Interfacial Engineering

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Lecture-08

Kelvin equation; Tutorial

Kelvin equation, vapour pressure, droplets, and bubbles

Welcome back.

So, in last class, we dealt with Young–Laplace equation, right. So, Young–Laplace equation was used to, you know, determine the Laplace pressure for any given equilibrium, I mean, a geometry, you know, in a equilibrium shape or It can be used to describe the equilibrium shape of any given geometry. Okay, so in today's lecture, we will look at the application of Young–Laplace equation, which is nothing but Kelvin equation. Okay, and we will see how Kelvin equation is used to describe the, you know, the phase equilibria, you know, wherein you can consider phenomena like boiling, you know, condensation, crystallization, all that. So we will look at how Kelvin equation can be used or how the curvature effect, okay, affect these phase equilibria or the kinetics of let's say boiling and condensation, crystallization etc.

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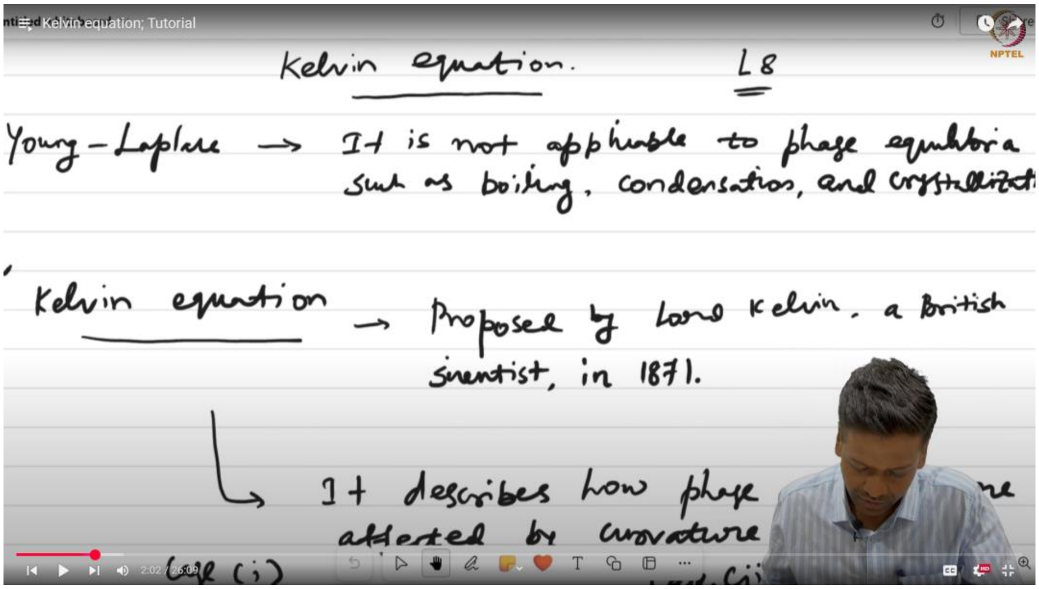

So in today's video lecture, we are going to look at the derivation of Kelvin equation and then we are going to look at tutorial session followed by the derivation part. Okay, let's begin. Yeah, so first let's look at the Kelvin equation. So we know that, we just now described that, you know, as such Young–Laplace equation is not applicable to phase equilibria.

I mean, You cannot use that equation as such to describe the radius of a given geometry, especially in the application of phase equilibria, like boiling, condensation, and crystallization. Kelvin equation does I mean helps us you know the find out you know the critical radius of the bubble okay and it also help us find out the you know the the pressure right of bubble or the droplet okay you know so in this equation One can also describe how phase equilibria are affected by what is known as the curvature effect. So this equation was proposed by Lord Kelvin himself. is none other than the scientist who discovered the absolute temperature scale. In 1871, he proposed this form of equation which we are going to derive very shortly.

 In his article in 1871, he described using the application of Young–Laplace, he proposed this equation. So, let us look at how it can be appreciated. This equation can be appreciated, you know, when it comes to the you know, phase equilibria, you know, phenomena like boiling point, crystallization and condensation, right How the curvature effect is going to play a role, major role in these processes, right? So, let's look at two scenarios. One is case one, where you have a flat interface, right Case two, you have a curved interface, right Now so we know that because the curved interface brings in some amount of compactness and therefore you can expect the pressure inside the bubble or droplet will be greater than pressure of you know at the flat interface. when similar conditions prevail.

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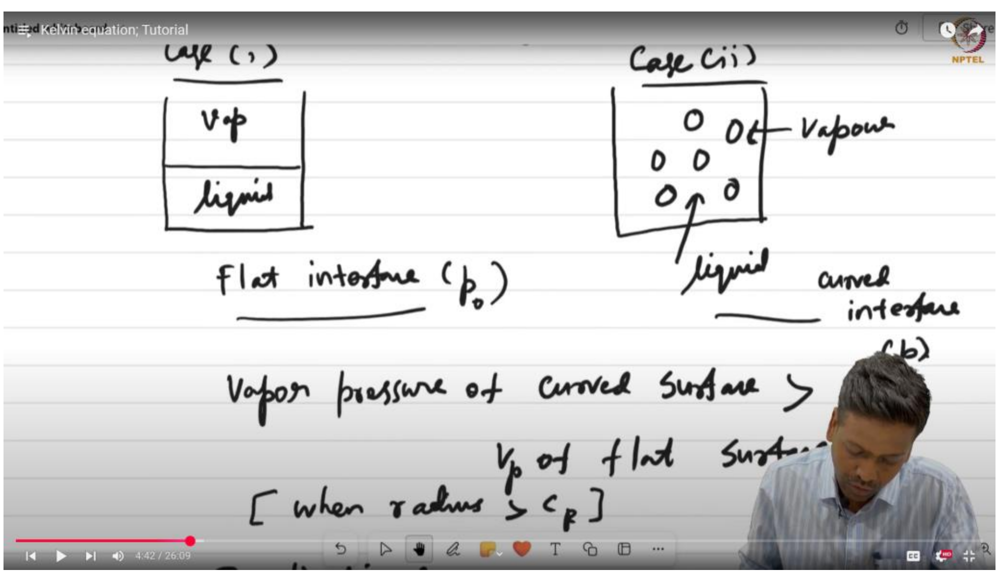

So in this case, let's look at the flat interface and the curved interface. So the vapor pressure of the curved surface is going to be greater than the vapor pressure of flat surface at any given temperature. So this condition is valid when the radius of the bubble is greater than the critical radius of the bubble. Okay.

Right. So we'll look at how this curvature effect plays a major role and how it affects the phase equilibria. So let's say we have a case where boiling phenomena is occurring. Okay. So as the droplet size we will see shortly in an equation using the Kelvin equation. As the droplet or bubble size goes down, the pressure goes up.

So that I explained through the compactness of the bubble just now. So as the vapor pressure of the bubble goes up, the boiling becomes easier, which means that the kinetics of boiling, evaporation, can be improved if the bubble size, you know, goes down, right Which means that vapor pressure goes up, okay Which is big. I mean, this is due to as the bubble size goes down, vapor pressure goes up. which can easily overcome the atmospheric pressure. Because it can easily overcome the atmospheric pressure you can expect that this bubble can promote the boiling quickly.

So this is actually quite useful. the curvature effect is quite useful if you want to accelerate the kinetics of boiling. Whereas on the other hand the increase in the vapor pressure is not going to help in terms of condensation because if vapor pressure goes up it actually it doesn't favor the condensation, right So, in this case, curvature effect provide, you know, negative consequence. So, one has to know, in this case, one has to understand that the bubble size one can, you know, tune so that the vapor pressure is not too high. Similar is the case when you deal with crystallization.

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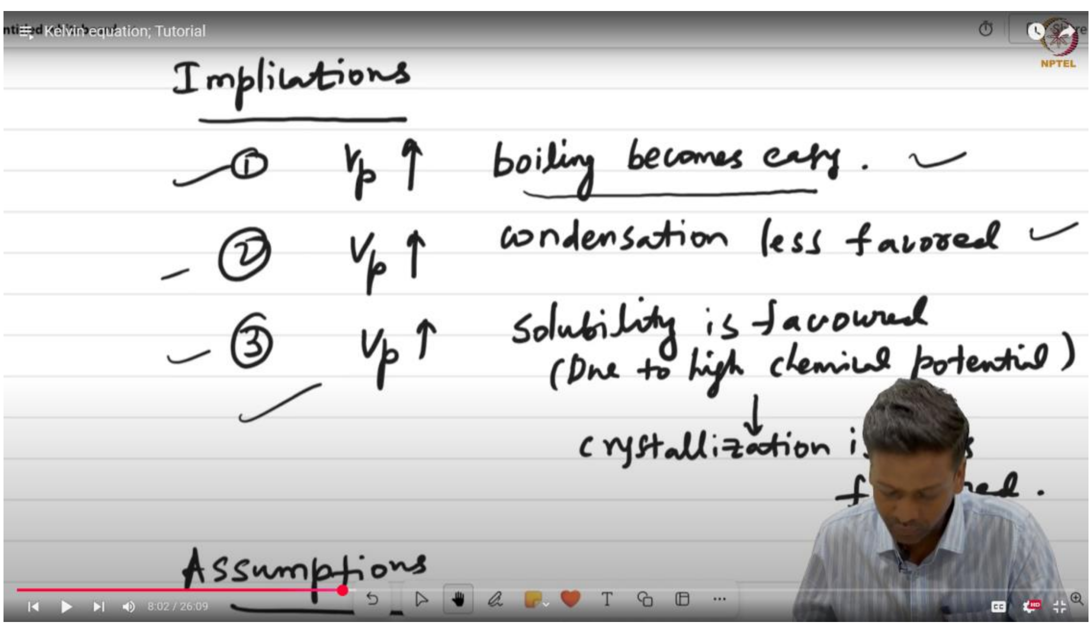

Here also, as the vapor pressure goes up, you can expect that the solubility is favored. This is because of the high chemical potential that exist I mean that drives the solubility you know to the greater extent that's why the solubility will be favored when the vapor pressure goes up the consequence of that will be crystallization will be less favored. So in the case of condensation and crystallization, increasing the vapor pressure is not going to help us, whereas there you need to tune such a way that the vapor pressure is not too high. So these are some of the consequences of curvature effect. So by knowing this, we can actually tune the size or the radius of the bubble or droplet so that we can tune the respective process.

So we are going to look at the derivation of Kelvin equation. In that Kelvin equation, you will see there is a relationship exists between the radius of bubble or droplet with the surface tension and the temperature. We will look at that shortly. Before that, Let us list out the assumptions involved when deriving this equation. The first and foremost assumption that we need to know is this equation is derived keeping in mind the equilibrium exists between vapor and liquid.

So, the equilibrium established between vapor and liquid That is the first and foremost assumption. The second one will be incompressible liquid. That you will know why we have to assume this, why we have to make this assumption. We know that shortly when we derive this equation. The other one is the, you know, in this case we are going to take ideal gas, the fluid obeys the ideal gas.

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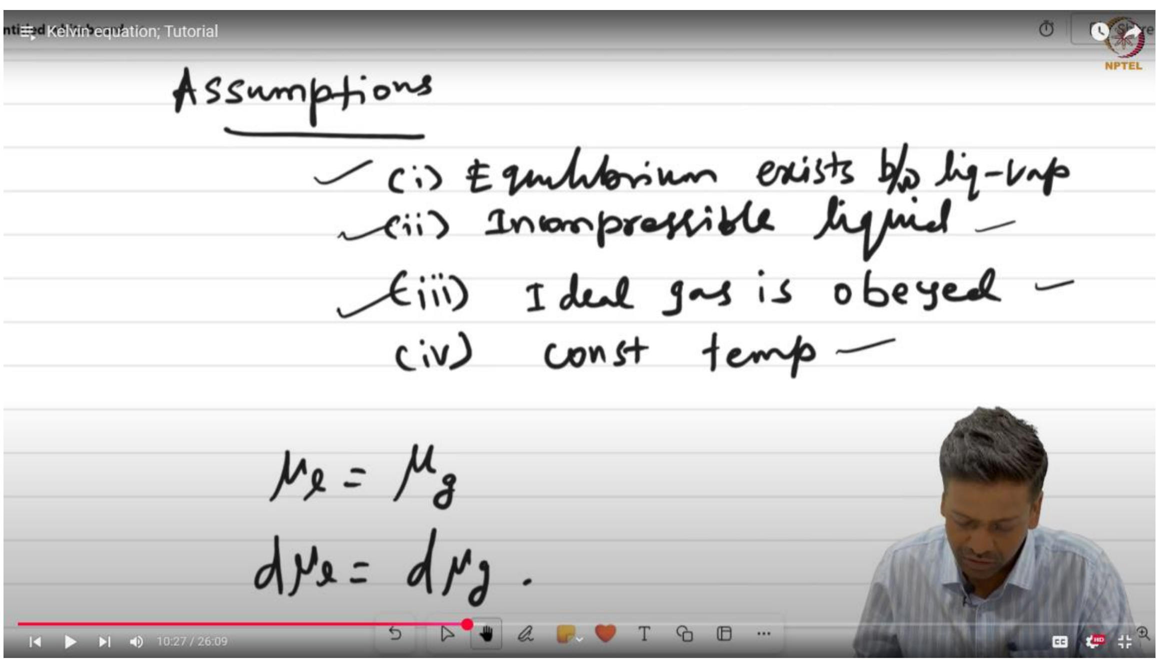

That is the assumption we are going to take. the last one is constant temperature. So these are the assumptions we need to note down so that this equation is only valid in these circumstances. So as we know the phase equilibria is the phase transition whenever we talk about their equilibrium process at equilibrium the chemical potential the change in chemical potential in liquid side and change in chemical potential in gas side, both will have to be equal. This is the essential criterion of equilibrium.

This we know, pretty much we know. So this is going to be our starting point. Now let's only look at the change in chemical potential on the liquid side. So if we look at the change in chemical potential on the liquid side at constant temperature, that is an assumption we have already mentioned. In that case, you will not have the entropy term in this; you will simply have the other term, which is Vdp. So remember, this is nothing but molar volume. So, this can be integrated using the limits p_0 to p. Here, this p_0 is the reference state.

Reference state for us in this case will be flat interface. So this is going from flat interface to at some pressure in curved surface. So this is our equation for the liquid side. So in this case, we know since we mentioned that it is incompressible liquid, so we can treat V bar as constant 1 so that V bar can be taken away from the integral. we will simply have p0 to p and dp.

Now, this is simply ΔP, and ΔP is nothing but the Laplace pressure. We know the Laplace pressure for a spherical geometry, because a bubble or droplet always assumes a spherical shape. So, we can safely assume the geometry to be spherical, and for that spherical geometry, the Laplace pressure that we know is:

$$\Delta P=2\gamma/r$$

Or, more specifically:

$$\Delta P=2\gamma/r_s$$

where r_s is the radius of the spherical bubble or droplet. Thus, the simplified equation for chemical potential on the liquid side is:

$$\mu_{liquid}=\bar{V}\cdot 2\gamma/r_s$$

This is Equation (1). Now, for the gas side, we have the similar equation.

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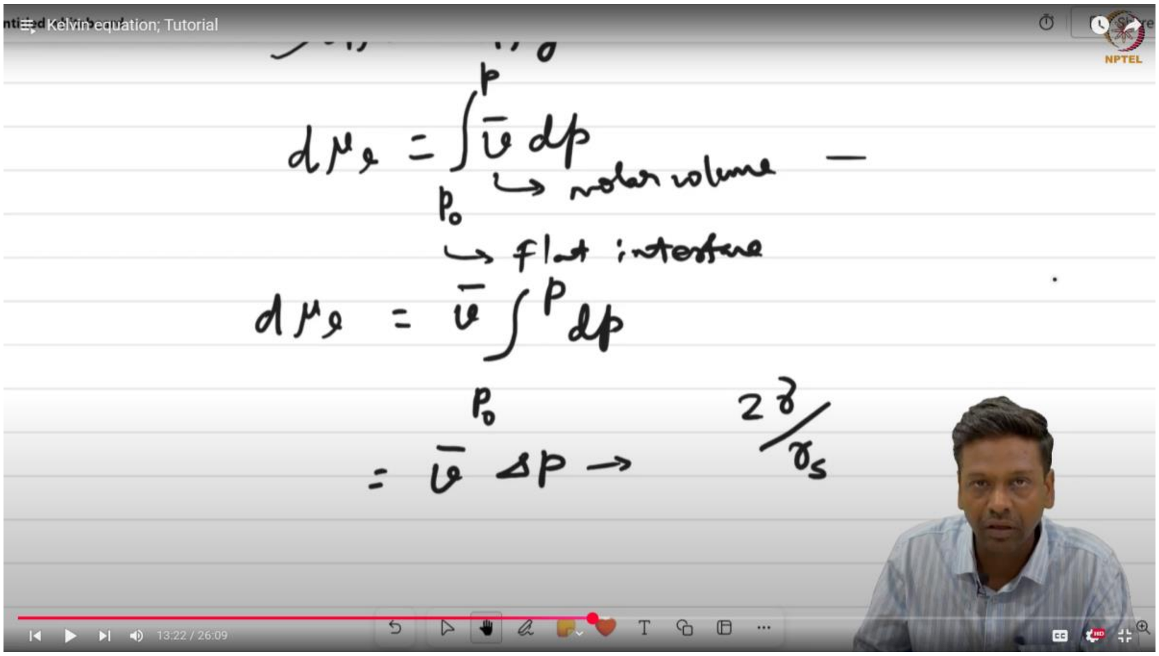

Here also, my integral limits are going from p_0 to p, where p_0 is a reference state (flat interface), and p is any pressure in a curved surface. Now, $\bar{V}$ is the molar volume, and here we will also look at the assumptions that we made in the beginning. One of the assumptions we made was ideal gas behavior, the fluid obeys the ideal gas law. So, in this case, we will simply have:

$$\bar{V} = RT / p$$

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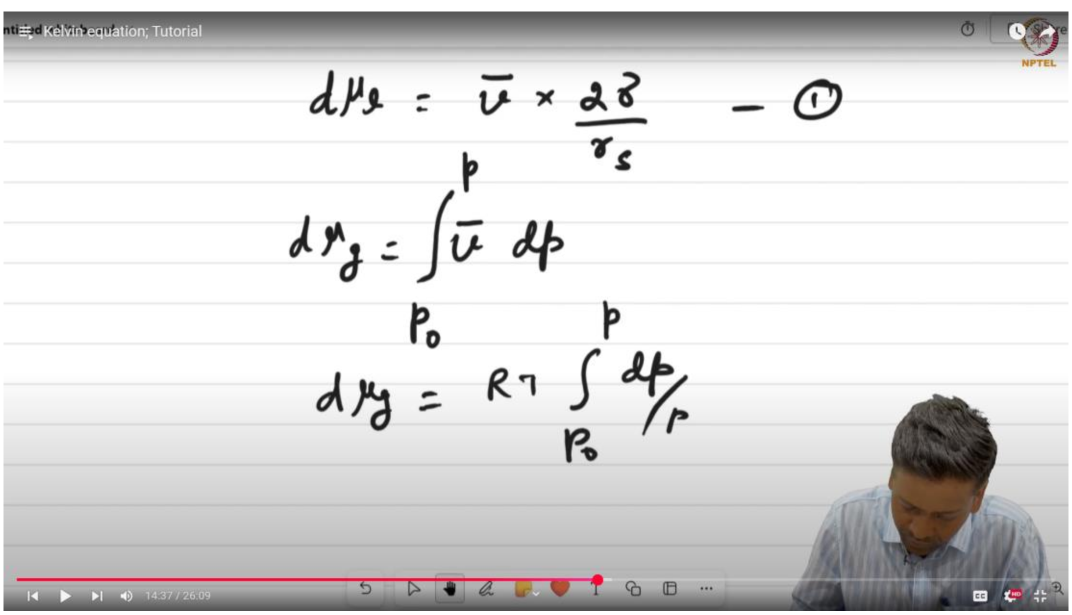

So, you can take RT out. Then you will have:

with limits going from p_0 to p. So, from the gas side, we will have:

$$d\mu g = RTln(P/P_0)$$

This is Equation (2). Since we know that at equilibrium, we have:

$$d\mu L = d\mu g$$

So, I can easily write:

$$ln\left(\frac{P}{P_0}\right) = \frac{V^{-} \cdot 2\gamma}{RT \cdot r_s}$$

Or, sometimes, you can replace V̄ with m/ρ, where m is the molecular weight and ρ is the density. In that case, we will simply have:

$$\frac{\text{m } 2\gamma}{\rho RTr_s}$$

So, this is the Kelvin equation, which is used for phase equilibria such as boiling, condensation, and crystallization. This equation is usually used for a droplet, and when we talk about bubbles up to the critical size, this equation, when evaluated using the natural logarithm, will always be negative. This means that:

$$\frac{P}{P_0}$$

will be a fraction, and thus the logarithm will yield a negative value. So, for bubbles, this equation takes a negative sign. The rest of the equation remains the same, but the negative sign is included to ensure that the radius of the bubble is a positive quantity. So, Equation (3) is applicable for droplets, and Equation (4) is applicable for bubbles. Now, we can stop here and move on to the tutorial part. We have a couple of exercises.

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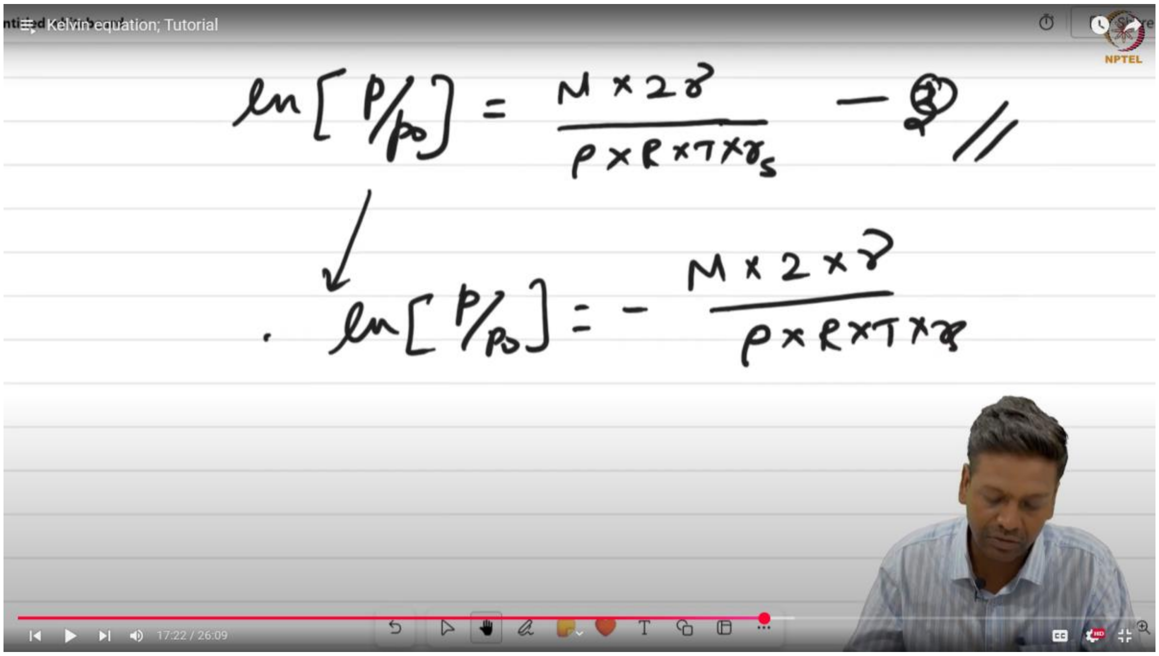

We can look at them one by one. Let's say the equation that we know is, sorry, the problem number one (exercise number one) is based on the Kelvin equation. Here, we are going to calculate the vapor pressure of spherical water droplets of radius 1, 10, and 100 nanometers. The temperature is given as 280 K, and the surface tension of water at this temperature is given as 74.6 milliNewtons per meter.

The equation we will use is:

$$ln\left(\frac{P}{P_0}\right) = \frac{\mathrm{m}\ 2\gamma}{\rho R T r_s}$$

The data required for the calculations are provided, and we need to calculate the vapor pressure P of spherical water droplets. Specifically, we need to calculate the ratio of P/P_0 for different droplet radii.

Given:

- Temperature T=280K
- Surface tension of water at this temperature γ = 74.6mN/m
- Radius of spherical droplets: 1 nm, 10 nm, 100 nm

Now, let's calculate P/P_0 for these droplet radii:

1. For a 100 nm droplet radius:

$P/P_0 = 1.011$

2. For a 10 nm droplet radius:

   $P/P_0 = 1.12$

   (This is one order of magnitude higher than the previous one.)

3. For a 1 nm droplet radius:

   $P/P_0 = 3.16$

These are the P/P_0 values for different droplet radii. You can verify these answers yourself by applying the Kelvin equation.

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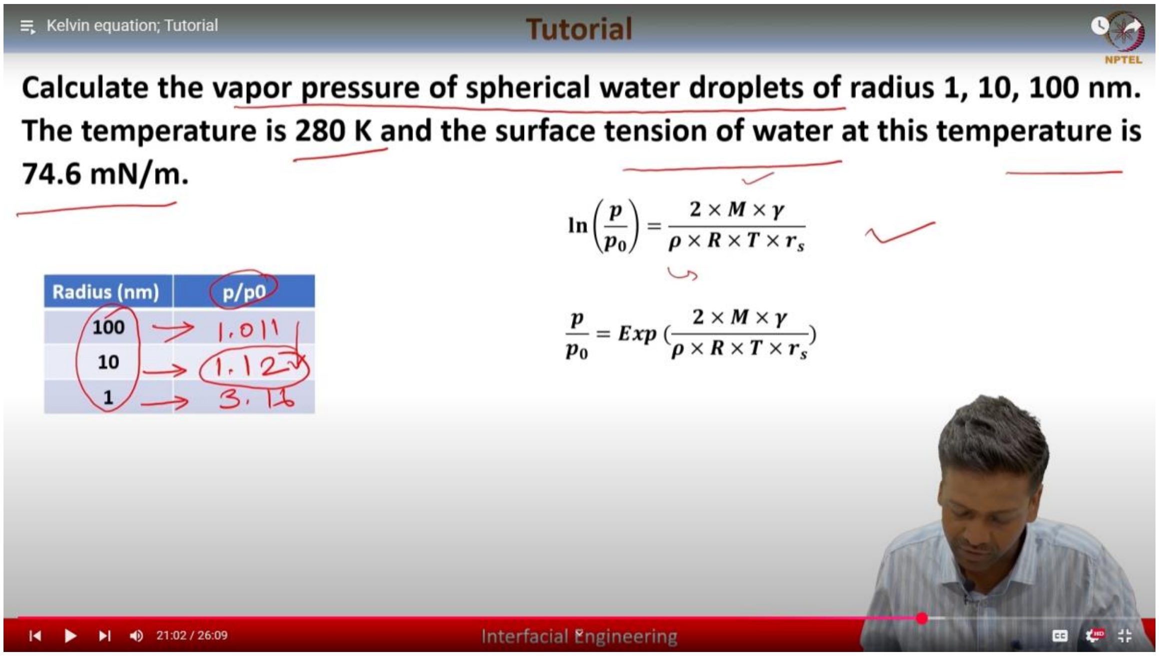

So, if I look at this, when you change the droplet radius, you know, down drastically, when it goes down, the $\frac{P}{P_0}$ also, you know, goes down. I mean, it increases by one order, I mean, it increases drastically. You can see at least one order difference higher than the previous one. So, which comes to say that, I mean, which highlights the curvature effect of, we know, the droplet. So, the lower the droplet size, the $\frac{P}{P_0}$ value will become higher and higher. As you go down $\frac{P}{P_0}$, the pressure of the vapor pressure of the water droplet will become higher and higher, right? So this is one exercise wherein we can understand the application of the Kelvin equation. In another exercise, we can even calculate the radius of the bubble. The radius of the bubble can be calculated using the equation:

$$r_s = \frac{\mathrm{m}\ 2\gamma}{\rho RT}$$

Where:

- MMM is the molecular weight (since it is water vapor, M=0.018 kg/mol)
- γ is the surface tension, which is 0.0585 N/m
- ρ is the density, which is 957 kg/m^3
- R is the gas constant, 8.314 J/ mol·K
- T is the temperature in Kelvin.

Now, there is a condition given here. Calculate the minimum size for a bubble of water vapor forming 10 cm beneath the surface of water. This means that the condition is there is a bubble, so which is just below the water surface, but the height of this water surface is the bubble is kept below, I mean, 10 centimeters below the water surface. So, you will have the bubble will have to overcome both the atmospheric pressure that is acting on the water, and then there is also called hydrostatic pressure, which is nothing but:

Hydrostatic Pressure=h·ρ·g

Where:

- h is the height of the water column (10 cm = 0.1 m),
- ρ is the density of water (957 kg/m^3),
- g is the acceleration due to gravity (9.81 m/s^2).

And you have atmospheric pressure and the hydrostatic pressure. So, if you assume that your initial pressure is given, which is P_0, which is 108.8 kilopascal, but what we need to know is for this condition, which means that the actual pressure for this condition, which is given here, which is atmospheric pressure plus the hydrostatic pressure. So, for this case, the actual pressure is going to be 102 kilopascal.

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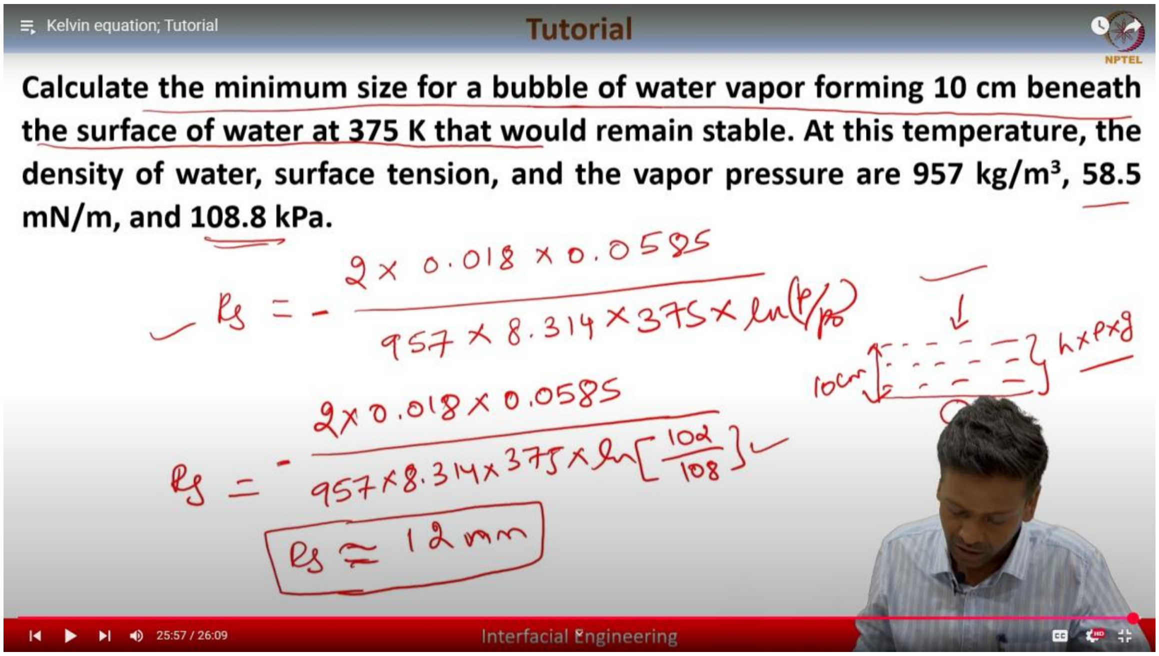

Okay, so if you substitute these values here, we know that P_0 is 108 kPa and so P is nothing but 102 kPa. So in that case, how do we deal with it? This will be:

$$r_s = 2 \cdot 0.018 \cdot 0.0585 / 957 \cdot 8.314 \cdot 375 \cdot ln\left(\frac{P}{P_0}\right)$$

So if I substitute this value in p by p0, the rest of the values are already known. So, finally, the radius of the spherical bubble is going to be 12 nanometers in this case. Approximately 12 nanometers. So, you can understand that for a given condition, the spherical bubble is going to be 12 nanometers. We have a negative sign here because of this fraction. The logarithm of this fraction turned out to be negative, and minus and minus finally result in the radius of the spherical bubble being a positive quantity. Here, it is simply nothing but 12 nanometers.

Okay. So, I am sure these exercises will help you understand the application of the Kelvin equation in a much better way. So, I will stop here. We will continue from the next lecture. Thank you.