# Cloud formation and condensational growth of cloud droplets

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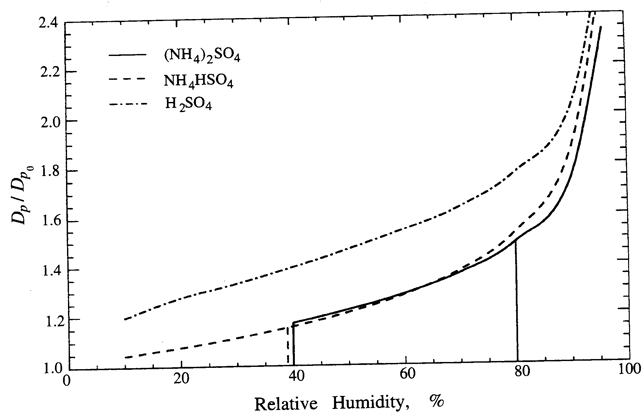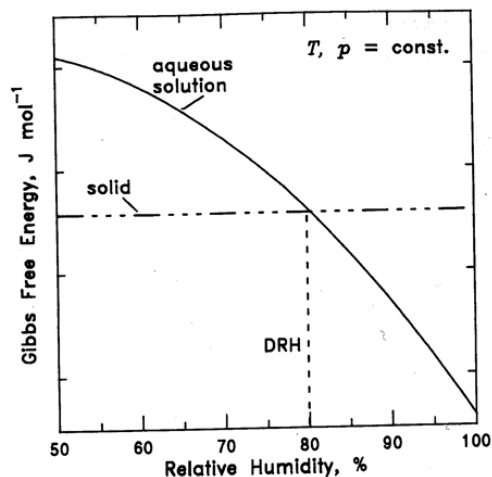


**FIGURE 9.4** Diameter change of $(NH_4)_2SO_4$, $NH_4HSO_4$, and $H_2SO_4$ particles as a function of relative humidity. $D_{p_0}$ is the diameter of the particle at 0% RH.

## 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:

$$\Delta G = G_{droplet} - G_{pure\ vapor} \tag{1}$$

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:

▶

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

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

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

▶ Start from

$$dg = \alpha de - s dT \tag{3}$$

▶ with constant temperature:

$$dg = \alpha de = (\alpha_l - \alpha_v) de \tag{4}$$

▶ 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 $\alpha_v = k\,T/e$

$$g_l - g_v = -\alpha_v de = -kT \int_{e_s(\infty)}^{e_s(r)} \frac{de}{e} = -kT\ln\frac{e_s(r)}{e_s(\infty)} \tag{5}$$

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

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

$$\Delta G = -\frac{4\pi r^3 kT}{3\alpha_l}\ln S + 4\pi r^2 \sigma \tag{6}$$

▶ 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:

▶

$$e_s(r) = e_s(\infty)\exp\left(\frac{2\sigma\alpha_l}{kTr}\right) = e_s(\infty)\exp\left(\frac{2\sigma}{R_v \rho_l Tr}\right) \tag{7}$$

▶ where $\sigma$ is the surface tension $\approx 0.075$ 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 $r$ for $e - e_s(r) > 0$ and decay for $e - e_s(r) < 0$. Here $e$ is the actual ambient vapor pressure.

Cloud formation
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Kelvin equation
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Raoult's law
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Köhler curve
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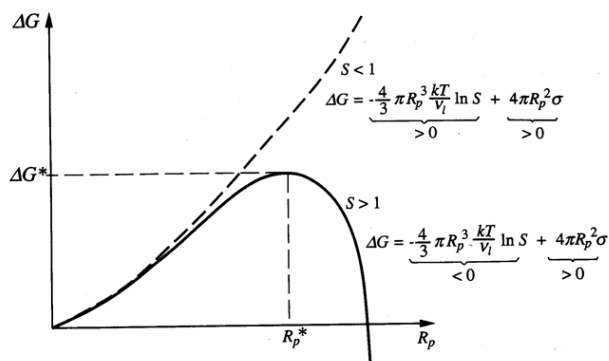Condensation
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# Gibbs free energy (Fig. 9.10 Seinfeld&Pandis)



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

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Cloud formation
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Kelvin equation
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Raoult's law
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Köhler curve
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# Kelvin equation

Critical radii for droplet formation in clean air:

$$r^* = \frac{2\sigma}{R_v \rho_l \, T \ln S} \; ; \; S = \frac{e}{e_{sat}(\infty)} \tag{8}$$

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

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Cloud formation
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Kelvin equation
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# 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:

$$\frac{e'}{e_s(\infty)} = \frac{n_o}{n + n_o} \tag{9}$$

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:

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

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

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

$$n = iN_o m_s / M_s \tag{11}$$

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

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

$$n_o = N_o m_w / M_w \tag{12}$$

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

$$\frac{e'}{e_s(\infty)} = 1 - \frac{3 i m_s M_w}{4\pi M_s \rho_l r^3} = 1 - \frac{b}{r^3} \tag{13}$$

where

$$b = \frac{3 i m_s M_w}{4\pi \rho_l M_s} \approx \frac{4.3 \cdot 10^{-6} i \, m_s}{M_s} [m^3] \tag{14}$$

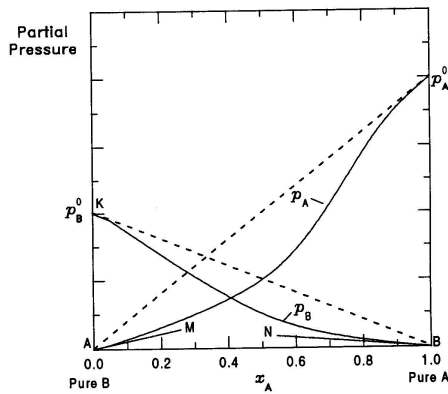## Raoult's Law (Fig. 9.3 Seinfeld&Pandis)



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:

▶

$$\frac{e'(r)}{e_s(\infty)} = \left(1 - \frac{b}{r^3}\right) exp\left(\frac{a}{r}\right) \tag{15}$$

with

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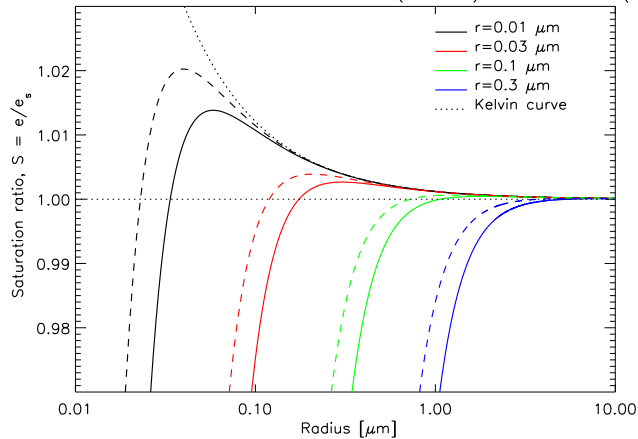
▶ For $r$ not too small, a good approximation is $exp(\frac{a}{r}) \sim 1 + \frac{a}{r}$

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

▶ 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)

Legend:
— r=0.01 $\mu$m
— r=0.03 $\mu$m
— r=0.1 $\mu$m
— r=0.3 $\mu$m
...... Kelvin curve

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# Köhler curve

▶ The critical radius $r^*$ and critical supersaturation $S_s^*$ ($S_s = S - 1$) are given by:

$$r^* = \sqrt{\frac{3b}{a}} \tag{18}$$

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

▶ 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.

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# 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 again.

▶ If droplet grows beyond r*, its equilibrium saturation ratio falls below S*. 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 $S^*$ 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.
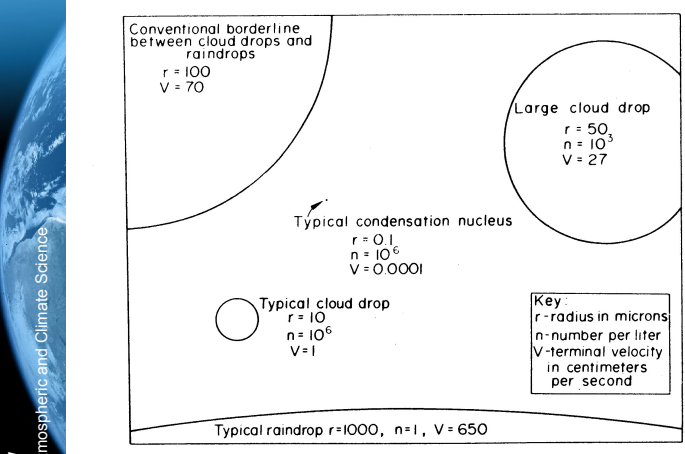
FIG. 6.1. Comparative sizes, concentrations, and terminal fall velocities of some of the particles included in cloud and precipitation processes. (From McDonald, 1958.)

# Droplet growth condensation

- ▶ $r^*$ must be exceeded for a small solution droplet to become a cloud drop.

- ▶ Before and after the droplet reaches the critical size, it grows by diffusion of water molecules from the vapor onto its surface.
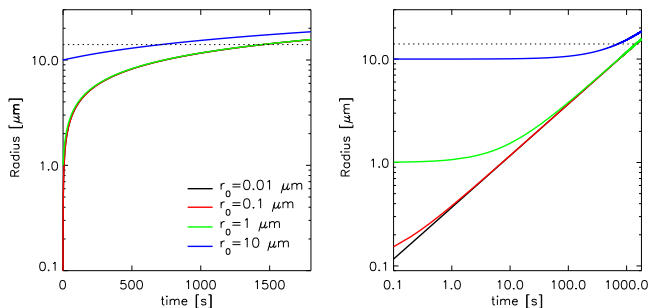
- ▶ Droplet growth equation:

$$r\frac{dr}{dt} = \frac{(S-1) - \frac{a}{r} + \frac{b}{r^3}}{F_k + F_d} \qquad (20)$$

- ▶ $F_k$ = thermodynamic term: $\left(\frac{L}{R_v T} - 1\right)\frac{L\rho_l}{KT}$; "-1" can be neglected

- ▶ $F_d$ = vapor diffusion term: $\frac{\rho_l R_v T}{De_s}$.

- ▶ Equation (20) cannot by solved analytically. Thus, for sufficiently large droplets it can be approximated by neglecting the solution and curvature effects on the drop's equilibrium pressure:

# Droplet growth equation

$$r\frac{dr}{dt} = \frac{S-1}{F_k + F_d} \qquad (21)$$

## Droplet growth condensation

▶ Then the cloud droplet radius increases with time according to:

$$r(t) = \sqrt{r_0^2 + 2\xi t} \qquad (22)$$

where $\xi = (S-1)/(F_k + F_d)$.

▶ $\xi$ depends on temperature and pressure. The larger $T$, the lower $p$, the higher $\xi$

▶ The parabolic form of (22) leads to a narrowing of the drop-size distribution as growth proceeds.

▶ Consider 2 cloud droplets with initial radii of $r_1(0)$ and $r_2(0)$ with $r_2 > r_1$. From (22) it follows:

$$r_2(t) - r_1(t) = \frac{r_2^2(0) - r_1^2(0)}{r_2(t) + r_1(t)} \qquad (23)$$

because the difference between the squares of the initial radii remains constant, at any time $t$, the difference in radii becomes smaller.

## Growth of droplet population

▶ Take interactions between cloud droplets with each other and with the environment by mixing into account

▶ In the early development of a cloud the droplets are too small for sedimentation or coalescence to be important $\Rightarrow$ growth is dominated by condensation

▶ This process is controlled by ambient $S_{max}$, thus we need to examine the vapor budget of a developing cloud

▶ Assume that the vapor is provided by saturated air that is cooled in ascent and that it is lost by condensation on the growing cloud droplet. Then the rate of change of the saturation ratio $S$ is given by:

$$\frac{dS}{dt} = P - C = Q_1 \frac{dz}{dt} - Q_2 \frac{d\chi}{dt} \qquad (24)$$

where $P$ = production, $C$ = condensation, $\frac{dz}{dt}$ = vertical air velocity, $\frac{d\chi}{dt}$: condensation rate [mass condensate per mass of air and unit time], $Q_1 = \frac{1}{T}\left[\frac{\epsilon L g}{R_d c_p T} - \frac{g}{R_d}\right]$, $Q_2 = \rho\left[\frac{R_d T}{\epsilon e_s} + \frac{\epsilon L^2}{p T c_p}\right]$
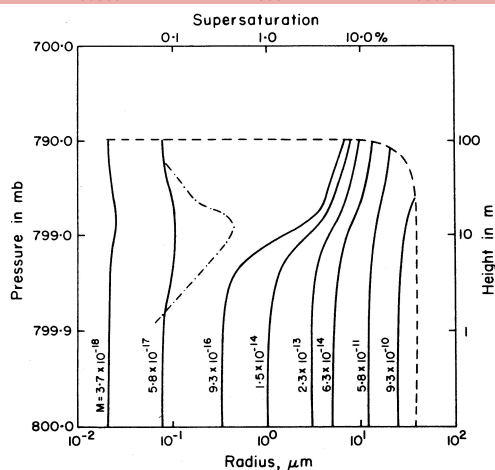
FIG. 7.3. Initial formation of cloud droplets and the variation of super-saturation above cloud base. (Adapted from Mordy, 1959.)

## Initial cloud formation (Figure 7.3)

- ▶ peak updraft speed of 15 cm/s
- ▶ Aerosols with different mass of solute
- ▶ dashed envelop termination of these curves
- ▶ smaller drops move with air at 15 cm/s, but the larger ones fall relative to air and do not rise to same altitude
- ▶ dot-dashed line: supersaturation [%]
- ▶ all cloud droplet grow as they ascent from cloud base
- ▶ $S$ increases, reaching a max of 0.5% at 10m above cloud base
- ▶ smallest droplets grow initially but evaporate after $S$ passes $S_{max}$ ($S^* > S_{max}$ for those)
- ▶ droplets in larger categories are activated, experience rapid growth
- ▶ as they continue to grow their spread becomes narrower because of parabolic form of the growth equation
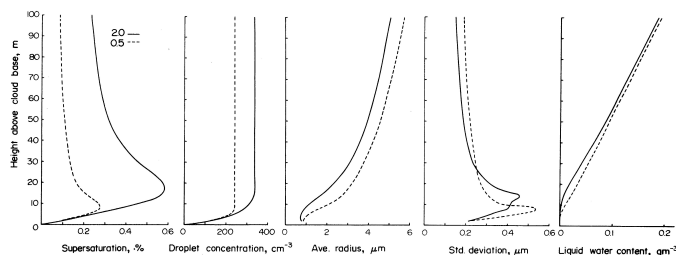
## Early cloud development



FIG. 7.4. Early development of cloud properties in air ascending at constant velocity of 0.5 m/s or 2 m/s.

## Early cloud development (Figure 7.4)

- ▶ sharp rise and gentle settling down of $S$
- ▶ rapid increase in cloud droplet number concentration initially, then settles to steady state at $S_{max}$
- ▶ relative narrowness of size distribution as measured by standard deviation
- ▶ $S_{max}$ lies within about 100 m of cloud base above which $S$ decreases and approaches constant value (where the rate of condensation equals $S$ produced in updrafts)
- ▶ $S_{max}$ determines number of CCN activated.
- ▶ The cloud droplet number concentration is controlled in lowest cloud layer.