D

Thermodynamics of ideal gases

An ideal gas is a nice “laboratory” for understanding the thermodynamics of a fluid with a non-trivial equation of state. In this section we shall recapitulate the conventional thermodynamics of an ideal gas with constant heat capacity. For more extensive treatments, see for example [67, 66].

D.1 Internal energy

In section 4.1 we analyzed Bernoulli’s model of a gas consisting of essentially non-interacting point-like molecules, and found the pressure $p = \frac{1}{3}\rho v^2$ where v is the root-mean-square average molecular speed. Using the ideal gas law (4-26) the total molecular kinetic energy contained in an amount $M = \rho V$ of the gas becomes,

$$\frac{1}{2}Mv^2 = \frac{3}{2}pV = \frac{3}{2}nRT \ , \tag{D-1}$$

where $n = M/M_{\mathsf{mol}}$ is the number of moles in the gas. The derivation in section 4.1 shows that the factor 3 stems from the three independent translational degrees of freedom available to point-like molecules. The above formula thus expresses that in a mole of a gas there is an internal kinetic energy $\frac{1}{2}RT$ associated with each translational degree of freedom of the point-like molecules.

Whereas monatomic gases like argon have spherical molecules and thus only the three translational degrees of freedom, diatomic gases like nitrogen and oxygen have stick-like molecules with two extra rotational degrees of freedom orthogonally to the bridge connecting the atoms, and multiatomic gases like carbon dioxide and methane have the three extra rotational degrees of freedom. According to the *equipartition theorem* of statistical mechanics these degrees of freedom will also carry a kinetic energy $\frac{1}{2}RT$ per mole. Molecules also possess vibrational degrees of freedom that may become excited at high temperatures, but we shall disregard them here.

The *internal energy* of n moles of an ideal gas is defined to be,

$$\boxed{\mathcal{U} = \frac{k}{2}\, nRT \ ,} \tag{D-2}$$

where k is the number of molecular degrees of freedom. A general result of thermodynamics (Helmholtz' theorem [67, p. 154]) guarantees that for an ideal gas $\mathcal{U}$ cannot depend on the volume but only on the temperature. Physically a gas may dissociate or even ionize when heated, and thereby change its value of k, but we shall for simplicity assume that k is in fact constant with $k = 3$ for monatomic, $k = 5$ for diatomic, and $k = 6$ for multiatomic gases. For mixtures of gases the number of degrees of freedom is the molar average of the degrees of freedom of the pure components (see problem D.1).

D.2 Heat capacity

Suppose that we raise the temperature of the gas by δT without changing its volume. Since no work is performed, and since energy is conserved, the necessary amount of heat is $\delta Q = \delta\mathcal{U} = C_V \delta T$ where the constant,

$$C_V = \frac{k}{2}\, nR \ , \tag{D-3}$$

is naturally called the *heat capacity at constant volume.*

If instead the pressure of the gas is kept constant while the temperature is raised by δT, we must also take into account that the volume expands by a certain amount δV and thereby performs work on the surroundings. The necessary amount of heat is now larger by this work, $\delta Q = \delta U + p\delta V$. Using the ideal gas law (4-26) we have for constant pressure $p\delta V = \delta(pV) = nR\delta T$. Consequently, the amount of heat which must be added per unit of increase in temperature at constant pressure is

$$C_p = C_V + nR \ , \tag{D-4}$$

called the *heat capacity at constant pressure.* It is always larger than C_V because it includes the work of expansion.

The adiabatic index

The dimensionless ratio of the heat capacities,

$$\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{k} \ , \tag{D-5}$$

is for reasons that will become clear in the following called the *adiabatic index*. It is customary to express the heat capacities in terms of γ rather than k,

$$C_V = \frac{1}{\gamma - 1} nR \ , \qquad\qquad C_p = \frac{\gamma}{\gamma - 1} nR \ . \tag{D-6}$$

Given the adiabatic index, all thermodynamic quantities for n moles of an ideal gas are completely determined. The value of the adiabatic index is $\gamma = 5/3$ for monatomic gases, $\gamma = 7/5$ for diatomic gases, and $\gamma = 4/3$ for multiatomic gases.

D.3 Entropy

When neither the volume nor the pressure are kept constant, the heat that must be added to the system in an infinitesimal process is,

$$\delta Q = \delta U + p\delta V = C_V \delta T + nRT\frac{\delta V}{V} \ . \tag{D-7}$$

It is a mathematical fact that there exists no function, $Q(T, V)$, which has this expression as differential (see problem D.2). It may on the other hand be directly verified (by insertion) that

$$\delta \mathcal{S} = \frac{\delta Q}{T} = C_V \frac{\delta T}{T} + nR\frac{\delta V}{V} \ , \tag{D-8}$$

can be integrated to yield a function,

$$\boxed{\mathcal{S} = C_V \log T + nR \log V + \text{const} \ ,} \tag{D-9}$$

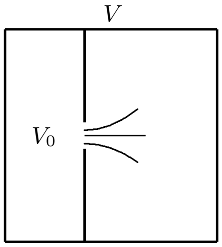
called the *entropy* of the amount of ideal gas. Being an integral the entropy is only defined up to an arbitrary constant. The entropy of the gas is, like its energy, an abstract quantity which cannot be directly measured. But since both quantities depend on the measurable thermodynamic quantities, ρ, p, and T, that characterize the state of the gas, we can calculate the value of energy and entropy in any state. But why bother to do so at all?

The two fundamental laws of thermodynamics

The reason is that the two fundamental laws of thermodynamics are formulated in terms of the energy and the entropy. Both laws concern processes that may take place in an *isolated* system which is not allowed to exchange heat with or perform work on the environment.

The *First Law* states that the energy is unchanged under any process in an isolated system. This implies that the energy of an open system can only change by exchange of heat or work with the environment. We actually used this law implicitly in deriving the heat capacities and the entropy.

The *Second Law* states that the entropy cannot decrease. In the real world, the entropy of an isolated system must in fact grow. Only if all the processes taking place in the system are completely *reversible* at all times, will the entropy stay constant. Reversibility is an ideal which can only be approached by very slow *quasistatic* processes, consisting of infinitely many infinitesimal reversible steps. Essentially all real-world processes are *irreversible* to some degree.



A compartment of volume V_0 inside an isolated box of volume V. Initially, the compartment contains an ideal gas with vacuum in the remainder of the box. When the wall breaks, the gas expands by itself to fill the whole box. The reverse process would entail a decrease in entropy and never happens by itself.

James Prescott Joule (1818-1889). *English physicist. Gifted experimenter who as the first demonstrated the equivalence of mechanical work and heat, a necessary step on the road to the First Law. Demonstrated (in continuation of earlier experiments by Gay-Lussac) that the irreversible expansion of a gas into vacuum does not change its temperature.*

Example D.3.1 (Joule's expansion experiment): An isolated box of volume V contains an ideal gas in a walled-off compartment of volume V_0. When the wall is opened, the gas expands into vacuum and fills the full volume V. The box is completely isolated from the environment, and since the internal energy only depends on the temperature, it follows from the First Law that the temperature must be the same before and after the event. The change in entropy then becomes

$$\Delta\mathcal{S} = (C_V \log T + nR \log V) - (C_V \log T + nR \log V_0) = nR \log(V/V_0)$$

which is evidently positive (because $V/V_0 > 1$). This result agrees with the Second Law, which thus appears to be unnecessary.

The strength of the Second Law becomes apparent when we ask the question of whether the air in the box could ever — perhaps by an unknown process to be discovered in the far future — by itself enter the compartment of volume V_0, leaving vacuum in the box around. Since such an event would entail a negative change in entropy which is forbidden by the Second Law, it never happens.

Isentropic processes

Any process in an open system which does not exchange heat with the environment is said to be *adiabatic*. If the process is furthermore reversible, it follows that $\delta Q = 0$ in each infinitesimal step, so that the $\delta\mathcal{S} = \delta Q/T = 0$. The entropy (D-9) must in other words stay constant in any reversible, adiabatic process. Such a process is for this reason called *isentropic*.

By means of the adiabatic index (D-5) we may write the entropy (D-9) as,

$$\mathcal{S} = C_V \log\left(TV^{\gamma-1}\right) + \text{const} . \tag{D-10}$$

From this it follows that

$$T\,V^{\gamma-1} = \text{const} , \tag{D-11}$$

for any isentropic process in an ideal gas. Using the ideal gas law to eliminate $V \sim T/p$, this may be written equivalently as,

$$T^{\gamma} p^{1-\gamma} = \text{const} . \tag{D-12}$$

Eliminating instead $T \sim pV$, the isentropic condition takes its most common form,

$$\boxed{p\,V^\gamma = \text{const}\ .} \tag{D-13}$$

Notice that the constants are different in these three equations.

> **Example D.3.2:** When the air in a bicycle pump is compressed from V_0 to V_1 (while you block the valve with your finger), the adiabatic law implies that $p_1 V_1^\gamma = p_0 V_0^\gamma$. For $p_0 = 1\ \mathsf{atm}$ and $V_1 = V_0/2$ we find $p_1 = 2.6\ \mathsf{atm}$. The temperature simultaneously rises about 100 degrees, but the hot air quickly becomes cold again during the backstroke. One may wonder why the fairly rapid compression stroke may be assumed to be reversible, but as long as the speed of the piston is much smaller than the velocity of sound, this is in fact a reasonable assumption. Conversely, we may conclude that the air expands with velocity close to the speed of sound when the wall is opened in example D.3.1.

Isothermal versus isentropic bulk modulus

We have formerly seen that the bulk modulus of a strictly isothermal ideal gas with $p = \rho R T_0 / M_{\mathsf{mol}}$ is equal to the pressure,

$$K_T = \rho \left(\frac{\partial p}{\partial \rho}\right)_T = p\ . \tag{D-14}$$

Here the index T (in the usual thermodynamic way of writing derivatives) signals that the temperature must be held constant while we differentiate.

In terms of the mass density $\rho = M/V$, the isentropic condition may be written in any of three different ways (with three different constants),

$$\boxed{p\,\rho^{-\gamma} = \text{const}\ , \qquad T\rho^{1-\gamma} = \text{const}\ , \qquad T^\gamma p^{1-\gamma} = \text{const}\ .} \tag{D-15}$$

Using the first we find the isentropic bulk modulus of an ideal gas,

$$K_S = \rho \left(\frac{\partial p}{\partial \rho}\right)_S = \gamma\, p\ , \tag{D-16}$$

where the index S now signals that the entropy must be held constant. The distinction between the isothermal and isentropic bulk modulus is necessary in all materials, but for nearly incompressible liquids there is not a great difference between K_S and K_T.

> Among Isaac Newton's great achievements was the first calculation of the speed of sound in air, using essentially the ideal gas law with constant temperature. His result did not agree with experiment, because normal sound waves oscillate so rapidly that compression and expansion are essentially isentropic processes. In section 16.2 we shall find that the speed of sound is $c = \sqrt{K/\rho}$, such that the ratio between the isentropic and isothermal sound velocities is $c_S/c_T = \sqrt{\gamma}$. For air with $\gamma \approx 1.4$ this amounts to an 18% error in the sound velocity. Much later in 1799, Laplace derived the correct value for the speed of sound.

D.4 Specific quantities

In classical thermodynamics we always think of a macroscopic volume of matter with the same thermodynamic properties throughout the volume. Volume, mass, energy, entropy, and the specific heats are all *extensive* quantities, meaning that the amount of any such quantity in a composite system is the sum of the amounts in the parts. Pressure, temperature, and density are in contrast *intensive* quantities, that may not be added when a system is put together from its parts.

In continuum physics, an intensive quantity becomes a field that may vary from place to place, whereas an extensive quantity becomes an integral over the density of the quantity. Since a material particle with a fixed number of molecules has a fixed mass (subject to the reservations set down in chapter 1), the natural field to introduce for an extensive quantity like the energy is the *specific internal energy*, $u = d\mathcal{U}/dM$, which is the amount of energy per unit of mass in the neighborhood of a given point. The actual energy density becomes $d\mathcal{U}/dV = \rho\, u$, and the total energy in a volume

$$\mathcal{U} = \int_V \rho\, u\, dV \ . \tag{D-17}$$

The specific energy is an intensive quantity like temperature, pressure or density.

Similarly, we define the *specific heat* as the local heat capacity per unit of mass. Since the heat capacities (D-6) of an ideal gas are directly proportional to the mass $M = nM_{\mathsf{mol}}$, the specific heats of an ideal gas become,

$$c_V = \frac{1}{\gamma - 1}\frac{R}{M_{\mathsf{mol}}} \ , \qquad\qquad c_p = \frac{\gamma}{\gamma - 1}\frac{R}{M_{\mathsf{mol}}} \ . \tag{D-18}$$

They are constants which only depend on the properties of the gas. For air we have $c_V = 718$ J/K/kg and $c_p = 1005$ J/K/kg. From (D-2) we obtain after dividing by M,

$$u = c_V T \ . \tag{D-19}$$

The specific energy of an ideal gas is the specific heat times the absolute temperature.

Finally, we define the *specific entropy*, $s = d\mathcal{S}/dM$, from which the total entropy may be calculated as an integral,

$$\mathcal{S} = \int_V \rho\, s\, dV \ . \tag{D-20}$$

For an ideal gas, the specific entropy is obtained by dividing (D-10) by $M = nM_{\mathsf{mol}}$. It may be written in three different forms related by the ideal gas law,

$$s = c_V \log\left(T\rho^{1-\gamma}\right) + \text{const} \tag{D-21a}$$

$$= c_V \log\left(T^{\gamma}p^{1-\gamma}\right) + \text{const} \tag{D-21b}$$

$$= c_V \log\left(p\,\rho^{-\gamma}\right) + \text{const} \ . \tag{D-21c}$$

Notice, however, that the constants are different in the three cases.

Problems

D.1 An ideal gas mixture contains $n = \sum_i n_i$ moles.

(a) Show that the mixture obeys the equation of state (4-27) when the molar mass of the mixture is defined as

$$M_{\mathsf{mol}} = \sum_i c_i M_{\mathsf{mol},i} \ . \tag{D-22}$$

where $c_i = n_i/n$ of the molar fraction of the i-th component.

(b) Show that the number of degrees of freedom of a mixture is

$$k = \sum_i c_i k_i \ , \tag{D-23}$$

where k_i is the degrees of freedom of the i-th component.

D.2 a) Show that for a function $Q = Q(T, V)$ the differential takes the form $dQ = AdT + BdV$ where $\partial A/\partial V = \partial B/\partial T$. b) Prove that this is not fulfilled for (D-7).