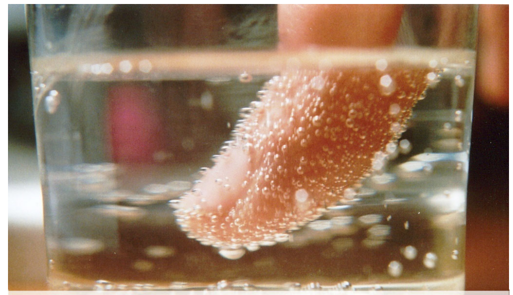
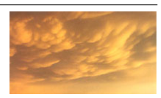
Nucleation of water vapor

Nucleation



Definition: The onset of a phase transition, i.e., condensation of water vapor into liquid in the atmosphere

Making clouds…



- Clouds form when air becomes *supersaturated* with respect to liquid water or ice
- Supersaturation most commonly occurs in the atmosphere when air parcels ascend, resulting in expansion and adiabatic cooling
- Water vapor condenses onto aerosols, forming a cloud of small water droplets

Formation of cloud droplets

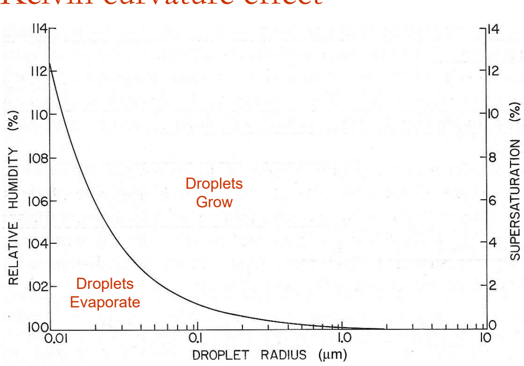
- Homogeneous (spontaneous) nucleation
  - Embryonic water droplets form through chance collisions of molecules of water vapor (no aerosols).
    - Will this happen spontaneously? _______________
    - Will the droplets grow to raindrops? _______________
  - Requires supersaturation with respect to a plane surface of water: Kelvin's formula

$$r = \frac{2\sigma}{nkT\ln(e/e_s)}$$

r: droplet radius
e: vapor pressure
e_s: saturation vapor pressure
σ: interfacial (surface) energy of water
n: # H_2O molecules per unit vol. of liquid
k: Boltzmann constant
T: temperature

The droplet radius is dependent upon the relative humidity (e/e_s)!

Kelvin curvature effect



Relative humidity with which pure water droplets are in unstable equilibrium at 5°C

Kelvin curvature effect

- Water molecules are less strongly attached to a curved water surface, so they evaporate more readily!
- Kelvin's formula can be used to:
  - Calculate the radius *r* of a droplet which will be in unstable equilibrium with air with a given water vapor pressure *e*
  - Determine the saturation vapor pressure *e* over a droplet of specified radius *r*
    - *r* = 0.01 micrometers requires a RH of 112.5%
    - *r* = 1.0 micrometer requires a RH of 100.12%

Supersaturation (S)

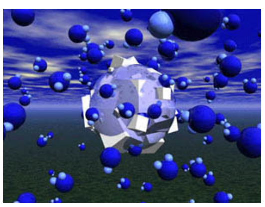
- S = (RH-100%)
- Supersaturation levels that develop in natural clouds due to the adiabatic ascent of air rarely exceed 1% (RH=101%)
- S is typically ~0.1%

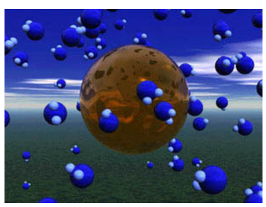
→ Droplets do not form in natural clouds by the homogeneous nucleation of pure water!

Formation of cloud droplets

- Heterogeneous nucleation
  - Cloud droplets grow on wettable (non-hydrophobic) atmospheric aerosols
  - Some hygroscopic aerosols (e.g., sea salt, sodium chloride, ammonium sulfate, etc.) are water soluble; aerosols dissolve when wet, lowering the equilibrium saturation vapor pressure (the Köhler solute effect)
  - Droplets can form and grow on aerosols at much lower supersaturation levels than are required for homogeneous nucleation

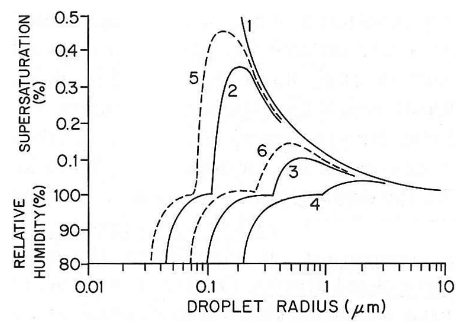
Hygroscopic vs. hydrophobic aerosols


Hygroscopic nucleus (affinity for water)


Hydrophobic nucleus (resists condensation)

- Salt is hygroscopic
  - Can see a sea salt haze at the beach when relative humidity < 100%
  - Condensation begins at RH≈75% for sulfuric and nitric acid particles

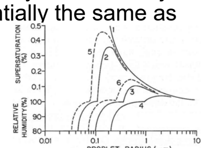
Köhler curve



Describes the variation of relative humidity of air adjacent to a *solution* droplet as a function of its radius

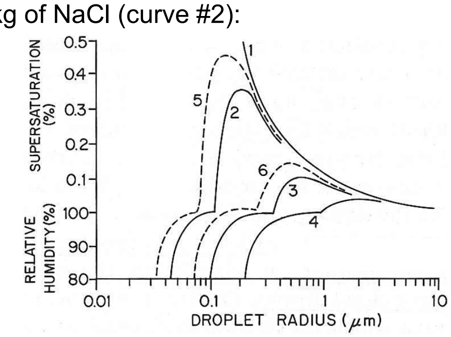
Köhler curve

- Below a certain droplet size, the vapor pressure of the air adjacent to a solution droplet is less than that which is in equilibrium with a plane surface of water at the same temperature
- As the droplets increase in size, the solutions become weaker, the Kelvin curvature effect becomes the dominant influence
- At large radii, the relative humidity of the air adjacent to the droplets becomes essentially the same as that over pure water droplets



Köhler curve

- Consider a solution droplet containing 10^{-19} kg of NaCl (curve #2):



Köhler curve

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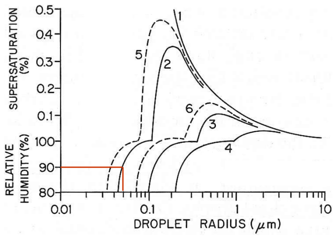
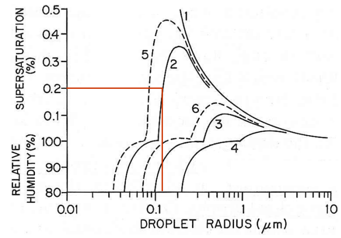


If an initially dry NaCl particle of mass 10^{-19} kg were placed in air with RH = 90%, water vapor would condense onto the particle, the salt would dissolve, and a solution droplet of r = 0.05 μm would form!

Köhler curve

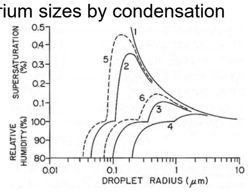
- Consider a solution droplet containing 10^{-19} kg of NaCl (curve #2):



If an initially dry NaCl particle of mass 10^{-19} kg were placed in air with RH = 100.2%, a solution droplet of r = 0.13 μm would form on the NaCl particle.

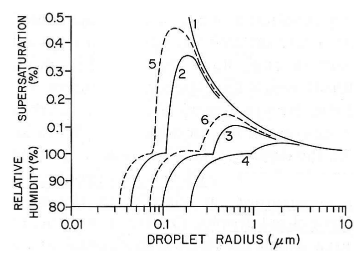
Köhler curve

- In both examples the droplets that form are in stable equilibria with the air:
  - If the drops grew a bit more, the vapor pressures adjacent to their surfaces would rise above that of the ambient air and they would evaporate back to their equilibrium sizes
  - If the drops evaporated a bit, the vapor pressures would fall below that of the ambient air and they would grow back to their equilibrium sizes by condensation



Köhler curve

- Droplets small enough to be in stable equilibrium with the air are called haze droplets. All droplets in a state represented by points on the left-hand side of the maxima in the Köhler curves are haze.

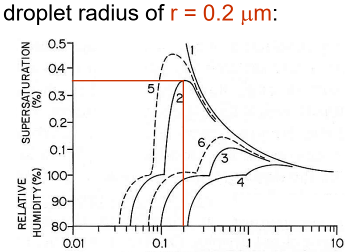


Haze

Source: http://www.nps.gov/shen/naturescience/visibility_and_haze.htm

Köhler curve

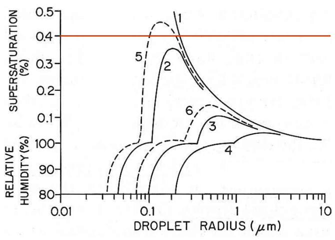
- Again consider curve #2, but with RH = 100.36% and a droplet radius of r = 0.2 μm:



a) Slight evaporation → growth by condensation back to its original size
b) Slight growth → growth by condensation → continued growth → activated droplet (droplet has passed peak in its Köhler curve)

Köhler curve

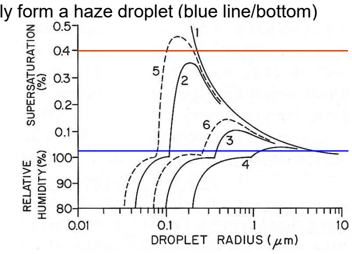
- Again consider curve #2, but with RH = 100. 4%:



A NaCl solution droplet would continue growing by condensation at any radius

Köhler curve

- Any droplet growing along a curve which has a peak supersaturation lying *below* the supersaturation of the ambient air can form a cloud droplet (red line/top)
- Any droplet growing along a Köhler curve which *intersects* a horizontal line, corresponding to the supersaturation of the air, can only form a haze droplet (blue line/bottom)



Cloud condensation nuclei (CCN)

- Small particles upon which cloud droplets condense
- Soluble particles
  - At least 0.01 μm in radius for 1% supersaturation, depending on salt concentration (see Köhler curve)
  - Larger size or solubility → serves as CCN at lower supersaturation
- Insoluble particles
  - At least 0.1 μm in radius for 1% supersaturation (see Kelvin's formula)
  - Larger size or more readily wetted by water → serves as CCN at lower supersaturation

Recall : Atmospheric particulates

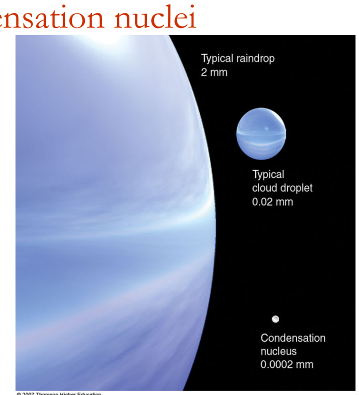
Type	Size range	Concentration (# cm^{-3})
Aitken particles	< 0.1 μm	up to 10^5
Large particles	0.1–1.0 μm	up to 10^3
Giant particles	> 1.0 μm	up to 10^1
Fog/cloud droplets	10–200 μm	20–600

Cloud condensation nuclei

Equivalent spherical diameters of raindrops, cloud droplets, and CCN

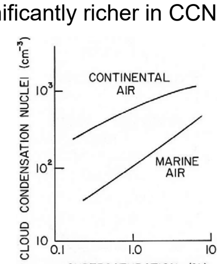
Large aerosols (0.2 to 1.0 μm diameter) are most important in natural cloud formation

Typical CCN have a number concentration between 100 and 1000 per cm^3



Cloud condensation nuclei

- ~1% of aerosols serve as CCN in continental air
- ~10–20% of aerosols serve as CCN in maritime air
- Near the earth's surface, continental air masses are generally significantly richer in CCN than are marine air masses



Cloud condensation nuclei

- Concentrations of CCN over land decline by about a factor of 5 from the surface to 5 km
- Concentrations of CCN over the ocean remain fairly constant with height from the surface to 5 km

Miniature CCN counter (http://www.arm.gov/acrf/updates101507.stm)

Cloud condensation nucleus sources

- Sources include:
  - Wind-generated dust
  - Volcanoes
  - Industrial operations
  - Forest fires
  - Sea salt
  - Sulfate particles
    - Conversion of gaseous components to small particles through chemical/photochemical processes