



Lecture Ch. 5a

- Surface tension (Kelvin effect)
 - Hygroscopic growth (subsaturated humidity)
 - Saturation
- Chemical potential (Raoult effect)
- Nucleation
 - Competition between surface and chemical effects
 - Köhler curves
- Aerosol-cloud interactions

Curry and Webster, Ch. 5 (skip 5.6, 5.7)

Pruppacher and Klett, Ch. 6

For Tuesday: Homework Problem 3, p. 157

Macro-Thermodynamics

- Hot air rises
- Rising air cools
- Cooled moist air saturates
- (Sub & Super)-saturated water vapor condenses
- Condensation liberates heat

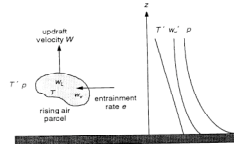


FIGURE 12.12 Schematic description of the cloud formation mathematical framework

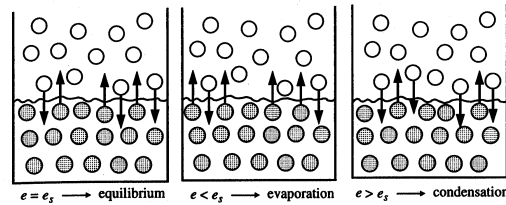
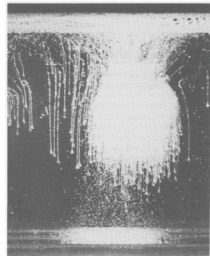


Figure 4.5 Schematic representation illustrating how the relative magnitudes of the vapor pressure of the water vapor layer, e and the saturation vapor pressure of the liquid below it, e_s determine the phase transitions between water and water vapor. When $e = e_s$, the vapor and liquid are in equilibrium and there is no net exchange between water and water vapor. When $e < e_s$, there is a net transfer of water into water vapor (i.e., net evaporation). When $e > e_s$, there is a net transfer of water vapor into water (i.e., net condensation).

Micro-Thermodynamics

- Saturation has the most possible dissolved species
- Equilibrium means two phases are balanced
- Supersaturated states are not stable
- Nucleation initiates a change of "phase" (from particle to droplet)



Bohren, 1987

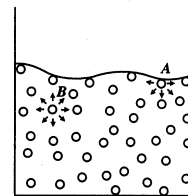


Figure 5.1 Water molecules at the surface of a liquid are subjected to a different attractive force field than those in the interior. A surface molecule, A , experiences a net attractive force towards the interior of the liquid. An interior molecule, B , experiences a symmetric force field exerted by its neighboring molecules and therefore does not freely move to the surface.

Surface Thermodynamics

- Surfaces require energy to form
- Smaller particles have
 - higher surface-to-volume ratios
 - higher curvature
- Higher curvature requires more energy per mass

$$S_{v,w} \equiv \frac{e_{a,w}}{e_{sat,w}} = \exp\left(\frac{4M_w\sigma_w/a}{RT\rho_w D_p}\right)$$

Kelvin Equation

- vapor pressure over a curved interface always exceeds that of the same substance over a flat surface
 - vapor pressure of a liquid = energy necessary to separate a molecule from the attractive force of its neighbors
 - curvature - increases the distance between a molecule and its neighbors so it has fewer neighbors – therefore it is easier for molecules to break free
- for pure water Kelvin effects are important <0.05 μm diameter droplets

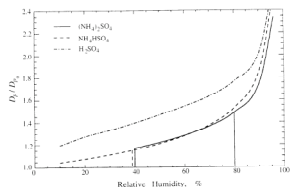
$$RH = \frac{P_w}{P_w^{sat}} = x_w \gamma_w \exp\left[\frac{4M_w\sigma_w}{RT\rho_w D_p}\right]$$

Ambient conditions
 RH relative humidity
 T temperature
 P_w vapor pressure
 P_w^{sat} saturation pressure

Particle composition
 x_w mole fraction of water
 γ_w activity coefficient for water
 σ_w surface tension of solution
 ρ_w density of aqueous solution
 M_w molecular weight
 D_p particle diameter

Hygroscopic Growth of Particles

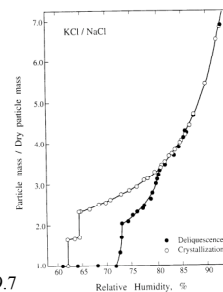
- Normalized diameter change (growth factor) of sulfate species
 - Relative to particle size at 0% RH



Seinfeld and Pandis, Fig. 9.3

Measured Hygroscopic Growth

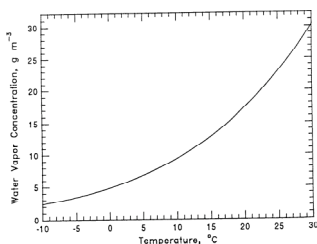
- Particle balance for levitating particles (Tang et al., 1987)
- Growth compensated by change in electric field
- Deliquescence occurs at transition from dry to wet



Seinfeld and Pandis, Fig. 9.7

Water Saturation

- Saturation concentration of water over a flat water surface



Seinfeld and Pandis, Fig. 15.1

Table 4.3 Coefficients of the sixth-order polynomial fits to saturation vapor pressure for the temperature range -50° to 50°C for both liquid water and ice. (After Flatau *et al.*, 1992.)

| Coefficient | Liquid water | Ice |
|----------------|-----------------|-----------------|
| a ₁ | 6.11176750 | 6.10952665 |
| a ₂ | 0.443986062 | 0.501948366 |
| a ₃ | 0.143053301E-01 | 0.186288989E-01 |
| a ₄ | 0.265027242E-03 | 0.403488906E-03 |
| a ₅ | 0.302246994E-05 | 0.539797852E-05 |
| a ₆ | 0.203886313E-07 | 0.420713632E-07 |
| a ₇ | 0.638780966E-10 | 0.147271071E-09 |

Free Energy Equation

- Surface energy $dW_{\sigma} = \sigma dA$ (5.1)

$$dW_{\sigma} = \sigma_n 8\pi r dr \quad (5.3)$$

where σ_n is the surface tension between the liquid and vapor phases. Since the work

$$\sigma_n dA = \Delta p dV \quad (5.4)$$

- Free energy at constant T, P

$$dG = -\eta dT + V dp + \sigma_n dA + \mu_l dn_l + \mu_v dn_v \quad (5.8)$$

If we assume that nucleation occurs at constant temperature and pressure, and that $dn_l = -dn_v$, we have

$$dG = \sigma_n 8\pi r dr + (\mu_l - \mu_v) dn_l \quad (5.9)$$

Chemical Potential

- From Maxwell's equations

$$\left(\frac{\partial g}{\partial p}\right)_T = v \quad \left(\frac{\partial g}{\partial T}\right)_p = -\eta \quad (2.48)$$

- Integrating from vapor to liquid

The term $(\mu_l - \mu_v)$ can be evaluated as follows. For an isothermal process involving one mole of water vapor, we can write

$$d\mu_v = dG = R^* T d(\ln e)$$

$$\mu_v = \mu_v^0 + R^* T \ln \frac{e}{e_0}$$

Since $\mu_l = \mu_v$ when the two phases are in equilibrium over a plane surface, we can therefore write

$$\mu_l - \mu_v = R^* T \ln \left(\frac{e}{e_0}\right) \quad (5.10)$$