

sketch, text chewy

## 1 Background

### 1.1 Why aerosols are important

[ARG1998]

### 1.2 Volatility

Low volatility means a substance has less tendency to form vapor and is more stable in liquid phase. In effect is the tendency of a substance to vaporize. Volatility is directly related to a substance vapor pressure. Vapor pressure is the pressure at which its gas phase is in equilibrium with its condensed phases.

## 2 Aerosol types

### 2.1 Organic Aerosol

Oxidation of organic vapors emitted by plants could lead to the formation of organic aerosols. (Donahue, Robinson, and Pandis 2009) Photooxidation of olefins could form organic aerosols.

#### 2.1.1 Secondary organic aerosol (SOA)

These are formed from the atmospheric transformation of organic species (???). SOA can be formed via oxidation of volatile organic compounds (VOCs) that

usually form products of lower volatility that then partition into the condensed phase. Oxidation of organic vapours can create products with low volatility

#### **2.1.1.1 Semivolatiles**

Semivolatiles are compounds that may be present in appreciable amounts in both the gas and particle phases. Some of the secondary organic aerosols are of low volatility (semivolatiles) that are governed by a complex series of reactions. Reactions in less volatile organics may lead to the formation of particulate matter as well. Compounds that are present entirely in the condensed phase (nonvolatile organics)

### **3 Aerosol Activation**

Aerosol activation is the process in which particles that are suspended in the atmosphere grow to form cloud droplets. Aerosol activation influences cloud droplet number concentration, mean droplet size, cloud reflectivity and autoconversion of cloud droplets to form precipitation. (Abdul-Razzak and Ghan 2000) A droplet that has passed over the peak in its Kohler curve and continues to grow is said to be activated

### **4 Kohler theory**

Kohler theory describes the processes in which water vapor condenses and forms liquid drops and it is based on equilibrium thermodynamics. The original idea behind it looking at the net increase in the energy of a “droplet system” associated with work done in creating the surface area of the droplet and the energy decrease in droplets Gibbs free energy due to the condensation associated

with a volume term. So that for droplet of radius R the increase in free energy is given by:

$$\Delta E = 4\pi R^2 \sigma - \frac{4}{3}\pi R^3 nkT \ln \frac{e}{e_s}$$

It combines the Kelvin effect which describes the change in saturation pressure due to a curved surface and Rault's law that relates saturation vapor pressure to the solute.

It shows what the supersaturation exactly adjacent the droplet surface is, so if this supersaturation is less than the ambient supersaturation the droplet will continue growing.

Predicts CCN activity based on the aerosol physiochemical properties.

The saturation ratio S over aqueous solution droplet can be calculated from:

$$S = a_w \exp\left(\frac{4\sigma_a M_w}{RT\rho_w D}\right) \quad (1)$$

Where  $a_w$  is the activity of water in solution,  $\rho_w$  is the density of water,  $M_w$  is the molecular weight of water,  $\sigma_a$  is the surface tension of the solution-air interface, R is the universal gas constant, T is the temperature, D is the diameter of the droplet.

#### 4.1 Kohler curve

This is the visual representation of the Kohler equation. (It shows what the supersaturation exactly adjacent the droplet surface is, so if this supersaturation is less than the ambient supersaturation the droplet will continue growing.) Kohler curves are different depending on the solute you have dissolved in the droplet and its concentration. When relative humidity is above 100% the droplet will grow

**Kohler Theory: Describes  
the process in which water  
vapor forms liquid drops**

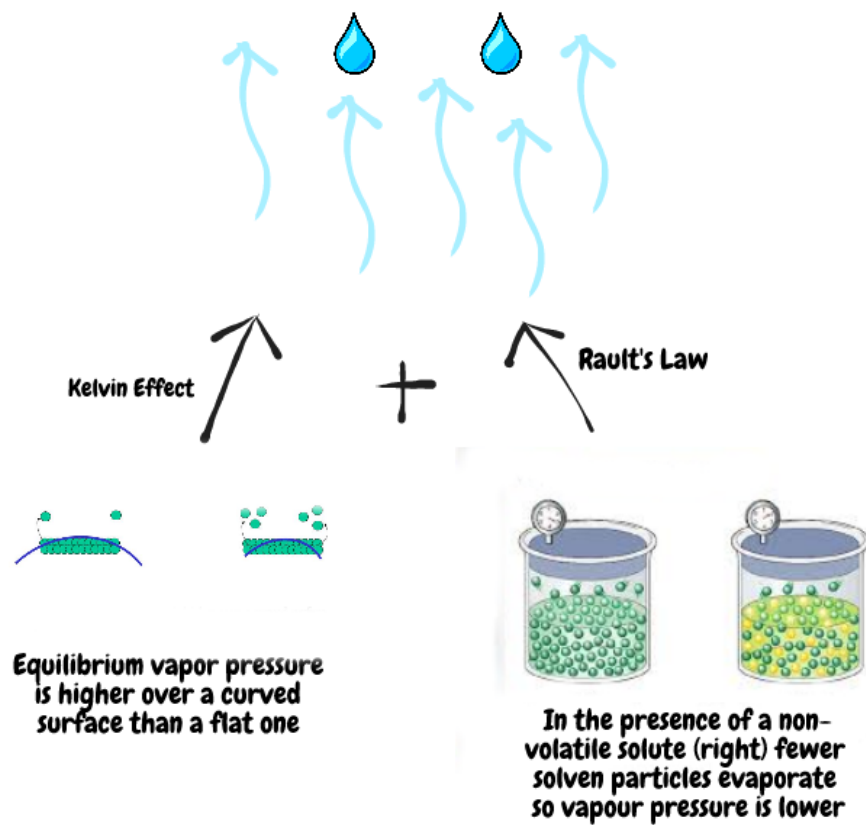
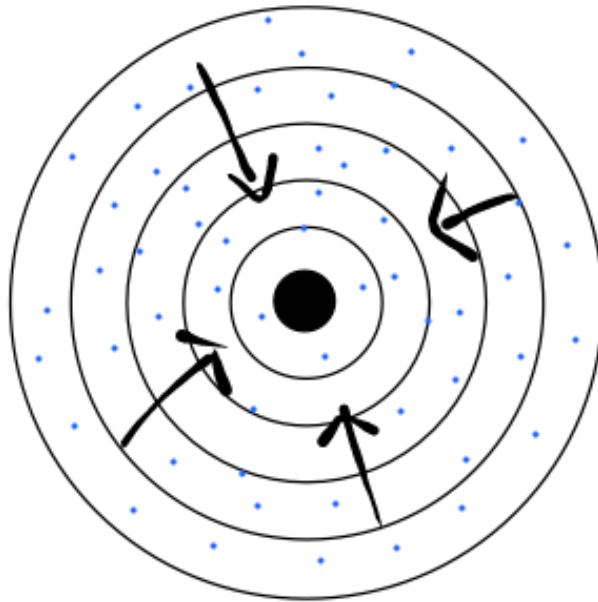
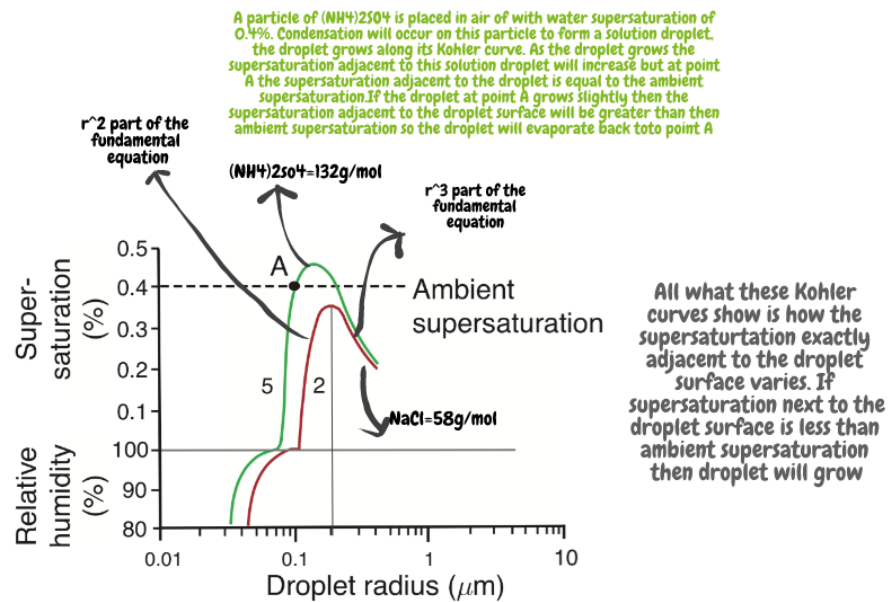


Figure 1: Kohler Theory Explained



**All Kohler equation does is that it solves for the supersaturation EXACTLY adjacent to the droplet surface as the droplet grows (factoring in shape variation as droplet grows–Kelvin effect and the fact that a solute is dissolved within the drop–Raoult's law). IF THE SUPERSATURATION adjacent to the droplet is less than the ambient supersaturation droplet will continue growing.**

Figure 2: Kohler made simple



A particle of  $\text{NaCl}$  is placed in air of with water supersaturation of 0.4%. Condensation will occur on this particle to form a solution droplet. the droplet grows along the red curve. As the droplet grows the supersaturation adjacent to this solution droplet will increase but event the peak of its Kohler curve the supersaturation adjacent to the droplet is less than the ambient supersaturation so the droplet will continue to grow

Figure 3: Kohler example

until it is in thermodynamic equilibrium. As the droplet grows however and its wet diameter increases its equilibrium pressure decreases (kelvin effect). **Kohler equation really is a calculation of the supersaturation adjacent to a solution droplet**

## 4.2 Kelvin Effect

See p55 in book

Kelvin equation can be used to determine the saturation vapor pressure  $e$  over a droplet of specified radius.

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

write more on kelvin effect and calculation.

## 4.3 Raoult's Law

## 4.4 water activity

Water activity  $a_w$  describes the escaping tendency of water in a sample and indicates how tightly water is bound in a solution. Water activity is used to calculate the supersaturation see 1.

$$\frac{1}{a_w} = \frac{n_w + \nu n_s}{n_w} \quad (3)$$

Where,  $n_w$  is the number of moles of water (the droplet contains),  $n_s$  is the number of moles of non volatile solute,  $\nu$  is the number of ions of solute present in the solution ( $\nu > 1$  if the solution dissociates). (Petters and Kreidenweis 2007)

Calculations of water activity used in the “simple Kohler” theory have been based of Rault’s law that states that water activity equals to the mole fraction of water in the solution. (McDonald 1953) and (Low 1969) introduced more general expressions of Rault’s law that use the van’t Hoff factor  $i$  or the molar osmotic coefficient  $\phi$ :

$$a_w^{-1} = 1 + i \frac{M_w m_s}{M_s m_w} \approx 1 + \nu \Phi \frac{n_s}{n_w} \quad (4)$$

Where  $M_s$  is the molecular weight of the solute,  $m_s(n_s)$  and  $m_w(n_w)$  are the masses in moles of solute and water ,repsectively, $\nu$  is the total number of ions per dissociation molecule.

#### 4.4.1 Vant Hoff factor $i$

#### 4.4.2 Moral osmotic coefficient $\phi$

### 4.5 Mole fraction.

### 4.6 k-Kohler Theory

In this variation of the Kohler theory in effect we substitute the water activity term with the hydroscopicity parameter, $kappa$  that incorporates dry and wet diameters.

$$S = \frac{D^3 - D_d^3}{D^3 - D_d^3(1 - k)} \exp\left(\frac{4\sigma_s M_w}{RT \rho_w D}\right) \quad (5)$$



#### 4.6.1 Kappa-Hydroscopicity

This is the hydroscopicity parameter (and is part of the k-Kohler theory). The higher its value the more hydroscopic a substance is (this means the more this substance wants water molecules). It can be used to model the CCN activity of atmospheric particles. Solute hydroscopicity was built in Kohler theory. (Petters and Kreidenweis 2007)

Description	k range
Non hydroscopic	0
slightly to very hydroscopic.	0.01-0.5
Highly-CCN active salts	0.5-1.4
NaCl	1.4
Atmospheric Particulate matter	0.1-0.9

The hydroscopicity parameter  $k$  is defined through its effect on water activity of the solution:

$$\frac{1}{a_w} = 1 + k \frac{V_s}{V_w} \quad (6)$$

Where  $V_s$  is the volume of the dry particulate matter and  $V_w$  is the volume of water.

##### 4.6.1.1 Relevance to model

Combine equation 3 and eq 6

$$\frac{n_w + \nu n_s}{n_w} = 1 + k \frac{V_s}{V_w} \quad (7)$$

#### 4.6.1.2 How to measure Kappa-Hydroscopicity parameter

Values of  $k$  can be determined experimentally by fitting CCN activity or hydroscopic growth factor data. Values of  $k$  for individual components may be combined to represent the hydroscopic behaviour of multicomponent aerosols. Kappa was determined based on CCN measurements 420 at 0.24% Critical supersaturation leading to a kappa of 0.31

## 5 Activation based on Abdul-Razzak

From Kohler theory the parameterization establishes a relationship between  $S_{max}$  reached in updraft and a critical supersaturation  $S_m$  for the radius of mode  $m$  see (Milbrandt and Morrison 2015):

$$\frac{1}{S_{max}^2} = \sum \frac{1}{S_m^2} \left[ f_m \left( \frac{\zeta}{\eta_m} \right)^{\frac{3}{2}} + g_m \left( \frac{S_m^2}{\eta_m + 2\zeta} \right)^{\frac{3}{4}} \right] \quad (8)$$

Where  $\zeta$  and  $\eta$  are two-non dimensional parameters dependant on vertical velocity, growth coefficient (accounting for diffusion of heat and moisture to particles), surface tension etc.  $S_m$  depends on size, hydroscopicity and surface tension characteristics of the particles.  $f_m$  and  $g_m$  depends on the geometric deviation of the mode (this is what i manage to deduce when plotting the lognormal functions)

where the activated aerosol concentration is given by:

$$N_{act} = \frac{1}{2} \sum N_{aero} [1 - erf(z_m)] \quad (9)$$

Where:

$$z_m = 2 \frac{\ln(\frac{S_m}{S_{max}})}{3\sqrt{2}\ln\sigma_m} \quad (10)$$

Activation Depends on:	Implementation
aerosol concentration $N_{aero}$	grid scale vertical velocity
aerosol mean radius $r_{aero}$	one aerosol mode/type
aerosol hygroscopicity $\kappa$	$\kappa=0.4$
aerosol size distribution $\sigma$	$\sigma=1.8$
updraft velocity $w$	$r_{aero} = 0.04\mu$
temperature and Pressure	$N_{aero}$ 3-D climatology

## 5.1 A-R scheme

Assumes that the aerosol size distribution is distributed lognormally with respect to size, (see (Connolly et al. 2014)):

$$n_{ap}(d_{ap}) = \frac{N_{ap}}{\sqrt{2\pi}\ln\sigma} \exp\left[-\frac{\ln^2(\frac{d_{ap}}{d_m})}{2\ln^2\sigma}\right] \quad (11)$$

where  $n_{ap}$  is the number of aerosols per unit volume, per logarithmic interval;  $d_{ap}$  is the particle diameter;  $\ln\sigma$  is the standard deviation of  $\ln\frac{d_{ap}}{d_m}$ ;  $d_m$  is the median diameter and  $N_{ap}$  is the total number of particles per unit volume. The equation above is modified to introduce critical supersaturation  $S_{crit}$  as shown below:

$$n_{ap}(d_{ap}) = \frac{2N_{ap}}{3S_{crit}\sqrt{2\pi}\ln\sigma} \exp\left[-\frac{\ln^2(\frac{d_{ap}}{d_m})}{2\ln^2\sigma}\right] \quad (12)$$

where:

$$S_{crit} = \frac{2}{\sqrt{B}} \left( \frac{2A}{3d_{ap}} \right)^{\frac{3}{2}} \quad (13)$$

## 6 Organic Aerosol volatility quantification

This methodology is based on (Cappa and Jimenez 2010) where the ambient organic aerosol volatility is quantified by determining distributions of ambient-temperature **effective saturation concentrations**  $C_i(\frac{\mu g}{m^3})$ .  $C_i$  is directly proportional to vapor pressure through the relationship:

$$C_i = \frac{MW_i 10^6 p_{i,L} \zeta_i}{RT} \quad (14)$$

Where  $MW_i$  is the molecular weight ( $\frac{g}{mol}$ ),  $R$  is the ideal gas constant ( $8.314 J mol^{-1} K^{-1}$ ),  $T$  is the temperature (K),  $\zeta_i$  is the activity coefficient of the OA phase and  $p_{i,L}$  is the (sub-cooled liquid) saturation vapor pressure (Pa) of compound  $i$  (that can also represent a class of compounds)

## 7 Direct effect

The reduction in solar radiation due to the scattering and absorption of aerosols is known as the direct effect that decreases the amount of radiation reaching the surface (Steiner et al. 2013)

## 8 Indirect effect

## 9 Closure experiment

A closure study is a combination of different measurement techniques to describe the current state of the investigation system as fully as possible and find inaccuracies in one or some of the methods involved.

## 10 Aerosol activation parameterizations

### 10.1 ARG 1998

(Abdul-Razzak Steven J. Ghan 1988) This parameterization produces the **fraction** of aerosol activated to form cloud droplets in a parcel of air rising adiabatically. Aerosols must have lognormal size distribution.

$$n(a_{ap}) = \frac{N_{ap}}{\sqrt{2\pi} \ln \sigma} \exp \left[ - \frac{\ln^2 \left( \frac{a_{ap}}{a_m} \right)}{2 \ln^2 \sigma} \right] \quad (15)$$

Where:

- $N_{ap}$  is the total aerosol concentration
- $N$  number concentration of activated aerosols
- $a_m$  is the geometric mean radius
- $\sigma$  is the geometric standard deviation
- $a_{ap}$  is the dry aerosol particle radius

Activation fraction  $N/N_{ap}$  is obtained by integrating 15 to get:

$$\frac{N}{N_{ap}} = \frac{1}{2} [1 - \text{erf}(u)] \quad (16)$$

Where:

$$u = \frac{\ln(\frac{S_m}{S_{max}})^2}{3\sqrt{2}\ln\sigma} \quad (17)$$

Where  $S_m$  is the critical supersaturation of a particle with radius  $a_m$  (that is the geometric mean radius of the size distribution) and is given by:

$$S_m = \frac{2}{\sqrt{B}} \left( \frac{A}{3a_m} \right)^{\frac{3}{2}}$$

#### 10.1.1.1 Points:

- produces the fraction of activated aerosol
- aerosol size ditribution must be lognormal
- 4 dimensionless parameters that affect the activation fraction

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