Book Reviews

Measurement of the Thermodynamic Properties of Multiple Phases. R. D. Weir and T. W. de Loos, Editors. Elsevier: Amsterdam, The Netherlands, 2005. 450 pp. $US 220. ISBN 0-444-51977-7.

This book is Volume VII in the IUPAC Experimental Thermodynamics series which began in 1968. Volume VII replaces Volume II (1975) and gives an up-to-date description of current experimental techniques to measure and analyze phase equilibrium data and thermodynamic properties of multiple phases of pure components and mixtures. Knowledge of these methodologies is essential for researchers and graduate students in chemical engineering and physical chemistry and for industrial practitioners who need to measure phase equilibria for effective design and operation of chemical process units.

The Editors have produced a valuable and comprehensive reference by calling upon 25 international thermodynamics experts to survey recent developments and the theoretical background of 15 types of multiphase properties, which are usually measured over a broad range of temperature and pressure.

After a brief overview of the history and impact of IUPAC thermodynamic publications in Chapter 1, Chapter 2 describes experimental methods to measure the vapor pressure of pure components. Of particular interest is ebulliometry, which is the most frequently employed technique for measurement of vapor pressures > 0.1 kPa. Chapter 2 also gives a careful and complete discussion of methods to measure vapor pressures at or well below 1 Pa. These low-pressure techniques include Knudsen effusion, Langmuir effusion, and transpiration (gas-saturation) methods. Chapter 2 concludes with a brief discussion of direct calorimetric measurements of the enthalpy of vaporization.

Chapter 3 discusses measurement of the enthalpy and density change during the solid−liquid (melting) phase transition for pure materials. Also included is a description of the high-temperature, high-pressure apparatus needed to measure the melting curve of high-melting materials such as uranium. Chapter 4 on pure component solid−solid phase transitions begins with an extensive discussion on the classification and thermodynamics of different types of solid−solid phase transitions including plastic crystals and fullerenes. Experimental techniques including thermal, optical, scattering, ultrasonic, and magnetic resonance methods are briefly reviewed. The chapter concludes with an interesting survey of recent developments (mostly after 1995), which is sorted by type of material.

Chapter 5 on low pressure vapor−liquid equilibrium (VLE) is divided equally between expositions on static total pressure $P-T-x$ measurements (where no samples of the coexisting phases are taken) and dynamic one-stage re-circulating equilibrium still $P-T-x-y$ measurements. A useful analysis of the pressure and temperature sensitivity of $P-T-x$ measurements is given. Chapter 6 also considers closed-circuit (static) and open-circuit (forced circulation) methods in the measurement of VLE at high pressure. A discussion of literature apparatus and sampling techniques (with the original schematic diagrams) gives a comprehensive overview of the myriad and difficult choices facing the experimentalist who plans VLE measurements at pressures > 200 kPa.

A complete thermodynamic analysis of gas solubility measurements at low pressures (< 200 kPa) is given in Chapter 7 along with a discussion of low imprecision (0.1 %) apparatus, significant recent measurements, and the use of derived and measured partial molar enthalpy change data. Chapter 8 on liquid−liquid equilibrium (LLE) measurement is divided between measurements on binary systems (where synthetic or other indirect measurements are possible) and measurements on ternary and multicomponent systems (where sampling and analysis is essential). As in other chapters, extensive schematic diagrams from recent literature are used to give an overview of the current alternatives for LLE measurement including measurement of octanol−water partition coefficients.

Chapters 9 to 12 comprise an extensive review of condensed phase equilibrium of mixtures divided by type of material. (Chapter 9 is the longest in the book: 74 pages). The four types of materials discussed are organic systems, metallic systems, ceramic systems, and molten salts. A large variety of experimental methods are described; their particular application is dictated by the properties of the different materials and the thermodynamic objectives of the study. These methods are calorimetry including differential scanning calorimetry (DSC), combustion calorimetry, drop calorimetry, solution calorimetry, X-ray diffraction, microscopy, electrochemical measurement, vapor pressure measurement including Knudsen cell methods, mass spectroscopy, and cryoscopy. Industrial thermodynamic applications of mixture solid−solid and solid−liquid equilibria are found principally in metallurgical engineering including nuclear reactor design.

Measurement of infinite-dilution activity coefficients (γ^{∞}) by methods that do not required chemical analysis is the subject of Chapter 13. The principal technique, differential ebulliometry, is examined in detail including a complete mathematical analysis of ebulliometer holdup corrections. Dew-point γ^{∞} methods and static $P-x$ routes to γ^{∞} are discussed. Chapter 14 also discusses infinite-dilution activity coefficients but describes methods that require analytical tools. These methods include gas chromatographic retention time, headspace gas chromatography, static mass balance, gas-stripping, and distillation methods. The chapter concludes with an interesting analysis of γ^{∞} versus temperature data for the system 1-butanol dilute in water measured by several different techniques from Chapters 13 and 14.

Chapter 15 describes static, quasi-static, and dynamic methods to measure surface (gas−liquid) and interfacial (liquid−liquid) tension. Recent developments such as bubble and oscillating drop methods are discussed in addition to well-known techniques such as capillary rise, drop shape and weight, spinning drop, du Noüy ring, Wilhemy plate, bubble pressure, oscillating jet, and capillary wave methods.

Concluding Chapter 16 describes experimental techniques to measure vapor−liquid critical point parameters: critical temperature, critical pressure, and critical density. Of particular importance are recent developments such as improved flow

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methods and spontaneous boiling methods that can be used for more accurate measurements on thermally unstable substances.

This book is a unique and indispensable reference for anyone who needs to measure phase equilibria and thermodynamic properties of multiple phases. Of the 1307 literature references in the 16 chapters, more than 50 % are more recent than 1990. This shows that the book indeed concentrates on current developments and also indicates that thermodynamic and phase equilibria research is thriving (contrary to many pessimistic claims that data measurement is no longer a current topic of research).

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