

A Course in Thermodynamics

MOLECULAR THERMODYNAMICS OF PHASE EQUILIBRIA

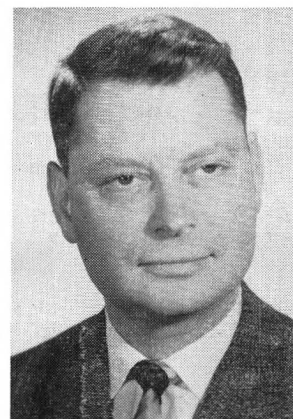
J. M. PRAUSNITZ

*University of California, Berkeley
Berkeley, Calif.*

Chemical thermodynamics started with J. Willard Gibbs nearly 100 years ago but its significant influence on chemists and chemical engineers in the United States, starting about 50 years ago, is due in large measure to the work of G. N. Lewis, who introduced fugacity and activity. For many years Lewis' strong personality dominated the College of Chemistry at the University of California at Berkeley; he served as its dean from 1912 until shortly before his death in 1946. It is therefore not surprising that Berkeley's College of Chemistry (which includes the Department of Chemical Engineering) has retained a tradition of strong interest in the application of thermodynamics to chemical problems.

While Lewis' early work in thermodynamics was along classical lines, in his middle and later years he devoted much attention to relations between molecular physics and thermodynamic properties. Classical thermodynamics establishes broad relations between macroscopic equilibrium properties but, by itself, it cannot generate numerical values of these properties; further, it is limited in its ability to suggest useful techniques for interpreting and correlating them. For such purposes, we must call on the insights provided by statistical mechanics and molecular physics. Lewis' efforts in this area were accompanied and continued by various collaborators, including W. F. Giaque (who won the Nobel prize for his low-temperature work) and later, Leo Brewer and K. S. Pitzer (now president of Stanford University). But, with respect to chemical engineering education and research in thermodynamics, the most important of Lewis' collaborators was (and is) Joel H. Hildebrand, who at age 88 is still active in research on the properties of liquid solutions.

Hildebrand's numerous publications have shown that when thermodynamics is coupled with



J. M. Prausnitz (BChE Cornell, PhD Princeton) has been a member of the Chemical Engineering faculty at the University of California, Berkeley since 1955. His research interests are concerned with the application of thermodynamics and molecular physics to chemical engineering design. He has published extensively in this area and serves as a consultant to petroleum, petrochemical and cryogenic industries. He has been honored with a Guggenheim fellowship, Miller Research Professorship, ACS Honor Scroll and with the Colburn and Walker Awards of the AIChE.

simple (often semiempirical) molecular models, many practical phase-equilibrium problems can be solved with a minimum of effort, and what is more important, with a minimum of experimental data. It is this feature of Hildebrand's work that has become the major influence on the course "Phase Equilibria" in the Chemical Engineering Department at Berkeley.

The course is normally taken by graduate students in their first quarter at Berkeley. It meets twice a week; each meeting is for one and a half hours. Prerequisites for the course are a one-year course in undergraduate physical chemistry and at least a one-quarter course in undergraduate chemical engineering thermodynamics; almost all entering graduate students satisfy these prerequisites. **The two main purposes of the course are: (1) to give students the background needed to apply thermodynamics and molecular physics toward the solution of practical phase equilibrium problems as required in typical chemical engineering design practice, and (2) to provide an introduction to applied molecular science for tackling new problems on the frontier of modern chemical engineering.** The student acquires some feeling for the physical (as opposed to the merely mathematical) significance of thermodynamic functions and some insight into the intermolecular forces which determine the magnitude of these

Table 1. Berkeley's Course in Phase-Equilibrium Thermodynamics

1. The Phase Equilibrium Problem
2. Classical Thermodynamics of Phase Equilibria
3. Thermodynamic Properties from Volumetric Data
4. Intermolecular Forces
5. Fugacities in Gas Mixtures
6. Fugacities in Liquid Mixtures; Excess Functions
7. Fugacities in Liquid Mixtures: Theories of Solutions
8. Solubility of Gases in Liquids
9. Solubility of Solids in Liquids
10. High-Pressure Equilibria

functions. He gains practice in reduction and interpretation of experimental data and in devising efficient and physically meaningful methods for data correlation. Most important, he achieves some perspective on what kind of experimental information he requires for a given problem and, lacking that information, he gains experience in quantitatively estimating desired phase equilibrium relations from a minimum of experimental data. Finally, he becomes acquainted with some of the literature on phase equilibrium thermodynamics and learns, often to his great surprise, that he must be critical of what he reads since this literature, unfortunately, is not free of errors.

The course is divided into ten somewhat arbitrary sections which are given in Table 1. These sections correspond to the ten chapters of a recent textbook*. The lectures summarize, focus and illustrate the material in the text which the student reads concurrently.

The first section introduces the student to the phase equilibrium problem: what are we trying to do and what connection is there between thermodynamics and the distribution of several components between two (or more) phases? The importance of this problem is discussed not only with respect to typical chemical engineering operations (distillation, extraction, etc.) but also with respect to physiology, meteorology and everyday experiences such as brewing coffee or dry cleaning a piece of clothing. The second section reviews the classical work of Gibbs and Lewis: the concept of open systems; definition and utility of the chemical potential; fugacity and activity; a worked-out simple example (Raoult's law as a special case of the general equation of equilibrium). The third section deals with the calculation of thermodynamic functions (espe-

*J. M. Prausnitz, "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969.

cially fugacity) from experimental P-V-T data (or empirical equations of state) for pure gases, for gas mixtures and for pure liquids and solids. Attention is given to the general procedure of calculating vapor-liquid equilibria using only an equation of state assumed to be valid for both gas and liquid phases (e.g., the Benedict-Webb-Rubin equation).

After the third section the student begins to understand that for finding successful solutions to phase equilibrium problems, the important bottleneck has little to do with thermodynamics; the real problem is not thermodynamics, which is (essentially) all worked out, but molecular physics: How do we obtain, with a minimum of experimental work, the various constants in the equations? The student recognizes the need for constants which appear because real substances, unlike ideal gases, consist of finite-size molecules which attract and repel one another. He is made aware of the main difficulty in applied thermodynamics: to use thermodynamics for obtaining numerical results we must add physical understanding to our thermodynamic formalism. And while the thermodynamic formalism is beautiful, exact and complete, our understanding of molecular behavior is still very limited.

Section four presents a simplified survey of what is known about intermolecular forces. The nature and origin of intermolecular forces is presented along with the concept and significance of potential energy functions and the microscopic law of corresponding states. A brief discussion is given of such "chemical" forces as hydrogen bonding and charge-transfer complex formation. Emphasis is given to qualitative and semiquantitative relations between intermolecular forces and macroscopic properties.

Section five begins with a critical discussion of the virial equation of state: its theoretical significance, its utility and limitations for calculating fugacity coefficients in gas mixtures. Attention is given to the exact relations between virial coefficients and intermolecular potential functions and to the composition dependence of virial coefficients. The "chemical" theory of gas imperfections is discussed. Semiempirical methods (e.g., the Redlich-Kwong equation) are presented for finding fugacity coefficients at high densities, and it is shown how these are used to calculate solubilities of liquids and solids in compressed gases.

Excess functions and their application to liquid mixtures are considered in section six. Various

equations for representing activity coefficients (van Laar, Margules, Wilson, NRTL, etc.) are discussed. Consideration is given to multicomponent mixtures and to systems with partial miscibility. The significance and uses of the Gibbs-Duhem equation are given special attention.

Section seven is an introduction to the theory of liquid solutions. Brief attention is given to the lattice theory of simple mixtures and of polymer solutions; emphasis is placed on the theory of regular solutions, on applications of corresponding states theory, and on the "chemical" theory of associated and solvated solutions. All theories are regarded critically; advantages and disadvantages are pointed out.

Sections eight and nine are concerned with the solubilities of gases and solids in pure solvents and in solvent mixtures. Physical and chemical effects on solubility are pointed out and special attention is given to the importance of the standard-state fugacity of the solute.

The course ends with a brief discussion of the uses of thermodynamics to describe systems at high pressure. Special emphasis is given to the important role of the partial molar volume. Vapor-liquid, liquid-liquid and gas-gas equilibria are considered.

As outlined above, the course appears to contain a lot of material. However, experience has shown that well-prepared first-year graduate students can handle the course without difficulty provided their total course load is not large.

Typical first-year graduate students at Berkeley usually take only a total of two lecture courses plus one seminar course per quarter. Careful reading of the text (which was available in mimeographed form until its recent publication) is augmented with reading of "classical" original articles which are kept on reserve in the College of Chemistry library. Eight problem sets give the student practice in applying what he has learned to the solution of practical phase equilibrium problems. All problem sets are corrected by a teaching assistant and the more difficult problems are discussed in class.

The course provides a good partial foundation for subsequent graduate courses in separation operations, in process design and in medical engineering. For those students interested in doing research in molecular science and engineering it provides background and perspective for subsequent courses in statistical mechanics and in advanced chemistry, physics, and materials science.

The often-praised versatility of the chemical engineer, his ability to tackle a wide variety of new problems, is in large measure due to his knowledge of applied physical chemistry. Berkeley's course in phase equilibrium thermodynamics aims to contribute to that knowledge while at the same time providing the student with some of the skills for the practice of conventional chemical engineering.

LETTERS (Cont'd from p. 167.)

AN ADVENTURE IN TEACHING

Sir: During a recent conversation one of my graduate students described a course he was taking. The professor wrote everything down on the blackboard. He defined each symbol of every equation. Definitions were given of each technical word. Discussion was limited to students asking for clarification of the professor's handwriting. And then he added, "It wasn't like the Rate Processes course you taught last year". That had been an exciting learning experience for him. It had been the same for me.

I was teaching the second quarter of Rate Processes to first-year graduate students of varied backgrounds. In the first quarter we had covered the Momentum Transport section of "Transport Phenomena" by Bird, Stewart, and Lightfoot (BSL). This quarter I decided to teach Energy and Mass Transfer by the "row" approach. As the authors point out in the preface this alternate approach is suitable for graduate students. It emphasizes the type of transport and the analogies between the transport phenomena. Realistically it also eliminated the possibility that only

a week or two at the end of the quarter would be left for Mass Transport.

The first topic covered was methods for predicting thermal conductivities and binary diffusivities. Since this touched on the area of my doctoral research, I added current literature methods to the text material and the students evaluated:

- Variation of thermal conductivity for sulfur dioxide, carbon tetrafluoride, and tungsten hexafluoride over the temperature range of 0 to 1000°C.
- Comparison of thermal conductivities of ammonia, carbon tetrafluoride, and hydrogen at three elevated pressures with experimental values.
- Variation of the binary diffusivities of tungsten hexafluoride and hydrogen fluoride over the temperature range of 0 to 1000°C.

Three lessons were learned from this exercise. First, beware of phase changes when computing transport properties (melting point of tungsten hexafluoride is 2°C and critical point is 178°C). Second, use of available sources of or estimation techniques for intermolecular force parameters. Finally, a feel for the accuracy of generalized correlations for transport properties.