CHAPTER THREE

Early experiments and laws

At the end of Chapter 2 we derived theoretically the equation of state or the ideal gas law. This law was first derived experimentally. The relevant experiments provide many interesting insights about the properties of ideal gases and confirm the theory. As such a little discussion is necessary.

3.1 The first law of Gay-Lussac

Through experiments Gay-Lussac was able to show that, when pressure is constant, the increase in volume of an ideal gas, dV, is proportional to the volume V_0 that it has at a temperature (measured in the Celsius scale) of $\theta = 0\,°\mathrm{C}$ and proportional to the temperature increase, $d\theta$:

$$dV = \alpha V_0 d\theta. \tag{3.1}$$

The coefficient α is called the volume coefficient of thermal expansion at a constant pressure and it has the value of $1/273\,\mathrm{deg}^{-1}$ for all gases. The physical meaning of α can be understood if we solve equation (3.1) for α:
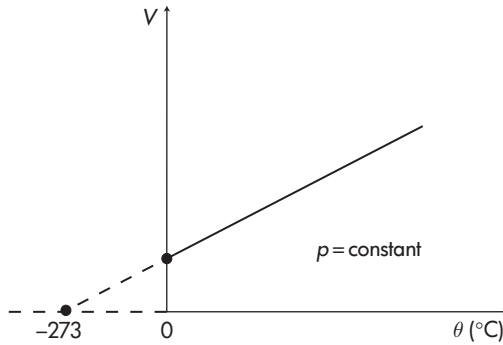
$$\alpha = \frac{1}{d\theta}\frac{dV}{V_0}.$$

From the above equation it follows that if we increase the temperature of an ideal gas by $1\,°\mathrm{C}$, while we keep the pressure constant, the volume will increase by $1/273$ of the volume the gas occupies at $0\,°\mathrm{C}$. By integrating equation (3.1) we obtain the relationship between V and θ:

$$\int_{V_0}^{V} dV = \int_{0}^{\theta} \alpha V_0 d\theta$$

or

$$V - V_0 = \alpha V_0 \theta$$

Figure 3.1
Graphical representation
of the first law of
Gay-Lussac.

or

$$V = V_0(1 + \alpha\theta). \tag{3.2}$$

This is a linear relationship and its graph is shown in Figure 3.1.

3.2 The second law of Gay-Lussac

Again through experimentation Gay-Lussac was able to show that for a constant volume the increase in pressure of an ideal gas, dp, is proportional to the pressure p_0 that it has at a temperature of $0\,^\circ$C and proportional to the increase in temperature $d\theta$:

$$dp = \beta p_0 d\theta.$$

The coefficient β is the pressure coefficient of thermal expansion at a constant volume and has the value $1/273$ deg^{-1} for all gases:

$$\beta = \frac{1}{d\theta}\frac{dp}{p_0}.$$

The above formula indicates that an increase in temperature by $1\,^\circ$C (while V is constant) results in an increase in pressure by $1/273$ of the pressure the gas had at $0\,^\circ$C.

As in the first law again it follows that (Figure 3.2)

$$p = p_0(1 + \beta\theta). \tag{3.3}$$

Application

The second law of Gay-Lussac can easily explain why, in the winter, heating a house at a much greater temperature than the outside temperature does not increase the pressure enough to break the windows. A difference of $20\,^\circ$C between the inside and the outside air increases the pressure inside the house by 7.3%. Glass can withstand such pressure changes easily.

Figure 3.2
Graphical representation
of the second law of
Gay-Lussac.
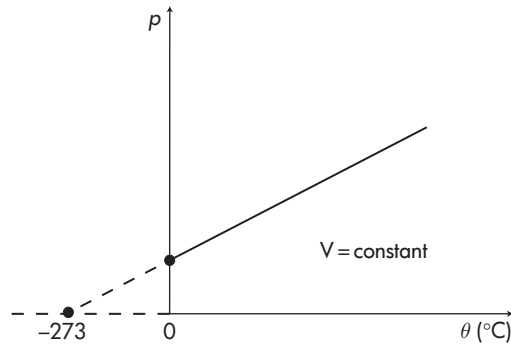
3.3 Absolute temperature

From equation (3.2) it follows that if we extrapolate to $\theta = -273\,^\circ$C, then $V = 0$. This means that if we were able to cool an ideal gas to $-273\,^\circ$C, while keeping the pressure constant, the volume would become zero. Similarly, from equation (3.3) it follows that if we were able to cool an ideal gas to the temperature of $-273\,^\circ$C, while keeping the volume constant, the pressure would become zero. This temperature of $-273\,^\circ$C we call *absolute zero*. Up to now for the measurement of temperature the Celsius scale has been used, starting from the temperature "zero Celsius". If we extend the Celsius scale to the absolute zero (i.e. $-273\,^\circ$C), then the temperature measured from the absolute zero is called absolute temperature, T. This defines a new scale called the Kelvin scale ($T = 273 + \theta$).

3.4 Another form of the Gay-Lussac laws

Using the absolute temperature we can present the Gay-Lussac laws as follows. From Figure 3.3 it follows from the similarity of triangles ABC and $AB'C'$ that his first law can be expressed as

$$\text{for } p = \text{constant}, \quad \frac{V}{V'} = \frac{T}{T'}. \tag{3.4}$$

Similarly from Figure 3.4, his second law can be expressed as

$$\text{for } V = \text{constant}, \quad \frac{p}{p'} = \frac{T}{T'}. \tag{3.5}$$

Verbally stated, the volumes of an ideal gas under constant pressure and the pressures under constant volume are proportional to the absolute temperatures.

Figure 3.3
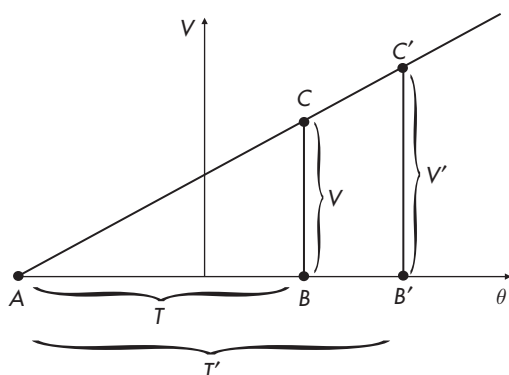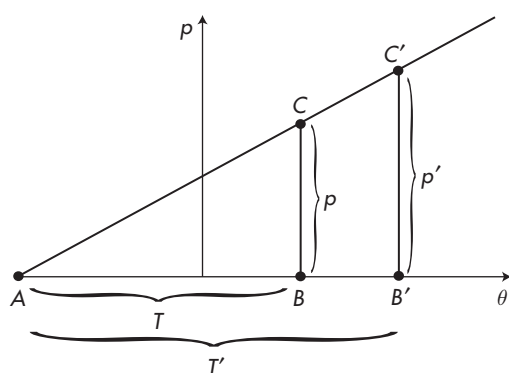Expressing Gay-Lussac's
first law for two states C
and C'.

Figure 3.4
Expressing Gay-Lussac's
second law for two states
C and C'.

3.5 Boyle's law

While Gay-Lussac's laws provide the change in volume or pressure as a function of temperature, Boyle's law provides the change in pressure as the volume varies at a constant temperature. The law is expressed as follows:

$$pV = p'V'. \tag{3.6}$$

3.6 Avogadro's hypothesis

The formal definition of a *mole* is the amount of substance which contains the same number of particles (atoms, molecules, ions, or electrons) as there are in 12 grams of ^{12}C. This number of atoms is equal to $N = 6.022 \times 10^{23}$ and it is known as Avogadro's number. It is obtained under the condition that one mole of carbon weighs 12 grams. In general, a substance of a weight equal to its molecular weight contains one mole of the substance. Thus 25 grams of water contain $27/18 = 1.5$ mole of water. In 1811 the Italian physicist

and mathematician Amedeo Avogadro proposed his hypothesis that the volume of a gas, V, is directly proportional to the number of molecules of the gas, N',

$$V = aN'$$

where a is a constant. To relate to this hypothesis, simply imagine inflating a balloon. The more the air you pump into it, the bigger the volume. It follows that at constant temperature and pressure, equal volumes of gases contain the same number of molecules. For one mole $N' = N$. Since N is the same for one mole of any gas, Avogadro's hypothesis (actually a law by now) can be stated simply as: *A mole of any gas at constant temperature and pressure occupies the same volume.* This volume for the standard state $T_0 = 0\,°\mathrm{C}$, $p_0 = 1$ atmosphere has the value (see equation (2.13))

$$V_{T_0,p_0} = 22.4 \quad \text{liters mol}^{-1}$$
$$= 22\,400\,\text{cm}^3\,\text{mol}^{-1}.$$

3.7 The ideal gas law

Let us consider an ideal gas at a state p, V, T which is heated under constant volume to a state p_1, V, T' (Figure 3.5). Then, according to Gay-Lussac's second law

$$p_1 = p\frac{T'}{T}.$$

If subsequently we keep the temperature constant and increase the volume to V' the gas goes to a state $p'V'T'$. Then, according to Boyle's law,

$$p'V' = p_1 V.$$

By combining the above two equations we obtain

$$p'V' = p\frac{T'}{T}V$$

or

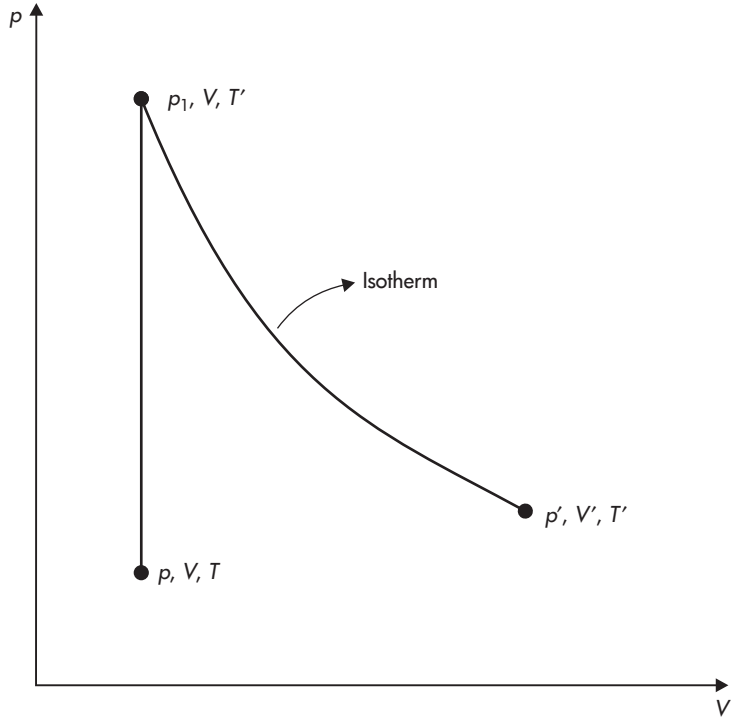$$\frac{pV}{T} = \frac{p'V'}{T'}. \tag{3.7}$$

This is called the Boyle–Gay-Lussac law and it indicates that if we change the pressure, the volume, and the temperature the value of PV/T remains constant. Thus, equation (3.7) can be written as

$$pV = AT \tag{3.8}$$

where A is, according to equation (3.7), a constant depending on the type and mass of the gas. The dependence on the mass follows

from the fact that if we consider twice the mass and keep the pressure and the temperature constant, then the volume will double (Avogadro's hypothesis). Therefore, the value of pV/T (i.e. A) will double. Accordingly, we can write $A = mR$ where m is the mass of the gas and R is a constant independent of the mass but dependent on the gas. This constant is called the specific gas constant. We can then write equation (3.8) as

$$pV = mRT. \tag{3.9}$$

Since $m = Nm_\mathrm{p}$ (where N is the total number of molecules each having mass m_p), equation (3.9) is identical to equation (2.13) with $R = k/m_\mathrm{p}$. Equation (3.9) is thus the equation of state or ideal gas law which is now derived experimentally. Equation (3.9) can be written as $p = \rho RT$ where $\rho = m/V$ is the mass density. By defining the specific volume $a = 1/\rho$, the ideal gas law takes the form

$$pa = RT.$$

If M denotes the molecular weight of the gas then the number of moles is $n = m/M$. It follows that

$$pV = nMRT$$

or

$$pV = nR^*T \tag{3.10}$$

or

$$pa = \frac{R^*}{M}T$$

where $R^* = MR$. Considering that $R = k/m_{\rm p}$ it follows that $R^* = Mk/m_{\rm p} = mk/nm_{\rm p} = Nk/n$. Now recall that the number of molecules in one mole, N_A, is equal to 6.022×10^{23} (Avogadro's number). Then, $N = nN_{\rm A}$. In this case $R^* = N_{\rm A}k$, which is the product of two constants. This new constant is called the universal gas constant and its value is $8.3143\,\mathrm{J\,K^{-1}mol^{-1}}$.

3.8 A little discussion on the ideal gas law

- Because the ideal gas law relates three variables (rather than two), we have to be careful when we interpret changes in one of the variables. For example, temperature increases when pressure increases but only if the volume (density) increases (decreases) or remains constant or decreases (increases) by a smaller amount compared with pressure. Let us consider the ideal gas law $pV = mRT$ or $p = \rho RT$ and differentiate it:

$$pdV + V dp = mRdT$$

$$dp = RTd\rho + R\rho dT.$$

We can easily see that if $dp > 0$ and $dV \geq 0$ then $dT > 0$. Also, if $dp > 0$ and $dV < 0$ and $|Vdp| > |pdV|$ then $dT > 0$. And so on! It follows that cold air is denser than warm air only if pressure remains constant or if its change does not offset the temperature difference.

Similarly, if we consider the ideal gas law in the form

$$pa = \frac{R^*}{M}T$$

or

$$p = \rho\frac{R^*}{M}T$$

we can reason that moist air (in which some of the dry air of molecular weight $28\,\mathrm{g\,mol^{-1}}$ has been replaced by water vapor of molecular weight $18\,\mathrm{g\,mol^{-1}}$) is less dense than dry air at more or less the same pressure and temperature. This explains some interesting statistics in the American game of baseball where more home runs occur when the weather is hot and humid. In a warmer and more moist environment where $p = $ constant, the density of air is smaller. Therefore, the ball has less resistance.

For a path of 400 feet or so the effect can be significant, resulting in higher chances for a home run.

- Recall equations (2.9) and (3.2). According to equation (2.9) $T = 0\,\text{K}$ when $v = 0$. Because of this one might interpret the zero absolute temperature as the temperature where all motion in an ideal gas ceases. On the other hand, when equation (3.2) is extrapolated to the temperature at which $V = 0$ it results in $T_{\text{absolute}} = (-\frac{1}{\alpha})\,°\text{C} = -273\,°\text{C} = 0\,\text{K}$. While this temperature corresponds to vanishing volumes, it is not necessarily the temperature at which motion ceases. If both $V = 0$ and $v = 0$ are true when $T = 0\,\text{K}$, then pressure can be anything, but this does not invalidate the ideal gas law, both sides of which will equal zero. To avoid confusion, we must keep in mind that these issues emerge when these equations are extrapolated to states where one cannot assume that a gas behaves as an ideal gas. At those states, equations (2.9) and (3.2) simply do not mean much.

3.9 Mixture of gases – Dalton's law

Consider a mixture of two gases occupying a volume V and consisting of N_1 molecules of gas 1 and N_2 molecules of gas 2. The total pressure on the walls will be the result of all the collisions, i.e. the collisions by the molecules of gas 1 and the collisions by the molecules of gas 2. Thus we can write equation (2.13) as

$$p = \frac{(N_1 + N_2)}{V} kT$$

or

$$p = \frac{N_1 kT}{V} + \frac{N_2 kT}{V}.$$

The first term on the right-hand side of the above equation is exactly the pressure that gas 1 would create if all its N_1 molecules occupied the volume V, i.e. the partial pressure of gas 1. The same is valid for the second term. We thus conclude that the total pressure is the sum of the partial pressures. This expresses Dalton's law which states that for a mixture of K components, each one of which obeys the ideal gas law, the total pressure, p, exerted by the mixture is equal to the sum of the partial pressures which would be exerted by each gas if it alone occupied the entire volume at the temperature of the mixture, T:

$$p = \sum_{i=1}^{K} p_i.$$

If the volume of the mixture is V and the mass and molecular weight of the ith constituent are m_i and M_i respectively, then for each constituent

$$p_i = \frac{R^*}{M_i}\frac{m_i}{V}T.$$

Applying Dalton's law, we then can write that for a mixture

$$p = \sum_{i=1}^{K}\frac{R^*T}{V}\frac{m_i}{M_i}$$

or

$$p = \frac{R^*T}{V}\sum_{i=1}^{K}\frac{m_i}{M_i}.$$

Since the total mass of the mixture $m = \sum_{i=1}^{K}m_i$, the above equation becomes

$$p = \frac{R^*Tm}{V}\frac{\sum_{i=1}^{K}\frac{m_i}{M_i}}{\sum_{i=1}^{K}m_i}$$

or

$$p = \frac{R^*T}{a}\frac{\sum_{i=1}^{K}\frac{m_i}{M_i}}{\sum_{i=1}^{K}m_i} \qquad (3.11)$$

In order for the mixture to obey the ideal gas law, it must satisfy the equation

$$p = \frac{RT}{a} = \frac{R^*T}{a\overline{M}} \qquad (3.12)$$

where $\overline{M}$ is the mean molecular weight of the mixture. By comparing equations (3.11) and (3.12) we see that this would be possible if

$$\overline{M} = \frac{\sum_{i=1}^{K}m_i}{\sum_{i=1}^{K}\frac{m_i}{M_i}}. \qquad (3.13)$$

This provides the proper way to compute the mean molecular weight for a mixture and indicates that the mixture follows the ideal gas law as long as there is no condensation (if there is, then some m_i's may not remain constant).

Examples

(3.1)   Determine the mean molecular weight of dry air.

For our planet, the lowest $25\,\mathrm{km}$ of the atmosphere is made up almost entirely by nitrogen (N_2), oxygen (O_2), argon (A), and carbon dioxide (CO_2) (75.51%, 23.14%, 1.3%, and 0.05%

by mass, respectively). Thus, for dry air the mean molecular weight is

$$\overline{M} = \frac{m_{N_2} + m_{O_2} + m_A + m_{CO_2}}{\frac{m_{N_2}}{M_{N_2}} + \frac{m_{O_2}}{M_{O_2}} + \frac{m_A}{M_A} + \frac{m_{CO_2}}{M_{CO_2}}}$$

or

$$\overline{M} = \frac{75.51 + 23.16 + 1.3 + 0.05}{\frac{75.51}{28.02} + \frac{23.14}{32.0} + \frac{1.3}{39.94} + \frac{0.05}{44.01}} \, \mathrm{g\,mol}^{-1}$$

or

$$\overline{M} = 28.97 \, \mathrm{g\,mol}^{-1}$$

or

$$\overline{M} = 0.02897 \, \mathrm{kg\,mol}^{-1}.$$

It follows that the specific gas constant for dry air is

$$R_d = R^*/\overline{M} = 287 \, \mathrm{J\,kg}^{-1}\,\mathrm{K}^{-1}.$$

(3.2)   Determine the mean molecular weight of a mixture of dry air saturated with water vapor at $0\,°C$ and 1 atmosphere pressure. The partial pressure of water vapor at $0\,°C$ is 6.11 mb.

The mixture consists of dry air and water vapor. If p_d is the pressure due to dry air and p_v the pressure due to water vapor, then the pressure of the mixture is $p = p_d + p_v$. If we recall that the number of moles $n = m/M$, then we can write equation (3.13) as

$$\overline{M} = \frac{\sum_{i=1}^{K} n_i M_i}{\sum_{i=1}^{K} n_i} = \frac{\sum_{i=1}^{K} n_i M_i}{n} = \sum_{i=1}^{K} \frac{n_i}{n} M_i \qquad (3.14)$$

where n_i and n are the corresponding number of moles of the constituents of the mixture and the total number of moles in the mixture. Assuming that both dry air and water vapor are ideal gases we have that

$$pV = nR^*T \qquad \text{for the mixture}$$
$$p_i V = n_i R^*T \qquad \text{for each of the constituents.}$$

From these two equations it follows that

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

Combining the above relationship and equation (3.14) yields

$$\overline{M} = \sum_{i=1}^{K} \frac{p_i}{p} M_i.$$

In our case $i = 1, 2$. Thus,

$$\overline{M} = \frac{p_1}{p} M_1 + \frac{p_2}{p} M_2$$

or changing $1 \to d$ (dry air) and $2 \to v$ (water vapor)

$$\overline{M} = \frac{p_d}{p} M_d + \frac{p_v}{p} M_v$$

or

$$\overline{M} = \frac{p - p_v}{p} M_d + \frac{p_v}{p} M_v$$

or

$$\overline{M} = 28.9 \, \mathrm{g \, mol^{-1}}.$$

The above estimated mean molecular weight is not very much different from the mean molecular weight of dry air. The difference becomes more apparent for higher temperatures. For example for $T = 35\,°\mathrm{C}$ the partial pressure of water vapor is $57.6\,\mathrm{mb}$ and $\overline{M} = 28.3\,\mathrm{g\,mol^{-1}}$.

(3.3) Two containers A and B of volumes $V_A = 800\,\mathrm{cm^3}$ and $V_B = 600\,\mathrm{cm^3}$, respectively, are connected with a tube that closes and opens by a hinge. The containers are filled with a gas under pressures of 1000 mb and 800 mb, respectively. If we open the connection what will the final pressure be in each of the containers? Assume that the temperature remains constant.

Once the connection is open, each gas will expand to fill the total volume $V = V_A + V_B$ thereby equalizing the difference in pressure between the two containers. Thus the final pressure in each container will be the same. Let us first assume that container B is empty. Since the gas in container A expands at a constant temperature we have (Boyle's law)

$$p_f V_f = p_i V_i$$

where i and f stand for initial and final. It follows that $p_f = 571\,\mathrm{mb}$.
Similarly if we assume that container A is empty the final pressure in both containers will be

$$p'_f = \frac{p_i V_i}{V_f} = 343\,\mathrm{mb}.$$

Since $p_f (p'_f)$ is the pressure the gas in A(B) would exert if it occupied the total volume $V_A + V_B$, p_f and p'_f can be considered as partial pressures of two gases. Then from Dalton's law it follows that the final pressure in each container should be $914\,\mathrm{mb}$.

(3.4)   If Boyle had observed $\sqrt{p}V = $ constant, what would the equation of state for an ideal gas be? In this case calculate the temperature of a sample of nitrogen which has a pressure of 800 mb and a specific volume of 1200 cm³ g⁻¹. How does this temperature differ from that estimated when the correct law $pV = $ constant is observed? Can you explain the difference?

If we follow the procedure to arrive at equation (3.7) but with the new Boyle's law, we have that

$$p_1 = p\frac{T'}{T}$$

$$\sqrt{p'}V' = \sqrt{p_1}V.$$

By combining the above equations we have that

$$\sqrt{p'}V' = \sqrt{p}\sqrt{\frac{T'}{T}}V$$

or

$$\frac{\sqrt{p'}V'}{\sqrt{T'}} = \frac{\sqrt{p}V}{\sqrt{T}} = \text{constant}.$$

As we know, if we keep the temperature and pressure constant and double the mass, the volume will double. As such, here as well the ratio $\sqrt{p}V/\sqrt{T}$ will double. Then we can write that $\sqrt{p}V/\sqrt{T} = mR$ where m is the total mass and R is the specific gas constant. Thus, the ideal gas law in this case will be

$$\sqrt{p}a = \frac{R^*}{M}\sqrt{T}.$$

Solving for T we have that

$$\sqrt{T} = 1.143$$

or

$$T = 1.07\,\text{K}.$$

Under normal circumstances (i.e. when $pa = (R^*/M)T$), we find that $T = 323.3\,\text{K}$ which makes more sense. The tremendous difference is due to the fact that the square root in $\sqrt{p}a = $ constant introduces two corrections to the ideal gas law (both pressure and temperature appear under a square root) having the net result of significantly reducing T.

Problems

(3.1) What is the mass of dry air occupying a room of dimensions $3 \times 5 \times 4\,\mathrm{m}$ at $p = 1$ atmosphere and $T = 20\,°\mathrm{C}$? ($72.3\,\mathrm{kg}$)

(3.2) Graph the relationship $V = f(T)_p = \mathrm{constant}$ from absolute zero up to high temperatures, for two samples of the same gas which at $0\,°\mathrm{C}$ occupy volumes of 1000 and $2000\,\mathrm{cm}^3$, respectively.

(3.3) In a 2-D coordinate system with axes the absolute temperature and volume, graph (a) an isobaric (constant pressure) change of one mole of an ideal gas for $p = 1$ atmosphere, and (b) the same when $p = 2$ atmospheres.

(3.4) Determine the molecular weight of the Venusian atmosphere assuming that it consists of 95% CO_2 and 5% N_2 by volume. What is the gas constant for $1\,\mathrm{kg}$ of such an atmosphere? ($43.2\,\mathrm{g\,mol^{-1}}$, $192.5\,\mathrm{J\,kg^{-1}\,K^{-1}}$)

(3.5) If $p = 1$ atmosphere and $T = 0\,°\mathrm{C}$ how many molecules are there in $1\,\mathrm{cm}^3$ of dry air? (2.6884×10^{19} molecules)

(3.6) Given the two states p, V, T and p', V', T', define on a (p, V) diagram the state p_1, V, T' that was used to arrive at the ideal gas law (section 3.7).

(3.7) An ideal gas of p, V, T undergoes the following successive changes: (1) it is warmed under a constant pressure until its volume doubles, (2) it is warmed under constant volume until its pressure doubles, and (3) it expands isothermally until its pressure returns to p. Calculate in each case the values of p, V, T and plot all three changes in a (p, V) diagram.