation, you do yourself at your home. So, you get P in P constant or P = $P_{initial}$ exp $\left(\frac{\gamma V\kappa}{Rt}\right)$ So, you get an exponential relationships. And this can be written as P = $P_{initial}\exp(\frac{\gamma V}{rRt})$, one is capital R, one is small r, capital R is the gas constant, small r is the particle radius. So, you have understood, right. This is something, these two relationships are very important for pure component temperature and the pressure related to the size of the particle. This can be derived directly from thermodynamics.

So, therefore, before I stop for today's lecture, we started Thermodynamics of Nanoparticle discussion today, and we used only one equation dG = VdP - SdT for derivation of everything. You can imagine that. Thus, stability equation tells me to derive everything in this world, ok.

Let me stop here. We will come back and do the mathematics again, ok.