A Course in

EQUILIBRIUM THEORY OF FLUIDS

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Equilibrium Theory of Fluids is one of the beginning courses we offer the new graduate students in the Fall Semester. The course is an evolution of thermodynamics which has been in more or less the same position in the graduate curriculum for many years at Purdue. We changed the name of the course a few years ago to reflect its changed emphasis and contents.

The objective of this course is the study of the equilibrium properties of gases and liquids that are of interest in chemical process calculations. The properties are defined and interrelated in the context of classical thermodynamics. The interpretation, correlation, and prediction of properties are made by appealing to molecular considerations. A coincident objective of the course is to impart training in classical and statistical thermodynamics. The usefulness of the training should go beyond the understanding of equilibrium properties.

The contents of the course belong in three broad areas: 1. Principles of thermodynamics and statistical mechanics, 2. Properties of homogeneous fluid phases, and 3. Phase and chemical equilibria. The progression of the course coincides with the above sequence so that the semester starts with the basic principles and ends up at the frontier of current engineering literature. Table 1 shows the breakdown of the course contents in parts and sections.

PART 1 CONTAINS a concise presentation of the fundamental concepts and laws of thermodynamics. These are shown to lead to criteria of physico-chemical equilibria, and to functions that are useful for the description of physico-chemical processes. The concept of equilibrium in physico-chemical systems is inherently more abstract than that in many other types of systems such as the mechanical or electrical. But it is central to chemical process systems. We therefore think it worthwhile to go through a development starting from scratch. (We are aware of the risk of repeating a substantial part of undergraduate material. Hence, we depend on the use of hand-outs to keep lecturing to a minimum.)

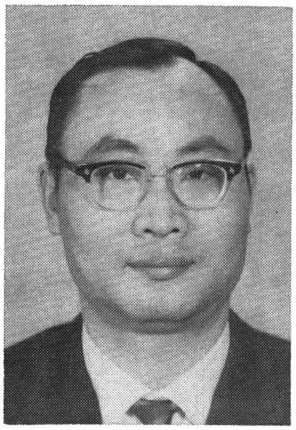
The first section of Part 1 is in the nature of definitions. A discussion is then made of exact and inexact differentials. Thermodynamic laws are presented on the basis of this discussion regarding state functions. The zeroth, first, and second laws are stated in terms of the state function introduced — temperature, internal energy, and entropy respectively.

The usefulness of the thermodynamic laws is greatly extended with the introduction of the energy functions. The concept of their association with certain natural variables is basic to this usefulness. Since these functions are related to the reversible shaft work under various conditions of constraint they provide the point of departure for the development of criteria of equilibrium and stability of physico-chemical systems.

IN PART 2 WE RELATE the equilibrium properties of matter in bulk to the properties of the constituent molecules. Our main concern is to develop the formalism and to present a set of useful formulas. These are illustrated extensively with examples drawn from simple systems.

A dual function is served in relating the thermodynamic properties to the molecular properties: (1) a deeper understanding is gained of thermodynamics as the manifestations of large collections of particles. (2) the molecular viewpoint provides the basis for the interpretation, correlation, and prediction of properties.

We begin Part 2 with a discussion of the meaning of the micro and macro states. The micro function (for isolated systems), the canonical partition function (for closed systems), and the grand partition function (for open systems) are introduced for the representation of the system. When the statistical averages are evaluated the thermodynamic properties become expressed in terms of the partition functions. The equivalence of the partition functions is demonstrated.



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Equilibrium properties of fluids are conveniently considered as made up of contributions due to the motion of the isolated molecules, and the cooperative motion of the molecules in interaction. The former make up the ideal gas properties and the latter determine the deviations from ideal gas behavior. Since we are interested in real fluids, we discuss intermolecular forces in Section 4. We then separate in Section 5 the thermodynamic properties due to intermolecular forces and express them in terms of configurational integrals.

All the example systems studied in Part 2 are simple and elementary, such as non-interacting particles, Einstein's crystal, one-dimensional lattice solutions, etc. Nevertheless they serve more than purposes of illustration. The simple results become useful when re-combined and developed for the description of real fluids of considerable complexity. We might compare these possibilities to the mechanical engineer's tinkering with simple links and bars, for out of these are made complex machines.

Table 1. Contents of Equilibrium Theory of Fluids

1. Thermodynamic Principles and Functions
   - 1.1 Systems and processes
   - 1.2 Exact and inexact differentials
   - 1.3 Zeroth law, temperature, and ideal gas
   - 1.4 First law and internal energy
   - 1.5 Second law and entropy
   - 1.6 Energy functions
   - 1.7 Shaft work
   - 1.8 Criteria of equilibrium and stability
   - 1.9 Partial quantities
   - 1.10 Jacobians
2. Partition Functions, Intermolecular Forces, and Configurational Properties
   - 2.1 Micro and macro states
   - 2.2 Micro partition function
   - 2.3 Canonical partition function
   - 2.4 Grand partition function
   - 2.5 Intermolecular forces
   - 2.6 Configurational properties
3. Gases and Gas Mixtures
   - 3.1 P-V-T behavior and principle of corresponding states of pure fluids
   - 3.2 Generalized correlation of volumetric behavior
   - 3.3 Properties derived from generalized correlations
   - 3.4 Virial equation of state and properties of gases at low densities
   - 3.5 Equations of state
   - 3.6 Properties derived from equations of state
   - 3.7 Low pressure gas mixtures
   - 3.8 Fugacity and partial functions
   - 3.9 Equation of state for mixtures
   - 3.10 Properties of gas mixtures from pseudo-criticals
   - 3.11 Amagat's law and Dalton's law
   - 3.12 Sublimiation equilibrium
4. Liquids and Liquid Solutions
   - 4.1 The liquid state
   - 4.2 Principle of Corresponding States of pure liquids
   - 4.3 Raoult's law, Henry's law, and ideal solutions
   - 4.4 Activity and activity coefficients in real solutions
   - 4.5 Mixing and excess properties
   - 4.6 Empirical representation of excess functions
   - 4.7 Nearly-ideal systems
   - 4.8 Regular solutions
   - 4.9 Polymer solutions
   - 4.10 Group contributions
5. Phase Equilibrium
   - 5.1 Gibbs phase rule
   - 5.2 Vapor liquid equilibria at low pressures
   - 5.3 Vaporization equilibrium ratio
   - 5.4 Solid-liquid solubility equilibrium
   - 5.5 Liquid-liquid extraction equilibrium
   - 5.6 Adsorption equilibrium
6. Chemical Equilibrium
   - 6.1 The third law
   - 6.2 Standard free energy and the chemical equilibrium constant
   - 6.3 Thermodynamic restrictions on the rate expression
   - 6.4 Transition state theory
   - 6.5 Calculation of complex chemical equilibria

. . . this course is the study of the equilibrium properties of gases and liquids that are of interest in chemical process calculations.

IN PART 3 WE STUDY the properties of gases and their mixtures. The properties can be clearly classified into two categories: the energy functions of the entire fluid, and the chemical-potential related functions of the components in the fluid. The first type of properties are of general interest to many disciplines. The second type of properties fall within the special interest of the chemical engineer.

The energy functions are needed for the determination of heat and work quantities that are associated with processes. Heat is always an important concern with any fluids. The mechanical work of compression and expansion can also be an important consideration in the processing of gas. This consideration sets the gases apart from the condensed phases for which compressibility effects are usually of secondary importance.

The chemical-potential-related functions (μ, fugacity, activity, etc) are the partial properties needed for the calculation of phase and chemical equilibria. Other partial properties, such as $\overline{H}_i$ and $\overline{V}_i$, are of interest mainly in so far as they reflect the effect on equilibrium due to changes of conditions.

Thermodynamic properties of gases are discussed in terms of their differences from their ideal gas values. We do not belabor the ideal gas values. Instead, we depend on the extensive tabulations of such properties in the literature. We are therefore free from considerations of the isolated molecules and their modes of internal motion which are adequately described in physical chemistry. Here we concentrate on the effects of intermolecular forces which determine real fluid behavior in contrast to that of the ideal gas.

The principle of corresponding states is the single most important tool for the general description of properties of fluids. Accordingly we emphasize generalized correlations (tabular and graphical) and generalized equations of state expressed in dimensionless reduced forms. For the treatment of gases, the reduced variables are formed with the critical properties. With the aid of correlations of the criticals with molecular structure, it becomes possible to make quantitative calculations for diverse substances from no more information than their structural formulas, if that should be the only piece of information available.

We include liquids in this Part where it is feasible to treat them as an extension of the gas phase. It is well known that a liquid partakes of the properties of both a gas and a solid to varying degrees depending on its state relative to the critical point and the triple point. Part 4 will be concerned entirely with liquids but from a different view point.

The first six sections of this Part deal with pure gases. After an introductory discussion of the general qualitative features of the properties of fluids, we develop the formalism of their quantitative analysis in two ways: with (T,p) and with (T,V) respectively as the independent variables. With generalized correlations, (and tabular and graphical data) the set (T,p) serves well. The necessary development is adequately covered in most texts. However, a corresponding development is usually lacking with (T,V) as the independent variables. These are required in equations of state calculations with the electronic computer and are of increasing importance as the use of computers is increased. We therefore go to some length to present the general working formulas, and to show their use with example equations of state.

In the second part of the Part starting with 3.7 we discuss gas mixtures. The limiting behavior of low pressure gas mixtures is always completely determined by the pure component properties. From there on the formalism relating the energy functions of real gas mixtures to their low pressure limits remain the same as for pure gases.

With mixtures, however, there is the additional task of evaluating the partial properties. including the chemical-potential and related functions in equilibrium calculations. Even though it is possible in principle to do so with the generalized correlations, the calculations are too tedious to be practical. As a result equations of state assume added significance when applied to mixtures, for the equations are far more suited for computer applications.

IN PART 4 WE STUDY liquids and their solutions. Liquids are probably the most common and least understood state of matter that occur in chemical processes. However, a systematic understanding of their behavior is basic to the rational design of separation operations involving liquids such as distillation, crystallization, extraction, and so on.

A liquid shares the properties of gases and solids to varying extents depending on the relative

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proximity of its state to the critical point and the triple point. Our main interest in Part 4 is about liquids at states far removed from the critical. Liquid states close to the critical were part of the discussion of the preceeding Part. In the introductory part of Part 4 we present a general molecular view of liquids. Reflecting recent progress, the cell theory is developed into useful generalizations of the properties of non-polar liquids, including simple molecules, and chain molecules. We then discuss properties of pure liquids that will be needed in subsequent studies of liquid solutions.

The remainder of Part 4 concerns solutions. In §3 to §5 we present the formal framework for the description of solution properties on the basis of classical thermodynamics. Then, starting with §6 we discuss the various procedures for the quantitative interpretation, correlation, and prediction of non-ideal behavior of solutions.

The molecular viewpoint provides us with a most useful classification of liquid solutions. Our quantitative description of their non-ideal behavior is based on the same classification. Thus in §7 we describe nearly-ideal systems in which the molecules are highly similar. A linear perturbation theory adequately describes their non-ideality. This theory applies to almost all superfractionation systems as well as a number of other close-boiling mixture systems of exceptional importance such as propane/propylene.

From there on we proceed to systems showing progressively larger non-ideality. We describe solutions of non-polar molecules of appreciably different interaction energies in §8, and of appreciably different sizes in §9. The procedures provide useful descriptions of hydrocarbon mixtures.

The highly non-ideal behavior of solutions containing polar molecules is the basis of azeotropic and extractive distillations. A simple example would be the relative volatility of methanol to ethanol which can be controlled by adding water so that either methanol or ethanol can be distilled as the overhead product. All liquid-liquid extraction processes similarly depend on the utilization of non-ideal solution behavior. Such highly non-ideal solution systems individually required specific and extensive experimental studies until relatively recent times. Then investigations along the lines of group contributions began to bear fruit, until today many general results have been obtained for the description of chain molecules with attached polar groups. We describe this development in §10 to conclude Part 4.

IN THE LAST TWO PARTS of this course, Parts 5 and 6, the materials of the first four Parts are applied to the study of phase and chemical equilibria. Relatively few new principles are introduced here, but the applications serve as an effective review of the preceeding materials, as well as to make more sense of them.

In summary, Equilibrium Theory of Fluids hopefully gives the students:

(1) A systematic understanding of the equilibrium properties of fluids that are needed in the analysis of chemical processes, with some appreciation of what is critically important and where, and what is not so critical.

(2) Some experience in the application of physico-chemical principles to industrial problems.

(3) Reinforced training in thermodynamics.

(4) A fair amount of factual information regarding current industrial and engineering practice in property estimation.

We prepared a set of notes for this course which has been added on and revised each time it was used during the last three years. The notes are dittoed for distribution so we do not require any textbooks. The most often cited reference books are listed below:

1. Prigogine, I., and Defay, R., "Chemical Thermodynamics," Longmans, 1954—for our Parts 1 and 6.
2. Rowlinson, J.S., "Liquids and Liquid Mixtures," 2nd ed. Butterworths, 1969—for our Parts 1, 2, 4, 5.
3. Hill, T.L., "Introduction to Statistical Thermodynamics," Addison-Wesley, 1960—for our Parts 2, 3.
4. Prigogine, I., "The Molecular Theory of Solutions," Interscience, 1957—for our Parts 2, 4.
5. Prausnitz, J.M., "Molecular Thermodynamics," Prentice-Hall, 1969—for our Parts 3, 4, 5.
6. Denbigh, K., "Chemical Equilibrium," Cambridge, 1964—for our Parts 1, 2, 6.
7. Stull, D.R., Westrum, E.F., Jr., and Sinke, G.C., "The Chemical Thermodynamics of Organic Compounds," Wiley, 1969—for our Part 6.
8. "Applied Thermodynamics," Am. Chem. Soc. 1968—for our Parts 3, 4, 5, 6. □