

# Thermodynamics

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# Preface

# Chapter 1

## Temperature & Heat

### 1.1 Thermal Equilibrium

When two systems are in **thermal contact**, they are able to exchange energy with each other. The one that loses energy is said to be hotter/higher temperature. If two systems are in **thermal equilibrium**, it means that there is no *net* energy transfer.

### 1.2 The 0<sup>th</sup> Law

**Definition 1.1** (0<sup>th</sup> Law of Thermodynamics). If two systems are each in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.

### 1.3 Measuring Temperature

To measure temperature, we can make use of the fact that properties of materials are often a function of temperature. We pick a property of a system, measure it, and compare to measurements made at other known temperatures. For example, the Kelvin temperature scale uses the triple point of water (defined as 273.16K) and absolute zero to define a scale. A good thermometer for calibrating is a fixed-volume gas thermometer, because there is a linear relationship between pressure and temperature (for an ideal gas).

### 1.4 The 1<sup>st</sup> Law

We denote the **internal energy** of a system  $U$ . Energy can be transferred into or out of the system by **heat** ( $Q$ ) or **work** ( $W$ ). Heat is the energy transferred due to a difference in temperature, and work is the usable mechanical energy.

**Definition 1.2** (1<sup>st</sup> Law of Thermodynamics). The change in internal energy of a system is equal to the sum of the change in heat and the work done on the system.

$$\Delta U = Q + W \tag{1.1}$$

If  $Q$  is positive, the system is being heated up, if  $Q$  is negative, the system is heating something else. Likewise, if  $W$  is positive, then work is being done on the system and if  $W$  is negative, then work is being done by the system.

## 1.5 Crystal Structure & Interatomic Forces

Without interatomic forces, everything would be a gas. In a solid, energy of the atom is minimised by the bonding. For example, in ionic bonding, an electron is transferred from one atom to another, and the pair are held together by Coulomb's law. In covalent bonding, the energy of bonding electrons is minimised by sharing between atoms. There is also the van der Waals interaction which is due to dipole-dipole interactions.

Consider two atoms in a solid. When they get very close, there must be a repulsive force (otherwise matter would be infinitely dense). However, the force must become attractive further away (but still very close on a macroscopic scale). A simple model of an intermolecular force like this is the **Lennard-Jones potential**. It is given by

$$V(x) = 4\alpha \left[ \left( \frac{\beta}{x} \right)^{12} - \left( \frac{\beta}{x} \right)^6 \right] \quad (1.2)$$

This potential only really describes bonding between electrically neutral atoms or molecules, however the same is very similar for all types of bonding.

Close to the equilibrium separation, we can describe the Lennard-Jones potential can be approximated with a parabola.

$$V \propto (x - x_0)^2 \quad (1.3)$$

$$\implies F \propto -(x - x_0). \quad (1.4)$$

When looking at the stretching of materials, we can define two quantities. The **stress** is defined as the force per unit area.

$$\sigma = \frac{F}{A}. \quad (1.5)$$

The **strain** is defined as the proportional deformation of the material.

$$\varepsilon = \frac{\Delta L}{L}. \quad (1.6)$$

We can then define Young's modulus, which is a property that measures the stiffness of a solid material.

$$E = \frac{\sigma}{\varepsilon}. \quad (1.7)$$

## 1.6 Thermal Expansion

Near absolute zero, the average spacing of atoms is near  $x_0$ , but as energy is increased, more atoms will be sitting at higher energies so the average atomic separation will get larger (because of the asymmetry of the potential). Let  $L_0$  be the length of a solid bar at a temperature  $T$ .

Suppose that the length of the bar increases linearly with temperature (first approximation). If the temperature increases by  $\Delta T$ , the length increases by  $\Delta L$  and we write

$$\frac{\Delta L}{L_0} = \alpha \Delta T. \quad (1.8)$$

$\alpha$  is called the **coefficient of linear expansion** and may be different at different temperatures. Analogously, if a volume  $V_0$  increases by  $\Delta V$ , then we can write

$$\frac{\Delta V}{V_0} = \beta \Delta T, \quad (1.9)$$

where  $\beta$  is the **coefficient of volume expansion**. How is  $\beta$  related to  $\alpha$ ?

$$V_1 = V_0 + \Delta V \quad (1.10)$$

$$= (1 + \beta \Delta T) V_0. \quad (1.11)$$

Similarly,  $L_1 = (1 + \alpha \Delta T) L_0$ , and using  $V_1 = L_1^3$ , we get

$$V_1 = L_0^3 (1 + \alpha \Delta T)^3 \quad (1.12)$$

$$1 + \beta \Delta T = (1 + \alpha \Delta T)^3 \quad (1.13)$$

$$1 + \beta \Delta T \approx 1 + 3\alpha \Delta T \quad (1.14)$$

$$\beta \approx 3\alpha. \quad (1.15)$$

Where in the third line we have used the approximation  $(1 + x)^n \approx 1 + nx$  for small  $x$ .

**Example 1.1.** Consider a doughnut-shaped block of material which expands linearly with temperature. It has an initial inner and outer diameter  $r_0$  and  $R_0$  respectively. Find the new area of the block in terms of  $r_0$  and  $R_0$  after a temperature increase of  $\Delta T$ , and hence show that they increase linear with the change in temperature.

## 1.7 Heat Transfer

The transfer of energy by heating is always due to a temperature difference. The specific mechanism depends on the the material properties. For example, in a fluid the heating is caused by molecular collisions which transfer energy. In solids, energy is transferred by electrons or lattice vibrations known as phonons, depending on whether the material is electrically insulating or not. Fourier's heat conduction law states that

$$\frac{Q}{\Delta t} = P = -\kappa A \frac{dT}{dx}. \quad (1.16)$$

$P$  is the power transferred and  $\kappa$  is the thermal conductivity (measured in W/m/K). Under **steady state** conditions, meaning the temperature of the system and the surroundings at every point does not change with time (there may still be energy transfer), the law becomes

$$P = -\kappa A \frac{\Delta T}{\Delta x}. \quad (1.17)$$

An object that is so big that its temperature can be assumed to remain constant, no matter how much we heat or cool it, is known as a **thermal reservoir**. For example, a cup of tea will exchange heat with the air in the room that it sits in. It will cool down, but the room will not noticeably heat up.

**Example 1.2.** Consider three solid blocks between two thermal reservoirs which have temperatures  $T_1$  and  $T_2$  respectively.

**Example 1.3.** Consider two concentric cylinders.

## 1.8 Radiation

When it comes to heat transfer by radiation, the most important equation is the **Stefan-Boltzmann Law**,

$$P = \sigma \varepsilon A T^4. \quad (1.18)$$

$A$  is the surface area of the object,  $T$  is the surface temperature,  $\varepsilon$  is the emissivity, a dimensionless constant between 0 and 1 that determines how efficiently the object radiates energy, and  $\sigma$  is the Stefan-Boltzmann constant. A perfectly reflecting object has  $\varepsilon = 0$  and a perfectly absorbing and emitting object has  $\varepsilon = 1$ .

## Chapter 2

# Kinetic Theory

### 2.1 The Ideal Gas Law

An ideal gas is one where the particles can be considered point-like, meaning the average distance between particles is very large compared to particle size. We also assume that the particles interact only in perfectly elastic collisions (there are no intermolecular forces). This might sound like a very simplistic set of assumptions, but it turns out to be a very useful model. From these assumptions, we get the ideal gas law:

$$PV = nRT, \quad (2.1)$$

where  $R$  is the gas constant, equal to  $N_A K_B$ . Using this we can write the physicists version of the ideal gas law:

$$PV = NK_B T. \quad (2.2)$$

The ideal gas law is an example of an equation of state, one that relates state variables of a system to each other. Due to the assumptions that we have made, this equation only holds in the real world for gases that are in equilibrium (or very close to it). Note that a “state variable” is a property of the system that depends only on the current state, and not the past states.

Let’s focus on a single particle in an ideal gas in a container. If the particle hits the wall in the  $y - z$  plane, only the  $x$  component of the velocity will change since it is an elastic collision. Thus the pressure on the wall is due to the  $x$  component of the momentum. The particle’s momentum changes by  $\Delta p_{x,i} = -2mv_{x,i}$  so due to conservation of momentum there is  $\Delta p_{x,i} = 2mv_{x,i}$  imparted to the wall. The change in momentum is equal to the force multiplied by the time interval  $\Delta p = F\Delta t$ , so since pressure is defined as force per unit area, we get

$$\Delta p_{x,i} = P_i A \Delta t_i. \quad (2.3)$$

$P_i$  is the pressure due to particle  $i$  on the wall and  $\Delta t_i$  is the time interval between collisions for particle  $i$ . Now if we imagine the particle bouncing back and forth in the box of width  $L$ , then the time between collisions is given by

$$\Delta t_i = \frac{2L}{v_{x,i}}. \quad (2.4)$$

Substituting this into the equation above we get

$$P_i V = mv_{x,i}^2, \quad (2.5)$$



where  $V = AL$ . The total pressure on the wall is simply equal to the sum of this quantity for all particles:

$$PV = \sum_{i=1}^N mv_{x,i}^2 = m \underbrace{\sum_{i=1}^N v_{x,i}^2}_{N\bar{v}_x^2} \quad (2.6)$$

The bar above the velocity denotes the mean. Now, note that

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2, \quad (2.7)$$

so assuming the velocity of the particles is **isotropic** (meaning there is not preferred direction),

$$\bar{v}_x^2 = \frac{1}{3}\bar{v}^2, \quad (2.8)$$

and hence by using the ideal gas law,

$$PV = \frac{1}{3}Nm\bar{v}^2 = Nk_B T \quad (2.9)$$

$$\implies \bar{v}^2 = \frac{3k_B T}{m}. \quad (2.10)$$

If we take the square root of both sides, we get the **root mean square velocity**:

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}. \quad (2.11)$$

## 2.2 Equipartition Theorem

The internal energy of a gas is a state variable. It is the sum of all of the types of energy contained in the gas; kinetic, potential, mass, and chemical. For a monatomic ideal gas, we only have kinetic energy, and moreover the kinetic energy is purely translational:

$$U = \frac{1}{2}Nm\bar{v}^2 = \frac{3}{2}Nk_B T. \quad (2.12)$$

Note that this is a constant times  $N$ , meaning that on average each atom has an energy of  $\frac{3}{2}k_B T$ , or  $\frac{1}{2}k_B T$  for each translational degree of freedom. This is known as the **equipartition theorem**. In general, an ideal gas with  $N$  particles and  $f$  quadratic degrees of freedom will have an internal energy of

$$U = \frac{f}{2}Nk_B T. \quad (2.13)$$

Note that a quadratic degree of freedom is one where the associated energy is proportional to the square of a position or momentum variable. For example, translation motion  $E = \frac{1}{2}mv^2$ , elastic potential energy  $E = \frac{1}{2}kx^2$ , or rotational kinetic energy  $E = \frac{1}{2}I\omega^2$ . A diatomic gas has 3 translational degrees of freedom, along with 2 rotational and 2 vibrational (one for the kinetic energy and one for the potential energy). This makes 7 in total, however at lower temperatures some of these modes will not be excited and the degrees of freedom will be “frozen out”. For example, at room temperature, diatomic oxygen and nitrogen have 5 degrees of freedom.

Let's look at the average distance between collisions, also known as the **mean free path**. A collision between two particles occurs if a particle comes within a diameter  $d$  of another. Identically, we can consider a particle with cross-sectional area  $2d$  and ask about the probability that a particle enters the volume traced out:

$$\pi d^2 \lambda \frac{N}{V} = 1 \quad (2.14)$$

$$\implies \lambda = \frac{V}{N\pi d^2}. \quad (2.15)$$

If we remember that all particles are moving, this gets reduced by a factor of  $\frac{1}{\sqrt{2}}$ :

$$\lambda = \frac{V}{\sqrt{2}N\pi d^2} = \frac{1}{\sqrt{2}n\pi d^2}. \quad (2.16)$$

Note that we have defined the number density  $n = \frac{N}{V}$ .

It can be shown that in an ideal gas, the velocities are distributed according to the **Maxwell-Boltzmann Distribution**. This takes the form

$$p(v) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{\frac{3}{2}} v^2 \exp \left( -\frac{mv^2}{2k_B T} \right), \quad (2.17)$$

where  $p(v)$  is the probability density of a single particle having speed  $v$ . Note that this probability distribution is properly normalised so that  $\int_0^\infty p(v)dv = 1$ . At higher temperatures, the tail drops off much less i.e. there are a much wider range of velocities. From this distribution, we can measure some characteristic speeds. The most probable speed is found at the peak of the distribution, which is found by differentiating:

$$\frac{dp}{dv} = 0 = 2Ave^{-av^2}(1 - av^2) \quad (2.18)$$

$$\implies av_{\text{mp}}^2 = 1 \quad (2.19)$$

$$v_{\text{mp}} = \sqrt{\frac{1}{a}} = \sqrt{\frac{2k_B T}{m}}. \quad (2.20)$$

The mean speed will be to the right of the most probable speed since the distribution is asymmetric. It is found by integrating the distribution multiplied by  $v$ :

$$\bar{v} = \int_0^\infty vp(v)dv = A \int_0^\infty v^3 e^{-av^2} dv \quad (2.21)$$

$$= \frac{1}{2} A a^{-2} \quad (2.22)$$

$$= \sqrt{\frac{8k_B T}{\pi m}}. \quad (2.23)$$

Finally, we can calculate the root mean square speed just to check our answer from before:

$$v_{\text{rms}} = \sqrt{\int_0^\infty v^2 p(v)dv} = \sqrt{A \int_0^\infty v^4 e^{-av^2} dv} \quad (2.24)$$

$$= \sqrt{A \frac{3}{8} \sqrt{\pi} a^{-\frac{5}{2}}} \quad (2.25)$$

$$= \sqrt{\frac{3k_B T}{m}}. \quad (2.26)$$

## Chapter 3

# Thermodynamic Processes

### 3.1 Reversible & Irreversible Processes

A reversible process is one in which after it is carried out, the system can be restored to its starting conditions without any change in the rest of the universe. For irreversible processes, this is not possible. For example, free expansion of an ideal gas is irreversible (a gas won't contract by itself). The gas does no work as it expands, its internal energy does not change and neither does its temperature. We call processes where no energy is transferred by heating **adiabatic**.

$$Q = 0, \quad \Delta U = W. \quad (3.1)$$

Free expansion is adiabatic, but not all adiabatic processes are irreversible.

Imagine we have an ideal gas contained in a box with a piston on the top face. If we decrease the force on the piston, the gas will be allowed to expand slowly. The work done by the gas on the piston is equal to  $W$ , which is equivalent to  $-W$  being done on the gas.

$$dW = -Fdz. \quad (3.2)$$

The force on the piston  $F$  is equal to the gas pressure times area  $PA$ , and noting that  $Adz = dV$ , we get

$$dW = -PdV. \quad (3.3)$$

Using the first law (since  $Q = 0$ ), we get that

$$dU = -PdV, \quad (3.4)$$

and hence

$$W = - \int_{V_i}^{V_f} P(V)dV. \quad (3.5)$$

This is valid for an adiabatic process of slow expansion/compression, which is also reversible. This integral can be visualised as the area under a plot of pressure  $P$  as a function of volume  $V$  (a  $P$ - $V$  diagram).

On a  $P$ - $V$  diagram, two different paths can have the same set of initial and final conditions and yet the work can be different because work is not a function of state, it is **path dependent**. For some processes, like free expansion, the process is not even continuous so it is impossible to draw the path of the system on a  $P$ - $V$  diagram. In the last chapter, we saw that  $dU = \frac{f}{2} Nk_B dT$ . Using this and the ideal gas law, we get

$$-\frac{dV}{V} = \frac{f}{2} \frac{dT}{T} \quad (3.6)$$

$$-\int_{V_i}^{V_f} \frac{dV}{V} = \frac{f}{2} \int_{T_i}^{T_f} \frac{dT}{T} \quad (3.7)$$

$$\Rightarrow T_i V_i^{\frac{2}{f}} = T_f V_f^{\frac{2}{f}} \quad (3.8)$$

$$P_i V_i^{1+\frac{2}{f}} = P_f V_f^{1+\frac{2}{f}}. \quad (3.9)$$

If we define  $\gamma = 1 + \frac{2}{f}$ , we get

$$P_i V_i^\gamma = P_f V_f^\gamma. \quad (3.10)$$

Se reversible adiabatic processes for an ideal gas follow lines where this quantity  $PV^\gamma$  is constant. These lines are called **adiabats**. On the other hand, **isothermal processes**, ones that occur at constant temperature follow **isotherms**, which are given by  $P \propto V^{-1}$ . Thus adiabats always drop off faster with volume than isotherms since  $\gamma > 1$ .

## 3.2 Heat Capacity

Heat capacity tells us the amount of heat we need to add to raise a system's temperature by one unit.

$$C = \frac{dQ}{dT}. \quad (3.11)$$

Note that this depends on how much substance our system contains. Specific heat capacity is defined for a unit mass:

$$c = \frac{C}{m} = \frac{1}{m} \frac{dQ}{dT}. \quad (3.12)$$

From the first law of thermodynamics, we know that

$$dQ = dU - dW, \quad (3.13)$$

and hence,

$$C = \frac{dU - dW}{dT}. \quad (3.14)$$

This means that heat capacity can be different depending on the work done. We need to specify some more conditions so that heat capacity is useful. Using  $dW = -PdV$ , we get

$$C = \frac{dU}{dT} + P \frac{dV}{dT}. \quad (3.15)$$

Now we can define two different heat capacities, one at constant volume where  $dV = 0$  and one at constant pressure.

$$C_v = \left( \frac{\partial U}{\partial T} \right)_V \quad (3.16)$$

$$C_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial P} \right)_P. \quad (3.17)$$

Now using the equipartition theorem  $U = \frac{f}{2}Nk_B T$ , we get

$$C_V = \frac{f}{2}Nk_B \quad (3.18)$$

$$C_p = \frac{f}{2}Nk_B + P \frac{\partial}{\partial T} \left( \frac{Nk_B T}{P} \right) \quad (3.19)$$

$$= \left( 1 + \frac{f}{2} \right) Nk_B. \quad (3.20)$$

So, we see that the ratio of the two specific heats is

$$\frac{C_P}{C_V} = 1 + \frac{2}{f} = \gamma. \quad (3.21)$$

Sometimes we can add or remove energy from a system without changing the temperature e.g. during a first-order phase transition. These transitions involve **latent heat**, which is the amount of heat needed to make a unit mass of substance undergo the phase change.

$$L = \frac{Q}{m}. \quad (3.22)$$

However, this is still ambiguous as it doesn't specify the conditions that the system is in during the phase change. We usually say that the substance is under constant pressure and the only work done in the process is expansion against the atmosphere.

# Chapter 4

## Entropy

### 4.1 Multiplicity, Macrostates, & Microstates

Why does heat transfer only take place from hot to cold? Technically, the first law does not disallow heat flowing from cold to hot. If we want to examine how systems exchange energy, it makes sense to first look at how energy is spread out in a system. Consider a system which is comprised of many particles but which can be described by a few state parameters which describe the system as a whole. These bulk properties define the **macrostate** of the system (for example, having a certain temperature, pressure, volume). A different approach would be to specify the properties of every single particle e.g. the position and momentum. This defines the **microstate** of the system. For any given macrostate, there will be many possible microstates. The number of microstates consistent with the macrostate of the system is called the **multiplicity**.

For a isolated system in thermal equilibrium, all the accessible microstates are equally probable. For example, consider a system of  $N$  coins. We can define the macrostate of the system as how many heads we have after tossing all of them.

Imagine a 2-egg egg box and the macrostate of 2 eggs in the box. There is only 1 way to arrange these eggs so the multiplicity is 1. Consider increasing the volume of the box to 4 eggs. Now there are 6 different ways to arrange the two eggs in the box, so the multiplicity has increase. This is a general feature, multiplicity of a given macrostate will increase when the volume or “size” of the system is increased.

Now consider an ideal gas at pressure  $P$  and volume  $V$  in thermal equilibrium with a reservoir at temperature  $T$ . If there is a movable frictionless insulating piston on top and the force on the piston is reduced, the gas expands to volume  $V + dV$ . The gas goes work, but its temperature stays constant, so  $\Delta U = 0$ . Thus, we have

$$dQ = -dQ_R, \tag{4.1}$$

where  $Q_R$  stands for heat added in a reversible process. The larger the volume, the greater the multiplicity. Let  $x$  be the number of positions available for the particles. Note that  $x \gg N$  since we have an ideal gas which must be at low density. There are approximately  $x^N$  ways of

arranging the particles, so the multiplicity is proportional to  $x^N$

$$\Omega \propto x^N. \quad (4.2)$$

$x$  is proportional to  $V$ , so  $\Omega \propto V^N$ . Hence we can write

$$\frac{\Omega_{V+dV}}{\Omega_V} = \left( \frac{V+dV}{V} \right). \quad (4.3)$$

Since we know from the last chapter that the work done by the gas is  $dW = PdV$ , we have that

$$dQ_R = PdV \quad (4.4)$$

$$= Nk_B T \frac{dV}{V} \quad (4.5)$$

$$\implies \frac{dV}{V} = \frac{dQ_R}{Nk_B T}. \quad (4.6)$$

Combining this with the relation above we get

$$\ln \left( \frac{\Omega_{V+dV}}{\Omega_V} \right) = N \ln \left( 1 + \frac{dQ_R}{Nk_B T} \right). \quad (4.7)$$

Note that  $\frac{dQ_R}{Nk_B T} \ll 1$ , so we can use the Taylor expansion for  $\ln(1+x) \approx x$ , and we get

$$k_B \ln \Omega_{V+dV} - k_B \ln \Omega_V = \frac{dQ_R}{T}. \quad (4.8)$$

What about free expansion? As we saw before, no work is done by the gas and there is no heat transfer to the gas, so  $\Delta U = 0$ . The start and end macrostates under an expansion from  $V$  to  $V+dV$  are the same for the isothermal reversible expansion considered above. Thus the quantity  $k_B \ln \Omega_{V+dV} - k_B \ln \Omega_V$  must be the same for both processes.

Consider adding a small amount of heat to an ideal gas but keeping the volume constant. The average momentum of the particles changes, so the number of ways that momenta can be assigned to individual particles changes, meaning the multiplicity changes. Assuming that  $U = \frac{3}{2}k_B T$ , we have

$$\frac{3}{2}k_B T = \frac{\bar{p}^2}{2m} \quad (4.9)$$

$$\implies \bar{p} \propto \sqrt{T}. \quad (4.10)$$

The number of allowed momentum values in any given direction is proportional to  $\bar{p}$  (the width of the probability curve is proportional to  $\bar{p}$ ). Thus the total number of allowed momentum values, which is proportional to the multiplicity, is given by

$$\Omega \propto \bar{p}^3 \propto T^{\frac{3}{2}}. \quad (4.11)$$

For  $N$  particles, this means

$$\Omega \propto T^{\frac{3N}{2}}. \quad (4.12)$$

From everything we have seen, we can say that the general expression for multiplicity is

$$\Omega = F(N)V^N T^{\frac{3N}{2}} \ln \Omega = \ln F(N) + N \ln V + \frac{3N}{2} \ln T. \quad (4.13)$$

Note that

$$\ln(T + dT) - \ln T = \frac{dT}{T}, \quad (4.14)$$

so

$$k_B \ln \Omega_{T+dT} - k_B \ln \Omega_T = \frac{3N}{2} k_B \frac{dT}{T} \quad (4.15)$$

$$k_B \ln \Omega_{T+dT} - k_B \ln \Omega_T = \frac{dQ_R}{T}, \quad (4.16)$$

where in the last line we have used  $dU = dQ_R$ .

What we have shown is that this quantity  $k_B \ln \Omega$ , which we will call  $S$  is a state variable (path independent). We call  $S$  the **entropy**. We have found that the change in entropy is the same for slow heating, where heat is added reversibly, and in free expansion, where no heat is added. In general, for any isothermal process, we have

$$\Delta S \geq \frac{Q}{T}. \quad (4.17)$$

**Definition 4.1** (Second Law of Thermodynamics). The entropy of a thermally isolated system increases in any irreversible process and stays the same in a reversible one.

$$\Delta S \geq 0. \quad (4.18)$$

An isolated system will always evolve to the state of highest entropy and stay there. The energy in the system “spreads out”. We now have a new definition for a reversible process, one where the entropy of the system and the rest of the universe stays the same.

**Example 4.1.** Consider two blocks in thermal contact between two thermal reservoirs of temperature  $T_1$  and  $T_2$  respectively. If  $T_2 > T_1$ , then heat will flow through the blocks. We have that

$$\Delta S_1 = \frac{Q}{T_1} \quad (4.19)$$

$$\Delta S_2 = -\frac{Q}{T_2}. \quad (4.20)$$

But since we know  $|\Delta S_1| > |\Delta S_2|$ , we have

$$\Delta S_1 + \Delta S_2 > 0. \quad (4.21)$$

## 4.2 Entropy & Temperature

Recall that when a gas is heated slowly at constant volume,

$$dS = \frac{dQ_R}{T}. \quad (4.22)$$

In this case, the work done is 0, so by the first law we have

$$dS = \frac{dU}{T}, \quad (4.23)$$



or alternatively,

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}. \quad (4.24)$$

From this we get an alternative definition of the first law:

$$dU = TdS - PdV. \quad (4.25)$$

This is the first law defined completely in terms of state variables. To calculate entropy changes for a reversible process, we have

$$\Delta S = \int dS = \int \frac{dQ_R}{T}. \quad (4.26)$$

If our process is irreversible, free expansion for example, then we need to identify an equivalent reversible process with the same start and end conditions. This works because we know the entropy change will always be the same.

At constant volume with no work done, we have

$$dS = \frac{dU}{dT} \frac{dT}{T} \quad (4.27)$$

$$= C_V \frac{dT}{T} \quad (4.28)$$

$$\Rightarrow C_V = T \left(\frac{\partial S}{\partial T}\right)_V. \quad (4.29)$$

# Chapter 5

## Heat Cycles

### 5.1 Heat Engines

A heat engine is a generic name for a system that absorbs heat and converts some of it into useful work. Heat engines contain a working substance which we do processes on. The process in the engine must be cyclic to be practical. Heat is added to the working substance, the entropy of the working substance increases, then we dump the extra entropy into a cold reservoir to return the substance to its original state.

An alternative way of stating the second law is that no series of processes which transfer energy to a body as heat and the completely converts the energy to work is possible. One of the most historically significant and well-known heat engines is the **Carnot cycle**.

- (i) Isothermal expansion, gas is doing work on outside world.
- (ii) Adiabatic expansion, gas is doing work again.
- (iii) Isothermal compression, outside world is doing work on the gas.
- (iv) Adiabatic compression, outside world is doing work on the gas again.

The work extracted from this cycle is given by the area enclosed by the process in a  $P$ - $V$  diagram. The isothermal expansion is propelled by absorption of heat. In the second phase, the gas is allowed to expand, doing work and losing energy. The the gas is cooled by the reservoir and compressed, which takes less energy to the expansion phase due to the gas being at lower pressure. Finally, the gas is adiabatically compressed to bring its internal energy back to where it started. Let's look at the change in entropy during the Carnot cycle. We already know what the entropy change is from processes we have studied before. In the isothermal expansion phase, the entropy change is

$$\Delta S_{\text{gas}} = \frac{Q_{\text{hot}}}{T_{\text{hot}}}, \quad \Delta S_{\text{hot}} = -\frac{Q_{\text{hot}}}{T_{\text{hot}}}, \quad (5.1)$$

where  $Q_{\text{hot}}$ , is the heat transferred from the hot reservoir and  $T_{\text{hot}}$  is the temperature of the hot reservoir. In the next phase, the expansion is adiabatic so the entropy change is zero.

$$\Delta S_{\text{gas}} = 0. \quad (5.2)$$

Now in the isothermal compression phase, the gas is exchanging heat with the cold reservoir:

$$\Delta S_{\text{gas}} = -\frac{Q_{\text{cold}}}{T_{\text{cold}}}, \quad \Delta S_{\text{cold}} = \frac{Q_{\text{cold}}}{T_{\text{cold}}}. \quad (5.3)$$

Finally, in the last phase, the entropy change is once again zero since the compression is adiabatic.

$$\Delta S_{\text{gas}} = 0. \quad (5.4)$$

In total, since the gas starts and finishes in the exact same configuration, the entropy change over the whole cycle must be zero. This implies that

$$\frac{Q_{\text{hot}}}{T_{\text{hot}}} = \frac{Q_{\text{cold}}}{T_{\text{cold}}}. \quad (5.5)$$

We can define the efficiency of the Carnot cycle as the work done by the gas during phase 2 compared to the heat transferred from the hot reservoir to the gas.

$$\varepsilon = -\frac{W_{\text{cycle}}}{Q_{\text{hot}}}. \quad (5.6)$$

By the first law of thermodynamics we have

$$Q_{\text{hot}} - Q_{\text{cold}} + W_{\text{cycle}} = 0, \quad (5.7)$$

since the total change in internal energy is zero. By dividing this equation by  $Q_{\text{hot}}$  and rearranging, we get

$$\varepsilon = 1 - \frac{Q_{\text{cold}}}{Q_{\text{hot}}} \quad (5.8)$$

$$= 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}. \quad (5.9)$$

It can be proven that this is actually an upper limit on the efficiency of *any* reversible process!

## 5.2 Refrigerators

We can also model thermodynamic cycles which *remove* energy from a substance (i.e. a refrigerator) by looking at a heat engine in reverse. For example, a simple model of a refrigerator is as a Carnot cycle in reverse. The refrigerator remove energy from a cold reservoir and dumps it in a hot reservoir by using work. A hypothetical perfect fridge would not need energy to run i.e.  $W = 0$ . In this case, the entropy changes of the hot and cold reservoirs are given by

$$\Delta S_{\text{cold}} = -\frac{Q}{T_{\text{cold}}}, \quad \Delta S_{\text{hot}} = \frac{Q}{T_{\text{hot}}}. \quad (5.10)$$

Note that  $Q_{\text{cold}} = Q_{\text{hot}} = Q$  since  $W = 0$ . Then the total entropy change of the entire system is

$$\Delta S_{\text{total}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} \quad (5.11)$$

$$= \frac{Q}{T_{\text{hot}}} - \frac{Q}{T_{\text{cold}}}. \quad (5.12)$$

Since  $T_{\text{hot}} > T_{\text{cold}}$ ,  $\Delta S_{\text{total}} < 0$  which is disallowed by the second law, so a perfect fridge *cannot* exist. In other words, the second law says that no series of processes that transfers energy from a cold body to a hot body purely by heat transfer is possible.

We can define a coefficient of performance analogously to the efficiency of a heat engine as the heat extracted from the cold reservoir divided by the work input to the cycle.

$$\kappa = \frac{Q_{\text{cold}}}{W_{\text{cycle}}}. \quad (5.13)$$

Using the first law again just like before, we get

$$W_{\text{cycle}} = Q_{\text{hot}} - Q_{\text{cold}} \quad (5.14)$$

$$\kappa = \frac{Q_{\text{cold}}}{Q_{\text{hot}} - Q_{\text{cold}}}. \quad (5.15)$$

### 5.3 Heat Pumps

For a heat pump, where the objective of the cycle is to take energy from a cold reservoir and “pump” it into a hot reservoir, the cycle is equivalent to that of a refrigerator. We define the coefficient of performance differently to reflect the different purpose of the cycle.

$$\text{C.O.P.} = \frac{Q_{\text{hot}}}{W} \quad (5.16)$$

$$= \frac{Q_{\text{cold}} + W}{W} \quad (5.17)$$

$$= \frac{T_{\text{hot}}}{T_{\text{hot}} - T_{\text{cold}}}. \quad (5.18)$$