

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 (except 4.5.1), 4.6)
 For Tuesday: Homework Problem Ch.4 Prob. 4, 5

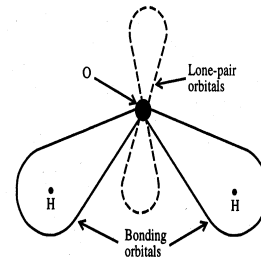


Figure 4.1 Atomic configuration of the water molecule. Bonding with unshared electrons in lone-pair orbitals forms a roughly tetrahedral configuration, with an H-O-H bond angle of 104.5°.

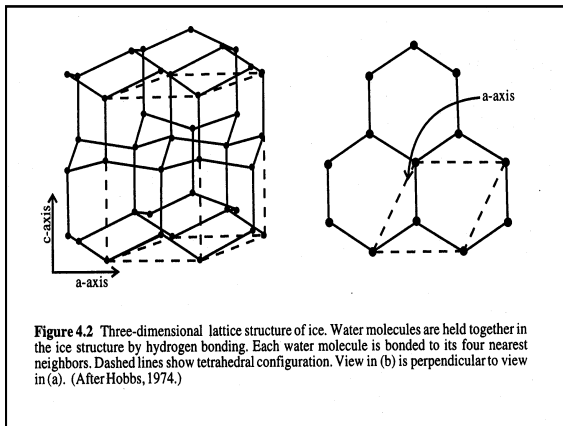


Figure 4.2 Three-dimensional lattice structure of ice. Water molecules are held together in the ice structure by hydrogen bonding. Each water molecule is bonded to its four nearest neighbors. Dashed lines show tetrahedral configuration. View in (b) is perpendicular to view in (a). (After Hobbs, 1974.)

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

Phase Diagrams

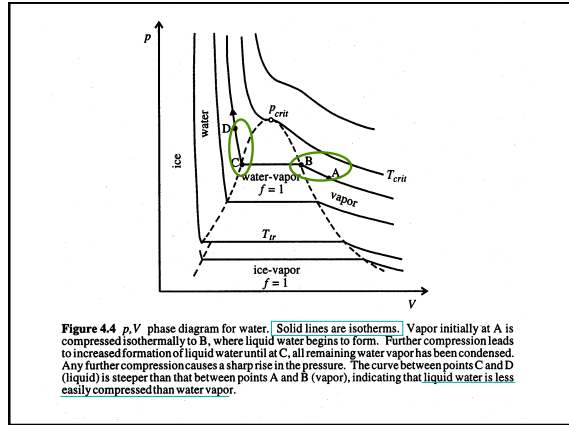
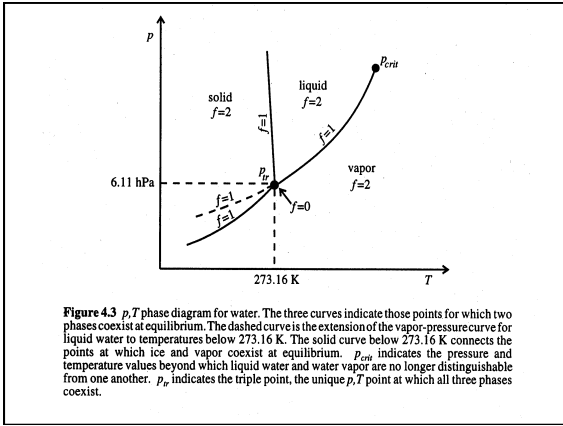
- Pressure-temperature diagrams
- Degrees of freedom

by $\chi(\phi - 1)$. 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:

$$f = 2 + \phi(\chi - 1) - \chi(\phi - 1) = \chi - \phi + 2 \quad (4.2)$$

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



Phase Equilibrium

- Thermal equilibrium $T_1 = T_2$.
- Mechanical equilibrium $p_1 = p_2$.
- Chemical equilibrium $\mu_1 = \mu_2$.

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

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

$$dG = \sum \mu_i dn_i = 0 \quad (4.9)$$

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?

Reminders

- **Virtual Temperature:** The temperature air would have at the given pressure and density if there were no water vapor in it

$$T_v = T(1 + 0.608q_v)$$
- **Potential Temperature:** The temperature a parcel would have if it were brought adiabatically and reversibly to p_0 (usually 1 atm)

$$\theta = T \left(\frac{p_0}{p} \right)^{R_d / c_{pd}}$$
- **Virtual Potential Temperature:** The temperature a parcel would have if there were no water vapor in it (only condensed water) and if it were brought adiabatically and reversibly to p_0 (usually 1 atm)

$$\theta_v = T(1 + 0.608q_v) \left(\frac{p_0}{p} \right)^{R_d / c_{pd}}$$

Water Vapor Metrics

	Mixing ratio	Specific humidity	Relative humidity
Water vapor by mass	$w_v = \frac{m_v}{m_d} = \frac{\rho_v}{\rho_d}$	$q_v = \frac{m_v}{m_d + m_v}$	$H \approx \frac{w_v}{w_s}$
Water vapor by partial pressure		$q_v = 0.622 \left(\frac{e}{p - (1 - 0.622)e} \right)$	$H = \frac{e}{e_s}$
Water saturation	$w_s = 0.622 \left(\frac{e_s}{p - e_s} \right)$		
Virtual temperature		$T_v = T(1 + 0.608q_v)$	
Virtual potential temperature		$\theta_v = T(1 + 0.608q_v) \left(\frac{p_0}{p} \right)^{R_d / c_{pd}}$	

Water Vapor Metrics

The *water vapor mixing ratio*, w_v , is the ratio of the mass of water vapor present to the mass of dry air. It is thus defined, after substituting from the ideal gas law, as

$$w_v = \frac{m_v}{m_d} = \frac{p_v}{p_d} = \frac{e}{p-e} \quad (4.36)$$

where $e = M_v/M_d = 0.622$ (Section 1.7). A value of the *saturation mixing ratio*, w_s , is given by

$$w_s = \frac{e_s}{p-e_s} \quad (4.37)$$

Since $p \gg e$ and $p \gg e_s$,

$$\mathcal{H} \approx \frac{w_v}{w_s} \quad (4.38)$$

is an approximate definition of the relative humidity.

The *water vapor mixing ratio* can be related to the *specific humidity*, q_v , which was originally defined in Section 1.7, as

$$q_v = \frac{m_v}{m_d + m_v} = \frac{e}{p - (1-e)e} = \frac{w_v}{1 + w_v} \quad (4.39)$$

Since both w_v and q_v are always smaller than 0.04, $q_v \approx w_v$.

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:

- vapor pressure
- mixing ratio
- specific humidity
- specific heat at constant pressure
- virtual temperature

Chemical Equilibrium

- Two phases in equilibrium $\Delta G_{T,P} = 0$
– Constant T, P
- Phase changes $\Delta G_{T,P} = 0$
– 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

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

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

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

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

Enthalpy Change

- Enthalpy for phase transition $dh = Td\eta + v dp$ (2.32)
- Define latent heat
transition, entropy and the specific volume will increase. The enthalpy change during the phase transition is $\Delta h = L$ (4.10)
where L is the *latent heat* of the phase transition (sometimes called the *molar heat*) of phase transition. Note that $L_{ij} = L_{iv} - L_{iv}$. In a phase change process at constant pressure, the entropy change can easily be shown from (2.32) and (4.10) to be $\Delta\eta = \frac{\Delta h}{T} = \frac{L}{T}$ (4.11)

Clapeyron Equation

- Enthalpy change for any phase transition $\left(\frac{\partial p}{\partial T}\right)_s = -\frac{\eta}{v}$ (2.40) $dG = -\eta dT + v dp$ (4.4)
- Since $dg_1 = dg_2$ at equilibrium, we may write $-\eta_1 dT + v_1 dp = -\eta_2 dT + v_2 dp$ (4.13)
- Collecting terms we have **Exact!** (Not exact but usually good) $\frac{dp}{dT} = \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{\Delta\eta}{\Delta v} = \frac{\Delta h}{T\Delta v} = \frac{L}{T\Delta v}$ (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

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

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

$$\frac{dp}{dT} = \frac{L_{lv}}{T v_g} \quad (4.18)$$

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

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

Equation (4.19) is the Clausius-Clapeyron equation.

Phase Change Relationships

- Clapeyron equation

– All phase changes

– Non-ideal equations of state

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

- Clausius-Clapeyron equation

– Liquid-vapor equilibrium only: $v_l \ll v_v$

– Ideal gas law for vapor: $v_v = RT/p$

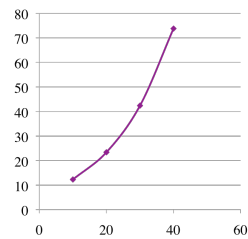
$$\frac{dp}{dT} = \frac{L_{lv} p}{R_v T^2} \quad (4.19)$$

Water Saturation Pressures

es doubles with every 10C!

T(C)	e_s (hPa)
10	12.3
20	23.4
30	42.4
40	73.8

(this is one consequence of Clausius-Clapeyron's 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 $287 \text{ J K}^{-1} \text{ kg}^{-1}$. The gas constant for water vapor is $461 \text{ J K}^{-1} \text{ kg}^{-1}$.

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.