

4.3, 4.4

Phase Equilibrium

Determine the slopes of the $f = 1$ lines

Relate p and T at equilibrium between two phases

Lets consider the Gibbs function

$$dG = -\eta dT + V dp$$

Applies to a homogeneous system

An open system where a new phase may form or a new component can be added

$$dG = -\eta dT + V dp + \sum_i \sum_j \frac{\partial G}{\partial n_{ij}} dn_{ij}$$

i

Number of components

j

Number of phases

$$dG = -\eta dT + V dp + \sum_i \sum_j \frac{\partial G}{\partial n_{ij}} dn_{ij}$$

$$\frac{\partial G}{\partial \eta}$$

Is the chemical potential

$$\mu = \frac{\partial G}{\partial n}$$

Change in the Gibbs function of the system with a change in the number of moles of a given component or phase

$$\mu = g$$

$$dG = -\eta dT + V dp + \sum_i \sum_j \mu_{ij} dn_{ij}$$

constant temperature

constant pressure

One component

$$dG = \sum_j \mu_j dn_j$$

closed system

One component

3 phases

The number of moles of a given phase can vary under possible phase transitions

Total number of moles

$$n = n_1 + n_2 + n_3 = \text{constant}$$

$$dn = 0$$

For a closed system at
constant temperature
constant pressure

$$dG = \sum_j \mu_j dn_j = 0$$

Conditions for equilibrium between two phases 1 and 2

★ Thermal equilibrium $T_1 = T_2$

if $T_1 \neq T_2$ Heat would flow from one phase to the other \longrightarrow No equilibrium

★ Mechanical equilibrium $p_1 = p_2$

if $p_1 \neq p_2$ One phase would be expanding at the expense of the other \longrightarrow No equilibrium

★ Chemical equilibrium $\mu_1 = \mu_2$

if $\mu_1 \neq \mu_2$ A transfer on n moles would change the Gibbs function

During a phase change heat is added to (or remove) from the system

No change of temperature or pressure

Enthalpy change during the phase transition is

$$\Delta h = L$$

L

Latent heat of the phase in transition

Latent heat of fusion

$$L_{il} = h_l - h_i$$

solid-liquid
phase transition

Latent heat of vaporization

$$L_{lv} = h_v - h_l$$

liquid-vapor
phase transition

Latent heat of sublimation

$$L_{iv} = h_v - h_i$$

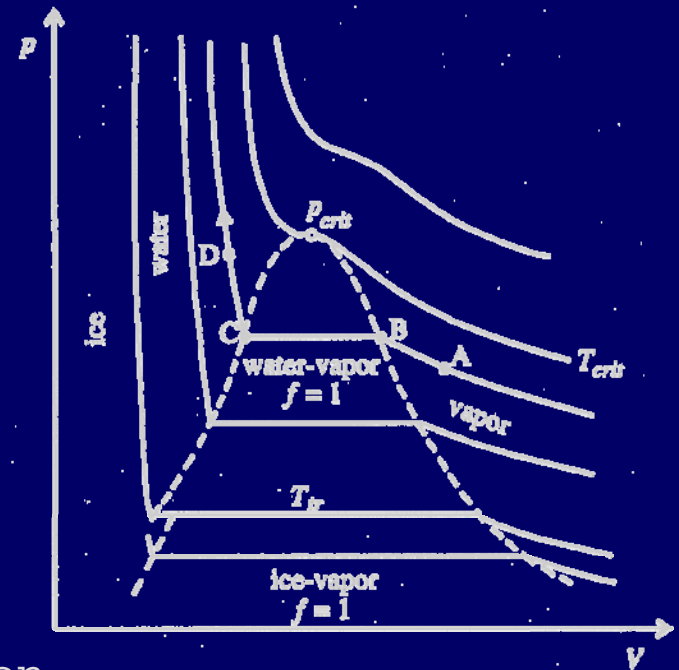
solid-vapor
phase transition

$$L_{il} = L_{iv} - L_{lv}$$

l liquid

i ice

v vapor



Phase change process



Constant pressure

$$dh = Td\eta + vdp$$

$$\Delta h = L$$

$$\Delta\eta = \frac{\Delta h}{T} = \frac{L}{T}$$

Latent heat

molecular interactions

Strong in liquid

Weak in a gas

During vaporization

The majority of latent heat is used to overcome the cohesive forces holding the molecules together in the liquid

Latent heat of fusion is much less than the heat of vaporization

Density difference between solid and liquid is relative small

Determine the slopes of the $f = 1$ lines

$$\mu_1 = \mu_2$$

$$G_1 = G_2$$

$$dg_1 = dg_2$$

$$\Delta\eta = \frac{\Delta h}{T} = \frac{L}{T}$$

$$dg_1 = -\eta_1 dT + v_1 dp$$

$$dg_2 = -\eta_2 dT + v_2 dp$$

$$-\eta_1 dT + v_1 dp = -\eta_2 dT + v_2 dp$$

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

Clapeyron equation



First latent heat equation

$$\frac{dp}{dT} = \frac{L}{T\Delta v}$$

Evaluate the slope
 $f = 1$ lines

Solid-liquid
equilibrium line

$$\frac{dp}{dT} = \frac{L_{il}}{T(v_l - v_i)}$$

Inverting

$$\frac{dT}{dp} = \frac{T(v_l - v_i)}{L_{il}}$$

Variation of the melting point with pressure

Liquid-vapor equilibrium line

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

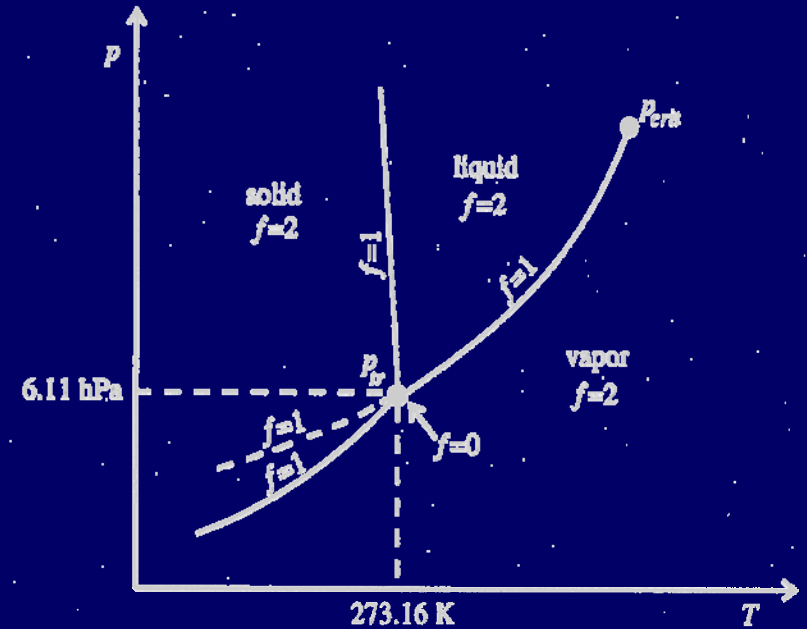
At the triple point

$$v_v = 206 \text{ m}^3\text{kg}^{-1}$$

$$v_l = 10^{-3} \text{ m}^3\text{kg}^{-1}$$

$$v_v \gg v_l$$

$$\frac{dp}{dT} \approx \frac{L_{lv}}{Tv_v}$$



$$\frac{dp}{dT} \approx \frac{L_{lv}}{Tv_v}$$

If we use the
ideal gas law

$$\frac{dp}{dT} = \frac{L_{lv} p}{R_v T^2}$$

Clausius Clapeyron equation

The boiling point temperature

The temperature at which the vapor pressure is
equal to the atmospheric pressure

$$\frac{dT}{dp} = \frac{R_v T^2}{L_{lv} p}$$

Decrease of boiling point temperature with decreasing pressure

To integrate

$L_{lv}(T)$ Lets assume L_{lv} constant e Water vapor pressure

$$\int_{e_1}^{e_2} d(\ln e) = \int_{T_1}^{T_2} \frac{L_{lv}}{R_v T^2} dT$$

$$\ln \frac{e_2}{e_1} = -\frac{L_{lv}}{R_v} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$e_2 = e_1 \exp \left[-\frac{L_{lv}}{R_v} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

e_1 e_2

Saturation vapor pressure at

T_1 T_2

Remember we assume

Vapor phase obeys the ideal gas

L_{lv} constant

Vapor-ice
equilibrium line

$$\frac{de}{dT} = \frac{L_{iv}}{T(v_v - v_i)}$$

$$v_i = 1.091 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$$

$$v_v \gg v_i$$

$$\frac{de}{dT} \approx \frac{L_{lv}}{Tv_v}$$

integrating

$$e_2 = e_1 \exp \left[-\frac{L_{lv}}{R_v} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

To integrate Clausius clapeyron equation more precisely

Including the variation of

L_{lv} L_{iv} With T

$$d\Delta h = \left(\frac{\partial \Delta h}{\partial T} \right) dT + \left(\frac{\partial \Delta h}{\partial p} \right) dp \quad dh = c_p dT$$

$$\frac{d\Delta h}{dT} = \frac{\partial \Delta h}{\partial T} + \left(\frac{\partial \Delta h}{\partial p} \right) \frac{dp}{dT} = \Delta c_p + \left(\frac{\partial \Delta h}{\partial p} \right) \frac{dp}{dT}$$

small

$$\frac{dL_{lv}}{dT} = c_{pv} - c_{pl}$$

Kirchoff's law

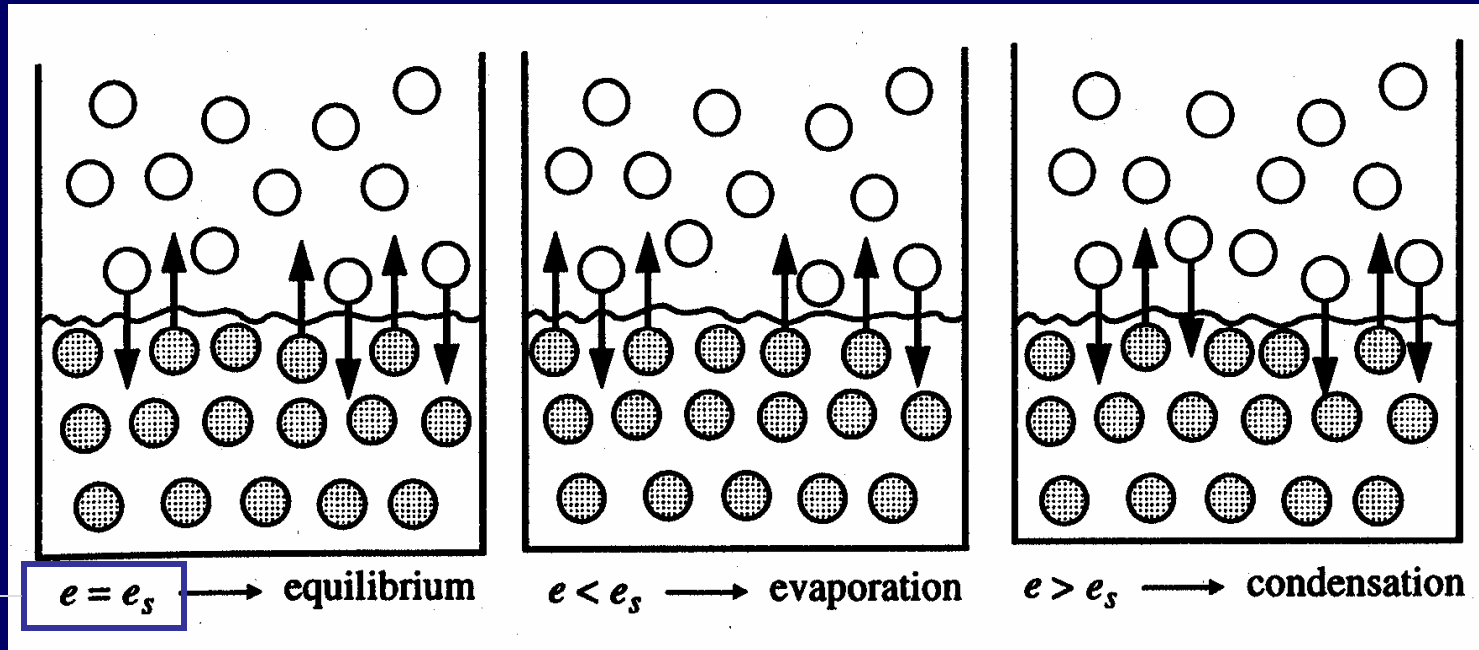
second latent heat equation

The variation of the Latent heat of fusion

$$\frac{dL_{il}}{dT} = c_{pl} - c_{pi}$$

Consider a system

Layer of liquid water overlain by a layer of water vapor



Vapor pressure equal to the saturation vapor pressure of the liquid

Condensation

decreases

Entropy

Evaporation

increases

Liquid is a "less random" state

Atmospheric humidity variables

Last sections

Pure water vapor as the gaseous phase under consideration

In the atmosphere

Mixture of dry air gases and water vapor

Partial pressure of the water vapor

e

Partial pressure of dry air

p_d

Total atmospheric pressure

p

The saturation vapor pressure with respect to liquid

e_s

The saturation vapor pressure with respect to ice

e_{si}

Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{L_{lv} p}{R_v T^2}$$

Integrating the Clausius-Clapeyron equation for atmospheric water vapor

$$e_s = e_{s,tr} \exp \left[-\frac{L_{lv}}{R_v} \left(\frac{1}{T_{tr}} - \frac{1}{T} \right) \right]$$

saturation vapor
pressure with
respect to liquid

$$e_{si} = e_{s,tr} \exp \left[-\frac{L_{iv}}{R_v} \left(\frac{1}{T_{tr}} - \frac{1}{T} \right) \right]$$

saturation vapor
pressure with
respect to ice

Reference pressure and temperature

Triple point

$$e_{s,tr} = 6.11 \text{ hPa}$$

$$T_{tr} = 273.16 \text{ K}$$

Application of the Clausius-Clapeyron equation to determining the saturation vapor pressure in the atmosphere is not strictly valid

Dalton's law of partial pressures is not strictly valid

The total pressure is not the sum of the partial pressures of two ideal gases

The condensed phase is under a total pressure that is augmented by the presence of dry air

The condensed phase is not purely liquid water, but contains dissolved air

Departure from ideal gas

Less than 1%

When high accuracy is needed

Empirical values

$$e_s = a_1 + \sum_{n=2}^7 a_n (T - T_{tr})^{n-1}$$

Values of saturation vapor pressure

Used to determine commonly used atmospheric variables

Relative humidity

$$H = \frac{e}{e_s}$$

Partial pressure of the water vapor

saturation vapor pressure with respect to liquid

Relative humidity with respect to ice saturation

$$H_i = \frac{e}{e_{si}}$$

Multiplied by 100 percentage

Function only of

e T

If we compare

saturation vapor pressure with respect to liquid

e_s

saturation vapor pressure with respect to ice

e_{si}

$$e_s = e_{s,tr} \exp\left[-\frac{L_{lv}}{R_v}\left(\frac{1}{T_{tr}} - \frac{1}{T}\right)\right]$$

$$e_{si} = e_{s,tr} \exp\left[-\frac{L_{iv}}{R_v}\left(\frac{1}{T_{tr}} - \frac{1}{T}\right)\right]$$

$$\frac{e_s}{e_{si}} = \exp\left[\frac{L_{il}}{R_v T_{tr}}\left(\frac{T_{tr}}{T} - 1\right)\right]$$

For subfreezing temperatures!!

$$\frac{e_s(T)}{e_{si}(T)} > 1$$

Ratio increases as the temperature decreases

Atmosphere saturated with respect to liquid water

→ $H = 1$

T (C)	H_i
0	1.0
-10	1.10
-20	1.22
-30	1.34
-40	1.47

Supersaturated with respect to ice

Water mixing ratio

$$w_v$$

Ratio of the mass of water vapor present to the mass of dry air

$$w_v = \frac{m_v}{m_d} = \frac{\rho_v}{\rho_d} = \varepsilon \frac{e}{p-e} \quad \varepsilon = \frac{M_v}{M_d}$$

Saturation mixing ratio

$$w_s$$

$$w_s = \varepsilon \frac{e_s}{p-e_s}$$

$$p \gg e$$

$$p \gg e_s$$



$$H = \frac{w_v}{w_s}$$

$$H = \frac{e}{e_s}$$

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

$$w_v \quad q_v$$

Are always smaller than 0.04

$$q_v \approx w_v$$

Given T, p, and one of the humidity variable all the other humidity variables can be determined

Precipitable water
Water vapor path

$$W_v$$

The total mass of water vapor in a column of unit cross-sectional area extending from the surface to the top of the atmosphere

$$W_v = \int_0^{\infty} \rho_v dz$$

If all the vapor in the column were to be condensed the depth would be

$$\frac{W_v}{\rho}$$

The relationship between precipitable water and specific humidity

$$W_v = \int_0^{\infty} \rho_v dz$$

$$\frac{dp}{dz} = -\rho g$$

$$W_v = \frac{1}{g} \int_p^{p_0} \frac{\rho_v}{\rho_a} dp$$

$$q_v = \frac{m_v}{m_d + m_v}$$

$$W_v = \frac{1}{g} \int_p^{p_0} q_v dp$$