

# Thermodynamics Notes

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# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	What is thermodynamics? . . . . .	1
1.2	The atmosphere . . . . .	1
<b>2</b>	<b>The Equation of State</b>	<b>1</b>
2.1	State variables . . . . .	1
2.2	Charles' Law and absolute temperature . . . . .	2
2.3	Boyle's Law . . . . .	3
2.4	Equation of state of an ideal gas . . . . .	3
2.5	Mixtures of gases . . . . .	4
2.6	Ideal gas law: molecular viewpoint . . . . .	6
<b>3</b>	<b>Conservation of Energy</b>	<b>8</b>
3.1	Conservation of energy in mechanics . . . . .	8
3.2	Conservation of energy: A system of point masses . . . . .	8
3.3	Kinetic energy exchange in molecular collisions . . . . .	9
3.4	Working and Heating . . . . .	9
<b>4</b>	<b>The Principles of Thermodynamics</b>	<b>11</b>
4.1	Conservation of energy and the first law of thermodynamics . . . . .	11
4.1.1	Conservation of energy . . . . .	11
4.1.2	The first law of thermodynamics . . . . .	11
4.1.3	Work . . . . .	12
4.1.4	Energy transferred by heating . . . . .	13
4.2	Quantity of energy transferred by heating . . . . .	14
4.3	The first law of thermodynamics for an ideal gas . . . . .	15
4.4	Applications of the first law . . . . .	16
4.4.1	Isothermal process . . . . .	16
4.4.2	Isobaric process . . . . .	17
4.4.3	Isosteric process . . . . .	18
4.5	Adiabatic processes . . . . .	18
<b>5</b>	<b>The Thermodynamics of Water Vapor and Moist Air</b>	<b>21</b>
5.1	Thermal properties of water substance . . . . .	21
5.2	Equation of state of moist air . . . . .	21
5.3	Mixing ratio . . . . .	22
5.4	Moisture variables . . . . .	22
5.5	Changes of phase and latent heats . . . . .	24
5.6	Adiabatic processes of saturated air . . . . .	24
5.7	More moisture variables . . . . .	27

5.8	Skew $T$ -log $p$ diagram . . . . .	28
<b>6</b>	<b>Hydrostatic Equilibrium</b>	<b>30</b>
6.1	The hydrostatic equation . . . . .	30
6.2	Height computations for upper-air soundings . . . . .	30
6.3	The hydrostatics of special atmospheres . . . . .	31
6.3.1	The isothermal atmosphere . . . . .	32
6.3.2	The constant-lapse-rate atmosphere . . . . .	32
6.3.3	The U. S. Standard Atmosphere . . . . .	32
<b>7</b>	<b>Hydrostatic Stability and Convection</b>	<b>34</b>
7.1	The dry and moist adiabatic lapse rates . . . . .	34
7.1.1	The dry-adiabatic lapse rate . . . . .	34
7.1.2	The saturation-adiabatic lapse rate . . . . .	35
7.2	Stability criteria: The parcel method . . . . .	36
7.3	Convective Available Potential Energy (CAPE) . . . . .	38
	<b>Useful Constants</b>	<b>39</b>

# 1 Introduction

## 1.1 What is thermodynamics?

Thermodynamics is the study of the equilibrium states of a system subject to a specified process. A *system* is a specific sample of matter. The *equilibrium state* of a system can be completely specified by a small number of properties such as pressure, temperature, and volume. These properties are known as *state variables* or *thermodynamic variables*.

An example of the type of question that we can answer using the laws of thermodynamics is the following: What is the final temperature of 1 kg of air saturated with water vapor, initially at a pressure of 1000 mb and a temperature of 0° C, if it is allowed to expand, without the addition of or loss of energy from or to its surroundings, until its pressure is 500 mb?

It will be useful to set down at the outset the *laws of thermodynamics*, even though they can not be fully understood until they are actually applied.

**Equation of state of a perfect gas** An equation of state is a relationship among the state variables that defines the state of a system. The simple form that applies to an idealized or perfect gas is sufficiently accurate for real gases. The most common form expresses the relationship between the pressure, temperature, and volume of a sample of gas.

**First law of thermodynamics** This is the law of conservation of energy for a thermodynamic system.

**Second law of thermodynamics** This law specifies the direction in which heat (molecular kinetic energy) may flow during a thermodynamic process.

## 1.2 The atmosphere

The earth's atmosphere is a mixture of gases. The chief variable constituent is water vapor. It may occupy up to 4 per cent of the volume of a sample of air. The composition of pure *dry* air in the troposphere and lower stratosphere is given in Table 1.

# 2 The Equation of State

## 2.1 State variables

A small sample of matter is described thermodynamically by its volume  $V$ , mass  $M$ , pressure  $p$ , temperature  $T$ , and composition. For the cases we will consider, a sample's mass and composition will remain constant.

Table 1: Composition of pure dry air up to 25 km (Hess 1959). The units for molecular weight are  $\text{g mol}^{-1}$ .

<i>Constituent</i>	<i>Per cent by volume</i>	<i>Per cent by mass</i>	<i>Molecular weight</i>
Nitrogen	78.09	75.51	28.02
Oxygen	20.95	23.14	32.00
Argon	0.93	1.3	39.94
Carbon dioxide (var)	$\sim 0.03$	$\sim 0.05$	44.01
Neon	$180. \times 10^{-5}$	$120. \times 10^{-5}$	20.18
Helium	$52. \times 10^{-5}$	$8. \times 10^{-5}$	4.00
Krypton	$10. \times 10^{-5}$	$29. \times 10^{-5}$	83.7
Hydrogen	$5.0 \times 10^{-5}$	$0.35 \times 10^{-5}$	2.02
Xenon	$0.8 \times 10^{-5}$	$3.6 \times 10^{-5}$	131.3
Ozone (var)	$\sim 0.1 \times 10^{-5}$	$\sim 0.17 \times 10^{-5}$	48.00

It is more convenient to use the specific volume,  $\alpha \equiv V/M$ , or the density,  $\rho \equiv M/V = 1/\alpha$ , in place of the volume  $V$ . Then  $\alpha$ ,  $p$ , and  $T$  completely describe the state of the system.

In a gas, the *pressure* is the force per unit area produced by gas molecules hitting a plane surface. The pressure is independent of the orientation of the plane surface, and is considered to be uniform within a thermodynamic system. However, in atmospheric dynamics, small variations of pressure are very important.

Temperature is a concept with which we are familiar. To define a precise temperature scale, we must find certain fixed and reproducible temperatures. A mixture of ice and water in equilibrium at a pressure of 1 atmosphere (1013.25 mb) has a temperature of  $0^\circ\text{C}$ . Steam (water vapor) in equilibrium with boiling water at a pressure of 1 atmosphere has a temperature of  $100^\circ\text{C}$ . If these two temperatures are marked on a mercury thermometer, we can subdivide the interval between the two marks into 100 equal degrees.

## 2.2 Charles' Law and absolute temperature

By measuring the specific volume of a gas at any two temperatures, both at the same pressure, Charles found that the corresponding change in specific volume is directly proportional to the change in temperature. If one temperature is  $0^\circ\text{C}$  and the second temperature is the Celsius temperature  $t$ , then

$$t = k(\alpha_t - \alpha_0), \tag{1}$$

where  $k$  is a constant. We can determine  $k$  by measuring  $\alpha$  at  $100^\circ\text{C}$ . At that temperature,

$$100^\circ\text{C} = k(\alpha_{100} - \alpha_0),$$

so

$$k = \frac{100^\circ\text{C}}{\alpha_{100} - \alpha_0}.$$

The temperature  $t$  in (1) is essentially independent of the gas used. This equation forms the basis for *gas thermometers*. The international standard of thermometry is a gas thermometer using helium.

Rewrite (1) as

$$t + k\alpha_0 = k\alpha_t. \tag{2}$$

This suggests that we can define a new temperature scale so that the temperature  $T$  is directly proportional to the specific volume:

$$T = t + k\alpha_0 = t + T_0 = t + 273.16^\circ\text{C}.$$

This temperature scale is the *absolute temperature scale* or the *Kelvin temperature scale*. Absolute temperatures are measured in degrees Kelvin. Note that one Kelvin degree (K) is the same size as one Celsius degree ( $^\circ\text{C}$ ). When  $t = 0^\circ\text{C}$ ,  $T = T_0 = 273.16$  K.

Use the absolute temperature scale and  $k = T_0/\alpha_0$  in (2), and divide the result by  $\alpha_T$  to obtain

$$\frac{T}{\alpha_T} = \frac{T_0}{\alpha_0},$$

or

$$\frac{\alpha_T}{T} = \frac{\alpha_0}{T_0}.$$

This form of *Charles' Law* shows most clearly that at constant pressure the specific volume is directly proportional to the absolute temperature.

### 2.3 Boyle's Law

For a sample of dry air at a fixed temperature, Boyle found that the specific volume and the pressure are inversely proportional to each other:

$$p\alpha = C,$$

where  $C$  depends on the temperature.

### 2.4 Equation of state of an ideal gas

Real gases follow Charles' and Boyle's Laws only approximately. An *ideal* or *perfect* gas follows them exactly. Charles' and Boyle's Laws can be combined to produce the equation of state of an ideal gas, which is

$$p\alpha = RT, \tag{3}$$

where  $R$ , the *specific gas constant*, is a constant for the gas (such as oxygen) being considered.

Another form of the equation of state is

$$p\alpha = \frac{R^*}{m}T, \quad (4)$$

where  $R^*$ , the *universal gas constant*, is a constant for *all* gases, and  $m$  is the molecular weight (the weight of 1 mole) of the gas. Either of these forms of the equation of state is sometimes called the *ideal gas law*.

To derive (4) from (3), consider a sample of gas with  $M = m$ . From the definition of  $\alpha$  it follows that  $V = m\alpha$ , so (3) becomes  $pV = mRT$ . Next, use Avogadro's Law which is an empirical law that states that at the same  $p, T$  a mole of *any* gas has the same volume. (For example, at  $p = 1$  atm and  $T = 0^\circ$  C,  $V = 22.415$  liters.) Consider two gases with molecular weights  $m_1$  and  $m_2$  and specific gas constants  $R_1$  and  $R_2$ . If the gases are at the same  $p, T$ , then the equation of state for gas 1 is  $pV_1/T = m_1R_1$ , while for gas 2 it is  $pV_2/T = m_2R_2$ . According to Avogadro's Law,  $V_1 = V_2$ , so

$$m_1R_1 = m_2R_2 \equiv R^* = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$$

is a constant for *all* gases. We see that for any gas,  $mR = R^*$ . Using this in (3) gives (4).

The equation of state (4) can be displayed graphically by plotting lines of constant temperature (isotherms) on a graph of specific volume versus pressure ( $\alpha, p$  diagram). We will prefer to make the ordinate  $-p$  so that pressure decreases upward as it does in the atmosphere. The resulting  $\alpha, -p$  diagram is shown schematically in Fig. 1.

## 2.5 Mixtures of gases

Dalton's Law states the total pressure  $p$  of a mixture of  $k$  gases is equal to the sum of the *partial pressures*  $p_n$ :

$$p = \sum_1^k p_n.$$

The partial pressure is the pressure that each constituent gas would have if it were the only gas present. It is therefore given by (4), the equation of state:

$$p_n = \frac{R^*}{m_n} \frac{M_n}{V} T,$$

where  $M_n$  is the mass of the  $n$ th gas, and  $m_n$  its molecular weight, and we used  $\alpha = V/M_n$ .

From Dalton's Law,

$$p = \sum p_n = \frac{R^*T}{V} \sum \frac{M_n}{m_n},$$

or, after multiplying by  $\alpha = V/\sum M_n$ ,

$$p\alpha = R^*T \frac{\sum \frac{M_n}{m_n}}{\sum M_n}. \quad (5)$$

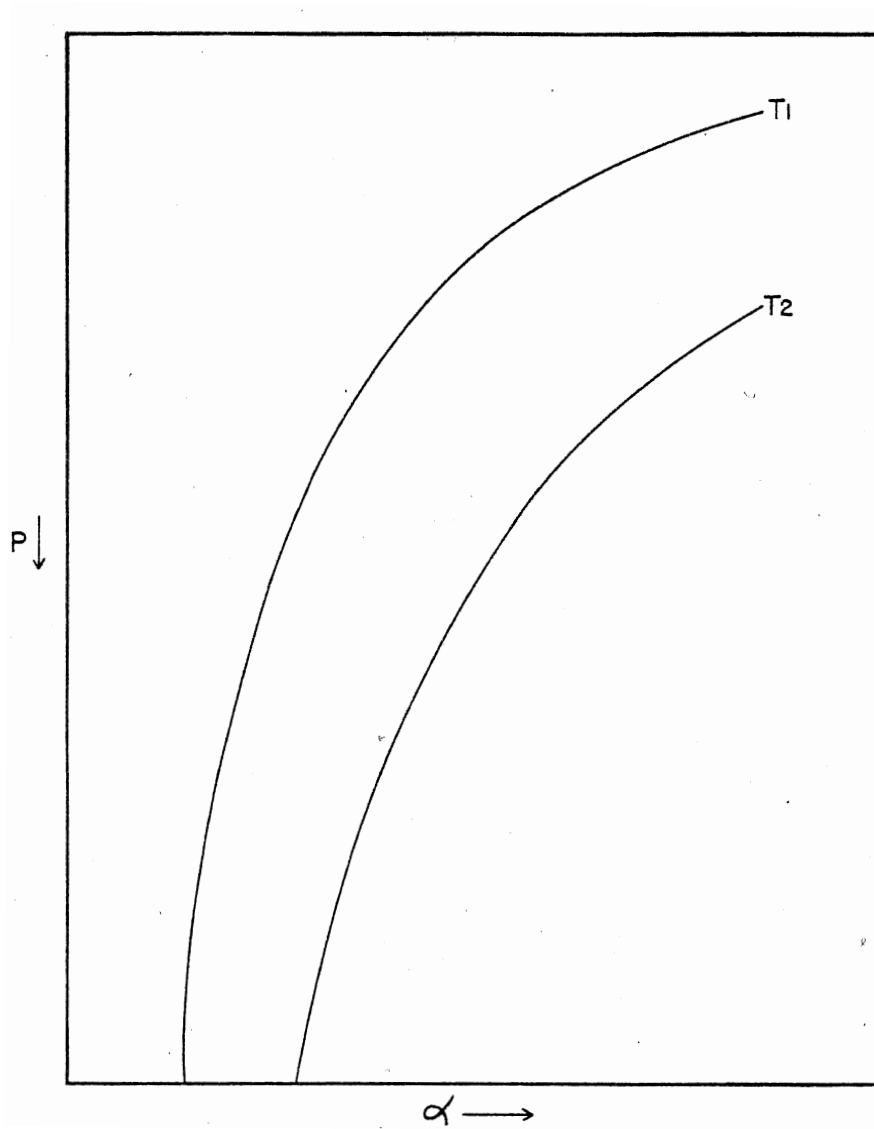


Figure 1: Isotherms on an  $\alpha, -p$  diagram (Hess 1959).



This will have the same form as the ideal gas law if we define the *mean molecular weight*  $\bar{m}$  as the total mass divided by the total number of moles:

$$\bar{m} \equiv \frac{\sum M_n}{\sum \frac{M_n}{m_n}}. \quad (6)$$

Then

$$p\alpha = \frac{R^*}{\bar{m}}T.$$

For dry air,  $\bar{m} = 28.966 \text{ g mol}^{-1}$ , and  $R = R^*/\bar{m} = 287.04 \text{ J kg}^{-1} \text{ K}^{-1}$ .

The expression for the mean molecular weight given by (6) can be simplified by recognizing that the number of moles of the  $n$ th gas is  $N_n = M_n/m_n$  and that the total number of moles in the mixture is

$$N = \sum N_n = \sum \frac{M_n}{m_n}.$$

Then (6) becomes

$$\bar{m} = \frac{\sum M_n}{N} = \frac{\sum N_n m_n}{N} = \sum \frac{N_n}{N} m_n = \sum \frac{V_n}{V} m_n. \quad (7)$$

Note that  $N_n/N$  is the *molar fraction* of the  $n$ th gas. Since a mole of any gas at the same temperature and pressure occupies the same volume,  $V_n/V = N_n/N$ , where  $V_n/V$  is the *volume fraction* of the  $n$ th gas.

## 2.6 Ideal gas law: molecular viewpoint

Consider  $N$  identical molecules in a cubical container of volume  $V$ . The edges of the container are parallel to a Cartesian coordinate system. We assume that the molecules do not attract or repel each other. However, they do collide with each other and with the walls of the container.

The number of molecules per unit volume is called the *number density* of molecules,  $n \equiv N/V$ . We assume that the molecules are moving in all directions with equal probability, so that only half of them will be moving toward a particular wall of the container at any instant. Let this wall be parallel to the  $y-z$  plane. Then the number of molecules colliding with the wall per unit area and time is  $nv_x/2$ , where  $v_x$  is the  $x$  component of the molecular velocity.

We assume that each molecule undergoes no change in kinetic energy upon collision (such a collision is "elastic"), and that the molecule's angle of incidence equals its angle of reflection. With these assumptions, the molecule's  $x$  component of momentum after collision is  $-mv_x$ , where  $m$  is the molecule's mass. (The  $y$  and  $z$  components of momentum are unchanged.) Therefore, the change in momentum is  $2mv_x$ .

Newton's second law of motion for a mass acted upon by a force  $\mathbf{F}$  is

$$\frac{d\mathbf{p}}{dt} = \mathbf{F},$$

where  $\mathbf{p}$  is the momentum. The molecule's change of momentum is due to a force exerted upon it by the wall. But if the wall exerts a force on the molecule, the molecule must exert an equal and opposite force  $F_x$  on the wall. The time integral of this force is the momentum change:

$$\int F_x dt = \Delta p_x = 2mv_x.$$

During the time interval  $t$ ,  $Atnv_x/2$  molecules hit an area  $A$  of the wall. The time-integrated force acting on this area is

$$\int_0^t F_x dt = (2mv_x)(Atnv_x/2).$$

The average force acting on the area  $A$  over time  $t$  is

$$\frac{1}{t} \int_0^t F_x dt = Anmv_x^2.$$

The average force divided by the area over which it acts is the *pressure*,  $p$ :

$$p = nmv_x^2.$$

We assumed that all molecules have the same speed. In reality, their speeds are distributed about an average. We simply replace  $v_x^2$  by its average, so that

$$p = nm\langle v_x^2 \rangle, \tag{8}$$

where the angle brackets denote an average over the distribution of molecular speeds. If the molecules are moving randomly, averages for the three velocity components must be the same:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle.$$

Since

$$\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle,$$

we can write (8) as

$$p = \frac{1}{3}nm\langle v^2 \rangle = \frac{1}{3} \frac{N}{V} m\langle v^2 \rangle.$$

The pressure of a gas is 2/3 of its molecular kinetic energy density.

At this point we define *absolute temperature*,  $T$ , by

$$\frac{1}{3}m\langle v^2 \rangle = kT,$$

where  $k$ , called *Boltzmann's constant*, has the value  $1.38 \times 10^{-23}$  J K<sup>-1</sup>. With this definition,

$$pV = NkT.$$

This is the fundamental form of the ideal gas law, from which all other forms can be derived.

### 3 Conservation of Energy

#### 3.1 Conservation of energy in mechanics

Newton's Second Law for a single point mass in a gravitational field is

$$m \frac{d\mathbf{v}}{dt} = m\mathbf{g},$$

where  $m$  is the mass,  $\mathbf{v}$  is its velocity, and  $\mathbf{g} = -g\mathbf{k}$  is gravity. If we multiply this equation by  $\mathbf{v}$ , we obtain

$$\frac{d}{dt} \left( \frac{1}{2} m v^2 \right) = -\frac{d}{dt} (mgz),$$

which can be written as

$$\frac{d}{dt} K = -\frac{d}{dt} P,$$

where  $K$  is the kinetic energy and  $P$  is the potential energy. This relation implies that the total energy  $E = K + P$  is constant, or conserved.

We see that the dimensions of energy are those of mass  $\times$  velocity<sup>2</sup>, or force  $\times$  distance.

The conservation of kinetic plus potential energy is (approximately) exhibited by a tennis ball thrown into the air and allowed to bounce. However, what if we replace the tennis ball with a ball of putty? When the ball of putty hits the ground, both its kinetic energy and its potential energy become zero. Is energy not conserved in this case?

#### 3.2 Conservation of energy: A system of point masses

Consider a system consisting of interacting point masses, each with a fixed mass  $m_i$  ( $i = 1, 2, \dots$ ) and position  $\mathbf{x}_i$ . The  $j$ th point mass exerts a force  $\mathbf{F}_{ji}$  on the  $i$ th point mass. In addition, an external force  $\mathbf{F}_i^e$  may act on the  $i$ th point mass. The equation of motion for the  $i$ th point mass is

$$m_i \frac{d^2 \mathbf{x}_i}{dt^2} = \sum_{j \neq i} \mathbf{F}_{ji} + \mathbf{F}_i^e. \quad (9)$$

By summing (9) over all  $i$ , the sum of the internal forces vanishes, leaving only the sum of the external forces:

$$\sum_i m_i \frac{d^2 \mathbf{x}_i}{dt^2} = \sum_i \mathbf{F}_i^e = \mathbf{F}^e. \quad (10)$$

If we define the *center of mass* by

$$\mathbf{X} = \frac{\sum_i m_i \mathbf{x}_i}{M},$$

where  $M = \sum_i m_i$  is the total mass of the system, then (10) can be written

$$M \frac{d^2 \mathbf{X}}{dt^2} = \mathbf{F}^e, \quad (11)$$

which shows that the motion of the center of mass of the system of point masses is determined only by the external forces.

By multiplying (9) by  $\mathbf{v}_i$  and summing over  $i$ , we find that

$$K_{cm} + K_{int} + P_{int} + P^e = \text{const}, \quad (12)$$

where  $K_{cm}$  is the kinetic energy of a body with mass  $M$  moving with the center-of-mass velocity,  $K_{int}$  is the kinetic energy of the point masses due to their motion relative to the center of mass (their average velocity relative to the center of mass is zero),  $P_{int}$  is the sum of all potential energies of mutual interaction, and  $P^e$  is the sum of the external potential energies.

Now we see that when the ball of putty hits the ground, its center-of-mass kinetic energy,  $K_{cm}$ , is converted into internal kinetic energy,  $K_{int}$ , so that energy is conserved.

For another example of energy conservation, consider a fan that is causing air to circulate in a room. What happens to the kinetic energy of the breeze after the fan is turned off? As with the putty,  $K_{cm}$  is converted to  $K_{int}$ .

After one turns on a hot plate, an air current will rise above it. In this case,  $K_{int}$  is (partly) converted into  $K_{cm}$ . A similar process produces many atmospheric circulations.

### 3.3 Kinetic energy exchange in molecular collisions

What happens on average when two molecules of unequal kinetic energy interact (i.e., collide)? For now, consider molecules to be point masses (later, we will abandon this to understand the specific heats of gas molecules). In an *elastic* collision, the total momentum and total kinetic energy of the molecules are conserved. There are six unknowns: the velocity components of the two molecules after the collision. But we have only four equations: three for the components of the total momentum, and one for the total kinetic energy. Therefore, we cannot uniquely determine the velocities of the two molecules after the collision from their velocities before the collision. However, it can be shown that, *on average*, the molecule that has the lower kinetic energy before the collision gains kinetic energy due to the collision.

### 3.4 Working and Heating

In section 3.2, interactions between a system and its surroundings was described by the external potential energy,  $P^e$ , which is often unknown, or too complicated to be useful. We therefore use an alternative description of the interaction between a macroscopic system (i.e., a large collection of molecules) and its surroundings (another large collection of molecules).

The equation of motion for a point mass acted upon by a force  $\mathbf{F}$  is

$$m \frac{d\mathbf{v}}{dt} = \mathbf{F}.$$

As before in section 3.1, we take the scalar product of this equation with  $\mathbf{v}$  to obtain the equation for the kinetic energy of the point mass,  $K = mv^2/2$ :

$$m\mathbf{v} \cdot \frac{d\mathbf{v}}{dt} = \frac{dK}{dt} = \mathbf{v} \cdot \mathbf{F} = W,$$

where  $W$  is the rate of *working*, since *work* is defined as force acting over a distance. This equation is another way of stating energy conservation: The kinetic energy of the point mass does not change unless work is done on it by an external force. This can be extended to a system of point masses:

$$\frac{d}{dt}(K_{cm} + K_{int} + P_{int}) = \sum_i \mathbf{v}_i \cdot \mathbf{F}_i^e, \quad (13)$$

which is Eq. (12) written using

$$-\frac{dP^e}{dt} = \sum_i \mathbf{v}_i \cdot \mathbf{F}_i^e.$$

We can decompose the right side of Eq. (13) into two components. One component, denoted by  $\dot{H}$ , *the rate of heating*, is the contribution from external forces,  $\mathbf{F}_i^e$ , that vanish on average, although

$$\sum_i \mathbf{v}_i \cdot \mathbf{F}_i^e$$

may not vanish. In particular, this sum does not vanish if the average kinetic energy of the surrounding molecules is different from that of the system molecules. The other component, denoted by  $-\dot{W}$ , *the rate of working*, is the contribution from external forces that do not vanish on average (such as gravity).

If we define  $U = K_{int} + P_{int}$ , we can write Eq. (13) as

$$\frac{dU}{dt} + \frac{dK_{cm}}{dt} = \dot{H} - \dot{W}. \quad (14)$$

Under many conditions, we may ignore the rate of change of  $K_{cm}$  in Eq. (14) and write

$$\frac{dU}{dt} = \dot{H} - \dot{W}. \quad (15)$$

Equation (15) can be summarized in words as follows:  $U$  is an *internal energy* of a system of molecules in the sense that it is the sum of a potential energy arising from forces exerted by the system molecules upon each other and a kinetic energy of motion about the system's center of mass.  $U$  may change due to two types of interactions of the system with its surroundings: (1) those interactions for which the force vanishes on average yet the energy of the system changes because of random collisions with surrounding molecules that have a different average kinetic energy; (2) those interactions for which the force does not vanish on average.

## 4 The Principles of Thermodynamics

### 4.1 Conservation of energy and the first law of thermodynamics

#### 4.1.1 Conservation of energy

In section 3.2, we found that for a macroscopic system (i.e., for a large collection of molecules)

$$\frac{d}{dt}(K_{cm} + K_{int} + P_{int}) = \dot{H} - \dot{W}, \quad (16)$$

where  $K_{cm}$  is the kinetic energy of a body with the mass of the system moving with the center-of-mass velocity,  $K_{int}$  is the kinetic energy of the molecules due to their motion relative to the center of mass (their average velocity relative to the center of mass is zero),  $P_{int}$  is the sum of all potential energies of mutual molecular interaction, and  $\dot{H} - \dot{W}$  represents the rate of energy change due to interactions between the system and its environment.

If we define  $U = K_{int} + P_{int}$ , we can write Eq. (16) as

$$\frac{dU}{dt} + \frac{dK_{cm}}{dt} = \dot{H} - \dot{W}. \quad (17)$$

The energy  $U$  is called the *internal energy*.

Joule showed by experiment that kinetic energy and internal energy are two forms of energy. Joule used falling weights to turn paddles which stirred water in a container and raised the water's temperature. In Joule's experiment,  $dU/dt = -dK_{cm}/dt$ .

#### 4.1.2 The first law of thermodynamics

Under many conditions, we may ignore the rate of change of  $K_{cm}$  in Eq. (17) and write

$$\frac{dU}{dt} = \dot{H} - \dot{W}. \quad (18)$$

A thermodynamic process changes a system from an initial state to a final state over an unspecified time interval. If we integrate Eq. (18) over such a time interval, from a time  $t_1$  when the system is in its initial state to a time  $t_2$  when it is in its final state, we obtain

$$U_f - U_i = \Delta U = H - W. \quad (19)$$

Equation (19) is the *first law of thermodynamics*.

$$H = \int_{t_1}^{t_2} \dot{H} dt$$

is the energy added by heating (often called the "heat added"), and

$$-W = - \int_{t_1}^{t_2} \dot{W} dt$$

is the work done on the system.

Any number of processes may produce the same change in the system. If  $H - W$  is calculated for any one of these processes, we find that  $H - W$  is always the same. This is because  $H - W$  is the change in the *internal energy*,  $U$ , of the system, which is a function of thermodynamic state variables (i.e., of  $p, \alpha, T$ ). We write this as

$$U_f - U_i = \Delta U = H - W. \quad (20)$$

This is *the first law of thermodynamics* in its most general form. Recall that if  $H > 0$ , heat is added to the system, while if  $W > 0$ , work is done by the system. If we divide (20) by the mass of the system, the first law can be written

$$u_f - u_i = \Delta u = h - w.$$

For small amounts of heat added or work done, we write the first law as

$$du = dh - dw. \quad (21)$$

The first law of thermodynamics expresses the conservation of internal energy. When energy is added to (or extracted from) a system, the internal energy of the system is increased (or decreased). The energy added is equal to the energy added by heating minus the work done. The first law cannot tell us whether a process can actually occur. The second law is needed to for that.

In contrast to energy transfer between a system and its surroundings by heating, which always involves a temperature difference, work is energy that is transmitted in such a way that a temperature change is not directly involved. The energy added or lost by the system by heating,  $H$ , and the work done by or on the system,  $W$ , are characteristics of the *thermodynamic process* by which a system moves from one equilibrium state to another, by interacting with its environment.

### 4.1.3 Work

*Work* is defined as follows: When a force  $\mathbf{F}$  is applied to a mass which moves a distance  $d\mathbf{S}$ , the work done is  $dW = \mathbf{F} \cdot d\mathbf{S}$ . The only force with which a sample of nonviscous fluid can do work on the surrounding fluid is that due to the pressure along its surface. Each surface element of area  $dA$  exerts a force on the surrounding fluid equal to  $p dA$ . This force is normal to the surface element. Suppose the fluid sample expands so that a surface element moves a distance  $dS$  normal to the surface. Then

$$dW = \mathbf{F} \cdot d\mathbf{S} = pA dS = p dV, \quad (22)$$

where  $dV = A dS$  is the differential change in the volume of the sample.

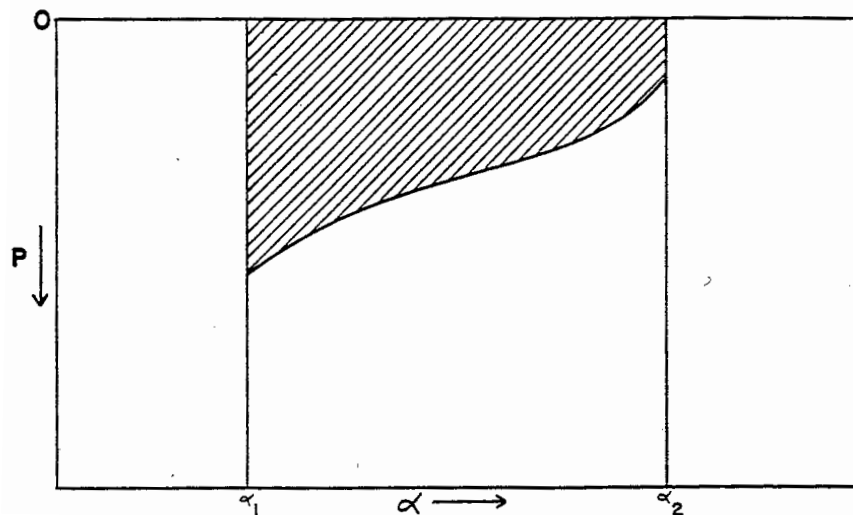


Figure 2: Graphical representation of work done in an arbitrary process of expansion from  $\alpha_1$  to  $\alpha_2$ . (Hess 1959).

We denote quantities that refer to the entire mass of a sample with capital letters, and quantities that refer to a unit mass with small letters. If we divide (22) by the mass of the sample, we get

$$dw = p d\alpha, \quad (23)$$

where  $dw$  is the *specific work* done.

If the system (the fluid sample) expands and does work its environment (the surrounding fluid), then  $dw$  is positive. If the system is compressed, then work has been done on the system and  $dw$  is negative.

The total specific work done during a finite expansion from  $\alpha_1$  to  $\alpha_2$ , during which  $p$  may vary, is

$$w = \int_{\alpha_1}^{\alpha_2} p d\alpha.$$

This may be shown graphically on an  $\alpha, -p$  diagram as in Fig. 2. The work done is shown by the hatched area. Since there are many different ways in which a system can be taken from the initial state  $(\alpha_1, p_1)$  to the final state  $(\alpha_2, p_2)$ , *the work done by a system depends not only on the initial and final states but also on the intermediate states, that is, on the path of the process.*

#### 4.1.4 Energy transferred by heating

Energy transferred by heating,  $H$ , is that which is transferred between a system and its surroundings as a result of temperature differences only.



## 4.2 Quantity of energy transferred by heating

The unit of energy transferred by heating is defined quantitatively in terms of a specified change produced in a body by a specified process. If the temperature of one kg of water is raised from 14.5 to 15.5°C by heating, one *kilocalorie* (kcal) of energy has been added. The *calorie* ( $= 10^{-3}$  kcal) is also used as an energy unit. Joule's experiment shows that 1 kcal = 4186 joules.

The ratio of the energy  $\Delta H$  supplied to a body by heating to its corresponding temperature change  $\Delta T$  is called the *heat capacity*  $C$  of the body:

$$C = \frac{\Delta H}{\Delta T}.$$

The heat capacity per unit mass of a body, called the *specific heat*  $c$ , is characteristic of the material of which the body is composed:

$$c = \frac{\Delta H}{M\Delta T}.$$

Thus, we properly speak of the heat capacity of a penny, and of the specific heat capacity of copper.

Neither the heat capacity of a body nor the specific heat capacity of a material is constant. They both depend on the temperature. At any temperature, the specific heat is defined by

$$c = \frac{dH}{MdT} = \frac{dh}{dT}, \quad (24)$$

where  $dh = dH/M$  is the energy added by heating per unit mass.

Eq. (24) does not define specific heat uniquely. We must also specify the conditions under which the energy  $\Delta H$  is added to the sample by heating. If the heating is isobaric, we obtain the specific heat at constant pressure  $c_p$  from (24):

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

If the heat is isosteric, then we obtain the specific heat at constant volume  $c_v$ :

$$c_v = \left( \frac{dh}{dT} \right)_\alpha.$$

Thus, the amount of energy that is transferred to a system depends on how the system is heated. Just as for the work done by a system, *the amount of energy transferred to or from a system by heating depends not only on the initial and final states but also on the intermediate states, that is, on the path of the process.*

For dry air,  $c_p = 1004 \text{ J kg}^{-1} \text{ K}^{-1}$ , and  $c_v = 717 \text{ J kg}^{-1} \text{ K}^{-1}$ . The variation of the specific heat capacities of dry air with temperature is negligible. We expect that  $c_p > c_v$

Table 2: Specific heat capacities at constant pressure ( $p = 1$  atm).

<i>Substance</i>	<i>Temperature</i> (°C)	<i>Specific heat capacity</i> (kcal kg <sup>-1</sup> K <sup>-1</sup> )
pure water	0	1.007
	30	0.998
pure ice	0	0.503
Al	20	0.215
Cu	20	0.092
Ag	20	0.056

since in a constant pressure process some of the energy added by heating is used to perform work on the surroundings as the gas expands, while in a constant volume process all of the energy added by heating is used to raise the temperature of the gas. Table 2 lists the specific heat capacities of various other substances at constant pressure.

### 4.3 The first law of thermodynamics for an ideal gas

For an ideal gas, internal energy is a function of temperature only, since energy added by heating at constant volume only increases the random molecular motion, which is proportional to the temperature. Thus,

$$du = c_v dT.$$

We can substitute this and  $dw = p d\alpha$  into (21) to obtain

$$c_v dT = dh - p d\alpha,$$

or, after rearranging,

$$dh = c_v dT + p d\alpha. \tag{25}$$

We can use the equation of state for an ideal gas to write the first law in an alternate form. From the equation of state, we obtain

$$p d\alpha + \alpha dp = R dT.$$

Using this, the first law (25) becomes

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

For an isobaric process,

$$dh = (c_v + R) dT.$$

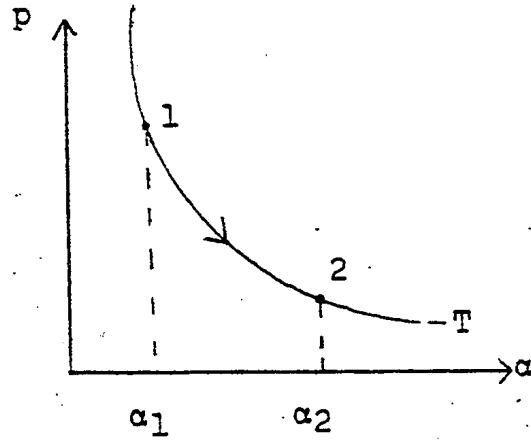


Figure 3: Graphical representation of an isothermal process.

But from the definition of  $c_p$ ,

$$dh = c_p dT.$$

Thus,  $c_v + R = c_p$ , and we obtain the alternate form of the first law:

$$dh = c_p dT - \alpha dp. \quad (26)$$

The enthalpy of an ideal gas, like the internal energy, is a function of temperature only. In differential form the *specific enthalpy* is

$$db = c_p dT.$$

In meteorology, the quantity  $c_p dT$  is also called the *sensible heat*. It is the energy transferred to a system by heating during an isobaric process.

#### 4.4 Applications of the first law

We will compute the specific energy added by heating  $h$ , the specific work done  $w$ , and the changes in specific internal energy  $\Delta u$  and specific enthalpy  $\Delta b$  for isothermal, isobaric, and isosteric (constant volume) process of an ideal gas.

##### 4.4.1 Isothermal process

Fig. 3 is a graphical representation of an isothermal process. Since  $dT = 0$  during an isothermal process, the changes in specific internal energy,  $\Delta u = c_v \Delta T$ , and enthalpy,  $\Delta b = c_p \Delta T$ , are both zero.

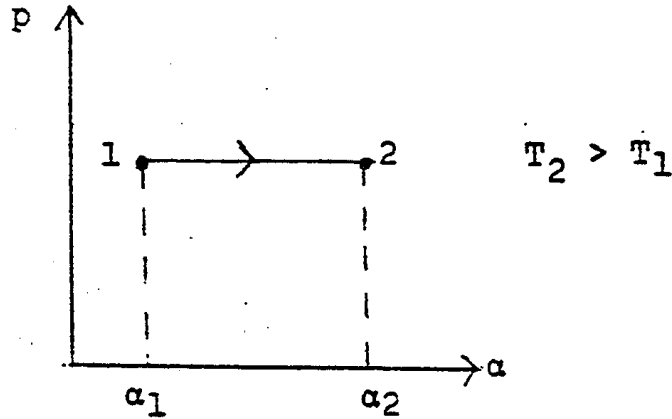


Figure 4: Graphical representation of an isobaric process.

Since  $\Delta u = 0$  for this process, the first law (4.1.2) becomes simply

$$h = w = \int_{\alpha_1}^{\alpha_2} p d\alpha = RT \ln \frac{\alpha_2}{\alpha_1}.$$

All of the energy transferred to the system by heating during an isothermal expansion is used by the system to do work on the surroundings.

#### 4.4.2 Isobaric process

Fig. 4 is a graphical representation of an isobaric process. Since  $\Delta T > 0$  for an isobaric expansion, the changes in specific internal energy,  $\Delta u = c_v \Delta T$ , and enthalpy,  $\Delta b = c_p \Delta T$ , are also positive.

The specific work done by the system is

$$w = p(\alpha_2 - \alpha_1).$$

To calculate the energy transferred to the system by heating, we use the alternate form of the first law (26),

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

Since  $dp = 0$  during an isobaric process, the first law becomes simply

$$h = \Delta b.$$

All of the energy transferred to the system by heating during an isobaric process is used to increase the specific enthalpy of the system.

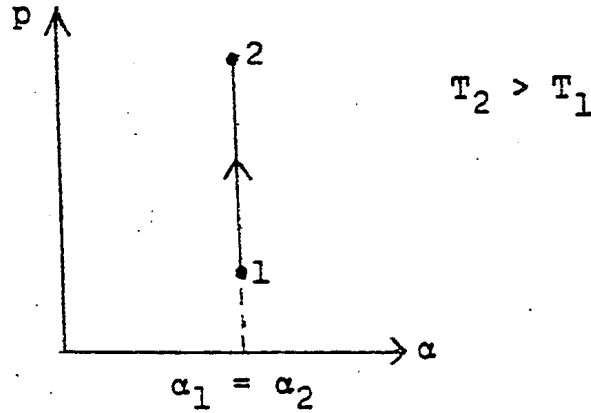


Figure 5: Graphical representation of an isosteric process.

#### 4.4.3 Isosteric process

Fig. 5 is a graphical representation of an isosteric process. Since  $\Delta T > 0$  for an isosteric (constant volume) process during which the pressure increases, the changes in specific internal energy,  $\Delta u = c_v \Delta T$ , and enthalpy,  $\Delta h = c_p \Delta T$ , are also positive.

The specific work done by the system is zero since  $d\alpha = 0$  during an isosteric process. The first law (4.1.2) becomes simply

$$h = \Delta u.$$

All of the energy transferred to the system by heating during an isosteric process is used to increase the specific internal energy of the system.

#### 4.5 Adiabatic processes

Heating in the atmosphere can be due to radiation, condensation, freezing, or conduction from the underlying surface. Heating is often of secondary importance for synoptic scale motions for one to two day time periods. Processes that include heating are *diabatic*; those without heating are *adiabatic*.

For adiabatic processes, the first law in its alternate form (26) is

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

Using the ideal gas law for  $\alpha$  and dividing by  $c_p T$ , this becomes

$$0 = \frac{dT}{T} - \frac{R}{c_p} \frac{dp}{p}.$$

By integrating between state 1 and state 2, we get

$$\ln \frac{T_2}{T_1} = \frac{R}{c_p} \ln \frac{p_2}{p_1}.$$

By exponentiating, we get

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{R/c_p} = \left( \frac{p_2}{p_1} \right)^\kappa, \quad (27)$$

where  $\kappa \equiv R/c_p = 0.286$ . This is *Poisson's equation*. It describes how  $T$  and  $p$  are related during an adiabatic process. Similar equations relate  $T$  and  $\alpha$  and  $\alpha$  and  $p$ :

$$\frac{T_2}{T_1} = \left( \frac{\alpha_2}{\alpha_1} \right)^{-R/c_v},$$

$$\frac{\alpha_2}{\alpha_1} = \left( \frac{p_2}{p_1} \right)^{-c_v/c_p}.$$

If  $p_1 = p_0 \equiv 100 \text{ kPa} = 1000 \text{ mb}$ ,  $T_1 = \theta$ ,  $p_2 = p$ , and  $T_2 = T$ , then (27) becomes

$$\frac{T}{\theta} = \left( \frac{p}{p_0} \right)^\kappa. \quad (28)$$

The temperature  $\theta$  is called the *potential temperature*. It is the temperature a parcel of dry air would have if it was brought adiabatically to a pressure of 1000 mb. It is a characteristic property of a parcel of air which is invariant during adiabatic processes and is a *conservative* property.

The potential temperature is also a state variable, since it is a function of two state variables. Lines of constant  $\theta$  can therefore be drawn on an  $\alpha, -p$  diagram. Such a line is called a *dry adiabat*. Fig. 6 shows schematically some adiabats and isotherms on an  $\alpha, -p$  diagram. With the aid of such a diagram, one can graphically portray changes of state during adiabatic processes.

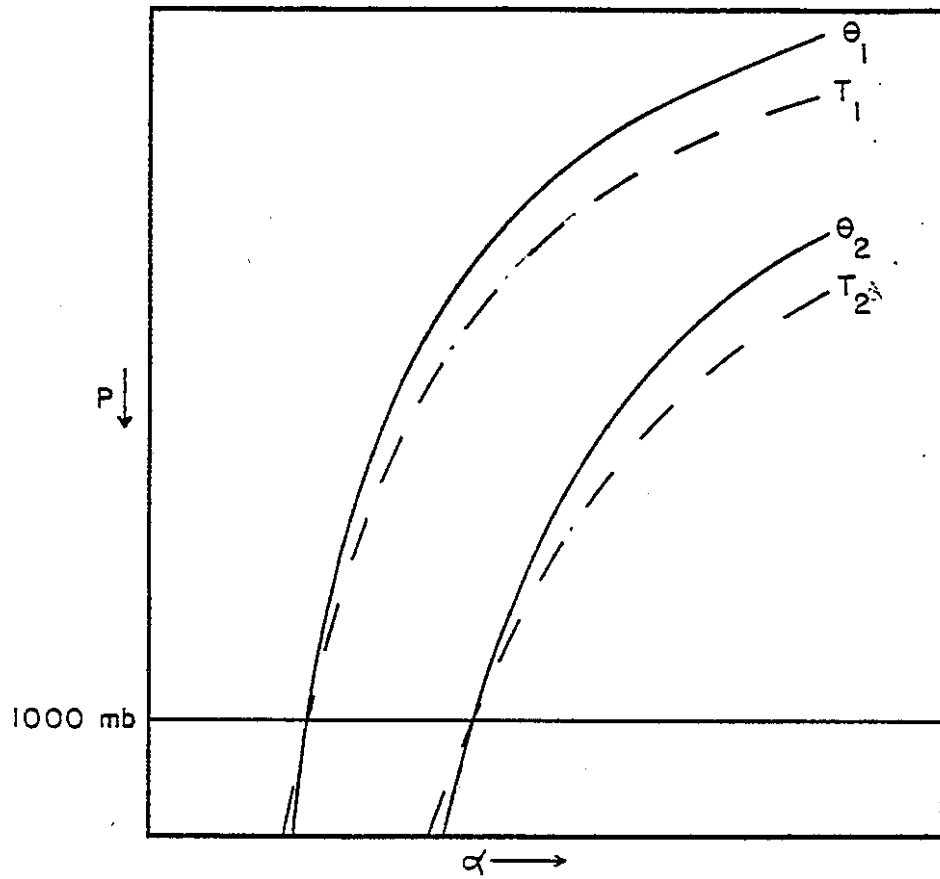


Figure 6: Schematic representation of dry adiabats (solid lines) and isotherms (dashed lines) on an  $\alpha, -p$  diagram (Hess 1959).

## 5 The Thermodynamics of Water Vapor and Moist Air

### 5.1 Thermal properties of water substance

Water vapor is an exceptional gas in the earth's atmosphere because it can coexist with liquid water and solid water (ice). The specific volume of ice at  $0^\circ\text{C}$  is  $1.091 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ . The specific heat capacity of ice at  $0^\circ\text{C} = 0.503 \text{ kcal kg}^{-1} \text{ K}^{-1}$ . The specific volume of water is  $1.00 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ . The specific heat capacity of water at  $15^\circ\text{C}$  is exactly  $1.00 \text{ kcal kg}^{-1} \text{ K}^{-1}$ . The properties of liquid water vary so little with temperature that we may neglect the variations.

We will assume that water vapor satisfies the equation of state of an ideal gas. The specific heat capacities of water vapor at low concentrations (partial pressures) are  $c_{vv} = 0.331 \text{ kcal kg}^{-1} \text{ K}^{-1}$  and  $c_{pv} = 0.441 \text{ kcal kg}^{-1} \text{ K}^{-1}$ . The subscript  $v$  indicates that these are values for water vapor. These quantities may vary appreciably with temperature, so that water vapor does not satisfy the second condition for an ideal gas (i.e., that the specific heat capacities are independent of temperature). However, we will always be concerned with a mixture of dry air and a small amount of water vapor, so the specific heat capacities of the mixture will not be seriously affected by the variations in the vapor properties.

### 5.2 Equation of state of moist air

Moist air is a mixture of dry air and water vapor. Therefore, the mean molecular weight of moist air is (see section 2.5)

$$\frac{1}{\bar{m}} = \frac{1}{M_d + M_v} \left( \frac{M_d}{m_d} + \frac{M_v}{m_v} \right),$$

where subscript  $d$  indicates dry air and subscript  $v$  indicates water vapor. Expressing  $\bar{m}$  in terms of  $m_d$  gives

$$\frac{1}{\bar{m}} = \frac{1}{m_d} \frac{M_d}{M_d + M_v} \left( 1 + \frac{M_v/M_d}{m_v/m_d} \right).$$

$M_v/M_d$  is the water vapor *mixing ratio*. It is the mass of water vapor per unit mass of dry air. Using  $w \equiv M_v/M_d$ , we can write the equation above as

$$\frac{1}{\bar{m}} = \frac{1}{m_d} \frac{1 + w/\epsilon}{1 + w},$$

where  $\epsilon = m_v/m_d$ . The equation of state for a mixture of water vapor and dry air may now be written as (see section 2e)

$$p\alpha = \frac{R^*}{m_d} \left( \frac{1 + w/\epsilon}{1 + w} \right) T.$$



Instead of using a variable gas constant for moist air, we define a new temperature,

$$T_v \equiv \left( \frac{1 + w/\epsilon}{1 + w} \right) T,$$

called the *virtual temperature*. It satisfies the equation of state for dry air,

$$p\alpha = \frac{R^*}{m_d} T_v = R T_v.$$

The virtual temperature is the temperature that dry air would have if its pressure and specific volume (or density) were equal to those of a given sample of moist air.

The virtual temperature is always greater than the actual temperature. Using  $\epsilon = 0.622$ , we may write

$$T_v = \left( \frac{1 + 1.609w}{1 + w} \right) T \approx (1 + 0.61w)T.$$

### 5.3 Mixing ratio

According to Dalton's law, each gas in a mixture of gases behaves as if it were the only gas present. Thus in a mixture of water vapor and dry air, water vapor obeys the ideal gas law,

$$e\alpha_v = \frac{R^*}{m_v} T,$$

where  $e$  is the partial pressure of water vapor, or the *vapor pressure*. Likewise in such a mixture, dry air obeys the ideal gas law,

$$(p - e)\alpha_d = \frac{R^*}{m_d} T,$$

where  $p - e$  is the partial pressure of dry air. We can use these relations to express the mixing ratio in terms of  $e$  and  $p$ :

$$w \equiv \frac{M_v}{M_d} = \frac{\rho_v}{\rho_d} = \frac{\alpha_d}{\alpha_v} = \frac{m_v}{m_d} \frac{e}{p - e} \approx \frac{m_v}{m_d} \frac{e}{p}.$$

### 5.4 Moisture variables

**Vapor pressure,  $e$**  The pressure exerted by water vapor in a mixture of air and water vapor.

**Saturation vapor pressure,  $e_s(T)$**  The vapor pressure of water that is in equilibrium with a plane surface of water. It is a function of temperature only. Bolton's (1980) formula for  $e_s(T)$  is sufficiently accurate for most purposes:

$$e_s(T) = 611.2 \exp \left( \frac{17.67 T_c}{T_c + 243.5} \right),$$

where  $e_s$  is in Pa and  $T_c \equiv T - T_0$  is temperature in degrees Celsius.

**Mixing ratio,  $w$**  The ratio of the mass of water vapor present to the mass of dry air:

$$w = \frac{\rho_v}{\rho_d} = \frac{m_v}{m_d} \frac{e}{p - e} = \epsilon \frac{e}{p - e} \approx \epsilon \frac{e}{p}.$$

**Saturation mixing ratio,  $w_s(T, p)$**  The mixing ratio for which water vapor is in equilibrium with a plane surface of water. It is a function of temperature and pressure:

$$w_s = \epsilon \frac{e_s(T)}{p - e_s(T)} \approx \epsilon \frac{e_s(T)}{p}.$$

**Relative humidity,  $r$**  The ratio of the actual vapor pressure to the saturation vapor pressure:

$$r = \frac{e}{e_s} \approx \frac{w}{w_s}.$$

**Dew-point temperature,  $T_d$**  The temperature at which moist air becomes just saturated after being cooled during a process in which  $p$  and  $w$  remain constant. Alternatively, the temperature at which the mixing ratio equals the saturation mixing ratio:

$$w = w_s(T_d, p).$$

The dew-point temperature may be calculated from

$$T_d = \frac{T}{1 - \frac{TR_v}{L_e} \ln(e/e_s)},$$

where  $R_v \equiv R^*/m_v = R/\epsilon$  and  $L_e$  is the latent heat of evaporation (see section 5.5).

**Saturation pressure,  $p_s$**  Also called the *lifting condensation level* or *LCL*. The pressure at which unsaturated air becomes saturated after a dry adiabatic ascent (expansion).

**Saturation temperature,  $T_s$**  The temperature at the saturation pressure. At  $p = p_s, T = T_s$ , the mixing ratio becomes the saturation mixing ratio, so

$$w = w_s(T_s, p_s).$$

An approximation for  $T_s$  is

$$T_s = \left( \frac{1}{T - 55} - \frac{\log r}{2840} \right)^{-1} + 55.$$

**Height of LCL,  $z_{\text{LCL}}$  (m)** This is approximately

$$z_{\text{LCL}} - z \approx \frac{T(z) - T_d(z)}{8}.$$

A more accurate formula is Lawrence’s formula:

$$z_{\text{LCL}} - z \approx 100 \left( 20 + \frac{T_c(z)}{5} \right) (1 - r(z)).$$

M. G. Lawrence, 2005: The relationship between relative humidity and the dew point temperature in moist air: A simple conversion and applications, *Bull. Am. Meteorol. Soc.*, **86**, 225–233.

**Virtual temperature,  $T_v$**  The temperature at which dry air would have the same density as a sample of moist air, at the same pressure:

$$T_v = \left( \frac{1 + 1.609w}{1 + w} \right) T \approx (1 + 0.61w)T.$$

## 5.5 Changes of phase and latent heats

In the atmosphere, liquid water and water vapor can coexist in thermodynamic equilibrium, as can ice and water vapor. Vapor, liquid, and solid are called *phases*. The following *phase changes* of water substance occur in the atmosphere: evaporation, condensation, sublimation, deposition, melting, and freezing. Evaporation occurs when liquid water changes to water vapor, while condensation is the opposite. Sublimation occurs when ice changes to water vapor, while deposition is the opposite. Melting occurs when ice changes to liquid water, while freezing is the opposite. Both condensation and freezing require “nuclei” to initiate the phase change. If sufficient nuclei are not present, *supersaturation* of water vapor, or *supercooling* of liquid water, may occur.

Heating or cooling of the environment occurs during phase changes, even though the phase change is isothermal. The energy transferred is called the *latent heat*. Cooling occurs during evaporation, sublimation, and melting, while heating occurs during condensation, deposition, and freezing. At 0°C the latent heat of evaporation is  $L_e = 2.5 \times 10^6 \text{ J kg}^{-1}$ , the latent heat of melting is  $L_m = 0.334 \times 10^6 \text{ J kg}^{-1}$ , and the latent heat of sublimation is  $L_s = 2.834 \times 10^6 \text{ J kg}^{-1}$ .

## 5.6 Adiabatic processes of saturated air

When condensation occurs during ascent, the latent heat that is released significantly reduces the rate of temperature decrease due to adiabatic expansion. Consider two cases:

All condensed water remains suspended. This is called a *moist adiabatic* or *saturation adiabatic* process, and is *reversible*.

All condensed water falls out of the parcel immediately. This is called a *pseudo-adiabatic* process, and is *irreversible*.

The real situation lies between these two extremes. The rate of cooling in a pseudo-adiabatic process is essentially equal to that in a truly moist adiabatic one.

We will now consider a pseudo-adiabatic process in which the amount of water vapor condensed is  $-dw_s$  so the latent heating is  $-Ldw_s$ . Here we use  $L = L_e$  for simplicity. The first law for the mixture of dry air and water vapor is

$$-Ldw_s = c_p dT - RT \frac{dp}{p}. \quad (29)$$

Since  $w_s$  and  $e_s$  are known functions of  $T$  and  $p$ , this is a differential relationship between  $T$  and  $p$  during a pseudo-adiabatic process.

We will use the definition of potential temperature given by Eq. (28) to write another form of the first law. Take the logarithm of (28) to get

$$\ln \frac{T}{\theta} = \frac{R}{c_p} \ln \frac{p}{p_0}.$$

Differentiate this to obtain

$$d \ln T - d \ln \theta = \frac{R}{c_p} (d \ln p - d \ln p_0),$$

which becomes

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

Rearrange this to get

$$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R \frac{dp}{p}. \quad (30)$$

By comparing (29) and (30), we see that the first law of thermodynamics for a pseudo-adiabatic process is

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

which can also be written as

$$d\theta + \frac{L}{c_p \pi} dw_s = 0,$$

where  $\pi$  is the *Exner function*:

$$\pi = \left( \frac{p}{p_0} \right)^{R/c_p}. \quad (31)$$

It can be shown that (see Wallace and Hobbs, First Edition, Problem 2.33)

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

so

$$-L d\left(\frac{w_s}{T}\right) \approx c_p \frac{d\theta}{\theta} = c_p d \ln \theta.$$

Integrate from the original, *saturated* state  $(p, T, w_s(T, p), \theta(T, p))$  to a state where  $w_s = 0$  and  $\theta = \theta_e$ :

$$\frac{Lw_s}{c_p T} = \ln(\theta_e/\theta),$$

then exponentiate and rearrange to obtain

$$\theta = \theta_e \exp(-Lw_s/c_p T).$$

This describes a *pseudo-adiabat* which is characterized by  $\theta_e$ , the *equivalent potential temperature*:

$$\theta_e = \theta \exp(Lw_s/c_p T). \tag{32}$$

## 5.7 More moisture variables

The thermodynamic processes that define the following four variables are easily visualized on a skew  $T$ -log  $p$  diagram, as shown in Fig. 7.

**Equivalent potential temperature,  $\theta_e$**  The potential temperature of a parcel that has ascended pseudo-adiabatically until all water vapor has been condensed. Eq. (32):

$$\theta_e = \theta \exp(Lw_s/c_p T) \approx \theta + Lw_s/c_p.$$

**Equivalent temperature,  $T_e$**  The temperature of a parcel that has first ascended pseudo-adiabatically until all water vapor has been condensed, then descended (dry adiabatically) to its original pressure:

$$T_e = \theta_e \left( \frac{p}{p_0} \right)^{R/c_p} = T \exp(Lw_s/c_p T) \approx T + Lw_s/c_p.$$

**Wet-bulb temperature,  $T_w$**  (i) The temperature of a parcel that has been isobarically cooled by evaporation until saturated. (ii) The temperature of a parcel that has first ascended dry adiabatically to its LCL, then descended moist (saturated) adiabatically to its original pressure.

**Wet-bulb potential temperature,  $\theta_w$**  (i) The temperature of a parcel that has first been isobarically cooled by evaporation until saturated, then descended moist (saturated) adiabatically to 1000 hPa. (ii) The temperature of a parcel that has first ascended dry adiabatically to its LCL, then descended moist (saturated) adiabatically to 1000 hPa.

**Liquid water mixing ratio,  $w_l$**  The mass of liquid water (droplets) per unit mass of dry air.

**Total water mixing ratio,  $w_t$**  The mass of water vapor plus liquid water (droplets) per unit mass of dry air:  $w_t = w + w_l$ .

During a *reversible* process, the *total water mixing ratio* ( $w_t = w + w_l$ ) in a parcel remains constant. During a *pseudo-adiabatic* process, any condensed water immediately falls out of the parcel (as precipitation) so that the *liquid water mixing ratio* ( $w_l$ ) is always zero.

Naturally occurring processes are usually neither exactly reversible nor pseudo-adiabatic, but somewhere in between: some, but not all, of the condensed water falls out of the parcel as precipitation so that the *liquid water mixing ratio* may be greater than zero, but the *total water mixing ratio* is reduced by the loss due to precipitation.

Given the *total water mixing ratio*, one can then determine the remaining unknown mixing ratios. We will assume that the parcel is either exactly saturated, or unsaturated with no liquid water. If a parcel is exactly saturated:  $w = w_s(T, p)$ , so  $w_l = w_t - w_s(T, p)$ . If a parcel is unsaturated with no liquid water:  $w_l = 0$ , so  $w = w_t$ .

## 5.8 Skew $T$ -log $p$ diagram

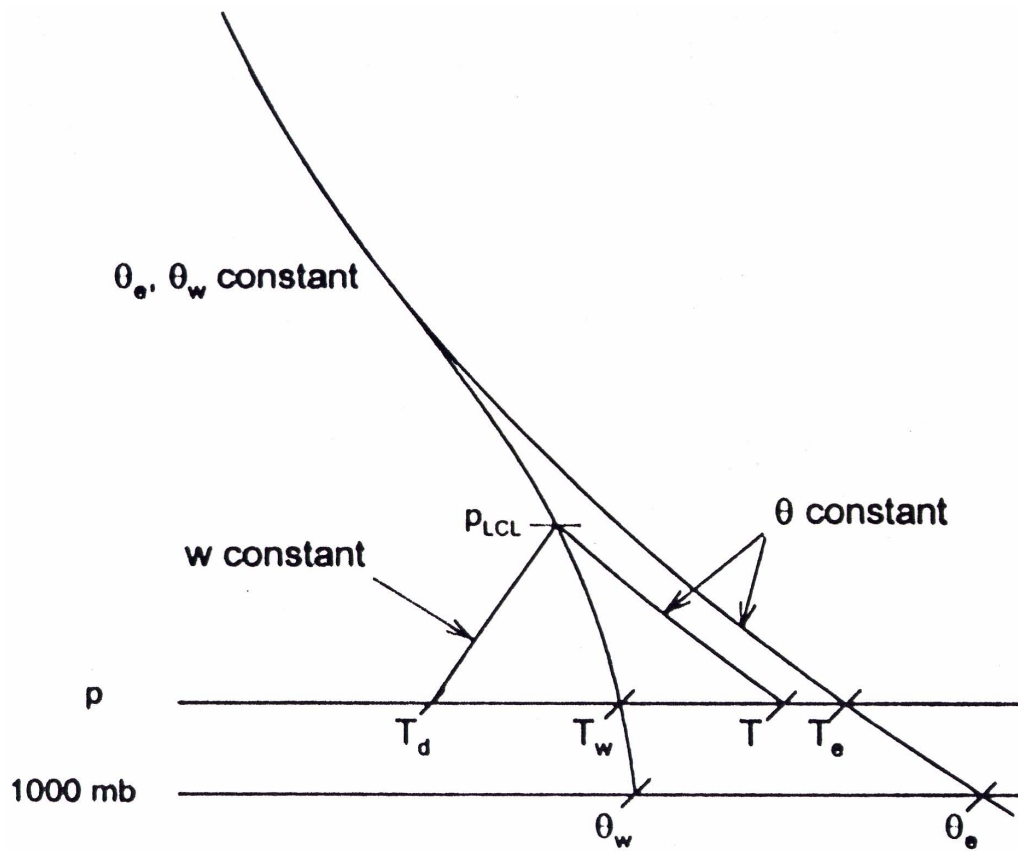


Figure 7: Depiction of thermodynamic variables and processes on a skew  $T$ -log  $p$  diagram (Bohren and Albrecht 1998).

## Graphical Operations

The most frequently evaluated quantities on the skew  $T$ - $\log p$  diagram are illustrated in Fig. 5-1. This is a part of a complete chart, with lines selected for evaluating several of the variables in the example that follows. Usage of the graph can be demonstrated with a parcel of air having pressure  $p = 900 \text{ mb} = 9\text{E}4 \text{ Pa}$ , temperature  $T = 15^\circ\text{C} = 288 \text{ K}$ , and relative humidity  $r = 50\%$ . These variables could be directly measured by the radiosonde. In the diagram in Fig. 5-1,  $p$  and  $T$  are represented by the doubly circled point A.

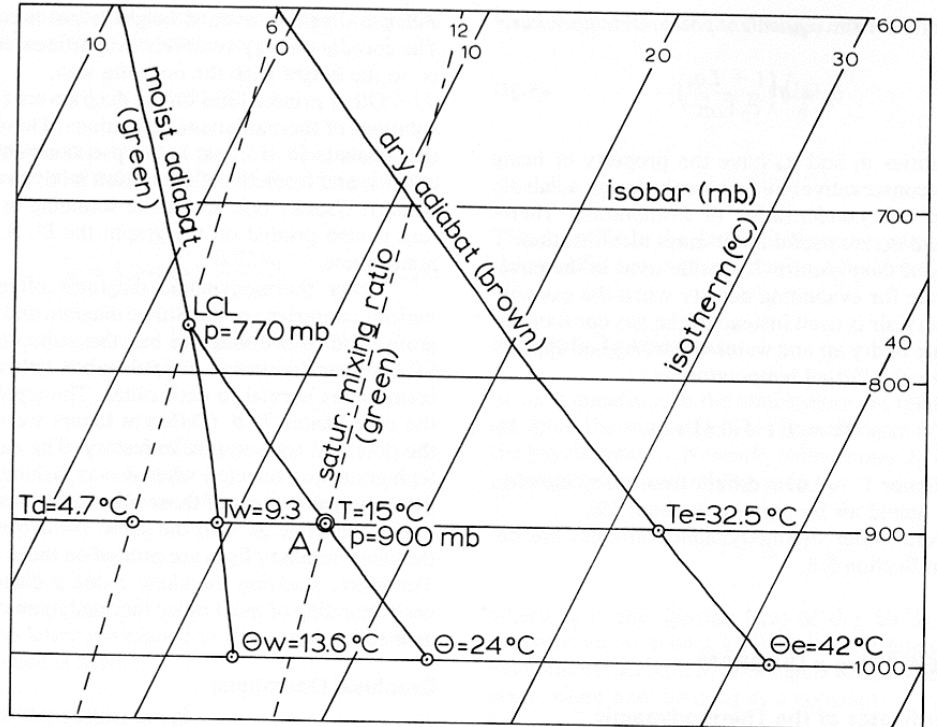
The quantities that follow can be evaluated using the diagram:

- The saturation mixing ratio  $w_s$  can be read directly from the chart using the printed isopleths of  $w_s$ . In original diagrams these lines are dashed and green. In our example we have  $w_s = 12 \text{ g kg}^{-1}$ . This ratio is a function of temperature and pressure. Units of  $\text{g kg}^{-1}$  are commonly used. In equations,  $w_s$  must be used as the original ratio. In this example,  $w_s = 0.012$ .
- The mixing ratio  $w$ , the ratio of densities of water vapor and dry air, is evaluated from the definition of relative humidity (5-4):

$$w = r w_s$$

In our example  $w = 6 \text{ g kg}^{-1}$ .

- The dew point  $T_d$  can be found at the same pressure (900 mb), but at the isopleth  $w_s = 6 \text{ g kg}^{-1}$ . This value is equal to 50% (observed relative humidity) of the evaluated mixing ratio. The dew point is the temperature where the current mixing ratio  $w$  becomes the saturation mixing ratio ( $w_s = w$ ).
- The potential temperature  $\theta$  is at the intersection of the dry adiabat through A and the isobar of 1000 mb. Here we have  $\theta = 24^\circ\text{C}$ . Potential temperature is commonly expressed in kelvins; therefore, here also  $\theta = 297 \text{ K}$ .
- The pressure at the lifting condensation level  $p_{\text{LCL}}$  is found at the intersection of the printed  $w_s$  isopleth for the evaluated  $w$  (that is  $w = 6 \text{ g kg}^{-1}$  in our example) and dry adiabat through A. In our example,  $p_{\text{LCL}}$  is at 770 mb.
- The wet-bulb temperature  $T_w$  is at the intersection of the moist adiabat through the point indicated as LCL and the isobar through A;  $T_w = 9.3^\circ\text{C}$ .



**FIGURE 5-1.** Evaluation of thermodynamic variables on a skew  $T$ - $\log p$  diagram. The observations of temperature and pressure are at A; other circled points show evaluated quantities.

- The wet-bulb potential temperature  $\theta_w$  is equal to  $T$  on the continuation of the moist adiabat through the LCL point to 1000 mb;  $\theta_w = 13.6^\circ\text{C}$ .
- The equivalent temperature  $T_e$  can be found by following the moist adiabat through LCL until very low values of temperature are found near the upper left corner of the complete chart, outside the domain shown in Fig. 5-1. There the wet adiabat becomes tangent to a dry adiabat. From there we follow that tangent dry adiabat to the original pressure of 900 mb. In this way we find  $T_e = 32.5^\circ\text{C}$ . The choice of printed adiabats and moist adiabats is such that the same values appear in both sets of lines. In this way, we may see which are the pairs of adiabats (one moist, one dry) that are tangent to each other, even if they touch outside of the printed diagram.
- The equivalent potential temperature  $\theta_e$  is on the same dry adiabat as  $T_e$ , but at 1000 mb. Therefore, in Fig. 5-1 we have  $\theta_e = 42^\circ\text{C} = 315 \text{ K}$ .



## 6 Hydrostatic Equilibrium

### 6.1 The hydrostatic equation

Up to this point we have dealt with the properties and physical processes of individual air parcels. Now we shall consider some aspects of the spatial distribution of these properties.

Thermodynamic variables in the atmosphere usually change more rapidly vertically than horizontally. Forces acting along the vertical include gravity. The acceleration of gravity,  $g$ , is approximately equal to  $9.8 \text{ m s}^{-2}$ . No downward acceleration of the atmosphere is observed so another force must balance gravity.

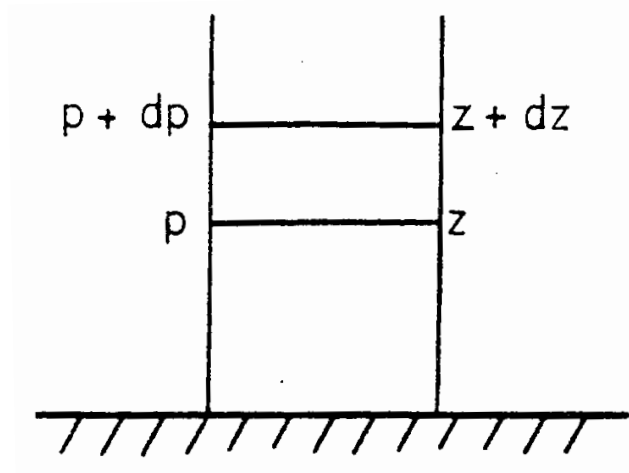


Figure 8: Change of pressure with height.

We know that pressure decreases with height in the atmosphere. Fig. 8 shows that over a small height interval  $dz$  the pressure changes by  $dp$  (negative). This pressure difference produces an upward directed force on the layer between heights  $z$  and  $z + dz$ . The force per unit volume is  $dp/dz$ , while the force per unit mass is  $\alpha dp/dz$ .

Observations show that the vertical pressure gradient force almost exactly balances gravity. This balance is called *hydrostatic equilibrium*. It is expressed by the *hydrostatic equation*:

$$\alpha \frac{dp}{dz} = -g \text{ or } \frac{dp}{dz} = -\rho g. \quad (33)$$

### 6.2 Height computations for upper-air soundings

Numerical weather prediction requires extensive information on the distribution of pressure, temperature, and water vapor in the upper atmosphere. An upper-air sounding is taken

by releasing a balloon carrying a *radiosonde*. This is an inexpensive instrument which measures pressure, temperature, and relative humidity and transmits radio signals to a ground station. Such soundings are taken at least twice a day at several hundred locations around the world.

To make these soundings useful, one must determine the heights at which the measurements are made. To do this one uses the hydrostatic equation,

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

We will use the hydrostatic equation in the form

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

To account for the effect of water vapor on density, we substitute for  $\rho$  from the equation of state for moist air to get

$$dz = -\frac{RT_v}{g} \frac{dp}{p}.$$

and integrate this differential equation between two heights  $z_1$  and  $z_2$  where the pressures are  $p_1$  and  $p_2$  to obtain

$$z_2 - z_1 = -\frac{R}{g} \int_{p_1}^{p_2} T_v \frac{dp}{p}.$$

One can always find a mean virtual temperature  $\bar{T}_v$  so that

$$\int_{p_1}^{p_2} T_v \frac{dp}{p} = \bar{T}_v \int_{p_1}^{p_2} \frac{dp}{p} = \bar{T}_v (\ln p_2 - \ln p_1) = \bar{T}_v \ln \frac{p_2}{p_1}.$$

Then

$$z_2 - z_1 = -\frac{R\bar{T}_v}{g} \ln \frac{p_2}{p_1}. \tag{34}$$

This is called the *hypso metric equation*. For dry air,  $T_v = T$ , so (34) becomes

$$z_2 - z_1 = -\frac{R\bar{T}}{g} \ln \frac{p_2}{p_1}. \tag{35}$$

### 6.3 The hydrostatics of special atmospheres

It is often useful to apply the hydrostatic equation to special cases of atmospheric structure. Two such cases are considered in this section. For these cases, we will assume that the air contains no water vapor.

### 6.3.1 The isothermal atmosphere

If the hydrostatic equation for dry air (35) is integrated from a level  $z_1$  with pressure  $p_1$  to a height  $z_2$  where the pressure is  $p_2$ , while assuming that the temperature  $T$  is constant, one obtains

$$p_2 = p_1 \exp\left(-\frac{z_2 - z_1}{H}\right), \quad (36)$$

where  $H \equiv RT/g$ .

### 6.3.2 The constant-lapse-rate atmosphere

In this case, we assume that temperature varies linearly between heights  $z_1$  and  $z_2$  where the temperatures are  $T_1$  and  $T_2$ . Then

$$T(z) = T_1 - \gamma(z - z_1)$$

where the *lapse rate*  $\gamma \equiv -dT/dz$  is a constant. Integrate the hydrostatic equation for dry air from  $z_1$  at pressure  $p_1$  to  $z_2$  at pressure  $p_2$  to obtain

$$p_2 = p_1 \left(\frac{T_2}{T_1}\right)^{\frac{g}{R\gamma}}. \quad (37)$$

### 6.3.3 The U. S. Standard Atmosphere

The U. S. Standard Atmosphere is meant to represent the average conditions over the United States at latitude 40°N. The following are the basic specifications of the U. S. Standard Atmosphere up to an altitude of 32 km:

1. The surface temperature is 15.0°C and the surface pressure is 1013.25 mb.
2. The air is assumed to be dry and to obey the ideal gas law.
3. The acceleration of gravity is assumed to be constant and equal to 9.80665 m s<sup>-2</sup>.
4. From sea level to 10.769 km the temperature decreases at a constant rate of 6.5 K km<sup>-1</sup>. This region is the troposphere.
5. From 10.769 km to 32 km the temperature is constant at -55.0°C. This region is the stratosphere.

The standard atmosphere is a combination of the two special cases already discussed: constant-lapse-rate and isothermal. Therefore, the pressure at any level can be computed from Eqs. (36) and (37). The calculated characteristics of this atmosphere are listed in Table 3.

Table 3: Properties of the U. S. Standard Atmosphere up to 20 km. (Hess 1959).

<i>Altitude</i> (km)	<i>Pressure</i> (mb)	<i>Temperature</i> (°C)	<i>Density</i> (kg m <sup>-3</sup> )
0	1013.25	15.0	1.226
1	898.71	8.5	1.112
2	794.90	2.0	1.007
3	700.99	-4.5	0.909
4	616.29	-11.0	0.819
5	540.07	-17.5	0.736
6	471.65	-24.0	0.660
7	410.46	-30.5	0.590
8	355.82	-37.0	0.525
9	307.24	-43.5	0.466
10	246.19	-50.0	0.413
(10.769)	(234.53)	(-55.0)	(0.375)
11	226.19	-55.0	0.361
12	193.38	-55.0	0.309
13	165.33	-55.0	0.264
14	141.35	-55.0	0.226
15	120.86	-55.0	0.193
16	103.30	-55.0	0.165
17	88.34	-55.0	0.141
18	75.53	-55.0	0.121
19	64.57	-55.0	0.103
20	55.21	-55.0	0.088

## 7 Hydrostatic Stability and Convection

### 7.1 The dry and moist adiabatic lapse rates

The criteria for stability involve the lapse rates for a parcel moving dry adiabatically and moist adiabatically. Therefore we will derive expressions for these lapse rates. In the following descriptions, a variable with an overbar is a property of the environment; a variable without an overbar is a property of the parcel.

The first law of thermodynamics is

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

for the parcel. The pressure change  $dp$  experienced by the parcel depends upon the environment. We assume that the pressure of the parcel is always the same as that of the environment, and that the environment is in hydrostatic equilibrium, so that

$$dp = d\bar{p} = -\frac{1}{\bar{\alpha}} g dz. \quad (38)$$

Use this in the first law to obtain

$$dh = c_p dT + \frac{\alpha}{\bar{\alpha}} g dz.$$

The ratio  $\alpha/\bar{\alpha} = T_v/\bar{T}_v$  is close to one, so that to a good approximation the first law of thermodynamics for a parcel in a hydrostatic environment is

$$dh = c_p dT + g dz. \quad (39)$$

#### 7.1.1 The dry-adiabatic lapse rate

Unsaturated air moving vertically changes state dry adiabatically. Therefore, we use the adiabatic form of Eq. (39):

$$0 = c_p dT + dz$$

to obtain the lapse rate for a dry-adiabatic process,

$$\Gamma_d \equiv -\frac{dT}{dz} = \frac{g}{c_p}.$$

The value of  $\Gamma_d$  for dry air is  $9.76 \text{ K km}^{-1}$ .

### 7.1.2 The saturation-adiabatic lapse rate

As saturated air ascends, heating due to condensation occurs. Therefore, we use Eq. (39) with  $dh = -Ldw_s$ :

$$-L dw_s = c_p dT + g dz. \quad (40)$$

Expand  $dw_s$  to make its dependence on  $dp$  and  $dT$  explicit:

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

Substitute this into (40), substitute for  $dp$  from (38), divide the result by  $c_p dz$ , and assume that  $\alpha/\bar{\alpha} \approx 1$  to obtain:

$$-\frac{L}{c_p} \left[ - \left( \frac{\partial w_s}{\partial p} \right)_T \rho g + \left( \frac{\partial w_s}{\partial T} \right)_p \frac{dT}{dz} \right] = \frac{dT}{dz} + \frac{g}{c_p}.$$

Then solve for  $dT/dz$  to obtain the lapse rate for a saturation-adiabatic process,

$$\Gamma_s \equiv -\frac{dT}{dz} = \frac{g}{c_p} \frac{1 - \rho L \left( \frac{\partial w_s}{\partial p} \right)_T}{1 + \frac{L}{c_p} \left( \frac{\partial w_s}{\partial T} \right)_p}. \quad (41)$$

Equation (41) may be rewritten in terms of  $w_s$  by using the approximation

$$w_s \approx \epsilon \frac{e_s}{p}$$

and the *Clausius-Clapeyron equation*,

$$\frac{de_s}{dT} = \frac{m_v L e_s}{R^* T^2}.$$

The result is

$$\Gamma_s \equiv -\frac{dT}{dz} = \frac{g}{c_p} \frac{1 + \frac{L}{R} \frac{w_s}{T}}{1 + \frac{\epsilon L^2}{c_p R} \frac{w_s}{T^2}}.$$

Note that  $\Gamma_s$  is not a constant, but is equal to  $\Gamma_d$  multiplied by a factor that depends on temperature and pressure. Values of  $\Gamma_s$  for various pressures and temperatures are given in Table 4.

Table 4: Values of the saturated pseudoadiabatic lapse rate in  $\text{K km}^{-1}$  calculated from Eq. (41) for saturation with respect to water (Hess 1959).

$T$ ( $^{\circ}\text{C}$ )	$P$ (mb)		
	1000	700	500
-30	9.2	9.0	8.7
-20	8.6	8.2	7.8
-10	7.7	7.1	6.4
0	6.5	5.8	5.1
+10	5.3	4.6	4.0
+20	4.3	3.7	3.3

## 7.2 Stability criteria: The parcel method

If a parcel of air is displaced from its initial position in an atmosphere in hydrostatic balance, the parcel's resulting motion determines the atmospheric *stability* at that location. If the parcel moves further away from its initial position, then the atmosphere is *unstable*. If the parcel returns towards its initial position, then the atmosphere is *stable*. If the parcel does not move, then the atmosphere is *neutral*.

We will use the equation for the vertical acceleration of an air parcel to calculate a displaced parcel's velocity and height as a function of time. In the following description, a variable with an overbar is a property of the environment; a variable without an overbar is a property of the parcel.

We assume that the environment of the parcel is in hydrostatic equilibrium:

$$\frac{d\bar{w}}{dt} = -g - \bar{\alpha} \frac{d\bar{p}}{dz} = 0.$$

The parcel itself will have a specific volume  $\alpha$  and an acceleration  $dw/dt$ . We assume that the pressure of the parcel is the same as that of its environment so that

$$\frac{dw}{dt} = -g - \alpha \frac{d\bar{p}}{dz}.$$

We use the hydrostatic equation to eliminate  $d\bar{p}/dz$  from this equation:

$$\frac{dw}{dt} = g \frac{\alpha - \bar{\alpha}}{\bar{\alpha}}.$$

The right hand side is called the *buoyancy* and is due to the difference in specific volume (or density) between the parcel and the environment. Substitute for  $\alpha$  and  $\bar{\alpha}$  from the

equation of state for dry air,  $p\alpha = RT$ , (for simplicity, we ignore the effect of water vapor on density) to obtain

$$\frac{dw}{dt} = g \frac{T - \bar{T}}{\bar{T}}. \quad (42)$$

Let  $z = 0$  denote the parcel's equilibrium location. Then at  $z = 0$ ,  $T = \bar{T}$ , and  $dw/dt = 0$ . Assume that the temperature in the environment varies linearly with height. Then the temperature at any height  $z$  in the environment is

$$\bar{T}(z) = \bar{T}(0) - \gamma z,$$

where  $\gamma = -d\bar{T}/dz$  is the *environmental lapse rate*. Similarly, the parcel temperature at any height  $z$  is

$$T(z) = T(0) - \Gamma_d z = \bar{T}(0) - \Gamma z,$$

where  $\Gamma = -dT/dz$  is the *parcel lapse rate*. When these expressions are substituted in Eq. (42), we obtain

$$\frac{dw}{dt} = \frac{g}{\bar{T}(0) - \gamma z} (\gamma - \Gamma) z \approx \frac{g}{\bar{T}(0)} (\gamma - \Gamma) z = bz. \quad (43)$$

Eq. (43) describes how  $w$  changes with time. By definition,

$$\frac{dz}{dt} = w. \quad (44)$$

Eqs. (43) and (44) are coupled linear differential equations which are easy to solve analytically for  $z(t)$ . If the coefficient  $b$  in Eq. (43) is negative (i.e.,  $\gamma < \Gamma$ ), the solution  $z(t)$  is sinusoidal. The parcel will oscillate about its original position with period

$$\tau = \frac{2\pi}{\sqrt{-b}} = \frac{2\pi}{\sqrt{\frac{g}{\bar{T}(0)}(\Gamma - \gamma)}}. \quad (45)$$

The atmosphere is thus stable in this case. If the coefficient  $b$  is positive (i.e.,  $\gamma > \Gamma$ ), the solution  $z(t)$  is exponentially increasing, and the atmosphere is unstable. If  $b = 0$  (i.e.,  $\gamma = \Gamma$ ), the atmosphere is neutral.

Recall that for unsaturated air,  $\Gamma = \Gamma_d$ , while for saturated air,  $\Gamma = \Gamma_s$ . Because  $\Gamma_s < \Gamma_d$ , the atmosphere can have five responses with respect to parcel displacement in an atmospheric layer of lapse rate  $\gamma$ . The atmosphere is said to be:

<i>absolutely stable</i> if	$\gamma < \Gamma_s$ ,
<i>saturated neutral</i> if	$\gamma = \Gamma_s$ ,
<i>conditionally unstable</i> if	$\Gamma_s < \gamma < \Gamma_d$ ,
<i>dry neutral</i> if	$\gamma = \Gamma_d$ ,
<i>absolutely unstable</i> if	$\gamma > \Gamma_d$ .



### 7.3 Convective Available Potential Energy (CAPE)

Suppose the atmosphere is conditionally unstable (i.e.,  $\Gamma_s < \gamma < \Gamma_d$ ). An initially unsaturated parcel will be stable to *small* upward displacements. If the parcel's lifting condensation level (LCL) is reached, the parcel lapse rate becomes  $\Gamma_s$ . If the parcel is lifted further, it will become positively buoyant at its *level of free convection* (LFC). Thus the parcel is unstable to *large* upward displacements. Above the LFC, the parcel will eventually become negatively buoyant at its *level of neutral buoyancy* (LNB). The parcel will overshoot, then oscillate about this level.

*Convective Available Potential Energy* (CAPE) is proportional to the area between a sounding and the parcel's temperature plotted on a skew  $T$ -log  $p$  diagram. CAPE depends on the parcel properties, which in turn depend on the parcel's originating level. Thus,

$$\text{CAPE}_i \equiv \int_{z_i}^{\text{LNB}} g \frac{T - \bar{T}}{\bar{T}} dz = \int_{p_n}^{p_i} R(T - \bar{T}) d \ln p,$$

where  $z_i$  is the parcel's initial height,  $p_i$  its initial pressure, and  $p_n$  the pressure at the LNB.

We can also define *negative area* (NA) and *positive area* (PA):

$$\text{NA}_i \equiv - \int_{p_f}^{p_i} R(T - \bar{T}) d \ln p,$$

$$\text{PA}_i \equiv \int_{p_n}^{p_f} R(T - \bar{T}) d \ln p,$$

so

$$\text{CAPE}_i = \text{PA}_i - \text{NA}_i.$$

Here,  $p_f$  is the pressure at the LFC.

The negative area is the amount of vertical kinetic energy per unit mass required for a parcel to reach the LFC from  $z_i$ . In this case,  $w_f = 0$  and  $w_i^2/2 = \text{NA}_i$ . The positive area is the amount of vertical kinetic energy per unit mass that is acquired by the parcel as it ascends from the LFC to LNB. If  $w_{\text{LFC}} = 0$ , then  $w_n^2/2 = \text{PA}_i$ . In particular, the maximum updraft speed (which is attained at the LNB) is then just

$$w_n = \sqrt{2\text{PA}_i}.$$

*Exercise.* Derive  $\text{CAPE}_i$  from (42).

## Useful Constants

$$0\text{ }^{\circ}\text{C} = 273.15\text{ K}$$

$$R^* = 8.31\text{ J mol}^{-1}\text{ K}^{-1}\text{ (universal gas constant)}$$

$$R = R_d = c_p - c_v = 287\text{ J kg}^{-1}\text{ K}^{-1}\text{ (gas constant for dry air)}$$

$$m_v = 18.02\text{ g mol}^{-1}\text{ (molecular weight of water vapor)}$$

$$m_d = 28.97\text{ g mol}^{-1}\text{ (mean molecular weight of dry air)}$$

$$\epsilon \equiv m_v/m_d = 0.622$$

$$g = 9.81\text{ m s}^{-2}\text{ (acceleration of gravity)}$$

$$c_p = 1004\text{ J kg}^{-1}\text{ K}^{-1}\text{ (specific heat at constant pressure for dry air)}$$

$$c_v = 717\text{ J kg}^{-1}\text{ K}^{-1}\text{ (specific heat at constant volume for dry air)}$$

$$L_e = 2.5 \times 10^6\text{ J kg}^{-1}\text{ (latent heat of evaporation)}$$

$$L_m = 0.334 \times 10^6\text{ J kg}^{-1}\text{ (latent heat of melting)}$$

$$L_s = 2.834 \times 10^6\text{ J kg}^{-1}\text{ (latent heat of sublimation)}$$

$$\rho = 1.2\text{ kg m}^{-3}\text{ (density of air near sea level)}$$

$$1\text{ mb} = 100\text{ Pa}$$