

Overhead Slides for
Chapter 15
of
Fundamentals of
Atmospheric Modeling

by

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January 30, 2002

Aerosol Emissions

Sources of new particles

volcanic eruptions (sulfuric acid - water)

natural fires (ash, organic carbon)

wind (pollen, dust, sea spray)

combustion (soot, organic carbon)

Table 15.1. Concentrations of major constituents in sea water (data from Lide, 1993).

Constituent	Sea Water Concentration (mg L ⁻¹)	Constituent	Sea Water Concentration (mg L ⁻¹)
Water	1.00×10^6	Sulfur	9.05×10^2
Sodium	1.08×10^4	Calcium	4.12×10^2
Chloride	1.94×10^4	Potassium	3.99×10^2
Magnesium	1.29×10^3	Carbon	2.80×10^1

Urban Aerosol Emissions

Table 15.1. Aerosol emissions (kg day⁻¹) in the Los Angeles basin.

Substance	-----Particle Diameter-----					Total %
	< 1 μm	1-2.5 μm	2.5-10 μm	> 10 μm	all sizes	
Other (O, H, etc.)	147,884	86,431	380,221	712,049	1,326,585	53.167
Silicon	37,312	37,086	183,641	166,527	424,566	17.015
Organic carbon	28,462	9,363	69,967	58,111	165,903	6.649
Aluminum	14,550	14,644	67,991	58,216	155,401	6.228
Iron	7,090	7,189	37,210	38,947	90,436	3.624
Calcium	5,587	5,511	32,619	34,028	77,745	3.116
Sulfates	45,922	894	3,998	3,122	53,936	2.162
Potassium	7,364	3,586	16,266	18,989	46,205	1.852
Elemen. carbon	28,467	1,095	7,247	7,429	44,238	1.773
Unknown	9,919	6,745	11,110	11,903	39,677	1.590
Chloride	11,318	814	4,535	4,796	21,463	0.860
Titanium	1,048	877	4,241	4,716	10,882	0.436
Sulfur	618	573	3,216	2,129	6,536	0.262
Carbonate ion	306	162	2,514	1,879	4,861	0.195
Sodium	569	233	2080	1916	4,798	0.192
Manganese	899	521	1,511	1,824	4,755	0.191
Phosphorous	130	286	1,660	1,148	3,224	0.129
Nitrates	1,237	147	935	782	3,101	0.124
Zinc	226	154	729	674	1,783	0.071
Lead	173	156	758	653	1,740	0.070
Barium	79	88	544	856	1,567	0.063
Ammonium	841	51	120	136	1,148	0.046
Strontium	25	42	308	364	739	0.030
Vanadium	94	66	274	280	714	0.029
Copper	132	60	203	208	603	0.024
Cobalt	127	52	158	212	549	0.022
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Totals	350,776	176,958	834,725	1,132,673	2,495,132	100.00
% of total	14.06	7.09	33.45	45.40	100.00	

Nucleation

Homogeneous homomolecular

Single gas nucleates away from a surfaces

Homogeneous binary

Two gases nucleate in tandem away from a surfaces

Heterogeneous homomolecular

Single gas nucleates on an existing surface

Heterogeneous binary

Two gases nucleate in tandem on a surface

Classical Nucleation Theory

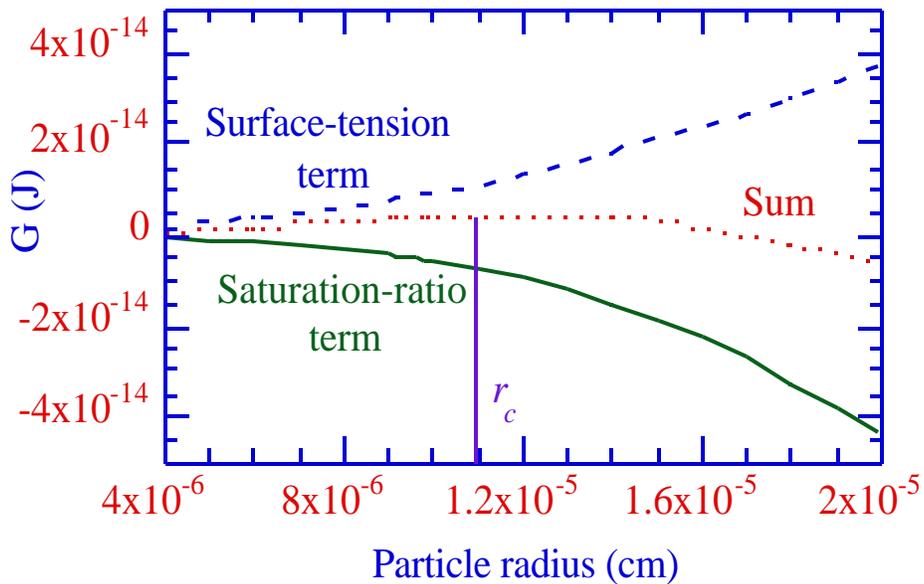
Change in Gibbs free energy (J) during cluster aggregation

$$G = 4\pi r_p^2 \sigma - \frac{4}{3}\pi r_p^3 \rho \frac{R^* T}{m_q} \ln S_q \quad (15.1)$$

Saturation ratio

$$S_q = p_q / p_{q,s}$$

Fig 15.2. Change in free energy versus cluster radius.



Critical Radius

Minimize Gibbs free energy

$$\frac{dG}{dr_p} = 8 \pi r_p^2 p - 4 \pi r_p^2 p \frac{R^* T}{m_q} \ln S_q = 0 \quad (15.3)$$

Solve for critical radius

$$r_c = \frac{2 \pi m_q^2 A}{p R^* T \ln S_q} \quad (15.4)$$

Number of molecules in a critical cluster

Divide $\frac{4}{3} \pi r_c^3$ by molecular volume $[m_q / (\rho A)]$

$$n_c = \frac{32 \pi^2 m_q^2 A}{3 p (R^* T \ln S_q)^3} \quad (15.5)$$

Table 15.3. Critical radii and number of water molecules in a critical cluster when $T = 288 \text{ K}$, $\sigma = 7.5 \times 10^{-6} \text{ J cm}^{-2}$, $\rho = 1.0 \text{ g cm}^{-3}$, and $m_q = 18 \text{ g mole}^{-1}$.

Saturation Ratio (S)	Critical Radius (μm)	Number of Molecules
1	Infinite	Infinite
1.01	0.11	2.03×10^8
1.10	0.011	2.32×10^5
1.5	0.0028	3.01×10^3
2	0.0016	6.03×10^2
5	0.0007	48
10	0.00048	16

Homogeneous Homomolecular Nucleation

Rate (partic. cm⁻³ s⁻¹)

$$J_{hom} = 4 r_c^2 N_x Z_n N_x \exp \left(- \frac{G_{hom}^*}{k_B T} \right) \quad (15.6)$$

Combine (15.1) and (15.3)

$$G_{hom}^* = \frac{4}{3} r_c^2 p \quad (15.7)$$

Number of gas molecules striking cluster surface per second

$$Z_n = N_x \frac{k_B T}{2 \bar{M}_x}^{1/2} \quad (15.8)$$

Equilibrium no. concentration of clusters of critical radius

$$N_x \exp \left(- G_{hom}^* / k_B T \right)$$

Zeldovich non-equilibrium factor

Accounts for the difference between an equilibrium and nonequilibrium cluster concentration

$$Z_n = \frac{\bar{M}_x}{2 r_c^2 N_x} \sqrt{\frac{p}{k_B T}} \quad (15.9)$$

Homogeneous Binary Nucleation

Rate (partic. cm⁻³ s⁻¹)

$$J_{hom} = 4 r_c^2 N_x N_y \exp\left(-\frac{G_{hom}^*}{k_B T}\right) \quad (15.10)$$

Number of gas molecules striking cluster surface per second

$$N_y = N_y \frac{k_B T}{2 \bar{M}_y}^{1/2} \quad (15.11)$$

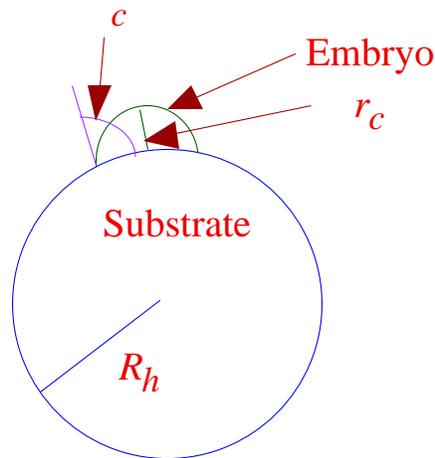
Equilibrium no. concentration of cluster of critical radius

$$(N_x + N_y) \exp\left(-G_{hom}^*/k_B T\right)$$

$$N_x \gg N_y \quad \rightarrow N_x \exp\left(-G_{hom}^*/k_B T\right)$$

Heterogeneous Nucleation Rate

Fig. 15.3. Formation of critical embryo on a surface



Contact angle (θ_c)

= 0 --> surface wettable, embryo forms easily

= 180° --> surface non-wettable, no embryo forms

Heterogeneous nucleation rate (no. embryos $\text{cm}^{-2} \text{s}^{-1}$)

$$J_{het} = 4 \cdot r_c^2 \cdot y \cdot x \cdot \exp \left(\frac{-G_{het}^*}{k_B T} \right) \quad (15.15)$$

Time a gas molecule spends on surface before bouncing off

$$= \tau_0 \exp \left(\frac{E}{R^* T} \right)$$

Change in Gibb's free energy

$$G_{het}^* = G_{hom}^* f_h(x_h, m_h) \quad (15.13)$$

Correction Factor

$$f_h(x_h, m_h) = 1 + \frac{1 - m_h x_h}{g_h} + x_h^3 \left[2 - 3 \frac{x_h - m_h}{g_h} + \frac{x_h - m_h}{g_h} \right] + 3m_h x_h^2 \frac{x_h - m_h}{g_h} - 1 \quad (15.14)$$

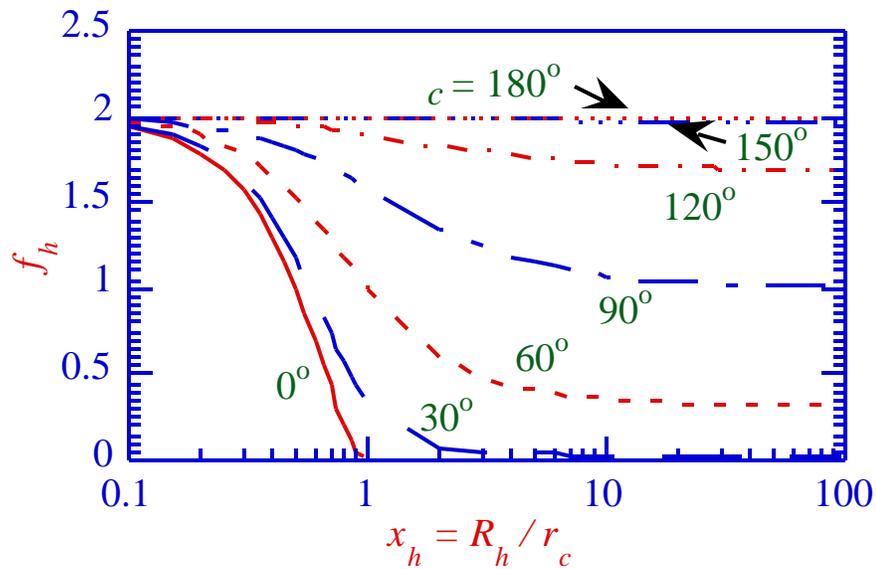
$$g_h = \sqrt{1 + x_h^2 - 2m_h x_h} \quad x_h = R_h / r_c$$

$$m_h = \cos c$$

Contact angle

$$c = \cos^{-1} \frac{S_a - S_w}{w, a} \quad (15.12)$$

Fig. 15.4. Correction factor versus x_h for different contact angles.



Parameterized Nucleation

Parameterized remote marine boundary layer homogeneous binary nucleation rate (sulfuric acid-water)

$$J_{hom} = 10^{7.0 - (64.24 + 4.7 f_r) + (6.13 + 1.95 f_r) \log_{10} N_{H_2SO_4}} \quad (15.16)$$

Example 15.1.

$$f_r = 0.9$$

$$m_{H_2SO_4} = 0.005 \mu\text{g m}^{-3}$$

$$\text{---> } N_{H_2SO_4} = 3.1 \times 10^7 \text{ molec cm}^{-3}$$

$$\text{---> } J_{hom} = 2.6 \times 10^{-5} \text{ partic. cm}^{-3} \text{ s}^{-1}$$

$$m_{H_2SO_4} = 0.05 \mu\text{g m}^{-3}$$

$$\text{---> } N_{H_2SO_4} = 3.1 \times 10^6 \text{ molec cm}^{-3}$$

$$\text{---> } J_{hom} = 3.1 \times 10^5 \text{ partic. cm}^{-3} \text{ s}^{-1}$$