Maithripala D. H. S.,
Dept. of Mechanical Engineering,
Faculty of Engineering,
University of Peradeniya,
Sri Lanka.

Lecture Notes on Classical Thermodynamcis

Class notes for GP111

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Preface

The word 'thermodynamics' is derived from the greek words 'thermo' meaning heat and 'dynamics' meaning power. Today it is used to describe the interplay between energy and work. It arose out of the attempt to get work out of energy and was the driving force behind the industrial revolution. The formal study of thermodynamics is based on the quest for describing empirical observations using the fewest number of laws or axioms. These laws are, basically, general statements about the behavior of the universe as we perceive it through our senses. They are expressed using the universal language of mathematics. This quest that intensified in the 17th century gave rise, by the mid of the 19th century, to four fundamental axioms that describe the thermodynamic behavior of everyday systems. All hitherto conducted experiments have verified these axioms and no experiment has ever been able to contradict these axioms. Thus they have been accepted as fundamental laws that govern the thermodynamic behavior of observable physical systems. In the following notes I will attempt to describe these laws, the road to their discovery, their implications, and limitations. The road to the discovery of these four fundamental laws of thermodynamics was not clean. It was iterative. The discussion will not follow its chronological development but will follow an axiomatic development that is similar to that of euclidean geometry that you are familiar with. We will begin by making a few definitions and making a few assumptions. Then we will state the laws using these definitions, discuss the motivation for the statement of the laws, and then consider the physical implications of these laws. Specifically we will see that these laws enforce constraints on the amount of energy that can be converted into work.

Historically the laws of thermodynamics were developed phenomenologically using a *systems* perspective[1]. Later towards the end of the 19th century and the beginning of the 20th century it was established that everything was made-up of 'particles'. In this context it became a challenge to interpret or validate the four fundamental laws of thermodynamics using this microscopic picture of matter. The quest was successfully completed by Maxwell, Boltzmann, and Gibbs. In this notes we will consider both the phenomenological and microscopic aspects in an attempt to gain a better understanding of the four fundamental laws of thermodynamics. The topic is a classic example of the application of the process of logic and reasoning. I invite the reader to think it through for themselves and reason out the plausibility of these four fundamental laws and deduce the many physical implications of these laws of nature.

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[1] This point of view is also called the macroscopic view.

Through this process we will also hope to gain a better understanding of key thermodynamic notions such as temperature, internal energy, heat, and entropy.

This is a compilation of notes that originated as class notes for GP111 at the University of Peradeniya in the year 2015. It is an attempt by me to present thermodynamics in an intuitive axiomatic way. I have tried to strike a balance between simplicity and rigor. They are far from complete and I will be frequently updating them as time permits. I am deeply indebted to all the students who have suffered through them and have tried out the exercises and have provided me with valuable input. I am sure there are many errata and will greatly appreciate if you can please bring them to my notice by sending an e-mail to mugalan at gmail.com. The treatment contained in the book is based on the excellent lecture notes by R. P. Feynman [5] and H. Gould and J. Tobochnik [6]. For an interesting historical perspective I refer the reader to the freely available e-book by J. M. Powers [1] while I refer the reader to [4, 3] for a more advanced mathematically rigorous axiomatic treatment of the subject.

Peradeniya, Sri Lanka,   *D. H. S. Maithripala*
                                                                     June 25, 2019

Contents

Chapter 1
The System, Surrounding, and the Universe

It turns out that all of the fundamental concepts of thermodynamics can be understood quite intuitively if we take for granted that everything is made up of particles. This assumption is thought to be the most fundamental hypothesis of nature. Thus let us begin our quest by stating it as an axiom.

Axiom 1.1 Particle Hypothesis: *Everything is made-up of indivisible units called particles that are never still.*

Before proceeding any further let us ask if it is reasonable to make such a daring assumption. What evidence do we have to justify such a claim? For instance is the air that we breath made of particles? The zig-zag random dance that a speck of dust does in a beam of sunlight that falls into a dark room tells us that air is indeed made out of particles that are moving in a never ending manner[1]. Around the early 1800s, while looking through a microscope at pollen trapped in cavities, the botanist Robert Brown noticed that the pollen moved through the water in a random zig-zag irregular kind of way similar to that of the dust particles[2]. Albert Einstein explained this, mathematically, as a consequence of the particle nature of water. He showed that the very high energy motion of the water molecules was the cause of the random zig-zag motion of pollen in water and thereby establishing the particle nature of matter. Today this particle hypothesis of matter has been experimentally and theoretically justified irrefutably and we will take it as one of the mysterious ways in which we perceive nature to behave. Specifically, as of now it has been established that matter in the Universe is made of particles that we call *atoms* and that each of these atoms are made up of more fundamental particles called *electrons, protons, and neutrons*[3]. Armed with this basic assumption of the particle nature of matter, let us proceed to define a few terms that are necessary when one has to deal with getting work out of something[4].

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[1] Can you reason out why?

[2] This type of motion is called Brownian Motion.

[3] It is also known that protons and neutrons are made up of even more fundamental particles called *Quarks*.

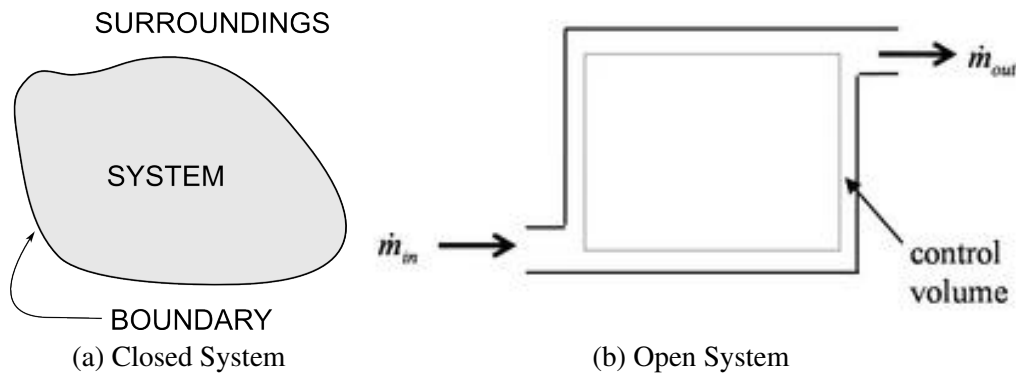[4] The driving force behind the study of thermodynamics.

Fig. 1.1 Schematic representation of a system.

Definition 1.1. Closed System: A specific set of particles will be called a closed system.

Definition 1.2. Open System: A specified volume in space where particles are allowed to move in and out of the volume will be called an open system. The specified volume in space is usually called the *control volume*.

Definition 1.3. Macroscopic System: Roughly speaking, a macroscopic system is a system with a volume that is visible to the naked eye. A little more precisely stated a macroscopic system is a system of a large number of particles so that statistical properties of the collection of particles can be defined sufficiently accurately.

Typically the number of particles contained in such a system is of the order of the Avogadro's number[5], $\mathscr{N}_A = 6.0221 \times 10^{23}$. In this course we will only consider the thermodynamics of *macroscopic* systems and hence we will often omit the word macroscopic when referring to such systems and call them simply systems. The size of an atom and the interatomic distances in solids is of the order of 10^{-10}m. Thus we see that even a tiny speck of dust[6] that is of roughly the volume of $10^{-1} \times 10^{-1} \times 10^{-1}\, mm^3$, has about 10^{18} particles.

Definition 1.4. Surrounding: The surrounding is defined to be everything else other than the system of interest.

Definition 1.5. Universe: The universe is defined to be the system and the surroundings. That is everything there is in existence.

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[5] This peculiar looking number was traditionally chosen by Chemists since the mass of this many number of carbon atoms of isotope 12 turned out to be exactly 12 grams.
[6] The smallest objects that are visible to the naked eye are about $60\mu m = 0.06\, mm$.

Definition 1.6. System Boundary: The interface between a system and the surrounding is defined to be the system boundary.

Note that the universe, being everything there is in existence, can be considered a closed system by definition.

Chapter 2
Kinetic Theory of Gases and the Ideal Gas Law

Having defined a few terms of interest let us begin our study of thermodynamics by investigating the behavior of a collection of a large number of *gas* particles. The experience we have with observing the irregular zig-zag motion[1] of specks of dust and the many scientific experiments and observations regarding a system of gas particles tell us that the gas particles are moving incessantly. As a first step we will assume that these moving gas particles do not interact with each other except when they 'collide' with each other. Such a system is called an *ideal gas* and they do not exist in reality. However there are certain gases that behave approximately in this fashion. Furthermore consideration of this ideal situation may allow us to derive explicit expressions to model its behavior. Doing so will help us understand the thermodynamic behavior of more general systems a little more clearly. Thus we will consider this ideal situation first. The particles that makeup a gas are called the gas *molecules*. A molecule can be a single atom like in He or Ar or a molecule can be made up of several atoms like in H_2, O_2, CO_2 or NH_3.
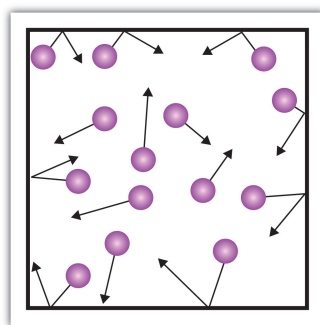

Fig. 2.1 The irregular motion of widely spaced gas particles inside a container. Figure courtesy of http://2012books.lardbucket.org/books/the-basics-of-general-organic-and-biological-chemistry/

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[1] Brownian motion.

2.1 Thermodynamic equilibrium

How can we define the behavior of a collection of an extremely large number[2] of moving molecules? Clearly, from a practical point of view, the extremely large number prevents us from keeping track of each and every molecule. Thus the best that we can hope for is to find a few number of quantities that in some sense will capture the collective behavior of the molecules. In this search, the first question that we need to answer is: do such quantities exist?

May be the best way to answer these questions for ourselves is to think of our ordinary experience with gaseous systems and use our imagination to hypothesize a situation that will give rise to the observations we make. For instance consider a balloon filled with air. We have observed that there are some properties of the entire collection of gas molecules in the ballon that can be easily quantified[3] such as the *mass* and *volume* of the entire system of particles. We have observed that these quantities do not change with time. We have also noticed that the more air we blow into the balloon the heavier it gets and the bigger it gets. Thus could these quantities be used to represent the collective behavior of all the molecules. Well, why not? Such quantities that define some measure of the collective steady behavior of a large number of particles are called *thermodynamic properties* or *macroscopic properties* of the system.

Do there exist other quantities such as the mass and the volume? If we think a little bit more about the balloon we would realize that something inside the balloon is preventing the balloon from collapsing in. That is, these moving molecules, some how, apply a force on the inside surface of the balloon. We will also notice that the magnitude of the force that we have to exert in order to squeeze the balloon is pretty much the same everywhere on its surface and that this force remains the same over time. Thus the force per unit area, which is called *pressure*, acting on the surface of the ballon could also serve as another macroscopic property that captures the collective behavior of the system of molecules.

How does this pressure arise? It is not too hard to imagine that may be, similarly to what might happen if we throw a bunch of pebbles at a screen, the constant bombardment of the moving gas molecules is the reason for this pressure exerted on the inside surface of the balloon. More specifically each molecule upon collision with the molecules of the inside surface of the balloon 'bounces' off causing a change in the momentum of the gas molecules. But the principle of conservation of momentum of *Galelian mechanics* tells us that there should be an equal and opposite change in the momentum of the molecules of the balloon that take part in the collision as well. The rate of the change of the momentum of the molecules of the balloon is by definition the force felt by the balloon. Hence the rate of change of momentum of the molecules of the balloon per unit area that occurs due to the constant bombardment of the air molecules on the balloon is the cause of the pressure inside the balloon. But why is this pressure the same everywhere on the inside surface? Well the only plausible explanation for this observation is that the molecules must behave, in some sense, more or less in the same manner every where inside the balloon. Therefore resulting in, on average, the same *rate of change* of momentum transfer due to collisions. We will use the term *thermodynamic equilibrium state* or *macroscopic state* to denote such a condition of 'uniform time invariant collective behav-

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[2] Of the order of the Avogadro's number.

[3] Measured.

ior' of the set of molecules. More specifically we use the term thermodynamic equilibrium state[4] to refer to a certain steady collective behavior of the molecules.

At this point we should ask ourselves, under what circumstances would the individual behavior of billions and billions of moving molecules give rise to such uniform time invariant collective behavior? It will also be very useful if we can quantify this steady collective behavior. If we assume that energy of the universe is conserved then we could imagine that in this steady state all particle collisions must be elastic. That is, in this steady state, the total sum of the center of mass kinetic energy[5] of the molecules involved in the collision are the same before and after the collision. If this were not true then we should observe that either the balloon molecules increase in energy and the gas molecules decrease in energy or the balloon molecules decrease in energy and the gas molecules increase energy. Furthermore we observe that in such a steady condition the gas does not flow in any particular direction. That is, in this steady state, on average there are no preferred directions for the motion of the molecules. That is we specifically assume that

 i.) particle collisions are elastic,
 ii.) there are no preferred directions of motion for the molecules.

Under these reasonable assumptions one can use the principle of conservation of linear momentum[6] to show that the magnitude of the velocity of a particle with respect to the center of mass frame does not change in a collision and that the only thing that changes is its direction of motion and consequently the *time average of the center of mass kinetic energy* of a molecule remains constant over time and that this quantity is the same for all the molecules. Thus it is reasonable to assume that center of mass kinetic energy, averaged over all the molecules, at any particular instant of time is in fact independent of time and that this quantity is the same as the center of mass kinetic energy of any particular molecule averaged over time. This is called the *ergodic hypothesis*. The profound consequence of this hypothesis is that the average center of mass kinetic energy of a molecule, measured with respect to a frame fixed to the centre of mass of the molecules constituting the system, will now have a well defined meaning. Thus we could use it as the quantifying and defining property of thermodynamic equilibrium. We state this formally below:

Definition 2.1. Thermodynamic Equilibrium: A collection of molecules (a closed system) is said to be in thermodynamic equilibrium if the center of mass kinetic energy of a molecule is well defined.

Sticking to the convention used by Physicists we will use $\langle x \rangle$ to denote the average of a given property x of a molecule. For instance if v denotes the magnitude of the center of mass velocity of a molecule $\langle v \rangle$ will denote the average of it. Using this notation the well defined

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[4] Or thermodynamic state for short.

[5] The kinetic energy is computed with respect to an inertial frame with origin coinciding with the center of mass of the collection of molecules.

[6] Newton's laws.

average center of mass kinetic energy of a given molecule can be denoted by $\left\langle \frac{m_p v^2}{2} \right\rangle$ where m_p is the mass of the molecule and v denotes the magnitude of the center of mass velocity of the molecule. It can also be shown that item ii.) of the above assumptions also imply that at thermodynamic equilibrium

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle,$$
$$\langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle,$$

where v_x, v_y, v_z are the components of the velocity of a molecule expressed in the inertial frame with origin coinciding with the center of mass of the collection of molecules.

Exercise 2.1. A cylinder contains a mixture of CO_2 and O_2. What can you say about the average center of mass speed of the molecules when the mixture is in thermodynamic equilibrium.

2.2 Absolute Temperature

The fact that the average kinetic energy of the center of mass motion of all the interacting molecules are the same implies that one can assign this number to describe the equilibrium condition itself. Historically the term *temperature* was used to define this steady collective behavior of the molecules called thermodynamic equilibrium way before people came to realize the particle nature of matter[7]. To coincide with the historically defined notion of temperature one defines in this microscopic picture the *absolute temperature* to be a certain fraction of the average center of mass kinetic energy of the molecules. That is one can define the absolute temperature, T, to be given by

$$T = \frac{2}{3k_B} \left\langle \frac{m_p v^2}{2} \right\rangle,$$

where k_B is the Boltzmann constant[8].

For a mono-atomic gas such as Ar the three degrees of freedom of the center of mass motion comprises the only degrees of freedom and hence the total kinetic energy, that we will abbreviate as KE, of the Ar gas molecule is the total average kinetic energy of the center of mass motion of the molecule. For other complicated gasses such as O_2 or NH_3 there exists degrees of freedom other than the center of mass motion and hence the total average kinetic energy of the entire molecule is more than the kinetic energy of the center of mass motion. For instance there may be rotations and vibrations internal to the molecule due to the increased degrees of freedom in the molecule. A single atom has three degrees of freedom. Thus a molecule that is made of m number of atoms will, in general, have $3m$ degrees of freedom. For instance a O_2 molecule has six degrees of freedom, a CO_2 molecule has nine degrees of freedom while a NH_3 molecule has twelve degrees of freedom. In general consider the total kinetic energy of a molecule that contains r degrees of freedom. Since we can imagine that each degree of freedom interacts with each other and that when in equilibrium the average

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[7] We will discuss this viewpoint a little later.
[8] $k_B = 1.38066 \times 10^{-23} \text{JK}^{-1}$

kinetic energy of each degree of freedom must also be the same, one sees that the total kinetic energy of a molecule, KE, must be equally distributed among all of its degrees of freedom. Thus the total kinetic energy of a molecule per degree of freedom must equal to one third of the center of mass kinetic energy of the molecule:

$$\frac{\text{KE}}{r} = \frac{1}{3}\left\langle \frac{m_p v^2}{2} \right\rangle.$$

Thus we have $\text{KE}/r = k_B T/2$, which says that $k_B T/2$ is equal to the total average kinetic energy of the molecule per degree of freedom. For the convenience of remembering we take this as the formal definition of absolute temperature and state it formally.

Definition 2.2. Absolute Temperature: The absolute temperature of a system in thermodynamic equilibrium, denoted by T, is defined by the following expression.

The average total kinetic energy of a molecule **per degree of freedom** $= \dfrac{1}{2}k_B T.$ (2.1)

Observe that this quantity is not well defined unless the spatial averages and the time averages of the kinetic energy of the center of mass are the same. That is, the above quantity is well defined only if the system is in thermodynamic equilibrium. This definition of temperature allows us to conclude that two systems of particles in contact with each other will have the same absolute temperature when they are in equilibrium. However they may not have the same kinetic energy if the molecules have different number of degrees of freedom.

Note that the notion of thermodynamic equilibrium is what allowed us to precisely define the macroscopic property called absolute temperature. However the notion of temperature was well established way before the knowledge of the particle nature of matter. This notion was developed by pure reasoning and was also based on a phenomenological definition of equilibrium. Below we visit this interpretation of thermodynamic equilibrium and discuss how it gave rise to the notion of a temperature of a system. Reflecting its origin, this notion of temperature is called *empirical temperature* and we will see later that it has a definte correspondence with the absolute temperature that is defined using the microscopic picture.

In the empirical formulation we define the thermodynamic equilibrium state of closed system to be the steady state that satisfies the following properties:

Axiom 2.1 - Zeroth Law of Thermodynamics: *Consider three thermodynamic systems A, B and C. If A and B are in thermal equilibrium and A and C are in thermal equilibrium then necessarily B and C are in thermal equilibrium.*

Notice that this assumption follows easily from the notion of thermodynamic equilibrium defined using the particle nature of matter. The zeroth law allows one to assign an empirical

temperature, θ^o, to a thermodynamic state as follows. Define a system, called a thermometer Θ, that allows the easy measurement of a variation of a single measurable macroscopic thermodynamic variable, such as volume, while its other macroscopic properties remain constant. Thus this measurable quantity will serve to define its thermodynamic state (that is if x is the thermodynamic state of Θ then there exists a function $\theta^o(x)$ that uniquely prescribes the state x). Two systems B and C will be defined to have the same empirical temperature if B is in thermal equilibrium with Θ in a particular state, x, and C is in thermal equilibrium with Θ in the same state, x. The zeroth law now allows us to say that both systems are at the same temperature $\theta^o(x)$. We will see later that all such defined $\theta^o(x)$ will have a linear variation with T.

2.3 Pressure

Recall that the rate of change of momentum of the molecules of the balloon that is caused by the never ending collision of the air molecules on the balloon is what gives rise to the pressure inside a balloon. Let us try to estimate this pressure. Specifically let us consider a N number of gas molecules contained in a cube of volume V and estimate the pressure exerted by the gas molecules on the inside surface of the cube. Consider a single gas molecule colliding with one of the faces of the cube as shown in figure-2.2. Let A be the cross sectional
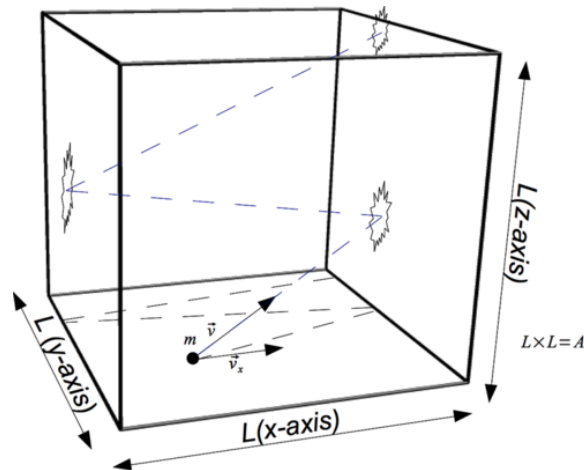
Fig. 2.2 The motion of a gas particle in a box. Figure courtesy of http://www.ck12.org

area of this face and denote by v_x the velocity of the center of mass of the molecule in the x-direction (the direction perpendicular to the surface of collision). Recall that when a collection of particles is in thermodynamic equilibrium particle collisions are elastic and there are no preferred directions for the motion of particles and that consequently in collisions the only thing that changes is the direction of motion and not the magnitude of the velocity. Thus it can be seen that when a molecule bounces off the surface its velocity in the x direction changes sign but must remain the same in magnitude. Consider the collision of a particular molecule

p that has a x velocity component equal to v_x. The change of momentum of this molecule due to its collision with the face is $2m_p v_x$ where m_p is the mass of the molecule. Thus, the law of conservation of momentum tells us that, $2m_p v_x$ of momentum is transferred to the face of the cube due to the collision of the molecule p that has a x component of the velocity equal to v_x. If we know the number of such molecules that hit the surface per unit time then multiplying $2m_p v_x$ by this number gives us the total rate of change of momentum given to the surface of the cube due to the collision of molecules that have a x-velocity equal to v_x. In a unit time interval only half of the molecules with a x-velocity equal to v_x that lies [9] within a distance v_x from the face have the chance of hitting the face. Thus the total rate of change of momentum occurring in the molecules on the face of the cube due to a collision with a molecule that has a x component of the velocity equal to v_x is

$$\frac{1}{2}\left(n_{v_x}\frac{Av_x}{V}\right)2m_p v_x = \frac{A}{V}n_{v_x}m_p v_x^2,$$

where n_{v_x} is the number of molecules per unit volume with the magnitude of the x component of the velocity equal to $|v_x|$. Since the rate of change of momentum is equal to the force we would see that the above expression gives the total force acting on one of the faces due to the effect of the collision of the gas particles with the x component of the velocity equal to v_x. Thus the total force on the wall due to the collision of particles of all possible velocities is given by

$$F = \sum_{v_x}\frac{A}{V}n_{v_x}m_p v_x^2 = \sum_{v_x}\frac{2AN}{V}\left(\frac{n_{v_x}}{N}\frac{m_p v_x^2}{2}\right) = 2A\frac{N}{V}\left\langle\frac{m_p v_x^2}{2}\right\rangle,$$

where we have denoted the average of the quantity $m_p v_x^2$ by

$$\left\langle\frac{m_p v_x^2}{2}\right\rangle \triangleq \sum_{v_x}\left(\frac{n_{v_x}}{N}\frac{m_p v_x^2}{2}\right).$$

Recall that since equilibrium implies there are no preferred directions we also have $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$, and $\langle v^2\rangle = \langle v_x^2 + v_y^2 + v_z^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle$. Thus we see that $\langle\frac{m_p v_x^2}{2}\rangle = \frac{1}{3}\langle\frac{m_p v^2}{2}\rangle$ and hence that:

The pressure, P, exerted by an ideal gas on its boundary is given by

$$P = \frac{N}{V}\frac{2}{3}\left\langle\frac{m_p v^2}{2}\right\rangle,$$

where N is the number of gas molecules in the system, m_p is the mass of a single molecule, V is the volume occupied by the gas molecules, and v is the magnitude of the center of mass velocity of a molecule.

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[9] Why half?

2.4 The ideal gas law

From the above expression for pressure we see that

$$PV = N\frac{2}{3}\left\langle\frac{m_p v^2}{2}\right\rangle.$$

Recall that since the center of mass motion of a molecule has three degrees of freedom $\left\langle\frac{m_p v^2}{2}\right\rangle = 3\frac{1}{2}k_B T$. Substituting this in the above expression we have:

The **ideal gas law:**

$$PV = Nk_B T. \tag{2.2}$$

Let us briefly try to summarize some of the amazing implications of this law.

(a) Equal volumes of gasses at the same temperature and pressure have the same number of molecules irrespective of the type of gas[10].
(b) The pressure in a closed ideal gas system undergoing a constant temperature change is inversely proportional to the volume[11].
(c) The volume of a closed ideal gas system at constant pressure is proportional to the absolute temperature[12].

Let us re-write the ideal gas law (2.2) in terms of the number of Moles, n, or the total mass m of the gas instead of the number of molecules contained in the gas N. Recall that $\mathcal{N}_A = 6.0221 \times 10^{23}$ denotes the Avogadro's number. By definition the number of moles, n, is given by $n = N/\mathcal{N}_A$. Then the ideal gas law (2.2) becomes $PV = n\mathcal{N}_A k_B T$. Defining $R = \mathcal{N}_A k_B \approx 8.3145\,\mathrm{JK}^{-1}$, we have the following form of the ideal gas law used by chemists:

$$PV = nRT. \tag{2.3}$$

The constant R is a universal constant and is referred to as the *universal gas constant*.

Note that this expression describing the equilibrium state of a closed system of ideal gas particles was known well before the knowledge of the particle nature of matter. It was purely derived from an effort to interpret various observed phenomena and experimental results that were summarized by Avogadro, Boyle, and Charles.

Exercise 2.2. A sample of an ideal gas is contained in a certain vessel at a pressure of 1 atm. What is the pressure of this sample of gas when the volume is halved and the absolute temperature is doubled?

Exercise 2.3. Two types of ideal gasses are contained in an insulated cylinder. There are N_A number of gas molecules of type A and N_B number of gas molecules of type B. The temperature of the inside of the cylinder surface is measured to be T kelvins while the volume of

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[10] Avogadro's law
[11] Boyle's law
[12] Charle's law

the cylinder is measured to be V m^3. What is the total pressure acting on the piston? State all assumptions made.

Exercise 2.4. Consider a closed system consisting of k types of different ideal gases. The total volume of the system is V and it is found that the temperature of the inside boundary of the system is T and the total pressure acting on the inside of the boundary is P. If there are N_i number of molecules of type i show that the equilibrium thermodynamic properties of the system satisfy $PV = Nk_BT$ where $N = \sum_{i=1}^{k} N_i$.

Exercise 2.5. Find the volume, in mL, when 7.00 g of O_2 and 1.50 g of Cl_2 are mixed in a container with a pressure of 482 atm and at a temperature of 22°C.

In engineering it is usually convenient to express the ideal gas law in terms of the total mass, m, of the gas. We see that the total mass of the gas of N molecules is $m = Nm_p$, where N is the number of gas molecules and m_p is the mass of a molecule. Then $PV = (m/m_p)k_BT$. Defining $R_s = k_B/m_p$ we have

$$PV = mR_sT. \tag{2.4}$$

The constant $R_s = k_B/m_p$ depends on the type of gas and is referred to as the *specific gas constant* of the gas. Using exercise-2.4 one can find R_s for a mixture of gases. A fairly accurate estimate for air is $R_s = 0.287\,kJ/kgK$.

Exercise 2.6. Stating all assumption, estimate R_s for air.

Exercise 2.7. [13] Consider the piston cylinder arrangement shown in figure-2.3. The piston is frictionless with area A = 0.2 m^2. The cylinder is initially filled with air with the piston positioned at a height of 2 m, initial pressure $P_1 = 200\,$kPa and temperature $T_1 = 500^o$ C. The air inside the cylinder is slowly cooled. Find

(a) the temperature when the piston reaches the stops that are positioned at a height of 1 m,
(b) the pressure if the cooling continues to $T = 20^o$ C.

In a closed ideal gas system the total number of molecules, N, in the system is fixed. Thus the ideal gas law also tells us that when a closed system is in thermodynamic equilibrium the observable macroscopic properties that define the thermodynamic state (the condition) of the system such as V, P, T are not entirely independent. The ideal gas law implies that the knowledge of two properties are sufficient to uniquely describe the rest of the properties[14]. For example the knowledge of P and V for a closed system of N particles uniquely determines T. It turns out that this observation is in general true for any system that consists of a single type of molecules.

It is interesting to know if there exists other macroscopic variables of interest such as V, T, P. Below we define another set of such quantities.

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[13] Example-3.3 of the lecture notes by J. M. Powers.
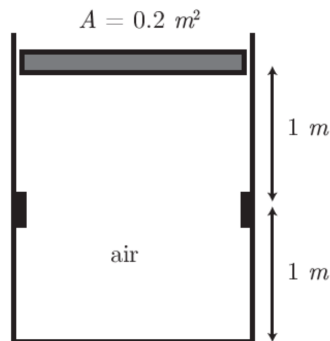[14] This is popularly known as the two property rule.

Fig. 2.3 The ideal gas exercise -2.7. Figure courtesy of http://www3.nd.edu/~powers/ame.20231/notes.pdf

2.5 Internal Energy

Recall that absolute temperature measures the amount of average kinetic energy per degree of freedom of a molecule and the pressure is the average rate of momentum transfer per unit area due to molecular collisions with the boundary. For an ideal gas of N molecules we will now define the total energy of all the molecules to be a new macroscopic thermodynamic property called the *internal energy U* of the system. Assuming that the molecules behave according to the classical Galelian laws of mechanics, it can be defined to be the total sum of the potential plus kinetic energy of the molecules. A system of ideal gas molecules, by assumption, do not interact with each other except when they collide with each other. Thus there is no potential energy associated with the ideal gas molecules and we have that the internal energy is the total kinetic energy of all the molecules. That is $U = Nr\frac{1}{2}k_BT$ where r is the degrees of freedom of a single molecule. For historical reasons we will denote $\frac{r}{2} = \frac{1}{(\gamma-1)}$ and hence formally define internal energy of an ideal gas as:

Definition 2.3. Internal Energy: Internal energy of an ideal gas is defined to be

$$U \triangleq \frac{Nk_BT}{(\gamma-1)}.$$

The parameter γ is called the *adiabatic constant* of the gas.

Note that in the ideal condition $\gamma = \frac{(r+2)}{r}$. For instance for a mono-atomic gas like Ar or He $r = 3$ and hence $\gamma = 5/3 \approx 1.66$. It might be useful to keep in mind that for molecules

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made up of more than one atom the potential energy due to the forces between the atoms in the molecule may not be negligible.

Using this newly defined thermodynamic property, internal energy U, we can re-write the ideal gas equation for a N number of gas molecules as

$$PV = (\gamma - 1)U. \tag{2.5}$$

The ideal gas law and the above expression are the only expressions that one needs to estimate the macroscopic properties of an equilibrium state of an ideal gas.

Considering the microscopic picture one sees that the definition of thermodynamic variables V, P and T for the ideal gases can naturally be extended to other materials that exist in other conditions as well. However we need to be careful when we consider internal energy U of a general system. For an ideal gas this is equal to the total kinetic energy of the gas particles since ideal gas molecules do not interact with each other and hence there exists no potential energy of interaction. However if the molecules interact like in a liquid or a solid the potential energy of the interactions should also be counted when one calculates the internal energy. In such an instance the potential energy U will not depend only on T. Even then one can still show that U is uniquely determined by the knowledge of only two thermodynamic variables. Thus the two property rule still holds for pure materials other than ideal gases.

2.6 Enthalpy

In Section-6 we will see that, when dealing with open systems the term $U + PV$ will naturally start appearing where the term PV is equal to the work done by the flow. Thus it turns out to be convenient to define a new thermodynamic property to define this quantity.

Definition 2.4. Enthalpy: The enthalpy H of a closed system, is defined to be

$$H \triangleq U + PV.$$

Computing H for an ideal gas we see that

$$H = U + PV = m\frac{R_s}{\gamma - 1}T + mR_sT = m\frac{R_s\gamma}{\gamma - 1}T.$$

Note that this quantity, enthalpy, has no physical significance other than being simply $U + PV$.

2.7 Specific heat capacities of ideal gasses

Let us define the two parameters c_v and c_p as follows

$$c_v \triangleq \frac{R_s}{\gamma - 1}, \tag{2.6}$$

$$c_p \triangleq \frac{\gamma R_s}{\gamma - 1} \tag{2.7}$$

then we can write the internal energy, U, and the enthalpy, H, as

$$U = mc_vT,$$
$$H = mc_pT.$$

These two parameters are called the specific heat capacities[15] of the ideal gas. From the above relationships it easily follows that, for an ideal gas the specific heat capacities must also satisfy,

$$\frac{c_p}{c_v} = \gamma, \tag{2.8}$$

$$c_p - c_v = R_s. \tag{2.9}$$

Note that for an ideal gas the two specific heat capacities are a constant for a given particular gas.

Observe that by measuring c_p and c_v of an ideal gas one can find the adiabatic constant γ. Such experimental estimates of γ deviate significantly from the theoretical estimate of $\gamma = \frac{(r+2)}{r}$. Note that the internal energy was defined based on the assumption that molecules of an ideal gas behave according to the laws of classical Galelian laws of mechanics. Thus this experimental disagreement was one of the earliest clues of the failure of the classical Galelian laws of mechanics to accurately describe the motion of small particles. The interested reader is referred to Chapter-40 of the excellent text, Feynman lectures on physics [5].

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[15] The meaning of this term will be clearer in Section-3.3.

Chapter 3
Limits of energy conversion

Up to this point we have seen how one could go about characterizing the average collective behavior of a large number of particles using a few number of quantities that we call thermodynamic properties (or equivalently macroscopic properties) of a system. We have seen that this can be done only if the system of particles are in a particular special condition called thermodynamic equilibrium where the notion of average center of mass kinetic energy of all the particles is well defined. We have seen that two thermodynamic properties uniquely define the thermodynamic equilibrium state of a given closed ideal gas system. It turns out that this is also true for sufficiently simple systems consisting of molecules of the same type that are in the same condition[1]. Thus we see that the space of all possible equilibrium states of a given simple closed system can be identified with a point in $\mathbb{R}^2$. Thus, once we pick a suitable pair of thermodynamic variables[2], we can identify an equilibrium state of the closed system with a point in the plane.

A key property of a closed system is internal energy. It represents the total energy of the collection of particles. The question that we will try to answer in this section is how much of this energy can be converted into mechanical work. A machine that converts energy to mechanical work is called an *engine*. From a practical point of view we would like to find out what the best possible engine is. The search for the answer to this question was the driving force behind the study of thermodynamics and the industrial revolution.

3.1 Thermal Processes

We will begin by considering what changes happens to a system when it is made to interact with the surrounding. In general a transition of a closed system from one equilibrium state to another is called a *thermal process*.

If all the intermediate states in such a transition are also equilibrium states we have a special name for it:

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[1] What is known as the two property rule.
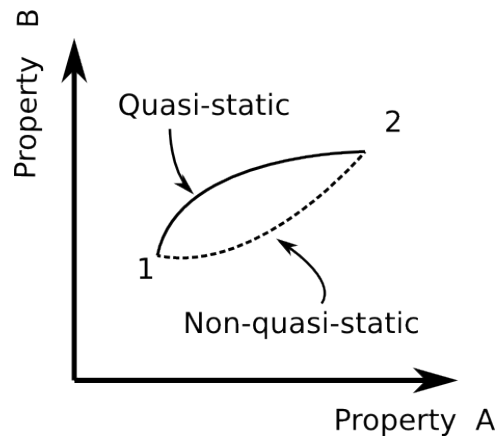
[2] Coordinates.

Fig. 3.1 Schematic representation of a Quasi-Static thermal process and a non-Quasi-Static thermal process.

Definition 3.1. Quasi-Static Process: A closed system undergoing a transition in from one thermodynamic equilibrium state to another in such a way that all the intermediate states are also in thermodynamic equilibrium is called a Quasi-Static thermal process.

Real processes never satisfy this idealized condition. However we may imagine that if changes are done sufficiently slowly[3] the process may be close to such conditions. On the other hand in a process that involves stirring or mixing we clearly see that there is a preferred direction of motion for the particles. Thus stirring or mixing is not a quasi-static process. Recall that the equilibrium state of a sufficiently simple system can be represented as a point in a plane. Thus, since all intermediate states of a quasi-static process are also equilibrium states we can represent a quasi-static process as a curve in the plane as shown in figure-3.1. However since the intermediate states of a non-quasi-static process are not in equilibrium we can not represent such a process as a curve in the plane. We will adhere to the convention of using a dotted curve to represent non-quasi-static processes as shown in figure-3.1.

A reasonable question to ask at this moment is if all processes are reversible?

Definition 3.2. Reversible Process: If a certain quasi-static process can be reversed such that both the system and the surrounding are both restored back to their original equilibrium states at every stage of the process, the process is said to be reversible. Notice that by definition all reversible processes are necessarily quasi-static. However not all quasi-static processes need to be reversible.

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[3] How slowly is slow here?

In a thermal process the energy of the molecules of a system can increase, decrease or remain the same due to the interaction of the system of particles with its surrounding. Two distinct types of interactions occur between the molecules comprising the system and the surrounding. In one case the molecules of the system will interact directly with the particles of the surrounding[4] through 'collisions'. If these interactions are negligible we will say that the system is *thermally insulated* or insulated to be brief. Another way the molecules of the system can interact with the surrounding is through the boundary or a shaft that connects the inside of the system to the outside surrounding. For example if the volume of the system changes due to a deformation of the system boundary the system molecules and the surrounding particles will both be affected. Such deformations of the system boundary involve the movement of forces through certain distances and thus result in mechanical work. The work interaction that occurs between a closed system and the surrounding due to the deformation of the boundary will be called *volume work*. Recall that mechanical work is defined as follows.
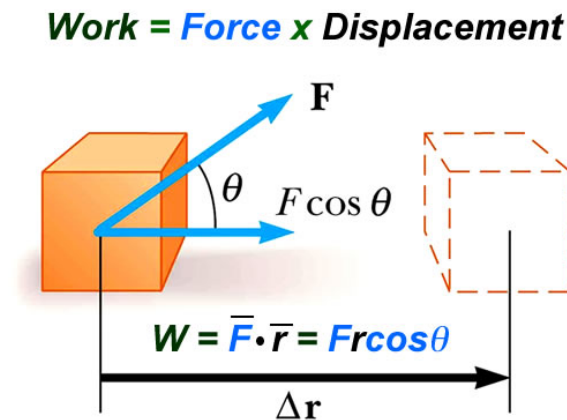
Fig. 3.2 The work done by a constant force. Figure courtesy of http://www.sdsu-physics.org

Definition 3.3. Mechanical Work: The net effect caused by a force moved by a distance in the direction of the force is defined to be the work done by the force. Specifically if a force F acting on a mass is moved along a path c, then the work done by the force along path c is defined to be the line integral

$$\Delta W \triangleq \int_c F \cdot dr.$$

Note that, in general, mechanical work is path dependent.

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[4] Note that at a microscopic level electromagnetic radiation occurs through photon transport.

There exists other types of indirect interactions that may arise and result in mechanical work. For instance, by stirring a system of gas particles using a shaft we can do work on a system and by allowing a set of gas particles to expand through a nozzle that has a kind of a fan at the end[5] the system will do work on the surrounding. Note that this kind of work will be referred to as *shaft work* and that in such a process the intermediate states of the system are not in thermodynamic equilibrium since the process involves a flow of molecules.

We can associate a real number referred to as the *work done* or simply work during a thermal process for those interactions a system has with the surrounding that involve mechanical work.

Definition 3.4. Work Done: The work done by a closed system during a thermal process corresponds to the maximum possible mechanical work that can be extracted during the process. Conventionally the work done **by** the system during a process will be taken to be **positive** while the work done on the system will be taken to be negative.

Note that the sign convention for the work used in this note is different from the convention used by Prof. Sivasegaram where he uses the convention that work done on the system to be positive. Since mechanical work is path dependent the work done during a thermal process is generally path dependent and is not necessarily a function of only the two end states.

Let us try to estimate the volume work that arises in a given process due to the deformation of the system boundary. The incremental[6] work done due to an infinitesimal (very small) change in the boundary caused by the deformation of a point R on the boundary with position r to a point R+δR with position $r + \delta r$ is given by $\delta W = P\delta A n \cdot \delta r$. Here δA is the small area of the boundary at R, P is the pressure acting at the point R, and n is the unit normal to the boundary at R. Since $\delta A n \cdot \delta r = \delta V$ we see that the incremental work due to the infinitesimal change δr in the boundary is given by $\delta W = P\delta V$. Since pressure can only be defined for a system in equilibrium we can use this formula to calculate boundary work only if all intermediate states of a process are also equilibrium states and hence the process is quasi-static.

For a quasi-static process from an equilibrium state 1 to an equilibrium state 2 the *volume work* done **by** the system can thus be defined to be the integral

$$\Delta W \triangleq \int_1^2 PdV. \tag{3.1}$$

Observe that this expression says that a system will do volume work on the surrounding only if its volume changes. This also says that the volume work done by the system in a quasi-static process is equal to the area under the $P - V$ curve of the quasi-static process as shown in

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[5] What we call a turbine.

[6] Alternatively referred to as differential changes.

figure-3.3. Note that in order to analytically find the volume using the above expression one needs to know how P varies as a function of V.
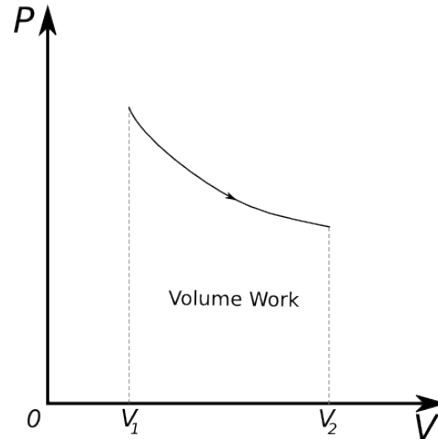
Fig. 3.3 The volume work done by the system in a quasi-static process is the area under the $P - V$ curve of the process.

Exercise 3.1. Find the volume work done by a closed ideal gas system in the following processes:

(a) quasi-static isochoric[7] process.
(b) isobaric[8] process.
(c) isothermal[9] process.

A system where its particles do not interact with the particles of the surrounding are particularly simple in nature. Recall that we call such systems thermally insulated systems. We saw that in a thermally insulated system the possible interactions occur only as a consequence of the deformation of the boundary or as a consequence of the interaction with a shaft. A process that a thermally insulated systems undergoes will be called an *adiabatic process*. That is:

Definition 3.5. Adiabatic Process: A process is said to be adiabatic if throughout the process the only interaction the system has with the surrounding is mechanical work.

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[7] Constant volume
[8] Constant pressure
[9] Constant temperature

3.2 Conservation of Energy and the First Law of Thermodynamics

Let us consider a thermally insulated glass container filled with an ideal gas and a stirrer. If we stir the gas for a while we will notice that the temperature of the gas will go up. Which implies that the internal energy of the gas has increased due to the effect of the shaft work done on the system. This is reasonable since stirring the gas would cause the gas molecules to move faster due to the constant rate of momentum transfer that is resulting from the collision between the gas molecules and the rotating stirrer. Thus we can conclude that doing work on a thermally insulated (isolated) system increases its internal energy. But by how much does it increase? One of the fundamental laws of classical mechanics is the belief that the total energy of all the particles of the Universe is conserved[10]. Recall that the internal energy of a system was defined to be the total energy of all the particles in a system. Thus it is reasonable to assume that in an adiabatic process the increase in the internal energy of an isolated system must be equal to the work done on the system. Experience and extensive experimentation indicates that this assertion is indeed true and we take it as a fundamental behavior of nature. This statement is one of the most fundamental forms of the *First Law of Thermodynamics* and we state it formally.

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[10] The principle of conservation of energy.

Axiom 3.1 - First Law of Thermodynamics: *The internal energy increase, denoted by ΔU, in an adiabatic process is equal to the work done on the system during the adiabatic process. That is, for an adiabatic process,*

$$\Delta U = -\Delta W,$$

where ΔW is the work done **by** *the system during the process. Here we use the convention that work done by the system is positive.*

We know that mechanical work is path dependent. Thus will the work done in an adiabatic transition of an isolated system between two specific equilibrium states be the same for any adiabatic process? Or in other words is adiabatic work path independent? It better be so. Otherwise the internal energy of a system will not be a property of the equilibrium state of a system[11]. Thus the particle nature of the universe and the law of conservation of energy of the universe imply that adiabatic work is path independent.

Historically the thermodynamic behavior of systems was well understood way before the realization that everything is made up of particles. This was made possible by conversely assuming that all adiabatic transitions of a system between two equilibrium states result in the same work. Before the turn of the 20$^{\text{th}}$ century, this assumption was taken to be the most fundamental form of the first law of thermodynamics. Notice from the preceding discussion that it also establishes the fact that one can assign a property of the equilibrium thermodynamic state of a system called internal energy such that the increase in the internal energy in an adiabatic process is equal to the work done on the system.

For non-isolated systems the surrounding particles interact with the system particles and hence can cause the internal energy of the system particles to change. Thus for non-isolated systems undergoing a general process the internal energy increase will not be equal to the work done on the system during the process. That is, for a general non adiabatic process $\Delta U + \Delta W \neq 0$. This difference will be defined as the heat interaction[12] of the process. Formally we have the following definition.

Definition 3.6. Heat Interaction: For a closed system undergoing a transition from an thermodynamic equilibrium state x to a state y, the heat interaction, ΔQ, between the system and the environment during the process is defined to be

$$\Delta Q \triangleq \Delta U + \Delta W,$$

where $\Delta U = U(y) - U(x)$ and ΔW is the work done by the system during the process.

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[11] Show that the the law of conservation of energy implies that adiabatic work is path independent.
[12] Traditionally referred to as the heat transfer.

Note that this is nothing but a statement that says heat is the amount of thermal energy that is transferred to the system due to non mechanical (that does not involve work) interactions the particles of the system have with the surrounding. Through experience we have found that the manner in which the particles of the surrounding can interact with the particles in the system are very limited. If the interaction is through collision of surrounding molecules with the system molecules we call it *conduction energy transfer*. The other type of common interaction that occurs is when electromagnetic waves, or photons, in the surrounding interact with the electrons of the molecules of the system. This second type of interaction is called *radiation energy transfer*. Thus it is clear that heat is not something that can flow in an out of a system. Before the knowledge of the particle nature of matter people in fact believed that there was some invisible fluid called heat that flowed between 'hot' bodies and 'cold' bodies. Hence the traditional use of the terms such as heat flow, heat addition or heat removal. In this note we will try as much as possible to avoid such terms. Instead, if in a process the energy of the system increases due to the direct interaction of the molecules with the surrounding we will say a *a positive heat interaction* has occurred instead of the words heating or heat addition and if the energy of the system decreases due to the direct interaction of the molecules with surrounding we will say a *a negative heat interaction* has occurred instead of the words cooling or heat removal. In the following discussions we will adopt the following notations.

Consider a process where the system undergoes a change from an equilibrium state i to an equilibrium state j. We will let ΔW_{ij} denote the total work done by the system, ΔQ_{ij} denote the total heat interaction between the system and the surrounding, and ΔU_{ij} denote the total change in the internal energy of the system during the process.

Exercise 3.2. Find the heat interaction that occurs in a closed ideal gas system in the following processes:

(a) quasi-static isochoric[13] process.
(b) isobaric[14] process.
(c) isothermal[15] process.

Exercise 3.3. Consider a closed ideal gas system. Find the heat interaction between the system and surrounding for the following processes of the system:

(a) isochoric process with stirring where the initial temperature and the temperature after stirring is the same.
(b) isobaric and isothermal process.

Exercise 3.4. Consider a closed and insulated ideal gas system contained in a rigid cylinder. If the system is mixed using a shaft and the mechanical work involved in the mixing was estimated to be W_s Joules find the temperature change in the system due to mixing.

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[13] Constant volume
[14] Constant pressure
[15] Constant temperature

3.2.1 Quasi-static adiabatic ideal gas process

Let us apply the knowledge that we have developed so far to estimate the work done by a closed system of ideal gas particles undergoing a quasi-static adiabatic process. For a system of N particles at equilibrium defined by the thermodynamic properties (P, V, T) that undergoes an infinitesimal change and ends up at the equilibrium state $(P + \delta P, V + \delta V, T + \delta T)$ the incremental changes must satisfy

$$P\delta V + V\delta P = Nk_B\delta T = (\gamma - 1)\delta U.$$

For an adiabatic process, since the only interaction the system has with the surrounding is work, the principle of *conservation of energy*, or what is known as the first law of thermodynamics, tells us that the incremental increase in the internal energy δU of the particles must be equal to the incremental work done on the system. That is

$$\delta U = -\delta W = -P\delta V.$$

Substituting this in the above incremental expression we have

$$P\delta V + V\delta P = -(\gamma - 1)P\delta V,$$

and by re-arranging the terms we have

$$\gamma \frac{1}{V}\delta V + \frac{1}{P}\delta P = 0.$$

Now for a quasi-static process from an equilibrium state-1 to an equilibrium state-2 we can integrate the above expressions and obtain,

$$0 = \gamma \int_1^2 \frac{1}{V}\delta V + \int_1^2 \frac{1}{P}\delta P = \gamma\ln\left(\frac{V_2}{V_1}\right) + \ln\left(\frac{P_2}{P_1}\right)$$

$$= \ln\left(\frac{V_2}{V_1}\right)^\gamma + \ln\left(\frac{P_2}{P_1}\right) = \ln\left(\left(\frac{V_2}{V_1}\right)^\gamma \frac{P_2}{P_1}\right) = \ln\left(\frac{P_2 V_2^\gamma}{P_1 V_1^\gamma}\right),$$

and hence that

$$\frac{P_2 V_2^\gamma}{P_1 V_1^\gamma} = 1.$$

Which says that PV^γ is equal to a constant along a quasi-static adiabatic ideal gas process. Thus the volume work done **by** an ideal gas system in a quasi-static adiabatic process is

$$\Delta W_{12}^{\text{volume}} = \int_1^2 PdV = \int_1^2 \frac{c}{V^\gamma}dV = \frac{c}{(1-\gamma)V^{(1-\gamma)}}\Big|_1^2 = -\frac{1}{(\gamma-1)}\left(\frac{P_2 V_2^\gamma}{V_2^{(\gamma-1)}} - \frac{P_1 V_1^\gamma}{V_1^{(\gamma-1)}}\right)$$

$$= -\frac{1}{(\gamma-1)}(P_2 V_2 - P_1 V_1) = -\frac{Nk_B}{(\gamma-1)}(T_2 - T_1).$$

However we have seen that adiabatic work is path independent. Thus it follows that one can use the above formula to estimate the work done by an ideal gas system under going even a non-quasi-static process. We summarize the above result in the following:

For an ideal gas quasi-static adiabatic process

$$PV^\gamma = c \text{ (constant)},$$

and the work done **by** an ideal gas system in any (quasi-static or not) adiabatic process is

$$\Delta W_{12}{}^{\text{volume}} = -\frac{1}{(\gamma-1)}(P_2 V_2 - P_1 V_1) = -\frac{Nk_B}{(\gamma-1)}(T_2 - T_1). \qquad (3.2)$$
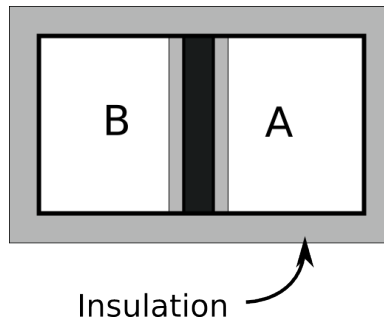

Fig. 3.4 An insulated piston cylinder arrangement. The piston cylinder interface is smooth and the piston is free to move.

Exercise 3.5. Consider the rigid piston cylinder arrangement shown in figure-3.4. Assume that the cylinder and the piston are covered by a perfectly insulating material and that the piston cylinder interface is very smooth and the piston is free to move. Two types of ideal gasses are separated in the cylinder by the piston. The number of gas molecules of type A are equal to N and the number of gas molecules of type B are twice as that of A. At thermal equilibrium one finds that the volume occupied by each of the gases is the same and equal to V, the temperature of the gas A is T and the pressure of the gas A is P. After a certain time a door in the piston is opened and the gases are allowed to mix.

(a) Find the initial temperature and pressure of gas B, in terms of the variables N, V and T.
(b) Find the pressure, after mixing is complete, in terms of the variables N, V and T.
(c) Show that the temperature, T_2, and pressure, P_2, after mixing must satisfy

$$\frac{1}{2}T < T_2 < T,$$
$$\frac{3}{4}P < P_2 < \frac{3}{2}P.$$

Exercise 3.6. Consider the rigid piston cylinder arrangement shown in figure-3.5. Assume that the cylinder and the piston are covered by a perfectly insulating material and that the piston cylinder interface is very smooth and the piston is free to move. Two types of ideal gasses are separated in the cylinder by the piston. The number of gas molecules of type A
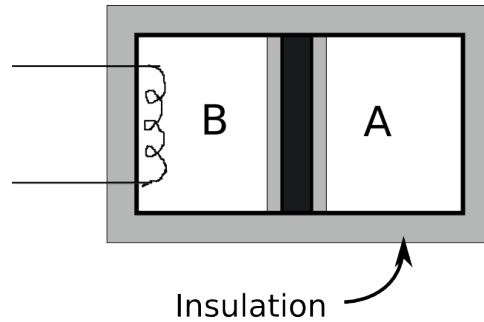
Fig. 3.5 The piston cylinder arrangement for exercise-3.6

are equal to N and the number of gas molecules of type B are twice as that of A. At thermal equilibrium one finds that the volume occupied by each of the gases is the same and equal to V, the temperature of the gas A is T and the pressure of the gas A is P. A high current is sent through the coil that is inside the left hand side of the cylinder for a certain amount of time. The current is switched off and after a while the system attains an equilibrium state where the pressure of the gas B is P_2 and the temperature of the gas B is T_2. The electric energy used by the coil while it was switched on was estimated to be E Joules. Find the variables that define the end equilibrium state and estimate the work done by the gas B.
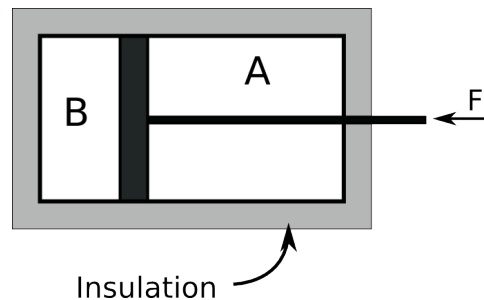
Fig. 3.6 The piston cylinder arrangement for exercise-3.7

Exercise 3.7. Consider the uniform cross section rigid insulated cylinder shown in figure-3.6. Two types of ideal gasses are separated in the cylinder by a piston of negligible volume and cross sectional area a_p. The piston cylinder interface can be assumed to be very smooth. There are N number of gas molecules of type A. At thermal equilibrium we find that the volume occupied by both gasses is the same and that the absolute temperature of the gas A is T and the force F exerted on the piston is zero. If we slowly move the piston so that the volume of gas A is twice that of gas B and the temperature of gas A has increased to T_2, answer the following:

(a) What is the force that we have to apply to the piston to keep it in place?
(b) Estimate the work done on the system.

Exercise 3.8. Consider the uniform cross section rigid cylinder shown in figure-3.7. The piston is uninsulated and the cylinder is insulated from three sides. Two types of ideal gasses
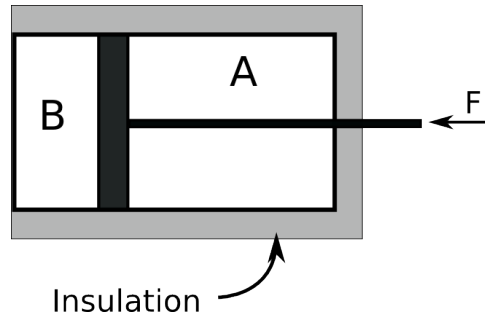
Fig. 3.7 The piston cylinder arrangement for exercise-3.8

are separated in the cylinder by a piston of negligible volume and cross sectional area a_p. The piston cylinder interface can be assumed to be very smooth. There are N number of gas molecules of type A. At thermal equilibrium we find that the volume occupied by both gasses is the same and that the absolute temperature of the gas A is T and that the force F acting on the piston is zero. If we slowly move the piston so that the volume of gas A is twice that of gas B. Answer the following:

(a) What is the force that we have to apply to the piston to keep it in place?
(b) Estimate the work done on the system.
(c) What can you say about the heat interaction between the gases and the surrounding?

Compare this answer with that of exercise-3.7.
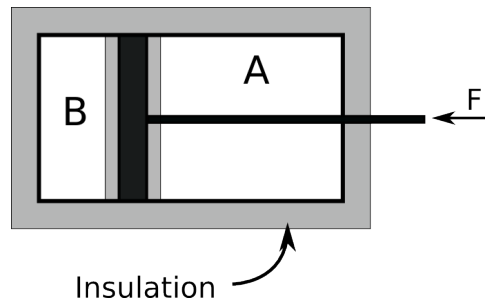
Fig. 3.8 An insulated piston cylinder arrangement. The piston cylinder interface is smooth.

Exercise 3.9. Consider the rigid insulated cylinder shown in figure-3.8. Two types of ideal gasses are separated in the cylinder by an insulated piston of negligible volume and/or negligible heat capacity. There are N_A number of gas molecules of type A and N_B number of gas molecules of type B. Initially the piston is kept in place by applying a force. The initial equilibrium state of the two gases is then given by the thermodynamic variables T_{A_1}, P_{A_1} and T_{B_1}, P_{B_1} respectively. We consider three cases:

3.9.a   The insulation of the piston and the force acting on the piston are suddenly removed.
3.9.b   The insulation of the piston is kept in tact and the force acting on the piston is removed suddenly.

3.9.c   A door in the piston is slowly opened so that the intermediate states are guaranteed to be equilibrium states while the piston is kept in place.

In each of the three cases find the final equilibrium state of the system in terms of the thermodynamic properties of the initial state. Estimate the internal energy change occurring in each gas and comment about the work done by each gas for all the three cases above.

Fig. 3.9 A heating and cooling process. Figure courtesy of Feynman Lectures on Physics.
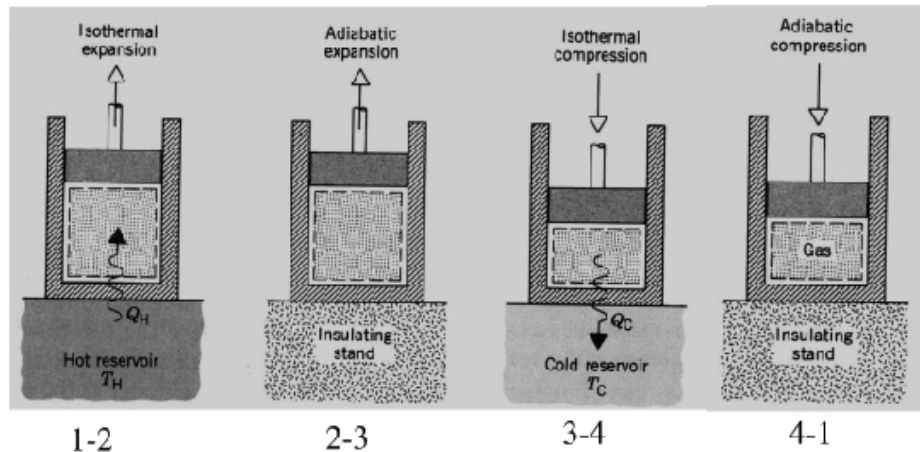
Exercise 3.10. Consider a piston cylinder arrangement where the cylinder is insulated from the sides and the piston is insulated at the top while the bottom of the cylinder is uninsulated. An ideal gas is trapped inside the cylinder. Initially the gas is at an absolute temperature T_H, pressure P_1 and volume V_1 when it is placed on a hotplate at temperature T_H. Consider the following sequence of process:

Step 1:   While the cylinder is on the hot plate the piston is moved by applying an external force on the piston in such a way that the temperature of the gas remains constant at T_H until the volume inside the cylinder reaches V_2.

Step 2:   When the volume inside the cylinder reaches V_2 the cylinder is immediately moved on to a mound of sand and the piston is allowed to move freely until the temperature inside the cylinder reaches T_C. Let the volume at this point be V_3.

Step 3:   As soon as the temperature reaches T_C the piston is moved onto a cold plate that is also at a temperature of T_C and the piston is moved by applying an external force in such a way that the temperature of the gas remains constant at T_C. This process is continued until the volume inside the cylinder reaches V_4.

Step 4:   The moment the volume inside the cylinder reaches V_4 the cylinder is moved on to the mound of sand and the piston is moved until the volume reaches V_1.

The volume V_4 is chosen such that when the volume inside the cylinder reaches V_1 the pressure of the gas is also P_1. This process is shown in figure-3.9. Answer the following with respect to this process.

(a) Illustrate the process using a curve in $P - V$ space.

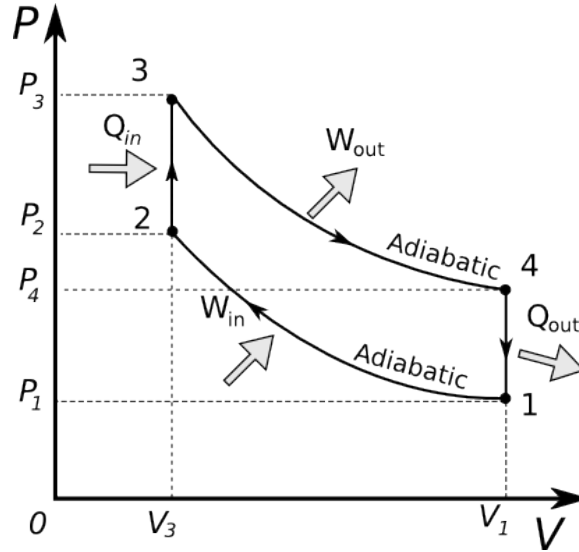(b) Find the heat and work interaction occurring in each stage of the process.

Fig. 3.10 The cycle on which the spark ignition gasoline engines are based on. This is an idealization of the cycle called the Otto air standard cycle.

Exercise 3.11. A closed system consisting of air undergoes a cyclic process as shown in figure-3.10. The processes $3 \to 4$ and $1 \to 2$ are quasi-static adiabatic processes. The pressure and the volume when the system is in state 1 is P_1, V_1 respectively while the pressure and the volume of the system when it is in state 3 is P_3, V_3 respectively. The mass of the air particles that makeup the system is m, specific gas constant of air is R_a, and the adiabatic constant of air is γ. Find the heat and work interactions occurring in one complete cycle of the system in terms of the above data. Also show that the efficiency of the engine that is modelled by the cyclic system is given by

$$\eta = \left(1 - \left(\frac{V_3}{V_1} \right)^{(\gamma-1)} \right) \times 100\%$$

Exercise 3.12. A closed system consisting of air undergoes a cyclic process as shown in figure-3.11. The processes $3 \to 4$ and $1 \to 2$ are quasi-static adiabatic processes. The pressure and the volume when the system is in state 1 is P_1, V_1 respectively while the pressure and the volume of the system when it is in state 3 is P_3, V_3 respectively. The mass of the air particles that makeup the system is m, specific gas constant of air is R_a, and the adiabatic constant of air is γ. Find the heat and work interactions occurring in one complete cycle of the system in terms of the above data. Also show that the efficiency of the system is given by

$$\eta = \left(1 - \frac{1}{r^{\gamma-1}} \left(\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)} \right) \right) \times 100\%.$$

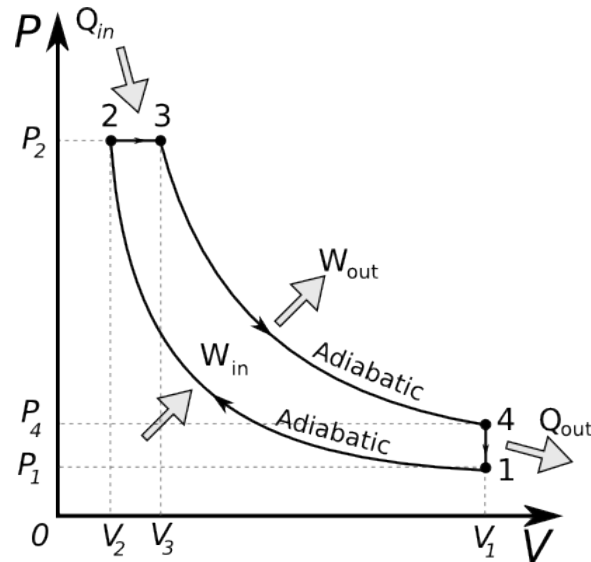where $\alpha = V_3/V_2$ and $r = V_1/V_2$.

36

Fig. 3.11 This is an idealization of the cycle on which the diesel engines are based on.

Exercise 3.13. An closed system of N number of ideal gas molecules are contained in an insulated rigid container with a stirrer. It is initially in a state (P_1, V_1). Upon stirring the system for a while and allowing it to settle one finds that the pressure in the system has increased to P_2. Justifying your answer clearly estimate the total work done on the system during stirring.

Exercise 3.14. An ideal gas undergoes a two-step process. Beginning at state-1, it is isothermally compressed to state-2. Then it is iso-barically compressed to state-3. The system experiences no shaft work. Stating all assumptions being made, find the total work done by the system during the process. What can you say about the total heat interaction that has occurred in the process. Has the system absorbed energy or lost energy during the process.

Exercise 3.15. [16] Consider the spring loaded piston cylinder arrangement shown in Figure-3.12. Initially the air inside the piston is at $P_1 = 100\,kPa$, $V_1 = 0.002\,m^3$ and the spring is unstretched (ie. $x_1 = 0\,m$) and we find the system to be in an equilibrium state. The atmospheric pressure is $P_{atm} = 100\,kPa$, and the cross sectional area of the piston is $A = 0.018\,m^2$. Energy is supplied to the air from outside so that the air expands until $V_2 = 0.003\,m^3$. We know the spring is linear with a spring constant $k = 16.2\,kN/m$. Find the final pressure of the air inside the cylinder and the work done by the air on the piston.

Exercise 3.16. [17] A spherical balloon contains air at $P_1 = 150\,kPa$ and is placed in a vacuum. It has an initial diameter of $d_1 = 0.3\,m$. The balloon is 'heated' until its diameter is $d_2 = 0.4\,m$. It is known that the pressure in the balloon is proportional to its diameter. Calculate the work of expansion.

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[16] Example 4.12 of the lecture notes by J. M. Powers.
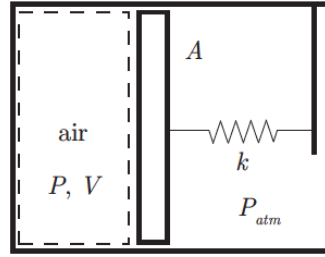[17] Example 4.14 of the lecture notes by J. M. Powers.

Fig. 3.12 A spring loaded piston cylinder arrangement. Figure courtesy of the e-book by J. M. Powers.

3.3 Processes of non-ideal gas systems

For non-ideal gas systems the particle interactions are not negligible and hence the potential energy between particles also contribute to the internal energy. Thus the internal energy, U, is not only a function of absolute temperature. The two property rule tells us that for sufficiently simple systems the internal energy of a the system in an equilibrium state is only a function of two independent variables. It is customary to pick T and V as the two independent variables. That is let $U(T,V)$. On the other hand since the Enthalpy, H, is defined to be $H = U + PV$ it is customary to consider H to be a function of T and P. We know that these properties depend on the number of molecules in the system and hence on the total mass of the system. Thus it turns out to be convenient to consider the per unit mass quantities of these. That is $u(T,V) \triangleq U(T,V)/m$ and $h(T,P) \triangleq H(T,P)/m$ that we will call the *specific internal energy* and the *specific enthalpy* of the system.

Then the incremental change in the specific internal energy due to an incremental change in the equilibrium state of the system is given by

$$\delta u = \frac{\partial u}{\partial T} \delta T + \frac{\partial u}{\partial V} \delta V,$$

and thus for *constant volume* processes

$$\delta u = \left(\left. \frac{\partial u}{\partial T} \right|_{V=\text{const}} \right) \delta T.$$

Similarly we also have

$$\delta h = \frac{\partial h}{\partial T} \delta T + \frac{\partial h}{\partial P} \delta P,$$

and thus for *constant pressure* processes

$$\delta h = \left(\left. \frac{\partial h}{\partial T} \right|_{P=\text{const}} \right) \delta T.$$

Therefore it is customary to define the following as the specific heat capacities of non-ideal gas system.

$$c_v(T,V) \triangleq \left. \frac{\partial u}{\partial T} \right|_{V=\text{const}}$$

$$c_p(T,P) \triangleq \left. \frac{\partial h}{\partial T} \right|_{P=\text{const}}$$

Using these quantities we can write for an iso-choric process

$$dU = m c_v(T,V) \, dT,$$

and for an iso-baric process

$$dH = m c_p(T,P) \, dT.$$

In section-2.7 we have seen that for an ideal gas the specific heat capacities do not depend on the equilibrium properties of the system and are only a property of the type of gas. This is not the case for a general non-ideal gas process. Therefore for general processes one may consider these specific heat capacities also as properties of the equilibrium state.

Since the incremental volume change is zero for an iso-choric process without shaft work, we have from the definition of heat interaction that

$$\delta Q = dU + PdV = m c_v(T,V) \, dT,$$

and for an iso-baric process,

$$\delta Q = dU + PdV = dU + d(PV) = d(U+PV) = dH = m c_p(T,P) \, dT.$$

Thus the knowledge of how the the specific heat capacities depend on the properties of the equilibrium state allows one to estimate the heat interaction in constant volume and constant pressure quasi-static processes by integrating the above expressions. Let us summarize these results below:

For a general *quasi-static iso-choric* process V is a constant and

$$\Delta U_{12} = m \int_1^2 c_v(T,V) \, dT, \tag{3.3}$$

$$\Delta Q_{12} = m \int_1^2 c_v(T,V) \, dT. \tag{3.4}$$

For a general *quasi-static iso-baric* process P is a constant and

$$\Delta H_{12} = m \int_1^2 c_p(T,P) \, dT, \tag{3.5}$$

$$\Delta Q_{12} = m \int_1^2 c_p(T,P) \, dT. \tag{3.6}$$

For most solids and liquids at moderate pressures it turns out that c_v and c_p depend only on temperature and if one knows this dependence one can analytically or numerically evaluate the above integrals to obtain the heat interactions in iso-choric and iso-baric processes.

Exercise 3.17. A certain non ideal gas undergoes an iso-baric process from an equilibrium state (P_1, V_1, T_1) to an equilibrium state (V_2, T_2). The specific heat capacity of the gas at constant pressure, c_p, is found to approximately satisfy the relationship $c_p(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3$. Find the heat interaction occurring in the process.

Unlike ideal gas systems non-ideal gas systems do not, in general, have simple relationships between the various thermodynamic variables that describe the thermodynamic equilibrium state. Thus in order to determine the volume work one needs to evaluate the integral $\Delta W_{12}^{\text{volume}} = \int_1^2 P dV$ using quadratures.

In certain quasi-static processes it may turn out to be possible to approximate the behavior of the process by the relationship $PV^n = \text{constant}$. Such quasi-static processes are called *Polytropic Processes*. Then we see that the volume work done by the system in a polytropic process is given by

$$\Delta W_{12}^{\text{volume}} = -\frac{1}{(n-1)}(P_2 V_2 - P_1 V_1), \tag{3.7}$$

for $n \neq 1$.

Exercise 3.18. A closed system initially at an equilibrium state (P_1, V_1) undergoes a polytropic expansion process that satisfies PV^n and ends up in a state (P_2, V_2). The specific heat capacities of the substance that makes up the system vary only with temperature for the pressures under consideration. These relationships are known. That is $c_v(T)$ and $c_p(T)$ are known as a function of the temperature (this function could either be given as an explicit formula or in a table as in the case of most substances). The temperature, T, of the substance is also known as a function of the pressure and volume of the system. That is, we know $T = \tau(P, V)$ either explicitly, graphically or in a tabular form. Show that the heat interaction during the process is given by the expression

$$\delta Q_{12} = \delta U_{12} + \delta W_{12}$$

$$= -P_2(V_2 - V_1) + \int_{T_1}^{T_0} c_v(T) dT + \int_{T_0}^{T_2} c_p(T) dT - \frac{P_1 V_1}{(n-1)}\left(\left(\frac{V_1}{V_2}\right)^{(n-1)} - 1\right),$$

where $P_2 = P_1\left(\frac{V_1}{V_2}\right)^n$, $T_1 = \tau(P_1, V_1)$, $T_0 = \tau(P_2, V_1)$, and $T_2 = \tau(P_2, V_2)$.

3.4 Heat Engines and the Second Law of Thermodynamics

So far we have seen that a closed system can, through its heat and work interactions with the surrounding, convert the energy absorbed from the surrounding into work and convert work back into energy. Machines that convert energy from the surrounding into work are called *heat engines*. It is not too difficult to see that such an engine that uses a closed system should preferably operate in a *cyclic* manner. That is, the process must visit all its intermediate states[18] periodically. Using the notion of a cyclic process we will formally define a heat engine to be:

Definition 3.7. Heat Engine: A Heat Engine is a closed thermodynamic system that undergoes a cyclic process.

Since internal energy is only a property of the equilibrium state we see that in one complete cycle the total internal energy change that occurs in the system must be equal to zero. Thus the first law of thermodynamics says that the total work done by the system, in one cycle, must be equal to the total heat interaction the system has with the surrounding. Therefore the first law says that you can not get work out of nothing or that more than 100% efficient engines do not exist. We have encountered our first limitation of nature in terms of converting energy to work and we see that it is a pure consequence of the first law of thermodynamics. From a practical point of view the next question that we would like to ask is if it is possible to construct 100% efficient engines. The second law of thermodynamics, that we will find below, states that even this is impossible.

Just like the first law the second law can not be derived. It is simply a summary statement of how nature behaves. All hitherto made observations and experiments have confirmed this assertion and no experiments or observations have contradicted it. Therefor we take it as a fundamental law of nature. Below, following Kelvin and Planck, we will state this law in the most general form possible.

Axiom 3.2 - Kelvin-Planck Statement of the Second Law of Thermodynamics:
There exists no cyclic process that can convert a given amount of energy entirely into mechanical work by only means of positive heat interactions. In other words it is impossible to construct a cyclic process with a net effect equal to the one that is schematically depicted in figure 3.13.

Note that the Kelvin and Planck version of the second law does not preclude the possibility of converting work entirely into energy. In fact the burning sensation you feel when you rub your finger over a table or the temperature rise inside an insulated cylinder due to constant stirring indicates that work can be converted entirely into energy.

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[18] Note that all the intermediate states need not be equilibrium states.
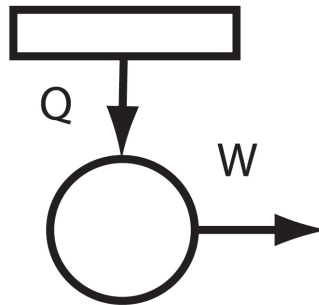
Fig. 3.13 A cyclic processes that only absorbs energy due to positive heat interactions with the surroundings. The first law says that the work done by the system in the process must be equal to the total energy absorbed by the system due to heat interactions. The Second Law of Thermodynamics states that such a cyclic processes do not exist.

If a cyclic process depicted in figure-3.13 is impossible then what is possible is that some energy from the system must also be lost to the the surrounding due to heat interactions. This is shown schematically in the figure-3.14. Using the first law it can be easily shown that the
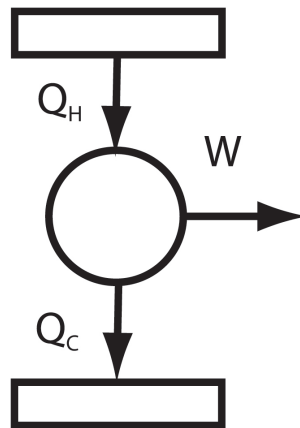
Fig. 3.14 The second law of thermodynamics says that a cyclic process that absorb energy from the surrounding due to heat interactions and converts it into mechanical work will necessarily loose some of the absorbed energy back to the surrounding due to heat interactions with the surrounding.

efficiency of such a heat engine is

$$\eta \triangleq \frac{W}{Q_H} \times 100 = \left(1 - \frac{Q_C}{Q_H} \right) \times 100 \ \%.$$

The second law implies that efficiency of a heat engine is always less than 100%. If that is the case then what cyclic process will give us the best possible efficiency? The French Engineer Sadi Carnot provided an ingenious answer to this question. He showed that for a given energy

source and an energy sink[19] the maximum possible efficiency will result if and only if the heat engine is a *reversible cyclic process*. You are invited to prove these statements in the exercises given below.

Exercise 3.19. Show that all reversible engines operating between a particular choice of energy source and an energy sink will have the same efficiency.

Exercise 3.20. Consider an irreversible engine and a reversible engine operating between the same energy source and energy sink. Show that the irreversible engine will have a lesser efficiency than the reversible one.

In the next exercise you are invited to show that energy will not flow from a 'cold' place to a 'hot' place without the aid of mechanical work. This assertion is also commonly referred to as a version of the second law of thermodynamics.

Exercise 3.21. Show that, in agreement with our observations, an energy transfer process that occurs from a hot source to a cold sink without the aid of mechanical work is irreversible[20].

In essence what these results imply is that reversible cyclic processes give the maximum possible efficiency irrespective of the type of process and thus the efficiency must only depend on the properties of the reservoirs. Therefore we see that the quantity Q_C/Q_H must be the same for all reversible cyclic processes that operate between the same source and sink and that it should only depend on the properties of the two reservoirs. Reservoirs are by definition very large thermodynamic systems in a given unchanging equilibrium state and thus the property that defines the state of a reservoir is its absolute temperature. Consequently the second law of thermodynamics implies that for any reversible cyclic process we must necessarily have

$$\frac{Q_C}{Q_H} = f(T_C, T_H).$$

What we would like to find out is what this function $f(T_C, T_H)$ is. To answer this question we will assume that we deal with a particularly simple class of systems called *simple thermodynamic systems*. All macroscopic systems of practical interest satisfy this property. Such systems are characterized by the assumptions that: i.) if x and y are any two equilibrium states of the system then either y can be reached from x in an adiabatic process or x can be reached from y in an adiabatic process or both are possible, and ii.) given any equilibrium state x there exits a pure heat interaction process[21] that passes through x [3, 4].

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[19] Without loss of generality the sources and sinks are assumed to be reservoirs. A reservoir is a very large thermodynamic system that is in thermal equilibrium where its interaction with other systems occur only through heat interactions and the loss or gain of thermal energy through these interactions will not result in a noticeable change in its equilibrium thermodynamic state. Since by assumption the equilibrium state of a reservoir does not change, its temperature completely characterizes its state.
[20] Hint: Show that if this statement is not true then that the Kelvin-Planck version of the second law must be false.
[21] Fo example it is reasonable to assume that we can always have a constant volume 'heating' and 'cooling' process starting from any equilibrium state.

Exercise 3.22. Consider an arbitrary equilibrium state x of an arbitrary simple thermodynamic system. The above assumption implies that there exists a pure heat interaction process[22] that passes through x. Let y and z be two equilibrium states that lie on this pure heat interaction process as shown in figure-3.15. Show that:

(a) y can not be reached from x adiabatically.
(b) x can not be reached from z adiabatically.

Purely Positive Heat Interaction, Processs
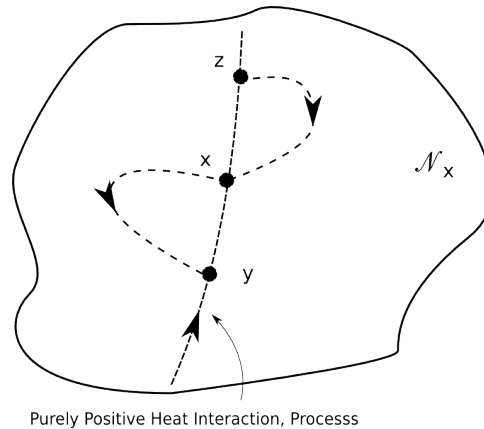
Fig. 3.15 Adiabatically non-reachable states.

Using the results of exercise-3.22 it is easy to show that the second law as stated by Kelvin and Planck implies that:

Axiom 3.3 - Caratheodory Statement of the Second Law of Thermodynamics: *In every neighborhood of every equilibrium state x of a simple thermodynamic system there exists an equilibrium state y that is not adiabatically accessible from x and conversely there also exists an equilibrium state z in every neighbourhood of x such that x is not adiabatically accessible from z.*

This statement is a weaker version of the second law and is attributed to Caratheodory. In the first of the two exercises below we invite you to prove that the Kelvin-Planck version implies the Caratheodory version of the second law.

Exercise 3.23. Prove that the Kelvin and Planck version of the second law implies the Caratheodory's version[23].

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[22] A process where there is no work interaction.
[23] Hint: Use the results of exercise-3.22

3.5 What does Entropy tell us?

The Caratheodory statement of the second law says that there exists states near any given state x that can not be adiabatically reached from x. What can we say about the states that can be adiabatically and reversibly reached from x? It is possible to show that the states that can be adiabatically and reversibly reached from x have a smooth structure[24]. One can also show that there exists a *reversible pure heat interaction* process that is transversal to all such curves of adiabatically and reversibly accessible states[25]. The existence of a transversal pure heat interaction process implies that these smooth curves of adiabatically and reversibly accessible states do not intersect each other[26]. Thus these smooth curves provide us with a new ruled structure[27] for the space of equilibrium states. This allows us to define a new thermodynamic property by insisting it to be constant along these smooth curves of reversibly and adiabatically accessible states. This new property of the equilibrium state is called *entropy*[28] and will be denoted by the symbol S. By computing the heat interaction that occurs along the transversal pure heat interaction process one can quantify this property. We summarize these observations below by defining entropy formally.

Entropy denoted by S satisfies:

(i) The entropy of two states x and y is the same, that is $S(x) = S(y)$, if and only if y can be reached from x by a *reversible adiabatic* processes.

(ii) There exists a *reversible pure heat interaction* process that is transversal to all the constant entropy surfaces.

(iii) There exists a unique non-negative quantity, T, referred to as the absolute temperature such that for a *reversible* processes, c_r, from an equilibrium state x to an equilibrium state y the total entropy change is given by

$$S(y) - S(x) = \int_{c_r} \frac{\delta Q}{T}. \tag{3.8}$$

It can be shown that this absolute temperature coincides with the notion developed before. Figure-3.16 provides a pictorial summary of these statements.

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[24] A smooth curve in the space of equilibrium states.

[25] The proof of these two sentences is beyond the scope of these lecture notes and requires advanced mathematical notions in differential geometry [3]. However you should convince yourself that this must at least be true for an ideal gas system.

[26] Prove this statement.

[27] A new coordinate system.

[28] The word entropy was coined by Rudolf Clausius in 1850.
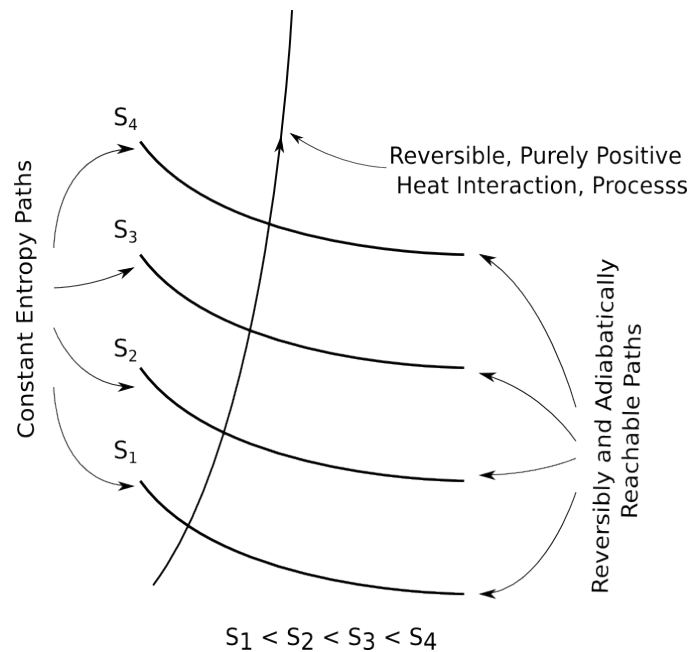
Fig. 3.16 Implications of the Caratheodory Version of the Second Law of Thermodynamics.

Exercise 3.24. By constructing suitable reversible processes find the entropy difference between the two states of a closed system of N number of ideal gas particles for each of the cases given below:

(a) (T,V_i) and (T,V_f).
(b) (P,V_i) and (P,V_f).
(c) (V,P_i) and (V,P_f).

In the following exercise you are asked to prove[29] several key properties of Entropy. In the process you will show that for adiabatic processes entropy increase is an indication of irreversibility. We have seen above that by definition an adiabatic process is reversible if and only if the entropy of the system remains constant though out the process. A process where the entropy remains constant is commonly called an *isentropic* process.

Exercise 3.25. Prove the following statements.

If x and y are two arbitrary equilibrium states of a simple closed system, show the following:

(a) whenever y is reachable from x by an *irreversible* adiabatic process then $S(y) > S(x)$.
(b) if entropy of the two states satisfy $S(y) > S(x)$ then x can not be reached from y adiabatically and thus any adiabatic process from x to y must be necessarily *irreversible*.

---

[29] Using the first law and the Kelvin-Planck version of the second law.

(c) whenever y can be reached from x by a process of only *positive heat interaction* (not necessarily quasi-static), then $S(y) > S(x)$.

These conclusions are illustrated in figure-3.17. Note that these conclusions also imply that entropy can not reduce in an adiabatic process or in other words that one can not reach a lower entropy state from a higher entropy state by a pure work interaction process. This also states that since the entire Universe taken as a system undergoes only adiabatic transitions[30], the entropy of the universe is always increasing.

The exercises below will demonstrate how we can use these properties of entropy to determine the reversibility or irreversibility of common *adiabatic* processes.
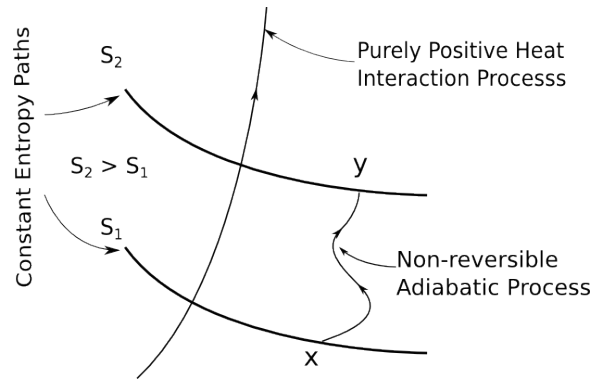
Fig. 3.17 Irreversible adiabatic processes, purely positive heat interaction processes, and Entropy.

Exercise 3.26. Show that 1 kg of water has less entropy when it is in a solid form than in a liquid form under atmospheric conditions. Also comment about its entropy when it is in a gaseous form.

Exercise 3.27. Show that the entropy of an ideal gas is given by:

$$S(V,T) = Nk_B \left(\ln(V) + \frac{1}{\gamma - 1} \ln(T) \right) + a, \qquad (3.9)$$

where V is the volume of the gas, T is the absolute temperature, N is the umber of gas particles, k_B is the Boltzmann constant, γ is the adiabatic index, a is the integration constant known as the chemical potential of the gas.

Exercise 3.28. Consider an ideal gas contained in an insulated rigid cylinder initially at a temperature T_1. The gas is stirred using a shaft. Show that the process is irreversible.

Exercise 3.29. Consider a gas contained inside a rigid cylinder and initially separated by a piston. The piston is uninsulated and free to move. A trap door in the piston is opened and the two gases are allowed to mix. Prove that this process is irreversible.

---

[30] Is this a reasonable assumption?

Exercise 3.30. Consider a hot metal block of mass m, specific heat capacity c_b, and initial temperature T_i and a large mass of water (reservoir) at an temperature of T_c. Find the maximum amount of work that can be extracted from the metal block.

Using (3.8) we are now in position to answer the question what $\frac{Q_C}{Q_H} = f(T_C, T_H)$ is for a reversible cyclic process operating between two reservoirs. Since $\frac{Q_C}{Q_H}$ is the same for all reversible cyclic process between the same reservoirs the reversible process we use to compute $\frac{Q_C}{Q_H}$ is immaterial. In any such one complete cycle of the process let the positive heat interaction the system has with the source reservoir at temperature T_H be Q_H and let the negative heat interaction the system has with the sink reservoir at temperature T_C be Q_C. Since the cyclic process is reversible we can use (3.8) to estimate the entropy change in the system due to the heat interactions. The entropy increase in the system, in one cycle, due to the positive heat interaction occurring at temperature T_H is $(\Delta S)_{increase} = Q_H/T_H$ and the entropy decrease in the system due to the negative heat interaction occurring at temperature T_H, in one cycle, is $(\Delta S)_{decrease} = Q_C/T_C$. Thus since entropy depends only on the thermodynamic state, in one complete cycle of the process we must have $0 = (\Delta S)_{increase} - (\Delta S)_{decrease} = Q_H/T_H - Q_C/T_C$. Thus we have shown the following:

For any reversible cyclic process operating between two reservoirs at temperature T_H and T_C, where $T_C < T_H$ we must necessarily have

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}.$$

Hence the maximum possible efficiency of a heat engine operating between two reservoirs is given by

$$\eta_{\text{carnot}} = \left(1 - \frac{T_C}{T_H}\right) \times 100\,\%, \tag{3.10}$$

and is termed the Carnot Efficiency, η_{carnot}. Any engine that operates at the Carnot efficiency is in general referred to as a Carnot Engine.

Recall that we have shown in exercise-3.19 and exercise-3.20 that such an engine has to be a reversible cyclic process. Thus any reversible cyclic process is a Carnot engine.

Exercise 3.31. Justifying each step explain why the cycle shown in figure-3.18 is a Carnot cycle. Illustrate the process using a $P - V$ curve.

Observe that (3.10) says that in order to extract work from a system undergoing a cyclic process we necessarily need an energy source and an energy sink and that they should be at different temperatures. Larger the difference larger the amount of work that can be extracted.

Thus the second law also says that if no thermal gradients exists in the universe, the conversion of energy into work would be impossible.
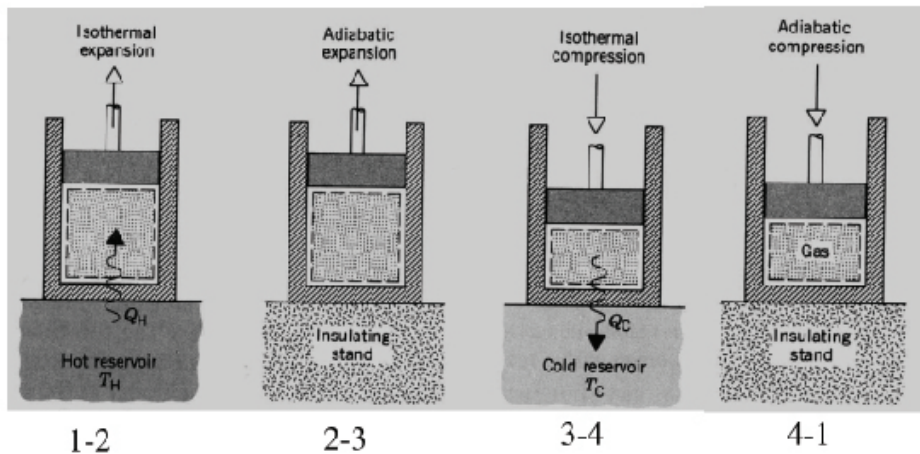
Fig. 3.18 Example of a Carnot Cycle. Figure courtesy of Feynman lectures on physics.

3.6 Clausius statement and irreversibility

At this point we have come across many profound implications of the second law of thermodynamics. What more does the second law tell us. By definition of the Entropy we see that for a reversible cyclic process $\oint \frac{\delta Q}{T} = 0$. It is interesting to know what happens if a quasi-static cyclic process is not necessarily reversible. Rudolf Clausius showed that the Kelvin-Planck version of the second law implies that this quantity has to be necessarily less than or equal to zero for any general quasi-static cyclic processes. That is:

Clausius Inequality: For any quasi-static cyclic process

$$\oint \frac{\delta Q}{T} \leq 0,$$

where the equality holds if the process is reversible.

This says that if $\oint \frac{\delta Q}{T} < 0$ then the cyclic process must be necessarily irreversible. However note that this theorem does not say that $\oint \frac{\delta Q}{T} = 0$ implies that the cyclic process is reversible. Thus there could exist irreversible cyclic processes for which $\oint \frac{\delta Q}{T} = 0$. In fact verify that $\oint \frac{\delta Q}{T} = 0$ for both the Otto cycle discussed in exercise 3.11 and the diesel cycle discussed in exercise 3.12, both of which are non reversible since the heat interactions occur at non-constant temperature.

Exercise 3.32. Show that the Kelvin-Planck version of the second law implies the Clausius inequality.

Let us investigate what the Clausius inequality tells us in addition to what we have deduced so far. Consider any quasi-static process (reversible or not) from an equilibrium state x to an equilibrium state y as shown by the curve c in figure-3.19. Let c_r be a reversible process from
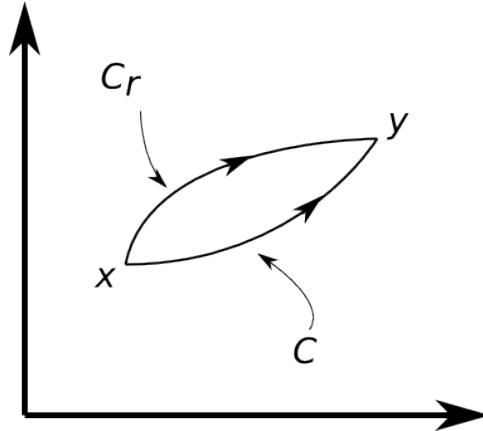
Fig. 3.19 Implications of the Clausius inequality.

x to y. Then we have that

$$S(y) - S(x) = \int_{c_r} \frac{\delta Q}{T}.$$

Now let us consider the cyclic process of going from x to y along the general possibly irreversible process c and then coming back to x by reversing the process c_r. Then

$$\oint \frac{\delta Q}{T} = \int_c \frac{\delta Q}{T} + \int_{-c_r} \frac{\delta Q}{T} = \int_c \frac{\delta Q}{T} - \int_{c_r} \frac{\delta Q}{T} = \int_c \frac{\delta Q}{T} - (S(y) - S(x)).$$

Since the Clausius inequality says that $\oint \frac{\delta Q}{T} \leq 0$ we have that $\int_c \frac{\delta Q}{T} - (S(y) - S(x)) \leq 0$ where the equality hold if the process c is also reversible. We summarize this in the following statement.

For a general quasi-static process, c, from x to y the Clausius inequality implies that

$$\int_c \frac{\delta Q}{T} \leq S(y) - S(x),$$

where the equality holds if the process, c, is reversible.

From a practical point of view this implies that the quantity

$$\int_c \frac{\delta Q}{T} - (S(y) - S(x))$$

can be used as a measure of irreversibility and the impossibility of a process. That is:

If $\left(\int_c \frac{\delta Q}{T} - (S(y) - S(x)) \right)$ is strictly greater than zero then the process is impossible while if it is strictly less than zero then the process is irreversible. Note that even though

for a reversible process this quantity must be zero the converse is not implied by the Clausius statement. Thus this quantity being equal to zero will only indicate that the process 'might' be reversible.

Exercise 3.33. A hot metal block initially at a temperature T_i is immersed in a large body of water that is at a temperature of T_C ($T_C < T_i$). Prove that the process is irreversible. You may assume that the specific heat capacity c_b of the block remains constant in this temperature range.

Exercise 3.34. A hot metal block initially at a temperature T_b is immersed in a rigid and insulated container of water that is initially at a temperature of T_w ($T_w < T_b$). After a while it is noticed that both the block and the water have attained a steady temperature of T_f. Prove that the process is irreversible. You may assume that the specific heat capacity c_b of the block and c_w of the water remains constant in this temperature range and that the mass and specific heat capacity of the container is negligibly small compared to the mass of the water.

3.7 The microscopic interpretation of entropy

Recall that since a thermodynamic system is a collection of a large number of particles of the order of the Avogadro's number, it is impractical to keep track of what happens to each and every particle in such a collection. Thus we have seen that the best one can do is to prescribe the average collective behavior of the system using quantities such as the number of particles, the energy, temperature, volume, and pressure. This average collective behavior is referred to as the *macroscopic* state. Various different combinations of the individual behavior of each of the individual particles will give rise to this collective behavior. A certain combination of the individual behaviors of the particles is referred to as a *microscopic* state. In terms of this terminology we say that there exists many micro-states that correspond to a given macro-state.

Ludwig Boltzmann[31] showed that for closed and insulated systems[32] the entropy is a measure of the different number of micro-states that correspond to a given macro-state. That is:

The entropy S of a macroscopic state of an isolated system is given by

$$S \triangleq k_B \ln(\Omega), \tag{3.11}$$

where Ω is the number of microscopic states that correspond to the given macroscopic state and k_B is the Boltzmann constant.

This shows that higher the number of possible micro-states higher the value of entropy of a closed system. From this definition of entropy it is easy to see that the entropy can not be

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[31] One of the pioneers of the atomic theory of matter.
[32] Isolated systems.

a negative quantity. In the following, we will see using a simple example, that Entropy is an increasing function of the number of particles, N, the total energy, E, and the volume, V.

The subsequent part of the notes closely follows Chapter-4 of the excellent text by Gould and Tobochnik titled Thermal and Statistical Phyisics [6]. We will begin by considering a hypothetical situation that is very close to 'reality'. We will assume, along with Einstein, that particles of nature are distinguishable[33]. In reality they are not. However considering this hypothetical situation gives us considerable insight into how nature might behave and hence we will look at it first. Quantum mechanics tells us that the energy of a particle is quantized. Again for simplicity we will assume that a particle can have only integer values of energy $0, 1, 2, \cdots$. In addition if the spatial configurations of the particles can not change then such a system is called an *Einstein Solid*.

Let us denote by $\Omega_V(N, E)$ the total number of different energy configurations that correspond to the macroscopic state of N number of particles, sharing a total energy of E, occupying a volume V in space. Einstein proved the following result:

$$\Omega_V(N, E) = {}^{(E+N-1)}C_E = \frac{(E+N-1)!}{E!(N-1)!}.$$

Exercise 3.35. Prove the above Einstein formula for the number of distinct energy configurations corresponding to a macroscopic state of N number of particles, sharing a total energy of E, occupying a volume V in space.

We will consider below, the total number of spatial configurations that correspond to a macroscopic state of N number of particles occupying a total volume V in the case where the spatial configurations of the particles are allowed to change (ie. the material is not a solid). We will assume a very simplified situation where each particle has an identical volume V_p and the space that the particles occupy is divided into boxes which are just big enough to fit a particle. Then the number of such boxes, n, define the total volume $V = nV_p$ of the system. We will also assume that the particles can move around and occupy any of the boxes and that no two particles can occupy the same box. Then it is easy to see that the number of spatial configurations that correspond to the macroscopic state of N particles, with fixed energy E, occupying the volume V is given by,

$$\Omega_E(N, V) = N! \, {}^{V}C_N = \frac{V!}{(V-N)!}.$$

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[33] Can be separately identified. For example they could be of various different colors or may have labels on them.

This formula shows that $\Omega_E(N,V)$, with fixed energy E, is an increasing function of both N and V while the above Einstein formula shows that $\Omega_V(N,E)$ is an increasing function of both N and E.

From the above two results we have that, for the simplified situation of an isolated set of *distinguishable* particles each having *discrete energy levels* and *discrete spatial configurations*, the total number of microscopic states corresponding to the macroscopic state of N particles sharing a total energy E occupying a volume V is given by

$$\Omega(N,E,V) = \Omega_V(N,E)\Omega_E(N,V) = \frac{(E+N-1)!}{E!(N-1)!}\frac{V!}{(V-N)!}.$$

Thus the total Entropy S corresponding to the macroscopic state of N particles sharing a total energy E occupying a volume V is given by

$$S = k_B \ln(\Omega) = k_B \ln(\Omega_V \Omega_E) = k_B \ln(\Omega_V) + k_B \ln(\Omega_E).$$

This shows that the entropy of a macroscopic state is larger if the number of particles and/or the total energy and/or the volume is larger. It turns out that these conclusions are true in general as well. We summarize this below:

The number of microscopic states corresponding to a given macroscopic state of an isolated system of particles have an increasing dependence on the number of particles N, the volume V, and the total energy E. That is $\Omega(N,E,V)$ is an increasing function of the number of particles N, the volume V, and the total energy E.

For an Einstein solid there is only one spatial configuration and hence $\Omega_E(N,V) = 1$. The Einstein formula shows that when the Energy E is zero then $\Omega_V(N,0) = 1$ for any number of particles[34]. Thus for an Einstein solid the entropy tends to zero when the energy tends to zero. For a non-solid system of particles $\Omega_E(N,V) > 1$ and thus, for a non-solid system when the energy tends to zero the entropy approaches a minimum. We have seen that the temperature, T, is a measure of the energy of a particle thus when the temperature T tends to zero it implies that the energy also tends to zero and hence the volume also tends to zero therefore we have the following result that is commonly stated as the *third-law of thermodynamics*.

Axiom 3.4 - Third Law of Thermodynamics: *The entropy of a state tends to a minimum as the absolute temperature tends to zero.*

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[34] Obviously.

It is an empirically observed fact that the absolute temperature T of a system can not reach zero and this is sometimes considered as the *fourth law of thermodynamics*.

3.7.1 Adiabatic Processes and Entropy

In order to develop an intuition about what happens to the entropy in an adiabatic process we will consider two distinct examples of adiabatic mixing processes: 1.) Energy mixing or what is commonly referred to as thermalization, and 2.) Particle mixing or what is commonly known as diffusion. We will see that entropy increases in both these adiabatic processes. We will also see that entropy is greater for states that are most likely to occur. Thus demonstrating that entropy increase is an indication of irreversibility.

Example-1: Thermalization
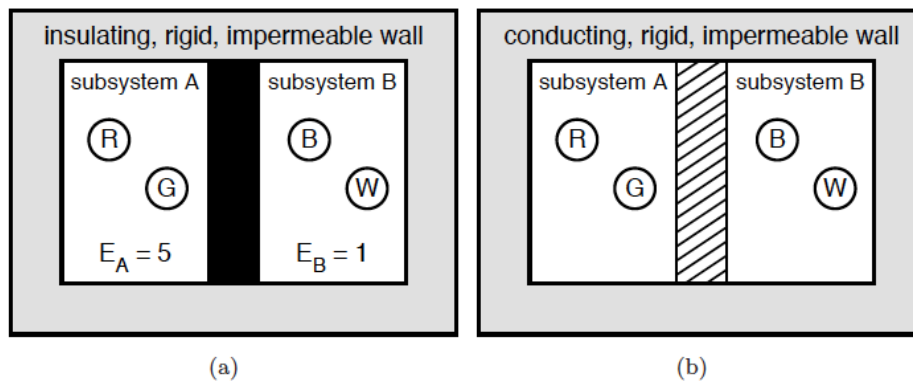
Fig. 3.20 Two systems, of two particle Einstein solids, separated by a rigid wall: a) The wall is thermally insulated. b) The wall is thermally conducting. Figure is copied from Chapter-3 of the text by Harvey Gould and Jan Tobochnik titled '*Thermal and Statistical Physics*' [6].

As an approximation of the case of two gases separated by a piston inside a cylinder let us consider a specific example of a set of four distinguishable particles contained in a box that is separated into two distinct parts by means of a rigid partition as shown in figure-3.20. Each side contains two particles each and for simplicity of computations we will assume that each of these pairs exist like in a solid. That is, particles of each of the pairs have a definite spatial configuration. The two particles on the left side will be labelled R and G while the two on the right hand side will be labelled B and W. We will also assume that the only information that we can get[35] is the total energy of the particles on each side. Since the particles are isolated from the rest of the Universe the total sum of the energies of all the four particles always remains

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[35] The only measurements that we can make.

the same[36]. Thus the total energy of the particles on one side specifies a certain macroscopic state of the collection of particles.

Initially the system is in the macroscopic state shown in figure-3.20(a). The total energy of the particles on the left side A is $E_{A1} = 5$ and the total energy of the particles on the right side B is $E_{B1} = 1$. The number of micro-states that correspond to this macro-state is thus $\Omega(E_A = 5 \ \& \ E_B = 1) = 6 \times 2 = 12$ and the corresponding entropy of the system is $S(E_A = 5 \ \& \ E_B = 1) = k_B \ln(12)$.

Let us consider what happens if we remove the insulation of the partition. That is, we assume that the particles can exchange energy through collisions with the partition. If we insist on that the total energy is conserved (First law of thermodynamics) then we should have that $E_A + E_B = 6$ and that the total number of micro-states that will correspond to this macroscopic state is equal to $\Omega(E_A + E_B = 6) = {}^9C_6 = 84$. Thus we have that $S(E_A + E_B = 6) = k_B \ln(84) > S(E_A = 5 \& E_B = 1)$. This corresponds to the observation that when two systems at two different temperatures are allowed to interact the entropy of the composite system increases.

If the occurrence of a given micro-state is assumed to be random let us investigate the probability of finding a system with a given energy partition of E_A and $E_B = (E - E_A)$. It is reasonable to assume that each microscopic state corresponding to a given macroscopic state is equally likely to occur. That is there is nothing special about any of the microscopic states that correspond to a given macroscopic state. Let us compute the probability of finding the system in a micro-state such that the total energy of the particles in the left side is E_A and on the right side is $E_B = E - E_A$. We see that the total number of microscopic states that will result in a total energy of E_A on the left side is ${}^{E_A+1}C_{E_A} \times {}^{6-E_A+1}C_{6-E_A} = (E_A + 1) \times (6 - E_A + 1)$. Thus the probability of finding the system in a micro-state where the total energy of the particles in the left side is E_A is given by $p(E_A) = (E_A + 1) \times (6 - E_A + 1)/84$. In the table below we compute this quantity for the various different possibilities of $E_A = 0, 1, 2, 3, 4, 5, 6$.

E_A	0	1	2	3	4	5	6
$\Omega(E_A)$	7	12	15	16	15	12	7
$S(E_A)$	$\ln(7)$	$\ln(12)$	$\ln(15)$	$\ln(16)$	$\ln(15)$	$\ln(12)$	$\ln(7)$
$p(E_A)$	$\frac{7}{84}$	$\frac{12}{84}$	$\frac{15}{84}$	$\frac{16}{84}$	$\frac{15}{84}$	$\frac{12}{84}$	$\frac{7}{84}$

Thus we see that the most probable and hence the most likely situation that would occur is when the energies of the two sides are the same. In fact the expectation[37] of E_A, that is the value that you expect to 'mostly' get if you repeatedly measure the energy of the left hand side, is:

$$\langle E_A \rangle = \sum_{E_A=0}^{6} E_A p(E_A) = 0 \times \frac{7}{84} + 1 \times \frac{12}{84} + 2 \times \frac{15}{84} + 3 \times \frac{16}{84} + 4 \times \frac{15}{84} + 5 \times \frac{12}{84} + 6 \times \frac{7}{84} = 3.$$

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[36] The first law of thermodynamics.

[37] The average value.

Note that the entropy of this equally shared energy macro-state is also the maximum entropy macro-state. Figure-3.21 shows the probability distribution for each of the macroscopic states corresponding to subsystem A having a total energy $E_A = 0, 1, 2, \cdots, 20$ for $N_B = N_A = 60$ and $E = 20$ and it is clear that the macroscopic state where the energy is equally shared on each side is the most likely to occur. We also find in this case that $\langle E_A \rangle = 10$ and that entropy of this state is also a maximum.

We find that these conclusions are true in general as well. That is, for an isolated system, the most likely possibility is for the energy to be equally shared (equipartition of energy) and that the entropy of this state is a maximum. Since the energy shared state is the most likely to occur if one starts with the state where the energy was unevenly distributed and allow the energies to be shared then the initial state is less likely to occur after equilibrium has set in. Thus indicating an irreversibility of the energy mixing process.
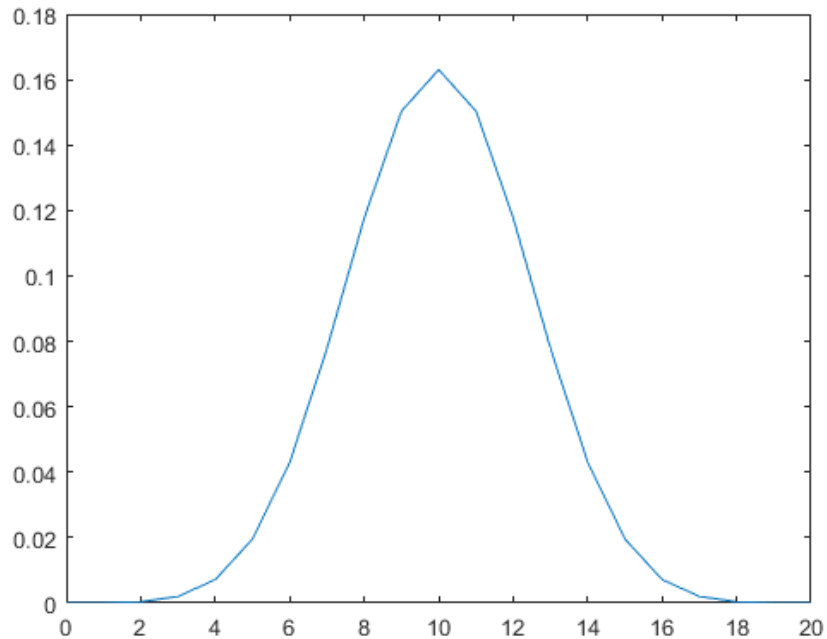
Fig. 3.21 The probability distribution $p(E_A)$ Vs E_A for the macroscopic state of subsystem A having a total energy E_A for $N_B = N_A = 60$ and $E = 20$.

Example-2: Diffusion

Consider a box made of two identical compartments separated by a partition with several holes in it. Each of the holes are big enough for a particle (you may visualize them as marbles) to move through it and we will assume that no particle will ever get stuck in a hole. A total of

$n = 2N$ number of distinguishable particles of identical mass are contained in the box. We will assume that the mass of a particle is m. A scale is fixed to the bottom of the left hand side compartment of the box so that it displays the total weight of the particles on the left hand side of the box. Consider the problem of randomly shaking the box. The mass of the left hand side of the box, read out using the scale, can be considered to be a measurement or in other words a macroscopic variable of the system. Denote this measurement by M_L. We will call a particular configuration where $M_L = m_k = km$, that is the situation where there are k number of particles in the left hand side, the macroscopic state denoted by m_k. If we randomly shake the system and then stop and read out the reading on the scale (that is the total mass of the particles on the left hand side) what is the value that we would expect to get?

To answer this question we proceed as follows. Let us call a particular distribution of the particles in the box a microscopic state. Since we are only interested in knowing if a given particle is in the left or right we see that there are a total of 2^n number of possible configurations or microscopic states of the system. If the shaking is random, given the information we have, the most reasonable (unbiased) conclusion that we can make is that each micro-state of the system (a particular distribution of the particles) is equally likely to occur at any given moment. Then the probability of finding the system in any one of the micro-states is $1/2^n$. The total number of microscopic states that will result in the macroscopic state $M_L = m_k$, denoted by $\Omega(m_k)$ is given by the number of k choices that we can make from n options:

$$\Omega(m_k) = {}^nC_k.$$

The entropy of the system when in the macroscopic state x_k is by definition

$$S(m_k) = k_B \ln(\Omega(m_k)) = k_B \ln({}^nC_k).$$

The probability of finding the system in the macroscopic state m_k is given by

$$p(m_k) = {}^nC_k \frac{1}{2^n}.$$

Then the mass reading that we would expect to get, $\langle M_L \rangle$, is given by

$$\langle M_L \rangle = \sum_{k=0}^{n} m k\, p(m_k).$$

We have computed $\Omega(m_k), p(m_k), S(m_k)$ for $n = 6$ in the table below.

k	$\Omega(m_k)$	$p(m_k)$	$S(m_k)$
0	1	$\frac{1}{2^6}$	0
1	6	$\frac{6}{2^6}$	$k_B \ln(6)$
2	15	$\frac{15}{2^6}$	$k_B \ln(15)$
3	20	$\frac{20}{2^6}$	$k_B \ln(20)$
4	15	$\frac{15}{2^6}$	$k_B \ln(15)$
5	6	$\frac{6}{2^6}$	$k_B \ln(6)$
6	1	$\frac{1}{2^6}$	0

From the results we see that the condition where an equal number of particles are in the left and right hand side has the maximum probability of occurring and hence is the most likely state to occur. Notice that the entropy of this state is also the maximum. Furthermore we also see that the expected value of the mass on the left hand side is given by

$$\langle M_L \rangle = m \left(0 \times \frac{1}{2^6} + 1 \times \frac{6}{2^6} + 2 \times \frac{15}{2^6} + 3 \times \frac{20}{2^6} + 4 \times \frac{15}{2^6} + 5 \times \frac{6}{2^6} + 6 \times \frac{1}{2^6} \right) = 3m,$$

confirming our intuition that on average we would expect to read the value $3m$ on the scale. This shows that the probability of finding half the marbles in one side is the most likely configuration that could occur if we randomly shake the box for a while and then stop. It is easy to show that this is in fact true for any $n = 2N$.

Let us try to see what all of this means. Imagine the case where initially all the particles are in the left hand side partition of the box. Recall that we do not care about how a particle is positioned in each side and that we only care about whether it is in the left or the right side of the box. Thus the initial entropy of the system, according to Boltzmann, is zero. Then let us start shaking the box for a long time and then open it to see how many marbles are in the left side of the partition. From the probability calculations shown above we see that the most likely state that would occur is the condition where the marbles are evenly distributed between the two halves and that the entropy of this state corresponds to a maximum. This agrees very well with our previous experience of what happens when a gas is confined to one side of a container and then allowed to diffuse over the entire cylinder. Thus the most mixed state is the one that is the most likely to occur and the entropy corresponding to this maximally mixed state is the maximum. We also see that how ever much you shake the box, obtaining the initial configuration of all the particles being in the left side is less unlikely.

Thus we see that if microscopic states of an isolated system occur in a random fashion the macroscopic state that are most likely to occur have the maximum entropy.

3.7.2 What does Boltzmann Entropy tell us ?

(a) Entropy is greater than or equal to zero.
(b) Higher the number of microscopic states higher the entropy.
(c) Entropy is a measure of the uncertainty about the microscopic state of the system.
(d) Entropy is an increasing function of the number of particles, the volume, and the total energy.
(e) The macroscopic state where the energy and the number of particles are evenly distributed is the most likely to occur and has the highest entropy.

Chapter 4
Introduction to Statistical Thermodynamics

Though accessible, the material covered in this section may be considered as beyond the scope of the GP111 syllabus. We have seen that that there exists many micro-states that correspond to a given macro-state. A macro-state is characterized by some average behavior of the collection of particles. Variables such as the number of particles, energy, temperature, pressure, and volume are some quantities that represent this average behavior and hence help characterize the macroscopic state. Given such information what is the best estimate that we can make of any other unknown property of the system? What we mean by best here is that those estimates must be unbiased. We will see that maximizing entropy gives us such an unbiased estimate [7]. That is we shall see that by starting with entropy as a fundamental property and applying notions of statistical inference allows us to recover the principles of statistical mechanics without having to invoke any additional assumptions other than the classically known laws of nature.

Let us denote by $\mathscr{X}$ the set made up of all possible situations that the system and the surrounding can exist[1]. Since there is practically no way of inferring the microscopic state of a system nor the exact influence the surrounding has on the system the best we can do is to assume that the microscopic states of the system occur according to some random probability distribution. Or more precisely, we will assume that the micro-state of the system is a random variable $X : \mathscr{X} \to \{x_1, x_2, \cdots, x_k\}$ where $\{x_1, x_2, \cdots, x_k\}$ is a list of all possible micro-states[2]. Denote by $P(\{X = x_j\}) = p_j$ the probability of the random variable X taking the value x_j. That is, denote by p_j the probability of finding the system in the microscopic state denoted by x_j. We see that any measurement of the system must also be a random variable that only depends on the random variable X.

Formally stated, measurements of the system are random variables that are only a function of the random variable X that prescribes the microscopic state of the system.

For a given system the number of particles and the energy of the system are some such random variables. Depending on what information (the measurements) we have about the system we can classify systems into three distinct groups.

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[1] That is all possible outcomes of the system plus surrounding

[2] Here k can be infinite.

Open Systems: Systems that can exchange both particles and energy with the surrounding. Both the energy and the number of particles of the system can change and can be measured. That is the measurements we have are the number of particles $N(X)$ and the Energy $E(X)$.

Closed Systems: Systems that can exchange *only energy* with the surrounding. The energy of the system can change $E(X)$ while the number of particles N remains fixed. Thus the only measurement we have is the energy $E(X)$.

Isolated Systems: Systems that *can not* exchange particles nor energy with the surrounding. We have no information of the system other than that the energy E and the number of particles N remain fixed.

In each of these macroscopic circumstances what is the best that we can say about the microscopic state of the system. That is the question that we will try to address in the following. Specifically what we will answer is: if the only information we can obtain is the expectations of $f_i(X)$ for some set of m number of functions of X what is the best that can be said about the expectation of $g(X)$?. What we know is the expectation (average) of f_i that we will denote by $\langle f_i(x) \rangle$ or $\bar{f}_i$. What we do not know is the probability distribution $\{p_j\}_{j=1}^k$ of X. That is, we know that

$$\bar{f}_i = \langle f_i(x) \rangle \triangleq \sum_{j=1}^k f_i(x_j) p_j, \tag{4.1}$$

$$1 = \sum_{j=1}^k p_j, \tag{4.2}$$

but we do not know the $\{p_j\}_{j=1}^k$. Note that condition (4.2) is a consequence of $\{p_j\}_{j=1}^k$ being a probability distribution and correspond to the simple statement that the probability of some microscopic state occurring must be one. The problem we need to solve is to find the most unbiased probability distribution $\{p_j\}_{j=1}^k$ given the information (4.1). Intuitively the most unbiased distribution should be the one with the most uncertainty. Claude Shannon [8] proved that the the notion of entropy used in thermodynamics is a measure of the intuitive notion of the *uncertainty of the probability distribution of the random variable*. Or in other words he proved that the most unbiased probability distribution $\{p_j\}_{j=1}^k$ of the random variable X must maximize the entropy.

In the general setting of probability and statistics, the entropy of a random variable X was defined by Claude Shannon to be

$$S(X) \triangleq -k_B \sum_{j=1}^k p_j \ln p_j. \tag{4.3}$$

We will see later that this definition reduces to the one given by Boltzmann for isolated systems. Thus the way that one should proceed to solve the problem of finding the most unbiased probability distribution $\{p_j\}_{j=1}^{k}$ given the information (4.1) is to find the probability distribution $\{p_j\}_{j=1}^{k}$ that maximizes the entropy of X subjected to the constraint (4.1). This is known as *maximum entropy inference*. Formally stated we find the probability distribution that solves the optimization problem

$$\{p_j^*\} = \max_{\{p_j\}} \left(S + \tilde{\gamma}\left(1 - \sum_{j=1}^{k} p_j\right) + \sum_{i=1}^{m} \tilde{\lambda}_i\left(\bar{f}_i - \sum_{j=1}^{k} p_j f_i(x_j)\right)\right).$$

The constants $\tilde{\gamma}$ and $\tilde{\lambda}_i$ are known as the Lagrange multipliers associated with the respective constraints. The solution to this constrained optimization problem is given by the solution of

$$0 = dS + \sum_{i=1}^{m} \tilde{\lambda}_i d\left(\bar{f}_i - \sum_{j=1}^{k} p_j f_i(x_j)\right) + \tilde{\gamma} d\left(1 - \sum_{j=1}^{k} p_j\right),$$

$$= \sum_{j=1}^{k}\left(-k_B(1 + \ln p_j) - \tilde{\gamma} - \sum_{i=1}^{m} \tilde{\lambda}_i f_i(x_j)\right) dp_j.$$

Thus we see that the probability distribution that maximizes the entropy and satisfies (4.1) and (4.2) must satisfy

$$\left(-k_B(1 + \ln p_j) - \tilde{\gamma} - \sum_{i=1}^{m} \tilde{\lambda}_i f_i(x_j)\right) = 0,$$

for every j. Thus probability distribution that maximizes the entropy and satisfies (4.1) and (4.2) takes the form

$$p_j^* = e^{-\gamma - \lambda_1 f_1(x_j) - \lambda_2 f_2(x_j)\cdots},$$

where we have defined $\gamma = 1 + \tilde{\gamma}/k_B$ and $\lambda_i = \tilde{\lambda}_i/k_B$. Then by defining $Z \triangleq e^{\gamma}$, we have that the constraint (4.2) implies:

$$Z(\lambda_1, \cdots, \lambda_m) = \sum_{j=1}^{k} \exp\left(-\lambda_1 f_1(x_j) - \lambda_2 f_2(x_j)\cdots\right), \tag{4.4}$$

$$p_j^* = \frac{1}{Z} \exp\left(-\lambda_1 f_1(x_j) - \lambda_2 f_2(x_j)\cdots\right). \tag{4.5}$$

The variable $Z(\lambda_1, \cdots, \lambda_m)$ is known as the *Partition Function* and depends only on the Lagrange multipliers $\lambda_1, \cdots, \lambda_m$.

Thus if one knows how to list the possible values of $f_i(x_j)$ for all i and j (that is we know the value that the measurement f_i will take if the system is in the state x_j) then one can uniquely determine the maximum entropy probability distribution, $\{p_j^*\}_{j=1}^{k}$, of the random variable X in terms of the Lagrange multipliers λ_i.

From (4.4) and (4.5) we also find that

$$\langle f_i(x) \rangle = -\frac{\partial}{\partial \lambda_i} \ln Z, \tag{4.6}$$

$$S = k_B \left(\ln Z + \lambda_1 \langle f_1(x) \rangle + \lambda_2 \langle f_2(x) \rangle + \cdots \right), \tag{4.7}$$

$$\lambda_i = \frac{\partial S}{\partial \langle f_i(x) \rangle} \tag{4.8}$$

$$\langle f_i^2(x) \rangle - \langle f_i(x) \rangle^2 = \frac{\partial^2}{\partial \lambda_i^2} \ln Z. \tag{4.9}$$

In addition if the functions $f_i(x, \alpha_1, \cdots, \alpha_k)$ also depend on some other parameters α_r then by taking the partial derivative of $\ln Z$ it follows that

$$\sum_{i=1}^{m} \lambda_i \left\langle \frac{\partial f_i}{\partial \alpha_r} \right\rangle = -\frac{\partial}{\partial \alpha_r} \ln Z. \tag{4.10}$$

Thus from a thermodynamics point of view, these expressions, demonstrate that analytically finding the partition function Z determines the Entropy and all the measurements. In turn to find the partition function Z what one needs are the Lagrange multipliers and the knowledge of what each of the measurements f_i will take if the system is in any of its particular microscopic states x_j. By computing the differential of S from (4.7) we also find that

$$dS = \sum_{i=1}^{m} k_B \lambda_i \left(d \langle f_i \rangle - \langle d f_i \rangle \right) = \sum_{i=1}^{m} k_B \lambda_i \left(d \langle f_i \rangle - \sum_r \left\langle \frac{\partial f_i}{\partial \alpha_r} \right\rangle d\alpha_r \right),$$

$$= \sum_{i=1}^{m} k_B \lambda_i d \langle f_i \rangle + k_B \sum_r \frac{\partial \ln Z}{\partial \alpha_r} d\alpha_r. \tag{4.11}$$

Picking the measurements f_i, which denotes the measured quantities, entirely determines the thermodynamics of the problem. If both the number of particles and the total energy of the particles remains fixed in a system (an isolated system) then the resulting maximum entropy probability distribution (4.5) is simply the uniform distribution of $p_j^*(x_j) = 1/\Omega$ where $Z = \Omega$ is the total number of micro-states. This distribution is referred to as the *Micro-canonical Ensemble*. On the other hand if only the number of particles of the system is fixed (a closed system) and the system can exchange energy with the surrounding through heat interactions then picking f to be the energy results in the maximum entropy probability distribution known as the *Canonical Ensemble*. Similarly if the system interacts with the surrounding by exchanging both particles and energy (open systems) then by picking f_1 to be the energy and f_i to be the number of particles of the ith type results in the probability distribution what is knows as the *Grand Canonical Ensemble*. Below we will derive these results and take a brief look at the thermodynamics of these three ensembles. We will start with the Canonical Ensemble then look at the more general Grand Canonical Ensemble and finally look at the Micro-canonical Ensemble.

4.1 Thermodynamics of the Canonical Ensemble

Let us consider a closed system that is thermally interacting with a reservoir (or thermal bath). That is a system that can only exchange energy with the thermal bath. A thermal bath, by definition being a system of a very large number of particles, has invariant properties that do not change due to its interaction with the system. The energy of the system also depends on the volume V occupied by the particles. For a given system of particles, the volume V of the system and the invariant properties of the thermal bath uniquely define the problem. If what we can measure is only the average energy, $U \triangleq \langle E \rangle$, of the system and we know what the energy is for each of the microscopic states then by setting $f_1(x_j, V) = E(x_j, V) = E_j$ we have from (4.4) that the corresponding partition function is given by

$$Z = \sum_j e^{-\lambda E_j}, \tag{4.12}$$

and from (4.5) we see that the corresponding maximum entropy probability distribution of finding the system in the jth state x_j is given by

$$p(x_j) = \frac{1}{Z} e^{-\lambda E_j}. \tag{4.13}$$

This is known as the *Canonical Ensemble*. The partition function Z will depend only V, and the invariant properties that characterize the thermal bath.

The Lagrange multiplier λ corresponding to the energy measurement of the system is a constant. Thus we can use it to characterize the invariant properties of the thermal bath. That is we will see that defining

$$T \triangleq \frac{1}{k_B \lambda},$$

to be the 'temperature' of the thermal bath allows us to recover all of the conventional notions of thermodynamics as well as some more.

With this definition of temperature of the thermal bath from (4.12), (4.13), (4.7), and (4.8) we have that

$$Z(T, V) = \sum_j e^{-\frac{E_j}{k_B T}},$$

$$p(x_j) = \frac{1}{Z} e^{-\frac{E_j}{k_B T}},$$

$$S(U, T, V) = k_B \ln Z + \frac{1}{T} U,$$

$$\frac{\partial S}{\partial U} = \frac{1}{T}.$$

Note that if we set $F(T, V) \triangleq -k_B T \ln Z$ then we find from the above expressions that

$$S = -\frac{\partial F}{\partial T},$$

$$U = TS + F.$$

The function $F(T,V)$ is called the the *Helmholtz free energy* of the system and it uniquely determines the entropy S and the total energy U of the closed system.

From (4.7) and (4.11) we also find that

$$dS = \frac{1}{T}\left(dU - \left\langle \frac{\partial E}{\partial V}\right\rangle dV\right) = \frac{1}{T}\left(dU + k_B T \frac{\partial \ln Z}{\partial V} dV\right) = \frac{1}{T}\left(dU - \frac{\partial F}{\partial V} dV\right).$$

From which we have

$$dU = TdS + \frac{\partial F}{\partial V} dV.$$

On the other hand the principle of conservation of energy (the 1st-law) for a closed system says that $dU = \delta Q - \delta W = \delta Q - PdV$ where P is the pressure of the system. Thus comparing with the above total differential dU we may define

$$\delta Q = TdS,$$
$$P \triangleq -\frac{\partial F}{\partial V} = \left\langle \frac{\partial E}{\partial V}\right\rangle = T\frac{\partial S}{\partial V} - \frac{\partial U}{\partial V}.$$

Therefore we see that:

Defining the temperature of the thermal bath to be $T = 1/k_B \lambda$ and the knowledge of the Helmholtz free energy $F(T,V) \triangleq U - TS$ allows us to recover all the classical thermodynamic notions of a closed system.

From (4.11) we also have

$$dS = \frac{1}{T}(dU - \langle dE \rangle).$$

Thus by comparing with the first law of thermodynamics we also see that $\langle dE \rangle = \delta W$.

From $U = TS + F$ we have that the heat capacity of the closed system is given by

$$C_V = \frac{\partial U}{\partial T} = T\frac{\partial S}{\partial T}.$$

From (4.9)

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2}{\partial \lambda^2} \ln Z = -\frac{\partial^2}{\partial \lambda^2} \lambda F = -2\frac{\partial F}{\partial \lambda} - \lambda \frac{\partial^2 F}{\partial \lambda^2}$$
$$= 2k_B T^2 \frac{\partial F}{\partial T} - \frac{k_B^2 T^2}{k_B T}\left(2T\frac{\partial F}{\partial T} + T^2 \frac{\partial^2 F}{\partial T^2}\right)$$
$$= -k_B T^3 \frac{\partial^2 F}{\partial T^2} = k_B T^3 \frac{\partial S}{\partial T} = k_B T^2 C_V.$$

Thus we have that the heat capacity of the system is

$$C_V = \frac{1}{k_B T^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right).$$

This shows that the heat capacity of the closed system is a measure of the variance of the energy distribution of the system among its micro-states.

Example: A Single Quantum Harmonic Oscillator

In this section we will find the thermodynamic properties of a single quantum harmonic oscillator thermally interacting with a thermal bath at temperature T. We know that a quantum harmonic oscillator has the energy levels

$$E_j = \hbar \omega \left(\frac{1}{2} + j \right).$$

Thus we have that the partition function is given by

$$Z(T) = \sum_{j=0}^{\infty} e^{-\frac{E_j}{k_B T}} = e^{-\frac{\hbar \omega}{2k_B T}} \sum_{j=0}^{\infty} \left(e^{-\frac{\hbar \omega}{k_B T}} \right)^j = \frac{e^{-\frac{\hbar \omega}{2k_B T}}}{1 - e^{-\frac{\hbar \omega}{k_B T}}}$$

Then the Helmholtz free energy, the entropy, and the average energy are given by

$$F(T) = \left(\frac{\hbar \omega}{2} + k_B T \ln \left(1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right),$$

$$S = -k_B \left(\ln \left(1 - e^{-\frac{\hbar \omega}{k_B T}} \right) - \frac{\hbar \omega}{k_B T} \frac{1}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)} \right),$$

$$U = \hbar \omega \left(\frac{1}{2} + \frac{1}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)} \right),$$

$$C_V = \frac{1}{k_B} \left(\frac{\hbar \omega}{T} \right)^2 \left(\frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2} \right) = \frac{1}{k_B} \left(\frac{\hbar \omega}{T} \right)^2 \left(\frac{1}{\left(\sinh \sqrt{\frac{\hbar \omega}{k_B T}} \right)^2} \right).$$

4.2 Thermodynamics of the Grand Canonical Ensemble

Let us consider an open system that is thermally interacting with a reservoir. That is a system that can exchange both energy and particles with the reservoir. For convenience we will assume that the reservoir and the system has only one type of particles. A reservoir, by definition

being a system of a very large number of particles, has invariant properties that do not change due to its interaction with the system. For an given open system the energy of the system depends on the pressure P of the system.Thus the pressure P of the system and these invariant properties of the thermal bath uniquely define the problem. If what we can measure is the average number of particles, $N \triangleq \langle n \rangle$ and the average energy, $U \triangleq \langle E \rangle$, of the system and we know what the the number of particles and the energy are for each of the microscopic states then by setting $f_1(x_j) = E(x_j, P) = E_j$ and $f_2(x_j, P) = n(x_j, P) = n_j$ we have from (4.4) and (4.5) that the maximum entropy probability distribution of finding the system in the micro-state x_j is given by

$$Z = \sum_j e^{-\lambda_1 E_j - \lambda_2 n_j}, \tag{4.14}$$

$$p(x_j) = \frac{1}{Z} e^{-\lambda_1 E_j - \lambda_2 n_j}. \tag{4.15}$$

This is known as the *Grand Canonical Ensemble*. We will see that it is completely determined by the pressure P and the invariant properties of the reservoir.

Again as in the previous section since the Lagrange multipliers λ_1 and λ_2 are constant we take them to characterize the invariant properties of the reservoir. Thus we define the temperature T and the chemical potential μ of the reservoir as

$$T \triangleq \frac{1}{k_B \lambda_1}, \quad \mu \triangleq -k_B T \lambda_2.$$

Then we have that (4.14), (4.15), (4.7), and (4.8) become

$$Z = \sum_j e^{\left(\frac{\mu n_j - E_j}{k_B T} \right)},$$

$$p(x_j) = \frac{1}{Z} e^{\left(\frac{\mu n_j - E_j}{k_B T} \right)},$$

$$S = k_B \ln Z + \frac{1}{T} U - \frac{\mu}{T} N,$$

$$\frac{\partial S}{\partial U} = \frac{1}{T},$$

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}.$$

Note that if we define $G(\mu, T, P) \triangleq -k_B T \ln Z$ then from the above expressions we have that

$$S = -\frac{\partial G}{\partial T},$$

$$N = -\frac{\partial G}{\partial \mu}$$

$$U = TS + \mu N + G.$$

The function $G(\mu, T, P)$ is called the the *Gibbs free energy* of the system and if known it uniquely determines the entropy S, the average number of particles N, and the total energy U.

From (4.7) and (4.11) we also find that

$$dS = \frac{1}{T}\left(dU - \left\langle \frac{\partial E}{\partial P} \right\rangle dP\right) - \frac{\mu}{T}\left(dN - \left\langle \frac{\partial n}{\partial P} \right\rangle dP\right)$$

$$= \frac{1}{T}\left(dU - \mu dN + k_B T \frac{\partial \ln Z}{\partial P} dP\right)$$

From the above expression we have

$$dU = TdS + \mu dN + \frac{\partial G}{\partial P} dP.$$

On the other hand the principle of conservation of energy (the 1st-law) for an open system says that

$$dU = \delta Q - \delta W + \delta H_f = \delta Q - P\delta V + \delta H_f = \delta Q - d(PV) + VdP + \delta H_f,$$

where δH_f is the net flow of enthalpy into the system and hence

$$dH = \delta Q + VdP + \delta H_f.$$

In light of this re-arranging the previous expression for dU we have

$$d(U - \mu N) = TdS + \frac{\partial G}{\partial P} dP - Nd\mu.$$

Thus from the above expression we have

$$\delta Q = TdS,$$
$$V \triangleq \frac{\partial G}{\partial P},$$
$$\delta H_f = -Nd\mu,$$
$$H \triangleq U - \mu N.$$

Thus notice that defining the temperature as $T = 1/k_B\lambda_1$ and the chemical potential as $\mu = -\lambda_2 k_B T$ we recover the classical definition of Entropy and that the volume is equal to $\frac{\partial G}{\partial P}$. Thus we see that:

Defining the temperature to be $T = 1/k_B\lambda_1$ and the chemical potential as $\mu = \lambda_2 k_B T$ and the knowledge of the Gibbs free energy $G(\mu, T, P) = H - TS$ allows us to recover all the classical thermodynamic notions of an open system.

4.3 Thermodynamics of the Microcanonical Ensemble

Consider a closed system of N fixed number of particles contained in a volume V that is isolated from the rest of the Universe. The total energy of the system E and the total number of particles N are a constant for all microscopic states. Then there are no constraints of the form (4.1) and thus the maximum entropy probability distribution (4.5) is simply the uniform distribution of $p_j^*(x_j) = 1/\Omega$ where $Z \triangleq \Omega$ is the total number of micro-states. This in fact makes perfect sense if there is no information available other than the number of states there is no reason to believe that any one of the states is any special than any other. Thus the best we can conclude is that all states are equally likely.

Thus for isolated systems, since $p_j^*(x_j) = 1/\Omega$ we immediately have that

$$S = k_B \ln \Omega,$$

in agreement with the Boltzmann definition of Entropy we saw in (3.11).

By taking the derivations of the Section-4.2 as formal definitions one can then define T, P and μ of the isolated system using the Entropy $S(N, V, T, \mu)$ as

$$G = -k_B T \ln Z = -TS$$
$$U = TS + \mu N + G = \mu N,$$
$$\frac{\partial S}{\partial U} = \frac{1}{T},$$
$$\frac{\partial S}{\partial V} = \frac{P}{T} + \frac{1}{T}\frac{\partial U}{\partial V},$$
$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}.$$

Chapter 5
Summary: What do the laws of thermodynamics tell us?

Finally let us summarize below all the consequence of the laws of thermodynamics that we have encountered in this study:

(A) Work can not be created out of nothing since energy can not be created or destroyed.
(B) Reversible heat engines are the best in terms of efficiency and result in the maximum amount of energy conversion.
(C) The maximum amount of energy that can be converted into work in a cyclic process depends only on the temperatures of the reservoirs.
(D) If no thermal gradients existed in the universe, the conversion of energy into work would be impossible.
(E) Energy transfer from a cold body to a hot body without the aid of mechanical work is impossible.
(F) There exists a property of the thermodynamic equilibrium state of a system called entropy, S, such that:
   (a) For reversible processes $\Delta S = \int \frac{\delta Q}{T}$.
   (b) For reversible adiabatic processes entropy remains a constant.
   (c) Entropy never decreases in an Adiabatic processes.
   (d) For pure positive heat interaction processes the entropy of the system increases.
(G) The quantity $\left(\int_c \frac{\delta Q}{T} - (S(y) - S(x)) \right)$ serves as a measure of the irreversibility of a general process, c.
(H) Entropy measures the number of possible micro-states that correspond to a given macro-state and hence has to be a non-negative quantity.
(I) Entropy is an increasing function of the number of particles, the volume, and the total energy.
(J) Entropy is a measure of the uncertainty of the knowledge of the microscopic state of the system.
(K) A maximally mixed state is the most likely to occur and the entropy corresponding to this state is the maximum. This means that isolated systems tend to a maximally mixed state (thermalization and diffusion) and that this process is irreversible.

Chapter 6
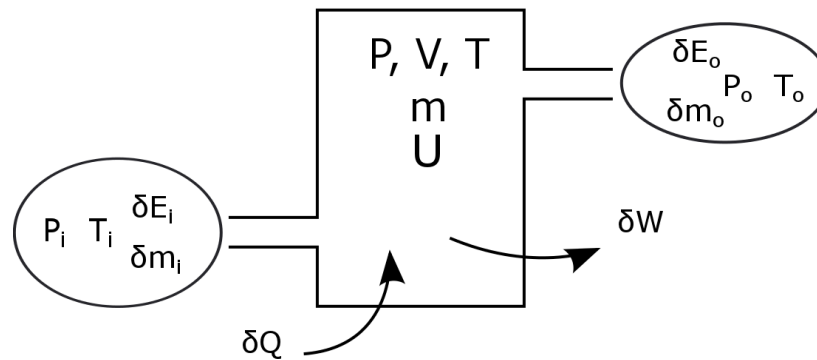# Thermodynamics of open systems

Fig. 6.1 Open thermodynamic system.

Consider the open system with one inlet and one outlet as shown in figure-6.1. We are interested in estimating the thermodynamic properties of the system. Let us consider the effects on the system during a small time interval δt. This is shown in figure-6.2. Let us apply the principles of conservation of mass and conservation of energy for the system at t and at $t + \delta t$. Let P_i, T_i be the inlet pressure and temperature and let δm_i and δE_i be the mass and the total energy that comes into the system (the control volume) through the inlet during the time interval δt. Similarly let P_o, T_o be the outlet pressure and temperature and let δm_o and δE_o be the mass and the total energy that goes out of the system through the oulet during the time interval δt. Also let δQ be the heat coming into the system and δW the work done by the system during the time interval δt. Then for non-nuclear reactions the mass of the system is conserved and the energy of the system is conserved and we have:

$$m + \delta m_i = m + \delta m + \delta m_o,$$
$$\delta E_i + U + \delta Q - \delta W = \delta E_o + U + \delta U$$

Which gives us

$$\delta m = \delta m_i - \delta m_o, \tag{6.1}$$
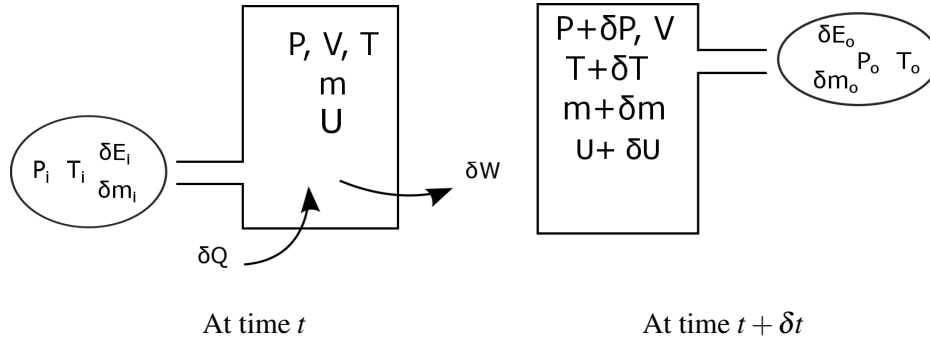$$\delta U = \delta Q - \delta W + (\delta E_i - \delta E_o). \tag{6.2}$$

Fig. 6.2 Open thermodynamic system energy and mass balance during a small time interval δt.

The inlet and outlet energy consists of the internal energy, the kinetic energy, potential energy, chemical energy, other forms of energy and the work done by the flow. Recall that the in flow work is equal to $\delta m_i P_i v_i$ and the out flow work is equal to $\delta m_o P_o v_o$ where v_i and v_o are the specific volumes of the inlet and outlet flow respectively. Also notice that the internal energy inflow is $\dot{m}_i u_i \delta t$ and the internal energy outflow is $\dot{m}_o u_o \delta t$ where u_i and u_o are the specific internal energies of the inlet and outlet flow respectively. Thus it turns out to be convenient to combine the two terms $u + Pv$ which is termed the specific enthalpy. Thus

$$\delta E_i = \delta m_i u_i + \delta m_i P_i v_i + \frac{\delta m_i}{2} c_i^2 + E_{\text{other}i} = \delta m_i h_i + \frac{\delta m_i}{2} c_i^2 + E_{\text{other}i}, \qquad (6.3)$$

$$\delta E_o = \delta m_o u_o + \delta m_o P_o v_o + \frac{\delta m_o}{2} c_o^2 + E_{\text{other}o} = \delta m_o h_o + \frac{\delta m_o}{2} c_o^2 + E_{\text{other}o}, \qquad (6.4)$$

where h_i, c_i denotes the inlet specific enthalpy, the inlet speed while h_o, c_o denotes the outlet specific enthalpy and the outlet speed.

Equations (6.1)–(6.4) are all you need for problems involving closed and open systems. A flow process is said to be steady if $\delta m = 0$ and $\delta U = 0$ and un-steady otherwise.

If the system is insulated then the heat interaction can be neglected and we would have $\delta Q \equiv 0$. If the system has no work output and the control volume does not change then $\delta W \equiv 0$.

6.1 Steady flow processes

For steady flow processes $\delta m = 0$ and $\delta U = 0$. For convenience we will only consider processes where the other forms of energy do not change during the process.

6.1.1 ideal gas steady flow processes

From (6.1)–(6.4) and $h = c_p T$ we have

$$\delta m_i = \delta m_o \triangleq \delta m_{fl}, \qquad (6.5)$$

74

$$\delta W - \delta Q = \delta m_{fl}(h_i - h_o) + \frac{\delta m_{fl}}{2}(c_i^2 - c_o^2) = \delta m_{fl}c_p(T_i - T_o) + \frac{\delta m_{fl}}{2}(c_i^2 - c_o^2). \quad (6.6)$$

Exercise in Prof. Sivasegaram's tutorial on steady flow: Q 1 *Air enters a nozzle at a pressure of P_i, temperature T_i, and mass flow rate $\dot{m}_{fl}$. It leaves the nozzle with an exit pressure of P_o. The mean velocity at entry is c_i and exit is c_o. Find the exit temperature T_o.*

Exercise in Prof. Sivasegaram's tutorial on steady flow: Q 3 *Air flows through a uniform pipe heated from the outside. The temperature and pressure are respectively T_i and P_i at inlet and T_o and P_o at exit. If the mass flow rate is $\dot{m}_{fl}$ and the pipe cross sectional area is A, calculate the mean velocity at inlet and exit and the rate of heat gain of the air.*

Exercise in Prof. Sivasegaram's tutorial on steady flow: Q 4 *A mixing device is required to cool hot air at temperature T_h and pressure P_h with a mass flow rate of $\dot{m}_h$ by mixing it with cool air at temperature T_c and pressure P_c. Neglecting heat interactions between the vessel and the surroundings answer the following:*

(a) Neglecting kinetic energy and assuming an exit pressure of P_m find the necessary rate of flow of cold air.
(b) If the entry velocity is c_h and c_c for the hot and cold air, and the exit velocity of the mixture leaving at P_m is c_m, calculate the exit temperature of the mixture for the air flow rates above.

Exercise in Prof. Sivasegaram's tutorial on steady flow: Q 8 *Helium enters a gas turbine at a temperature of T_i and pressure P_i with a mass flow rate of $\dot{m}_{fl}$ and after expansion leaves at a temperature of T_o and pressure of P_o. If the entry velocity is c_i and the exit velocity is c_o, calculate the power produced by the turbine. (Neglect heat interaction with the surrounding).*

6.1.2 Non-ideal gas steady flow processes

The difference is that now you can not use $h = c_p T$ and $u = c_v T$ and any of the ideal gas relationships. You should basically apply the mass and energy balance given by the expressions (6.1)–(6.4). For steam-and water use the steam tables to estimate the enthalpies.

Exercise in Prof. Sivasegaram's tutorial on steady flow: Q 5 *A separator is used to remove water droplets from steam of dryness fraction x_s. Steam with a flow rate of $\dot{m}_s$ enters the device at a pressure of P_s and on removal leaves at the same pressure and a dryness fraction of x_d.*

(a) If the condensed water leaves at a pressure of P_s find the rate of removal of water. (Neglect the heat interaction with the surrounding).
(b) If the condensed water leaves at a pressure of P_o, corresponding to atmospheric conditions, find the rate of removal of water. (Neglect the heat interaction with the surrounding).

Exercise in Prof. Sivasegaram's tutorial on steady flow: Q 7 *Steam of dryness fraction $x_s = 0.85$ at a pressure of $P_s = 1$ bar is condensed at the rate of $\dot{m}_s = 30$ kg/s in a condenser using cooling water entering the condenser at an temperature $T_i = 25^o C$.*

(a) *If the exit cooling water temperature is $T_o = 33^oC$ find the necessary rate of supply of cooling water. (Neglect changes in Kinetic and Potential energies).*

(b) *If the coolant supply rate is increased by $\Delta\dot{m} = 80kg/s$ what will be the exit temperature of the coolant?*

Exercise 6.1. A closed system consisting of H_2O undergoes a cyclic process as shown in figure-6.3. Assume that the processes $3 \to 4$ and $1 \to 2$ are reversible adiabatic processes. The boiler pressure is 100 kPa while the condenser pressure is 1kPa. The H_2O leaving the condenser is at saturated liquid conditions and the H_2O entering the turbine are at saturated vapor conditions. You may also assume that the specific heat capacity of sub-cooled water at 100 kPa is approximately $c_{fp} = 4.2$ kJ/kg.K. Answer the following:
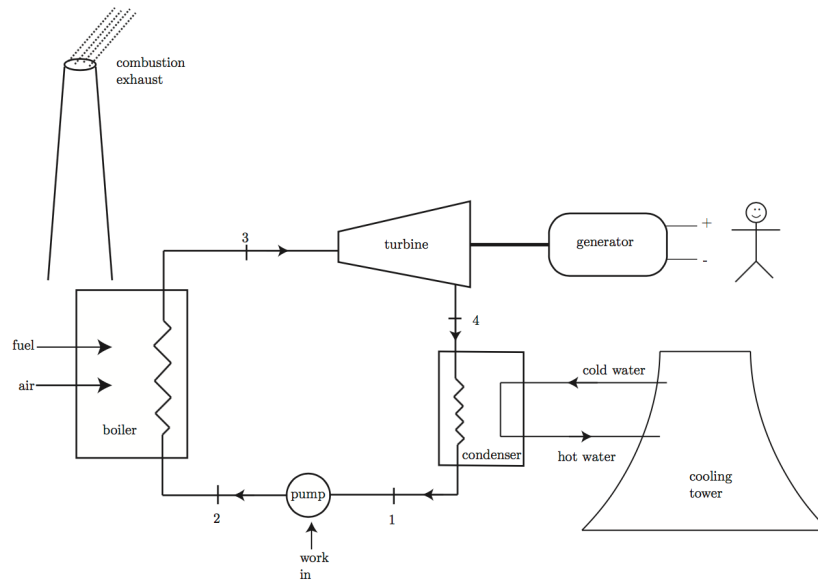
Fig. 6.3 The schematic of a cyclic process on which the steam engines are based on.

P	T	v_g	u_f	u_g	h_f	h_{fg}	h_g	s_f	s_{fg}	s_g
kPa	C	m³/kg	kJ/kg	kJ/kg	kJ/kg	kJ/kg	kJ/kg	kJ/kg.K	kJ/kg.K	kJ/kg.K
1	99.6	1.694	417	2506	418	2257	2675	1.3028	6.0560	7.3588
10	179.9	0.194	762	2583	763	2015	2778	2.1381	4.4469	6.5850

Table 6.1 Steam table extracts for exercise-6.1.

1. Sketch the cyclic process in a Temperature versus specific entropy space (ie. in T Vs s space).

76

2. Show that the efficiency η of the cycle is given by

$$\eta = 1 - \left(\frac{h_4 - h_1}{h_3 - h_2} \right),$$

where h_i denotes the specific enthalpy of the i^t state.

3. Find the efficiency of the cyclic process.

4. Sketch the modifications that you will do to this cyclic process, without changing the operating pressures, in order to obtain the maximum possible efficiency and find this efficiency.

6.2 Unsteady flow ideal gas processes

Though accessible and is a simple consequence of the law of conservation of energy, the material covered in this section may be considered as beyond the scope of GP111. For convenience we will assume that the flow velocities are very small and hence the kinetic energies can be neglected. Recall that for an ideal gas we have $u = c_v T$, $h = c_p T$, $PV = (\gamma - 1)U$ and $(\gamma - 1) = \frac{R}{c_v}$. Then from (6.1)–(6.4) we have

$$\delta m = \delta m_i - \delta m_o, \tag{6.7}$$
$$\delta U = \delta Q - \delta W + \delta m_i c_p T_i - \delta m_o c_p T_o. \tag{6.8}$$

6.2.1 Filling a rigid bottle with an ideal gas

Since there is no out flow $\delta m_o = 0$. Recall that

$$(\gamma - 1)\delta U = (P\delta V + V\delta P),$$
$$(\gamma - 1) = \frac{R}{c_v}.$$

Since the bottle is rigid we have that $\delta W = 0$ and $\delta V = 0$. Thus from (6.7) we have that $\delta m_i = \delta m$ and from equation (6.8) we have

$$V\delta P = \frac{c_p}{c_v} RT_i \, \delta m + \frac{R}{c_v} \delta Q = \gamma RT_i \, \delta m + \frac{R}{c_v} \delta Q,$$

and hence

$$V \int_{P_1}^{P_2} \delta P = \gamma RT_i \int_{m_1}^{m_2} \delta m + \frac{R}{c_v} \int_1^2 \delta Q,$$

where we have assumed that the inlet conditions remain constant. Which gives

$$V(P_2 - P_1) = \gamma RT_i(m_2 - m_1) + \frac{R}{c_v} \int_1^2 \delta Q. \tag{6.9}$$

Using the ideal gas law we have $P_2 V = m_2 RT_2$ and $P_1 V = m_1 RT_1$ and hence that the above equation becomes

$$m_2 T_2 - m_1 T_1 = \gamma T_i(m_2 - m_1) + \frac{1}{c_v} \int_1^2 \delta Q. \tag{6.10}$$

Exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 1 *An insulated gas cylinder of capacity V litres has air at pressure P_1 and temperature T_1. Air is added from an air supply line of pressure P_i and temperature T_i.*

(a) Find the pressure inside the bottle and the mass of air added when the cylinder temperature reaches T_2.

(b) Find the temperature inside the bottle and the mass of air added when the cylinder pressure reaches P_2.

Exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 2 *If the air in the cylinder in the previous question was maintained at a constant T through out the filling process what will be the mass of air added when the pressure reaches P_2. Also determine the heat interaction of the contents of the cylinder and the surroundings.*

6.2.2 Emptying a rigid bottle filled with an ideal gas

Since there is no in flow $\delta m_i = 0$. Since the bottle is rigid $\delta W = 0$ and $\delta V = 0$. Thus from (6.7) we have that $\delta m_o = -\delta m$ and from equation (6.8) we have

$$V \delta P = \gamma R T_o \, \delta m + \frac{R}{c_v} \delta Q,$$

and hence

$$V(P_2 - P_1) = \gamma R T_o (m_2 - m_1) + \frac{R}{c_v} \int_1^2 \delta Q, \tag{6.11}$$

where we have assumed that the outlet conditions remain constant. Using the ideal gas law we have $P_2 V = m_2 R T_2$ and $P_1 V = m_1 R T_1$ and hence that the above equation becomes

$$m_2 T_2 - m_1 T_1 = \gamma T_o (m_2 - m_1) + \frac{1}{c_v} \int_1^2 \delta Q. \tag{6.12}$$

Exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 3 *An insulated gas cylinder of volume V contains helium at a pressure of P_1 and a temperature of T_1. A leak is developed in the valve and was discovered when ice started to form on the surface of the bottle.*

(a) Estimate the mass of helium that would have leaked at the time of the discovery of the leak. (The pressure-density relationship for the gas in the cylinder during the process may be assumed to satisfy $P/\rho^\gamma = $ constant.

(b) What do you expect the heat interaction to be?

Chapter 7
Solutions to selected exercises

7.1 Solutions to selected exercises on Elementary Thermodynamics

Solution to exercise-2.6

Air is a mixture of several different ideal gases. Close to 80% of air is N_2 and a close to 20% of air is O_2. Thus we can approximately consider air to be a 4:1 mixture of N_2 and O_2.

Consider a closed system of air of mass m contained in a volume of V that is at a temperature of T and a total pressure of P. Since

$$m = M_{N_2} + M_{O_2},$$
$$P = P_{N_2} + P_{O_2},$$

where M_{N_2} is the mass of N_2 in the system M_{O_2} is the mass of O_2 in the system. If m_{N_2} is the mass of a N_2 molecule and m_{O_2} is the mass of a O_2 molecule we have

$$PV = (N_{N_2} + N_{O_2})k_B T = \left(\frac{M_{N_2}}{m_{N_2}} + \frac{M_{O_2}}{m_{O_2}} \right) k_B T.$$

We see that

$$m_{N_2} \mathcal{N}_A = 28 \times 10^{-3} \, kg$$
$$m_{O_2} \mathcal{N}_A = 32 \times 10^{-3} \, kg$$

where $\mathcal{N}_A = 6.0221 \times 10^{23}$ is the Avogadro's number. Thus we have

$$PV = \left(\frac{M_{N_2}}{28} + \frac{M_{O_2}}{32} \right) \mathcal{N}_A k_B T \times 10^{23}.$$

Since $M_{N_2} = 0.8 \times M$ and $M_{O_2} = 0.2 \times M$ we have

$$PV = m \left(\frac{0.8}{28} + \frac{0.2}{32} \right) RT \times 10^3,$$

where $R = \mathcal{N}_A k_B = 8.3145 \, JK^{-1}$. Thus we have that

$$PV = mR_aT,$$

where

$$R_a = \left(\frac{0.8}{28} + \frac{0.2}{32}\right) \times R \times 10^3 = 0.289\,kJ/kgK.$$

A more accurate consideration of the percentages gives $R_a = 0.287\,kJ/kgK$ that agrees quite well with experimental estimates.

Solution to Exercise-3.2

The heat interaction that occurs in an ideal gas system in the following processes:

(a) quasi-static isochoric process.

In an isochoric process the volume work is zero. Since the process is quasi-static there can not be any shaft work. Thus the total work done by the system $\Delta W_{12} = 0$ we then see that the first law implies that

$$\Delta Q_{12} = \Delta U_{12} + \Delta W_{12} = \frac{Nk_B}{(\gamma - 1)}(T_2 - T_1).$$

(b) isobaric process.

In an isobaric process the pressure is constant. Thus since the process is by definition quasi-static we have that the volume work done by the system is

$$\Delta W_{12}{}^{\text{v}} = \int_1^2 PdV = P(V_2 - V_1).$$

Since the process is quasi-static there can not be any shaft work. Thus the total work done by the system is $\Delta W_{12} = \Delta W_{12}{}^{\text{v}}$. Since the system is an ideal gas the total internal energy increase is

$$\Delta U_{12} = \frac{Nk_B}{(\gamma - 1)}(T_2 - T_1).$$

Thus from the first law of thermodynamics we have that the positive heat interaction during the process is

$$\Delta Q_{12} = \Delta U_{12} + \Delta W_{12} = \frac{Nk_B}{(\gamma - 1)}(T_2 - T_1) + P(V_2 - V_1).$$

$$= \frac{Nk_B}{(\gamma - 1)}(T_2 - T_1) + Nk_B(T_2 - T_1) + W_s = \frac{\gamma Nk_B}{(\gamma - 1)}(T_2 - T_1).$$

(c) isothermal process.

In an iso-thermal process the temperature is constant. Then the internal energy change

in the process is zero. Thus the first law says that the total energy transferred to the system due to positive heat interactions must be equal to the work done by the system thus we must have $\Delta Q_{12} = \Delta W_{12}$. Thus since isothermal processes are by definition quasi-static and since in a quasi-static process the shaft work must be zero we have

$$\Delta Q_{12} = \Delta W_{12} = \int_1^2 PdV = W_s + Nk_BT \int_1^2 \frac{1}{V}dV = Nk_BT \ln\left(\frac{V_2}{V_1}\right)$$

Solution to Exercise-3.3

Consider a closed ideal gas system. The heat interaction between the system and surrounding for the following processes of the system are:

(a) isochoric process with stirring where the temperature of the initial state and the state after stirring is complete is the same.

Since the process is isochoric the volume work is zero. Since the initial and final temperatures are the same the total internal energy change is zero. Thus the first law says that the work done on the system due to stirring must be equal to the negative heat interaction the system had with the system. That is, if the work done on the system due to stirring is W_{stir} then the energy lost by the system to the surrounding is equal to W_{stir}. Hence

$$\Delta Q_{12} = -W_{\text{stir}}.$$

(b) iso-baric and iso-thermal process with no mixing.

In such a process the internal energy change is zero and the work interaction is zero. Thus the first law says that the total heat interaction that occurs between the system and the surrounding must be zero. That is

$$\Delta Q_{12} = 0.$$

In fact in this process the system does not change state!!! It is the trivial stationary process.

Solution to Exercise-3.4

For a closed and insulated ideal gas system contained in a rigid cylinder the total heat interaction during a process is negligible and hence can be considered to be zero. If the system is mixed using a shaft and the mechanical work involved in the mixing was estimated to be W_m Joules then the first law of thermodynamics says that the total internal energy increase in the system must be equal to the shaft work W_m. Thus we have

$$W_m = \Delta U_{12} = \frac{Nk_B}{(\gamma - 1)}(T_2 - T_1).$$

Thus the temperature increase due to mixing is

$$\Delta T = (T_2 - T_1) = \frac{(\gamma - 1)}{Nk_B} W_m.$$

Solution to Exercise-3.5

Since the system is initially in thermal equilibrium $P_{A_1} = P_{B_1} = P$. From the ideal gas law for the initial states we find

$$PV = Nk_BT,$$
$$PV = 2Nk_BT_{B_1}.$$

This shows that $T_{B_1} = T/2$. Let P_{A_2} and P_{B_2} be the partial pressures of the gasses after they mix. Then assuming thermal equilibrium from the ideal gas law for the final state we find

$$P_{A_2}2V = Nk_BT_2,$$
$$P_{B_2}2V = 2Nk_BT_2,$$
$$P_2 = P_{A_2} + P_{B_2} = \frac{3Nk_BT_2}{2V}.$$

Since the system does not interact with the surrounding the first law implies that the internal energy in the system does not change during the process. Thus we have

$$Nk_BT \left(\frac{1}{(\gamma_B - 1)} + \frac{1}{(\gamma_A - 1)} \right) = Nk_BT_2 \left(\frac{2}{(\gamma_B - 1)} + \frac{1}{(\gamma_A - 1)} \right).$$

Which implies that

$$\frac{T_2}{T} = \frac{(\gamma_A - 1) + (\gamma_B - 1)}{2(\gamma_A - 1) + (\gamma_B - 1)} = \alpha.$$

The total pressure after mixing is thus $P_2 = \frac{\alpha 3Nk_BT}{2V}$. Furthermore we see that

$$P_2 = \frac{3Nk_BT_2}{2V} = \frac{\alpha 3Nk_BT}{2V} = \alpha \frac{3}{2}P.$$

Since we see that $1/2 < \alpha < 1$ we have that

$$\frac{1}{2}T < T_2 < T,$$
$$\frac{3}{4}P < P_2 < \frac{3}{2}P$$

Solution to Exercise-3.6

Since the system the initial equilibrium state is the same as for exercise-3.5 we have

$$PV = Nk_BT,$$
$$PV = 2Nk_BT_{B_1},$$
$$T_{B_1} = \frac{T}{2}.$$

At the equilibrium state following the switching off of the current through the coil $P_{B_2} = P_{A_2} = P_2$ and

$$P_2V_{A_2} = Nk_BT_{A_2},$$
$$P_2V_{B_2} = 2Nk_BT_{B_2}.$$

Since the gas A undergoes an adiabatic process we have

$$P_2V_{A_2}^{\gamma_A} = PV^{\gamma_A}.$$

Since the piston is rigid

$$V_{A_2} + V_{B_2} = 2V.$$

Since the cylinder is rigid and if we assume no shaft work, the first law implies that the internal energy increase in the system is equal to the positive heat interaction with the surrounding E. Thus we have

$$E = Nk_BT \left(\frac{1}{(\gamma_B - 1)} + \frac{1}{(\gamma_A - 1)} \right) - Nk_B \left(\frac{2T_{B_2}}{(\gamma_B - 1)} + \frac{T_{A_2}}{(\gamma_A - 1)} \right).$$

Solving the above five equations for the five unknowns $(P_2, T_{A_2}, V_{A_2}, T_{B_2}, V_{B_2})$ we can now estimate the work done by the gas B since the work done by gas B is equal to the work done on the gas A and since gas A undergoes an adiabatic process we have

$$W^B{}_{12} = -W^A{}_{12} = \frac{Nk_B}{(\gamma_A - 1)} (T_{A_2} - T).$$

Solution to Exercise-3.7

Initially $V_{A_1} = V_{B_1} = V/2$ where V is the entire volume of the cylinder. Initially the pressure on both sides of the cylinder is the same since the system is in equilibrium and the piston is stationary with no other external forces acting on it.

Let P_1 be this initial pressure inside the cylinder. Also since the piston is not insulated equilibrium also implies that both gases are at the same temperature T_1. From the ideal gas law we find

$$\frac{P_1 V}{2} = N k_B T_1,$$

for both gases. In particular this says that both gases have the same number of molecules. When you slowly move the piston such that $V_{A_2} = 2 V_{B_2}$ we see that $V_{A_2} = 2V/3$ and $V_{B_2} = V/3$. When the system is at equilibrium in this state the temperature of both gases are the same since the piston is not insulated. Let this temperature be T_2. Then from the ideal gas law we have that

$$P_{A_2} = \frac{3 N k_B T_2}{2V},$$
$$P_{B_2} = \frac{3 N k_B T_2}{V}.$$

Hence the force that has to be applied to keep the piston in place is

$$F = a_p (P_{B_2} - P_{A_2}) = \frac{3 a_p N k_B T_2}{2V}.$$

Total internal energy increase inside the cylinder during the process is $\Delta U_{12} = \Delta U_{12}^A + \Delta U_{12}^B$ where

$$\Delta U_{12}^A = \frac{N k_B (T_2 - T_1)}{(\gamma_A - 1)}$$
$$\Delta U_{12}^B = \frac{N k_B (T_2 - T_1)}{(\gamma_B - 1)}.$$

Since the cylinder is insulated the heat interactions between the gases and the surrounding is negligible and we can ignore them. Thus from the 1st law of thermodynamics the total work done on the two gases is equal to $-\Delta W_{12} = \Delta U_{12}$. That is the total work done on the system is

$$-\Delta W_{12} = N k_B (T_2 - T_1) \left(\frac{1}{(\gamma_A - 1)} + \frac{1}{(\gamma_B - 1)} \right).$$

Solution to Exercise-3.8

The initial conditions satisfy the same relationships as that of the above solution to exercise-3.7. Since the left end of the cylinder is uninsulated and if we assume that the process happens slowly so that all intermediate states are also equilibrium states then the temperature insider the cylinder is equal to the atmospheric temperature, $T_1 = T_{atm} = T_2$.

Then from the ideal gas law we have that at the final stae

$$P_{A_2} = \frac{3 N k_B T_{atm}}{2V},$$
$$P_{B_2} = \frac{3 N k_B T_{atm}}{V}.$$

Hence the force that has to be applied to keep the piston in place is

$$F = a_p(P_{B_2} - P_{A_2}) = \frac{3a_p N k_B T_{atm}}{2V}.$$

Total internal energy increase inside the cylinder during the process is $\Delta U_{12} = \Delta U_{12}^A + \Delta U_{12}^B = 0$ since there is no temperature change inside the cylinder through out the process. The work done by each of the gases throughout the process is

$$\Delta W_{12}^A = N k_B T_{atm} \ln\left(\frac{4}{3}\right)$$

$$\Delta W_{12}^B = N k_B T_{atm} \ln\left(\frac{2}{3}\right).$$

Thus the total work heat interaction the system has with the surrounding is

$$\Delta Q_{12} = \Delta W_{12} = N k_B T_{atm} \ln\left(\frac{8}{9}\right).$$

Solution to Exercise-3.9

Denote by $(T_{A_2}, P_{A_2}, V_{A_2})$ the thermodynamic properties of the end state of gas A and $(T_{B_2}, P_{B_2}, V_{B_2})$ the thermodynamic properties of the end state of gas B. From the ideal gas law we have that in all the above three cases:

$$\frac{P_{A_2} V_{A_2}}{T_{A_2}} = \frac{P_{A_1} V_{A_1}}{T_{A_1}} = N_A k_B, \tag{7.1}$$

$$\frac{P_{B_2} V_{B_2}}{T_{B_2}} = \frac{P_{B_1} V_{B_1}}{T_{B_1}} = N_B k_B. \tag{7.2}$$

We also note from the rigidity of the cylinder that

$$V_{A_2} + V_{B_2} = V_{A_1} + V_{B_1}. \tag{7.3}$$

Observe that the cylinder is assumed to be fully insulated and rigid and that there is no shaft work. Therefore throughout the process the total system does not exchange energy or work with the surroundings. Furthermore the assumption that the volume of the piston is negligible (or the specific heat capacity of the piston is negligible) implies that the internal energy change in the piston is negligible. Thus from the principle of conservation of energy we have that the initial total internal energy $U_1 = U_{A_1} + U_{B_1}$ is equal to the final total internal energy $U_2 = U_{A_2} + U_{B_2}$. Recalling that internal energy is given by $U = \frac{N k_B T}{(\gamma - 1)}$ we then have

$$\frac{N_A k_B}{(\gamma_A - 1)}(T_{A_2} - T_{A_1}) = -\frac{N_B k_B}{(\gamma_B - 1)}(T_{B_2} - T_{B_1}). \tag{7.4}$$

We now have four equations in six unknowns and thus need two more equations in order to be able to solve for the six unknowns $V_{A_2}, P_{A_2}, T_{A_2}, V_{B_2}, P_{B_2}, T_{B_2}$. It is clear that the equilibrium state corresponding to the final state of the three different cases described by a), b) and c) in exercise-3.9 are in general different. Thus we consider each of these cases separately.

3.9.a   The insulation of the piston and the force acting on the piston are both removed suddenly.

In this case at equilibrium, since the piston has to be stationary we see that

$$P_{A_2} = P_{B_2} = P_2. \tag{7.5}$$

Furthermore we also see that at equilibrium the average kinetic energy of the center of mass motion of all the particles that constitute gas A, gas B and the piston are the same and hence

$$T_{A_2} = T_{B_2} = T_2. \tag{7.6}$$

Thus we have six equations (7.1)—(7.6) in the six unknowns $(T_{A_2}, P_{A_2}, V_{A_2})$ and $(T_{B_2}, P_{B_2}, V_{B_2})$. We can now solve the six equations (7.1)—(7.4) for the six unknowns $(T_{A_2}, P_{A_2}, V_{A_2})$ and $(T_{B_2}, P_{B_2}, V_{B_2})$.

From (7.6) and (7.4) we obtain

$$T_2 = T_{A_2} = T_{B_2} = \left[\frac{N_A}{(\gamma_A - 1)} + \frac{N_B}{(\gamma_B - 1)} \right]^{-1} \left(\frac{N_A T_{A_1}}{(\gamma_A - 1)} + \frac{N_B T_{B_1}}{(\gamma_B - 1)} \right).$$

From (7.1) and (7.2) and (7.5) and (7.6) we have

$$\frac{V_{A_2}}{V_{B_2}} = \frac{N_A}{N_B},$$

and hence from (7.3) we have

$$V_{A_2} = \frac{N_A}{N_A + N_B} (V_{A_1} + V_{B_1}),$$

$$V_{B_2} = \frac{N_B}{N_A + N_B} (V_{A_1} + V_{B_1}).$$

Finally from (7.2) we have

$$P_2 = P_{A_2} = P_{B_2} = \frac{N_B k_B T_{B_2}}{V_{B_2}} = \frac{(N_A + N_B) k_B T_2}{V_{A_1} + V_{B_1}}.$$

Furthermore we can also compute the internal energy changes of the individual gases by

$$\Delta U_{12}^A = U_2^A - U_1^A = \frac{N_A k_B}{(\gamma_A - 1)} (T_2 - T_{A_1}),$$

$$\Delta U_{12}^B = U_2^B - U_1^B = \frac{N_B k_B}{(\gamma_B - 1)} (T_2 - T_{B_1}).$$

However we do not know enough information to compute the work done by each sub system since the work depends on the process and not only on the end states. For instance, the work done by the sub systems when the insulation is removed slowly without changing the force and then removing the force slowly, is different from the work done when the force is removed first and the insulation is removed next.

3.9.b   The insulation of the piston is kept in tact and the force acting on the piston is removed suddenly. In this case at equilibrium, since the piston has to be stationary we see that

$$P_{A_2} = P_{B_2} = P_2. \tag{7.7}$$

Thus we have five equations (7.1), (7.2), (7.3), (7.4) and (7.7) in the six unknowns $(T_{A_2}, P_{A_2}, V_{A_2})$ and $(T_{B_2}, P_{B_2}, V_{B_2})$. Hence to be able to solve for these six unknowns we need one more expression.

Before finding this expression lets find out what we can say about the system with the information and the expressions we have so far. From (7.1), (7.2) and (7.4) we obtain

$$\frac{1}{(\gamma_A - 1)} (P_{A_2} V_{A_2} - P_{A_1} V_{A_1}) = -\frac{1}{(\gamma_B - 1)} (P_{B_2} V_{B_2} - P_{B_1} V_{B_1}),$$

and from (7.7)

$$P_2 \left(\frac{V_{A_2}}{(\gamma_A - 1)} + \frac{V_{B_2}}{(\gamma_B - 1)} \right) = \left(\frac{P_{A_1} V_{A_1}}{(\gamma_A - 1)} + \frac{P_{B_1} V_{B_1}}{(\gamma_B - 1)} \right).$$

and

$$T_{A_2} = \frac{P_2 V_{A_2}}{k_B N_A}, \quad T_{B_2} = \frac{P_2 V_{B_2}}{k_B N_B}.$$

We find this by noting that each gas undergoes an adiabatic process and assuming that the removal of the force was done in such a way that the intermediate states of the process are guaranteed to be equilibrium states and hence that

$$P_2 V_{A_2}^{\gamma_A} = P_{A_1} V_{A_1}^{\gamma_A}. \tag{7.8}$$

or equivalently

$$P_2 V_{B_2}^{\gamma_B} = P_{B_1} V_{B_1}^{\gamma_B}. \tag{7.9}$$

We can now solve the six equations (7.1), (7.2), (7.3), (7.4), (7.7) and (7.8) (or (7.9)) for the six unknowns $(T_{A_2}, P_{A_2}, V_{A_2})$ and $(T_{B_2}, P_{B_2}, V_{B_2})$.

Substituting for V_{A_2} and V_{B_2} from (7.8) and (7.9) and (7.7) we end up with the following nonlinear expression for $P_{A_2} = P_2$.

$$P_2 \left(\left(\frac{P_{A_1} V_{A_1}^{\gamma_A}}{P_2} \right)^{\frac{1}{\gamma_A}} \frac{1}{(\gamma_A - 1)} + \left(\frac{P_{B_1} V_{B_1}^{\gamma_B}}{P_2} \right)^{\frac{1}{\gamma_B}} \frac{1}{(\gamma_B - 1)} \right) = \left(\frac{P_{A_1} V_{A_1}}{(\gamma_A - 1)} + \frac{P_{B_1} V_{B_1}}{(\gamma_B - 1)} \right).$$

Once you solve this for P_2, we can obtain V_{A_2} from (7.8) and V_{B_2} from (7.9), and finally T_{A_2} and T_{B_2} from (7.1) and (7.2) respectively.

Now we can also compute the internal energy changes of the individual gases by

$$\Delta U_{12}^A = U_2^A - U_1^A = \frac{N_A k_B}{(\gamma_A - 1)}(T_2 - T_{A_1}),$$

$$\Delta U_{12}^B = U_2^B - U_1^B = \frac{N_B k_B}{(\gamma_B - 1)}(T_2 - T_{B_1}).$$

Furthermore since the gasses undergo an adiabatic process we also have that the work done by the gasses are given by

$$\Delta W_{12}^A = -\Delta U_{12}^A = -\frac{N_A k_B}{(\gamma_A - 1)}(T_2 - T_{A_1}),$$

$$\Delta W_{12}^B = -\Delta U_{12}^B = -\frac{N_B k_B}{(\gamma_B - 1)}(T_2 - T_{B_1}).$$

3.9.c   A door in the piston is opened slowly.

In this case at equilibrium,

$$T_{A_2} = T_{B_2} = T_2. \tag{7.10}$$

Thus we have five equations (7.1), (7.2), (7.3), (7.4) and (7.10) in the six unknowns $(T_{A_2}, P_{A_2}, V_{A_2})$ and $(T_{B_2}, P_{B_2}, V_{B_2})$. Hence to be able to solve for these six unknowns we need one more expression. We find this by noting that each gas at equilibrium occupies the entire volume of the cylinder. That is

$$V_{A_2} = V_{B_2} = V_{A_1} + V_{B_1}. \tag{7.11}$$

From (7.10) and (7.4) we obtain

$$T_2 = \left[\frac{N_A}{(\gamma_A - 1)} + \frac{N_B}{(\gamma_B - 1)} \right]^{-1} \left(\frac{N_A T_{A_1}}{(\gamma_A - 1)} + \frac{N_B T_{B_1}}{(\gamma_B - 1)} \right).$$

From (7.1) and (7.2) we thus have

$$P_{A_2} = \frac{N_A k_B T_2}{V_{A_1} + V_{B_1}},$$

$$P_{B_2} = \frac{N_B k_B T_2}{V_{A_1} + V_{B_1}},$$

$$P_2 = P_{A_2} + P_{B_2} = k_B T_2 \frac{N_A + N_B}{V_{A_1} + V_{B_1}},$$

$$\frac{P_{A_2}}{P_{B_2}} = \frac{N_A}{N_B}.$$

Now we can also compute the internal energy changes of the individual gases by

$$\Delta U_{12}^A = U_2^A - U_1^A = \frac{N_A k_B}{(\gamma_A - 1)}(T_2 - T_{A_1}),$$

$$\Delta U_{12}^B = U_2^B - U_1^B = \frac{N_B k_B}{(\gamma_B - 1)}(T_2 - T_{B_1}).$$

Lecture notes by D. H. S. Maithripala, Dept. of Mechanical Engineering, University of Peradeniya
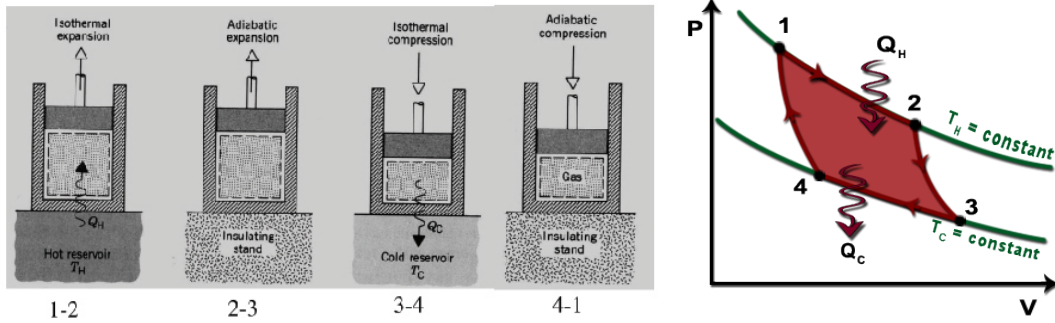
Solution to Exercise-3.10

Fig. 7.1 The $P - V$ curve of the process discussed in exercise-3.10.

Note that the given data are P_1, V_1, T_H, V_2, T_C In order to maintain the temperature at T_H during the part of the process from $1 \to 2$ one needs to maintain the internal energy at a constant thus from the first law we see that the energy that is coming in from the hot plate to the system through the bottom of the cylinder must be expended as work. That is the energy absorbed by the system $\Delta Q_{12} = Q_H$ during this part must be equal to the work done by the system during the process ΔW_{12}. Thus the volume V must increase. Since the temperature remains constant through this part of the process the pressure and volume must satisfy $PV = mR_aT_H$ during the process $1 \to 2$. Then assuming that the process is quasi-static and there is no shaft work we have

$$Q_H = \Delta W_{12} = \int_1^2 PdV = \int_1^2 \frac{mR_aT_H}{V}dV = mR_aT_H \ln\left(\frac{V_2}{V_1}\right).$$

The process from $2 \to 3$ that occurs on the sand pit is an adiabatic process. Thus from the first law of thermodynamics we have that the work done by the system, ΔW_{23}, during this process is equal to the internal energy decrease. Thus

$$\Delta W_{23} = -\Delta U_{23} = \frac{mR_a}{(\gamma - 1)}(T_H - T_C).$$

During this part of the process since the internal energy is decreasing the temperature must drop during this part of the process. We allow this expansion to occur until the temperature drops to T_C at which point we transfer the cylinder to a cold plate at temperature T_C. During the process $3 \to 4$ on the cold plate we need to maintain the temperature at a constant value T_C. From the argument made before we see that we need to compress the gas. Since this part of the process is iso-thermal and the gas is an ideal gas the total internal energy change during this part of the process is zero and thus from the first law of thermodynamics we have that the energy lost by the system, $Q_C = -\Delta Q_{34}$ is equal to the work done on the system $-W_{34}$. Assuming this part of the process is quasi-static we then have

$$Q_C = -\Delta Q_{34} = -\Delta W_{34} = -\int_3^4 PdV = -\int_3^4 \frac{mR_aT_C}{V}dV = -mR_aT_C \ln\left(\frac{V_4}{V_3}\right) = mR_aT_C \ln\left(\frac{V_3}{V_4}\right).$$

Note that in order to compute Q_C we need to know V_3, and V_4.

Now for the part of the process, from $2 \to 3$, on the sand pit since there are no other interactions other than work the process is adiabatic. Assuming that the process is quasi-static we see that PV^γ is a constant during this part of the process. On the other hand from the ideal gas law we have $P_2 V_2 / T_H = P_3 V_3 / T_C$ and hence

$$\frac{P_2}{P_3} = \left(\frac{V_3}{V_2}\right)^\gamma = \left(\frac{V_3 T_H}{V_2 T_C}\right)$$

and hence that

$$V_3 = V_2 \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}}.$$

Similarly for the last part of the process, from $4 \to 1$, $P_1 V_1^\gamma = P_4 V_4^\gamma$ and $P_1 V_1 / T_H = P_4 V_4 / T_C$ and hence

$$\frac{P_1}{P_4} = \left(\frac{V_4}{V_1}\right)^\gamma = \left(\frac{V_4 T_H}{V_1 T_C}\right)$$

and hence that

$$V_4 = V_1 \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}}.$$

Note that this shows that

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}.$$

Since the process is adiabatic the work done on the system $-\Delta W_{41}$ is equal to the internal energy increase of the system. That is

$$\Delta W_{41} = -\frac{mR_a}{(\gamma-1)}(T_H - T_C).$$

Taking Prof. Sivasegaram's advice we will summarize these results in the two tables below.

State	P	V	T
1	P_1	V_1	T_H
2	—	V_2	T_H
3	—	$V_2 \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}}$	T_C
4	—	$V_1 \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}}$	T_C

Process	ΔQ_{ij}	ΔW_{ij}
$1 \to 2$	$mR_a T_H \ln\left(\frac{V_2}{V_1}\right)$	$mR_a T_H \ln\left(\frac{V_2}{V_1}\right)$
$2 \to 3$	0	$\frac{mR_a}{(\gamma-1)}(T_H - T_C)$
$3 \to 4$	$-mR_a T_C \ln\left(\frac{V_3}{V_4}\right)$	$-mR_a T_C \ln\left(\frac{V_3}{V_4}\right)$
$4 \to 1$	0	$-\frac{mR_a}{(\gamma-1)}(T_H - T_C)$

The efficiency of the engine is

$$\eta = \left(\frac{\Delta W_{12} + \Delta W_{23} + \Delta W_{34} + \Delta W_{41}}{\Delta Q_{12}} \right) \times 100\% = \left(\frac{\Delta Q_{12} + \Delta Q_{34}}{\Delta Q_{12}} \right) \times 100\%$$

$$= \left(1 + \frac{\Delta Q_{34}}{\Delta Q_{12}} \right) \times 100\% = \left(1 + \frac{-mR_a T_C \ln\left(\frac{V_3}{V_4}\right)}{mR_a T_H \ln\left(\frac{V_2}{V_1}\right)} \right) \times 100\%$$

$$= \left(1 - \frac{T_C}{T_H} \right) \times 100$$

Solution to Exercise-3.11 – [Otto standard cycle]:

Consider the quasi-static adiabatic compression process from $1 \to 2$. Assuming that air behaves like an ideal gas we have $T_1 = P_1 V_1 / mR_a$ and since $P_1 V_1^\gamma = P_2 V_2^\gamma = P_2 V_3^\gamma$, that

$$P_2 = \frac{P_1 V_1^\gamma}{V_3^\gamma},$$

$$P_2 V_2 = \frac{P_1 V_1^\gamma}{V_3^{\gamma-1}},$$

$$T_2 = \frac{P_2 V_2}{mR_a} = \frac{P_1 V_1^\gamma}{mR_a V_3^{\gamma-1}}.$$

The volume work done **by** the system, ΔW_{12} during this part of the process is thus

$$\Delta W_{12} = -\frac{1}{\gamma-1}(P_2 V_2 - P_1 V_1) = \frac{P_1 V_1}{\gamma-1}\left(1 - \left(\frac{V_1}{V_3} \right)^{\gamma-1} \right)$$

Consider the constant volume process from $2 \to 3$. Since air is assumed to be an ideal gas the ideal gas law gives:

$$T_3 = \frac{P_3 V_3}{mR_a}.$$

Since the volume is constant the pressure can increase only if the temperature increases. That is the internal energy must increase during this process. Since there is no volume change the volume work is zero. Thus the first law says that the internal energy increase in this part of the process must equal the positive heat interaction ΔQ_{23} that the system has with the surrounding. Since we assume air is an ideal gas we then have that

$$\Delta Q_{23} = U_3 - U_2 = \frac{mR_a}{(\gamma-1)}(T_3 - T_2) = \frac{1}{(\gamma-1)}(P_3 V_3 - P_2 V_2) = \frac{P_3 V_3}{(\gamma-1)}\left(1 - \frac{P_1 V_1^\gamma}{P_3 V_3^\gamma} \right).$$

Consider the quasi-static adiabatic expansion process from $3 \to 4$. Assuming that air behaves like an ideal gas we have since $P_3 V_3^\gamma = P_4 V_4^\gamma = P_4 V_1^\gamma$, that

$$P_4 = \frac{P_3 V_3^\gamma}{V_1^\gamma},$$

$$P_4 V_4 = \frac{P_3 V_3^\gamma}{V_1^{\gamma-1}},$$

$$T_4 = \frac{P_4 V_4}{mR_a} = \frac{P_3 V_3^\gamma}{mR_a V_1^{\gamma-1}}.$$

The volume work done **by** the system, ΔW_{34} during this part of the process is thus

$$\Delta W_{34} = -\frac{1}{\gamma-1}(P_4 V_4 - P_3 V_3) = \frac{P_3 V_3}{\gamma-1}\left(1 - \left(\frac{V_3}{V_1}\right)^{\gamma-1}\right).$$

Consider the constant volume process from $4 \to 1$. Since the volume is constant the pressure can decrease only if the temperature decreases. That is the internal energy must decrease during this process. Since there is no volume change the volume work is zero. Thus the first law says that the internal energy decrease in this part of the process must equal the negative heat interaction $-\Delta Q_{41}$ that the system has with the surrounding. Since we assume air is an ideal gas we then have that

$$\Delta Q_{41} = U_1 - U_4 = \frac{mR_a}{(\gamma-1)}(T_1 - T_4) = \frac{1}{(\gamma-1)}(P_1 V_1 - P_4 V_4) = \frac{P_1 V_1}{(\gamma-1)}\left(1 - \frac{P_3 V_3^\gamma}{P_1 V_1^\gamma}\right).$$

We will summarize these results in the two tables below.

State	P	V	T
1	P_1	V_1	$\frac{P_1 V_1}{mR_a}$
2	$\frac{P_1 V_1^\gamma}{V_3^\gamma}$	V_3	$\frac{P_1 V_1^\gamma}{mR_a V_3^{\gamma-1}}$
3	P_3	V_3	$\frac{P_3 V_3}{mR_a}$
4	$\frac{P_3 V_3^\gamma}{V_1^\gamma}$	V_1	$\frac{P_3 V_3^\gamma}{mR_a V_1^{\gamma-1}}$

Process	ΔQ_{ij}	ΔW_{ij}
$1 \to 2$	0	$\frac{P_1 V_1}{\gamma-1}\left(1 - \left(\frac{V_1}{V_3}\right)^{\gamma-1}\right)$
$2 \to 3$	$\frac{P_3 V_3}{(\gamma-1)}\left(1 - \frac{P_1 V_1^\gamma}{P_3 V_3^\gamma}\right)$	0
$3 \to 4$	0	$\frac{P_3 V_3}{\gamma-1}\left(1 - \left(\frac{V_3}{V_1}\right)^{\gamma-1}\right)$
$4 \to 1$	$\frac{P_1 V_1}{(\gamma-1)}\left(1 - \frac{P_3 V_3^\gamma}{P_1 V_1^\gamma}\right)$	0

Note that for one entire cycle of the process the first law says that

$$0 = (\Delta Q_{23} + \Delta Q_{41}) - (\Delta W_{12} + \Delta W_{34}),$$

and hence that

$$(\Delta Q_{23} + \Delta Q_{41}) = (\Delta W_{12} + \Delta W_{34}).$$

The efficiency of the engine is

$$\eta = \frac{\Delta W_{12} + \Delta W_{34}}{\Delta Q_{23}} \times 100\% = \left(\frac{(\Delta Q_{23} + \Delta Q_{41})}{\Delta Q_{23}} \right) \times 100\% = \left(1 + \frac{\Delta Q_{41}}{\Delta Q_{23}} \right) \times 100\%$$

$$= \left(1 + \frac{\frac{P_1 V_1}{(\gamma-1)} \left(1 - \frac{P_3 V_3^\gamma}{P_1 V_1^\gamma} \right)}{\frac{P_3 V_3}{(\gamma-1)} \left(1 - \frac{P_1 V_1^\gamma}{P_3 V_3^\gamma} \right)} \right) \times 100\% = \left(1 - \left(\frac{V_3}{V_1} \right)^{(\gamma-1)} \right) \times 100\%.$$

Solution to Exercise-3.13

Since the cylinder is insulated and rigid the only interaction the system has with the surrounding is the work due to stirring. Thus the fist law tells us that $\Delta U_{12} = -\Delta W_{12}$. Thus the work done on the system due to stirring is

$$\Delta W_{12} = -\Delta U_{12} = \frac{N k_B}{(\gamma-1)} (T_2 - T_1) = \frac{1}{(\gamma-1)} (P_2 - P_1) V_1.$$

Solution to Exercise-3.14

Let $x_i = (P_i, V_i, T_i, U_i)$ denote the ith equilibrium state of the system during the described process. Iso-thermal or iso-baric process means that intermediate states are also equilibrium states. Thus iso-thermal processes or iso-baric processes are quasi-static process.

Thus for the iso-thermal part of the process

$$\Delta W_{12} = \int_1^2 P dV = P_1 V_1 \int_1^2 \frac{1}{V} dV = P_1 V_1 \ln \left(\frac{V_2}{V_1} \right) < 0,$$
$$\Delta U_{12} = (U_2 - U_1) = 0.$$

and for the iso-baric part

$$\Delta W_{23} = \int_2^3 P dV = P_2 \int_2^3 dV = P_2 (V_3 - V_2) < 0,$$
$$\Delta U_{23} = (U_3 - U_2) = \frac{N k_B}{(\gamma-1)} (T_3 - T_2) = \frac{1}{(\gamma-1)} P_2 (V_3 - V_2).$$

Thus the heat interaction during each stage is

$$\Delta Q_{12} = \Delta U_{12} + \Delta W_{12} = P_1 V_1 \ln \left(\frac{V_2}{V_1} \right) < 0$$

$$\Delta Q_{32} = \Delta U_{23} + \Delta W_{23} = \frac{1}{(\gamma-1)} P_2 (V_3 - V_2) + P_2 (V_3 - V_2) = \frac{\gamma}{(\gamma-1)} P_2 (V_3 - V_2) < 0.$$

Solution to Exercise-3.15

Assume that the process occurs sufficiently slowly so that all the intermediate states of the system are also in equilibrium. Consider an intermediate state of the system described by the variables (P, V, T) at which the spring is compressed by x. Consider an infinitesimal change in the system that results in an equilibrium state $(P + \delta P, V + \delta V, T + \delta T)$ and the spring to be compressed by $x + \delta x$. Then the incremental work done by the gas is

$$\delta W = P\delta V = \left(P_{atm} + \frac{kx}{A} \right) A\delta x = (AP_{atm} + kx)\,\delta x.$$

When the system changes from (P_1, V_1, T_1) to (P_2, V_2, T_2) the spring is compressed from $x_1 = 0$ to $x_2 = (V_2 - V_1)/A$. Thus we find the work done by the system to be

$$\Delta W_{12} = \int_{x_1}^{x_2} (AP_{atm} + kx)\,dx = P_{atm}(V_2 - V_1) + \frac{k}{2A^2}(V_2 - V_1)^2.$$

The internal energy increase in the system is

$$\Delta U_{12} = \frac{1}{(\gamma - 1)}(P_2 V_2 - P_1 V_1).$$

Thus the total heat interaction between the gas and the surrounding is

$$\Delta Q_{12} = \Delta U_{12} + \Delta W_{12} = \frac{1}{(\gamma - 1)}(P_2 V_2 - P_1 V_1) + P_{atm}(V_2 - V_1) + \frac{k}{2A^2}(V_2 - V_1)^2.$$

Solution to Exercise-3.17

Since the process is iso-baric and if we assume the process to be quasi-static then

$$\Delta Q_{12} = \int_{T_1}^{T_2} c_p dT = \int_{T_1}^{T_2} (c_0 + c_1 T + c_2 T^2 + c_3 T^3)dT$$
$$= \left(c_0(T_2 - T_1) + \frac{c_1}{2}(T_2 - T_1)^2 + \frac{c_1}{3}(T_2 - T_1)^3 + \frac{c_1}{4}(T_2 - T_1)^4) \right),$$

and

$$\Delta W_{12} = \int_{V_1}^{V_2} PdV = P_1(V_2 - V_1).$$

Thus from the first law we have that the increase in the internal energy of the system is

$$\Delta U_{12} = \Delta Q_{12} - \Delta W_{12}$$
$$= \left(c_0(T_2 - T_1) + \frac{c_1}{2}(T_2 - T_1)^2 + \frac{c_2}{3}(T_2 - T_1)^3 + \frac{c_3}{4}(T_2 - T_1)^4 \right) - P_1(V_2 - V_1).$$

Solution to Exercise-3.18

Since the process satisfies $PV^n = $ constant we see that

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^n .$$

Since by definition polytropic processes are quasi-static we have that the work done by the system is

$$\Delta W_{12} = -\frac{1}{(n-1)} (P_2 V_2 - P_1 V_1)$$

$$= -\frac{P_1 V_1}{(n-1)} \left(\left(\frac{V_1}{V_2} \right)^{(n-1)} - 1 \right)$$

Consider the following process $x_1 = (P_1, V_1) \to x_0 = (P_2, V_1) \to x_2 = (P_2, V_2)$ where the first is a quasi-static iso-choric process and the second is a quasi-static iso-baric process. Thus

$$\Delta U_{10} = \Delta Q_{10} = \int_{T_1}^{T_0} c_v(T) dT,$$

$$\Delta U_{02} = \Delta Q_{02} - \Delta W_{02} = \int_{T_0}^{T_2} c_p(T) dT - P_2(V_2 - V_1),$$

where $T_1 = \tau(P_1, V_1)$, $T_0 = \tau(P_2, V_1)$, and $T_2 = \tau(P_2, V_2)$. Hence we have

$$\Delta U_{12} = \Delta U_{10} + \Delta U_{02} = -P_2(V_2 - V_1) + \int_{T_1}^{T_0} c_v(T) dT + \int_{T_0}^{T_2} c_p(T) dT,$$

and thus that the heat interaction during a process is given by

$$\Delta Q_{12} = \Delta U_{12} + \Delta W_{12}$$

$$= -P_2(V_2 - V_1) + \int_{T_1}^{T_0} c_v(T) dT + \int_{T_0}^{T_2} c_p(T) dT - \frac{P_1 V_1}{(n-1)} \left(\left(\frac{V_1}{V_2} \right)^{(n-1)} - 1 \right),$$

where $T_1 = \tau(P_1, V_1)$, $T_0 = \tau(P_2, V_1)$, and $T_2 = \tau(P_2, V_2)$.

Solution to Exercise-3.23: [Kelvin-Planck implies Caratheodory]

Let x be a given equilibrium state of a given simple thermodynamic system and $\mathcal{N}_x$ be any neighborhood of x.

   If Kelvin-Planck is true but the Caratheodory statement is false then every equilibrium state $y \in \mathcal{N}_x$ can be adiabatically and quasi-statically reached from x. Let $y \in \mathcal{N}_x$ be such that x
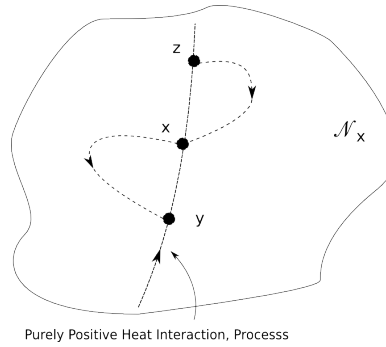
Purely Positive Heat Interaction, Processs

Fig. 7.2 A small neighborhood $\mathcal{N}_x$ about x and a pure heat interaction process through x.

can be reached from y by only a positive heat interaction (purely heat addition) process. Such points exist by assumption. Refer to figure-7.2 for an illustration. Then if we consider the process of going from y to x by pure positive heat interaction and then coming back to y from x adiabatically results in a cyclic process that can convert a given amount of energy (absorbed by the system due to the pure positive heat interaction) entirely into work (see figure-7.2) and hence is a contradiction of the Kelvin-Planck statement. Thus if Kelvin-Planck is true then there must exist equilibrium states near x that can not be adiabatically reached from x. This proves that the Kelvin-Planck statement implies that in any neighborhood of x there exists equilibrium states near x that can not be adiabatically reached from x.

Let us consider the case if Kelvin-Planck is true and further that x can be reached from any state near x in an adiabatic process. Let $z \in \mathcal{N}_x$ be a state that can be reached from x by a only a positive heat interaction process. Then one can reach z from x by only positive heat interaction and then come back to x in an adiabatic process that results in a cyclic process that can convert a given amount of energy (absorbed as a result of the pure positive heat interaction) entirely into work (see figure-7.2) and is thus a contradiction of the Kelvin-Planck statement. Thus if the Kelvin-Planck statement is true then there must exist states z in any neighborhood of x from which you can not reach x in an adiabatic process. Thus proving that the Kelvin-Planck statement implies the Caratheodory statement.

Solution to Exercise-3.27: [Entropy of an ideal gas]

Since entropy S is a property of the thermodynamic equilibrium state the entropy change that occurs in any ideal gas process from state (P_1, V_1, T_1) to (P_2, V_2, T_2) is the same. Since we know how to compute the entropy change that occurs in a reversible process, c_r, using $\Delta S = \int_{c_r} \frac{\delta Q}{T}$, we can estimate the entropy difference between the two states by constructing such a process. For any reversible ideal gas process we have

$$dS = \frac{1}{T}\delta Q = \frac{1}{T}(dU + \delta W) = \frac{1}{T}(dU + PdV).$$

Since the internal energy U of an ideal gas depends only on the temperature T we see that

$$dU = \frac{Nk_B}{(\gamma - 1)} dT.$$

Furthermore from the ideal gas law we have that $P = Nk_B T/V$ and thus we have that

$$dS = \frac{1}{T} \frac{Nk_B}{(\gamma - 1)} dT + Nk_B \frac{1}{V} dV$$

Integrating the above equation over the reversible process, c_r, we see that

$$S(V,T) = \frac{Nk_B}{(\gamma - 1)} \ln(T) + Nk_B \ln(V) + a, \tag{7.12}$$

where a is an integration constant and finally we have

$$S(V,T) = Nk_B \left(\ln(V) + \frac{1}{\gamma - 1} \ln(T) \right) + a.$$

Solution to Exercise-3.29

Since the piston is uninsulated and free to move the initial temperatures of both gases must be the same. Denote by (T, P_i, V_A) the thermodynamic properties of the initial state of gas A and (T, P_i, V_B) the thermodynamic properties of the initial state of gas B. Denote by (T, P_{A_2}, V) the thermodynamic properties of the end state of gas A and (T, P_{B_2}, V) the thermodynamic properties of the end state of gas B where $V = V_A + V_B$.

Let ΔS_A and ΔS_B be the entropy difference between the initial and final state of gas A and gas B. From the entropy for an ideal gas given by

$$S(V,T) = Nk_B \left(\ln(V) + \frac{1}{\gamma - 1} \ln(T) \right) + a,$$

we see that

$$\Delta S_A = N_A k_B \left(\ln\left(\frac{V_A + V_B}{V_A} \right) + \frac{1}{\gamma_A - 1} \ln\left(\frac{T_f}{T_A} \right) \right)$$

$$\Delta S_B = N_B k_B \left(\ln\left(\frac{V_A + V_B}{V_B} \right) + \frac{1}{\gamma_B - 1} \ln\left(\frac{T_f}{T_B} \right) \right)$$

Thus the entropy difference between the initially separated state and the mixed state is

$$\Delta S = \Delta S_A + \Delta S_B,$$
$$= N_A k_B \left(\ln\left(\frac{V_A + V_B}{V_A} \right) + \frac{1}{\gamma_A - 1} \ln\left(\frac{T_f}{T_A} \right) \right) + N_B k_B \left(\ln\left(\frac{V_A + V_B}{V_B} \right) + \frac{1}{\gamma_B - 1} \ln\left(\frac{T_f}{T_B} \right) \right),$$
$$= k_B \left(N_A \ln\left(\frac{V_A + V_B}{V_A} \right) + N_B \ln\left(\frac{V_A + V_B}{V_B} \right) \right) + k_B \left(\frac{N_A}{\gamma_A - 1} \ln\left(\frac{T_f}{T_A} \right) + \frac{N_B}{\gamma_B - 1} \ln\left(\frac{T_f}{T_B} \right) \right).$$

where from the solution to Exercise-3.9 we have seen that

$$T_f = \left[\frac{N_A}{(\gamma_A - 1)} + \frac{N_B}{(\gamma_B - 1)} \right]^{-1} \left(\frac{N_A T_A}{(\gamma_A - 1)} + \frac{N_B T_B}{(\gamma_B - 1)} \right).$$

If this ΔS is greater than zero then the adiabatic process must be necessarily irreversible. We should be able to verify that this is true. The first two terms in the expression for ΔS is positive while one of the last two terms is negative. Proving that the sum of the last two terms is positive in this general setting is algebraically hard. However, below we will show that this can be easily verified for the special case where gas A and gas B is the same and have the same number of particles.

If both gases are of the same type then we have

$$T_f = \frac{(N_A T_A + N_B T_B)}{(N_A + N_B)},$$

Let $r_n = N_B/N_A$, $r_T = T_B/T_A$ then it can be shown that the last two terms of the expression for ΔS becomes

$$\begin{aligned}
\frac{k_B}{\gamma - 1} &\left(N_A \ln \left(\frac{(N_A T_A + N_B T_B)}{T_A (N_A + N_B)} \right) + N_B \ln \left(\frac{(N_A T_A + N_B T_B)}{T_B (N_A + N_B)} \right) \right) \\
&= \frac{N_A k_B}{\gamma - 1} \left(\ln \left(\frac{(1 + r_n r_T)}{(1 + r_n)} \right) + r_n \ln \left(\frac{(1 + r_n r_T)}{r_T (1 + r_n)} \right) \right) \\
&= \frac{N_A k_B}{\gamma - 1} \ln \left(\frac{1}{r_T^{r_n}} \left(\frac{1 + r_n r_T}{1 + r_n} \right)^{1 + r_n} \right).
\end{aligned}$$

Now if both sides initially had the same number of particles then $r_n = 1$ and thus

$$\begin{aligned}
\frac{k_B}{\gamma - 1} &\left(N_A \ln \left(\frac{(N_A T_A + N_B T_B)}{T_A (N_A + N_B)} \right) + N_B \ln \left(\frac{(N_A T_A + N_B T_B)}{T_B (N_A + N_B)} \right) \right) = \frac{N_A k_B}{\gamma - 1} \ln \left(\frac{1}{r_T} \left(\frac{1 + r_T}{2} \right)^2 \right) \\
&= \frac{2 N_A k_B}{\gamma - 1} \ln \left(\frac{\left(\frac{1}{\sqrt{r_T}} + \sqrt{r_T} \right)}{2} \right) > 0.
\end{aligned}$$

Solution to Exercise-3.30

Let us assume that the specific heat capacity of the metal block and the temperature of the water remains constant (since the water mass is assumed very large the temperature change is very small and this assumption is valid).

We have seen that the maximum efficiency that one can obtain is with a reversible engine. Thus the maximum work that can be extracted from this hot block and the cold reservoir

is given by a reversible engine running between the block and the reservoir at a constant temperature T_c. We will construct such a cycle as follows:

Let the block and the reservoir be connected by a reversible engine such that in one of its complete cycles only an incremental change occurs in the block. That is in one complete cycle let δQ_{Hb} be the total energy absorbed by the system due to its positive heat interaction and let δQ_{Cw} be the total energy lost to the pool of water due to negative heat interaction. Let δT be the incremental temperature *increase* of the block at the end of one cycle of the reversible engine.

Then by the First Law we have that the incremental work done in one complete cycle of the process is

$$\delta W = \delta Q_{Hb} - \delta Q_{Cw}.$$

The incremental energy lost by the block to the cyclic system at a particular stage is $-mc_b dT$[1]. Thus since the total energy added to the system during one complete cycle due to its interaction with the block is equal to the energy lost by the block we have

$$\delta Q_{Hb} = -mc_b \delta T.$$

In order to find the incremental negative heat interaction, δQ_{Cw}, the engine has we proceed as follows. Observe that since the cycle is reversible, we can use $\Delta S = \int \frac{\delta Q}{T}$ to compute the Entropy change in the reversible system at each stage and use the fact that the total entropy change in one cycle of the process is zero. Thus we have that

$$0 = \frac{\delta Q_{Hb}}{T} - \frac{\delta Q_{Cw}}{T_C} = \frac{-mc_b \delta T}{T} - \frac{\delta Q_{Cb}}{T_C}.$$

Which gives us that the incremental energy absorbed **by** the pool of water in one complete cycle of the process is

$$\delta Q_{Cw} = -mc_b T_C \frac{\delta T}{T}.$$

Thus the incremental work done in one cycle of the reversible process is

$$\delta W = -mc_b dT + mc_b T_C \frac{\delta T}{T}.$$

Thus the maximum extractable work is

$$W_{\max} = \int \delta W = -\int_{T_i}^{T_C} mc_b dT + \int_{T_i}^{T_C} mc_b T_C \frac{dT}{T}$$
$$= mc_b \left((T_i - T_C) - T_C \ln \left(\frac{T_i}{T_C} \right) \right).$$

Note that since $T_C < T_i$ we see that

$$W_{\max} < mc_b (T_i - T_C).$$

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[1] This is negative because we have considered δT to be the temperature increase in the block in the course of one complete cycle of the process
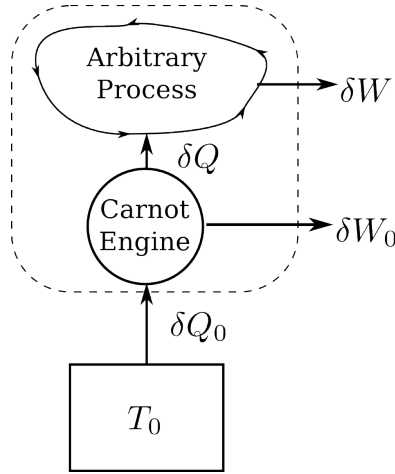
Fig. 7.3 An arbitrary system undergoing a quasi-static cyclic process while interacting with a Carnot Engine at every intermediate stage of the process.

Solution to Exercise-3.32:[Proof that Kelvin's version of the second law implies the Clausius inequality]

Consider an arbitrary system undergoing an arbitrary quasi-static cyclic process. Consider an incremental (small) part of this process. During this incremental part of the process, let δQ be the heat interaction the system has with the surrounding, δW be the work done by the system, and let the temperature of the system at this part of the process be T. Since it does not matter how the system interacts with the surrounding we may assume without loss of generality that the δQ amount of energy interaction the system has with the surrounding is given by a Carnot engine operating at a constant temperature T_0 as shown in figure-7.3. Let the corresponding energy absorbed by the Carnot engine due to its heat interaction with a reservoir at a temperature T_0 be δQ_0 and let the corresponding work done by the Carnot engine be δW_0. We will assume that when the system in the Carnot engine undergoes one cyclic process our original system makes the incremental transition defined above. We have shown that for the Carnot engine $\frac{\delta Q}{T} = \frac{\delta Q_0}{T_0}$. Furthermore from the first law for the composite system of the arbitrary system plus the Carnot engine we have

$$\oint \delta Q_0 = \oint (\delta W_0 + \delta W).$$

But the second law says that a given amount of energy absorbed by a system through a positive heat interaction can not be converted entirely to its mechanical equivalent work thus necessarily $\oint \delta Q_0 = \oint (\delta W_0 + \delta W) \leq 0$. Thus

$$\oint \frac{\delta Q}{T} = \oint \frac{\delta Q_0}{T_0} = \frac{1}{T_0} \oint \delta Q_0 \leq 0.$$

Now if the process is reversible $\frac{\delta Q}{T} = dS$ and hence $\oint \frac{\delta Q}{T} = 0$. Hence if the process is reversible the equality holds.

Solution to Exercise-3.33

Assume that the specific heat capacity of the metal block and the temperature of the water remains constant (since the water mass is assumed very large the temperature change is very small and this assumption is valid). Recall that the incremental internal energy increase in a solid is equal to $mc_b\delta T$ where δT is the incremental temperature *increase* in the solid.

When the block is directly immersed in the water, since the water mass is assumed to be very large it is reasonable to assume that the water temperature will remain constant at T_c and that the block will eventually cool to a temperature of T_c.

Since Entropy is only a function of the state we can compute the entropy change in the block by constructing a reversible process that brings the block from a temperature T_i to a temperature T_c, as done in the solution to exercise-3.30, by connecting a reversible cyclic process between the block and the reservoir. Thus the Entropy increase in the block is

$$\Delta S_b = \int_1^2 \frac{\delta Q_b}{T} = \int_{T_i}^{T_c} \frac{mc_b dT}{T} = mc_b \ln\left(\frac{T_c}{T_i}\right) = -mc_b \ln\left(\frac{T_i}{T_c}\right).$$

Note that since $T_c < T_i$ this quantity is negative.

The energy absorbed by the reservoir, due to heat interaction with the block may not be a reversible process. However the Clausius inequality implies that the entropy increase in the reservoir, ΔS_w, must be greater than or equal to $\int \frac{\delta Q_w}{T}$ over the process of energy transfer through heat interaction the reservoir has with the block. Since the energy transfer to the reservoir is equal to the energy lost by the block due to heat interactions we see that $\delta Q_w = -\delta Q_b = -mc_b dT$. Thus, as pointed out before, the Clausius inequality implies that the entropy increase in the reservoir must satisfy

$$\Delta S_w \geq \int_1^2 \frac{\delta Q_w}{T_c} = -\int_{T_i}^{T_c} \frac{mc_b dT}{T_c} = mc_b\left(\frac{T_i - T_c}{T_c}\right).$$

Thus the total Entropy increase in the closed system consisting of the block+pool of water must satisfy

$$\Delta S = \Delta S_b + \Delta S_w \geq mc_b\left(-\ln\left(\frac{T_i}{T_c}\right) + \left(\frac{T_i - T_c}{T_c}\right)\right) = \frac{mc_b}{T_c}\left((T_i - T_c) - T_c \ln\left(\frac{T_i}{T_c}\right)\right)$$

Since $T_c < T_i$ we can show that the right hand side is greater than zero. That is $\Delta S > 0$. Thus the total entropy of the system where the block is immersed in the water is greater than the entropy of the block+water with the block sitting outside the water. Consider the reservoir and the block as one single system. This composite system is a closed system and it does not interact with the surrounding in any way and hence in particular the entire process of the composite system is an adiabatic process. Thus from the property of the entropy proven in Exercise-3.25 we see that this entire process is irreversible. Confirming our empirical observations.

7.2 Solutions to exercises on steady flow processes

Solution to exercise in Prof. Sivasegaram's tutorial on steady flow: Q 1 *Since the flow though the nozzle is adiabatic $\delta Q \equiv 0$. Inlet conditions T_i, P_i are given. The entry and exit velocities c_i and c_o are given. Since the device is a nozzle there is no shaft work and the control volume does not change and hence $\delta W \equiv 0$. Assuming air to behave as an ideal gas from equation (6.6) we have that*

$$T_o = T_i + \frac{1}{2c_p}(c_i^2 - c_o^2).$$

Solution to exercise in Prof. Sivasegaram's tutorial on steady flow: Q 3 *Let T_i, P_i be the inlet conditions and let T_o, P_o be the outlet conditions of the pipe and they are given. The mass flow rate $\dot{m}$ and the pipe cross section A is given. Let the inlet velocity be c_i and the outlet velocity be v_o. If v_i and v_o denote the inlet and outlet specific volumes we have*

$$c_i = \frac{\dot{m}v_i}{A} = \frac{\dot{m}RT_i}{AP_i},$$
$$c_o = \frac{\dot{m}v_o}{A} = \frac{\dot{m}RT_o}{AP_o}.$$

Since the control volume of interest does not change $\delta W \equiv 0$ and thus from (6.6) we have

$$-\delta Q = \dot{m}c_p(T_i - T_o) + \frac{\dot{m}}{2}(c_i^2 - c_o^2).$$

Solution to exercise in Prof. Sivasegaram's tutorial on steady flow: Q 4 *There are two inputs and one output of the system. Denote the inlet hot air properties by T_h, P_h and the flow rate by $\dot{m}_h$ while the cool air properties by T_c, P_c and the flow rate by $\dot{m}_c$. Denote by T_m, P_m the mixture properties.*

(a) In the first case all data mentioned above except $\dot{m}_c$ is given and you are asked to find the cold air flow rate $\dot{m}_c$.
    Assuming that the kinetic energies of the inlet and outlet flows are negligible and that the heat interactions are negligible due to insulation(that is $\delta Q \equiv 0$) the equations (6.1)–(6.4) gives (inlet enthalpy-outlet enthalpy)=0 and thus.

$$0 = \dot{m}_c h_c + \dot{m}_h h_h - (\dot{m}_c + \dot{m}_h)h_m,$$

Assuming air to behave close to an ideal gas we can use $h = c_p T$ and hence the above equation becomes
$$0 = \dot{m}_c c_p T_c + \dot{m}_h c_p T_h - c_p(\dot{m}_c + \dot{m}_h)T_m$$

Which gives
$$\dot{m}_c = \dot{m}_h \frac{(T_h - T_m)}{(T_m - T_c)}$$

(b) In the next part you are given the inlet and outlet velocities of the flow and they are of non-negligible magnitude. Furthermore the flow rates are assumed to be the flow rates

obtained in the previous section. What is unknown now is the exit mixture temperature T_m. Applying the energy balance as before we have

$$0 = \dot{m}_c c_p T_c + \dot{m}_h c_p T_h - c_p (\dot{m}_c + \dot{m}_h) T_m + \frac{\dot{m}_c}{2} c_c^2 + \frac{\dot{m}_h}{2} c_h^2 - \frac{\dot{m}_c + \dot{m}_h}{2} c_m^2.$$

The only unknown in this expression is T_m and it can be solved for.

$$T_m = \frac{1}{c_p (\dot{m}_c + \dot{m}_h)} \left(\dot{m}_c c_p T_c + \dot{m}_h c_p T_h + \frac{\dot{m}_c}{2} c_c^2 + \frac{\dot{m}_h}{2} c_h^2 - \frac{\dot{m}_c + \dot{m}_h}{2} c_m^2 \right).$$

Solution to exercise in Prof. Sivasegaram's tutorial on steady flow: Q 5 *Let the inlet wet steam conditions be denoted by T_w, P_w, x_w and the outlet dry steam conditions be denoted by T_d, P_d, x_d and the condensed water conditions be T_c, P_c. Lets the respective mass flow rates be denoted by $\dot{m}_w, \dot{m}_d, \dot{m}_c$.*

Since the separator volume does not change and there is no shaft work $\delta W \equiv 0$. Assume that the heat interactions are negligible and hence $\delta Q \equiv 0$. Assume that the kinetic energies of the flows are negligible the equations (6.1)–(6.4) give

$$\dot{m}_w = \dot{m}_d + \dot{m}_c,$$
$$0 = \dot{m}_w h_w - \dot{m}_d h_d - \dot{m}_c h_c$$

(a) Let the pressures of all the flows be the same $P_w = P_c = P_d = P$. Let the saturated liquid and vapor enthalpies corresponding to a pressure P be h_f and h_g respectively and can be found from the steam tables. Then we have

$$h_w = x_w h_f + (1 - x_w) h_f,$$
$$h_d = x_d h_f + (1 - x_d) h_f,$$
$$h_c = h_f$$

where we have assumed that the condensed water is at saturated liquid conditions. Then plugging these in the above mass and energy balance equations we have

$$0 = \dot{m}_w (x_w h_g + (1 - x_w) h_f) - (\dot{m}_w - \dot{m}_c)(x_d h_g + (1 - x_d) h_f) - \dot{m}_c h_f$$

The only unknown in this expression is $\dot{m}_c$ and can be solved for to give.

$$(-\dot{m}_c)(x_d h_g + (1 - x_d) h_f) + \dot{m}_c h_f = \dot{m}_w (x_w h_g + (1 - x_w) h_f) - (\dot{m}_w)(x_d h_g + (1 - x_d) h_f)$$

$$-\dot{m}_c x_d (h_g - h_f) = \dot{m}_w (x_w - x_d)(h_g - h_f).$$

And finally

$$\dot{m}_c = \dot{m}_w \left(\frac{x_d - x_w}{x_d} \right).$$

Note that you only need the dryness fraction data to solve this.

(b) *On the other hand if the exit water conditions were saturated conditions an the exit water is at atmospheric conditions then $P_w = P_d = P$. Denote as before the saturated liquid and vapor enthalpies corresponding to a pressure P as h_f and h_g respectively. Let $P_c = P_0$ the atmospheric pressure and let h_{f_0} be the saturated liquid enthalpy at atmospheric pressure then we have from the mass balance and energy balance*

$$0 = \dot{m}_w(x_w h_g + (1 - x_w)h_f) - (\dot{m}_w - \dot{m}_c)(x_d h_g + (1 - x_d)h_f) - \dot{m}_c h_{f_0}.$$

Simplifying as before

$$(-\dot{m}_c)(x_d h_g + (1 - x_d)h_f) + \dot{m}_c h_{f_0} = \dot{m}_w(x_w h_g + (1 - x_w)h_f) - (\dot{m}_w)(x_d h_g + (1 - x_d)h_f)$$

$$-\dot{m}_c x_d(h_g - h_f) + \dot{m}_c(h_{f_0} - h_f) = \dot{m}_w(x_w - x_d)(h_g - h_f).$$

and finally

$$\dot{m}_c = \dot{m}_w \left(\frac{(x_d - x_w)(h_g - h_f)}{(h_f - h_{f_0}) + x_d(h_g - h_f)} \right).$$

Solution to exercise in Prof. Sivasegaram's tutorial on steady flow: Q 7 *Denote inlet conditions of steam as T_s, P_s, x_s and let the conditions of the condensate that is leaving be T_c, P_c. Assume that $P_c = P_s = P$ since in a typical condenser the pressure differences between the inlet and outlet are small. For an optimal condenser design the condensate should be at saturated liquid conditions. The mass flow rate of steam is denoted by $\dot{m}_s$ and denote the cooling water supply rate by $\dot{m}_w$. Let the inlet cooling water conditions be T_i, P_i and the outlet cooling water conditions be T_o, P_o.*

Denote by h_s, h_c, h_i, h_o be the specific enthalpies of the steam, condensate, inlet cooling water, and the outlet cooling water respectively.

The two flows do not mix in the condenser. Assuming that the kinetic energy of the flows are negligible and the condenser is insulated we have from the energy balance

$$0 = \dot{m}_s h_s + \dot{m}_w h_i - (\dot{m}_s h_c + \dot{m}_w h_o).$$

From which we have

$$0 = \dot{m}_s(h_s - h_c) + \dot{m}_w(h_i - h_o).$$

Thus

$$\dot{m}_w = \dot{m}_s \left(\frac{h_s - h_c}{h_o - h_i} \right).$$

(a) *Consider the problem of finding the coolant supply rate $\dot{m}_w$ given all inlet and outlet conditions and the steam mass flow rate $\dot{m}_s$.*

To find the solution what one needs is to find the specific enthalpies. Since all inlet and outlet conditions are given this can be done. From the steam tables we can obtain the specific enthalpy of saturated liquid and vapor at $P = .1$ bar. Denote them by h_{fP} and h_{gP} respectively. (from steam tables $h_{fP} = 192$ kJ and $h_{gP} = 2584$ kJ) Then

$$h_s = x_s h_{gP} + (1 - x_s)h_{fP} = (0.85 \times 2584 + (1 - 0.85) \times 192)\,\text{kJ} = 2225.2\,\text{kJ}.$$

Since for an optimum condenser design the condense should be in saturated liquid conditions and there is no appreciable pressure loss

$$h_c = h_{fP} = 192\,\text{kJ}.$$

Recall that we can approximate the sub cooled enthalpies at a temperature T by the saturated liquid enthalpies at the saturation temperature of $T_s = T$. Let the saturation pressure corresponding to a saturation temperature of T be P_{T_i}. Then we have $h_i \approx h_{f P_{T_i}}$ and $h_o \approx h_{f P_{T_o}}$. (From steam tables for a saturation temperature of $T_i = 25^oC$ the pressure should be $P_{T_i} = 0.03166$ bar and $h_i \approx h_{f P_{T_i}} = 104.8kJ$ and for a saturation temperature of $T_o = 33^oC$ the pressure should be $P_{T_o} = 0.05036$ bar and $h_o \approx h_{f P_{T_o}} = 138.2kJ$ — note that you need interpolations to get P_{T_o} and $h_{f P_{T_o}}$). Thus

$$\dot{m}_w \approx 30 \times \left(\frac{2225.2 - 192}{138.2 - 104.8} \right)\,\text{kg/s} = 1826\,kg/s.$$

(b) Consider the problem of finding the exit cooling water conditions if the desired cooling water rate is $\dot{m}_w = 80$ kg/s given and all inlet conditions are given.
In this case since the outlet cooling water conditions are not known h_o is not known and this is the only unknown hence from

$$1906 \approx 30 \times \left(\frac{2225.2 - 192}{h_o - 104.8} \right).$$

we have that $h_o \approx 136.8$ kJ. Reversing the process we did before to find h_o we find from steam tables that this values is approximately equal to the saturated liquid enthalpy corresponding to the saturation temperature of 32.7^o C. Thus the exit temperature of the coolant is close to 32.7^o C if the coolant flow rate is increased 80 kg/s.

Solution to exercise in Prof. Sivasegaram's tutorial on steady flow: Q 8 *Hellium enters a gas turbine. The entry conditions T_i, P_i and c_i are given. The exit conditions T_o, P_o, and c_o are also given. The mass flow rate $\dot{m}_{fl}$ is given. Assuming that the heat interaction with the surrounding is negligible we have from equation (6.6)*

$$\dot{W} = \dot{m}_{fl} c_p (T_i - T_o) + \frac{\dot{m}_{fl}}{2}(c_i^2 - c_o^2).$$

7.3 Solutions to exercises on un-steady flow processes

Solution to exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 1 *In this problem the initial conditions of the cylinder V, T_1, P_1 are given. The inflow conditions P_i, T_i are also given and the cylinder is said to be insulated. Thus $\delta Q \equiv 0$.*

(a) *First you are asked to find P_2 and m_2 for a given T_2. Since P_1, T_1, V is given we can find m_1 using the ideal gas law, $m_1 = \frac{P_1 V}{RT_1}$. Then from equation (6.10) we have*

$$m_2 = \left(\frac{\gamma T_i - T_1}{\gamma T_i - T_2} \right) m_1$$

and from the ideal gas law

$$P_2 = \frac{m_2 R T_2}{V}.$$

(b) *Then you are asked to find T_2 and m_2 for a given P_2. Once again from equation (6.9) we have*

$$m_2 = m_1 + \frac{V}{\gamma R T_i}(P_2 - P_1),$$

and then from (6.10)

$$T_2 = \frac{m_1}{m_2} T_1 + \gamma T_i \frac{(m_2 - m_1)}{m_2}.$$

Solution to exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 2 *If since temperature inside is maintained at a constant then $T_2 = T_1$ (then necessarily there should be some heat interaction). The question is, what is m_2 when the pressure inside the cylinder, P, reaches a certain value P_2. From the ideal gas law we have*

$$(m_2 - m_1) = \frac{V(P_2 - P_1)}{RT_1},$$

and hence

$$m_2 = m_1 + \frac{V(P_2 - P_1)}{RT_1}.$$

Finally from equation (6.10) we have that the heat interaction

$$\int_1^2 \delta Q = c_v (T_1 - \gamma T_i)(m_2 - m_1) = \frac{c_v}{R}(T_1 - \gamma T_i)\frac{V(P_2 - P_1)}{T_1} = \frac{(T_1 - \gamma T_i)}{(\gamma - 1)} \frac{V(P_2 - P_1)}{T_1}.$$

Solution to exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 3 *The initial P_1, T_1 and the volume V of the tank are given. A leak is supposed to have formed and noticed only when ice starts to form. That means at the moment of discovery the inside temperature $T_2 = 0^o C$. Since the gas leaks to the atmosphere at a temperature of T_o and pressure P_o. Since the leaked gas eventually is at atmospheric conditions and before it leaked it was at a different condition there is a heat interaction that occurs between the leaked gas and the atmosphere thus the heat interaction can not be ignored even though the tank is insulated. Thus from (6.12) we can find the heat interaction if m_1 and m_2 are known. Since the initial conditions are known and from the ideal gas law we have that*

$$m_1 = \frac{RT_1}{P_1 V}.$$

Similarly from the ideal gas law we could also find m_2 if we knew P_2. To find this we notice that it is given that the gas inside the tank can be assumed to behave as $P/\rho^\gamma = $ constant. From this we have that

$$\frac{P_1}{\left(\frac{m_1}{V}\right)^\gamma} = \frac{P_2}{\left(\frac{m_2}{V}\right)^\gamma}.$$

From this and using the ideal gas law we have

$$\frac{m_1 T_1}{m_1{}^\gamma} = \frac{m_2 T_2}{m_2{}^\gamma},$$

and hence that

$$m_2 = m_1 \left(\frac{T_2}{T_1}\right)^{\frac{1}{(\gamma-1)}} = \frac{RT_1}{P_1 V}\left(\frac{T_2}{T_1}\right)^{\frac{1}{(\gamma-1)}}$$

Hence the leaked mass is $(m_2 - m_1)$ and finally from (6.12) the total heat interaction is

$$\int_1^2 \delta Q = -c_v(m_1 T_1 - m_2 T_2) + \gamma T_o(m_1 - m_2).$$

Solution to exercise in Prof. Sivasegaram's tutorial on un-steady flow: Q 4 *The process of finding the answer is similar to that of Q2 but use (6.11) and (6.12) instead.*

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