

## Physical Meteorology

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## Part 2

## Atmospheric Thermodynamics

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## Atmospheric Thermodynamics

Thermodynamics plays an important role in our quantitative understanding of atmospheric phenomena, ranging from the smallest cloud microphysical processes to the general circulation of the atmosphere.

The purpose of this section of the course is to introduce some fundamental ideas and relationships in thermodynamics and to apply them to a number of simple, but important, atmospheric situations.

The course is based closely on the text of *Wallace & Hobbs*

## Outline of Material

- 1 The Gas Laws
- 2 The Hydrostatic Equation
- 3 The First Law of Thermodynamics
- 4 Adiabatic Processes
- 5 Water Vapour in Air
- 6 Static Stability
- 7 The Second Law of Thermodynamics

# The Kinetic Theory of Gases

The atmosphere is a gaseous envelope surrounding the Earth. The basic source of its motion is *incoming solar radiation*, which drives the general circulation.

To begin to understand atmospheric dynamics, we must first understand the way in which a gas behaves, especially when heat is added or removed. Thus, we begin by studying thermodynamics and its application in simple atmospheric contexts.

Fundamentally, a gas is an agglomeration of molecules. We might consider the dynamics of each molecule, and the interactions between the molecules, and deduce the properties of the gas from direct dynamical analysis. However, considering the enormous number of molecules in, say, a kilogram of gas, and the complexity of the inter-molecular interactions, such an analysis is utterly impractical.

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We resort therefore to a statistical approach, and consider the average behaviour of the gas. This is the approach called the kinetic theory of gases. The laws governing the bulk behaviour are at the heart of thermodynamics. We will not consider the kinetic theory explicitly, but will take the thermodynamic principles as our starting point.

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## I. The Gas Laws

The pressure, volume, and temperature of any material are related by an equation of state, the ideal gas equation. For most purposes we may assume that atmospheric gases obey the ideal gas equation exactly.

The ideal gas equation may be written

$$pV = mRT$$

Where the variables have the following meanings:

$p$  = pressure (Pa)

$V$  = volume ( $\text{m}^3$ )

$m$  = mass (kg)

$T$  = temperature (K)

$R$  = gas constant ( $\text{J K}^{-1} \text{kg}^{-1}$ )

Again, the gas law is:

$$pV = mRT$$

The value of  $R$  depends on the particular gas.  
For dry air, its value is  $R = 287 \text{ J K}^{-1} \text{ kg}^{-1}$ .

**Exercise:** Check the dimensions of  $R$ .

Since the density is  $\rho = m/V$ , we may write

$$p = R\rho T.$$

Defining the *specific volume*, the volume of a unit mass of gas, as  $\alpha = 1/\rho$ , we can write

$$p\alpha = RT.$$

# Special Cases

**Boyle's Law:** We may write

$$V = \frac{mRT}{p}.$$

For a fixed mass of gas at *constant temperature*,  $mRT$  is constant, so volume is *inversely proportional* to pressure:

$$V \propto 1/p.$$

**Charles Law:** We may write

$$V = \left(\frac{mR}{p}\right)T.$$

For a fixed mass of gas at *constant pressure*,  $mR/p$  is constant, so volume is *directly proportional* to temperature:

$$V \propto T.$$

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# Avogadro's Hypothesis

One *mole* (mol) of a gas is the molecular weight in grams. One *kilomole* (kmol) of a gas is the molecular weight in kilograms. For example, the molecular weight of nitrogen  $N_2$  is 28 (we ignore the effects of isotopic variations). So:

One mole of  $N_2$  corresponds to 28 g

One kilomole of  $N_2$  corresponds to 28 kg

According to **Avogadro's Hypothesis**, equal volumes of different gases at a given temperature and pressure have the same number of molecules; or, put another way, gases with the same number of molecules occupy the same volume at a given temperature and pressure.

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The number of *molecules* in a *mole* of any gas is a universal constant, called **Avogadro's Number**,  $N_A$ . The value of  $N_A$  is  $6.022 \times 10^{23}$ . So:

28 g of nitrogen contains  $N_A$  molecules of  $N_2$

28 kg contains  $10^3 \times N_A$  molecules.

For a gas of molecular weight  $M$ , with mass  $m$  (in kilograms) the number  $n$  of kilomoles is

$$n = \frac{m}{M}.$$

So, we use  $m = nM$  in the gas law to write it

$$pV = n(MR)T$$

By Avogadro's hypothesis, equal volumes of different gases at a given temperature and pressure have the same number of molecules. Therefore, the value of  $MR$  is the same for any gas. It is called the **universal gas constant**, denoted:

$$R^* = MR = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 8314.5 \text{ J K}^{-1} \text{ kmol}^{-1}.$$

Then the gas law may be written in the form normally found in texts on chemistry:

$$pV = nR^*T.$$

with  $n$  the number of moles of gas and  $R^* = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The gas constant for a single molecule of a gas is also a universal constant, called **Boltzmann's constant**,  $k$ . Since the gas constant  $R^*$  is for  $N_A$  molecules (the number in a kilomole), we get

$$k = \frac{R^*}{N_A}$$

Now, for a gas containing  $n_0$  molecules per unit volume, the equation of state is

$$p = n_0 kT.$$

# Virtual Temperature

The mean molecular weight  $M_d$  of dry air is about 29 (average of four parts  $N_2$  (28) and one part  $O_2$  (32)).

The molecular weight  $M_v$  of water vapour ( $H_2O$ ) is about 18 (16 for O and 2 for  $H_2$ ).

Thus, the mean molecular weight,  $M_m$ , of *moist air*, which is a mixture of dry air and water vapour, is less than that,  $M_d$ , of dry air and more than that of water vapour:

$$M_v < M_m < M_d$$

The gas constant for water vapour is larger than that for dry air:

$$R_d = \frac{R^*}{M_d}, \quad \text{and} \quad R_v = \frac{R^*}{M_v}$$

so that

$$M_v < M_d \implies R_v > R_d.$$

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The numerical values of  $R_d$  and  $R_v$  are as follows:

$$R_d = \frac{R^*}{M_d} = 287 \text{ J K}^{-1} \text{ kg}^{-1}, \quad R_v = \frac{R^*}{M_v} = 461 \text{ J K}^{-1} \text{ kg}^{-1}.$$

We define the ratio of these as:

$$\varepsilon \equiv \frac{R_d}{R_v} = \frac{M_v}{M_d} \approx 0.622.$$

For *moist air*, which is a mixture of dry air and water vapour, the mean molecular weight  $M_m$ , and therefore also the gas 'constant'  $R_m$ , depends on the amount of moisture in the air.

It is inconvenient to use a gas 'constant' which varies in this way. It is simpler to retain the constant  $R = R_d$  for dry air, and to use a *modified temperature*,  $T_v$ , in the ideal gas equation. We call this the *virtual temperature*.

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# Mixing Ratio

Let's consider a fixed volume  $V$  of moist air at temperature  $T$  and pressure  $p$  which contains a mass  $m_d$  of dry air and a mass  $m_v$  of water vapour. The total mass is  $m = m_d + m_v$ .

The *mixing ratio* is defined by

$$w = \frac{m_v}{m_d}.$$

The mixing ratio is a dimensionless number. It is usually given as grams of water vapour per kilogram of air.

In middle latitudes,  $w$  is typically a few grams per kilogram. In the tropics it can be greater than  $20 \text{ g kg}^{-1}$ . If there is no evaporation or condensation, the mixing ratio is a *conserved quantity*.

# Mixing Ratio and Vapour Pressure

By the ideal gas law, the partial pressure exerted by a constituent of a mixture of gases is proportional to the number of kilomoles of the constituent in the mixture. Thus:

$$\begin{aligned} p_d &= n_d R^* T && \text{dry air} \\ e &= n_v R^* T && \text{water vapour} \\ p &= n R^* T && \text{moist air} \end{aligned}$$

where  $p_d$  is the pressure due to dry air,  $e$  the pressure due to water vapour and  $p$  the total pressure.

Therefore,

$$\frac{e}{p} = \frac{n_v}{n} = \frac{n_v}{n_v + n_d} = \frac{m_v/M_v}{m_v/M_v + m_d/M_d}$$

Dividing by  $M_v/m_d$ , this gives

$$\frac{e}{p} = \frac{w}{w + \varepsilon}$$

**Problem:** If the mixing ratio is  $5.5 \text{ g kg}^{-1}$ , and the total pressure is  $p = 1026.8 \text{ hPa}$ , calculate the vapour pressure.

**Solution:** We have

$$e = \left( \frac{w}{w + \varepsilon} \right) p \approx \frac{w}{\varepsilon} p$$

where  $\varepsilon = 0.622$ . Substituting  $w = 5.5 \text{ g kg}^{-1} = 0.0055 \text{ g g}^{-1}$ , we find that  $e = 9 \text{ hPa}$ .

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# Virtual Temperature

The density of the mixture of air and water vapour is

$$\rho = \frac{m_d + m_v}{V} = \rho_d + \rho_v$$

where  $\rho_d$  is the value the density would have if *only* the mass  $m_d$  of dry air were present and  $\rho_v$  is the value the density would have if *only* the mass  $m_v$  of water vapour were present.

We apply the ideal gas law to each component:

$$\begin{aligned} p_d &= R_d \rho_d T \\ e &= R_v \rho_v T \end{aligned}$$

where  $p_d$  and  $e$  are the *partial pressures* exerted by the dry air and water vapour respectively.

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By Dalton's law of partial pressure,

$$p = p_d + e.$$

Combining the above results,

$$\begin{aligned} \rho &= \rho_d + \rho_v = \frac{p_d}{R_d T} + \frac{e}{R_v T} \\ &= \frac{p - e}{R_d T} + \frac{R_d}{R_v} \frac{e}{R_d T} \\ &= \frac{p}{R_d T} - \frac{e}{R_d T} + \varepsilon \frac{e}{R_d T} \\ &= \frac{p}{R_d T} \left[ 1 - \frac{e}{p} (1 - \varepsilon) \right]. \end{aligned}$$

We may write this equation as

$$p = R_d \rho T_v$$

where the *virtual temperature*  $T_v$  is defined by

$$T_v = \frac{T}{1 - (e/p)(1 - \varepsilon)}.$$

Again,

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$$T_v = \frac{T}{1 - (e/p)(1 - \varepsilon)}.$$

The great advantage of introducing virtual temperature is that the total pressure and total density of the mixture are related by the ideal gas equation with the gas constant the same as that for dry air,  $R_d$ .

The virtual temperature is the temperature that dry air must have in order to have the same density as the moist air at the same pressure. Note that the virtual temperature is *always greater* than the actual temperature:

$$T_v \geq T.$$

Typically, the virtual temperature exceeds the actual temperature by only a few degrees.

# Approximate Expressions for $T_v$

We can assume that  $e \ll p$  and also that  $w$  is small. By the binomial theorem,

$$\frac{1}{1 - (e/p)(1 - \varepsilon)} \approx 1 + (e/p)(1 - \varepsilon)$$

and the virtual temperature is

$$T_v \approx T \left[ 1 + \frac{e}{p}(1 - \varepsilon) \right].$$

Now substituting for  $e/p$ , we get

$$\left[ 1 + \frac{e}{p}(1 - \varepsilon) \right] = \left[ 1 + \frac{w}{w + \varepsilon}(1 - \varepsilon) \right]$$

But we assume that  $w \ll \varepsilon$ , so we get

$$\left[ 1 + \frac{w}{w + \varepsilon}(1 - \varepsilon) \right] \approx \left[ 1 + \frac{1 - \varepsilon}{\varepsilon}w \right]$$

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End of §2.1

Again,

$$\left[ 1 + \frac{w}{w + \varepsilon}(1 - \varepsilon) \right] \approx \left[ 1 + \frac{1 - \varepsilon}{\varepsilon}w \right]$$

Since  $\varepsilon = 0.622$  we have  $(1 - \varepsilon)/\varepsilon = 0.608$ . Thus,

$$T_v \approx T [1 + 0.608w].$$

**Problem:** Calculate the virtual temperature of moist air at  $30^\circ\text{C}$  having a mixing ratio of  $20 \text{ g kg}^{-1}$ .

**Solution:** First,  $T = 30 + 273 = 303 \text{ K}$  and  $w = 20 \text{ g kg}^{-1} = 0.02 \text{ g g}^{-1}$ . Then

$$T_v \approx 303 [1 + 0.608 \times 0.02] = 306.68 \text{ K}$$

So, the virtual temperature is  $(306.68 - 273) = 33.68^\circ\text{C}$ , an elevation of  $3.68^\circ\text{C}$  above the actual temperature.

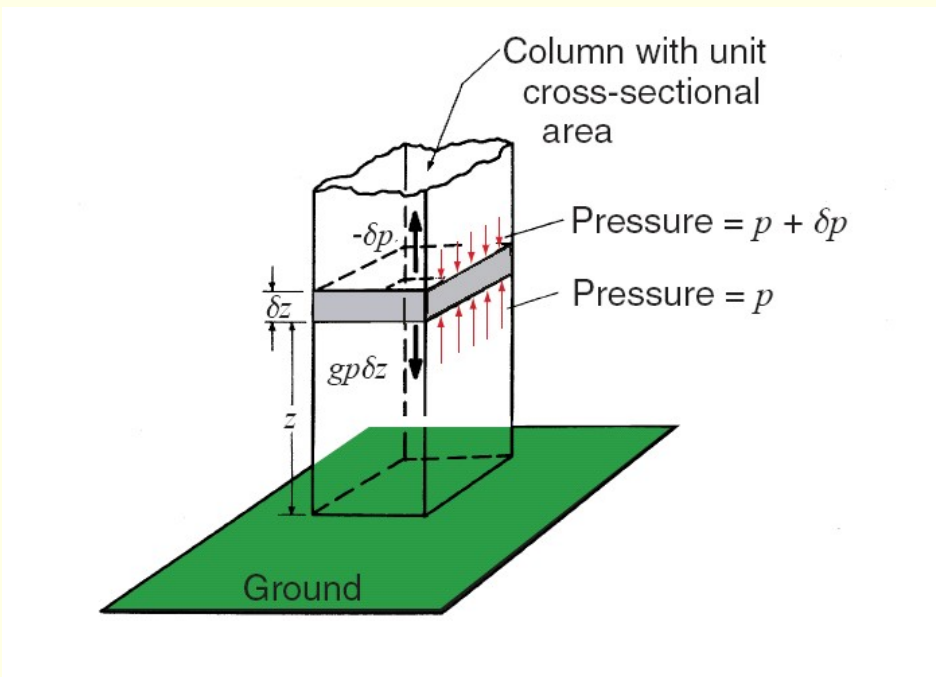
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## II. The Hydrostatic Equation

Air pressure at any height in the atmosphere is due to the force per unit area exerted by the weight of all of the air lying above that height. Consequently, atmospheric pressure decreases with increasing height above the ground.

The net upward force acting on a thin horizontal slab of air, due to the decrease in atmospheric pressure with height, is generally very closely in balance with the downward force due to gravitational attraction that acts on the slab.

If the net upward pressure force on the slab is equal to the downward force of gravity on the slab, the atmosphere is said to be in *hydrostatic balance*.



Balance of vertical forces in an atmosphere in hydrostatic balance.

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The mass of air between heights  $z$  and  $z + \delta z$  in the column of air is  $\rho \delta z$ .

The downward gravitational force acting on this slab of air, due to the weight of the air, is  $g\rho\delta z$ .

Let the change in pressure in going from height  $z$  to height  $z + \delta z$  be  $\delta p$ . Since we know that pressure decreases with height,  $\delta p$  must be a *negative* quantity.

The upward pressure on the lower face of the shaded block must be slightly greater than the downward pressure on the upper face of the block.

Therefore, the net vertical force on the block due to the vertical gradient of pressure is upward and given by the positive quantity  $-\delta p$  as indicated in the figure.

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For an atmosphere in hydrostatic equilibrium, the balance of forces in the vertical requires that

$$-\delta p = g\rho \delta z$$

In the limit as  $\delta z \rightarrow 0$ ,

$$\frac{\partial p}{\partial z} = -g\rho.$$

This is the *hydrostatic equation*.

The negative sign ensures that the pressure decreases with increasing height.

Since  $\rho = 1/\alpha$ , the equation can be rearranged to give

$$g dz = -\alpha dp$$

Integrating the hydrostatic equation from height  $z$  (and pressure  $p(z)$ ) to an infinite height:

$$-\int_{p(z)}^{p(\infty)} dp = \int_z^{\infty} g\rho dz$$

Since  $p(\infty) = 0$ ,

$$p(z) = \int_z^{\infty} g\rho dz$$

That is, the pressure at height  $z$  is equal to the *weight of the air* in the vertical column of unit cross-sectional area lying above that level.

If the mass of the Earth's atmosphere were uniformly distributed over the globe, the pressure at sea level would be 1013 hPa, or  $1.013 \times 10^5$  Pa, which is referred to as 1 *atmosphere* (or 1 atm).



# Geopotential

The geopotential  $\Phi$  at any point in the Earth's atmosphere is defined as *the work* that must be done against the Earth's gravitational field to raise a mass of 1 kg from sea level to that point.

In other words,  $\Phi$  is the **gravitational potential energy per unit mass**. The units of geopotential are  $\text{J kg}^{-1}$  or  $\text{m}^2 \text{s}^{-2}$ .

The work (in joules) in raising 1 kg from  $z$  to  $z + dz$  is  $g dz$ . Therefore

$$d\Phi = g dz$$

or, using the hydrostatic equation,

$$d\Phi = g dz = -\alpha dp$$

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Geopotential height is used as the vertical coordinate in most atmospheric applications in which energy plays an important role. It can be seen from the Table below that the values of  $Z$  and  $z$  are almost the same in the lower atmosphere where  $g \approx g_0$ .

**Table 3.1**  
Values of the geopotential height ( $Z$ ), and acceleration due to gravity ( $g$ ), at  $40^\circ$  latitude for geometric height ( $z$ )

$z(\text{km})$	$Z(\text{km})$	$g(\text{m s}^{-2})$
0	0	9.81
1	1.00	9.80
10	9.99	9.77
100	98.47	9.50
500	463.6	8.43

The geopotential  $\Phi(z)$  at height  $z$  is thus given by

$$\Phi(z) = \int_0^z g dz.$$

where the geopotential  $\Phi(0)$  at sea level ( $z = 0$ ) has been taken as zero.

The geopotential at a particular point in the atmosphere depends only on the height of that point and not on the path through which the unit mass is taken in reaching that point.

We define the **geopotential height**  $Z$  as

$$Z = \frac{\Phi(z)}{g_0} = \frac{1}{g_0} \int_0^z g dz$$

where  $g_0$  is the globally averaged acceleration due to gravity at the Earth's surface.

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# The Hypsometric Equation

In meteorological practice it is not convenient to deal with the density of a gas,  $\rho$ , the value of which is generally not measured. By making use of the hydrostatic equation and the gas law, we can eliminate  $\rho$ :

$$\frac{\partial p}{\partial z} = -\frac{pg}{RT} = -\frac{pg}{R_d T_v}$$

Rearranging the last expression and using  $d\Phi = g dz$  yields

$$d\Phi = g dz = -RT \frac{dp}{p} = -R_d T_v \frac{dp}{p}$$

Integrating between pressure levels  $p_1$  and  $p_2$ , with geopotentials  $Z_1$  and  $Z_2$  respectively,

$$\int_{\Phi_1}^{\Phi_2} d\Phi = - \int_{p_1}^{p_2} R_d T_v \frac{dp}{p}$$

or

$$\Phi_2 - \Phi_1 = -R_d \int_{p_1}^{p_2} T_v \frac{dp}{p}$$



Dividing both sides of the last equation by  $g_0$  and reversing the limits of integration yields

$$Z_2 - Z_1 = \frac{R_d}{g_0} \int_{p_2}^{p_1} T_v \frac{dp}{p}$$

The difference  $Z_2 - Z_1$  is called the geopotential **thickness** of the layer.

If the virtual temperature is constant with height, we get

$$Z_2 - Z_1 = H \int_{p_2}^{p_1} \frac{dp}{p} = H \log \left( \frac{p_1}{p_2} \right)$$

or

$$p_2 = p_1 \exp \left[ -\frac{Z_2 - Z_1}{H} \right]$$

where  $H = R_d T_v / g_0$  is the **scale height**. Since  $R_d = 287 \text{ J K}^{-1} \text{ kg}^{-1}$  and  $g_0 = 9.81 \text{ m s}^{-2}$  we have, approximately,  $H = 29.3 T_v$ .

If we take a *mean* value for virtual temperature of  $T_v = 255 \text{ K}$ , the scale height  $H$  for air in the atmosphere is found to be about 7.5 km.

**Exercise:** Check these statements.

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The temperature and vapour pressure of the atmosphere generally vary with height. In this case we can define a **mean virtual temperature**  $\bar{T}_v$  (see following Figure):

$$\bar{T}_v = \frac{\int_{\log p_2}^{\log p_1} T_v d \log p}{\int_{\log p_2}^{\log p_1} d \log p} = \frac{\int_{\log p_2}^{\log p_1} T_v d \log p}{\log(p_1/p_2)}$$

Using this in the thickness equation we get

$$Z_2 - Z_1 = \frac{R_d}{g_0} \int_{p_2}^{p_1} T_v d \log p = \frac{R_d \bar{T}_v}{g_0} \log \frac{p_1}{p_2}$$

This is called the **hypsothetic equation**:

$$Z_2 - Z_1 = \frac{R_d \bar{T}_v}{g_0} \log \frac{p_1}{p_2}$$

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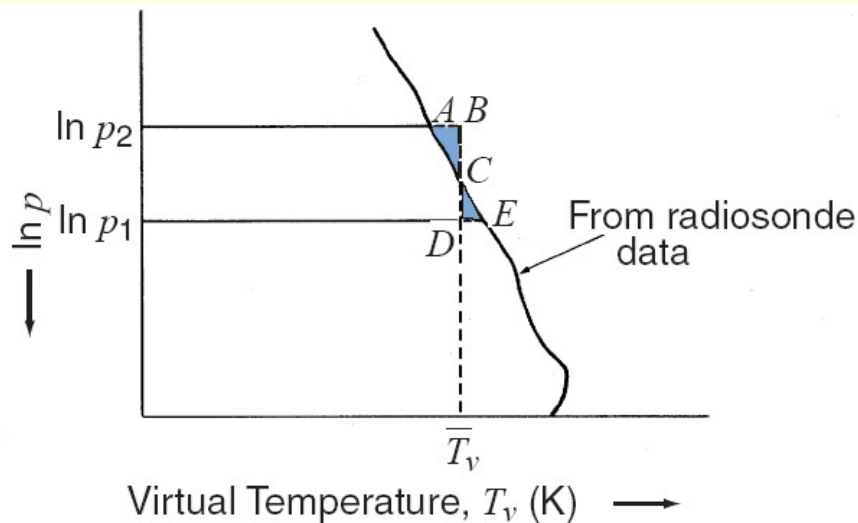


Figure 3.2. Vertical profile, or sounding, of virtual temperature.

If area  $ABC$  is equal to area  $CDE$ , then  $\bar{T}_v$  is the mean virtual temperature with respect to  $\log p$  between the pressure levels  $p_1$  and  $p_2$ .

## Constant Pressure Surfaces

Since pressure decreases monotonically with height, pressure surfaces never intersect. It follows from the hypsothetic equation that the thickness of the layer between any two pressure surfaces  $p_2$  and  $p_1$  is proportional to the mean virtual temperature of the layer,  $\bar{T}_v$ .

Essentially, the air between the two pressure levels expands and the layer becomes thicker as the temperature increases.

**Exercise:** Calculate the thickness of the layer between the 1000 hPa and 500 hPa pressure surfaces, (a) at a point in the tropics where the mean virtual temperature of the layer is  $15^\circ\text{C}$ , and (b) at a point in the polar regions where the mean virtual temperature is  $-40^\circ\text{C}$ .

**Solution:** From the hypsometric equation,

$$\Delta Z = Z_{500} - Z_{1000} = \frac{R_d \bar{T}_v}{g_0} \ln \left( \frac{1000}{500} \right) = 20.3 \bar{T}_v \text{ metres}$$

Therefore, for the tropics with virtual temperature  $\bar{T}_v = 288 \text{ K}$  we get

$$\Delta Z = 5846 \text{ m.}$$

For polar regions with virtual temperature  $\bar{T}_v = 233 \text{ K}$ , we get

$$\Delta Z = 4730 \text{ m.}$$

In operational practice, thickness is rounded to the nearest 10 m and expressed in **decameters (dam)**. Hence, answers for this exercise would normally be expressed as 585 dam and 473 dam, respectively.

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Using soundings from a network of stations, it is possible to construct topographical maps of the distribution of geopotential height on selected pressure surfaces.

If the three-dimensional distribution of virtual temperature is known, together with the distribution of geopotential height on one pressure surface, it is possible to infer the distribution of geopotential height of any other pressure surface.

The same hypsometric relationship between the three-dimensional temperature field and the shape of pressure surface can be used in a qualitative way to gain some useful insights into the three-dimensional structure of atmospheric disturbances, as illustrated by the following examples:

- Warm-core hurricane
- Cold-core upper low
- Extratropical cyclone

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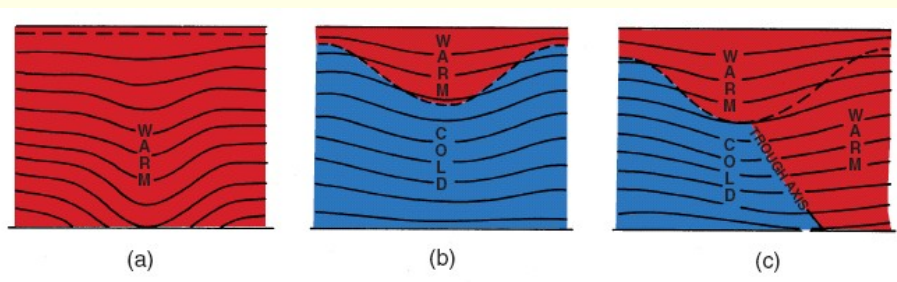


Figure 3.3. Vertical cross-sections through (a) a hurricane, (b) a *cold-core* upper tropospheric low, and (c) a middle-latitude disturbance that tilts westward with height.

## Reduction of Pressure to Sea Level

In mountainous regions the difference in surface pressure from one measuring station to another is largely due to **differences in elevation**.

To isolate that part of the pressure field that is due to the passage of weather systems, it is necessary to reduce the pressures to a *common reference level*. For this purpose, sea level is normally used.

Let  $Z_g$  and  $p_g$  be the geopotential and pressure at ground level and  $Z_0$  and  $p_0$  the geopotential and pressure at sea level ( $Z_0 = 0$ ).

Then, for the layer between the Earth's surface and sea level, the hypsometric equation becomes

$$(Z_g - Z_0) = Z_g = \bar{H} \ln \frac{p_0}{p_g}$$

where  $\bar{H} = R_d \bar{T}_v / g_0$ .

Once again,

$$Z_g = \bar{H} \ln \frac{p_0}{p_g}$$

where  $\bar{H} = R_d \bar{T}_v / g_0$ .

This can be solved to obtain the sea-level pressure

$$p_0 = p_g \exp\left(\frac{Z_g}{\bar{H}}\right) = p_g \exp\left(\frac{g_0 Z_g}{R_d \bar{T}_v}\right)$$

The last expression shows how the sea-level pressure depends on the mean virtual temperature between ground and sea level.

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If  $Z_g$  is small, the scale height  $\bar{H}$  can be evaluated from the ground temperature.

Also, if  $Z_g \ll \bar{H}$ , the exponential can be approximated by

$$\exp\left(\frac{Z_g}{\bar{H}}\right) \approx 1 + \frac{Z_g}{\bar{H}}.$$

Since  $\bar{H}$  is about 8 km for the observed range of ground temperatures on Earth, this approximation is satisfactory provided that  $Z_g$  is less than a few hundred meters.

With this approximation, we get

$$p_0 \approx p_g \left(1 + \frac{Z_g}{\bar{H}}\right) \quad \text{or} \quad p_0 - p_g \approx \left(\frac{p_g}{\bar{H}}\right) Z_g$$

Since  $p_g \approx 1000$  hPa and  $\bar{H} \approx 8$  km, the pressure correction (in hPa) is roughly equal to  $Z_g$  (in meters) divided by 8.

$$p_0 - p_g \approx \frac{1}{8} Z_g$$

In other words, near sea level the pressure decreases by *about 1 hPa for every 8 m of vertical ascent*.

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**Exercise:** Calculate the geopotential height of the 1000 hPa pressure surface when the pressure at sea level is 1014 hPa. The scale height of the atmosphere may be taken as 8 km.

**Solution:** From the hypsometric equation,

$$Z_{1000} = \bar{H} \ln\left(\frac{p_0}{1000}\right) = \bar{H} \ln\left(1 + \frac{p_0 - 1000}{1000}\right) \approx \bar{H} \left(\frac{p_0 - 1000}{1000}\right)$$

where  $p_0$  is the sea level pressure and the approximation

$$\ln(1+x) \approx x$$

for  $x \ll 1$  has been used.

Substituting  $\bar{H} \approx 8000$  m into this expression gives

$$Z_{1000} \approx 8(p_0 - 1000)$$

Therefore, with  $p_0 = 1014$  hPa, the geopotential height  $Z_{1000}$  of the 1000 hPa pressure surface is found to be 112 m above sea level.

**Exercise:** Derive a relationship for the height of a given pressure surface  $p$  in terms of the pressure  $p_0$  and temperature  $T_0$  at sea level assuming that the *temperature decreases uniformly* with height at a rate  $\Gamma$  K km<sup>-1</sup>.

**Solution:** Let the height of the pressure surface be  $z$ ; then its temperature  $T$  is given by

$$T = T_0 - \Gamma z$$

Combining the hydrostatic equation with the ideal gas equation gives

$$\frac{dp}{p} = -\frac{g}{RT} dz$$

From these equations it follows that

$$\frac{dp}{p} = -\frac{g}{R(T_0 - \Gamma z)} dz$$

Again:

$$\frac{dp}{p} = -\frac{g}{R(T_0 - \Gamma z)} dz$$

Integrating this equation between pressure levels  $p_0$  and  $p$  and corresponding heights 0 and  $z$ , and neglecting the variation of  $g$  with  $z$ , we obtain

$$\int_{p_0}^p \frac{dp}{p} = -\frac{g}{R} \int_0^z \frac{dz}{T_0 - \Gamma z}.$$

Aside:

$$\int \frac{dx}{ax+b} = \frac{1}{a} \log(ax+b).$$

Thus:

$$\log \frac{p}{p_0} = \frac{g}{R\Gamma} \log \left( \frac{T_0 - \Gamma z}{T_0} \right).$$

Therefore

$$z = \frac{T_0}{\Gamma} \left[ 1 - \left( \frac{p}{p_0} \right)^{R\Gamma/g} \right]$$

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**Exercise (Hard!):** Show that, in the limit  $\Gamma \rightarrow 0$ , the altimetry equation is consistent with the relationship

$$p = p_0 \exp \left( -\frac{z}{H} \right)$$

already obtained for an isothermal atmosphere.

**Solution (Easy!):** Use l'Hôpital's Rule.

Note: If you are unfamiliar with l'Hôpital's Rule, either ignore this exercise or, better still, try it using more elementary means.

# Altimetry

The *altimetry equation*

$$z = \frac{T_0}{\Gamma} \left[ 1 - \left( \frac{p}{p_0} \right)^{R\Gamma/g} \right]$$

forms the basis for the calibration of altimeters on aircraft. An altimeter is simply an aneroid barometer that measures the air pressure  $p$ .

However, the scale of the altimeter is expressed as the height above sea level where  $z$  is related to  $p$  by the above equation with values for the parameters in accordance with the U.S. Standard Atmosphere:

$$T_0 = 288 \text{ K}$$

$$p_0 = 1013.25 \text{ hPa}$$

$$\Gamma = 6.5 \text{ K km}^{-1}$$

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End of §2.2

# III. First Law of Thermodynamics

A mass of gas possesses **internal energy** due to the kinetic and potential energy of its molecules or atoms. Changes in internal energy are manifested as changes in the **temperature** of the system.

Suppose that a closed system of **unit mass** takes in a certain quantity of thermal energy  $q$ , which it can receive by thermal conduction and/or radiation. As a result the system may do a certain amount of external work  $w$ .

The excess of the energy supplied to the body over and above the external work done by the body is  $q - w$ . It follows from the *principle of conservation of energy* that the internal energy of the system must increase by  $q - w$ .

That is,

$$\Delta u = q - w$$

where  $\Delta u$  is the change in internal energy of the system.

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Again, let  $\Delta u$  be the change in internal energy of the system:

$$\Delta u = q - w$$

In differential form this becomes

$$du = dq - dw$$

where  $dq$  is the differential increment of heat added to the system,  $dw$  the differential element of work done by the system, and  $du$  the differential increase in internal energy of the system.

This is a statement of the *First Law of Thermodynamics*. In fact, it provides a *definition* of  $du$ .

The change in internal energy  $du$  depends only on the initial and final states of the system, and is therefore independent of the manner by which the system is transferred between these two states. Such parameters are referred to as *functions of state*

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Consider a substance, the *working substance*, contained in a cylinder of fixed cross-sectional area that is fitted with a movable, frictionless piston.

The volume of the substance is proportional to the distance from the base of the cylinder to the face of the piston, and can be represented on the horizontal axis of the graph shown in the following figure. The pressure of the substance in the cylinder can be represented on the vertical axis of this graph.

Therefore, every state of the substance, corresponding to a given position of the piston, is represented by a point on this pressure-volume ( $p$ - $V$ ) diagram.

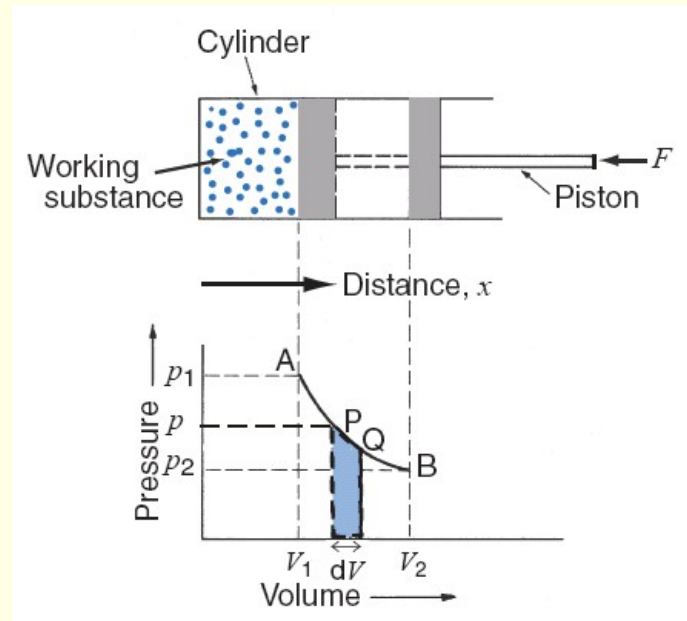


Figure 3.4: Representation of the state of a working substance in a cylinder on a  $p$ - $V$  diagram.

If the piston moves outwards through an incremental distance  $dx$ , the work  $dW$  done by the substance in pushing the external force  $F$  through the distance  $dx$  is

$$dW = F dx$$

Since  $F = pA$ , where  $A$  is the cross-sectional area,

$$dW = pAdx = p dV$$

In other words, the work done is equal to the **pressure of the substance multiplied by its increase in volume**. Note that  $dW = p dV$  is equal to the shaded area in the graph, the area under the curve PQ.

When the substance passes from state A with volume  $V_1$  to state B with volume  $V_2$ , the work  $W$  done by the material is equal to the area under the curve AB. That is,

$$W = \int_{V_1}^{V_2} p dV$$

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Again,

$$W = \int_{V_1}^{V_2} p dV$$

If  $V_2 > V_1$ , then  $W$  is positive, indicating that the substance does work on its environment. If  $V_2 < V_1$ , then  $W$  is negative, which indicates that the environment does work on the substance.

The  $p$ - $V$  diagram is an example of a *thermodynamic diagram*, in which the physical state of a substance is represented by two thermodynamic variables. Such diagrams are very useful in meteorology; we will discuss other examples later, in particular, the *tephigram*.

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If we are dealing with a *unit mass* of a substance, the volume  $V$  is replaced by the specific volume  $\alpha$  and the work  $w$  that is done when the specific volume increases by  $dw$  is

$$dw = p d\alpha$$

The thermodynamic equation may be written

$$dq = du + dw$$

Using this with the equation above, we get

$$dq = du + p d\alpha$$

which is an alternative statement of the **First Law of Thermodynamics**.

## Joule's Law

**When a gas expands without doing external work, into a chamber that has been evacuated, and without taking in or giving out heat, the temperature of the gas does not change.**

This statement is strictly true only for an *ideal gas*, but air behaves very similarly to an ideal gas over a wide range of conditions.

Joule's Law leads to an important conclusion concerning the internal energy of an ideal gas. If a gas neither does external work nor takes in or gives out heat,  $dq = 0$  and  $dw = 0$ , so that, by the First Law of Thermodynamics,  $du = 0$ .

According to Joule's law, under these conditions the temperature of the gas does not change, which implies that the kinetic energy of the molecules remains constant.



Therefore, since the total internal energy of the gas is constant, that part of the internal energy due to the potential energy must also remain unchanged, even though the volume of the gas changes.

In other words, the internal energy of an ideal gas is independent of its volume if the temperature is kept constant.

This can be the case only if the molecules of an ideal gas do not exert forces on each other.

In this case, the **internal energy** of an ideal gas will depend only on its **temperature**:

$$u = u(T)$$

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## Specific Heats

Suppose a small quantity of heat  $dq$  is given to a unit mass of a material and, as a consequence, the temperature of the material increases from  $T$  to  $T + dT$  without any changes in phase occurring within the material.

The ratio  $dq/dT$  is called the **specific heat** of the material. However, the specific heat defined in this way could have any number of values, depending on how the material changes as it receives the heat.

If the *volume* of the material is kept constant, a **specific heat at constant volume**,  $c_v$ , is defined

$$c_v = \left( \frac{dq}{dT} \right)_V$$

But if the volume of the material is constant, the thermodynamic equation gives  $dq = du$ .

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Again,  $c_v = (dq/Dt)_V$ . But  $V$  constant implies  $dq = du$ . Therefore

$$c_v = \left( \frac{du}{dT} \right)_V$$

For an ideal gas, Joule's law applies and therefore  $u$  depends only on temperature. Therefore, regardless of whether the volume of a gas changes, we may write

$$c_v = \frac{du}{dT}.$$

Since  $u$  is a function of state, no matter how the material changes from state 1 to state 2, the change in its internal energy is

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT$$

In differential form, we have:

$$du = c_v dT.$$

The First Law of Thermodynamics for an ideal gas can now be written in the form

$$dq = c_v dT + p d\alpha$$

We can also define a **specific heat at constant pressure**

$$c_p = \left( \frac{dq}{dT} \right)_p$$

where the material is allowed to expand as heat is added to it and its temperature rises, but its pressure remains constant.

In this case, some of the heat added to the material will have to be expended to do work as the system expands against the constant pressure of its environment.

Therefore, a larger quantity of heat must be added to the material to raise its temperature by a given amount than if the volume of the material were kept constant.



Therefore

$$c_p > c_v$$

For the case of an ideal gas, this inequality can be seen mathematically as follows. We write the thermodynamic equation as

$$dq = c_v dT + p d\alpha = c_v dT + d(p\alpha) - \alpha dp$$

From the equation of state,  $d(p\alpha) = d(RT) = R dT$ .

Therefore,

$$dq = (c_v + R)dT - \alpha dp$$

At constant pressure, the last term vanishes; therefore,

$$c_p = \left( \frac{dq}{dT} \right)_p = c_v + R$$

Using this in the equation above it, we obtain an alternative form of the **First Law of Thermodynamics**:

$$dq = c_p dT - \alpha dp.$$

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## Mnemonics

For air,  $c_p : c_v : R = 7 : 5 : 2$ .

$$\begin{array}{ll} \gamma = c_p/c_v & \text{Indices in alphabetical order} \\ R = c_p - c_v & \text{Indices in alphabetical order} \end{array}$$

$$c_p \approx 1000 \text{ J K}^{-1} \text{ kg}^{-1}$$

(true value  $1004 \text{ J K}^{-1} \text{ kg}^{-1}$ )

Therefore,

$$c_v \approx \frac{5}{7} \times 1000 \approx 714 \text{ J K}^{-1} \text{ kg}^{-1}$$

(true value  $717 \text{ J K}^{-1} \text{ kg}^{-1}$ )

Moreover,

$$R \approx \frac{2}{7} \times 1000 \approx 286 \text{ J K}^{-1} \text{ kg}^{-1}$$

(true value  $287 \text{ J K}^{-1} \text{ kg}^{-1}$ )

The specific heats at constant volume and at constant pressure for dry air are  $717$  and  $1004 \text{ J K}^{-1} \text{ kg}^{-1}$ , respectively, and the difference between them is  $287 \text{ J K}^{-1} \text{ kg}^{-1}$ , which is the gas constant for dry air.

Again,

$$c_v = 717 \quad c_p = 1004 \quad R = 287$$

(all in units  $1004 \text{ J K}^{-1} \text{ kg}^{-1}$ ).

For an ideal *monatomic gas*  $c_p : c_v : R = 5 : 3 : 2$ , and for an ideal *diatomic gas*  $c_p : c_v : R = 7 : 5 : 2$ .

Since the atmosphere is comprised primarily of diatomic gases ( $\text{N}_2$  and  $\text{O}_2$ ), we have

$$\gamma = \frac{c_p}{c_v} \approx \frac{7}{5} = 1.4, \quad \kappa = \frac{R}{c_p} \approx \frac{2}{7} = 0.286.$$

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## Enthalpy

Suppose heat is added to a unit mass of material at constant pressure. Suppose the resulting expansion causes the (specific) volume to increase from  $\alpha_1$  to  $\alpha_2$ .

Then the work done by a unit mass of the material is

$$\int_{\alpha_1}^{\alpha_2} p d\alpha = p(\alpha_2 - \alpha_1)$$

Therefore, the finite quantity of heat  $\Delta q$  added is given by

$$\begin{aligned} \Delta q &= (u_2 - u_1) + p(\alpha_2 - \alpha_1) \\ &= (u_2 + p\alpha_2) - (u_1 + p\alpha_1) \end{aligned}$$

where  $u_1$  and  $u_2$  are the initial and final internal energies for unit mass.

We define the *enthalpy* of a unit mass of the material by

$$h = u + p\alpha.$$

Again, the specific enthalpy is defined as:

$$h = u + p\alpha$$

Since  $u$ ,  $p$ , and  $\alpha$  are functions of state,  $h$  is also a function of state.

From above it follows that, at constant pressure,

$$\Delta q = (h_2 - h_1)$$

or, in other words,

$$\Delta q = \Delta h.$$

Differentiating the defining equation,  $h = u + p\alpha$ , we obtain

$$\begin{aligned} dh &= du + d(p\alpha) \\ &= du + p d\alpha + \alpha dp \\ &= dq + \alpha dp \end{aligned}$$

Transferring terms to the other side, we get:

$$dq = dh - \alpha dp.$$

This is another form of the First Law of Thermodynamics.

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Repeating,

$$dq = dh - \alpha dp.$$

But we already had the equation

$$dq = c_p dT - \alpha dp.$$

Comparing these last two equations, we conclude that

$$dh = c_p dT$$

or, in integrated form,

$$h = c_p T$$

where  $h$  is taken as zero when  $T = 0$ .

In view of this,  $h$  is sometimes called the *heat at constant pressure*, because it corresponds to the heat given to a material to raise its temperature from 0 to  $T$  Kelvins at constant pressure.

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## Dry Static Energy

The hydrostatic equation gives

$$\frac{dp}{dz} = -g\rho, \quad \text{or} \quad \alpha dp = -g dz$$

Using this in the thermodynamic equation, we have

$$\begin{aligned} dq &= c_p dT - \alpha dp \\ &= c_p dT + g dz \\ &= d(h + \Phi) \end{aligned}$$

Hence, if the material is a parcel of air with a fixed mass that is moving about in an hydrostatic atmosphere, the quantity

$$(h + \Phi)$$

which is called the *dry static energy*, is constant provided the parcel neither gains nor loses heat (that is,  $dq = 0$ ).

For *adiabatic changes*, the dry static energy is constant.

## Exercises:

End of §2.3

## IV. Adiabatic Processes

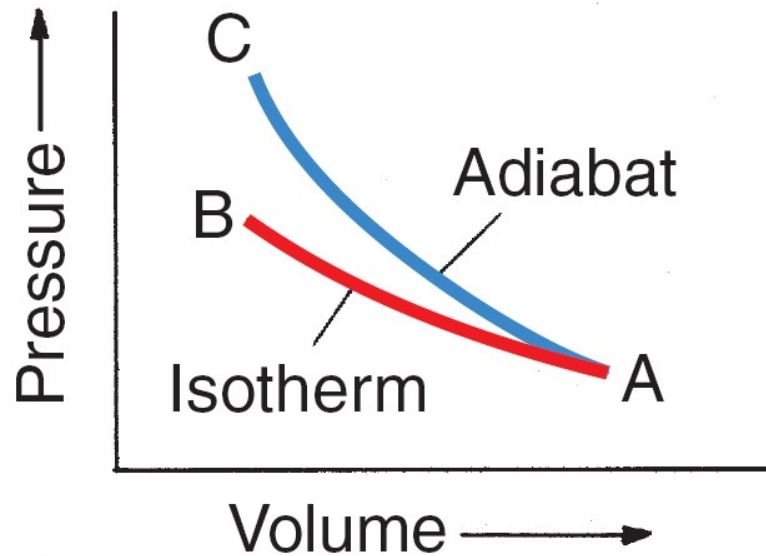
If a material undergoes a change in its physical state (e.g., its pressure, volume, or temperature) without any heat being added to it or withdrawn from it, the change is said to be *adiabatic*.

Suppose that the initial state of a material is represented by the point A on the thermodynamic diagram below, and that when the material undergoes an *isothermal* transformation it moves along the line AB.

If the same material undergoes a similar change in volume but under *adiabatic* conditions, the transformation would be represented by a curve such as AC, which is called an *adiabat*.

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An *isotherm* and an *adiabat* on a  $p$ - $V$ -diagram.

The adiabat AC is steeper than the isotherm AB. The reason for this is easily seen.

During the *adiabatic compression* ( $d\alpha < 0$ ) the internal energy increases:

$$dq = du + p d\alpha \quad \text{and} \quad dq = 0 \quad \Rightarrow \quad du = -p d\alpha > 0$$

and therefore *the temperature of the system rises*:

$$du = c_v dT > 0 \quad \Rightarrow \quad T_C > T_A$$

However, for the *isothermal compression* from A to B, the *temperature remains constant*:  $T_B = T_A$ . Hence,  $T_B < T_C$ . But  $\alpha_B = \alpha_C$  (the final volumes are equal); so

$$p_B = \frac{RT_B}{\alpha_B} < \frac{RT_C}{\alpha_C} = p_C$$

that is,  $p_B < p_C$ .

Thus, the adiabat is steeper than the isotherm.

# The Idea of an Air Parcel

In the atmosphere, molecular mixing is important only within a centimeter of the Earth's surface and at levels above the turbopause ( $\sim 105$  km).

At intermediate levels, virtually all mixing in the vertical is accomplished by the exchange of macroscale *air parcels* with horizontal dimensions ranging from a few centimeters to the scale of the Earth itself.

That is, mixing is due not to molecular motions, but to **eddies** of various sizes.

Recall Richardson's rhyme:

Big whirls have little whirls that feed on their velocity,  
And little whirls have lesser whirls and so on to viscosity  
--- in the molecular sense.

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To gain some insights into the nature of vertical mixing in the atmosphere it is useful to consider the behavior of an *air parcel* of infinitesimal dimensions that is assumed to be:

- thermally insulated from its environment, so that its temperature changes *adiabatically* as it rises or sinks
- always at exactly the same pressure as the environmental air at the same level, which is assumed to be in hydrostatic equilibrium
- moving slowly enough that the macroscopic kinetic energy of the air parcel is a negligible fraction of its total energy.

This simple, idealized model is helpful in understanding some of the physical processes that influence the distribution of vertical motions and vertical mixing in the atmosphere.

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# The Dry Adiabatic Lapse Rate

We will now derive an expression for the rate of change of temperature with height of a *parcel of dry air* as it moves about in the Earth's atmosphere.

Since the air parcel undergoes only adiabatic transformations ( $dq = 0$ ), and the atmosphere is in hydrostatic equilibrium, for a unit mass of air in the parcel we have:

$$\begin{aligned}c_v dT + p d\alpha &= 0 \\c_v dT + d(p\alpha) - \alpha dp &= 0 \\c_v dT + d(RT) - \alpha dp &= 0 \\(c_v + R)dT + g dz &= 0 \\c_p dT + g dz &= 0\end{aligned}$$

Dividing through by  $dz$ , we obtain

$$-\left(\frac{dT}{dz}\right) = \frac{g}{c_p} \equiv \Gamma_d$$

where  $\Gamma_d$  is called the *dry adiabatic lapse rate*.

Since an air parcel expands as it rises in the atmosphere, its temperature will decrease with height so that  $\Gamma_d$  is a positive quantity.

Substituting  $g = 9.81 \text{ m s}^{-2}$  and  $c_p = 1004 \text{ J K}^{-1} \text{ kg}^{-1}$  gives

$$\Gamma_d = \frac{g}{c_p} = 0.0098 \text{ K m}^{-1} = 9.8 \text{ K km}^{-1} \approx 10 \text{ K km}^{-1}$$

which is the dry adiabatic lapse rate.

It should be emphasized again that  $\Gamma_d$  is the rate of change of temperature following a *parcel of dry air* that is being raised or lowered *adiabatically* in the atmosphere.

The *actual lapse rate* of temperature in a column of air, which we will indicate by

$$\Gamma = -\frac{dT}{dz},$$

as measured for example by a radiosonde, averages 6 or  $7 \text{ K km}^{-1}$  in the troposphere, but it takes on a wide range of values at individual locations.

# Potential Temperature

**Definition:** The *potential temperature*  $\theta$  of an air parcel is the temperature that the parcel of air would have if it were expanded or compressed adiabatically from its existing pressure to a standard pressure of  $p_0 = 1000 \text{ hPa}$ .

We will derive an expression for the potential temperature of an air parcel in terms of its pressure  $p$ , temperature  $T$ , and the standard pressure  $p_0$ .

For an adiabatic transformation ( $dq = 0$ ) the thermodynamic equation is

$$c_p dT - \alpha dp = 0$$

Using the gas equation  $p\alpha = RT$  yields

$$c_p dT - \frac{RT}{p} dp = 0 \quad \text{or} \quad \frac{dT}{T} = \frac{R}{c_p} \frac{dp}{p}$$

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Integrating from standard pressure  $p_0$  (where, by definition,  $T = \theta$ ) to  $p$  (with temperature  $T$ ), we write:

$$\int_{\theta}^T \frac{dT}{T} = \frac{R}{c_p} \int_{p_0}^p \frac{dp}{p}$$

Evaluating the integrals, we get:

$$\log\left(\frac{T}{\theta}\right) = \frac{R}{c_p} \log\left(\frac{p}{p_0}\right) = \log\left(\frac{p}{p_0}\right)^{R/c_p}$$

Taking the exponential (antilog) of both sides

$$\frac{T}{\theta} = \left(\frac{p}{p_0}\right)^{R/c_p}$$

Solving for  $\theta$ ,

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

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Defining the thermodynamic constant  $\kappa = R/c_p$ , we get

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

This equation is called *Poisson's equation*.

For dry air,  $R = R_d = 287 \text{ J K}^{-1} \text{ kg}^{-1}$  and  $c_p = 1004 \text{ J K}^{-1} \text{ kg}^{-1}$ .

Recall that, for a diatomic gas,  $R : c_p = 2 : 7$ , so

$$\kappa = \frac{2}{7} \approx 0.286$$

\* \* \*

# Conservation of $\theta$

Recall the thermodynamic equation in the form

$$ds \equiv \frac{dq}{T} = c_p \frac{dT}{T} - R \frac{dp}{p} = c_p \frac{d\theta}{\theta} \quad (*)$$

The quantity  $ds$  is the change in *entropy* (per unit mass).

By definition, *adiabatic* changes have  $dq = 0$ .

Therefore, we also have  $ds = 0$  and  $d\theta = 0$ .

Thus,

$$\left[ \begin{array}{l} \text{Adiabatic} \\ \text{Changes} \end{array} \right] \quad \text{correspond to} \quad \left[ \begin{array}{l} \text{Isentropic} \\ \text{Changes} \end{array} \right]$$

We can write the thermodynamic equation (\*) as:

$$\frac{dq}{dt} = c_p T \frac{d\theta}{dt}$$

*The potential temperature is constant for adiabatic flow.*

*The entropy is constant for adiabatic flow.*

Parameters that remain constant during certain transformations are said to be *conserved*. Potential temperature is a conserved quantity for an air parcel that moves around in the atmosphere under adiabatic conditions.

Potential temperature is an extremely useful parameter in atmospheric thermodynamics, since *atmospheric processes are often close to adiabatic*, in which case  $\theta$  remains essentially constant.

Later, we will consider a more complicated quantity, the *isentropic potential vorticity*, which is approximately conserved for a broad range of atmospheric conditions.

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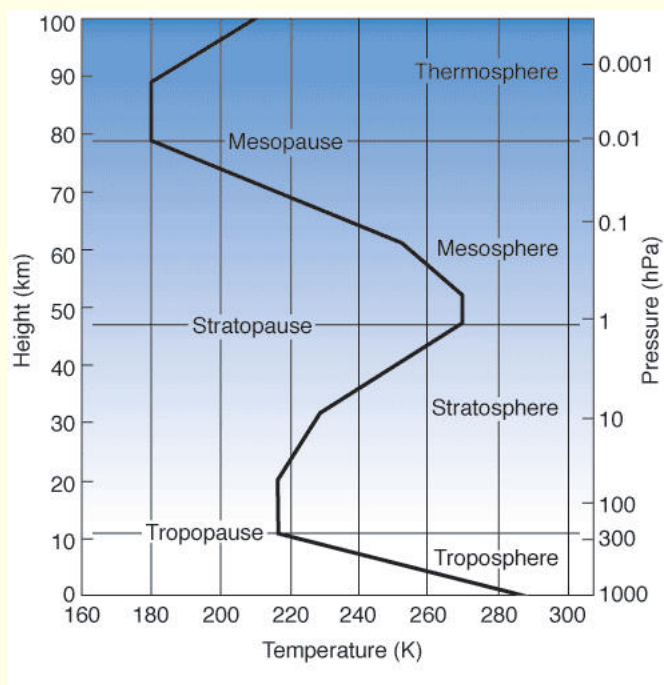
# Thermodynamic Diagrams

To examine the variation of temperature in the vertical direction, the most obvious approach would be to plot  $T$  as a function of  $z$ .

It is customary to use  $T$  as the abscissa and  $z$  as the ordinate, to facilitate interpretation of the graph.

For the mean conditions, we obtain the familiar picture, with the troposphere, stratosphere, mesosphere and thermosphere.

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Atmospheric stratification.

# The Tephigram

There are several specially designed diagrams for depiction of the vertical structure. The one in common use in Ireland is the *tephigram*.

The name derives from  $T$ - $\phi$ -gram, where  $\phi$  was an old notation for entropy. It is a *temperature-entropy* diagram.

The tephigram was introduced by Napier Shaw (1854–1945), a British meteorologist, Director of the Met Office.

Shaw founded the Department of Meteorology at Imperial College London, and was Professor there from 1920 to 1924. He did much to establish the scientific foundations of meteorology.

We owe to Shaw the introduction of the millibar (now replaced by the hectoPascal).

We define the change in *specific entropy* due to the addition of heat to a unit mass of material:

$$ds = \frac{dq}{T}$$

By the first law of thermodynamics, this can be written

$$ds = \frac{c_p dT - \alpha dp}{T} = c_p \frac{dT}{T} - R \frac{dp}{p} \quad (*)$$

But recall the definition of potential temperature:

$$\theta = T \left( \frac{p}{p_0} \right)^{-\kappa} \quad \text{or} \quad \log \theta = \log T - \kappa(\log p - \log p_0)$$

Differentiating and multiplying by  $c_p$ , we have

$$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R \frac{dp}{p} \quad (**)$$

From (\*) and (\*\*) it follows that

$$ds = c_p \frac{d\theta}{\theta} = c_p d \log \theta$$

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Again,

$$ds = c_p d \log \theta$$

Integrating from a reference value  $\theta_0$  where  $s = s_0$ , we get

$$s = c_p \log(\theta/\theta_0) + s_0$$

\* \* \*

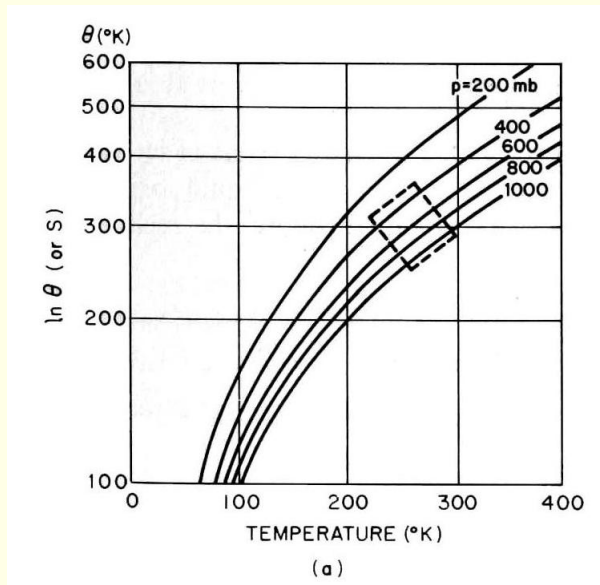
We will now consider a straightforward plot of  $T$  against  $s$  (figure to follow).

The entropy is linearly related to the logarithm of potential temperature  $\theta$ . Thus

$$s = c_p \log \theta + \text{const.}$$

We can thus plot  $\theta$  instead of  $s$  on the vertical axis, on a logarithmic scale.

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The temperature-entropy diagram or tephigram. The region of primary interest is indicated by the small box.

Next, recall the definition of potential temperature:

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

Taking logarithms of both sides,

$$\log \theta = \log T - \kappa \log p + \text{const.}$$

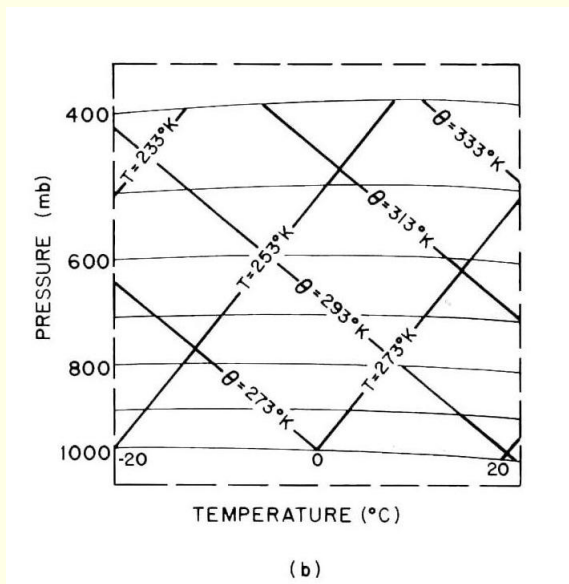
or

$$s = c_p \log T - R \log p + \text{const.}$$

So, for a constant value of *pressure*,  $s$  is given by the logarithm of *temperature*. We can plot a series of such curves of  $s$  against  $T$  for a range of values of pressure, and get the picture shown above.

The region of interest for the lower atmosphere is indicated by a small square. This region is extracted and used in the design of the tephigram. Since surfaces of constant pressure are approximately horizontal, it is convenient to rotate the diagram through  $45^\circ$ .





The temperature-entropy diagram or tephigram. Zoom and rotation of area of interest (*Wallace & Hobbs, 1st Edn, p. 96*).

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### Notes on Tephigram:

- The spacing on the temperature axis is uniform.
- $\log \theta$  is uniformly spaced, so that  $\theta$  is not. However, on the restricted range, the spacing of  $\theta$  appears nearly uniform.
- The isobars are fairly close to horizontal.
- We can think of the chart as a plot of temperature as a function of pressure. However, its special design enables us to deduce stability properties by inspection.
- Lines of constant temperature are called *isotherms*.
- Lines of constant potential temperature are called *adiabats* or *isentropes*.
- Lines of constant pressure are called *isobars*.

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### EXTRACT FROM THE MET ÉIREANN WEB-SITE (9 August, 2004)

A TEPHIGRAM IS A GRAPHICAL REPRESENTATION OF OBSERVATIONS OF PRESSURE, TEMPERATURE AND HUMIDITY MADE IN A VERTICAL SOUNDING OF THE ATMOSPHERE. VERTICAL SOUNDINGS ARE MADE USING AN INSTRUMENT CALLED A RADIOSONDE, WHICH CONTAINS PRESSURE, TEMPERATURE AND HUMIDITY SENSORS AND WHICH IS LAUNCHED INTO THE ATMOSPHERE ATTACHED TO A BALLOON.

THE TEPHIGRAM CONTAINS A SET OF FUNDAMENTAL LINES WHICH ARE USED TO DESCRIBE VARIOUS PROCESSES IN THE ATMOSPHERE. THESE LINES INCLUDE:

- ISOBARS — LINES OF CONSTANT PRESSURE
- ISOTHERMS — LINES OF CONSTANT TEMPERATURE
- DRY ADIABATS — RELATED TO DRY ADIABATIC PROCESSES (POTENTIAL TEMPERATURE CONSTANT)
- SATURATED ADIABATS — RELATED TO SATURATED ADIABATIC PROCESSES (WET BULB POTENTIAL TEMPERATURE CONSTANT)

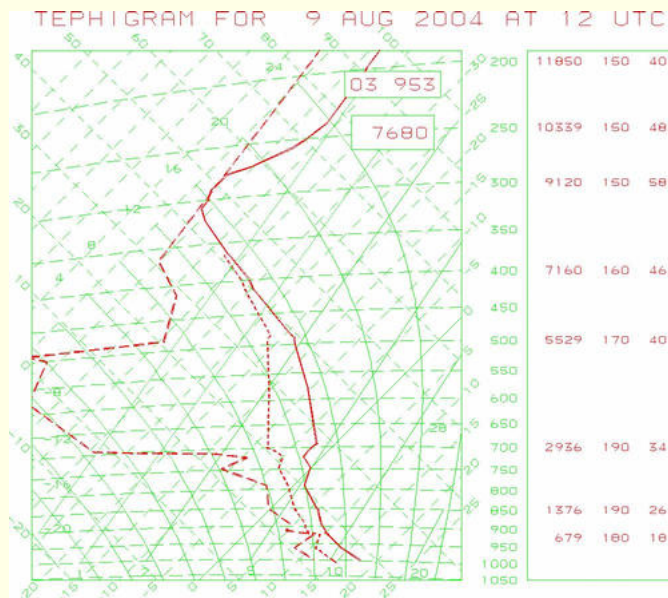
ON THE TEPHIGRAM THERE ARE TWO KINDS OF INFORMATION REPRESENTED

- THE ENVIRONMENT CURVES (RED) WHICH DESCRIBES THE STRUCTURE OF THE ATMOSPHERE
- THE PROCESS CURVES (GREEN) WHICH DESCRIBES WHAT HAPPENS TO A PARCEL OF AIR UNDERGOING A PARTICULAR TYPE OF PROCESS (E.G. ADIABATIC PROCESS)

IN ADDITION, THE RIGHT HAND PANEL DISPLAYS HEIGHT, WIND DIRECTION AND SPEED AT A SELECTION OF PRESSURE LEVELS.

TEPHIGRAMS CAN BE USED BY THE FORECASTER FOR THE FOLLOWING PURPOSES

- TO DETERMINE MOISTURE LEVELS IN THE ATMOSPHERE
- TO DETERMINE CLOUD HEIGHTS
- TO PREDICT LEVELS OF CONVECTIVE ACTIVITY IN THE ATMOSPHERE
- FORECAST MAXIMUM AND MINIMUM TEMPERATURES
- FORECAST FOG FORMATION AND FOG CLEARANCE



Sample Tephigram based on radiosonde ascent from Valentia Observatory for 1200 UTC, 9 August, 2004.

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End of §2.4

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## V. Water Vapour in Air

So far we have indicated the presence of water vapour in the air through the *vapour pressure*  $e$  that it exerts.

We have quantified its effect on the density of air by introducing the concepts of *mixing ratio* and of *virtual temperature*.

However, the amount of water vapour present in a certain quantity of air may be expressed in many different ways, some of the more important of which are considered now.

## A Bewildering Variety

- Vapour Pressure
- Mixing Ratio
- Specific Humidity
- Absolute Humidity
- Relative Humidity
- Dew Point Temperature/Dew Point Depression
- Wet-bulb Temperature/Wet-bulb Depression
- Wet-bulb Potential Temperature
- Virtual Temperature
- Saturation Level

# Why So Many Moisture Variables?

- Some are useful because they are easy to measure.

Wet-bulb temperature is easy to measure, but it is not easy to convert to more useful parameters, so psychrometric tables have been devised.

- Some are *conserved quantities* describing physical characteristics of the air.

The mixing ratio is not measured directly, but it is useful because it is conserved for an air parcel moving vertically (or horizontally) without mixing.

- Some are fundamental quantities, related simply to other thermodynamic variables.

Vapour pressure is hard to measure and not directly useful in applications. But it is theoretically important, describing how saturation humidity varies with temperature.

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# Mixing Ratio & Specific Humidity

The *mixing ratio*  $w$  is the ratio of the mass  $m_v$  of water vapour to the mass  $m_d$  of dry air in a parcel of air.

That is,

$$w = \frac{m_v}{m_d}$$

Clearly, the mixing ratio  $w$  is a dimensionless quantity. It is generally expressed in *grams of water vapour per kilogram of dry air*.

In the atmosphere the magnitude of  $w$  typically ranges from a few grams per kilogram in middle latitudes to values of around  $20 \text{ g kg}^{-1}$  in the tropics.

It should be noted that if neither condensation nor evaporation takes place, the mixing ratio of an air parcel is constant (i.e., it is a *conserved quantity*).

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The mass of water vapour  $m_v$  in a unit mass of air (dry air plus water vapour) is called the *specific humidity*  $q$ .

That is,

$$q = \frac{m_v}{m_v + m_d}$$

Since the magnitude of  $w$  is only a few percent ( $w \ll 1$ , or  $m_v \ll m_d$ ), it follows that  $w$  and  $q$  are nearly equal:

$$q = \frac{m_v}{m_v + m_d} \approx \frac{m_v}{m_d} = w$$

**Exercise:** If air contains water vapour with a mixing ratio of  $5.5 \text{ g kg}^{-1}$  and the total pressure is  $1026.8 \text{ hPa}$ , calculate the vapour pressure  $e$ .

**Exercise:** Calculate the virtual temperature correction for moist air at  $30^\circ\text{C}$  that has a mixing ratio of  $20 \text{ g kg}^{-1}$ .

**Exercise:** If air contains water vapour with a mixing ratio of  $5.5 \text{ g kg}^{-1}$  and the total pressure is  $1026.8 \text{ hPa}$ , calculate the vapour pressure  $e$ .

**Solution:** Recall that we had

$$e \approx \frac{p}{\varepsilon} w$$

where  $\varepsilon = R_d/R_v = 0.622$ .

Now  $w = 5.5 \text{ g kg}^{-1} = 0.0055 \text{ g g}^{-1}$

And  $p = 1026.8 \text{ hPa} = 102680 \text{ Pa}$ .

So

$$e = \frac{102680}{0.622} \times 0.0055 = 908 \text{ Pa} \approx 9 \text{ hPa}$$

**Exercise:** Calculate the virtual temperature correction for moist air at  $30^\circ\text{C}$  that has a mixing ratio of  $20\text{ g kg}^{-1}$ .

**Solution:** First, convert the temperature and mixing ratio:

$$T = 30^\circ\text{C} = 303\text{ K}$$

$$w = 20\text{ g kg}^{-1} = 0.02\text{ g g}^{-1}$$

By a result already obtained,

$$T_v \approx T[1 + 0.608w]$$

where  $0.608 = (1 - \varepsilon)/\varepsilon$ .

Thus

$$T_v - T \approx 0.608 w T = 0.608 \times 0.02 \times 303 = 3.68\text{ K}$$

Therefore, the virtual temperature elevation is  $3.68^\circ\text{C}$ .

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## Saturation Vapour Pressures

Consider a small closed box containing a shallow layer of water at temperature  $T$  (draw a picture).

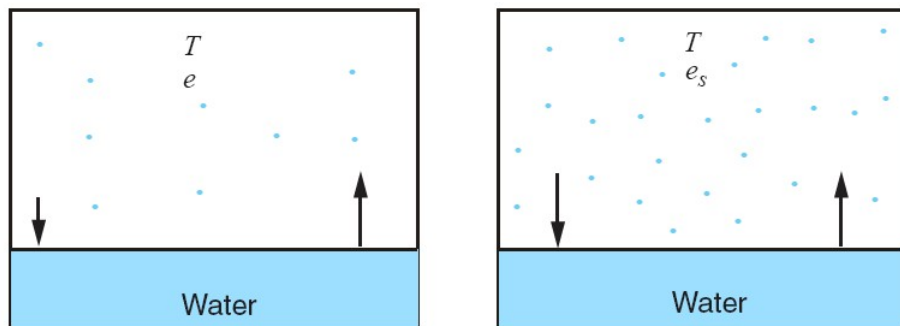
Initially assume there is dry air above the water. Water will begin to evaporate and, as it does, the number of water molecules in the box, and therefore the water vapour pressure, will increase.

As the water vapour pressure increases, so will the rate at which the water molecules condense from the vapour phase back to the liquid phase.

If the rate of condensation is less than the rate of evaporation, the box is said to be *unsaturated*.

When the water vapour pressure in the box increases to the point that the rate of condensation is equal to the rate of evaporation, the air is said to be *saturated*.

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(a) Unsaturated

(b) Saturated

Figure 3.8. A box (a) unsaturated and (b) saturated with respect to a plane surface of pure water at temperature  $T$ . The vapour pressure over a plane surface of pure water at temperature  $T$  is  $e_s$ .

More precisely, the air is said to be *saturated with respect to a plane surface of pure water at temperature  $T$* .

The pressure  $e_s$  that is then exerted by the water vapour is called the *saturation vapour pressure* over a plane surface of pure water at temperature  $T$ .

Similarly, if the water were replaced by a plane surface of *pure ice* at temperature  $T$ , and the rate of condensation of water vapour were equal to the rate of evaporation of the ice, the pressure  $e_{si}$  exerted by the water vapour would be the *saturation vapour pressure over a plane surface of pure ice* at temperature  $T$ .

Since, at any given temperature, the rate of evaporation from ice is less than from water,  $e_{si}(T) < e_s(T)$ .

The rate at which water molecules evaporate from either water or ice *increases with increasing temperature*.

Consequently, both  $e_s$  and  $e_{si}$  increase with increasing temperature, and their *magnitudes depend only on temperature*.

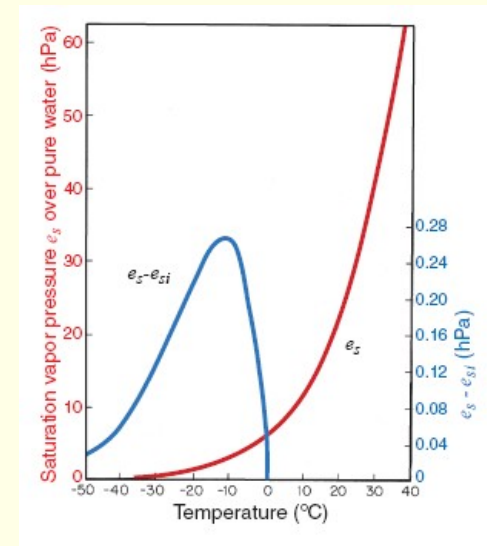
$$e_s = e_s(T), \quad e_{si} = e_{si}(T)$$

The variations with temperature of  $e_s$  and  $e_s - e_{si}$  are shown in the following figure [not differing scales].

It can be seen that the magnitude of  $e_s - e_{si}$  reaches a peak value at about  $-12^\circ\text{C}$ .

It follows that if an ice particle is in water-saturated air it will grow due to the deposition of water vapour upon it.

We will see later that this phenomenon plays a role in the growth of precipitable particles in some clouds.



Variations with temperature of the saturation vapour pressure  $e_s$  over a plane surface of pure water (red line). Difference  $e_s - e_{si}$  between saturation vapour pressures over water and ice (blue line).

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## Saturation Mixing Ratio

**Definition:** The *saturation mixing ratio*  $w_s$  is the ratio of the mass  $m_s$  of water vapour in a given volume of air that is *saturated* to the mass  $m_d$  of the dry air:

$$w_s = \frac{m_s}{m_d}$$

Since water vapour and dry air both obey the ideal gas equation,

$$w_s = \frac{\rho_s}{\rho_d} = \frac{e_s/R_v T}{(p - e_s)/R_d T} = \frac{R_d}{R_v} \frac{e_s}{p - e_s}$$

where  $\rho_s$  is the partial density of water vapour required to saturate air with respect to water at temperature  $T$ ,  $\rho_d$  is the partial density of the dry air, and  $p$  is the total pressure.

Again,

$$w_s = \frac{R_d}{R_v} \frac{e_s}{p - e_s}$$

Recall that we defined the ratio of gas constants

$$\varepsilon = \frac{R_d}{R_v} = 0.622$$

so the saturation mixing ratio can be written

$$w_s = \varepsilon \times \frac{e_s}{p - e_s}$$

For the range of temperatures observed in the Earth's atmosphere, the saturation vapour pressure is much smaller than the total pressure,  $e_s \ll p$ ; therefore,

$$w_s \approx \varepsilon \times \frac{e_s}{p}$$

Hence, at a given temperature, the saturation mixing ratio is *inversely proportional to the total pressure*.

Repeat:

$$w_s \approx \varepsilon \times \frac{e_s}{p} = 0.622 \times \frac{e_s}{p}$$

Since  $e_s$  depends only on temperature, it follows that  $w_s$  is a function of temperature and pressure.

Lines of constant saturation mixing ratio are printed as *dashed lines on the tephigram* and are labeled with the value of  $w_s$  in grams of water vapour per kilogram of dry air.

It is apparent from the slope of these lines that at constant pressure  $w_s$  increases with increasing temperature, and at constant temperature  $w_s$  increases with decreasing pressure.

**Exercise:** Check the above statement (1) by examination of the tephigram and (2) by analytical means (requiring the Clausius-Clapeyron Equation).

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It follows that the humidity at temperature  $T$  and pressure  $p$  is given by

$$RH = 100 \times \left[ \frac{w_s \text{ at temperature } T_d \text{ and pressure } p}{w_s \text{ at temperature } T \text{ and pressure } p} \right]$$

The **frost point** is defined as the temperature to which air must be cooled at constant pressure to saturate it with respect to a plane surface of pure ice.

Saturation mixing ratios and relative humidities with respect to ice may be defined in analogous ways to their definitions with respect to liquid water.

**Exercise:** Air at 1000 hPa and 18°C has a mixing ratio of 6 g kg<sup>-1</sup>. What are the relative humidity and dew point of the air?

**Solution:** 46%, 6.5°C. This exercise may be solved using the tephigram chart.

# Relative Humidity and Dew Point

The **relative humidity** (RH) with respect to water is the ratio — expressed as a percentage — of the actual mixing ratio  $w$  of the air to the saturation mixing ratio  $w_s$  with respect to a plane surface of pure water at the same temperature and pressure.

That is,

$$RH = 100 \times \frac{w}{w_s} \approx 100 \times \frac{e}{e_s}$$

The **dew point**  $T_d$  is the temperature to which air must be cooled at constant pressure for it to become saturated with respect to a plane surface of pure water.

In other words, the dew point is the temperature at which the saturation mixing ratio  $w_s$  with respect to liquid water becomes equal to the actual mixing ratio  $w$ .

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# Thermal Comfort

At the Earth's surface, the pressure varies only slightly from place to place and from time to time. Therefore, the dew point is a good indicator of the moisture content of the air.

In warm, humid weather the **dew point** is also a convenient indicator of the level of **human discomfort**.

For example, most people begin to feel uncomfortable when the dew point rises above 20°C, and air with a dew point above about 22°C is generally regarded as extremely humid or “sticky”.

Fortunately, dew points much above this temperature are rarely observed even in the tropics.

In contrast to the dew point, relative humidity depends as much upon the temperature of the air as upon its moisture content.



On a sunny day the relative humidity may drop by as much as 50% from morning to afternoon, just because of a rise in air temperature.

Relative humidity is not a good indicator of the level of human discomfort.

For example, a relative humidity of 70% may feel quite comfortable at a temperature of 20°C, but it would cause considerable discomfort to most people at a temperature of 30°C.

The highest dew points occur over warm bodies of water or vegetated surfaces from which water is evaporating.

In the absence of vertical mixing, the air just above these surfaces would become saturated with water vapour, at which point the dew point would be the same as the temperature of the underlying surface.

Complete saturation is rarely achieved over hot surfaces, but dew points in excess of 25°C are sometimes observed over the warmest regions of the oceans.

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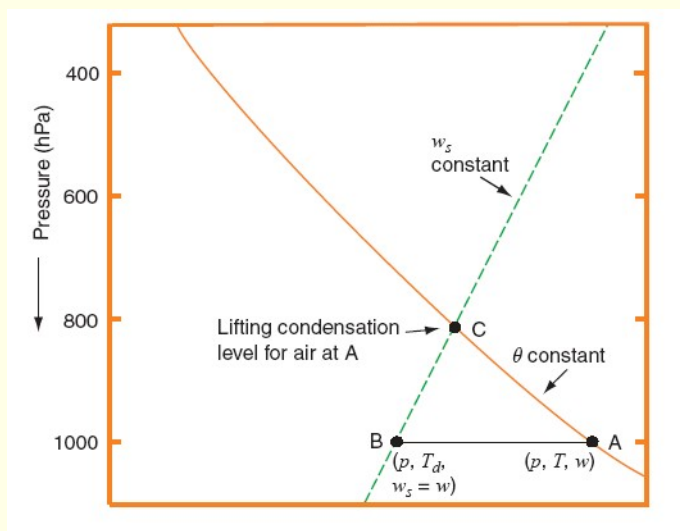
# Lifting Condensation Level

The *lifting condensation level* (LCL) is the level to which an unsaturated parcel of air can be lifted adiabatically before it becomes saturated.

During lifting the mixing ratio  $w$  and potential temperature  $\theta$  of the air parcel remain constant, but the saturation mixing ratio  $w_s$  decreases until it becomes equal to  $w$  at the LCL.

Therefore, the LCL is located at the intersection of the potential temperature line passing through the temperature  $T$  and pressure  $p$  of the parcel of air, and the  $w_s$  line that passes through the pressure  $p$  and dew point  $T_d$  of the air parcel (see figure).

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The lifting condensation level of a parcel of air at A, with pressure  $p$ , temperature  $T$  and dew point  $T_d$ , is at point C.

Since the *dew point* and *LCL* are related in the manner indicated in the figure, *knowledge of either one is sufficient to determine the other*.

Similarly, a knowledge of pressure, temperature and *any one moisture parameter* is sufficient to determine all the other moisture parameters we have defined.



# Wet-bulb Temperature

The *wet-bulb temperature* is measured with a thermometer, the glass bulb of which is covered with a moist cloth over which ambient air is drawn.

The heat required to evaporate water from the moist cloth to saturate the ambient air is supplied by the air as it comes into contact with the cloth.

When the difference between the temperatures of the bulb and the ambient air is steady and sufficient to supply the heat needed to evaporate the water, the thermometer will read a steady temperature, which is called the *wet-bulb temperature*.

If a raindrop falls through a layer of air that has a constant wet-bulb temperature, the raindrop will eventually reach a temperature equal to the wet-bulb temperature of the air.

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The definition of the wet-bulb temperature is rather similar to that of the dew point, but there is a distinct difference.

If the unsaturated air approaching the wet bulb has a mixing ratio  $w$ , the dew point  $T_d$  is the temperature to which the air must be cooled at constant pressure to become saturated.

The air that leaves the wet bulb has a mixing ratio  $w'$  that saturates it at temperature  $T_w$ .

If the air approaching the wet bulb is unsaturated,  $w'$  is greater than  $w$ ; therefore,  $T_d \leq T_w \leq T$ .

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# Latent Heat

Under certain conditions heat supplied to a system may produce a *change in phase*, rather than a change in temperature.

In this case, the increase in internal energy is associated entirely with a change in molecular configurations in the presence of intermolecular forces, rather than an increase in the kinetic energy of the molecules.

For example, if heat is supplied to ice at 1000 hPa and  $0^\circ\text{C}$ , the temperature remains constant until all of the ice has melted.

**Definition:** The *latent heat of melting* ( $L_m$ ) is defined as the heat that has to be given to a unit mass of a material to convert it from the solid to the liquid phase without a change in temperature.

The temperature at which this phase change occurs is called the *melting point*.

At 1000 hPa and  $0^\circ\text{C}$ , the latent heat of melting of the water substance is  $3.34 \times 10^5 \text{ J kg}^{-1}$ . Note that:

$$\left[ \begin{array}{c} \text{latent heat} \\ \text{of melting} \end{array} \right] = \left[ \begin{array}{c} \text{latent heat} \\ \text{of fusion} \end{array} \right] = \left[ \begin{array}{c} \text{latent heat} \\ \text{of freezing} \end{array} \right].$$

**Definition:** The latent heat of vapourization or evaporation ( $L_v$ ) is the heat that has to be given to a unit mass of material to convert it from the liquid to the vapour phase without a change in temperature.

The temperature at which this phase change occurs is called the *boiling point*.

For water at 1000 hPa and  $100^\circ\text{C}$  the latent heat of vapourization is  $2.25 \times 10^6 \text{ J kg}^{-1}$ .

$$\left[ \begin{array}{c} \text{latent heat} \\ \text{of vaporization} \end{array} \right] = \left[ \begin{array}{c} \text{latent heat} \\ \text{of condensation} \end{array} \right] = \left[ \begin{array}{c} \text{latent heat} \\ \text{of boiling} \end{array} \right].$$

# Saturated Adiabatic Processes

When an air parcel rises in the atmosphere its temperature decreases with altitude at the dry adiabatic lapse rate until it becomes saturated with water vapour.

Further lifting results in the condensation of liquid water (or the deposition of ice), which releases *latent heat*. Consequently, the rate of decrease in the temperature of the rising parcel is reduced.

If all of the condensation products remain in the rising parcel, the process may still be considered to be *adiabatic* (and *reversible*), even though latent heat is released in the system.

The air parcel is then said to undergo a *saturated adiabatic process*.

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If, on the other hand, all the condensation products immediately fall out of the air parcel, the process is *irreversible*, and not strictly adiabatic, since the condensation products carry some heat.

The air parcel is then said to undergo a *pseudoadiabatic process*.

However, the amount of heat carried by condensation products is small compared to that carried by the air itself.

Therefore, the saturated-adiabatic lapse rate is essentially the same as the pseudoadiabatic lapse rate.

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# Saturated Adiabatic Lapse Rate

We will derive an expression for the rate of change in temperature with height of a parcel of air undergoing a saturated adiabatic process.

The hydrostatic and thermodynamic equations allow us to write

$$dq = c_p dT + g dz$$

If the saturation mixing ratio of the air with respect to water is  $w_s$ , the quantity of heat  $dq$  released into a unit mass of dry air due to condensation of liquid water is  $-L_v dw_s$ , where  $L_v$  is the latent heat of condensation.

Therefore,

$$-L_v dw_s = c_p dT + g dz$$

Again,

$$-L_v dw_s = c_p dT + g dz$$

Dividing both sides by  $c_p dz$  and rearranging terms, we obtain

$$\frac{dT}{dz} = -\frac{L_v}{c_p} \frac{dw_s}{dz} - \frac{g}{c_p}$$

The chain rule gives

$$dw_s = \left( \frac{\partial w_s}{\partial p} \right)_T dp + \left( \frac{\partial w_s}{\partial T} \right)_p dT$$

We will assume that the first right-hand term is negligible in comparison with the second: the dependence of  $w_s$  on pressure is much weaker than its dependence on temperature. [Note that lines of constant saturated mixing ratio  $w_s$  and isotherms are fairly close to parallel on the tephigram.]

Then

$$\frac{dT}{dz} = -\frac{L_v}{c_p} \left( \frac{\partial w_s}{\partial T} \right)_p \frac{dT}{dz} - \frac{g}{c_p}$$

Rearranging the last expression yields

$$\frac{dT}{dz} = \frac{-g/c_p}{1 + \frac{L_v}{c_p} \left( \frac{\partial w_s}{\partial T} \right)_p}$$

We write this as

$$\Gamma_s \equiv -\frac{dT}{dz} = \frac{\Gamma_d}{1 + \frac{L_v}{c_p} \left( \frac{\partial w_s}{\partial T} \right)_p}$$

where  $\Gamma_s$  is called the saturated adiabatic lapse rate, which is the rate of decrease in temperature with height of an air parcel undergoing a saturated adiabatic process.

The magnitude of  $\Gamma_s$  is not constant but depends on the pressure and temperature. Since  $(\partial w_s/\partial T)_p$  is always positive, it follows that

$$\Gamma_s < \Gamma_d$$

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Actual values of  $\Gamma_s$  range from about  $4 \text{ K km}^{-1}$  near the ground in warm, humid air masses to typical values of  $6\text{--}7 \text{ K km}^{-1}$  in the middle troposphere.

For typical temperatures near the tropopause,  $\Gamma_s$  is only slightly less than  $\Gamma_d$  because the moisture capacity is so small that the effect of condensation is negligible.

Lines that show the decrease in temperature with height of a parcel of air that is rising or sinking in the atmosphere under saturated adiabatic (or pseudoadiabatic) conditions are called *saturated adiabats* (or pseudoadiabats).

On the tephigram, these are the curved lines that diverge upward and tend to become parallel to the dry adiabats at lower pressure values.

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**Exercise:** A parcel of air with an initial temperature of  $15^\circ\text{C}$  and dew point  $2^\circ\text{C}$  is lifted adiabatically from the 1000 hPa level. Determine its LCL and temperature at that level. If the air parcel is lifted a further 200 hPa above its LCL, what is its final temperature and how much liquid water is condensed during this rise?

**Solution:** Solve using a tephigram chart.



William Thomson (Lord Kelvin) was the first (in 1862) to derive quantitative estimates of the dry and saturated adiabatic lapse rates based on theoretical arguments.

# Equivalent Potential Temperature

Combining the gas law ( $p\alpha = RT$ ) and the thermodynamic equation ( $dq = c_p dT - \alpha dp$ ) we have

$$\frac{dq}{T} = \left\{ c_p \frac{dT}{T} - R \frac{dp}{p} \right\}$$

The potential temperature  $\theta$  is given by

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

or, taking logarithms of both sides,

$$\log \theta = \log T - \frac{R}{c_p} \log p + \text{const}$$

Differentiating this equation gives

$$c_p \frac{d\theta}{\theta} = \left\{ c_p \frac{dT}{T} - R \frac{dp}{p} \right\}$$

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We will define the constant of integration by requiring that at low temperatures, as  $w_s \rightarrow 0$ ,  $\theta \rightarrow \theta_e$ .

Then

$$- \left( \frac{L_v w_s}{c_p T} \right) \approx \log \frac{\theta}{\theta_e}$$

or

$$\theta_e = \theta \exp \left( \frac{L_v w_s}{c_p T} \right)$$

The quantity  $\theta_e$  is the *equivalent potential temperature*.

It can be seen that  $\theta_e$  is the potential temperature  $\theta$  of a parcel of air when its saturation mixing ratio  $w_s$  is zero.

Since the expressions in braces in the above two equations are identical, the left hand sides must be equal:

$$\frac{dq}{T} = c_p \frac{d\theta}{\theta}$$

Substituting the heating rate  $dq = -L_v dw_s$ , we obtain

$$-\frac{L_v}{c_p T} dw_s = \frac{d\theta}{\theta}$$

*“It can be shown that”*

$$\frac{L_v}{c_p T} dw_s \approx d \left( \frac{L_v w_s}{c_p T} \right)$$

*(see Wallace & Hobbs, Exercise 3.52. Not for exams!)*

It follows from this that

$$-d \left( \frac{L_v w_s}{c_p T} \right) \approx \frac{d\theta}{\theta}$$

This last expression can be integrated to give

$$- \left( \frac{L_v w_s}{c_p T} \right) \approx \log \theta + \text{const}$$

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The equivalent potential temperature of an air parcel may be found as follows.

- The air is expanded pseudo-adiabatically until all the vapour has condensed, released its latent heat, and fallen out.
- The air is then compressed dry adiabatically to the standard pressure of 1000 hPa when it will attain the temperature  $\theta_e$ .

[Illustrate on tephigram]

(If the air is initially unsaturated,  $w_s$  and  $T$  are the saturation mixing ratio and temperature at the point where the air first becomes saturated after being lifted dry adiabatically.)

*The equivalent potential temperature is conserved during both dry and saturated adiabatic processes.*

# Wet-bulb Potential Temperature

If the line of constant equivalent potential temperature (that is, the pseudoadiabat) that passes through the wet-bulb temperature of a parcel of air is traced back on a tephigram to the point where it intersects the 1000 hPa isobar, the temperature at this intersection is called the *wet-bulb potential temperature*  $\theta_w$  of the air parcel.

Like the equivalent potential temperature, the wet-bulb potential temperature is *conserved during both dry and saturated adiabatic processes*. Both  $\theta_w$  and  $\theta_e$  are valuable as *tracers* of air masses.

When height, rather than pressure, is used as the independent variable, the conserved quantity during adiabatic or pseudoadiabatic ascent or descent with water undergoing transitions between liquid and vapour phases is the *moist static energy*.

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# Moist Static Energy

The *moist static energy* (MSE) is defined as

$$MSE = c_p T + \Phi + L_v q$$

where  $T$  is the temperature of the air parcel,  $\Phi$  is the geopotential and  $q$  the specific humidity (recall  $q \approx w$ ).

- The first term ( $c_p T$ ) is the enthalpy per unit mass of air
- The second term ( $\Phi$ ) is the potential energy
- The third term ( $L_v q$ ) the latent heat content.

The first two terms comprise the *dry static energy*.

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Recall the definition of moist static energy:

$$MSE = c_p T + \Phi + L_v q$$

When air is lifted dry adiabatically, enthalpy is converted into potential energy and the latent heat content remains unchanged.

In saturated adiabatic ascent, energy is exchanged among all three terms: potential energy increases, while enthalpy and latent heat content both decrease. However, the sum of the three terms remains constant.

# Normand's Rule

*Normand's Rule:* On a tephigram, the lifting condensation level (LCL) of an air parcel is located at the intersection of:

- The *potential temperature line* that passes through the point located by the temperature and pressure of the air parcel
- The *equivalent potential temperature line* (that is, the pseudo-adiabat) that passes through the point located by the wet-bulb temperature and pressure of the air parcel and
- The *saturation mixing ratio line* that passes through the point determined by the dew point and pressure of the air.

This rule is illustrated in the following figure.

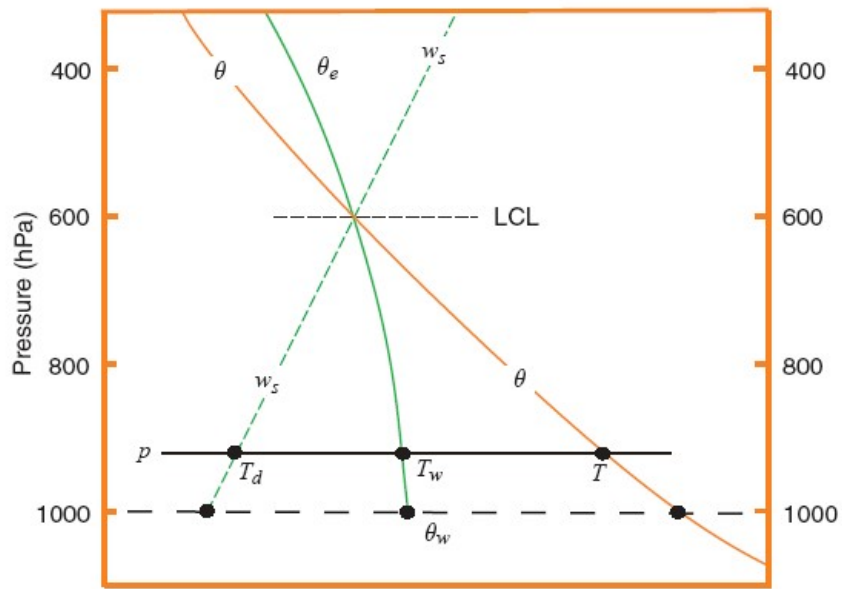


Figure 3.11. Illustration of Normand's rule.

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Consider an air parcel with temperature  $T$ , pressure  $p$ , dew point  $T_d$ , and wet-bulb temperature  $T_w$ .

It can be seen that, if  $T$ ,  $p$ , and  $T_d$  are known,  $T_w$  may be readily determined using Normand's rule.

Also, by extrapolating the  $\theta_e$  line that passes through  $T_w$  to the 1000 hPa level, the wet-bulb potential temperature  $\theta_w$ , may be found (see figure).

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## Ascent Followed by Descent

If a parcel of air is lifted above its LCL so that condensation occurs, and if the products of the condensation fall out as precipitation, the latent heat gained by the air during this process will be retained by the air if the parcel returns to its original level.

The effects of the saturated ascent coupled with the adiabatic descent are:

- Net increases in the temperature and potential temperature of the parcel
- A decrease in moisture content (as indicated by changes in the mixing ratio, relative humidity, dew point and wet-bulb temperature)
- No change in the equivalent potential temperature or wet-bulb potential temperature, which are conserved quantities for air parcels undergoing both dry and saturated processes.

## Exercise

The following exercise illustrates the effects of ascent and descent.

- (1) An air parcel at 950 hPa has a temperature of  $14^\circ\text{C}$  and a mixing ratio of  $8\text{ g kg}^{-1}$ . What is the wet-bulb potential temperature of the air?
- (2) The air parcel is lifted to the 700 hPa level by passing over a mountain, and 70% of the water vapour that is condensed out by the ascent is removed by precipitation. Determine the temperature, potential temperature, mixing ratio, and wet-bulb potential temperature of the air parcel after it has returned to the 950 hPa level on the other side of the mountain.



## Solution

On a tephigram, locate the initial state of the air at 950 hPa and 14°C. The saturation mixing ratio for an air parcel with temperature and pressure is found from the chart to be 10.6 g kg<sup>-1</sup>.

Therefore, since the air has a mixing ratio of only 8 g kg<sup>-1</sup>, it is unsaturated. The wet-bulb potential temperature can be determined using the following method: Trace the constant potential temperature line that passes through the initial state of the air parcel up to the point where it intersects the saturation mixing ratio line with value 8 g kg<sup>-1</sup>. This occurs at a pressure of about 890 hPa, which is the LCL of the air parcel. Now follow the equivalent potential temperature line that passes through this point back down to the 1000 hPa level and read off the temperature on the abscissa — it is 14°C. This is in the wet-bulb potential temperature  $\theta_w$  of the air.

When the air is lifted over the mountain, its temperature and pressure up to the LCL at 890 hPa are given by points on the potential temperature line that passes through the point 950 hPa and 14°C. With further ascent of the air parcel to the 700 hPa level, the air follows the saturated adiabat that passes through the LCL. This saturated adiabat intersects the 700 hPa level at a point where the saturation mixing

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ratio is 4.7 g kg<sup>-1</sup>. Therefore,  $8 - 4.7 = 3.3$  g kg<sup>-1</sup> of water vapour has to condense out between the LCL and the 700 hPa level, and 70% of this, or 2.3 g kg<sup>-1</sup>, is precipitated out. Therefore, at the 700 hPa level there is 1 g kg<sup>-1</sup> of liquid water in the air. The air parcel descends on the other side of the mountain at the saturated adiabatic lapse rate until it evaporates all of its liquid water, at which point the saturation mixing ratio will have risen to  $4.7 + 1 = 5.7$  g kg<sup>-1</sup>. The air parcel is now at a pressure of 760 hPa and a temperature of 1.8°C. Thereafter, the air parcel descends along a dry adiabat to the 950 hPa level, where its temperature is 20°C and the mixing ratio is still 5.7 g kg<sup>-1</sup>. If the method indicated in the Figure above is applied again, the wet-bulb potential temperature of the air parcel will be found to be unchanged at 14°C.

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## Mountain Winds

The heating of air during its passage over a mountain, 6°C in the above example, is responsible for the remarkable warmth of the *Föhn* and *Chinook* winds, which often blow downward along the lee side of mountain ranges.

*Aside:* The person who first explained the Föhn wind in this way appears to have been Julius F. von Hann in his classic book *Lehrbuch der Meteorologie* (Leipzig, 1901). J. von Hann (1839-1921) was an Austrian meteorologist, who introduced thermodynamic principles into meteorology. He developed theories for mountain and valley winds. He also published the first comprehensive treatise on climatology (1883).

*Comment:* Remark on mean winds in Rio and Buenos Aires.

End of §2.5



# VI. Static Stability

Consider a parcel of *unsaturated air*. Assume the actual lapse rate is less than the dry adiabatic lapse rate:

$$\Gamma < \Gamma_d$$

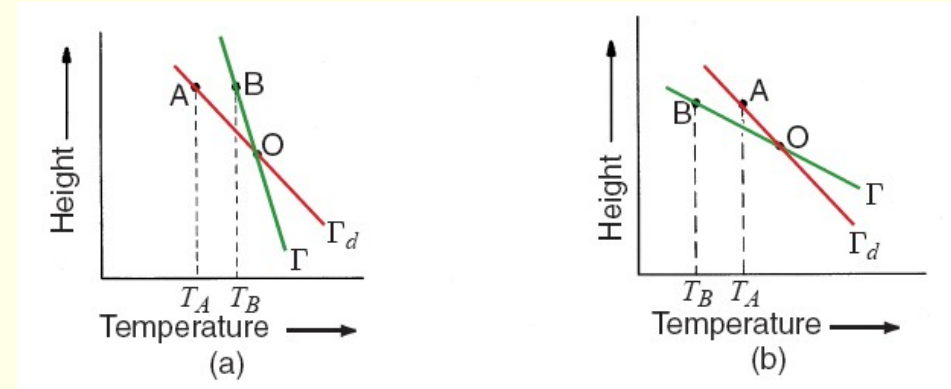
If a parcel of unsaturated air is raised vertically, its temperature will be lower than the ambient temperature at the higher level.

The colder parcel of air will be denser than the warmer ambient air and will tend to return to its original level.

If the parcel is displaced downwards, it becomes warmer than the ambient air and will tend to rise again.

In both cases, the parcel of air encounters a *restoring force* after being displaced, which *inhibits vertical mixing*. Thus, the condition  $\Gamma < \Gamma_d$  corresponds to stable stratification (or positive *static stability*) for unsaturated air parcels.

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Conditions for (a) positive static stability ( $\Gamma < \Gamma_d$ ) and (b) negative static instability ( $\Gamma > \Gamma_d$ ) for the displacement of unsaturated air.

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**Exercise:** An unsaturated parcel of air has density  $\rho'$  and temperature  $T'$ , and the density and temperature of the ambient air are  $\rho$  and  $T$ . Derive an expression for the downward acceleration of the air parcel in terms of  $T$  and  $T'$ .

**Sketch of Solution:** The downward buoyancy force on the parcel is

$$F = (\rho' - \rho)g$$

Therefore, the downward acceleration is

$$a = \frac{F}{\rho'} = \left( \frac{\rho' - \rho}{\rho'} \right) g$$

or, using the gas equation,

$$a = g \left( \frac{T - T'}{T} \right)$$

By the definitions of the lapse rates, we have

$$T' = T_0 - \Gamma_d z \quad T = T_0 - \Gamma z$$

Therefore, the downward acceleration is

$$a = g \left( \frac{\Gamma_d - \Gamma}{T} \right) Z$$

where  $Z$  is the upward displacement of the parcel.

Then the upward acceleration is  $\ddot{Z}$ . Thus, by Newton's second law of motion,

$$\ddot{Z} + \left\{ \frac{g}{T} (\Gamma_d - \Gamma) \right\} Z = 0$$

If  $(\Gamma_d - \Gamma) > 0$ , this equation has solutions corresponding to bounded oscillations with (squared) frequency  $\omega^2 = \frac{g}{T} (\Gamma_d - \Gamma)$ . **The oscillations are stable.**

If  $(\Gamma_d - \Gamma) < 0$ , the solutions are exponentially growing with time. This corresponds to *static instability*.

**Exercise:** Find the period of oscillation of a parcel of air displaced vertically, where the ambient temperature and lapse rate are

- $T = 250 \text{ K}$  and  $\Gamma = 6 \text{ K km}^{-1}$ , typical tropospheric values
- $T = 250 \text{ K}$  and  $\Gamma = -2 \text{ K km}^{-1}$ , typical of strong inversion

**Solution:** The equation of motion for the parcel is

$$\ddot{z} + \omega^2 z = 0$$

where  $\omega^2 = (g/T)(\Gamma_d - \Gamma)$ .

Assuming  $\Gamma_d = 10 \text{ K km}^{-1} = 0.01 \text{ K m}^{-1}$  and  $g = 10 \text{ m s}^{-2}$ ,

$$\omega^2 = \frac{g}{T}(\Gamma_d - \Gamma) = \left(\frac{10}{250}\right) \left(\frac{10 - 6}{10^3}\right) = 0.00016$$

Thus the period of the motion is

$$\tau = \frac{2\pi}{\omega} \approx 500 \text{ sec}$$

For  $\Gamma = -2 \text{ K km}^{-1}$ ,  $\omega^2$  is tripled. Thus,  $\tau \approx 290 \text{ s}$ .

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## Inversions

Layers of air with negative lapse rates (i.e., temperatures increasing with height) are called *inversions*. It is clear from the above discussion that these layers are marked by very strong static stability.

A low-level inversion can act as a *lid* that traps pollution-laden air beneath it (See following figure).

The layered structure of the stratosphere derives from the fact that it represents an inversion in the vertical temperature profile.

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## Static Instability

If  $\Gamma > \Gamma_d$ , a parcel of unsaturated air displaced upward will have a temperature *greater than* that of its environment. Therefore, it will be less dense than the ambient air and will continue to rise.

Similarly, if the parcel is displaced downward it will be cooler than the ambient air, and it will continue to sink if left to itself.

Such unstable situations generally do not persist in the free atmosphere, since **the instability is eliminated** by strong vertical mixing as fast as it forms.

The only exception is in the layer just above the ground under conditions of very strong heating from below.



Looking down onto widespread haze over southern Africa. The haze is confined below a temperature inversion. Above the inversion, the air is remarkably clean and the visibility is excellent.

**Exercise:** Show that if the potential temperature  $\theta$  increases with increasing altitude the atmosphere is stable with respect to the displacement of unsaturated air parcels.

**Solution:** By the gas equation

$$p = R\rho T$$

The hydrostatic equation is

$$\frac{dp}{dz} = -g\rho \quad \frac{dp}{\rho} = -g dz$$

Poisson's equation is

$$\theta = T \left( \frac{p}{p_0} \right)^{-R/c_p} \quad \text{or} \quad c_p \log \theta = c_p \log T - R \log p + \text{const}$$

Differentiating this yields

$$\begin{aligned} c_p T \frac{d\theta}{\theta} &= c_p dT - RT \frac{dp}{p} \\ &= c_p dT - \frac{dp}{\rho} \\ &= c_p dT + g dz. \end{aligned}$$

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Again,

$$c_p T \frac{d\theta}{\theta} = c_p dT + g dz.$$

Consequently,

$$\frac{1}{\theta} \frac{d\theta}{dz} = \frac{1}{T} \left( \frac{dT}{dz} + \frac{g}{c_p} \right)$$

or

$$\frac{1}{\theta} \frac{d\theta}{dz} = \frac{1}{T} (\Gamma_d - \Gamma)$$

Thus, *if the potential temperature  $\theta$  increases with altitude* ( $d\theta/dz > 0$ ) we have  $\Gamma < \Gamma_d$  and the atmosphere is *stable* with respect to the displacement of unsaturated air parcels.

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## Conditional & Convective Instability

If a parcel of air is **saturated**, its temperature will decrease with height at the saturated adiabatic lapse rate  $\Gamma_s$ .

It follows that if  $\Gamma$  is the actual lapse rate, saturated air parcels will be stable, neutral, or unstable with respect to vertical displacements, according to the following scheme:

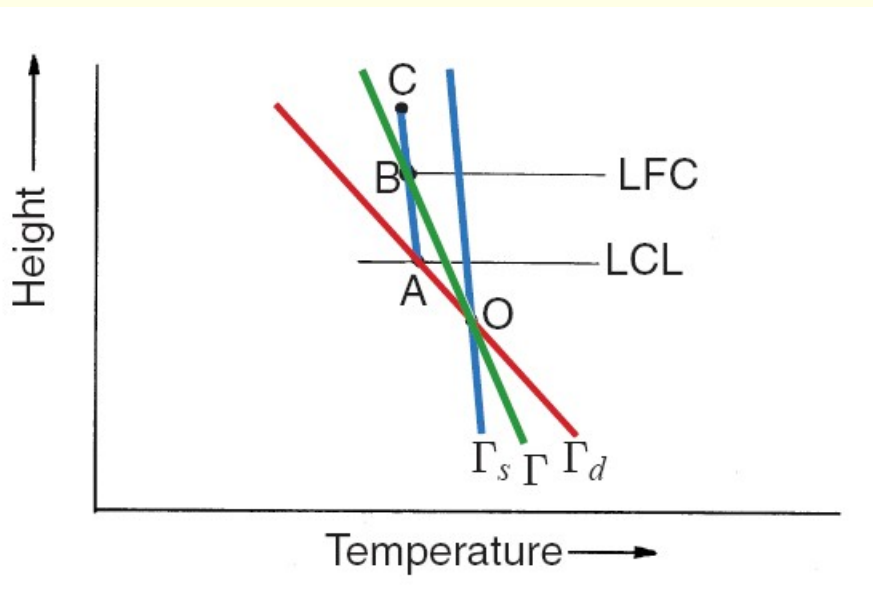
$\Gamma < \Gamma_s$	stable
$\Gamma = \Gamma_s$	neutral
$\Gamma > \Gamma_s$	unstable

When an environmental temperature sounding is plotted on a **tephigram**, the distinctions between  $\Gamma$ ,  $\Gamma_d$  and  $\Gamma_s$  are clearly discernible.

If the actual lapse rate  $\Gamma$  of the atmosphere lies *between* the saturated adiabatic lapse rate and the dry adiabatic lapse rate,

$$\Gamma_s < \Gamma < \Gamma_d$$

a parcel of air that is lifted *sufficiently far* above its equilibrium level will become warmer than the ambient air. This situation is illustrated in the following figure.



Conditions for conditional instability ( $\Gamma_s < \Gamma < \Gamma_d$ ). LCL is the lifting condensation level and LFC is the *level of free convection*.

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If the vertical displacement of the parcel is **small**, the parcel will be heavier than its environment and will return to its original height.

However, if the vertical displacement is **large**, the parcel develops a positive buoyancy that carries it upward even in the absence of further forced lifting.

For this reason, the point where the buoyancy changes sign is referred to as the *level of free convection (LFC)*.

The level of free convection depends on the amount of moisture in the rising parcel of air as well as the magnitude of the lapse rate  $\Gamma$ .

It follows that, for a layer in which  $\Gamma_s < \Gamma < \Gamma_d$ , vigorous convective overturning will occur if vertical motions are large enough to lift air parcels beyond their level of free convection. Clearly, **mountainous terrain is important here**.

Such an atmosphere is said to be *conditionally unstable* with respect to convection.

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If vertical motions are weak, this type of stratification can be maintained indefinitely.

The stability of the atmosphere may be understood in broad terms by considering a mechanical analogy, as illustrated below.

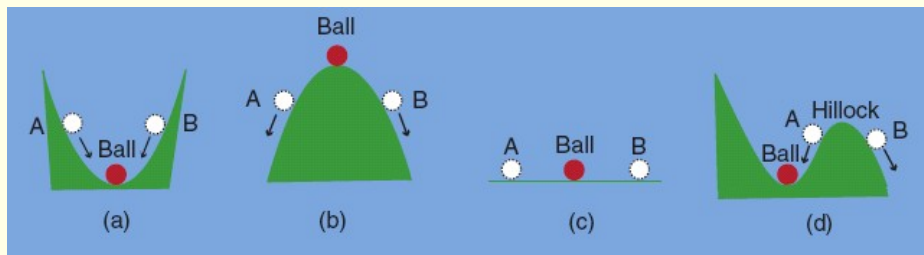
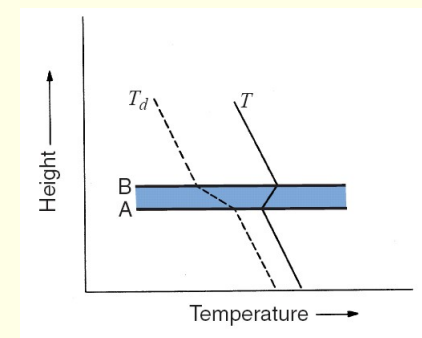


Figure 3.15. Analogs for (a) stable, (b) unstable, (c) neutral, and (d) conditional instability.

## Convective Instability

The potential for instability of air parcels is related also to the *vertical stratification of water vapour*.

In the profiles shown below, the dew point decreases rapidly with height within the inversion layer AB that marks the top of a moist layer.



Convective instability. The blue shaded region is a dry inversion layer.

Now, suppose that the moist layer is lifted. An air parcel at A will reach its LCL almost immediately, and beyond that point it will cool moist adiabatically.

But an air parcel starting at point B will cool dry adiabatically through a deep layer before it reaches its LCL.

Therefore, *as the inversion layer is lifted, the top part of it cools much more rapidly than the bottom part, and the lapse rate quickly becomes destabilized.*

Sufficient lifting may cause the layer to become conditionally unstable, even if the entire sounding is absolutely stable to begin with.

The criterion for this so-called *convective (or potential) instability* is that  $d\theta_e/dz$  be negative within the layer.

Throughout *large areas of the tropics*  $\theta_e$  decreases markedly with height from the mixed layer to the much drier air above. Yet deep convection breaks out only within a few percent of the area where there is sufficient lifting.

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End of §2.6

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## Second Law of Thermodynamics

The First Law of Thermodynamics is a statement of the principle of conservation of energy. The *Second Law of Thermodynamics* is concerned with the maximum fraction of a quantity of heat that can be converted into work.

A discussion of the *Carnot cycle* can be found in *Wallace & Hobbs*. It is also described in most standard texts on thermodynamics.

We will provide only an outline here.

## The Carnot Cycle

A cyclic process is a series of operations by which the state of a substance changes but finally returns to its original state.

If the volume of the working substance changes, *the substance may do external work*, or work may be done on the working substance, during a cyclic process.

Since the initial and final states of the working substance are the same in a cyclic process, and internal energy is a function of state, *the internal energy of the working substance is unchanged in a cyclic process.*

Therefore, the net heat absorbed by the working substance is equal to the external work that it does in the cycle.



A working substance is said to undergo a *reversible transformation* if each state of the system is in equilibrium, so that a reversal in the direction of an infinitesimal change returns the working substance and the environment to their original states.

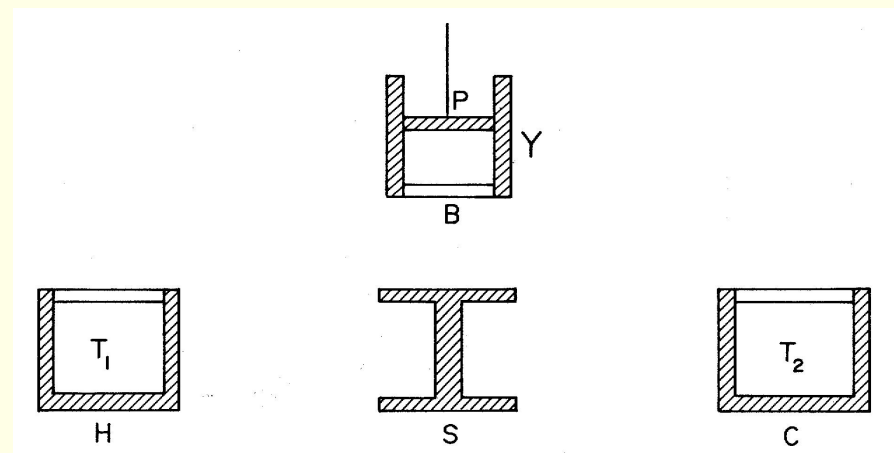
A heat engine is a device that does work through the agency of heat.

If during one cycle of an engine a quantity of heat  $Q_1$  is absorbed and heat  $Q_2$  is rejected, the amount of work done by the engine is  $Q_1 - Q_2$  and its *efficiency*  $\eta$  is defined as

$$\eta = \frac{\text{Work done by the engine}}{\text{Heat absorbed by the working substance}} = \frac{Q_1 - Q_2}{Q_1}$$

Carnot was concerned with the efficiency with which heat engines can do useful mechanical work. He envisaged an ideal heat engine consisting of a working substance contained in a cylinder (figure follows).

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The components of Carnot's ideal heat engine.

By means of this contraption, we can induce the working substance to undergo transformations which are either *adiabatic* or *isothermal*.

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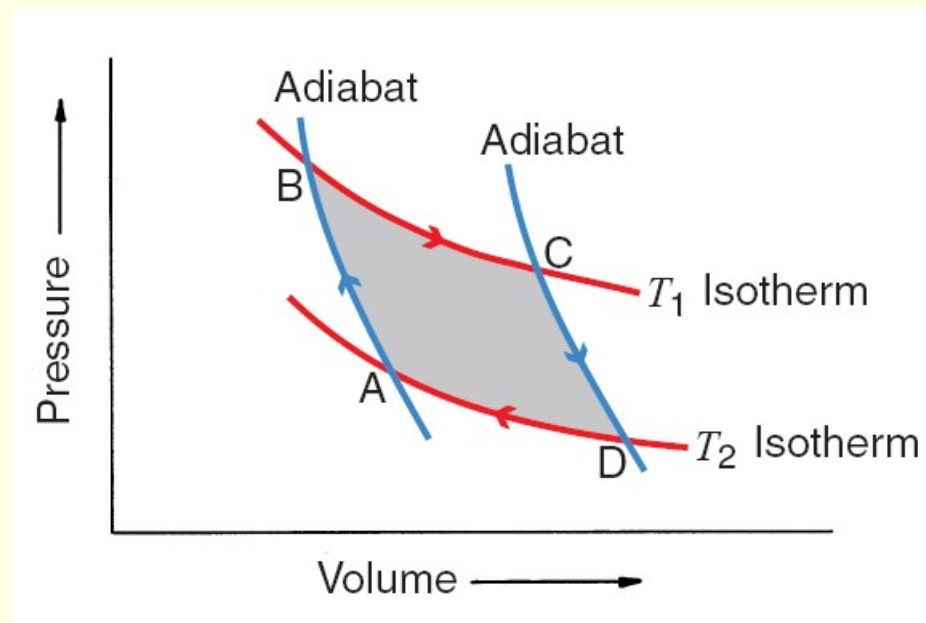
An infinite warm reservoir of heat (H) at constant temperature  $T_1$ , and an infinite cold reservoir for heat (C) at constant temperature  $T_2$  (where  $T_1 > T_2$ ) are available.

Also, an insulating stand S to facilitate adiabatic changes.

Heat can be supplied from the warm reservoir to the working substance contained in the cylinder, and heat can be extracted from the working substance by the cold reservoir.

As the working substance expands, the piston moves outward and external work is done by the working substance.

As the working substance contracts, the piston moves inward and work is done *on* the working substance.



Representations of a Carnot cycle on a  $p - V$  diagram. The red lines are isotherms and the blue lines adiabats.



**Carnot's cycle** consists of taking the working substance in the cylinder through the following four operations that together constitute a reversible, cyclic transformation

1. The substance starts at point A with temperature  $T_2$ . The working substance is compressed adiabatically to state B. Its temperature rises to  $T_1$ .
2. The cylinder is now placed on the warm reservoir H, from which it extracts a quantity of heat  $Q_1$ . The working substance expands isothermally at temperature  $T_1$  to point C. During this process the working substance does work.
3. The working substance undergoes an adiabatic expansion to point D and its temperature falls to  $T_2$ . Again the working substance does work against the force applied to the piston.
4. Finally, the working substance is compressed isothermally back to its original state A. In this transformation the working substance gives up a quantity of heat  $Q_2$  to the cold reservoir.

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The net amount of work done by the working substance during the Carnot cycle is equal to the area contained within the figure ABCD. This can be written

$$W = \oint_C p dV$$

Since the working substance is returned to its original state, the net work done is equal to  $Q_1 - Q_2$  and the efficiency of the engine is given by

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

In this cyclic operation the engine has done work by transferring a certain quantity of heat from a warmer ( $H$ ) to a cooler ( $C$ ) body.

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One way of stating the Second Law of Thermodynamics is: "only by transferring heat from a warmer to a colder body can heat can be converted into work in a cyclic process."

It can be shown that no engine can be more efficient than a reversible engine working between the same limits of temperature, and that all reversible engines working between the same temperature limits have the same efficiency.

The validity of these two statements, which are known as Carnot's Theorems, depends on the truth of the Second Law of Thermodynamics.

**Exercise:** Show that in a Carnot cycle the ratio of the heat  $Q_1$  absorbed from the warm reservoir at temperature  $T_1$  to the heat  $Q_2$  rejected to the cold reservoir at temperature  $T_2$  is equal to  $T_1/T_2$ .

**Solution:** See *Wallace & Hobbs*.

## Heat Engines

A heat engine is a device that does work through the agency of heat.

Examples of real heat engines are the steam engine and a nuclear power plant.

The warm and cold reservoirs for a steam engine are the boiler and the condenser. The warm and cold reservoirs for a nuclear power plant are the nuclear reactor and the cooling tower.

In both cases, water (in liquid and vapour forms) is the working substance that expands when it absorbs heat and thereby does work by pushing a piston or turning a turbine blade.

# The Atmospheric Heat Engines

Why do we study heat engines and Carnot Cycles?

The atmosphere itself can be regarded as the working substance of an enormous heat engine.

- Heat is added in the tropics, where the temperature is high.
- Heat is transported by atmospheric motions from the tropics to the temperate latitudes
- Heat is emitted in temperate latitudes, where the temperature is relatively low.

We can apply the principles of thermodynamic engines to the atmosphere and discuss concepts such as its efficiency.

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# Alternative Statements of 2nd Law

One way of stating the Second Law of Thermodynamics is as follows:

Heat can be converted into work in a cyclic process only by transferring heat from a warmer to a colder body.

Another statement of the Second Law is:

Heat cannot of itself pass from a colder to a warmer body in a cyclic process.

That is, the “uphill” heat-flow cannot happen without the performance of work by some external agency.

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# Entropy

We define the increase  $dS$  in the *entropy* of a system as

$$dS = \frac{dQ}{T}$$

where  $dQ$  is the quantity of heat that is added reversibly to the system at temperature  $T$ .

For a unit mass of the substance,

$$ds = \frac{dq}{T}$$

( $s$  is the *specific entropy*).

Entropy is a function of the state of a system and not the path by which the system is brought to that state.

The First Law of Thermodynamics for a reversible transformation may be written as

$$dq = c_p dT - \alpha dp,$$

Therefore,

$$ds = \frac{dq}{T} = c_p \frac{dT}{T} - \frac{\alpha}{T} dp = \left( c_p \frac{dT}{T} - R \frac{dp}{p} \right)$$

In this form the First Law contains functions of state only.

From the definition of potential temperature  $\theta$  (Poisson's equation) we get

$$c_p \frac{d\theta}{\theta} = \left( c_p \frac{dT}{T} - R \frac{dp}{p} \right)$$

Since the right hand sides of the above two equations are equal, their left hand sides are too:

$$ds = c_p \frac{d\theta}{\theta}.$$

Integrating, we have

$$s = c_p \log \theta + s_0$$

where  $s_0$  is a reference value for the entropy.

Transformations in which entropy (and therefore potential temperature) are constant are called *isentropic*.

Therefore, adiabats are generally referred to as *isentropes*.

The potential temperature can be used as a surrogate for entropy, and this is generally done in atmospheric science.

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# The Clausius-Clapeyron Equation

[The subject matter of this section (CC Equation) will not form part of the examinations.]

We can use the Carnot cycle to derive an important relationship, known as the Clausius-Clapeyron Equation.

The Clausius-Clapeyron equation describes how the saturated vapour pressure above a liquid changes with temperature. [Details will not be given here. See *Wallace & Hobbs*.]

In approximate form, the Clausius-Clapeyron Equation may be written

$$\frac{de_s}{dT} \approx \frac{L_v}{T\alpha}$$

where  $\alpha$  is the specific volume of water vapour that is in equilibrium with liquid water at temperature  $T$ .

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The vapour exerts a pressure  $e_s$  given by the ideal gas equation:

$$e_s\alpha = R_v T$$

Eliminating  $\alpha$ , we get

$$\frac{1}{e_s} \frac{de_s}{dT} \approx \frac{L_v}{R_v T^2}$$

If we write this as

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

we can immediately integrate it to obtain

$$\log e_s = \frac{L_v}{R_v} \left( -\frac{1}{T} \right) + \text{const}$$

Taking the exponential of both sides,

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

Since  $e_s = 6.11 \text{ hPa}$  at  $273 \text{ K}$   $R_v = 461 \text{ J K}^{-1} \text{ kg}^{-1}$  and  $L_v = 2.500 \times 10^6 \text{ J kg}^{-1}$ , the saturated vapour pressure  $e_s$  (in hPa) of water at temperature  $T$  (Kelvins) is given by

$$e_s = 6.11 \exp \left[ 5.42 \times 10^3 \left( \frac{1}{273} - \frac{1}{T} \right) \right]$$

**Exercise:** Using MATLAB, draw a graph of  $e_s$  as a function of  $T$  for the range  $-20^\circ\text{C} < T < +40^\circ\text{C}$ .

# Generalized Statement of 2nd Law

The Second Law of Thermodynamics states that

- for a *reversible transformation* there is no change in the entropy of the universe.

In other words, if a system receives heat reversibly, the increase in its entropy is exactly equal in magnitude to the decrease in the entropy of its surroundings.

- the entropy of the universe *increases* as a result of *irreversible transformations*.

The Second Law of Thermodynamics cannot be proved. It is believed to be valid because it leads to deductions that are in accord with observations and experience.

Evidence is overwhelming that the Second Law is true. Deny it at your peril!

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# Quotes Concerning the 2nd Law

Sir Arthur Eddington, one of the most prominent and important astrophysicists of the last century.



*If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations, then so much the worse for Maxwell's equations. And if your theory contradicts the facts, well, sometimes these experimentalists make mistakes. But if your theory is found to be against the Second Law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.*

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Charles Percy Snow (1905-1980) a scientist and novelist, most noted for his lectures and books regarding his concept of *The Two Cultures*.



*A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: it was also negative.*

*Nothing in life is certain except death, taxes and the second law of thermodynamics. All three are processes in which useful or accessible forms of some quantity, such as energy or money, are transformed into useless, inaccessible forms of the same quantity. That is not to say that these three processes don't have fringe benefits: taxes pay for roads and schools; the second law of thermodynamics drives cars, computers and metabolism; and death, at the very least, opens up tenured faculty positions.*

[Seth Lloyd, Professor, Department of Mechanical Engineering, MIT. Nature 430, 971 (26 August 2004)]

Entropy is a measure of the *disorder* (or randomness) of a system. The Second Law implies that **the disorder of the universe is inexorably increasing**.

The two laws of thermodynamics may be summarised as follows:

- (1) The energy of the universe is constant
- (2) The entropy of the universe tends to a maximum.

They are sometimes parodied as follows:

- (1) You can't win
- (2) You can't break even
- (3) You can't get out of the game.

End of §2.7