

Experimental Atmospheric Chemistry

(12.335/12.835)

Section 3, Lecture 2:

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Tuesday, Nov 18, 2014

- ❖ RH & Saturation
- ❖ Liquid water from 0 – 100% RH
- ❖ RH of 100% +
- ❖ Kelvin Köhler curve
- ❖ Cloud droplets
- ❖ CCN counter

A term used to describe the amount of water vapor that exists in a gaseous mixture of air and water vapor.

The relative humidity of an air-water mixture defined as the ratio of :

$$\text{Relative Humidity (RH)} = \frac{\text{Actual Vapor Density (amount of moisture in air)}}{\text{Saturation Vapor Density (amount in saturated air)}} \times 100\%$$

Relative Humidity ~ Saturation

The relative humidity of an air-water mixture defined as the ratio of :

$$\frac{e}{e_s}$$

e - vapor pressure of environment

e_s - vapor pressure of saturated environment

$\frac{e}{e_s} < 1$ sub-saturated

$\frac{e}{e_s} > 1$ supersaturated

$\frac{e}{e_s} = 1$ saturated

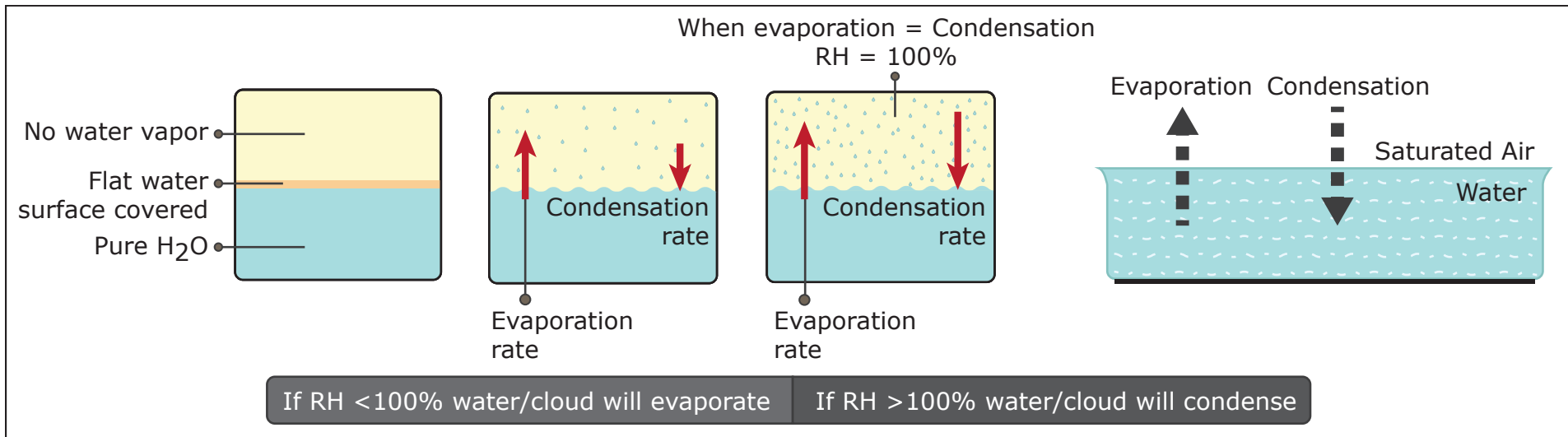
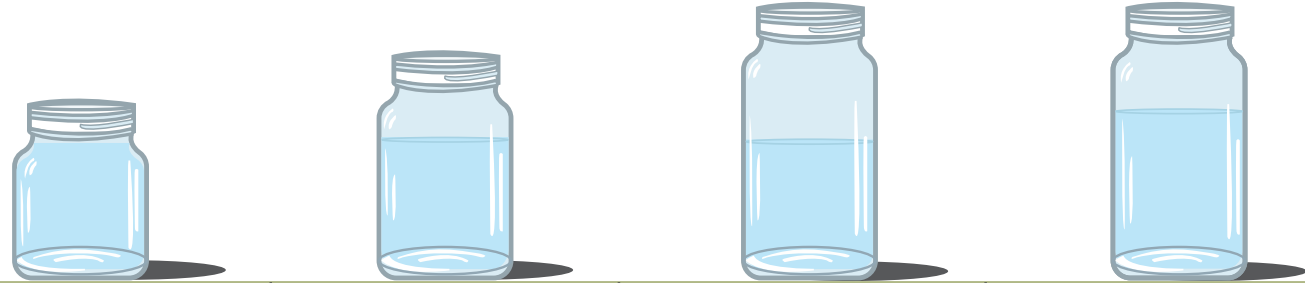


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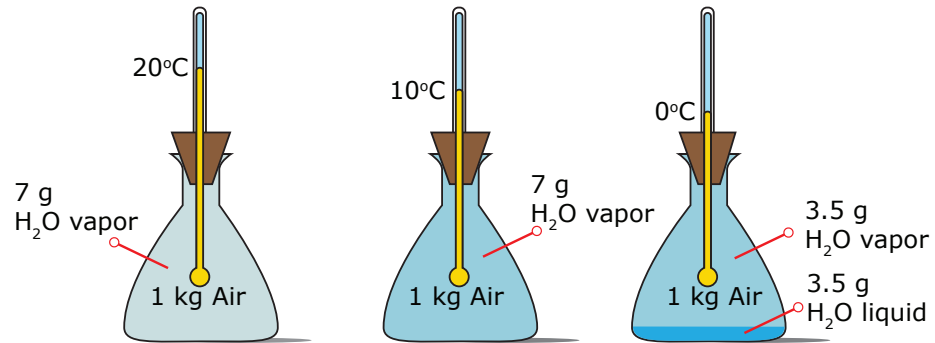
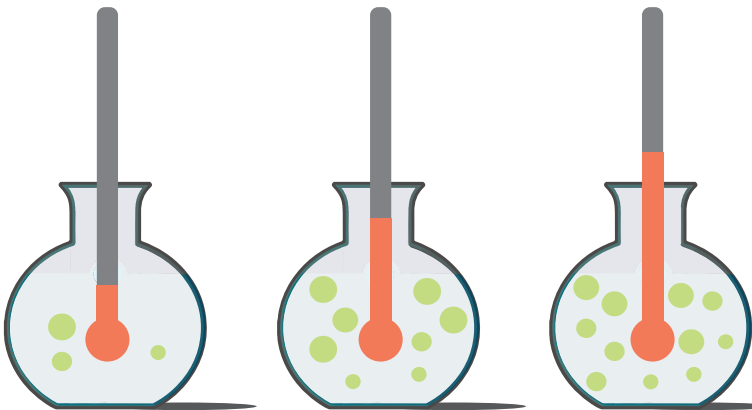
Content	6 oz water	6 oz water	6 oz water	9 oz water
Capacity	6 oz glass	9 oz glass	12 oz glass	12 oz glass
Relative Humidity	$6/6 \times 100 = 100\%$	$6/9 \times 100 = 67\%$	$6/12 \times 100 = 50\%$	$9/12 \times 100 = 75\%$

Temperature

Low

Medium

High



	(A) Initial Condition	(B) Cooled to 10°C	(C) Cooled to 0°C
Temperature	20°C	10°C	0°C
Air	1 kg	1 kg	1 kg
Capacity	At 20°C=14 grams	At 10°C=7 grams	At 0°C=3.5 grams
H ₂ O Vapor Content	7 grams	7 grams	3.5 grams
Relative Humidity	$7/14=50\%$	$7/7=100\%$	$3.5/3.5=100\%$

Figure by MIT OpenCourseWare.

Deliquescence (DRH) - process by which a substance absorbs moisture from the atmosphere until it dissolves in the absorbed water and forms a solution.

Efflorescence (ERH) - spontaneous loss of water by a hydrated salt, which occurs when the aqueous vapor pressure of the salt is greater than the partial pressure of the water vapour in the air.

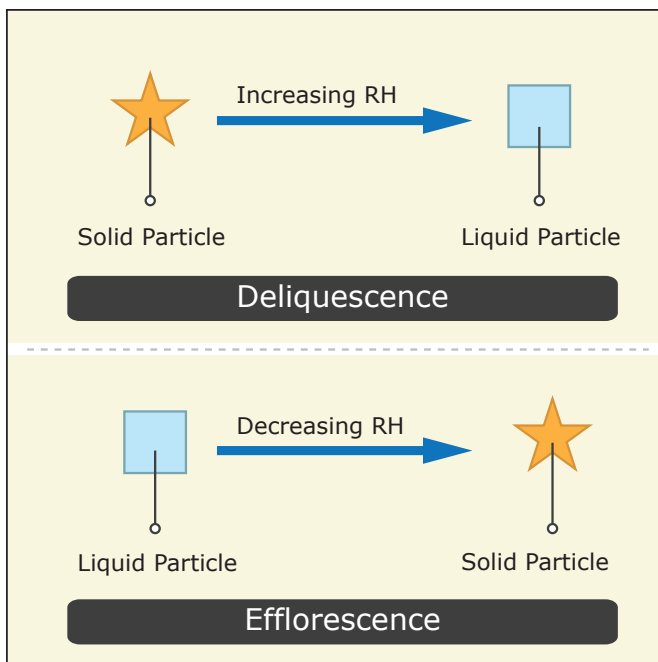
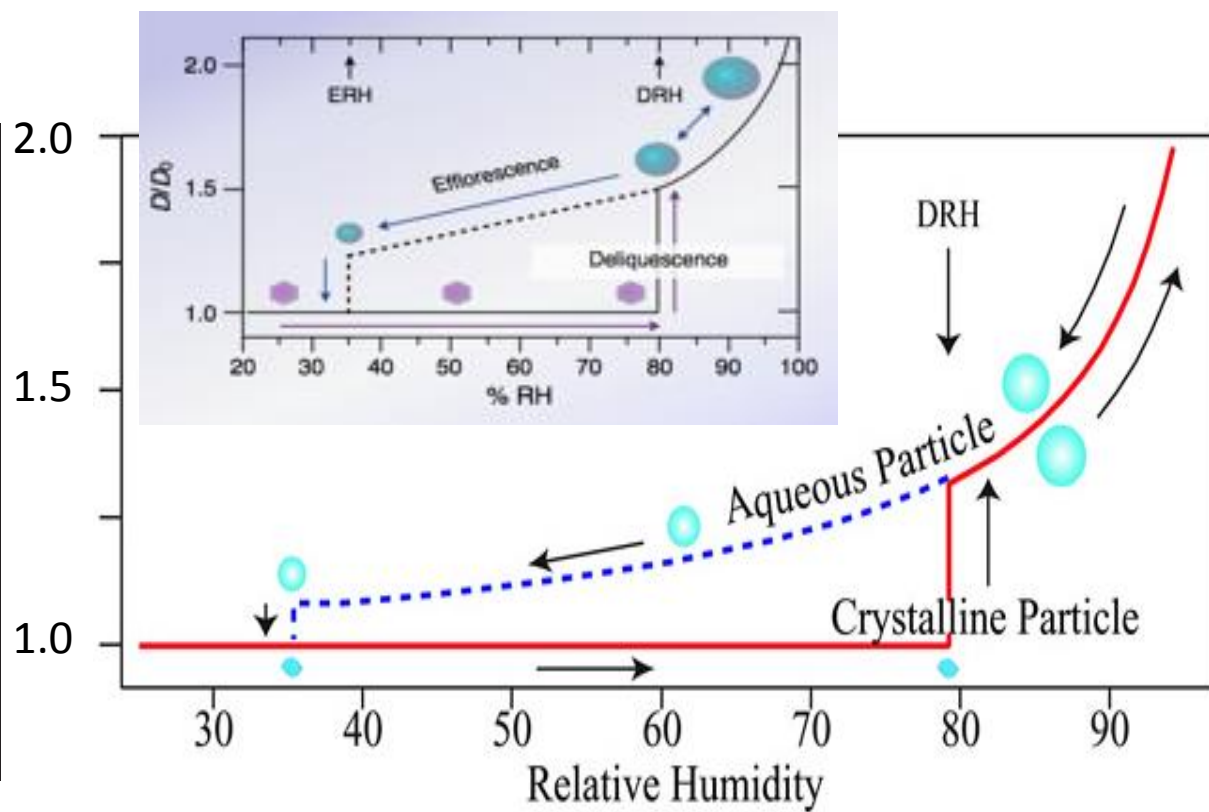


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$(\text{NH}_4)_2\text{SO}_4$ Ammonium sulfate

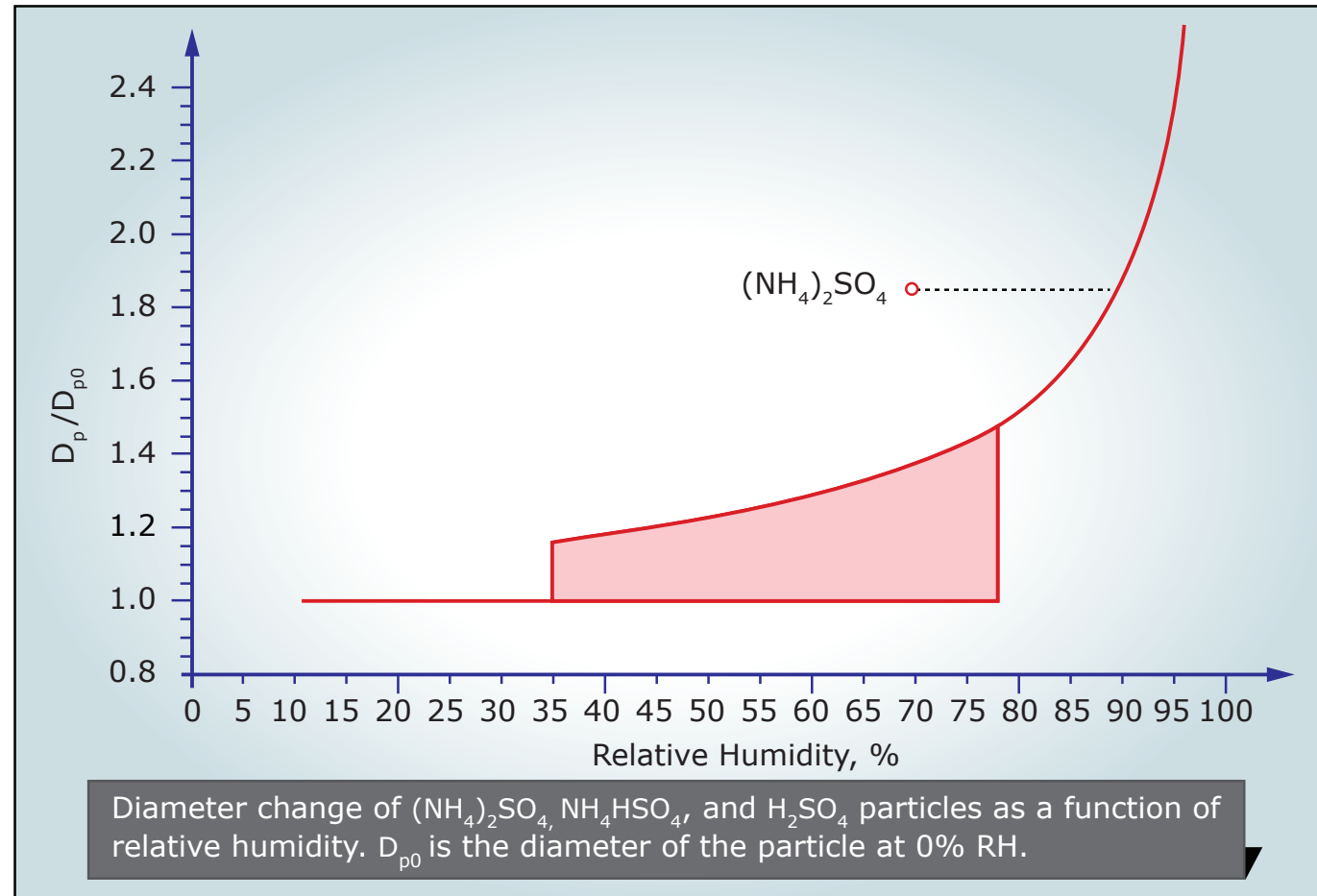


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DRH is material specific

DRH changes with T per “Clausius-Clapyeron” relation

ERH is not predictable but follows nucleation theory

Deliquescence and Efflorescence

TABLE: Deliquescence Relative Humidities of Electrolyte Solutions at 298 K

Salt	DRH (%)
NaCl	75.3 ± 0.1
NaHSO ₄	52.0
NaNO ₃	74.3 ± 0.4
Na ₂ SO ₄	84.2 ± 0.4
NH ₄ Cl	80.0
NH ₄ HSO ₄	40.0
(NH ₄) ₃ H(SO ₄) ₂	69.0
NH ₄ NO ₃	61.8
(NH ₄) ₂ SO ₄	79.9 ± 0.5
KCl	84.2 ± 0.3

Source: Tang (1980) and Tang and Munkelwitz (1993).

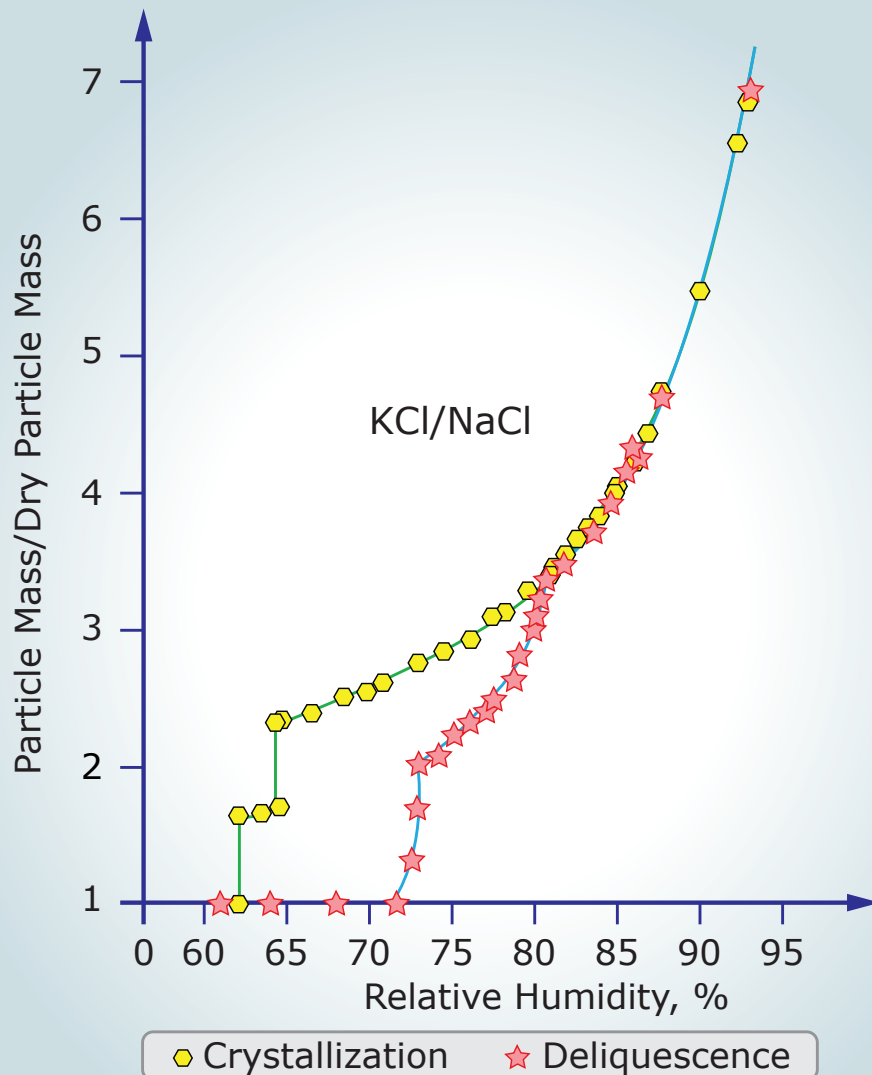
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TABLE: Efflorescence Relative Humidity at 298 K

Salt	ERH (%)
NaCl	43 ± 3
NaNO ₃	Not Observed
Na ₂ SO ₄	56 ± 1
NH ₄ Cl	45
NH ₄ HSO ₄	Not Observed
(NH ₄)H(SO ₄) ₂	35
NH ₄ NO ₃	Not Observed
(NH ₄) ₂ SO ₄	35 ± 2
KCl	59

Source: Martin (2000).

Figures by MIT OpenCourseWare.



Hygroscopic growth and evaporation of a mixed-salt particle composed initially of 66% mass KCl and 34% mass NaCl.

Two (or more) components

More favorable state is solution sooner when a second component is added (regardless of the DRH)

DRH

NaCl (Sodium chloride) 75.3%

KCl (potassium chloride) 84.2%

ERH

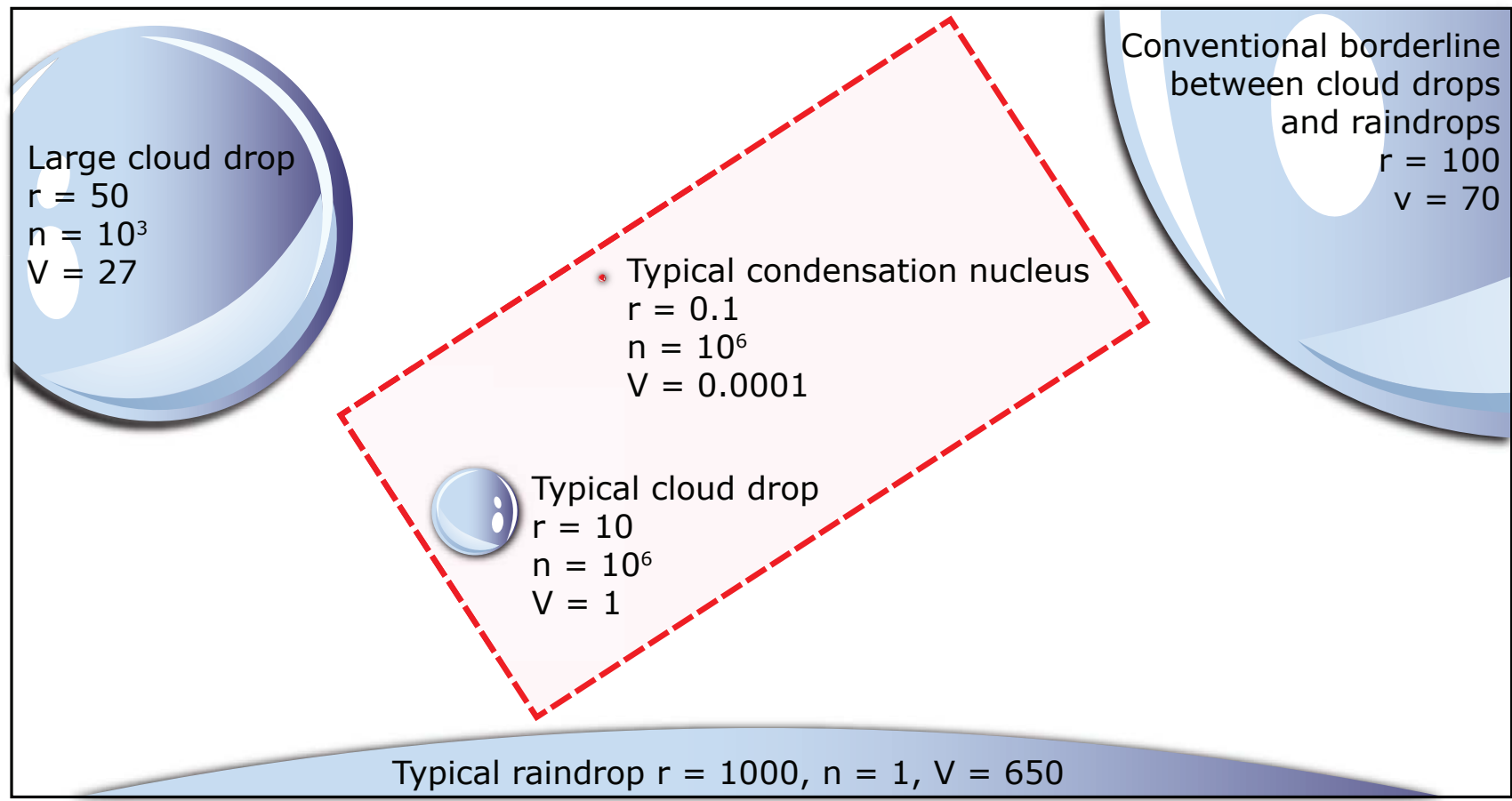
NaCl (Sodium chloride) 43%

KCl (potassium chloride) 59%

Figure by MIT OpenCourseWare.

'Haze' or Deliquesced -> Droplet

Comparative sizes, concentrations, and terminal fall velocities of some of the particles included in cloud and precipitation processes



KEYS

r - radius in microns
n - number per liter
V - terminal velocity in centimeters per second

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Please see: http://www.harding.edu/lmurray/113_files/html/d2_earth%20revised/img037.jpg.

Heating reduces RH, cooling increases RH
(day/night variation and concept of dew point and frost point)

Parcel rise or fall ('adiabatic') results in condensation or evaporation

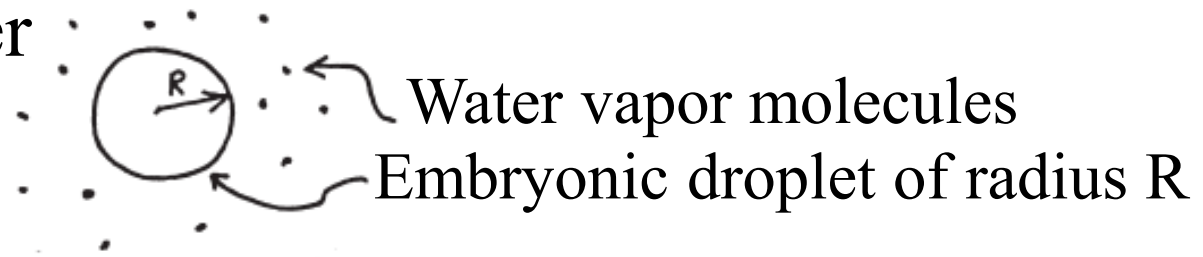
Homogeneous Nucleation

Drop of pure water forms from vapour

Heterogeneous Nucleation

Collection of water molecules on a foreign substance

There are a lot of molecule in the air in supersaturation, in order to create a drop the molecule need to become attached to each other



Growth of the pure water embryo depend on the difference between e_s and e

$e < e_s$ **→** decay (vapor moves away from the drop)

$e > e_s$ **→** growth (vapor moves toward the drop)

When the pure water embryo drop radius is $e = e_s$
The droplet is just large enough to be stable

Saturation above a pure water droplet of a known radius is:

r - embryo drop radius

T - temperature

k - Boltzmann constant

σ_{LV} - surface tension of water molecules

e - vapor pressure of environment

e_s - vapor pressure of saturated environment (water molecules)

n_L - number of water molecules/unit volume in the liquid phase

$$\frac{e}{e_s} = \exp \left[\frac{2\sigma_{LV}}{n_L k T r} \right]$$

$e/e_s < 1$ sub-saturated $e/e_s > 1$ super-saturated

$e < e_s$ decay (vapor moves away from the drop)

$e > e_s$ growth (vapor moves toward the drop)

Kelvin's equation for critical radius for initial droplet to “survive”, strongly dependent on supersaturation

R_c - critical radius

ρ_L - liquid density

T - temperature

R_v - gas constant ($8.314472\text{JK}^{-1}\text{mol}^{-1}$)

e - vapor pressure of environment

e_s - vapor pressure of saturated environment

σ_{LV} - surface tension between the liquid-vapor phases (0.076Jm^{-2})

$$R_c = \frac{2\sigma_{vl}}{R_v \rho_L T \ln\left(\frac{e}{e_s}\right)}$$

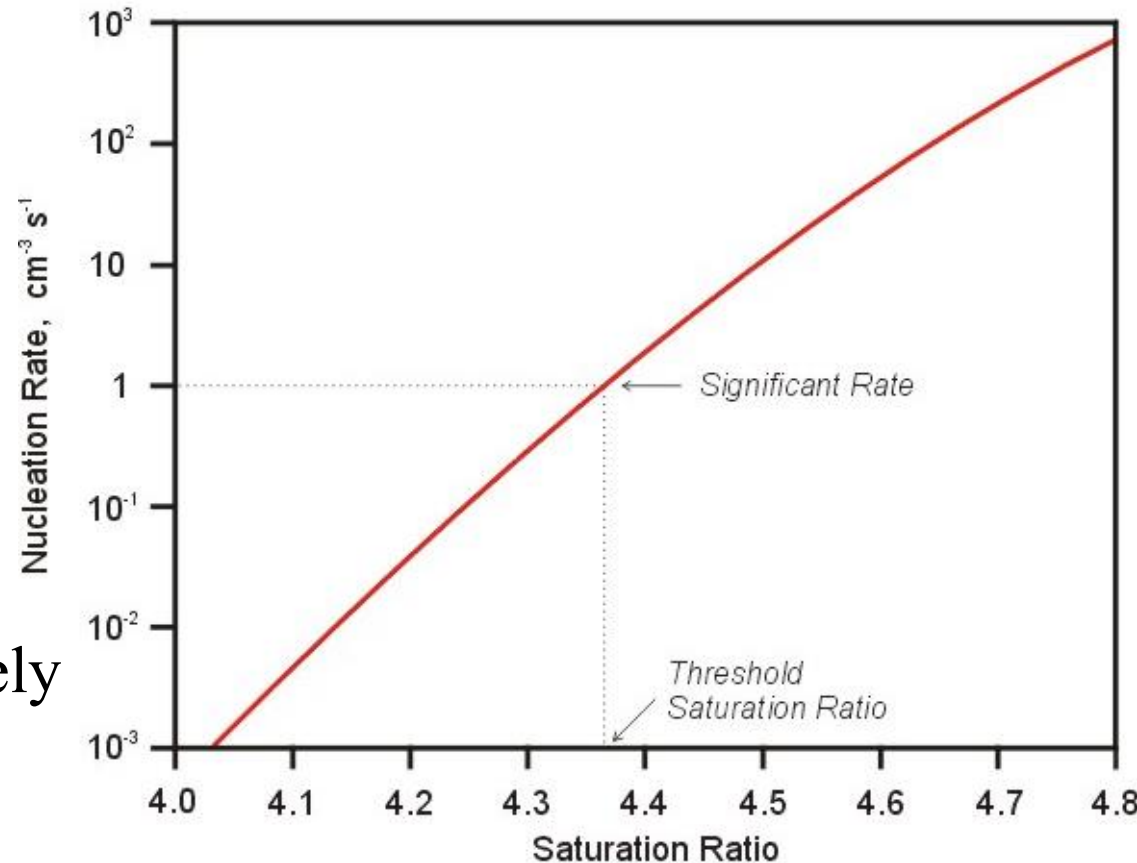
TABLE: Radii and Number of Molecules in Droplets of Pure Water in Equilibrium with the Vapor at 0°

Saturation Ratio S	Critical Radius r_c (μm)	Number of Molecules n
10	5.221×10^{-4}	20
5	7.468×10^{-4}	58
4	8.671×10^{-4}	91
3	1.094×10^{-3}	183
2	1.734×10^{-3}	730
1.5	2.964×10^{-3}	3.645×10^3
1.10	1.261×10^{-2}	2.807×10^5
1.01	1.208×10^{-1}	2.468×10^8
1	∞	∞

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Smaller pure drop need higher supersaturation, and less molecules in order to grow.

- Statistical thermodynamic calculations show that Saturation ratio must be 300-600% for one homogeneous nucleation event per cm^3 per second in the natural atmosphere.
- Since Saturation ratio rarely exceeds 1-2%,



Homogeneous nucleation is never consistently achieved.

In this section we will examine the production of small water droplets nucleated with the aid of a foreign particle.

Since nucleation takes place with something in addition to pure water vapor, the nucleation process is called *heterogeneous*.

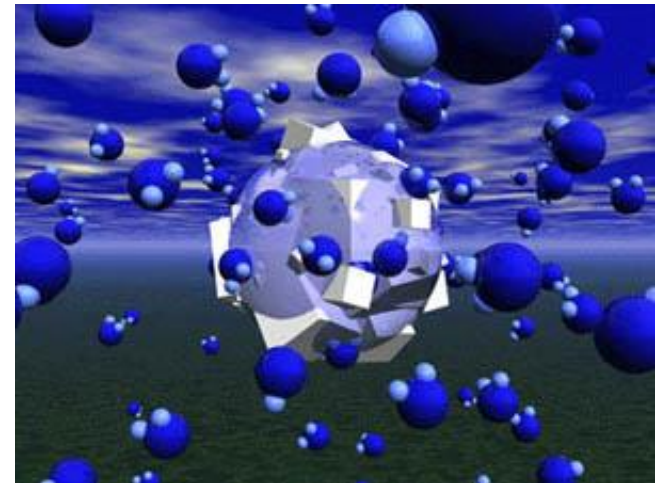


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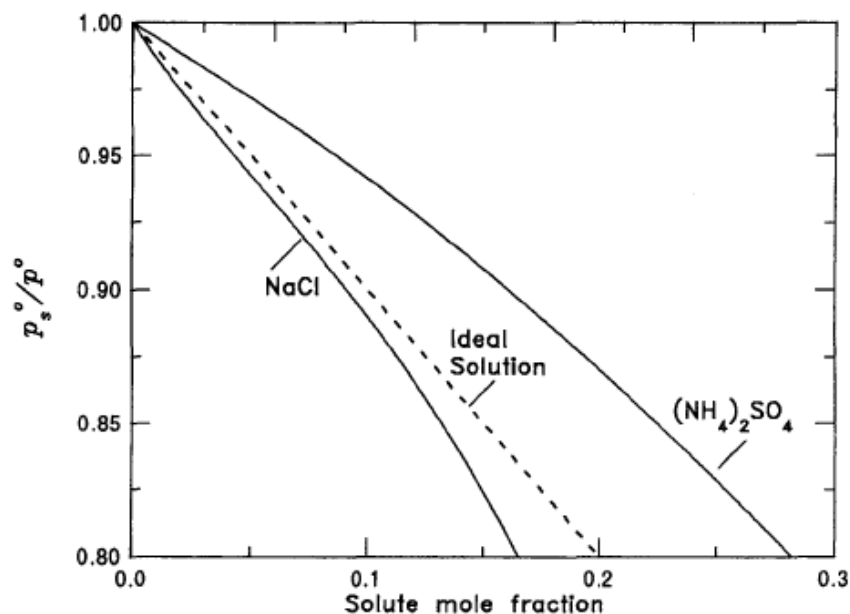


FIGURE 17.3 Variation of water vapor pressure ratio (p_s^o/p^o) as a function of the solute mole fraction at 25°C for solution of NaCl and $(\text{NH}_4)_2\text{SO}_4$ and an ideal solution. The mole fraction of the salts has been calculated taking into account their complete dissociation.

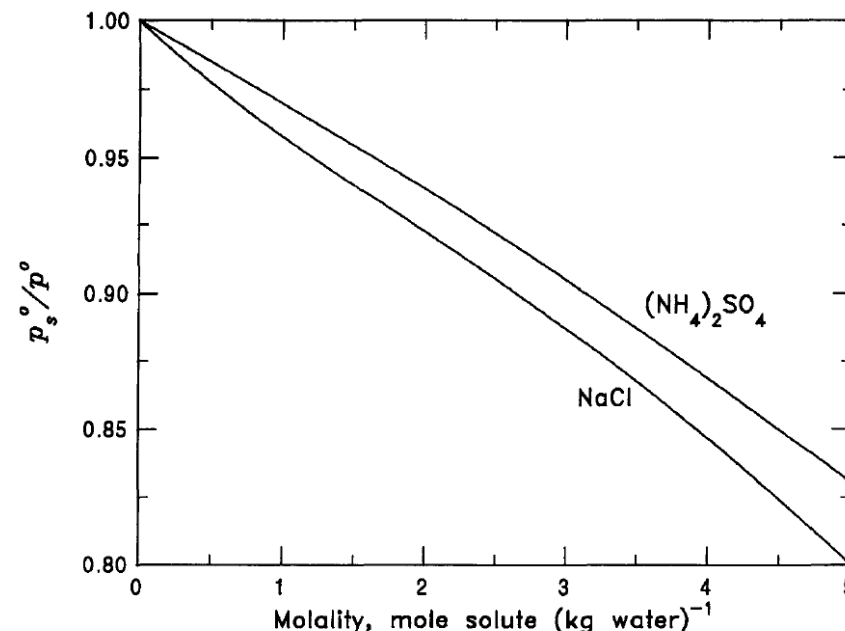


FIGURE 17.4 Variation of water vapor pressure ratio (p_s^o/p^o) as a function of the salt molality (mol of salt per kg of water) of NaCl and $(\text{NH}_4)_2\text{SO}_4$ at 25°C.

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The vapor pressure of water over NaCl and $(\text{NH}_4)_2\text{SO}_4$ solutions is shown in Figure 17.3. Also shown is the ideal solution behavior. Note that because NaCl dissociates into two ions, the number of equivalents in solution is twice the number of moles of NaCl. For $(\text{NH}_4)_2\text{SO}_4$, the number of ions in solution is three times the number of dissolved salt moles. In calculating the number of moles in solution, n_s , a dissociated molecule that has dissociated into i ions is treated as i molecules, whereas an undissociated molecule is counted only once. A similar diagram is given in Figure 17.4, using now the concentration of salt as the independent variable. Solutes that dissociate (e.g., salts) reduce the vapor pressure of water more than do solutes that do not dissociate, and this reduction depends strongly on the type of salt.

- The saturation ratio for a solution droplet must still be given by this relation since we must require the droplet to be in equilibrium with the vapor

$$\frac{e_r}{e_s} = \exp \left[\frac{2\sigma'}{n'_L k T r} \right] \left[1 + \frac{i m_s M_0}{(4/3\pi r^3 \rho' - m_s) \times M} \right]^{-1}$$

For sea salt \longrightarrow $\frac{e_r}{e_s} = \exp \left(\frac{A}{r} - \frac{B}{r^3} \right)$

$$A = 2\sigma / \rho_w R_v T$$

$$B = (3i m_s M_w) / (4\pi M_s \rho_w)$$

r- drop radius

m_s - masses of salt

M_s – molecular weight

i = Van't Hoff factor

$$A \approx \frac{3.3 \times 10^{-5}}{T} \text{ (cm)}$$

$$B \approx 4.3 \frac{i m_s}{M_s} \text{ (cm}^3\text{)}$$

Saturation rate as a function of the drop size

$$S = \frac{e_r}{e_s} = 1 + \frac{A}{r} - \frac{B}{r^3}$$

e_r - Vapor pressure

e_s - saturation vapor pressure over a plane surface of pure water.

RH (Relative Humidity) = $s \times 100\%$

Supersaturation = $S = (s + 1)$

Kelvin Köhler curve

If we plot the saturation with r for a given salt type and salt mass, we obtain a set of curves known as the **Köhler curves**.

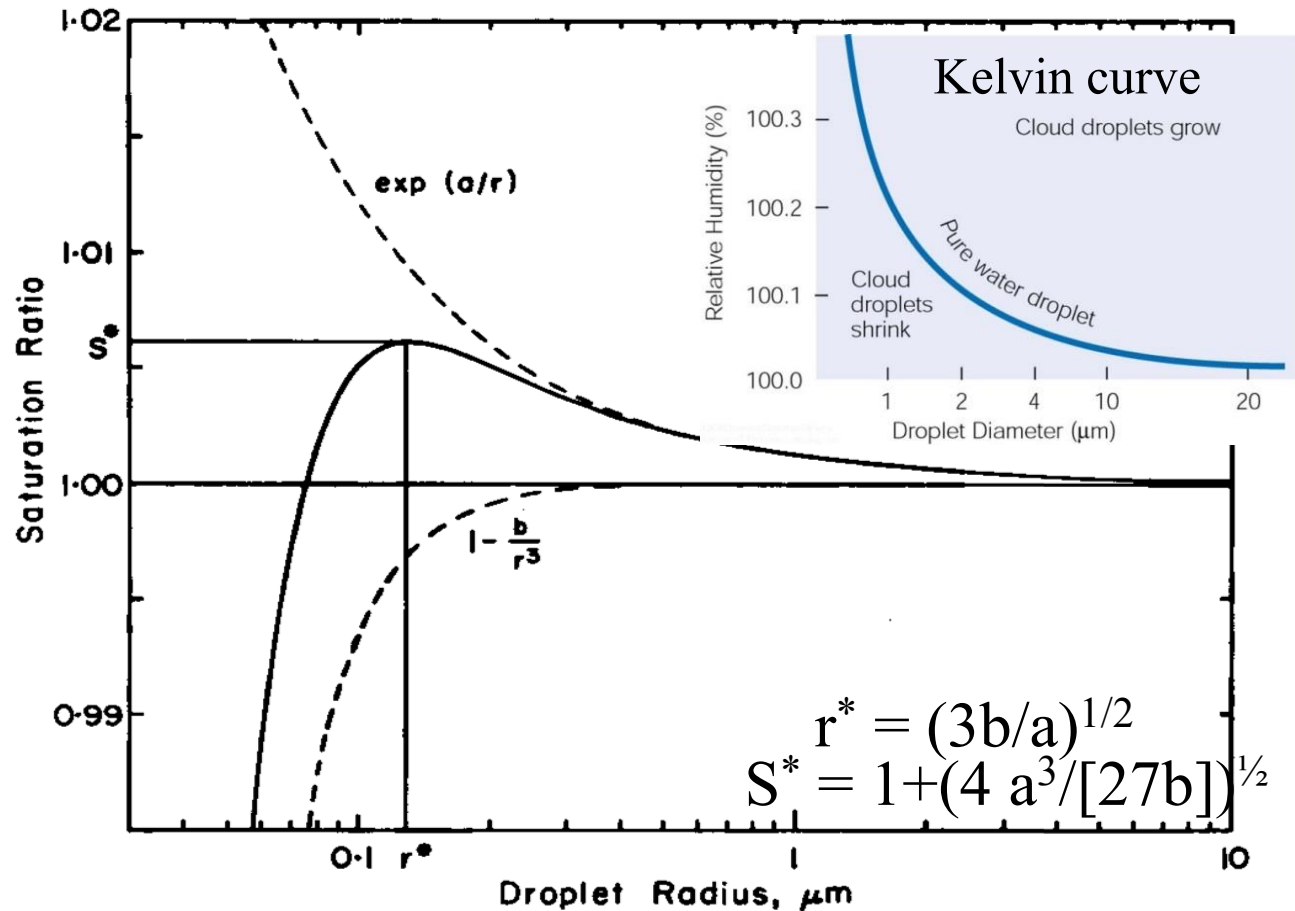
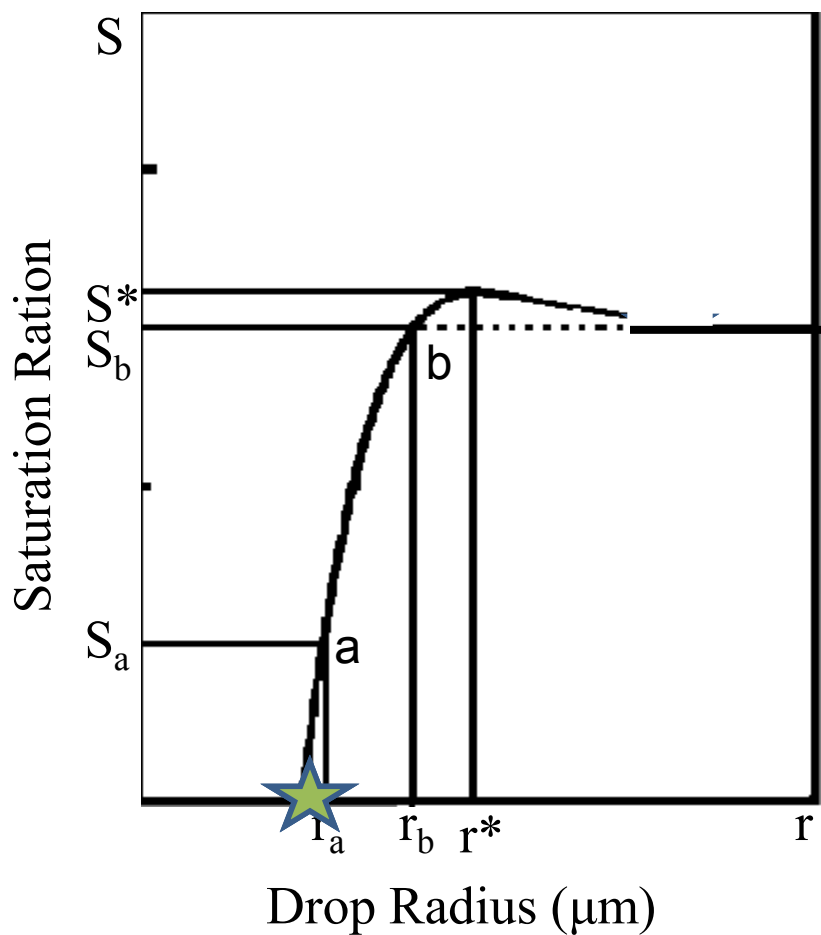
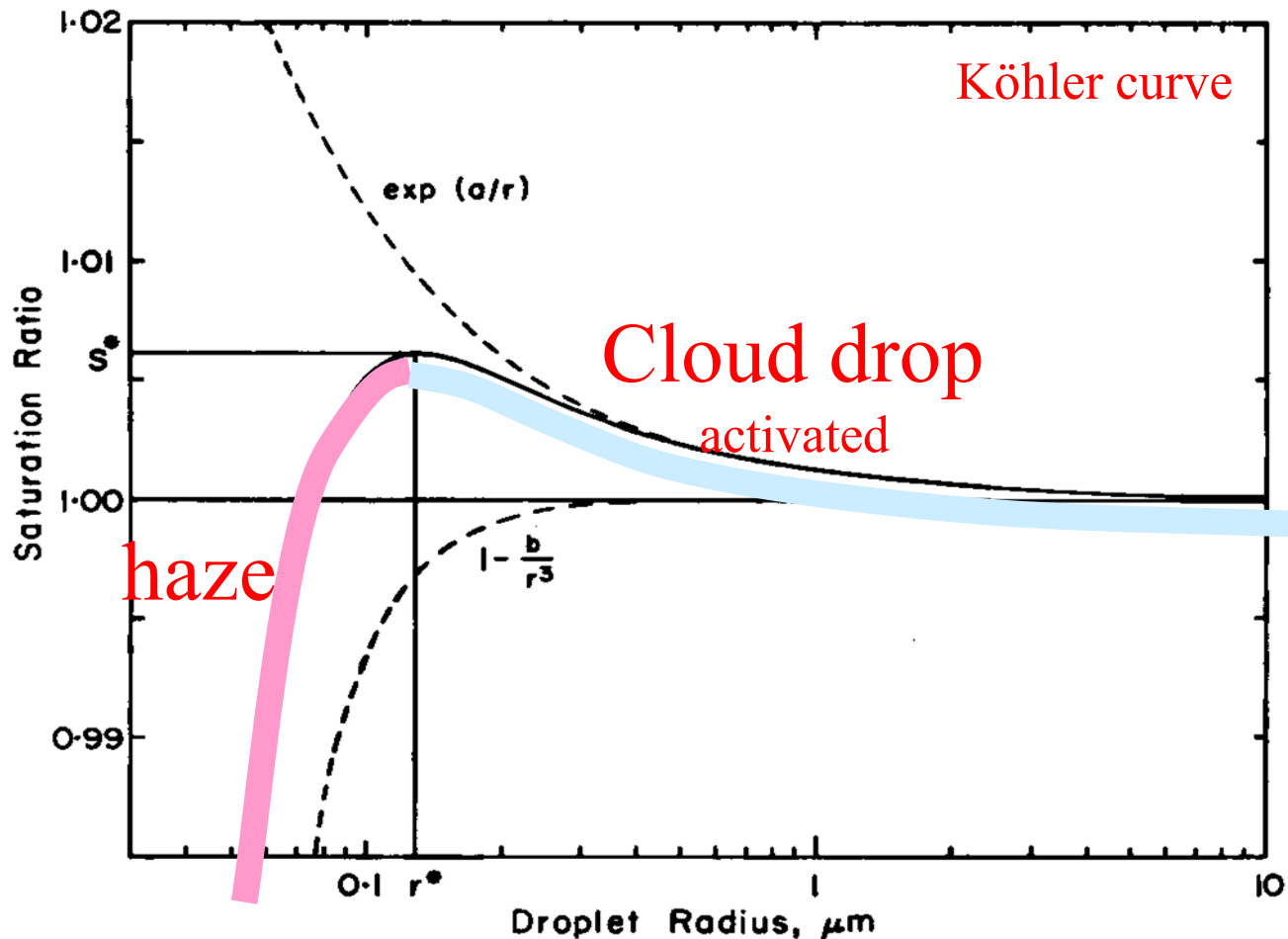


FIG. 6.2. Equilibrium saturation ratio of a solution droplet formed on an ammonium sulfate condensation nucleus of mass 10^{-16} g.

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- A drop at point a ($r=r_a$, $S=S_a$). Let the Supersaturation to increase to S_b , the drop will grow to radius r_b . If the Supersaturation drops again, the drop will get smaller.
- But if the Supersaturation will increase to the critical Supersaturation condition ($r=r^*$, $S=S^*$) the drop will grow to a critical radius.
- From now on the drop will continue growing spontaneously (by diffusion), even if the Supersaturation decrease.

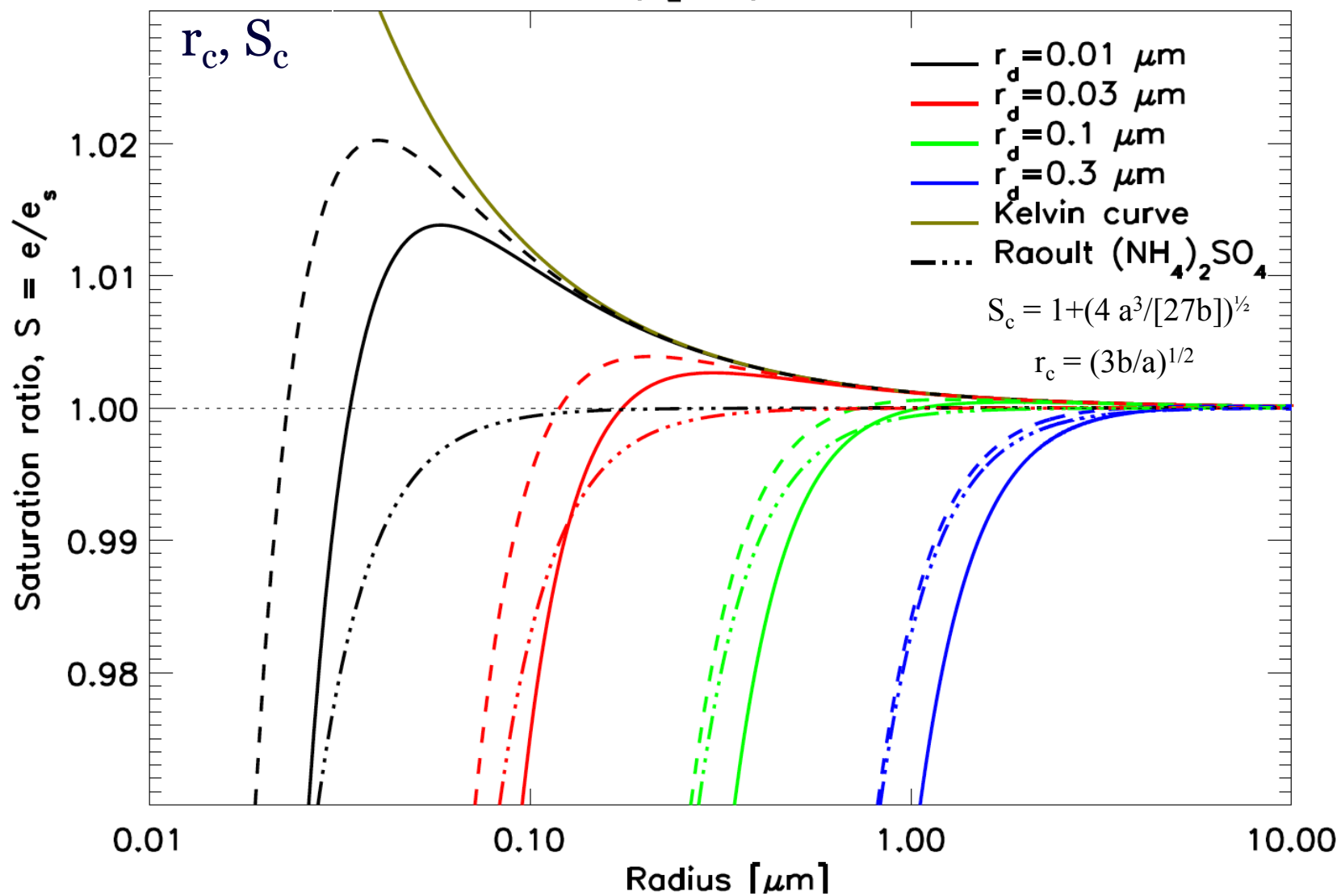


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Drop below the critical radius called haze particle

Drop above the critical radius called clouds drop their aerosol are activated aerosol

Koehler curves for $(\text{NH}_4)_2\text{SO}_4$ (dashed) and NaCl (solid)



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Please see: Figure 17.5 of the book *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. Wiley-Interscience, 2006. ISBN: 9780471720188.

Bigger particle are more effective than small ones, but their concentration in the cloud is lower

SS vs. Critical Diameter

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Mass of dissolved salt [gr]	$r_{\text{salt}} [\mu\text{m}]$	$r^* [\mu\text{m}]$	$S^* [\%]$
10^{-16}	0.0223	0.19	0.42
10^{-15}	0.0479	0.61	0.13
10^{-14}	0.103	1.9	0.042
10^{-13}	0.223	6.1	0.013
10^{-12}	0.479	19	0.0042

$r^* \uparrow, S^* \downarrow$ as dry particle diameter (or mass) increases

$r^* \downarrow, S^* \uparrow$ as dry solute molecular weight increases

Most atmospheric particles contain both water-soluble and water-insoluble substances (dust, elemental carbon, etc.).

The effect of the insoluble material is to increase in absolute terms the solute effect. Physically, the insoluble material is responsible for part of the droplet volume, displacing the equivalent water. Therefore, for the same overall droplet diameter, the solution concentration will be higher and the solute effect more significant.

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Köhler curves for a particle consisting of various combinations of $(\text{NH}_4)_2\text{SO}_4$ and insoluble material

We see that the smaller the water-soluble fraction the higher the supersaturation needed for activation of the same particle, and the lower the critical diameter.

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The smaller the ϵ_m the higher the supersaturation needed for activation of the same particle size

The ability of a given particle to serve as a nucleus for water droplet formation will depend on its:

- Size
- Chemical composition
- Local supersaturation

Aerosol that consider as a “good candidate” for condensation nuclei are:

- Hygroscopic aerosol.
- Bigger Aerosol with a critical radius can nucleate at low supersaturation (according to Köhler curve)

Hygroscopic aerosol can be larger than $\sim 0.01 \mu\text{m}$ in order to nucleate.

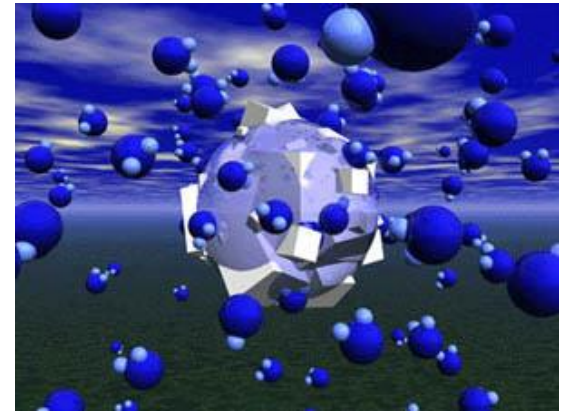
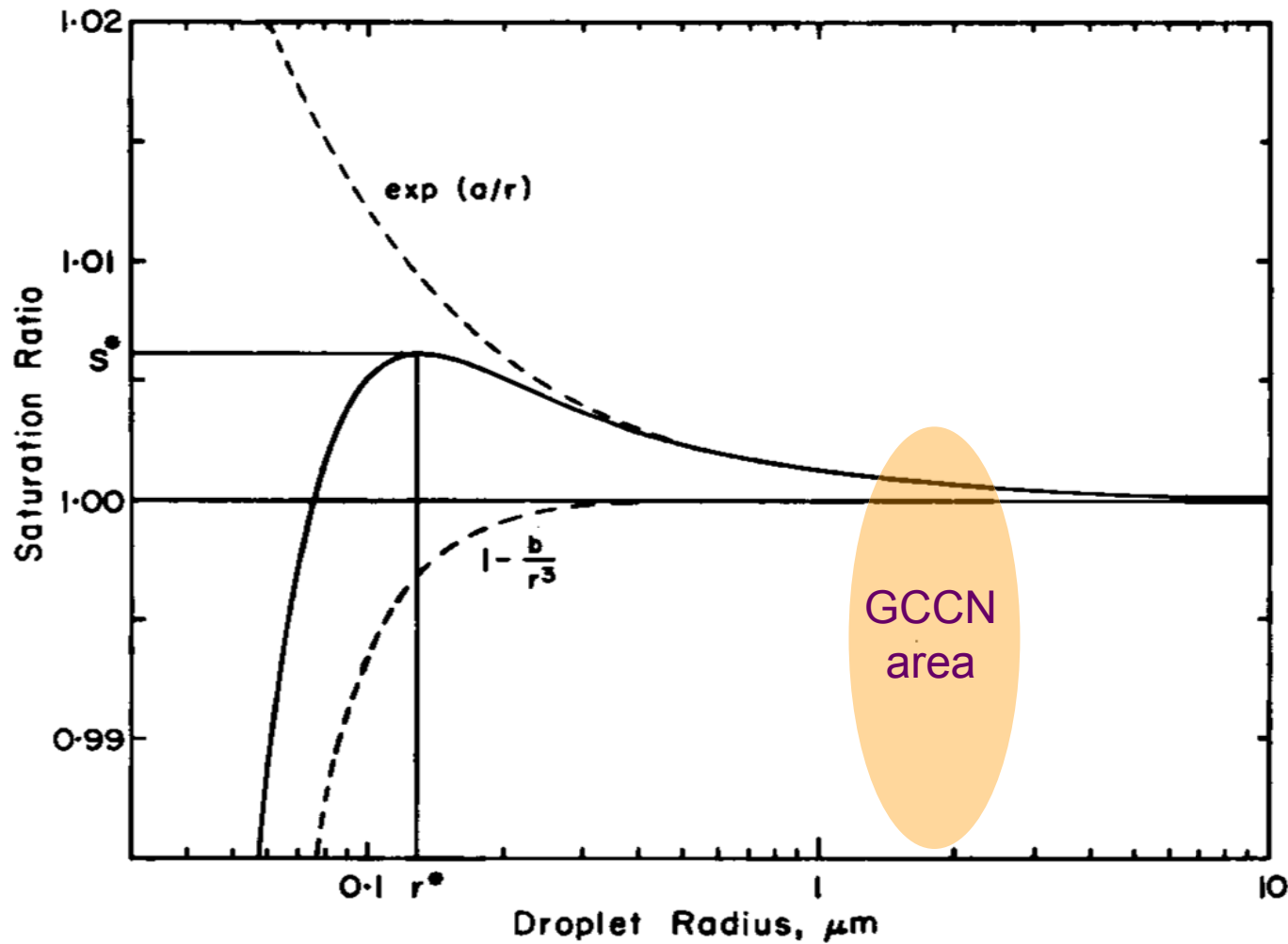


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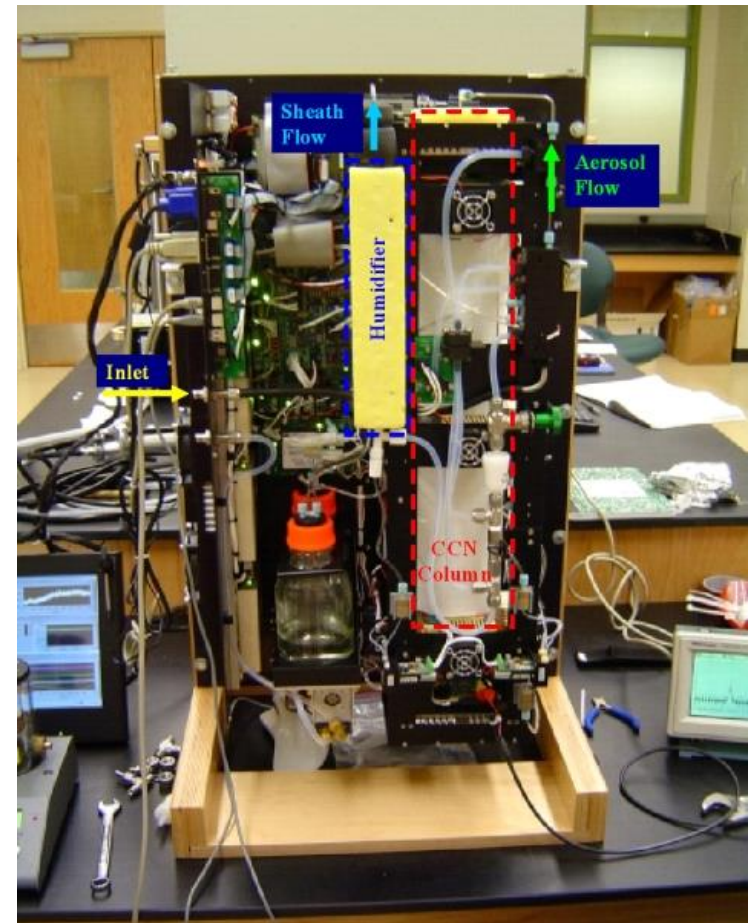
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The CCN Counter is a continuous-flow thermal-gradient diffusion chamber for measuring aerosols that can act as cloud condensation nuclei.

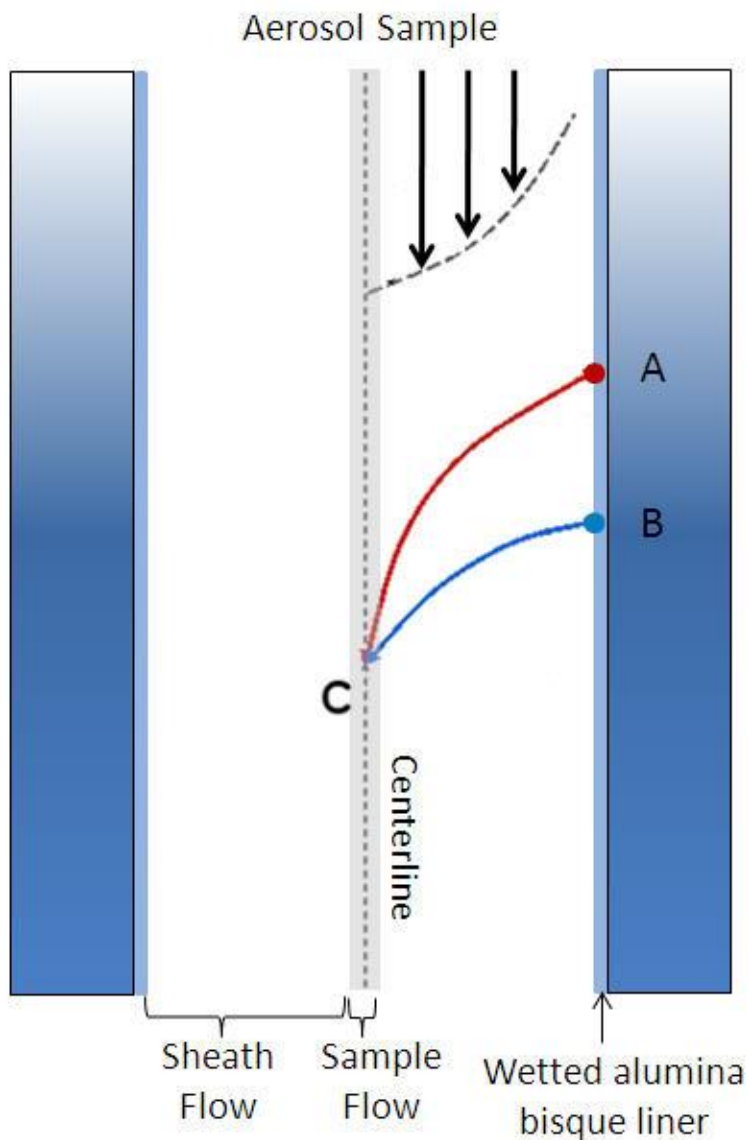
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Please see: <http://www.dropletmeasurement.com/sites/default/files/pictures/Products/CCN/CCN.png>.



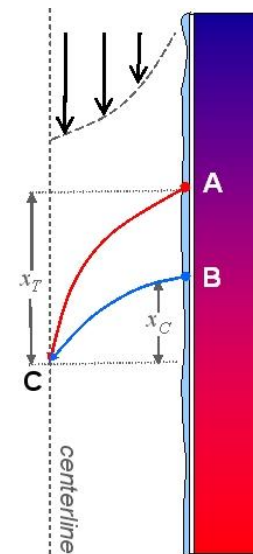
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http://acd.ucar.edu/~jimsmith/POP/instruments_files/CCNc.htm

<http://www.dropletmeasurement.com/>



- Water vapor is saturated at the column wall at all points.
- Diffusing heat originates at Point A, while diffusing mass originates at Point B.
- The actual partial water pressure of water vapor at C equals the partial pressure of water vapor at B.
- However, the temperature at C is lower than at B, meaning there is more water vapor than thermodynamically allowed.



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Please see Figure 1 on page: <http://www.tandfonline.com/doi/full/10.1080/02786820903289780>.

Initial size is selected with a
DMA

Supersaturation due to T
gradient used for activation

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$n(D_p)$ - number distribution of the aerosol population

D_s - activation diameter for $s\%$ supersaturation of these particles

$f_s(D_p)$ - fraction of the aerosol particles of diameter D_p that are activated at $s\%$

Historically, one counted aerosol and determined number activated as a function of s (atmospheric supersaturation, %).

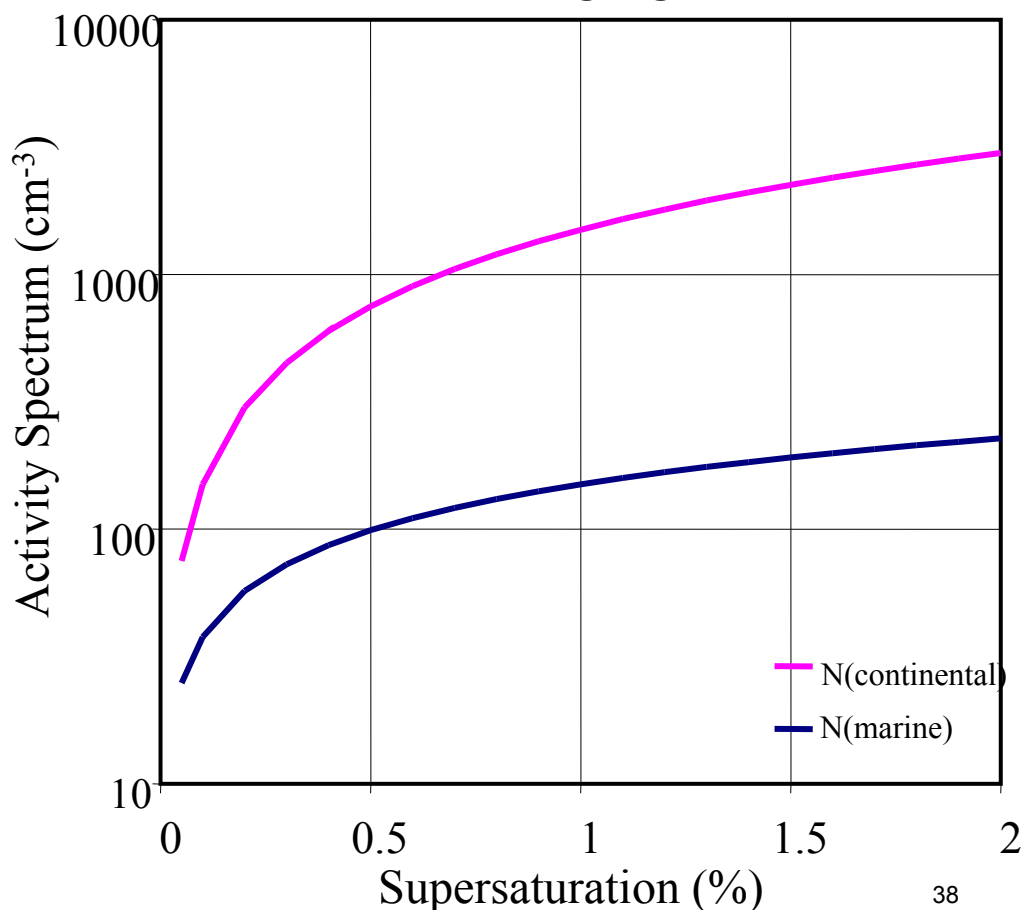
$$\text{Relationship: } \text{CCN}(s) = c s^k$$

CCN(s) - particles cm^{-3}

s - supersaturation expressed as a percentage

C - constant c corresponds to the CCN(1%), the particles active at 1% supersaturation.

Number of aerosol going to nucleation



$$N_c = C s^k$$

Marine: $C=150$
 $k=0.6$

Continental: $C=1500$
 $k=1.1$

maritime: $C=10-300 \text{ cm}^{-3}$
 $k=0.3-1.0$

Continental: $C=200-1000 \text{ cm}^{-3}$
 $k=0.2-2.0$

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Please see: Figure 5 on page, http://olympic.atmos.colostate.edu/AT620/papers/Hudson_and_Yum.pdf.

The saturation ratio, S , over an aqueous solution droplet can be calculated from

$$S = a_w \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right) \quad \rightarrow \quad S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1 - \kappa)} \exp\left(\frac{A}{D}\right)$$

where a_w is the activity of water in solution, ρ_w is the density of water, M_w is the molecular weight of water, $\sigma_{s/a}$ is the surface tension of the solution/air interface, R is the universal gas constant, T is temperature, and D is the diameter of the droplet.

where $A=8.69251 \times 10^{-6} \sigma_{s/a} / T$ is a constant that is evaluated at $\sigma_{s/a} = 0.072 \text{ Jm}^{-2}$ and $T = 298.15 \text{ K}$ (PK07)

PK07 proposed a hygroscopicity parameter that is defined through its effect on the water activity of the solution: $\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w}$,

where V_s is the volume of the dry particulate matter (both soluble and insoluble) and V_w is the volume of the water.

$$D_d^3 = 6V_s / \pi \quad \text{and} \quad D^3 = 6V_T / \pi,$$

Fig. 2. Predicted CCN activity for single- and two-component mixtures. Blue: assumed hygroscopicity and solubility of dominant component, succinic acid having $\kappa=0.23$ and $C=0.056$. Solid line: pure component; activation proceeds based on the deliquescence RH, which is determined by the water activity of the saturated solution. Dashed lines: addition of 0.2% and 2% by volume of sodium chloride. Red: hygroscopicity and solubility of calcium carbonate, $\kappa=0.97$ and $C=2.3 \times 10^{-6}$. Solid line: pure component. Dashed line: addition of 0.1% by volume of sodium chloride.

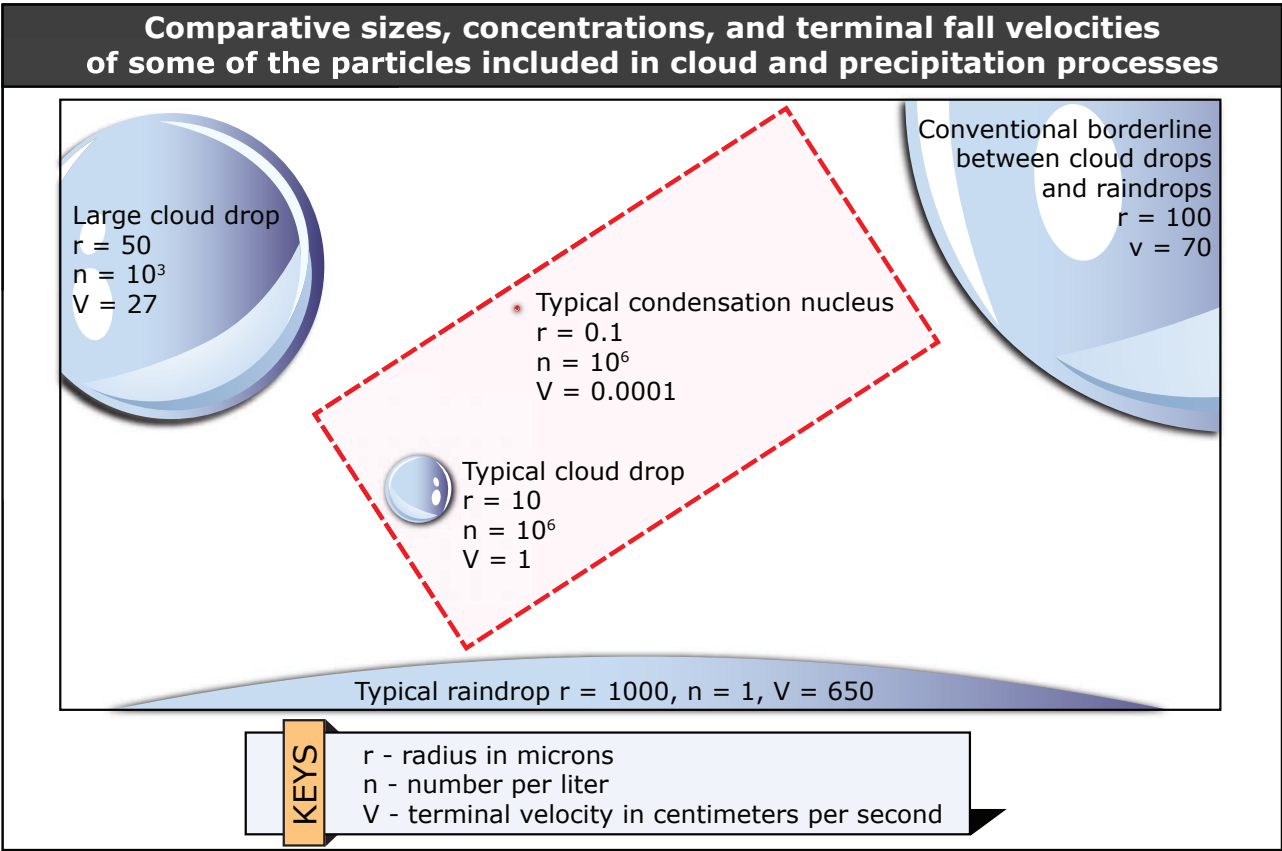
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Lower k indicate on less
hygroscopic or less CCN activity

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Figure 5. Critical supersaturation as a function of size for dry-generated ATD. Raw data (black) are shown along with charge corrections (magenta) and charge and shape corrections (green). Dashed cyan curves are lines of constant κ . Particle sizes are corrected for their non-spherical shape by estimating their surface area from EM. After shape correction, particles are classified by their surface area equivalent diameters instead of by their mobility diameters. The y-error bars indicate the standard deviation of measured supersaturation. The x-error bars indicate the range of possible values of surface area equivalent diameter as observed with EM.

Until now we only create small cloud drop



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As result of the raising air and cooling the droplets are going through:

1. Evaporation
2. Gravity
3. Condensation
4. Collision-coalescence

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Please see the first image on page: <http://conveccion.at.fcen.uba.ar/practicas/NUBES.pdf>.

1 mm drop is a product of 100,000
Collisions and Coalescences

In order for the Collision –
Coalescence process to be
effective, a minimum 20 μm drop
is needed. From this size the drop
can collect smaller drops.

For 30 μm drop collision is the main growing
process.

Larger particles sweep out smaller cloud droplets.

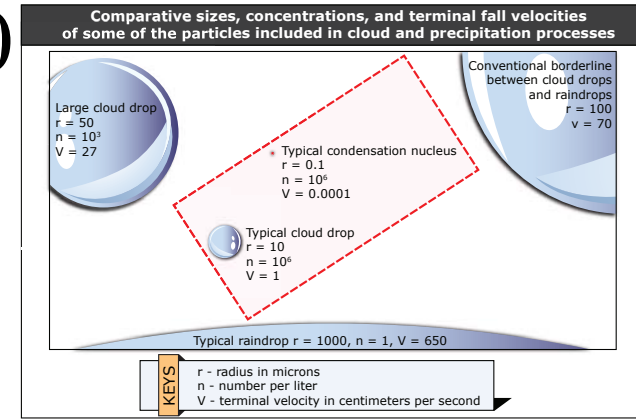


Figure by MIT OpenCourseWare.

Questions?

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12.335 / 12.835 Experimental Atmospheric Chemistry
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