Add an Atmosphere!

- Atmosphere is transparent to non-reflected portion of the solar beam
- Atmosphere in radiative equilibrium with surface
- Atmosphere absorbs all the IR emission

\[
F_{\text{surf}} = 2F_{\text{atm}} 
\]

TOA:
\[
F_{\text{atm}} = F_{\text{sun}} \left( 1 - \alpha_p \right) = \sigma T_{\text{atm}}^4 \quad T_{\text{atm}} = 255K
\]

Atmos:
\[
F_{\text{surf}} = 2F_{\text{atm}}  \quad \sigma T_{\text{surf}}^4 = 2\sigma T_{\text{atm}}^4 
\]

\[
T_{\text{surf}} = 303K
\]

Kiehl and Trenberth, 1997 (posted on course site)

Hydrostatic Balance

- Applicable to most atmospheric situations (except fast accelerations in thunderstorms)

\[
p = \rho g \frac{\partial z}{\partial z} 
\]

\[
\rho = \rho_0 \frac{p}{R_d T_0} 
\]

Curry and Webster, Ch. 1

Homogeneous Atmosphere

- Density is constant
- Surface pressure is finite
- Scale height \( H \) gives where pressure=0

\[
T = \frac{1}{p} \rho \partial \frac{p}{\partial z} 
\]

\[
\int_0^H \frac{dp}{\rho} = \int_0^H \rho dp \\
\rho H = \rho_0 \frac{p}{R_d T_0} 
\]

Curry and Webster, Ch. 1

Hydrostatic + Ideal Gas + Homogeneous

- Evaluate lapse rate by differentiating ideal gas law

\[
\Gamma = -\frac{\partial T}{\partial z} = \frac{L}{R_d} = 34.1^\circ\text{C/km} 
\]

Curry and Webster, Ch. 1

Lecture Ch. 4a

- Equilibrium
- Phase changes
- Enthalpy changes from phase changes
  - Latent heat
  - Clapeyron equation
  - Clausius-Clapeyron equation

Curry and Webster, Ch. 4 (pp. 96-115; skip 4.5, 4.6)
For Tuesday: Homework Problem Ch.4 Prob. 4, 5
Atmospheric "Components"

In our studies of the atmosphere and oceans, we will consider the following systems:

1) moist air (dry air + water vapor); \( x = 2; \ p = 1 \);
2) liquid cloud (dry air + water vapor + liquid water droplets); \( x = 2; \ p = 2 \);
3) cloud drop (liquid water + a macroscopic aerosol particle): \( x = 2; \ p = 1 \);
4) mixed-phase cloud (dry air + water vapor + liquid water droplets + ice particles): \( x = 2; \ p = 2 \);
5) ice cloud (dry air + water vapor + ice particles): \( x = 2; \ p = 2 \);
6) ocean (water + salt, with or without ice): \( x = 2; \ p = 2 \).

Table 4.1 Examples of some thermodynamic systems and their associated numbers of components and phases.

<table>
<thead>
<tr>
<th>Examples</th>
<th>Components</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid water with ice</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Mixture of two gases</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Oil and vinegar</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Water and alcohol</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Sugar in water</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sand in water</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Two blocks of copper</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Phase Diagrams

- Pressure-temperature diagrams
- Degrees of freedom
  
  by \( p(x - 1) \). The \( p(x - 1) \) denotes the number of degrees of freedom, \( p \), the number of phases, \( x \), and the number of components, \( p \), in the following way:

\[
f = 2 + g(x - 1) - g(y - 1) = x - p + 2
\]

where the number "2" refers to the degrees of freedom associated with temperature and pressure of all phases. The Gibbs phase rule states that the total number of degrees

- Pressure-volume diagrams

![Figure 4.1 Atomic configuration of the water molecule. Bonding with unshared electrons in lone-pair orbitals forms a roughly tetrahedral configuration, with an H-O-H bond angle of 104.5°.](image)

![Figure 4.2 Three-dimensional lattice structure of ice. Water molecules are held together in the ice structure by hydrogen bonding. Each water molecule is bonded to its four nearest neighbors. Dashed lines show tetrahedral configuration. View in (b) is perpendicular to view in (a). (After Hobbs, 1974.)](image)

![Figure 4.3 p-T phase diagram for water. The three curves indicate those points for which two phases coexist in equilibrium. The dashedcurve is the boundary where the vapor pressure equals the liquid water temperature below 273.15 K. The solid curve below 273.15 K connects the points at which ice and vapor coexist in equilibrium. \( \rho_{fw} \) indicates the pressure and temperature values beyond which liquid water and water vapor are no longer distinguishable from one another. \( \rho_{t} \) indicates the triple point, the unique point at which all three phases coexist.](image)
**Degrees of Freedom Example**

Name the five main components of the atmosphere: (a) If all components are in the gas phase, how many degrees of freedom are there in the system? (b) If water condenses or freezes, does that number increase or decrease? (c) If new components are added by pollution, how does that change (i) the number of possible phases and (ii) the degrees of freedom of the atmosphere?

**Chemical Equilibrium**

- Two phases in equilibrium: \( \Delta G_{T,P} = 0 \)
  - Constant T, P
- Phase changes: \( \Delta G_{T,P} = 0 \)
- (What was \( G' \)?)

**Gibbs (Free) Energy**

For many applications in the atmosphere and ocean, it is useful to define a new state function whose natural independent variables are temperature and pressure. The Gibbs energy, \( G \), is defined as:

\[
G = U - T S + P V
\]

or in extensive form:

\[
G = N \overline{U} - T \overline{S} + P \overline{V}
\]

where \( \overline{U} \) is the internal energy, \( \overline{S} \) is the entropy, and \( \overline{V} \) is the volume. In differential form we have:

\[
\frac{dG}{dV} = -T \frac{dS}{dV} + \overline{p}
\]

The natural independent variables of the Gibbs energy are temperature and pressure.

**Entropy Change**

- Entropy for phase transition:
  \[
  \frac{dH}{dV} = T \frac{dS}{dV} + \overline{p}
  \]
- Define latent heat:
  - latent heat of the phase transition (sometimes called the molar heat of transition) is the change in entropy when the volume remains constant. The entropy change can be shown to have the same form as the (2.32) and (4.10) to be:
  \[
  \Delta S = \int \frac{dH}{T}
  \]

**Phase Equilibrium**

- Thermal equilibrium: \( T_1 = T_2 \)
- Mechanical equilibrium: \( \rho_1 = \rho_2 \)
- Chemical equilibrium: \( \beta_1 = \beta_2 \)

\[
\mu = \frac{\Delta G}{\Delta F}
\]

and \( \Delta H = 0 \). For a closed system at constant temperature and pressure, we therefore have:

\[
\frac{dG}{dV} = \sum_{i=1}^{\infty} \frac{dH}{dV} = 0
\]
Clapeyron Equation

- Enthalpy change for any phase transition

\[ \Delta H = -\Delta S \rho dT + \Delta V \rho dP \]  
(4.13)

Since \( dT = -\frac{\Delta T}{\rho} \rho dT = -\frac{\Delta T}{\rho} \rho dT + \frac{\Delta T}{T} \rho dT \]
Collecting terms we have

\[ \Delta H = \frac{\Delta H}{\rho} \frac{\Delta T}{\rho} = \frac{\Delta V}{\rho} \frac{\Delta T}{T} \]
(4.14)

which is known as the Clausius-Clapeyron equation or the first latent heat equation. This equation can be used to evaluate the slope of each of the \( T = T \) lines on the T-P phase diagram (Figure 4.3).

Phase Change Relationships

- Clapeyron equation
  - All phase changes
  - Non-ideal equations of state

\[ \frac{d\rho}{dT} = \frac{\Delta T}{\rho} \frac{\Delta T}{\rho} = \frac{\Delta S}{\Delta T} \frac{\Delta T}{T} = \frac{\Delta V}{\rho} \frac{\Delta T}{T} \]
(4.14)

- Clausius-Clapeyron equation
  - Liquid-vapor equilibrium only: \( v_L \ll v_V \)
  - Ideal gas law for vapor: \( v_V = RT/\rho \)

\[ \frac{d\rho}{dT} = \frac{\Delta V}{\rho} \frac{\Delta T}{T} \]
(4.15)

Clausius-Clapeyron Equation

- Latent heat of vaporization

For the liquid-vapor phase transition

\[ \frac{d\rho}{dT} = \frac{\Delta H}{\rho} \]
(4.16)

At the triple point \( v_L = 200 \text{ cm}^3/\text{kg} \) and \( v_V = 10 \text{ cm}^3/\text{kg} \), so that \( v_L \approx v_L \) and \( v_V \) can be neglected relative to \( v_V \). We may then write the Clausius equation as

\[ \frac{d\rho}{dT} = \frac{\Delta H}{\rho} \]
(4.17)

If we substitute the ideal gas law \( \rho = \frac{RT}{V} \), we obtain

\[ \frac{d\rho}{dT} = \frac{\Delta H}{\rho} \]
(4.18)

Equation (4.15) is the Clausius-Clapeyron equation.

Clausius Clapeyron Example

The saturation vapor pressure at a temperature of 30°C is 42.4 hPa. The gas constant for dry air is 287 J K\(^{-1}\) kg\(^{-1}\). The gas constant for water vapor is 461 J K\(^{-1}\) kg\(^{-1}\).

In addition to the constants given above, here is one more: the saturation vapor pressure at a temperature of 40°C is 73.8 hPa. Assuming that the latent heat of vaporization is constant, use this information to calculate the numerical value for this latent heat.