1.1.2.7 Column abundance

The column abundance of a gas, $N(z)$, is the number of molecules per unit area above a surface at altitude z, given by

$$N_c(z) = \int_z^\infty n(z)dz \qquad (1.19)$$

where $n(z)$ is the number of molecules of the gas per unit volume at altitude z.

The column mass is $N_c(z)\bar{m}$, so the pressure at altitude z, is $p(z) = N_c(z)\bar{m}g$. Using this, we obtain an expression for the column abundance in terms of scale height H:

$$N_c(z) = \frac{p(z)}{\bar{m}g} = \frac{n(z)kT(z)}{\bar{m}g} \implies N_c(z) = n(z)H(z) \qquad (1.20)$$

Column abundance is usually expressed in units of **molecules per cm^2**. However, planetary science also employs the unit "cm-atm" or "cm-amagat". This is the number of centimeters of a column produced if the gas were taken to standard temperature and pressure. The relationship with the column abundance $N_c(z)$ is as follows:

$$\mathcal{N} \text{ cm-atm} = \frac{N_c(z)}{n_0} \text{ where } n_0 = \frac{p_{STP}}{kT_{STP}} = 2.687 \times 10^{19} \text{ molecules cm}^{-3} \qquad (1.21)$$

where $N_c(z)$ is in units of molecules cm^{-2}. Here, n_0 is the *Loschmidt number*, the molecular number density in cm^{-3} of an ideal gas at standard conditions of $p = 1$ atm = 101325 Pa and $T = 273.15$ K.

EXAMPLE: Observations of peak ozone levels on Mars by NASA's Mariner 9 orbiter spacecraft are reported in the literature as a column abundance of ~10 μm-atm. How does this compare with a typical O_3 column abundance on Earth of ~8×10^{18} cm^{-2}? What does it mean for UV fluxes on Mars? What does it mean for life on Mars?

The Dobson Unit (DU) *for ozone*

A DU is the depth in thousandths of centimeters of a column of ozone taken to 1 atm and 0°C. So column abundance in DU is related to $\mathcal{N}$ by the following expression:

$$\text{Dobson Units} = 1000\mathcal{N} \text{ cm-atm } O_3 = \frac{1000N(z)}{n_0} \qquad (1.22)$$

One DU refers to a layer of ozone that would be 0.01 mm (or 0.001 cm) thick at STP. Earth's ozone column abundance varies with latitude and time, but is typically about 300 DU, equivalent to a layer of pure ozone that is 3 mm thickness at STP.

Precipitable Microns

For atmospheric water vapor there is yet another measure of column abundance, which is the depth of water that would result if all the water were condensed out from an atmospheric column onto the surface. This is measured as **precipitable centimeters** (pr cm) on Earth, and on Mars as **precipitable microns** (pr µm). On Earth, a typical water column abundance is 3 pr cm. In contrast, the Martian atmosphere contains an average 10 pr µm of water.

EXAMPLE:
How many kilograms of water are there per sq. meter on Mars, typically?
Given the surface area of Mars of 144.8 x 10^6 km^2, how much water is there on Mars in the atmosphere? Express it in terms of the size of an equivalent cube of liquid water?

1.1.3 Convection and Stability

What determines the vertical thermal structure? Two physical processes mainly: radiation and convection. These interact with each other and aspects of atmospheric dynamics.

Convection occurs when air parcels become buoyant. Several processes drive buoyancy:
1.
2.
3.
4.

Buoyant air parcels rise and displace adjacent air, which mixes an atmosphere. Sinking parcels contract and warm.

The rate that temperature *T*, decreases with altitude *z*, is **the *lapse rate*, $\Gamma = -(dT/dz)$**, usually given in K per km. For example, on Earth, the global average tropospheric lapse rate is ~6 K km^{-1}. Thus, the minus sign convention makes Γ positive.

In an idealized case where the temperature of the air parcel warms by contraction or cools by expansion with no exchange of energy with its surroundings either by conduction or

radiation, the temperature change is *adiabatic*. In this case, the temperature change with altitude is the *adiabatic lapse rate*, $\Gamma_a = -(dT/dz)_a$.

The condition for convection is that the ambient lapse rate exceeds the adiabatic rate, $\Gamma > \Gamma_a$. Then a parcel rising adiabatically will be at a warmer temperature than surroundings (which have cooled more rapidly with height) and the parcel continue to rise. An *unstable* atmosphere mixes quickly so temperatures adjust to the adiabatic profile.

Thus, Γ_a = a limiting lapse rate. We expect to find *stable* atmospheres with $\Gamma \leq \Gamma_a$.

We do: On average this is observed in planetary atmospheres. However, we should be wary of *superadiabatic* conditions:
(i) in Earth's tropics Γ > a moist adiabatic lapse rate. What kind of weather results?

(ii) within a few meters of planetary surfaces in daytime Γ can exceed Γ_a by a factor of hundreds or thousands. On Mars the atmosphere cannot keep up with the daytime warming of the surface and gives rise to dust devils or thermal vortices commonly.
(iii) superadiabatic conditions near ground-level means that gases released at the surface travel upwards and are dispersed.
    In the cloudless terrestrial atmosphere, the ambient lapse rate is often superadiabatic near the ground and nearly adiabatic at higher levels. Consequently, gases released at the surface travel upwards and are dispersed. However, sometimes an *inversion* arises, meaning that the lapse rate is negative and temperature increases with height. In this case, the atmosphere is highly stable, and gases get trapped near the ground.
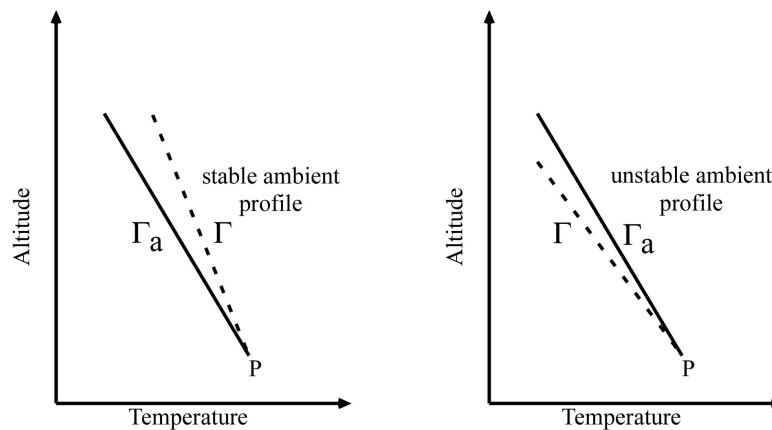

Fig. 1.5. The adiabatic lapse rate (Γ_a) as a solid line and the ambient lapse rate ($\Gamma = -dT/dz$) as a dashed line. The left-hand profile is stable because $\Gamma < \Gamma_a$, i.e. the decrease of temperature with altitude is smaller than in the adiabatic case (think of the x-y axes the other way around, if it helps). A parcel displaced *adiabatically* from point P will be colder and denser than its surroundings and so will tend to return to P. In the right-hand graph when $\Gamma > \Gamma_a$, the atmosphere is unstable to convective mixing. A parcel will continue rising from point P. However, the adiabatic assumption will break down, so the

parcel will lose its heat to the air aloft and the ambient profile will move towards adiabatic.

1.1.3.1 The (dry) adiabatic lapse rate and observed lapse rate: Derivation

The adiabatic lapse rate comes from energy conservation&hydrostatic eq. &ideal gas law.

Start with conservation of energy (the first law of thermodynamics), which is

$$\text{heat input} = (\text{change in internal energy}) + (\text{work done})$$
$$dq = du + dw$$

(1.23)

Here the dq, du and dw are energy changes **per unit mass**, which we indicate through using lower case letters. Now, the definition of specific heat at constant volume is $c_v = (du/dT)_v$, where the v subscript indicates constant volume, from which we get $du = c_v\, dT$. Also a small increment of work dw is given by "force $\times$ incremental distance", which is equivalent to "pressure $\times$ incremental volume change". If we define specific volume (volume per unit mass) as $\alpha = 1/\text{density} = 1/\rho$, we have $dw = pd\alpha$. Consequently, substituting for du and dw, we have

$$dq = c_v dT + pd\alpha$$

(1.24)

$\underbrace{}_{\text{heat added / kg (zero for adiabatic)}}$ $\underbrace{}_{\text{change in internal heat /kg}}$ $\underbrace{}_{\text{work done / kg}}$

In this equation, dq is a very small heat input (e.g., from sunlight), dT is a small rise in temperature, and $d\alpha$ is a small increase in parcel volume. From the ideal gas law $p = \rho\bar{R}T$, it follows that $p\alpha = \bar{R}T$, so $\alpha = \bar{R}T / p$. By applying the product rule [$d(xy) = x\, dy + y\, dx$] to both sides of this, gives us:

$$d\alpha = (\bar{R}/p)dT - (\bar{R}T/p^2)dp$$

Substituting in the conservation of energy equation for $d\alpha$:

$$dq = c_v dT + p\left[\frac{\bar{R}}{p}dT - \frac{\bar{R}T}{p^2}dp\right] = (c_v + \bar{R})dT - \left(\frac{\bar{R}T}{p}\right)dp \implies dq = c_p dT + gdz \quad (1.25)$$

In the middle expression, we've inserted $c_p = c_v + \bar{R}$ from kinetic theory, which relates specific heat at constant pressure (c_p) to specific heat at constant volume. We also substituted -gdz for $(\bar{R}T/p)dp$ using the hydrostatic equation, i.e., $dp = -g\rho dz$.

Now consider an adiabatic parcel of air that moves up or down. First of all, adiabatic means no exchange of heat with the surroundings so $dq = 0$. Thus, when we rearrange, we get the definition of the **(dry) adiabatic lapse rate**:

$$\Gamma_a = -\left(\frac{dT}{dz}\right) = \frac{g}{c_p} \tag{1.26}$$

EXAMPLE:

Given the specific heat capacities of the atmospheres of Venus, Earth and Mars as 930, 1004 and 850 J K^{-1} kg^{-1}, and g values of 8.87, 9.81 and 3.72 m s^{-2}, respectively, what are their adiabiatic lapse rates?

Typical observed lapse rates in the lower atmospheres of these planets are Γ (K km^{-1}) = 6.5 (Earth), ~8.0 (Venus), ~2.5 (Mars). What is going on?

On Earth, where in the troposphere is Γ close to dry adiabatic? Where (in latitude) will tropospheric Γ be smallest?

1.1.3.2 Potential temperature

A parameter that is useful in determining if an atmosphere is stable against convection is called *potential temperature*. If we set $dq = 0$ in eq. (1.25) and substitute $-(\bar{R}T/p)dp$ for gdz from the hydrostatic eq:

$$\frac{dT}{T} = \left(\frac{\bar{R}}{c_p}\right)\frac{dp}{p} = \kappa\frac{dp}{p} \qquad \Rightarrow d(\ln T) = \kappa d(\ln p) \tag{1.27}$$

This equation says that fractional changes in temperature and pressure are in direct proportion for adiabatic processes, with a constant of proportionality given by $\kappa \equiv \bar{R}/c_p$.

Integrating eq. (1.27), we have

$$\left[\ln T\right]_\theta^T = \kappa\left[\ln p\right]_{p_{\text{ref}}}^p \Rightarrow \ln\left(\frac{T}{\theta}\right) = \kappa \ln\left(\frac{p}{p_{\text{ref}}}\right) = \ln\left(\frac{p}{p_{\text{ref}}}\right)^\kappa$$

Thus,

$$T = \theta\left(\frac{p}{p_{\text{ref}}}\right)^\kappa \tag{1.28}$$

and

$$\theta = T\left(\frac{p_{\text{ref}}}{p}\right)^\kappa \tag{1.29}$$

Eq. (1.29) is called *Poisson's (adiabatic state) Equation* and defines variable θ, which is *potential temperature*.

- Mathematically, θ is a constant of integration equivalent to the actual temperature at a reference pressure p_{ref}. In a sense, it's a reference temperature.
- **Physically, θ is the temperature a parcel of air would have if it were taken to pressure p_{ref} dry adiabatically.** On Earth, usually $p_{ref} = 1000$ mbar $= 10^5$ Pa and $\kappa = 287$ J K^{-1} kg^{-1} /1004 J K^{-1} kg^{-1} = 0.286; potential temperature θ is greater than actual temperature when the pressure is less than 1000 mbar, and vice versa.

θ can be regarded as an alternative thermodynamic variable to temperature so that eq. (1.28) is an alternative equation of state and defines T vs. P for the convective part of a troposphere. The importance of θ is that it is constant if a parcel undergoes adiabatic change of pressure. Thus, when the lapse rate is adiabatic, θ is constant with altitude ($\partial\theta / \partial z = 0$). Deviations from this constancy indicate conditions of convective stability and instability, which we now examine.
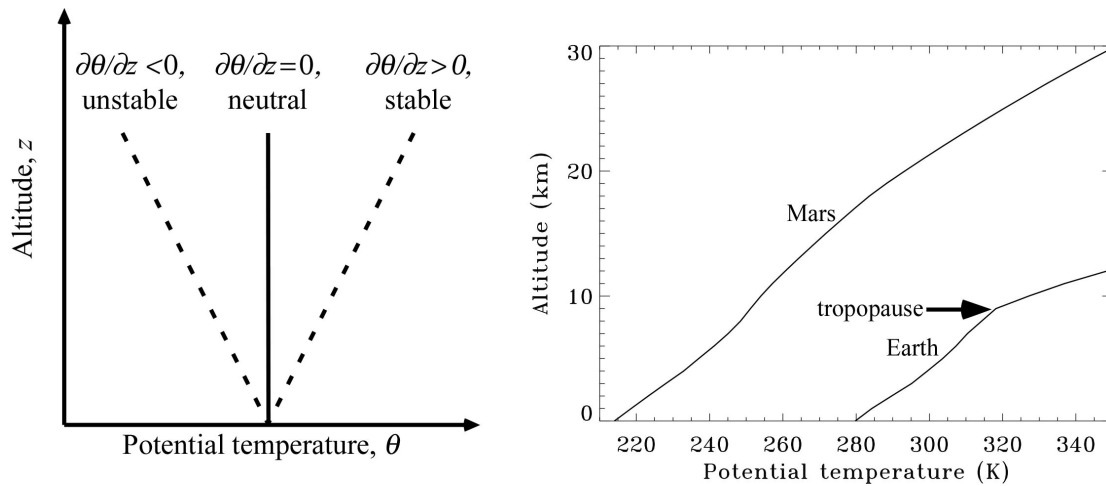

Fig. 1.6. Left: The relationship between profiles of potential temperature θ, and stability. Right: Averaged potential temperature profiles on Mars and Earth. Note the marked increase in static stability above the terrestrial tropopause.

Qu.) Where is a tropopause on Mars in Fig. 1.6?

Application to general structure of planetary and exoplanetary troposphere:
We can rewrite eq. (1.28) as

$$T = T_{ref}\left(\frac{p}{p_{ref}}\right)^{\bar{R}/c_p} \Rightarrow T = T_{ref}\left(\frac{p}{p_{ref}}\right)^{(\gamma-1)/\gamma}$$

where we've replaced the exponent with the ratio of specific heats, $\gamma = c_p/c_v$, from:

$$\bar{R} = c_p - c_v \quad \Rightarrow \frac{\bar{R}}{c_p} = 1 - \frac{1}{\gamma} = \frac{(\gamma-1)}{\gamma}$$

Kinetic theory allows us to relate the ratio of specific heats γ to the degrees of freedom, N_{dof}, for the primary atmospheric gas or gases, where

$$\gamma = 1 + \frac{2}{N_{\text{dof}}}$$

Often atmospheres are dominated by **linear diatomic** gases, such as H_2 (Jupiter, Saturn, Uranus, and Neptune), N_2 (Titan), or an N_2-O_2 mixture (Earth). These molecules have 3 translational and 2 rotational degrees of freedom, so that $N_{\text{dof}} = 5$ and $\gamma = 7/5 = 1.4$ for these worlds. In the case of the CO_2-dominated atmospheres of Venus and Mars, there are 3 translational, 2 rotational, and ~0.3 vibrational degrees of freedom, so $N_{\text{dof}} = 6.3$ and $\gamma = 1.3$. Consequently, **the dry adiabatic temperature T varies with altitude expressed as pressure as $p^{0.3}$ and $p^{0.2}$ for diatomic and CO_2 dominated atmospheres**, respectively. Such a relationship for dry adiabats is general and will also apply to dry tropospheres of exoplanets. In reality, latent heat and lowers the lapse rate below that of the dry adiabatic lapse rate, which can be accommodated by putting a factor ~0.6-0.9 in the exponent.
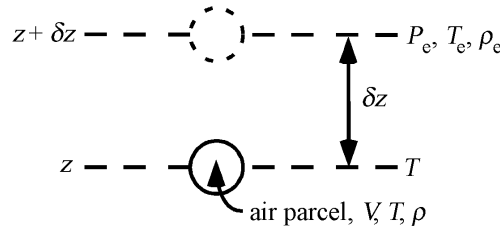
1.1.3.3 Static stability

Fig. 1.7. Diagram indicating conditions for an air parcel displaced adiabatically.

In convectively stable atmospheres, a buoyancy force causes vertically displaced parcels to return to their original altitude, but overshooting creates oscillations at an angular frequency called the *Brunt-Väisälä* frequency, N_B.

Consider a parcel of air of volume V and temperature T that is displaced by height δz from height z at environmental temperature T to a place where the environmental temperature is T_e. The parcel cools adiabatically to a new temperature $T_p = T - \Gamma_a \delta z$, while the environment cools *less* at the ambient lapse rate as $T_e = T - \Gamma \delta z$. The difference in density between the parcel (ρ_p) and air (ρ_e) drives a buoyancy force, which we can write as Newton's second law:

$$\underbrace{(V\rho_p)}_{\text{mass}}\underbrace{\frac{d^2(\delta z)}{dt^2}}_{\text{acceleration}} = \underbrace{-g(\rho_p - \rho_e)V}_{\text{buoyancy force}} \quad \Rightarrow \quad \frac{d^2(\delta z)}{dt^2} = g\left(\frac{\rho_e}{\rho_p} - 1\right) = g\left(\frac{T_p}{T_e} - 1\right) \qquad (1.30)$$

We used $\rho_e = P_e / \bar{R} T_e$ and $\rho_p = P_e / \bar{R} T_p$. Substituting for temperatures T_p and T_e, we get:

$$\frac{d^2(\delta z)}{dt^2} = g\left(\frac{T - \Gamma_a \delta z}{T - \Gamma \delta z} - 1\right) = g\left(\frac{\Gamma \delta z - \Gamma_a \delta z}{T - \Gamma \delta z}\right) \approx g\left(\frac{\Gamma - \Gamma_a}{T - \Gamma \delta z}\right)\delta z \Rightarrow \ddot{\delta z} + \frac{g}{T}(\Gamma_a - \Gamma)\delta z = 0$$

We recognize simple harmonic motion, i.e., the "$\ddot{x} + \omega^2 x = 0$" of elementary physics. This is an equation of motion, i.e.,

$$\frac{d^2(\delta z)}{dt^2} + N^2(\delta z) = 0 \qquad (1.31)$$

where

$$N^2 \equiv \frac{g}{T}(\Gamma_a - \Gamma) \equiv \frac{g}{T}(\frac{dT}{dz} + \frac{g}{c_p}) \equiv \frac{g}{T}S \qquad (1.32)$$

Here, S (K km^{-1}) = *static stability*, measures the difference between the adiabatic lapse rate (g/c_p) and actual lapse rate ($-dT/dz$).
- In a statically stable atmosphere, $\Gamma < \Gamma_a$; thus $N^2 > 0$ and solutions to eq. (1.31) are simple harmonic motion. The parcel, which we initially displaced, oscillates up and down at a natural (angular) frequency N = the "buoyancy frequency" = *Brunt-Väisälä* frequency. The higher this frequency, the greater the atmospheric stability.

-In a statically unstable atmosphere, $\Gamma > \Gamma_a$ and $N^2 < 0$. This means that N is imaginary and leads to exponential solutions of eq. (1.31). A displaced parcel would continue to rise with increasing speed. The resulting convection would drive the lapse rate down towards Γ_a by carrying warmer parcels upwards and cooler parcels downward.

EXAMPLE:
Calculate this frequency for Earth's lower troposphere, with $dT/dz \sim$ -6.5 K km^{-1} and $T \sim$ 270 K, g = 9.81 m s^{-2}, cp =1004 J K^{-1} kg^{-1}. Then try Mars, with $dT/dz \sim$ -2.5 K km^{-1}, $T \sim$ 190 K, cp =850 J K^{-1} kg^{-1}, g = 3.72 m s^{-2}.

Buoyancy oscillations occur in association with *buoyancy waves* (= *gravity waves*) which can be excited by flow over orographic features. Commonly, we see *lee wave clouds* on Earth and Mars, the latter in the lee of crater rims.

The Brunt-Väisälä frequency can also be expressed in terms of potential temperature. If we take logs of eq. (1.29), we get

$$\ln\theta = \ln T + \kappa(\ln p_{ref}) - \kappa(\ln p)$$

Now if we differentiate w.r.t. z, and remember that $d(\ln x) = (1/x)dx$, we have

$$\frac{d(\ln\theta)}{dz} = \frac{d(\ln T)}{dz} + \kappa\frac{d(\ln p_{ref})}{dz} - \kappa\frac{d(\ln p)}{dz}$$

$$\frac{1}{\theta}\frac{d\theta}{dz} = \frac{1}{T}\frac{dT}{dz} - \frac{\kappa}{p}\frac{dp}{dz} = \frac{1}{T}\frac{dT}{dz} + \frac{\kappa\rho g}{p}$$

In the very last step we have used the hydrostatic equation to substitute for dp/dz. Using the definition of $\kappa = \bar{R}/c_p$ and the ideal gas law, $p = \rho\bar{R}T$, we have

$$\frac{1}{\theta}\frac{d\theta}{dz} = \frac{1}{T}\frac{dT}{dz} + \frac{g}{c_p T} \quad\Rightarrow\quad \underbrace{\frac{g}{\theta}\frac{d\theta}{dz}}_{N^2} = \frac{g}{T}\left(-\Gamma + \Gamma_a\right) \qquad (1.33)$$

Comparing eq. (1.32), we see that the square of the Brunt-Väisälä frequency is given by

$$\boxed{N^2 = \frac{g}{\theta}\frac{d\theta}{dz}} \qquad (1.34)$$

- **Stable** atmosphere solutions have positive N^2 and positive $d\theta/dz$, when a displaced parcel experiences a restoring force and return to its previous position, albeit with oscillations.
- **Neutral stability** is when $d\theta/dz = 0$, then $N = 0$, where the atmosphere is just stable and the lapse rate equals the adiabatic lapse rate.
- **Convective instability** occurs if $d\theta/dz < 0$, N^2 is negative, and the atmosphere undergoes free convection.

1.1.2.4 The Planetary Boundary Layer

A *boundary layer* is a zone in which flow is significantly affected by the presence of a boundary and distinguished from relatively free fluid beyond. On rocky planets, the *Planetary Boundary Layer* (PBL) is a near-surface region where turbulence generated by thermal convection produces an air-ground temperature differential and rapid change with height of temperature and wind. PBL fluxes of heat, mass and momentum drive circulations in an atmosphere.
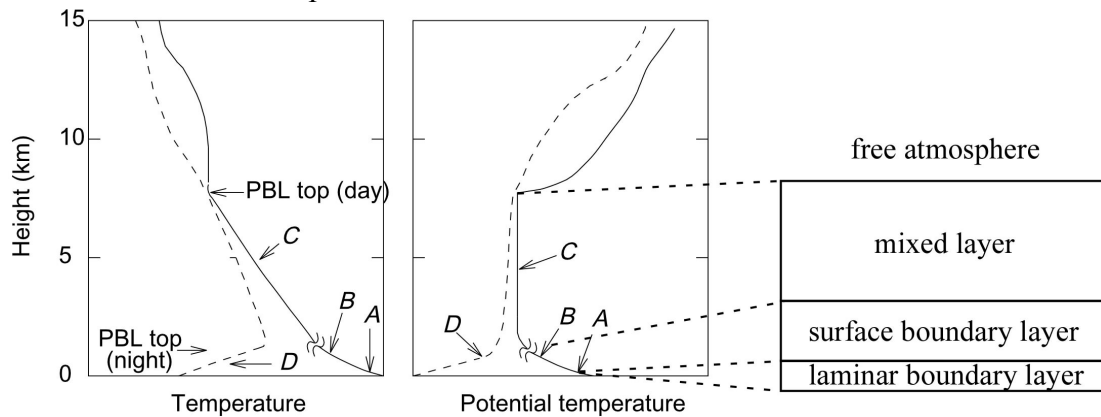
Fig. 1.8. Schematic depiction of the planetary boundary layer (PBL) on Mars, indicating day and night conditions. Based on a schematic by Leovy (1982).

Just above the surface, air is so strongly restrained by friction with the ground and by its own intermolecular friction (viscosity), that its motion is nearly nonexistent. This is the *laminar boundary layer* (point **A**) where momentum, heat and volatiles are transported mainly by molecular diffusion. It has depth ~1 cm on Mars and ~0.5-few mm on Earth.

The next region (marked **B**) is the turbulent or *surface boundary layer* (or *Prandtl layer*), which on Earth extends up to altitude 5-50 m. On Mars, it reaches a height of a few to a few hundred meters. This is the most turbulent part of the atmosphere. Flow is in planes parallel to the surface and strongly shears (i.e. changes direction and/or magnitude) with height. After sunset, radiational cooling may lead to a temperature inversion (**D**).

Further up is a much thicker convective layer (**C**) called the *mixed layer* (or *Ekman layer*) that extends up to the top of the well-mixed (constant θ, adiabatic) zone. In this layer, away from the equator, the local vertical component of the angular momentum of a rotating planet can become important in affecting the direction of flow. Above C, the PBL ends and an increase of θ (i.e., static stability) greatly reduces turbulent mixing. The region above the PBL is called the *free atmosphere* or *geostrophic level*. On Earth, the PBL extends typically up to 0.5-1 km, but can be tens of meters or ~2-4 km in certain circumstances. In early morning on Mars, the PBL may be less than 100 m deep but on a clear, summer afternoon typical thermal convection produces a PBL 5-10 km thick (based on afternoon cumulus cloud shadows, probe entry measurements, dust devil shadows, and atmospheric models).
During Martian nighttime, a "nocturnal jet" (10-20 m/s) at a height of ~100 m may form above the inversion layer because the temperature inversion decouples the winds from the surface friction. After sunrise, convection in the PBL destroys the jet.

1.1.3.5 Condensable Species, Entropy, and the Clausius-Clapeyron Equation

H_2O on Earth
CH_4 on Titan, Uranus, Neptune
H_2O and CO_2 on Mars,
H_2SO_4 (SO_3 + H_2O) on Venus,
H_2O and NH_3 on Jupiter and Saturn.
N_2, CH_4 on Triton and Pluto
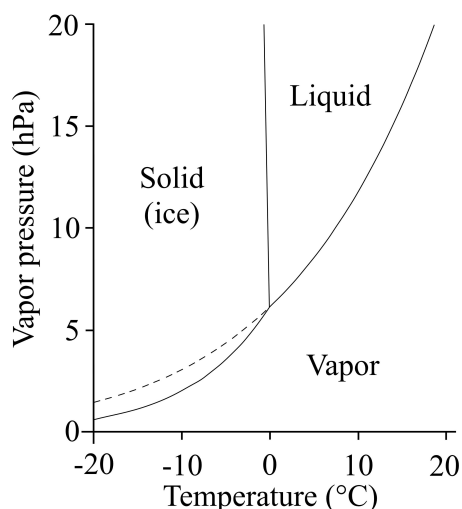
Which form snow? Rain? Clouds?

Fig. 1.9. The saturation vapor pressure (SVP) between liquid and vapor (and also solid and vapor) for water. The dashed line shows the SVP with supercooled water, which produces a higher SVP than ice and evaporates more rapidly.

The first step towards understanding the behavior of a condensable species is to consider the *saturation vapor pressure* (SVP): the vapor pressure exerted in equilibrium with the liquid phase. If we plot the SVP versus temperature, a curve is defined that represents the transition between vapor and liquid phases; once a condensable gas vapor reaches SVP, it must condense into liquid. T**he *Clausius-Clapeyron Equation* mathematically defines the SVP** as a function of temperature for a condensable gas or a change in the melting point of a solid with pressure, such as CO_2 on Mars. On Earth, we are accustomed to think of the Clausius-Clapeyron equation as defining the vapor pressure of water, but an analogous equation can be written for any condensable gas.

Before discussing how condensable species affect lapse rates, we visit the concept of entropy. Rudolf Clausius (1822-1888) introduced the word *entropy*, from the Greek τροπη, meaning *transformation*. Entropy is that the integral of the quantity dQ/T (= heat absorbed (or lost)/ temperature) along a reversible path between two states A and B and independent of path. If S_A and S_B are the values of this function in the states A and B, S is defined as

$$S_B - S_A = \int_A^B \frac{dQ}{T} \qquad \text{or } dS = \frac{dQ}{T} \tag{1.35}$$

If we define a reference state O, the state S can be defined for any state X as:

$$S_X = S_0 + \int_0^X \frac{dQ}{T} \tag{1.36}$$

The Third Law of thermodynamics give us an entropy reference value S_0 as follows: at the absolute zero of temperature (0 K) the entropy of every chemically homogeneous

solid or liquid body is zero. In the real world, the transformation from state O to state X involves irreversible processes along a path, as opposed to a reversible path. In thermodynamics, it is often assumed that every irreversible transformation that occurs in nature can also be achieved through a reversible process for which eq. (1.36) is valid.

The above seems fairly abstract but entropy is a measurable physical quantity and has units of J K^{-1}. For example, when one mole of water ice turns into liquid water the entropy change is 22 J K^{-1} mol^{-1} (= 6008 J mol^{-1}/273.15 K), where we have used a melting temperature of 273.15 K, the latent heat of fusion of water 6008 J mol^{-1}, and eq. (1.35) in the form $\Delta S = \Delta Q / T$.

Derivation of Clausius-Clapeyron
(The *key concept is that two phases are in equilibrium along the SVP versus T line, so the Gibbs free energy change of the phase transition is zero everywhere along the line*.)

In order to change unit mass of condensable from liquid (or ice) to vapor at constant temperature and pressure, a certain amount of energy, called the *latent heat* or, more properly, *enthalpy l_c*, is absorbed. Enthalpy per unit mass has units J kg^{-1}.

- from liquid to vapor, l_c is the *enthalpy (latent heat) of vaporization*
- from ice to liquid it is the *enthalpy (latent heat) of fusion*
- from ice to vapor it is the *enthalpy (latent heat) of sublimation*.
-

Imagine going from condensed phase to vapor phase. The first law of thermodynamics, eq. (1.23), gives the heat input as

$$l_c = \int_{q_1}^{q_2} dq = \int_{u_1}^{u_2} du + p\int_{\alpha_1}^{\alpha_2} d\alpha = u_2 - u_1 + p(\alpha_2 - \alpha_1)$$

(1.37)

  = (change in internal energy in making vapor) + (work done in making vapor)

where u is the internal energy per unit mass, $p = e_s$ is the equilibrium or saturation vapor pressure, and α is the specific volume. Subscript 1 refers to the condensed phase and subscript 2 to the vapor phase. The change of phase takes place at constant temperature, so from the definition of entropy (eq. (1.35)), it follows that $l_c = T\delta s = T(s_2 - s_1)$, which can be substituted on the L.H.S. of (1.37) to give

$$T(s_2 - s_1) = u_2 - u_1 + p(\alpha_2 - \alpha_1)$$
$$\Rightarrow u_1 + p\alpha_1 - Ts_1 = u_2 + p\alpha_2 - Ts_2$$

(1.38)

The combination $u + p\alpha - Ts$ is called the Gibbs function, or G, which is a function of state and, from eq. (1.38), constant during an isothermal change of phase. Now if the phase change takes place at a higher temperature, $T + dT$, and a correspondingly higher equilibrium vapor pressure, $e_s + de_s$, we can write the Gibbs function as $G + dG$. To obtain dG we take the derivative of $u + p\alpha - Ts$, which gives

$$dG = du + pd\alpha + \alpha dp - Tds - sdT \qquad \text{; sub. for } dq = du + pd\alpha$$
$$= \quad dq \quad + \alpha dp - Tds - sdT \qquad \text{; sub. for } dq = Tds \qquad (1.39)$$
$$= \alpha dp - sdT$$

Since G remains constant during the isothermal change of phase, $G_1 + dG_1 = G_2 + dG_2$ and $dG_1 = dG_2$. So from eq. (1.39)

$$\alpha_1 dp - s_1 dT = \alpha_2 dp - s_2 dT$$
$$\Rightarrow dp(\alpha_2 - \alpha_1) = dT(s_2 - s_1) \qquad (1.40)$$

Thus, replacing p above with e_s (the saturation vapor pressure), the slope of the Clausius-Clapeyron curve is defined by

$$\frac{de_s}{dT} = \frac{\delta s}{\delta \alpha} = \frac{\text{entropy gained per kg from condensed to vapor}}{\text{volume increase per kg from condensed to vapor}} \qquad (1.41)$$

Since $l_c = T\delta s$, it follows that

$$\frac{de_s}{dT} = \frac{l_c}{T\delta\alpha} = \frac{l_c}{T(\alpha_{\text{vapor}} - \alpha_{\text{condensed}})} \approx \frac{l_c}{T\alpha_{\text{vapor}}}$$

The specific volume of vapor is much larger than the specific volume of the condensed phase ($\alpha_{\text{vapor}} \gg \alpha_{\text{condensed}}$), so we ignore the latter. By substituting for $\alpha_{\text{vapor}} = R_c T / e_s$, where R_c is the specific gas constant for the condensable species vapor, we obtain

$$\frac{de_s}{dT} = \frac{l_c e_s}{R_c T^2}, \qquad \text{or} \quad \frac{d(\ln e_s)}{dT} = \frac{l_c}{R_c T^2} \qquad (1.42)$$

This eq. can be integrated from a reference temperature T_0 to temperature T, to give

$$\boxed{e_s(T) = e_s(T_0)\exp\left(\int_{T_0}^{T} \frac{l_c}{R_c} \frac{dT}{T^2}\right) \approx e_s(T_0)\exp\left[\frac{l_c}{R_c}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]} \qquad (1.43)$$

The second expression is approximate because l_c changes slightly with T. The exponential form of the equation shows that SVP is very sensitive to temperature. Noting that $R_c = k/m_c$, and given that exponents are additive, we can deduce from eq. (1.43) that $e_s \propto \exp(-m_c l_c / kT)$. This is a Boltzmann equation, which gives us the insight that the numerator in the exponent is the energy input required to free a water molecule from its neighbors while the denominator is the average molecular energy. For water vapor above liquid water, we use $T_0 = 273.15$ K, $e_s(T_0) = 611$ Pa, $R_c = 461$ J K^{-1} kg^{-1}, and latent heat of vaporization $l_c = 2.5 \times 10^6$ J kg^{-1}, finding that SVP roughly doubles for every 10 K temperature rise.

To consider the behavior of condensable species in atmospheres, we define the volume mixing ratio, f_c, of the condensable species according to eq. (1.4),

$$f_c = \frac{n_c}{n} = \frac{e_c}{p}$$

where the n's are number densities, e_c is the partial pressure of the condensable species, and p is the total pressure. Similarly, we can define a mass mixing ratio according to eq. (1.5) as

$$\mu_{cm} = \varepsilon f_c = \varepsilon \frac{e_c}{p}, \quad \text{where } \varepsilon = \frac{m_c}{\bar{m}} = \frac{\text{molecular mass of condensable}}{\text{mean molecular mass of air}} \approx \frac{m_c}{m_d} \quad (1.44)$$

For water vapor in Earth's atmosphere, $\varepsilon = 0.622$. We can also define saturation mixing ratios as

$$f_{cs} = \frac{e_s(T)}{p}, \qquad \mu_{cms} = \varepsilon \frac{e_s(T)}{p} \qquad (1.45)$$

Example of usage: NASA's *Galileo* probe measured 5×10^{-5} mixing ratio of water at 5 bar and 0 C on Jupiter. What was (a) the specific humidity (g/kg), (b) the relative humidity (%)? ($\bar{m} = 2.22\text{g/mol}$).

Let us consider a parcel that rises adiabatically from the surface, which is at pressure p_{ref} and temperature T_{ref}. In the adiabatic parcel, potential temperature θ, starts out as T_{ref} and remains constant at T_{ref}, while the actual temperature will fall via eq. (1.28) as $T = T_{\text{ref}}(p/p_{\text{ref}})^{\kappa}$, or equivalently, $p = p_{\text{ref}}(T/T_{\text{ref}})^{1/\kappa}$. Substituting for p in eq. (1.44) gives

$$e_{\text{parcel}}(T) = \frac{\mu_{cm} p_{\text{ref}}}{\varepsilon} \left(\frac{T}{T_{\text{ref}}}\right)^{1/\kappa} \qquad (1.46)$$

The parcel behaves as dry air until it reaches the SVP temperature, when $e_{\text{parcel}} = e_s$, at an altitude called the *lifting condensation level*. After this point, the lapse rate changes discontinuously to become a saturation lapse rate on the SVP curve. Cloud particles form from the condensable and the parcel is warmed. Instead of the temperature dropping at the adiabatic lapse rate, the temperature drops less sharply with altitude at a *saturated adiabatic lapse rate* (or moist lapse rate).
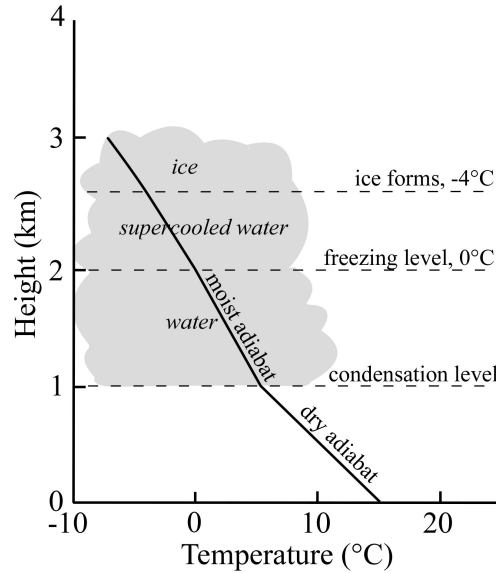
Fig. 1.10. A rising air parcel and the lifting condensation level, which forms the base of cloud (shown schematically in shade).

Reading: See Sanchez-Lavega et al. (2004) on planets & clouds.

1.1.3.6 The Saturated Adiabatic Lapse Rate

The saturated adiabatic lapse rate occurs when chilled moist air is held at saturation by warming associated with continual condensation of excess vapor. It is common for textbooks and papers to talk of "*release of latent heat*". Physically, condensation is a warming process because as water vapor molecules approach with a few molecular diameters of liquid water they are attracted to it and increase their K.E.

Recall the equation used in deriving the adiabatic lapse rate in Sec. 1.1.3.1 for a unit mass air parcel,

$$dq = c_p dT + gdz$$

Let's consider the specific heat capacity, c_p, to be that for an air-water vapor mixture. If mass $\delta\mu_{cms}$ condenses then $dq = -l_c\delta\mu_{cms}$, from the definition of the enthalpy ("latent heat") of phase change. Hence, substitution for dq in the above equation gives,

$$l_c\delta\mu_{cms} + c_p dT + gdz = 0 \tag{1.47}$$

At saturation, the condensable species mass mixing ratio is equal to the saturation mass mixing ratio given by eq. (1.45), $\mu_{cms} = \varepsilon e_s / p$. Taking logs and differentiating (1.45),

$$\frac{\delta\mu_{cms}}{\mu_{cms}} = \frac{\delta e_s}{e_s} + \frac{\delta\varepsilon}{\varepsilon} - \frac{\delta p}{p} \tag{1.48}$$

Now, $\delta e_s = (de_s / dT)\delta T$ and from eq. (1.42), $(1/e_s)(de_s/dT) = l_c/(R_cT^2)$. Also $\delta p/p = -g\delta z/(\bar{R}T)$ from the hydrostatic equation. Putting all of these in eq. (1.48) gives

$$\frac{\delta\mu_{cms}}{\mu_{cms}} = \frac{l_c\delta T}{R_cT^2} + \frac{g\delta z}{\bar{R}T} \tag{1.49}$$

We can substitute $\delta\mu_{cms}$ from (1.49) into eq. (1.47), as follows,

$$c_p\delta T + gdz + l_c\mu_{cms}\left(\frac{l_c\delta T}{R_cT^2} + \frac{g\delta z}{\bar{R}T}\right) = 0$$

$$\Rightarrow \delta Tc_p\left(1 + \frac{l_c^2\mu_{cms}}{c_pR_cT^2}\right) + g\delta z\left(1 + \frac{l_c\mu_{cms}}{\bar{R}T}\right) = 0$$

If we now divide through by δz and rearrange we get

$$\Gamma_{sa} \equiv \text{saturated adiabatic lapse rate} = -\left(\frac{dT}{dz}\right)_{sa} = \frac{g}{c_p}\frac{\left(1 + \dfrac{l_c\mu_{cms}}{\bar{R}T}\right)}{\left(1 + \dfrac{l_c^2\mu_{cms}}{c_pR_cT^2}\right)} \tag{1.50}$$

This eq. does not allow for the thermodynamics and fate of the condensate (precipitation or retention or further phase change) and so is only approximate.

However, the mass of the condensate is usually small compared to the gas phase. This lapse rate is also called the *pseudo-adiabatic lapse rate* if condensation products are assumed to fall out of the parcel.

Static stability is controlled by Γ_{sa} under saturated conditions. For example, saturated air is stable if $\Gamma < \Gamma_{sa}$. On Earth, in warm humid air near the ground, $\Gamma_{sa} \approx 4$ K km^{-1}, whereas $\Gamma_{sa} \approx 6\text{-}7$ K km^{-1} in the middle troposphere, and Γ_{sa} is close to dry adiabatic Γ_a near the top of the troposphere where the air is cold and dry.

This theory has limits through its assumptions
(1) that the condensable mass mixing ratio is small, so we can ignore the condensate (which is not true for CO_2 on Mars),
(2) that precipitation can be neglected (violated by rain on Earth),
(3) that phase change is an equilibrium process (which is not always true for more exotic substances).