The Properties of Gases and Liquids

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Preface

Reliable values of the properties of materials are necessary for the design of industrial processes. An enormous amount of data has been collected and correlated over the years, but the rapid advance of technology into new fields seems always to maintain a significant gap between demand and availability. The engineer is still required to rely primarily on common sense, experience, and a variety of methods for estimating physical properties.

This book presents a critical review of various estimation procedures for a limited number of properties of gases and liquids: critical and other pure component properties, *PVT* and thermodynamic properties of pure components and mixtures, vapor pressures, and phase-change enthalpies, standard enthalpies of formation, standard Gibbs energies of formation, heat capacities, surface tensions, viscosities, thermal conductivities, diffusion coefficients, and phase equilibria. Comparisons of experimental and estimated values are normally shown in tables to indicate reliability. Most methods are illustrated by examples.

The procedures described are necessarily limited to those which appear to the authors to have the greatest validity and practical use. Wherever possible, we have included recommendations delineating the best methods for estimating each property and the most reliable techniques for extrapolating or interpolating available data. Recommended methods are often illustrated by detailed examples.

Although the book is intended to serve primarily the practicing engineer, especially the process or chemical engineer, other engineers and scientists concerned with gases and liquids may find it useful.

The first edition of this book was published in 1958, the second in 1966, and the third in 1977. Each revision is essentially a new book, because many estimation methods are proposed each year and, over an 8- to 10-year span, most earlier methods are modified or displaced by more accurate or more general techniques. Most new methods are still empirical in nature, although there are often theoretical bases for the correlation;

whenever possible, the theory is outlined to provide the user with the foundation of the proposed estimation method.

The data bank, Appendix A, is now about 15 percent larger than that in the third edition. More important, many estimated quantities in the earlier version have now been replaced by experimental results.

Many colleagues and students have contributed data, advice, examples, or illustrative calculations; we are grateful to them all. For their helpful contributions, we want to record our thanks to C. Baroncini, M. R. Brulé, R. Lopes Cardozo, T. -H. Chung, J. H. Dymond, W. Hayduk, J. B. Irving, J. D. Isdale, D. T. Jamieson, K. G. Joback, J. Kestin, D. Klingenberg, D. Kyser, G. Latini, L. L. Lee, K. Lucas, D. Reichenberg, R. L. Rowley, A. S. Teja, T. P. Thinh, R. Topliss, A. Vetere, and J. Wong.

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Chapter

1

The Estimation of Physical Properties

1-1 Introduction

The structural engineer cannot design a bridge without knowing the properties of steel and concrete. Similarly, scientists and engineers often require the properties of gases and liquids. The chemical or process engineer, in particular, finds knowledge of physical properties of fluids essential to the design of many kinds of industrial equipment. Even the theoretical physicist must occasionally compare theory with measured properties.

The physical properties of every substance depend directly on the nature of the molecules of the substance. Therefore, the ultimate generalization of physical properties of fluids will require a complete understanding of molecular behavior, which we do not yet have. Though its origins are ancient, the molecular theory was not generally accepted until about the beginning of the nineteenth century, and even then there were setbacks until experimental evidence vindicated the theory early in the twentieth century. Many pieces of the puzzle of molecular behavior have now fallen into place, but as yet it has not been possible to develop a complete generalization.

In the nineteenth century, the laws of Charles and Gay-Lussac were combined with Avogadro's hypothesis to form the gas law, $PV = NRT$, which was perhaps the first important correlation of properties. Deviations from the ideal-gas law, though often small, were tied to the fundamental nature of the molecules. The equation of van der Waals, the virial equation, and other equations of state express these quantitatively. These extensions of the ideal-gas law have not only facilitated progress in the development of a molecular theory but, more important for our purposes here, have provided a framework for correlating physical properties of fluids.

The original "hard-sphere" kinetic theory of gases was a significant contribution to progress in understanding the statistical behavior of a system containing a large number of molecules. Thermodynamic and transport properties were related quantitatively to molecular size and speed. Deviations from the hard-sphere kinetic theory led to studies of the interaction of molecules based on the realization that molecules attract at intermediate separations and repel when they come very close. The semiempirical potential functions of Lennard-Jones and others describe attraction and repulsion in an approximate quantitative fashion. More recent potential functions allow for the shapes of molecules and for asymmetric charge distribution in polar molecules.

Although allowance for the forces of attraction and repulsion between molecules is primarily a development of the twentieth century, the concept is not new. In about 1750, Boscovich suggested that molecules (which he referred to as atoms) are "endowed with potential force, that any two atoms attract or repel each other with a force depending on their distance apart. At large distances the attraction varies as the inverse square of the distance. The ultimate force is a repulsion which increases without limit as the distance decreases without limit, so that the two atoms can never coincide" [3].

From the viewpoint of mathematical physics, the development of a comprehensive molecular theory would appear to be complete. J. C. Slater [4] observes that, while we are still seeking the laws of nuclear physics, "in the physics of atoms, molecules and solids, we have found the laws and are exploring the deductions from them." However, the suggestion that, in principle (the Schrödinger equation of quantum mechanics), everything is known about molecules is of little comfort to the engineer who needs to know the properties of some new chemical to design a commercial plant.

Paralleling the continuing refinement of the molecular theory has been the development of thermodynamics and its application to properties. The two are intimately related and interdependent. Carnot was an engineer interested in steam engines, but the second law of thermodynamics was shown by Clausius, Kelvin, Maxwell, and Gibbs to have broad applications in all branches of science.

Thermodynamics by itself cannot provide physical properties; only molecular theory or experiment can do that. But thermodynamics reduces experimental or theoretical efforts by relating one physical property to another. For example, the Clausius-Clapeyron equation provides a useful method for obtaining enthalpies of vaporization from more easily measured vapor pressures.

The second law led to the concept of chemical potential which is basic to an understanding of chemical and phase equilibria, and Maxwell's equations provide ways to obtain important thermodynamic properties of a substance from $PVTx$ relations. Since derivatives are often required, the $PVTx$ function must be known accurately.

In spite of impressive developments in molecular theory, the engineer frequently finds a need for physical properties which have not been measured and which cannot be calculated from existing theory. The *International Critical Tables*, Beilstein, Landolt-Börnstein, and many other handbooks provide convenient data sources, and there exists an increasing number of journals devoted to compilation and critical review of physical property data. Further, computerized data banks are now becoming routine components of computer-aided process design. But it is inconceivable that all desired experimental data will ever be available for the hundreds or thousands of compounds of interest in science and industry: while the number of possibly interesting compounds is already very large, the number of mixtures formed by these compounds is much larger.

While the need for accurate design data is increasing, the rate of accumulation of new data is not increasing fast enough. Data on multicomponent mixtures are particularly scarce. The process engineer who is frequently called upon to design a plant to produce a new chemical (or a well-known chemical in a new way) often finds that the required physical property data are not available. It may be possible to obtain the desired properties from new experimental measurements, but that is often not practical because such measurements tend to be expensive and time-consuming. To meet budgetary and deadline requirements, the process engineer almost always must estimate at least some of the properties required for design.

1-2 Estimation of Properties

In the all-too-frequent situation in which no experimental value of the needed property is at hand, the value must be estimated or predicted. "Estimation" and "prediction" are often used as if they were synonymous, although the former properly carries the frank implication that the result may be only approximate. Estimates may be based on theory, on correlations of experimental values, or on a combination of both. A theoretical relation, although not generally valid, may nevertheless serve adequately in specific cases.

To relate mass and volumetric flow rates of air through an air-conditioning unit, the engineer is justified in using $PV = NRT$. Similarly, he or she may properly use Dalton's law and the vapor pressure of water to calculate the mass fraction of water in saturated air. However, the engineer must be able to judge the operating pressure when such simple calculations lead to unacceptable error.

Completely empirical correlations are often useful, but one must avoid the temptation to use them outside the narrow range of properties on which they are based. In general, the stronger the theoretical basis, the more reliable the correlation.

Most of the better estimation methods use equations based on the form of an incomplete theory with empirical correlations of the constants that are not provided by that theory. Introduction of empiricism into parts of a theoretical relation provides a powerful method for developing a reliable correlation. For example, the van der Waals equation of state is a modification of the simple $PV = NRT$; setting $N = 1$,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1-2.1}$$

Equation (1-2.1) is based on the idea that the pressure on a container wall, exerted by the impinging molecules, is decreased because of the attraction by the mass of molecules in the bulk gas; that attraction rises with density. Further, the available space in which the molecules move is less than the total volume by the excluded volume b due to the size of the molecules themselves. Therefore, the "constants" a and b have some theoretical basis. The correlation of a and b in terms of other properties of a substance is an example of the use of an empirically modified theoretical form.

Empirical extension of theory can often lead to a correlation useful for estimation purposes. For example, several methods for estimating diffusion coefficients in low-pressure binary gas systems are empirical modifications of the equation given by the simple kinetic theory. Almost all the better estimation procedures are based on correlations developed in this way.

1-3 Types of Estimation

An ideal system for the estimation of a physical property would (1) provide reliable physical and thermodynamic properties for pure substances and for mixtures at any temperature, pressure, and composition, (2) indicate the state (solid, liquid, or gas), (3) require a minimum of input data,

(4) choose the least-error route (i.e., the best estimation method), (5) indicate the probable error, and (6) minimize computation time. Few of the available methods approach this ideal, but some serve remarkably well.

In numerous practical cases, the most accurate method may not be the best for the purpose. Many engineering applications properly require only approximate estimates, and a simple estimation method requiring little or no input data is often preferred over a complex but more accurate correlation. The simple gas law is useful at low to modest pressures, although more accurate correlations are available. Unfortunately, it is often not easy to provide guidance on when to reject the simpler in favor of the more complex (but more accurate) method.

Although a variety of molecular theories may be useful for data correlation, there is one theory which is particularly helpful. This theory, called the theory of corresponding states, was originally based on macroscopic arguments, but in its modern form it has a molecular basis.

The law of corresponding states

Proposed by van der Waals in 1873, the law of corresponding states expresses the generalization that equilibrium properties which depend on intermolecular forces are related to the critical properties in a universal way. Corresponding states provides the single most important basis for the development of correlations and estimation methods. In 1873, van der Waals showed it to be theoretically valid for all pure substances whose *PVT* properties could be expressed by a two-constant equation of state such as Eq. (1-2.1). As shown by Pitzer in 1939, it is similarly valid if the intermolecular potential function requires only two characteristic parameters. Corresponding states holds well for fluids containing simple molecules and, upon semiempirical extension, it also holds for many other substances where molecular orientation is not important, i.e., for molecules that are not strongly polar or hydrogen-bonded.

The relation of pressure to volume at constant temperature is different for different substances; however, corresponding states theory asserts that if pressure, volume, and temperature are related to the corresponding critical properties, the function relating reduced pressure to reduced volume becomes the same for all substances. The reduced property is commonly expressed as a fraction of the critical property: $P_r = P/P_c$; $V_r = V/V_c$; and $T_r = T/T_c$.

To illustrate corresponding states, Fig. 1-1 shows the law of corresponding states for *PVT* data for methane and nitrogen. In effect, the critical point is taken as the origin. The data for saturated liquid and saturated vapor coincide well for the two substances. The isotherms (constant T_r), of which only one is shown, agree equally well.

Successful application of the law of corresponding states for correlation

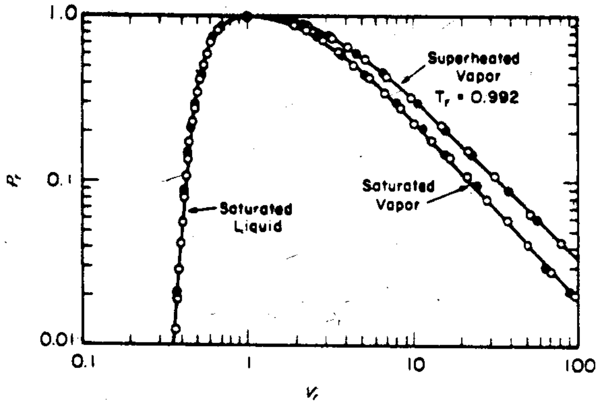

Figure 1-1 The law of corresponding states applied to the *PVT* properties of methane and nitrogen. Experimental values [3]: ○ methane, ● nitrogen.

of *PVT* data has encouraged similar correlations of other properties which depend primarily on intermolecular forces. Many of these have proved valuable to the practicing engineer. Modifications of the law are common to improve accuracy or ease of use. Good correlations of high-pressure gas viscosity have been obtained by expressing η/η_c as a function of P_r and T_r. But since η_c is seldom known and not easily estimated, this quantity has been replaced in other correlations by η_c°, η_T°, or the group $M^{1/2}P_c^{2/3}T_c^{1/6}$, where η_c° is the viscosity at T_c and low pressure, η_T° is the viscosity at the temperature of interest, again at low pressure, and the group containing M, P_c, and T_c is suggested by dimensional analysis. Other alternatives to the use of η_c might be proposed, each modeled on the law of corresponding states but essentially empirical as applied to transport properties.

The law of corresponding states can be derived from statistical mechanics when severe simplifications are introduced into the partition function. Sometimes other useful results can be obtained by introducing less severe simplifications into statistical mechanics toward providing a framework for the development of estimation methods. Fundamental equations describing various properties (including transport properties) can sometimes be derived, provided that an expression is available for the potential-energy function for molecular interactions. This function may be, at least in part, empirical; but the fundamental equations for properties are often insensitive to details in the potential function from which they stem, and two-constant potential functions frequently serve remarkably well for some systems. Statistical mechanics may at present be far removed from engineering practice, but there is good reason to believe that it will become increasingly useful, especially when combined with computer simulations.

Nonpolar and polar molecules

Spherically symmetric molecules (for example, CH_4) are well fitted by a two-constant law of corresponding states. Nonspherical and weakly polar molecules do not fit poorly, but deviations are often great enough to encourage the development of correlations using a third parameter, e.g., the acentric factor. The acentric factor is obtained from the deviation of the experimental vapor pressure–temperature function from that which might be expected for a similar substance consisting of spherically symmetric molecules. Typical corresponding states correlations express the dimensionless property as a function of P_r, T_r, and the chosen third parameter.

Unfortunately, the properties of strongly polar molecules are often not satisfactorily represented by the two- or three-constant correlations which do so well for nonpolar molecules. An additional parameter based on the dipole moment has often been suggested but with limited success, since polar molecules are not easily characterized by using only the dipole moment and critical constants. As a result, although good correlations exist for properties of nonpolar fluids, similar correlations for polar fluids are often not available or else are of restricted reliability.

Structure

All macroscopic properties are related to molecular structure, which determines the magnitude and predominant type of the intermolecular forces. For example, structure determines the energy storage capacity of a molecule and thus the molecule's heat capacity.

The concept of structure suggests that a macroscopic property can be calculated from group contributions. The relevant characteristics of structure are related to the atoms, atomic groups, bond type, etc.; to them we assign weighting factors and then determine the property, usually by an algebraic operation which sums the contributions from the molecule's parts. Sometimes the calculated sum of the contributions is not for the property itself but instead is for a correction to the property as calculated by some simplified theory or empirical rule. For example, Lydersen's method for estimating T_c starts with the loose rule that the ratio of the normal boiling temperature to the critical temperature is about 2:3. Additive structural increments based on bond types are then used to obtain empirical corrections to that ratio.

Some of the better correlations of ideal-gas heat capacities employ theoretical values of C_p° (which are intimately related to structure) to obtain a polynomial expressing C_p° as a function of temperature; the constants in the polynomial are determined by contributions from the constituent atoms, atomic groups, and types of bonds.