CHAPTER I

REVIEW OF BASIC CONCEPTS AND SYSTEMS OF UNITS

1.1. Systems

Every portion of matter, the study of whose properties, interaction with other bodies, and evolution is undertaken from a thermodynamical point of view, is called a *system*. Once a system is defined, all the material environment with which it may eventually interact is called its *surroundings*.

Systems may be *open* or *closed*, depending on whether they do or do not exchange matter with their surroundings. A closed system is said to be *isolated* if it obeys the condition of not exchanging any kind of energy with its surroundings.

The systems in Atmospheric Thermodynamics will be portions of air undergoing transformations in the atmosphere. They are obviously open systems. They will be treated, however, as closed systems for the sake of simplicity; this is legitimate insofar as we may consider volumes large enough to neglect the mixture of the external layers with the surroundings. Or we may consider, which is equivalent, small portions typical of a much larger mass in which they are imbedded; provided we are taking a constant mass for our portion (e.g. the unit mass), any exchange with the surroundings will not affect our system, as the surroundings have the same properties as itself. This approximation is good for many purposes but it breaks down when the whole large air mass considered becomes modified by exchanges with the surroundings. This may happen, due to turbulent mixing, in convective processes that we shall consider later on; this is made visible, for instance, when ascending turrets from a cumulus cloud become thinner throughout their volume and finally disappear by evaporation of the water droplets.

1.2. Properties

The complete description of a system at a certain instant is given by that of its properties, that is by the values of all the physical variables that express those properties. For a closed system, it is understood that the mass, as well as the chemical composition, define the system itself; the rest of the properties define its *state*.

Properties are referred to as *extensive*, if they depend on the mass, or as *intensive*, if they do not. Intensive properties can be defined for every point of the system; specific properties (extensive properties referred to unit mass or unit volume) among others, are intensive properties. We shall use, with some exceptions, capital letters for extensive properties and for specific properties when they are referred to one mole :

V (volume), U (internal energy), etc.; and small letters for specific properties referred to an universal unit of mass: v (specific volume), u (specific internal energy), etc. The same criterion will be followed with the work and the heat received by the system from external sources: A, a and Q, q, respectively. m for mass and T for temperature will be exceptions to this convention.

1.3. Composition and State of a System

If every intensive variable has the same value for every point of the system, the system is said to be *homogeneous*. Taking different portions of a homogeneous system, their values for any extensive property Z will be proportional to their masses:

$$Z = mz$$

where z is the corresponding specific property.

If there are several portions or sets of portions, each of them homogeneous, but different from one another, each homogeneous portion or set of portions is called a *phase* of the system, and the system is said to be *heterogeneous*.

For a heterogeneous system

$$Z = \sum_{\alpha} m_{\alpha} z_{\alpha}$$

where the sum is extended over all the phases.

We shall not consider, unless otherwise stated, certain properties that depend on the shape or extension of the separation surfaces between phases, or 'interfaces'. Such is the case, for instance, of the vapor pressure of small droplets, which depends on their curvature or, given a certain mass, on its state of subdivision; this is an important subject in microphysics of clouds.

It may also happen that the values of intensive properties change in a continuous way from one point to another. In that case the system is said to be *inhomogeneous*. The atmosphere, if considered in an appreciable thickness, is an example, as the pressure varies continuously with height.

1.4. Equilibrium

The state of a system placed in a given environment may or may not remain constant with time. If it varies, we say that the system is not in equilibrium. Independence of time is therefore a necessary condition in defining equilibrium; but it is not sufficient.

Stationary states have properties which by definition are independent of time. Such would be the case, for instance, of an electrical resistance losing to its surroundings an amount of heat per unit time equivalent to the electrical work received from an external source. We do not include these cases, however, in the definition of equilibrium. They may be excluded by making the previous criterion more stringent: the constancy of properties with time should hold for every portion of the system, even if we isolate it from the rest of the system and from the surroundings.

The criterion would provide a definition including certain states of *unstable* and of *metastable* equilibria. An example of unstable equilibrium is that which may exist between small droplets and their vapor, when this is kept at a constant pressure. It may be shown that if a droplet either grows slightly by condensation or slightly reduces its size by evaporation, it must continue doing so, thereby getting farther and farther away from equilibrium. A small fluctuation of the vapor pressure around the droplet could thus be enough to destroy the state of equilibrium in this case.

Examples of metastable equilibria are supercooled water in mechanical and thermal equilibrium (see Section 5) with its surroundings or a mixture of hydrogen and oxygen in similar conditions, at room temperature. In the first example, the freezing of a very small portion of water or the introduction of a small ice crystal will lead to the freezing of the whole mass. In the second one, a spark or the presence of a small amount of catalyst will be enough to cause an explosive chemical reaction throughout the system. These two systems, therefore, were in equilibrium with respect to small changes in temperature, pressure, etc. but not with respect to freezing in one case and to chemical reaction in the other. They did not change before our perturbations because of reasons which escape a purely thermodynamic consideration and which should be treated kinetically; for the molecular process to occur, an energy barrier had to be overcome. The initial ice crystal or the catalyst provide paths through which this barrier is lowered enough to allow a faster process.

We might exclude unstable and metastable cases from the definition, if we add the condition that if means are found to cause a small variation in the system, this will not lead to a general change in its properties. If this is true for whatever changes we can imagine we have a *stable* or *true thermodynamic equilibrium*. This is better treated with the help of the Second Principle, which, by considering imaginary or 'virtual' displacements of the values of the variables, provides a suitable rigorous criterion to test an equilibrium state (cf. Chapter III).

The lack of equilibrium can manifest itself in mechanical changes, in chemical reactions or changes of physical state, or in changes in the thermal state. In that sense we speak of mechanical, chemical, or thermal equilibrium. The pressure characterizes the mechanical equilibrium. Thermal equilibrium will be considered in the following section, and chemical equilibrium in Chapter IV.

1.5. Temperature. Temperature Scales

Experience shows that the thermal state of a system may be influenced by the proximity of, or contact with, external bodies. In that case we speak of *diathermic* walls separating the system from these bodies. Certain walls or enclosures prevent this influence; they are called *adiabatic*.

If an adiabatic enclosure contains two bodies in contact or separated by a diathermic wall, their properties will in general change towards a final state, reached after a long enough period of time, in which the properties remain constant. They are then said to be in thermal equilibrium. It is a fact of experience that if a body A is in thermal equilibrium with a body B, and B is in its turn in thermal equilibrium with C, A and C are also in thermal equilibrium (the transitive property, sometimes called the 'zeroth principle' of Thermodynamics).

All the bodies that are in thermal equilibrium with a chosen reference body in a well defined state have, for that very reason, a common property. It is said that they have the same *temperature*. The reference body may be called a *thermometer*. In order to assign a number to that property for each different thermal state, it is necessary to define a *temperature scale*. This is done by choosing a thermometric substance and a thermometric property X of this substance which bears a one-to-one relation to its possible thermal states. The use of the thermometer made out of this substance and the measurement of the property X permits the specification of the thermal states of systems in thermal equilibrium with the thermometer by values given by an arbitrary relation, such as

$$T = cX \tag{1}$$

or

$$t = aX + b\,. \tag{2}$$

The thermometer must be much smaller than the system, so that by bringing it into thermal equilibrium with the system, the latter is not disturbed. We may in this way define *empirical scales* of temperature. Table I-1 gives the most usual thermometric substances and properties.

TABLE I-1

Empirical scales of temperature

Thermometric substance	Thermometric property X
Gas, at constant volume	Pressure
Gas, at constant pressure	Specific volume
Thermocouple, at constant pressure and tension	Electromotive force
Pt wire, at constant pressure and tension	Electrical resistance
Hg, at constant pressure	Specific volume

The use of a scale defined by Equation (2) requires the choice of two well-defined thermal states as 'fixed points', in order to determine the constants a and b. These had conventionally been chosen to be the equilibrium (air-saturated water)-ice (assigned value $t=0$) and water-water vapor (assigned value $t=100$), both at one atmosphere pressure. Equation (1) requires only one fixed point to determine the constant c, and this is chosen now as the triple point of water, viz. the thermal state in which the equilibrium ice-water-water vapor exists.

The different empirical scales do not coincide and do not bear any simple relation with each other. However, the gas thermometers (first two examples in Table I-1) can be used to define a more general scale; for instance, taking the first case, pressures can be measured for a given volume and decreasing mass of gas. As the mass tends to 0, the pressures tend to 0, but the ratio of pressures for two thermal states tend to a finite value. Equation (1), applied to any state and to the triple point, would give $T = T_t(p/p_1)$; we now modify the definition so that

$$T = T_t \lim_{p \to 0} \frac{p}{p_t} \tag{3}$$

where the subscript t refers to the triple point as standard state. The temperature thus defined is independent of the nature of the gas. This universal scale is the *absolute temperature scale of ideal gases*. The choice of T_t is arbitrary; in order to preserve the values assigned to the fixed points in the previous scales, it is set to $T_t = 273.16\,\mathrm{K}$. Here the symbol K stands for *kelvin*, the temperature unit in this scale (referred to as *degree Kelvin* prior to 1967).

The two fixed points mentioned above in connection with formula (2) have the values $T_0 = 273.15\,\mathrm{K}$ and $T_{100} = 373.15\,\mathrm{K}$. Another scale, the Celsius temperature, is now defined by reference to the previous one through the formula

$$t = T - 273.15 \tag{4}$$

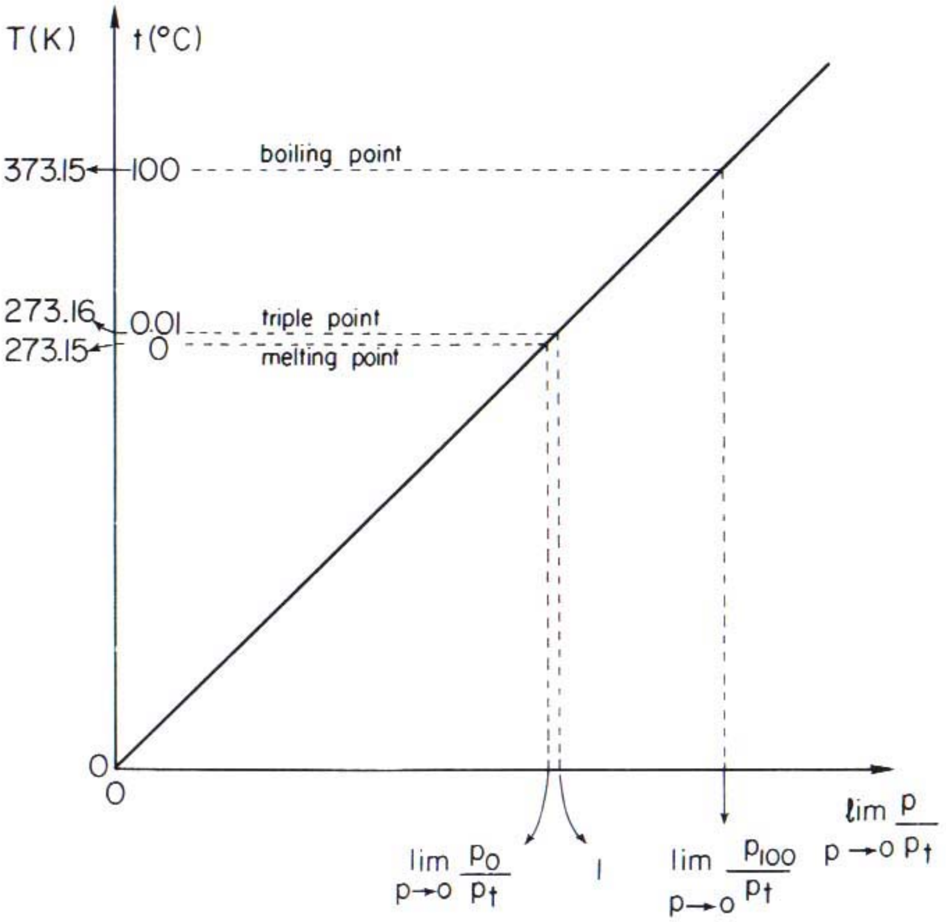

Fig. I-1. Temperature scales.

so that the two fixed points have in this scale the values $t_0 = 0\,°\text{C}$, $t_{100} = 100\,°\text{C}$. The symbol °C stands for *degrees Celsius*. The relation between both scales is represented schematically in Figure I-1.

The absolute gas scale is defined for the range of thermal states in which gases can exist. This goes down to 1 K (He at low pressure). The Second Principle allows the introduction of a new scale, independent of the nature of the thermodynamic system used as a thermometer, which extends to any possible thermal states and coincides with the gas scale in all its range of validity. This is called the *absolute thermodynamic* or *Kelvin* scale of temperature (Chapter III, Section 2).

The Fahrenheit scale, t_F (in degrees Fahrenheit, °F), is defined by

$$t_F = \tfrac{9}{5}t + 32\,.$$

1.6. Systems of Units

The current systems of units for mechanical quantities are based on the choice of particular units for three fundamental quantities: length, mass, and time.

The choice of the 'MKS system' is: *metre* (m), *kilogramme* (kg) and *second* (s). The metre is defined as 1 650 763.73 wavelengths in vacuum of the orange-red line of the spectrum of krypton-86. The kilogramme is the mass of a standard body (kilogramme prototype) of Pt-Ir alloy kept by the International Bureau of Weights and Measures at Paris. The second is the duration of 9 192 631 770 cycles of the radiation associated with a specified transition of Cs^{133}. The International System of Units ('SI-Units'), established by the Conférence Générale des Poids et Mesures in 1960, adopts the MKS mechanical units and the kelvin for thermodynamic temperature.

The 'cgs system', which has a long tradition of application in Physics, uses *centimetre* (cm), *gramme* (g) and *second*, the two first being the corresponding submultiples of the previous units for length and mass.

Units for the other mechanical quantities derive from the basic ones. Some of them receive special denominations. A selection is given in Table I-2.

A third system of units, whose use was recommended at one time (International Meteorological Conference, 1911) but is now of historical significance only, is the mts, with metre, tonne (t) (1 t = 1000 kg) and second as basic units. The pressure unit in this system is the centibar (cbar): 1 cbar = 10^4 μbar.

Other units, not recommended in these systems, find frequent use and must also be mentioned. Thus we have for pressure:

Bar (bar): $1\ \text{bar} = 10^6\ \mu\text{bar} = 10^5\ \text{Pa}$
Millibar (mb): $1\ \text{mb} = 10^3\ \mu\text{bar} = 10^2\ \text{Pa}$
Torricelli or mm Hg (torr): $1\ \text{torr} = 133.322\ \text{Pa}$
Atmosphere (atm): $1\ \text{atm} = 1.01325\ \text{bar} = 760\ \text{torr} = 1.01325 \times 10^5\ \text{Pa}$
Pounds per square inch (p.s.i.): $1\ \text{p.s.i.} = 6894.76\ \text{Pa}$

The equivalence from atmosphere to bar is now the definition of the former, chosen

TABLE I-2

Derived mechanical units

Physical quantity	Unit	
	SI(MKS System)	cgs-system
Acceleration	m s^{-2}	cm s^{-2}
Density	kg m^{-3}	g cm^{-3}
Force	newton (N) N = kg m s^{-2}	dyne (dyn) dyn = g cm s^{-2}
Pressure	pascal (Pa) Pa = N m^{-2} = kg m^{-1} s^{-2}	microbar or barye (μbar) μbar = dyn cm^{-2} = g cm^{-1} s^{-2}
Energy	joule (J) J = N m = kg m^2 s^{-2}	erg (erg) erg = dyn cm = g cm^2 s^{-2}
Specific energy	J kg^{-1} = m^2 s^{-2}	erg g^{-1} = cm^2 s^{-2}

in such a way as to be consistent with the original definition in terms of the pressure exerted by 760 mm of mercury at 0°C and standard gravity $g_0 = 9.80665$ m s^{-2}.

The millibar is the unit which has been used most commonly in Meteorology. The listing of pressure equivalents shows that a convenient true SI unit would be the hectopascal (hPa), identically equal to a millibar. This is the pressure unit being adopted by ICAO (International Civil Aviation Organisation), effective from 26 November 1981.

Historically, an important unit for energy has been the *calorie* or *gramme calorie* (cal). Classically, it was defined as the heat necessary to raise by 1 K the temperature of one gramme of water at 15°C (cf. Chapter II, Section 2); 1 cal_{15} = 4.1855 J. Sometimes its multiple *kilocalorie* or *kilogramme calorie* (kcal or Cal) is used. Other definitions giving slightly different equivalences are:

International Steam Table calorie: (IT cal) 1 IT cal = 4.1868 J
Thermochemical calorie (TC cal): 1 TC cal = 4.1840 J.

The international calorie was introduced in Engineering, in connection with the properties of water substance. The thermochemical calorie was agreed upon by physical chemists, and defined exactly by the previous equivalence. Meteorologists have generally used the IT cal. However, the fundamental SI energy unit is the joule, and scientists are encouraged to avoid the use of calorie (or, as a minimum, to quote the conversion factor to joules whenever calories have had to be employed). Since the meteorological literature, and even textbooks in this area, still prefer to maintain the 'abandoned' unit (calorie), we have adopted a rather ambivalent stance in this book, and have frequently employed the symbol *cal* to denote an energy unit of 4.1868 J.

Finally, we must mention a rational chemical mass unit: the *mole* (mol). It is defined as the amount of substance of a system which contains as many elementary units (molecules, atoms, ions or electrons, as the case may be) as there are C atoms in exactly 12 g of C^{12}. It is equal to the formula mass taken in g. This 'unified definition' is slightly different from the older 'physical scale' which assigned the value 16 (exactly) to the atomic mass of O^{16} and the 'chemical scale', which assigned the same value to the natural mixture of isotopes of O.

1.7. Work of Expansion

If a system is not in mechanical equilibrium with its surroundings, it will expand or contract. Let us assume that S is the surface of our system, which expands infinitesimally to S' in the direction ds (Figure I-2). The element of surface dσ has performed against the external pressure p the work

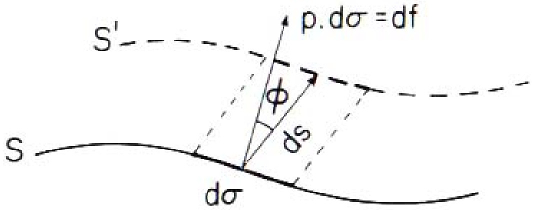

Fig. I-2. Work of expansion.

$$(\mathrm{d}W)_{\mathrm{d}\sigma} = p\,\mathrm{d}\sigma\,\mathrm{d}s\cos\varphi = p(\mathrm{d}V)_{\mathrm{d}\sigma} \tag{5}$$

where $(\mathrm{d}V)_{\mathrm{d}\sigma}$ is the volume element given by the cylinder swept by dσ. If the pressure exerted by the surroundings over the system is constant over all its surface S, we can integrate for the whole system to

$$\mathrm{d}W = p\int(\mathrm{d}V)_{\mathrm{d}\sigma} = p\,\mathrm{d}V \tag{6}$$

$\mathrm{d}V$ being the whole change in volume.

For a finite expansion,

$$W = \int_{\mathrm{i}}^{\mathrm{f}} p\,\mathrm{d}V \tag{7}$$

where i, f stand for initial and final states. And for a cycle (see Figure I-3):

$$W = \oint p\,\mathrm{d}V = \left(\int_{\mathrm{a}}^{\mathrm{b}} p\,\mathrm{d}V\right)_1 - \left(\int_{\mathrm{a}}^{\mathrm{b}} p\,\mathrm{d}V\right)_2 \tag{8}$$

positive if described in the clockwise sense. This is the area enclosed by the trajectory in the graph.

The work of expansion is the only kind of work that we shall consider in our atmospheric systems.

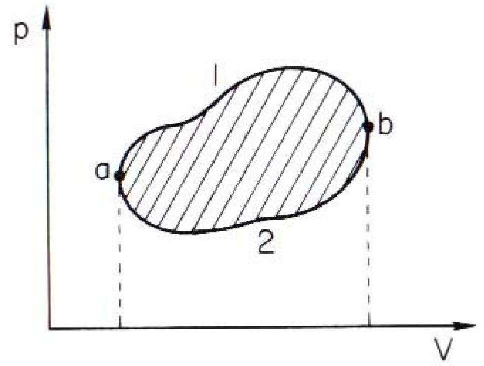

Fig. I-3. Work of expansion in a cycle.

1.8. Modifications and Processes. Reversibility

We shall call a *modification* or a *change* in a given system any difference produced in its state, independent of what the intermediate stages have been. The change is therefore entirely defined by the initial and final states.

By *process* we shall understand the whole series of stages through which the system passes when it undergoes a change.

Thermodynamics gives particular consideration to a very special, idealized type of

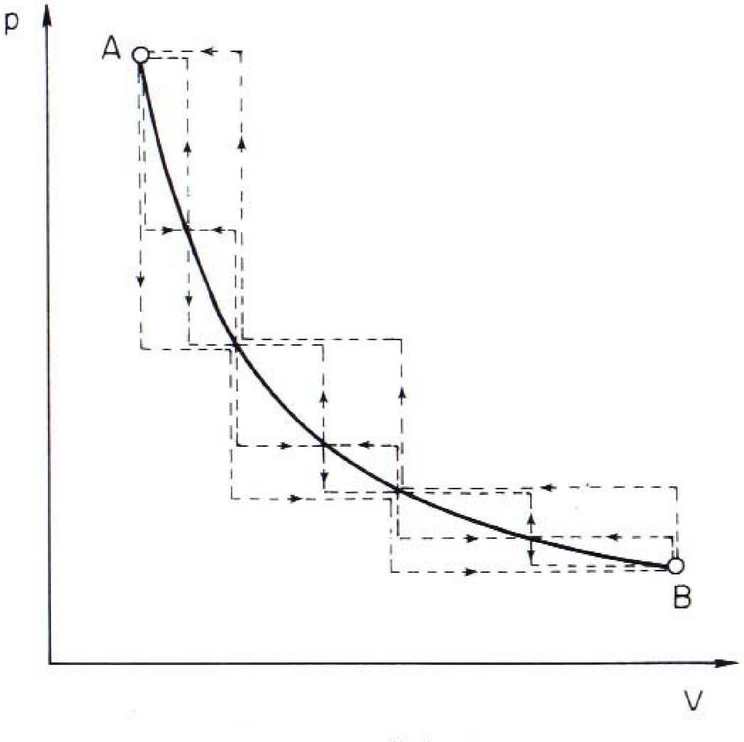

Fig. I-4. Reversible process as a limit of irreversible processes.

processes: those along which, at any moment, conditions differ from equilibrium by an infinitesimal in the values of the state variables. These are called *reversible* or *quasi-static* processes*. As an example, we may consider the isothermal expansion or compression of a gas (Figure I-4). The curve AB represents the reversible process, which appears as a common limit to the expansion or the compression as they might be performed through real processes consisting in increasing or decreasing the pressure by finite differences (zigzag trajectories). In this graph p is the external pressure exerted over the gas. The internal pressure is only defined for equilibrium states over the continuous curve AB, and in that case is equal to the external pressure.

1.9. State Variables and State Functions. Equation of State

Of all the physical variables that describe the state of a system, only some are independent. For homogeneous systems of constant composition (no chemical reactions), if we do not count the mass (which may be considered as a part of the definition of the system), only two variables are independent. These can be chosen among many properties; it is customary to choose them among pressure, volume and temperature, as readily measured properties. They are called *state* variables. All the other properties will depend on the state defined by the two independent variables, and are therefore called *state functions*. Between state variables and state functions there is no difference other than the custom of choosing the independent variables among the former.**

The equation for homogeneous systems

$$f(p, V, T) = 0$$

relating the three variables, p, V, T (two of them independent) is called the equation of state.

1.10. Equation of State for Gases

The equation of state that defines the ideal behavior for gases is

$$pV = nR^*T = mR^*T/M = mRT \tag{9}$$

where n = number of moles, M = molecular weight, R^* is the universal gas constant and $R = R^*/M$ is the specific gas constant.

$$\begin{aligned} R^* &= 8.3143 \text{ J mol}^{-1}\text{K}^{-1} \\ &= 1.986 \text{ cal mol}^{-1}\text{K}^{-1}. \end{aligned}$$

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* These two terms are not always used as synonymous.

** It should be remarked, however, that the *thermodynamic* functions (internal energy, entropy and derived functions) differ in one fundamental aspect from the others in that their definitions contain an arbitrary additive constant. They are not really point (state) functions, but functions of pairs of points (pairs of states) (cf. following chapters).

The equation can also be written (introducing the density, ϱ) as

$$pv = \frac{p}{\varrho} = RT. \tag{10}$$

The behavior of real gases can be described by a number of empirical or semi-empirical equations of state. We shall only mention the equation of van der Waals:

$$\left(p + \frac{a}{V^2}\right)(V - b) = R^*T \quad (1\ \text{mol}) \tag{11}$$

where a and b are specific constants for each gas, and the equation of Kammerlingh-Onnes, which allows a better approximation to experimental data by representing pV as a power series in p:

$$\begin{aligned} pV &= A + Bp + Cp^2 + Dp^3 + \ldots \\ &= A(1 + B'p + C'p^2 + D'p^3 + \ldots) \quad (1\ \text{mol}). \end{aligned} \tag{12}$$

A, B, C, ... are called the virial coefficients and are functions of the temperature. The first virial coefficient is $A = R^*T$ for all gases, as it is the value of pV for $p \to 0$. The other coefficients are specific for each gas. For instance, we have for N_2 the values indicated in Table I-3.

TABLE I-3

Virial coefficients for N_2

T(K)	$B'(10^{-3}\ \text{atm}^{-1})$	$C'(10^{-6}\ \text{atm}^{-2})$	$D'(10^{-9}\ \text{atm}^{-3})$	pV/R^*T ($p = 1$ atm)
200	− 2.125	− 0.0801	+ 57.27	0.9979
300	− 0.183	+ 2.08	+ 2.98	0.9998

It may be seen that for pressures up to 1 atm and in this range of temperature, only the first correction term (second virial coefficient) needs to be considered.

1.11. Mixture of Ideal Gases

In a mixture of gases, the partial pressure p_i of the ith gas is defined as the pressure that it would have if the same mass existed alone at the same temperature and occupying the same volume. Similarly, the partial volume V_i is the volume that the same mass of ith gas would occupy, existing alone at the same pressure and temperature*. Dalton's law for a mixture of ideal gases may be expressed by

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* This definition of partial volume, valid for ideal gases, would not be the proper one for real gases. The general rigorous definition of partial extensive properties, including the volume (e.g., the *partial molar* volume and the *partial specific* volume), will be considered in Chapter IV.

$$p = \sum p_i \tag{13}$$

where p is the total pressure and the sum is extended over all gases in the mixture, or by

$$V = \sum V_i \tag{14}$$

where V is the total volume.

For each gas

$$p_i V = n_i R^* T = m_i R_i T\,;$$
$$M_i = \frac{m_i}{n_i} = \frac{R^*}{R_i}. \tag{15}$$

Applying Dalton's law, we have

$$pV = (\sum n_i) R^* T = (\sum m_i R_i) T \tag{16}$$

where $\sum n_i = n$ is the total number of moles, and if we define a mean specific gas constant $\bar{R}$ by

$$\bar{R} = \frac{\sum m_i R_i}{m}, \tag{17}$$

the equation of state for the mixture has thus the same expressions as for a pure gas:

$$pV = nR^*T = m\bar{R}T. \tag{18}$$

The mean molecular weight of the mixture $\bar{M}$ is defined by

$$\bar{M} = \frac{\sum n_i M_i}{n} = \frac{m}{n} \tag{19}$$

so that

$$\bar{M} = R^*/\bar{R}. \tag{20}$$

The molar fraction of each gas $N_i = n_i/n$ will be

$$N_i = p_i/p = V_i/V. \tag{21}$$

Since the introduction of the mole as a fundamental unit in 1971, this ratio is often referred to as the *mole fraction*.

1.12. Atmospheric Air Composition

We may consider the atmospheric air as composed of:

(1) a mixture of gases, to be described below;
(2) water substance in any of its three physical states; and
(3) solid or liquid particles of very small size.

Water substance is a very important component for the processes in the atmosphere.

Its proportion is very variable, and we shall postpone its consideration, as well as that of its changes of state producing clouds of water droplets or of ice particles.

The solid and liquid particles in suspension (other than that of water substance) constitute what is called the atmospheric aerosol. Its study is very important for atmospheric chemistry, cloud and precipitation physics, and for atmospheric radiation and optics. It is not significant for atmospheric thermodynamics, and we shall disregard it.

The mixture of gases mentioned in the first place is what we shall call *dry air*. The four main components are listed in Table I-4; the minor components in Table I-5.

Except for CO_2 and some of the minor components, the composition of the air is remarkably constant up to a height of the order of 100 km, indicating that mixing processes in the atmosphere are highly efficient. The CO_2 has a variable concentration near the ground, where it is affected by fires, by industrial activities, by photosynthesis and by the exchange with the oceans, which constitute a large reservoir of the dissolved gas. Above surface layers, however, its proportion is also approximately constant, and can be taken as 0.03% by volume. This proportion is slowly increasing with time, and is expected to reach 0.04% by about 1990.

It may be seen that the two main gases constitute more than 99% in volume of the air; if we add Ar we reach 99.97% and if we also consider the CO_2, the rest of the trace components only amounts to less than 0.003%. For all our purposes, which are mainly restricted to the troposphere, we shall consider dry air as a constant mixture which can be treated as a pure gas with a specific constant (see Equation (17) and Table I-4)

TABLE I-4

Main components of dry atmospheric air

Gas	Molecular weight[a]	Molar (or volume) fraction	Mass fraction	Specific gas constant (J kg^{-1} K^{-1})	$m_i R_i/m$ (J kg^{-1} K^{-1})
Nitrogen (N_2)	28.013	0.7809	0.7552	296.80	224.15
Oxygen (O_2)	31.999	0.2095	0.2315	259.83	60.15
Argon (Ar)	39.948	0.0093	0.0128	208.13	2.66
Carbon dioxide (CO_2)	44.010	0.0003	0.0005	188.92	0.09
		1.0000	1.0000	$\frac{\Sigma m_i R_i}{m}$ =	287.05

[a] Based on 12.000 for C^{12}.

$$R_d = 287.05 \text{ J kg}^{-1} \text{K}^{-1}$$

and a mean molecular weight (see Equation (20)):

$$M_d = R^*/R_d = 0.028964 \text{ kg mol}^{-1} = 28.964 \text{ g mol}^{-1}.$$

The subscript d shall always stand for 'dry air'.

TABLE I-5

Minor gas components of atmospheric air

Gas		Molar (or volume) fraction
Neon	(Ne)	1.8×10^{-5}
Helium	(He)	5.2×10^{-6}
Methane	(CH_4)	1.5×10^{-6}
Krypton	(Kr)	1.1×10^{-6}
Hydrogen	(H_2)	5.0×10^{-7}
Nitrous oxide	(N_2O)	2.5×10^{-7}
Carbon monoxide	(CO)	1.0×10^{-7}
Xenon	(Xe)	8.6×10^{-8}
Ozone	(O_3)	Variable. Up to 10^{-5} in stratosphere.
Sulfur dioxide	(SO_2)	Variable, under 10^{-8}
Hydrogen sulfide and other reduced sulfur compounds	(H_2S, etc.)	
Nitric oxide	(NO)	
Nitrogen dioxide	(NO_2)	
Ammonia	(NH_3)	
Formaldehyde	(CH_2O)	

Amongst the minor components, O_3 has a variable concentration and its molar fraction shows a maximum of 10^{-6} to 10^{-5} with height in the layers around 25 km; it plays an important role in radiation phenomena.

Above about 100 km, the air composition can no longer be considered constant. Firstly, molecular diffusion becomes more important than mixing, which leads to a gradual increase in the proportion of lighter gases with height; secondly, at those heights photochemical reactions produced by solar radiation play an important role in determining the chemical composition. This, however, is of no concern for the subject of this book, which essentially deals with the lower layers of the atmosphere.

Table I-6 gives the value of the second virial coefficient for dry air, and the ratio $pV/R^*T = pv/R_d T$ for two pressures. Virial coefficients of higher order may be neglected, and these data show that we may consider dry air in the troposphere as a perfect gas within less than 0.2% error.

TABLE I-6

Second virial coefficient B' for dry air

t(°C)	B' (10^{-9} cm^2 dyn^{-1})	$pv/R_d T$	
		$p = 500$ mb	$p = 1000$ mb
-100	-4.0	0.9980	0.9960
-50	-1.56	0.9992	0.9984
0	-0.59	0.9997	0.9994
50	-0.13	0.9999	0.9999

PROBLEMS

1. Suppose we define an empirical scale of temperature t' by Equation (2), based on the saturation vapor pressure e_w (thermometric property) of water (thermometric substance). Construct the graph defining t', using the same 0 and 100 points as for the Celsius temperature t. Starting from this graph, construct a second graph giving t as a function of t' between 0 and 100°.

   What would be the temperature t' corresponding to 50°C?

t(°C)	0	25	50	75	90	100
e_w(mb)	6.11	31.67	123.40	385.56	701.13	1013.25

2. (a) Find the equivalences between MKS and cgs units for the physical quantities listed in Table I-2,

   (b) Show that the definition of the atmosphere is consistent with the original definition in terms of the pressure exerted by a column of 760 mm of Hg at 0°C (density: 13.5951 g cm^{-3}) and standard gravity $g_0 = 9.80665$ m s^{-2}.
3. At what pressure is the ideal gas law in error by 1%, for air at 0°C?
4. Prove that $p = \sum p_i$ and $V = \sum V_i$ (p_i = partial pressure of gas i; V_i = partial volume of gas i) are equivalent statements of Dalton's law.
5. Find the average molecular weight $\overline{M}$ and specific constant $\overline{R}$ for air saturated with water vapor at 0°C and 1 atm of total pressure. The vapor pressure of water at 0°C is 6.11 mb.