

As a further step, we can investigate the buoyancy force on the parcel and its acceleration.

The upward buoyancy force on the parcel is g times the difference between the mass of air displaced and the mass of the parcel, i.e.

$$gV_1(\rho_{e1}-\rho_{p1})$$

at height  $z_1$ , where  $V_1$  is the volume of the parcel there. By Newton's second law, this force can be equated to the mass of the parcel times its acceleration, i.e.

$$\rho_{\rm pl} V_1 \, \frac{d^2(\delta z)}{dt^2}$$

We therefore have

$$\frac{d^2(\delta z)}{dt^2} = g\left(\frac{\rho_{\rm cl}}{\rho_{\rm pl}} - 1\right) = g\left(\frac{T_{\rm pl}}{T_{\rm cl}} - 1\right)$$

$$= g\left(\frac{T - \Gamma_{a} \delta z}{T - \Gamma \delta z} - 1\right) = g\left(\frac{\Gamma - \Gamma_{a}}{T - \Gamma \delta z}\right) \delta z = -\frac{g}{T} \left(\Gamma_{a} - \Gamma\right) \delta z$$

to leading order in the small quantity dz.

(The ideal gas law  $P = R_a T P$  the second to the third expression here.)

has been used to go from

We therefore have an equation of the form

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

$$N^{2} = \frac{g}{T} \left( \Gamma_{a} - \Gamma \right) = \frac{g}{T} \left( \frac{dT}{dz} + \frac{g}{c_{p}} \right)$$

and the temperature T in this equation is that of the environment.

In the case of a statically stable region of the atmosphere, in which  $\Gamma_{\rm a}>\Gamma$  , equation indicates that  $N^2>0$  and equation

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

 $N^2 > 0 \rightarrow$  represents simple harmonic motion, with sinusoidal solutions.

 $N^2 < 0 \rightarrow$  So that N is imaginary, which leads to exponential

The parcel then oscillates up and down at an angular frequency N, where N is called the buoyancy frequency or the Brunt-Väisälä frequency;

For a statically unstable region of the atmosphere, in which  $\Gamma_a > \Gamma$ ,  $N^2 < 0$  So that N is imaginary, which leads to exponential solutions of the equation.

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

one of which corresponds to the displaced parcel continuing to move at an increasing speed.

The quantity  $N^2$  is a useful measure of atmospheric stratification.

It can be related to the potential temperature of the environment as follows.

Taking logarithms of equation

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

$$\ln \theta = \ln T + k \ln p_0 - k \ln p$$
  
and differentiating, we obtain

$$\frac{d\theta}{\theta} = \frac{dT}{T} + k(0) - k\frac{dp}{p}$$

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

using the ideal gas law

and the relation

$$P = R_a T P$$

$$CP = R_a K$$

$$CP = R_a^{K}$$

$$= \frac{1}{T} \frac{dT}{dz} + \frac{g}{c_p T},$$

On combining equations

$$N^{2} = \frac{g}{T} \left( \Gamma_{a} - \Gamma \right) = \frac{g}{T} \left( \frac{dT}{dz} + \frac{g}{c_{p}} \right)$$

and above equ. we obtain the equation

$$N^2 = \frac{g}{\theta} \, \frac{d\theta}{dz}.$$

$$N^2 = \frac{g}{\theta} \frac{d\theta}{dz} > 0 \qquad \Rightarrow \Gamma_a > \Gamma \qquad \text{Stable case}$$
 
$$\frac{d\theta}{dz} > 0 \qquad \Rightarrow \Gamma_a < \Gamma \qquad \text{Unstable case}$$
 
$$\frac{d\theta}{dz} = 0 \qquad \Rightarrow \Gamma_a = \Gamma \qquad \text{Neutral case}$$
 Thus a region of the atmosphere is statically stable if  $\theta$  height and is statically unstable if  $\theta$  decreases with height

Thus a region of the atmosphere is statically stable if  $\theta$  increases with height and is statically unstable if  $\theta$  decreases with height.

## The available potential energy

$$E_{\rm P} = \int_{z_0}^{\infty} \rho g z \, dz.$$
  $\rho g = -dp/dz$ 

$$\rho g = -dp/dz$$

$$E_{\rm P} = -\int_{z_0}^{\infty} z \, \frac{dp}{dz} \, dz = \int_{p=0}^{p=p_0} z \, dp,$$
 p=p<sub>0</sub>

$$E_P = [zp]_{p=0}^{p=p_0} + \int_{z_0}^{\infty} p \, dz.$$
 Now assuming that  $zp \to 0$  as  $z \to \infty$  and  $p \to 0$ ,

This holds in all reasonable cases; for example, p decays exponentially with z in an isothermal atmosphere, as shown in equation

$$p = p_0 \exp\left(-\frac{gz}{R_a T_0}\right) = p_0 e^{-z/H},$$

$$E_{\rm P} = \int_{z_0}^{\infty} p \, dz + E_0,$$
 where  $E_0 = z_0 p_0.$ 

The boundary term  $E_0=0$  if the surface elevation  $z_0=0$ , but in general we must allow for topography of varying height over the Earth's surface, with  $z_0\neq 0$ 

We now consider the internal energy of the air in the column. As noted in equation  $U=c_vT$  the internal energy per unit mass is  $c_vT$ ,

so the integral of this over the mass of the column is

$$E_{\rm I} = \int_{z_0}^{\infty} \rho c_v T dz = \frac{c_v}{R_{\rm a}} \int_{z_0}^{\infty} p dz, \qquad P = R_{\rm a}^{\rm T} P$$

We define the total potential energy  $E_T$  of the column as the sum of the potential and internal energies

$$E_{\rm T} = E_{\rm P} + E_{\rm I} = \frac{c_v + R_{\rm a}}{R_{\rm a}} \int_{z_0}^{\infty} p \, dz + E_0 = \frac{1}{\kappa} \int_{z_0}^{\infty} p \, dz + E_0,$$

since 
$$c_{
m v}+R_{
m a}=c_p$$
 =  $R_{
m a}/\kappa$ 

since the enthalpy per unit mass is

$$c_pT$$

$$H = c_{\rm v}T + R_{\rm a}T = c_pT$$

so that the enthalpy per unit volume is

$$P = R_a^T P$$

$$c_p \rho T = c_p p / R_a$$

We can extend these ideas to the atmosphere as a whole by integrating the column values over the Earth's surface area; for example, the global total energy is

 $\langle E_{\rm T} \rangle = \iint_{\text{surface}} E_{\rm T} \, dx \, dy,$ 

where x and y are horizontal coordinates.

$$M_1 = \iint_{\text{surface}} dx \, dy \int_{z_1}^{\infty} \rho \, dz,$$

where  $z_1(x, y)$  is the height of the isentrope.

$$M_1 = \frac{1}{g} \iint_{\text{surface}} dx \, dy \int_0^{p_1} dp = \frac{1}{g} \iint_{\text{surface}} p_1(x, y) \, dx \, dy = \frac{1}{g} \langle p_1 \rangle,$$

where  $p_1(x, y)$  is the pressure on the isentrope.

In particular the total mass of the atmosphere is

$$M_s = \frac{1}{g} \iint_{\text{surface}} p_0(x, y) dx dy = \frac{1}{g} \langle p_0 \rangle.$$

The same results must hold for the reference state so that, under an adiabatic redistribution of mass, the global integral  $p_1$  (or global mean) of the pressure on the  $\theta_1$  isentrope (and therefore on every isentrope) must remain unchanged.

Together with other arguments, this allows the reference state and also the difference in total potential energy between the actual and reference states to be calculated.

This difference is called the available potential energy and represents the maximum amount of potential energy that might be released for conversion into, say, kinetic energy.

The details of the calculation are generally quite complicated; however, a simple special case is considered in Problem 2.9.

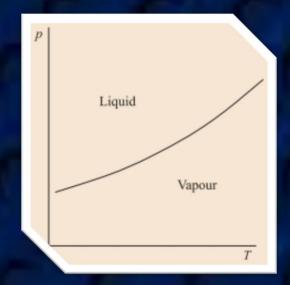
## Moisture in the atmosphere

## Clausius-Clapeyron equation

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

$$L=T\delta S$$

$$dV \approx V_v = 1/\rho_v = R_v T/p$$



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

$$\frac{dp}{dT} = \frac{Lp}{R_{\rm v}T^2},$$

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

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

$$e_{\rm s}(T) = e_{\rm s}(T_0) \exp \frac{L}{R_{\rm v}} \left(\frac{1}{T_0} - \frac{1}{T}\right)$$

where  $T_0$  is a constant reference temperature.

We can relate the partial pressure e of water vapour to its volume mixing ratio v and mass mixing ratio  $\mu$ , say, using equations:

$$\mu_i = \frac{nm_ip_i}{mp} = \frac{m_i}{\overline{m}}\frac{p_i}{p}, \qquad v_i = \frac{n_i}{n} = \frac{p_i}{p}.$$

$$v_i = \frac{n_i}{n} = \frac{p_i}{p}.$$

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

where p is the total air pressure, as usual, and

$$\epsilon = \frac{m_{\rm v}}{\overline{m}} \approx \frac{m_{\rm v}}{m_{\rm d}} = \frac{18.02}{28.97} = 0.622.$$

$$(\mu < 3 \times 10^{-2})$$
,  $\overline{m} \approx m_d$ .

Another important measure of the moisture content of air is the relative humidity, defined by

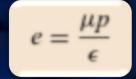
$$RH = \frac{e}{e_s(T)}$$

Now consider a parcel of moist air, of unit mass, containing mass  $\mu$  of water vapour, so that  $\mu$  is the mass mixing ratio of water vapour according to our definition

$$\mu_i = \frac{m_i n_i}{m}.$$

So long as no condensation or evaporation takes place, this mass  $\mu$  remains constant.

The vapour pressure of the parcel satisfies



$$v = e/p$$

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

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 previouse Figure.

Suppose that the parcel rises adiabatically from the surface

(at pressure  $p_0$  and temperature  $T_0$ )

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

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

by equation

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

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:

$$e_{\mathrm{parcel}}(T) = \frac{\mu p_0}{\epsilon} \left(\frac{T}{T_0}\right)^{1/\kappa}$$

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

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

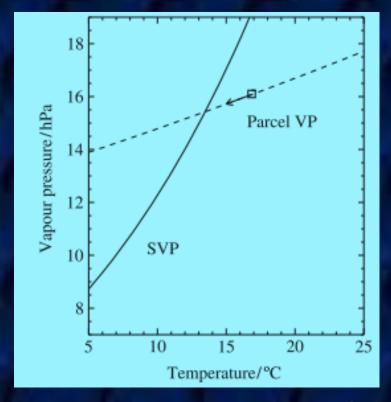
$$T = T_0 \left(\frac{p}{p_0}\right)^{\kappa}$$

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

$$\mu_{s}(T,p) = \frac{e_{s}(T)\epsilon}{p}$$

(g kg<sup>-1</sup>)



## If, at temperature T and pressure p, the mixing ratio

$$\mu < \mu_s(T, p), \implies e < e_s$$

from

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

Air is unsaturated

$$\mu = \mu_{\rm s}(T, p),$$

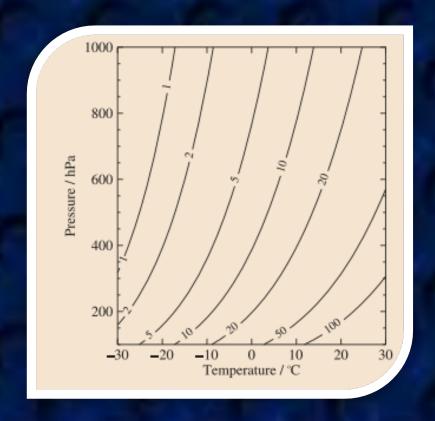
Air is saturated

$$\mu > \mu_{\rm s}(T, p),$$

Air is supersaturated

Fig. gives a plot of  $\mu_s$  as a function of temperature and pressure.

The overall behaviour of  $\mu s$  is clearly consistent with the facts that it is inversely proportional to pressure and proportional to  $e_s$ , which increases with temperature (see prviouse Fig.).



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  $\mu$ , the dew point  $T_d$  satisfies the implicit equation

$$\mu_{s}(T_{d},p) = \mu$$

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

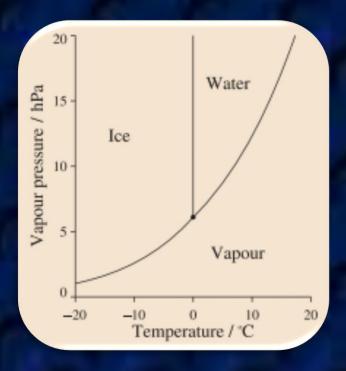
$$e_s(T_d) = e$$
.

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.

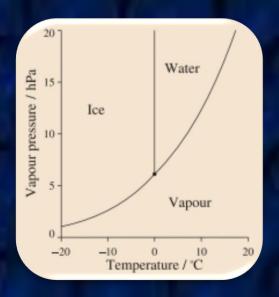
The three transition lines meet at the triple point,

$$T_t = 273 \text{ K}$$
 and  $p_t = 6.1 \text{ hPa}$ .



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  $-1.4 \times 10^5$  hPa K<sup>-1</sup> 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

$$V_1 = 1.00 \times 10^{-3} \text{m}^3 \text{kg}^{-1}$$

the specific volume of ice is

$$V_{\rm i} = 1.09 V_{\rm I}$$

(unlike most substances, waterexpands on freezing)

the specific volume of water vapour is  $V_{
m v} pprox 2 imes 10^5 \ 
m V_1$ 

The basic form

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

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

Since 
$$V_{\rm v}>>V_i$$

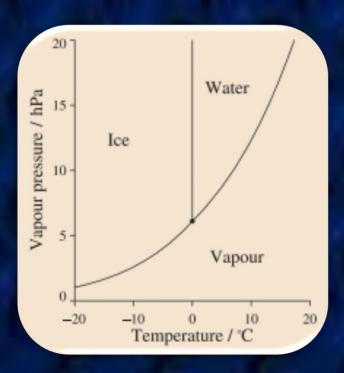
and the latent heat of sublimation (ice-vapour) is approximately constant, an approximate form of the sublimation curve can be found as in equ.

$$e_s(T) = e_s(T_0) \exp \frac{L}{R_v} \left( \frac{1}{T_0} - \frac{1}{T} \right)$$

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  $\delta V$  is sma and negative, since  $V_{\parallel}$  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.



Many of the concepts developed above for condensation of water vapour at the vapour-liquid transition can be applied also to sublimation at the vapour - ice transition.

These include

the saturation vapour pressure,

saturation mixing ratio

the frost point

the temperature to which moist air must be cooled at constant pressure for sublimation to occur.

