Book Review

Chemical Thermodynamics
Fifth Edition
by Irving M. Klotz and Robert M. Rosenberg
John Wiley & Sons, INC.
New York-Chichester-Brisbane-Toronto-Singapore, 1994
560 pages, Price: £54

Chemical Thermodynamics is the fifth edition of a textbook that appeared originally forty-four years ago. Although there have not been fundamental changes in thermodynamics since the first edition was published, convention and pedagogical approaches have changed, and new applications have been introduced.

The authors, Irving M. Klotz, Morrison Professor Emeritus at Northwestern University, and Robert M. Rosenberg, MacMillen Professor Emeritus at Lawrence University and Visiting Professor of Chemistry at Northwestern University, have revised and updated the book, maintaining the spirit and format of the previous editions. In the fifth edition, numerous new biological and geological applications have been included together with problems that reflect these applications. New topics, such as the thermodynamics of the electrochemical cell and Eh/pH diagrams, have also been introduced. The symbols used in previous editions have changed to conform with new conventions.

Chemical Thermodynamics has been written in the language of a classical or phenomenological approach. The mathematical tools necessary for an understanding are presented in great detail and demonstrated in sample problems. The extensive use of subheadings, indicating the position of each topic within the general sequence of presentation, enables readers to retain information effectively. Useful exercises for practice are also provided extensively.

Chemical Thermodynamics consists of 24 chapters.

Chapter 1 is the Introduction, in which the origins and the objectives of chemical thermodynamics are outlined and the limitations of classical thermodynamics are presented.

Chapter 2 is devoted to the mathematical preparation for thermodynamics. Extensive and intensive variables of thermodynamics, and mathematical methods (total differential, exact and inexact differential, and Euler's theorem) are discussed.

In *Chapter 3*, basic concepts (systems, surroundings, variables of state, equation of state, temperature, work, energy and heat) are defined and the first law of thermodynamics is described.

In *Chapter 4*, the reader can find the definitions of essential functions and equations for enthalpy, enthalpy of reaction and heat capacity. In detail: the relationship between QV and QP; standard states; the additivity of enthalpies of reaction; the calculation of bond energies; the heat capacities of gases, solids and liquids;, the relationship between CP and CV; and the variation of enthalpy with temperature.

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In *Chapter 5*, the application of the first law of thermodynamics to gases is to be found. The properties of ideal and real gases are surveyed, calculations of the thermodynamic changes in isothermal and adiabatic expansion processes, semiempirical equations (van der Waals, Barthelot, and Redlich-Kwong) for real gases and the Joule-Thomson effect are
presented.
Chapter 6 is devoted to essential concepts in thermodynamics, such as the second law of thermodynamics, Camot's theorem, the thermodynamic temperature scale, the definition of entropy (S), entropy changes in reversible and irreversible processes, the entropy of ideal and real gases, and entropy as an index of exhaustion.
In *Chapter 7*, the reversibility, spontaneity and equilibrium of systems at constant temperature, Helmholz free energy (A), Gibbs free energy (G) and the equilibrium constant (K) are characterized, and free energy and useful work in electric cell and biological systems are described.
Chapter 8 deals with the changes of phase in one-component systems. The Clapeyron and Clausius-Clapeyron equations are derived in this section.
In *Chapter 9*, statements on the third law of thermodynamics (Nerst heat theorem, Planck's formulation, the statement of Lewis and Randall, and the unattainability of absolute zero) are listed, and thermodynamic properties (G, H, CP, CV and S) at absolute zero are characterized.
In *Chapter 10*, the authors discuss the applications of the Gibbs free energy criterion to chemical transformations. The following calculations are considered: the addition of known ΔG_m values for suitable chemical equations leading to the desired equation, the determination of ΔG_m from equilibrium measurements, the determination from measurements of cell potentials, and the calculation of standard free energies from standard entropies and standard enthalpies.
In *Chapter 11*, the discussion is extended to systems of variable composition. Variables of state, criteria of equilibrium, relationships between partial molar quantities and the spontaneous direction of transport (escaping tendency) are considered.
In *Chapter 12*, the concepts developed in Chapter 11 are applied to gaseous systems: first to mixtures of ideal gases, then to pure real gases, and finally to mixtures of real gases.
Chapter 13 deals with a presentation of the Gibbs phase rule and its application to multiphase-multicomponent systems. The phase rule and its graphical representation are derived.
Chapter 14 considers the analytical descriptions of ideal solutions. Definitions, thermodynamics of mixing, and equilibrium between ideal solutions are discussed.
In *Chapter 15*, limiting laws (Henry's law, Nernst's distribution law, Rault's law, and van't Hoff's law of osmotic pressure, freezing point depression and boiling point elevation) which describe the thermodynamic behavior of dilute solutions of nonelectrolyte systems are to be found.
In *Chapter 16*, the description on nonelectrolyte solutions is extended over the entire range of composition. Activity, standard states, equilibrium constant, and the dependence of activity on pressure and temperature are discussed.
In *Chapter 17*, methods by which values of partial molar quantities can be obtained from experimental data are presented. Special emphasis is placed on the partial molar volume and the partial molar enthalpy, since these quantities are needed to determine the pressure and temperature coefficients of the chemical potential.

Chapter 18 is devoted to the determination of the numerical values of nonelectrolyte activities by using experimental methods: measurement of vapor pressure; concentration-distribution measurements; measurements of cell potentials; and calculation of the activity of one component from known values of the activity of the other.
Chapter 19 contains a characterization of strong electrolytes. Definitions and standard states for dissolved electrolytes, and the determination of activities of strong electrolytes are treated in the section.
Chapter 20 presents some typical calculations of free energy changes in real solutions.
In *Chapter 21*, the authors focus on processes subject to gravitational and centrifugal fields.
In *Chapter 22*, some semiempirical methods of estimation of thermodynamic quantities associated with chemical transformations are surveyed.
Chapter 23 reviews practical mathematical techniques, and numerical and graphical methods.
Chapter 24 comprises the concluding remarks.

Chemical Thermodynamics can be valuable reading for chemists, material scientists, geologists and biologists who require detailed information on the basic theory and methods of the subject, but first and foremost it is a textbook. I can recommend it to students and teachers in chemistry, geology, biology and material science.

Thermodynamics of Irreversible Processes is one of the volumes in the Wiley Tutorial Series in Theoretical chemistry. Originally, this was a textbook based on the lectures of the author, G.D.C. Kuiken, at Delft University of Technology in The Netherlands. The book can be divided into two parts. In the first part, the author describes the methodology of the thermodynamics of irreversible processes (TIP) in general. The second half of the book discusses the application of the general theory of the TIP to multicomponent diffusion and rheology. Thus, it can be considered to be the first advanced textbook dealing with this kind of application. However, the reader should bear in mind that the book has principally been prepared for theoretical use.
Thermodynamics of Irreversible Processes consist of 7 chapters and 2 appendices, supplemented by an Author Index and a Subject Index. examples are to be found at the end of each chapter.
The first chapter outlines the continuum or macroscopic view of matter and the range of its applicability.
In the second chapter, basic concepts familiar in classical thermodynamics, such as equilibrium, system and the laws of thermodynamics, are recapitulated. The first law of thermodynamics is described for both closed and open systems. The second law of thermodynamics is described for both closed and open systems. The second law of thermodynamics is defined according to Kelvin-Planck, Clausius and Carathéodory. Still in this section, the reader can find a description of irreversible and reversible processes, Carnot cycles, internal energy and entropy.
In the third chapter, the six basic axioms (the validity of classical thermodynamics, local and instantaneous equilibrium, balance equations, entropy balance, phenomenological equations and Onsager-Casimir reciprocal relations) and the four supplementary axioms

(Galilean invariance, coordinate invariance, dimensional invariance and material isomorphism) of the TIP are included. The structure of the theory is summarized and its applications are given in a diagram. Application to anisotropic heat conduction and membrane permeability is presented.

In the fourth chapter, fundamental equations and quantities to the thermodynamics of multicomponent fluids are summarized, and balance equations for mass, diffusion, electromagnetic field, momentum, energy and entropy are derived. The process fluxes and forces are defined by these equations.

The fifth chapter is devoted to the statistical foundation of the Onsager-Casimir reciprocal relations for homogeneous systems. Fundamentals of stochastic processes and microscopic reversibility are summarized and the regression axiom of fluctuation theory is described in this chapter. The reciprocal relations are derived, using the solutions of the Fokker-Planck equation, which satisfies the microscopic reversibility and the regression axiom.

The next two chapters deal with the application of the TIP theory.

The sixth chapter discusses multicomponent diffusion, often important in mass transfer processes by determining their rate. The Maxwell-Stefan description of diffusion processes and its aplications to ideal and non-ideal binary systems (Fick Description) are detailed. Molar diffusion flux with respect to the mass average velocity is also considered and simplified diffusion equations are presented.

The whole of the seventh chapter is devoted to the thermodynamic theory of relaxation processes, in detail: phenomenological experiments. Rheological models or ideal models, the TIP model of rheological bodies, thermostatics of linear rheological bodies, etropy production, phenomenological equations, basic equations for internal vector and scalar processes, relaxation equations, characterization of rheological bodies i.e. Burgers body, Poynting-Thomson body, Jeffreys body, Maxwell body, Kelvin-Voigt body, classical bodies, basic equations for bodies with a number of internal processes, general linear rheological equations of state for isotropic bodies (retardation and relaxation) and linear bodies with continuous spectra.

In Appendix A, the Maxwell electromagnetic field equations are summarized. Electrostatic and magnetostatic laws are described, and electric and magnetic polarizations are characterized. Appendix B is a summary of vector and tensor notations and definitions.

Thermodynamics of Irreversible processes can be valuable reading for scientists working in the field of irreversible phenomena. It can also be a useful book for researchers and university students in chemistry, chemical technology, polymer and material science, physics and rheology.

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