**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 interactions

Curry and Webster, Ch. 5 (skip 5.6, 5.7); also 4.5.1
Pruppacher and Klett, Ch. 6
For Thursday: Homework Problem 3 and 7 (Ch. 5) (optional!)
Tuesday, Oct. 27: Midterm
Thursday, Oct. 29: meet to work on ROAST!

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**Macro-Thermodynamics**

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

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**Water Saturation**

- Saturation concentration of water over a flat water surface

Seinfeld and Pandis, Fig. 15.1

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**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

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**Table 4.3** Coefficients of the sixth-order polynomial fits to saturation vapor pressure for the temperature range -50°C to 50°C for both liquid water and ice.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Liquid water</th>
<th>Ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>6.11176750</td>
<td>6.10952665</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.44396062</td>
<td>0.50194366</td>
</tr>
<tr>
<td>$a_3$</td>
<td>0.143053010E-01</td>
<td>0.186288989E-01</td>
</tr>
<tr>
<td>$a_4$</td>
<td>0.265027242E-03</td>
<td>0.403488906E-03</td>
</tr>
<tr>
<td>$a_5$</td>
<td>0.302346994E-05</td>
<td>0.539797812E-05</td>
</tr>
<tr>
<td>$a_6$</td>
<td>0.203886313E-07</td>
<td>0.420713632E-07</td>
</tr>
<tr>
<td>$a_7$</td>
<td>0.638780966E-10</td>
<td>0.147271071E-09</td>
</tr>
</tbody>
</table>

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N.B. Equilibrium is in but is NOT the same as “steady state.”
Surface Thermodynamics

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

\[ S_{v,w} \equiv \frac{e_{a,w}}{e_{sat,w}} = \exp \left( \frac{4Mw \sigma v}{RT \rho w Dp} \right) \]

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

Free Energy Equation

- Surface energy
  \[
  d\gamma_s = \gamma_s d\xi_s
  \]
  \[
  d\gamma_v = \gamma_v d\xi_v
  \]

  where \( \gamma \) is the surface tension between the liquid and vapor phases. Since the work
  \[
  \sigma_{v,s} = \Sigma_{v,s} - \Sigma_{v,sw}
  \]

- Free energy at constant T, P
  \[
  dG = -RT \xi + \sigma_{v,s} \xi_{v,s} + \sigma_{v,sw} \xi_{v,sw} + \sigma_{s,s} \xi_{s,s} + \sigma_{s,ps} \xi_{s,ps}
  \]
  \[
  \xi_{s,ps} = \gamma_{s,ps} \xi_{s,ps}
  \]
  \[
  \sigma_{s,ps} = \gamma_{s,ps} \xi_{s,ps}
  \]

Bubbles

- Liquid (H\(_2\)O/EtOH) supersaturated with vapor (CO\(_2\)) nucleates on salt to form bubbles

Clouds

- Vapor (air) supersaturated with liquid (H\(_2\)O) nucleates on particles to form droplets
Kelvin Equation

- vapor pressure over a curved interface always exceeds that of the same substance over a flat surface
- vapor pressure of a liquid is 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

\[ RH = \frac{P}{P_{\text{w}}^{\text{sat}}} = x_w \exp \left( \frac{4 M_w \sigma}{RT \rho D_p} \right) \]

**Ambient conditions**
- RH: relative humidity
- \( T \): temperature
- \( P_{\text{v}} \): vapor pressure
- \( P_{\text{w}}^{\text{sat}} \): saturation pressure

**Particle composition**
- \( x_w \): mole fraction of water
- \( \gamma_w \): activity coefficient for water
- \( \sigma_w \): surface tension of solution
- \( M_w \): molecular weight
- \( D_p \): particle diameter

Simulating Atmospheric Humidity using Molecular Dynamics

- NaCl solution reservoir
  - Simulates a grand canonical (constant RH) ensemble
  - Equilibrates with humid air
  - Ambient pressure fixed by nitrogen molecules

Raoult’s Law

- Vapor Pressure Depression
  - This effect, the net increase in the vapor pressure of the solvent is given by Raoult’s law. The law states that the vapor pressure \( P_{\text{w}} \) of a solution is given by the sum of the increase in the vapor pressure due to the presence of the solute:

\[ P_{\text{w}} = P_{\text{w}}^{\text{sat}} \exp \left( \frac{-\Delta H_{\text{fus}}}{RT} \right) \]

**Ambient conditions**
- \( \rho \): density of aqueous solution
- \( M_w \): molecular weight
- \( D_p \): particle diameter

Raoult’s Law

- Fluctuations/noise introduced due to individual evaporation/condensation events but overall RH is held constant
- Due to the small number of water molecules removed, reservoir concentration does not change.

\[ \frac{\text{Humidity as controlled by solutions of differing concentrations}}{\text{Fluctuations/noise introduced due to individual evaporation/condensation events but overall RH is held constant}} \]

\[ \text{Due to the small number of water molecules removed, reservoir concentration does not change.} \]

\[ \text{Humidity is controlled closely to value expected from bulk thermodynamics, within a small margin of error.} \]
Chemical Potential

- From Maxwell's equations
  \[
  \left( \frac{dP}{dT} \right)_T = \frac{dH}{dT} - \frac{dS}{dV}
  \]  
  (5.46)

- Interpreting from vapor to liquid
  The term \( \left( \frac{dS}{dV} \right) \) can be evaluated as follows. For an isothermal process involving one mole of water vapor, we can write
  \[
  d\mu = dU = \frac{N}{RT} dT
  \]
  \[
  \mu = \mu^0 + \frac{N}{RT} \ln \left( \frac{P}{P^0} \right)
  \]
  Since \( \mu = \mu^0 \) when the two phases are in equilibrium over a flat surface, we can therefore write
  \[
  \mu - \mu^0 = N \left( \frac{1}{2} \right)
  \]  
  (5.49)

Condensed Water Molecules

- Change in number of liquid molecules
  The number of moles of water vapor, \( d_n \), that condense onto spherical drops can be written
  \[
  d_n = \frac{1}{3\pi} \frac{dS}{dV} = \frac{d\mu}{R}
  \]  
  (5.11)

Substitution of (5.10) and (5.11) into (5.8) yields
  \[
  d\mu = \left( -R \ln \left( \frac{P}{P^0} \right) \right) d\mu
  \]  
  (5.12)

Critical Radius and Supersaturation

- Integrate then find maximum
  \[
  \Delta G = 4\pi R_0^2 \rho_L \int_0^\infty \frac{d\mu}{R}
  \]  
  (5.13)

where \( \sigma = \gamma / \rho \) is the surface tension and \( \eta \) is the saturated vapor pressure over a plane surface \( \sigma / \gamma \). \( \left( \frac{d\mu}{R} \right)_{\sigma} \)

Solving for \( \tau \)

\[
\tau = \frac{2\rho L}{R \rho R^2}
\]

(5.14)

We can write equivalently

\[
\ln S = \frac{2\rho L}{R \rho R^2}
\]

(5.14a)

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Figure 5.3: Equilibrium saturation ratio for pure water drop as a function of radius. Values are calculated from the Kelvin equation (5.14). The curve represents an unstable equilibrium. A drop above the equilibrium curve will grow, while a drop below the equilibrium curve will evaporate.
Cloud Droplet Nucleation
• **particle activation** - process by which droplets (several micron in size) are formed (or activated) from primarily submicron particles; also called heterogeneous nucleation or just nucleation by cloud physicists
  – process illustrates the conditions required for growth to droplets
  – the approach used assumes that this formation is an equilibrium process

Activation of CCN to Droplets
• Variation of the equilibrium vapor pressure of an aqueous solution drop containing ammonium sulfate and insoluble material
  – Initial dry particle diameter 0.1 µm
  – Soluble mass fractions 0.2, 0.4, 0.6, 1.0 at 293K

Köhler Curves
• Köhler curves for sodium chloride and ammonium sulfate
  – Dry diameters 0.05, 0.1, 0.5 µm
  – Supersaturation of 1% is equivalent to 101% relative humidity

Pressure Altitude Calculator
Let’s compare the hydrostatic equation to the atmosphere

\[ p = p_0 \left( \frac{T_0}{T} \right) \]

\[ J = T - T_G \rightarrow p = p_0 \left( \frac{T_G}{T} \right) \]

http://www.csgnetwork.com/pressurealtcalc.html
Pressure-Altitude Dependence

Radiation Balance Example

It has been estimated from satellite observations that variations in solar radiation during the last 20 years amounted to ≤0.2 W m⁻², or less than 0.1% of the incoming shortwave radiation. Calculate the approximate change in the temperature at the Earth’s surface for a 0.1% decrease in solar luminosity for a simplified climate model. State all assumptions, simplifications, and equations used. Values of constants that you may need are Earth’s albedo 0.31, solar luminosity 3.92x10²⁶ W, Earth-sun distance 1.50x10¹¹ m, Stefan-Boltzmann constant 5.67x10⁻⁸ W m⁻² K⁻⁴.

Terminology Review

- Synoptic: large phenomena, hundreds of kilometers in length
- Isentropic: Adiabatic-reversible
- For adiabatic, ideal:
  - p determines T and vice versa
- Potential temperature: temperature that air would have if raised/lowered to a reference pressure.

Definition Example

Define the following terms, briefly and clearly, in light of their use in the kinetic theory of gases and the first and second laws of thermodynamics:

- an ideal gas: vapor whose molecular interactions are perfect, specific at low pressures (≤1 atm) and high temperatures (≥300K); vapor that satisfies pV=RT and has the properties that dh=c_p dT, du=c_v dT, c_p-c_v=R (p. 44).
- temperature: the intensive property describing the internal energy of a gas, which for an ideal gas depends only on the average speed of the molecules.
- entropy: a state property whose differential describes the amount of energy that is not available for doing work for a reversible process (in which maximum work is done) and satisfies the criteria of an exact differential; it can be evaluated from Eqn. 2.25a and 2.26b:
  \[ \text{d} \eta = \frac{dQ}{T} \]
  \[ \int_{\text{rev}} = c_p d(ln T) - R d(ln p) \]
- exact differential: a function for which \( \text{d} f \) has the properties (1) for any closed path \( k \circ (k) = 0 \) and (2) for \( f(x,y) \) when x and y are independent, then
  \[ \frac{\partial f}{\partial x} \text{ at } x=a \equiv \frac{\text{d} f}{\text{d} x} \text{ at } x=a \]
  \[ \frac{\partial f}{\partial y} \text{ at } y=b \equiv \frac{\text{d} f}{\text{d} y} \text{ at } y=b \]
- enthalpy: a state property whose differential describes the change in heat for a constant-pressure process and satisfies the criteria of an exact differential; it is defined as \( U+pV \) (Eqn. 2.12).
Radiation Balance Example

It has been estimated from satellite observation that variations in solar radiation during the last 70 years amounted to a 0.3 W/m² in less than 1% of the incoming shortwave radiation. Calculate the approximate change in temperature at the Earth’s surface for a perfect blackbody, neglecting the greenhouse effect and the albedo of the Earth. Assume that: (1) the Earth behaves as a perfect blackbody, (2) the Earth’s albedo is 0.31, (3) the atmosphere is transparent to the incoming shortwave radiation, (4) the atmosphere absorbs all the infrared emission. Then, at equilibrium, the temperature on the Earth’s surface is given by Eqn. 5.7:

\[ T_{surf} = \frac{2S \sigma}{\varepsilon} \]

where \( S \) is the solar luminosity, \( \varepsilon \) is the Earth’s albedo, and \( \sigma \) is the Stefan-Boltzmann constant.

The resulting cooling of 0.06 K associated with a 0.1% reduction in solar radiation is negligible for this simplified climate model.

Water Vapor Metrics

<table>
<thead>
<tr>
<th>Water vapor by mass</th>
<th>Specific humidity</th>
<th>Relative humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w_e = \frac{m_e}{m_o} )</td>
<td>( q_e = \frac{m_e}{m_o} )</td>
<td>( H = \frac{w_e}{w_v} )</td>
</tr>
<tr>
<td>Water vapor by partial pressure</td>
<td>( q_e = 0.622 \left( \frac{T}{T_0} - 1 \right) )</td>
<td>( H = \frac{w_e}{w_v} )</td>
</tr>
<tr>
<td>Water saturation</td>
<td>( w_s = 0.622 \left( \frac{T_0}{T} \right) )</td>
<td></td>
</tr>
<tr>
<td>Virtual temperature</td>
<td>( T_v = T(1 + 0.608 q_v) )</td>
<td></td>
</tr>
<tr>
<td>Virtual potential temperature</td>
<td>( \theta_v = T(1 + 0.608 q_v) )</td>
<td></td>
</tr>
</tbody>
</table>

Ch. 4: Problem 5

Consider moist air at a temperature of 30°C, a pressure of 1,000 hPa, and a relative humidity of 50%. Find the values of the following quantities:

a) vapor pressure
b) mixing ratio
c) specific humidity
d) specific heat at constant pressure
e) virtual temperature

The saturation vapor pressure at a temperature of 30°C is 42.4 hPa. The gas constant for dry air is 287 K J/K/kg. The gas constant for water vapor is 461 K J/kg.

a) vapor pressure = 0.90*42.4 = 31.2 hPa [Eqn. 4.36]
b) mixing ratio = \( \frac{m_v}{m_o} = \frac{M_v \rho_v \sigma_l}{M_o \rho_o} \) [Eqn. 4.36]
c) specific humidity = \( q_v = \frac{m_v}{m_o} = \frac{M_v \rho_v \sigma_l}{M_o \rho_o} = 0.0135 \) [Eqn. 1.20]
d) specific heat at constant pressure = \( c_v = \frac{7}{2} R_v = 1,331 J/K/kg \) [Eqn. 2.65]
e) virtual temperature = \( T_v = (1+0.608 q_v) / T = 385.6 K \) [Eqn. 1.25]

Homework Ch. 5 Prob. 3

\[ S^* = 1 + \frac{4a^2}{27b} \]

<table>
<thead>
<tr>
<th>( a )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600</td>
<td>81</td>
</tr>
<tr>
<td>200</td>
<td>600</td>
</tr>
<tr>
<td>1</td>
<td>3000</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>1.00E-10</td>
<td>132.1</td>
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<tr>
<td>1.00E-10</td>
<td>132.1</td>
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</tr>
<tr>
<td>1.00E-10</td>
<td>132.1</td>
</tr>
</tbody>
</table>

\( \text{kg/m}^3 \) \( \text{mm}^3/\text{mol} \text{K} \) \( \text{mm}^3/\text{mol} \text{K} \)