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Atmospheric Thermodynamics

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1. Introduction

Thermodynamics deals with the transformations of the energy in a system and between the system and its environment. Hence, it is involved in every atmospheric process, from the large scale general circulation to the local transfer of radiative, sensible and latent heat between the surface and the atmosphere and the microphysical processes producing clouds and aerosol. Thus the topic is much too broad to find an exhaustive treatment within the limits of a book chapter, whose main goal will be limited to give a broad overview of the implications of thermodynamics in the atmospheric science and introduce some of its jargon. The basic thermodynamic principles will not be reviewed here, while emphasis will be placed on some topics that will find application to the interpretation of fundamental atmospheric processes. An overview of the composition of air will be given, together with an outline of its stratification in terms of temperature and water vapour profile. The ideal gas law will be introduced, together with the concept of hydrostatic stability, temperature lapse rate, scale height, and hydrostatic equation. The concept of an air parcel and its enthalpy and free energy will be defined, together with the potential temperature concept that will be related to the static stability of the atmosphere and connected to the Brunt-Vaisala frequency.

Water phase changes play a pivotal role in the atmosphere and special attention will be placed on these transformations. The concept of vapour pressure will be introduced together with the Clausius-Clapeyron equation and moisture parameters will be defined. Adiabatic transformation for the unsaturated and saturated case will be discussed with the help of some aerological diagrams of common practice in Meteorology and the notion of neutral buoyancy and free convection will be introduced and considered referring to an exemplificative atmospheric sounding. There, the Convective Inhibition and Convective Available Potential Energy will be introduced and examined. The last subchapter is devoted to a brief overview of warm and cold clouds formation processes, with the aim to stimulate the interest of reader toward more specialized texts, as some of those listed in the conclusion and in the bibliography.

2. Dry air thermodynamics and stability

We know from experience that pressure, volume and temperature of any homogeneous substance are connected by an *equation of state*. These physical variables, for all gases over a

wide range of conditions in the so called *perfect gas approximation*, are connected by an equation of the form:

$$pV=mRT \tag{1}$$

where p is pressure (Pa), V is volume (m^3), m is mass (kg), T is temperature (K) and R is the *specific gas constant*, whose value depends on the gas. If we express the amount of substance in terms of number of moles $n=m/M$ where M is the gas molecular weight, we can rewrite (1) as:

$$pV=nR^*T \tag{2}$$

where R^* is the *universal gas constant*, whose value is $8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$. In the kinetic theory of gases, the perfect gas is modelled as a collection of rigid spheres randomly moving and bouncing between each other, with no common interaction apart from these mutual shocks. This lack of reciprocal interaction leads to derive the internal energy of the gas, that is the sum of all the kinetic energies of the rigid spheres, as proportional to its temperature. A second consequence is that for a mixture of different gases we can define, for each component i , a partial pressure p_i as the pressure that it would have if it was alone, at the same temperature and occupying the same volume. Similarly we can define the partial volume V_i as that occupied by the same mass at the same pressure and temperature, holding *Dalton's law* for a mixture of gases i :

$$p=\sum p_i \tag{3}$$

Where for each gas it holds:

$$p_iV=n_iR^*T \tag{4}$$

We can still make use of (1) for a mixture of gases, provided we compute a specific gas constant R as:

$$\bar{R} = \frac{\sum m_i R_i}{m} \tag{5}$$

The atmosphere is composed by a mixture of gases, water substance in any of its three physical states and solid or liquid suspended particles (aerosol). The main components of dry atmospheric air are listed in Table 1.

Gas	Molar fraction	Mass fraction	Specific gas constant (J Kg ⁻¹ K ⁻¹)
Nitrogen (N2)	0.7809	0.7552	296.80
Oxygen (O2)	0.2095	0.2315	259.83
Argon (Ar)	0.0093	0.0128	208.13
Carbon dioxide (CO2)	0.0003	0.0005	188.92

Table 1. Main component of dry atmospheric air.

The composition of air is constant up to about 100 km, while higher up molecular diffusion dominates over turbulent mixing, and the percentage of lighter gases increases with height. For the pivotal role water substance plays in weather and climate, and for the extreme variability of its presence in the atmosphere, with abundances ranging from few percents to

millionths, it is preferable to treat it separately from other air components, and consider the atmosphere as a mixture of dry gases and water. In order to use a state equation of the form (1) for moist air, we express a specific gas constant R_d by considering in (5) all gases but water, and use in the state equation a *virtual temperature* T_v defined as the temperature that dry air must have in order to have the same density of moist air at the same pressure. It can be shown that

$$T_v = \frac{T}{1 - \frac{e}{p} \left(1 - \frac{M_w}{M_d}\right)} \quad (6)$$

Where M_w and M_d are respectively the water and dry air molecular weights. T_v takes into account the smaller density of moist air, and so is always greater than the actual temperature, although often only by few degrees.

2.1 Stratification

The atmosphere is under the action of a gravitational field, so at any given level the downward force per unit area is due to the weight of all the air above. Although the air is permanently in motion, we can often assume that the upward force acting on a slab of air at any level, equals the downward gravitational force. This *hydrostatic balance* approximation is valid under all but the most extreme meteorological conditions, since the vertical acceleration of air parcels is generally much smaller than the gravitational one. Consider an horizontal slab of air between z and $z + \delta z$, of unit horizontal surface. If ρ is the air density at z , the downward force acting on this slab due to gravity is $g\rho\delta z$. Let p be the pressure at z , and $p + \delta p$ the pressure at $z + \delta z$. We consider δp as negative, since we know that pressure decreases with height. The hydrostatic balance of forces along the vertical leads to:

$$-\delta p = g\rho\delta z \quad (7)$$

Hence, in the limit of infinitesimal thickness, the *hypsometric equation* holds:

$$-\frac{\partial p}{\partial z} = -g\rho \quad (8)$$

leading to:

$$p(z) = \int_z^\infty g\rho dz \quad (9)$$

As we know that $p(\infty)=0$, (9) can be integrated if the air density profile is known.

Two useful concepts in atmospheric thermodynamic are the geopotential Φ , an exact differential defined as the work done against the gravitational field to raise 1 kg from 0 to z , where the 0 level is often taken at sea level and, to set the constant of integration, $\Phi(0)=0$, and the *geopotential height* $Z = \Phi/g_0$, where g_0 is a mean gravitational acceleration taken as 9.81 m/s².

We can rewrite (9) as:

$$Z(z) = \frac{1}{g_0} \int_z^\infty g dz \quad (10)$$

Values of z and Z often differ by not more than some tens of metres.

We can make use of (1) and of the definition of virtual temperature to rewrite (10) and formally integrate it between two levels to formally obtain the geopotential thickness of a layer, as:

$$\Delta Z = \frac{R_d}{g_0} \int_{p_1}^{p_2} T_v \frac{dp}{p} \quad (11)$$

The above equations can be integrated if we know the virtual temperature T_v as a function of pressure, and many limiting cases can be envisaged, as those of constant vertical temperature gradient. A very simplified case is for an isothermal atmosphere at a temperature $T_v = T_0$, when the integration of (11) gives:

$$\Delta Z = \frac{R_d T_0}{g_0} \ln \left(\frac{p_1}{p_2} \right) = H \ln \left(\frac{p_1}{p_2} \right) \quad (12)$$

In an isothermal atmosphere the pressure decreases exponentially with an e-folding scale given by the *scale height* H which, at an average atmospheric temperature of 255 K, corresponds roughly to 7.5 km. Of course, atmospheric temperature is by no means constant: within the lowest 10-20 km it decreases with a *lapse rate* of about 7 K km⁻¹, highly variable depending on latitude, altitude and season. This region of decreasing temperature with height is termed *troposphere*, (from the Greek “turning/changing sphere”) and is capped by a region extending from its boundary, termed *tropopause*, up to 50 km, where the temperature is increasing with height due to solar UV absorption by ozone, that heats up the air. This region is particularly stable and is termed *stratosphere* (“layered sphere”). Higher above in the *mesosphere* (“middle sphere”) from 50 km to 80-90 km, the temperature falls off again. The last region of the atmosphere, named *thermosphere*, sees the temperature rise again with altitude to 500-2000K up to an isothermal layer several hundreds of km distant from the ground, that finally merges with the interplanetary space where molecular collisions are rare and temperature is difficult to define. Fig. 1 reports the atmospheric temperature, pressure and density profiles. Although the atmosphere is far from isothermal, still the decrease of pressure and density are close to be exponential. The atmospheric temperature profile depends on vertical mixing, heat transport and radiative processes.

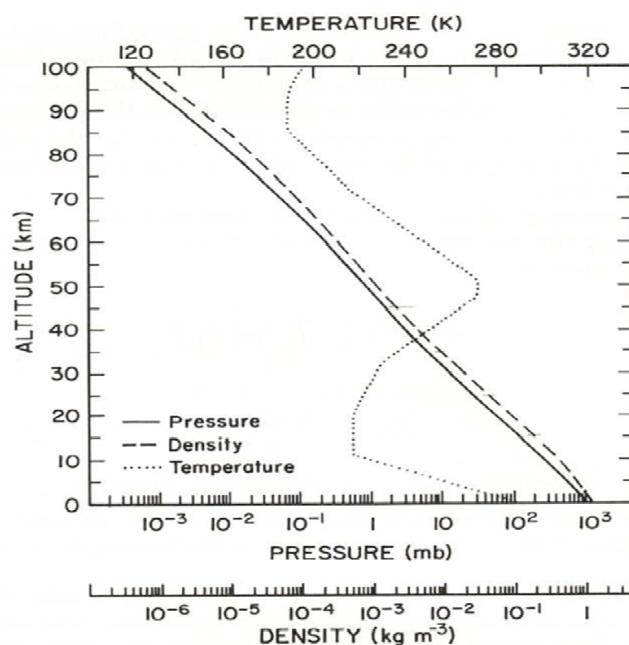


Fig. 1. Temperature (dotted line), pressure (dashed line) and air density (solid line) for a standard atmosphere.

2.2 Thermodynamic of dry air

A system is *open* if it can exchange matter with its surroundings, *closed* otherwise. In atmospheric thermodynamics, the concept of “air parcel” is often used. It is a good approximation to consider the air parcel as a closed system, since significant mass exchanges between airmasses happen predominantly in the few hundreds of metres close to the surface, the so-called *planetary boundary layer* where mixing is enhanced, and can be neglected elsewhere. An air parcel can exchange energy with its surrounding by work of expansion or contraction, or by exchanging heat. An *isolated* system is unable to exchange energy in the form of heat or work with its surroundings, or with any other system. The first principle of thermodynamics states that the *internal energy* U of a closed system, the kinetic and potential energy of its components, is a state variable, depending only on the present state of the system, and not by its past. If a system evolves without exchanging any heat with its surroundings, it is said to perform an *adiabatic* transformation. An air parcel can exchange heat with its surroundings through diffusion or thermal conduction or radiative heating or cooling; moreover, evaporation or condensation of water and subsequent removal of the condensate promote an exchange of latent heat. It is clear that processes which are not adiabatic ultimately lead the atmospheric behaviours. However, for timescales of motion shorter than one day, and disregarding cloud processes, it is often a good approximation to treat air motion as adiabatic.

2.2.1 Potential temperature

For adiabatic processes, the first law of thermodynamics, written in two alternative forms:

$$c_v dT + p dv = \delta q \quad (13)$$

$$c_p dT - v dp = \delta q \quad (14)$$

holds for $\delta q = 0$, where c_p and c_v are respectively the specific heats at constant pressure and constant volume, p and v are the specific pressure and volume, and δq is the heat exchanged with the surroundings. Integrating (13) and (14) and making use of the ideal gas state equation, we get the Poisson's equations:

$$T v^{\gamma-1} = \text{constant} \quad (15)$$

$$T p^{-\kappa} = \text{constant} \quad (16)$$

where $\gamma = c_p/c_v = 1.4$ and $\kappa = (\gamma-1)/\gamma = R/c_p \approx 0.286$, using a result of the kinetic theory for diatomic gases. We can use (16) to define a new state variable that is conserved during an adiabatic process, the *potential temperature* θ , which is the temperature the air parcel would attain if compressed, or expanded, adiabatically to a reference pressure p_0 , taken for convention as 1000 hPa.

$$\theta = T \left(\frac{p_0}{p} \right)^\kappa \quad (18)$$

Since the time scale of heat transfers, away from the planetary boundary layer and from clouds is several days, and the timescale needed for an air parcel to adjust to environmental pressure changes is much shorter, θ can be considered conserved along the air motion for one week or more. The distribution of θ in the atmosphere is determined by the pressure and temperature fields. In fig. 2 annual averages of constant potential temperature surfaces

are depicted, versus pressure and latitude. These surfaces tend to be quasi-horizontal. An air parcel initially on one surface tend to stay on that surface, even if the surface itself can vary its position with time. At the ground level θ attains its maximum values at the equator, decreasing toward the poles. This poleward decrease is common throughout the troposphere, while above the tropopause, situated near 100 hPa in the tropics and 3-400 hPa at medium and high latitudes, the behaviour is inverted.

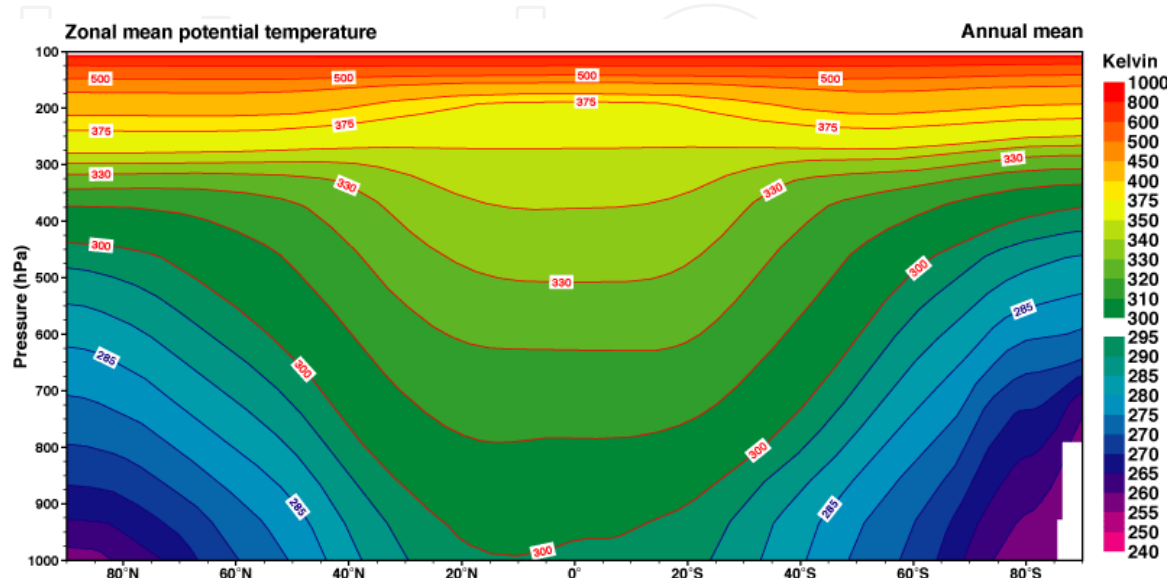


Fig. 2. ERA-40 Atlas : Pressure level climatologies in latitude-pressure projections (source: http://www.ecmwf.int/research/era/ERA40_Atlas/docs/section_D25/charts/D26_XS_YEA.html).

An adiabatic vertical displacement of an air parcel would change its temperature and pressure in a way to preserve its potential temperature. It is interesting to derive an expression for the rate of change of temperature with altitude under adiabatic conditions: using (8) and (1) we can write (14) as:

$$c_p dT + g dz=0 \tag{19}$$

and obtain the *dry adiabatic lapse rate* Γ_d :

$$\Gamma_d = -\left(\frac{dT}{dz}\right)_{adiabatic} = \frac{g}{c_p} \tag{20}$$

If the air parcel thermally interacts with its environment, the adiabatic condition no longer holds and in (13) and (14) $\delta q \neq 0$. In such case, dividing (14) by T and using (1) we obtain:

$$d \ln p - \kappa d \ln p = -\frac{\delta q}{c_p T} \tag{21}$$

Combining the logarithm of (18) with (21) yields:

$$d \ln \theta = \frac{\delta q}{c_p T} \tag{22}$$

That clearly shows how the changes in potential temperature are directly related to the heat exchanged by the system.

2.2.2 Entropy and potential temperature

The second law of the thermodynamics allows for the introduction of another state variable, the *entropy* s , defined in terms of a quantity $\delta q/T$ which is not in general an exact differential, but is so for a reversible process, that is a process proceeding through states of the system which are always in equilibrium with the environment. Under such cases we may pose $ds = (\delta q/T)_{rev}$. For the generic process, the heat absorbed by the system is always lower than what can be absorbed in the reversible case, since a part of heat is lost to the environment. Hence, a statement of the second law of thermodynamics is:

$$ds \geq \frac{\delta q}{T} \quad (23)$$

If we introduce (22) in (23), we note how such expression, connecting potential temperature to entropy, would contain only state variables. Hence equality must hold and we get:

$$d \ln \theta = \frac{ds}{c_p} \quad (24)$$

That directly relates changes in potential temperature with changes in entropy. We stress the fact that in general an adiabatic process does not imply a conservation of entropy. A classical textbook example is the adiabatic free expansion of a gas. However, in atmospheric processes, adiabaticity not only implies the absence of heat exchange through the boundaries of the system, but also absence of heat exchanges between parts of the system itself (Landau et al., 1980), that is, no turbulent mixing, which is the principal source of irreversibility. Hence, in the atmosphere, an adiabatic process always conserves entropy.

2.3 Stability

The vertical gradient of potential temperature determines the stratification of the air. Let us differentiate (18) with respect to z :

$$\frac{\partial \ln \theta}{\partial z} = \frac{\partial \ln T}{\partial z} + \frac{R}{c_p} \left(\frac{\partial p_0}{\partial z} - \frac{\partial p}{\partial z} \right) \quad (25)$$

By computing the differential of the logarithm, and applying (1) and (8), we get:

$$\frac{T}{\theta} \frac{\partial \theta}{\partial z} = \frac{\partial T}{\partial z} + \frac{g}{c_p} \quad (26)$$

If $\Gamma = -(\partial T/\partial z)$ is the environment lapse rate, we get:

$$\Gamma = \Gamma_d - \frac{T}{\theta} \frac{\partial \theta}{\partial z} \quad (27)$$

Now, consider a vertical displacement δz of an air parcel of mass m and let ρ and T be the density and temperature of the parcel, and ρ' and T' the density and temperature of the surrounding. The restoring force acting on the parcel per unit mass will be:

$$f_z = -\frac{\rho' - \rho}{\rho'} g \quad (28)$$

That, by using (1), can be rewritten as:

$$f_z = -\frac{T - T'}{T} g \quad (29)$$

We can replace $(T-T')$ with $(\Gamma_d - \Gamma) \delta z$ if we acknowledge the fact that the air parcel moves adiabatically in an environment of lapse rate Γ . The second order equation of motion (29) can be solved in δz and describes buoyancy oscillations with period $2\pi/N$ where N is the Brunt-Vaisala frequency:

$$N = \left[\frac{g}{T} (\Gamma_d - \Gamma) \right]^{1/2} = \left[\frac{g}{c_p} \frac{\partial \theta}{\partial z} \right]^{1/2} \quad (30)$$

It is clear from (30) that if the environment lapse rate is smaller than the adiabatic one, or equivalently if the potential temperature vertical gradient is positive, N will be real and an air parcel will oscillate around an equilibrium: if displaced upward, the air parcel will find itself colder, hence heavier than the environment and will tend to fall back to its original place; a similar reasoning applies to downward displacements. If the environment lapse rate is greater than the adiabatic one, or equivalently if the potential temperature vertical gradient is negative, N will be imaginary so the upward moving air parcel will be lighter than the surrounding and will experience a net buoyancy force upward. The condition for atmospheric stability can be inspected by looking at the vertical gradient of the potential temperature: if θ increases with height, the atmosphere is stable and vertical motion is discouraged, if θ decreases with height, vertical motion occurs. For average tropospheric conditions, $N \approx 10^{-2} \text{ s}^{-1}$ and the period of oscillation is some tens of minutes. For the more stable stratosphere, $N \approx 10^{-1} \text{ s}^{-1}$ and the period of oscillation is some minutes. This greater stability of the stratosphere acts as a sort of damper for the weather disturbances, which are confined in the troposphere.

3. Moist air thermodynamics

The conditions of the terrestrial atmosphere are such that water can be present under its three forms, so in general an air parcel may contain two gas phases, dry air (d) and water vapour (v), one liquid phase (l) and one ice phase (i). This is an heterogeneous system where, in principle, each phase can be treated as an homogeneous subsystem open to exchanges with the other systems. However, the whole system should be in thermodynamical equilibrium with the environment, and thermodynamical and chemical equilibrium should hold between each subsystem, the latter condition implying that no conversion of mass should occur between phases. In the case of water in its vapour and liquid phase, the chemical equilibrium imply that the vapour phases attains a saturation vapour pressure e_s at which the rate of evaporation equals the rate of condensation and no net exchange of mass between phases occurs.

The concept of chemical equilibrium leads us to recall one of the thermodynamical potentials, the *Gibbs function*, defined in terms of the *enthalpy* of the system. We remind the definition of enthalpy of a system of unit mass:

$$h = u + pv \quad (31)$$

Where u is its specific internal energy, v its specific volume and p its pressure in equilibrium with the environment. We can think of h as a measure of the total energy of the system. It includes both the internal energy required to create the system, and the amount of energy required to make room for it in the environment, establishing its volume and balancing its pressure against the environmental one. Note that this additional energy is not stored in the system, but rather in its environment.

The First law of thermodynamics can be set in a form where h is explicited as:

$$\delta q = dh - v dp \quad (32)$$

And, making use of (14) we can set:

$$dh = c_p dT \quad (33)$$

By combining (32), (33) and (8), and incorporating the definition of geopotential Φ we get:

$$\delta q = d(h + \Phi) \quad (34)$$

Which states that an air parcel moving adiabatically in an hydrostatic atmosphere conserves the sum of its enthalpy and geopotential.

The specific Gibbs free energy is defined as:

$$g = h - Ts = u + pv - Ts \quad (35)$$

It represents the energy available for conversion into work under an isothermal-isobaric process. Hence the criterion for thermodynamical equilibrium for a system at constant pressure and temperature is that g attains a minimum.

For an heterogeneous system where multiple phases coexist, for the k -th species we define its *chemical potential* μ_k as the partial molar Gibbs function, and the equilibrium condition states that the chemical potentials of all the species should be equal. The proof is straightforward: consider a system where n_v moles of vapour (v) and n_l moles of liquid water (l) coexist at pressure e and temperature T , and let $G = n_v \mu_v + n_l \mu_l$ be the Gibbs function of the system. We know that for a virtual displacement from an equilibrium condition, $dG > 0$ must hold for any arbitrary dn_v (which must be equal to $-dn_l$, whether its positive or negative) hence, its coefficient must vanish and $\mu_v = \mu_l$.

Note that if evaporation occurs, the vapour pressure e changes by de at constant temperature, and $d\mu_v = v_v de$, $d\mu_l = v_l de$ where v_v and v_l are the volume occupied by a single molecule in the vapour and the liquid phase. Since $v_v \gg v_l$ we may pose $d(\mu_v - \mu_l) = v_v de$ and, using the state gas equation for a single molecule, $d(\mu_v - \mu_l) = (kT/e) de$. In the equilibrium, $\mu_v = \mu_l$ and $e = e_s$ while in general:

$$(\mu_v - \mu_l) = kT \ln \left(\frac{e}{e_s} \right) \quad (36)$$

holds. We will make use of this relationship we we will discuss the formation of clouds.

3.1 Saturation vapour pressure

The value of e_s strongly depends on temperature and increases rapidly with it. The celebrated Clausius -Clapeyron equation describes the changes of saturated water pressure above a plane surface of liquid water. It can be derived by considering a liquid in equilibrium with its saturated vapour undergoing a Carnot cycle (Fermi, 1956). We here simply state the result as:

$$\frac{de_s}{dT} = \frac{L_v}{T\alpha} \quad (37)$$

Retrieved under the assumption that the specific volume of the vapour phase is much greater than that of the liquid phase. L_v is the latent heat, that is the heat required to convert

a unit mass of substance from the liquid to the vapour phase without changing its temperature. The latent heat itself depends on temperature – at 1013 hPa and 0°C is 2.5×10^6 J kg⁻¹, - hence a number of numerical approximations to (37) have been derived. The World Meteorological Organization bases its recommendation on a paper by Goff (1957):

$$\begin{aligned} \text{Log}_{10} e_s = & 10.79574 (1 - 273.16 / T) - 5.02800 \text{Log}_{10}(T / 273.16) + \\ & + 1.50475 \cdot 10^{-4} (1 - 10(-8.2969 * (T / 273.16 - 1))) + 0.42873 \cdot 10^{-3} \\ & - 3 (10(4.76955 * (1 - 273.16 / T)) - 1) + 0.78614 \end{aligned} \quad (38)$$

Where T is expressed in K and e_s in hPa. Other formulations are used, based on direct measurements of vapour pressures and theoretical calculation to extrapolate the formulae down to low T values (Murray, 1967; Bolton, 1980; Hyland and Wexler, 1983; Sonntag, 1994; Murphy and Koop, 2005) uncertainties at low temperatures become increasingly large and the relative deviations within these formulations are of 6% at -60°C and of 9% at -70°.

An equation similar to (37) can be derived for the vapour pressure of water over ice e_{si} . In such a case, L_v is the latent heat required to convert a unit mass of water substance from ice to vapour phase without changing its temperature. A number of numerical approximations holds, as the Goff-Gratch equation, considered the reference equation for the vapor pressure over ice over a region of -100°C to 0°C:

$$\begin{aligned} \text{Log}_{10} e_{si} = & -9.09718 (273.16 / T - 1) - 3.56654 \text{Log}_{10}(273.16 / T) + \\ & + 0.876793 (1 - T / 273.16) + \text{Log}_{10}(6.1071) \end{aligned} \quad (39)$$

with T in K and e_{si} in hPa. Other equations have also been widely used (Murray, 1967; Hyland and Wexler, 1983; Marti and Mauersberger, 1993; Murphy and Koop, 2005).

Water evaporates more readily than ice, that is $e_s > e_{si}$ everywhere (the difference is maxima around -20°C), so if liquid water and ice coexists below 0°C, the ice phase will grow at the expense of the liquid water.

3.2 Water vapour in the atmosphere

A number of moisture parameters can be formulated to express the amount of water vapour in the atmosphere. The *mixing ratio* r is the ratio of the mass of the water vapour m_v , to the mass of dry air m_d , $r = m_v / m_d$ and is expressed in g/kg⁻¹ or, for very small concentrations as those encountered in the stratosphere, in parts per million in volume (ppmv). At the surface, it typically ranges from 30-40 g/kg⁻¹ at the tropics to less than 5 g/kg⁻¹ at the poles; it decreases approximately exponentially with height with a scale height of 3-4 km, to attain its minimum value at the tropopause, driest at the tropics where it can get as low as a few ppmv. If we consider the ratio of m_v to the total mass of air, we get the *specific humidity* q as $q = m_v / (m_v + m_d) = r / (1 + r)$. The *relative humidity* RH compares the water vapour pressure in an air parcel with the maximum water vapour it may sustain in equilibrium at that temperature, that is $RH = 100 e / e_s$ (expressed in percentages). The dew point temperature T_d is the temperature at which an air parcel with a water vapour pressure e should be brought isobarically in order to become saturated with respect to a plane surface of water. A similar definition holds for the frost point temperature T_f , when the saturation is considered with respect to a plane surface of ice.

The *wet-bulb temperature* T_w is defined operationally as the temperature a thermometer would attain if its glass bulb is covered with a moist cloth. In such a case the thermometer is

cooled upon evaporation until the surrounding air is saturated: the heat required to evaporate water is supplied by the surrounding air that is cooled. An evaporating droplet will be at the wet-bulb temperature. It should be noted that if the surrounding air is initially unsaturated, the process adds water to the air close to the thermometer, to become saturated, hence it increases its mixing ratio r and in general $T \geq T_w \geq T_d$, the equality holds when the ambient air is already initially saturated.

3.2 Thermodynamics of the vertical motion

The saturation mixing ratio depends exponentially on temperature. Hence, due to the decrease of ambient temperature with height, the saturation mixing ratio sharply decreases with height as well.

Therefore the water pressure of an ascending moist parcel, despite the decrease of its temperature at the dry adiabatic lapse rate, sooner or later will reach its saturation value at a level named *lifting condensation level* (LCL), above which further lifting may produce condensation and release of latent heat. This internal heating slows the rate of cooling of the air parcel upon further lifting.

If the condensed water stays in the parcel, and heat transfer with the environment is negligible, the process can be considered reversible – that is, the heat internally added by condensation could be subtracted by evaporation if the parcel starts descending – hence the behaviour can still be considered adiabatic and we will term it a *saturated adiabatic process*. If otherwise the condensate is removed, as instance by sedimentation or precipitation, the process cannot be considered strictly adiabatic. However, the amount of heat at play in the condensation process is often negligible compared to the internal energy of the air parcel and the process can still be considered well approximated by a saturated adiabat, although it should be more properly termed a *pseudoadiabatic* process.

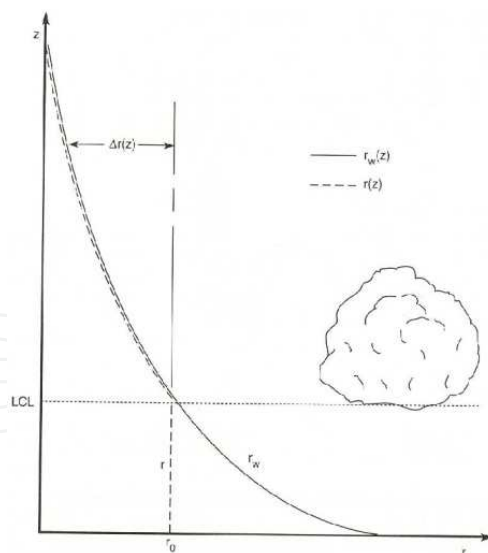


Fig. 3. Vertical profiles of mixing ratio r and saturated mixing ratio r_s for an ascending air parcel below and above the lifting condensation level. (source: Salby M. L., Fundamentals of Atmospheric Physics, Academic Press, New York.)

3.2.1 Pseudoadiabatic lapse rate

If within an air parcel of unit mass, water vapour condenses at a saturation mixing ratio r_s , the amount of latent heat released during the process will be $-L_w dr_s$. This can be put into (34) to get:

$$-L_w dr_s = c_p dT + g dz \quad (40)$$

Dividing by $c_p dz$ and rearranging terms, we get the expression of the *saturated adiabatic lapse rate* Γ_s :

$$\Gamma_s = -\frac{dT}{dz} = \frac{\Gamma_d}{\left(1 + \left(\frac{L_w}{c_p}\right)\left(\frac{dr_s}{dz}\right)\right)} \quad (41)$$

Whose value depends on pressure and temperature and which is always smaller than Γ_d , as should be expected since a saturated air parcel, since condensation releases latent heat, cools more slowly upon lifting.

3.2.2 Equivalent potential temperature

If we pose $\delta q = -L_w dr_s$ in (22) we get:

$$\frac{d\theta}{\theta} = -\frac{L_w dr_s}{c_p T} \simeq -d\left(\frac{L_w r_s}{c_p T}\right) \quad (42)$$

The approximate equality holds since $dT/T \ll dr_s/r_s$ and L_w/c_p is approximately independent of T. So (41) can be integrated to yield:

$$\theta_e = \theta \exp\left(\frac{L_w r_s}{c_p T}\right) \quad (43)$$

That defines the *equivalent potential temperature* θ_e (Bolton, 1990) which is constant along a pseudoadiabatic process, since during the condensation the reduction of r_s and the increase of θ act to compensate each other.

3.3 Stability for saturated air

We have seen for the case of dry air that if the environment lapse rate is smaller than the adiabatic one, the atmosphere is stable: a restoring force exist for infinitesimal displacement of an air parcel. The presence of moisture and the possibility of latent heat release upon condensation complicates the description of stability.

If the air is saturated, it will cool upon lifting at the smaller saturated lapse rate Γ_s so in an environment of lapse rate Γ , for the saturated air parcel the cases $\Gamma < \Gamma_s$, $\Gamma = \Gamma_s$, $\Gamma > \Gamma_s$ discriminates the absolutely stable, neutral and unstable conditions respectively. An interesting case occurs when the environmental lapse rate lies between the dry adiabatic and the saturated adiabatic, that is $\Gamma_s < \Gamma < \Gamma_d$. In such a case, a moist unsaturated air parcel can be lifted high enough to become saturated, since the decrease in its temperature due to adiabatic cooling is offset by the faster decrease in water vapour saturation pressure, and starts condensation at the LCL. Upon further lifting, the air parcel eventually get warmer than its environment at a level termed *Level of Free Convection (LFC)* above which it will develop a positive buoyancy fuelled by the continuous release of latent heat due to condensation, as long as there is vapour to condense. This situation of *conditional instability* is most common in the atmosphere, especially in the Tropics, where a forced finite uplifting of moist air may eventually lead to spontaneous convection. Let us refer to figure 4 and follow such process more closely. In the figure, which is one of the meteograms discussed later in the chapter, pressure decreases vertically, while lines of constant temperature are tilted 45° rightward, temperature decreasing going up and to the left.

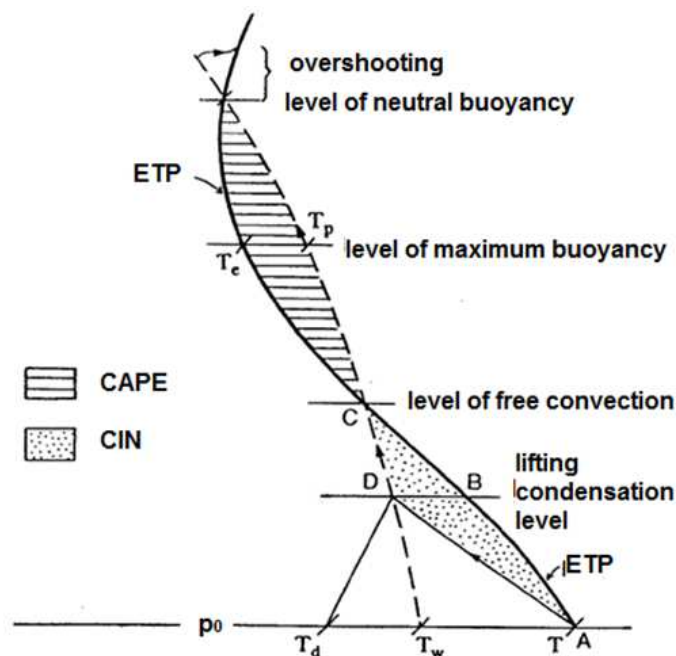


Fig. 4. Thick solid line represent the environment temperature profile. Thin solid line represent the temperature of an ascending parcel initially at point A. Dotted area represent CIN, shaded area represent CAPE.

The thick solid line represent the environment temperature profile. A moist air parcel initially at rest at point A is lifted and cools at the adiabatic lapse rate Γ_d along the thin solid line until it eventually get saturated at the Lifting Condensation Level at point D. During this lifting, it gets colder than the environment. Upon further lifting, it cools at a slower rate at the pseudoadiabatic lapse rate Γ_s along the thin dashed line until it reaches the Level of Free Convection at point C, where it attains the temperature of the environment. If it gets beyond that point, it will be warmer, hence lighter than the environment and will experience a positive buoyancy force. This buoyancy will sustain the ascent of the air parcel until all vapour condenses or until its temperature crosses again the profile of environmental temperature at the *Level of Neutral Buoyancy (LNB)*. Actually, since the air parcel gets there with a positive vertical velocity, this level may be surpassed and the air parcel may overshoot into a region where it experiences negative buoyancy, to eventually get mixed there or splash back to the LNB. In practice, entrainment of environmental air into the ascending air parcel often occurs, mitigates the buoyant forces, and the parcel generally reaches below the LNB.

If we neglect such entrainment effects and consider the motion as adiabatic, the buoyancy force is conservative and we can define a potential. Let ρ and ρ' be respectively the environment and air parcel density. From Archimede's principle, the buoyancy force on a unit mass parcel can be expressed as in (29), and the increment of potential energy for a displacement δz will then be, by using (1) and (8):

$$dP = f_b = \left(\frac{T' - T}{T} \right) g \delta z = R(T' - T) d \log p \quad (44)$$

Which can be integrated from a reference level p_0 to give:

$$dP(p) = -R \int_{p_0}^p (T' - T) d \log p = -RA(p) \quad (45)$$

Referring to fig. 4, $A(p)$ represent the shaded area between the environment and the air parcel temperature profiles. An air parcel initially in A is bound inside a “potential energy well” whose depth is proportional to the dotted area, and that is termed *Convective Inhibition (CIN)*. If forcibly raised to the level of free convection, it can ascent freely, with an available potential energy given by the shaded area, termed *CAPE (Convective Available Potential Energy)*.

In absence of entrainment and frictional effects, all this potential energy will be converted into kinetic energy, which will be maximum at the level of neutral buoyancy. CIN and CAPE are measured in J/Kg and are indices of the atmospheric instability. The CAPE is the maximum energy which can be released during the ascent of a parcel from its free buoyant level to the top of the cloud. It measures the intensity of deep convection, the greater the CAPE, the more vigorous the convection. Thunderstorms require large CAPE of more than 1000 Jkg^{-1} .

CIN measures the amount of energy required to overcome the negatively buoyant energy the environment exerts on the air parcel, the smaller, the more unstable the atmosphere, and the easier to develop convection. So, in general, convection develops when CIN is small and CAPE is large. We want to stress that some CIN is needed to build-up enough CAPE to eventually fuel the convection, and some mechanical forcing is needed to overcome CIN. This can be provided by cold front approaching, flow over obstacles, sea breeze.

CAPE is weaker for maritime than for continental tropical convection, but the onset of convection is easier in the maritime case due to smaller CIN.

We have neglected entrainment of environment air, and detrainment from the air parcel, which generally tend to slow down convection. However, the parcels reaching the highest altitude are generally coming from the region below the cloud without being too much diluted.

Convectively generated clouds are not the only type of clouds. Low level stratiform clouds and high altitude cirrus are a large part of cloud cover and play an important role in the Earth radiative budget. However convection is responsible of the strongest precipitations, especially in the Tropics, and hence of most of atmospheric heating by latent heat transfer.

So far we have discussed the stability behaviour for a single air parcel. There may be the case that although the air parcel is stable within its layer, the layer as a whole may be destabilized if lifted. Such case happen when a strong vertical stratification of water vapour is present, so that the lower levels of the layer are much moister than the upper ones. If the layer is lifted, its lower levels will reach saturation before the uppermost ones, and start cooling at the slower pseudoadiabatic rate, while the upper layers will still cool at the faster adiabatic rate. Hence, the top part of the layer cools much more rapidly of the bottom part and the lapse rate of the layer becomes unstable. This *potential (or convective) instability* is frequently encountered in the lower levels in the Tropics, where there is a strong water vapour vertical gradient.

It can be shown that condition for a layer to be potentially unstable is that its equivalent potential temperature θ_e decreases within the layer.

3.4 Tephigrams

To represent the vertical structure of the atmosphere and interpret its state, a number of diagrams is commonly used. The most common are *emagrams*, *Stüve diagrams*, *skew T- log p diagrams*, and *tephigrams*.

An *emagram* is basically a T - z plot where the vertical axis is $\log p$ instead of height z . But since $\log p$ is linearly related to height in a dry, isothermal atmosphere, the vertical coordinate is basically the geometric height.

In the *Stüve diagram* the vertical coordinate is $p^{(R_d/c_p)}$ and the horizontal coordinate is T : with this axes choice, the dry adiabats are straight lines.

A *skew T- $\log p$ diagram*, like the emagram, has $\log p$ as vertical coordinate, but the isotherms are slanted. *Tephigrams* look very similar to skew T diagrams if rotated by 45° , have T as horizontal and $\log \theta$ as vertical coordinates so that isotherms are vertical and the isentropes horizontal (hence tephigram, a contraction of T and Φ , where $\Phi = c_p \log \theta$ stands for the entropy). Often, tephigrams are rotated by 45° so that the vertical axis corresponds to the vertical in the atmosphere.

A tephigram is shown in figure 5: straight lines are isotherms (slope up and to the right) and isentropes (up and to the left), isobars (lines of constant p) are quasi-horizontal lines, the dashed lines sloping up and to the right are constant mixing ratio in g/kg, while the curved solid bold lines sloping up and to the left are saturated adiabats.

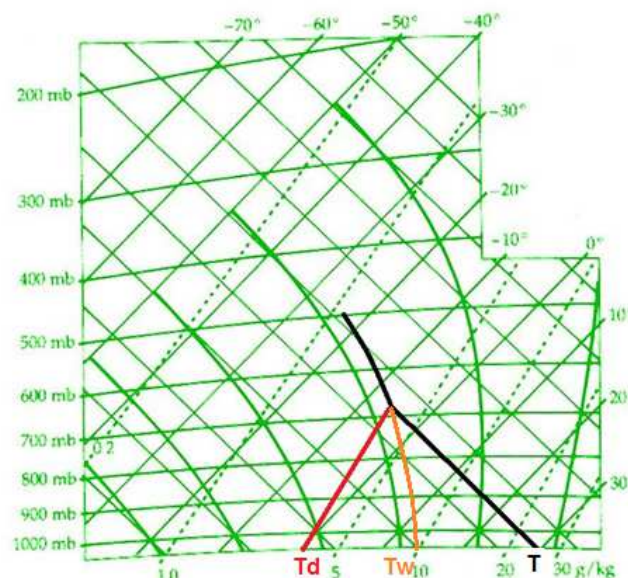


Fig. 5. A tephigram. Starting from the surface, the red line depicts the evolution of the Dew Point temperature, the black line depicts the evolution of the air parcel temperature, upon uplifting. The two lines intersect at the LCL. The orange line depicts the saturated adiabat crossing the LCL point, that defines the wet bulb temperature at the ground pressure surface.

Two lines are commonly plotted on a tephigram – the temperature and dew point, so the state of an air parcel at a given pressure is defined by its temperature T and T_d , that is its water vapour content. We note that the knowledge of these parameters allows to retrieve all the other humidity parameters: from the dew point and pressure we get the humidity mixing ratio w ; from the temperature and pressure we get the saturated mixing ratio w_s , and relative humidity may be derived from $100 \cdot w / w_s$, when w and w_s are measured at the same pressure.

When the air parcel is lifted, its temperature T follows the dry adiabatic lapse rate and its dew point T_d its constant vapour mixing ratio line - since the mixing ratio is conserved in

unsaturated air - until the two meet at the LCL where condensation may start to happen. Further lifting follows the Saturated Adiabatic Lapse Rate. In Figure 5 we see an air parcel initially at ground level, with a temperature of 30° and a Dew Point temperature of 0° (which as we can see by inspecting the diagram, corresponds to a mixing ratio of approx. 4 g/kg at ground level) is lifted adiabatically to 700 mb which is its LCL where the air parcel temperature following the dry adiabat meets the air parcel dew point temperature following the line of constant mixing ratio. Above 700 mb, the air parcel temperature follows the pseudoadiabat. Figure 5 clearly depicts the *Normand's rule*: The dry adiabatic through the temperature, the mixing ratio line through the dew point, and the saturated adiabatic through the wet bulb temperature, meet at the LCL. In fact, the saturated adiabat that crosses the LCL is the same that intersect the surface isobar exactly at the wet bulb temperature, that is the temperature a wetted thermometer placed at the surface would attain by evaporating - at constant pressure - its water inside its environment until it gets saturated.

Figure 6 reports two different temperature soundings: the black dotted line is the dew point profile and is common to the two soundings, while the black solid line is an early morning sounding, where we can see the effect of the nocturnal radiative cooling as a temperature inversion in the lowermost layer of the atmosphere, between 1000 and 960 hPa. The state of the atmosphere is such that an air parcel at the surface has to be forcedly lifted to 940 hPa to attain saturation at the LCL, and forcedly lifted to 600 hPa before gaining enough latent heat of condensation to become warmer than the environment and positively buoyant at the LFB. The temperature of such air parcel is shown as a grey solid line in the graph.

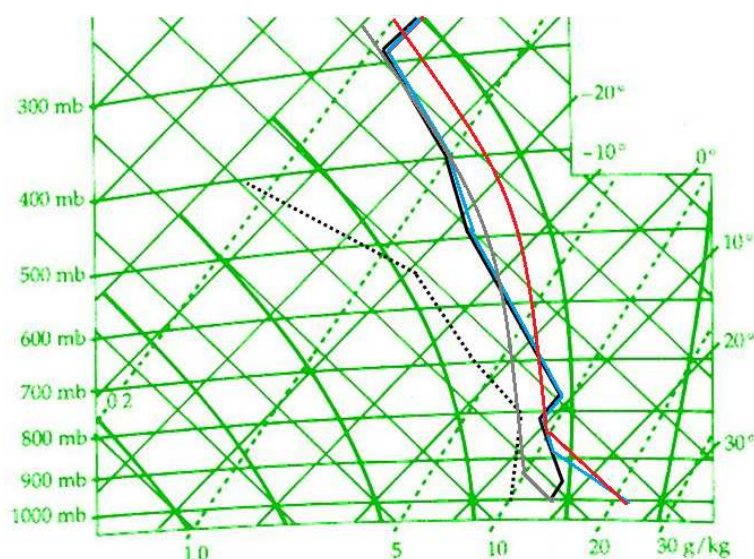


Fig. 6. A tephigram showing with the black and blue lines two different temperature soundings, and with the grey and red lines two different temperature histories of an air parcel initially at ground level, upon lifting. The dotted line is the common T_d profile of the two soundings.

The blue solid line is an afternoon sounding, when the surface has been radiatively heated by the sun. An air parcel lifted from the ground will follow the red solid line, and find itself immediately warmer than its environment and gaining positive buoyancy, further increased by the release of latent heat starting at the LCL at 850 hPa. Notice however that a

second inversion layer is present in the temperature sounding between 800 hPa and 750 hPa, such that the air parcel becomes colder than the environment, hence negatively buoyant between 800 hPa and 700 hPa. If forcedly uplifted beyond this stable layer, it again attains a positive buoyancy up to above 300 hPa.

As the tephigram is a graph of temperature against entropy, an area computed from these variables has dimensions of energy. The area between the air parcel path is then linked to the CIN and the CAPE. Referring to the early morning sounding, the area between the black and the grey line between the surface and 600 hPa is the CIN, the area between 600 hPa and 400 hPa is the CAPE.

4. The generation of clouds

Clouds play a pivotal role in the Earth system, since they are the main actors of the atmospheric branch of the water cycle, promote vertical redistribution of energy by latent heat capture and release and strongly influence the atmospheric radiative budget.

Clouds may form when the air becomes supersaturated, as it can happen upon lifting as explained above, but also by other processes, as isobaric radiative cooling like in the formation of *radiative fogs*, or by mixing of warm moist air with cold dry air, like in the generation of airplane contrails and *steam fogs* above lakes.

Cumulus or *cumulonimbus* are classical examples of convective clouds, often precipitating, formed by reaching the saturation condition with the mechanism outlined hereabove.

Other types of clouds are *alto-cumulus* which contain liquid droplets between 2000 and 6000m in mid-latitudes and cluster into compact herds. They are often, during summer, precursors of late afternoon and evening developments of deep convection.

Cirrus are high altitude clouds composed of ice, rarely opaque. They form above 6000m in mid-latitudes and often promise a warm front approaching. Such clouds are common in the Tropics, formed as remains of anvils or by in situ condensation of rising air, up to the tropopause. *Nimbo-stratus* are very opaque low clouds of undefined base, associated with persistent precipitations and snow. *Strato-cumulus* are composed by water droplets, opaque or very opaque, with a cloud base below 2000m, often associated with weak precipitations.

Stratus are low clouds with small opacity, undefined base under 2000m that can even reach the ground, forming fog. Images of different types of clouds can be found on the Internet (see, as instance, <http://cimss.ssec.wisc.edu/satmet/gallery/gallery.html>).

In the following subchapters, a brief outline will be given on how clouds form in a saturated environment. The level of understanding of water cloud formation is quite advanced, while it is not so for ice clouds, and for glaciation processes in water clouds.

4.1 Nucleation of droplets

We could think that the more straightforward way to form a cloud droplet would be by condensation in a saturated environment, when some water molecules collide by chance to form a cluster that will further grow to a droplet by picking up more and more molecules from the vapour phase. This process is termed *homogeneous nucleation*. The survival and further growth of the droplet in its environment will depend on whether the Gibbs free energy of the droplet and its surrounding will decrease upon further growth. We note that,

by creating a droplet, work is done not only as expansion work, but also to form the interface between the droplet and its environment, associated with the *surface tension* at the surface of the droplet of area A . This originates from the cohesive forces among the liquid molecules. In the interior of the droplet, each molecule is equally pulled in every direction by neighbouring molecules, resulting in a null net force. The molecules at the surface do not have other molecules on all sides of them and therefore are only pulled inwards, as if a force acted on interface toward the interior of the droplet. This creates a sort of pressure directed inward, against which work must be exerted to allow further expansion. This effect forces liquid surfaces to contract to the minimal area.

Let σ be the energy required to form a droplet of unit surface; then, for the heterogeneous system droplet-surroundings we may write, for an infinitesimal change of the droplet:

$$dG = -SdT + Vdp + (\mu_v - \mu_l)dm_v + \sigma dA \quad (46)$$

We note that $dm_v = -dm_l = -n_l dV$ where n_l is the number density of molecules inside the droplet. Considering an isothermal-isobaric process, we came to the conclusion that the formation of a droplet of radius r results in a change of Gibbs free given by:

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 n_l K T \ln\left(\frac{e}{e_s}\right) \quad (47)$$

Where we have used (36). Clearly, droplet formation is thermodynamically unfavoured for $e < e_s$, as should be expected. If $e > e_s$, we are in supersaturated conditions, and the second term can counterbalance the first to give a negative ΔG .

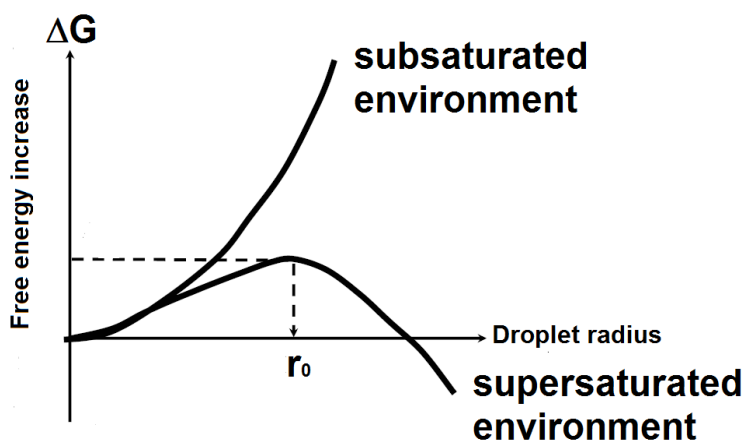


Fig. 7. Variation of Gibbs free energy of a pure water droplet formed by homogeneous nucleation, in a subsaturated (upper curve) and a supersaturated (lower curve) environment, as a function of the droplet radius. The critical radius r_0 is shown.

Figure 7 shows two curves of ΔG as a function of the droplet radius r , for a subsaturated and supersaturated environment. It is clear that below saturation every increase of the droplet radius will lead to an increase of the free energy of the system, hence is thermodynamically unfavourable and droplets will tend to evaporate. In the supersaturated case, on the contrary, a critical value of the radius exists, such that droplets that grows by casual collision among molecules beyond that value, will continue to grow: they are said to get *activated*. The expression for such *critical radius* is given by the *Kelvin's formula*:

$$r_0 = \frac{2\sigma}{n_l K T \ln\left(\frac{e}{e_s}\right)} \quad (48)$$

The greater e with respect to e_s , that is the degree of supersaturation, the smaller the radius beyond which droplets become activated.

It can be shown from (48) that a droplet with a radius as small as $0.01 \mu\text{m}$ would require a supersaturation of 12% for getting activated. However, air is seldom more than a few percent supersaturated, and the homogeneous nucleation process is thus unable to explain the generation of clouds. Another process should be invoked: the *heterogeneous nucleation*. This process exploits the ubiquitous presence in the atmosphere of particles of various nature (Kaufman et al., 2002), some of which are soluble (hygroscopic) or wettable (hydrophilic) and are called *Cloud Condensation Nuclei (CCN)*. Water may form a thin film on wettable particles, and if their dimension is beyond the critical radius, they form the nucleus of a droplet that may grow in size. Soluble particles, like sodium chloride originating from sea spray, in presence of moisture absorb water and dissolve into it, forming a droplet of solution. The saturation vapour pressure over a solution is smaller than over pure water, and the fractional reduction is given by *Raoult's law*:

$$f = \frac{e'}{e} \quad (49)$$

Where e is the vapour pressure over pure water, and e' is the vapour pressure over a solution containing a *mole fraction* f (number of water moles divided by the total number of moles) of pure water.

Let us consider a droplet of radius r that contains a mass m of a substance of molecular weight M_s dissolved into i ions per molecule, such that the effective number of moles in the solution is im/M_s . The number of water moles will be $((4/3)\pi r^3 \rho - m)/M_w$ where ρ and M_w are the water density and molecular weight respectively. The water mole fraction f is:

$$f = \frac{\frac{(4/3)\pi r^3 \rho - m}{M_w}}{\frac{(4/3)\pi r^3 \rho - m}{M_w} + \frac{im}{M_s}} = \left(1 + \frac{imM_w}{M_s((4/3)\pi r^3 \rho - m)}\right)^{-1} \quad (50)$$

Eq. (49) and (50) allows us to express the reduced value e' of the saturation vapour pressure for a droplet of solution. Using this result into (48) we can compute the saturation vapour pressure in equilibrium with a droplet of solution of radius r :

$$\frac{e'}{e_s} = \exp\left(\frac{2\sigma}{n_l K T r}\right) \left(1 + \frac{imM_w}{M_s((4/3)\pi r^3 \rho - m)}\right)^{-1} \quad (51)$$

The plot of supersaturation $e'/e_s - 1$ for two different values of m is shown in fig. 8, and is named *Köhler curve*.

Figure 8 clearly shows how the amount of supersaturation needed to sustain a droplet of solution of radius r is much lower than what needed for a droplet of pure water, and it decreases with the increase of solute concentration. Consider an environment supersaturation of 0.2%. A droplet originated from condensation on a sphere of sodium chloride of diameter $0.1 \mu\text{m}$ can grow indefinitely along the blue curve, since the peak of the curve is below the environment supersaturation; such droplet is *activated*. A droplet originated from a smaller grain of sodium chloride of $0.05 \mu\text{m}$ diameter will grow until

when the supersaturation adjacent to it is equal to the environmental: attained that maximum radius, the droplet stops its grow and is in stable equilibrium with the environment. Such *haze droplet* is said to be *unactivated*.

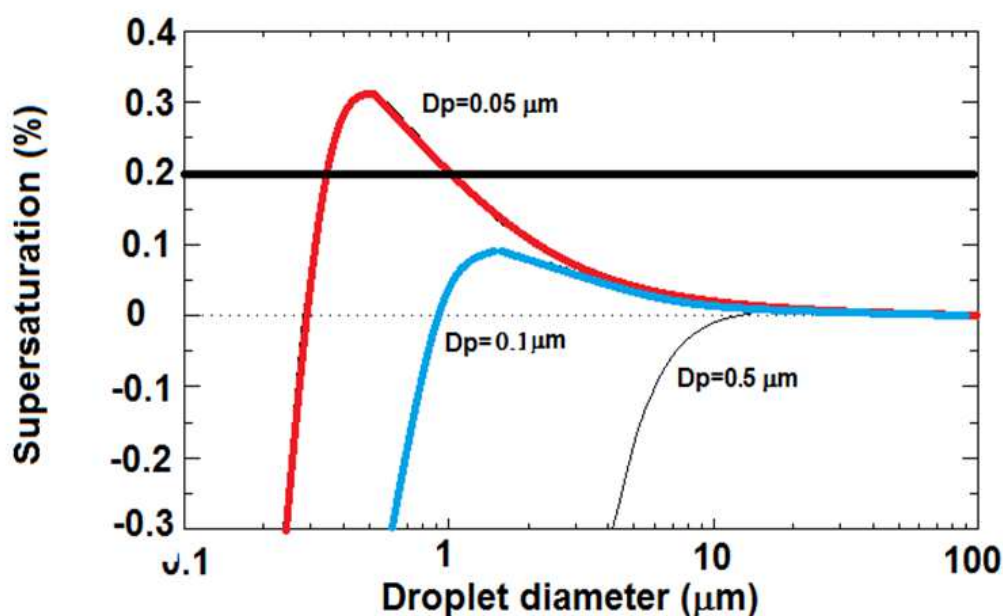


Fig. 8. Köhler curves showing how the critical diameter and supersaturation are dependent upon the amount of solute. It is assumed here that the solute is a perfect sphere of sodium chloride (source: http://en.wikipedia.org/wiki/Köhler_theory).

4.2 Condensation

The droplet that is able to pass over the peak of the Köhler curve will continue to grow by condensation. Let us consider a droplet of radius r at time t , in a supersaturated environment whose water vapour density far from the droplet is $\rho_v(\infty)$, while the vapour density in proximity of the droplet is $\rho_v(r)$. The droplet mass M will grow at the rate of mass flux across a sphere of arbitrary radius centred on the droplet. Let D be the diffusion coefficient, that is the amount of water vapour diffusing across a unit area through a unit concentration gradient in unit time, and $\rho_v(x)$ the water vapour density at a distance $x > r$ from the droplet. We will have:

$$\frac{dM}{dt} = 4\pi x^2 D \frac{d\rho_v(x)}{dx} \quad (52)$$

Since in steady conditions of mass flow this equation is independent of x , we can integrate it for x between r and ∞ to get:

$$\frac{dM}{dt} \int_r^\infty \frac{dx}{x^2} = \int_{\rho_v(r)}^{\rho_v(\infty)} d\rho_v(x) \quad (53)$$

Or, expliciting M as $(4/3)\pi r^3 \rho_l$:

$$\frac{dr}{dt} = \frac{D}{r \rho_l} (\rho_v(\infty) - \rho_v(r)) = \frac{D \rho_v(\infty)}{r \rho_l e(\infty)} (e(\infty) - e(r)) \quad (54)$$

Where we have used the ideal gas equation for water vapour. We should think of $e(r)$ as given by e' in (49), but in fact we can approximate it with the saturation vapour pressure over a plane surface e_s , and pose $(e(\infty)-e(r))/e(\infty)$ roughly equal to the supersaturation $S=(e(\infty)-e_s)/e_s$ to come to:

$$\frac{dr}{dt} r = \frac{D \rho_v(\infty)}{\rho_l} S \quad (55)$$

This equation shows that the radius growth is inversely proportional to the radius itself, so that the rate of growth will tend to slow down with time. In fact, condensation alone is too slow to eventually produce rain droplets, and a different process should be invoked to create droplet with radius greater than few tens of micrometers.

4.3 Collision and coalescence

The droplet of density ρ_l and volume V is suspended in air of density ρ so that under the effect of the gravitational field, three forces are acting on it: the gravity exerting a downward force $\rho_l V g$, the upward Archimede's buoyancy ρV and the *drag force* that for a sphere, assumes the form of the *Stokes' drag* $6\pi\eta r v$ where η is the viscosity of the air and v is the steady state terminal fall speed of the droplet. In steady state, by equating those forces and assuming the droplet density much greater than the air, we get an expression for the terminal fall speed:

$$v = \frac{2}{9} \frac{\rho_l g r^2}{\eta} \quad (56)$$

Such speed increases with the droplet dimension, so that bigger droplets will eventually collide with the smaller ones, and may entrench them with a *collection efficiency* E depending on their radius and other environmental parameters, as for instance the presence of electric fields. The rate of increase of the radius r_1 of a spherical collector drop due to collision with water droplets in a cloud of *liquid water content* w_l , that is is the mass density of liquid water in the cloud, is given by:

$$\frac{dr}{dt} = \frac{(v_1 - v_2) w_l E}{4 \rho_l} \cong \frac{v_1 w_l E}{4 \rho_l} \cong \quad (57)$$

Since v_1 increases with r_1 , the process tends to speed up until the collector drops became a rain drop and eventually pass through the cloud base, or split up to reinitiate the process.

4.4 Nucleation of ice particles

A cloud above 0° is said a *warm cloud* and is entirely composed of water droplets. Water droplet can still exists in *cold clouds* below 0° , although in an unstable state, and are termed *supercooled*. If a cold cloud contains both water droplets and ice, is said *mixed cloud*; if it contains only ice, it is said *glaciated*.

For a droplet to freeze, a number of water molecules inside it should come together and form an *ice embryo* that, if exceeds a critical size, would produce a decrease of the Gibbs free energy of the system upon further growing, much alike the homogeneous condensation from the vapour phase to form a droplet. This glaciations process is termed *homogeneous freezing*, and below roughly -37°C is virtually certain to occur. Above that temperature, the

critical dimensions of the ice embryo are several micrometers, and such process is not favoured. However, the droplet can contain impurities, and some of them may promote collection of water droplets into an ice-like structure to form a ice-like embryo with dimension already beyond the critical size for glaciations. Such particles are termed *ice nuclei* and the process they start is termed *heterogeneous freezing*. Such process can start not only within the droplet, but also upon contact of the ice nucleus with the surface of the droplet (*contact nucleation*) or directly by deposition of ice on it from the water vapour phase (*deposition nucleation*). Good candidates to act as ice nuclei are those particle with molecular structure close to the hexagonal ice crystallography. Some soil particles, some organics and even some bacteria are effective nucleators, but only one out of 10^3 - 10^5 atmospheric particles can act as an ice nucleus. Nevertheless ice particles are present in clouds in concentrations which are orders of magnitude greater than the presence of ice nuclei. Hence, ice multiplication processes must be at play, like breaking of ice particles upon collision, to create ice splinterings that enhance the number of ice particles.

4.5 Growth of ice particles

Ice particles can grow from the vapour phase as in the case of water droplets. In a mixed phase cloud below 0°C , a much greater supersaturation is reached with respect to ice that can reach several percents, than with respect to water, which hardly exceed 1%. Hence ice particles grows faster than droplets and, since this deplete the vapour phase around them, it may happen that around a growing ice particle, water droplets evaporate. Ice can form in a variety of shapes, whose basic habits are determined by the temperature at which they grow. Another process of growth in a mixed cloud is by *riming*, that is by collision with supercooled droplets that freeze onto the ice particle. Such process is responsible of the formation of hailstones.

A process effective in cold clouds is the *aggregation* of ice particles between themselves, when they have different shapes and/or dimension, hence different fall speeds.

5. Conclusion

A brief overview of some topic of relevance in atmospheric thermodynamic has been provided, but much had to remain out of the limits of this introduction, so the interested reader is encouraged to further readings. For what concerns moist thermodynamics and convection, the reader can refer to chapters in introductory atmospheric science textbooks like the classical Wallace and Hobbs (2006), or Salby (1996). At a higher level of deepening the classical reference is Iribarne and Godson (1973). For the reader who seeks a more theoretical approach, Zdunkowski and Bott (2004) is a good challenge. Convection is thoughtfully treated in Emmanuel (1994) while a sound review is given in the article of Stevens (2005). For what concerns the microphysics of clouds, the reference book is Pruppacher and Klett (1996). A number of seminal journal articles dealing with the thermodynamics of the general circulation of the atmosphere can be cited: Goody (2003), Pauluis and Held (2002), Renno and Ingersoll (2008), Pauluis et al. (2008) and references therein. Finally, we would like to suggest the Bohren (2001) delightful book, for which a scientific or mathematical background is not required, that explores topics in meteorology and basic physics relevant to the atmosphere.

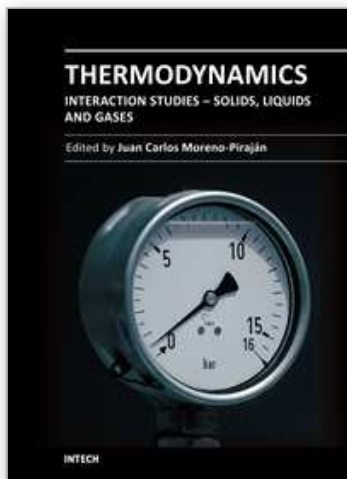
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