Condensation and Evaporation

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List of Symbols

p_A: the partial pressure of gas A;
p_T: the total pressure of the gas mixture;
p_s: saturation vapor pressure (vapor pressure);
p: pressure; T: temperature; v: volume;
p_1, p_2, T_1, T_2, v_1, v_2: the above parameters at different statuses;
S_R: saturation ratio; κ: the specific heat ratio;
d^*: critical diameter for a droplet at equilibrium;
K_R : Kelvin ratio;
p_d: partial pressure near the droplet surface pressure to maintain the equilibrium according to the Kelvin equation;
γ : surface tension; M: molecular weight of the vapors;
ρ_l: density of the liquid; $\hat{R}$: gas constant 8.314 Joule K^{-1} $mole^{-1}$;
ρ_v: density of the vapor; h: height of liquid;
d : the droplet diameter; g: gravitational acceleration;

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List of Symbols

J : molecular flux per unit area;
N: molecular number concentration;
$\bar{c}$: mean thermal speed of gas molecules;
k : Boltzmann's constant; p_∞ : the ambient partial pressure;
n_z : the net rate of molecules added to (or leave) the droplet;
d_p : the droplet diameter;
α_c : the condensation coefficient or the coefficient for the molecules to stick on the droplet; N_a : Avogadro's number;
M : molecular weight, mass per mole (kg/mole);
m : molecular weight, mass per molecule;
v_m: volume of a molecule;
λ : mean free path of vapor molecules;
D : the diffusion coefficient for vapor molecules;
Φ : the flux on a surface; r : generic radial direction location;

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List of Symbols

N_d : molecular concentration at the surface of the droplet;
N_∞ : molecular concentration in the ambient;
T_d : temperature at the surface of the droplet;
T_∞ : temperature in the ambient;
ϕ : correction term for the diffusional growth rate;
m_s: mass of the dissolved salt;
i: number of ions each molecule of salt forms when it dissolves (2)
M_w: molecular weight of solvent;
M_s: molecular weight of salt;
ρ: solvent density;
t : time

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Outline

Condensation, evaporation and saturation
Kelvin effect
Homogeneous nucleation
Condensation grow rate
Nucleated condensation
Evaporation
Condensation particle counters

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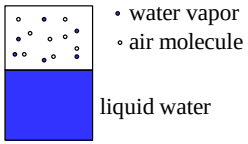
Importance

Cloud physics
Humidification
Combustion
Aerosol generation
Spray drying
Particle measurement



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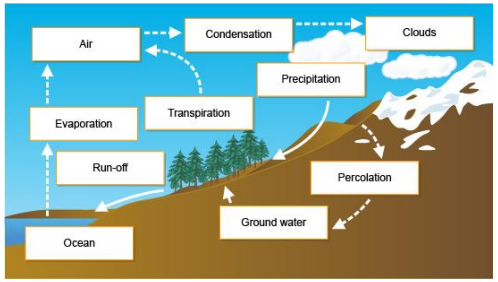
Water Cycle



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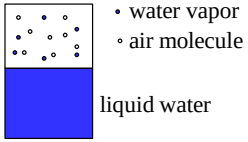
Definitions

Partial pressure: the pressure of a gas (or vapor) in a gas mixture would have if it were to occupy, by itself, the entire volume occupied by the gas mixture.

The volume fraction of gas A is p_A/p_T, where p_A is the partial pressure of gas A, and p_T is the total pressure of the mixture.

Saturation vapor pressure (vapor pressure) p_s, when the condensation of the vapor is in equilibrium with the evaporation from the plane liquid surface.



Function of temperature

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Water Vapor Pressure

Empirical equation for water (accurate within 0.5% for 273 – 373 K)

$$p_s = \exp(16.7 - \frac{4060}{T-37}) \quad \text{kPa}$$

p_s = 2.3 kPa at T = 293K, p_s = 101 kPa (1 atm) at T = 373 K.

Saturation ratio $S_R = \frac{p}{p_s}$ S_R < 1 unsaturated, S_R >1 supersaturated.

S_R = 0.5, relative humidity (RH) = 50%, S_R =1.1, RH = 110%.

How to achieve supersaturation?

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Supersaturation

Cooling, adiabatic expansion, mixing

Adiabatic expansion: change of volume without heat exchange.

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\kappa-1}$$ where κ is the specific heat ratio, κ =1.4 for air.

Example: air saturated with water vapor at 20 °C is expanded adiabatically by 18%. What are the new temperature and saturation ratio?

$$\frac{v_2}{v_1} = 1.18 \qquad T_2 = T_1\left(\frac{v_1}{v_2}\right)^{\kappa-1} = 293(1/1.18)^{0.4} = 274.2$$

$$p_s(T_1) = \exp(16.7 - \frac{4060}{293-37}) = 2.3 \qquad p_s(T_2) = 0.66$$

$$S_R = \frac{2.3 * p_2/p_1}{0.66} = \frac{2.3*(1/1.18)^{1.4}}{0.66} = 2.8$$

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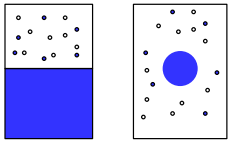
Kelvin Effect

p_s is the equilibrium pressure for a flat liquid surface. For surface of a droplet, the attractive forces between surface molecules need to account for surface tension, thus it is easier for molecules to leave the droplet surface.



To maintain the equilibrium for a droplet with diameter d^* (no condensation, no evaporation), the partial pressure must be higher than p_s. This saturation ratio is the Kelvin ratio K_R,

$$K_R = \frac{p_d}{p_s} = \exp\left(\frac{4\gamma M}{\rho_l \hat{R} T d^*}\right)$$

p_d: partial pressure near the droplet surface

γ surface tension

M: molecular weight of the vapors

ρ_l: density of the liquid

$\hat{R}$: 8.314 Joule K^{-1} $mole^{-1}$

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Kelvin Equation Derivation

$$dp = -\rho_v g dh$$

Assume perfect gas law for vapor

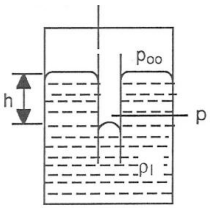
$$p = \rho_v \frac{\hat{R}}{M} T \qquad dp = -\frac{pMg}{\hat{R}T} dh$$

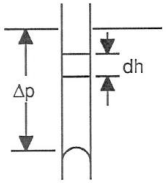
$$\ln\frac{p_d}{p_s} = \frac{Mgh}{\hat{R}T} \qquad \Delta p = \rho_l g h$$

Surface tension $\Delta p \pi d^2/4 = \gamma \pi d$

Thus

$$\frac{p_d}{p_s} = \exp\left(\frac{4\gamma M}{\rho_l \hat{R} T d}\right)$$





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Example for Kelvin Effect

What saturation ratio is needed to maintain the size of 50 nm pure water droplets at 20 °C?

$$K_R = \frac{p_d}{p_s} = \exp\left(\frac{4\gamma M}{\rho_l \hat{R} T d^*}\right)$$

γ=0.0727 N/m, surface tension between air and water at NTP.

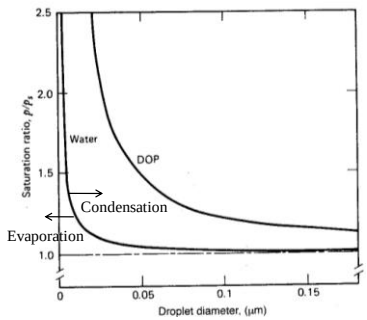
M=18/1000 kg/mol

ρ_l =1000 kg/m^3

$\hat{R}$ = 8.314 Joule K^{-1} mole^{-1}

T=293 K; d^* = 50×10^{-9} m.

K_R =1.044



Even at saturation, small droplets evaporate and disappear.

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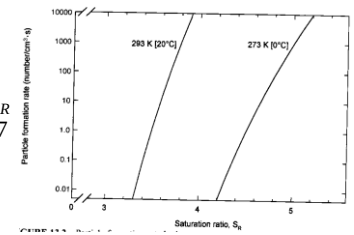
Homogeneous Nucleation

Homogeneous nucleation (self-nucleation) is the formation of particles from the supersaturated vapor without the assistance of condensation nuclei or ions.

What is the value of S_R if condensation were to start from individual water molecules?

Homogeneous nucleation usually starts with clusters of molecules. Pure water at 293 °C will form particles when S_R > 3.5, corresponding to d^*=1.7 nm.



Homogeneous nucleation contributes to photochemical smog.

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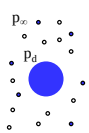
Condensation Growth: free molecular

$$j = \frac{1}{4} N\bar{c} \qquad \bar{c} = \sqrt{\frac{8kT}{\pi m}} \qquad p_\infty = NkT$$



Thus the net rate of molecules added to the droplet is

$$n_z = \pi d_p^2 \frac{p_\infty - p_d}{\sqrt{2\pi mkT}} \alpha_c$$

d_p is the droplet diameter, p_∞ is the ambient partial pressure, p_d is the pressure to maintain the equilibrium according to the Kelvin equation, α_c is the condensation coefficient or the coefficient for the molecules to stick on the droplet, 0.04 is often used.

$$v = \frac{\pi}{6} d_p^3 \qquad \frac{dv}{dt} = n_z v_m \qquad v_m = \frac{M}{\rho_l N_a}$$

N_a = Avogadro's number

Thus $$\frac{d(d_p)}{dt} = \frac{2M\alpha_c(p_\infty - p_d)}{\rho_l N_a \sqrt{2\pi mkT}} \quad \text{for } d_p < \lambda.$$

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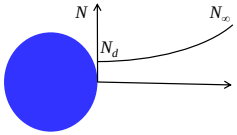
Condensation Growth: diffusion limited

When $d_p > \lambda$, diffusion of vapor molecules determines the growth rate. D is the diffusion coefficient for vapor molecules.



$$j = -D\frac{dN}{dr} \qquad j = \frac{\Phi}{4\pi r^2}$$

For steady state diffusion, the flux Φ is constant

$$-\int_{r=d_p/2}^{r=\infty} \frac{dr}{4\pi r^2} = \int_{N=N_d}^{N=N_\infty} \frac{DdN}{\Phi} \qquad \Phi = 2\pi d_p D(N_\infty - N_d)$$

Using perfect gas law and $n_z = \Phi$ at the droplet surface

$$n_z = \frac{2\pi d_p D}{k}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right) \qquad \frac{d(d_p)}{dt} = \frac{4DM}{\rho_l d_p \hat{R}}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right) \text{ for } d_p > \lambda.$$

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Correction and Temperature Effect

The diffusion limited growth equation needs to be corrected because the diffusion equation breaks down within one free path of the droplet surface. The correction given by Fuchs (1959) and Davies (1978) is

$$\frac{d(d_p)}{dt} = \frac{4DM}{\rho_l d_p \hat{R}}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right)\phi \quad \text{and} \quad \phi = \frac{2\lambda + d_p}{d_p + 5.33(\lambda^2/d_p) + 3.42\lambda}$$

The correction reduces the growth rate.

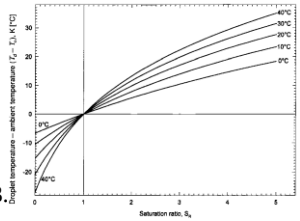
For slow growth $1.0 < S_R < 1.05$

$$T_\infty \cong T_d$$

For fast growth, empirical equation

$$T_d - T_\infty = \frac{(6.65 + 0.345T_\infty + 0.0031T_\infty^2)(S_R - 1)}{1 + (0.082 + 0.00782T_\infty)S_R}$$

T_∞ in °C, for $0<S_R<5$ and $273<T_\infty<313$.



Nucleated Condensation

Nucleated condensation, or heterogeneous nucleation is the formation and growth of particles in the presence of condensation nuclei or ions.

- Insoluble nuclei: passive site for vapors to condense on
  behaves like a droplet of the same size
  Under favorable conditions, d^* and critical S_R determined by Kelvin equation

- Ions: clusters of air molecules with electrical charges
  slightly changes the relation between d^* and critical S_R
  facilitate droplet formation when $S_R > 2.0$.

- Soluble nuclei: most important formation mechanism.
  significantly promotes droplet formation even at saturation or unsaturated conditions.
  NaCl is most important nuclei.

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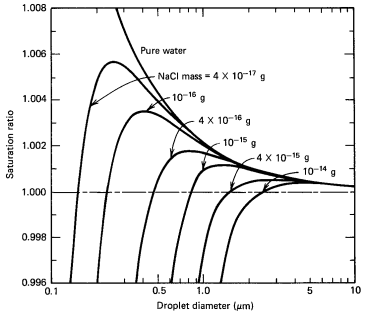
Effect of Salt on Condensation

The salt has high affinity with water. Dissolved salt molecules lower the vapor pressure at the water surface, thus promote condensation.

$$S_R = \frac{p_d}{p_s} = \exp\left(\frac{4\gamma M_w}{\rho R T d_p}\right) \Big/ \left(1 + \frac{6 i m_s M_w}{M_s \rho \pi d_p^3}\right)$$



m_s: mass of the dissolved salt
i: number of ions each molecule of salt forms when it dissolves (2 for NaCl).
M_w: molecular weight of solvent (water)
M_s: molecular weight of salt
ρ: solvent density

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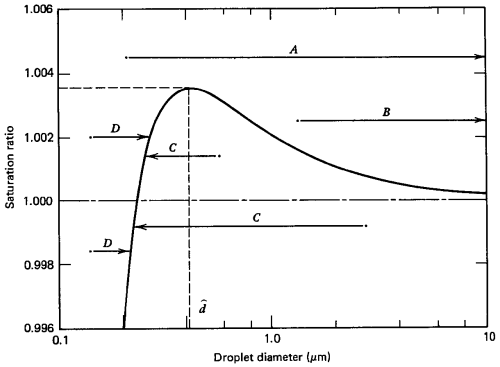
Kohler Curve

Saturation ratio vs. droplet size for 10^{-16} g NaCl (Solid sphere of 45 nm in diameter). At saturation, the particle becomes a stable 0.23-μm droplet.



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Evaporation Rate and Time

A pure liquid droplet under S_R below the Kelvin ratio, will completely evaporate. The time for this is the droplet lifetime or drying time.

Evaporation is the opposite of condensation. The right-hand side is negative and d_p is decreasing

$$\frac{d(d_p)}{dt} = \frac{4DM}{\rho_l d_p \hat{R}}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right)\phi \quad \text{for } d_p > \lambda.$$

Time t for a droplet with diameter d_1 to completely evaporate

$$\int_{d_1}^{0} d_p d(d_p) = \int_0^t \frac{4DM}{\rho_l \hat{R}}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right)dt \qquad t = \frac{\hat{R}\rho_l d_p^2}{8DM\left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty}\right)}$$

for $d_p > 1\mu$m.

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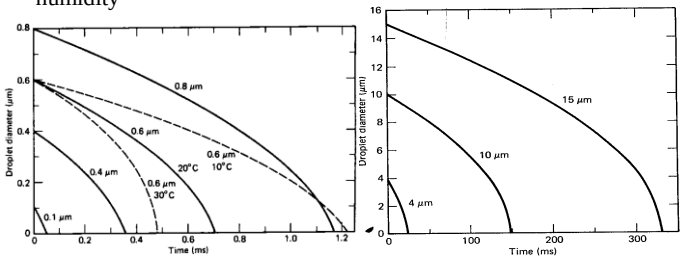
Evaporation Time

Evaporation of pure water droplet at 293 K and 50% of relative humidity



Droplets of 0.1 – 0.8 μm. Dashed lines show the effect of T_∞.

Droplets of 4 – 15 μm.

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Example

Example: how long does it take a 20-μm droplet of pure water to evaporate completely in dry air at 293 K?

$$t = \frac{\hat{R}\rho_l d_p^2}{8DM\left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty}\right)} \qquad \text{Dry air} \quad p_\infty = 0 \quad T_\infty = 293K = 20^\circ\text{C}$$

$$T_d - 20 = \frac{(6.65 + 0.345\times 20 + 0.0031\times 20^2)(0-1)}{1 + (0.082 + 0.00782\times 20)0} \qquad T_d = 5.2^\circ\text{C} = 278.2K$$

$$p_d = \exp(16.7 - \frac{4060}{278.2 - 37}) = 0.876\text{kPa}$$

The diffusion coefficient of water vapors at 293 K and 1 atm $D = 2.4\times 10^{-5}$ m^2/s

$$t = \frac{8.31\times 1000\times(20\times 10^{-6})^2}{8\times 2.4\times 10^{-5}\times\frac{18}{1000}\left(\frac{876}{278.2} - \frac{0}{293}\right)} = 0.31\text{s}$$

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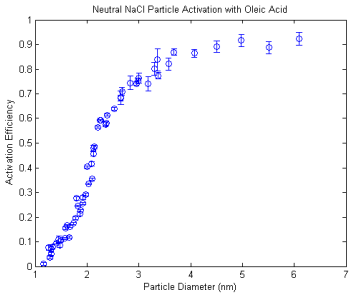
Condensation Particle Counters

CPC grows aerosols by condensing vapors of working fluid onto them, then detects the aerosol by optical scattering. It is the primary method to detect and count aerosols in the nm range.

Lower detection limit 1 nm – 20 nm, depending on the nuclei, working liquid and temperatures



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CPC Design

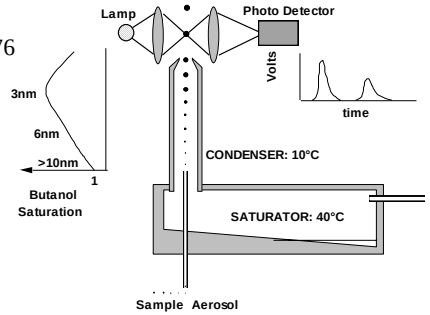
Nuclei grow to about 10 μm, regardless of their initial sizes.

Specification for TSI 3776

Flowrate: 0.3 or 1.5 lpm
Response time ~ 1 sec

Concentration:
single particle counting < 3×10^5 p/cc;
photometric counting up to 10^6 p/cc.
error ± 10 % at < 3×10^5 p/cc

Schematic of unltrafine CPC (TSI 3025, Stolzenburg & McMurry, 1991)



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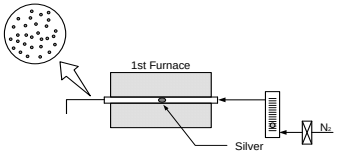
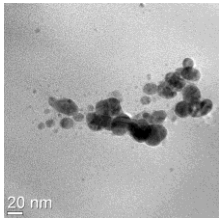
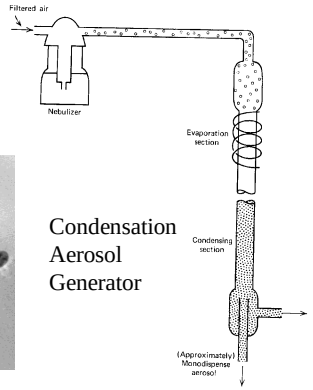
Aerosol Generation



Evaporation and condensation generation of metal nanoparticles



Silver nanoparticles



Condensation Aerosol Generator

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