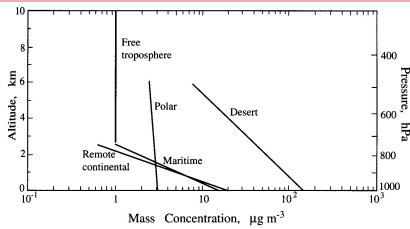# Cloud formation

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FIGURE 7.25   Representative vertical distribution of aerosol mass concentration (Jaenicke, 1993).
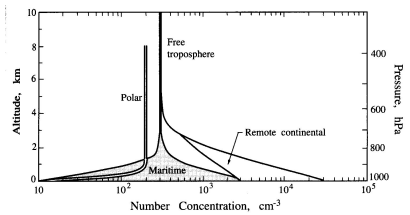

FIGURE 7.26   Representative vertical distribution of aerosol number concentration (Jaenicke, 1993).
A range of concentrations is shown for marine and remote continental aerosols.

Source: Figures 7.25 & 7.26 Seinfeld&Pandis

Formation of aerosols

► Gas-to-particle conversion: nucleation of aerosols from supersaturated gases

► Bulk-to-particle conversion: wind blown dust (arid regions), emissions of pollens and spores by plants

► Liquid-to-particle conversion: Sea salt aerosols originate from drops ejected into the air when air bubbles in breaking waves burst at ocean surface.
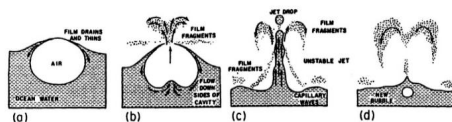

Fig. 8-12: Four stages in the production of sea salt particles by the bubble-burst mechanism. (a) Film cap protrudes from the ocean surface and begins to thin. (b) Flow down the sides of the cavity thins the film which eventually ruptures into many small fragments. (c) Unstable jet breaks into few drops. (d) Tiny salt particles remain as drops evaporate; new bubble is formed. (From Day, 1965, with changes.)

►

Global Source Strength, Lifetime and Burden

	Aerosol Type		Flux (Tg/yr)	Lifetime (d)	Burden (mg/m^2)
Natu-ral	Pri-mary		900-1500	4	19-33
			2300	1	3
			50	4	1
	Sec.		70	5	2
			20	10	1
			(40)	(400)	(80)
			20	5	0.6
	Total		3400-4000		27-41
Anth-ropo-genic	Pri.		40-640	4	1-14
			14	7	0.6
			54	6	1.8
	Sec.		140	5	3.8
			20	7	0.8
	Total		270-870		8-21
Sum			3670-4870		35-62

(Source: Ramanathan et al., Science, 2001)

Removal of aerosols

► 80%-90% of the aerosol mass is removed from the atmosphere by precipitation particles (wet scavenging)

► prior to that aerosols serve as cloud condensation nuclei (CCN). As these particles grow, aerosols tend to be forced onto their surface by diffusion fields associated with the flux of water vapor to the growing cloud droplet (diffusiophoretic force)

► precipitation particles collect aerosols by direct impaction, the better the larger the aerosols (best for aerosols > 2 μm).

► aerosols are also removed by gravitational settling and subsequent impaction onto obstacles on Earth's surface (dry deposition) which accounts for 10-20% of aerosols mass removed from the atmosphere.
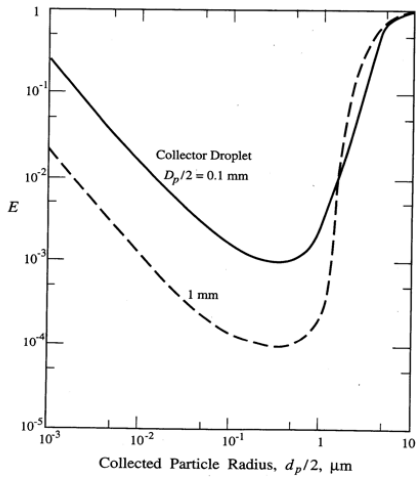

Dry deposition (Fig 19.3 Seinfeld&Pandis)
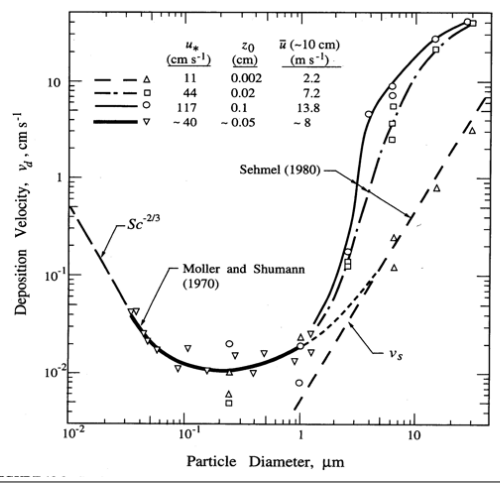
Wet deposition (Fig 20.10 Seinfeld&Pandis)

Nucleation scavenging (Fig 17.8 Pruppacher&Klett)
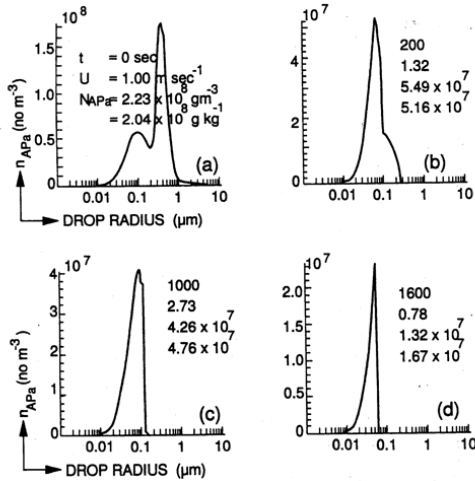
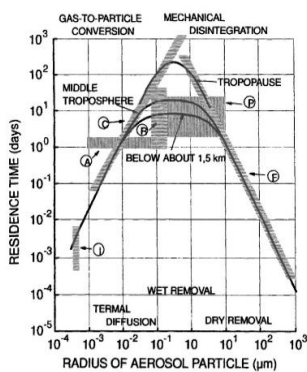# Residence time of aerosols (Fig 8.14 Pruppacher&Klett)

Fig. 8-14: Residence time of aerosol particles as a function of their radius. I: Small ions, A: Aitken particles, C: from thermal diffusion of aerosol particles, R: based on radioactivity data, P: removal by precipitation, F: removal by sedimentation. (From Jaenicke, 1978a, 1988, with changes.)

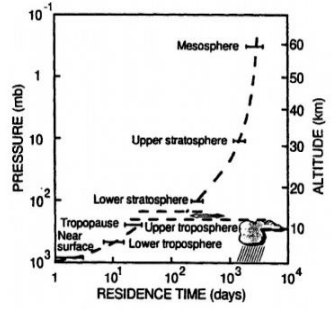# Residence time of aerosols (Fig 8.15 Pruppacher&Klett)

Fig. 8-15: Residence time of aerosol particles as a function of altitude in the atmosphere. (From Jaenicke, 1978c, 1988, based on Flohn, 1973, with changes.)

Importance of aerosol particles (AP)

- Aerosol particles act as centers for cloud droplets and ice particles
- Effects on pollution:
  - photochemical smog (ozone)
  - degradation of visibility
  - winter smog (solid aerosols provide surface upon which trace gases can be absorbed and then react, e.g. _London smog_)
- Effects on climate - effects on radiative transfer (direct and indirect effect)

London smog
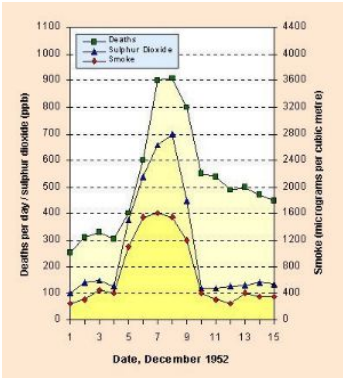
Aerosol radiative effects

Phase changes

▶ Phase changes of water are basic to cloud microphysics:

▶ vapor ↔ liquid
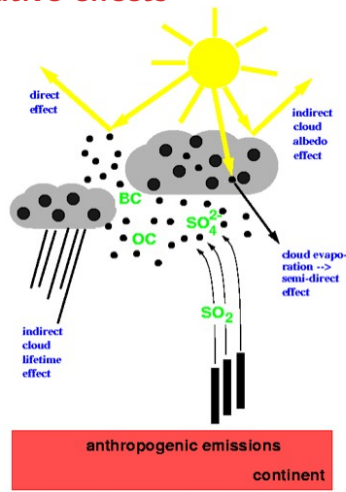
▶ liquid ↔ solid

▶ vapor ↔ solid

▶ the changes from left to right correspond to increasing molecular order.

▶ these transitions do not occur at thermodynamic equilibrium, but in presence of a strong free energy barrier. I.e. for a water droplet to form by condensation from the vapor, the surface tension must be overcome by a strong gradient of vapor pressure.

▶ The Clausius-Clapeyron equation describes the equilibrium condition for a thermodynamic system consisting of bulk water and its vapor.

▶ Saturation is defined as the equilibrium situation in which the rates of evaporation and condensation are equal.

▶ However, for small droplets, because of the energy barrier, phase transitions do not generally occur at the equilibrium saturation of bulk water.

Nucleation

▶ **nucleation**: Any process in which a free energy barrier must be overcome, such as vapor to liquid or liquid to ice transitions.

▶ **homogeneous nucleation**: Cloud droplets form directly from the vapor phase

▶ homogeneous nucleation requires several hundred percent supersaturation

▶ instead cloud droplet form when the ascending air just reaches equilibrium saturation, because of the presence of CCN.

▶ **heterogeneous nucleation**: Cloud droplets form on nuclei from the vapor phase

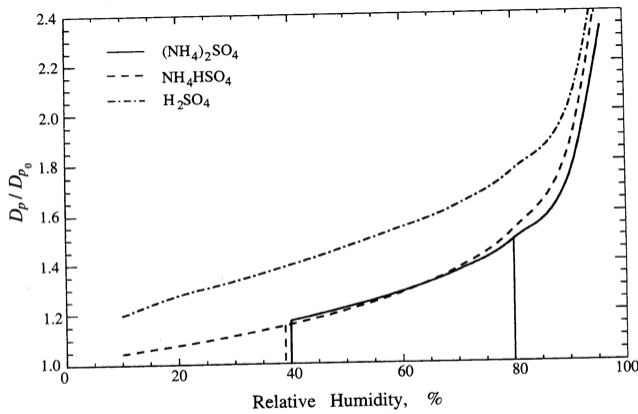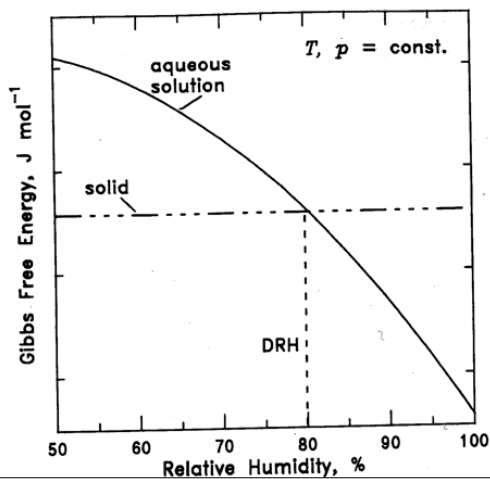## Water uptake of aerosols (Fig. 9.4 Seinfeld&Pandis)

FIGURE 9.4 Diameter change of $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4 particles as a function of relative humidity. D_{p_0} is the diameter of the particle at 0% RH.

Gibbs free energy (Fig. 9.5 Seinfeld&Pandis)

Kelvin equation

▶ So far we have ignored the curvature effect. We introduce it by starting from Gibbs free energy:

$$\Delta G = G_{droplet} - G_{pure\ vapor} \qquad (1)$$

where the drop with radius r contains n molecules.

▶ Let N_T the initial number of molecules of vapor. After the drop forms, number of vapor molecules is reduced to: $N_v = N_T - n$. Then, if g_v and g_l are the Gibbs free energies of a molecule in the vapor and liquid phase:

▶

$$\Delta G = n(g_l - g_v) + 4\pi r^2 \sigma = \frac{4\pi r^3}{3\alpha_l}(g_l - g_v) + 4\pi r^2 \sigma \qquad (2)$$

where $4\pi r^2 \sigma$ is the free energy associated with an interface with radius of curvature r and surface tension σ.

▶ Now evaluate, $g_l - g_v$, the difference in Gibbs free energy per molecule of the liquid and vapor state:

▶ Start from

$$dg = \alpha de - s dT \qquad (3)$$

▶ with constant temperature:

$$dg = \alpha de = (\alpha_l - \alpha_v) de \qquad (4)$$

▶ since $\alpha_v >> \alpha_l$ for all condition of interest to us $dg = -\alpha_v de$ and applying the ideal gas law of water vapor $\alpha_v = R_v\, T/e$

$$g_l - g_v = -\alpha_v de = -R_v\, T \int_{e_s(\infty)}^{e_s(r)} \frac{de}{e} = -R_v\, T \ln\frac{e_s(r)}{e_s(\infty)} \qquad (5)$$

where $e_s(\infty)$ is the pure water vapor pressure over a flat surface, and $e_s(r)$ is the actual equilibrium partial pressure over the liquid

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▶ Define saturation ratio $S = \frac{e_s(r)}{e_s(\infty)}$:

$$\Delta G = -\frac{4\pi r^3 R_v\, T}{3\alpha_l} \ln S + 4\pi r^2 \sigma \qquad (6)$$

▶ From $\frac{\partial \Delta G}{\partial r} = 0.$ obtain **Kelvin equation** which says that the vapor pressure in equilibrium is larger over a droplet with radius r than over a bulk surface:

▶

$$e_s(r) = e_s(\infty) exp(\frac{2\sigma}{\rho_w R_v\, Tr}) \qquad (7)$$

▶ where σ is the surface tension = 0.075 N/m.
Def: Surface tension: free energy per unit surface area of the liquid. Work per unit area required to extend the surface of liquid at constant temperature

▶ net growth of droplet with radius r is $e - e_s(r)$, where e is the actual ambient vapor pressure, $e - e_s(r) > 0$ (growth), $e - e_s(r) < 0$ (decay).

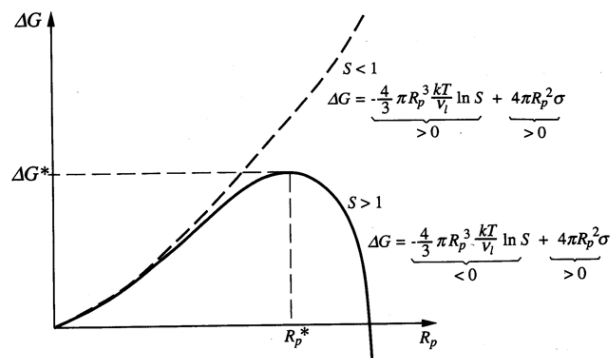## Gibbs free energy (Fig. 9.10 Seinfeld&Pandis)

FIGURE 9.10 Gibbs free energy change for formation of a droplet of radius R_p from a vapor with saturation ratio S.

Kelvin equation

Critical radii for droplet formation in clean air:

$$r_c = \frac{2\sigma}{R_v \rho_w T \ln S} \;;\; S = \frac{e}{e_{sat}(\infty)} \qquad (8)$$

Saturation ratio S	Critical radius $r_c(\mu m)$	number of molecules n
1	∞	∞
1.01	0.12	2.47×10^8
1.1	0.0126	2.81×10^5
1.5	2.96×10^{-3}	3645
2	1.73×10^{-3}	730
3	1.09×10^{-4}	183
10	5.22×10^{-4}	20

Raoult's Law

▶ For a plane water surface the reduction in vapor pressure due to the presence of a non-volatile solute may be expressed:

$$\frac{e^*}{e_s(\infty)} = \frac{n_o}{n + n_o} \qquad (9)$$

where e^* is the equilibrium vapor pressure over a solution consisting of n_o molecules of water and n molecules of solute.

▶ If the vapor pressure of the solute is less than that of the solvent, the vapor pressure is reduced in proportion to the amount of solute present.

▶ For solutions in which the dissolved molecules are dissociated n must be multiplied by the degree of ionic dissociation i (van't Hoff factor).

Raoult's Law

▶ For dilute solutions:

$$\frac{e^*}{e_s(\infty)} = \frac{1}{n/n_o + 1} \sim 1 - \frac{n}{n_o} \; (Taylorseries) \qquad (10)$$

▶ For both NaCl and $(NH_4)_2SO_4$: $i \approx 2$.

▶ The number of effective ions in a solute of mass m is given by:

$$n = iN_o m/M_s \qquad (11)$$

where N_o is the Avogadro's number, and M_s is the molecular weight of the solute.

▶ The number of water molecules in mass m_w may likewise be written as:

$$n_o = N_o m_w/M_w \qquad (12)$$

with $m_w = 4/3\pi r^3 \rho_w$, Raoult's law can be written as:

$$\frac{e^*}{e_s(\infty)} = 1 - \frac{3imM_w}{4\pi M_s \rho_w r^3} = 1 - \frac{b}{r^3} \qquad (13)$$

where

$$b = \frac{3imM_w}{4\pi \rho_w M_s} \approx \frac{4.3 \cdot 10^{-6} i \; m}{M_s}[m^3] \qquad (14)$$
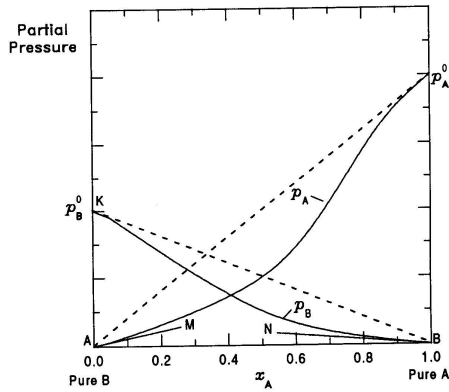
Raoult's Law (Fig. 9.3 Seinfeld&Pandis)

FIGURE 9.3 Equilibrium partial pressures of the components of a nonideal mixture of A and B. Dashed lines correspond to ideal behavior.

Köhler curve

▶ Combination (multiplication) of Kelvin and Raoult's equation (evaluating it for $e^*(r)/e_s(r)$) gives the Koehler curve:

▶
$$\frac{e^*(r)}{e_s(\infty)} = (1 - \frac{b}{r^3}) * exp(\frac{a}{r}). \qquad (15)$$

with

$$a = \frac{2\sigma}{\rho_w R_v T} \approx \frac{3.3 \cdot 10^{-7}}{T}[m] \qquad (16)$$
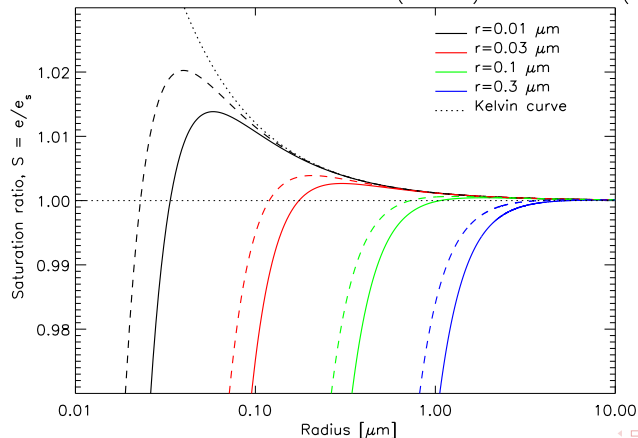
▶ For r not too small, a good approx. is $\left(exp(\frac{a}{r}) \sim 1 + \frac{a}{r}\right)$

$$\frac{e^*(r)}{e_s(\infty)} = 1 + \frac{a}{r} - \frac{b}{r^3} \qquad (17)$$

▶ 1. term: surface molecules possess extra energy
2. term: solute molecules displacing surface water molecules

Köhler curve

Koehler curves for ammonium sulfate (dashed) and sea salt (solid)

Köhler curve

- The critical radius r_c and critical supersaturation S_c are given by:

$$r_c = \sqrt{\frac{3b}{a}} \tag{18}$$

$$S_c = \sqrt{\frac{4a^3}{27b}} \tag{19}$$

- Köhler curve represents equilibrium conditions
- Large particles have large equilibrium radii and may have insufficient times to grow to their equilibrium size in clouds with strong updrafts.
- As the size of a droplet increases, the equilibrium vapor pressure above its surface decreases (Kelvin's equation).
- The curves for droplets containing fixed masses of salt approach the Kelvin curve as they increase in size, since the droplets become increasingly dilute solutions.

Köhler curve

- Solution effect dominates when radius is small: a very small solution droplet is in equilibrium with the vapor at RH less 100%. If RH is increased a small amount, droplet will grow until it reaches equilibrium one again.
- If droplet grows beyond r_c, its equilibrium saturation ratio falls below S_c. Consequently vapor will diffuse to the droplet and it will continue to grow without the need for further increase in the ambient saturation ratio → **activated drop**. I.e. drops for which supersaturation in the atmosphere is larger than S_c can be activated.
- If cloud droplet is not activated and grows slightly, then supersaturation of air adjacent to drop needs to be higher than that of ambient air to maintain that state. Since it isn't drop will shrink again and vice versa.
- general conclusion: the higher the supersaturation, the more and the smaller CCN can be activated.
- smaller aerosols would need larger saturation ratios than exist in the free atmosphere
- larger aerosols serve easier as CCN, but are much fewer in number

Activity spectrum

- number of aerosols per unit volume that are activated to become cloud droplet, expressed as a function of supersaturation
- Measure CCN in chamber where S can be fixed. Usually evaluate the range from 0.3% to 1%.
- Activated nuclei are called CCN. Subset of total aerosols population that can account for formation of natural clouds.
- CCN are always present in the atmosphere in ample concentration . Clouds form whenever there is vertical air motion and sufficient moisture
- in atmosphere $S \leq$ a few %.
- The nucleus counts may often be approximated by the power-law relation:

Example of an activation spectrum
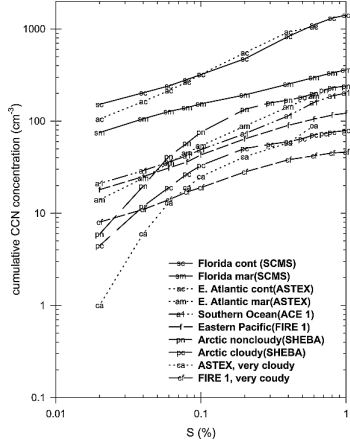
[Hudson and Yum, JGR, 2002]

$$CCN = C \cdot S^k \quad (20)$$

CCN=cloud condensation nuclei

- ▶ in marine air:
  C = 30-300 cm^{-3},
  k=0.3-1
- ▶ in continental air:
  C = 300-3000 cm^{-3},
  k=0.2-2