Add an Atmosphere!

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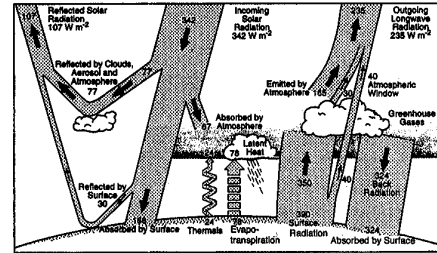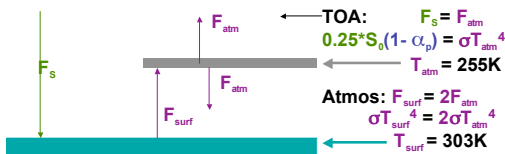- Atmosphere absorbs all the IR emission

TOA: $F_S = F_{atm}$
$0.25 \cdot S_0 (1 - \alpha_p) = \sigma T_{atm}^4$
$T_{atm} = 255K$

Atmos: $F_{surf} = 2 F_{atm}$
$\sigma T_{surf}^4 = 2\sigma T_{atm}^4$
$T_{surf} = 303K$

Figure 12.2 Estimated annual mean global energy balance for the Earth. Units are W m^{-2} (Kiehl and Trenberth, 1997).

Kiehl and Trenberth, 1997 (posted on course web site)

Hydrostatic Balance

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

$$g = -\frac{1}{\rho}\frac{\partial p}{\partial z}$$

$$\partial p = -\frac{pg}{R_d T}\partial z$$

Curry and Webster, Ch. 1

Homogeneous Atmosphere

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

$$g = -\frac{1}{\rho}\frac{\partial p}{\partial z}$$
$$dp = -\rho g dz$$
$$\int_{p_0}^{0} dp = -\int_{0}^{H} \rho g dz$$
$$0 - p_0 = -(\rho g H - 0)$$

$$p_0 = \rho g H$$
$$H = \frac{p}{\rho g} = \frac{R_d T_0}{g}$$

Curry and Webster, Ch. 1

Hydrostatic + Ideal Gas + Homogeneous

- Evaluate lapse rate by differentiating ideal gas law

Ideal gas
$$p = \rho R_d T$$

Density constant
$$\frac{\partial p}{\partial z} = \rho R_d \frac{\partial T}{\partial z}$$
$$\left(-\frac{1}{\rho}\frac{\partial p}{\partial z}\right) = R_d \left(-\frac{\partial T}{\partial z}\right)$$

Hydrostatic
$$g = -\frac{1}{\rho}\frac{\partial p}{\partial z}$$

$$\Gamma = -\frac{\partial T}{\partial z} = \frac{g}{R_d} = 34.1°C/km$$

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)
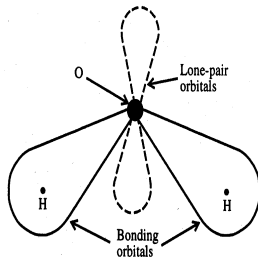For Tuesday: Homework Problem Ch.4 Prob. 4, 5

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°.
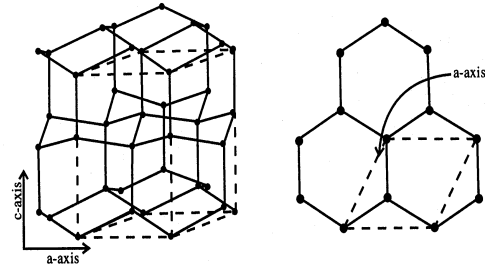

Figure 4.2 Three-dimensional lattice structure of ice. Water molecules are held together in the ice structure by hydrogen bonding. Each water molecule is bonded to its four nearest neighbors. Dashed lines show tetrahedral configuration. View in (b) is perpendicular to view in (a). (After Hobbs, 1974.)

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

Examples	Components	Phases
Liquid water with ice	1	2
Mixture of two gases	2	1
Oil and vinegar	2	2
Water and alcohol	2	1
Sugar in water	2	1
Sand in water	2	2
Two blocks of copper	1	1

Atmospheric "Components"

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

1) moist air (dry air + water vapor): $\chi = 2$; $\varphi = 1$;
2) liquid cloud (dry air + water vapor + liquid water drops): $\chi = 2$; $\varphi = 2$;
3) cloud drops (liquid water + a soluble aerosol particle): $\chi = 2$; $\varphi = 1$;
4) mixed-phase cloud (dry air + water vapor + liquid water drops + ice particles): $\chi = 2$; $\varphi = 3$;
5) ice cloud (dry air + water vapor + ice particles): $\chi = 2$, $\varphi = 2$;
6) ocean (water + salt, with or without sea ice): $\chi = 2$; $\varphi = 1, 2$.

Phase Diagrams

- Pressure-temperature diagrams
- Degrees of freedom

by $\chi(\varphi - 1)$. The Gibbs phase rule relates the number of degrees of freedom, f, the number of phases, φ, and the number of components, χ, in the following way:

$$f = 2 + \varphi(\chi - 1) - \chi(\varphi - 1) = \chi - \varphi + 2 \qquad (4.2)$$

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
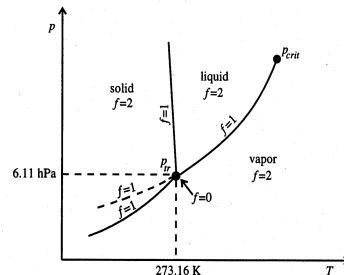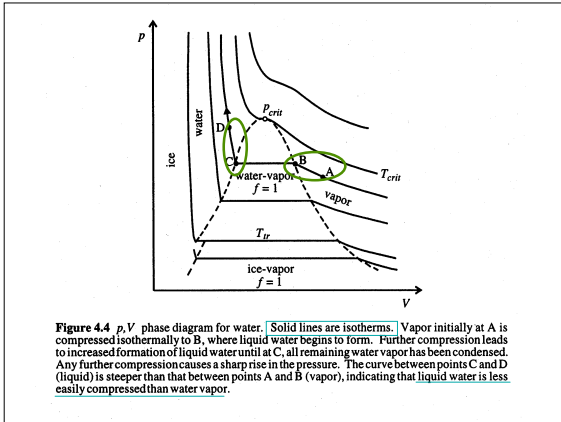
- Pressure-volume diagrams

Figure 4.3 p,T phase diagram for water. The three curves indicate those points for which two phases coexist at equilibrium. The dashed curve is the extension of the vapor-pressure curve for liquid water to temperatures below 273.16 K. The solid curve below 273.16 K connects the points at which ice and vapor coexist at equilibrium. p_{crit} indicates the pressure and temperature values beyond which liquid water and water vapor are no longer distinguishable from one another. p_{tr} indicates the triple point, the unique p,T point at which all three phases coexist.

Figure 4.4 p,V phase diagram for water. Solid lines are isotherms. Vapor initially at A is compressed isothermally to B, where liquid water begins to form. Further compression leads to increased formation of liquid water until at C, all remaining water vapor has been condensed. Any further compression causes a sharp rise in the pressure. The curve between points C and D (liquid) is steeper than that between points A and B (vapor), indicating that liquid water is less easily compressed than water vapor.

Phase Equilibrium

- Thermal equilibrium $\qquad T_1 = T_2.$

- Mechanical equilibrium $\qquad p_1 = p_2.$

- Chemical equilibrium $\qquad \mu_1 = \mu_2.$

$$\mu = \frac{\partial G}{\partial n} \qquad (4.6)$$

and $dn = 0$. For a closed system at constant temperature and pressure, we therefore have

$$dG = \sum_j \mu_j\, dn_j = 0 \qquad (4.9)$$

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 $\qquad \Delta G_{T,P} = 0$
  - Constant T, P

- Phase changes $\qquad\qquad\quad \Delta G_{T,P} = 0$
  - Constant T, P

- (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

$$g = u - T\eta + pv = h - T\eta \qquad (2.33)$$

or in extensive form

$$G = H - T\eta$$

where $\eta = m\eta$ is used to denote extensive entropy and $G = mg$ is the extensive Gibbs energy. In differential form we have

$$dg = -\eta\, dT + v\, dp \qquad (2.34)$$

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

Entropy Change

- Entropy for phase transition

$$dh = T d\eta + v\, dp \qquad (2.32)$$

- Define latent heat

transition, entropy and the specific volume will increase. The enthalpy change during the phase transition is

$$\Delta h = L \qquad (4.10)$$

where L is the *latent heat* of the phase transition (sometimes called the *molar heat*) phase transition. Note that $L_{il} = L_{iv} - L_{lv}$. In a phase change process at constant pressure, the entropy change can easily be shown from (2.32) and (4.10) to be

$$\Delta \eta = \frac{\Delta h}{T} = \frac{L}{T} \qquad (4.11)$$

Clapeyron Equation

- Enthalpy change for any phase transition

$$\left(\frac{\partial p}{\partial T}\right)_g = -\frac{\eta}{v} \qquad (2.40)$$

$$dG = -\eta\, dT + V\, dp \qquad (4.4)$$

Since $dg_1 = dg_2$ at equilibrium, we may write

$$-\eta_1\, dT + v_1\, dp = -\eta_2\, dT + v_2\, dp \qquad (4.13)$$

Collecting terms we have

Exact!   **(Not exact but usually good)**
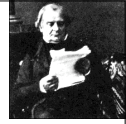
$$\frac{dp}{dT} = \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{\Delta\eta}{\Delta v} = \frac{\Delta h}{T\Delta v} = \frac{L}{T\Delta v} \qquad (4.14)$$

which is known as the *Clapeyron equation* or the *first latent heat equation*. This equation can be used to evaluate the slope of each of the $f = 1$ lines on the p, T phase diagram (Figure 4.3).

Clausius-Clapeyron Equation

- Latent heat of vaporization

For the liquid–vapor equilibrium,

$$\frac{dp}{dT} = \frac{L_{lv}}{T(v_v - v_l)} \qquad (4.17)$$

At the triple point $v_v = 206\ \text{m}^3\,\text{kg}^{-1}$ and $v_l = 10^{-3}\ \text{m}^3\,\text{kg}^{-1}$, so that $v_v \gg v_l$ and v_l can be neglected relative to v_v. We may then write the Clapeyron equation as

$$\frac{dp}{dT} = \frac{L_{lv}}{T v_v} \qquad (4.18)$$

If we substitute the ideal gas law for v_v, we obtain

$$\frac{dp}{dT} = \frac{L_{lv}\, p}{R_v T^2} \qquad (4.19)$$

Equation (4.19) is the *Clausius–Clapeyron equation.*

Phase Change Relationships

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

$$\frac{dp}{dT} = \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{\Delta\eta}{\Delta v} = \frac{\Delta h}{T\Delta v} = \frac{L}{T\Delta v} \qquad (4.14)$$

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

$$\frac{dp}{dT} = \frac{L_{lv}\, p}{R_v T^2} \qquad (4.19)$$

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.