

2.1: What is Thermodynamics?

Thermodynamics is the study of relations among the *state variables* describing a thermodynamic system, and of transformations of heat into work and *vice versa*.

Thermodynamic systems and state variables

Thermodynamic systems contain large numbers of constituent particles, and are described by a set of *state variables* which describe the system's properties in an average sense. State variables are classified as being either *extensive* or *intensive*.

Extensive variables, such as volume V , particle number N , total internal energy E , magnetization M , , scale linearly with the system size, as the first power of the system volume. If we take two identical thermodynamic systems, place them next to each other, and remove any barriers between them, then all the extensive variables will double in size.

Intensive variables, such as the pressure p , the temperature T , the chemical potential μ , the electric field \mathbf{E} , , are independent of system size, scaling as the zeroth power of the volume. They are the same throughout the system, if that system is in an appropriate state of *equilibrium*. The ratio of any two extensive variables is an intensive variable. For example, we write $n = N/V$ for the number density, which scales as V^0 . Intensive variables may also be *inhomogeneous*. For example, $n(\mathbf{r})$ is the number density at position \mathbf{r} , and is defined as the limit of $\Delta N/\Delta V$ of the number of particles ΔN inside a volume ΔV which contains the point \mathbf{r} , in the limit $V \gg \Delta V \gg V/N$.

Classically, the full motion of a system of N point particles requires $6N$ variables to fully describe it ($3N$ positions and $3N$ velocities or momenta, in three space dimensions)¹. Since the constituents are very small, N is typically very large. A typical solid or liquid, for example, has a mass density on the order of $\rho \sim 1 \text{ g/cm}^3$; for gases, $\rho \sim 10^{-3} \text{ g/cm}^3$. The constituent atoms have masses of 10^0 to 10^2 grams per mole, where one mole of X contains N_A of X , and $N_A = 6.0221415 \times 10^{23}$ is Avogadro's number². Thus, for solids and liquids we roughly expect number densities n of $10^{-2} - 10^0 \text{ mol/cm}^3$ for solids and liquids, and $10^{-5} - 10^{-3} \text{ mol/cm}^3$ for gases. Clearly we are dealing with fantastically large numbers of constituent particles in a typical thermodynamic system. The underlying theoretical basis for thermodynamics, where we use a small number of state variables to describe a system, is provided by the microscopic theory of statistical mechanics, which we shall study in the weeks ahead.

Intensive quantities such as p , T , and n ultimately involve averages over both space and time. Consider for example the case of a gas enclosed in a container. We can measure the pressure (relative to atmospheric pressure) by attaching a spring to a moveable wall, as shown in Fig. [pressure]. From the displacement of the spring and the value of its spring constant k we determine the force F . This force is due to the difference in pressures, so $p = p_0 + F/A$. Microscopically, the gas consists of constituent atoms or molecules, which are constantly undergoing collisions with each other and with the walls of the container. When a particle bounces off a wall, it imparts an impulse $2\hat{\mathbf{n}}(\hat{\mathbf{n}} \cdot \mathbf{p})$, where \mathbf{p} is the particle's momentum and $\hat{\mathbf{n}}$ is the unit vector normal to the wall. (Only particles with $\mathbf{p} \cdot \hat{\mathbf{n}} > 0$ will hit the wall.) Multiply this by the number of particles colliding with the wall per unit time, and one finds the net force on the wall; dividing by the area gives the pressure p . Within the gas, each particle travels for a distance ℓ , called the *mean free path*, before it undergoes a collision. We can write $\ell = \bar{v}\tau$, where \bar{v} is the average particle speed and τ is the *mean free time*. When we study the kinetic theory of gases, we will derive formulas for ℓ and \bar{v} (and hence τ). For now it is helpful to quote some numbers to get an idea of the relevant distance and time scales. For O_2 gas at standard temperature and pressure ($T = 0^\circ \text{ C}$, $p = 1 \text{ atm}$), the mean free path is $\ell \approx 1.1 \times 10^{-5} \text{ cm}$, the average speed is $\bar{v} \approx 480 \text{ m/s}$, and the mean free time is $\tau \approx 2.5 \times 10^{-10} \text{ s}$. Thus, particles in the gas undergo collisions at a rate $\tau^{-1} \approx 4.0 \times 10^9 \text{ s}^{-1}$. A measuring device, such as our spring, or a thermometer, effectively performs time and space averages. If there are N_c collisions with a particular patch of wall during some time interval on which our measurement device responds, then the root mean square relative fluctuations in the local pressure will be on the order of $N_c^{-1/2}$ times the average. Since N_c is a very large number, the fluctuations are negligible.

individual particles
classical mechanics
variables: $\{x_i, p_i\}$

$\xrightarrow{\text{statistical mechanics}}$

gases, liquids, solids
thermodynamics
variables: T, p, V, \dots

individual people
psychology
variables: ???

$\xrightarrow{????}$

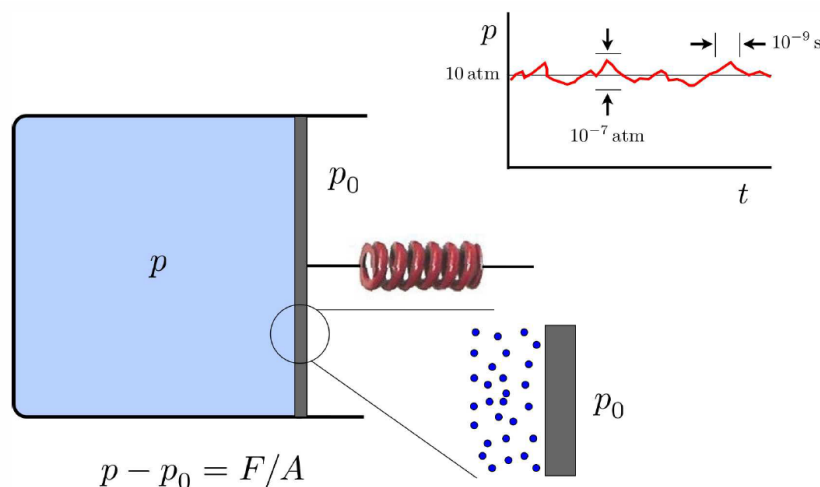
human populations
sociology/politics
variables: ???

[politics] From microscale to macroscale : physical *versus* social sciences.

If the system is in *steady state*, the state variables do not change with time. If furthermore there are no macroscopic currents of energy or particle number flowing through the system, the system is said to be in *equilibrium*. A continuous succession of equilibrium states is known as a *thermodynamic path*, which can be represented as a smooth curve in a multidimensional space whose axes are labeled by state variables. A thermodynamic *process* is any change or succession of changes which results in a change of the state variables. In a *cyclic* process, the initial and final states are the same. In a *quasistatic* process, the system passes through a continuous succession of equilibria. A *reversible* process is one where the external conditions and the thermodynamic path of the system can be reversed; it is both quasi-static *and* non-dissipative (no friction). The slow expansion of a gas against a piston head, whose counter-force is always infinitesimally less than the force pA exerted by the gas, is reversible. To reverse this process, we simply add infinitesimally more force to pA and the gas compresses. An example of a quasistatic process which is not reversible: slowly dragging a block across the floor, or the slow leak of air from a tire. Irreversible processes, as a rule, are dissipative. Other special processes include isothermal ($dT = 0$), isobaric ($dp = 0$), isochoric ($dV = 0$), and adiabatic ($dQ = 0$, no heat exchange):

$\backslash \text{sl reversible: } dQ = T dS$ $\backslash \text{sl spontaneous: } dQ < T dS$ $\backslash \text{sl adiabatic: } dQ = 0$	$\backslash \text{sl isothermal: } dT = 0$ $\backslash \text{sl isochoric: } dV = 0$ $\backslash \text{sl isobaric: } dp = 0$
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We shall discuss later the entropy S and its connection with irreversibility.



[pressure] The pressure p of a gas is due to an average over space and time of the impulses due to the constituent particles.

How many state variables are necessary to fully specify the equilibrium state of a thermodynamic system? For a single component system, such as water which is composed of one constituent molecule, the answer is three. These can be taken to be T , p , and V . One always must specify at least one extensive variable, else we cannot determine the overall size of the system. For a multicomponent system with g different species, we must specify $g + 2$ state variables, which may be $\{T, p, N_1, \dots, N_g\}$, where N_a is the number of particles of species a . Another possibility is the set $\{T, p, V, x_1, \dots, x_{g-1}\}$, where the *concentration* of species a is $x_a = N_a/N$. Here, $N = \sum_{a=1}^g N_a$ is the total number of particles. Note that $\sum_{a=1}^g x_a = 1$.

It then follows that if we specify more than $g + 2$ state variables, there must exist a relation among them. Such relations are known as *equations of state*. The most famous example is the ideal gas law,

$$pV = Nk_B T, \quad (2.1.1)$$

relating the four state variables T , p , V , and N . Here $k_B = 1.3806503 \times 10^{-16} \text{ erg/K}$ is Boltzmann's constant. Another example is the van der Waals equation,

$$\left(p + \frac{aN^2}{V^2}\right)(V - bN) = Nk_B T, \quad (2.1.2)$$

where a and b are constants which depend on the molecule which forms the gas. For a third example, consider a paramagnet, where

$$\frac{M}{V} = \frac{CH}{T}, \quad (2.1.3)$$

where M is the magnetization, H the magnetic field, and C the Curie constant.

Any quantity which, in equilibrium, depends only on the state variables is called a *state function*. For example, the total internal energy E of a thermodynamics system is a state function, and we may write $E = E(T, p, V)$. State functions can also serve as state variables, although the most natural state variables are those which can be directly measured.

Heat

Once thought to be a type of fluid, heat is now understood in terms of the kinetic theory of gases, liquids, and solids as a form of energy stored in the disordered motion of constituent particles. The units of heat are therefore units of energy, and it is appropriate to speak of *heat energy*, which we shall simply abbreviate as *heat*.³

$$1 \text{ J} = 10^7 \text{ erg} = 6.242 \times 10^{18} \text{ eV} = 2.390 \times 10^{-4} \text{ kcal} = 9.478 \times 10^{-4} \text{ BTU}. \quad (2.1.4)$$

We will use the symbol Q to denote the amount of heat energy absorbed by a system during some given thermodynamic process, and dQ to denote a differential amount of heat energy. The symbol dQ indicates an 'inexact differential', about which we shall have more to say presently. This means that heat is not a state function: there is no 'heat function' $Q(T, p, V)$.

Work

In general we will write the differential element of work dW done by the system as

$$dW = \sum_i F_i dX_i, \quad (2.1.5)$$

where F_i is a *generalized force* and dX_i a *generalized displacement*.⁴ The generalized forces and displacements are themselves state variables, and by convention we will take the generalized forces to be *intensive* and the generalized displacements to be *extensive*. As an example, in a simple one-component system, we have $dW = p dV$. More generally, we write

$$dW = \overbrace{\left(p dV - \mathbf{H} \cdot d\mathbf{M} - \mathbf{E} \cdot d\mathbf{P} - \sigma dA + \dots\right)}^{-\sum_j y_j dX_j} - \overbrace{\left(\mu_1 dN_1 + \mu_2 dN_2 + \dots\right)}^{\sum_a \mu_a dN_a} \quad (2.1.6)$$

Here we distinguish between two types of work. The first involves changes in quantities such as volume, magnetization, electric polarization, area. The conjugate forces y_i applied to the system are then $-p$, the magnetic field \mathbf{H} , the electric field \mathbf{E} , the surface tension σ , respectively. The second type of work involves changes in the number of constituents of a given species. For example, energy is required in order to dissociate two hydrogen atoms in an H_2 molecule. The effect of such a process is $dN_{H_2} = -1$ and $dN_H = +2$.

As with heat, dW is an inexact differential, and work W is not a state variable, since it is path-dependent. There is no 'work function' $W(T, p, V)$.

Pressure and Temperature

The units of pressure (p) are force per unit area. The SI unit is the Pascal (Pa): $1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg/m s}^2$. Other units of pressure we will encounter:

$$\begin{aligned} 1 \text{ bar} &\equiv 10^5 \text{ Pa} \\ 1 \text{ atm} &\equiv 1.01325 \times 10^5 \text{ Pa} \\ 1 \text{ torr} &\equiv 133.3 \text{ Pa} . \end{aligned}$$

Temperature (T) has a very precise definition from the point of view of statistical mechanics, as we shall see. Many physical properties depend on the temperature – such properties are called *thermometric properties*. For example, the resistivity of a metal $\rho(T, p)$ or the number density of a gas $n(T, p)$ are both thermometric properties, and can be used to define a temperature scale. Consider the device known as the ‘constant volume gas thermometer’ depicted in Fig. [CVGTa], in which the volume or pressure of a gas may be used to measure temperature. The gas is assumed to be in equilibrium at some pressure p , volume V , and temperature T . An incompressible fluid of density ρ is used to measure the pressure difference $\Delta p = p - p_0$, where p_0 is the ambient pressure at the top of the reservoir:

$$p - p_0 = \rho g(h_2 - h_1) , \quad (2.1.7)$$

where g is the acceleration due to gravity. The height h_1 of the left column of fluid in the U-tube provides a measure of the change in the volume of the gas:

$$V(h_1) = V(0) - Ah_1 , \quad (2.1.8)$$

where A is the (assumed constant) cross-sectional area of the left arm of the U-tube. The device can operate in two modes:

- Constant pressure mode : The height of the reservoir is adjusted so that the height difference $h_2 - h_1$ is held constant. This fixes the pressure p of the gas. The gas volume still varies with temperature T , and we can define

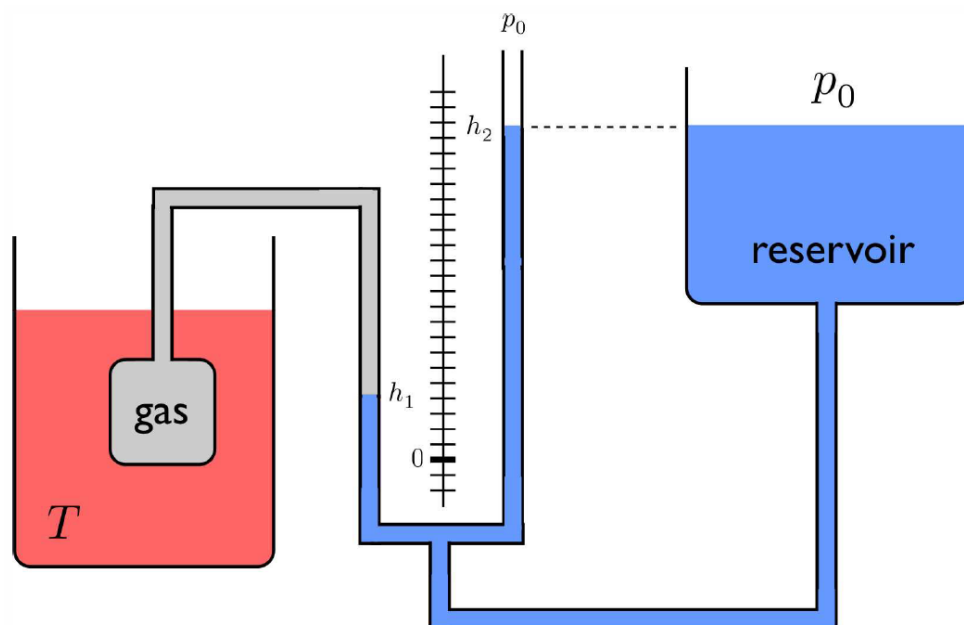
$$\frac{T}{T_{ref}} = \frac{V}{V_{ref}} , \quad (2.1.9)$$

where T_{ref} and V_{ref} are the reference temperature and volume, respectively.

- Constant volume mode : The height of the reservoir is adjusted so that $h_1 = 0$, hence the volume of the gas is held fixed, and the pressure varies with temperature. We then define

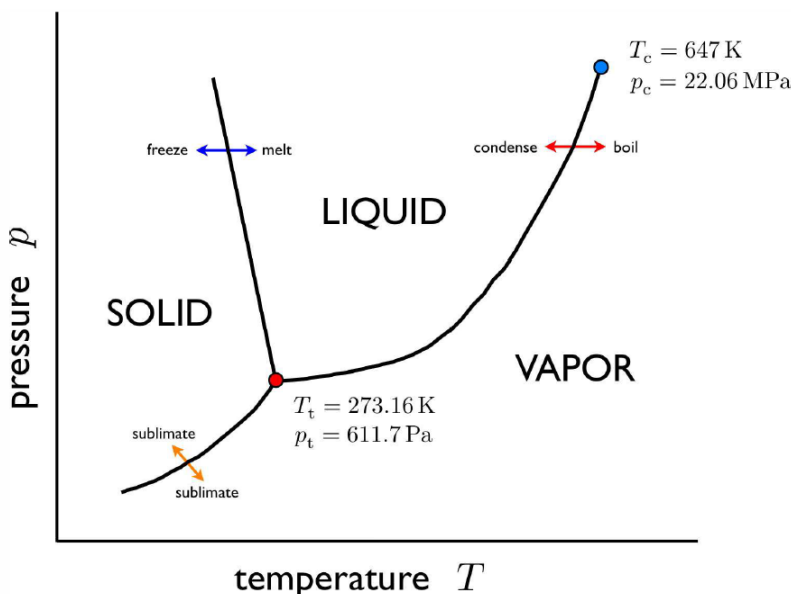
$$\frac{T}{T_{ref}} = \frac{p}{p_{ref}} , \quad (2.1.10)$$

where T_{ref} and p_{ref} are the reference temperature and pressure, respectively.



[CVGTa] The constant volume gas thermometer. The gas is placed in thermal contact with an object of temperature T . An incompressible fluid of density ρ is used to measure the pressure difference $\Delta p = p_{\text{gas}} - p_0$.

What should we use for a reference? One might think that a pot of boiling water will do, but anyone who has gone camping in the mountains knows that water boils at lower temperatures at high altitude (lower pressure). This phenomenon is reflected in the *phase diagram* for H_2O , depicted in Fig. [H2Opd]. There are two special points in the phase diagram, however. One is the *triple point*, where the solid, liquid, and vapor (gas) phases all coexist. The second is the *critical point*, which is the terminus of the curve separating liquid from gas. At the critical point, the *latent heat of transition* between liquid and gas phases vanishes (more on this later on). The triple point temperature T_t is thus *unique* and is by *definition* $T_t = 273.16 \text{ K}$. The pressure at the triple point is $611.7 \text{ Pa} = 6.056 \times 10^{-3} \text{ atm}$.



[H2Opd] A sketch of the phase diagram of H_2O (water). Two special points are identified: the triple point (T_t, p_t) at which there is three phase coexistence, and the critical point (T_c, p_c), where the latent heat of transformation from liquid to gas vanishes. Not shown are transitions between several different solid phases.

A question remains: are the two modes of the thermometer compatible? if we boil water at $p = p_0 = 1 \text{ atm}$, do they yield the same value for T ? And what if we use a different gas in our measurements? In fact, all these measurements will in general be *incompatible*, yielding different results for the temperature T . However, in the limit that we use a very low density gas, all the results converge. This is because all low density gases behave as *ideal gases*, and obey the ideal gas equation of state $pV = Nk_B T$.

Standard temperature and pressure

It is customary in the physical sciences to define certain standard conditions with respect to which any arbitrary conditions may be compared. In thermodynamics, there is a notion of *standard temperature and pressure*, abbreviated STP. Unfortunately, there are two *different* definitions of STP currently in use, one from the International Union of Pure and Applied Chemistry (IUPAC), and the other from the U.S. National Institute of Standards and Technology (NIST). The two standards are:

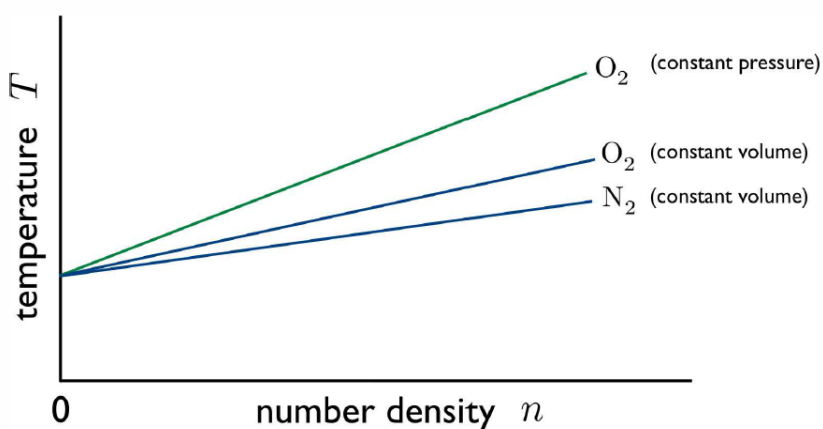
$$\begin{aligned} \text{IUPAC} &: T_0 = 0^\circ \text{C} = 273.15 \text{ K} \quad , \quad p_0 = 10^5 \text{ Pa} \\ \text{NIST} &: T_0 = 20^\circ \text{C} = 293.15 \text{ K} \quad , \quad p_0 = 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} \end{aligned}$$

To make matters worse, in the past it was customary to define STP as $T_0 = 0^\circ \text{C}$ and $p_0 = 1 \text{ atm}$. We will use the NIST definition in this course. Unless I slip and use the IUPAC definition. Figuring out what I mean by STP will keep you on your toes.

The volume of one mole of ideal gas at STP is then

$$V = \frac{N_A k_B T_0}{p_0} = \begin{cases} 22.711 \ell & (\text{IUPAC}) \\ 24.219 \ell & (\text{NIST}) \end{cases} \quad (2.1.11)$$

where $1 \ell = 10^6 \text{ cm}^3 = 10^{-3} \text{ m}^3$ is one liter. Under the old definition of STP as $T_0 = 0^\circ \text{C}$ and $p_0 = 1 \text{ atm}$, the volume of one mole of gas at STP is 22.414ℓ , which is a figure I remember from my 10^{th} grade chemistry class with Mr. Lawrence.



[CVGTb] As the gas density tends to zero, the readings of the constant volume gas thermometer converge.

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