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Thermodynamics and Statistical Mechanics

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**Thermodynamics and
Statistical
Mechanics**

Preface

The object of this text is to provide the reader with a comprehensive introduction to the basic concepts of thermodynamics and statistical mechanics. It is intended for science and engineering undergraduates.

The emphasis throughout is on simplicity and clarity, the order of presentation and the explanations given being those which have been found most successful with students and acceptable to them. It is often found that ideas are presented to students which are not wholly true. This may either be in order to gloss over certain difficulties or possibly from a lack of understanding. Despite the simplicity of approach of the present text, the truth has not been overlooked.

SI units have been used, and for the convenience of those unfamiliar with them an appendix on this topic has been included.

The approach to thermodynamics is, of necessity, mathematical. Quite often, students lose themselves in the mathematics, not appreciating that it is merely a tool used to obtain the end-result. Basically, all the mathematics that is required is a little algebraic manipulation and a small amount of elementary calculus.

The classical approach to entropy of Chapter 4 may be omitted with no loss of continuity, this being provided by the alternative approach of Chapter 5. The modern practice of chemists is to avoid the classical approach. Probability has been introduced in Chapter 5 in order to clarify the concept of entropy. The third law is presented soon after the first and second laws, rather than being left as an afterthought, as is often the case. All types of solutions – gas, liquid and solid, ideal and non-ideal – are dealt with as a whole in Chapter 13, thus avoiding unnecessary repetition. Because of the importance of chemical equilibria, an elementary derivation of the van't Hoff isotherm is given in Chapter 8 in order that the reader be familiar

with it at an early stage. In addition, a more general approach is given in Chapter 14.

Asterisks have been employed at section headings to indicate sections of interest to readers wishing to have a more thorough knowledge. These may be omitted without any loss of continuity.

I should like to acknowledge the assistance given to me by many colleagues and past students, and to thank Dr. K. P. Kyriakou for his encouragement. It is also a great pleasure to acknowledge the vast amount of assistance I have received from my wife, Jeanne, not only in the form of helpful discussions and encouragement, but also in the typing of the manuscript.

Brunel University
April 1971

G.S.



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1

Introductory Concepts

1.1 Introduction

In thermodynamics, when we talk of a *system* we mean a specific portion of matter, with definite boundaries, on which our attention is focused. Other terms which will be referred to frequently are:

Surroundings. All space and matter external to the system, which may or may not interact with the system.

Open systems. Those systems in which mass may be transferred between the system and the surroundings.

Closed systems. Those systems of constant mass, i.e. in which no transfer of mass occurs.

Universe. The system plus its surroundings (no celestial connotations being implied).

Isolated systems. Systems which cannot exchange energy of any kind, including mass, with their surroundings. In other words, an isolated system is not allowed to exchange heat, work or mass with its surroundings.

A process. Any transformation of a system from one equilibrium state to another over an interval of time. (Work and heat transfers may possibly occur during a process.)

The path of a process. The specific series of equilibrium states through which the system passes during the process.

A complete description of a system defines the existing condition or *state* of the system. There are two ways of giving a complete description of a system, microscopic and macroscopic. For simplicity, let us consider a system that consists of a single homogeneous substance. (By homogeneous, we mean chemically and physically uniform throughout.)

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MICROSCOPIC DESCRIPTION

A homogeneous system may be thought of as consisting of a very large number of particles (atoms or molecules) of the same mass. The position and velocity of each particle are both needed for a complete description. That is, for each particle we need three cartesian coordinates x , y , z and the velocity components v_x , v_y , v_z . Therefore, for N particles we need $6N$ values to determine the state of the system. The state defined in this manner is known as a microstate. Because of the motions of the molecules and atoms this type of description would only be true for a single instant in time. The microscope description leads to a *statistical* approach to thermodynamics.

MACROSCOPIC DESCRIPTION

To give this type of description, we need a knowledge of the properties of the system such as mass M , pressure P , volume V , temperature T , etc. These measurable properties may, in theory, be determined from a knowledge of the microscopic state. For instance, pressure is the average force due to the impact of molecules on unit area, i.e. the average rate of change of momentum for all the molecular impacts on unit area. A state defined by using measurable quantities is known as a macrostate.

The *microscopic description* has the following *disadvantages*:

- (1) We assume a knowledge of the nature of matter, for example that the system is composed of molecules;
- (2) The description of the state of the system requires the knowledge of a large number of values ($6N$);
- (3) The quantities required to describe the system (e.g. the positions and velocities of all the molecules) cannot be easily determined;
- (4) The description is only true for a single instant in time.

An *advantage* of the microscopic approach, and therefore a *disadvantage* of the macroscopic approach, is that the conceptual insight on the molecular scale given by statistical thermodynamics cannot be attained in any other way.

The *advantages* of the macroscopic description are:

- (1) No assumption about the composition of matter is necessary;
- (2) Only a relatively small number of quantities is required to describe the state of the system;
- (3) The description is given in terms of quantities which can be easily measured (M , P , V , etc.).

Of course, the results obtained from both the microscopic and macroscopic approaches to thermodynamics must agree.

1.2 Functions of state

Consider a system consisting of a single homogeneous substance. In giving a precise macroscopic description of the state of the system, we could use the properties mass M , volume V , pressure P , temperature T , density ρ , viscosity η , refractive index n , etc. These *functions of state*, as they are known, are used to define the state of the system. Functions of state are independent of the previous history of the system. We say that a system is in an *equilibrium state* if its functions of state (i.e. properties) remain constant, provided that its external environment is not altered.

1.3 Extensive and intensive quantities

The properties of a system may be classed as intensive or extensive. If we consider a system which has been divided into two identical parts, then those properties which have not been altered by the division are *intensive* properties (e.g. pressure, temperature, density, viscosity, refractive index) whereas those properties which have been exactly halved are *extensive* properties (e.g. mass, volume, energy, charge). Intensive properties, as opposed to extensive properties, are therefore independent of the amount of material present. Extensive thermodynamic properties which we shall meet with in the course of this book are internal energy U , enthalpy H , entropy S , the Helmholtz function A , and the Gibbs function G .

Intensive analogues of extensive properties do exist, for example, specific volume v (i.e. volume per unit mass) or molar volume v (volume per unit amount of substance), molar internal energy u , molar enthalpy h , etc. Note that we use lower-case letters for the specific or molar quantities of functions, e.g. volume V and specific volume v , enthalpy H and specific enthalpy or molar enthalpy h , entropy S and molar entropy s . Specific or molar properties are all intensive functions of state.

1.4 Independent variables

The question now arises as to how many functions of state are needed to define the state of a system consisting of a single, homogeneous substance. From our own experience it is obvious that we

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do not need to know all the properties of the system. It has been found by experiment that, in general, if we fix the mass of the substance and any two other functions of state such as volume and pressure, or volume and temperature, or pressure and density, or volume and viscosity, then all the other functions of state are fixed automatically. That is, we need only know the values of three variables to define the state of the system. We therefore say that the system has *three independent variables*. By independent variable, we mean that the property cannot be calculated from a knowledge of the other functions of state used to define the state of the system. For instance, M cannot be calculated from P and T . On the other hand, density is not independent of M and V , and T^2 is not independent of T . At least one of the three independent variables must be an extensive property if the amount of substance present is to be known. For a system of *given* mass, only *two* independent variables are required to define the state. This means that if we choose any two independent variables (say P and V) then there exists an equation relating these variables and any one of the other functions of state (say T). That is, for a given mass, T may be considered a mathematical function of P and V only,

$$T = f(P, V) \quad (1.1)$$

Similarly, we may have

$$\eta = f(P, V)$$

and

$$\rho = f(P, V)$$

For a given system, these relations may be very complex, so much so that we may never know them explicitly.

Any function of state ψ may be written as a function of the independent variables of a system,

$$\psi = f(\text{independent variables}) \quad (1.2)$$

Such equations are known as equations of state. We are, of course, all familiar with the equation of state of an ideal gas, i.e. for one mole,

$$Pv = RT$$

where T is the temperature on the *ideal gas temperature scale* (absolute zero on this scale being the temperature at which the volume of an ideal gas vanishes) and R is the *universal gas constant*.

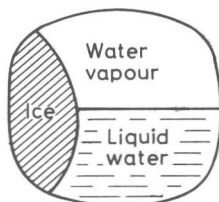
Although, in general, only two functions of state are required to define the state of a pure homogeneous substance of given mass, there are systems for which *any* two properties will *not* define the state. For example, pressure and density are not sufficient to define the

state of liquid water near 277 K, since the density of water goes through a maximum at this temperature.

1.5 Phase

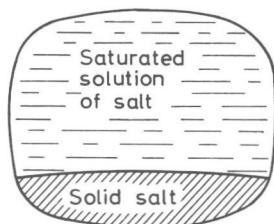
A *phase* is a homogeneous part of a system separated from other parts by physical boundaries, i.e. a phase is physically and chemically uniform throughout. By a *heterogeneous system* we mean that the system is composed of more than one phase.

Example 1 In the system shown there are three phases (solid, liquid and vapour).



A solution (whether solid, liquid or gas) is considered as a single phase since it is chemically and physically uniform throughout.

Example 2 The system shown contains two phases.



Sometimes people use such terms as 'the gaseous state' and 'the solid state'. Strictly speaking, these are incorrect; one should refer to 'the gaseous *phase*' and 'the solid *phase*'.

1.6 Thermodynamic state

To define the thermodynamic state of a homogeneous system containing more than one substance, we must specify the amount of each component in the system and two other independent variables such as P and T .

To define the state of a heterogeneous system containing more than one substance, we must consider and describe each of the phases

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of the system. For each phase we must specify the content, i.e. the amount of each substance present, and two other independent variables.

1.7 Thermal equilibrium

A system is in *thermodynamic* equilibrium if the properties of the system do not alter so long as the external environment remains unchanged.

Consider two systems A and B, each in a state of equilibrium. Let them be brought into thermal contact by means of a *diathermic wall*, i.e. a wall allowing the transfer of heat from one system to another. The systems are thermally insulated from the rest of the universe by a surrounding *adiabatic wall*, i.e. a thermally insulating wall (see Figure 1.1). If the systems A and B were not in mutual equilibrium originally, then their properties would change until eventually

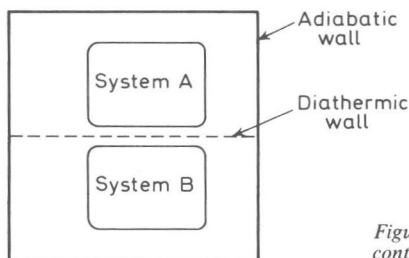


Figure 1.1 Systems A and B in thermal contact and surrounded by an insulating wall

they were so. Once this equilibrium is attained, no further change in the properties of the system will occur so long as the external conditions are not altered. The two systems are then said to be in *thermal equilibrium*.

It is possible to define a 'new' property which will show that the two systems are in thermal equilibrium, this property being known as temperature. By definition, two systems have equal temperatures if, when brought into thermal contact, their properties do not change. In other words, two systems in thermal equilibrium have the same temperature.

1.8 Zeroth law

Let us apply the concept of temperature equality of systems in thermal equilibrium to the following experiment. Two systems A and B, separated by an adiabatic wall, i.e. a thermally insulating

wall, are both brought into thermal contact with a third system C by means of a diathermic wall (Figure 1.2).

Eventually, systems A and B will come into thermal equilibrium with system C and then there will be no further change in their properties. At equilibrium, systems A and C must have the same temperature, and similarly systems B and C must have the same

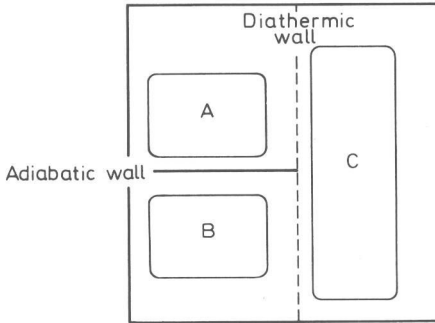


Figure 1.2. Systems A and B in thermal contact with system C but insulated from each other

temperature. Therefore, the temperatures of systems A and B must also be equal.

This experiment demonstrates the *zeroth law* of thermodynamics which states that *if each of two systems is in thermal equilibrium with a third, then they are also in thermal equilibrium with each other.*

Although this statement seems obvious, it cannot be derived from other observations of nature and is for this reason known as a *law*. The zeroth law is, of course, the basis of temperature measurement.

1.9 Temperature scales

Any system in a well-defined state may be used as a reference for temperature measurement, all other systems in thermal equilibrium with it having the same temperature. If a system is to be used as a thermometer, numerical values must be given to the temperatures of two well-defined states of the system and the thermometric property of the system must be measured in those states. A few of the commonest thermometric properties are volume, pressure, electrical resistance and length.

The Kelvin (or absolute) temperature scale, which is also known as the thermodynamic temperature scale, will be discussed later.

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It is unique in that it is independent of the thermometric properties of any system and it will be shown to be identical with the ideal-gas temperature scale.

1.10 **Thermodynamic equilibrium**

For simplicity, consider a system that consists of a single homogeneous substance. If the properties of the system are uniform throughout, then, so long as the external conditions are unaltered, the system is said to be in *thermodynamic equilibrium*. For example, if the pressure were not uniform, turbulence would occur until the system reached equilibrium. It is only under equilibrium conditions that the state of a homogeneous system of given mass may be described by only two functions of state, each function having only one value.

A system is in thermodynamic equilibrium if it is in mechanical, thermal and chemical equilibrium.

Mechanical equilibrium exists if there are no net forces between the system and the surroundings and if also there are none within the system.

Thermal equilibrium exists if the temperature of the system is uniform throughout and equal to that of the surroundings with which it is in thermal contact.

Chemical equilibrium exists if the composition of each compound present is constant and if diffusion and solution do not occur.

1.11 **Reversible and irreversible processes**

A *quasi-static process* is one performed infinitely slowly.

A *reversible process* is a quasi-static process in which all means of energy dissipation are absent.

Energy dissipation may be due to friction, viscosity, electrical resistance, magnetic hysteresis, plastic deformation, etc. Reversible processes are hypothetical processes which are useful for comparison purposes. The concept of a reversible process may be compared with that of frictionless pulleys, weightless strings, etc. that are used in mechanics. Since the state of the system changes infinitely slowly during a reversible process, the system goes through a *continuous series of equilibrium states*. *A reversible process may be defined as one for which the system is always in equilibrium.*

Any process that is not reversible is known as an *irreversible process*. All naturally occurring (i.e. spontaneous) processes are non-equilibrium processes and therefore irreversible. We shall,

in fact, show in Chapter 3 that irreversible processes cannot be reversed without leaving the surroundings permanently changed.

For the reversible expansion of a gas in a vessel fitted with a frictionless piston, the gas must always be in equilibrium, and therefore the pressure on the piston must be released infinitely slowly, so that at any instant in time the pressure and temperature are uniform throughout the gas. The state of the gas at any time may then be given by the single values of two variables, e.g. pressure 10^5 N m^{-2} , temperature 300 K.

If the piston were withdrawn rapidly, the gas would perform no work in rushing in to fill the vacuum left by the piston, pressure differences would be set up and turbulence would occur. In this case, the state of the gas cannot be given by the single values of two variables. Instead, an infinite number of values of the two variables would be required since the state of each point within the gas must be described. Only the initial and final states of the gas would then be equilibrium states. The rapid expansion described is an irreversible process.

The path of a reversible process can be shown by a line on a graph with suitable axes. However, we cannot do the same for an irreversible process since the state of the system cannot be described by the single values of two variables.

If the piston is released rapidly, (1) pressure differences will occur in the gas, and (2) the pressure opposing the change will increase. Both (1) and (2) will oppose the expansion and, hence, work is necessary to overcome them. For a *reversible expansion*, the *maximum possible work* is obtained since neither (1), (2) nor friction occur. Similarly, for a rapid compression, (1) and (2) would occur. Hence, for a *reversible compression*, the *minimum possible work* is used.

It is only for a *reversible* process that the *maximum work output* or the *minimum work input* can be achieved, that is, when the forces responsible for the change of state of the system are essentially always at equilibrium and energy dissipation does not occur.

In a reversible process, a system must be in thermal equilibrium. Therefore, if it is in thermal contact with its surroundings, it must be in thermal equilibrium with them at all times.

Since a system must be in equilibrium during a reversible process, all chemical reactions carried out under normal conditions are irreversible. Chemical reactions may be carried out reversibly only if the reaction is essentially at equilibrium. One very good and simple way of doing this is to construct an electrochemical cell in which the reaction that occurs produces an electromotive force (e.m.f.). If an opposing voltage is applied to the cell which is infinitesimally less than the e.m.f. of the cell, the reaction will proceed infinitely

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slowly. If the applied voltage equals the e.m.f. of the cell, no reaction will occur; if it is infinitesimally greater than the e.m.f., the reverse reaction will occur infinitely slowly.

Consider a system consisting of ice and liquid water in equilibrium at 273.15 K and $101\,325\text{ N m}^{-2}$. The ice may be melted reversibly by absorbing heat from a heat reservoir, the temperature of which is infinitesimally greater than 273.15 K.

A spring whose tension is increased infinitesimally will extend by an infinitesimal amount. If this tension is relaxed, the spring will return to its original position provided the elastic limit has not been exceeded. The work done in loading the spring equals the work recovered on unloading. The original extension was therefore reversible. If the elastic limit were exceeded, plastic deformation would occur and the spring would not return to its original position. Also, the work recovered would be less than that put in, the plastically deformed state being one of higher energy.

Some other examples of irreversible processes are:

- (1) a metastable phase changing to the stable form of a substance (e.g. freezing of a super-cooled liquid, condensation of a super-saturated vapour);
- (2) mixing of substances (e.g. mixing of gases or miscible liquids);
- (3) transportation across a phase boundary (e.g. osmosis, dissolution of a solid);
- (4) all naturally occurring processes, i.e. all spontaneous processes (e.g. all reactions occurring under normal conditions, the mixing of gases).

1.12 **Work done by volume change**

Consider a fluid in a cylinder with a frictionless piston. The fluid may do work on the surroundings by expansion.

Suppose the fluid at a pressure P expands by an infinitesimal amount dV , the piston moving by dx , against an opposing pressure P_{opp} . The work done, δw (the significance of the line through the work differential will be explained later), is given by

work done = force opposing the change \times distance moved

$$\delta w = F_{\text{opp}} \times dx$$

We may write

$$\delta w = \frac{F_{\text{opp}}}{A} \cdot A dx$$

where A is the cross-sectional area of the piston.

Since the opposing pressure P_{opp} is the opposing force per unit area