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Equilibrium Properties of Fluids and Fluid Mixtures

By Aleksander Kreglewski

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By ALEKSANDER KREGLEWSKI

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In Memoriam

Aleksander Kreglewski passed away on February 3, 1984, at the age of 56, having seen only the galley proofs of this book, his major work. The tragedy of this situation was, in many ways, consistent with his entire life.

Alek was Polish by birth and retained a love for his homeland along with that for his adopted country, the United States. He received his education in Poland and as a teenager witnessed and participated in the Second World War. While he was attempting to disarm a land mine, it exploded, and he incurred a serious hearing loss which became almost total in the years immediately preceding his death. His accomplishments in life were made even more remarkable by the presence of that handicap.

He received his Doctor of Chemistry degree from the Polish Academy of Sciences in 1956 and remained there as a research chemist until 1958. He then spent two years at Carnegie Institute in a postdoctoral capacity and subsequently returned to Poland as Head of the Phase Equilibria Laboratory in the Warsaw Institute of Physical Chemistry. In 1966, he emigrated to the United States (becoming a citizen in 1972) and joined the staff of Texas A&M University. During an eighteen-month period in 1966–68, he was a visitor at Ohio State and, upon returning to Texas A&M, completed his career as a member of the Thermodynamics Research Center staff. During his scientifically active years, he published 55 papers and contributed to several collective works. His efforts received wide recognition for excellence and gained him the respect of his peers. This book represented an opportunity for him to record those works he considered to be most important and to share his insight with the scientific and engineering community.

On a personal basis, Alek was an interesting intellect and a man of gentlemanly manner. He was a devoted and loving father to his daughter, Agnesieke, and he was a kind and loyal friend to those who knew him. Truly, we are all diminished both personally and professionally by his passing.

Kenneth R. Hall
Andrew R. McFarland
College Station, Texas
April 4, 1984

List of Symbols

Subscripts

$i, j, k, \ldots$	running suffixes for different species (or 1, 2, . . . , also used for individual molecules)
$\alpha, \beta, \gamma, \ldots$	running suffixes for different molecules (of the same or different species)
m	molar or per mole of an m-component mixture; also an average value of a molecular property of a mixture (the excess functions are also molar, but the subscript is deleted)
σ	property along the saturation curve
o, oo	property of a reference substance
x	see f_x, h_x; also pseudocritical constants

Superscripts

none	configurational property
r	residual property
E	excess property
c	gas-liquid critical locus
cs	critical solution temperature (liquid-liquid or gas-gas); e.g., T^{ucs} (upper), T^{lcs} (lower)
b	normal boiling point
v	vaporization
∞	infinite dilution
$-$	bar over a symbol: extremum value, e.g., $\bar{x}_i$, the azeotropic composition
$\ominus$	the values at $T/T^c = 0.6$ or any "standard" quantity
$*$	reduced quantity, Eqs. (4.22) and (4.23)
$'$ $''$	primes, double primes indicate phases in the order of decreasing molar density
L, μ, Q	London, dipole, quadrupole energy contributions

Symbols

N_0	Avogadro number, 6.02205×10^{23} molecules $\cdot \text{mol}^{-1}$
k	Boltzmann constant, $1.38066 \times 10^{-23}\ \text{J} \cdot \text{K}^{-1}$
R	$= N_0k$, gas constant, $8.31441\ \text{J} \cdot \text{mol}^{-1}\text{K}^{-1}$
h	Planck constant, $6.62618 \times 10^{-34}\ \text{J} \cdot s$
M	molar mass
P	pressure
V	volume
T	thermodynamic temperature (Kelvins)
Z	compressibility factor
N	number of molecules (total)
n	amount in moles
ρ	density, $1/V$
ρ_n	number density, N/V
A	Helmholtz free energy
G	Gibbs free energy
U	internal energy, Eq. (1.12a)
H	enthalpy (heat content)
S	entropy
f_i	fugacity
μ_i	chemical potential
h_i, v_i	partial molar enthalpy, volume
H_{ij}	Henry's constant
β, $\beta(T)$	second virial coefficient
$\beta^{(3)}$	third virial coefficient
K_i	vaporization equilibrium constant
α_{ij}	volatility ratio, Eq. (8.2)
z	coordination number
z_{ij}	frequency of collisions
m_c	number of chain links (also number of carbon atoms)
x_i	mole fraction
q_i	contact fraction, Eq. (5.20)
φ_i	g-fraction, Eq. (5.17)
ϕ_i	site fraction, Eq. (5.28)
$u(r)$	intermolecular energy; $u(r)/k$ in Kelvins
$\bar{u}$	minimum value of $u(r)$
σ	collision diameter

η, δ	parameters of noncentral energy
f_x	$\tilde{u}_m/\tilde{u}_{oo}$
h_x	$(\sigma_m/\sigma_{oo})^3$
p_i	polarizability (mean)
μ_i	dipole moment (scalar)
Q_i	quadrupole moment (scalar)
ω	acentric factor
E	electronegativity
Ω	phase integral (partition function)
Ψ	wave function, Eq. (9.4); product of partition functions, Eq. (1.6)
Q	configurational integral
$\mathcal{U}$	configurational (potential) energy of an assembly of molecules
$d\mathbf{r}$	element of volume, $dxdydz$ or $r^2 \sin \Theta \, dr \, d\Theta \, d\varphi$

Units

The following practical SI units are used:

Pressure	1 bar = 10^5 Pa = 14.50377 lb(wt) · in^{-2}
Volume	1 liter = 10^3 cm^3 = 3.531467 × 10^{-2} ft^3 = 0.2641721 gal (U.S.)
Temperature	Kelvin (K); $T/\text{K} = 273.150 + t/°\text{C}$ where $t/°\text{C} = (t/°\text{F} - 32)/1.8$
Energy	1 kJ = 10^3 J = 0.2390057 × 10^3 cal = 0.9478172 BTU
Molar mass	1 mol = 1 g-mol = 2.20462 × 10^{-3} lb-mol

Preface

The physical properties of mixtures of fluids have been at the center of the research interests of many physical chemists and chemical engineers for more than a century. One of the important reasons was and continues to be the need for efficient and economical separation and purification of the components of raw materials, such as petroleum or coal tar, and also of synthetic products. Another reason is purely scientific: namely, fascination with the elusive properties of fluids and mixtures of fluids.

The theory of fluids has made great progress in recent years. These papers are scattered in journals of theoretical physics, however, and the equations seem hopelessly complex for a chemical engineer interested in simple practical solutions. Consequently, the gap between pure science and engineering in this field is growing.

The results obtained in recent years show that the accuracy of either smoothing or predicting phase equilibria in mixtures depends mostly on that of the equations of state, the extent of our knowledge of the intermolecular forces, and their temperature dependence. Equations of state of hard bodies were developed, accounting properly for the repulsion between molecules, as well as the perturbation theories and molecular dynamics simulations taking care of the intermolecular attraction. These accurate equations of state and fast computers allow solution of the Gibbs equilibrium conditions directly. Therefore, we shall return in this book to the original idea of van der Waals (1890, 1908) and his coworkers that the properties of fluids are determined to the same extent by repulsion and by attraction forces. Accordingly, this book could bear a subtitle, *Applications of the Augmented van der Waals Theory of Fluids*, to honor the name of the pioneering scientist.

Besides equations of state, the theory of intermolecular energy $u(r)$ will be considered to a far greater extent than it is in any of the existing monographs on mixtures. The considerations will be limited to fluids and mixtures of non-electrolytes with or without weak hydrogen bridges (bonds), but the theoretical foundations allow an extension to such substances as water, alcohols, and organic acids, the latter only in mixtures with inert solvents. The radial distribution functions $g(r)$, which are coupled with $u(r)$ and whose computation is very difficult, are replaced by functions of the reduced density ρ^* and reduced temperature T^*, $F(\rho^*, T^*)$, based on molecular dynamics or the *PVT* properties of a reference fluid (argon). The functions $F(\rho^*, T^*)$ for polar or quadrupolar fluids will be further simplified so that the dependence on ρ^* will be the same as for argon. All these simplifications seem to be necessary in routine computations. The application of the above concepts to the calculation of complete phase diagrams of mixtures at high pressures, including the critical locus curves, is the main object of my book.

The theories of mixtures that were published before the development of recent equations of state are now briefly reviewed. Hildebrand and coworkers developed the theory of regular solutions (also known as the Scatchard-Hildebrand theory), whose extensions and applications are summarized in three monographs by Hildebrand and Scott (1950, 1962) and by Hildebrand, Prausnitz, and Scott (1970). At the same time, Guggenheim (1952) applied the lattice model to mixtures;[†] in turn, Flory (1941, 1953) and Huggins (1941, 1958) published the first successful theory of polymer solutions based on the lattice model.

In the decade of the 1950s new approaches were proposed. The first, based on the cell model of the liquid state, was developed by Prigogine and Garikian and more recently by Prausnitz and his coworkers. The second approach, based on the principle of corresponding states, evolved from the theory of conformal mixtures developed by Longuet-Higgins (1951). Attempts to combine the advantages of the two approaches were made by Prigogine and Bellemans (the average potential model) and by Scott (the two-fluid model). The detailed accounts of these efforts are well summarized in the four books by Prigogine, Bellemans, and Mathot (1957), Rowlinson (1959), Prausnitz (1969), and King (1969), as well as in the review articles by Barker (1955), Brown (1965), Bellemans et al. (1967), Leland and Chappelear (1968), and R. L. Scott and Fenby (1969). During the same period, a surprisingly successful theory based on an abstract concept of

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[†] For comments on the lattice model, see Gokcen and Chang (1971).

equilibrium between gaslike and solidlike degrees of freedom in a liquid was proposed by Eyring, Ree, and coworkers (1958). It has been further extended to mixtures with similar success (Liang et al., 1964; Ma and Eyring, 1965).

The theories based on the principle of corresponding states are the only ones that may be applied without an equation of state to the calculation of phase equilibria at high pressures. They will be discussed later. The validity of the others is questionable even when the vapor pressures of the components are very low, because these theories did not consider repulsion. Although the repulsion and the attraction terms in the relation for the compressibility factor Z are equal at $P = 0$, they differ in the residual Helmholtz energy A^r_m of the mixture. The differences between the repulsion and the attraction terms in $Z(T, \rho)$ and $A^r(T, \rho)$ are essential in phase equilibria of fluids and mixtures. All other aspects in which the theories differ among themselves are of minor importance. For these reasons the theories of mixtures usually lead to wrong values of the excess functions G^E and V^E. The contribution of the repulsion term to the residual internal energy U^r is negligible, and so some of the theories yield good values of H^E. Nevertheless, there are concepts in these theories that become useful when incorporated into an accurate equation of state. They will be discussed in Chaps. 4 and 6.

The development of the equation of state for hard spheres seemed of little value for the theory of long-chain molecules, and the latter was treated independently. Flory and coworkers (1964, 1965, 1970) published a successful theory of mixtures of chain molecules based on a modified van der Waals equation of state. Huggins (1970, 1971) developed an accurate theory of polymer solutions based on detailed statistics of the surfaces and interaction energies of the contacting segments of the mixture. When the molecules of both components (i, j) are small, it is proper to evaluate the average minimum value of $u(r)$: namely, $\bar{u}_m$ of the mixture from $\bar{u}_{ii}$, $\bar{u}_{jj}$, and $\bar{u}_{ij}$ weighed by means of the mole fractions. On the other hand, when j or both i and j are large r-mers, the surface fractions or the site fractions are used, giving greater weight to the larger molecule. Various approximations for weighing the contributions to $\bar{u}_m$ of mixtures of intermediate-size molecules are considered in Chap. 5, but not polymer mixtures, as the scope of this book is limited to more or less volatile fluids.

In order to complete this brief survey of the earlier literature, it is appropriate to mention the monographs by Malesinski (1965), Hala, Pick, and Vilim (1958), and van Ness (1967), as well as the textbooks by Haase (1956) and Prigogine and Defay (1954) on the classical thermodynamics of mixtures, which devote little or no attention at all to the molecular behavior of the mixtures.

All the thermodynamic equilibrium and stability conditions needed in the calculations of phase equilibria in pure fluids and mixtures (except those of a tricritical point) were derived by Gibbs (1948) in 1870–80, the same decade as the van der Waals equation. In order to apply these conditions in practice, it is necessary to distinguish a perfect gas from a real fluid. The differences between the two, expressed by the residual functions, can be evaluated when the molecular properties of the fluid and the equation of state are known. The basic relations for the residual functions are given in Chap. 1, and those resulting from the theory of intermolecular forces and the recent equations of state are considered in Chaps. 4 and 6.

Most students of chemistry and chemical engineering wonder at the multitude of relations in their courses in thermodynamics, and later they wonder again that still other relations are used in practice. We need a few basic relations to calculate the phase diagrams of mixtures and the enthalpies and entropies. The relations for multicomponent systems (for example, for the excess functions) are derived; other functions obtained from thermodynamics, theories of intermolecular forces, and the theory of intermolecular repulsion are quoted without derivation.

Finally, let us note that the bibliography at the end of this book does not reflect the tremendous amount of work done by the experimentalists. The data for pure fluids and those for mixtures are equally important. Each set of constants of an equation results from the data in ten, twenty, or more papers that are not cited here; however, they are cited in the papers where the constants were determined. Also, the sources quoted here for mixtures are only a few among the hundreds of papers. This does not mean that the others are less important but simply that the author was able to interpret only some of them at the present time.

The foundations of science are empirical. Theories must be improved or discarded, whereas the results of careful experiments are always good.

Acknowledgments

I offer my thanks to Dr. Bruno J. Zwolinski, former Director of the Thermodynamics Research Center (TRC), for encouraging this part-time research on mixtures of fluids and to the Texas Engineering Experiment Station for partial financial support.

Most of my experimental research was done with a group of students and coworkers before 1966, at the Institute of Physical Chemistry in Warsaw, Poland. A collaboration with Prof. Webster B. Kay in 1968–69 was very fruitful, and I will always recall with nostalgia those eighteen months at Ohio State University.

An extensive evaluation of various theories of mixtures and equations of state was perhaps the most important task. This I did in the years 1970–77, with the assistance of Dr. Stephen S. Chen in 1975–77. Our work progressed rapidly, but unfortunately, Stephen died in September 1977 at the age of 39. I have continued this work with much assistance from Mrs. Carol Chen in computer programming. The assistance of Dr. R. C. Wilhoit in programming during 1973 and 1981 is also acknowledged.

Thanks to the emphasis put on the studies of mixtures by Dr. Kenneth R. Hall, the Director of TRC since 1979, and a large grant from the National Science Foundation, I have been able to expand this work greatly and to test the usefulness of basic concepts by the calculation of complete phase diagrams for many binary systems.

In a nice gesture, Mrs. Ann-Lin Risinger prepared all the graphs, with great care and concern for every detail. Ms. Renèe C. Ney typed all the references. Finally, I wish to thank the reviewers for friendly and constructive comments.

College Station
July 1983

Contents

Equilibrium Properties of Fluids and Fluid Mixtures

CHAPTER 1

Thermodynamic Residual and Configurational Functions

It is well known that a liquid will evaporate during an isothermal expansion of the space in which it is confined until the dew point is reached. Upon further expansion, the properties of the unsaturated vapor or gas, when its density or the pressure is low enough, may approach those of a perfect gas. However, even at the density $\rho = 0$ not all of the properties of a real fluid become equal to those of the *perfect gas*. One of the properties that become identical for a real gas and the perfect gas at this density is the pressure

$$P(T, V, n_i) = (RT/V) \sum_i n_i \tag{1.1}$$

This limiting behavior of real fluids was confirmed by precise measurements of the compressibility (compression) factors Z, shown schematically in Fig. 1.1. The straight lines can be expressed by the relation

$$Z = PV_m/RT = 1 + \beta(T)\rho_m \tag{1.2a}$$

or

$$Z = 1 + \beta(T)P/RT \qquad (\rho_m \to 0) \tag{1.2b}$$

where ρ_m is the molar density, $1/V_m$. The function $\beta(T)$ depends on the chemical nature of the gas and on the temperature only. It is called the *second virial coefficient*. As $\rho \to 0$, $(\partial Z/\partial \rho)_T = \beta(T)$, and it is zero at all temperatures for a perfect gas only. Let us note that at $P \to 0$ the equations above are not necessarily valid, because the state at this pressure may be that of a nonvolatile liquid or the crystalline state. It is then more proper to operate with densities than with pressures.

As shown by Kirkwood (1935) and independently by Mayer and Mayer (1940) and de Boer (1949), the second virial coefficient is

$$\beta_{ij} = -2\pi N_0 \int_0^\infty (e^{-u_{ij}(r)/kT} - 1)\, r^2\, dr \tag{1.3}$$

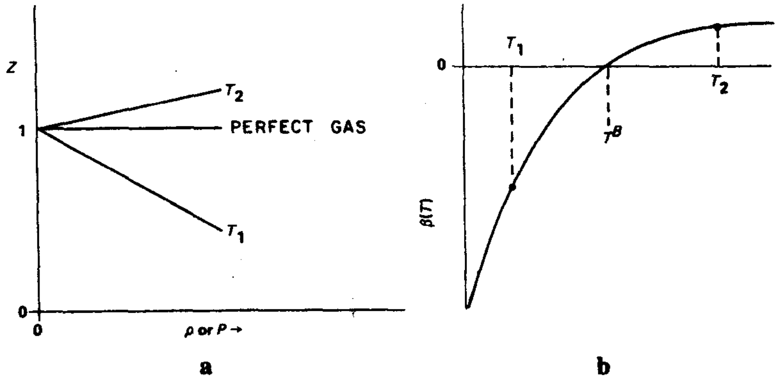

FIG. 1.1. (a) The compressibility factor Z of a real gas at two temperatures, T_1 and T_2, and low densities. (b) The second virial coefficient of a real gas as the function of temperature. T^B, at which β equals zero, is called the *Boyle temperature*.

The intermolecular energy $u_{ij}(r)$ between the molecules of species i and j depends on the geometric properties (size and shape) of the molecules and the intermolecular forces of attraction. Thus, the perfect gas is a hypothetical gas of point-molecules ($\sigma = 0$) between which there is no attraction, $u(r) = 0$, at all distances r.

The total of the thermodynamic functions of a substance is the sum of the *molecular functions* and the *configurational functions*; for example,

$$A^{\text{total}} = A + A^{\text{mol}};\ G^{\text{total}} = A^{\text{total}} + PV;$$

also

$$G = A + PV;$$

hence

$$G^{\text{mol}} = A^{\text{mol}} \qquad (1.4)$$

The total functions are derived from the phase integral (partition function) Ω, which is related to the mass and to the intra- and intermolecular energies of N_i molecules of species i. The fundamental relation for the Helmholtz energy[†] is

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[†] The basic relations of thermodynamics and statistical mechanics such as (1.6), (1.8), and (1.12) are quoted here without derivation. The reader is referred to the textbooks on the subject.