

Climate Dynamics

PartII: Atmospheric Dynamics

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This course consists of 15 lectures.

- At the end of each lesson, exercises will be given as homework and discussed in the beginning of the following lesson.
- Recommended textbooks:
 - S. R. de Groot and P. Mazur*: Non-Equilibrium Thermodynamics. Dover Publications, New York,
 - John A. Dutton*: The Ceaseless Wind. Dover Publications, INC., New York
 - James R. Holton*: Dynamic Meteorology, Third edition, Academic Press.
 - Joseph Pedlosky*: Geophysical Fluid Dynamics, Springer-Verlag.Others are suggested in the individual lectures. Many others are good as well, so choose!
- Lecture notes will be available at http://users.ictp.it/~kucharsk/lecture_notes_climate_units_section1_3.pdf, etc.
- If you find mistakes, corrections are highly appreciated!

Topics in the course

- Thermodynamic state and state variables; thermodynamics potentials; second law; thermodynamics equilibrium; multicomponent systems; hydrostatic equation; Application to dry air; Moist atmospheric thermodynamics [3 h]
- Vorticity equation for synoptic-scale motion; potential vorticity conservation (barotropic and general) [1.5 h]

- Rossby waves; free Rossby waves; forced Rossby waves; turning latitude [1.5 h]
- Equatorial waves; Rossby-gravity waves; Kelvin waves [1.5 h]
- ENSO atmosphere and ocean feedback mechanisms; Gill model; Reduced Gravity Model [1.5h]
- Rainfall responses to heating; Ekman pumping effect; upper-level divergence [1.5h]
- The General Circulation; Hadley Cell; Ferrell Cell; Tropical zonal and meridional circulations; Walker circulation; Sverdrup balance [1.5h]
- Modes of variability in the climate system: ENSO, PDO, NAO, AMO [1.5]

1 Thermodynamic state

The presentation of thermodynamics in this lecture is based in parts on a lecture course *Atmospheric Thermodynamics* which is part of the *Atmospheric Physics* lecture course developed at the ICTP. I have modified the presentation of the basics according to my own taste a little bit, by trying to separate the general basics of (thermo)dynamics and the specifics of a particular system. In particular there will be no dq , the *heat*, in this lecture course. Thermodynamics has a microscopic foundation, but when talking about a *thermodynamic state*, we are referring to its macroscopic state. A thermodynamic state is characterized by state variables. Examples of state variables (or simply variables) of a moving system are its velocity, temperature, density and pressure. Thermodynamics is usually referring to systems that are at rest (macroscopically, of course). But the interaction between dynamics and thermodynamics is important, and this interaction is one of the reasons why thermodynamics is of major interest in, for example, atmospheric dynamics. Examples of systems we are interested in are gases (atmosphere), fluids (oceans, water in atmosphere), and solid bodies (parts of the Earth). We will sometimes use the thermodynamics of systems of larger extends, but mostly adopt the *local* description. For example, one may define the density of a system (for example a gas) by its mass M divided by its volume V , but it is sometime convenient to consider *infinitesimal* small systems in a continuum. In this case we have the local density

$$\rho := \lim_{\Delta V \rightarrow 0} \frac{\Delta M}{\Delta V} \quad , \quad (1)$$

and $\rho = \rho(x, y, z, t)$. The specific volume v is just $1/\rho$. The same will be the case for all other state variables, such as pressure p , temperature T , etc.

1.1 Extensive and intensive variables

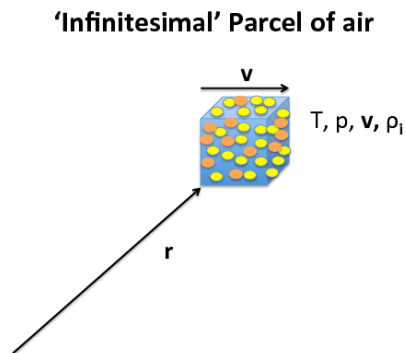
There are extensive and intensive state variables. Assume a system that we decompose into pieces. *Extensive* variables are then variables that if we add their parts, the result is the variable of the whole system. For example, volume and mass are extensive variables. Variables that do not add up after a decomposition are called *intensive variables*. If we divide an extensive variable by its mass, the results is the corresponding *specific* variable, i.e. the specific volume is $v = V/M$. Usually we will denote the specific variables with lower case letters and the corresponding variable with capital letters. Specific variables are intensive, they do not add up anymore (or only if properly weighted). We can divide an extensive quantity also by the amount of molecules present. Then is is called molar quantity. In the following we will mainly consider local, specific quantities. Also note that in particular cases also intensive quantities may be added up (in particular the specific intensive quantities, where we may sum up using a weighting).

1.2 Field quantities

For our application, the earth system, including the solid part, ocean and the atmosphere (which is mainly dealt with in this course), it is useful to consider the local specific quantities to describe the system that depend on space and time, e.g. $\rho = \rho(\mathbf{r}, t)$, $v = v(\mathbf{r}, t)$, etc., where $\mathbf{r} = x, y, z$ is the space position vector and t is time. Such quantities are called field quantities. To apply thermodynamics locally we have to assume that the infinitesimal system we are considering is small (so small that it can be considered to be in *local thermodynamics equilibrium*), but not too small. It has to be large enough to be able to apply the macroscopic thermodynamic laws to the system. Typically a few mm are certainly large enough in the not too thin atmosphere. There are two basic ways to describe changes of field quantities (this has been already extensively discussed in your GFD Course), one is the *lagrangian* form, in which you follow the infinitesimal element with its macroscopic motion, e.g. $d\rho/dt$, where d/dt is the *total* time derivative, and the *eulerian* form $\partial\rho/\partial t$, that is the local time derivative. Lagrangian and eulerian derivatives for any field ψ are related through the 3 dimensional velocity vector \mathbf{v}

$$\frac{d\psi}{dt} = \frac{\partial\psi}{\partial t} + \mathbf{v} \cdot \nabla\psi \quad , \quad (2)$$

where ∇ is the vector containing the 3 space derivatives $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$ and the scalar product has to be considered. The thermodynamic properties developed in the next sections are mostly valid for the infinitesimal mass element that we consider, but sometimes we also apply the field perspective.



1.3 Energy, first law and Gibbs equation

We will only provide a heuristic description of Thermodynamics in this course. The laws introduced may be interpreted as *axioms*, that is we cannot prove them within

the macroscopic framework, but they are postulates that have been proven to be true in every system that fulfills the properties outlined. The (specific) energy, e , can be attributed as variable to virtually all physical systems. It is also a function of a set of variables, called *natural variables*, lets say x_i , $i = 1, m$ that characterizes a physical system under consideration

$$e = e(x_i), \quad i = 1, m \quad (3)$$

The first law of thermodynamics is just a special case of the general conservation law of energy, and is therefore nothing really special to thermodynamics.

The Gibbs equation is an equation that can be derived by differentiating e with respect to its variables

$$de = \sum_{i=1}^m \frac{\partial e}{\partial x_i} dx_i \quad . \quad (4)$$

Note that the variations here are arbitrary, and can be in particular the total time derivative or local time derivatives. The same as above is also valid for finit volume system that are in *thermodynamic equilibrium* (see below). The more difficult part is to identify the natural variables of energy, and they are postulated here.

The natural variables of energy for a n component (multicomponent) system, composed, for example of gases or different phases of gases (e.g. the atmosphere), are the $n + 4$ quantities specific momentum \mathbf{v} , specific volume, v , and specific entropy, s , and the n mass fractions of each component $m_i = \rho_i/\rho$ (note that $\sum_{i=1}^n \rho_i = \rho$ and therefore $\sum_{i=1}^n m_i = 1$). This also means that a one-component system has 5 natural variables. It is usually assumed that in this case the gases and phases are well mixed in the infinitesimal mass or volume element, so that just one temperature and (total) pressure can be attributed.

In the presence of a gravity field, we have to include an explicit dependence of energy on the location through the potential energy, $\phi(\mathbf{r})$ The partial derivatives of energy with respect to its natural variables are the (3-dimensional) velocity vector, \mathbf{v} , negative pressure, $-p$ and temperature T , and the chemical potentials μ_i . Therefore the Gibbs equation 4 becomes

$$de = \mathbf{v} \cdot d\mathbf{v} - pdv + Tds + \sum_{i=1}^n \mu_i dm_i + d\phi \quad . \quad (5)$$

This equation, in particular the partial derivatives of energy with respect to entropy, may be interpreted as the defining equation for the absolute temperature. Note that all the above can be also formulated in terms of the non-specific quantities for a system in thermodynamic equilibrium (see below). In general, also in a nonequilibrium situation, we may define a global quantity (e.g. for the whole atmosphere) by an integral, e.g. $E = \int \rho e \, dx dy dz$. It is often convenient to consider another quantity, the internal energy, u , that is defined by $u := e - 1/2\mathbf{v}^2 - \phi$. The Gibbs equation for the internal energy is then

$$du = -pdv + Tds + \sum_{i=1}^n \mu_i dm_i \quad . \quad (6)$$

The internal energy is just dependent on the $n + 1$ quantities v, s, m_i , as can be seen from Eq. 6. Note that this is also true for the field quantities introduced in the previous section, the dependence of u on space and time is then through the quantities v, s, m_i . Traditionally, the term Tds has been expressed as exchanged heat q or dq . Particularly the latter one is misleading as it suggests the 'heat' to be a function of state. However, we may occasionally refer to Tds as the process of exchange of heat q . Other *thermodynamics potentials* may be derived from the internal energy by simple transformations (Legendre Transformation). The most common ones are the Enthalpy ($h := u + pv$), the Gibbs free energy ($g := u + pv - Ts$), Helmholtz free energy ($f := u - Ts$). With each of these definitions comes along a change of the natural variables (exercise!).

Note that the thermodynamic potentials are *homogenic* function of its extensive (or specific intensive) variables, which means, for example, for the Gibbs free energy

$$g(T, p, m_i) = \sum_{i=1}^n m_i \mu_i \quad , \quad (7)$$

with

$$dg(T, p, m_i) = vdp - sdT + \sum_{i=1}^n \mu_i dm_i \quad . \quad (8)$$

Using the transformation 7 and 8 it follows the *Gibbs-Duhem relation* (exercise!)

$$\sum_{i=1}^n m_i d\mu_i = vdp - sdT \quad , \quad (9)$$

which states that the intensive variables are not independent anymore.

A useful volume-specific (instead of mass specific) formulation of Eq. 5 is (exercise!)

$$d(\rho e) = \mathbf{v} \cdot d(\rho \mathbf{v}) + Td(\rho s) + \sum_{i=1}^n \mu_i^* d\rho_i + \rho d\phi \quad , \quad (10)$$

where

$$\mu_i^* := \mu_i - \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + \phi \quad , \quad (11)$$

is some kind of modified gibbs free energy (including the mechanical energies), with (exercise!)

$$\sum_{i=1}^n m_i d\mu_i^* = -\mathbf{v} \cdot d\mathbf{v} - sdT + vdp + d\phi \quad . \quad (12)$$

Note that for a one-component system Eq. 10 becomes

$$d(\rho e) = \mathbf{v} \cdot d(\rho \mathbf{v}) + Td(\rho s) + \mu^* d\rho + \rho d\phi \quad , \quad (13)$$

where

$$\mu^* := g - \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + \phi = e - \mathbf{v} \cdot \mathbf{v} - Ts + pv \quad , \quad (14)$$

with the Gibbs free energy $g = u - Ts + pv$ and Eq. 12 degenerates to

$$d\mu^* = -\mathbf{v} \cdot d\mathbf{v} - sdT + vdp + d\phi \quad . \quad (15)$$

1.4 Second law of thermodynamics; thermodynamics equilibrium; hydrostatic equation

The second law of thermodynamics is related to the entropy, S and states

$$dS \geq 0 \quad (16)$$

for a closed system (no exchanges with outside), and the total entropy can be calculated from the local specific entropy by $S = \int \rho s \, dx dy dz$. Processes for which the entropy increases are called irreversible, reversible processes are the limit case in which the entropy remains constant. The thermodynamic equilibrium state (of a closed system) is defined by the state in which the entropy reaches its maximum value. It is useful to calculate the equilibrium state of the atmosphere (assuming it as a well mixed dry gas, so that it can be considered as one-component system that only depends on $\rho = \sum_{i=1}^n \rho_i$); see next section. For this purpose we have to maximize the integrated specific entropy. We cannot require momentum conservation for the atmosphere (momentum may be lost through friction to the earth in order to get into the equilibrium state). However, there are constraints to consider regarding the conservation of global energy and mass. The standard technique to solve this problem is to introduce lagrange-multipliers and to maximize:

$$L = S + \lambda_e \left(\int_v \rho e dV - E \right) + \lambda_\rho \left(\int_v \rho dV - M \right) \quad (17)$$

Applying a variation to this *Lagrange Function* and using a re-formulation of Eq. 13

$$\delta(\rho s) = -\frac{1}{T} \mathbf{v} \cdot \delta(\rho \mathbf{v}) + \frac{1}{T} \delta(\rho e) - \frac{\mu^*}{T} \delta \rho . \quad (18)$$

Note, that the variation δ applied here only to the variables and is local at this stage, so that the variation of the only space-dependent geopotential vanishes. With this we get

$$\delta L = \int_v \left[\left(\lambda_e + \frac{1}{T} \right) \delta(\rho e) - \frac{\mathbf{v}}{T} \cdot \delta(\rho \mathbf{v}) + \left(\lambda_\rho - \frac{\mu^*}{T} \right) \delta \rho \right] dV \quad (19)$$

In order for the entropy to be maximized under the constraints of global energy and mass conservation, the variation of the Lagrangefunction 19 must vanish for arbitrary and independent variations. From this follows

$$\frac{1}{T_0} := -\lambda_e ; \quad \frac{\mathbf{v}_0}{T_0} = 0 , \quad \frac{\mu_0^*}{T_0} := \lambda_\rho , \quad (20)$$

where the 0 indicates the equilibrium state. The lambdas are constant in space and time. Using Eq. 15, and using the gradient operator ∇ it follows for the equilibrium state

$$\nabla \mu_0^* = -\nabla \left(\frac{1}{2} \mathbf{v}_0^2 \right) - s_0 \nabla T_0 + v_0 \nabla p_0 + \nabla \phi . \quad (21)$$

Therefore, we have because of $\mathbf{v}_0 = 0$, $T_0 = const.$ and $\mu_0^* = const.$

$$\nabla p_0 = -\rho_0 \nabla \phi . \quad (22)$$

It follows that the equilibrium state is isothermal, motionless and in hydrostatic equilibrium. Since in a coordinate system with z as the local vertical, the potential energy can be usually well expressed as $\phi = gz$, we have the hydrostatic equation in the known form

$$\frac{\partial p_0}{\partial z} = -\rho_0 g, \quad (23)$$

where $g = 9.81 \text{ m/s}^2$ is the acceleration due to gravity. It is interesting to note that all *contact variables*, temperature, velocities, assume constant values in the thermodynamic equilibrium, apart from the pressure, which is in the presence of a gravity field in hydrostatic equilibrium. Often, in thermodynamics it is assumed that also the pressure is constant in equilibrium. This approximation is valid if vertical displacements are small (i.e. just a few meters), so that the pressure variation according to Eq. 23 can be considered as very small.

The typical variation of pressure with height due to the usually well fulfilled hydrostatic condition is shown in Fig. 1,

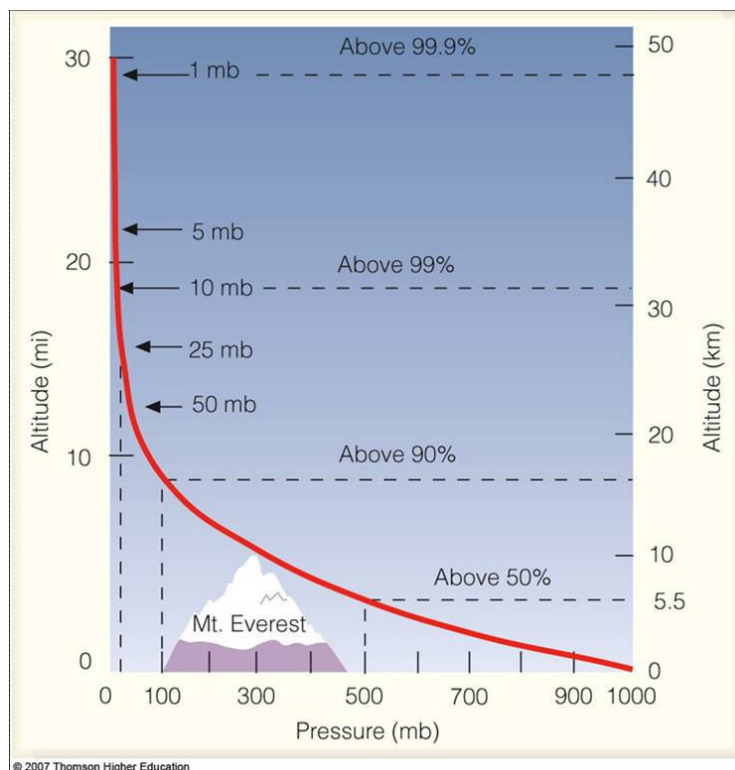


Figure 1: Typical change of pressure with height according to the hydrostatic equation. From http://www.physicalgeography.net/fundamentals/images/pressure_altitude.jpg

Questions: What are the processes that would bring an imaginary closed atmospheric system into thermodynamic equilibrium? Is the atmosphere typically in

thermodynamic equilibrium as a whole? The answer to this question is certainly NO!! Why? What are the processes that drive the atmosphere away from thermodynamic equilibrium?

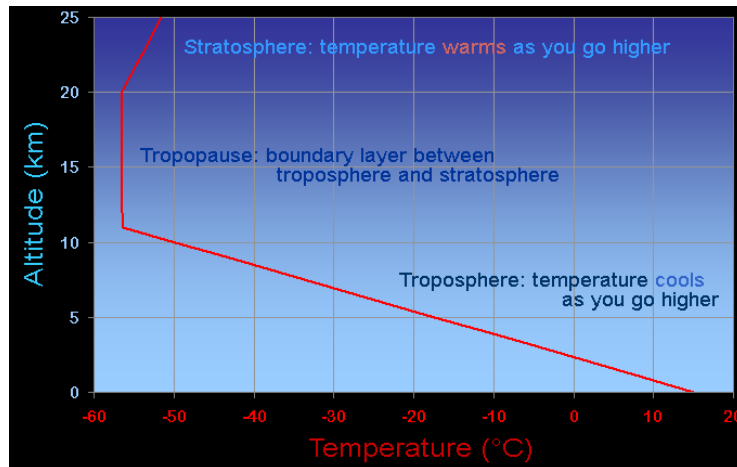


Figure 2: Typical change of temperature with height. From http://www.windows2universe.org/earth/Atmosphere/troposphere_temperature.html

Note that if a multicomponent system is considered including phase transitions an entropy maximization (representing local equilibrium conditions) yields the equilibrium chemical potentials for the exchanging substances (μ_l and μ_k) have to be equal and constant

$$\mu_l = \mu_k \quad . \quad (24)$$

Exercices

1. Derive the natural variables and the corresponding Gibbs equations (using Eq. 6) for the enthalpy $h = u + pv$, $f = u - Ts$ and $g = u + pv - Ts$ Also show the validity of Eq. 9.
2. Show that the variation of the volume specific total energy ρe obeys Eq. 10 (given that Eq. 5 is valid), and show also that Eq. 12 is valid.
3. Use the hydrostatic equation 23 to derive a relationship between the total mass of the atmosphere and the surface pressure.

2 Application to dry air

So far the thermodynamic concepts introduced are fairly general. Now we want to apply these concepts to the atmosphere. Let us first consider a truly one-component gas, then Eq. 6 is

$$du = -pdv + Tds . \quad (25)$$

Two more equations (usually the easily measurable relationships between T , p , v and u) are needed to completely characterise such a one-component system. Such equations are usually referred to as *equations of state*, and is dependent on the material considered. The *ideal gas law* is one of the equations of state. If the one component gas occupies the volume V we have

$$pV = NkT = \nu R^*T \quad , \quad (26)$$

where $k = 1.3806 \times 10^{-23} \text{J K}^{-1}$ is the Boltzmann's constant, N is the number of identical molecules, ν is the number of moles of gas, and $R^* = N_a k = 8.341 \text{J mol}^{-1} \text{K}^{-1}$ is the *Universal gas constant*. $N_a = 6.022 \times 10^{23} \text{mol}^{-1}$ is *Avogadro's number*, that is the number of molecules per mole of gas. If we divide Eq. 26 by the total mass M , we get

$$pv = RT \quad , \quad (27)$$

where $R = Nk/M = \nu R^*/M = R^*/M_m$ is the specific gas constant $M_m = M/\nu$ is the molar mass. Before we consider the atmosphere as a mixture of gases, it is useful to derive some relationships between thermodynamic variables for a one-component gas.

With the equation of state 27 one more equation is needed to solve Eq. 25 that specifies the dependence of u on T and v . It turns that the internal energy for an ideal gas just depends on temperature in the following way

$$u(T) = c_v T \quad , \quad (28)$$

where the constant c_v is called the *specific heat at constant volume* for historical reasons (it should really be referred to as partial derivative of internal energy with respect to temperature). From Eq. 28 follows for the specific enthalpy of a ideal gas because of $h = u + pv = (c_v + R)T = c_p T$, where c_p is called *specific heat at constant pressure*, also for historical reasons.

With the ideal gas law 27 and Eq. 28 the Gibbs Eq. 25 we can show the following relationships (exercise!)

$$s(T, v) = s_B + c_v \ln \left(\frac{T}{T_B} \right) + R \ln \left(\frac{v}{v_B} \right) \quad (29)$$

or

$$s(T, p) = s_B + c_p \ln \left(\frac{T}{T_B} \right) - R \ln \left(\frac{p}{p_B} \right) \quad , \quad (30)$$

where the subscript B indicates an arbitrary constant thermodynamic reference value. For the following considerations it is also useful to calculate Gibbs free energy $g = h - Ts$. It follows:

$$g(T, p) = T \left[c_p - s_B - c_p \ln \left(\frac{T}{T_B} \right) + R \ln \left(\frac{p}{p_B} \right) \right] , \quad (31)$$

Let us now assume that the atmosphere is a well mixed system of ideal gases. Although phase transitions may occur, for many purposes the dry atmosphere may be considered well mixed system of gases with $m_i = \text{const}$. For the typical composition, see Table 3.

TABLE 16.1 Composition of Dry Air near Sea Level		
Component*	Content (mole fraction)	Molar Mass
Nitrogen	0.78084	28.013
Oxygen	0.20948	31.998
Argon	0.00934	39.948
Carbon dioxide	0.000375	44.0099
Neon	0.00001818	20.183
Helium	0.00000524	4.003
Methane	0.000002	16.043
Krypton	0.00000114	83.80
Hydrogen	0.0000005	2.0159
Nitrous oxide	0.0000005	44.0128
Xenon	0.000000087	131.30

*Ozone, sulfur dioxide, nitrogen dioxide, ammonia and carbon monoxide are present as trace gases in variable amounts.

Figure 3: Composition of dry atmosphere at surface level. Source: http://wpscms.pearsoncmg.com/au_hss_brown_chemistry_1/57/14649/3750278.cw/content/index.html

According to *Dalton's Law* each gas in the mixture obeys its own equation of state and behaves as if it was alone in the volume V .

$$p_i = \frac{M_i R_i T}{V} = \rho_i R_i T = \rho m_i R_i T \quad , \quad (32)$$

where p_i is the *partial pressure* of the component i and R_i is the specific gas constant for that component (see Table 3). Note that the temperature in the infinitesimal volume of well mixed (and thermally equilibrated) gases is just T and recall the definition of mass fraction $m_i = \rho_i / \rho$. From Dalton's law we can add the partial pressures to get the total pressure

$$p = \sum_{i=1}^n p_i = \rho \sum_{i=1}^n m_i R_i T = \rho R T \quad , \quad (33)$$

where $R = \sum_{i=1}^n m_i R_i = 287 \text{ J kg}^{-1} \text{K}^{-1}$ is the specific gas constant for dry air. The complete thermodynamic treatment of an ideal gas mixture starts from the Gibbs free energy 7 with the fundamental equation 8. A mixture of ideal gases can be described according to 7 as

$$g(T, p, m_i) = \sum_{i=1}^n m_i \mu_i \quad , \quad (34)$$

this is we can add up the specific gibbs free energy (or chemical potentials). In general $\mu_i = \mu_i(T, p, m_i)$, however for an ideal gas mixture these relationships degenerate to

$$\mu_i(T, p, m_i) = \mu_i(T, p_i) \quad , \quad (35)$$

which can be interpreted as a consequence of Dalton's Law (each component behaves as if it was alone in the volume if we consider the partial pressures), thus we have

$$\mu_i(T, p_i) = T \left[c_{pi} - S_B - c_{pi} \ln \left(\frac{T}{T_B} \right) + R_i \ln \left(\frac{p_i}{p_B} \right) \right] \quad , \quad (36)$$

where we have used the relationship of the one-component gas for each component by replacing p by p_i , as well as the respective heat capacities and gas constants. Using

$$p_i = p \frac{m_i R_i}{R} := p y_i \quad , \quad (37)$$

where obviously $\sum_{i=1}^n y_i = 1$. The $y_i = m_i R_i / R = \nu_i / \nu$ may be interpreted as *molar fractions* of the respective component. Inserting this into 36 leads to

$$\mu_i(T, p, y_i) = T \left[c_{pi} - S_B - c_{pi} \ln \left(\frac{T}{T_B} \right) + R_i \ln \left(\frac{p}{p_B} \right) + R_i \ln y_i \right] \quad , \quad (38)$$

therefore

$$g(T, p, m_i) = \sum_{i=1}^n m_i T \left[c_{pi} - s_B - c_{pi} \ln \left(\frac{T}{T_B} \right) + R_i \ln \left(\frac{p}{p_B} \right) + R_i \ln y_i \right] \quad . \quad (39)$$

This tells us that apart from the Gibbs free energy of the well mixed gas (first 2 terms), there is a mixing Gibbs free energy (last term). From Eq. 8 we know that the entropy can be calculated as negative partial derivative of free energy, therefore

$$s = -\frac{\partial g}{\partial T} = -\sum_{i=1}^n m_i \left[c_{pi} - s_B - c_{pi} - c_{pi} \ln \left(\frac{T}{T_B} \right) + R_i \ln \left(\frac{p}{p_B} \right) + R_i \ln y_i \right] \quad . \quad (40)$$

Therefore

$$s = s_B + \sum_{i=1}^n m_i c_{pi} \ln \left(\frac{T}{T_B} \right) - \sum_{i=1}^n m_i R_i \ln \left(\frac{p}{p_B} \right) - \sum_{i=1}^n m_i R_i \ln y_i \quad . \quad (41)$$

If the definition of the specific entropy of the well mixed gas

$$s_i = s_B + c_{pi} \ln \left(\frac{T}{T_B} \right) - R_i \ln \left(\frac{p}{p_B} \right) \quad (42)$$

is made, then we see that apart from the entropy of the well mixed gas, $\sum_{i=1}^n m_i s_i$, there is an additional term for entropy in a gas mix

$$s = \sum_{i=1}^n m_i s_i - \sum_{i=1}^n m_i R_i \ln y_i . \quad (43)$$

the term

$$s_{mix} := - \sum_{i=1}^n m_i R_i \ln y_i \quad (44)$$

is called *mixing entropy* and is always positive because of $y_i < 1$. The existence of the mixing entropy is clearly due to the fact of the nonlinear dependence of entropy on pressure and temperature; (explain the meaning of mixing entropy for a mixture of 2 separated gases in volumes V_1 and V_2). Note that since we assume the dry atmosphere to be a well mixed gas, we also assume that the mass fractions m_i are constant for all components and therefore the mixing entropy is also constant (after the mixing!) and therefore this term can be combined with the constant s_B and with this we have the entropy according $\sum_{i=1}^n m_i s_i$ and 43 as for the one-component ideal gas Eq. 30 (or 29). For the enthalpy of the mixture we have because of $h = g + Ts$

$$\begin{aligned} h &= \sum_{i=1}^n m_i T \left[c_{pi} - s_B - c_{pi} \ln \left(\frac{T}{T_B} \right) + R_i \ln \left(\frac{p}{p_B} \right) + R_i \ln y_i \right] + \\ &T \left[s_B + \sum_{i=1}^n m_i c_{pi} \ln \left(\frac{T}{T_B} \right) - \sum_{i=1}^n m_i R_i \ln \left(\frac{p}{p_B} \right) - \sum_{i=1}^n m_i R_i \ln y_i \right] \\ &= \sum_{i=1}^n m_i c_{pi} T . \end{aligned} \quad (45)$$

Therefore the enthalpy is additive $h = c_p T = \sum_{i=1}^n m_i c_{pi} T = \sum_{i=1}^n m_i h_i$, with $h_i = c_{pi} T$, and there is no mixing enthalpy. It turns out that also internal energy can additively composed from the subsystems $u = c_v T = \sum_{i=1}^n m_i c_{vi} T = \sum_{i=1}^n m_i u_i$. For the Earth atmosphere with the gases listed in Table 3, we have $c_v = \sum_{i=1}^n m_i c_{vi} = 717 \text{ J kg}^{-1} \text{K}^{-1}$. For the specific enthalpy we have $h = u + pv = (c_v + R)T = c_p T$, where $c_p := c_v + R = 1004 \text{ J kg}^{-1} \text{K}^{-1}$.

In atmospheric physics and dynamics it is convenient to consider a quantity closely related to entropy, but with the dimension of temperature, the *potential temperature*. It can be defined as

$$ds = c_p d \ln \theta \text{ or } s = c_p \ln \theta + const. \quad (46)$$

It is usually derived as a process for which $ds = 0$, if ds is the total derivative following the particle. This is a stronger statement than that the global entropy is

constant (Eq. 16) and such a process is usually referred to as adiabatic reversible (i.e. no heat is exchanged between the parcel and its environment; no heatflux). Consider the specific enthalpy h , its derivative is

$$dh = vdp + Tds \quad (47)$$

Because of $ds = 0$, from Eq. 47 follows

$$\frac{T}{T_0} = \left(\frac{p}{p_0}\right)^{\frac{R}{c_p}} . \quad (48)$$

If we let $p_0 = 1000hPa$, the the interpretation of T_0 would be that it is the temperature that a particle would reach if it is adiabatic reversibly brought to the pressure p_0 , which approximately the surface. This temperature is then called *potential temperature* θ , and can be expressed as

$$\theta = T \left(\frac{p}{p_0}\right)^{-\frac{R}{c_p}} . \quad (49)$$

In expression 49 the potential temperature θ is obviously not constant. Comparing this with the expression for the entropy 30, we can easily verify the validity of 46, which means that entropy is a function of potential temperature alone and vice versa (exercise!). Fig. 12 shows a typical potential temperature distribution with height. Whereas temperature is typically decreasing with height, potential temperature (and therefore entropy!) is typically increasing with height. We will see in the next section that this is necessary if the dry atmosphere is in a stable condition.

Exercises

1. Assume the atmosphere has an initial density-weighted mean temperature of 270 K and a density-weighted mean kinetic energy of $100 \text{ m}^2/\text{s}^2$. Assume now that we close the atmosphere and all kinetic energy is dissipated. Calculate the resulting constant thermodynamic equilibrium temperature, T_0 of the final state in which entropy is maximal. (Hint: Note that the density-weighted mean can be evaluated as

$$\bar{\psi} := \frac{\int \rho \psi \, dv}{\int \rho \, dv} = \frac{1}{M} \int \rho \psi \, dv ,$$

where the integrals are done over the whole atmosphere. Note that the volume integral of the potential energy is just R/c_v times the integral of the internal energy, and you may use this without proof.)

2. Use the ideal gas law 27, Eq. 28 and Eq. 25 to calculate the dependence of entropy s on a) temperature and volume and on b) temperature and pressure.
3. Show that the potential temperature definition 49 is consistent with Eq. 46, with the entropy s of an ideal gas given by expression 30.

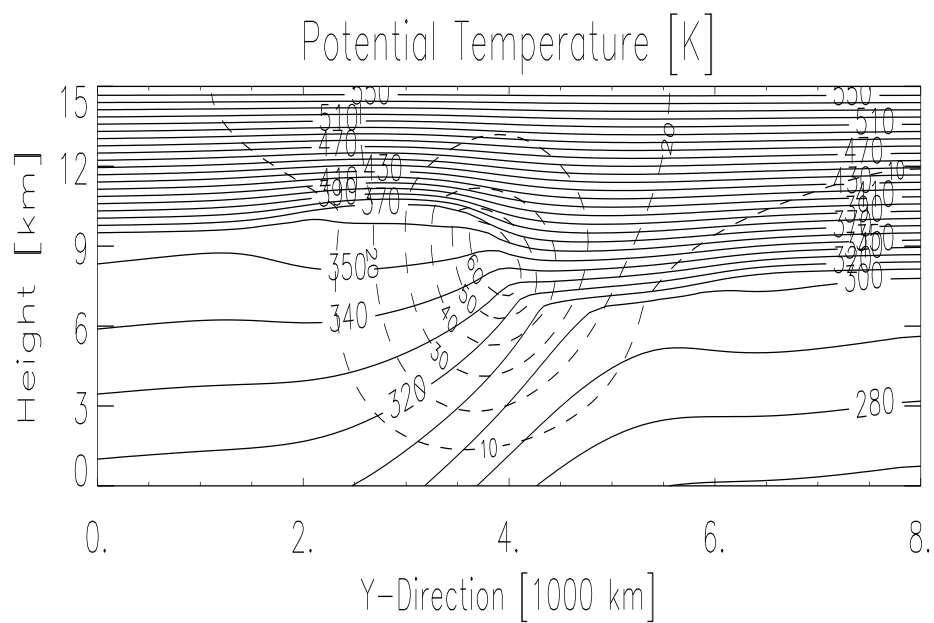


Figure 4: Idealised situation (meridional-vertical section) of the extratropical mean state. Potential temperature (solid lines, K) and zonal wind (dashed, m/s). As you know the wind approximately fulfills the thermal wind equation $\partial u_g / \partial z \approx -g / (fT) \partial T / \partial y$.

3 Moist Atmospheric Thermodynamics

In the previous sections the Atmosphere has been considered as a well-mixed perfect gas. Now we will introduce the water in the atmosphere. Water is special, because it can exist in its 3 phases: solid, liquid and vapour. Furthermore water vapor is anything but a well mixed gas and shows large spatial and temporal variations (see Fig. 5 for specific humidity or mass fraction; discuss distribution, why? Discuss magnitudes). Water in all phases is far from thermodynamic equilibrium mainly because there is the huge reservoir of the oceans that provide water to the atmosphere via evaporation and receives water via precipitation (section 3.3.1; see Fig. 8; discuss distribution, dimension). From Eq. 6 we know that in principle we should include in the thermodynamic description the additional variables of mass fractions m_i (or the densities) for dry air, water vapor, liquid and solid phases of water, where one follows from the other 3 because of $\sum_{i=1}^4 m_i = 1$ by definition. Therefore, the full description of such a system involves $n + 4 = 8$ natural variables, for which balance equations have to be established (momentum, thermal energy and mass continuity equations for total density and the 3 additional components). Of course, in principle even more components can be distinguished, such as ozone and other reacting gases. For the time being, the water components are considered, because they provide the most important feedbacks. However, in details the treatment of water in the atmosphere is already quite complicated.

It is first useful to discuss the effects of moisture in unsaturated air.

3.1 Moist unsaturated air

All air in the atmosphere contains some water vapor, but it is usually a very small fraction (up to 4%, but usually smaller, see Fig. 5). If in a volume, we have dry air with density $\rho_d = M_d/V$ and water vapor $\rho_v = M_v/V$ then we have for the densities

$$\rho = \frac{M_d + M_v}{V} = \rho_d + \rho_v \quad . \quad (50)$$

Therefore for the mass fractions $m_d = \rho_d/\rho = M_d/M$, $m_v = \rho_v/\rho = M_v/M$ we have

$$1 = m_d + m_v \quad . \quad (51)$$

Note that the mass fraction of vapor, m_v , is called *specific humidity*. We can now apply Daltons law 32 to water vapor as ideal gas if we are not near condensation

$$p_v = \rho_v R_v T \quad , \quad (52)$$

where p_v is the partial pressure of vapor and $R_v = 461.5 \text{ J kg}^{-1} \text{ K}^{-1}$ is the specific gas constant for vapor and we have assumed that the vapor temperature is equal to the temperature T . The dry air equation of state is

$$p_d = \rho_d R_d T \quad , \quad (53)$$

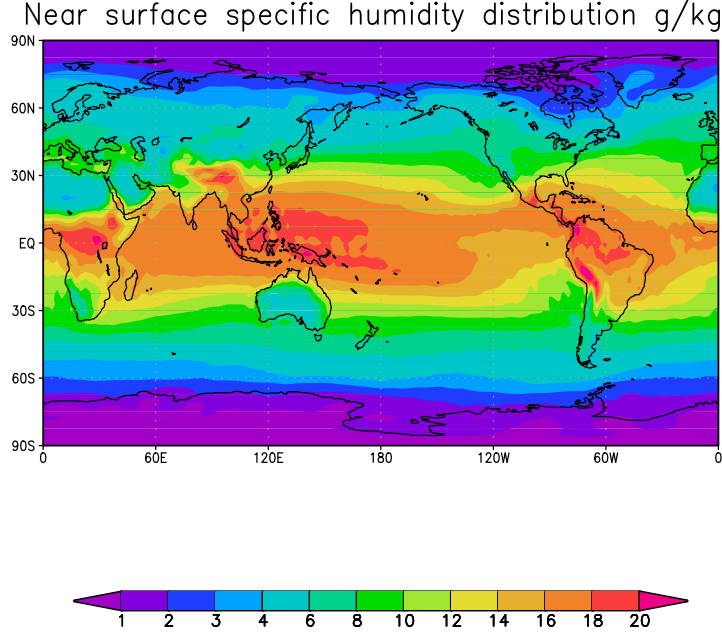


Figure 5: Near surface distribution of specific humidity (vapor mass fraction). Units are g/Kg.

where we have indicated dry air by the subscript d , but Eq. 53 is identical to Eq. 27. From Dalton's law 33 we can add the partial pressures

$$\begin{aligned}
 p &= p_d + p_v = (\rho_d R_d + \rho_v R_v) T \\
 &= \rho_d R_d \left(1 + \frac{r}{\epsilon} \right) T \quad , \quad (54)
 \end{aligned}$$

where the mixing ratio $r = \rho_v / \rho_d$ and the definition $\epsilon = R_d / R_v = 0.621 = 1/1.61$ have been introduced. With $\rho_d = \rho / (1 + r)$ it follows

$$p = \rho R_d \left(\frac{1 + \frac{r}{\epsilon}}{1 + r} \right) T \quad . \quad (55)$$

It is clear that the gas 'constant' of moist air is

$$R = R_d \left(\frac{1 + \frac{r}{\epsilon}}{1 + r} \right) \quad . \quad (56)$$

However, it is not a 'constant' anymore because it depends on the vapor mixing ratio, which is highly variable. Therefore, the *virtual Temperature* has been introduced in atmospheric physics to take into account the moisture correction into the temperature

$$T_v = T \left(\frac{1 + \frac{r}{\epsilon}}{1 + r} \right) \quad , \quad (57)$$

so that we have for moist air the gas law

$$p = \rho R_d T_v \quad . \quad (58)$$

It will be an exercise to estimate a typical value of the deviation $T_v - T$ due to the vapor in the atmosphere.

3.2 Specific heat of moist air

Moisture is also modifying somewhat the specific heat that we have for dry air. For an ideal gas mixture can add the internal energies according to the mass fractions by (see section 2; use $m_v = r/(1+r)$)

$$u = m_d u_d + m_v u_v = (m_d c_v + m_v c_{vv}) T = c_v \left(\frac{1 + \frac{c_{vv}}{c_v} r}{1+r} \right) T \quad , \quad (59)$$

such that the specific heat at constant volume of moist air c'_v can be expressed as

$$c'_v = c_v \left(\frac{1 + \frac{c_{vv}}{c_v} r}{1+r} \right) \quad , \quad (60)$$

where $c_{vv} = 1410 \text{Jkg}^{-1} \text{K}^{-1}$ is the specific heat of water vapor. A similar calculation for the enthalpies leads to

$$c'_p = c_p \left(\frac{1 + \frac{c_{pv}}{c_p} r}{1+r} \right) \quad . \quad (61)$$

$c_{pv} = 1870 \text{Jkg}^{-1} \text{K}^{-1}$ is the specific heat at constant pressure of water vapor. In practise, the differences of the specific heats of moist and dry air is often neglected because of $r \ll 1$.

3.3 Saturated air; Clausius Clapeyron Equation

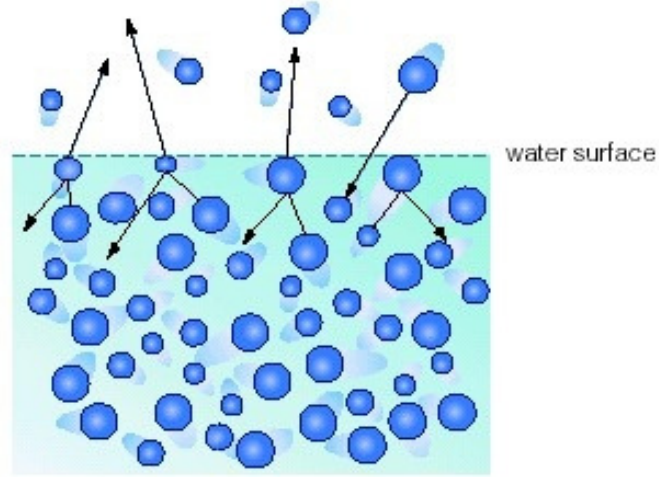
For saturation, the vapor and liquid (or solid) phases are in equilibrium. Let us for the time being just consider water vapor and the liquid phase. Saturation occurs when as many molecules leave the water surface as are absorbed by the water surface (Fig. 6).

Equilibrium means that the pressures and temperatures, as well as the Gibbs free enthalpy (or chemical potentials for just one component) are equal for the 2 pure phases (section 1.4; Eq.)

$$\mu_l = \mu_v \quad , \quad p_l = p_v \quad , \quad T_l = T_v \quad , \quad (62)$$

or

$$d\mu_l = d\mu_v \quad , \quad dp_l = dp_v \quad , \quad dT_l = dT_v \quad , \quad (63)$$



During evaporation, the more energetic particles escape from the surface leaving the less energetic ones behind.

Figure 6: Evaporation (condensation) from a water surface.

For each of the pure phases we have the Gibbs equation

$$d\mu_i = -s_i dT + v_i dp \quad , \quad (64)$$

where $i = v, l$, Note the v_i are the specific volumes $v_i = V_i/M_i$ for the phases. Thus

$$(s_l - s_v) dT = (v_l - v_v) dp \quad , \quad (65)$$

where T and p are the temperature and pressure. If we use the equilibrium condition Eq. 65 to define the *saturation vapor pressure* p_{sv} , then we have

$$\frac{dp_{sv}}{dT} = \frac{s_l - s_v}{v_l - v_v} \quad . \quad (66)$$

The 'heat' transferred during the phase transition is usually referred to as enthalpy of condensation or as *latent heat of condensation* and is

$$L_{lv} := h_v - h_l = T(s_v - s_l) + (\mu_v - \mu_l) = T(s_v - s_l) \quad . \quad (67)$$

L_{lv} is a function of temperature, but for meteorological purposes it can be approximated to a constant. Therefore

$$\frac{dp_{sv}}{dT} = \frac{L_{lv}}{T(v_v - v_l)} \quad . \quad (68)$$

This is the *Clausius-Clapeyron equation* specifying the temperature dependence of the saturation vapor pressure. If we use $v_v \gg v_l$ and the equation of state for water vapor (with $p_v = p_{sv}$)

$$p_{sv}v_v = R_v T \quad , \quad (69)$$

because the gas phase is only vapor ($V_v = V$), and therefore we have

$$\frac{1}{p_{sv}} \frac{dp_{sv}}{dT} = \frac{L_{lv}}{p_{sv}T^2} = \frac{L_{lv}}{R_v T^2} \quad . \quad (70)$$

Integration of this equation between p_{sv0}, T_{00} and p_{sv}, T using the approximately valid assumption $L_{lv} = \text{const} = 2.5008 \cdot 10^6 \text{ J kg}^{-1}$ leads to

$$p_{sv} = p_{sv0} e^{\frac{L_{lv}}{R_v T_{00}}} e^{-\frac{L_{lv}}{R_v T}} \quad . \quad (71)$$

We can immediately derive the formula for the phase transition vapor-ice by using the latent heat of sublimation $L_{iv} = 2834.1 \cdot 10^6 \text{ J kg}^{-1}$ instead of latent heat of condensation

$$p_{svi} = p_{vs0} e^{\frac{L_{iv}}{R_v T_{00}}} e^{-\frac{L_{iv}}{R_v T}} \quad . \quad (72)$$

For the constants of integrations we choose freezing point $T_{00} = 273.15K$, where the corresponding saturation vapor pressure is $p_{vs0} = 6.11 \text{ hPa}$. With this we have a expressions of the type

$$p_{sv} = A e^{-\frac{B}{T}} \quad ,$$

for the saturation pressure over water and ice and equations 71 and 72 indicate that air can only 'hold' a limited amount of water, and that this amount is a strong function of temperature (see Fig. 7).

If we have a mix of gases, as in the case of moist air, the same equations are valid, but the pressure pure p_{sv} becomes the partial pressure of water vapor instead (the pressure exerted by the dry air can be ignored).

3.3.1 Parametrization of evaporation over pure water surfaces

Assume now that the we have air over a water surface. In case the air is not saturated if the partial water vapor pressure is smaller that its saturation values $p_v < p_{vs}$, evaporation from the water surface will occur. This process is usually parameterized in a way that the evaporation rate is proportional to the saturation deficit of the air $p_{vs} - p_v$. A typical parameterization of the evaporative flux would be

$$f_{evap} = c_{evap} (p_{vs} - p_v) \quad , \quad (73)$$

where c_{evap} are usually empirical coefficients that usually depend on wind speed in the atmosphere and other properties, such as stability (usually for practical purposes in numerical models of the atmopshere/ocean these cannot be derived from microscopic (molecular) properties). Many models of the atmosphere use the vapor mass fraction (specific humidity) as variable, therefore it is an advantage to express the

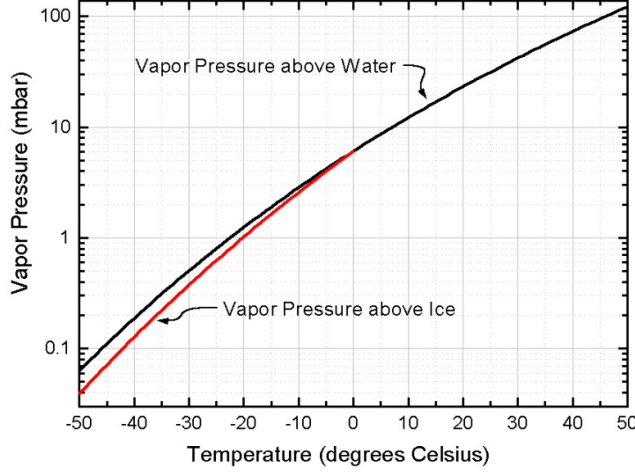


Figure 7: Saturation pressure versus temperature. Source: http://www.goes-r.gov/users/comet/tropical/textbook_2nd-edition/print_5.htm

evaporation rate f_{evap} in terms of difference in specific humidity and the saturation specific humidity. Since $p_v = \rho m_v R_v T$, and with the definition of the saturation specific humidity $m_{vs} := p_{vs}/(\rho R_v T)$ we can express Eq. 74 as

$$f_{evap} = c_{evap}^* (m_{vs} - m_v) \quad , \quad (74)$$

where $c_{evap}^* = c_{evap}/(\rho R_v T)$. The convergence of the evaporation rate (flux) should then increase the atmospheric vapor mass fraction

$$\left| \rho \frac{dm_v}{dt} \right|_{evap} = -\nabla \cdot (f_{evap} \mathbf{k}) = -\frac{\partial f_{evap}}{\partial z} \quad , \quad (75)$$

where we have used that the evaporation from a flat surface has only the vertical component. Note that the vapor mass flux from the surface may continue into the the atmosphere and only its convergence will lead to a change in mass fraction (explain this equation carefully). The convergence of these evaporation fluxes occur in the *atmospheric boundary layer*.

3.4 Ways to saturation

A useful measure that indicates if moist air is saturated is the *relative humidity*

$$RH = \frac{p_v}{p_{vs}} = \frac{m_v}{m_{vs}} \quad , \quad (76)$$

that is the ratio of partial vapor pressure to saturation vapor pressure or specific humidity and saturation specific humidity. A way to saturate unsaturated air is to

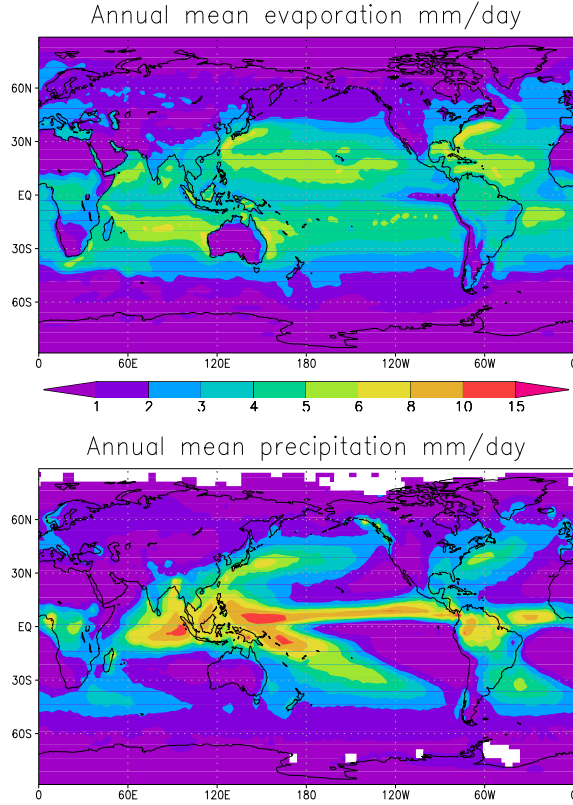


Figure 8: Annual mean observed evaporation (top) and precipitation (bottom). Units are mm/day (note that mm/day is equivalent to $\text{kg}/(\text{m}^2 \text{ day})$).

cool the air diabatically (e.g. fog formation at night through radiative surface cooling). The temperature defined by this cooling is defined as *dewpoint temperature* T_d . If p_{vs} is the measured atmospheric vapor pressure, the dewpoint temperature is defined by $p_v(T) = p_{sv}(T_d)$, because the cooling is assumed to take place at constant vapor pressure and we insert the measured vapor pressure of the into Eq. 71 in order to calculate the temperature at saturation T_d . An alternative and very important process to reach saturation is the adiabatic cooling through upward motion. However, in a rising parcel the vapor pressure it not constant (also decreasing; the mass fraction is constant), so the calculation of the *lifting condensation level* LCL is more complicated and may be derived from thermodynamics diagrams (an example is the tephigram in Fig. 9; explain how to calculate LCL through conservation of $m_v = M_v/M$; why is m_v conserved, is it?). Other important mechanisms to reach saturation are mixing of air and cooling and moistening by evaporation of water (leading to *Wet Bulb temperature*). We can do a little calculation to show that the

air is always going to saturate due to the adiabatic cooling if it is lifted high enough. For a rising parcel we have that its mass fraction m_v is conserved. Therefore, the relative humidity change with time for an unsaturated rising parcel will be

$$\frac{dRH}{dt} = -\frac{m_v}{m_{vs}^2} \frac{dm_{vs}}{dt} , \quad (77)$$

which tells us that in order for the relative humidity to increase in the rising parcel, the saturation specific humidity has to decrease. We have the saturation specific humidity

$$m_{vs} = \frac{p_{sv}}{\rho R_v T} = \frac{p_{sv} R}{\rho R T R_v} = \epsilon p_{sv} / p , \quad (78)$$

where the definition $\epsilon = R/R_v$ that has been used in Eq. 54 has been used (always approximating $R_d = R$). From Eq. 78 we can calculate

$$\begin{aligned} \frac{dm_{vs}}{dt} &= \frac{\epsilon}{p} \frac{dp_{sv}}{dt} - \frac{\epsilon p_{sv}}{p^2} \frac{dp}{dt} \\ &= \frac{\epsilon p_{sv}}{p} \left(\frac{L_{lv}}{R_v T^2} \frac{dT}{dt} + w \frac{\rho g}{p} \right) \\ &= m_{vs} \left(\frac{L_{lv}}{R_v T^2} \frac{dT}{dt} + w \frac{\rho g}{\rho R T} \right) \\ &= m_{vs} \left(\frac{L_{lv}}{R_v T^2} \frac{dT}{dt} + w \frac{g}{RT} \right) , \end{aligned} \quad (79)$$

where it has been assumed that the pressure change is hydrostatic. We have that the saturation specific humidity is decreasing with height if

$$\frac{dT}{dt} = -w \frac{g}{c_p} < -w \frac{g R_v T}{R L_{lv}} \quad \text{or} \quad \Gamma_d = \frac{g}{c_p} > \frac{g T}{\epsilon L_{lv}} , \quad (80)$$

where we have used that for the rising parcel the lapse rate is (nearly) the dry adiabatic one as long as the parcel is not saturated, which follows from $d\theta/dt = 0$ and the hydrostatic equation (explain!). This condition for the rising parcel is always fulfilled because we can easily verify that $c_p < (\epsilon L_{lv})/T \approx 5000 \text{ J kg}^{-1} \text{ K}^{-1}$ for all reasonable temperatures in the atmosphere. Therefore, an unsaturated rising parcel will saturate at some point. To estimate the level where saturation occurs, it is best to use the thepigram (Fig. 9).

3.5 Condensation for a saturated rising parcel

If we consider vertical motion, a parcel may be lifted until it is saturated, then supersaturation will occur, because the saturation pressure decreases faster than the parcels vapor pressure (see Fig. 9). If we lift the parcel further, condensation will occur. Note that a in-depth treatment would involve cloud drop formation (e.g. for cloud formation usually cloud nuclei are necessary, and their spherical form modifies the saturation vapor pressure, etc.). This is not a topic of this course.

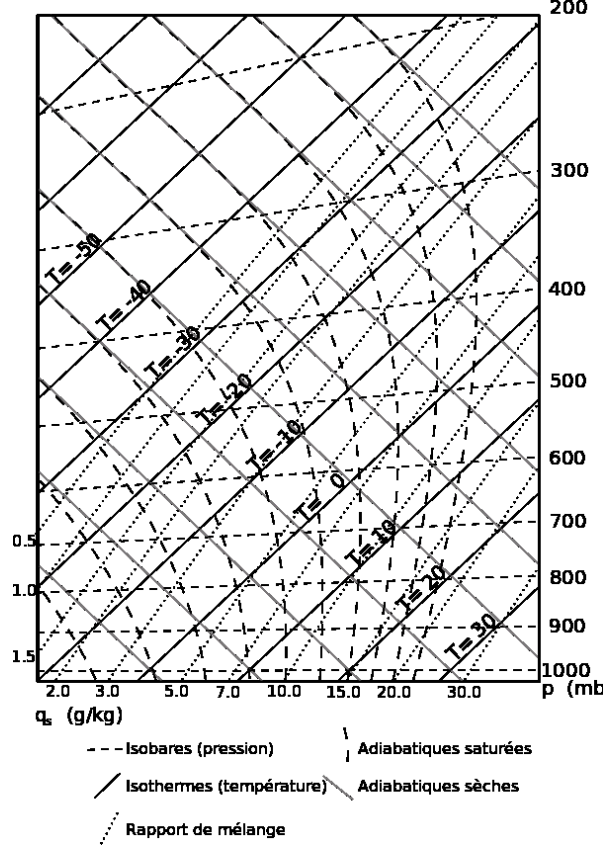


Figure 9: Thephigram

Here we provide a highly simplified treatment assuming that supersaturation will automatically and instantaneously lead to condensation until the parcel is saturated again. To evaluate this process, we may write the enthalpy of the moist air with condensate as (see section 2).

$$h = m_d h_d + m_v h_v + m_l h_l \quad . \quad (81)$$

Differentiation of this equation leads to

$$dh = m_d dh_d + m_v dh_v + m_l dh_l + h_d dm_d + h_v dm_v + h_l dm_l \quad . \quad (82)$$

If condensation is the only process for mass fraction changes considered here (i.e. no local diffusive mixing), then we may assume for the dry air $dm_d = 0$, for the phases of water we have $dm_l = -dm_v$, therefore

$$dh = m_d dh_d + m_v dh_v + m_l dh_l + (h_v - h_l) dm_v \quad . \quad (83)$$

Therefore we have because of the definition of the latent heat of condensation (67)

$$dh = m_d dh_d + m_v dh_v + m_l dh_l + L_{lv} dm_v \quad . \quad (84)$$

From this equation, we can already see that for a given dh the condensation (dm_v) will lead to changes of the temperature of the parcel additional to the other processes (pressure change in our case), because we have $m_d dh_d + m_v dh_v + m_l dh_l = (m_d c_p + m_v c_{pv} + m_l c_l) dT$, where c_p , c_{pv} , c_l are the heat capacities of dry air, vapor and liquid water, respectively. This addition of heat occurs because of the large value of L_{lv} .

With $m_d \approx 1$, and m_v, m_l small we get

$$dh = dh_d + L_{lv} dm_v \quad , \quad (85)$$

for an approximation of the *moist enthalpy* variation. With $dh = v dp + T ds$ (note that the term $(\mu_d dm_d + \mu_v dm_v + \mu_l dm_l) = 0$ because of $dm_d = 0$, $dm_v = -dm_l$ and 62) we get for adiabatic-reversible processes $ds = 0$ (our usual assumption for the rising parcel). Such a process is referred to as *saturated-adiabatic*, because it can be reversed as long as the water remains in the air/cloud. If the rain is falling out, the the process is called *pseudo-adiabatic*, because the heat released by the condensation remains irreversibly in the air.

$$v dp = c_p dT + L_{lv} dm_v \quad , \quad (86)$$

or

$$\frac{c_p}{T} dT - \frac{R}{p} dp = c_p d \ln \theta = -\frac{L_{lv}}{T} dm_v \quad , \quad (87)$$

where the potential temperature of dry air 49 has been used as approximation to the air-water mixture. If condensation occurs in the rising parcel, then $dm_v \leq 0$ it follows that the condensation process is increasing the potential temperature of the rising parcel though *latent heating*. Note, that the approximation 87 is used in many numerical models to represent the process of condensation. The change due to condensation dm_v is parameterized in some ways, e.g. if there is supersaturation it is assumed that the condensation removes the water vapor with a certain time scales until the parcel is saturated again. An extremely simple condensation parameterization would be

$$\left. \frac{dm_v}{dt} \right|_{condlift} = -\frac{m_v - m_{vs}}{\tau} \quad (88)$$

where τ is a time-scale empirically derived. Such a parameterization is used in some numerical models for *large-scale precipitation* (as opposed to *convective precipitation*). Of course, a more sophisticated parameterization would involve cloud microphysics, but we will not treat this topic in this course. For the purpose of this lecture, it is also useful consider the case that the air is always at saturation,

any supersaturation leads to instantaneous condensation until saturation is reached again, which means $m_v = m_{vs}$ and Eq. 87 becomes

$$\frac{c_p}{T} dT - \frac{R}{p} dp = c_p d \ln \theta = -\frac{L_{lv}}{T} dm_{sv} \quad , \quad (89)$$

and this equation can be used to derive the *equivalent potential temperature*. Note that the relationships 87 or 193 are of enormous importance for the atmosphere. We can interpret them as vertical redistribution of 'heat', because, in the global mean, the evaporation from the ocean surfaces cool that surface (which is heated, on the other hand by solar radiation) and the 'heat' is released in the troposphere through condensation (see Fig. 8), with following precipitation. The other importance of Eqs. 87 or 193 lies in driving the large-scale circulations, because we find most of the condensational heating in the tropical regions, and this gives rise to large-scale atmospheric motions that will be discussed later in this course.

3.6 Entropy of the mixture

If we ignore the mixing entropy (exercise!) we may calculate the entropy of the mixture dry air, water vapor and liquid water (see section 2) as

$$s = m_d s_d + m_v s_v + m_l s_l \quad , \quad (90)$$

where s_d, s_v, s_l are the specific entropies of dry air, water vapor and liquid water, respectively. If we calculate the derivative, we get

$$ds = m_d ds_d + m_v ds_v + m_l ds_l + s_d dm_d + s_v dm_v + s_l dm_l \quad , \quad (91)$$

and if we assume again only condensational mass fraction changes

$$ds = m_d ds_d + m_v ds_v + m_l ds_l + \frac{L_{lv}}{T} dm_v \quad , \quad (92)$$

because of Eq. 67. Using the same approximation as for the enthalpy changes we get

$$ds = ds_d + \frac{L_{lv}}{T} dm_v \quad , \quad (93)$$

which leads with Eq. 46 for the dry air to Eq. 87, if we again assume $ds = 0$.

3.7 Equivalent potential temperature

Assuming again that L_{lv} is a constant, Eq. 193 can be written as

$$\frac{c_p}{T} dT - \frac{R}{p} dp = -d \frac{L_{lv} m_{vs}}{T} - \frac{L_{lv} m_{vs}}{T^2} dT \quad , \quad (94)$$

or

$$\left(c_p + \frac{L_{lv} m_{vs}}{T} \right) \frac{1}{T} dT - \frac{R}{p} dp = -d \frac{L_{lv} m_{vs}}{T} \quad . \quad (95)$$

The term $\frac{L_{lv}m_{vs}}{T}$ is about 100 and therefore one order of magnitude smaller than c_p , and can be ignored in this first order calculation. We can integrate Eq. 95 by dropping the term just discussed to get

$$c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} = \frac{L_{lv}m_{vs0}}{T_0} - \frac{L_{lv}m_{vs}}{T} . \quad (96)$$

The reference pressure $p_0 = 1000$ hPa is as for the potential temperature definition. To define the *equivalent potential temperature*, θ_e it is assumed that the vapor is completely condensed and falls out, therefore $m_{vs0} = 0$ as the parcel arrived at the pressure p_0 . In this case we have

$$\theta_e = \theta e^{\frac{L_{lv}m_{vs}}{c_p T}} . \quad (97)$$

The equivalent potential temperature θ_e is a conservative quantity for a *pseudo-adiabatic* process, where ds has assumed to be zero, but we have included the latent heating due to condensation. Note that the equivalent potential temperature is also a measure of the entropy for the moist saturated ascent given all the approximations applied during its derivation and we have $ds = c_p d \ln \theta_e$ (in lecture: calculate logarithm θ_e according to 97 and differentiate and compare with 93). Note that within all approximations used here, the saturation mass fraction m_{vs} can be replaced by the saturation mixing ratio r_{rs} because of $m_{vs} = r_{sv}/(1 + r_{sv})$. Usually, using r_{vs} is the more commonly used formulation for θ_e . Because of $\frac{L_{lv}m_{vs}}{c_p T} \ll 1$, Eq. 97 can be further approximated using a Taylor series expansion to

$$\theta_e = \theta \left(1 + \frac{L_{lv}m_{vs}}{c_p T} \right) . \quad (98)$$

Note that we may evaluate the saturation specific humidity using Eq. 78.

Exercises

1. Assume a specific humidity of $m_v = 0.02$, calculate the virtual temperature difference $T_v - T$ according to 57, if $T=300$ K.
2. Assume a evaporation rate of $f_{evap} = 10^{-5} \text{kg m}^{-2} \text{s}^{-1}$ at the surface. Calculate how much vapor (in kg) is transferred to the whole column of the atmosphere for a surface of 1 m^2 within one day.