

Atmospheric Physics

Lecture 16

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Saturation Vapor Pressure

The saturation vapor pressure is defined over a plane (flat) surface of water.



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Curvature Effect

This reduced surface tension and the larger saturation vapor pressure required for the drop to remain in equilibrium with its surroundings is called the curvature effect.

This effect is enhanced for smaller drops.

In other words, the smaller the drop radius, the larger the curvature of the drop, and the larger the vapor pressure required to keep the drop in equilibrium at a given temperature.





Curvature Effect

The figure at the right shows the relationship between the supersaturation (the RH above 100 %) and the droplet radius.

The supersaturation increases exponentially as the droplet radius gets smaller.



Note: If the supersaturation is greater than the equilibrium curve for a given radius, then the drop will grow.

If the RH is less than the the equilibrium curve, the drop will evaporate. 20/12/2021

Curvature Effect

For droplets less than 1 μ m, which is larger than for homogeneous nucleation, the supersaturations must be very high, well above what we see in the atmosphere, for the droplet to grow.

This is a problem!!!

CCN to the rescue!

CCN give the water molecules a place to gather together. This "instantly" gives them a much larger size than without the CCN.

Some CCN are hygroscopic. Some salts begin to collect water at RH's as low as 75%. A solution is formed when water condenses onto a salt particle.

Formation of Cloud Droplets

Nucleation is the condensation, freezing, or deposition of water vapor <u>in free air</u> (air not in contact with the surface).

Homogeneous Nucleation : The formation of a cloud droplet by condensation of water vapor on an aerosol and Homogeneous nucleation unlikely

Aerosols important in cloud droplet formation

Heterogeneous Nucleation: almost all nucleation occurs on aerosol. condensation nuclei, ice nuclei.

Giant nuclei	1 - 10 µm
Large nuclei	0.1 - 1.0 µm
Aitken nuclei	0.01 - 0.1 µm

Heterogeneous Nucleation

Aerosols

Hydrophobic Water forms spherical drops on its surface

Wettable (Neutral)

Allows water to spread out on it

Hygroscopic

Have affinity for water Soluble







Solute Effect

Saturation vapor pressure over a solution droplet is less than that over pure water of the same size



Saturation vapor pressure is proportional to number of water molecules on droplet surface



Solute Effect

The saturation vapor pressure is defined over a plane (flat) surface of water. Let us now consider a droplet.



this is because salt is hygroscopic

Fractional decrease in vapor pressure



Consider a spherical droplet of radius a and volume

$$V_a = 4\pi a^3 / 3$$

containing

mass m of solute

molar mass M

 $n = i_d m / M$

Where i_d is the number of ions produced by the dissociation of one solute molecule

For example $i_d = 2$ for NaCl,

Which dissociates completely into Na⁺ and Cl⁻ ions $n_0 =
ho_l V_a \,/\, M_w$

 ρ_{l} density of the pure water

 M_w molar mass of pure water

(This approximation ignores the small mass m of solute within the droplet and the fact that the density of the solution is slightly different from ρ_{I} .)

We therefore obtain
$$\frac{e'}{e} = f = 1 - \frac{n}{n_o}$$
 $f = 1 - \frac{B}{a^3}$ $B = \frac{3i_d m M_w}{4\pi\rho_l M}$
Kelvin's formula $e = e_s(T) \exp{\frac{A}{a}}$ $A = \frac{2\gamma}{\rho_l R_v T}$

We obtain the relative humidity RH, given by

$$RH \equiv \frac{e}{e_{s}(T)} = \exp\left(\frac{A}{a}\right)\left(1 - \frac{B}{a^{3}}\right)$$

Solute Effect

0.035

0.025 (%) 0.020 (%) 0.015 (0.010)

0.005

The line represents the saturation vapor pressure curve for a solution drop.

 $f = 1 - \frac{B}{a^3}$

The vapor pressure for a solution drop is less than that for a plane of pure water.

The vapor pressure required to maintain equilibrium decreases as the drop radius decreases.

This is opposite of the effect for curvature.

e

Kelvin's formula

$$=e_s(T)\exp\frac{A}{a}$$



Fig. gives an example of this function of radius a Köhler curve

$$\mathrm{RH} \equiv \frac{e}{e_{\mathrm{s}}(T)} = \exp\left(\frac{A}{a}\right) \left(1 - \frac{B}{a^3}\right)$$

Equilibrium (Saturation) Curve e Near Drop = e of Environment (particle doesn't change size)



Kelvin factor exp(A/a) which decreases with increasing a,

> Raoult factor which increases with increasing a

Figure shows the Köhler equation applied to an NaCl particle that has the diameter 0.05 μ m when completely dry.



Grow e Near Drop < e of Environment (drop grows by condensation)

Shrink

e Near Drop > e of Environment (drop shrinks by evaporation)



If the RH increases a bit (move drop vertically), the drop will be supersaturated with respect to the equilibrium curve and will move to the right (grow) until it hits the curve again - and then it stops growing and reestablishes equilibrium.

If the drop increases in size for some reason at constant RH (move drop to the right), it will become sub-saturated with respect to the equilibrium curve and will shrink back to its original size (hit the equilibrium curve).







If the RH increases a bit (move drop vertically), the drop will be supersaturated with respect to the equilibrium curve and will grow (move to right). However, when it does so, it never reaches equilibrium with the environment again (never touches the curve), so the drop will simply continue to grow without bound (in reality it reaches a finite size because it competes with other drops for a finite amount of vapor).

The peak in the Kohler Curve is called the *critical radius* or (Imm activation radius.



