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Thermodynamics and Statistical Thermodynamics

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Preface

This book contains the material which we present, or refer to, during a one-year graduate course (three hours a week each semester) in Thermodynamics and Statistical Thermodynamics. We believe that the same material could be presented in a similar course to senior undergraduate honor students.

It has been our experience that lack of understanding of the First Law is often responsible for difficulty in using the Second Law. If the concept of thermodynamic temperature is properly understood, the full meaning of the Second Law is as easy to grasp intuitively as that of the first, if not easier. The order of presentation of subject matter of the first fifteen chapters has been governed entirely by these considerations. For this reason there is deliberate reiteration.

We have found, likewise, that the development of statistical thermodynamics using the distribution laws and energy levels to calculate the energy of a system *first* with many numerical examples has considerable advantage over a more general introduction. It is only after making such a start and deducing other thermodynamic properties from the energy (often clumsily perhaps) that the beginner can grasp the beauty of the general apology for thermodynamics that is summarized in our final chapter. The development of the latter half of the book, sometimes repetitiously, follows these considerations.

The first fifteen chapters are covered during the first semester, and the remainder of the book during the second semester. During the first semester the students always construct an entropy diagram; to lighten the work they do so in groups with two or three students in each. Very little time is spent on the general treatments of Gibbs or on the variables other than pressure, volume, temperature, and composition. In the second semester the students individually make calculations of thermodynamic properties using the accurate rotational-vibrational partition functions for diatomic gases and the approximate rotational and vibrational partition functions for complex molecules with internal rotation. For this purpose a rather complete chapter (Chapter 16) on energy levels is included along with an appendix giving selection rules and group theory tables.

There are about 260 numerical problems and about 130 problems involving derivations of the formulae stated but not fully derived in the text or of formulae which are an extension of those derived in the text. The Appendix contains outlines of mathematical methods as well as tables of functions and of data to supplement the material in the text.

Chemists should find the book sufficiently self-contained to be useful as a reference book and as a means of acquiring facility in advanced methods. With the exception of the treatment of crystals, the statistical thermodynamic treatment is limited to systems without interactions (i.e., to perfect gases). Systems with interactions are dealt with in more advanced books. For the same reason quantum mechanically degenerate gases are not discussed.

In the table below are suggestions concerning the most suitable material for a one-year graduate course and two senior one-semester courses, respectively dealing with thermodynamics and statistical thermodynamics. In each case it is assumed that the semester consists of approximately forty-five class hours.

The first four chapters of the book have proved very useful in our courses, for we have found that the historical approach is almost essential to a thorough understanding of the two laws of thermodynamics and to the proper understanding of thermodynamic temperatures.

There are two chapters dealing with the methods of Gibbs. One of these deals with his thermodynamic generalizations, the second deals with the application of statistical mechanics for the sole purpose of understanding the principles of thermodynamics. While these are not used directly in our class work, they are considered essential supplementary reading for the student and highly desirable for the general reader.

The last chapter gives a sufficiently general treatment of statistical thermodynamics to form an introduction to advanced study.

Suggested Chapters for Typical Courses

Type of Course	Chapters Covered Thoroughly	Chapters Covered Partially	**Chapters Omitted**
One-year graduate course	1 through 11; 16 through 20	12 through 15; 21	**22, 23**
One-semester senior course in thermodynamics	1 through 3; 6, 7, 12	4, 8, 10, 11, 13, 14	**15**
One-semester senior course in statistical thermodynamics	17, 18	19, 20	**16, and 21 through 23**

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J. J. F.

State College, Pennsylvania
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We are particularly indebted to Dr. D. M. Nace and Dr. W. A. Pavelich, who helped with the writing of Chapter 10 (Imperfect Gases; Fugacity and Entropy Diagrams); also to Dr. W. A. Steele, who helped with the writing of Chapter 15 (Systems Involving Other Variables). We wish to thank the Chemistry Department of this University for a great deal of help and consideration which materially aided in the preparation of the manuscript. We wish also to thank our past students who have contributed data which we have used in problems or have otherwise contributed to the development of this text. They are M. L. Eidinoff, E. Willihnganz, G. H. Messerly, C. W. Siller, S. C. Schumann,

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We wish also to thank Gwen Ray, who checked all references and tables against the original literature as well as prepared most of the index and otherwise helped with the proof.

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Contents

1.2 Chemical Thermodynamics

The role of thermodynamics in the designing of heat engines is widely known and apparent from a superficial inspection of the first and second laws. The manner in which it can place certain limitations on the physical and chemical conditions which may exist in a system and on the changes which may occur is not so apparent.

For example, it is not possible for sulfur vapor, liquid, rhombic, and monoclinic sulfur to exist together at equilibrium; if this were possible, the phenomenon could be made a basis for converting heat into work at constant temperature. At 280°C and at 1 atm NO_2 is 13% dissociated into NO and oxygen at equilibrium. If oxygen is added to this system, a certain fraction of it must combine with NO. This fraction can be calculated from thermodynamics. If it were possible to add oxygen at equilibrium without this fraction combining, this process could be used to invent a perpetual motion machine.

Thus from thermodynamics it is possible to calculate the maximum fraction of a mixture of nitrogen and hydrogen that can be converted into ammonia at any temperature and pressure; the maximum yield for any other chemical reaction can be calculated if the necessary data are available. The separation of components from a solution as solids, as gases, or in any other equilibrium fashion can be treated by thermodynamics. Thus we may predict the solubility of one compound in another.

When an electrolytic cell discharges against an opposing electromotive force under equilibrium conditions, electrical work is done. By thermodynamics we can calculate this work or, knowing its value, can predict the conditions of equilibrium in the chemical reaction of the cell.

By thermodynamics we are able to calculate only what may happen in a chemical reaction and to state what can never (or hardly ever) happen. We cannot predict whether a process will occur in a finite time, since thermodynamics deals only with equilibrium; many processes are so slow that equilibrium is never reached. From a practical point of view, it is extremely useful to know the conditions which favor appreciable amounts of reaction products at equilibrium. Such knowledge can save futile efforts to find a catalyst for a reaction which cannot possibly occur under the conditions employed. The application of the laws of thermodynamics to such problems is one of the principal tasks of chemical thermodynamics.

1.3 Statistical Thermodynamics

Count Rumford, among others, recognized the fact that heating a body increases the kinetic energy of the molecules within it. At present we have a fair understanding of the situation. With a complete knowledge of the energies that atoms or molecules may assume, we can calculate all the thermodynamic properties of actual systems involving such atoms and molecules, including the final state of a chemical reaction at equilibrium.

The study of the distribution of atoms and molecules among their energy levels and the consequent adjustments of the system with changes of pressure, volume, and temperature, including the ability to withdraw heat and do work, is called *statistical thermodynamics*.

1.4 Relation of Energy Levels and Spectroscopy to Thermodynamics

We now take for granted that atoms and molecules can acquire energy only in steps; that is, they can exist only in a discrete series of energy states. Other values of the energy are not allowed. In many instances there are closed mathematical expressions for these energies in terms of the masses of the atoms, the geometry of the molecules, and force laws which determine their motion.

These expressions will be discussed in a later chapter to justify their acceptance on faith. In the same chapter it will be shown how many of these energy levels may be obtained directly from lines observed in the absorption or emission spectra (for example, how the rotational and vibrational energy levels of hydrogen chloride may be obtained from its infrared spectrum).

In some cases energy levels or molecular structure may be deduced by working backwards from the thermodynamic properties. Thus statistical thermodynamics, spectroscopy, and the mechanics of atoms and molecules are all interdependent.

1.5 Scope and Nature of This Book

Our object has been to cover those important parts of thermodynamics and statistical thermodynamics which allow exact calculation and are now quite fully understood. It is intended that the following presentation, while primarily designed to constitute a textbook, should be understood and read with pleasure by the properly prepared reader without taking a formal course. It is suggested that such readers, as well as students using this book as a text, read the preface at this point. This preface not only explains in detail the reasons for our order of presentation, but also emphasizes the milestones along the way. For this reason frequent reference to the preface is advised, particularly where there is doubt about the relationship of one section of the book to another.

Physical Units, Accepted Constants, and Empirical Temperatures

CHAPTER 2

2.1 Fundamental Units

The basic units of measurement are those of length, mass, and time. The fundamental unit of *length* (l) is the *meter* (m); by convention, the meter represents the distance (at 0°C) between two ruled lines on a standard platinum-iridium bar maintained at the International Bureau of Weights and Measures at Sèvres, France. Similarly, the fundamental unit of *mass*, the kilogram (kg), is the mass of a standard block of platinum deposited at Sèvres. Copies of these standards have been deposited with the National Bureau of Standards in Washington, D.C.

The *centimeter* (cm) and *millimeter* (mm) correspond to one hundredth and one thousandth of a meter, respectively. Of the corresponding units of area (A), the square centimeter (1 cm^2) is the most commonly used. The *gram* (g) is one thousandth of a kilogram. The centimeter and gram are commonly considered standard units.

The *liter* (l) has been commonly accepted by chemists as the basic unit of volume (V). The liter is defined as the volume of one kilogram of pure water at the temperature corresponding to its maximum density under a pressure of one atmosphere. The *milliter* (ml) is one thousandth of a liter. From careful density measurements it has been established that 1 liter is equal to 1000.027 cubic centimeters (cm^3).

The fundamental unit of *time* (t), the *second* (sec), is defined as 1/86,400 of a *mean solar day*. (A mean solar day is the average, over a year, of the day as defined by the apparent transit of the sun through a vertical plane.)

The units of other physical quantities are derived in terms of those of length, mass, and time. The so-called cgs system is obtained when this is done in terms of the centimeter, gram, and second. Various derived quantities are considered in the following sections.

2.2 Force and Pressure

The numerical calculation of *force* (F) is based on Newton's second law of motion, which relates the force acting on a freely moving body to its rate of change of momentum. The *dyne* is the cgs unit of force, and it corresponds to the force which imparts to a freely moving mass of one gram an acceleration of one centimeter per second per second. The standard gravitational acceleration (g) is defined as 980.665 cm/sec^2. A *gram force* is the force required to give a mass of one gram the standard gravitational acceleration, and is thus equal to 980.665 dynes.

Pressure (P) is an important variable in the definition of the state of a chemical system. It is defined as the force acting on a unit area. The cgs unit of pressure is the *dyne per square centimeter*. Commonly, pressure is expressed and measured in terms of an equivalent height (h) of a fluid column of density ρ:

$$P = \frac{\mathrm{F}}{\mathrm{A}} = \rho g\mathrm{h}. \qquad (2.2\text{–}1)$$

The *normal* or *standard atmosphere* (atm) has been adopted as a practical unit of pressure. This unit is defined as the pressure exerted by a mercury column having a height of 760 mm and a density of 13.5951 g/cm^3. The latter is the density of mercury at 0°C, sea level, and 45° latitude (g = 980.665). The standard atmosphere is equal to 1,013,250 dynes/cm^2. Laboratory pressure data are frequently given in *millimeters of mercury* (mm Hg). An International millimeter of mercury is defined as 1/760 of a standard atmosphere. Pressures ranging up to 1000 atmospheres are employed in industrial chemical practice.

Problem 2.2-1. Calculate the height of mercury, in millimeters, corresponding to 1 atm in San Francisco, California, at 22°C. (*Note.* Values of g for representative localities are given in the *International Critical Tables.*[1]) If the scale is of silver and calibrated to read correctly at 0°C, what will be the height, in millimeters, observed on the scale at 22°C?

Problem 2.2-2. A weight of 15 g is placed on a circular slab of steel of weight 1 kg. By acting as a piston, this device prevents gas from escaping from a cylinder. If the

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[1] *International Critical Tables*, McGraw-Hill, New York, 1927.

slab and the cross section of the cylinder both have a diameter of 10 cm, calculate the difference between the pressure of the gas and that of the surrounding atmosphere for (a) Denver, Colorado; (b) San Francisco, California.

2.3 Work

When a body moves under the influence of a force, work (w) is done. In thermodynamic calculations, work is usually considered in terms of the displacement of a system against forces external to it. Thus, if a system is displaced a small amount dl in the same direction as, but opposed to, that of an external force F, the work performed, w, is given by the expression

$$w = \mathrm{F}\,\mathrm{d}l. \tag{2.3–1}$$

Over a specified path from A to B the work done by the system is

$$w = \int_{\mathrm{A}}^{\mathrm{B}} \mathrm{F}\,\mathrm{d}l, \tag{2.3–2}$$

which is obtained by taking the line integral corresponding to equation (2.3–1). Defined in this manner, work done by a system against external forces has a *positive sign.* In a general mechanical consideration, where X, Y, Z represent the rectangular components of the external forces and dx, dy, and dz the corresponding displacements of the system,

$$w = X\,\mathrm{d}x + Y\,\mathrm{d}y + Z\,\mathrm{d}z. \tag{2.3–3}$$

The work w done by the system is the line integral of w and is dependent on the path of integration.

Of special interest in thermodynamics is the work done by an expanding fluid. Using the definition of pressure P in Section 2.2 and the increment of volume dV = A dl,

$$\mathrm{d}w = P\mathrm{A}\,\mathrm{d}l = P\,\mathrm{d}V. \tag{2.3–4}$$

From (2.3–4), the work done by the system against the external pressure P is given by

$$w = \int_{V_1}^{V_2} P\,\mathrm{d}V. \tag{2.3–5}$$

In the case of constant external pressure,

$$w = P\int_{V_1}^{V_2} \mathrm{d}V = P\,\Delta V. \tag{2.3–6}$$

Equations (2.3–4) and (2.3–5) permit a simple geometrical interpretation as illustrated in Fig. 2.3–1. The points A and B correspond to the initial and final states of the system. The points A and A′ define an infinitesimal