# A primer in atmospheric thermodynamics
# Part I: "dry" atmospheres

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# Overview

State variables and equation of state

The hydrostatic relation

Atmospheric composition

Vertical structure of atmospheres

The First Law, entropy, potential temperature

# Basic thermodynamic state variables for atmospheres

- Pressure $p$ (Pa, $\mathrm{Nt/m^2}$)
- Density $\rho$ ($\mathrm{kg/m^3}$)
- Temperature $T$ (K)

# Ideal gas equation of state (EOS)

$$\begin{aligned} p &= \frac{N}{V} kT \\ &= nkT \\ &= (n\mu M)\frac{k}{\mu}\frac{1}{M}T \\ &= \rho\frac{R^*}{M}T \\ &= \rho RT \end{aligned} \tag{1}$$

In mks units $R^* = 8314$. For dry air $R = \frac{8314}{29} \approx 287$

# Partial pressure and Dalton's Law

$$p_A = n_A k T$$

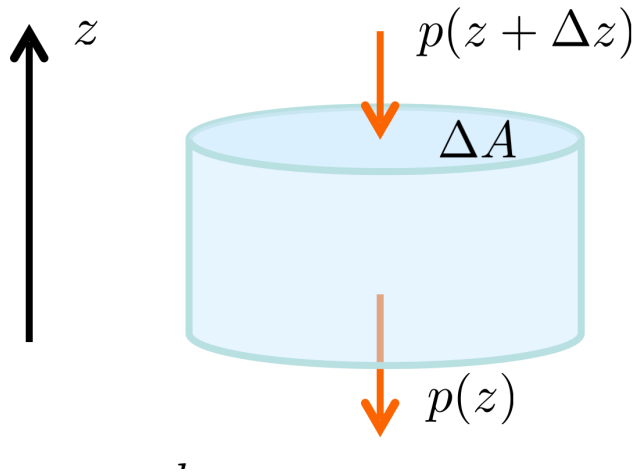
$$p_B = n_B k T$$

$$p = p_A + p_B = (n_A + n_B) k T = \rho \frac{R^*}{\overline{M}} T$$

where

$$\overline{M} \equiv \frac{n_A}{n_A + n_B} M_A + \frac{n_B}{n_A + n_B} M_B$$

# Derivation




$$p(z)\Delta A - p(z+\Delta z)\Delta A = \rho \Delta A \Delta z g$$

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

*Approximately valid for moving atmospheres if vertical acceleration is sufficiently small*

# Example: Mass of the atmosphere

Mass per unit area =

$$\int_0^\infty \rho dz = -\int_0^\infty \frac{1}{g}\frac{dp}{dz}dz = \frac{p_s}{g}$$

# Pressure as a vertical coordinate

*Because of hydrostatic relation $p(z)$ is monotonic in $z$, and so $p$ can be used as a vertical coordinate*

$\frac{\Delta p}{g}$ is mass per unit area in a layer of thickness $\Delta p$ in pressure coordinates

# Isothermal scale height

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

$$p(z) = p_s \exp\left(-\frac{z}{H}\right)$$

$$H \equiv \frac{RT}{g}$$

*Low molecular weight atmospheres have greater scale height* (cf $H_2$ vs $N_2$)

# Ways of measuring atmospheric composition

- Molar mixing ratio $\frac{n_A}{n_B}$ (often called "volume mixing ratio")
- Molar concentration $\frac{n_A}{n_A+n_B}$
- Mass mixing ratio $\frac{\rho_A}{\rho_B}$
- Mass concentration $\frac{\rho_A}{\rho_A+\rho_B}$

# Dalton's law and atmospheric composition

$$p_A = n_A k T$$

$$p_B = n_B k T$$

$$\frac{p_A}{p_B} = \frac{n_A}{n_B}$$

$$\frac{p_A}{p_A + p_B} = \frac{n_A}{n_A + n_B}$$

Multiply by $10^6$ to express as parts-per-million.
For historical reasons, called "ppmv" to distinguish from parts per million by mass.

# Dominant composition of some planetary atmospheres

## Earth: $g_s = 9.8\mathrm{m/s^2}$,$p_s = 10^5\mathrm{Pa}$

Dry air $\mathrm{N_2}$, 78% $\mathrm{O_2}$ 21%, Ar .93%, $\mathrm{CO_2}$ 416 ppmv (.0416 %);
+ condensible water vapour

## Venus: $g_s = 8.87\mathrm{m/s^2}$,$p_s = 93$ *times*$10^5\mathrm{Pa}$

$\mathrm{CO_2}$ 96.5%, $\mathrm{N_2}$, 3.5% 21%, $\mathrm{SO_2}$ 150ppmv (.015%)

## Jupiter (outer atmosphere)

$\mathrm{H_2}$ 86%, $\mathrm{He}$ 13.6% + ...

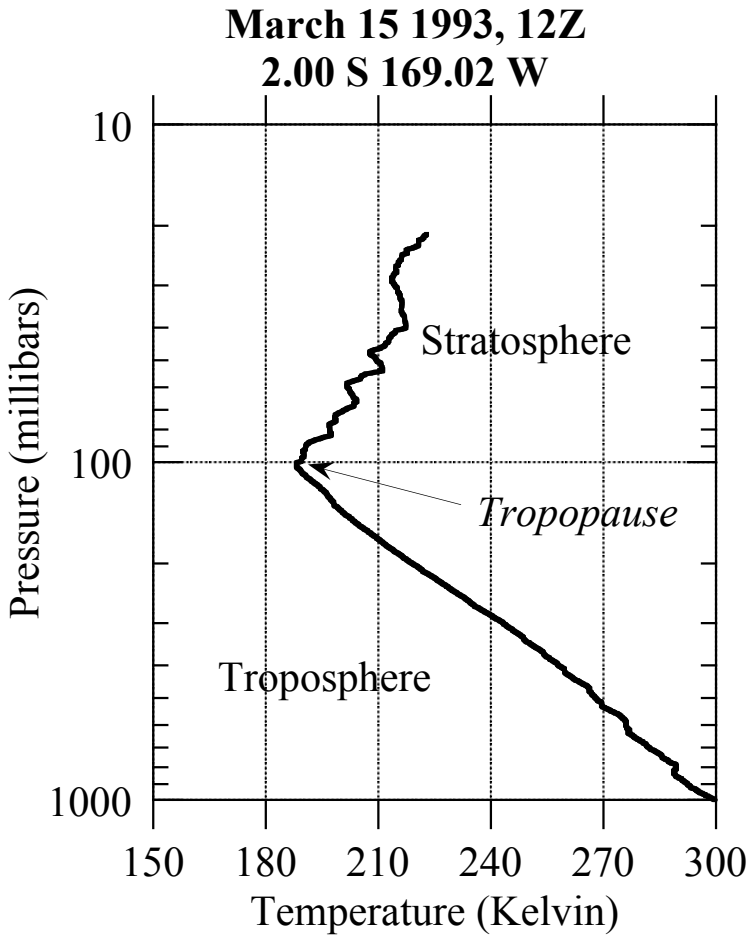
*(by count of molecules)*

# Examples:

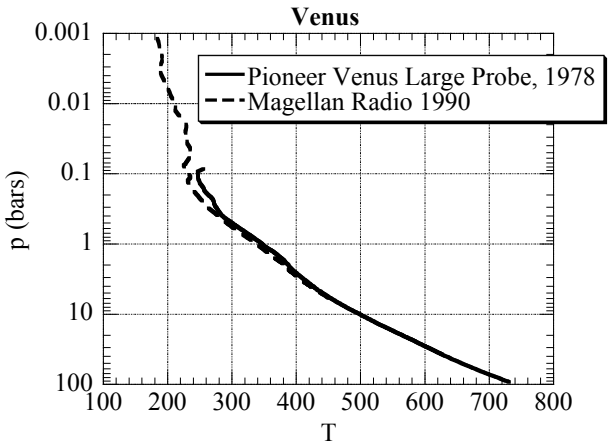
*How much carbon in the form of $\mathrm{CO}_2$ in Earth's atmosphere?*
*How much $\mathrm{N}_2$ does Venus have compared to Earth?*

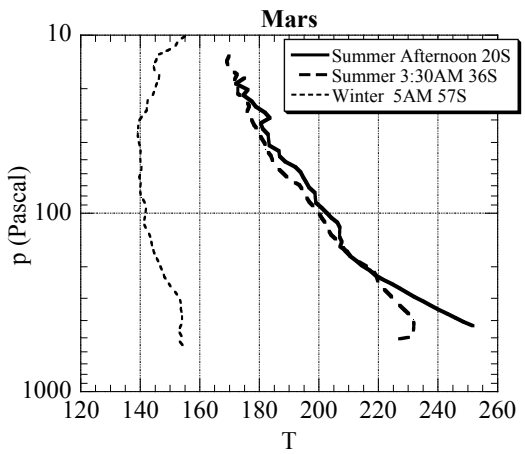
Done on $\mathbb{BLACKBOARD}$

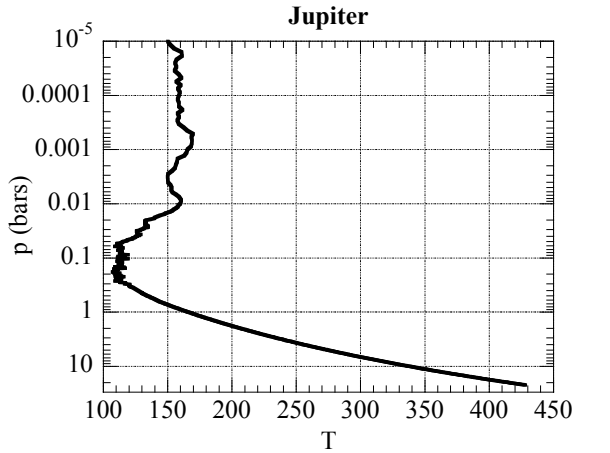
# Vertical structure of Earth atmosphere

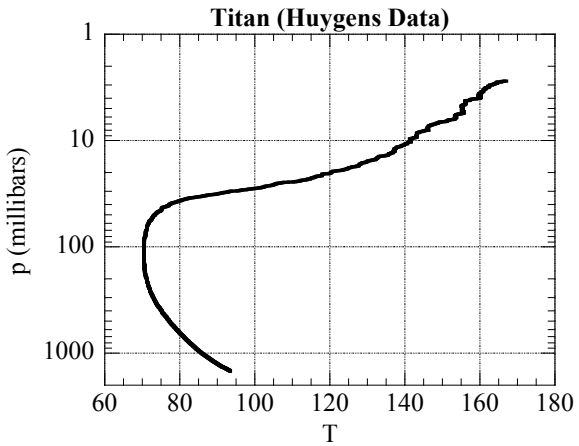


# Vertical structure of some other atmospheres

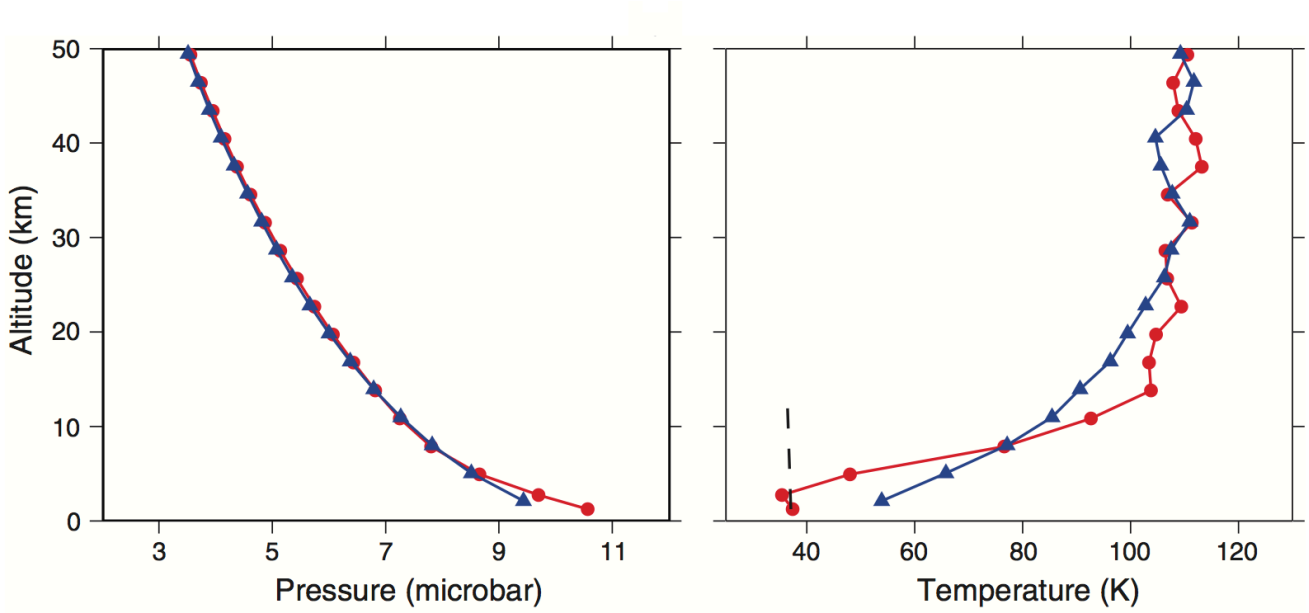


# New Horizons data for Pluto



*Why does temperature decrease with height in deep part of many atmospheres?*

# The First Law

Write in per-unit-mass form. $\frac{1}{\rho}$ is volume per unit mass.

$$du = \delta Q + dw = \delta Q - pd\frac{1}{\rho}$$

- For an ideal gas, the intensive form of the First Law remains valid even if there is mass loss from the system.
- For a non-ideal gas, if mass is lost or gained, there is an additiona "chemical potential" term.
- This is good to keep in mind for considering systems where mass can be lost, e.g. through condensation.

$$d(u + \frac{p}{\rho}) - \frac{1}{\rho}dp = \delta Q = TdS$$

$h \equiv u + \frac{p}{\rho}$ is the *enthalpy*

# The First Law, ideal gas case

In general $u = u(\rho, T)$, but for an ideal gas $u = u(T)$ and $du = c_v dT$

For ideal gas EOS, $\frac{p}{\rho} = RT$, so $du = (c_v + R)dT \equiv c_p dT$ .
$c_v$ generally dependes on $T$, but if constant, $h = c_p T$

# Entropy and adiabatic processes

$$c_p \frac{dT}{T} - R\frac{dp}{p} = \frac{1}{T}\delta Q \equiv dS$$

If $c_p$ is constant,

$$d(c_p \ln(T(\frac{p}{p_0})^{-R/c_p})) = dS$$

# Reversible processes, $dS = 0$

i.e. no heat added to or taken away from air parcel as it is expanded or compressed

$$\frac{d \ln T}{d \ln p} = \frac{R}{c_p}$$

Or, if $c_p$ is constant

$$d(c_p \ln(T(\frac{p}{p_0})^{-R/c_p})) = 0$$

*Potential temperature*:

$$\theta \equiv T(\frac{p}{p_0})^{-R/c_p}$$

is conserved, during expansion or compression.

# Air parcels: How this relates to an atmosphere

- "air parcel" = collection of molecules that stays together without mixing with surrounding environment
- For hydrostatic motion, pressure is a vertical coordinate, so changes in pressure correspond to changes in altitude
- If parcel is lifted or lowered rapidly enough that addition of heat by diffusion and radiation is insignicant, $dS = 0$ as the pressure adjusts to the ambient pressure at the new altitude.

# The dry adiabat in pressure coordinates

Constant $\theta$ implies

$$T(p) = T_0(\frac{p}{p_0})^{R/c_p}$$

$$\frac{R}{c_p} \approx \frac{2}{7}$$

(for diatomic gas at Earthlike temperatures)

For "well mixed" atmosphere, temperature goes down with altitude, and follows the dry adiabat

# The dry adiabat in z coordinates – "lapse rate"

$$\begin{aligned} 0 &= c_p dT - \frac{1}{\rho} dp \\ &= c_p dT - \frac{1}{\rho}\frac{dp}{dz} dz \\ &= c_p dT + g dz \end{aligned} \tag{2}$$

so

$$\frac{dT}{dz} = -\frac{g}{c_p}$$

(Important for observation of exoplanet atmospheres!)

*Can also derive from $T(p)$ expression by substituting in $p(z)$*

# Criterion for instability to convection

For a given temperature profile $T(p)$, if at a given point

$$\frac{d \ln T}{d \ln p} > \frac{R}{c_p}$$

then a parcel displaced adiabatically upwards (towards lower pressure) will be warmer than its surroundings and positively buoyant, and will continue to rise. A parcel displaced adiabatically downwards will be negatively buoyant relative to its surroundings and continue to sink. Convection will be triggered in the vicinity of all such points. (Valid even if $c_p$ depends on $T$)

# Conservation of enthalpy

**Theorem:**

$\frac{1}{g} \int \int \int h dx dy dp$ is conserved after mixing.

Assumes:

- Initial and final state are at rest and in hydrostatic balance (Kinetic energy is generated by buoyancy but later dissipated as heat)
- No energy or mass enters or leaves the domain
- This result does not require the ideal gas equation of state

Flow need not be hydrostic during mixing

# Conservation of enthalpy: Simplified derivation

For a fluid at rest, the only way to store energy is as internal energy $u$ and potential energy $gz$ (both per unit mass.) The column integral over the whole atmosphere gives the energy per unit cross-section area in the column:

$$E = \int_0^\infty \rho(u + gz)dz = \frac{1}{g}\int_0^{p_s} (u + gz)dp$$

if hydrostatic. Further, using the hydrostatic approximation and integration by parts on the $gz$ part of the integrand, and assuming a flat surface at $z = 0$,

$$\int_0^{p_s} zdp = \frac{1}{g}\int_0^{p_s} \frac{p}{\rho}dp$$

# Conservation of enthalpy: Simplified derivation, cont'd

whence

$$E = \frac{1}{g}\int_0^{p_s}(u + \frac{p}{\rho})dp = \frac{1}{g}\int_0^{p_s} h dp$$

See supplementary notes `DryEnthalpy.pdf` for a more complete derivation of enthalpy conservation, based on the equations of fluid dynamics.

# Temperature dependence of specific heat

- For ideal gas, energy can be stored only in kinetic energy of molecules and energy (potential and kinetic) of the internal motions of the molecules.
- *Equipartion* Each degree of freedom which can store energy gets a "fair share" of the available energy
- For degrees of freedom whose energy is quadratic in the corresponding coordinate, the "fair share" is $\frac{1}{2}kT$
- Examples of quadratic quantities: Kinetic energy ($\frac{1}{2}mv^2$), rigid rotation ($\frac{1}{2I}J^2$; $J$ ang. momentum, $I$ moment of inertia )

# Temperature dependence of specific heat, cont'd

If $n_d$ is number of degrees of freedom of a molecule of mass $m$, the internal energy per unit mass is

$$u = \frac{n_d}{2}\frac{k}{m}T = \frac{n_d}{2}RT$$

so $c_v = \frac{n_d}{2}R$ and $\frac{R}{c_p} = \frac{2}{n_d+2}$

- Monatomic gases (e.g. He), $n_d = 3$, $\frac{R}{c_p} = \frac{2}{5}$. Close to measured value, with no temperature dependence.
- Diatomic gases (e.g. $\mathrm{N}_2$ and $\mathrm{O}_2$ which dominate dry Earth air) should have 3 translational, 3 rotational and 2 vibrational d.f, so $\frac{R}{c_p} = \frac{2}{8}$, but at Earthlike temperatures measured value is close to $\frac{2}{7}$. Why the missing d.f.?

# Temperature dependence of specific heat, cont'd

The answer comes from quantum theory. For degrees of freedom that are quantized (i.e. everything other than translational kinetic energy) it takes a certain minimum of energy to excite a given degree of freedom.

- The three translational degrees of freedom are always excited. For monatomic gases these are the only degrees of freedom. (electron states are not excited except at high temperatures). Monatomic gases exhibit almost no temperature dependence of specific heat.
- Rotational degrees of freedom are generally fully excited, except quite close to absolute zero. However, for collinear molecules (all diatomic molecules, also $\mathrm{CO}_2$, the rotational d.f about the line joining the molecules (with very small moment of inertia) is never excited.

# Temperature dependence of specific heat, cont'd

- Collinear molecules therefore have only 2 rotational d.f.
- For diatomic molecules, vibrational modes are not significantly excited until temperatures much higher than Earthlike temperatures. There are thus 3+2=5 effective degrees of freedom. $R/c_p = 2/7$
- As temperature increases, more vibrational states are excited, leading to an increase in specific heat.
- Triatomic and higher molecules have more complex vibrational states, which are somewhat easier to excite.
- $H_2$ is a special case, because of the presence of ortho and para nuclear spin isomers.

# CAPE

CAPE $\equiv$ Convective Available Potential Energy

Lift parcel adiabatically from its initial level to a new level. Let $\rho_\ell$ be density of lifted parcel, $\rho_a$ the ambient density at the new level. The acceleration due to buoyancy experienced at the lifted level is

$$a = \frac{\rho_a - \rho_\ell}{\rho_\ell} g = \frac{1/T_a - 1/T_\ell}{1/T_\ell} g = \frac{T_\ell - T_a}{T_a} g$$

Kinetic energy (per unit mass) of nondilute parcel lifted by buoyancy from $z_0$ to $z_1$:

$$\frac{1}{2} w_1^2 = \int_{z_0}^{z_\ell} \frac{T_\ell - T_a}{T_a} g dz = \int_{p_\ell}^{p_0} R \cdot (T_\ell - T_a) d \ln p$$

... using ideal gas law and hydrostatic balance. (BLACKBOARD)

# CAPE, cont'd

## Level of free convection

$p_{\text{free}} \equiv$ Level $p_1$ where $a = 0$ ($T_\ell = T_a$) for first time as parcel is lifted from $p_0$

## Level of neutral buoyancy

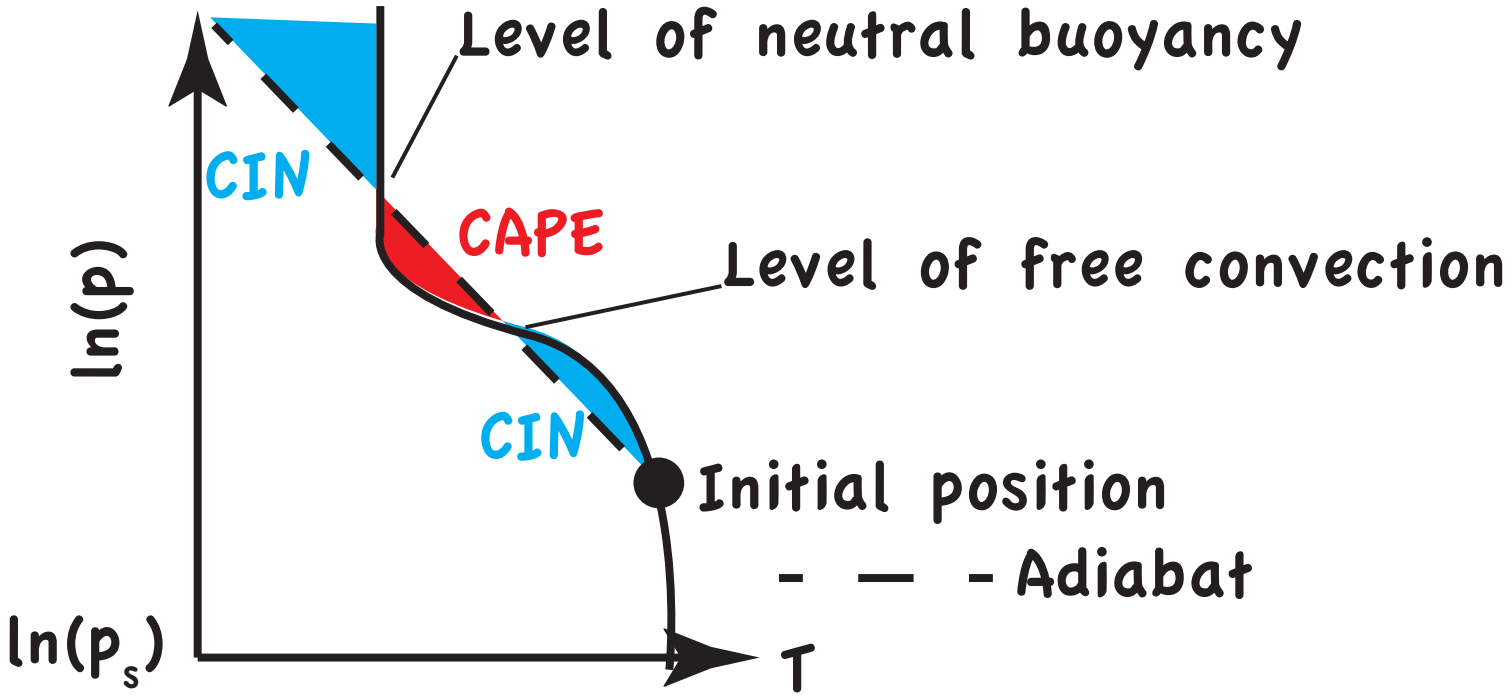
$p_n \equiv$ Level $p_1$ where $a$ returns to zero ($T_\ell = T_a$ again) as parcel is lifted further

## Definition of CAPE

$$\text{CAPE} \equiv \int_{p=p_n}^{p_{\text{free}}} R \cdot (T_\ell - T_a) d \ln p$$

$p_{\text{free}}$ is the boundary between negative and positive buoyancy. Buoyancy of the lifted parcel is positive for $p_{\text{free}} > p > p_n$

# CAPE, cont'd




Negative CAPE is also known as Convective Inhibition (CIN).

# (Dry) Convective Adjustment

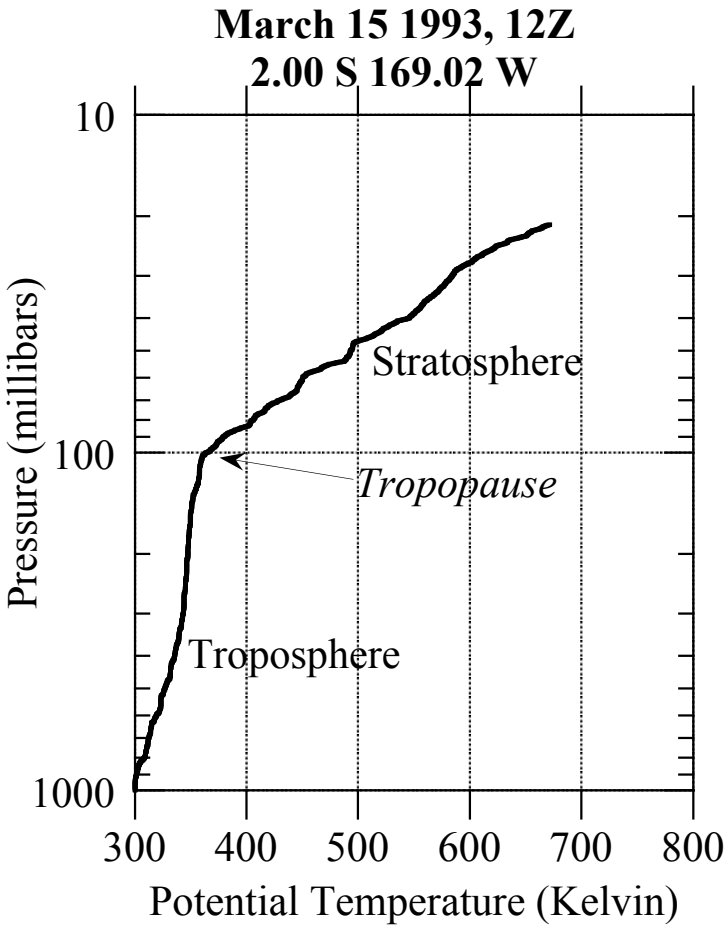
- If $\frac{d \ln T}{d \ln p} > \frac{R}{c_p}$, the fluid is unstable to convection at that point.
- The resulting turbulent mixing will adjust the local slope to $\frac{R}{c_p}$ while preserving enthalpy
- However, the local adjustment typically creates instability at other layers, so the process must be iterated until there is no instability left anywhere
- The final adjusted state has either slope $= \frac{R}{c_p}$ or slope unchanged from original state, at each $p$
- Additional *ansatz*: No "overstabilization"

# The main take-home point

In a region of strong convection, $T(p)$ relaxes towards the adiabat. Convection on terrestrial type planets can be driven by absorption of incoming light from the planet's star at the ground. Convection on gaseous planets (e.g. Jupiter) can be driven by absorption of starlight penetrating into the deep atmosphere, or by residual heat of formation escaping from the planetary interior

Heat escaping from the interior is significant on gaseous planets because fluid motions can efficiently transport heat. For rocky planets, heat can diffuse only slowly through the solid crust, or be transported only slowly by very slow motions in the planet's highly viscous rocky interior.

# The reality (for Earth)




Venus and Jupiter case explored in Problem Sheet 2

# Conservation of dry enthalpy during mixing

October 19, 2020

## 1 Simplified derivation done on whiteboard in lecture

A typical situation that we shall encounter is that a column of the atmosphere, which does not exchange energy or mass with adjacent columns, receives some energy that stirs up some motion in the column. We would like to be able to use energy conservation to constrain the state that the column settles into after the motion has dissipated (turning into heat), and the column has attained a state of rest. For example, in an initially stable column of air, some absorption of a stated amount of solar energy at the ground would heat the adjacent air, leading to buoyancy and subsequently convective mixing of some portion of the column. Energy conservation can help to determine the adjusted state of the column after the low level heat has been redistributed.

The potential energy of a column of atmosphere between altitude $z_1$ and $=z_2$ is

$$PE = \int_{z_1}^{z_2} \rho g z dz = \int_{p_2}^{p_1} z dp \tag{1}$$

where $z$ is altitude and the second equality assumes the hydrostatic relation. $p_1$ is the pressure at altitude $z_1$ and similarly for $p_2$. Integrating by parts and using the hydrostatic relation,

$$PE = p_1 z_1 - p_2 z_2 - \int_{p_2}^{p_1} p dz = p_1 z_1 - p_2 z_2 - \int_{p_2}^{p_1} p \frac{dz}{dp} dp \tag{2}$$

$$= p_1 z_1 - p_2 z_2 - \int_{p_2}^{p_1} p \frac{dz}{dp} dp \tag{3}$$

$$= p_1 z_1 - p_2 z_2 + \int_{p_2}^{p_1} \frac{p}{\rho} \frac{1}{g} dp \tag{4}$$

$$\tag{5}$$

We have not needed to make use of the ideal gas equation of state, so Eq. 5 is valid for an arbitrary substance. The boundary term $p_1 z_1$ is the work done at constant pressure to lift the entire column of atmosphere above $z_1$ to its current altitude, while the term $p_2 z_2$ subtracts the work done by the column between $z_1$ and $z_2$ on the air above $z_2$. For example, if heat were added to the layer, it would expand, increasing $z_2$, and the work

done to increase the potential energy over the overlying air would be taken from the change in internal energy $u$, just as in the classical thermodynamic thought-experiment involving a cylinder of gas topped by a movable piston that supports a weight. If the integral is taken over the entire atmosphere, $p_2 z_2 = 0$ and $p_1 z_1 = p_s z_s$, where $z_s$ is the elevation of the surface. Since the surface elevation can be considered unchanging, the remaining boundary term is a constant so long as $p_s$ doesn't change, which for a thin shell is assured for hydrostatic balance if the mass of the atmosphere does not change. $p_s z_s$ does, however represent an actual reservoir of potential energy which can be tapped to do work if the column of air were to be moved to a lower altitude, for example by flowing down a mountain slope.

Let $\Delta F$ be the change in a quantity $F$ between an initial state and a final state, with both considered to be at rest and in hydrostatic balance. Allowing for work done, the change in energy storage is

$$\Delta(\int_{p_2}^{p_1} u\frac{1}{g}dp + P.E.) = (p_1\Delta z_1 - p_2\Delta z_1) + \int_{p_2}^{p_1} \delta Q\frac{1}{g}dp \tag{6}$$

where the first term on the right hand side allows for the work done by and on the layer. The second term represents the heat added to or taken away from the layer, for example by absorption of solar energy or emission of infrared radiation. Substituting in Eq. 5 and canceling the work terms between the two sides,

$$\Delta \int_{p_2}^{p_1} h\frac{1}{g}dp = \int_{p_2}^{p_1} \delta Q\frac{1}{g}dp \tag{7}$$

where we have used the expression for enthalpy, $h \equiv u + p/\rho$. Eq. 7 is valid even for a non-ideal gas.

# 2 Derivation from equations of fluid motion

In this derivation we assume cartesion coordinates $x, y, z$, with $z$ in the vertical direction and $x$ and $y$ being horizontal. A local cartesian coordinate system is used because in this derivation we are concerned with mixing driven by convection, which typically occurs on a scale much smaller than the entire planet. The corresponding velocity vector is $\vec{v} = v_x\hat{x} + v_y\hat{y} + v_z\hat{z}$. Small scale convection is usually nonhydrostatic, so we do not make the hydrostatic approximation here.

Let $\frac{d}{dt}$ be the material derivative, which gives the total derivative of a quantity following along the trajectory of a fluid parcel. It is given by

$$\frac{d}{dt} = \partial_t + \vec{v}\cdot\nabla \tag{8}$$

Let $\rho$ be density $p$ be pressure and $T$ be temperature

The equation for conservation of mass is

$$\partial_t\rho + \nabla\cdot\vec{v}\rho = 0, \tag{9}$$

which can also be written as

$$\frac{d}{dt}\rho + \rho\nabla\cdot\vec{v} = 0 \tag{10}$$

The equation for momentum is

$$\rho \frac{d}{dt}\vec{v} = -\nabla p - \rho g \hat{z} \tag{11}$$

where $g$ is the acceleration of gravity The equation for the First Law of Thermodynamics following a fluid parcel is

$$\frac{d}{dt} c_v T + p \frac{d}{dt}\frac{1}{\rho} = \dot{Q} \tag{12}$$

We assume $c_v$ is constant here. The right hand side is the heat per unit mass per unit time added to or taken away from the fluid element. Later we will assume that it's integral over an entire column of atmosphere vanishes, but we do not require that it vanishes at every single point of the domain. The convection is redistributing heat within the column of atmosphere, but we will later assume no heat enters or leaves the column during the mixing.

First take the dot product of $\vec{v}$ with Eq. 11, and make use of the mass continuity equation to bring $\rho$ inside the derivative. This yields an equation for the rate of change of kinetic plus potential energy caused by the pressure work the fluid does:

$$\partial_t [\frac{1}{2}\rho v^2 + \rho g z] + \nabla \cdot [\frac{1}{2}\rho v^2 + \rho g z]\vec{v} = -\vec{v} \cdot \nabla p \tag{13}$$

In deriving this we have made use of the fact that $v_z = \frac{dz}{dt}$. The left hand side is in *flux form*, i.e the local time rate of change is expressed as a divergence of a flux. Thats nice, because we can use the divergence theorem to find the integral of the divergence over a volume in terms of the flux through the boundaries. . First write

$$\vec{v} \cdot \nabla p = \nabla \cdot \vec{v} p - p \nabla \cdot \vec{v} \tag{14}$$

The first term is the divergence of a flux, which we can later add in to the divergence on the left hand side of Eq. 13. We now need to do something to rewrite, and for this we turn to the heat equation, Eq. 12

Multiply the heat equation by $\rho$ and use the mass conservation to yield

$$\partial_t \rho c_v T + \nabla \cdot [\rho c_v T]\vec{v} - p \nabla \cdot \vec{v} = \rho \dot{Q} \tag{15}$$

The mass continuity equation is used in the form of Eq. 9 in rewriting the first term and in the form of Eq 10 in rewriting the second term. Now we add Eq 15 to Eq. 13 and use Eq 14. The result is that the $p \nabla \cdot \vec{v}$ term cancels out of both sides, leaving only terms in flux form. Gathering all the flux terms into one, we find

$$\partial_t [\frac{1}{2} v^2 + c_v T + g z)]\rho + \nabla \cdot \vec{\mathcal{F}} = \rho \dot{Q} \tag{16}$$

where the flux vector $\vec{\mathcal{F}}$ is given by

$$\vec{\mathcal{F}} = [\frac{1}{2} v^2 + g z + c_v T + \frac{p}{\rho}]\rho \vec{v} \tag{17}$$

This vector represents the flux of energy – the rate at which energy is carried from one place to another. Part of the flux is the energy density (kinetic plus potential plus thermal)

multiplied by the rate at which the flow carries the energy , but there is an additional flux term corresponding to transport of energy by pressure. If we now integrate over a column of atmosphere for which there is no flow through the boundaries, (think of it as convection in a box) and and assume that $\rho\dot{Q}$ integrates to zero over this region, then we find that the quantity

$$\mathcal{E} = \int\int\int [\frac{1}{2}v^2 + c_v T + gz)]\rho dz dy dx \tag{18}$$

has the same value between the initial and final state. We are assuming the initial state is at a state of rest, but is unstable to convection, so some of its potential energy is converted to kinetic energy which is used for mixing. In the absence of friction, the kinetic energy woud never go away, but if we assume that friction dissipates this kinetic energy as heat which stays in the domain (that frictional dissipation gets lumped into $\dot{Q}$) then the final state is at rest and has the same value of $\mathcal{E}$. Hence, the quantity

$$\int\int\int [c_v T + gz)]\rho dz dy dx \tag{19}$$

is the same between the initial and final state. This consists of the thermal energy and potential energy of the system.

So far we have not imposed the hydrostatic relation. Now let's assume that both the initial and final state are in hydrostatic balance. Then, we can write $\rho dz = -\frac{1}{g}dp$. Moreover,

$$\int_{z=0}^{\infty} gz\rho dz = -\int_{p=p_s}^{0} z dp = \int_{p=p_s}^{0} p dz = -\frac{1}{g}\int_{p=p_s}^{0} \frac{p}{\rho} dp = \frac{1}{g}\int_{p=0}^{p_s} RT dp \tag{20}$$

This assumes the lower boundary is flat. If the lower boundary is bumpy (i.e has a mountain) then we can no longer fix the lower boundary at $z = 0$ and an additional term arises from the boundary contribution when we do the integration by parts. The final step assumes the ideal gas law. Adding this term to the term arising from $c_v T$, we find that the following quantity is conserved between the inital and final state:

$$\int\int\int (c_v + R)T dp dy dx \tag{21}$$

Since $c_v + R = c_p$ we have shown that the net enthalpy is conserved between the initial and final state. Note that when we work in pressure coordinates and assume hydrostatic equlibrium, the potential energy term does not explicitly appear in the conservation equation.

Note that it is only in the final step that we invoked the ideal gas law, so this result very simply generalizes to the enthalpy of a non-ideal gas.

*Remark:* If we had put in the dissipation explicitly, the viscous term would appear as $\vec{\mathcal{D}}$ on the right hand side of Eq. 11, which would then contribute a kinetic energy dissipation term $\vec{v} \cdot \vec{\mathcal{D}}$ to the right hand side of Eq. 13. Since kinetic energy is dissipated as heat, a corresponding term $-\vec{v} \cdot \vec{\mathcal{D}}$ is added to the right hand side of Eq. 15. The two terms cancel when the equations are added. Note that the derivation can be simplified if

it is assumed that kinetic energy is rapidly dissipated into heat, so that the kinetic energy storage term can be neglected. In that case, the kinetic energy equation reduces to:

$$\partial_t[\rho g z] + \nabla \cdot [\rho g z \vec{v}] = -\vec{v} \cdot \nabla p + \vec{v} \cdot \vec{\mathcal{D}} \tag{22}$$

and the rest of the derivation proceeds as before, except that now the kinetic energy term no longer appears in the resulting conservation law.

# A primer in atmospheric thermodynamics
# Part II: "moist" atmospheres

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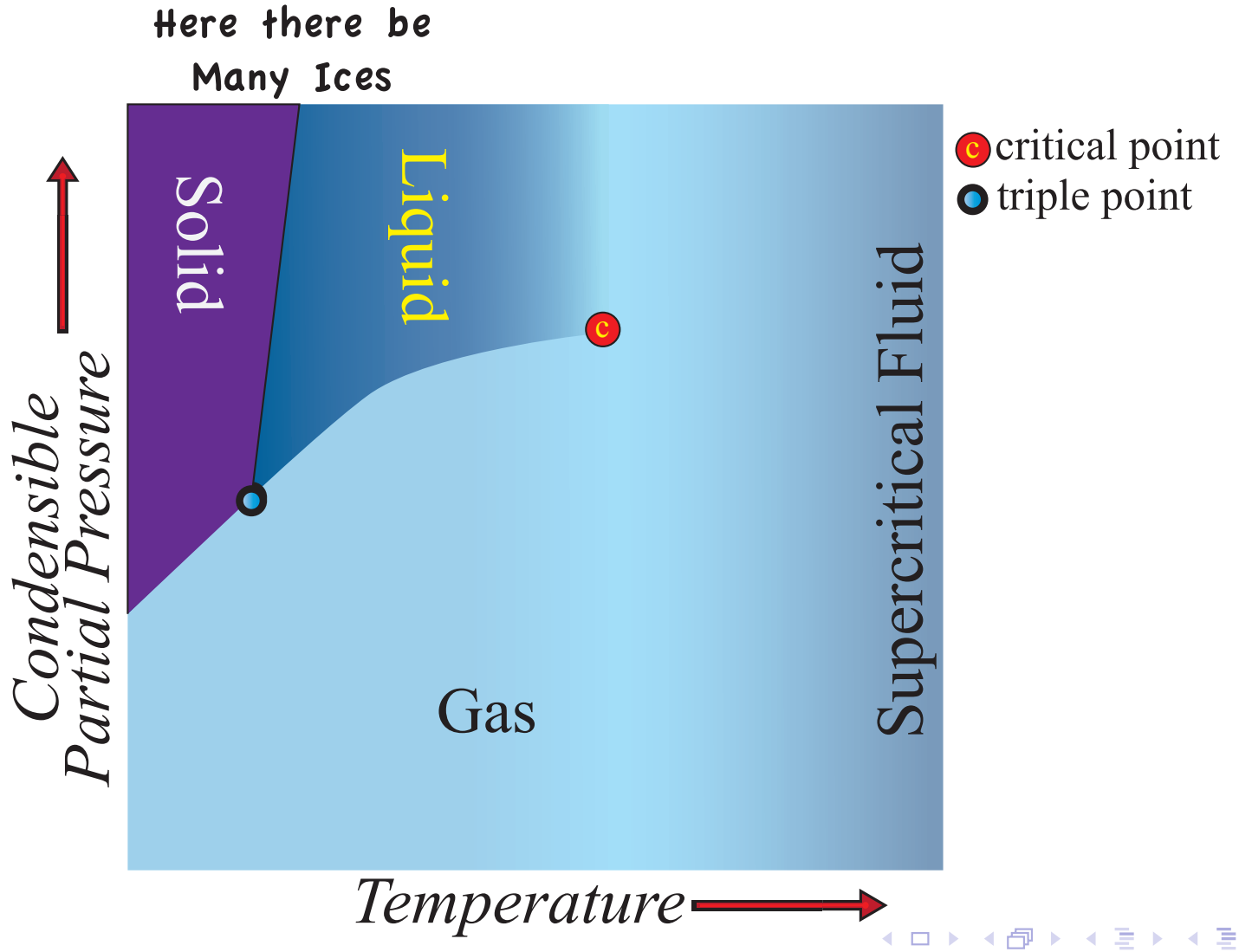
# Overview

Phase transitions and phase boundaries

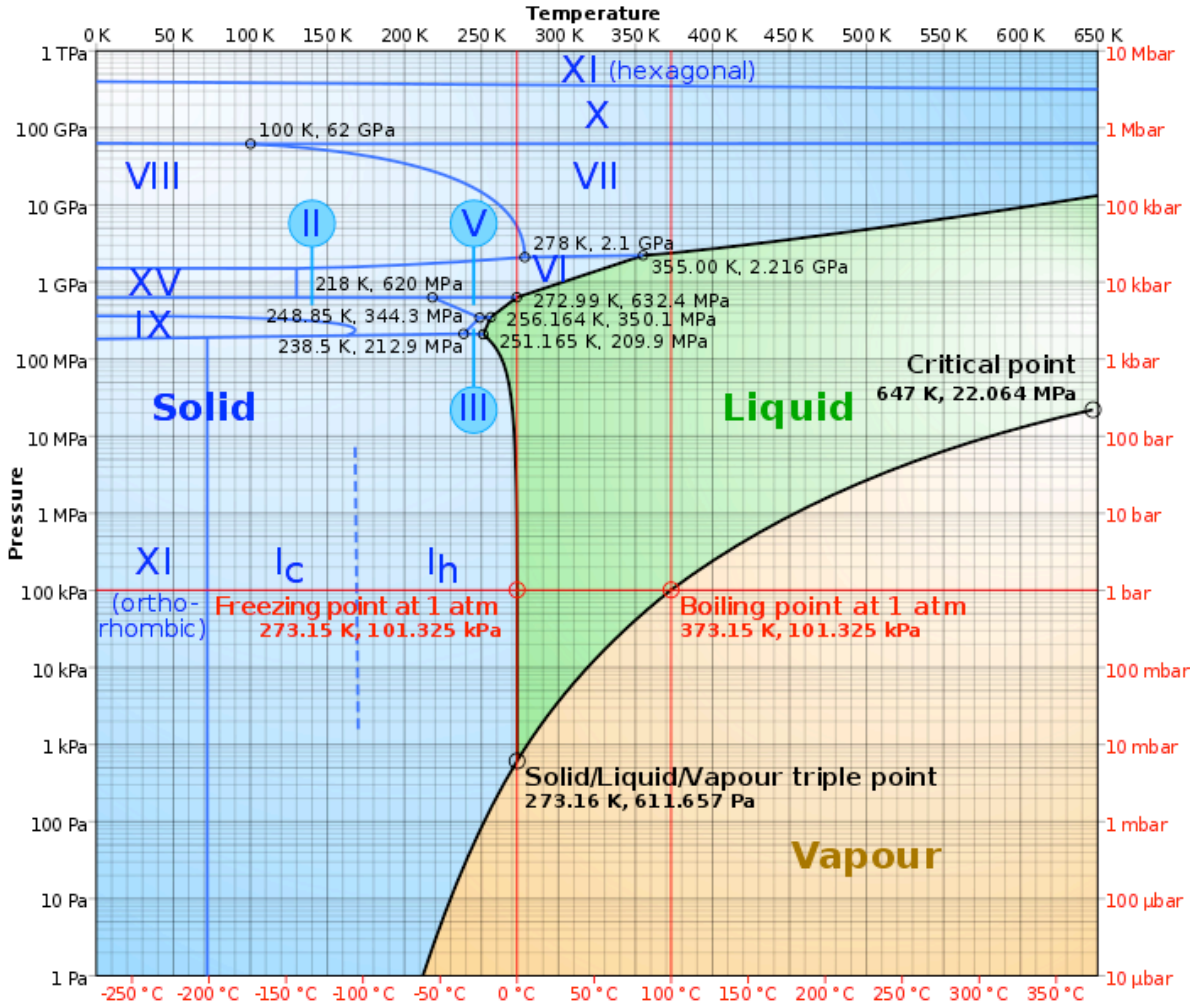
The moist pseudo-adiabat

Moist enthalpy and moist convection

# Generic Phase Diagram – pure substance



# Phase Diagram for Water



# Latent Heat

*(Specific) Latent heat $L_{A\to B}$ is the amount of energy released when a unit mass of a substance at temperature $T$ changes from Phase A to Phase B while keeping temperature fixed*

- Sign convention: Positive for energy released. E.g. for latent heat of vaporization vs condensation, $L_{\ell\to g} = -L_{g\to\ell} < 0$
- S.I. units are J/kg. Often quoted instead as molar latent heat, J/mol . Conversion factor from J/mol to J/kg is $1000/M$, where $M$ is molecular weight
- Same thing as enthalpy of phase change. Can get latent heat by taking differences in enthalpy of formation between two phases.

# On the BLACKBOARD...

- Sketch of two-phase system in a box with piston
- Examples of a few latent heats
- A few calculations using latent heat
  - How long to evaporate ocean during runaway greenhouse?
  - Ice ablation by melting vs. sublimation

# The Clausius-Clapeyron relation

$$\frac{d}{dT} p_{\mathrm{AB}} = \frac{1}{T} \frac{L_{\mathrm{AB}}}{\frac{1}{\rho_{\mathrm{A}}} - \frac{1}{\rho_{\mathrm{B}}}}$$

where $p_{\mathrm{AB}}$ is the phase boundary between phase A and phase B .

For ideal gas with A = gas phase, B = condensed phase and $\rho_g \ll \rho_B$,

$$\frac{dp_{\mathrm{sat}}}{dT} = \frac{L}{RT^2} p_{\mathrm{sat}}$$

where $R$ is gas constant for the substance undergoing phase change.

$\mathbb{BLACKBOARD}$ : Derivation of latter case, and exponential solution for constant $L$.

# Kirchoff relation for variation of latent heat with $T$

Approximate form for vapor to solid or liquid transition:

$$\frac{dL}{dT} = c_{p,g} - c_{p,\ell}$$

where subscript $\ell$ denotes condensed phase (solid or liquid).

Note: $L_{\text{vap}} \to 0$ at critical point.

# Why *pseudo* adiabat?

As we lift a parcel of atmosphere containing a condensible component, without allowing any external energy exchange, once condensation starts, the process will only be *reversible* if the condensate is retained, as happens with small cloud particles.

If we instead assume that condensate is instantaneously removed from the parcel, the resulting $T(p)$ is called the *pseudo-adiabat*. The process is not reversible, since the condensate mass has left the parcel, and is not available to re-evaporate if the parcel is compressed and warmed.

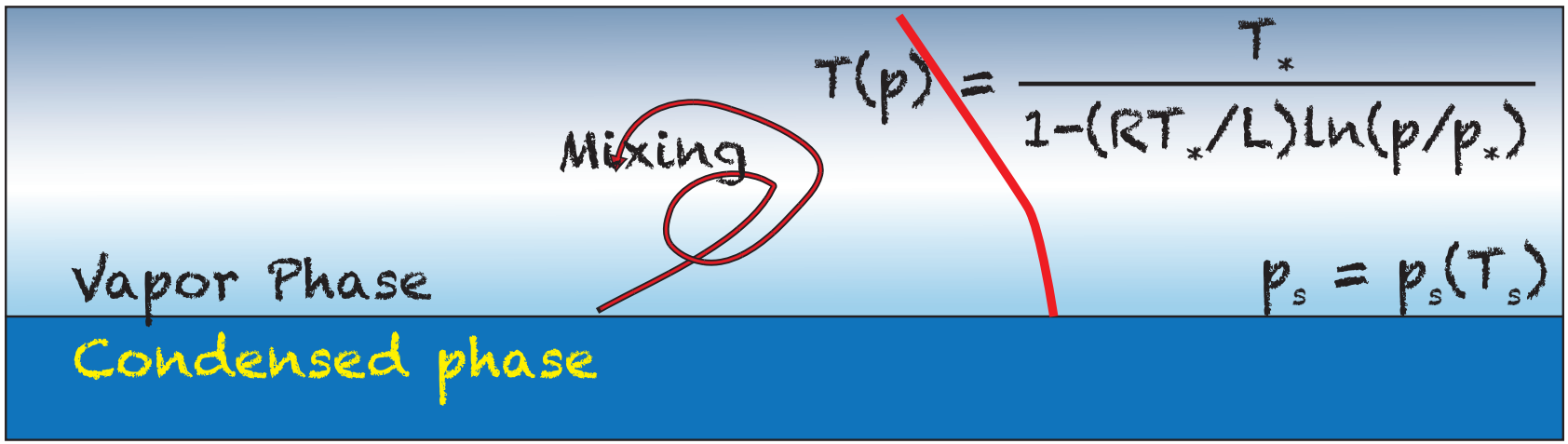
The pseudo-adiabat is nearly the same as the true adiabat if the amount of retained condensate mass is small (generally the case for Earth and many planetary clouds).

# Limiting case I: Moist pseudo-adiabat for a single-component atmosphere

Consider an atmosphere made up of a single chemical substance, which condenses somewhere in the temperature/pressure range encountered on the planet. e.g. $\mathrm{CO_2}$ condensing in a pure $\mathrm{CO_2}$ atmosphere, or $\mathrm{H_2O}$ condensing in a pure $\mathrm{H_2O}$ atmosphere (e.g. post-runaway steam atmosphere).

# Limiting case I: Moist pseudo-adiabat for a single-component atmosphere

Solve Clausius-Clapeyron for $T(p)$. This is also the *dew point* (or *frost point*) formula. For a single component saturated atmosphere total pressure $p$ is same as $p_{sat}$.




(constant $L$ approximation)

Mass of atmosphere determined by surface temperature!

# *Lifted Condensation Level* for a single-component atmosphere

If there is no condensed reservoir at the surface, then $p_s < p_{\rm sat}(T_s)$.
Lifted parcel follows dry adiabat $T_{\rm dry}(p) = T_s(\frac{p}{p_s})^{R/c_p}$ until we reach a pressure $p_{\rm LCL}$ where

$$T_{\rm dry}(p) = T_{\rm dew/frost}(p)$$

whereafter condensation starts and $T$ follows the single-component moist adiabat.

Sketch on BLACKBOARD

# Limiting case II: Moist pseudo-adiabat for an atmosphere with dilute condensible

- Atmosphere containing a gas "a" which doesn't condense anywhere
  (could be a mixture)
- ... mixed with a small amount of condensible "c"
- *Dilute* means $p_c/(p_a + p_c) \approx p_c/p_a \ll 1$
- Mass concentration $q \approx \epsilon(p_c/p_a)$, $\epsilon \equiv M_c/M_a$
- Diluteness $\rightarrow$ $p \approx p_a$, $c_p \approx c_{p,a}$, etc.

*e.g water vapor in present Earth atmosphere, which has concentrations of a few percent or less*

# Limiting case II: Moist pseudo-adiabat for an atmosphere with dilute condensible

Write first law per unit mass:

$$0 = c_p dT - R_a T d\ln p + L dq$$

If condensing, equilibrium with condensate maintains

$$q = q_{\rm sat} = \epsilon p_{\rm sat}(T)/p$$

Clausius-Clapeyron and algebra yield

$$\frac{d\ln T}{d\ln p} = \frac{R_a}{c_p}\frac{1+\frac{Lq_{\rm sat}}{R_a T}}{1+\frac{Lq_{\rm sat}}{c_p T}\frac{L}{R_c T}}$$

(Derivation, discussion on $\mathbb{BLACKBOARD}$ )

# The LCL for dilute moist atmospheres

- Suppose $p_c < p_{\rm sat}(T)$ at the surface (i.e. unsaturated) $q = q_0 = \epsilon(p_c/p_s)$
- Lifted parcel will follow dry adiabat $T_{\rm dry}(p)$
- $q$ fixed at $q_0$ so $p_{c,\rm lift} = \epsilon^{-1} q_0 p$
- Condensation begins when $p_{c,\rm lift} = p_{\rm sat}(T_{\rm dry}(p))$

Sketch on BLACKBOARD

# Digression: Measures of "humidity"

Let $p_c$ be partial pressure of the condensible

- *Specific humidity:* $q \equiv$ mass concentration of the condensible
- *Relative humidity:* $RH \equiv p_c / p_{c,sat}(T)$, often expressed as percent
  From $RH$, $T$ and total pressure $p$ you can compute $q$ or molar concentration, given the molecular weights of condensible and noncondensible gases.
- *Dew or frost point depression:* $T - T_{dew/frost}(p_c)$

Watch out for conventions about using saturation relative to liquid even when $T$ is below freezing point

# Moist enthalpy – sloppy approach for dilute condensible

For dilute case, $c_p \approx c_{p,a}$, unaffected by presence of condensible. Change in enthalpy is $c_p dT + L dq$. If $L$ can be regarded as approximately constant, then enthalpy change is

$$d(c_p T + Lq)$$

whence moist enthalpy is approximately $\boxed{c_p T + Lq}$.

Can estimate when $qdL$ is negligible using Kirchoff relation:

$$dL = (c_{p,g} - c_{p,\ell}) dT$$

where $c_{p,g}$ is the specific heat of the gas phase of the *condensible* component. So, need $(c_{p,g} - c_{p,\ell})q \ll c_p$; generally satisfied if $q \ll 1$.

# Moist CAPE, LFC, LNB

Moist CAPE is computed just the same as for dry CAPE, except that once the Lifted Condensation Level is reached and condensation begins, $T_{\rm lift}(p)$ is computed using the moist adiabat (or pseudo-adiabat) instead of the dry adiabat. Apart from this change, definition of CAPE, LFC and LNB are unchanged.

However, if the lifted air parcel starts off unsaturated, then it must be lifted along the dry adiabat, up until the Lifted Condensation Level (LCL) is reached, whereafter it is lifted along the saturated moist adiabat.

# Moist Convective adjustment – dilute case

Very similar to dry convective adjustment, except we need to keep track of the moisture budget

- Where $d \ln T / d \ln p >$ slope of saturated moist adiabat,reduce to the moist adiabatic slope while conserving moist enthalpy.
- ... but need to make an assumption about adjusted state moisture
- Typically assume $q = q_{sat}$ after adjustment, or sometimes adjust to specified fixed $RH$ instead of saturation
- Since $q_{sat}$ nonlinearly related to $T$, requires Newton iteration
- Excess moisture in initial vs. adjusted state is removed as precipitation

Nondilute case is really tricky: cf Feng & Pierrehumbert *ApJ*, and EXOCONDENSE

# But ... Complications!!!

- What if you need "negative rain" to reach the adjusted state, i.e. if there is not enough water vapor present in the initial state?
- Even if initial state has enough water, if it is subsaturated a finite amplitude lifting is required to cause condensation and trigger moist convection (unless initial state is unstable to dry convection) ...
- ... therefore, adjustment process should really be *nonlocal* ...
- ... and incorporate an assumption about level of "excitation"

# Compositional buoyancy and virtual temperature

Condensation changes $q$, affects mean molecular weight and $\rho$.

$$p = \rho R(q) T = \rho R_{\rm dry} (\frac{R(q)}{R_{\rm dry}}) T = \rho R_{\rm dry} T_v$$

(I prefer to work with potential density, instead of introducing $T_v$)

- On Earth, water vapor is "lighter than air"
- On Mars, because of Ar , sublimated $\mathrm{CO_2}$ is "heavier than air"
- In an $\mathrm{H_2}$ atmosphere water vapor is "heavier than air" (affects moist convection on Jupiter, Saturn)
- Similar things for many exoplanets

*Actually, compositional buoyancy can arise from any gas that is not well-mixed, not just from condensibles*

For many of the problems in this problem set, you will need thermodynamic data for various gases. Data for many substances can be found at the NIST Chemistry WebBook

`http://webbook.nist.gov/chemistry/`

and associated JANAF database

`http://kinetics.nist.gov/janaf/`

Note that "Enthalpy of vaporization" is the same thing as latent heat of vaporization. Also the JANAF database doesn't give latent heats directly, but these can be obtained by subtracting the enthalpy of formation for the gas vs liquid or solid phases. The NIST web-book has very good data on variation of specific heat with temperature, but in some cases JANAF is better. A convenient steam table giving latent heats for water all the way from freezing to the critical point is provided by Wikipedia:

`wikipedia.org/wiki/Water_(data_page)#Water.2Fsteam_equilibrium_properties`

Wikipedia also has useful latent heat data for $CO_2$:

`wikipedia.org/wiki/Carbon_dioxide_(data_page)`

Though $H_2$ is one of the most intensively studied gases, it is surprisingly hard to find low temperature thermodynamic data in public databases. The WebBook doesn't have specific heats below 298K, and the one datapoint in JANAF at 100K appears to be incorrect. I have provided some low-temperature data for $H_2$ where needed, courtesy of Pat Irwin's textbook, *Giant Planets in our Solar System*.

Hyperphysics has a good summary of the way "freezing out" of rotational modes and excitation of vibrational modes affects the specific heat at low temperatures and high temperatures, respectively. See

`http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/shegas.html`

In some cases you may need to convert from molar units to mass units. For example to convert to molar latent heat of $CO_2$ to mass-specific latent heat (i.e. J/kg) divide by .044, because 44 is the gram-molecular weight of $CO_2$.

Python computations can be carried out using the Physics Jupyter Notebook server at

`https://jhub.physics.ox.ac.uk:8000`.

Note that this now can be accessed through the Oxford VPN from any network, if you are not using the Physics subnet. Notebooks can also be run on the Google notebook server,

`https://colab.research.google.com` ,

which saves notebooks to your Google Drive space.

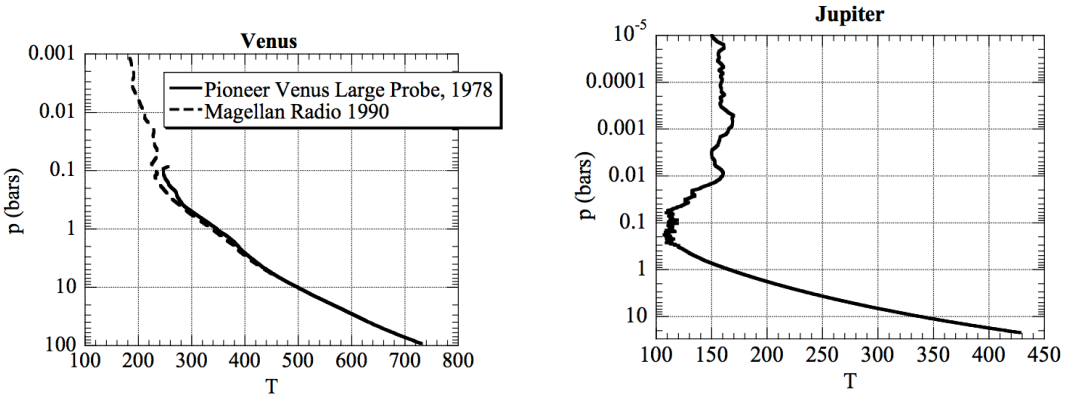



Figure 1: This figure shows temperature profiles for Venus and for Jupiter, as discussed in the lectures.

## Dry Atmospheric Thermodynamics

1. **Dry Adiabat**

   (a) Discuss the extent to which the temperature profiles follow the dry $CO_2$ adiabat in the Venus case, and a dry $H_2$ adiabat in the Jupiter case. Assume the ideal gas equation of state, and in your first attempt on the problem you may assume the specific heat $c_p$ to be constant. For $H_2$ on Jupiter, use the value of $c_p$ for $H_2$ at 300K, which is 14425. J/(kg-K), and for Venus use the value for $CO_2$ at 500K, which is 1015 J/(kg-K)

   (b) Extend your model of Jupiter by assuming the atmosphere to be a well-mixed mixture of $H_2$ and $He$. "Well mixed" means the mixing ratio is independent of height. Estimate the mole fraction (concentration by count of molecules) of He in the atmosphere by finding what value provides the best fit to the temperature profile. Compare this to the He mole fraction .137 measured *in situ* by the Galileo probe. Discuss possible reasons for any discrepancy you find. How does the result depend on the pair of pressure levels you use to do the estimate?

   (c) For the temperature range of the Jupiter sounding, $c_p$ is quite constant between 300K and 400K, but at lower temperatures, even though rotational degrees of freedom are more or less completely excited down to at least 150K, the temperature dependence of the proportion of ortho (aligned nuclear spin) vs. para (anti-aligned nuclear spin) hydrogen leads to a pronounced temperature dependence. Below 200K, the ortho:para ratio, and hence $c_p$, depends delicately on assumptions about whether the ratio has reached equilibrium, which takes a long time in the absence of catalysts such as provided by the surfaces of aerosol particles. Between 200K and 300K, $c_p$ increases from 13364 J/kg-K to 14425 J/kg-K, with an intermediate value of 14133.8 at 250 K. (Thanks to Pat Irwin for providing this data; the NIST webbook does not have data below 298K). Discuss how this temperature dependence would affect your estimate of the helium abundance.

   (d) In the case of Venus, the temperature range is great enough that vibrational modes begin to be excited, causing $c_p$ to increase with temperature. An empirical representation of $c_p(T)$ is given by the Shomate equation

$$c_p(T) = A + Bt + Ct^2 + Dt^3 + E/t^2$$

where $t \equiv T/1000$ with $T$ measured in Kelvins. You can look up the Shomate coefficients for $CO_2$ at `http://webbook.nist.gov/chemistry/`. Make sure to use the correct units (webbook values are given in $\mathrm{J}/(\mathrm{mol} \cdot \mathrm{K})$, where "mol" stands for gram-mole). You can use this equation to get a back-of-envelope estimate of how much difference the temperature dependance makes, but if you know how to solve a first order differential equation numerically using any programming language you can compute the actual dry adiabat, and are encouraged to do so. An example of how to use `SciPy` utilities to integrate an ordinary differential equation is provided in the collection of `Python` example scripts on the course web site.

If you want to use the data files from which the graphs were made, they can be found at `PlanetaryClimateBook.org`. Follow the link to the Data page, then the link for web access to individual data files. The data you want is in the Chapter 2 data collection.

**[Question Total 25]**

2. **Hydrostatics** Using the hydrostatic relation and the expression for dry potential temperature, show that for an isentropic (i.e. constant potential temperature) layer, the pressure and density go to zero at a finite altitude. Estimate what this altitude would be for a dry $O_2/N_2$ atmosphere on Earth with 300K surface temperature.

   Why doesn't the atmosphere abruptly terminate like this on Earth? (Note that the presence of moisture in Earth's atmosphere complicates the picture, but the essence of the answer is not there, since a parcel lifted a large distance gets cold enough to be essentially dry).

   **[Question Total 10]**

3. **Dry convective adjustment** A dry atmosphere consisting of a gas with temperature-independent $c_p$ and uniform composition (so $R$ does not vary with height) has the initial temperature profile

$$T(p) = T_\infty + \Delta T(\frac{p}{p_s})^a \tag{1}$$

   with $a > 0$, where $p_s$ is the surface pressure.

   (a) Under what circumstances is this atmosphere unstable to convection? When it is unstable, which portions of the atmosphere are unstable to small vertical displacements?

   (b) Discuss the pattern of CAPE and Convective Inhibition (CIN) for an air parcel lifted from the ground ($p = p_s$). Identify the level of free convection, the level of neutral buoyancy, and the level of maximum undilute ascent of an air parcel, and compute their values for a diatomic gas at Earthlike temperatures, for several values of $\Delta T/T_\infty$.

   (c) Now assume that convection adjusts the profile so as to eliminate the instability, leaving the atmosphere in a new state such that: (a) $T(p)$ is either replaced by the adiabat, or left unchanged, (b) $T(p)$ is continuous everywhere, and (c) enthalpy is the same between the initial and adjusted state. Determine the convectively adjusted state, for the case in which

the initial profile is unstable to convection. Discuss how the top ($p_1$) of the convectively adjusted region compares to the top of the initially unstable region. Do the two differ? If so, why? How does the top of the adjusted region compare to the level of neutral buoyancy and the level of maximum undilute ascent?

**[Question Total 25]**

## Moist Atmospheric Thermodynamics

4. **Condensation on ascent or descent?** From the case of clouds on Earth, we have come to expect that condensation occurs in the course of ascent, owing to the adiabatic cooling of the air parcel. However, it is not *a priori* obvious that this should be the case for atmospheres with different constituents having different thermodynamic properties. Cooling from ascent reduces the saturation vapor pressure, in accord with Clausius-Clapeyron, but ascent also reduces the pressure of the condensible gas being lifted which works against condensation. For example, if you compressed a gas isothermally (by bleeding off heat) instead of adiabatically, then condensation would occur on compression, not expansion. For Earthlike atmospheres, upon adiabatic ascent the cooling effect always wins, but are there atmospheres for which this would not be the case?

   Consider a parcel of atmosphere with total pressure $p_0$ and temperature $T_0$. The parcel contains a condensible component, which is saturated – i.e. its partial pressure equals the saturation vapor pressure for the substance in question given by Clausius-Clapeyron at temperature $T_0$. Now suppose the parcel is displaced adiabatically to a pressure $p_1$ only slightly different from $p_0$, without allowing condensation to occur. $p_1 > p_0$ corresponds to descent and $p_1 < p_0$ corresponds to ascent. In this problem you are to derive a criterion based on $T_0$, $p_0$ and the thermodynamic properties of the gases involved, which determines whether condensation occurs on ascent or descent.

   The basic approach is to derive expressions for $\frac{d\ln p}{d\ln T}$ on the dry adiabat and use that together with an expression for the change in saturation vapor pressure to determine whether the adiabatically displaced parcel becomes supersaturated on ascent or on descent. In essence, you are comparing the slope of the dry adiabat on a $\ln p$ vs. $\ln T$ thermodynamic diagram with the slope of the phase boundary between condensed and gaseous phases in the same coordinates.

   In carrying out this problem you may use the simplified form of Clausius Clapeyron in which the partial volume of the condensed phase $1/\rho_{\rm cond}$ is neglected.

   Assume that the condensible gas is the sole constituent of the atmosphere (e.g. a pure water vapor or pure $CO_2$ atmosphere). In this case, the total pressure is identical to the partial pressure of the condensible, so the phase boundary slope is given directly by Clausius-Clapeyron. You should find that the condensation criterion depends only on $c_p(T_0)$,$L(T_0)$ and $T_0$.

   Discuss the combinations of thermodynamic properties and temperatures for which condensation might happen upon compression (descent) rather than ascent, drawing on examples of typical values of $c_p$ and $L$ for various gases. Pay particular attention to the implications of the existence of a critical point, which limits the maximum temperature to be considered; it is also important that $L \to 0$ near the critical point. (Note that to compute the behavior very near the

critical point, one would need to use the full version of Clausius-Clapeyron, and also perhaps a non-ideal equation of state).

Evaluate your criterion for $H_2O$ at 300K, 400K, 500K and 600K. Do the same for $CO_2$ at 180K, 220K, 250K and 300K. Note that for 180K the phase transition is to solid, not liquid so you must use the latent heat appropriate to that case (which is relevant to the Martian atmosphere). Discuss

Explore other gases and temperatures to see if you can find a case that condenses on descent.

**[Question Total 20]**

5. **Moist adiabat basics**

The formula for the logarithmic slope of the dilute moist adiabat is

$$\frac{d\ln T}{d\ln p} = \frac{R_a}{c_{p,a}} \frac{1 + Lq/(R_a T)}{1 + L^2 q/(c_{p,a} R_c T^2)} \tag{2}$$

where $L$ is the latent heat of condensation , $q$ is the mass specific humidity at saturation (same as the mass mixing ratio in the dilute limit) and subscript $a$ denotes the noncondensible background gas. You can compute $q$ from the saturation vapor pressure given by the Clausius-Clapeyron relation. For the purposes of this problem, you may use the simplified form of Clausius-Clapeyron based on constant latent heat $L$ and neglecting the volume occupied by condensate. With those assumptions you can compute the saturation vapor pressure analytically, given $L$ and any point on the phase boundary. You should pick a point that has temperature representative of the general range of temperatures you are considering in the following calculations.

(a) For the case of water vapor in a background of Earth air, compute the behavior of the moist adiabatic slope defined above, as temperature ranges from 200K to 320K, with pressure fixed at $5 \times 10^4$Pa, and discuss the deviation from the dry adiabatic slope. Check how well the diluteness assumption is satisfied at 320K. You can present your results in the form of a table, or (better) as a graph. Next, carry out the same analysis for condensible methane in a background of noncondensing $N_2$, at a fixed pressure of $10^5$Pa. This case is relevant to Titan. In this case, explore the temperature range from 80K to 100K. (Since this range crosses the triple point, you should ideally switch from latent heat of sublimation to latent heat of vaporization at the triple point when computing saturation vapor pressure, but to keep things simple you can leave the latent heat fixed at the value for sublimation).

(b) Compute and plot the moist adiabat $T(p)$ for condensible water vapor in Earth air, assuming a surface pressure of 1 bar and a surface temperature of 305K. Plot the dry adiabat for comparison. Also plot a profile of the specific humidity corresponding to the moist adiabat. Make sure to extend your plot to sufficiently low pressures that you can see the slope transition to the dry adiabatic slope. The $T(p)$ plot works best if you use a logarithmic pressure axis, and the $q(p)$ plot works best as a log-log plot, owing to the very large range of $q$.

Do the same for condensible methane in an $N_2$ background, with surface pressure 2 bars and surface temperature 90K

**[Question Total 20]**