Book Review

CHEMICAL THERMODYNAMICS
Basic Concepts and Methods

Irving M. Klotz, Robert M. Rosenberg

This is the seventh edition of the book *Chemical Thermodynamics,* which was first published by professor Klotz in 1950. The fundamental objective of the book is to present to the student the logical foundations and interrelationships of thermodynamics and to teach the student the methods by which the basic concepts may be applied to practical problems. In the treatment of basic concepts, the authors adopted the classic, or phenomenological, approach to thermodynamics and have excluded the statistical viewpoint. This attitude permits the maintenance of a logical unity throughout the book. A great deal of attention is paid in this book to training the student in the application of the basic concepts to problems that are commonly encountered by the chemist, the biologist, the geologist, and the materials scientist.

The first chapter is an introduction that synthetically presents the origins of the chemical thermodynamics, objective of chemical thermodynamics and limitations of classic thermodynamics. The primary objective of chemical thermodynamics is to establish a criterion for determining the feasibility or spontaneity of a given physical or chemical transformation. Although the main objective of chemical thermodynamics is the analysis of spontaneity and equilibrium, the methods also are applicable to many other problems. For example, the study of phase equilibria, in ideal and nonideal systems, is basic to the intelligent use of techniques of extraction, distillation, and crystallization; to metallurgical operations; to the development of new materials; and to understanding of the species of minerals found in geological systems. Thermodynamic concept and methods provide a powerful approach to the understanding of such problems.

Chapter 2, *Mathematical preparation for thermodynamics* presents variables of thermodynamics (intensive and extensive variables) and analytic methods. As the state of a thermodynamic system generally is a function of more than one independent variable, it is necessary to consider the mathematical techniques for expressing these relationships. Many thermodynamic problems involve only two independent variables, and the extension to more variables is generally obvious, so authors limit our illustrations to functions of two variables.

The next three chapters present the first law of thermodynamics and this application to gases. The relationships developed for gases that are based on the first law will be useful in developing the second law will be useful in developing the second law of thermodynamics and in applying the second law to specific systems. As the behavior of many gases at low pressure can be approximated by the simple equation of state for ideal gas, and the ideal equation of state describes accurately the behavior of real gases at the limit of zero pressure, authors begin our discussion with a consideration of ideal gases.

The first law of thermodynamics, which is useful in keeping account of heat and energy balances, makes no distinction between reversible and irreversible processes and makes no statement about the natural direction of a chemical or physical transformation. The second law presented in chapter 6, like the first law, is a postulate that has not been derived from any prior principles. It is accepted because deductions from the postulate correspond to experience. Except in submicroscopic phenomena, to which classical thermodynamics does not apply, no exceptions to the second law have been found.

Chapters 7-9 present applications of the second law of thermodynamics in electrical, mechanical, biological and osmotic work. Mixtures of gases and equilibrium in gaseous mixtures are presented in chapter 10.

Chapter 11 deals with *The Third Law of Thermodynamics*. Lewis and Randal proposed the following statement of the third law of thermodynamics: "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances". The authors I. M. Klotz and R. M. Rosenberg adopt this statement as the working from of the third law of thermodynamics. This statement is the most convenient formulation for making calculations of changes in the Gibbs functions or the Planck function.

Chapter 12 present application of the Gibbs functions to chemical changes. As the Gibbs function is a thermodynamic property, values of ΔG do not depend on the intermediate chemical reactions that have been used to transform a set of reactants, under specified conditions, to a series of products. Thus, one can add known values of Gibbs function to obtain values for reactions for which direct data are not available.

In the chapter 13 authors present a deviation of the phase rule and apply the result to several examples (one-component systems, two-component systems and two phases at different pressures). Authors discussed multiphase-multicomponent systems in terms of the phase rule and its graphical representation. In the next two chapters this describes the equilibrium curves of a phase diagram in terms of analytic functions and begins by considering the ideal solutions and dilute solutions of nonelectrolytes.

Chapters 16 and 17 developed procedures for defining standard states for nonelectrolyte solutes and for determining the numeric values of the corresponding activities and activities and activity coefficients from experimental measurements.

In chapter 18, I. M. Klotz and R. M. Rosenberg shall consider the methods by which values of partial molar quantities and excess molar quantities can be obtained from experimental data. Most of the methods are applicable to any thermodynamic property *J*, but special emphasis will be placed on the partial molar volume and the partial molar enthalpy, which are needed to determine the pressure and temperature coefficients of the chemical potential, and on the excess molar volume and the excess molar enthalpy, which are needed to determine the pressure and temperature coefficients of the Gibbs function.

Chapter 19 describes the evaluation methods for activity, activity coefficients and osmotic coefficients of strong electrolytes. All methods used in the study of nonelectrolytes also can be applied in principle to the determination of activities of electrolytes solutes. However, in practice, several methods are difficult to adapt to electrolytes because it is impractical to obtain data for solutions sufficiently dilute to allow the necessary extrapolation to infinite dilution. Activity data for electrolytes usually are obtained by one or more of three independent experimental methods: measurement of the potentials of electrochemical cells, measurement of the solubility, and measurement of the properties of the solvent, such as vapor pressure, freezing point depression, boiling point elevation, and osmotic pressure. All these solvent property may be subsumed under the rubric *colligative properties*.

In chapter 20 authors been discussed of the principle of chemical thermodynamics with a consideration of some typical calculations of changes in Gibbs function in real solutions.

In most circumstance of interest to chemists, the dominant experimental variables are temperature, pressure, and composition, and our attention has been concentrated on the dependence of a transformation of these factors. On some occasions, however, a transformation takes place in a field: gravitational, electrical, or magnetic; chemists who work with macromolecules frequently use a centrifugal field in their work. Chapter 21 details the systems subject to a gravitational or a centrifugal field.

Chapter 22 *Estimation of thermodynamic quantities,* presents review some empirical and theoretical methods of estimation of thermodynamics quantities associated with chemical transformations. Precise thermodynamic data are available for relatively few compounds. However, in many situations, it is desirable to have some idea of the feasibility or impossibility of a given chemical transformation even though the necessary thermodynamic data are not available. Several groups of investigators have proposed empirical methods of correlation that allow us to estimate the thermodynamic properties required to calculate Gibbs functions and equilibrium constants. All of these methods are based on the assumption that a give thermodynamic property, such as entropy, of an organic substance can be resolved into contributions from each of the constituent groups in the molecule.

The last chapter of the book presents concluding remark. The point of view adopted toward thermodynamics in this book is the classic or phenomenological one. This approach is the most general but also the least illuminating in molecular insight. The three basic principles of phenomenological thermodynamics are extracted as postulated from general experience, and attempt is made to deduce them from equations describing the mechanical behavior of material bodies. As it is independent of the laws governing the behavior of material bodies, classic thermodynamics cannot be used to drive any of these laws. Generally, thermodynamics does not allow us to calculate a priori actual values of any of the quantities appearing in these relationships. Parallel with the phenomenological development, an alternative point

of view has developed toward thermodynamics, a statistical-mechanical approach. Its philosophy is more axiomatic and deductive than phenomenological. In principle, quantum mechanics permits the calculation of molecular energies and therefore thermodynamic properties. In practice, analytic solutions of the equations of wave mechanics are not generally accessible, especially for molecules with many atoms.

Each chapter of the book contains an up-to-date well documented list of references. The book is written in contemporary way and includes many illustrations which make the text more useful for specialists in chemical engineering. Also it is completed with Annexes containing practical analytical and graphical mathematical techniques. The book is necessary to people working into various field chemistry, biology, geology, and materials science.

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