

Thermodynamics

A Rigorous Postulatory Approach

S.H. Chue

*University of Malaya
Kuala Lumpur, Malaysia*

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To my parents

**‘And thou shalt teach them ordinances and laws and shalt
show them the way wherein they must walk’**

Exodus XVIII: 20

Preface

Thermodynamics is the branch of science dealing with our understanding of the properties of matter as they are affected by changes in temperature. It began as an experimental pursuit into the phenomena related to thermal interactions between bodies. However its usefulness was realized by different groups of people at different periods of its development (mainly because each area was then built up from a separate collection of experimental data that seemed to bear little resemblance to other areas. As a result, many textbooks on the subject have been written for each of its various specializations with little cross reference to other fields. For instance, texts on heat engines usually contain little other information beyond that strictly necessary for its exposition, and chemical or chemical engineering texts are primarily devoted to the study of topics in physical chemistry. However, a much wider theoretical basis now exists on the subject whereby each different topic can be neatly accommodated into a body of self-consistent theory. This systematic study of the subject was brought about by Hatsopoulos and Keenan (co-authors of the book entitled 'Principles of General Thermodynamics'). However, their work demands a level of sophistication generally higher than that possessed by undergraduate students.

In the belief that a rigorous development of the subject is of the highest importance in that it not only permits a more elegant exposition of the subject matter but also helps to cut across compartmentalized areas of specialization, thus stimulating interdisciplinary teaching, the author has taken this opportunity to introduce a text at the undergraduate level while retaining the rigour of Hatsopoulos and Keenan's presentation. Such an approach should be particularly beneficial to the physicist as this allows him to see with greater clarity the order of the physical world. In order to achieve the aim of injecting greater rigour into the undergraduate course, the text is based on the laws of thermodynamics rather than on the generalized principles of Hatsopoulos and Keenan. From these laws, the student will be guided to all other topics generally treated in a thermodynamics course by means of formal logic. Though some knowledge of calculus is necessary for the more advanced topics in the text the degree of dexterity required is not very great.

The author has felt free to tidy up some oddities that still persist in the thinking of many thermodynamicists. This should help to make the treatment of the subject more rational than it is at present. In the past, many writers had

maintained that the practical temperature scale and the theorists' concept of thermodynamic temperature referred to two different entities; indeed, both scales are accepted even today. Such a contention can be attributed to the fact that the first attempts to measure temperature were made long before any thermodynamic studies. To remove this anomaly, the present discussion on temperature begins with the qualitative definition of Maxwell. This is taken through the zero and first laws of thermodynamics to the second law, wherein it is evident that the logical exposition of thermodynamics does not require any quantitative measures of temperature before it can be so defined. It is hoped that eventually the kelvin alone will be used as the unit of temperature. The layman should in time have no difficulty in realizing that ice forms at about 273 kelvins, a heat wave sets in at about 310 kelvins and that our comfort range lies somewhere below 300 kelvins.

Similarly, since all experimentally observed laws in physical chemistry can be deduced as a consequence of a basic definition of an ideal solution, the treatment of ideal solutions in this text is considered more consistent than that of Hatsopoulos and Keenan.

The subject matter has been arranged in such a way that students following an applied thermodynamics course could proceed onto engineering cycle analysis, without confusion as to the choice of properties to be used in their calculations. To achieve this objective, the topic on properties of pure substances has been split into two parts, with cycle analysis inserted between them. Thus, students in engineering schools can be given a first course in thermodynamics by covering Chapters 1 to 6. More advanced topics on combustion and gas mixtures with an appropriate selection of materials, and more advanced topics on cycle analysis can be given in a second course. This arrangement does not break the continuity of presentation for students in chemical engineering schools as the topics on application are also well placed. Students of chemistry and physics may omit Chapter 6 or gloss over it with a few examples to gain an idea of the type of analysis that can be performed with the first and second laws.

The last two chapters present some topics of special interest. In particular some alternative schemes for energy conversion to those given in Chapter 6 have been included in greater detail than generally found in texts on thermodynamics, in the hope that it will encourage students to further study of the subject. It is impossible to give adequate acknowledgements to all those who have contributed either directly or indirectly to this book. However, much is owed to Professors George N. Hatsopoulos and Joseph H. Keenan, whose book inspired the writing of this text. The author is particularly indebted to them for their kind permission to produce in the abridged form their discussions on the *Phase Rule* and on the *effect of chemical equilibrium on the number of components* of a multi-component system. Their permission to use two of their problems, *Problems 11.5 and 12.1*, is also gratefully acknowledged.

S.H. Chue

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Contents

Preface	xi
1 Fundamental concepts	1
1.1 Introduction	1
1.2 Basic definitions	1
1.3 Work and heat	3
1.4 State of equilibrium	6
1.5 Reversibility	7
1.6 Principle of equivalence	7
Examples	9
Problems	10
2 Basic postulates in classical thermodynamics and their consequences	11
2.1 Zeroth law	11
2.2 First law	11
2.3 Second law	13
2.4 The state principle	27
2.5 Third law	28
Examples	29
Problems	30
3 Thermodynamics of one component systems	32
3.1 Simple systems	32
3.2 Energy of a simple system	32
3.3 Gibbs equation for a simple system	33
3.4 Other characteristic functions of simple systems	34
3.5 Maximum work and maximum useful work	36
3.6 Availability and irreversibility	38
3.7 Relations between properties of simple systems: Maxwell's equations	39
3.8 Criterion for equilibrium of a simple system	42
3.9 Coexistence of phases in a simple system: Clapeyron's equation	44

3.10	Realization of the true thermodynamic temperature	45
	Examples	47
	Problems	52
4	Extension to flow processes: thermodynamics of open systems	56
4.1	First law for open systems	56
4.2	Second law for open systems	58
	Examples	60
	Problems	64
5	Properties of ideal substances	66
5.1	Introduction	66
5.2	Ideal gases: semiperfect and perfect gases	66
5.3	Ideal liquids and solids	70
5.4	Tables of thermodynamic properties	72
	Examples	74
	Problems	80
6	Direct and reversed heat engines	82
6.1	Reversible and irreversible state changes on $p - v$ and $T - s$ diagrams	82
6.2	Vapour power cycles	88
6.3	Gas power cycles	99
6.4	Refrigeration cycles	112
	Examples	118
	Problems	131
7	Properties of real substances	134
7.1	Behaviour of real substances	134
7.2	Dense gases: van der Waals equation	136
7.3	Law of corresponding states	139
7.4	Other equations of state	140
7.5	Developing thermodynamic properties from experimental data	143
	Examples	151
	Problems	153
8	Thermodynamics of multi-component systems	156
8.1	The phase rule	156
8.2	Partial properties	158
8.3	Gibbs–Duhem equation	160
8.4	Equilibrium with respect to transfer of components	162
8.5	Chemical potential as an escaping tendency	163
8.6	Chemical potential of ideal and real gases	163
8.7	Effects of pressure and temperature on fugacity	165

8.8	Developing fugacity values from experimental data	166
	Examples	166
	Problems	169
9	Properties of ideal solutions	171
9.1	The concept of a solution	171
9.2	Amagat–Leduc law of additive volumes	172
9.3	Mixture of ideal gases	173
9.4	Mixture of an ideal gas and a condensable vapour: psychrometry	177
9.5	Mixture of dense gases	178
9.6	Sufficiency condition for an ideal gas mixture	183
9.7	Fugacity and ideal solutions	184
9.8	Equilibrium with respect to transfer of components in terms of fugacity	187
9.9	Effect of pressure on vapour pressure	187
9.10	Raoult's law	188
9.11	Henry's law	189
9.12	Law of boiling point elevation	190
9.13	Osmotic pressure	191
9.14	Chemical potentials of components in ideal solutions	193
9.15	Non-ideal solutions	194
	Examples	195
	Problems	202
10	Thermodynamics of reacting systems	205
10.1	First law analysis of chemical reaction	205
10.2	Effect of chemical reactions on number of components: chemical equilibrium	206
10.3	Equilibrium constant and the law of mass action	208
10.4	Systems in stable chemical equilibrium: Le Chatelier's Principle	210
10.5	Chemical potential and equilibrium constant of formation	211
10.6	Free energy change and equilibrium constant	212
10.7	Effect of temperature and pressure on equilibrium constant	213
10.8	Second law analysis of chemical reactions: work done by chemically reacting systems	214
10.9	Third law and equilibrium constants	215
	Examples	216
	Problems	220
11	Thermodynamics of special systems	223
11.1	Thermal radiation	223
11.2	The fuel cell	226
11.3	Inclusion of surface effects	235
11.4	Thermodynamics of general systems	242

Examples	243
Problems	244
12 Introduction to thermodynamics of irreversible processes	247
12.1 Introduction	247
12.2 Phenomenological laws and Onsager's reciprocal relations	247
12.3 Entropy production in systems involving heat and current flows	250
12.4 Application to thermoelectric circuits	251
12.5 Direct energy conversion from thermoelectric effects	256
Problems	263
Index	265

CHAPTER ONE

Fundamental Concepts

1.1 INTRODUCTION

Thermodynamics is the branch of science dealing with our understanding of matter as it is affected by changes in temperature. To date two approaches have been found successful in its description. These are;

- (i) postulatory (or classical);
- (ii) statistical.

The postulatory approach was originally developed primarily for the study of heat engines. However, its scope has since been extended to many other processes. It is not concerned with the form of matter but seeks to relate the observed physical properties of matter from using certain basic postulates. In contrast, the statistical approach is founded on the atomistic behaviour of matter and seeks through molecular dynamics to justify the postulates and other phenomenological laws taken for granted in the postulatory approach. We are not concerned here as to which of these two approaches is the more fundamental or more exact, or which approximates to the other, but since the mathematics required in the statistical approach is much more sophisticated, this will be left to more advanced courses.

Though historically classical thermodynamics began with experiments on a macroscopic scale, the results of which were then unified into a self-consistent theory, thermodynamic principles can best be explained from a purely logical viewpoint. Using this approach, we shall first familiarize ourselves with the basic definitions and fundamental concepts that are essential to our understanding of the subject matter to be presented in later chapters.

1.2 BASIC DEFINITIONS

To start, a *system* may be defined as an isolated region in space enclosed by well defined surfaces across which no mass can pass. The entire region which includes everything external to the system is called its *surroundings*. Surfaces separating the system from its surroundings are known as *boundaries*. Ideally, boundaries are mathematical surfaces which we endow with various ideal physical characteristics, such as rigidity and impermeability. If a system has been isolated

from its surroundings, all changes occurring in the system are considered to be independent of all changes that take place in the surroundings; hence if two systems are not isolated from each other, then changes in one will affect changes in the other. Since no mass can pass from one into the other, we invariably conclude that such changes are brought about by means of *boundary interactions* only.

As thermodynamics primarily deals with changes in systems, measures for identifying these changes are necessary. These measures are generally based on certain characteristics that can describe the condition of the system under investigation, and must be found by experience since many physical characteristics are irrelevant from the thermodynamic viewpoint, for examples, colour and shape. Any suitable characteristic whose value depends on the condition of a system and which is relevant to our thermodynamic investigation is known as a thermodynamic *property*.

There are two fundamentally different ways in which we can classify properties. From the standpoint of measurability, the properties may be termed *primitive* or *derived*. By primitive property, we mean any property that can be specified by an operation on the system that does not effect any noticeable change on the system. Any property that is not a primitive property is known as a derived property. Alternatively, from the computational viewpoint, the properties may be *intensive* or *extensive*. The former are essentially local in character and include such quantities as pressure, temperature, density and electric field. Mathematically, an intensive property is defined using the concept of a limit at a point, so that such properties are independent of the size of the system. Note that the mathematical definition deals with a hypothetical continuous substance, i.e., the continuum, and for the definitions to be valid, the 'point' taken for the limit should remain several orders larger than the molecular mean free path or distance so that coarseness in the fine structure of matter does not emerge. Properties of the extensive class in a sense convey a measure of the size or extent of the system, and include such quantities as mass, volume and internal energy. These quantities are generally proportional to the mass of the system if other conditions are kept constant. Thus, using the *additive rule*, the value of an extensive property is equal to the sum of its values for all parts of the system into which it may be subdivided.

It is often convenient to refer to extensive properties in terms of their values *per unit mass* of the system. These are known as *specific* properties. It has been the usual practice to denote extensive properties by capital letters and their derived specific properties by the corresponding small letters. For instance, we denote the volume of a system by V and the specific volume by v . Note that specific properties are also local in character and hence have often been referred to as intensive properties in many text books.

To continue, the *state* of a system is defined as that condition of the system which is capable of being completely specified by all its primitive properties. The entire series of states that a system undergoes during a change of state is called the *path* of the change, while the complete description of the change of a

system including the end states, the path and the boundary interactions constitutes a *process*. A process whose end states are identical is referred to as a *cycle*. It should be noted here that classical thermodynamics requires that processes should be carried out infinitely slowly, as shown in Section 1.5. The actual rate of a process is the concern of irreversible thermodynamics which will be examined briefly towards the end of this book.

As a consequence of the above definitions, we arrive at the following useful results, which we shall refer to as corollaries to the basic definitions.

Corollary 1 A change of state is fully described by means of the initial and final values of all the primitive properties of the system. A change occurs when at least one of its primitive properties changes value.

Corollary 2 A process is required for the determination of a derived property.

Corollary 3 The change in value of a property is fixed by the end states of a system undergoing a change of state and is independent of the path.

Corollary 4 Any quantity which is fixed by the end states of a process is a property of a system.

Corollary 5 When a system goes through a cycle, the change in value of any property is zero.

Corollary 6 Any quantity whose change in a cycle is zero is a property of a system.

These corollaries will be referred to many times in later discussions and students are therefore advised to become thoroughly familiar with them.

1.3 WORK AND HEAT

In mechanics, *work* is defined as the product of the displacement of a force and the component of the force in the direction of the displacement. Thus

$$W = F_x \cdot x \quad (1.1)$$

where F_x denotes the component of F in the x direction and x the displacement.

If F_x depends on x , then eqn. (1.1) can be written in the form of an integral

$$W = \int F_x dx \quad (1.2)$$

This is a useful definition as it enables us to evaluate the work done by a force.

However, in view of the fact that we are dealing primarily with interactions between systems in thermodynamics, the above definition is not directly applicable. If we examine this definition more closely, we note that even in the mechanical sense, work is done only when the force moves, no work being done when the force remains stationary, i.e., the definition of work involves a process. From this consideration, we conclude that work cannot be a property of a system. Rather, it is something that the system experiences while it changes from one state to another. We are now in a position to extend the mechanical definition of work to the thermodynamic sense; thus

Work is an interaction between two systems such that what happens in each system at the boundary could be repeated with the change in level of a weight as the sole effect external to each system.

As in mechanics, work can be a positive or negative quantity. We shall adopt the following convention which is now universal;

- work done by a system is positive;
- work done on a system is negative.

To amplify on the above definition, let us consider the following situations where work is done in the thermodynamical sense, though not necessarily in the mechanical sense.

- (1) Consider a system comprising a container filled with water as used in Joule's classical paddle-wheel experiment. Work is clearly done on the system if we rotate the paddle-wheel by means of descending weights, as performed by Joule, since what happens external to the system is the change in level of a weight.
- (2) If we use a motor to rotate the paddle-wheel instead, we may still argue that work is being done on the system since the rotation of the shaft could have been brought about by a falling weight as in (1).
- (3) If now we replace the paddle-wheel and spindle altogether by a resistive coil of wire with leads passing through the system boundary and connected to a battery. By such means we are able to bring about the same changes as occurred in (1). Is this work? The answer to this question cannot be provided by the purely mechanical definition. However, with our extended definition, we can show that work is being done, as follows: Let us consider the container with its mass of water and the battery as two interacting systems. If we short-circuit the resistance in the water and connect a motor in between these two systems (note that the motor is external to both), we could repeat the same phenomenon as occurred earlier, viz, the flow of electrons through the lead wires, and have the earlier result, viz, the change in state of the water, reduced to the change in level of a weight as the sole effect external to both systems. (Of course, we assume that the motor is 100 percent efficient! But the side effects lie with an imperfect motor rather than imperfect argument!)

This last illustration leads to the following important result: a flow of electricity *across* the boundary of a system represents a work interaction.

If we were to further modify our above system by having the resistance coil wound around the container on its outside wall, rather than immersed in the water as previously (see Figure 1.1a), by the above argument, work is done if we consider the system comprising the container and the coil as a whole. Now let us consider the system consisting of the mass of water in the container only, as in Figure 1.1(b); the argument of (3) above shows that work cannot be involved since the wires do not lead through the system boundary. What then is it that changes the state of our system? One point we note is that the water changes

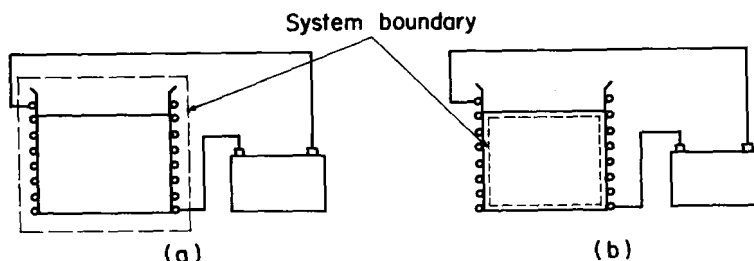


Figure 1.1

its state because it is 'colder' than the coils while the current is flowing. We could have brought about the same changes in the water by means of an alternative 'hotter' object such as a bunsen burner. (The terms hot or cold as used here are in their usual sense.) If between the two systems, one consists of the water and the other the hot object (either the resistance coil or the burner), we were to interpose a 'heat engine', we would invariably find that the weight-raising cannot be the sole effect external to these systems. There were always other side effects; either the water does not return to its initial state after passing through the engine or the surroundings become warmer in the process. Such a mode of changing the state of a system without work being done has been conventionally referred to as being brought about by *heat*. Though we accept this term in describing the above interaction between our two systems, we are immediately forced to forego the conventional idea that heat is a form of energy which can be added to or withdrawn from the system (the remnants of the caloric theory). Just as work is not a property of a system, neither is heat. From the above considerations, we arrive at the following definition for heat

Heat is an interaction between systems which occurs by virtue of their *temperature* difference when they are brought into contact with each other.

By temperature we mean the thermal state of a system considered with reference to its power of communicating heat to other systems. This latter definition for temperature was coined by Maxwell. In spite of its qualitative nature and its seemingly circular reference to heat, it is sufficient for our present understanding of the subject. The sign convention for heat is as follows;

- heat 'flow into' system is positive;
- heat 'flow out of' system is negative.

Before we close our discussion on work and heat, we shall sum up some of their important properties. Heat and work are not forms of energy; both are transient boundary phenomena which exist during the interaction only. Also, heat is not always necessary to cause a temperature rise, as both heat and work have the same end-effects.

Units of work

The unit for work can be inferred through its definition in mechanics. Since in SI units, the unit of force is the newton and the unit of length the metre, the unit of work is the newton-metre. This composite unit has also been called the joule. The same unit is used in thermodynamics.

Units of heat

In SI units, the unit of heat is also the joule. It is not immediately obvious why this should be so. This question will be answered when the formulation of the first law is discussed.

1.4 STATE OF EQUILIBRIUM

The concept of *equilibrium* is central to the study of thermodynamics. By equilibrium, we mean that no further perceptible changes can occur no matter how long we wait. This can be inferred from our definition of property. Since the value of a property changes if the state of the system is altered, property has meaning only when the system is no longer changing. As in mechanics, we distinguish four types of equilibrium. However, for our present purpose, there is no need for us to go into details of these. It suffices for us to say that a system is said to be in a state of equilibrium if after any slight temporary change in the surroundings it returns to its initial state. From this definition, it follows that a finite change from the equilibrium state cannot occur without leaving a permanent change of state in the surroundings. Such states are also known as stable states of equilibrium.

Without further definitions on the internal conditions of a system or assistance from certain fundamental postulates, we are not yet in a position to investigate the conditions of equilibrium within a system. The discussion is therefore confined at present to the equilibrium conditions existing between two systems in equilibrium.

If we take two isolated systems and allow them to come into equilibrium separately, and then bring them into communication with each other, there are two possible interactions between these two systems, viz. work and heat. Consider first that the surface of contact is an *adiabatic wall*, i.e. a surface across which only work interaction is allowed; if the pressures in the two systems on the two sides of this wall is unequal, an unbalanced force exists across this surface. Its magnitude is given by $p_1 A - p_2 A$. The adiabatic wall will move until it reaches a position where this unbalanced force vanishes. Thus, the condition of equilibrium for work interaction across two isolated systems to cease is that the pressure be equal on the two sides of their common adiabatic wall.

If now we replace the adiabatic wall by a *diathermal wall*, i.e. a surface across which only heat interaction is allowed, we find in general heat interaction occurs until the temperature difference across the diathermal wall becomes

zero. Thus, the condition of equilibrium for heat interaction across two isolated systems to cease is that the temperature be equal on the two sides of their common diathermal wall.

Note that at this stage we do not forbid the occurrence of temperature or pressure gradients within a system. Under such conditions, the equilibrium conditions discussed above are still valid provided that the same type of gradients occur on both sides of the surface separating the two systems.

1.5 REVERSIBILITY

Consider a system in equilibrium undergoing a certain change of state. We can determine the change in the properties of this system after it is allowed to settle in a new state of equilibrium. From Corollary (3) of our basic definitions, we are able to bring about the same changes by splitting the process up into stages. In order to describe the state of the system after any intermediate stage, we need to know its properties right after that stage. Thus, we require that if a complete description of the property at each point of the process be given, the system must be in a state of equilibrium throughout the process. Such a process is called a *reversible* process. It can only take place infinitely slowly since time has to be allowed for the system to reach equilibrium after an infinitesimally small interaction. As the system is in equilibrium at all times, forces exerted on the system by its surroundings must be balanced by internal forces within the system such that the direction of the process can be reversed and the initial state regained without any other change in the system or surroundings occurring. Because of this, we can also state the following alternative definition for a reversible process:

A process is *reversible* if means can be found to restore the system and its surroundings to their respective initial states.

This definition is very useful when we want to examine whether any given process is reversible or not. The method for such investigations will be given later, after we have studied the second law.

From the above discussion, it is clear that a reversible process is an ideal one and that all real processes are irreversible. Nevertheless, under laboratory conditions near reversible conditions can often be achieved although the types of experiments are not relevant in the present context. Irreversible processes cannot be retraced without leaving a permanent change in the surroundings.

1.6 PRINCIPLE OF EQUIVALENCE

Thermodynamics is a physical science. It is therefore a pursuit of logic just as any other science. There is a somewhat fundamental difference that distinguishes classical thermodynamics from other sciences. All other sciences depend heavily on mathematics as a language for expression. The principles of classical thermodynamics, on the other hand, are essentially verbal and not meaningful in a mathematical sense. Though these laws can be expressed in terms of certain