

1. Microphysics of Clouds

Changes in phase are basic to cloud microphysics. The possible changes are:

vapor-liquid evaporation, condensation

liquid-solid freezing, melting

vapor-solid deposition, sublimation

The changes from left to right correspond to increasing molecular order. These transitions *don't occur at thermodynamic equilibrium*. There is a strong free energy barrier that must be overcome for droplets to form - so even if a sample of moist air is cooled adiabatically to the equilibrium saturation point for bulk water, droplets should not be expected to form. In fact, water droplets do begin to condense in pure water vapor only when the relative humidity reaches several hundred percent!

The reason why cloud droplets are observed to form in the atmosphere when ascending air just reaches equilibrium saturation is because the atmosphere contains significant concentrations of particles of micron and sub-micron size which have an affinity for water .

A droplet will be stable if its size exceeds a certain critical value. What determines the critical value is the balance between the opposing rates of growth and decay. The decay process depends strongly upon the temperature of the droplet and its surface tension

1a. Droplet Growth by Condensation

i. Homogeneous nucleation (The curvature effect) The simplest means of forming cloud is through *homogeneous nucleation* wherein pure vapor condenses to form droplets. Survival of the droplet is determined by a balance between condensation and evaporation. The equilibrium between the droplet and surrounding vapor is described by the Gibbs free energy, but with one modification. In addition to expansion work, a spherical droplet performs work in association with its surface tension σ , which has dimensions of energy/area. σdA represents the work to form the incremental area dA of interface between vapor and liquid.

For a heterogeneous system composed of the droplet and surrounding vapor, the fundamental relation for the Gibbs free energy becomes:

$$dG = -SdT + Vdp + (\mu_v - \mu_w)dm_v + \sigma dA \quad (1)$$

where

$$dm_v = -dm_w \quad (2)$$

$$= -\rho_w dV_w \quad (3)$$

where n_w and V_w are the number density and volume of the droplet. The difference in the chemical potentials (this system is not necessarily in chemical equilibrium), can be expressed in terms of the vapor and saturation vapor pressures. $\mu_i \approx g_i$, so for an *isothermal, reversible* transformation:

$$d\mu_v = dg_v = -sdT + \alpha dp = \alpha de \quad (4)$$

$$d\mu_w = \alpha_w de \quad (5)$$

where e is the pressure. Subtracting gives

$$d(\mu_v - \mu_w) = (\alpha_v - \alpha_w)de \approx \alpha_v de \quad (6)$$

Applying the gas law to an individual molecule of water vapor

$$e\alpha_v = R_v T \quad (7)$$

$$d(\mu_v - \mu_w) = \frac{R_v T}{e} de = R_v T d \ln e \quad (8)$$

Integrating from the vapor pressure (e) to the saturation pressure e_s (at which $\mu_v = \mu_w$) we have

$$\mu_v - \mu_w = R_v T \ln \frac{e}{e_s} \quad (9)$$

Incorporating into Equation (1) and integrating from a reference state of pure vapor (with vapor pressure maintained) we have

$$\Delta G = -V_w \rho_w R_v T \ln \frac{e}{e_s} + \sigma dA \quad (10)$$

Forming a spherical droplet of radius a corresponds to the change of Gibbs free energy

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 R_v T \ln \frac{e}{e_s} \rho_w \quad (11)$$

For subsaturation $e/e_s < 1$, saturation $e/e_s = 1$ and supersaturation $e/e_s > 1$. The free energy as a function of droplet radius increases monotonically for subsaturated and saturated conditions, but a system approaches thermodynamic equilibrium by reducing its free energy so droplet formation is not favored for $e/e_s \leq 1$ - a droplet formed will spontaneously evaporate. For supersaturated conditions, there is a maximum energy at r_c and then the energy decreases and condensation is more efficient than evaporation.

$r < r_c$ droplet evaporates back to initial state.

$r > r_c$ droplet grows spontaneously through condensation of vapor and is said to be activated.

The critical radius for a given temperature is:

$$r_c = \frac{2\sigma}{n_w k T \ln(e/e_s(\infty))} \quad (12)$$

$$\frac{e}{e_s(\infty)} = \frac{2\sigma}{n_w k T r_c} \quad (13)$$

This is *Kelvin's Formula*. For critical or equilibrium supersaturation:

Above r_c the droplet grows spontaneously through condensation. r_c describes an unstable equilibrium - any perturbation will take the droplet away from this state. However, the requirements for supersaturation are very high (much higher than those observed). An embryonic droplet as large as $0.01 \mu m$ still requires a supersaturation of 12% to be sustained. Yet, supersaturations exceeding 1% are rarely observed. *Cloud formation cannot be explained by homogeneous nucleation.*

ii. Heterogeneous nucleation (Solution effect) water condenses onto existing particles of atmospheric aerosol termed *cloud condensation nuclei CCN*. These particles support condensation at supersaturation values well below those required for homogeneous nucleation - primarily because of their size.

Hygroscopic particles, like sodium chloride and ammonium sulfate are even more effective. In the presence of moisture $NaCl$ and $(NH_4)_2SO_4$ absorb vapor and readily dissolve. The resulting solution has a saturation vapor pressure below that

of pure water - because e_s is proportional to the absolute concentration of water molecules on the surface of the droplet. Consequently, a droplet containing dissolved salt favors condensation more than would a pure water droplet of the same size.

Saturation pressure over solution Droplets. Over a plane water surface, the reduction in vapor pressure due to the presence of non-volatile solute is:

$$\frac{e'}{e_s(\infty)} = \frac{n_0}{n + n_0} \quad (14)$$

e' is the equilibrium vapor pressure over a solution with n_0 molecules of water and n molecules of solute. For $n \ll n_0$:

$$\frac{e'}{e_s(\infty)} = 1 - \frac{n}{n_0} \quad (15)$$

This is Raoult's Law.

However, what really matters is not the number of molecules but the number of molecules formed in the solution (dissociation). If the number of effective ions in a solute of mass M is $n = iN_0M/m_s$. (N_0 is Avogadro's number and m_s is molecular weight). The number of water molecules of water in mass $m = n_0 = N_0m/m_v$. The solution effect (over a droplet) becomes:

$$\boxed{\frac{e'}{e_s(\infty)} = 1 - \frac{b}{r^3}} \quad (16)$$

where

$$b = \frac{3im_vM}{4\pi\rho_w m_s} \quad (17)$$

iii. Combining the Solution and Curvature effect: Köhler Curves Describe the equilibrium supersaturations for solutions containing specified amounts of solute.

$$\frac{e'(r)}{e_s(\infty)} = \left(1 - \frac{b}{r^3}\right) \exp^{a/r} \quad (18)$$

where

$$a = \frac{2\sigma}{\rho_w R_v T} \quad (19)$$

A good approximation is:

$$\boxed{\frac{e'(r)}{e_s(\infty)} = 1 + \frac{a}{r} - \frac{b}{r^3}} \quad (20)$$

Where the first term is the curvature term and the second term is the solution term. Using this expression we can obtain *Köhler Curves*.

For a fixed r , $e'(r)/e_s(\infty)$ decreases with increasing solute and eventually become negative ($RH < 100\%$).

At $r < r_t$ a droplet is in stable equilibrium - perturbed droplet is restored to original state. - *haze*

At $r > r_t$ a droplet is in unstable equilibrium - perturbed droplet is restored to original state.- *can enlarge into cloud drops*

Continental aerosols are the dominant source of CCNs - sea salt is not common in cloud droplets. Cumulus clouds have droplet number densities of order $10^2 cm^{-3}$ over maritime regions and $10^3 cm^{-3}$ for continental regions. This implies smaller size of the droplets in continental regions because the liquid water content doesn't differ much.

2. Aerosols

Radiative transfer is modified by clouds. Clouds represent cooling in the short-wave (SW) energy budget and warming in the longwave (LW) energy budget. Small particulates are produced and removed through a variety of processes, which make the composition, size and distribution of atmospheric aerosols widely variable. There is low density of aerosols over the oceans (*marine aerosols*) with number density $n = 10^3 cm^{-3}$ and greater over terrestrial areas (*continental*) with number densities $n > 10^5 cm^{-3}$ over industrial areas.

- Continental Aerosols**
1. Crustal species (subtropical deserts like Sahara and Southwestern US) $a > 1\mu m$
 2. Combustion (industrialized regions) (submicron-scale particles)
 3. Carbonaceous components (tropical regions through agricultural burning)

Has a bimodal distribution.

Marine Aerosol Are composed primarily of sea salt. Also has a bimodal distribution.

Stratospheric Aerosol Introduced into the stratosphere through penetrative convection and volcanic eruptions. Also by gas-to-particle conversions.

Some facts about aerosols...

- The larger the size of a particle, and the greater its solubility, the lower the supersaturation at which the particle can serve as a CCN. ($\approx .1\mu m$ for water insoluble, while $\approx .01\mu m$ for water soluble at 1% supersaturation)
- Number density decreases with height by about a factor of 5 between the PBL and the free troposphere.
- There is a diurnal variation in CCN concentrations with a minimum at about 6am and maximum about 6pm - apparently due to gas-to-particle conversions that require solar radiation.
- Soil particles and dust serve as CCN but are not really a dominant source.

2a. Size Distribution of Aerosols

Aerosols are characterized by its *size distribution* expressed as the distribution function $n_d(D)$ as a function of the diameter (of equi-volume spheres). $n_d(D)dD$ is the number of particles per unit volume whose diameters are between D and $D + dD$. We can also relate to the volume distribution function $n_v(v)dv$ for the number of particles with volumes between v and $v + dv$.

$$n_d(D)dD = n_v(v)dv \quad (21)$$

because $v = \frac{\pi D^3}{6}$,

$$n_d(D) = n_v(v) \frac{dv}{dD} = \frac{\pi}{2} D^2 n_v \left(\frac{\pi D^3}{6} \right) \quad (22)$$

The number of particles per unit volume with diameter smaller than D is

$$N(D) = \int_0^D n_d(D') dD' \quad (23)$$

where $n_d(D) = \frac{dN}{dD}$. It is also convenient to use the logarithmic scale by defining another distribution function $n_l(D)$ where $n_l(D)d(\log D)$ is the number of particles per unit volume whose diameters are in the interval $d(\log D)$ and $n_l(D) = \frac{dN}{d \log D}$. Plots of $\log n_l(D)$ versus $\log D$ for aerosol particles can be fit by straight lines over a limited range of diameters. This implies a power law dependence of n_l on D of the form

$$n_l(D) = cD^{-\beta} \quad (24)$$

$\beta = 3$ is often cited a typical over the diameter range from 10^{-1} to $10\mu m$. Aerosol populations having this form are said to follow a Junge distribution.

We can also write the distributions in terms of surface area or volume. Surface area of particles with diameters smaller than D is given by:

$$S(D) = \int_0^D \pi D'^2 n_d(D') dD' \quad (25)$$

The volume of particles with diameters smaller than D is:

$$V(D) = \int_0^D \frac{\pi}{6} D'^3 n_d(D') dD' \quad (26)$$

.1 to 1 μm Accumulation mode - collision as a result of Brownian motion. Most important for cloud formation. Larger particles close to $5\mu m$ are much fewer in number.

10 to 20 μm Coarse particle mode. Combustion sources or high winds.

.01 μm Nucleation mode