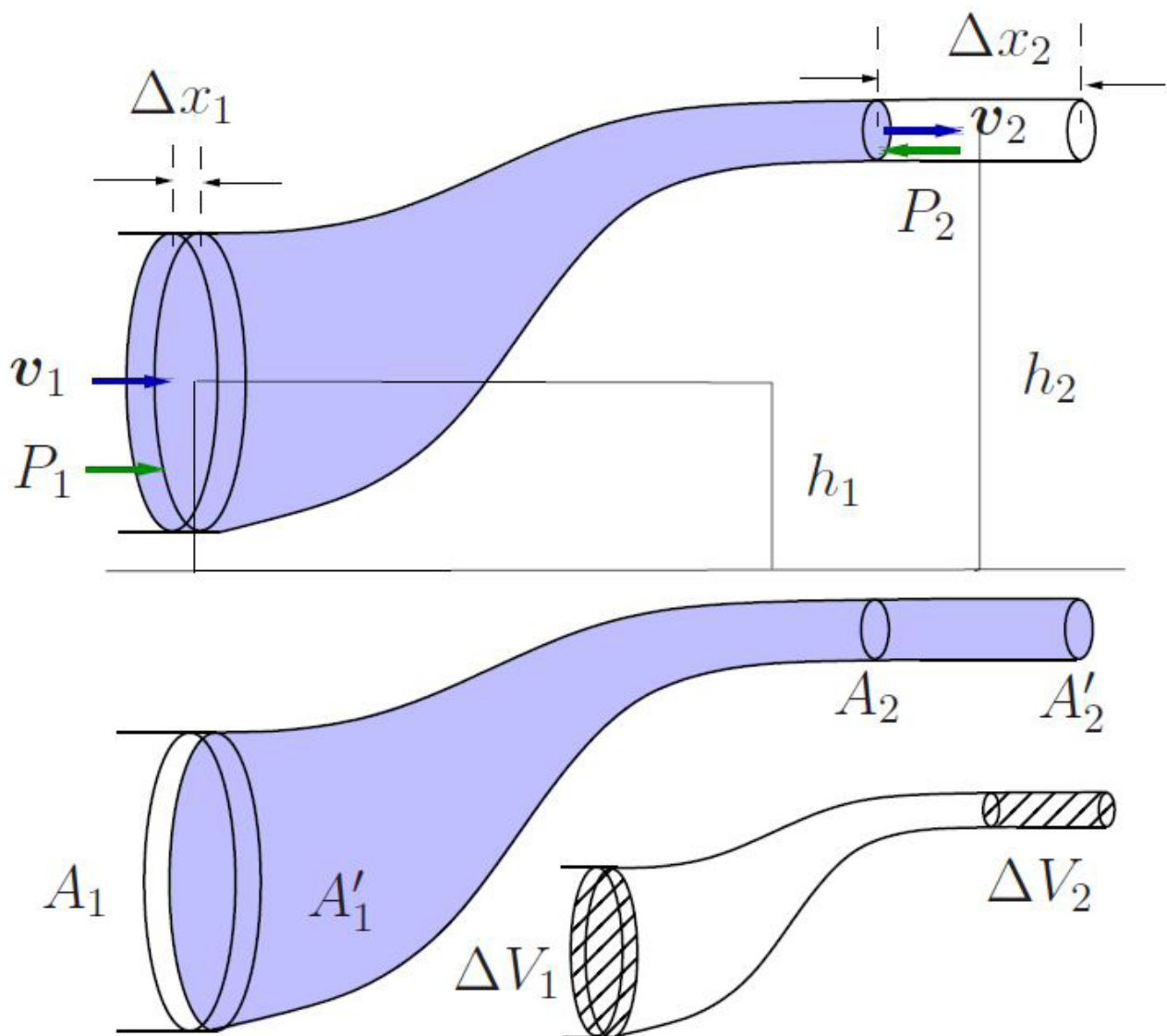


Basic Laws, Equations and Models II.



Gergely Nyitray

Basic Laws, Equations and Models II.

Pécs

2019

The Basic Laws, Equations and Models II. course material was developed under the project EFOP 3.4.3-16-2016-00005 "Innovative university in a modern city: open-minded, value-driven and inclusive approach in a 21st century higher education model".

Gergely Nyitray

Basic Laws, Equations and Models II.

Pécs

2019

A Basic Laws, Equations and Models II. tananyag az EFOP-3.4.3-16-2016-00005
azonosító számú,
„Korszerű egyetem a modern városban: Értékközpontúság, nyitottság és befogadó
szemlélet egy 21. századi felsőoktatási modellben” című projekt keretében valósul
meg.

DR. GERGELY NYITRAY

FUNDAMENTAL LAWS, EQUATIONS AND MODELS II

DEPARTMENT OF ELECTRICAL NETWORKS
FACULTY OF ENGINEERING AND INFORMATION TECHNOLOGY
UNIVERSITY OF PÉCS

2019

ISBN 978-963-429-348-4

THIS COURSE MATERIAL WAS DEVELOPED UNDER THE PROJECT "MODERN UNIVERSITY IN A MODERN CITY: MODEL FOR VALUE-ORIENTED, OPENNESS AND INCLUSIVE APPROACHES IN 21. CENTURY HIGHER EDUCATION". REGISTRATION NUMBER: EFOP-3.4.3-16-2016-00005

EFOP-3.4.3-16-2016-00005 MODERN UNIVERSITY IN A MODERN CITY:
MODEL FOR VALUE-ORIENTED, OPENNESS AND INCLUSIVE
APPROACHES IN 21. CENTURY HIGHER EDUCATION

Fundamental Laws, Equations and Models II

GENERAL COURSE
THERMODYNAMICS

BY
GERGELY NYITRAY

PÉCS
Published in The University of Pécs,
Faculty of Engineering
and Informattion Technology

Author

Gergely Nyitray dr.

assistant professor

University of Pécs

Faculty of Engineering and Information Technology

Hungary 7624 Pécs, Boszorkány Street 2.

nyitray@mik.pte.hu

Peer-review

László Pálfalvi, Dsc

Head of Department

full professor

University of Pécs

Faculty of Sciences

Institute of Physics

H-7624 Pécs, Ifjúság Str.6.

palfalvi@fizika.ttk.pte.hu

Copy Editor

Tímea Györök

Language Teacher

University of Pécs

Faculty of Engineering and Information Technology

Centre for Foreign Languages for Technical Purposes

Hungary 7624 Pécs, Boszorkány Street 2.

gyorok.timea@mik.pte.hu

ISBN:978-963-429-348-4

Contents

1	Classical Equilibrium Thermodynamics	7
1.1	Introduction	7
1.2	The Zeroth Law	9
1.2.1	System	9
1.2.2	Pressure, Temperature	9
1.2.3	The Zeroth Law	10
1.2.4	Constant-Volume Gas thermometer	11
1.3	Equation of state	11
1.3.1	Nonreactive Ideal-gas mixtures	12
1.4	Kinetic theory of ideal gases	13
1.4.1	Microscopic origin of Pressure	13
1.4.2	Temperature and Translational Kinetic Energy	14
1.4.3	Collisions between gas molecules	15
1.5	The First Law	16
1.5.1	Work	17
1.5.2	Quasi-static process	17
1.5.3	Internal Energy	17
1.5.4	Work in changing the volume	19
1.5.5	Heat	20
1.5.6	The mathematical form of the First Law	20
1.5.7	Sign convention during expansion and compression	21
1.5.8	Differential form of the First Law	21
1.5.9	Cyclic Processes	22
1.5.10	Heat Capacity and Specific Heat	22
1.5.11	Specific Heat	22
1.5.12	Specific Heat of Ideal Gases	22
1.5.13	Constant Pressure Processes	24
1.5.14	Constant Volume Processes	25
1.5.15	Constant Temperature Processes	25
1.5.16	Work on Solid and Liquid Phases	26
1.5.17	Other quasi-static forms of work	27
1.5.18	Generalized quasi-static work interactions	29
1.5.19	Equation of Adiabats of an ideal gas	29
1.5.20	Polytropic Processes	31
1.6	Applications of Classical Thermodynamics	34

1.7	The Second Law	46
1.7.1	Carnot Cycle	46
1.7.2	Absolute Temperature	48
1.7.3	The Principle of Increase of Entropy	49
1.8	Gibb's Equation	49
1.8.1	Fundamental Relations and State Equations	50
1.8.2	Euler's Relation	50
1.8.3	Gibbs–Duhem's Relation	51
1.8.4	Thermodynamic Potentials	51
1.8.5	Thermodynamic Potentials and Extremum Principles	53
1.8.6	Minimum Energy Principle	53
1.8.7	Minimum Helmholtz's Free Energy Principle	53
1.8.8	Minimum Enthalpy Principle	54
1.8.9	Minimum Gibbs' Free Energy Principle	54
1.8.10	Stability of Equilibrium States	55
1.8.11	Maxwell's Relations	56
1.8.12	Statistical Interpretation of Entropy	57
1.8.13	The Third Law	58
2	Phase Transitions	59
2.1	Introduction	59
2.2	Liquid and Its Saturated Vapour	60
2.3	The Critical State	60
2.4	Unphysical behavior of the van der Waals isotherms	61
2.5	The Clapeyron-Clausius Equation	62
2.6	Phase Diagram	63
3	Transport Processes	65
3.1	Streamlines and Flow Continuity	65
3.1.1	Bernoulli's Equation	66
3.1.2	Torricelli's formula	67
3.1.3	Forces of Internal Friction	68
3.1.4	Laminar and Turbulent Flow	70
3.2	Open systems	70
3.2.1	Conservation of energy principle for open systems	71
3.2.2	Nozzles and Diffusers	73
3.2.3	Turbines, Pumps, Compressors, and Fans	73
3.2.4	Throttling Devices	74
3.2.5	Heat Exchangers	74
3.3	Heat Transfer	75
3.3.1	Heat Conduction	75
3.3.2	Heat Convection	76
3.3.3	Thermal Radiation	77

4	Gas Power Cycles	79
4.1	The Otto Cycle	79
4.2	The Diesel Cycle	81
4.3	The Brayton Cycle	82
4.4	Aircraft Gas Turbines	83
	Bibliography	87

Chapter 1

Classical Equilibrium Thermodynamics

1.1 Introduction

Phenomenological or classical thermodynamics deals with the study of macroscopic properties of matter at *equilibrium*. It is sufficient to characterize it as a time-independent state, like a column of air at rest in absence of any flux of matter, energy, charge, or momentum. A *reversible process* represents a special class of idealized processes considered as a continuum sequence of equilibrium states.

Since time does not appear explicitly in the equations, it would be more appropriate to call it *thermostatistics* and to reserve the name *thermodynamics* to the study of processes taking place in the course of time outside equilibrium. However, for historical reasons, the name “thermodynamics” is widely used nowadays, even when referring to the equilibrium state.

Briefly speaking, *thermodynamics is the science that deals with heat and work and those properties matter that relate to heat and work*.

The course is a result of fourteen years of work in the Faculty of Engineering of the University of Pécs. While using this book, try not to memorize the material formalistically and mechanically, but rather logically. Make sure you memorize the material by thoroughly understanding it. I have tried to present physics not as a certain volume of information to be memorized, but as clever, logical, and attractive science. It is left to the reader to judge the extent to which I have succeeded in doing this.

I have done my utmost to limit the size of the course. This was achieved by carefully choosing the material which, in my opinion, should be included in a general course of physics. It is important to note that I have used the experiences of several books, lectures and online courses. They are listed at the end of this note (Bibliography).

The author is grateful to Professor László Pálfalvi and to Tímea Györök for their careful reading of the manuscript and their valuable suggestions and comments.

Historical background

Phenomenological thermodynamics is the natural extension of the more fundamental science, Mechanics. Mechanics is concerned with the study of motions of bodies such as mass particles and rigid solids. Two important notions, heat and temperature are absent in mechanics, which constitute the pillars of the establishment of classical thermodynamics as a branch of science. The need to develop a science beyond mechanics to cope with the reality of engineer's activities was born in the beginning of the nineteenth century. Thermodynamics began in 1822 with a Fourier's publication *Analytical theory of heat* wherein is derived the partial differential equation for the temperature distribution in a rigid body. Two, years later, in 1824, Sadi Carnot (1796-1832) put down further the foundations of thermodynamics with his renowned memoir *Reflection on the motive power of fire, and on machines fitted to develop that power*. Carnot recognized that steam power was a motor of industrial revolution that would prompt economical and social life. Despite its pioneering role, Carnot's work is based on several misconceptions, as for instance the identification of heat with a hypothetical indestructible weightless substance, the caloric. The notion of caloric was introduced by Lavoisier considered as the father of modern chemistry. James P. Joule identified heat as a form of energy transfer by showing experimentally that heat and work are mutually convertible. William Thomson (1827-1907) who has later become known as Lord Kelvin, realized that the work of Carnot was not contradicting the ideas of Joule. Kelvin developed the point of view that the mechanical action of heat could be interpreted by appealing to two laws. Rudolf Clausius (1822-1888), a contemporary of Joule and Kelvin, accomplished substantial advancement. Clausius was the first to introduce "internal energy" and "entropy", one of the most subtle notions of thermodynamics. It was the merit of Carnot, Joule, Kelvin, and Clausius to thrust thermodynamics towards the level of an undisputed scientific discipline. Another generation of scientists was needed to unify this new formalism and to link it with other currents of science. One of them was Ludwig Boltzmann (1844-1906) who put forward a decisive "mechanistic" interpretation of heat transport; his major contribution was to link the behaviour of the particles at the microscopic level to their consequences on the macroscopic level. Another prominent scientist, Josiah Williard Gibbs (1839-1903), deserves the credit to have converted thermodynamics into a deductive science. In fact he recognized soon that thermodynamics of the nineteenth century is a pure static science wherein time does not play any role. Among his main contributions, let us point out the theory of stability based on the use of the properties of convex (or concave) functions, the potential bearing his name, and the well-known Gibbs' ensembles. Gibbs' paper "*On the equilibrium of the heterogeneous substances*" ranks among the most decisive impacts in the developments of modern chemical thermodynamics. Other leading scientists have contributed to the development of equilibrium thermodynamics as a well structured, universal, and undisputed science since the pioneers laid down its first steps. Although the list is far from being exhaustive, let us mention the names of Caratheodory, Cauchy, Clapeyron, Duhem, Einstein, Helmholtz, Maxwell, Nernst, and Planck.

1.2 The Zeroth Law

1.2.1 System

By system is understood a portion of matter with a given mass, volume, and surface. An *open system* is able to exchange matter and energy through its boundaries, a *closed system* exchanges energy but not matter with the outside while an *isolated system* does exchange neither energy nor matter with its surroundings. It is admitted that the universe (the union of system and surroundings) acts as an isolated system. In this chapter, we will deal essentially with homogeneous systems, whose properties are independent of the position.

A macroscopic thermodynamic system is any three-dimensional region of space which is bounded by one or more arbitrary geometric surfaces. The bounding surfaces may be real or imaginary and may be at rest or in motion. The boundary may change its shape or size. The region of physical space which lies outside the arbitrarily selected boundaries of the system is called the *surroundings* or the *environment*. It is restricted to that specific localized region which interacts in some fashion with the system and hence has a detectable influence on the system.

The analysis of thermodynamic processes includes the study of the transfer of mass and energy across the boundaries of a system and the effect of these interactions on the state of the system. As mentioned previously, when the transfer of mass across the bounding surface of a system is prohibited, the system is called a closed system. Although the quantity of matter is fixed in a closed system, energy may be allowed to cross its boundaries in the form of *work* and *heat*.

- *Property* is any characteristic of a system which can in principle be specified by describing an operation or test to which the system is subjected.
- The term *State* is referred to an equilibrium state. There are many types of equilibrium, which include thermal, mechanical, phase, and chemical equilibrium.
- A *Process* is any transformation of a system from one state to another. A complete description of process typically involves specification of the initial and final equilibrium states, the path, and the interactions which take place across the boundaries of the system during the process.
- *Path* in thermodynamics refers to the specification of a series of states through which the system passes.
- *State functions* are independent of the past/history of the system.
- A *Cyclic Process* is defined as a process with identical end states. The change in the value of any state function for a cyclic process is zero.

1.2.2 Pressure, Temperature

Pressure P is defined as the normal force per unit area acting on some real or imaginary boundary. Normal forces in static equilibrium will always be considered as compressive, hence the pressure is a positive quantity.

Temperature is a property of great importance in thermodynamics, and its value can be obtained easily by indirect measurement with calibrated instruments. The temperature of a system is determined by bringing a second body, a thermometer, into contact with the system and allowing thermal equilibrium to be reached. The value of the temperature is found by measuring some temperature-dependent property of the thermometer such as

- Volume of gases, liquids, and solids
- Pressure of gases at constant volume
- Electric resistance of solids
- Intensity of radiation (at high temperature)
- Magnetic effects (at low temperature)

Any such property is called a *thermometric* property.

1.2.3 The Zeroth Law

The so called zeroth law refers to the introduction of the idea of empirical temperature, which is one of the most fundamental concepts of thermodynamics. When a system 1 is put in contact with a system 2 but no net flow of energy occurs, both systems are said to be in thermal equilibrium. If system 1 and 2 are put in contact, they will change the values of their parameters in such a way that they reach a state of thermal equilibrium, in which there is no net heat transfer between them.

The zeroth law of thermodynamics states that *if the systems 1 and 2 are separately in thermal equilibrium with 3, then 1 and 2 are in thermal equilibrium with one another*. The property of transitivity of thermal equilibrium allows one to classify the space of thermodynamic states in classes of equivalence, each of which constituted by states in mutual thermal equilibrium.

One distinguishes extensive and intensive state variables; extensive variables like mass, volume, and energy have values in a composite system equal to the sum of the values in each subsystem; intensive variables as temperature or chemical potential take the same values everywhere in a system at equilibrium. As a variable like temperature can only be rigorously defined at equilibrium, one may expect difficulties when dealing with situations beyond equilibrium. The general concept of intensive thermodynamic parameters plays a crucial role in classical thermodynamics and equilibrium statistical mechanics. For systems in contact, *intensive thermodynamic parameters like temperature, pressure or chemical potential equalize their values once the equilibrium state is reached*, provided that their associated quantities, energy, volume or number of particles, can be exchanged. Since this property holds even in the case of systems that exhibit different microscopic dynamics, *this equalization became the key criterion in equilibrium statistical mechanics* to study the influence of the environment on a given system, for example, when a reservoir is connected to it. Moreover, the theory of phase coexistence as well as the measurement of, for instance, temperature with a thermometer draw on this powerful concept.

Critical remarks

Tamás Matolcsi pointed out that the homogeneity of intensive parameters is not true in the following examples.

The pressure of a gas (liquid) in a container resting on the Earth is not homogeneous, growing downwards because of the gravity. Thus homogeneity in equilibrium does not hold necessarily in the presence of exterior volume force (which is proportional to the density).

The pressure of a gas consisting of electrically charged particles in equilibrium in a spherical container is not homogeneous, growing radially from the centre towards the container wall (gravity neglected). Thus homogeneity in equilibrium does not hold necessarily in the presence of interior volume force.

Let us take an elastic ball resting in the atmosphere, and let us neglect gravity. The three bodies in equilibrium, the air in the ball, the elastic hull and the atmosphere, have different pressures. The pressure of the air inside is larger than that of the atmosphere, and the pressure of the hull is not homogeneous (it is larger on the internal surface than on the external surface), though no volume force acts on the hull. Thus homogeneity in equilibrium does not hold necessarily even in the absence of volume force.

1.2.4 Constant-Volume Gas thermometer

A constant volume gas thermometer (see Fig.1.1) composed of a vessel on the left filled with dilute gas, which is connected to a mercury manometer. The right side can be moved up or down to keep the mercury level on the left at a fixed level, so the volume of gas is kept constant. The manometer is used to measure the pressure of the gas

$$P_{\text{gas}} = P_{\text{atm}} + \rho g \Delta h \quad (1.1)$$

1.3 Equation of state

An equation of state expresses the individual peculiarities of one system as compared with another system and must be determined either by experiment or by molecular theory. An equation of state, therefore, is not a theoretical deduction from thermodynamics, but is usually an experimental addition to thermodynamics. It expresses the result of experiments in which state variables of a system were measured as accurately as possible. A system consisting of a gas at very low pressure and sufficiently high temperature has the simple equation of state of an ideal gas,

$$PV = nRT,$$

where n is the number of moles and R is the molar gas constant. At higher pressures, the equation of state is more complicated, being well represented by the van der Waals equation, which takes into account intermolecular interactions and the finite size of the particles. Thus,

$$\left(P + a \frac{n^2}{V^2}\right) (V - nb) = nRT,$$

where a and b are positive constants appropriate to the specific gas.

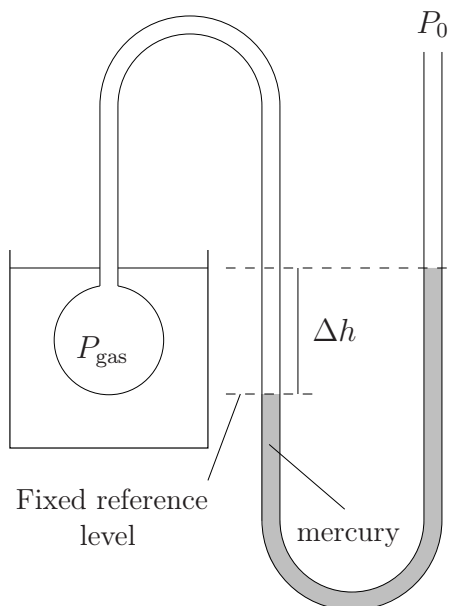


Figure 1.1: Constant-volume gas thermometer.

1.3.1 Nonreactive Ideal-gas mixtures

The PVT relationship for a mixture of gases is usually based on two models. The first of these is known as *Dalton's law* of additive pressures. This rule states that the total pressure exerted by a mixture of gases is the sum of the component pressure P_i , each measured alone at a temperature and volume of the mixture. Hence Dalton's rule can be written in the form

$$P = P_1 + P_2 + P_3 + \cdots + P_k = \sum_i P_i \quad (1.2)$$

where P_i is the partial pressure of the i th component. It would be expected that ideal gases fulfil Dalton's rule exactly, since the concept of ideal gas implies that intermolecular forces are negligible, and thus the gases act independently of one another.

The pressure exerted by an ideal gas in a gas mixture, in view of Dalton's rule, can be expressed as

$$P_i = \frac{N_i RT}{V} \quad (1.3)$$

where T and V are the absolute temperature and volume of the mixture, respectively. If the component pressures of each chemical species are now substituted into Eq.1.2, we find that

$$P = \frac{N_1 RT}{V} + \frac{N_2 RT}{V} + \cdots + \frac{N_i RT}{V} \quad (1.4)$$

$$= (N_1 + N_2 + \cdots + N_i) \frac{RT}{V} \quad (1.5)$$

1.4 Kinetic theory of ideal gases

In a gas, the interaction between two molecules weakens rapidly as the distance between the molecules increases. In a dilute gas, the average distance between gas molecules is large enough so we can ignore interactions between the molecules except when they collide. In addition, the volume of space occupied by the molecules themselves is a small fraction of the total volume of the gas. The *ideal gas* is a simplified model of a dilute gas in which we think of the molecules as point-like particles that move independently in free space with no interactions except for elastic collisions.

The simplified model is a good approximation for many gases under ordinary conditions. Many properties of gases can be understood from this model. The microscopic theory based on it is called the kinetic theory of the ideal gas.

1.4.1 Microscopic origin of Pressure

The force that a gas exerts on a surface is due to collisions that the gas molecules make with that surface. For instance, think of the air inside an automobile tire. Whenever an air molecule collides with the inner tire surface, the tire exerts an inward force to turn the air molecule around and return it to the bulk of the gas. By Newton's third law, the gas molecule exerts an outward force on the tire surface. The net force per unit area on the inside of the tire due to all the collisions of the many air molecules is equal to the air pressure in the tire. The pressure depends on three things: how many molecules there are, how often each one collides with the wall, and the momentum transfer due to collision.

We want to find out how the pressure of an ideal gas is determined by the motions of the gas molecules. To simplify the discussion, consider a gas contained in a box of length L and side area A . The result does not depend on the shape of the container. For an elastic collision, the x component of the molecule's momentum is reversed in direction since the wall is much more massive than the molecule. Since the gas exerts only an outward force on the wall the y - and z -components are unchanged. Thus, the molecule's momentum change is $\Delta p_x = 2m^*|v_x|$.

When does this molecule next collide with the same wall? Ignoring for now collisions with other molecules, its x -components of velocity never change magnitude. The time it takes the molecule to travel the length L of the container and hit the other wall is $L/|v_x|$. Then the round-trip time is

$$\Delta t = 2 \frac{L}{|v_x|}. \quad (1.6)$$

The average force exerted by the molecule on the wall during one complete round-trip is

$$\langle F \rangle = \frac{\Delta p_x}{\Delta t} = \frac{2m^*|v_x|}{2L/|v_x|} = \frac{m^*v_x^2}{L}. \quad (1.7)$$

The total force on the wall is the sum of the forces due to each molecule in the gas. If there are N molecules in the gas, we can multiply N by the average force due to one

molecule to get the total force on the wall.

$$F = N\langle F \rangle = \frac{Nm^*}{L}\langle v_x^2 \rangle \quad (1.8)$$

The Pressure is then

$$P = \frac{F}{A} = \frac{Nm^*}{AL}\langle v_x^2 \rangle \quad (1.9)$$

The volume of the container is $V = AL$, so

$$P = \frac{Nm^*}{V}\langle v_x^2 \rangle \quad (1.10)$$

which is true regardless of the shape of the container enclosing the gas. The product $m\langle v_x^2 \rangle$ suggest kinetic energy. It certainly makes sense that if the average kinetic energy of the gas molecules is larger, the pressure is higher. The average translational kinetic energy of a molecule in the gas belonging to the x direction is

$$\langle K_{\text{tr}} \rangle = \frac{1}{2}m^*\langle v_x^2 \rangle \quad (1.11)$$

For any gas molecule, $v^2 = v_x^2 + v_y^2 + v_z^2$, since the velocity is a vector. The gas as a whole is at rest, so there is no proffered direction of motion. Then the average value of v_x^2 must be the same as the averages of v_y^2 and v_z^2 , so

$$v_x^2 = \frac{1}{3}\langle v^2 \rangle$$

Therefore,

$$m\langle v_x^2 \rangle = \frac{1}{3}m^*\langle v^2 \rangle = \frac{2}{3}\langle K_{\text{tr}} \rangle$$

Substituting this into equation (1.45), the pressure is

$$P = \frac{2}{3}\frac{N\langle K_{\text{tr}} \rangle}{V} = \frac{2}{3}\frac{N}{V}\langle K_{\text{tr}} \rangle \quad (1.12)$$

Equation (1.12) says the pressure is proportional to the product of the number density N/V and the average molecular kinetic energy. The pressure of a gas increases if either the gas molecules are packed closer together or if the molecules have more kinetic energy. The derivation only relies on average quantities. So we assumed that the gas molecules never collide with each other.

1.4.2 Temperature and Translational Kinetic Energy

We found that in an ideal gas, the pressure, volume, and number of molecules are related to the average translational kinetic energy of the gas molecules:

$$P = \frac{2}{3}\frac{N}{V}\langle K_{\text{tr}} \rangle \quad (1.13)$$

Solving for the average kinetic energy,

$$\langle K_{\text{tr}} \rangle = \frac{3}{2} \frac{PV}{N} \quad (1.14)$$

The equation of state for ideal gas relates P , V , and N to the temperature:

$$PV = NkT$$

By rearranging the ideal gas law, we find that P , V , and N occur in the same combinations as in equation (1.14), we find that

$$\langle K_{\text{tr}} \rangle = \frac{3}{2} kT \quad (1.15)$$

Therefore, the absolute temperature of an ideal gas is proportional to the average translational kinetic energy of the gas molecules. Temperature then is the way to describe the average translational kinetic energy of the gas molecules. At higher temperatures, the gas molecules have greater kinetic energy. The Maxwell velocity distribution $f(v)$ as a function of molecular speed can be seen in Fig.1.2. The vertical axis shows the fraction of molecules moving at velocity v to $v + dv$. So $f(v)$ is a probability density function which gives the probability, per unit speed, of finding the particle with a speed near v . The speed of a gas molecule that has the average kinetic energy is called *rms* (root mean square) *speed*. The rms speed is not the same as the average speed. Instead, rms speed is the square root of the mean of the speed squared. Since

$$\langle K_{\text{tr}} \rangle = \frac{1}{2} m^* \langle v^2 \rangle = \frac{1}{2} m^* v_{\text{rms}}^2 \quad (1.16)$$

the rms speed is

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$$

Squaring before averaging emphasizes the effect of the faster-moving molecules, so the rms speed is about 9% higher as it turns out.

Since the average kinetic energy of molecules in an ideal gas depends only on temperature, equation (1.16) implies that more massive molecules move more slowly on average than the lighter ones at the same temperature. It can be shown that the root mean speed of the molecules takes the following form:

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m^*}},$$

where k is Boltzmann's constant and m^* is the mass of a molecule. Therefore, at a given temperature, the rms speed is inversely proportional to the square root of the mass of the molecule.

1.4.3 Collisions between gas molecules

How far does a gas molecule move, on average, between collisions? The mean (average) length of the path travelled by a gas molecule as a free particle is called *mean free path*

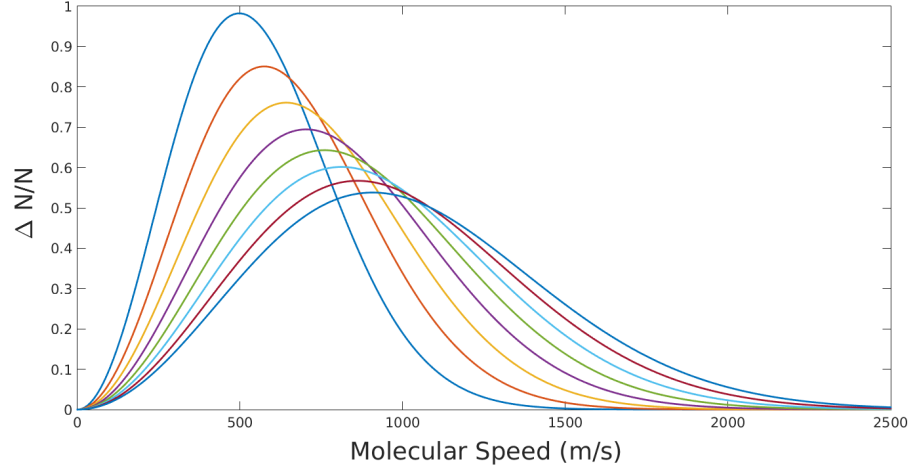


Figure 1.2: Velocity distributions of an ideal gas at different temperatures.

(Λ). The mean free path depends on two things: how large the molecules are and how many of them occupy a given volume. In a simplified model, imagine a molecule of diameter d . Its cross-sectional area is

$$A = \pi r^2 = \frac{1}{4}\pi d^2$$

As the molecule moves in a straight line, it sweeps out a cylinder volume of space. Once the volume it has swept out equals V/N , the total volume divided by the number of molecules, it has used up its own space and begins to infringe on the space belonging to another molecule—which means the collision is imminent. Thus, a collision occurs when

$$A\Lambda \approx \frac{V}{N}$$

or

$$\Lambda \approx \frac{1}{\frac{1}{4}\pi d^2 \frac{N}{V}}$$

This simplified calculation is correct except for the dimensionless constant of proportionality; a detailed calculation yields

$$\Lambda = \frac{1}{\sqrt{2}\pi d^2 \frac{N}{V}}$$

Typically the mean free path is much larger than the average distance between neighboring molecules.

1.5 The First Law

The first law of thermodynamics can be regarded as a generalization of the conservation of mechanical energy including many possible forms of energy associated with the system.

1.5.1 Work

If a system undergoes a displacement under the action of a force, work is said to be done. The amount of work being equal to the product of the force and the component of the displacement parallel to the force. If a system as a whole exerts a force on its surroundings and a displacement takes place, the work that is done either by the system or on the system is called *external work*. Thus, a gas, confined in a cylinder and at uniform pressure, while expanding and imparting motion to a piston does external work on its surroundings. The work done, however, by one part of the system on another part is called *internal work*. The interactions of molecules, atoms, or electrons on another constitute internal work.

1.5.2 Quasi-static process

The system in thermodynamic equilibrium satisfies the following requirements:

- *Mechanical equilibrium*. There are no unbalanced forces or torques acting on any part of the system or on the system as a whole.
- *Thermal equilibrium*. There are no temperature differences between parts of the system or between the system and its surroundings.
- *Chemical equilibrium*. There are no chemical reactions within the system and no motion of any chemical constituent from one part of a system to another part.

Once a system in thermal equilibrium and the surroundings are kept unchanged, no motion will take place and no work will be done. A finite unbalanced force may cause the system to pass through nonequilibrium states. A process is said to be *quasi-static* if the system is at all times infinitesimally near a state of thermodynamic equilibrium. A quasi-static process is an *idealization* that is applicable to all thermodynamic systems, including electric and magnetic systems. The conditions for such a process can never be rigorously satisfied in the laboratory, but they can be approached with almost any degree of accuracy.

1.5.3 Internal Energy

As we discussed earlier the average translational kinetic energy $\langle K_{\text{tr}} \rangle$ of an ideal gas is proportional to the absolute temperature of the gas:

$$\langle K_{\text{tr}} \rangle = \frac{3}{2}kT \quad (1.17)$$

The molecules move about in random directions even though, on macroscopic scale, the gas is neither moving nor rotating. Equation (1.17) also gives the average translational kinetic energy of the random motion of molecules in liquids, solids, and nonideal gases except at very low temperatures. This random microscopic kinetic energy is part of what we call the *internal energy* of the system:

The internal energy of the system is the total energy of all molecules in the system except for the macroscopic kinetic energy and the external potential energy.

Internal energy includes:

- Translational and rotational kinetic energy of molecules.
- Vibrational energy—both kinetic and potential—of molecules and of atoms within molecules due to random vibrations about their equilibrium points.
- Potential energy due to interactions between the atoms and molecules of the system.
- Chemical and nuclear energy

Internal energy does not include

- The kinetic energy of the molecules due to translation, rotation, or vibration of the whole system or of a macroscopic part of the system
- Potential energy due to interactions of the molecules of the system with something outside the system

The theorem of *equipartition of energy* says the internal energy is distributed equally among all the possible ways in which it can be stored (as long as the temperature is sufficiently high). Each independent form of energy has an average of $1/2kT$ of energy per molecule. Thus, the mean energy of a molecule should be

$$\langle \epsilon \rangle = \frac{f}{2}kT$$

where f is the sum of the number of translational, the number of rotational, and the double number of vibrational degrees of freedom of a molecule:

$$f = n_{\text{tr}} + n_{\text{rot}} + 2n_{\text{vib}}$$

In case of *monoatomic molecules* the atom can have only translational movement along the three axes in free space. In case of *diatomic molecules* the molecules can possess 3 translational (for the centre of mass of the molecule), 2 rotational (along axes perpendicular to the line joining the two atoms) and 1 vibrational motion along the line joining the two atoms. Vibration involves two more degrees of freedom, because during the oscillation both kinetic and potential energy $2n_{\text{vib}}$ contribute to f . It is worth noting that the vibration motion becomes significant only at high temperature.

Molecules of an ideal gas do not interact with one another. We can therefore find the internal energy of one mole of an ideal gas by multiplying the number of the particles by the mean energy of one molecule:

$$U = N \cdot \langle \epsilon \rangle = \frac{f}{2}NkT$$

It is very important to emphasize that the internal energy of ideal gases depend only on the absolute temperature $U = U(T)$. According to the equation of state ($PV = NkT$) the expression of U can be rewritten as follows

$$U = \frac{f}{2}PV$$

The internal energy is a function of state of a system. This signifies that whenever a system is in a given state, its internal energy takes on the value characterizing this state regardless of the previous history of the system.

$$\Delta U = \frac{f}{2}Nk\Delta T = \frac{f}{2}P_2V_2 - \frac{f}{2}P_1V_1$$

In other words, the change in the internal energy does not depend on the process or processes that caused the system to pass from one state to another.

1.5.4 Work in changing the volume

Imagine any hydrostatic system contained in a closed cylinder equipped with a frictionless movable piston on which the system and the surroundings may act. Suppose that the cylinder has a cross-sectional area A , and that the pressure exerted by the system at the piston face is P . The force on the internal face of the piston is, therefore, PA . The surroundings also exert an opposing force on the piston. It might be due to the force from a spring or a weight, or external friction, or a combination of these. The important condition that must be satisfied is that the force F of the surroundings must differ only slightly from the force PA of the system. If, under these conditions, the piston moves in an infinitesimal distance dx during compression, the surroundings perform an infinitesimal amount of positive work dW on the system equal to

$$dW = F dx = PA dx.$$

The differential symbol with the line drawn through it, and read “dee-bar W ” expresses that W is an inexact differential. During compression, the volume of the system is decreasing, so

$$A dx = -dV,$$

and, hence

$$dW = -P dV.$$

The presence of a minus sign before $P dV$ ensures that a negative dV gives rise to positive work done on the system and, conversely, a positive dV yields negative work done by the system.

In a finite quasi-static process in which the volume changes from V_1 to V_2 , the amount of work W done by the system is

$$W_{12} = - \int_{V_1}^{V_2} P(V) dV.$$

However, in contracting from state 2 to state 1, along the same path of integration but in opposite direction, the work done on the system is

$$W_{21} = \int_{V_2}^{V_1} P(V) dV.$$

1.5.5 Heat

Heat and work are similar in that both describe a particular kind of energy *transfer*. Work is an energy transfer due to a force acting through a displacement. Heat is a microscopic form of energy transfer involving a large number of particles. No macroscopic displacement occurs when heat flows and no macroscopic force is exerted by one object on the other. A system can possess *energy* in various forms, but it cannot possess heat or work. Heat and work are two ways of transferring energy from one system to another.

Heat flows from a system at higher temperature to one at lower temperature. Temperature is associated with the microscopic translation kinetic energy of the molecules. The flow of heat tends to equalize the average microscopic translational kinetic energy of the molecules. When two systems are in thermal contact and no net heat flow occurs, the systems are in thermal equilibrium and have the same temperature.

1.5.6 The mathematical form of the First Law

Consider first a system enclosed by a thermally isolated (adiabatic), impermeable wall, so that the sole interaction with the external world will appear under the form of a mechanical work W , for instance by expansion of its volume or by stirring. Referring to the famous experience of Joule, the work can be measured by the decrease in potential energy of a slowly falling weight and is given by $W = mgh$, where h is the displacement and g the acceleration of gravity. During the evolution of the system between the two given equilibrium states A and B , it is checked experimentally that the work W is determined exclusively by the initial and the final states A and B , independently of the transformation paths. This observation allows us to identify W with the difference $\Delta U = U(B) - U(A)$ of a state variable U which will be given the name of internal energy

$$W = \Delta U \tag{1.18}$$

This result provides a means to measure the internal energy of a system, whatever be its nature. Assume now that we remove the adiabatic wall enclosing the system, which again proceeds from state A to state B . When this is accomplished, it is observed that in general $W \neq \Delta U$, and calling Q the difference between these two quantities, one obtains

$$\Delta U - W = Q \tag{1.19}$$

where Q is referred to as the heat exchanged between the system and its surroundings. For a thermodynamic process without transfer of matter, the first law is often formulated as:

$$\Delta U = Q + W \tag{1.20}$$

1.5.7 Sign conversion during expansion and expression

As the volume of a hydrostatic system changes because of the motion of a piston in a cylinder, the position of the piston at any moment is proportional to the volume. Sign conversion during expansion and expression:

During the gas expansion we assume a piston is moving at velocity v , the magnitude of the velocity of the particle diminishes by $2v$ if the piston moves away from the particle catching up with it. If the average velocity of the gas is reduced, T and U must be reduced as well. Hence

$$\Delta U_{12} = Q_{12} - |W_{12}|$$

In case of compression after collision the magnitude of the velocity of the particle increases by $2v$ if the piston and the particle moved toward each other.

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

Heat absorption $Q_{12} > 0$, heat dissipation $Q_{12} < 0$.

1.5.8 Differential form of the First Law

A process involving only infinitesimal changes in the thermodynamic variables of a system is known as an infinitesimal process. For such a process, the general statement of the first law becomes

$$dU = \delta Q + \delta W. \quad (1.21)$$

Equation shows that the exact differential of dU is the sum of two inexact differentials, δQ and δW . It is important to note that dU refers to a property within the system, whereas δQ and δW are not related to the properties of the system; rather, they refer to the surroundings. We adopt the sign convention that $Q > 0$, $W > 0$ when heat and work are supplied to the system, $Q < 0$, $W < 0$ when heat and work are delivered by the system. It is important to stress that the domain of applicability of the first law is not limited to reversible processes between equilibrium states. The first law remains valid whatever the nature of the process is. Designated by $E = U + K + V$ the total energy of the system will be appear in a more general form:

$$dE = \delta Q + \delta W. \quad (1.22)$$

Microscopically, mechanical work is related to coherent correlated motions of the particles while heat represents that part of motion, which is uncorrelated, say incoherent. In equilibrium thermodynamics, the processes are reversible from which follows that the energy balance equation will take the form:

$$dU = \delta Q - P dV. \quad (1.23)$$

The first law introduces the notion of energy, which emerges as a unifying concept, and the notion of heat, related to the transfer of energy.

The mathematical formulation of the first law contains three related ideas: 1) the existence of an internal-energy function; 2) the principle of the conservation of energy; 3) the definition of heat.

1.5.9 Cyclic Processes

In a cyclic process, the system starts and returns to the same thermodynamic state. The net work involved is the closed area on the $P-V$ diagram. During a cyclic process of an ideal gas the net internal energy change must be zero.

$$\oint dU = 0 \quad \text{because } \Delta T = 0.$$

1.5.10 Heat Capacity and Specific Heat

Suppose we have a system on which no mechanical work is done, but we allow heat to flow into the system by placing it in thermal contact with another system at higher temperature. As the internal energy of the system increases, its temperature increases. If heat flows out of the system the internal energy decreases. We account for that possibility by making Q negative if heat flows out of the system.

For a large number of substances, under normal conditions, the temperature change ΔT is proportional to the heat Q . The constant proportionality is called heat capacity (symbol C):

$$C = \frac{\Delta Q}{\Delta T}$$

The heat capacity depends on the substance and on how much of it is present.

1.5.11 Specific Heat

Since the heat capacity of a system is proportional to the mass of the system, the *specific heat capacity* (symbol c) of a substance is defined as the heat capacity per unit mass:

$$c = \frac{C}{m} = \frac{1}{m} \frac{\Delta Q}{\Delta T}.$$

It is worth noting that the material is assumed to be homogeneous. Specific heat capacity is often abbreviated to specific heat. The SI unit of specific heat is $\text{Jkg}^{-1}\text{K}^{-1}$. In SI units, the specific heat is the number of joules of heat required to produce a 1 K temperature change in 1 kg of the substance. The specific heat of the water is $4186 \text{ Jkg}^{-1}\text{K}^{-1}$. The specific heat of water is quite a bit higher than many other common substances. For example, the specific heat of iron is $449 \text{ Jkg}^{-1}\text{K}^{-1}$, sand is $830 \text{ Jkg}^{-1}\text{K}^{-1}$, and oak timber is $\text{Jkg}^{-1}\text{K}^{-1}$.

1.5.12 Specific Heat of Ideal Gases

By definition the specific heat of ideal gases at constant volume is

$$c_v = \frac{1}{m} \left(\frac{dU}{dT} \right)_v$$

The subscript “V” is a reminder that the volume of the gas is held constant during the heat flow.

$$c_v = \frac{1}{m} \frac{dU}{dT} = \frac{1}{\mathfrak{M}} \frac{d}{dT} \left(\frac{f}{2} \frac{\mathfrak{M}}{M} RT \right)$$

$$c_v = \frac{f}{2} \frac{R}{M} \frac{d}{dT} (T) = \frac{f}{2} \frac{R}{M}$$

The molar specific heat of an ideal gas is independent of the material feature.

$$c_M = M c_v = \mathfrak{M} \frac{f}{2} \frac{R}{\mathfrak{M}} = \frac{f}{2} R$$

The internal energy can be expressed with c_v as follows

$$U(T) = \frac{f}{2} \frac{m}{M} RT = \frac{f}{2} \frac{R}{M} m T = c_v m T$$

By definition the specific heat of ideal gases at constant pressure is

$$c_p = \frac{1}{m} \left(\frac{dH}{dT} \right)_P$$

where H is a new quantity called enthalpy.

$$H = U + PV$$

Specific heat capacity at constant pressure can be written as:

$$c_p = \frac{1}{m} \left(\frac{dH}{dT} \right)_P = \frac{d}{dT} (U + PV)$$

$$c_p = \frac{1}{\mathfrak{M}} \frac{d}{dT} \left(\frac{f}{2} \frac{\mathfrak{M}}{M} RT + \frac{\mathfrak{M}}{M} RT \right)$$

$$c_p = \frac{d}{dT} \left(\frac{f}{2} \frac{RT}{M} + \frac{RT}{M} \right) = \frac{f+2}{2} \frac{R}{M}$$

The Robert Mayer’s relation expresses the connection between the two specific heats.

$$c_p - c_v = \frac{R}{M}.$$

We summarize the heat exchange calculation for arbitrarily quasi-static expansion

$$\Delta U_{12} = Q_{12} - |W_{12}| \text{ expansion}$$

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

$$Q_{12} = c_v m \Delta T_{12} + |W_{12}|$$

1.5.13 Constant Pressure Processes

A process by which the state of a system is changed while the pressure is held constant (see Fig.1.3) is called an *isobaric* process. The word *isobaric* comes from the same Greek root as the word *barometer*. The change of state from V_1 to V_2 along the line from 1 to 2 occurs at a constant pressure. A constant pressure process appears as a horizontal line on a PV diagram. The work done on the gas is

$$W = -P(V_2 - V_1)$$

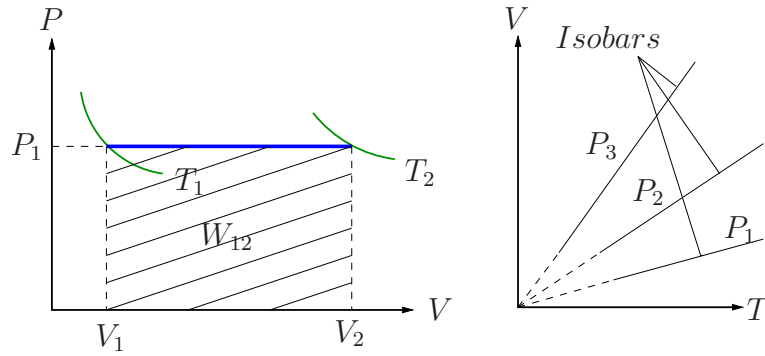


Figure 1.3: Isobaric processes. $P_3 < P_2 < P_1$.

On a $V - T$ plane the isobars are straight lines with zero intersection. The mathematical expression of these lines takes the following form:

$$V(T) = \left(\frac{NK}{P} \right) T.$$

During an isobaric process Charles's law applies:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The heat exchange can be calculated from the first law as follows:

$$\begin{aligned} \Delta U_{12} &= Q_{12} - |W_{12}| \\ Q_{12} &= \Delta U_{12} + |W_{12}| \\ Q_{12} &= c_v m \Delta T_{12} + p_1 \Delta V_{12} \end{aligned} \tag{1}$$

or using the the definition of the specific heat capacity:

$$Q_{12} = c_p m \Delta T_{12}$$

1.5.14 Constant Volume Processes

A process by which the state of a system is changed while the volume remains constant is called an *isochoric* process as it can be seen in Fig.1.4. No work is done during a constant volume process; without a displacement, work cannot be done. The area under the PV curve—a vertical line—is zero:

$$W = 0$$

If no work is done, then from the first law of thermodynamics, the change in internal energy is equal to the heat flow into the system:

$$\Delta U = Q$$

On a $P - T$ plane the isochores are straight lines with zero intersection. The mathematical expression of these lines takes the following form:

$$P(T) = \left(\frac{NK}{V} \right) T.$$

During an isochoric process Gay-Lussac law applies:

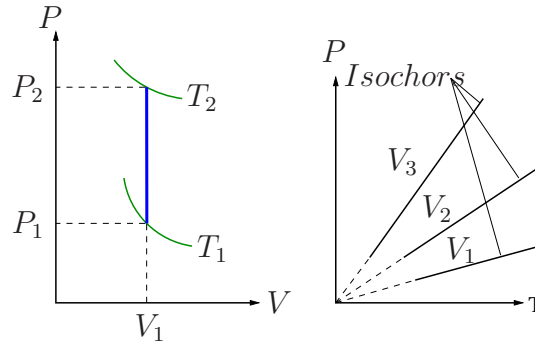


Figure 1.4: Isochoric processes. $V_3 < V_2 < V_1$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

According to the first law the heat exchange during an isochoric process is equal to the change in internal energy:

$$\begin{aligned} \Delta U_{12} &= Q_{12} - |W_{12}| \\ Q_{12} &= c_v m \Delta T_{12} \end{aligned} \tag{1}$$

1.5.15 Constant Temperature Processes

A process in which the temperature of the system remains constant (see Fig.1.5) is called an *isothermal* process. On a PV diagram, a path representing a constant temperature process is called an *isotherm*. All the points on an isotherm represent states

of the system with the same temperature. How can we keep the temperature of the system constant? One way is to put the system in thermal contact with a *reservoir*—something with a heat capacity so large that it can exchange heat in either direction without changing its temperature significantly. According to the Boyle's law during

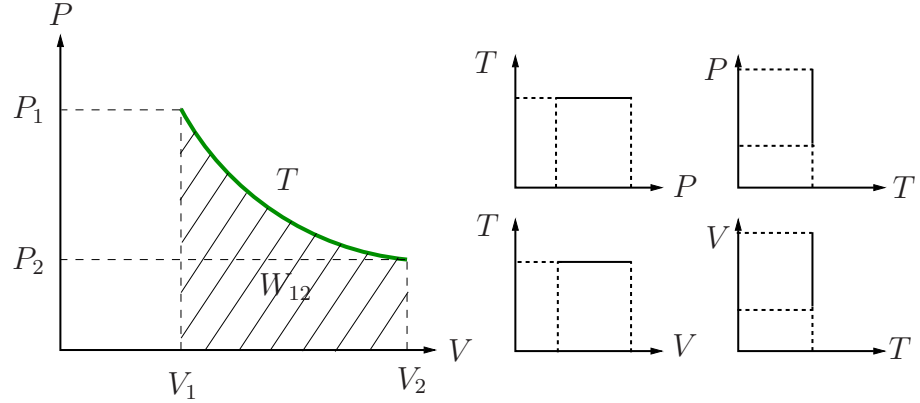


Figure 1.5: Isotherm processes.

the process

$$P_1 V_1 = P_2 V_2 \quad (1)$$

The first law reads as

$$\begin{aligned} \Delta U_{12} &= Q_{12} - |W_{12}| \\ \Delta U_{12} &= Q_{12} - |W_{12}| \\ 0 &= Q_{12} - |W_{12}| \\ Q_{12} &= |W_{12}| \\ |W_{12}| &= \int_{V_1}^{V_2} \frac{m}{M} R T \frac{dV}{V} = \frac{m}{M} R T \ln \frac{V_2}{V_1} = n R T \ln \frac{P_1}{P_2} \end{aligned} \quad (2)$$

1.5.16 Work on Solid and Liquid Phases

The integral of PdV may be used to evaluate the quasi-static expansion or compression work for any phase of interest. It is particularly appropriate in this form for the boundary work associated with gaseous systems, since the functional relation between P and v may be established by direct experimental measurements. The *specific volume* v is defined as the reciprocal of the density. Thus $v = 1/\rho = V/m = \text{volume/mass}$. For solids and liquids, the variation of pressure with volume is more frequently expressed indirectly in terms of a property called the *isothermal coefficient of compressibility* K_T . This property is defined as

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad (1.24)$$

It is an experimental observation that $(\partial v / \partial P)_T$ is always negative for all phases of matter. The negative in the definition of K_T is introduced so that tabulated values of the isothermal compressibility are always positive.

To accommodate the use of K_T in the evaluation of boundary work, it is necessary to replace dv in the integral of Pdv by an equivalent quantity. On the basis that v is solely a function of T and P , that is $v = v(T, P)$, the total differential is written as

$$dv = \left(\frac{\partial v}{\partial T} \right)_P dT + \left(\frac{\partial v}{\partial P} \right)_T dP \quad (1.25)$$

For isothermal processes ($dT = 0$) this total differential reduces to

$$dv = \left(\frac{\partial v}{\partial P} \right)_T dP = -v K_T dP \quad (1.26)$$

Therefore, the isothermal work of compression per unit mass is given by

$$w_T = - \int_1^2 P dv = \int_1^2 v K_T P dP \quad (1.27)$$

The coefficient K_T and the specific volume v are frequently nearly constant for liquids and solids over considerable ranges of temperature and pressure. Under this condition integration of the above expression yields

$$w_T = \frac{v K_T}{2} (P_2^2 - P_1^2) \quad (1.28)$$

This equation provides a means for estimating the work required to compress a solid or a liquid under isothermal conditions. Note that usually K_T is extremely small with the value in both cases being on the order of 10^{-6} Pa^{-1} .

1.5.17 Other quasi-static forms of work

There are a number of other quasi-statics forms of work developed in basic physics and chemistry. A brief summary of these is presented.

- Work of a reversible chemical cell

A *galvanic cell* is a device for converting chemical energy into electrical energy by means of a controlled chemical reaction. The electrical work delivered by the cell for the passage of a differential quantity of charge dQ_e is found in the following way. For a potential difference \mathcal{E} , a current I performs work at a rate

$$\frac{dW}{dt} = \mathcal{E} I \quad (1.29)$$

$$I = \frac{dQ_e}{dt} \quad (1.30)$$

Combination of these two expressions yields, for the electric work:

$$dW = \mathcal{E} dQ_e \quad (1.31)$$

- Work in stretching a liquid surface

In heterogeneous systems where gas and liquid may be in contact, the phenomenon of surface tension occurs. For a molecule well inside the liquid phase no resultant force is experienced as it moves around in the fluid because of the intermolecular attractions, there being an equal number of molecules immediately surrounding it. However, a molecule near the interface experiences a resultant force directed back into the liquid since the forces of attraction due to gas molecules above it are quite weak compared to those of the liquid phase. Hence additional work must be done on any molecule which is brought from the interior of the liquid to the surface as the surface area is increased. The quantity of work required is defined in terms of a thermodynamic property of the system called the surface tension. The surface tension γ of a liquid phase is defined as the work per unit change in area required to increase the surface area. Consequently, the change in surface energy of a liquid for a differential area change is given by

$$dW_{\text{s.tension}} = \gamma dA \quad (1.32)$$

- Work done on elastic solids.

In order to change the length of a spring or wire in tension or compression, it is necessary to exert a force F which alters the length L . The equation for the differential work required to alter the length from L to $L + dL$ follows directly from the mechanical definition of work, namely,

$$dW_{\text{s.tension}} = F dL = \frac{1}{2} k_s (x_2^2 - x_1^2), \quad (1.33)$$

where k_s is the spring constant and $x_2 = L_2 - L_0$ and $x_1 = L_1 - L_0$.

It is sometimes more convenient to express the work done on an elastic solid bar or wire in terms of the stress σ and the strain ϵ . The stress in the axial direction is defined by $\sigma = F/A$, where A is the cross-sectional area of the solid. The strain for a differential change in length is given by $d\epsilon = dL/L$.

$$dW_{\text{s.tension}} = F dL = (\sigma A) (L d\epsilon) = V_0 \sigma d\epsilon \quad (1.34)$$

where V_0 is the initial volume of the solid. If the work on the elastic solid is done isothermally, then the relation between stress and strain is given by Young's isothermal modulus, $E_T = \sigma/\epsilon$. When the elastic deformation occurs, then E_T is a constant.

- Work of polarization and magnetization

It may be shown from the theory of electromagnetic fields that work is done on a substance contained within an electric or magnetic field when the field is altered. For a dielectric material which lies within an electric field, the work supplied externally to increase the polarization of the dielectric is given by

$$dW_{\text{polarization}} = V \mathbf{E} d\mathbf{P} \quad (1.35)$$

where V is the volume, \mathbf{E} is the electric field strength, and \mathbf{P} is the polarization. In this equation the boldface type emphasizes that \mathbf{E} and \mathbf{P} are both vector quantities.

A similar equation for the work done in increasing the magnetization of a substance due to a change in the magnetic field is expressed by

$$dW_{\text{polarization}} = V\mu_0\mathbf{H}d\mathbf{M} \quad (1.36)$$

where \mathbf{H} is the magnetic field strength, \mathbf{M} represents the magnetization per unit volume, μ_0 stands for the permeability of free space.

1.5.18 Generalized quasi-static work interactions

In the preceding sections a number of work interactions were introduced. It is convenient to refer to all types of quasi-static work interactions as the products of force and displacement, even though the factors within a given work expression may not bring to mind physical forces and displacements. The intensive property that appears in the equations representing work will be called a *generalized force*, and will be symbolized by F_k . In an analogue fashion the extensive property found in these equations will be called a *generalized displacement*, represented by X_k . The subscript k simply refers to the k th type of a work interaction. The sum of the quasi-static work effects of these types is given by

$$dW_{\text{tot}} = \sum_k F_k dX_k = -PdV + FdL + \gamma dA + V\mu_0\mathbf{H}d\mathbf{M} \dots \quad (1.37)$$

It is a matter of experience when various work effects should be taken into account. In some instances their contributions may be so small as to be neglected. Most generalized forces do not have the dimensions of length, nor do the generalized displacements have the dimensions of length. Nevertheless, the product of the dimensions for any corresponding pair of a generalized force and displacement has the dimensions of work, i.e., energy.

1.5.19 Equation of Adiabatic of an ideal gas

A process going on without heat exchange with the surroundings is called adiabatic. When a closed system is completely surrounded by an adiabatic boundary, the system may still be coupled to the surroundings so that work may be done.

If a closed system is caused to change from an initial state to a final state by adiabatic means only, then the work done on the system is the same for all adiabatic paths connecting the two states.

Recall from mechanics that, in moving an object from one point in a gravitational field to another point, in the absence of friction the work done depends only on the positions of the two points and not on the path through which the body was moved. It was concluded that for a conservative force, there exists a potential-energy function whose final value minus the initial value is equal to the work done.

$$W_{\text{adiabatic}} = U_{\text{final}} - U_{\text{initial}}$$

Let us find an equation relating the parameters of an ideal gas in an adiabatic process.

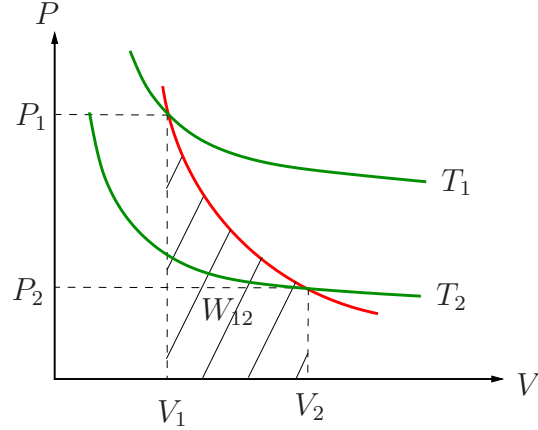


Figure 1.6: Quasi-static adiabatic process.

Adiabats connect isotherms together as it can be seen in Fig.1.6 and Fig.1.7. According to the first law of thermodynamics

$$dU = \cancel{dQ} - PdV \quad (1.38)$$

$$dU + PdV = 0 \quad (1.39)$$

$$c_v m dT + PdV = 0 \quad (1.40)$$

Now let us express P through V and T in accordance with the equation of state for an ideal gas

$$P = \frac{m}{M} \frac{RT}{V}$$

and introduce this expression into equation 1.40.

$$c_v dT + \frac{RT}{M} \frac{dV}{V} = 0$$

$$c_v \frac{dT}{T} + \frac{R}{M} \frac{dV}{V} = 0$$

According to Robert Mayer's relation instead of R/M we can substitute $c_p - c_v$, hence

$$\frac{dT}{T} + \frac{c_p - c_v}{c_v} \frac{dV}{V} = 0$$

This expression can be integrated, hence it follows that in adiabatic process

$$\ln(T) + \frac{c_p - c_v}{c_v} \ln(V) = \text{const}$$

$$TV^{\gamma-1} = \text{const}$$

where

$$\gamma = \frac{c_p}{c_v} = \frac{f+2}{f}$$

This expression is an equation of an adiabat of an ideal gas in variable T and V . We can pass over from this equation to one in variable P and V by replacing T in it with P and V in accordance with the equation of state for an ideal gas

$$T = \frac{M}{m} \frac{PV}{R}$$

Hence, we get

$$PV^\gamma = \text{const}'$$

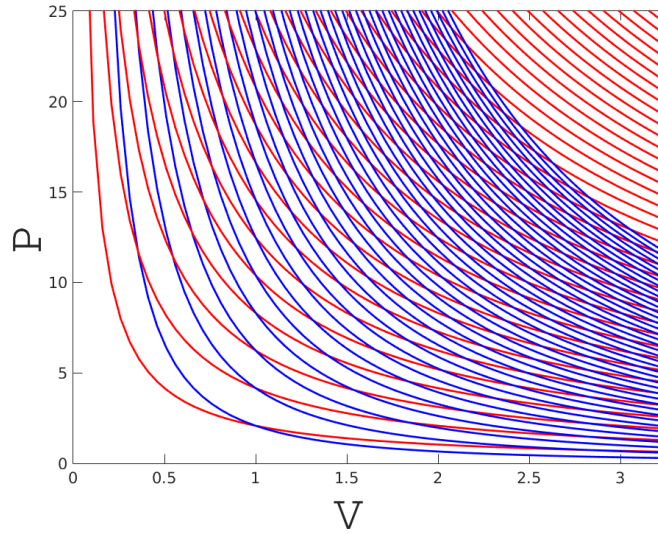


Figure 1.7: System of isotherms (red lines) and adiabats (blue lines). One can find that in every point on the $P - V$ plane the adiabat is always steeper than an isotherm.

1.5.20 Polytrropic Processes

Processes in which the heat capacity of a body remains constant are defined as *polytrropic* ones. Thus, the condition which is observed in a polytrropic process is

$$c = \text{constans}$$

Let us find the equation of a polytrope for an ideal gas. We shall write the equation of the first law, substituting $c m dT$ for dQ and $c_v m dT$ for dU :

$$c m dT = c_v m dT + P dV \quad (1.41)$$

This equation includes all three parameters: P , V and T . Let us differentiate the equation $PV = nRT$

$$PdV + VdP = nRdT \quad (1.42)$$

Excluding dT from equations (1.41) and (1.42) and bringing together similar terms, we get

$$\begin{aligned} PdV + VdP &= nR \frac{PdV}{(c - c_v)m} \\ PdV + VdP &= \frac{\mathfrak{M}}{M} R \frac{PdV}{(c - c_v)\mathfrak{M}} \end{aligned}$$

After rearranging terms we get

$$\begin{aligned} PdV + VdP - \frac{R}{M} \frac{PdV}{(c - c_v)} &= 0 \\ \left\{ (c - c_v) - \frac{R}{M} \right\} PdV + (c - c_v) VdP &= 0 \end{aligned}$$

According to Robert Mayer's relation we can rewrite $\frac{R}{M}$ as $(c_p - c_v)$.

$$\begin{aligned} \{(c - c_v) - (c_p - c_v)\} PdV + (c - c_v) VdP &= 0 \\ (c - \cancel{c_v} - c_p + \cancel{c_v}) PdV + (c - c_v) VdP &= 0 \\ (c - c_p) \frac{dV}{V} + (c - c_v) \frac{dP}{P} &= 0 \end{aligned}$$

After separation of variables we get the following equation:

$$\begin{aligned} (c - c_p) \int \frac{dV}{V} + (c - c_v) \int \frac{dP}{P} &= 0 \\ (c - c_p) \ln(V) + (c - c_v) \ln(P) &= \text{const} \\ \frac{c - c_p}{c - c_v} \ln(V) + \ln(P) &= \text{const}' \\ PV^{\frac{c - c_p}{c - c_v}} &= \text{const}' \end{aligned}$$

Introducing n as a polytropic index as follows:

$$n = \frac{(-1)(c - c_p)}{(-1)(c - c_v)} = \frac{(c_p - c)}{(c_v - c)}$$

the equation of a polytropic process reads as

$$PV^n = \text{const.}$$

Table 1.1: Summary of n and c for different quasi static processes.

Process	Equation	Polytropic index	Specific heat
Isobaric	$P_1 V_1^0 = P_2 V_2^0$	0	c_p
Isochoric	$V_1 = V_2$	∞	c_v
Isotherm	$P_1 V_1^1 = P_2 V_2^1$	1	∞
Adiabatic	$P_1 V_1^\gamma = P_2 V_2^\gamma$	$\frac{c_p}{c_v}$	0
Line with zero intersection	$P_1 V_1^{-1} = P_2 V_2^{-1}$	-1	$\frac{c_p + c_v}{2}$

1.6 Applications of Classical Thermodynamics

Thermodynamics is a science which aids the engineer in the design of processes and equipment which are useful to mankind. Engineering design involves a great deal of problem solving. Hence, it is important for a student early in his or her academic career to begin to acquire good habits with respect to problem solving procedures. There are certain steps and procedures which are fairly common to most engineering analysis. A general methodology for problem solving involves the following major points:

1. Problem-solving usually begins as a written or verbal statement. The information contained in this statement must be translated into sketches, diagrams, and symbols. Students frequently attempt to put numbers into equations without ever determining the nature of the problem.
2. Sketches of the system, with the appropriate system boundaries indicated, are of great value in approaching a problem in a consistent manner.
3. Process diagrams, such as a PV diagram, are extremely helpful as an aid in picturing the initial and final states and the path of the process.
4. Idealization or assumptions should be listed that might be necessary in order to solve the problem.
5. Determine what energy interactions are important, and recognize the sign conventions on these terms.
6. Complete the solution. Watch the units used in the various equations, so that they are consistent. Is the numerical answer reasonable in the light of your common experience?

Problem 1

A thermodynamic system consists of a vertically oriented double cylinder with different cross sections (see Fig.1.8). Both sides of the cylinders are opened and inside them there are two massive freely moving pistons. The mass of the pistons are 5 kg and they are connected with an ideal rope. The rope is under tension. The cross sectional area of the upper piston is $\Delta A = 10 \text{ cm}^2$ greater than that of the lower one. The pistons confine 1 mol of an ideal gas and the outer pressure is $P_0 = 10^5 \text{ Pa}$. What temperature difference is required for slowly displacing the pistons by $b = 5 \text{ cm}$?

During the displacement of the pistons the pressure of the confined gas remains constant. Hence the equations of mechanical equilibrium are

$$P_0 A_2 + mg + \mathcal{T} - P A_2 = 0 \quad (1.43)$$

$$P A_1 + mg - \mathcal{T} - P_0 A_1 = 0 \quad (1.44)$$

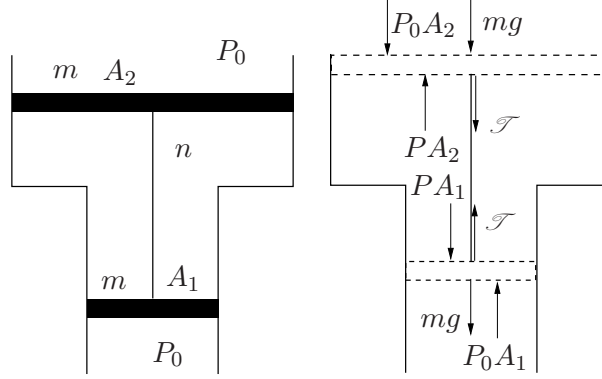


Figure 1.8: Vertically oriented double cylinder.

By adding these equations we can eliminate the constraint force \mathcal{T} hence

$$\begin{aligned}
 2mg + P_0(A_2 - A_1) - P(A_2 - A_1) &= 0 \\
 2mg + P_0\Delta A - P\Delta A &= 0 \\
 P &= \frac{2mg}{\Delta A} + P_0
 \end{aligned} \tag{1.45}$$

The equations of state of the confined gas are

$$PV_1 = nRT_1 \tag{1.46}$$

$$PV_2 = nRT_2 \tag{1.47}$$

By subtracting the two equations we get

$$\begin{aligned}
 P(V_2 - V_1) &= nR(T_2 - T_1) \\
 \Delta V &= A_2b - A_1b = b\Delta A \\
 P\Delta A &= nR\Delta T \\
 \Delta T &= \frac{P\Delta A}{nR}
 \end{aligned}$$

Substituting equation (1.45) into P , we get

$$\Delta T = \frac{\Delta A}{nR} \left(\frac{2mg}{\Delta A} + P_0 \right) \tag{1.48}$$

Problem 2

A hydrothermodynamic system consists of a vertically oriented double cylinder with different cross sections (see Fig.1.9). Both sides of the cylinders are opened and inside them there are two freely moving pistons. The mass of the pistons is negligible and they are connected with an ideal rope. The rope is under tension. The cross sectional area of the upper piston is ΔA greater than that of the lower one. The pistons confine ideal liquid. The mechanical density of the liquid ρ and the the outer pressure P_0 are known. Find the constraint force \mathcal{T}

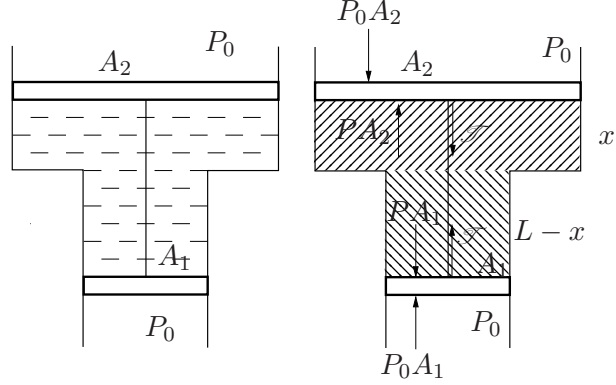


Figure 1.9: Vertically oriented double cylinder.

The water columns are in mechanical equilibrium so that the net force on them must be zero.

$$P_0 A_2 + m_2 g + \mathcal{T} - P A_2 = 0 \quad (1)$$

$$P A_1 + m_1 g - \mathcal{T} - P_0 A_1 = 0 \quad (2)$$

The masses of the water columns can be expressed in x and $L - x$ as follows:

$$P_0 A_2 + \rho A_2 x g + \mathcal{T} - P A_2 = 0 \quad (1')$$

$$P A_1 + \rho A_1 (L - x) g - \mathcal{T} - P_0 A_1 = 0 \quad (2')$$

By adding the equations we get

$$P_0 (A_1 - A_2) + \rho g (A_2 x + A_1 L - A_1 x) - P (A_2 - A_1) = 0$$

$$P_0 \Delta A - P \Delta A + \rho g A_1 L + \rho g \Delta A x = 0$$

We can express the length x of the upper water column as a function of ρ and the diameters of the pistons.

$$x = \frac{P - P_0}{\rho g} - L \frac{\rho g A_1}{\rho g \Delta A} = \frac{P - P_0}{\rho g} - L \frac{A_1}{\Delta A}$$

From Eq.(1) we get

$$\mathcal{T} = P A_2 - m_1 g - P_0 A_2$$

$$\mathcal{T} = (P - P_0) A_2 - m_2 g$$

$$\mathcal{T} = (P - P_0) A_2 - \rho A_2 x g$$

$$\mathcal{T} = (P - P_0) A_2 - \rho g A_2 \left(\frac{P - P_0}{\rho g} - L \frac{A_1}{\Delta A} \right)$$

Finally, the tension force reads

$$\mathcal{T} = \rho g L \frac{A_1 A_2}{A_2 - A_1}$$

Problem 3

A thermodynamic system consists of a horizontally oriented cylinder and a movable piston as it can be seen in Fig.1.10. The mass of the piston is 20 kg and confines a certain amount of a monoatomic ideal gas. Initially the piston is fixed. At a given moment the the piston is released with zero initial speed. The confined gas is heated in such a way that the piston gains $v = 0.8$ m/s speed and during the process it moves with constant acceleration. How much heat is exchanged if the outer pressure is negligible?

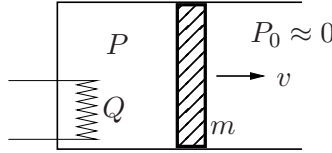


Figure 1.10: Piston with constant acceleration.

Since the acceleration is constant the pressure (and the net force) must be constant. One of our kinematic rules is applies

$$\begin{aligned}
 v^2 &= v_0^2 + 2a(x - x_0) \quad / a = F/m = PA/m/ \\
 v^2 &= 2 \frac{PA}{m} (x - x_0) \\
 v^2 &= 2 \frac{P}{m} Ax - 2 \frac{P}{m} Ax_0 \quad / V = Ax, V_0 = Ax_0/ \\
 v^2 &= 2 \frac{P}{m} V - 2 \frac{P}{m} V_0 \\
 \frac{mv^2}{2} &= PV - PV_0 \\
 \frac{mv^2}{2} &= P\Delta V
 \end{aligned}$$

According to the first law the internal energy change for expansion:

$$\begin{aligned}
 \Delta U &= Q - |W| \\
 Q &= \Delta U + |W|
 \end{aligned}$$

By definition the internal energy $\Delta U = f/2 P_2 V_2 - f/2 P_1 V_1 = 3/2 P \Delta V$. Because it is an isobaric process the calculation of work does not require integration $W = P \Delta V$.

$$\begin{aligned}
 Q &= \frac{3}{2} P \Delta V + P \Delta V \\
 Q &= \frac{5}{2} P \Delta V = \frac{5}{2} \frac{mv^2}{2}
 \end{aligned}$$

Problem 4

A thermodynamic system (see Fig.1.11) consists of a horizontally oriented, thermally isolated cylinder and two movable pistons. The masses of the pistons are 8.31 kg and confine a certain amount of a monoatomic ideal gas. At a given moment the pistons start to move with $3v$ and v initial speeds. What is the maximum temperature of the confined gas?

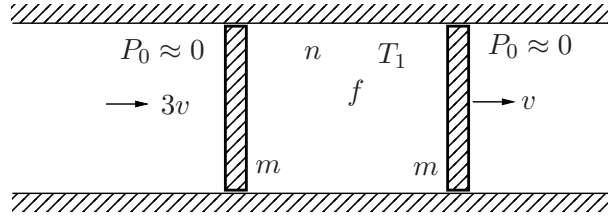


Figure 1.11: Two movable pistons.

At that state when $T = T_{\max}$ the distance between the pistons is minimum (see Fig.1.12) and they move with the same speed u . Since the conservation of momentum applies

$$m3v + mv = 2mu \quad (1.49)$$

$$u = 2v \quad (1.50)$$

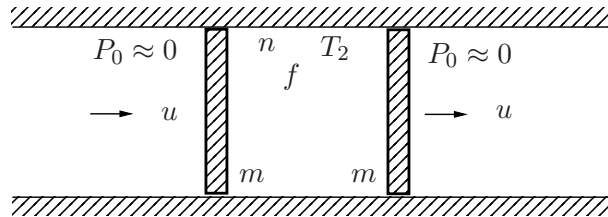


Figure 1.12: Pistons at the tightest position.

$$\Delta U_{12} = U_2 - U_1 = \frac{f}{2}P_2V_2 - \frac{f}{2}P_1V_1$$

$$K_2 - K_1 = 2\frac{mu^2}{2} - \left(\frac{m(3v)^2}{2} + \frac{mv^2}{2}\right)$$

$$K_2 - K_1 = m(2v)^2 - \left(\frac{9mv^2}{2} + \frac{mv^2}{2}\right)$$

$$K_2 - K_1 = 4mv^2 - 5mv^2$$

According to the conservation of mechanical energy $K_2 - K_1 = -\Delta U$, hence

$$\begin{aligned} -mv^2 &= \frac{f}{2}P_1V_1 - \frac{f}{2}P_2V_2 \\ -mv^2 &= \frac{f}{2}nRT_1 - \frac{f}{2}nRT_2 \\ T_2 &= T_1 + \frac{2mv^2}{fnR} \end{aligned}$$

Problem 5

Let us consider a tube which is bent and the horizontal part of the tube is partially filled with mercury. At a certain time instant the tube is rotated around the vertical axis as it can be seen in Fig.1.13. It is then spun around the axis shown until the mercury level is as high as $h = 2L$. During the acceleration a quarter of the mass of the confined air is leaked, hence the pressure and the temperature of the confined gas decreases. The temperature decreases to $4/5T_0$. The outer pressure $P_0 = \rho g(3/2)L$. Find the angular velocity ω .

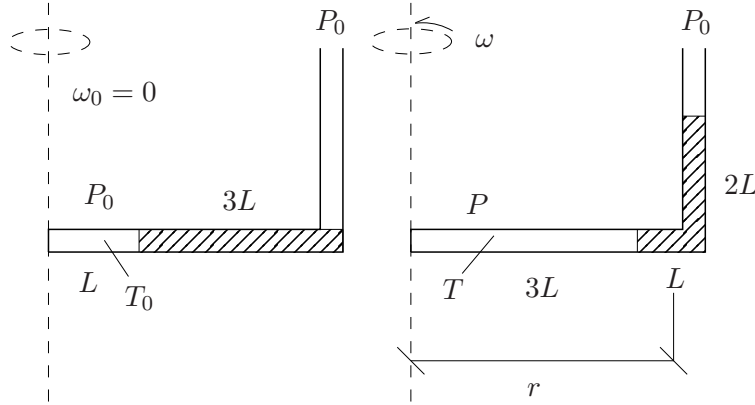


Figure 1.13: Rotating mercury column.

Applying the equation of state for the confined gas in the initial state

$$P_0AL = \frac{m}{M}RT, \quad (1)$$

and final state we get

$$P3AL = \frac{m - \frac{m}{4}}{M}R\frac{4}{5}T_0 \quad (2)$$

$$3PAL = \frac{3}{5}\frac{m}{M}RT_0. \quad (2')$$

By dividing the equations, we get

$$\begin{aligned} \frac{P_0}{3P} &= \frac{5}{3} \\ P &= \frac{P_0}{5} = \frac{4}{5}\rho g \end{aligned}$$

According to Newton's second Law for central mass of the horizontal part of the mercury

$$\begin{aligned}\sum F &= mr\omega^2 \\ \rho g 2LA + P_0A - PA &= mr\omega^2 \\ \rho g 2LA + P_0A - \frac{P_0}{5}A &= \rho AL \left(\frac{7}{2}L \right) \omega^2 \\ \rho g 2LA + \frac{4P_0}{5}A &= \frac{7}{2}\rho AL^2\omega^2 \\ \rho g 2L + \frac{4 \cdot 2}{5}\rho g \frac{3}{2}L &= \frac{7}{2}\rho L^2\omega^2 \\ 2g + \frac{6}{5}g &= \frac{7}{2}L\omega^2 \\ \omega &= \sqrt{\frac{32g}{35L}}\end{aligned}$$

Problem 6

A certain amount of monoatomic gas performs ABCA cycle shown in Fig.1.14. Find the thermal efficiency η .

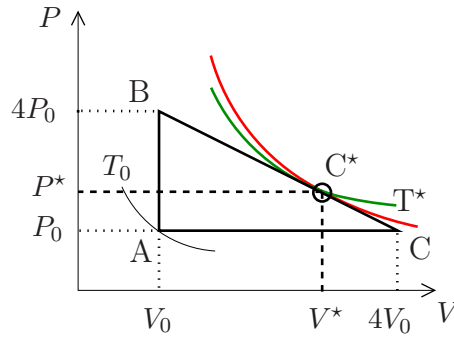


Figure 1.14: ABCA cycle.

The heat exchange during the BC process changes interestingly. An adiabat should be found, which just touches the BC process line.

Since mathematically the BC process is a linear function

$$P(V) = -\frac{P_0}{V_0}V + 5P_0$$

The slope of an adiabat is

$$\begin{aligned}PV^\gamma &= \text{CONST} \\ d(PV^\gamma) + P\gamma V^{\gamma-1}dV &= 0 \\ \frac{dP}{dV} &= -\gamma \frac{P}{V}\end{aligned}$$

If we equate the slope of the adiabat to the slope of the BC process we get

$$\begin{aligned} -\gamma \frac{P}{V^*} &= -\frac{P_0}{V_0} \\ -\gamma \frac{1}{V^*} \left(-\frac{P_0}{V_0} V + 5P_0 \right) &= -\frac{P_0}{V_0} \\ -\frac{\gamma}{V_0} + \frac{5\gamma}{V^*} &= \frac{1}{V_0} \\ V^* &= \frac{5\gamma V_0}{\gamma + 1} = \frac{25V_0}{8} \end{aligned}$$

The P^* reads as

$$\begin{aligned} P^*(V^*) &= -\frac{P_0}{V_0} V^* + 5P_0 \\ P^* &= -\frac{P_0}{V_0} \frac{25V_0}{8} + 5P_0 \\ P^* &= -\frac{P_0}{V_0} \frac{25V_0}{8} + 5P_0 \\ P^* &= \frac{15}{8} P_0 \end{aligned}$$

From the unified gas rule

$$\frac{P_0 V_0}{T_0} = \frac{P^* V^*}{T^*}$$

T^* can be obtained as follows:

$$\begin{aligned} \frac{P_0 V_0}{T_0} &= \frac{\frac{15P_0}{8} \frac{25V_0}{8}}{T^*} \\ T^* &= \frac{375}{64} T_0 \end{aligned}$$

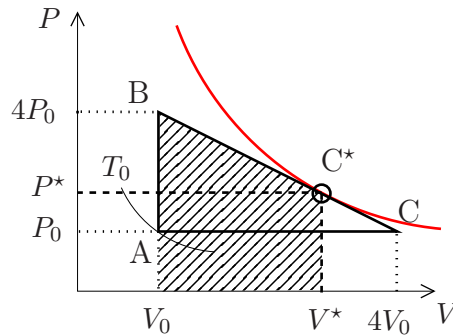


Figure 1.15: ABCA cycle.

The thermal efficiency by definition is

$$\eta = \frac{W}{Q_{\text{in}}}$$

$$\eta = \frac{W_{\text{ABCA}}}{Q_{AB} + Q_{\text{BC}^*}}$$

The absorbed heat during in the isochoric process:

$$Q_{AB} = c_v m \Delta_{AB} = \frac{3}{2} \frac{R}{M} m (4T_0 - T_0)$$

$$Q_{AB} = \frac{3}{2} \frac{R}{M} m (3T_0)$$

$$Q_{AB} = \frac{9}{2} P_0 V_0$$

The absorbed heat during in the BC^* process:

$$Q_{\text{BC}^*} = \Delta U_{\text{BC}^*} + |W_{\text{BC}^*}|$$

$$Q_{\text{BC}^*} = \frac{3}{2} \frac{R}{M} m (T^* - 4T_0) + \frac{4P_0 + P^*}{2} (V^* - V_0)$$

$$Q_{\text{BC}^*} = \frac{3}{2} \frac{R}{M} m \left(\frac{375}{64} T_0 - 4T_0 \right) + \frac{4P_0 + \frac{15P_0}{8}}{2} \left(\frac{25V_0}{8} - V_0 \right)$$

$$Q_{\text{BC}^*} = \frac{289}{32} P_0 V_0$$

So the thermal efficiency

$$\eta = \frac{W_{\text{ABCA}}}{Q_{AB} + Q_{\text{BC}^*}}$$

$$\eta = \frac{\frac{9P_0 V_0}{2}}{\frac{9P_0 V_0}{2} + \frac{289P_0 V_0}{32}} = \frac{16 \cdot 9}{9 \cdot 16 + 289}$$

$$\eta = \frac{144}{433}$$

Find the maximum temperature of the BC process. We should study the maximum of the PV multiplication, hence

$$P(V) = -\frac{P_0}{V_0} V + 5P_0 / \times V$$

$$PV = -\frac{P_0}{V_0} V^2 + 5P_0 V$$

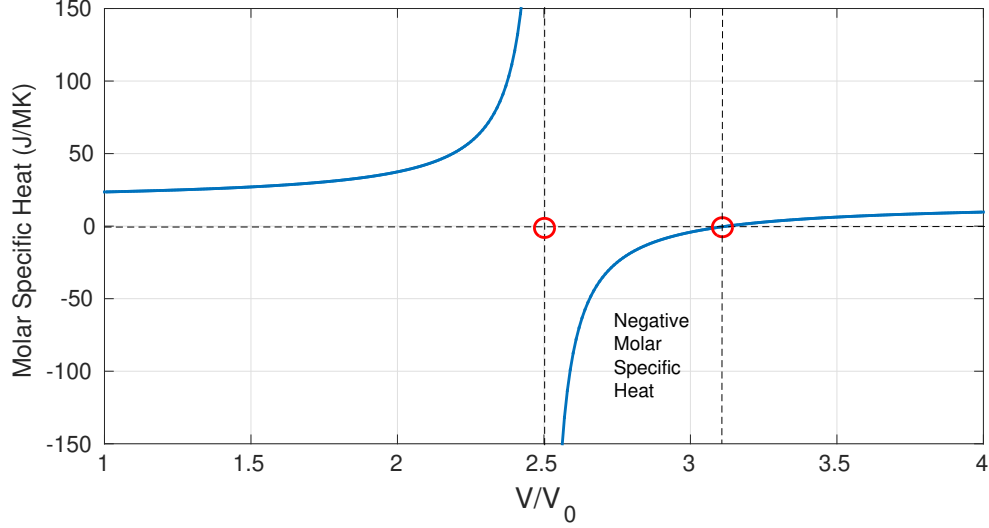


Figure 1.16: Behavior of specific heat.

Since at the point V' of extremum the derivative of the function vanishes

$$\begin{aligned}\frac{d}{dV}(PV) &= 0 \\ \frac{d}{dV}(PV) &= -\frac{P_0}{V_0}2V + 5P_0 \\ -\cancel{\frac{P_0}{V_0}}2V + 5\cancel{P_0} &= 0 \\ V' &= \frac{5}{2}V_0 = 2.5V_0 \\ P' &= 2.5P_0\end{aligned}$$

Hence the maximum temperature

$$\begin{aligned}\frac{P_0V_0}{T_0} &= \frac{2.5P_0 \cdot 2.5V_0}{T'} \\ T' &= 2.5^2 T_0 = 6.25T_0\end{aligned}$$

In comparison to $T^* = 5.86T_0$ we can see as the temperature decreases from $6.25T_0$ to $5.86T_0$ the gas absorbs heat. This means that the specific heat capacity of the gas can be negative as it can be seen in Fig.1.16.

Problem 7

A thermodynamic system consists of two fixed and identical cylinders and two movable pistons. The pistons are massless and they are joined by a rigid rod of negligible mass as it can be seen in fig.1.17. Both cylinders contain the same type of ideal gas. The cylinder on the left contains two times as much gas as the other one. Both gases are at the same temperature and the cross-sectional area of the cylinders A and the external

pressure P_0 are known. Find the P_1 , P_2 pressures of the confined gases and the F_1 , F_2 forces exerted by the pistons.

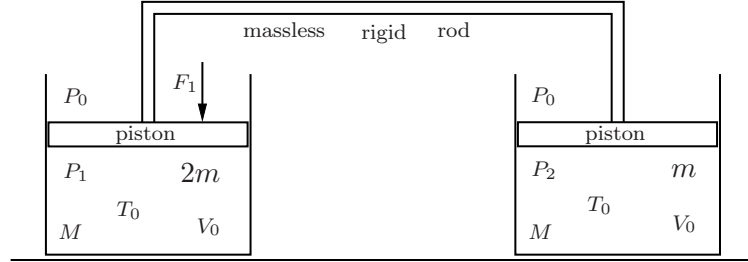


Figure 1.17: Joined pistons.

Because the piston is in mechanical equilibrium

$$P_0 A + F_1 - P_1 A = 0 \quad (1.51)$$

$$P_0 A - F_1 - P_2 A = 0 \quad (1.52)$$

By adding the two equations

$$P_1 + P_2 = 2P_0 \quad (1.53)$$

The equations of states are

$$P_1 V_0 = \frac{2m}{M} R T_0 \quad (1.54)$$

$$P_2 V_0 = \frac{m}{M} R T_0 \quad (1.55)$$

$$\frac{P_1}{P_2} = 2 \rightarrow P_2 = \frac{P_1}{2}$$

$$P_1 + P_2 = 2P_0 \quad (1.56)$$

$$P_2 = \frac{P_1}{2} \quad (1.57)$$

$$P_1 = \frac{4P_0}{3} \quad P_2 = \frac{2P_0}{3} \quad (1.58)$$

From equation (1.51)

$$F_1 = P_1 A - P_0 A$$

$$F_1 = \frac{4P_0}{3} A - P_0 A$$

$$F_1 = \frac{P_0 A}{3}$$

Problem 8

As Fig.1.18 shows a rigid insulated tank is divided into two equal volumes by a partition. Initially, 1 kg of a gas is introduced into one side of the partitioned tank, and the other side remains evacuated. In the equilibrium state the pressure and temperature are 2 bars and 100 °C, respectively. The partition is then pulled out, and the gas is allowed to expand into the entire tank. Determine the final pressure and temperature at equilibrium if the gas is ideal.

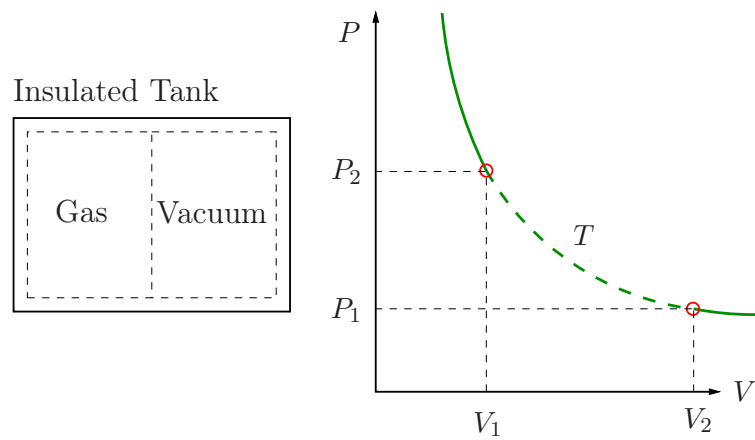


Figure 1.18: Free expansion.

SOLUTION The boundaries of the closed system will be selected to lie just inside the walls of the entire rigid, insulated tank, including the section which is initially evacuated. The system may be idealized as a simple compressible one. For such a system the energy equation is

$$Q + W = \Delta U$$

The boundary work associated with the rigid tank is zero, and all other work effects are absent. In addition, Q is zero for the insulated boundary. Because Q and W are zero for this process, we may write for the finite change of state that

$$\Delta U = 0$$

Consequently, the expansion of the gas in this case is one of constant internal energy; that is, U_2 equals U_1 .

For an ideal gas the internal energy is solely a function of the temperature for a given equilibrium state. Since the internal energy is constant, the initial and final temperatures of the ideal gas undergoing this expansion must be the same. Since the final volume is twice the initial volume, the final pressure is one-half the original value. The process is shown on the PV diagram. The path between states 1 and 2 is drawn as a dashed line, since the process is non-quasi-static and the temperature is not defined except at the equilibrium end states.

1.7 The Second Law

1.7.1 Carnot Cycle

Heat engines take heat from some hot reservoir, deliver heat to some cold reservoir, and perform an amount of work, i.e. they partially transform heat into work. Consider a Carnot's reversible engine (see Fig.1.19) operating between a single hot reservoir at empirical temperature T_1 and a single cold reservoir at temperature T_2 . The Carnot cycle is accomplished in four steps consisting in two isothermal and two adiabatic transformations (Fig.1.19)). During the first isothermal process, the Carnot's engine

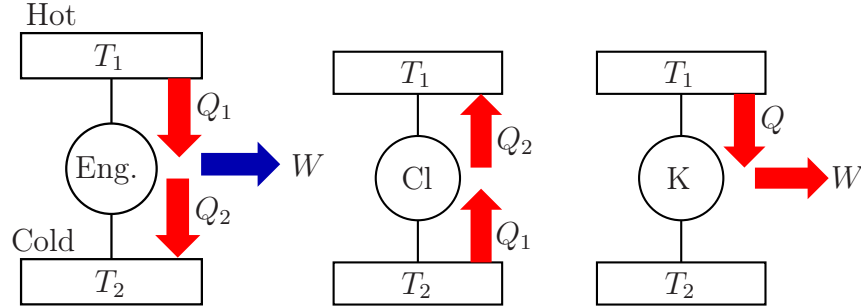


Figure 1.19: A typical heat engine and the Clausius and Kelvin engines.

absorbs an amount of heat Q_1 at temperature T_1 . In the second step, the system undergoes an adiabatic expansion decreasing the temperature from T_1 to T_2 . Afterwards, the system goes through an isothermal compression at temperature T_2 (step 3) and finally (step 4), an adiabatic compression which brings the system back to its initial state. After one cycle, the engine has performed a quantity of work W .

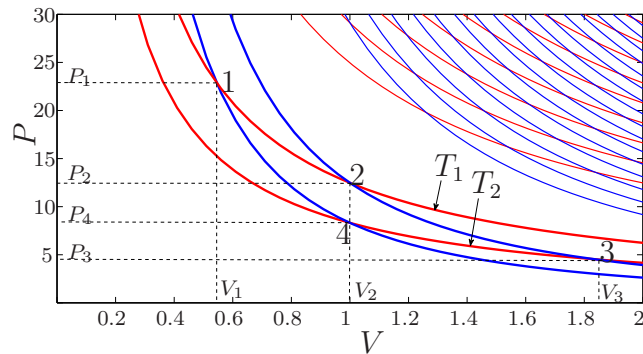


Figure 1.20: The Carnot Cycle.

The first law establishes the equivalence between heat and work but is silent about the restrictions on the transformation of one into the other. The role of the second law of thermodynamics is to place such limitations and to reflect the property that natural processes evolve spontaneously in one direction only. The first formulations of the second law were proposed by Clausius (1850, 1851) and Kelvin (1851) and were stated

in terms of the impossibility of some processes to be performed. Clausius' statement of the second law is enunciated as follows: *No process is possible whose sole effect is to transfer heat from a cold body to a hot body.* Kelvin's statement considers another facet: *it is impossible to construct an engine which can take heat from a single reservoir, and convert it entirely to work in a cyclic process.*

Constantin Declaratory formulated thermodynamics on a purely mathematical axiomatic foundation. His statement of the second law is known as the Principle of Declaratory, which may be formulated as follows: *In every neighborhood of any arbitrary initial state P_0 of a physical system, there exists neighboring states that are not accessible from P_0 along quasi-static adiabatic paths.*

We are going to build-up a formal definition of a new quantity, the entropy – so named by Clausius from the Greek words en (in) and trope (turning) for representing “capacity of change or transformation” – which is as fundamental and universal (for equilibrium systems) as the notion of energy. In the second part, which constitutes truly the essence of the second law, we shall enounce the principle of entropy increase during an irreversible process.

Consider a homogeneous system of constant mass undergoing a reversible transformation between two equilibrium states A and B. The quantity of

$$\int_A^B dQ_{\text{rev}}$$

depends on the path followed between states A and B (in mathematical terms, it is an imperfect differential) and therefore cannot be selected as a state variable. However, experimental observations have indicated that by dividing dQ_{rev} by a uniform and continuous function $T(\theta)$ of an empirical temperature θ , one obtains an integral which is independent of the path and may therefore be identified with a state function, called entropy and denoted S

$$\int_A^B \frac{dQ_{\text{rev}}}{T(\theta)} = S_B - S_A$$

Since in reversible processes, quantities of heat are additive, entropy is also additive and is thus an extensive quantity. A function like $T(\theta)$ which transforms an imperfect differential into a perfect one is called an integrating factor. The empirical temperature is that indicated by a mercury or an alcohol thermometer or a thermocouple and its value depends of course on the nature of the thermometer; the same remark is true for the entropy, as it depends on $T(\theta)$. It was the great merit of Kelvin to propose a temperature scale for T , the absolute temperature, independently of any thermodynamic system. In differential terms, it takes the form

$$dS = \frac{dQ_{\text{rev}}}{T}$$

This is a very important result as it introduces two new concepts; absolute temperature and entropy. The latter can be viewed as the quantity of heat exchanged by the system during a reversible process taking place at the equilibrium temperature T . Note that

only differences in entropy can be measured. Given two equilibrium states A and B, it is always possible to determine their entropy difference regardless of whether the process between A and B is reversible or irreversible. Indeed, it suffices to select or imagine a reversible path joining these initial and final equilibrium states. The question is how to realize a reversible heat transfer. Practically, the driving force for heat transfer is a temperature difference and for reversible transfer, we need only imagine that this temperature difference is infinitesimally small so that $dQ_{\text{rev}} = \lim_{\Delta T \rightarrow 0} dQ$. Nevertheless, when the process takes place between non-equilibrium states, the problem of the definition of entropy is open, and actually not yet definitively solved. The efficiency of a heat engine, in particular that of Carnot, is defined by the ratio of the work produced to the heat supplied

$$\eta = \frac{W}{Q_1}$$

for a cycle one has, in virtue of the first law, $W = Q_1 - |Q_2|$, so that

$$\eta = 1 - \frac{|Q_2|}{Q_1} \quad (1.59)$$

Finally, making use of equation (1.59), it is found that the efficiency of a reversible cycle is

$$\eta = 1 - \frac{T_2}{T_1} \quad (1.60)$$

As it will be seen, this is the maximum value for the efficiency of any heat engine working between the selected heat reservoirs.

1.7.2 Absolute Temperature

Consider a Carnot's reversible engine (see Fig.) operating between a single hot reservoir at the unknown empirical temperature θ_1 and a single cold reservoir at temperature θ_2 . The Carnot cycle is accomplished in four steps consisting in two isothermal and two adiabatic transformations.

During the first isothermal process, the Carnot's engine absorbs an amount of heat Q_1 at temperature θ_1 . In the second step, the system undergoes an adiabatic expansion decreasing the temperature from θ_1 to θ_2 . Afterwards, the system goes through an isothermal compression at temperature θ_2 (step 3) and finally (step 4), an adiabatic compression which brings the system back to its initial state. After one cycle, the engine has performed a quantity of work W but its total variation of entropy is zero

$$\Delta S_{\text{engine}} = \frac{|Q_1|}{T(\theta_1)} - \frac{|Q_2|}{T(\theta_2)} = 0 \quad (1.61)$$

Selecting the reference temperature as $T(\theta_2) = 273.16$, the triple point temperature of water, it follows from Eq.1.61

$$T(\theta_1) = 273.16 \frac{|Q_1|}{|Q_2|} \quad (1.62)$$

The ratio $|Q_1|/|Q_2|$ is universal in the sense that it is independent of the working substance. Therefore, Carnot cycles offer the opportunity to reduce temperature measurements to measurements of quantities of heat and to define an absolute scale of positive temperatures, independently of the measurement of temperature on any empirical temperature scale, which depends on thermometric substance.

1.7.3 The Principle of Increase of Entropy

The second law was formulated by Clausius (1865) for isolated systems in terms of the change of the entropy in the form

$$\Delta S \geq 0 \quad (1.63)$$

It is therefore concluded that entropy is increased as internal constraints are removed and that entropy reaches a maximum in the final state of equilibrium, i.e. the state of maximum “disorder”. In other terms, in isolated systems, one has

$$\Delta S = S_{\text{fin}} - S_{\text{in}} \geq 0 \quad (1.64)$$

Thus, entropy is continuously increasing when irreversible processes take place until it reaches a state of maximum value, the equilibrium state, which in mathematical terms is characterized by $dS = 0$, $d^2S < 0$. This statement constitutes the celebrated principle of entropy increase and is often referred to as the Second Law of thermodynamics. It follows that a decrease in entropy $dS < 0$ corresponds to an impossible process. Another consequence is that the entropy of an isolated system remains constant when reversible processes occur in it.

1.8 Gibbs' Equation

Let us now gather the results obtained for the first and second laws. Consider a reversible transformation, taking place in a closed system, for which the first law takes the form

$$dU = dQ_{\text{rev}} - PdV \quad (1.65)$$

and combine it with the definition of entropy $dQ_{\text{rev}} = TdS$, resulting in

$$dU = TdS - PdV \quad (1.66)$$

Expression (1.66) is known as Gibbs' equation; it is, however, not complete when there are matter exchanges as in open systems, or variations in composition as in chemical reactions. To calculate the reversible work corresponding to a chemical reaction involving n species, it is necessary to devise a reversible process of mixing.

$$dW_{\text{rev}}^{\text{ch}} = \sum_{k=1}^n \mu_k dN_k \quad (1.67)$$

where μ_k is defined as the chemical potential of substance k . The properties of the chemical potential will be explicitly examined below. With this additional term, one

is led to the generalized Gibbs' equations

$$dU = TdS - PdV + \sum_{k=1}^n \mu_k dN_k \quad (1.68)$$

As discussed in the forthcoming sections, the Gibbs' equation plays a fundamental role in equilibrium thermodynamics.

1.8.1 Fundamental Relations and State Equations

It follows directly from Gibbs' equation (1.68) that

$$U = U(S, V, N_1, N_2, \dots, N_n) \quad (1.69)$$

or, solving with respect to S ,

$$S = S(U, V, N_1, N_2, \dots, N_n) \quad (1.70)$$

Relations like (1.69) or (1.70) expressing that U or S are single-valued functions of extensive state variables are called fundamental relations because they contain all thermodynamic information about the system. When U (respectively, S) is expressed as a function of the variables, we are speaking of the "energy representation" (respectively, "entropy representation").

Another consequence of Gibbs' equation (1.66) is that the intensive variables, represented by temperature, pressure and chemical potentials, can be defined as partial derivatives of U :

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S,N} \quad \mu_k = \left(\frac{\partial U}{\partial N_k} \right)_{S,V,N_{j \neq k}} \quad (1.71)$$

Since U is a function of S, V, N_k , the same remains true for T, P , and μ_k so that

$$T = T(S, V, N) \quad (1.72)$$

$$P = P(S, V, N) \quad (1.73)$$

$$\mu_k = \mu_k(S, V, N) \quad (1.74)$$

Such relationships between intensive and extensive variables are called *state equations*. The knowledge of one single state equation is not sufficient to describe the state of a system, which requires the knowledge of all the equations of state. For instance in the case of a monoatomic perfect gas, $PV = nRT$ does not constitute the complete knowledge of the system but must be complemented by $U = \frac{3}{2}nRT$, R being the gas constant and n the mole number.

1.8.2 Euler's Relation

The extensive property of U implies that, from the mathematical point of view, it is a first-order homogeneous function of the extensive variables:

$$U(\lambda S, \lambda V, \lambda N_1, \dots, \lambda N_k) = \lambda U(S, V, N_1, \dots, N_k), \quad (1.75)$$

where λ is an arbitrary scalar. One obtains Euler's relation

$$U = TS - PV + \mu N \quad (1.76)$$

1.8.3 Gibbs–Duhem's Relation

A differential equation among the intensive variables can be derived directly from Euler's relation. Indeed, after differentiating (1.76), it is found that

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \quad (1.77)$$

which, after using Gibbs' equation (1.68), yields Gibbs–Duhem's relation

$$SdT - VdP + Nd\mu = 0 \quad (1.78)$$

By introducing $v = V/N$ and $s = S/N$ the Gibbs–Duhem's relation takes the following form:

$$\mu = vdP - sdT \quad (1.79)$$

This equation plays an important role to the study of first order phase transitions (see Chapter 2). This relation implies that natural variables of the chemical potential are P and T hence G and μ are connected to each other. Indeed, μ and G characterize the phase transitions.

1.8.4 Thermodynamic Potentials

In mathematics and physics, the Legendre (or canonical) transformation is an involutive transformation on the real-valued convex functions of one real variable. Canonical transformation is commonly used in classical mechanics to derive the Hamiltonian formalism out of the Lagrangian formalism. In thermodynamics to derive the thermodynamic potentials. The new variable (p) is the partial derivative of the original function (L) with respect to the original variable (\dot{q}). The new function (H) is the difference between the original function and the product of the old and new variables.

$$-H(q, p, t) = L(q, \dot{q}, t) - \dot{q} \left(\frac{\partial L}{\partial \dot{q}} \right) = L - \dot{q}p \quad (1.80)$$

Typically, this transformation is useful because it shifts the dependence of, e.g., the energy from an extensive variable to its conjugate intensive variable, which can usually be controlled more easily in a physical experiment.

Several Legendre transformations are known as the thermodynamic potentials. Starting from the fundamental relation, $U = U(S, V, N_k)$, replace the entropy S with $\partial U / \partial S \equiv T$ as independent variable, the corresponding Legendre transform is,

$$F = U - \left(\frac{\partial U}{\partial S} \right) S = U - TS \quad (1.81)$$

which is known as Helmholtz's free energy.

Replacing the volume V with $\partial U / \partial V \equiv -P$, one defines the *enthalpy* H as

$$H = U - \left(\frac{\partial U}{\partial V} \right) V = U + PV \quad (1.82)$$

The Legendre transform which simultaneously replaces S with T and V with $-P$ is the so-called *Gibbs' free energy* G given by

$$G = U - TS + PV \quad (1.83)$$

The fundamental relations of F , H , and G read in differential form:

$$dF = -SdT - PdV + \sum_{k=1}^n \mu_k dN_k \quad (1.84)$$

$$dH = TdS + VdP + \sum_{k=1}^n \mu_k dN_k \quad (1.85)$$

$$dG = -SdT + VdP + \sum_{k=1}^n \mu_k dN_k \quad (1.86)$$

Another set of Legendre transforms can be obtained by operating on the entropy $S = S(U, V, N_1, \dots, N_n)$, and are called the Massieu-Planck functions, particularly useful in statistical mechanics.

The Grand (Landau) potential

Finally, we introduce Φ as a grand (Landau) potential. By definition $\Phi = U - TS - \mu N$. The grand potential is a quantity used in statistical mechanics, especially for irreversible processes in open systems. The grand potential is the characteristic state function for the grand canonical ensemble.

The mathematical forms of the most important potentials in thermodynamics are as follows

$$\begin{aligned} U &= TS - PV + \mu N \\ H &= U + PV = TS + \mu N \\ F &= U - TS = -PV + \mu N \\ G &= H - TS = \mu N \\ \Phi &= U - TS - \mu N = -PV \end{aligned}$$

By the graphical representation (see Fig.1.21) it is easier to see the interrelations between the thermodynamic potentials. On the left hand side Fig.1.21 summarizes how the quantities have to be added or subtracted, while on the right hand side one can see the natural variables of the following physical quantities: $U = U(S, V, N)$, $H = H(S, P, N)$, $F = F(T, V, N)$ and $G = G(T, P, N)$.

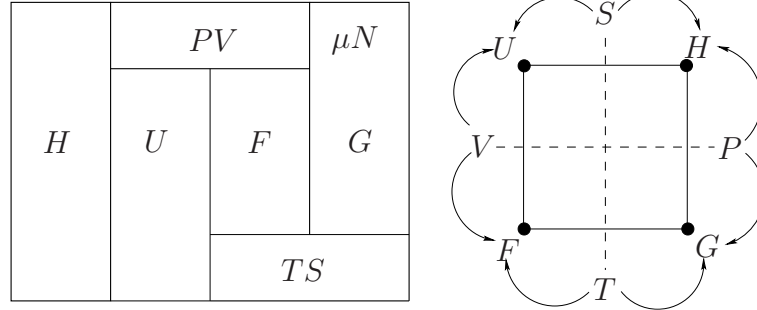


Figure 1.21: Relationships between thermodynamic potentials.

1.8.5 Thermodynamic Potentials and Extremum Principles

We have seen that the entropy of an isolated system increases until it attains a maximum value: the equilibrium state. Since an isolated system does not exchange heat, work, and matter with the surroundings, it will therefore be characterized by constant values of energy U , volume V , and mass N . In short, for a constant mass, the second law can be written as

$$dS \geq 0 \quad (1.87)$$

Because of the invertible roles of entropy and energy, it is equivalent to formulate the second principle in terms of U rather than S .

1.8.6 Minimum Energy Principle

Let us show that the second law implies that, in absence of any internal constraint, the energy U evolves to a minimum at S and V fixed:

$$dU \leq 0 \quad (1.88)$$

We will prove that if energy is not a minimum, entropy is not a maximum in equilibrium. Suppose that the system is in equilibrium but that its internal energy has not the smallest value possible compatible with a given value of the entropy. We then withdraw energy in the form of work, keeping the entropy constant, and return this energy in the form of heat. Doing so, the system is restored to its original energy but with an increased value of the entropy, which is inconsistent with the principle that the equilibrium state is that of maximum entropy. Since in most practical situations, systems are not isolated, but closed and then subject to constant temperature or (and) constant pressure, it is appropriate to reformulate the second principle by incorporating these constraints. The evolution towards equilibrium is no longer governed by the entropy or the energy but by the thermodynamic potentials.

1.8.7 Minimum Helmholtz's Free Energy Principle

For closed systems maintained at constant temperature and volume, the leading potential is Helmholtz's free energy F . In virtue of the definition of $F = U - TS$, one

has, at constant temperature,

$$dF = dU - TdS, \quad (1.89)$$

and, making use of the first law

$$dF = \delta Q - PdV - TdS \quad (1.90)$$

if V is maintained constant, the change of F is

$$dF = TdS \leq 0 \quad (1.91)$$

It follows that closed systems at fixed values of the temperature and the volume, are driven towards an equilibrium state wherein the Helmholtz's free energy is minimum. Summarizing, at equilibrium, the only admissible processes are those satisfying $dF \leq 0$ at T and V constant.

1.8.8 Minimum Enthalpy Principle

Similarly, the enthalpy $H = U + PV$ can also be associated with a minimum principle. At constant pressure, one has

$$dH = dU + PdV = \delta Q \quad (1.92)$$

When the system is not isolated, as in the case of closed and open systems, the entropy change in the system consists in two parts: dS_e due to exchanges of energy and matter with the outside, which may be positive or negative, and dS_i due to internal irreversible processes

$$dS = dS_e + dS_i \quad (1.93)$$

For closed systems, $\delta Q = TdS_e = T(dS - dS_i)$, whence, at fixed values of P and S ,

$$dH = TdS_i \leq 0, \quad (1.94)$$

as a direct consequence of the second law. Therefore, at fixed entropy and pressure, the system evolves towards an equilibrium state characterized by a minimum enthalpy, i.e.

$$dH = TdS_i \leq 0 \quad \text{at } S \text{ and } P \text{ constant} \quad (1.95)$$

1.8.9 Minimum Gibbs' Free Energy Principle

Similar considerations are applicable to closed systems in which both temperature and pressure are maintained constant but now the central quantity is Gibbs' free energy $G = U - TS + PV$. From the definition of G , one has at T and P fixed,

$$dG = dU - TdS + PdV = \delta Q - T(dS_e + dS_i) = -TdS_i \leq 0, \quad (1.96)$$

wherein use has been made of $dS_e = \delta Q/T$. This result tells us that a closed system, subject to the constraints T and P constant, evolves towards an equilibrium state where Gibbs' free energy is a minimum, i.e.

$$dG \leq 0 \text{ at } T \text{ and } P \text{ constant} \quad (1.97)$$

The above criterion plays a dominant role in chemistry because chemical reactions are usually carried out under constant temperature and pressure conditions.

It can be shown that the (maximum) work delivered in a reversible process at constant temperature is equal to the decrease in the Helmholtz's free energy:

$$dW_{\text{rev}} = -dF \quad (1.98)$$

This is the reason why engineers call frequently F the available work at constant temperature. Similarly, enthalpy and Gibbs' free energy are measures of the maximum available work at constant P , and at constant T and P , respectively. As a general rule, it is interesting to point out that the Legendre transformations of energy are a minimum for constant values of the transformed intensive variables.

1.8.10 Stability of Equilibrium States

Even in equilibrium, the state variables do not keep rigorous fixed values because of the presence of unavoidable microscopic fluctuations or external perturbations, like small vibrations of the container. We have also seen that irreversible processes are driving the system towards a unique equilibrium state where the thermodynamic potentials take extremum values. In the particular case of isolated systems, the unique equilibrium state is characterized by a maximum value of the entropy. The fact of reaching or remaining in a state of maximum or minimum potential makes that any equilibrium state be stable. When internal fluctuations or external perturbations drive the system away from equilibrium, spontaneous irreversible processes will arise that bring the system back to equilibrium.

$$C_V = \left(\frac{dQ}{dT} \right)_V > 0, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T > 0 \quad (1.99)$$

The first criterion is generally referred to as the condition of *thermal stability*; it means merely that, removing reversibly heat, at constant volume, must decrease the temperature. The second condition, referred to as *mechanical stability*, implies that any isothermal increase of pressure results in a diminution of volume, otherwise, the system would explode because of instability. Inequalities (1.99) represent mathematical formulations of *Le Chatelier's principle*, i.e. that any deviation from equilibrium will induce a spontaneous process whose effect is to restore the original situation. Suppose for example that thermal fluctuations produce suddenly an increase of temperature locally in a fluid. From the stability condition that C_V is positive, and heat will spontaneously flow out from this region ($dQ < 0$) to lower its temperature ($dT < 0$). If the stability conditions are not satisfied, the homogeneous system will evolve towards a state consisting of two or more portions, called phases, like liquid water and its vapour. Moreover, when systems are driven far from equilibrium, the state is no longer characterized by an extremum principle and irreversible processes do not always maintain the system stable.

1.8.11 Maxwell's Relations

As we have seen several important equations developed for the entropy change of simple, compressible systems by combining the first and second laws of thermodynamics. The first law in this particular case is $\delta Q + \delta W = dU$. For an internally reversible process, the heat and work interactions may be represented by TdS and $-PdV$. In order to summarize these four important relationships among properties of simple systems, they are collected together as a set and presented below:

$$dU = TdS - PdV + \sum_{k=1}^n \mu_k dN_k \quad (1.100)$$

$$dF = -SdT - PdV + \sum_{k=1}^n \mu_k dN_k \quad (1.101)$$

$$dH = TdS + VdP + \sum_{k=1}^n \mu_k dN_k \quad (1.102)$$

$$dG = -SdT + VdP + \sum_{k=1}^n \mu_k dN_k \quad (1.103)$$

These equations are sometimes referred to as the Gibbsian equations. They relate to the change in various properties of a simple compressible system during a differential change of equilibrium states. For the sake of simplicity we assume that N_k is kept constant hence $dN_k = 0$.

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad (1.104)$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \left(\frac{\partial F}{\partial V}\right)_T = -P \quad (1.105)$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad (1.106)$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad (1.107)$$

By applying the following mathematical theorem

$$\frac{\partial^2 f(x, y)}{\partial x \partial y} = \frac{\partial^2 f(x, y)}{\partial y \partial x} \quad (1.108)$$

we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (1.109)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (1.110)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (1.111)$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (1.112)$$

This set of equations is referred to as the Maxwell's relations. Their importance is not apparent at this point, but a simple example may help illustrate their usefulness. Consider a system at a given equilibrium state. For a differential change of state it is desirable to know the rate of change of entropy of the system as the volume is altered isothermally. This could apply, for example, to a gas contained within a piston-cylinder assembly which is expanded isothermally. It is not possible to measure $(\partial S/\partial V)_T$ directly for the process, since entropy variations cannot be evaluated directly. However, one of the Maxwell's relation states it is necessary only to measure the rate of change of pressure with temperature at constant value, since $(\partial P/\partial T)_V = (\partial S/\partial V)_T$.

1.8.12 Statistical Interpretation of Entropy

Thermodynamic systems are collections of huge numbers of atoms or molecules. How these atoms or molecules behave statistically determines the disorder in the system. In other words, the second law of thermodynamics is based on the statistics of systems with extremely large numbers of atoms or molecules.

As an analogy, suppose we take four identical coins, number them, and toss them. We could report the outcome in two different ways: either by specifying the outcome of each coin toss individually, or just by reporting the overall outcome as the number of heads.

Specifying the outcome of each coin toss individually is analogous to describing the *microstate* of a thermodynamic system. A microstate specifies the state of each constituent particle. For instance, in a monoatomic ideal gas with N atoms, a microstate is specified by the position and velocity of each of the N atoms. As the atoms move about and collide, the system changes from one microstate to another. The total number of heads for coin tossing is analogous to a *macrostate* of a thermodynamic system. A macrostate of an ideal gas is determined by the value of the macroscopic state variables (the pressure, volume, temperature, and internal energy).

In our four-coin model, each of the microstates is equally likely to occur on any toss. Each of the coins has equal probability of landing heads or tails. Since each of the 4 coins has 2 possible outcomes, there are $2^4 = 16$ different but equally probable microstates. There are only five macrostates: the number of heads can range from zero to four. The macrostates are not equally likely. A good guess would be that getting 2 heads is much more likely than 4 heads. To find the probability of a macrostate, we

count up the number of microstates corresponding to that macrostate and divide it by the the total number of microstates for all the possible macrostates.

It turns out, that the number of microstates for a given macrostate is related to the entropy of that macrostate in a simple way. Letting Ω stand for the number of microstates, the relationship is

$$S = k \ln \Omega \quad (1.113)$$

where k is Boltzmann's constant. The Boltzmann equation is inscribed on the tombstone of Ludwig Boltzmann, the Austrian physicist who made the connection between entropy and statistics in the late nineteenth century. The relationship between S and Ω has to be logarithmic because entropy is additive: if system 1 has entropy S_1 and system 2 has entropy S_2 , then the total entropy is $S_1 + S_2$. However, the number of microstates is *multiplicative*.

Entropy never decreases because the macrostate with the highest entropy is the one with the greatest number of microstates, and thus the highest probability.

1.8.13 The Third Law

The roots of this law appear in the study of thermodynamic quantities as the absolute temperature tends to zero. In 1909, Nernst formulated his heat theorem, later known as the third law of thermodynamics, to better understand the nature of chemical equilibrium. Nernst studied the operation of galvanic cells in low temperature. According to Nernst measurements as the temperature decreases the difference between G and H vanishes. Moreover, at the vicinity of absolute zero kelvin G and H have a mutual line tangent (with zero slope). Mathematically this is equivalent

$$\lim_{T \rightarrow 0} \left(\frac{\partial G}{\partial T} \right) = \lim_{T \rightarrow 0} \left(\frac{\partial H}{\partial T} \right) \quad (1.114)$$

Let us start with the definition of the Gibbs free energy

$$G = H - TS \rightarrow S = \frac{H - G}{T} \quad (1.115)$$

However, this ratio is indefinite because in the limit $T \rightarrow 0$ both the nominator and the denominator tends to zero:

$$S_{T \rightarrow 0} = \lim_{T \rightarrow 0} \left(\frac{H - G}{T} \right) = \frac{0}{0} \quad (1.116)$$

By using the L'Hospital rule one can eliminate this uncertainty:

$$S_{T \rightarrow 0} = \frac{\frac{\partial H}{\partial T} - \frac{\partial G}{\partial T}}{1} = 0 \quad (1.117)$$

Nernst's formulation states that the entropy change in any isothermal process approaches zero as the temperature at which the process occurs approaches zero, i.e.

$$(\Delta S)_{T \rightarrow 0} \rightarrow 0 \quad (1.118)$$

This statement is sufficient for any thermodynamic development, but sometimes the stronger Planck's statement ($S \rightarrow 0$ as $T \rightarrow 0$) is preferred. Since the third law is more of quantum statistical essence, it is not of the same nature as the other laws and no further reference will be made to it in this note.

Chapter 2

Phase Transitions

2.1 Introduction

A *phase* in thermodynamics is defined as a combination of homogeneous parts of a system having identical properties. A closed vessel contains water and a mixture of air and water vapour above it. The system consists of two phases: one is formed by the water, and the other by the mixture of air and water vapour. If we add a few pieces of ice to the water, then all these pieces form the third phase. Different crystalline modifications of a substance are also different phases. For instance, diamond and graphite are different solid phases of carbon.

In definite conditions, different phases of the same substance can be in equilibrium with one another while being in contact. The equilibrium of two phases is possible only within a definite temperature interval, and at a quite definite pressure P . Thus, the equilibrium states of two phases will be depicted in a $P - T$ diagram by the line

$$P = f(T) \tag{2.1}$$

Three phases of a single substance (solid, liquid, and gaseous, or liquid and two solid phases) can be in equilibrium only at single values of temperature and pressure which in the $P - T$ diagram correspond to what we call the *triple point*. It is proved in thermodynamics, in agreement with experiments, that the equilibrium of more than three phases of the same substance is impossible.

The transition from one phase to another is usually attended by the absorption or liberation of a certain amount of heat called the *latent heat of transition* or simply the *heat of transition*. Such transitions are called phase transitions of the first kind. There are also transitions from the crystalline modification to another that are not associated with the absorption or liberation of heat. These transitions are called phase transitions of the second kind. They include the transition to a superconductive state performed in the absence of a magnetic field, and also the transition between the two liquid phases of helium called helium-I and helium-II. The transition below the so-called Curie-temperature of paramagnetic materials to ferromagnetic one is also classified by phase transitions of the second kind. We shall consider only the phase transition of the first kind.

2.2 Liquid and Its Saturated Vapour

Let us consider the compression of a substance at a constant temperature (see Figure 2.1). Assume that the substance is initially gaseous. First, the pressure of the gas will grow with decreasing volume. When the volume V_g is reached, the pressure stops changing, and the substance stops being homogeneous—part of the gas condenses into a liquid. The substance separates into two phases: a liquid and a gaseous one. A further reduction of the volume is attended by more and more of the substance passing over into the liquid phase. After condensation of the substance terminates (this occurs when the volume V_{lg} is reached), a further reduction in the volume begins to be attended by a rapid growth of the pressure.

2.3 The Critical State

Figure (2.1) gives isotherms for several values of the temperature. The figure shows that the horizontal portion of the isotherm diminishes in length with elevation of the temperature, and contracts into a point at the temperature T_c called the *Critical* one. The difference between the densities of the liquid and its saturated vapour vanishes completely at the critical temperature. Simultaneously, any difference between a liquid and its vapour vanishes. Point C is the limit which the horizontal portions of the

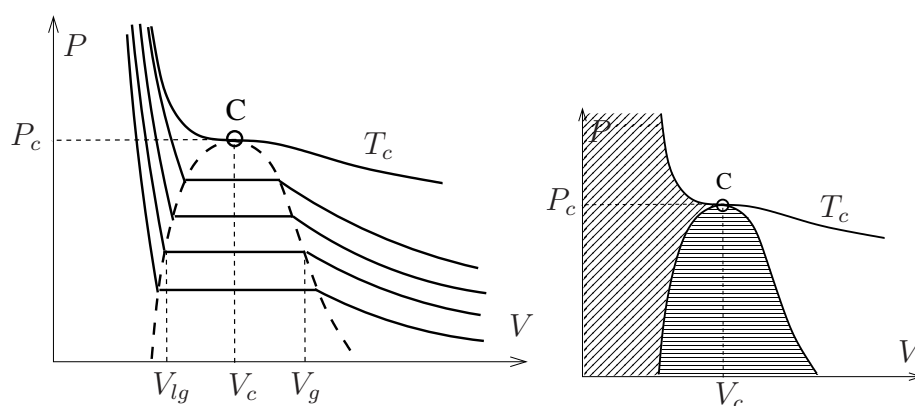


Figure 2.1: The real behavior of isotherms under the critical point.

isotherms tend to when the temperature tends to its critical value T_c . It is called the critical point. The volume V_c , pressure P_c , and temperature T_c corresponding to the critical state are called *critical quantities*. Point C is a point of inflection for the critical isotherm. A tangent to the isotherm at point C is parallel to the V -axis. It can be seen from figure (2.1) that the saturated vapour pressure grows with the temperature and reaches the value P_c at the critical temperature. At temperatures above the critical one, the concept of a 'saturated vapour' loses its meaning. Therefore, the curve showing the temperature dependence of the saturated vapour pressure terminates at the critical point. If we draw a line through the extreme points of the horizontal portions of the isotherms (figure 2.1), we get a bell-shaped curve confining the region of the two-phase states of a substance. At above critical temperatures, a substance cannot be liquefied,

no matter what pressure is applied to it. The bell-shaped curve and the portion of the critical isotherm to the left of the point C divide the $P - V$ diagram into three regions (figure 2.2). The diagonal hatching shows the region of homogeneous liquid states of a substance. Under a bell-shaped curve is the region of two-phase states, and finally, the region to the right of the bell-shaped curve and the upper branch of the critical isotherm is the region of homogeneous gaseous states of a substance.

2.4 Unphysical behavior of the van der Waals isotherms

In 1873 van der Waals proposed an equation of state which was an attempt to correct the ideal-gas equation so that it would be applicable to real gases. On the basis of the simple kinetic theory particles are assumed to be point masses, and there are no intermolecular forces between particles. However, as the pressure increases on a gaseous system, the volume occupied by the particles may become a significant part of the total volume. In addition, the intermolecular attractive forces become important under this condition. To account for the volume occupied by the particles, van der Waals proposed that the specific volume in the ideal-gas equation of state be replaced by the term $v - b$. At the same time the ideal pressure was to be replaced by the term $P + a/v^2$. The constant b is the covolume of the particles, and the constant a is a measure of the attractive forces. Thus the van der Waals equation is (for one mole substance)

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (2.2)$$

Both a and b have units which must be consistent with those employed for P , v and T . The van der Waals equation is moderately successful, but it has a weakness in that the constants a and b in actuality vary with temperature. Hence their values should be determined empirically for particular regions of pressure and temperature. One specific method of evaluating the two constants is based on the experimental facts that the critical isotherm on a Pv diagram has a zero slope at the critical state. On the basis that the critical isotherm goes through a point of inflection at the critical state, we may write the following equations which are valid at the critical state:

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \quad (2.3)$$

These equations permit the evaluation of the constants in any two-constant equation of state.

The van-der Waals isotherms have an S-shaped bend in whose region three different values of the volume correspond to a given pressure. Real isotherms do not have such a bend, but have a straight horizontal portion instead of it. Separation into two phases is explained by the lack of stability of the homogeneous states corresponding to bend 1-2-3-4. The instability of the states between points 2 and 3 becomes obvious if we take into account that the derivative dP/dV is positive on this part of the bend. Hence, a substance capable of passing consecutively through states 2-3 would have absolutely

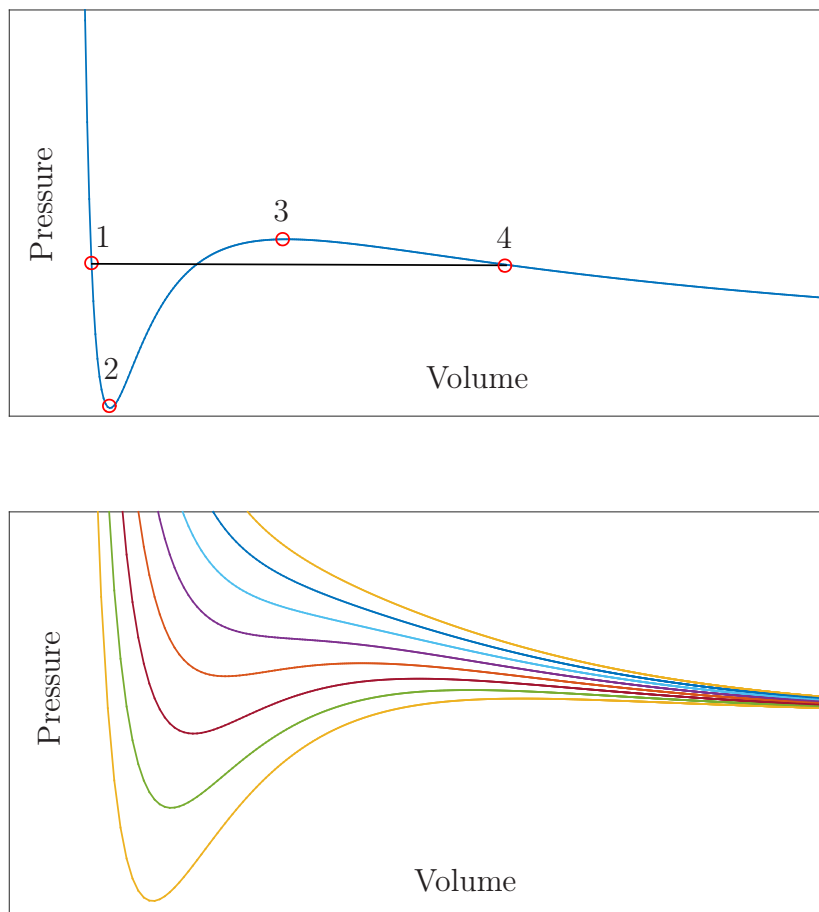


Figure 2.2: The behavior of isotherms of a real gas in the vicinity of the critical point

unnatural properties: an increase in the volume of the gas would be attended by a growth in pressure instead of a reduction in it.

The derivative dP/dV is negative on parts 1-2 and 3-4, so that it would seem possible for these portions of the curve to be realized. Indeed, in certain conditions, the states corresponding to these portions can be achieved. Such not fully stable states are called *metastable*. The substance in states 1-2 is called a *superheated liquid*, and in states 3-4 it is called a *supersaturated vapour*.

2.5 The Clapeyron-Clausius Equation

The Clapeyron-Clausius Equation in a hidden form appeared as a Maxwell's relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (2.4)$$

Strictly speaking the Clapeyron-Clausius equation is usually derived differently from

the Maxwell's relation. At a given pressure, the coexistence curve specifies the temperature at which the two phases can coexist. It is the temperature at which one phase begins to convert to the other; in the case of a liquid-vapour coexistence curve, the temperature corresponds to the boiling point at the given pressure. Thus, if we obtain an explicit relation between the pressure and the temperature that defines the coexistence curve, then we can know how the boiling point or freezing point changes with pressure. Using the condition for equilibrium $\mu_1 = \mu_2$, we can arrive at a more explicit expression for the coexistence curve. Let us consider two phases denoted by 1 and 2. Using the Gibbs-Duhem equation, $d\mu = -sdT + vdP$, one can derive a differential relation between P and T of the system as follows. It is clear that, for a component k , $d\mu_k^1 = d\mu_k^2$. Therefore,

$$-s_1dT + v_1dP = -s_2dT + v_2dP \quad (2.5)$$

in which the molar quantities for the two phases are indicated by the subscripts 1 and 2. From this it follows that

$$\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{\Delta h}{T(v_1 - v_2)} \quad (2.6)$$

in which we have expressed the difference in the molar entropy between the two phases in terms of the enthalpy of transition: $s_1 - s_2 = (\Delta h/T)$, where Δh trans is the molar enthalpy of the transition (vapourization, fusion or sublimation). More generally, then, we have the equation called the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta h}{T\Delta v} \quad (2.7)$$

Here, Δv is the difference in the molar volumes of the two phases. The temperature T in this equation is the transition temperature, i.e. boiling point, melting point, etc. This equation tells us how the transition temperature changes with pressure. For example, for a transition from a solid to a liquid in which there is an increase in the molar volume ($\Delta v > 0$), the freezing point will increase ($dT > 0$) when the pressure is increased ($dP > 0$); if there is a decrease in the molar volume, then the opposite will happen — as is the case when ice melts and becomes liquid water.

2.6 Phase Diagram

A useful tool in the study of phase transition is the $P - T$ diagram. A diagram on which pressure is plotted on the vertical axis and temperature on the horizontal axis. It is called *phase diagram* (see fig 2.3). A point on the phase diagram represents water in a state determined by the pressure and the temperature at that point. The curves on the phase diagram are the demarcations between the solid, liquid, and gas phases. For most temperatures, there is one pressure at which two particular phases can coexist in equilibrium.

The one exception is at the *triple point*, where all three phases (solid, liquid, and gas) can coexist in equilibrium. Triple points are used in precise calibrations of thermometers. The triple point of water is precisely $T = 0.01^\circ\text{C}$ $P = 611.657 \text{ Pa}$. If either the

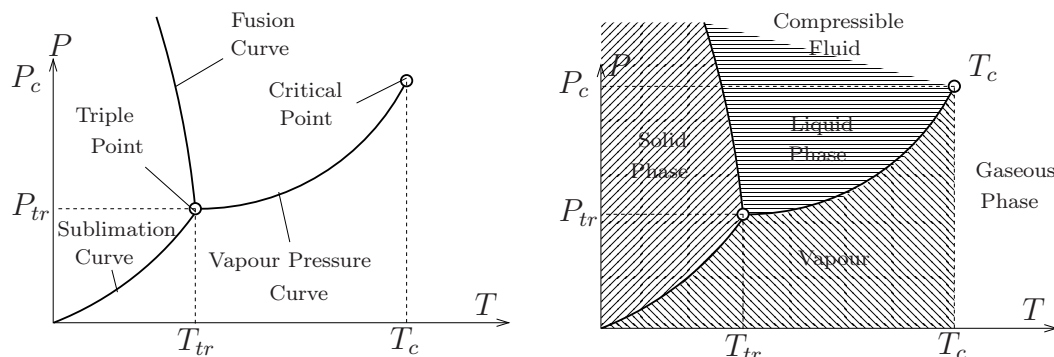


Figure 2.3: Phase diagram of first order phase transitions.

temperature or the pressure or both are changed, the point representing the state of the water moves along some path on the phase diagram. If the path crosses one of the curves, a phase transition occurs and the latent heat for that heat transition is either absorbed or released (depending on direction). Crossing the fusion curve represents freezing or melting; crossing the vapour pressure curve represents condensation or vapourization.

The vapour pressure curve ends at the *critical point*. Thus, if the path for changing a liquid to a gas goes around the critical point without crossing the vapour pressure curve, no phase transition occurs. At temperature above a critical temperature or pressure above the critical pressure, it is impossible to make a clear distinction between the liquid and gas phases.

The sublimation curve represents another phase change, called *sublimation*, that occurs when a solid becomes gas (or vice versa) without passing through the liquid phase. Sublimation occurs when ice on a car windshield becomes water vapour on a cold dry day. Dry ice (solid carbon dioxide) also passes directly from solid state to gas. Sublimation has its own latent heat; the latent heat for sublimation is not the sum of the latent heats for fusion and vapourization.

The phase diagram of water has an unusual feature: the slope of the fusion curve is negative. The fusion curve has a negative slope only for substances (such as water, gallium, and bismuth) that expand on freezing. In these substances the molecules are closer together in liquid phase than they are in solid. As liquid water starting at room temperature is cooled, it contracts until it reaches 3.98 °C. At this temperature water has its highest density (at a pressure of 1 atm); further cooling makes the water expand. When water freezes, it expands even more; ice is less dense than water. A layer of ice forms on top since ice is less dense than water; underneath the ice, liquid water remains, which permits fish, turtles, and other aquatic life to survive until spring. The water also has exceptionally high specific heat capacity (4.2 kJ/(kgK)), heat of fusion (333 kJ/kg), and heat of vaporization (2257 kJ/kg).

Chapter 3

Transport Processes

3.1 Streamlines and Flow Continuity

Mechanics of continuous media exists in addition to the mechanics of point particle and the mechanics of a rigid body which we dealt with in the preceding note. This science covers hydrodynamics, gas dynamics, the theory of elasticity. Hydrodynamics is the branch of mechanics of continuous media studying the motion of incompressible liquids and their interaction with solids.

To describe the motion of a liquid, we can set the position of each of its particles as a function of time. This method of description was worked out by J. Lagrange. But it is also possible to observe separate points of space instead of liquid particles and record the velocity with which separate particles of the liquid pass each given point. The second method is called the Euler method.

The state of motion of a liquid can be determined by indicating the velocity vector as a function of time for each point of space. The combination of the vectors \mathbf{v} given for all the points of space forms the so-called *velocity-vector field* that can be depicted as follows: Let us draw lines in a flowing liquid so that a tangent to them at each point coincides in direction with the vector \mathbf{v} . These lines are called *streamlines*. We shall agree to draw the streamlines so that their density is proportional to the magnitude of the velocity at a given place. The pattern of streamlines will thus allow us to assess not only the direction, but also the magnitude of the vector \mathbf{v} at different points of space. The streamlines will be closer together where the velocity is higher and, conversely, farther apart where the velocity is lower.

Since the magnitude and the direction of the vector \mathbf{v} may change with time at every point, then the pattern of the streamlines may also change continuously. If the velocity vector is constant at each point of space, then the flow is called *steady*. In steady flow, any particle of a liquid passes a given point of space with the same value of \mathbf{v} . The pattern of the streamlines in steady flow remains unchanged, and the streamlines in this case coincide with the trajectories of the particles. A portion of a liquid confined by streamlines is called a *flow tube*. The vector \mathbf{v} , being at each point tangent to a streamline, will also be tangent to the surface of the flow tube. Hence, the particles of the liquid in their motion do not intersect the “walls” of the flow tube.

Let us take a cross section A of a flow tube at right angles to the direction of the velocity.

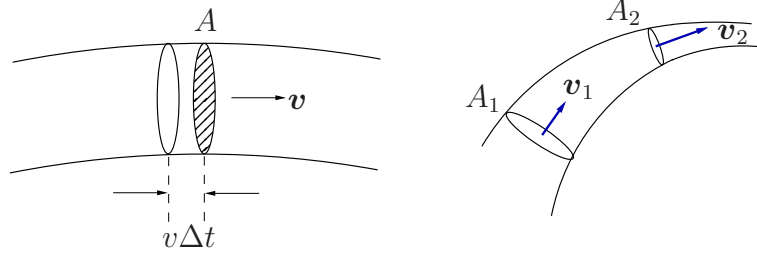


Figure 3.1: Flowing of an incompressible liquid.

We shall assume that the velocity of the liquid particles is the same at all points of this section. During the time Δt , all the particles whose distance from A at the initial moment did not exceed the value $v\Delta t$ will pass through section A . Consequently, a volume of the liquid equal to $Av\Delta t$ will pass through it in unit time. Let us take a flow tube so thin that at each section of it the velocity may be considered constant. If the liquid is incompressible (i. e. its density is the same everywhere and cannot change), then the amount of liquid between sections A_1 and A_2 will remain constant. Hence, it follows that the volumes of liquid flowing in a unit time through sections A_1 and A_2 must be the same:

$$A_1 v_1 = A_2 v_2 \quad (3.1)$$

$$Av = \text{const} \quad (3.2)$$

The result obtained forms the content of the theorem on flow continuity.

It can be seen from (3.1) that when a flow tube has a varying section the particles of an incompressible liquid will move with acceleration. Interestingly, the theorem on flow continuity can be applied to gases when their compressibility may be disregarded.

3.1.1 Bernoulli's Equation

Ideal fluids are incompressible and flow steadily without friction. The flow is laminar and can be represented graphically by streamlines. We shall consider the volume of the liquid confined by the “walls” of the flow tube and by cross sections A_1 and A_2 perpendicular to the streamlines (see Fig.3.2). During the time Δt , this volume will move along the flow tube. Section A_1 will move to the position A'_1 having covered the distance Δx_1 , and section A_2 will move to position A'_2 having covered the distance Δx_2 . Owing to flow continuity, the hatched volumes will be equal: $\Delta V_1 = \Delta V_2 = V$. The energy of each liquid particle consists of its kinetic energy and its potential energy in the field of the Earth's gravitational forces. Owing to the steady nature of the flow, a particle that after the time Δt is at any point in the unhatched part of the volume being considered has the same velocity as the particle did that was at the same point at the initial moment did. Hence, the energy increment ΔE of the entire volume being considered can be calculated as the difference between the energies of the small hatched volumes ΔV_1 and ΔV_2 .

Let us take a flow tube cross section and the lengths Δx so small that the same values of the velocity v , pressure P , and height h can be ascribed to all the points of each of

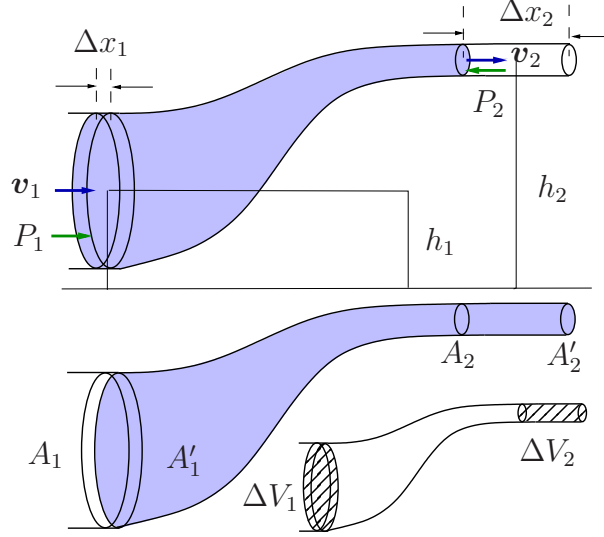


Figure 3.2: Applying conservation of energy to the flow of an ideal fluid.

the hatched volumes. Hence, the energy increment can be written as follows:

$$\Delta E = \left(\frac{\rho \Delta V v_2^2}{2} + \rho \Delta V g h_2 \right) - \left(\frac{\rho \Delta V v_1^2}{2} + \rho \Delta V g h_1 \right) \quad (3.3)$$

Forces of friction are absent in an ideal liquid. Therefore, the energy increment must equal the work done by the pressure forces on a separated volume. Only the work of the forces applied to sections A_1 and A_2 is not equal to zero. This work is

$$W = P_1 A_1 \Delta x_1 - P_2 A_2 \Delta x_2 = (P_1 - P_2) \Delta V \quad (3.4)$$

Equating equations (3.3) and (3.4), cancelling ΔV , and transferring terms with the same subscripts to the same side of the equation, we get

$$P_1 + \rho g h_1 + \frac{\rho v_1^2}{2} = P_2 + \rho g h_2 + \frac{\rho v_2^2}{2} \quad (3.5)$$

Sections A_1 and A_2 were taken absolutely arbitrarily. We can therefore assert the expression has the same value for any section of the flow tube. Equation (3.5) is called Bernoulli's equation, in honour of its discovery, the Swiss mathematician Daniel Bernoulli (1700-1782), who formulated it.

3.1.2 Torricelli's formula

Let us apply Bernoulli's equation to the flow of a liquid from a small hole in a wide open vessel (see fig.3.3). The water emerging from the spigot is also at atmospheric pressure since it is in contact with the air. If the pressure of the emerging water were different than that of the air, the stream would expand or contract until the atmospheric pressure is equal. We apply Bernoulli's equation to two points: points 1 at the water surface and point 2 in the emerging stream of water.

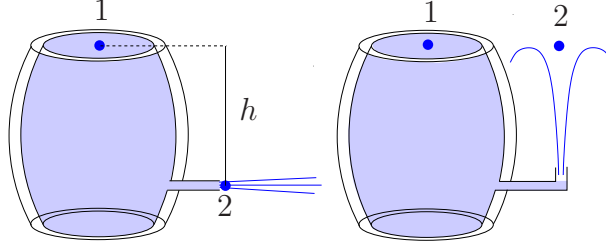


Figure 3.3: Full barrel of rainwater with open spigot (a) horizontal and (b) upward.

Since $P_1 = P_2$,

$$\rho gh_1 + \frac{1}{2}\rho v_1^2 = \frac{1}{2}\rho v_2^2 \quad (3.6)$$

The speed of the emerging water is v_2 . What is v_1 , the speed of the water at the surface? The water at the surface is moving slowly, since the barrel is drained. The continuity equation requires that

$$A_1 v_1 = A_2 v_2$$

Since the cross sectional area of the spigot A_2 is much smaller than the area of the top of the barrel A_1 , the speed of the water at the surface v_1 is negligibly small compared with v_2 . Setting $v_1 = 0$, Bernoulli's equation is reduced to

$$\rho gh_1 = \frac{1}{2}\rho v_2^2 \quad (3.7)$$

$$v = \sqrt{2gh_1} \quad (3.8)$$

Now take the point 2 to be at the top of the fountain. Then $v_2 = 0$ and the Bernoulli's equation is reduced to

$$\rho gh_1 = \rho gh_2 \quad (3.9)$$

A spurt of water goes right back up to the top of the water in the barrel. In reality, the 'fountain' does not reach as high as the original water level; some energy is dissipated due to viscosity and air resistance.

3.1.3 Forces of Internal Friction

An ideal liquid is an abstraction. Viscosity or internal friction is a property inherent to some extent or other in all real fluids (liquids and gases). Viscosity can be conceptualized as quantifying the frictional force that arises between adjacent layers of fluid that are in relative motion. Let us consider the following experiment to reveal the laws which forces of internal friction obey. Two parallel plates whose linear dimensions considerably exceed the distance d between them (see figure (3.4)) are immersed in a liquid. The bottom plate is held in place, while the top one is brought into motion relative to the bottom one with a certain velocity \mathbf{v}_0 . The experiment shows that to move the top plate with a constant velocity \mathbf{v}_0 , we have to exert on it a quite different force \mathbf{F} that is constant in magnitude. Since the plate receives no acceleration, this

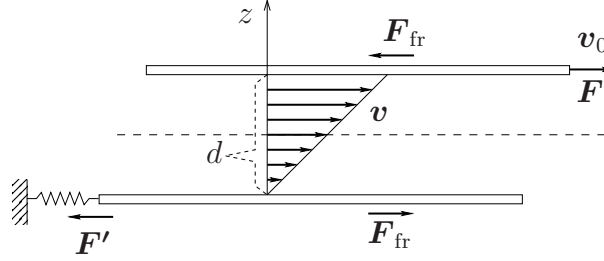


Figure 3.4: Experiment for viscosity.

signifies that the action of this force is balanced by a force equal to it in magnitude and opposite in direction which is evidently the force of friction acting on the plate when it moves in the liquid. It is denoted by \mathbf{F}_{fr}

By varying the velocity of the plate \mathbf{v}_0 , the area of the plate A , and the distance between them, we can find that

$$F_{\text{fr}} = \eta \frac{v_0}{d} A \quad (3.10)$$

where η is a constant of proportionality depending on the nature and state (for instance, the temperature) of the liquid and it is called the *coefficient of internal friction* or the *viscosity* of the liquid or gas. Sometimes η is called dynamic viscosity as distinct from the kinematic viscosity ν equal to η/ρ , where ρ is the density of the fluid.

If we study the velocity of the liquid particles in different layers, it will be found to change in the direction z at right angles to the plates according to the linear law:

$$v(z) = \frac{v_0}{d} z \quad (3.11)$$

The liquid particles in direct contact with the plates adhere to them have the same velocity as the plates themselves:

$$\left| \frac{dv}{dz} \right| = \frac{v_0}{d} \quad (3.12)$$

The value of v_0/d must be always positive, however, the derivative can be negative.

$$F_{\text{fr}} = \eta \frac{dv}{dz} A \quad (3.13)$$

This equation determines the magnitude of the force of friction. The quantity $|dv/dz|$ shows how fast the velocity changes in the direction of the z -axis.

It was found that the equation (3.13) also holds for any other law of the change in the velocity from layer to layer. The unit of viscosity in the SI system is the velocity at which the gradient of the velocity with a magnitude of 1 m/s per m leads to the appearance of a force of internal friction of 1 N per m² of contact surface of contact of the layers. This unit is called *pascal-second*.

$$1\text{Pa} \times \text{s} = 10\text{P}$$

Viscosity depends on the temperature. The nature of this dependence appreciably differs for liquids and gases. The viscosity of liquids greatly diminishes with increasing temperature. The viscosity of gases, however, grows with increasing temperature.

3.1.4 Laminar and Turbulent Flow

Two kinds of flow of a liquid or gas are observed. In some cases, the liquid separates, as it were, into layers that slide relative to one another without mixing. Such flow is called laminar. If we introduce a coloured stream into a laminar flow, it is retained without being washed out over the entire length of the flow because the liquid particles in a laminar flow do not pass over one layer to another. A laminar flow is steady.

With an increase in the velocity or cross-sectional dimensions of a flow, its nature changes quite appreciably. Vigorous stirring of the liquid appears. Such a flow is called *turbulent*. In a turbulent flow, the velocity of the particles at each given place constantly changes chaotically—the flow is not steady. If we introduce a coloured stream into a turbulent flow, already at a small distance from the place of its introduction the coloured liquid will be uniformly distributed over the entire cross section of the flow.

The British scientist Osborne Reynolds (1842-1912) established that the nature of a flow depends on the value of the dimensionless quantity

$$Re = \frac{\rho v l}{\eta} \quad (3.14)$$

where ρ is the mechanical density of the liquid (or gas), v is the average flow velocity, η stands for the viscosity of the liquid, and l characterizes the cross section.

The quantity Re is called the *Reynolds number*. At small values of the Reynolds number, laminar flow is observed. Beginning from a certain definite value of Re called critical one, the flow acquires a turbulent nature. If for a round pipe we take its radius r as the characteristic dimension, then the critical value of the Reynolds number equals approximately 1000. The Reynolds number can be used as a dimensionless or similarity number for the flow of liquids in pipes, channels. The nature of the flow of different liquids (or gases) in pipes of different cross sections will be absolutely the same if the same value of Re corresponds to each other.

3.2 Open systems

The first law of thermodynamics resulted from experimental observations on closed systems. The principle generally may be applied to any control mass which can be physically identified throughout a given process. However, a large number of engineering problems involve open systems where matter flows continuously in and out of a defined region of space. In most cases it is physically impossible to trace a given control mass, much less measure the heat and work interactions that might occur to the unit of mass. During its passage the velocity, pressure, and other macroscopic characteristics of the element are continually changing. It is impractical to attempt to measure all the interactions that occur between this fluid element and its neighbouring elements. Furthermore, in this case we are not interested in the behaviour of an individual element, but rather in the average behaviour of all the fluid elements.

The analysis of flow processes begins by selecting a region of space called a *controlled volume*. The boundary of the control volume may be in part a well-defined physical barrier, or all of it may be an imaginary envelope. We assume that the control volume will be fixed in size and shape.

When we consider open systems, a problem arises with regard to the significance of a property value at the control surface. Since the properties of an element of mass crossing the control surface, there is a tendency to question what is meant by a property in this case, and what its relation is to properties defined in thermostatic equilibrium. Are the results of the state postulate still valid? In most cases the answer to this last question is yes, if the physical situation fulfills the conditions for what is frequently called *local equilibrium*. By local equilibrium we mean to imply that the change in any property between two small adjacent fluid elements is very small compared with the average value of the property in this region.

We shall restrict our attention to one-dimensional steady-state flow problems. By definition of the system under analysis, the control mass at time t and $t + dt$ must be identical. Consequently, it is obvious that $m_A = m_B$. That is, under steady-state conditions the masses entering and leaving the control volume in a given time interval must be equal.

$$dm_1 = dm_2 \quad (3.15)$$

$$\rho_1 v_1 A_1 dt = \rho_2 v_2 A_2 dt \quad (3.16)$$

$$\frac{dm_1}{dt} = \rho_1 v_1 A_1 \quad \frac{dm_2}{dt} = \rho_2 v_2 A_2 \quad (3.17)$$

$$\rho_1 v_1 A_1 = \rho_2 v_2 A_2 \quad (3.18)$$

$$\sum_{\text{in}} (\rho v A) = \sum_{\text{out}} (\rho v A) \quad (3.19)$$

3.2.1 Conservation of energy principle for open systems

Because all properties of the fluid within the control volume are invariant with time at a given position during steady-state operation, the energy associated with the control volume must remain constant. This requires that the sum of the rates of energy transfer into and out of the control volume must add up to zero. Because mass flow rates are constant in steady-state processes, the rate of convection of energy associated with mass crossing every open boundary is also constant. Hence the rates of heat and work interactions must also remain constant in steady-state processes.

$$\dot{d}Q + \dot{d}W = dE \quad (3.20)$$

$$dE = e_2 \dot{m}_2 dt - e_1 \dot{m}_1 dt \quad (3.21)$$

$$\dot{d}Q + \dot{d}W = e_2 \dot{m}_2 dt - e_1 \dot{m}_1 dt \quad (3.22)$$

The energy e per unit mass represents the sum of the internal energy, the kinetic energy, and the potential energy due to conservative force fields. It is necessary to recognize that the term $\dot{d}W$ represents several distinct types of work interactions. One important form of work associated with open systems is called *shaft work*. This arises from the tangential shearing motions of the fluid at the boundary of blade on a rotating shaft. This quantity of work can be flown into or out of the control volume, as the situations

dictates. In addition, we must account for the work required to push mass into or out of the control volume.

Consider the work dW_1 necessary to push the mass in region A into the control volume. The force is exerted through a distance $v_1 dt$. Hence the required work is $P_1 A_1 v_1 dt$. Similarly, the work is $dW_2 = P_2 A_2 v_2 dt$. Recalling that $\dot{m} = \rho AV$.

$$dW_1 = P_1 A_1 v_1 dt = P_1 \boldsymbol{\nu}_1 \dot{m}_1 dt \quad (3.23)$$

$$dW_2 = P_2 A_2 v_2 dt = P_2 \boldsymbol{\nu}_2 \dot{m}_2 dt \quad (3.24)$$

where $\boldsymbol{\nu} = V/m$ is the specific volume.

$$dQ + dW = (e_2 + P_2 \boldsymbol{\nu}_2) \dot{m}_2 dt - (e_1 + P_1 \boldsymbol{\nu}_1) \dot{m}_1 dt \quad (3.25)$$

$$\frac{dQ}{dt} + \frac{dW}{dt} = (e_2 + P_2 \boldsymbol{\nu}_2) \dot{m}_2 - (e_1 + P_1 \boldsymbol{\nu}_1) \dot{m}_1 \quad (3.26)$$

$$\frac{dQ}{dt} + \frac{dW}{dt} = (e_2 + P_2 \boldsymbol{\nu}_2) \frac{dm_2}{dt} - (e_1 + P_1 \boldsymbol{\nu}_1) \frac{dm_1}{dt} \quad (3.27)$$

$$\dot{Q} + \dot{W} = (e + P \boldsymbol{\nu})_{\text{out}} \dot{m} - (e + P \boldsymbol{\nu})_{\text{in}} \dot{m} \quad (3.28)$$

$$dQ + dW = (e + P \boldsymbol{\nu})_2 dm - (e + P \boldsymbol{\nu})_1 dm \quad (3.29)$$

Integration of this equation over a time period during which a unit mass enters and another unit mass leaves, the control volume yields

$$q + w_{\text{shaft}} = (e + P \boldsymbol{\nu})_2 - (e + P \boldsymbol{\nu})_1 \quad (3.30)$$

where the subscripts 1 and 2 again refer to the inlet and outlet cross sections.

If we restrict ourselves to simple, compressible substances the energy e includes the internal energy, the linear kinetic energy, and the gravitational potential energy of the flow stream. In this case:

$$e = u + \frac{v^2}{2} + gz \quad (3.31)$$

Under this restrictions

$$q + w_{\text{shaft}} = \left(u + \frac{v^2}{2} + gz + P \boldsymbol{\nu} \right)_{\text{out}} - \left(u + \frac{v^2}{2} + gz + P \boldsymbol{\nu} \right)_{\text{in}} \quad (3.32)$$

At this point an important reason for introducing the enthalpy function \mathcal{H} is seen. At every control surface where mass transfer occurs, the sum of the internal energy and the flow work, $u + P \boldsymbol{\nu}$, is associated with each unit of mass crossing the boundary. Therefore, we may write the conservation of energy principle as

$$q + w_{\text{shaft}} = \left(\mathcal{H} + \frac{v^2}{2} + gz \right)_{\text{out}} - \left(\mathcal{H} + \frac{v^2}{2} + gz \right)_{\text{in}} \quad (3.33)$$

3.2.2 Nozzles and Diffusers

In many steady-flow processes there is a need to either increase or decrease the velocity of a flow stream. A device which increases the velocity of a fluid at the expense of a pressure drop in the direction of flow is called a *nozzle* as it can be seen in Fig.3.5. A *diffuser* is a device for increasing the pressure of a flow stream at the expense of a decrease in velocity. These defining conditions apply for both subsonic and supersonic flow. Note that a nozzle is a converging passage for subsonic flow, whereas the passage is diverging for supersonic flow. The opposite conditions hold for a diffuser. The actual shapes of these devices in practice are not as shown, but will probably have curved surfaces in the direction of flow. The true shape is unimportant for the overall energy balances that we wish to obtain. For a simple, compressible substance the steady-flow

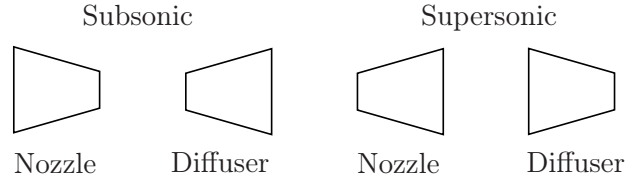


Figure 3.5: Nozzle and Diffuser.

energy equation per unit mass reduces to

$$q = \frac{v_2^2 - v_1^2}{2} + \mathcal{h}_2 - \mathcal{h}_1 \quad (3.34)$$

In some cases the duct may be insulated. Even without insulation, the fluid velocity may be so large that there is not enough time for the fluid to come to thermal equilibrium with the walls. Thus in many applications the assumptions of an adiabatic process is a good approximation for nozzles and diffusers.

$$-\Delta \mathcal{h} = \Delta K \quad (3.35)$$

$$-\Delta u - \Delta(Pv) = \Delta K \quad (3.36)$$

$$(3.37)$$

3.2.3 Turbines, Pumps, Compressors, and Fans

A turbine, whether the fluid is a gas or a liquid, is a device in which the fluids does work against some type of blade attached to a rotating shaft. As a result, the device produces work which may be used for some purpose in the surroundings. Pumps, compressors, and fans are devices in which work is done on the fluid, which results in an increase in the pressure of the fluid. Pumps are usually associated with liquids and compressors and fans are employed for gases. The ratio of outlet-to-inlet pressure across a fan will probably be just slightly above 1, whereas for a compressor the ratio will probably be between 3 and 10. For steady flow through any of these devices the energy equation reduces to

$$q + w = \mathcal{h}_2 - \mathcal{h}_1 + \frac{v_2^2 - v_1^2}{2} \quad (3.38)$$

The potential-energy change is normally negligible. Two other terms in this expression require comment. It is very important to note that the inclusion of a heat quantity depends upon the mode of operation. If the device is not insulated, the heat gained or lost by the fluid depends upon such factors as whether or not (1) a large temperature difference exists between the fluid and the surroundings, (2) a small flow-velocity exists, and (3) a large surface area is present.

3.2.4 Throttling Devices

There are circumstances in the design of systems where a decrease in pressure is desired, but no other useful effect occurs. This pressure drop is accomplished by inserting in the flow system a component called a throttling device see Fig.3.6. The main effect of a throttling process is a significant pressure drop without any work interactions or changes in kinetic or potential energy. Flow through a restriction such as a valve or a porous plug or a long capillary tube fulfils the necessary conditions.

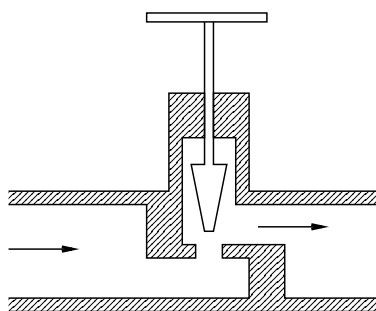


Figure 3.6: A throttle valve.

3.2.5 Heat Exchangers

One of the most important steady-flow devices of engineering interest is the heat exchanger. These devices (see Fig.3.7) serve two useful purposes. Either they are used to remove (or add) energy from some region of space or they are employed to change deliberately the thermodynamic state of a fluid. The radiator of an automobile is an example of a heat exchanger used for heat removal. Modern gas turbines and electric generators are frequently cooled internally, and their performance is greatly affected by the heat-transfer process. In steam power plants heat exchangers are used to remove heat from hot combustion gases and subsequently increase the temperature and enthalpy of the steam in the power cycle. This high-enthalpy fluid is then expanded with a resulting large power output. In the chemical industry, heat exchangers are extremely important in maintaining or attaining certain thermodynamic states as chemical processes are carried out. Modern applications of heat exchangers are numerous.

One of the primary applications of heat exchangers is the exchange of energy between two moving fluids. The changes of kinetic and potential energies are usually negligible and no work interactions are present. The pressure drop through a heat exchanger

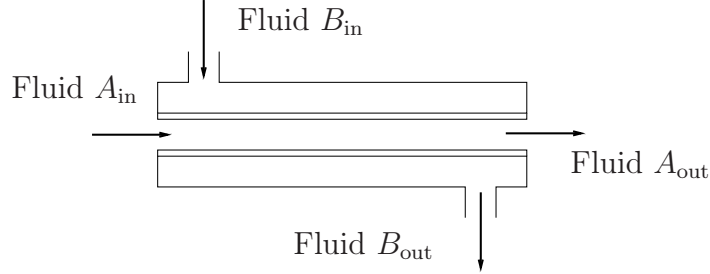


Figure 3.7: Heat exchanger.

is usually small, hence an assumption of constant pressure is often quite good as a first approximation. A heat exchanger composed of two concentric pipes is shown in Fig.3.7. One fluid A flows in the inner pipe, and a second fluid B flows in the annular space between the pipes. For this system the steady-state flow energy balance on a rate basis is applicable. We assume that the heat transfer external to the device is zero, and W is zero, no shaft work exists. In addition, the kinetic- and potential energy changes of the fluid streams are usually negligible.

$$\dot{m}_A(\mathcal{H}_{A1} - \mathcal{H}_{A2}) = \dot{m}_B(\mathcal{H}_{B2} - \mathcal{H}_{B1}) \quad (3.39)$$

Properly used, these equations may be applied to specific types of heat-exchanger equipment called boilers, evaporators, and condensers.

3.3 Heat Transfer

3.3.1 Heat Conduction

When two parts of a material substance are maintained at different temperatures, experiments show a continuous distribution of temperature. The energy transport between neighbouring volume elements by virtue of the temperature difference between them is known as *heat conduction*. The fundamental law of heat conduction is a generalization of the results of experiments on the linear heat flow through a slab perpendicular to the faces. A piece of material is made in the form of a slab of thickness Δx and of area A . One face is maintained at temperature T and the other at $T + \Delta T$. The heat Q flows in a direction perpendicular to the faces for a time t is measured. The experiment is repeated with other slabs of the same material but with different values of Δx and A . The results of such experiments show that, for a given value of ΔT , the conducted heat is proportional to the time and to the area. Also, for a given time and area, Q is proportional to the ratio $\Delta T/\Delta x$, provided that both ΔT and Δx are small. These results may be written

$$\frac{Q}{t} \propto A \frac{\Delta T}{\Delta x} \quad (3.40)$$

which is only approximately true when ΔT and Δx are finite but which is rigorously true in the limit as ΔT and Δx approach zero. If we generalize this result for an

infinitesimal slab of thickness dx , across which the temperature difference dT , and introduce a constant of proportionality κ , the fundamental law of heat conduction becomes

$$\frac{dQ}{dT} = -\kappa A \frac{dT}{dx} \quad (3.41)$$

The derivative dT/dx is called *temperature gradient*. The minus sign is introduced in order that the positive direction of flow of heat should coincide with the positive direction of x . For heat to flow in the positive direction of x , this must be the direction in which the temperature T decreases. The letter κ is called the *thermal conductivity*. A substance with a large thermal conductivity is known as a *thermal conductor* and one with a small value of κ as a *thermal insulator*.

Experiments show that the thermal conductivity of a metal is quite sensitive to impurities. The slightest trace of arsenic in copper reduces the thermal conductivity by a factor 3. Non-metallic solids at room temperature are poor conductors of heat. In the low temperature range, however, the behaviour is quite different. The thermal conductivity of sapphire rises to a maximum of approximately 6000 W/m·K at 35 K. The thermal conductivity of some metals remains quite constant over a wide temperature range. Thus, silver, copper and gold have thermal conductivities that remain practically constant in the temperature range from 100 to 1000 K. As a general rule, the thermal conductivity of metals increases as the temperature is lowered, until a maximum is reached.

Gases are by far the poorest heat conductors. The thermal conductivity of a gas always increases as the temperature is raised.

3.3.2 Heat Convection

A flow of a liquid or gas that absorbs heat at one place then moves to another place, where it mixes with a cooler portion of the fluid and rejects heat, is called a *convection current*. If the motion of the fluid is caused by a difference in density that accompanies a temperature difference, the phenomenon is called *natural convection*. If the fluid is made to move by the action of a pump or a fan, it is called forced convection.

Consider a fluid in contact with a flat or curved wall whose temperature is higher than that of the main body of the fluid. Although the fluid may be in motion, there is a relatively thin layer of stagnant fluid next to the wall, the thickness of the layer depending upon the character of the motion of the main body of fluid. The more turbulent the motion, the thinner the layer becomes. Heat is transferred from the wall to the fluid by a combination of conduction through the layer and convection in the fluid. Neglecting the transfer of heat by radiation, we may define *convection coefficient* h that includes the combined effects of conduction through the layer and convection in the fluid. Thus,

$$\frac{dQ}{dT} = hA\Delta T \quad (3.42)$$

where A is the area of the wall, and ΔT is the temperature difference between the surface of the wall and the main body of the fluid. The fundamental problem of heat convection is to find the value of h that is appropriate to a particular piece of equipment. Moreover, h is a function of density, viscosity, velocity, specific heat, and

thermal conductivity of the fluid. We can state that the rigorous calculation of the convection coefficient is an enormously complicated problem.

3.3.3 Thermal Radiation

Thermal radiation is important in thermometry since it is the basis of precisely measured high temperatures above the range of gas thermometers. By conduction and convection, the transfer of heat is accomplished through the medium of matter. During the process of radiation, however, heat is separated from its association with matter and can travel as radiation as far as empty space extends.

We shall focus on thermal radiation, namely, the radiation emitted by a solid or a liquid by virtue of its temperature. Experiment shows that the radiation depends on the temperature, on the area of the surface, and on the nature of the surface of the body. The total radiant power exiting from an infinitesimal element of surface, divided by the area of the surface, is called the *radiant exitance* \mathcal{R} of a body. For example, the radiant exitance of tungsten at 1000 K is 6.46 kW/m², at 2000 K it is 236 kW/m², and at 3000 K it is 1534 kW/m².

When thermal radiation is incident upon a body equally from all directions, the radiation is said to be *isotropic*. Some of the radiation is might be absorbed, some reflected, and some transmitted. In general, the incident isotropic radiation of all wavelengths that is *absorbed* depends on the temperature and the nature of the surface of the absorbing body. The fraction of the total incident radiant power that is absorbed is called *absorptivity*. In thermal equilibrium, the processes of absorption and emission of radiant power are equal and opposite. So, the total *emissivity* ϵ , equal to the absorptivity, is defined as the fraction of the power provided to a real body that is emitted through a material surface as thermal radiation. To summarize:

- Radiant exitance \mathcal{R} = total radiant power emitted per unit area;
- Total emissivity ϵ = fraction of the total radiant power that is emitted as thermal radiation.

The emissivity depends on both the temperature and the nature of the emitting surface. The emissive nature of surfaces is revealed by comparing emissivities at a given temperature. At 300 K, when all bodies emit only infrared radiation, the emissivity of polished steel is 0.09, the coefficient of rough oxidized steel is 0.81, and ocean water has an emissivity 0.96.

Stefan-Boltzmann Law

The first measurement of the heat transferred by radiation between a body and its surroundings was made by Tyndall. On the basis of these experiments, it was concluded by Stefan in 1879 that the heat radiated was proportional to the difference of the fourth powers of the absolute temperatures. This purely experimental result was later derived thermodynamically by Boltzmann, who showed that the radiant exitance of a body at any temperature T is equal to

$$\mathcal{R} = \epsilon \sigma T^4 \quad (3.43)$$

where σ is the Stefan-Boltzmann constant. $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$.

Chapter 4

Gas Power Cycles

An important use of thermodynamics is made in the study of cycles of devices used for power production. In this chapter we shall restrict ourselves to devices which employ a gas as the working fluid. Modern automotive, truck, and gas-turbine engines are examples of the extremely fruitful application of thermodynamic analysis.

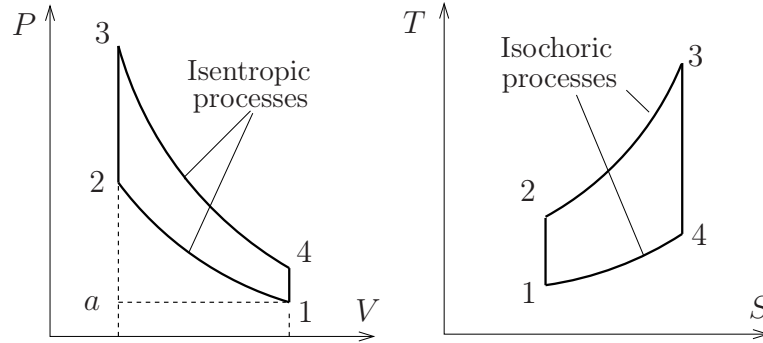
Because of the complexities of the actual processes, it is profitable in the initial study of gas power and refrigeration cycles to examine the general characteristics of each cycle without going into a detailed analysis.

4.1 The Otto Cycle

A number of applications make use of a piston-cylinder arrangement in which the piston is observed to undergo cycles, or revolutions. The *bore* of the piston is its diameter, and the distance the piston moves in one direction is known as the *stroke*. When the piston has moved to a position such that a minimum volume of the fluid is left in the cylinder, the piston is said to be at top dead centre (TDC). This minimum volume is called the *clearance volume*. When the piston has moved the distance of the stroke so that the fluid now occupies the maximum volume, the piston is in the bottom dead centre (BDC) position. The volume displaced by the piston as it moves the distance of the stroke between TDC and BDC is the displacement volume. The *compression ratio* r of a reciprocating device is defined as the volume of the fluid at BDC divided by the volume of the fluid at TDC $r = V_{\text{BDC}}/V_{\text{TDC}}$.

The four-stroke spark-ignition engine is an important component in the operation of a technology to meet the modern needs of society. Although it has undergone some modification in order to meet pollution standards for mobile equipment, the engine will continue to play a significant role as a device for producing relatively small quantities of power.

A theoretical cycle of interest in analysing the behavior of reciprocating spark-ignition engines is the Otto cycle. A four-stroke Otto cycle is composed of four internally reversible processes, plus an intake and an exhaust portion of the cycle. Both PV and TS diagrams are shown in Fig.4.1. Consider a piston-cylinder assembly containing air and a piston situated at the bottom dead centre position. This is shown as a point 1 on the diagrams. As the piston moves to the top dead centre position, compression

Figure 4.1: PV and TS diagrams for Otto cycle

of the air occurs adiabatically. Since the processes are reversible, the compression process is isentropic, ending at state 2. Heat is then added to the air instantaneously, so that both the pressure and the temperature rise to high values during a constant volume process 2-3. As the piston now moves toward the BDC position once more, the expansion is carried out adiabatically and internally reversibly, i.e., isentropically, to state 4. Now with the piston in its BDC position, heat is rejected at constant volume until the initial state is achieved.

In review, the theoretical Otto cycle is composed of the following internally reversible processes:

1. Adiabatic compression, 1-2
2. Constant-volume heat addition, 2-3
3. Adiabatic expansion, 3-4
4. Constant-volume heat rejection, 4-1

In addition, one may consider an exhaust stroke, 1- a , and an intake stroke, a -1, for completeness.

Without detailed calculations the thermal efficiency of an air-standard Otto cycle, it is seen that

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{V_2}{V_1} \right)^{(\gamma-1)} = 1 - \frac{1}{r^{\gamma-1}} \quad (4.1)$$

where r is the *compression ratio* for the theoretical cycle. The efficiency expression indicates that the major parameters governing the thermal efficiency of an Otto cycle are the compression ratio and the specific-heat ratio. For a given specific-heat ratio, the value of the thermal efficiency increases with increasing compression ratio. It should be noted, however, that the curves flatten out at compression ratio above 10 or so. Hence, the advantage of operating at high compression ratios lessens rapidly. From a practical viewpoint, the compression ratio is limited by the occurrence of preignition on engine knock when the compression ratio rises much above 10, for common hydrocarbon fuels.

4.2 The Diesel Cycle

In spark-ignition engine the fuel is ignited by energy supplied from an external source. An alternative method for initiating the combustion process in a reciprocating engine is to raise the fuel-air mixture above its autoignition temperature. An engine built on this principle is called a compression-ignition (CI) engine. By using compression ratios in the range of 14:1 to 24:1 and using diesel fuel instead of gasoline, the temperature of the air within the cylinder will exceed the ignition temperature at the end of the compression stroke. If the fuel were premixed with the air, as in a spark-ignition engine, combustion would begin throughout the mixture when the ignition temperature is reached. As a result, we would have no control over the timing of the combustion process. To overcome this difficulty, the fuel is injected into the cylinder in a separate operation. Injection begins when the piston is near the TDC position. Thus the CI engine differs from the spark-ignition (SI) engine primarily in the method of achieving combustion and in the adjustment of the timing of the combustion process.

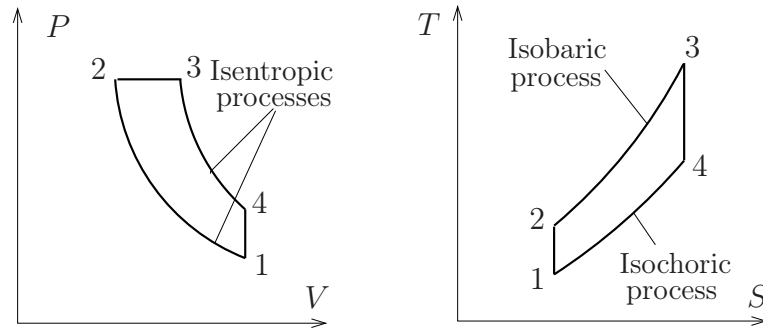


Figure 4.2: PV and TS diagrams for Diesel cycle

The theoretical Diesel cycle for a reciprocating engine is shown in Fig.4.2 on both PV and TS diagrams. The cycle, like the Otto cycle, is composed of four internally reversible processes. The only differences between the two cycles is that a Diesel cycle models the combustion as occurring at constant pressure, while the Otto cycle assumes constant-volume heat addition. A useful analysis of the Diesel cycle is made possible by a cycle based on constant specific heats. Without detailed derivation the heat efficiency is the following:

$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = \frac{c_p m (T_3 - T_2) - c_v m (T_4 - T_1)}{c_p m (T_3 - T_2)} = 1 - \frac{T_4 - T_1}{\gamma (T_3 - T_2)} \quad (4.2)$$

The above equation is more informative if one introduces the concept of the *cutoff ratio* r_c , which is defined as V_3/V_2 . By recalling that the compression ratio r is defined as V_1/V_2 , it can be shown that the preceding equation containing temperatures can be expressed in terms of volumes in the following manner:

$$\eta = 1 - \frac{1}{r^{\gamma-1}} \left(\frac{r_c^\gamma - 1}{\gamma (r_c - 1)} \right) \quad (4.3)$$

This equation indicates that the theoretical Diesel cycle is primarily a function of the compression ratio r , the cutoff ratio r_c , and the specific heat ratio γ .

Note that the thermal efficiency of a Diesel cycle is always less than that of an Otto cycle for the same compression ratio when r_c is greater than unity. In fact, an increase in the cutoff ratio has a drastic effect on the thermal efficiency of a Diesel cycle.

4.3 The Brayton Cycle

In a simple gas-turbine power cycle, separate equipment is used for the various processes of the cycle. Initially, air is compressed adiabatically in a rotating axial or centrifugal compressor. At the end of this process the air enters a combustion chamber where fuel is injected and burned at essentially constant pressure. The products of combustion are then expanded through a turbine until they reach the ambient pressure of the surroundings. A cycle composed of these three steps is called an open cycle, since new air must continually be introduced into the compressor. If one wishes to examine a closed cycle, the products of combustion which have expanded through the turbine must be sent through a heat exchanger, where heat is rejected from the gas until the initial temperature is attained.

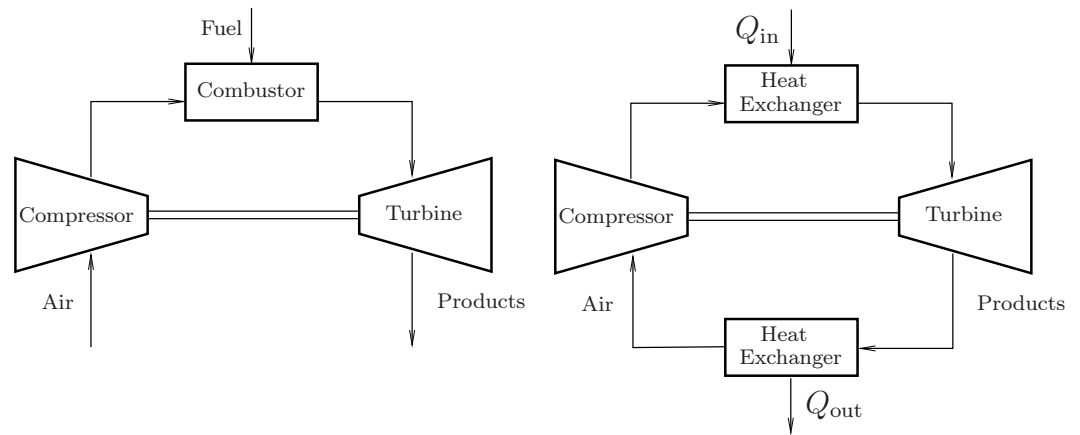


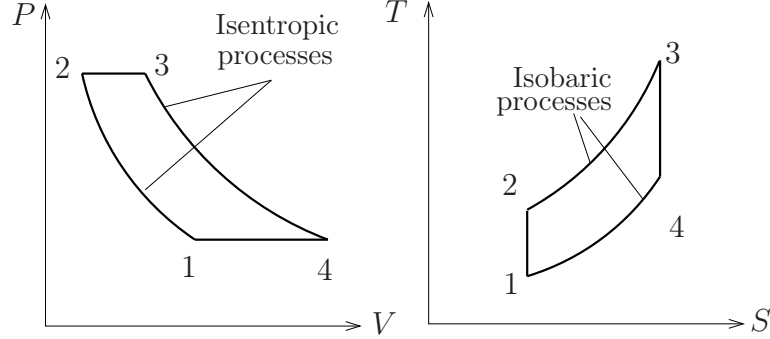
Figure 4.3: Gas turbine operating on the open and closed Brayton cycle.

The open and closed gas-turbine cycles are shown in Fig.4.3. In the Brayton cycle the compression and expansion processes are assumed to be isentropic, and the heat-addition and heat-removal processes occur at constant pressure. Both PV and TS diagrams for ideal cycle are shown in Fig.4.3.

In the Bryton cycle the compression and expansion processes are assumed to be isentropic, and the heat-addition and heat-removal processes occur at constant pressure. Both PV and TS diagrams for ideal cycle are shown in Fig.4.4. For processes 1-2 and 3-4, which are isentropic, the conservation of energy principle reduces to

$$w = \Delta \mathcal{H} + \Delta KE \quad (4.4)$$

where KE stands for the kinetic energy. A steady-flow energy balance for the heat

Figure 4.4: Typical PV and TS diagrams of the ideal Brayton cycle.

exchangers used in process 2-3 and 4-1 is of the form

$$q = \Delta h + \Delta KE \quad (4.5)$$

In the absence of appreciable kinetic-energy changes, the thermal efficiency of the ideal Brayton cycle is given by

$$\eta = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{h_{4s} - h_1}{h_3 - h_{2s}} \quad (4.6)$$

For an ideal Brayton cycle with constant specific-heat values, becomes

$$\eta_{\text{Bray}} = 1 - \frac{T_{4s} - T_1}{T_3 - T_{2s}} = 1 - \frac{1}{r^{\gamma-1}} = 1 - \frac{1}{r_p^{(\gamma-1)/\gamma}} \quad (4.7)$$

where r is defined as v_1/v_2 and r_p as P_1/P_2 . Thus the thermal efficiency of an ideal Brayton cycle is primarily a function of the overall pressure ratio.

The use of constant specific heat data, which led to η_{Bray} , is quite useful in the initial modelling of a gas-turbine power cycle. However, to obtain reasonable values for the heat and work terms in a cycle analysis, it is necessary to account for the variation of c_p with temperature.

In the ideal Brayton cycle, the ratio of the compressor work to the turbine work is roughly 0.44, or 44 percent. This quantity, W_c/w_T , is known as the *back work ratio* of a power cycle. In practice this ratio typically ranges from 40 to 80 percent. It can be shown that the effects of irreversibilities in the compressor and turbine are to greatly increase the back work ratio.

Compared with the Otto cycle, the Brayton cycle operates over a wider range of volume but a smaller range of pressures and temperatures.

4.4 Aircraft Gas Turbines

One of the most effective adaptations of the gas-turbine power cycle has been for the propulsion of aircraft. This is due to the favourable power to weight and power to volume ratios for a gas-turbine unit. The stationary gas-turbine cycle studied earlier

and the jet engine cycle do have some major differences, however. One of these is in the operation of compressors and turbines. In a turbojet propulsion unit there is no work output required from the turbine beyond that needed to drive the compressor and auxiliary equipment. Hence, the turbine drives the compressors, and there is no net shaft output. This is seen in Fig.4.5, which is a schematic of a turbojet engine.

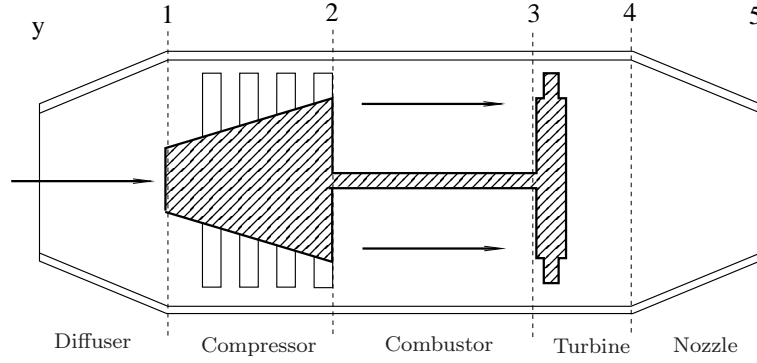


Figure 4.5: Turbojet engine schematic.

The centre section of the engine contains the three major components of a gas-turbine unit—compressor, combustor, and a turbine. Since the work requirement is less, the gas does not expand back to ambient pressure in the turbine. The final expansion occurs in the nozzle which follows the turbine. Here the fluid is accelerated to a relatively high velocity. The pressure ratio P_4/P_5 in the nozzle may be two or more. A third difference in operation is the placement of a diffuser in front of the compressor. Its purpose is to slow down the entering fluid and increase the pressure. A small pressure rise of a few decibars accompanies the decrease in kinetic energy. This pressure rise is referred to as a ram effect.

Compared to stationary gas-turbine power plants, turbojet engines operate at higher pressure ratios and higher inlet-turbine temperatures. Pressure ratios from 10:1 to 25:1 are common. Inlet-turbine temperatures are in the range of 1000-1400 K.

To an observer on the ground a jet aircraft does work in overcoming the resistance to motion known as a fluid drag. In addition, an energy analysis on the overall engine reveals enthalpy and kinetic energy terms at the inlet and exit of device. Finally, a heat term must be included to account for energy released by the combustion of fuel. For the surroundings of the engine in flight we may write

$$\mathcal{H}_{in} + KE_{in} + q_{in} = \mathcal{H}_{out} + KE_{out} + w_{out} \quad (4.8)$$

In terms of the notation of Fig.4.5, $\mathcal{H}_{in} = \mathcal{H}_y$ and $\mathcal{H}_{out} = \mathcal{H}_5$. The kinetic energy terms are based on the absolute velocities noted by the observer on the ground. For still air $KE_{in} = 0$, and KE_{out} is based on the relative velocity between the aircraft speed and the jet exhaust velocity. In still air the aircraft velocity is v_y , so that the relative exit velocity seen by the observer is $v_5 - v_y$. Hence, Eq.(4.8) becomes

$$\mathcal{H}_{in} + 0 + q_{in} = \mathcal{H}_{out} + \frac{(v_5 - v_y)^2}{2} + w \quad (4.9)$$

It is now desired to express this equation for w solely in terms of the inlet and exit velocities v_y and v_5 .

The enthalpy terms and the heat term can be replaced by making another energy analysis on the surroundings of the engine, except that the observer now is on the engine. In this case the steady-flow energy equation becomes

$$\mathcal{H}_{\text{in}} + \text{KE}_{\text{in}} + q_{\text{in}} = \mathcal{H}_{\text{out}} + \text{KE}_{\text{out}} \quad (4.10)$$

or

$$\mathcal{H}_y + \frac{v_y^2}{2} + q_{\text{in}} = \mathcal{H}_5 + \frac{v_5^2}{2} \quad (4.11)$$

If Eq.4.11 is solved for the quantity q_{in} , and the result is substituted into Eq.(4.9), then

$$w = \frac{v_5^2}{2} - \frac{v_y^2}{2} - \frac{(v_5 - v_y)^2}{2} \quad (4.12)$$

This equation is important in determining the propulsive efficiency of the engine, as well as the thrust.

The thrust developed by the engine is retrieved from the relations for the power developed, namely

$$\dot{W} = \dot{m}_a w = F v_y \quad (4.13)$$

where F is the thrust or force which acts to overcome fluid drag. When Eq.(4.12) is substituted into Eq.(4.13) we find that

$$F = \dot{m}_a (v_5 - v_y) \quad (4.14)$$

The propulsive efficiency η_p is a measure of how well energy available in the cycle is converted to work to overcome drag forces. It is defined as the ratio of the work done in flight divided by the sum of this work quantity and the kinetic energy of the exhaust stream relative to ground.

$$\eta_p = \frac{2}{1 + \frac{v_5}{v_y}} \quad (4.15)$$

The condition for maximum work or power can be determined by setting the first derivative of w with respect to v_y equal to zero. The result is

$$v_y = \frac{v_5}{2} \quad (4.16)$$

Hence, the maximum power is developed when the speed of the plane is one-half of the exhaust velocity.

Bibliography

- [1] Georgy Lebon, David Jou, José Casas-Vásquez *Understanding Non-equilibrium Thermodynamics Springer-Verlag* (2008) ISBN: 978-3-540-74251-7
- [2] Tamás Matolcsi *Ordinary Thermodynamics* 1st edition by Akadémiai Kiadó, Budapest, 2004, ISBN 963 05 8170 1
- [3] Mark W. Zemansky, Richard H. Dittman *Heat and Thermodynamics McGraw-Hill* (1997) ISBN 0-07-017059-2
- [4] László Kotek *Thermodynamics and Molecular Physics* Collection of Problems (only hungarian edition) (Janus Pannonius University Press) (1992)
- [5] Israel Ureli *Engineering thermodynamics* <https://www.ohio.edu/mechanical/thermo/>
- [6] Alan Giambattista, Betty Richardson, Robert C. Richardson, *College Physics* The MCGraw-Hill Companies, 2013.
- [7] I. V. Saveleyev, *Physics*, Mir Publisher Moscow, 1980.
- [8] Dilip Kondepudi, Ilya Prigogine *Modern Thermodynamics From Heat Engines to Dissipative Structure*
- [9] Ramamurti Shankar *Fundamentals of Physics*, ONLINE COURSE Yale University, in New Haven, Connecticut
- [10] Ramamurti Shankar *Fundamentals of Physics II*, Yale University Press, New Haven, London ISBN: 978-0-300-21236-5 (2016)
- [11] Venkataraman Balakrishnan, *Core Classical Physics and Nonequilibrium Statistical Physics* ONLINE COURSES, Indian Institute of Technology Madras.