Introduction to Atmospheric and Space Sciences

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Lecture – 38
Droplet Growth and Solute Effect

Hello dear students. So, we will continue the discussion on the curvature and the Solute Effects. So, we will try to see how does the solute effect a play an important role in deciding the growth of a cloud droplet into a rain droplet or let us say into the formation of a ice crystal let us say. So, like we have seen several number of times.

So far, the vapor to condense into a liquid phase will need water, what we call as the cloud condensation nuclei right. So, what are cloud condensation nuclei? Cloud condensation nuclei are class of particles or a class of aerosol particles. They make some of the let us say a aerosol population.

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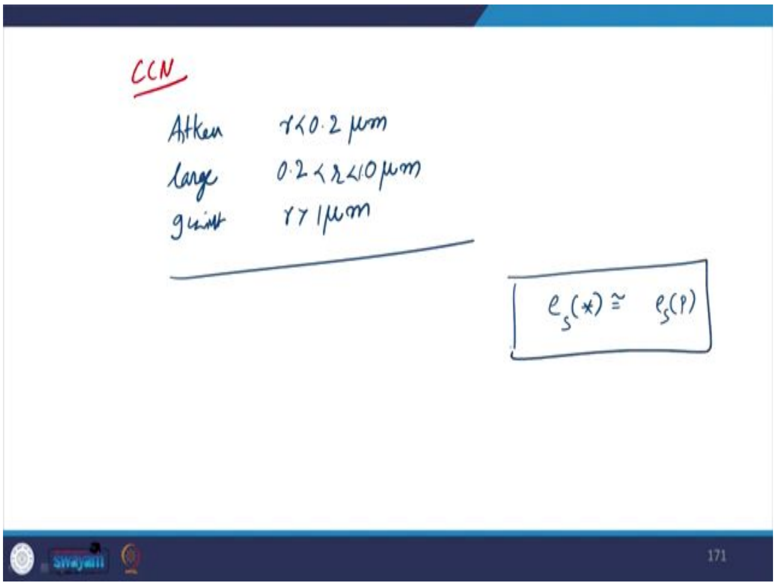

CCN

Atken $r < 0.2\ \mu m$
large $0.2 < r < 1.0\ \mu m$
giant $r > 1\ \mu m$

$$\boxed{e_s(*) \cong e_s(p)}$$

So, there are three different types of cloud condensation nuclei which are let us say Aitken nuclei which are typically of the size of less than 0.2 micro meters and large nuclei which are between 0.2 to 0 point let us say 1 micrometer. And another giant nuclei which are greater than 1 micrometer. Now, if you have this nuclei; we have to understand how the saturation vapor pressure with the solute varies or changes in comparison to saturation vapor pressure over let us say, over pure surface, pure or let us say pure water. In the way we have to understand how this changes.

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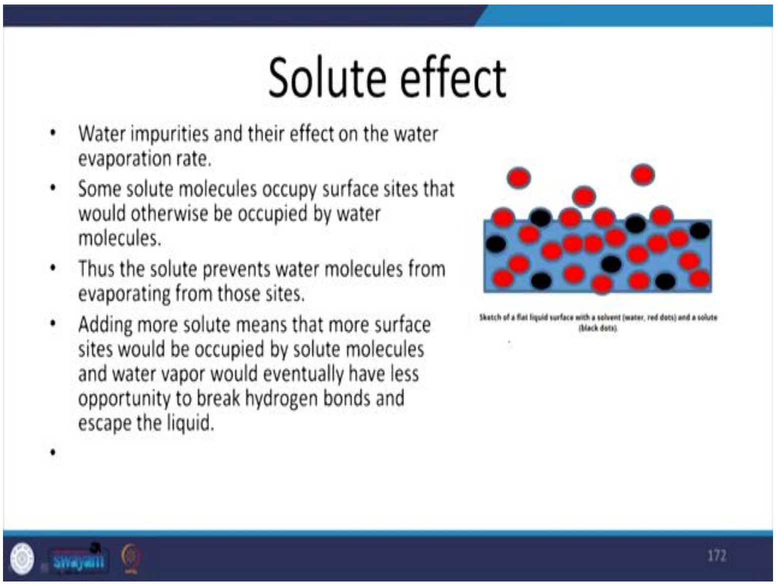

Solute effect

- Water impurities and their effect on the water evaporation rate.
- Some solute molecules occupy surface sites that would otherwise be occupied by water molecules.
- Thus the solute prevents water molecules from evaporating from those sites.
- Adding more solute means that more surface sites would be occupied by solute molecules and water vapor would eventually have less opportunity to break hydrogen bonds and escape the liquid.

Sketch of a flat liquid surface with a solvent (water, red dots) and a solute (black dots).

Now, what is the aspect that you want to understand when you add a solute. So, water impurities and their effect on the water evaporation rate is the basic idea. So, when you add some impurities on the water, in the water; what will happen? So, the impurities that I am talking about are the cloud condensation nuclei. So, if we have cloud condensation nuclei and condensation happens out of it. How will the vapor pressure change? Ok.

Some solute molecules occupies the surface slides; surface sites that would otherwise be occupied with water molecule. So, why are we interested in vapor phase? So, the evaporation rate depends on the amount of condensation and the amount of vaporization right. So, if we say that, if you replace some sites on the surface because, ideally the surface molecules are the ones which will be escaping or which are free to escape into the vapor phase.

So, if you replace some molecules with the solute molecules, let us say impurity molecules. Then, obviously; the rate at which the evaporation takes place will decrease. So, thus the solute prevents water molecules from evaporating from those sites. Now, adding more solute means that more surface sites would be occupied by the solute molecules and water vapor would eventually have less opportunity to break the bonds and go into the vapor phase right.

So, thereby by adding a solute you are decreasing the rate of evaporation. We do not talk about temperature here, but at any given temperature. If you add impurities; the rate at which evaporation will happen will decrease, simple. Now, because the evaporation rate is lowered which means that; there will be net condensation until the water vapor flux to the surface matches the water vapor flux leaving the surface right.

So, when the equilibrium is established between the lower evaporation rate and condensation. The condensation will obviously, be lesser this means the water vapor with saturation vapor pressure will be lower than what used to be only in the presence of water right. So, thus the equilibrium vapor pressure is less than the saturation vapor pressure with a pure water surface right.

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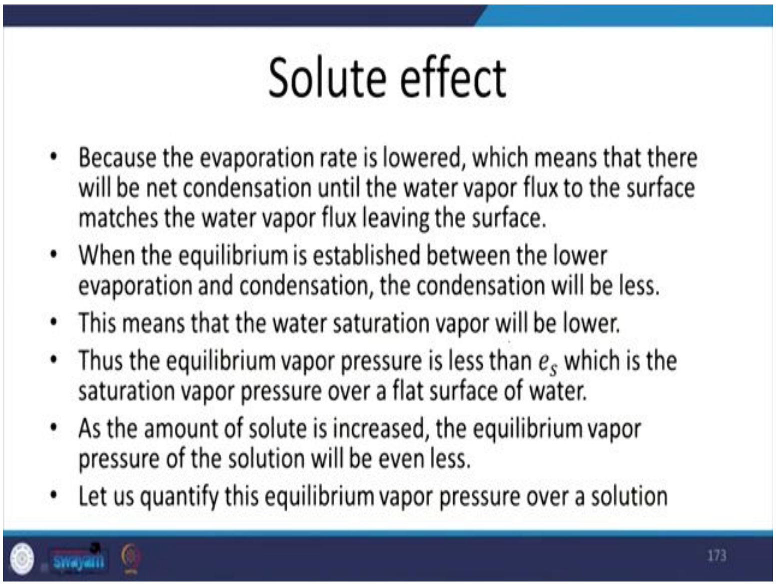

Solute effect

- Because the evaporation rate is lowered, which means that there will be net condensation until the water vapor flux to the surface matches the water vapor flux leaving the surface.
- When the equilibrium is established between the lower evaporation and condensation, the condensation will be less.
- This means that the water saturation vapor will be lower.
- Thus the equilibrium vapor pressure is less than e_s which is the saturation vapor pressure over a flat surface of water.
- As the amount of solute is increased, the equilibrium vapor pressure of the solution will be even less.
- Let us quantify this equilibrium vapor pressure over a solution

So, flat surface of water of course. So, as the amount of solute is increased the equilibrium vapor pressure of the solution becomes even more even lesser. So, let us quantify this equilibrium vapor pressure over a solution. So, let us see how we can put these effects into a mathematical treatment and how we can write an expression for the saturation vapor pressure with impurity in terms of saturation vapor pressure without impurity right. So, then an empirical relation expressing this variation is given by the Raoult’s law right.

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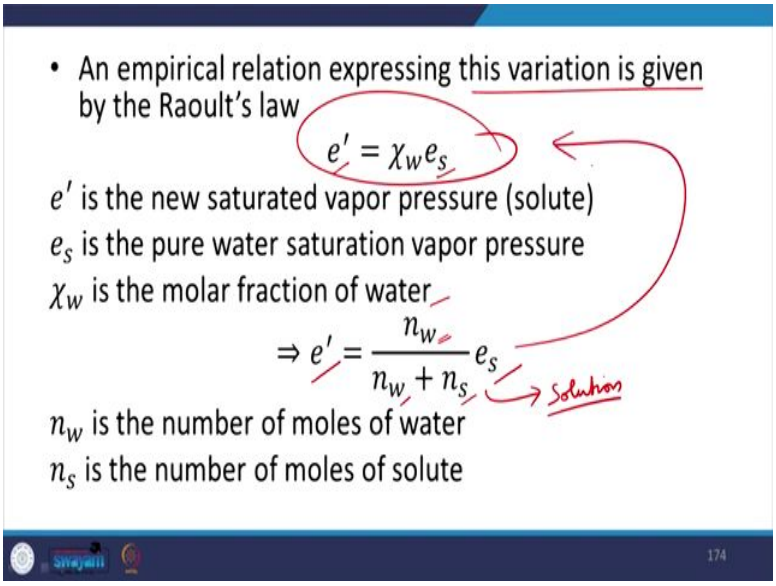

- An empirical relation expressing this variation is given by the Raoult's law

$$e' = \chi_w e_s$$

e' is the new saturated vapor pressure (solute)

e_s is the pure water saturation vapor pressure

χ_w is the molar fraction of water

$$\Rightarrow e' = \frac{n_w}{n_w + n_s} e_s$$

Solution

n_w is the number of moles of water

n_s is the number of moles of solute

So, we already have a relation let us say. So, the empirical relation expressing this variation; variation of we have seen what it is right. So, here e prime is the new saturation vapor pressure in the presence of a solute right, e s is the saturation vapor pressure in the absence of a solute or in pure water right. And chi w is the molar fraction of water. So, chi w will tell you what is the molar fraction of water, there is number of moles of water with respect to the total number of moles of let us say solute and water which is the solution. Total number of moles of the solution right.

So, this is the saturation vapor pressure in the presence of a solute and this is in the absence of a solute. Where n w is the number of moles of water, n s is the number of moles of solute right. So, if we continue this so, what we have is this, an empirical relation. So, this is an empirical relation. So, this relation needs to be substituted with this right.

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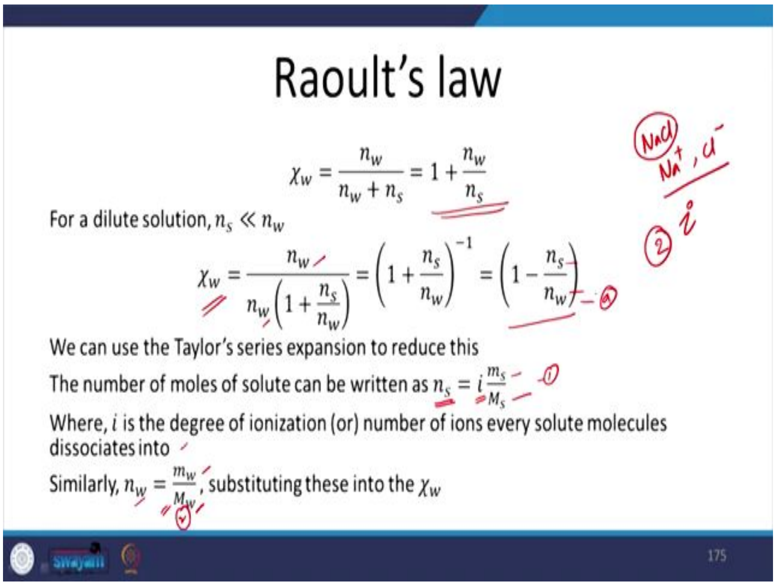

Raoult's law

$$\chi_w = \frac{n_w}{n_w + n_s} = 1 + \frac{n_w}{n_s}$$

For a dilute solution, $n_s \ll n_w$

$$\chi_w = \frac{n_w}{n_w\left(1 + \frac{n_s}{n_w}\right)} = \left(1 + \frac{n_s}{n_w}\right)^{-1} = \left(1 - \frac{n_s}{n_w}\right)$$

We can use the Taylor's series expansion to reduce this

The number of moles of solute can be written as $n_s = i\frac{m_s}{M_s}$ ①

Where, i is the degree of ionization (or) number of ions every solute molecules dissociates into

Similarly, $n_w = \frac{m_w}{M_w}$, substituting these into the χ_w

NaCl

Na^+, Cl^-

② i

So, this is the Raoult's law. So, where we have approximated this molar fraction n w by n w plus ns as 1 plus n w by n s. Now, let us say we take a very dilute solution where the number of moles of solute are very very less in comparison to the number of moles of water, very dilute solution. So, you have added a little impurity into the solution right. So, chi w; the molar fraction, chi w is the molar fraction can now be written as n w by n w, this is now written here right. So, then we can write it as 1 minus n s by n w. Now we can use the Taylor series expansion to reduce this. So, the number of moles of solute can be written as number of moles of solute. What is number of moles of a weight divided by the molecular weight of the particular substance divided by the molecular weight of that substance will give you the number of moles.

Now, when you add a solute, when you add a foreign substance. It may so happen that this substance may dissociate, let us say if you take NaCl, it might associate into Na plus and Cl minus right. So, this dissociation or the number of species that come out of the dissociation can be characterized by the degree of dissociation. Degree of ionization or degree of dissociation let us say. So, the number of moles of solute can be written as ns is i times ms by M s; m s is the molecular weight sorry weight divided by the M s is the capital ms is a molecular weight. Where i, is the degree of ionization or the number of ions every solute molecule will dissociate into.

So, in this case it is 2; that means, the solute molecule which is Na Cl, that you are adding is dissociated into 2 ions; which is Na plus and Cl minus right. So, nw will stay the same. n w is the number of moles of water is the amount of water and the molecular weight of water. Substituting these two things. So, now, we need ns and nw ns is now written as i times ms by M s; that means, that so, if it is we are not bothered about what is the ion which one is heavier or which one is lighter.

We are just bothered about the number of species which will be available let us say in terms of its molar fraction. So, let us say if you add NaCl; NaCl would not be as it is Na Cl molecule will not be the same when you add it in the water. So, it will be N a plus and Cl minus. So, eventually you have an an ion in Na plus and you have an ion which is Cl minus. And the other molecule that you have is H2O right.

So, if you substitute these two things here into the molar fraction chi w you write so, you have n s which is written like this and you have n w which is of course, written like this you substitute these two things let us say 1 and 2 into this expression which is a let us say.

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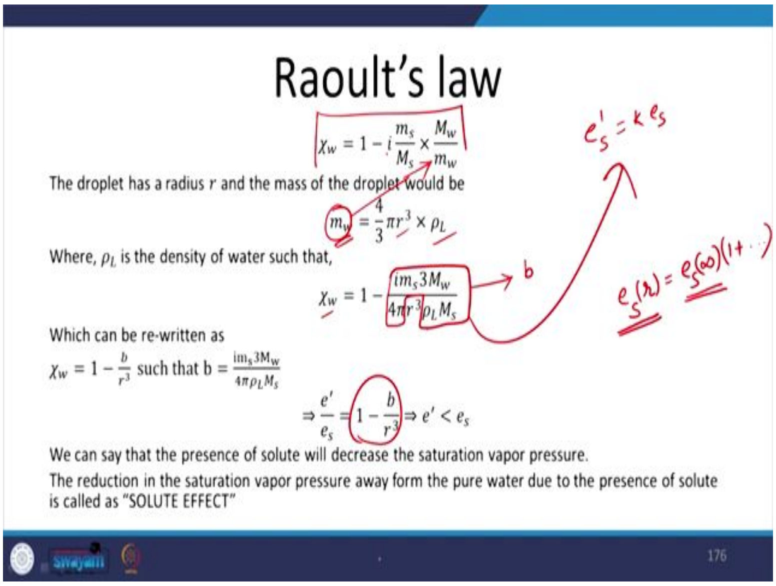

Raoult's law

$$\boxed{\chi_w = 1 - i\frac{m_s}{M_s} \times \frac{M_w}{m_w}}$$

The droplet has a radius r and the mass of the droplet would be

$$m_w = \frac{4}{3}\pi r^3 \times \rho_L$$

Where, ρ_L is the density of water such that,

$$\chi_w = 1 - \frac{i m_s 3 M_w}{4\pi r^3 \rho_L M_s} \xrightarrow{} b$$

Which can be re-written as

$\chi_w = 1 - \frac{b}{r^3}$ such that $b = \frac{i m_s 3 M_w}{4\pi \rho_L M_s}$

$$\Rightarrow \frac{e'}{e_s} = 1 - \frac{b}{r^3} \Rightarrow e' < e_s$$

We can say that the presence of solute will decrease the saturation vapor pressure.

The reduction in the saturation vapor pressure away form the pure water due to the presence of solute is called as "SOLUTE EFFECT"

$e_s' = k e_s$

$e_s(r) = e_s(\infty)(1 + \cdots)$

So, chi w is 1 minus i times m s by capital M s into M w by small mw right. So, now, what is this? This is just a molar fraction and we are still wanting to write an expression for the saturation vapor pressure in the in the presence of a solute with respect to the saturation vapor pressure in the absence of a solute.

So, now let us say we have this water as a droplet which has a radius r and then in the mass of the droplet mw we are trying to get the mass of the droplet. Where rho L is the density and if the droplet is of a radius r. . So, chi w; we substitute mw for m w, we substitute this. So, mw we substitute into this. So, chi w is 1 minus i, i is the degree of ionization, m s is the mass of solute times 3 M, capital M w mass molecular weight of water divided by 4 pi r is the droplets radius rho L is the density of water, capital M s is the molecular weight of the solute right.

So, this can be simply written as something let us say this, all this which can be constant for a given solution. So, chi w can be written as 1 minus b by r cube. So, all this is I am calling as b and r cubed remains such as i m s 3 M w by 4 pi rho L M s is going to be called as b. So, now, we substitute this into the empirical relation that we have right. So, e s, e prime divided by e s is 1 minus b by r cube.

So, this is one minus. So, in the case of curvature effect we see that the saturation vapor pressure over a curved surface in comparison to saturation vapor pressure over a flat surface was something like this 1 plus. That means, saturation vapor pressure over a curved surface will always be larger than the saturation group pressure over a flat surface. So, here you see the exactly opposite the saturation vapor pressure with respect to the solution is 1 minus; that means, is going to be lesser than pure phase.

Why because, there are more number of foreign molecules which are avoiding the water to evaporate so, thereby reducing the saturation vapor pressure. So, we can say that the presence of solute will decrease the saturation vapor pressure. The reduction in the saturation vapor pressure away from the pure water due to the presence of solute is called as this solute effect.

Now , we have eventually seen how we can write the saturation vapor pressure over a plain surface of water right. So, this is what is called as the solute effect right.

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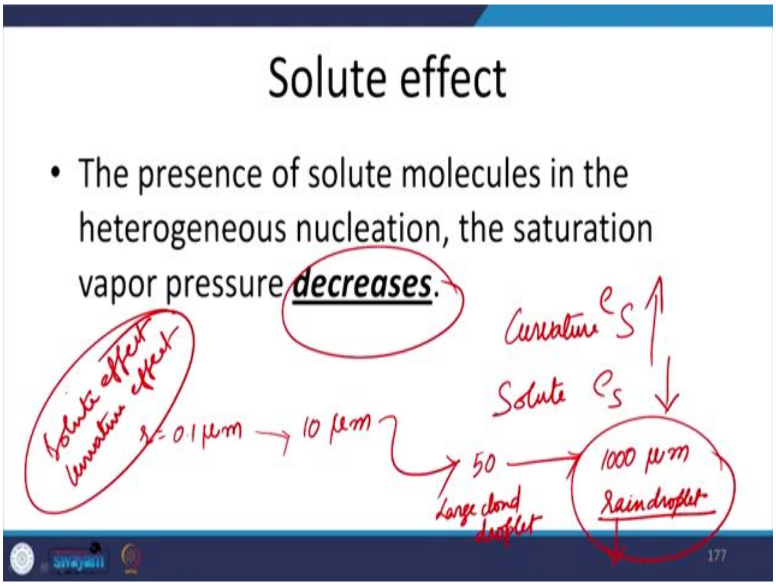

Solute effect

- The presence of solute molecules in the heterogeneous nucleation, the saturation vapor pressure **decreases**.

So, the presence of solute molecules in the heterogeneous nucleationmakes the saturation vapor pressure decrease. So, one thing for now what we can say is that, due to the curvature effect the saturation vapor pressure let us say e s is increasing and due to the solute effect the saturation vapor pressure is decreasing.

So, are these two effects important independently or are these two effects exist always together? That is the question. The question is; can you achieve nucleation, let us say can you think of a scenario where you achieve nucleation despite the lack of impurities, yes. But ideally no because the nucleation can be only be achieved at a relative humidities which are like several hundreds which are practically not possible right. Which are practically not possible in the sensor that how would you be able to create relative humidity of 400 percent or 500 percent in an air parcel which is suspended in the air.

But at any given time; the air parcel can never be free of any particles. The moment you have the particles 100 percent or 90 percent will still be sufficient to create nucleation. So, in any given situation, the saturation vapor pressure is always going to be influenced with the solute; that means, it will decrease as a result of the cloud condensation nuclei. And at the same time when the condensation happens over a surface over a particle

The condensation happens to result in the form of a droplet and when a droplet forms the evaporation will increase. That means, having the cloud condensation nuclei decreases the rate of evaporation from the droplet and droplet being present in the form of a sphere will increase the evaporation right. So, this droplet being present in the form of a sphere will increase the evaporation right.

So, these two effects will always be together, but how does it matter to us? I mean; our process our idea is to understand how the smallest cloud droplet will grow by diffusion, by collision or both collisions into the huge rain droplet right. So, if you put these things, how if you want to understand how this growth happens. It is very important, there are two processes which one is aiding the growth. One is aiding the growth by not allowing the water to evaporate which is the solute effect. And another is hampering the growth in the sense that it is allowing more evaporation

So, more evaporation happens the droplet will not be seen I mean; droplet will evaporate it will just vanish into the thin air right. Now we have to understand how the diffusional growth of a cloud droplet can be achieved if you have these two inter competing processes in the picture right.

Now, let us say for example, for a simple example so, we can always say that the radius of the cloud droplet let us say the radius of cloud droplet is you let us say in the units of let us say the radius of cloud condensation nuclei is 0.1 micrometer. The droplet will be of the order of ten micrometers, the cloud droplet.

Now, this has to grow to the sizes of let us say 50 micrometer to be called as a large cloud droplet, large cloud droplet and this has to further grow to the to the sizes of let us say 1000 micrometers to be called as a rain droplet. Now, once this process is complete only then you will see what is called as the precipitation. This is when the gravity kicks in and makes the rain droplet travel towards the surface right.

So, this process starting from 0.1 to 10 micrometers to 50 micrometers and 1000 micrometers is the process which facilitates the precipitation right. So, now, we will see how this growth of cloud condensation nuclei acquires moisture and becomes a cloud droplet then it becomes a large cloud droplet and then it becomes a rain droplet. So, we have two processes which are one is aiding the process, one is aiding this transformation and another is the hampering the transformation.

So, the process which is aiding is the is the solute effect. Of course, solute effect is helping it and the curvature effect. Now let us try to combine these two effects and try to see mathematically, what the relevance is I mean how the overall saturation vapor pressure changes with respect to plane surface or curved surface and in the presence of solute and in the absence of solute ok

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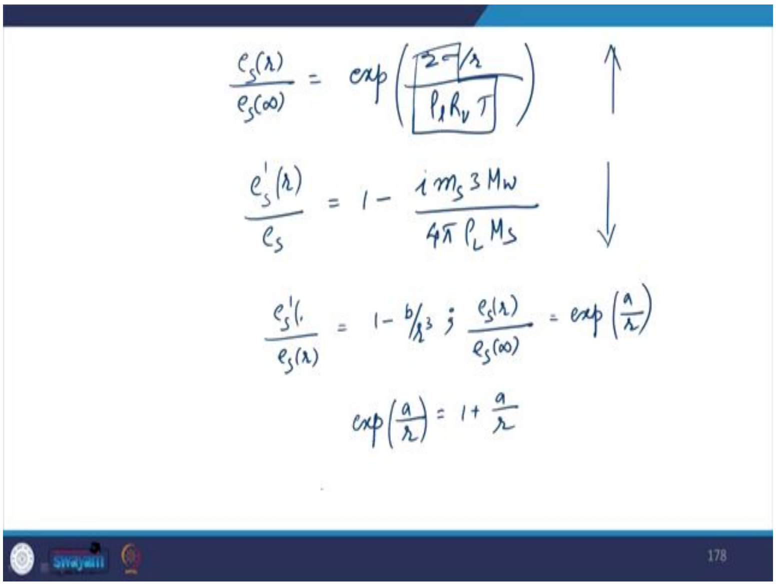

$$\frac{e_s(r)}{e_s(\infty)} = \exp\left(\boxed{\frac{2\sigma/r}{\rho_l R_v T}}\right) \quad \uparrow$$

$$\frac{e_s'(r)}{e_s} = 1 - \frac{i m_s 3 M_w}{4\pi \rho_L M_s} \quad \downarrow$$

$$\frac{e_s'(}{e_s(r)} = 1 - b/r^3 \; ; \; \frac{e_s(r)}{e_s(\infty)} = \exp\left(\frac{a}{r}\right)$$

$$\exp\left(\frac{a}{r}\right) = 1 + \frac{a}{r}$$

So, let us say we will write, let us say the Kelvin's equation e s of r by e s of infinite is equals to exponential 2 sigma by r divided by rho l R v T and the solute effect e s prime of r by e s is 1 minus i ms 3 M w divided by 4 pi rho L M s ok. So, what is this doing this is increasing the saturation vapor pressure and this is decreasing the saturation vapor pressure.

Let us try to combine these two equations ok. So, simply speaking, so we can write e s prime divided by e s of r it can be written as 1 minus b by r cube and e s of r divided by e s of infinite as exponential a by r. So, we have called everything this as a ok. So, for a very small radius of curvature, for very small radius of curvature, we can write exponential of a by r as 1 plus a by r right. Now, we can combine these two.

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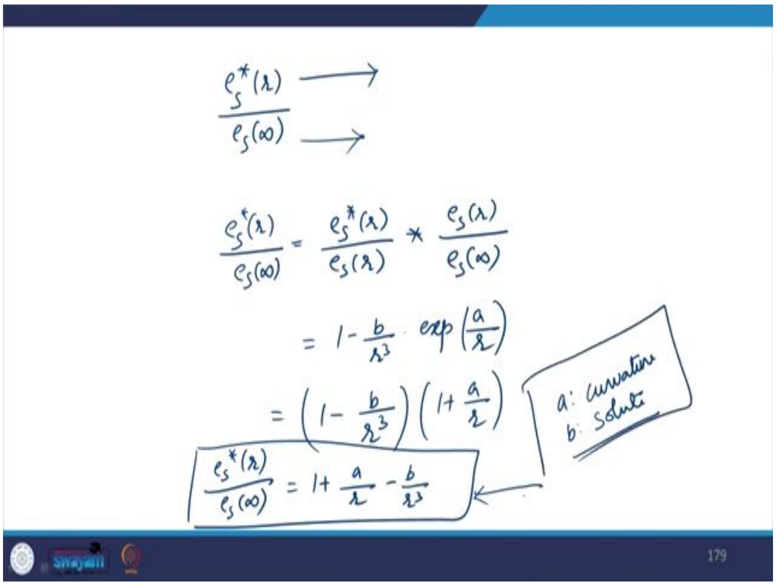

$$\frac{e_s^*(r)}{e_s(\infty)} \begin{matrix} \longrightarrow \\ \longrightarrow \end{matrix}$$

$$\frac{e_s^*(r)}{e_s(\infty)} = \frac{e_s^*(r)}{e_s(r)} * \frac{e_s(r)}{e_s(\infty)}$$

$$= 1-\frac{b}{r^3} \cdot \exp\left(\frac{a}{r}\right)$$

$$= \left(1-\frac{b}{r^3}\right)\left(1+\frac{a}{r}\right)$$

$$\boxed{\frac{e_s^*(r)}{e_s(\infty)} = 1+\frac{a}{r}-\frac{b}{r^3}}$$

a: curvature
b: solute

So, our objective is to write e s let us say star of r divided by e s of infinite. So, what is this equilibrium saturation vapor pressure in a solute over a droplet? So, that means; we have taken both the effects into consideration. So, how does the saturation vapor pressure changes in the presence of a solute over a droplet. In comparison to equilibrium, this is e s of infinity, equilibrium saturation vapor pressure over a plane surface of water right.

So, we can write that e s of e s star of r divided by e s of infinite is equals to e s star of r divided by e s of r in to e s of r into e s of infinite which is 1 minus b by r cube into exponential a by r which is 1 minus b by r cube into 1 plus a by r. Which is e s star of r divided by e s of infinite is equals to 1 plus a by r minus b by r cube right.

So, this is the combined effect . So, a represents things in curvature term and b represents parameters with respect to solute right. So, this is the basic idea. So, where we have summarized the both curvature effect and the solute effect right. So, now, the point is we will try to understand more about this equation, the final equation which is 1 plus a by r in 1 minus b y r cube.

Now, the most important thing is this seems to be dependent inversely along let us say 1 term along 1 by r and 1 by r cube ok. Now, we will try to understand more graphical implication of this and probably by combining the solute and curvature effects right. So, we can stop here. So that means that; we have some we have seen what is solute effect, what is curvature effect, what is the importance of these two effects in the formation of rain droplets or in the transformation of a single nucleus to the rain droplet right. So, we will continue this discussion more to understand the diffusional growth of a cloud droplet.