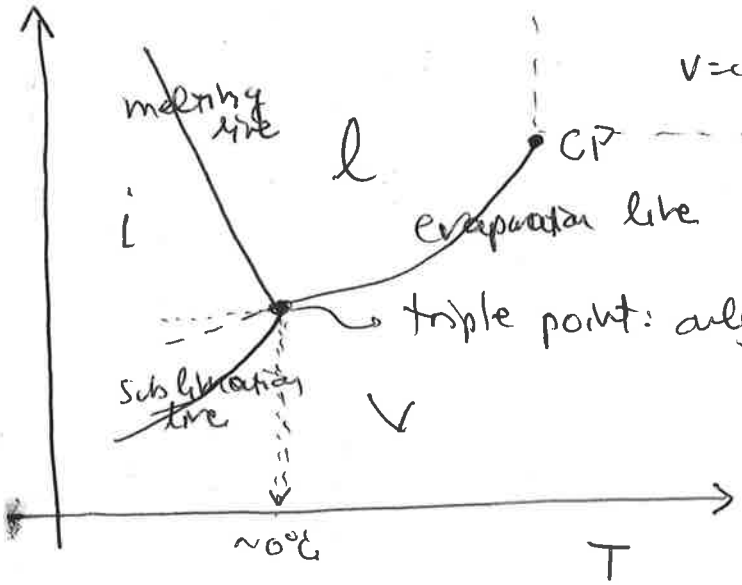
Recap of Atmospheric Thermodynamics

→ Basic Thermodynamics (1st, 2nd law, energy forms, Thermodynamic relationships ~ summary in slides, and reference to Chapter 2 of Curry and Webster.

→ Water phase diagram



V=cont. → fluid region (liquid indistinguishable from vapor)

triple point: only set of conditions where i, l, v are in equilibrium (i.e. $\mu_l = \mu_i = \mu_v$)

lines define sets of conditions where 2 phases can coexist (i.e. $\mu_i = \mu_l$ on the melting line, $\mu_v = \mu_l$ on the evaporation line and $\mu_i = \mu_v$ on the sublimation line). The equation that describes the i-v and l-v equilibrium lines was derived by clausius and clapeyron.

Clausius-clapeyron equation

take v-l equilibrium. We know that $\mu_v = \mu_l$ @ equilibrium. Since μ is the gibbs free energy per unit mol, we can then say:

$\mu_v = \mu_l \Rightarrow d\mu_v = d\mu_l$ (when in equilibrium, changes in μ_v are also equal to changes in μ_l)

$$\Rightarrow -s_v dT + v_v dp = -s_l dT + v_l dp \Rightarrow$$

$$\Rightarrow dp(v_v - v_l) = dT(s_v - s_l) \Rightarrow \frac{dp}{dT} = \frac{s_v - s_l}{v_v - v_l}$$

because $v_v \gg v_\ell$ (large difference in density means their molar volume differs alot)

and $s_v - s_\ell = \frac{L_{ev}}{T}$ (see chapter 4, eqn. 4.11 for derivation)

we have

$$\frac{dp}{dT} = \frac{L_{ev}}{T}\frac{1}{v_g} \xrightarrow[\text{ideal gas law}]{} \boxed{\frac{dp}{dT} = \frac{L_{ev}}{RT^2}p}$$

Clausius-Clapeyron Relationship

assumption to remember: $v_\ell \ll v_g$ (i.e. we are far away from CP)
ideal gas law

Integrated form of C-Clapeyron

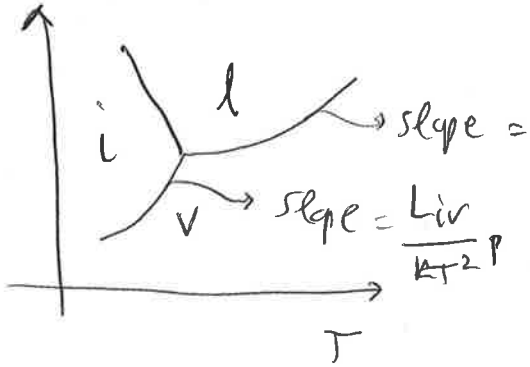
if $L_{ev} \neq f(T)$ then you can integrate the differential form of C-Clapeyron:

$$\int_{p(T_1)}^{p(T_2)} d\ln p = \int_{T_1}^{T_2} \frac{L_{ev}}{RT^2}\,dT \Rightarrow \boxed{p_1 = p_2 \exp\left\{-\frac{L_{ev}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\}}$$

these are saturation vapor pressures!

In the book, e_s is used to represent sat. vapor pressure over liquid

C-Clapeyron explains the steepness of curves on phase diagram



↳ difference in i-v, l-v slopes is governed by the difference in L_{ev}, L_{iv} ($L_{iv} > L_{ev}$)

Recap: We are interested in the partial pressure of water in atmosphere.

Clausius - Clapeyron:

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

latent heat

T_{ref}

psat @ T — p^{sat} @ tref — specific constant for water vap.

Usually the reference T, P are @ the triple point ∴ that both expressions for ice and liq. water have the same reference. The two curves only then differ in the "L", and its T-dependence.

However, C-C is not as accurate as we may want. Why? (go to assumptions made then ask for it):

→ ideal gas (may not be strictly valid)

→ $P = P^{w} + (P^{O_2} + P^{N_2})$ — changes total P, so phase equil. is affected a bit by this)

→ $L_{ev} = f(T)$

→ Empirical correlation of e_s should be used instead for calculations. e = six order polynomial or Antoine's equation

e_s is used to determine some commonly used variables for humidity. We have

relative humidity, $H = \frac{e}{e_s}$ ← e: vapor pressure of water; e_s: saturation v.p. @ ambient P, T.

relative humidity w.r.t. ice saturation:

$$H_i = \frac{e}{e_{si}}$$ ← e_{si}: saturation ratio

→ Q: if $H > 1$ (or 100%), what happens?

A: Liquid water can form (because you are in 2-phase region of phase diagram

→ Q: $H_i > 1$? A: ice forms

→ Q: how does H_i relate to H?

A: Take clausius clapeyron.

$$\frac{e_s}{e_{si}} = \exp\left\{ \frac{L_{ie}}{R_v T_{tr}} \left\{ \frac{T_{tr}}{T} - 1 \right\} \right\} \geq 1$$

(L_{ie}: latent heat of freezing)

if $T < T_{freezing}$

that also means that if $H \geq 1 \Rightarrow H_i > 1$

i.e. an atmosphere saturated with water is saturated with ice as well.

Q: How big is the transition between 99% and 101% supersaturation? → "shaky" airplane ride

A: 100.5% typical of cumulus clouds
105% very strong Thunderstorms

a "small" supersaturation ~~has a huge effect on~~ change reflects a long change in the dynamical activity of the atmosphere

→ Water vapor mass mixing ratio, w_v =

$$= \frac{m_v}{m_{dryair}} = \frac{\rho_v}{\rho_{dry}} = \varepsilon \frac{e}{p - e} \quad (1)$$

(ρ_v: water vapor; ρ_{dry}: dry air; ideal gas law)

$$\varepsilon = \frac{M_v}{M_d} \sim 0.62$$

→ saturation mixing ratio w_s is then given by:

$$w_s = \varepsilon \frac{e_s}{p - e_s} \quad (2)$$

Since there is little water in atmosphere relative to the O_i, N_i content, $p - e_s \simeq p$

from (2): $e_s \simeq p \frac{w_s}{\varepsilon}$

and from (1): $e \simeq p \frac{w_v}{\varepsilon}$ } (3)

so: $RH = \frac{e}{e_s} \overset{(3)}{\simeq} \frac{w_v}{w_s}$

w_v can also be related to specific humidity q_v (or water vapor mass fraction):

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

↑ ↑
e for $V = 1 m^3$

since $1 + w_v \sim 1$

↑ ... $w_v < 10^{-2}$

$\Rightarrow \boxed{q \simeq w_v}$

→ Precipitable water, W_v, is related to the maximum amount of water you can ever 'hope' to precipitate out of the atmosphere.

Q: what do you think it is?

A: $W_v = \int_0^\infty \rho_v \, dz$

W_v can be related to q_v by incorporating the hydrostatic eqn:

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

$\rho_a = \rho_v + \rho_d$

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