Fundamentals of Atmospheric Physics

Lecture 6

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Phase changes of water (latent heat transfer)



Equilibrium Curve

Equilibrium: Rate of condensation = Rate of evaporation e_s : water vapor pressure at equilibrium (saturation)



Water vapour is a minor constituent of the atmosphere It is responsible for the precipitation Volume mixing ratio (≤ 0.03)

Clausius-Clapeyron equation

 $\frac{dp}{dT} = \frac{\delta S}{\delta V} = \frac{L}{T \ \delta V} \qquad L = T \ \delta S$



 $\delta V \approx V_v = 1/\rho_v = R_v T/p$

Hence the Clausius-Clapeyron equation can be written in the more convenient form

$$\frac{dp}{dT} = \frac{Lp}{R_v T^2}$$

$$\frac{de_s}{dT} = \frac{Le_s}{R_v T^2}$$

Note that if L is constant (a fairly good approximation at typical atmospheric temperatures), this can be integrated to give

$$e_{s}(T) = e_{s}(T_{0}) \exp \frac{L}{R_{v}} \left(\frac{1}{T_{0}} - \frac{1}{T}\right)$$

where T_0 is a constant reference temperature.

v = e/v

We can relate the partial pressure e of water vapour to its volume mixing ratio v and mass mixing ratio μ , say:

$$\mu_i = \frac{nm_i p_i}{mp} = \frac{m_i}{\overline{m}} \frac{p_i}{p} \qquad \overline{m} = \frac{m}{n}$$

is the mean molecular mass for the sample. We also define the volume mixing ratio vi (also known as the mole fraction)by

 $\mu = \varepsilon(e/p)$

where p is the total air pressure, and

$$\varepsilon \approx \frac{m_V}{m_d} = \frac{18.02}{28.97} = 0.622$$
 $\mu < 0.03$

So long as no condensation or evaporation takes place, this mass μ remains constant.

The vapour pressure of the parcel satisfies

 $e = \frac{\mu p}{\varepsilon}$

and while this remains less than $e_s(T)$ saturation does not occur, since the water vapour in the parcel remains below the vapour pressure curve in Figure.



Suppose that the parcel rises adiabatically from the surface at p_0 and T_0

then the potential temperature of the parcel remains constant at $\theta = T_0$ while the temperature T of the parcel falls according to

$$\theta = T\left(\frac{p_0}{p}\right)^k \qquad T = T_0\left(\frac{p}{p_0}\right)^k$$

we can eliminate the pressure p of the parcel to find how the vapour pressure varies as a function of temperature T, following the motion of the parcel:

$$e = \frac{\mu p}{\varepsilon} \qquad e_{parcel}(T) = \frac{\mu p_0}{\varepsilon} \left(\frac{T}{T_0}\right)^{1/\ell}$$

As illustrated in Figure , eventually the temperature of the rising parcel falls enough for $e_{parcel} = e_s$ and saturation occurs.

The pressure level at which this happens can be calculated from equation:

 $T = T_0 \left(\frac{p}{p_0}\right)^k$

It is called the lifting condensation level. (However, it should be noted that in practice liquid need not form at saturation; the vapour may become supersaturated.

It is usually necessary for small 'condensation nuclei' to be present before liquid drops appear; see next Section.)

A useful related concept is the saturation mixing ratio, defined as:

$$\mu_s(T, p) = \frac{e_s(T)\varepsilon}{p} \qquad (g \text{ kg}^{-1})$$



If, at temperature T and pressure p, the mixing ratio $\mu < \mu_{s}(T, p) \implies e < e_{s} \quad \text{Air is unsaturated}$ $\mu = \mu_{s}(T, p), \implies e = e_{s} \quad \text{Air is saturated}$ $\mu > \mu_{s}(T, p), \implies e > e_{s} \quad \text{Air is supersaturated}$

from
$$\begin{cases} e = \frac{\mu p}{\varepsilon} \\ \mu_s(T, p) = \frac{e_s(T)\varepsilon}{p} \end{cases}$$

Fig. gives a plot of μ_s as a function of temperature and pressure.

The overall behaviour of μ_s is clearly consistent with the facts that it is inversely proportional to pressure and proportional to e_s , which increases with temperature (see prvious Fig.).

$$\mu_s(T, p) = \frac{e_s(T)\varepsilon}{p}$$





Contours of the saturation mixing ratio $\mu_s(T, p)$, in units of gkg⁻¹

The dew point T_d of a sample of air is the temperature to which the air must be cooled at constant pressure (i.e. not following a rising parcel), retaining its water vapour content, for it to become saturated.

Therefore, if the water vapour mixing ratio is μ , the dew pointT_d satisfies the implicit equation

$$\mu_s(T_d, p) = \mu$$

Equivalently, if the air sample initially has vapour pressure e, then

 $e_s(T_d) = e$

We now briefly mention the ice phase.

In addition to the vapour-water phase transition just considered, there are also ice-water and ice-vapour transitions, as shown in Fig. The three transition lines meet at the triple point,



p_t = 6.1 hPa.



The phase transitions between ice, liquid water and water vapour. The triple point is indicated by the small solid circle.

Note that the ice-water curve is not quite vertical, but has a large negative slope of about -1.4×10^5 hPa K⁻¹ near the triple point.

The densities and, therefore, the specific volumes V of the three phases are different at the triple point:



the specific volume of liquid water is $V_l = 1.00 \times 10^{-3} \text{m}^3 \text{kg}^{-1}$

the specific volume of ice is $V_{\rm i}$ = $1.09V_l$ (unlike most substances, water expands on freezing)the specific volume of water vapour is $V_{\rm v} \approx 2 \times 10^5 \ {
m V_1}$

The basic form

 $\frac{dp}{dT} = \frac{\delta S}{\delta V} = \frac{L}{T \ \delta V}$

 $V_{\rm v} >> V_i$

of the Clausius-Clapeyron equation applies to each of these transitions

and the latent heat of sublimation (ice-vapour) is approximately constant, an approximate form of the sublimation curve can be found as in equation

Since

$$e_{s}(T) = e_{s}(T_{0}) \exp{\frac{L}{R_{V}}(\frac{1}{T_{0}} - \frac{1}{T})}$$

indeed, since the two latent heats are fairly similar in size, the two curves are quite close. However, the form of the ice-water transition curve is very different: here δV is small and negative, since V_1 is slightly less than V_i , but the latent heat of fusion is positive and non-negligible.

Hence the ice-water transition has a large negative slope, as indicated in Fig.



 $\frac{dp}{dT} = \frac{L_{lv}}{T(V_v - V_l)}$

 $\frac{dp}{dT} = \frac{L_{iv}}{T(V_v - V_i)}$

 $\frac{dp}{dT} = \frac{L_{il}}{T(V_l - V_i)}$

The saturated adiabatic lapse rate

While the air in a rising parcel remains unsaturated, the derivation of the adiabatic lapse rate

$$-\left(\frac{dT}{dz}\right)_{\text{parcel}} = -\frac{R_{\text{a}}T}{c_{p}p}\left(\frac{dp}{dz}\right)_{\text{parcel}} = \frac{g}{c_{p}} \equiv \Gamma_{\text{a}},$$

remains unchanged, apart from the use of the specific heat capacity c_p for the mixture of dry air and water vapour: this is always close to that for dry air alone (see Problem 2.6).

However, once saturation takes place, the calculation of the lapse rate following the parcel must be changed significantly, because of the latent heat released.

So the dry adiabatic vertical temperature gradient is about -9.8 K/km The dry adiabatic lapse rate (defined as -dT/dz) is about +9.8 K/km

Moist Adiabatic Rate



considering a saturated parcel (which is taken for convenience to be of unit mass) that rises a distance dz.

At saturation, the mixing ratio equals the saturation mixing ratio

 $\mu = \mu_s(T, p)$

If a mass of water then $|\delta\mu_s| = -\delta\mu_s$ condenses during the rise through height δz , an amount of latent heat is given to the parcel.

 $\delta Q = L \left| \delta \mu_s \right| = -L \delta \mu_s$

Note that $\delta\mu_s$, as is usual for a small change, is defined as an increase in μ_s ; therefore $-\delta\mu$ is a decrease of μ_s .

The liquid water is assumed to fall out of the parcel and take no further part in its heat balance: this is an irreversible process and it also implies a loss of heat from the parcel.

Hence the parcel undergoes a non-adiabatic (and indeed a non adiathermal) change.

However, the amount of heat removed from the parcel by the liquid water is small compared with that remaining in the parcel, so the process is referred to as pseudo-adiabatic. The latent heat release δQ , given by previous equation, is equal to the heat input into the parcel while it rises a distance δz and its temperature increases by δT .

We assume that this heat input occurs reversibly so

$$\delta Q = c_p \, \delta T + g \, \delta z$$

where c_p is the value for the dry air-water vapour mixture.

$$c_p\,\delta T + g\,\delta z + L\,\delta\mu_{\rm s} = 0.$$

We now need to express $\delta\mu$ in terms of δT and δz .

$$\mu_{\rm s} = \epsilon e_{\rm s}/p.$$

Taking logarithms and differentiating gives

$$\frac{\delta\mu_{\rm s}}{\mu_{\rm s}} = \frac{\delta e_{\rm s}}{e_{\rm s}} - \frac{\delta p}{p}. \label{eq:scalar}$$

However, e_s depends only on T, so

$$\delta e_{\rm s} = (de_{\rm s}/dT) \, \delta T$$

moreover, from the Clausius-Clapeyron equation

$$\frac{1}{e_s}\frac{de_s}{dT} = \frac{L}{R_V T^2}$$

From the hydrostatic equation in the form

 $\delta p = -pg \, \delta z / (R_{\rm a}T),$

where p is the total pressure; by collecting these results we therefore get

$$\frac{\delta\mu_{\rm s}}{\mu_{\rm s}} = \frac{L\,\delta T}{R_{\rm v}T^2} + \frac{g\,\delta z}{R_{\rm a}T}.$$

By eliminating $\delta \mu_s$ from this equations (2.46) and

$$c_p\,\delta T + g\,\delta z + L\,\delta\mu_{\rm s} = 0.$$

we obtain

$$\left(c_p + \frac{L^2 \mu_{\rm s}}{R_{\rm v} T^2}\right) \delta T + g \left(1 + \frac{L \mu_{\rm s}}{R_{\rm a} T}\right) \delta z = 0.$$

Letting $\delta z \rightarrow 0$, we get the saturated adiabatic lapse rate (SALR) Γ_s :

$$\Gamma_{\rm s} = -\frac{dT}{dz} = \frac{g}{c_p} \frac{\left(1 + \frac{L\mu_{\rm s}}{R_{\rm a}T}\right)}{\left(1 + \frac{L^2\mu_{\rm s}}{c_pR_{\rm v}T^2}\right)}.$$

Note that the factor g/c_p on the right-hand side of equation equals the DALR Γ_a .

For typical atmospheric values of T and μ_s it is found that $\Gamma_s \leq \Gamma_a$.

Because of the latent heat given to the air by condensation of the water vapour, the temperature drops off less rapidly with height (by about 6-9Kkm⁻¹) at the SALR than it does at the DALR (\sim 9.8Kkm⁻¹

Note that Γs depends on the temperature and pressure, through its dependences on T and μ_s (T, p).

Working in terms of the pressure of the parcel, rather than its height, we may show (again using

$$g \, \delta z = -R_{\rm a} T \, \delta p/p)$$

that, following the ascending parcel,

$$\frac{dT}{dp} = \frac{\Gamma_{\rm s} R_{\rm a} T}{gp} = \Gamma_{\rm s}'(T,p),$$

say. Curves in the T, p plane whose slopes at each point are given by this equation are called saturated adiabatics.

Given the expression for Γ'_s and suitable starting values of T and p, they may readily be calculated numerically.

In particular, it follows that, if the actual lapse rate Γ is less than the SALR Γ s, then the region is statically stable even if the air is saturated. However, if Γ > Γ s, a saturated parcel will be unstable.

Moreover, if $\Gamma s < \Gamma < \Gamma a$, a saturated parcel is unstable but an unsaturated one is not: this situation is called conditional instability.

See Figure for a graphical representation of the various cases considered here: this should be contrasted with the much simpler Figure 2.4 for a dry atmosphere.







