Gas-Particle Partitioning to OA

Advanced Atmospheric chemistry
CHEM-5152
Prof. J.L. Jimenez

Last updated: Spring 2017

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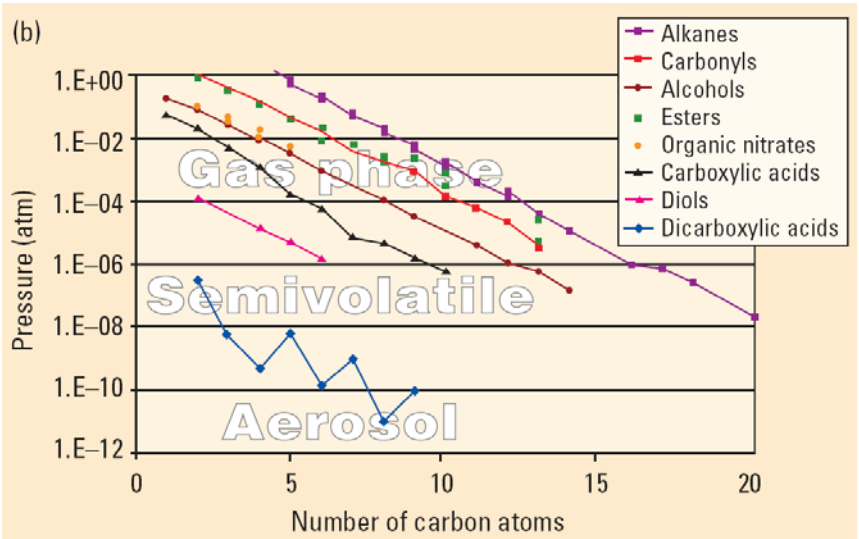
Gas-Phase vs Aerosol Compounds



- For monofunctional compounds, alkanes beyond C_{20} and acids beyond C_3 will partition to aerosols

Goldstein & Galbally, ES&T 2007

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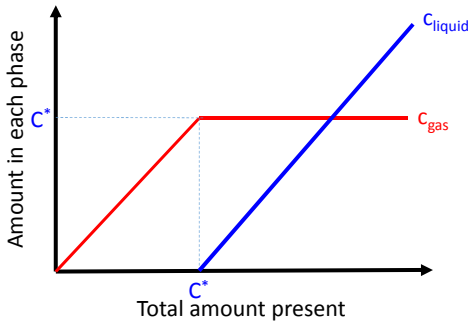
Partitioning of a Pure Compound

DO THE ACTUAL GRAPH IN IGOR

- If c < c*, then all in gas phase
  - $c_{gas} = c_{tot}$
- If c > c*, the excess above c* in the liquid
  - $c_{gas} = c^*$
  - $c_{liq} = c_{tot} - c^*$
- E.g. H_2O:
  - RH < 100%, all in gas phase
  - If more H_2O present, then RH = 100% and excess as a liquid (cloud)



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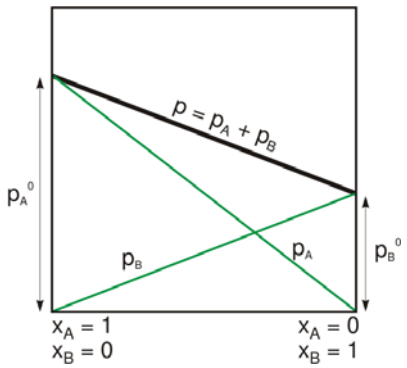
Dealing w/ Mixtures: Raoult's Law

- The partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.
  - $P_i = P_i^0 x_i$



https://en.wikipedia.org/wiki/Raoult%27s_law

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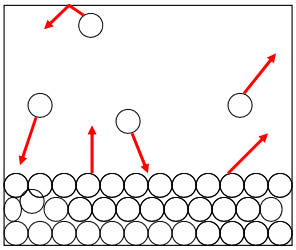
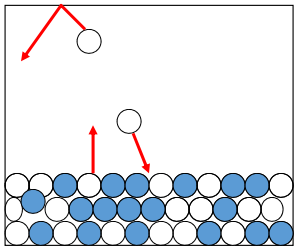
Graphical Illustration of Raoult's Law

$P^o_{H2O,SAT}$



water saturation vapor pressure over pure liquid water surface

$P_{H2O,SAT} = x_{H2O} P^o_{H2O,SAT}$



solute molecules in green

water saturation vapor pressure over aqueous solution of water mixing ratio x_{H2O}

An atmosphere of relative humidity *RH* can contain at equilibrium aqueous solution particles of water mixing ratio

$$x_{H2O} = \frac{P_{H2O,SAT}}{P^o_{H2O,SAT}} = \frac{RH}{100}$$

Slide from Jacob (I think)

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Deviations from R's Law: Activity coeff.

- $P_i = \gamma_i P_i^0 x_i$
- Q: What is the value of γ_i in the upper curve?
- Is γ_i dependent on the mixture?

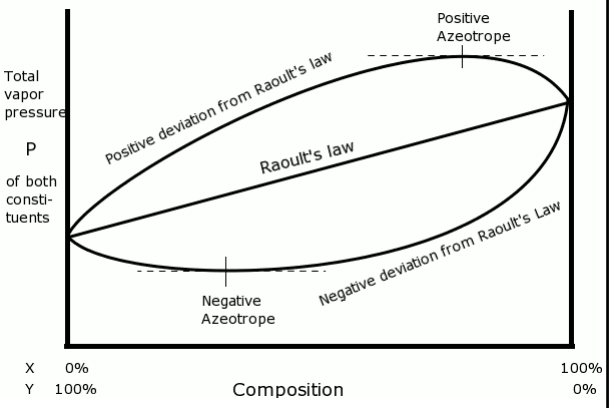

Figure from https://en.wikipedia.org/wiki/Raoult%27s_law

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Gas/particle partitioning Theory

Data: Fraction in particle-phase, F_p

$$F_p = \frac{Particle}{Gas + Particle}$$

Model: Absorptive partitioning theory using effective saturation concentration (C_i^*, µg m^{-3})

$$F_{p,i} = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

$$C_i^* = \frac{M_i 10^6 \zeta_i P_{L,i}^o}{760\ RT} = \frac{1}{K_p}$$

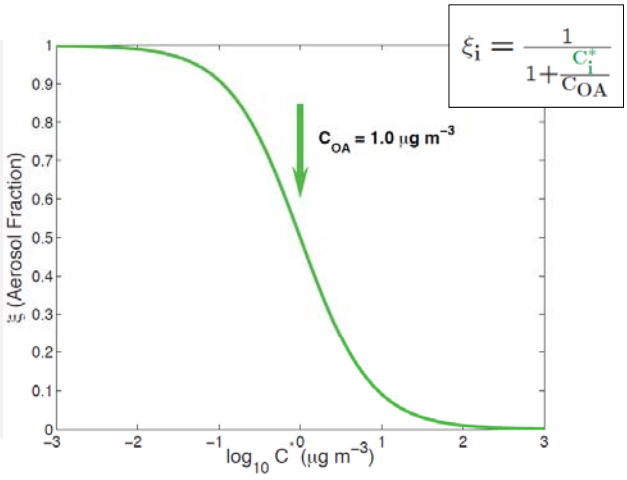
Model Inputs: T (K) = Ambient temperature
C_{OA} (µg m^{-3}) = Organic aerosol mass concentration
$P_{L,i}^o$ (Torr) = Vapor pressures of compound i (at T)
ζ_i = Activity coefficient of compound i = 1
M_i (g mol^{-1}) = Molecular weight of compound i

(Pankow, *Atmos. Environ*. 1994; Donahue et al., *ES&T* 2006)

Partitioning of an individual species vs c*

Clicker Q: what is F_p (= ξ_i) for a species with *Pvap* = 0.1 ppb & MW = 244 g mol^{-1} when C_{OA} = 10 $\mu g\ m^{-3}$

A. 1%
B. 3%
C. 7%
D. 10%
E. I don't know



The bottom line is that an individual component only 'cares' about the *total* mass of the solution compared to its saturation concentration. For example, a 1 $\mu g\ m^{-3}$ C* component will be 50-50 partitioned if there is 1 $\mu g\ m^{-3}$ total organic aerosol, no matter what its composition.

Donahue et al., ES&T 2006. Slide courtesy of Neil Donahue

Partitioning: Pankow Formulation

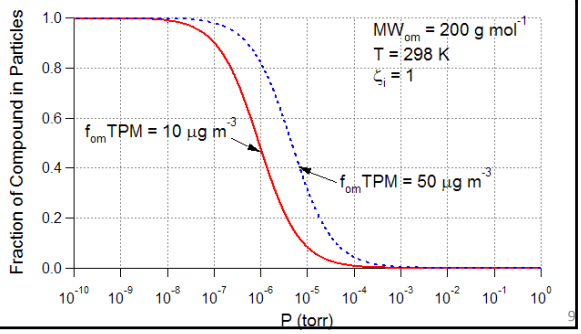
Once a multicomponent system contains enough condensable material to form aerosol, equilibrium G/P partitioning is governed by the equation for absorptive gas/liquid partitioning in a potentially nonideal system

1) $p_i = X_i \zeta_i p^o_{L,i}$

2) $K_{p,i} = \frac{(ng/\mu g)_{ParticlePhase}}{(ng/m^3)_{GasPhase}} = \frac{F_i / TSP}{A_i} = \frac{760RTf_{om}}{10^6 \mathbf{MW_{om}} \zeta p^o_{L,i}}$

p_i (torr): the gas-phase partial pressure of species *i*
X_i: the mole fraction of *i* in the particle phase
ζ_i: the activity coefficient of species *i* in the particle phase typically lie in the range 0.3~ 3.
$p^o_{L,i}$ (torr): the compound's vapor pressure as a pure liquid (subcooled if necessary) at the temperature of interest.
A_i (ng m^{-3}): gas phase conc.
F_i (ng m^{-3}): OM phase conc.
TSP (μg m^{-3}): total suspended PM conc.

R: the ideal gas constant (8.2E-5 m^3 atm mol^{-1} K^{-1})
T (K): temperature
f_{om}: the weight fraction of the TSP that comprises the absorbing OM phase
MW_{om} (g mol^{-1}): the number-average molecular weight of the absorbing OM phase.



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Iterative partitioning equil. calculations

- Let's start with 3 μg m^{-3} of reacted α-pinene
- There is no pre-existing aerosol seed
- Consider only the 2 lowest volatility bins
- Calculate the final amount of SOA formed

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Kinetics of Condensation & Evaporation

$SVOC_g \rightarrow SVOC_p$ k_c estimated from size dist.

$SVOC_g \leftarrow SVOC_p$ k_e?

$k_e/k_c = c^*/c_{OA}$ *(equil., Matsunaga & Ziemann, 2010)*

$\Rightarrow \boxed{k_e = k_c\, c^* / c_{OA}}$

Let's do this in KinSim for a-pinene VBS products

- $P_{\underline{0.01}}$ and P_{10}
- When OA = 0.1 and 10 μg m^{-3}

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Estimation of Vapor Pressures

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Effects of Functional Groups on P_{vap}

Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007)

Functional group	Structure	Change in vapor pressure (298 K)[a]
Ketone	–C(O)–	0.10
Aldehyde	–C(O)H	0.085
Hydroxyl	–OH	5.7×10^{-3}
Hydroperoxyl	–OOH	2.5×10^{-3}
Nitrate	$-ONO_2$	6.8×10^{-3}
Carboxylic acid	–C(O)OH	3.1×10^{-4}
Peroxyacid	–C(O)OOH	3.2×10^{-3}
Acyl peroxynitrate	$-C(O)OONO_2$	2.7×10^{-3}
Extra carbon[b]	$-CH_2-$, etc.	0.35[b]

[a]Multiplicative factor.
[b]For comparison between changes in polarity (by addition of a functional group) and changes to size of the carbon skeleton. Vapor pressure also depends on carbon skeleton structure; see Pankow and Asher (2007).

- Kroll & Seinfeld, 2008
- http://doi.org/10.1016/j.atmosenv.2008.01.003

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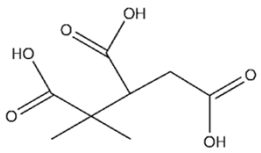
SIMPOL

- E.g. for a C_{15} Hydroxynitrate:
- $\log_{10}(P_{vap}\ (Atm)) = 1.79 - N_C * 0.438 - (N_{OH} + N_{ONO2}) * 2.23 = -9.24$
- Practice
  - C_{10} linear keto acid



- Pankow & Asher (2008)
- http://www.atmos-chem-phys.net/8/2773/2008/

Table 6. Values at T = 293.15 K of the b_k group contribution terms from this work, Müller (2006), and for each method whether each group value $d\Delta h_{vap}/dT < 0$ at T=293.

groups	k	coefficient	this work value of b_k T=293.15	$\frac{d\Delta h_{vap,k}(T)}{dT} < 0$? T=293.15 K
zeroeth group (constant term)	0	b_0	1.79	NO
carbon number	1	b_1	−0.438	YES
carbon number, acid-side of amide	2	b_2	−0.0338	NO
number of aromatic rings	3	b_3	−0.675	NO
number of non-aromatic rings	4	b_4	−0.0104	YES
C=C (non-aromatic)	5	b_5	−0.105	YES
C=C–C=O in non-aromatic ring	6	b_6	−0.506	YES
hydroxyl (alkyl)	7	b_7	−2.23	NO
aldehyde	8	b_8	−1.35	YES
ketone	9	b_9	−0.935	NO
carboxylic acid	10	b_{10}	−3.58	NO
ester	11	b_{11}	−1.20	YES
ether	12	b_{12}	−0.718	NO
ether (alicyclic)	13	b_{13}	−0.683	NO
ether, aromatic	14	b_{14}	−1.03	NO
nitrate	15	b_{15}	−2.23	YES
nitro	16	b_{16}	−2.15	NO
aromatic hydroxyl (e.g., phenol)	17	b_{17}	−2.14	YES
amine, primary	18	b_{18}	−1.03	NO
amine, secondary	19	b_{19}	−0.849	YES
amine, tertiary	20	b_{20}	-0.608	NO
amine, aromatic	21	b_{21}	−1.61	YES
amide, primary	22	b_{22}	−4.49	YES
amide, secondary	23	b_{23}	−5.26	NO
amide, tertiary	24	b_{24}	-2.63	NO
carbonylperoxynitrate	25	b_{25}	−2.34	YES
peroxide	26	b_{26}	−0.368	YES
hydroperoxide	27	b_{27}	-2.48	NO
carbonylperoxyacid	28	b_{28}	−2.48	NO
nitrophenol	29	b_{29}	0.0432	YES
nitroester	30	b_{30}	−2.67	NO

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2D VBS for P_{vap}

- Murphy et al., 2011 & Pandis et al. 2013)

Table 1. Carbon number as a function of effective saturation concentration and O:C in the 2D-VBS.

O:C	Effective saturation concentration ($\mu g\,m^{-3}$)											
	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}
1.2	6.9	6.5	6.1	5.7	5.3	4.9	4.5	4.1	3.7	3.3	3.0	2.6
1.1	7.4	7.0	6.5	6.1	5.7	5.3	4.9	4.4	4.0	3.6	3.2	2.7
1.0	8.0	7.5	7.0	6.6	6.1	5.7	5.2	4.8	4.3	3.9	3.4	3.0
0.9	8.6	8.1	7.6	7.1	6.7	6.2	5.7	5.2	4.7	4.2	3.7	3.2
0.8	9.4	8.9	8.3	7.8	7.3	6.7	6.2	5.6	5.1	4.6	4.0	3.5
0.7	10.4	9.8	9.2	8.6	8.0	7.4	6.8	6.2	5.6	5.0	4.4	3.8
0.6	11.5	10.9	10.2	9.5	8.9	8.2	7.6	6.9	6.3	5.6	5.0	4.4
0.5	13.0	12.2	11.5	10.7	10.0	9.3	8.5	7.8	7.0	6.3	5.6	4.9
0.4	14.8	14.0	13.1	12.3	11.4	10.6	9.7	8.9	8.1	7.2	6.3	5.6
0.3	17.3	16.3	15.3	14.4	13.4	12.4	11.4	10.4	9.4	8.4	7.4	6.4
0.2	20.8	19.6	18.5	17.3	16.1	14.9	13.7	12.5	11.3	10.1	8.9	7.7
0.1	30.5	28.8	27.1	25.3	23.6	21.9	20.1	18.3	16.6	14.9	13.1	11.4

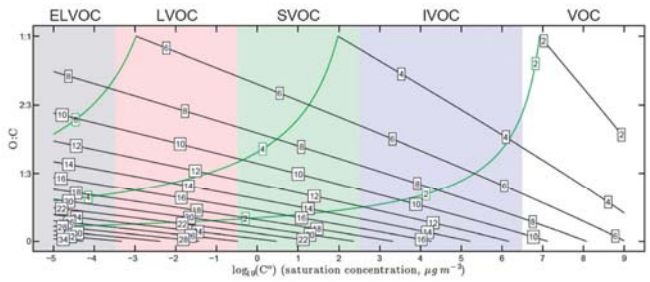

Fig. 1 The 2D Volatility Basis Set space with the volatility (expressed as the logarithm of the saturation concentration) as the *x*-axis and the O : C ratio as the *y*-axis (based on Fig. 4 of Donahue *et al.*[21]). The black isopleths are the number of carbon atoms and the green isopleths the number of oxygen atoms.

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The Volatility Basis Set

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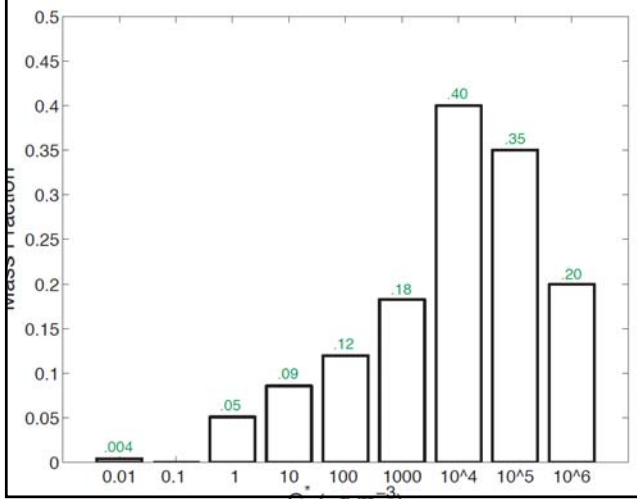
Basis Set 101: Calculate % Mass Yield from α-pinene + O_3 SOA when C_{OA} = 10 μg m^{-3}

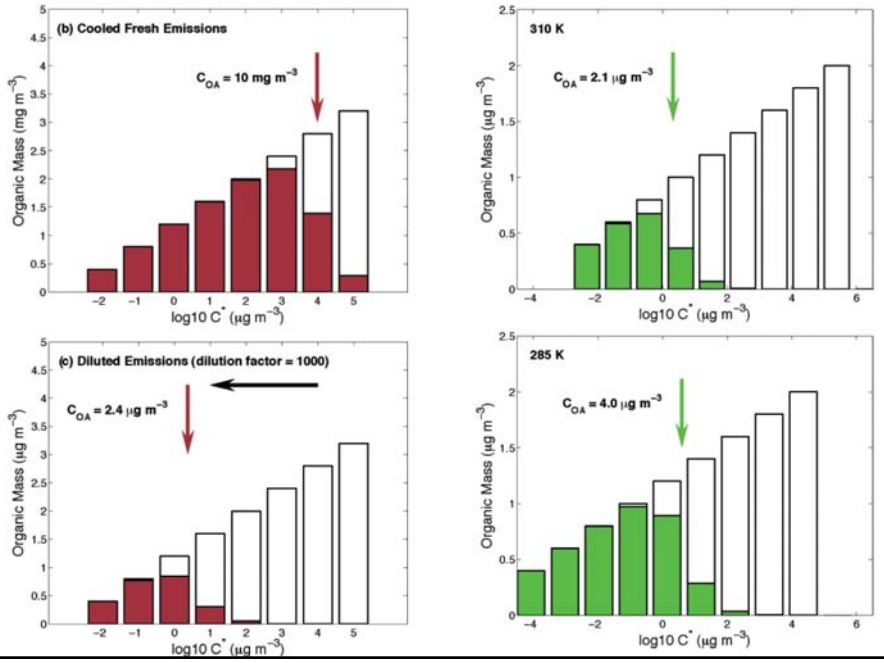
- α-pinene + O_3 → 0.004 $P_{0.01}$ + 0.05 P_1 + 0.09 P_{10} + …



P_x= group of products with the same c (many different species)*

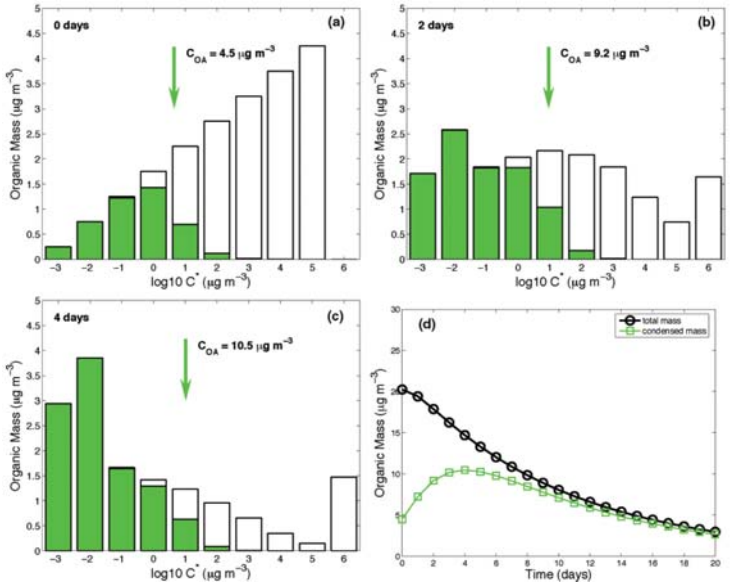
Adapted from Neil Donahue

Cooling & Dilution in VBS



Donahue et al. 2006

Aging in the Volatility Basis Set



As VOCs go through successive oxidation steps, products become more oxygenated and less volatile, but eventually smaller and more volatile

Donahue et al. 2006; Jimenez et al. 2009

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VBS-based SOA Mechanisms

Table 2. SOA yield scenarios using a four-product basis set with saturation concentrations of 1, 10, 100, and 1000 $\mu g\,m^{-3}$ at 298 K.

V-SOA precursors	Aerosol Yield[1] High-NO_X Parameterization				Aerosol Yield Low-NO_X Parameterization				Molecular Weight
	1	10	100	1000	1	10	100	1000	(g mol^{-1})
ALK4	0.000	0.038	0.000	0.000	0.000	0.075	0.000	0.000	120
ALK5	0.000	0.150	0.000	0.000	0.000	0.300	0.000	0.000	150
OLE1	0.001	0.005	0.038	0.150	0.005	0.009	0.060	0.225	120
OLE2	0.003	0.026	0.083	0.270	0.023	0.044	0.129	0.375	120
ARO1	0.003	0.165	0.300	0.435	0.075	0.225	0.375	0.525	150
ARO2	0.002	0.195	0.300	0.435	0.075	0.300	0.375	0.525	150
ISOP	0.001	0.023	0.015	0.000	0.009	0.030	0.015	0.000	136
SESQ	0.075	0.150	0.750	0.900	0.075	0.150	0.750	0.900	250
TERP	0.012	0.122	0.201	0.500	0.107	0.092	0.359	0.600	180

[1] The SOA yields are based on an assumed density of 1.5 g cm^{-3}.

- This is an example, many other sets of parameters have been proposed in the literature

- Tsimpidi et al., ACP 2010 - http://www.atmos-chem-phys.net/10/525/2010/

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Gas-Particle Partitioning to Liquid Water

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Henry's Law

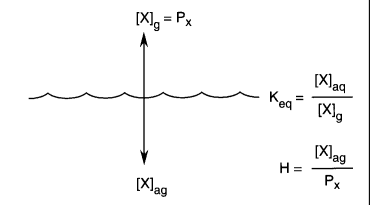

FIGURE 8.1 Henry's law applied to atmospheric systen

- Pure H_2O concentration in M (moles l^{-1})?
- O_3 aqueous concentration at 50 ppb in gas?
- H_2O_2 a.c. at 1 ppb?
- CO_2?
- Fractions for 1 g m^{-3} liquid H_2O?

TABLE 8.1 Henry's Law Coefficients (H) for Some Atmospheric Gases Dissolving in Liquid Water at 20–25°C[a]

Gas	H (mol L^{-1} atm^{-1})	Reference
O_2	1.3×10^{-3}	Loomis, 1928
NO	1.9×10^{-3}	Loomis, 1928
C_2H_4	4.9×10^{-3}	Loomis, 1928
NO_2[b]	1×10^{-2}	Schwartz and White, 1983
N_2O_4	1.4	Schwartz and White, 1981
N_2O_3	0.6	Schwartz and White, 1981
O_3	$(0.82–1.3) \times 10^{-2}$	Shorter *et al.*, 1995; Briner and Perrottet, 1939
N_2O	2.5×10^{-2}	Loomis, 1928
CO_2[c]	3.4×10^{-2}	Loomis, 1928
SO_2[c]	1.2	Sillén and Martell, 1964; Maahs, 1982; Shorter *et al.*, 1995
HONO[c]	49	Schwartz and White, 1981
NH_3[c]	62	Van Krevelen *et al.*, 1949
HNO_3[d]	2.1×10^5	Schwartz and White, 1981
HO_2	$(1–3) \times 10^3$	Schwartz, 1984b
OH	30	Golden *et al.*, 1990; Hanson *et al.*, 1992
PAN	5	Holdren *et al.*, 1984
CH_3SCH_3	0.48–0.56	Shorter *et al.*, 1995; De Bruyn *et al.*, 1995; Dacey *et al.*, 1984
NO_3	0.6–1.8	Rudich *et al.*, 1996; Thomas *et al.*, 1998
CH_3SH	0.20	De Bruyn *et al.*, 1995
H_2O_2	8.3×10^4 1.1×10^5	O'Sullivan *et al.*, 1996 Zhou and Lee, 1992; Staffelbach and Kok, 1993
CH_3OOH	3.1×10^2	O'Sullivan *et al.*, 1996
$HOCH_2OOH$	1.7×10^6 1.7×10^6 5×10^5	O'Sullivan *et al.*, 1996 Staffelbach and Kok, 1993 Zhou and Lee, 1992
$HOCH_2OOCH_2OH$	6×10^5	Zhou and Lee, 1992
$CH_3C(O)OOH$	8.4×10^2	O'Sullivan *et al.*, 1996
C_2H_5OOH	3.4×10^2	O'Sullivan *et al.*, 1996
H_2S	0.087	Shorter *et al.*, 1995; De Bruyn *et al.*, 1995
COS	0.022	Shorter *et al.*, 1995; De Bruyn *et al.*, 1995
CS_2	0.055	De Bruyn *et al.*, 1995

[a] Adapted from Schwartz, 1984a; see also Web site in Appendix IV.
[b] Physical solubility; reacts with liquid water.
[c] Physical solubility; exclusive of acid–base equilibria.
[d] See Clegg and Brimblecombe (1988) and Brimblecombe and Clegg (1988) for temperature dependence.

Reformulating Henry's Law

- Partitioning into an organic liquid phase: $F_{p,i}^{OA} = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$
- Partitioning into liquid water phase: $F_{p,i}^{w} = \left(1 + \frac{C_{w,i}^*}{C_w}\right)^{-1}$

$C_{w,i}^* = LWC\ x\ H_i$ *(not totally sure about this one, will check)*

Ervens et al. 2011: http://www.atmos-chem-phys.net/11/11069/2011/

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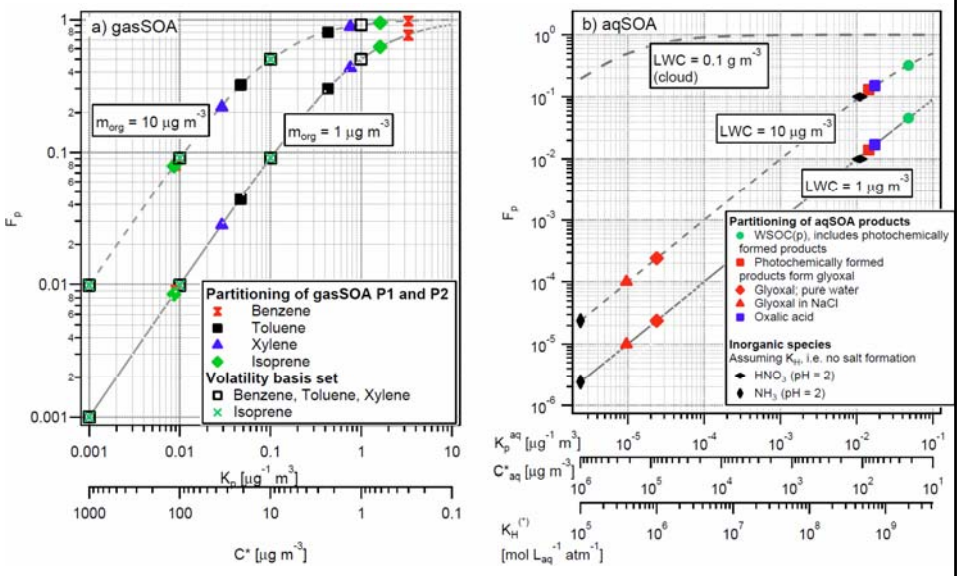
Partitioning to water vs OA



Ervens et al. 2011: http://www.atmos-chem-phys.net/11/11069/2011/

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Size Distributions and Particle Loss Calculations

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Some slides adapted from lectures from Qi Zhang, UC-Davis

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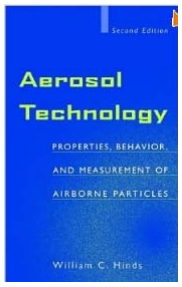
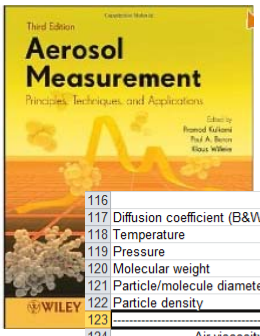
Practical Aerosol Resources

Great intro to medium book



Measurement "bible"



- For practical aerosol calculations
  - Aerosol calculator from Willeke and Baron
  - Linked on course page

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117	Diffusion coefficient (B&W 4-12; W&B 3-12; Hinds 2-35, 7-7), mechanical mobility (B&W 4-14; W&B 3-14;			
118	Temperature	293.15	Kelvin	
119	Pressure	101.3	kPa	
120	Molecular weight	0.02896	kg/mole	= 0.02896 for air
121	Particle/molecule diameter	4	µm	
122	Particle density	1000	kg/m^3	
123	----------	----------	----------	
124	Air viscosity =	1.80711E-05	Pa*s	
125	Slip correction factor =	1.04148201		
126	Diffusion coefficient =	1.51E-13	m^2/s	molecular range
127	Diffusion coefficient =	6.18E-12	m^2/s	particle range
128	Mechanical mobility =	1.53E+09	m/(N*s)	
129	Mean thermal velocity =	0.000554454	m/s	
130				
131	**********	**********	**********	

Quick exercise: calculate losses of 10 nm particles in 10m meters of circular tubing under laminar flow (outer tube diameter = ¼"; flow rate = 1 lpm)

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Size Distribution of Ambient Aerosols

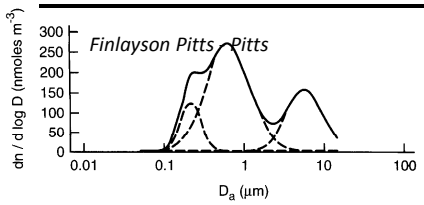

FIGURE 9.8 Typical size distribution of nitrate in southern California in 1987 fitted by the sum of three log-normal distributions with peaks at 0.2, 0.7, and 4.4 μm (adapted from John *et al.*, 1990).

$$\frac{dN}{d\ln D_p} = \sum_{i=1}^{I} \frac{N_i}{(2\pi)^{1/2}\ln\sigma_{g,i}} \exp\left(-\frac{(\ln D_p - \ln \overline{D}_{pg,i})^2}{2\ln^2\sigma_{g,i}}\right)$$

I – number of modes

$\overline{D}_{pg,i}$ – the median diameter of mode *i*

$\sigma_{g,i}$ – geometric standard deviation of mode

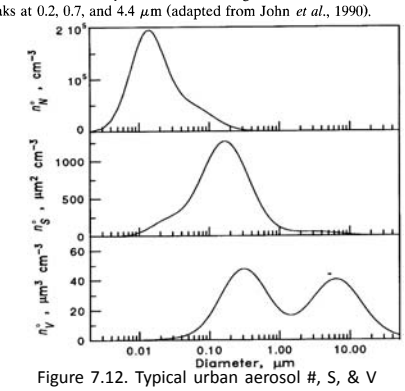

Figure 7.12. Typical urban aerosol #, S, & V distributions. *Seinfeld & Pandis*

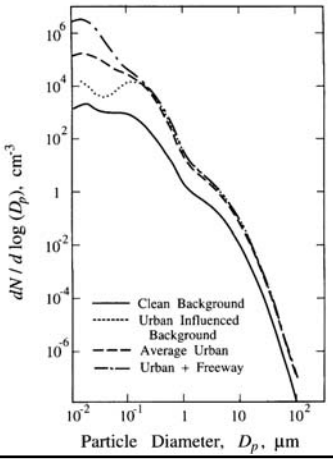

Figure 7.13. Aerosol number distributions next to a source (freeway), for average urban, for urban influences background, and for background conditions. *Seinfeld & Pandis*

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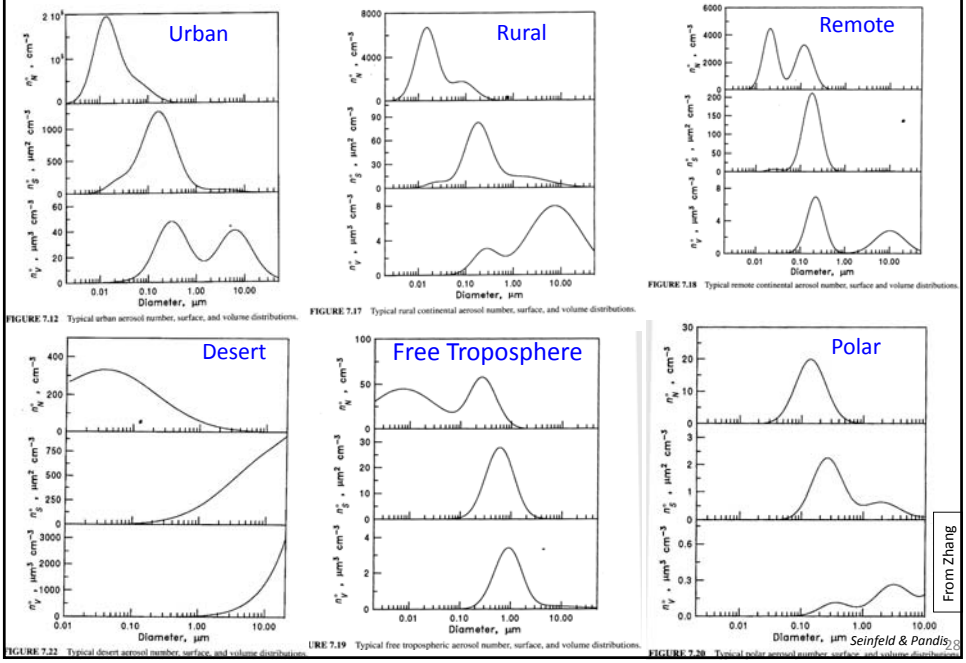
Typical PM Size Distributions in Various Atmospheres



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Clicker Questions

- The number of particles in the polar atmosphere below 1 micron is
  - A. 2 cm^{-2}
  - B. 2 cm^{-3}
  - C. 20 cm^{-3}
  - D. 2000 cm^{-3}
  - E. I don't know
- The typical volume of particles in the free troposphere below 200 nm is
  - A. 0.02 μm^3 cm^{-3}
  - B. 0.2 μm^3 cm^{-3}
  - C. 20 μm^3 cm^{-3}
  - D. 200 μm^3 cm^{-3}
  - E. I don't know

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Dry Deposition Velocity

$$J_{dd} = v_{dep} C$$

J_{dd}: dry deposition flux of particles (p/cm² s^{-1})
v_{dep}: "deposition velocity" (cm/s)
C: particle concentration (cm^{-3})

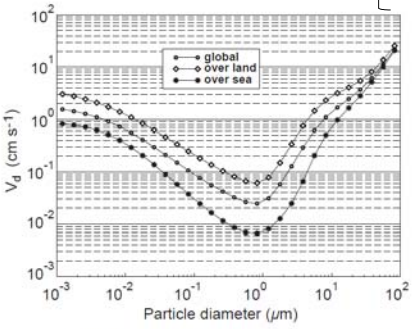

Fig. 1. Annual mean deposition velocities by particle size and surface type (particle density 1000 kg m^{-3}).

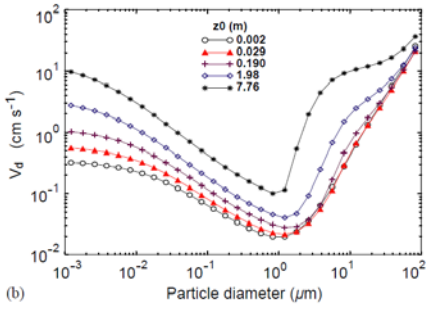

Fig. 6. Effect of surface roughness on deposition velocity: (a) unstable and (b) stable and neutral cases (particle density 1000 kg m^{-3}).

Clicker Q: timescale of loss of 100 nm from a 1 km boundary layer over a forest? A. 100 s B. 1 hr C. 1 day D. 1 century E. I don't know

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Condensation

Atmospheric chemistry 2
CHEM-5152
Prof. J.L. Jimenez

Some slides adapted from lectures from Qi Zhang, UC-Davis

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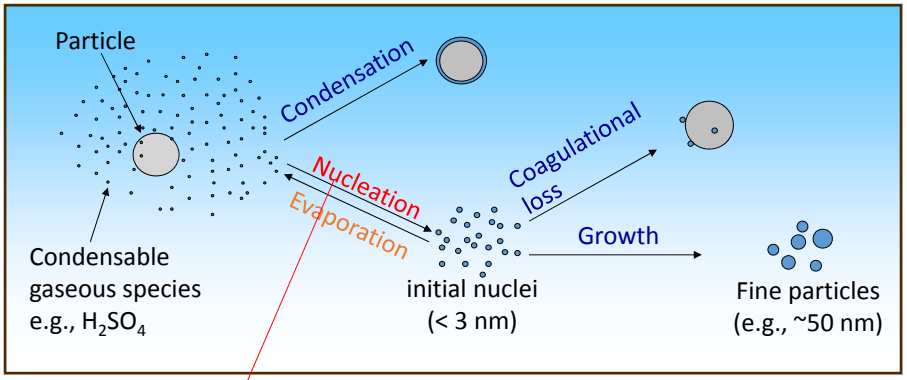
Gas to Particle Conversion: Condensation & Nucleation



- Nucleation
- Condensation and nucleation are competing processes.
- Nucleation dominate when PM condensational sink is low.

Possible nucleation mechanisms
a) Binary nucleation (H_2SO_4 + H_2O)
b) Ternary nucleation (H_2SO_4 + NH_3 + H_2O)
c) Organic compounds nucleation
d) Ion-induced nucleation

Adapted from Zhang

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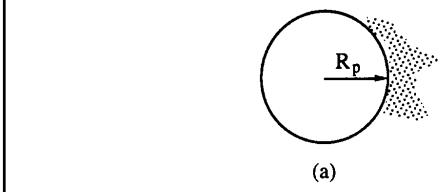
Regimes of Gas – Particle Interactions

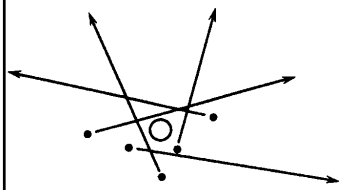
- Knudsen number: $Kn = 2\lambda/D_p$

  λ – Mean free path: the average distance traveled by a molecule btw collisions with other molecules. $\lambda_{air} \approx 65$ nm (1 atm)

  D_p – Particle diameter



(a)



(b)

(c)

Fig. 8.1 Seinfeld & Pandis

Three Regimes

a. The continuum regime: $\lambda << D_p$
   - ambient, $D_p > 1.3$ µm

b. The free molecular (kinetic regime): $\lambda >> D_p$
   - ambient, $D_p < 13$ nm

c. The transition regime: $\lambda \approx D_p$
   - ambient, $0.013 < D_p < 1.3$ µm

Mass transfer processes (i.e., condensation & coagulation) are function of *Kn*.

Adapted from Zhang

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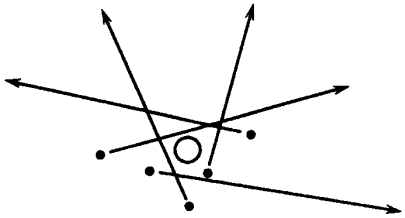
Condensation in Free Molecular Regime

- J_k: flux of A(g) (molec. cm^{-3} s^{-1}) toward particle in free molec. regime:

$$J_k = \gamma \frac{\bar{c}_A}{4} S\,(C_\infty - C_s)$$



- $\bar{c}_A$: mean molecular speed of A (m/s)
- S: surface area density (µm^2 cm^{-3})
- γ : accommodation coefficient, i.e., probability of A to stick on particle. $0 \le \gamma \le 1$

c_∞ : vapor conc. of A far from the particle

c_s: vapor conc. of A at the particle surface

$$\bar{c}_A = \left(\frac{8kT}{\pi m_A}\right)^{1/2}$$

- What is k (s^{-1})?
- Why is there a ¼?

- Expression in molec. s^{-1} towards 1 particle: $J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s)$

Adapted from Zhang

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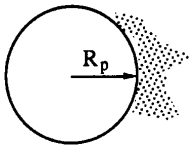
Condensation in the Continuum Regime

Mass transfer of gas molecules to particles (i.e., condensation):

- J_c: the total flow of A(g) (moles time^{-1}) toward 1 particle in continuum regime

$$J_c = 4\pi R_p D_g (c_\infty - c_s)$$



R_p: Particle radius
D_g: Diffusivity of gas A
c_∞ : Conc. of A far from the particle
c_s: Vapor phase conc. of A at the particle surface

- Ratio of free molecular to continuum fluxes:

Adapted from Zhang

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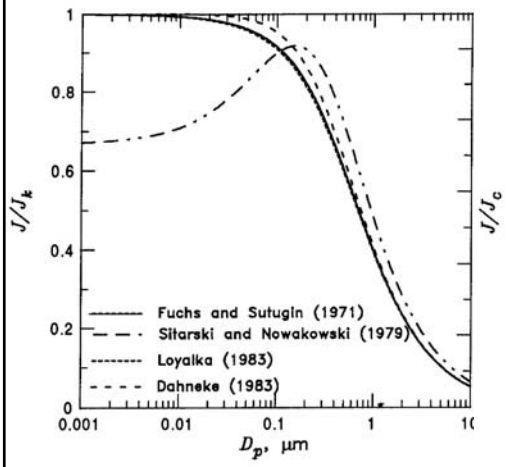
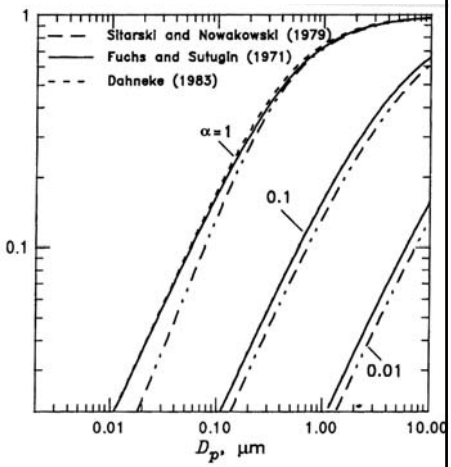
Transition Regime Corrections

- No general solution exists from solving distribution of gas molecules

➔ Use flux matching to determine J





Q: when are we ok using just one of the regimes?

From Seinfeld & Pandis
Slide adapted from Zhang

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Transition Regime: Fuchs-Sutugin

$$\frac{J}{J_c} = \frac{0.75\,\alpha(1+\mathrm{Kn})}{\mathrm{Kn}^2 + \mathrm{Kn} + 0.283\,\mathrm{Kn}\alpha + 0.75\,\alpha}$$

$$\frac{J_k}{J_c} = \frac{\alpha \bar{c}_A}{4 D_g} R_p$$

- See Seinfeld & Pandis – Chapter 12 for further details

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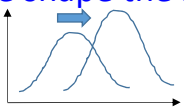
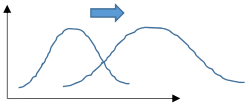
How Does Condensation Affect Size Distribution?

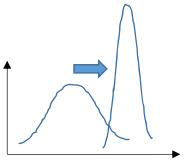
A. It will keep the shape the same (grow all particles equally)



B. It will widen the shape (grow larger particles more)



C. It will narrow the shape (grow smaller particles more)



D. It depends on free molecular vs continuum regime

E. I don't know

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Resistor method for more complex siuations

- Other effects act as resistances to mass transfer

$$\frac{1}{\gamma_{meas}} = \frac{1}{\Gamma_{diff}} + \frac{1}{\gamma_o} = \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\Gamma_b}$$

- Same approach is used to calculate dry deposition

Davidovits et al. 1999, JPCA
http://pubs.acs.org/doi/pdf/10.1021/jp991696p

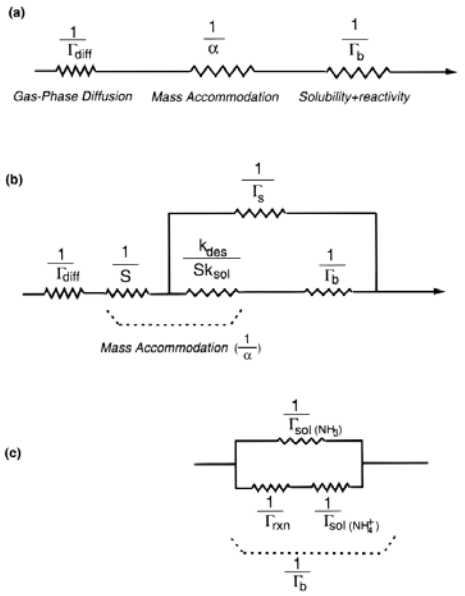

Figure 1. (a) Electrical circuit analogue for the gas uptake process governed by gas-phase diffusion, mass accommodation, and bulk phase solubility and reactivity. Explanation is found in the text. (b) Electrical circuit analogue for the gas uptake process including surface reactivity. (c) Expanded electrical circuit analogue for the gas uptake process in the bulk liquid phase.

9

Question

- Calculate and plot the surface area distribution for the rural size distribution from Seinfeld & Pandis
- Plot the "effective surface area" distribution
  - $dS/d\log D_p * J/J_k$
- Calculate k (s^{-1}) for

  γ = 1 and 0.1

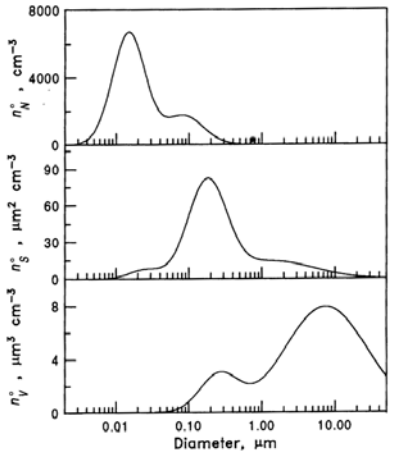

FIGURE 7.17 Typical rural continental aerosol number, surface, and volume distributions.

10

How Does Condensation Affect Size Distribution?

- Condensation/Evaporation → D_p change & size dist. change shape.
- Under condensation, smaller particles grow much faster than larger ones → The size distribution becomes much narrower

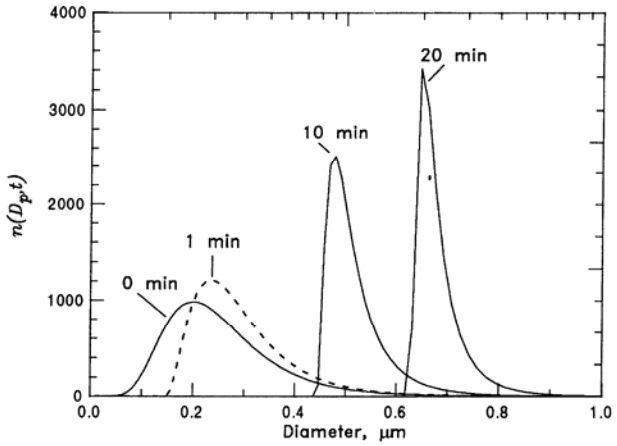

FIGURE 12.3 Evolution of a log-normal distribution (initially $\tilde{D}_p = 0.2\ \mu m$, $\sigma_g = 1.5$) assuming $D_i = 0.1\ cm^2\ s^{-1}$, $M_i = 100\ g\ mol^{-1}$, $(p_i - p_{eq,i}) = 10^{-9}$ atm(1 ppb), $T = 298$ K and $\rho_p = 1\ g\ cm^{-3}$.

From Seinfeld and Pandis

From Zhang

41

Chemical Reactions in / on Particles

- Chemistry
  - Solid aerosol provide surfaces upon which trace gases can be absorbed and then react
  - Liquid aerosols absorb gases which may then react together in solution

  e.g. SO_2 → H_2SO_4

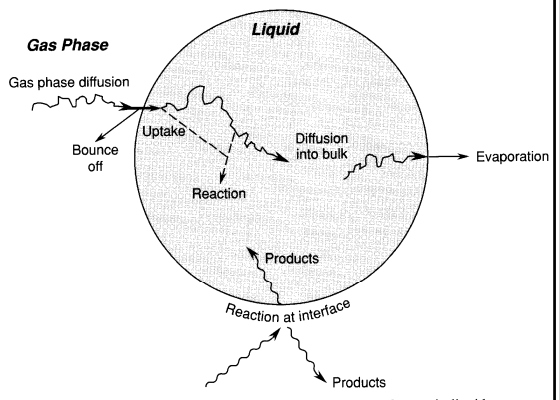

FIGURE 5.12 Schematic diagram of uptake and reaction of gases in liquids.

From Finlayson-Pitts and Pitts

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Wall Losses in Chambers

Atmospheric chemistry 2
CHEM-5152
Prof. J.L. Jimenez

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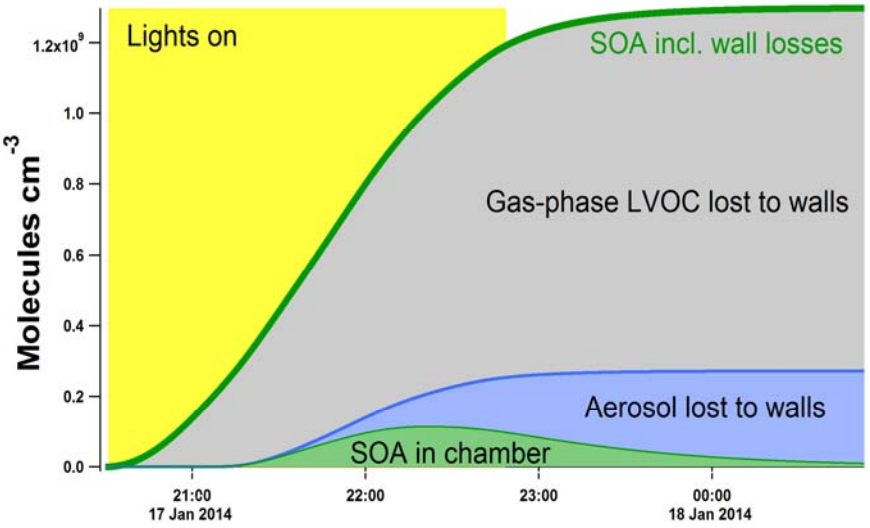
Losses of LVOC to walls at ~1 μg m^{-3}



Q: what is the ratio of aerosol / wall surface areas?
Chamber is cube with V ~ 25 m^3

Krechmer et al., in prep. 2015

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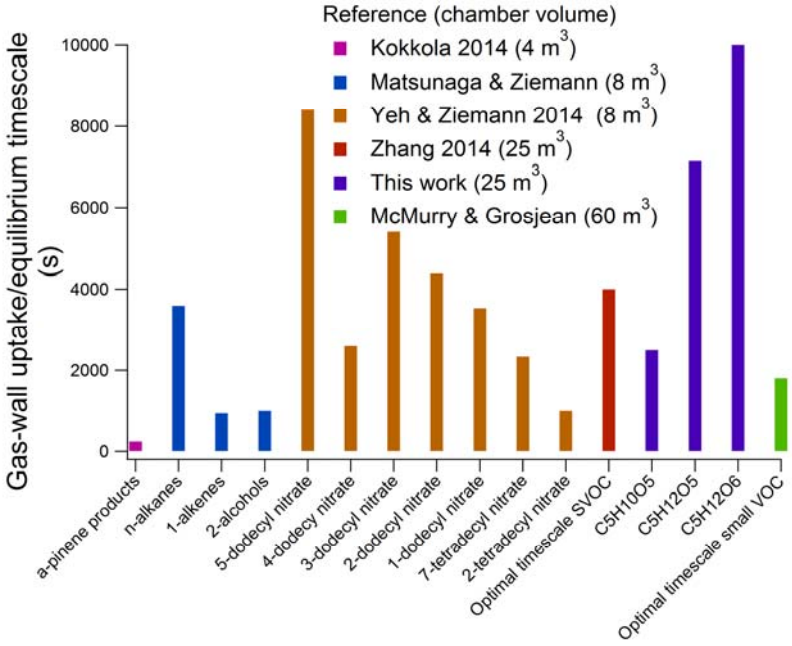
Timescales of losses to chamber walls



Krechmer et al., in prep. 2015

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HW: Simulate Condensation & Wall Losses

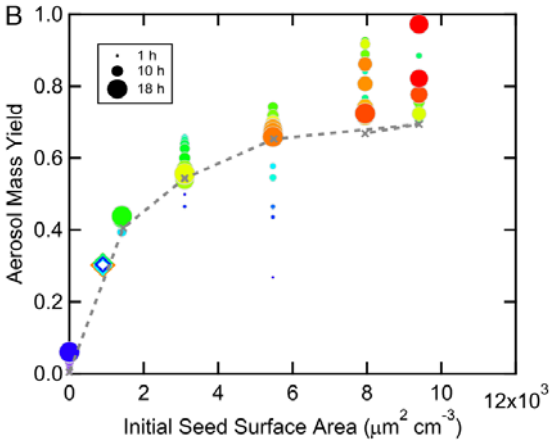

Fig. 1. Hourly averaged lower bound SOA yields over the course of a toluene photooxidation experiment as a function of initial ammonium sulfate seed surface area for (*A*) high-NO_x and (*B*) low-NO_x conditions. Symbol color indicates the SOA mass concentration and symbol size the time after lights were turned on. The filled circles are from the current experiments and the open diamonds from ref. 21. The dashed gray line and × are the end-of-experiment yields from the optimized best-fit SOM simulations.

Zhang et al., PNAS 2014

- Implement the a-pinene basis set in KinSim
- Oxidize 1 ppb of a-pinene with 100 ppb O_3 in the presence of variable amounts of seed

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