Calculation of properties

using corresponding-state methods

Z. ŠTĚRBÁČEK, B. BISKUP, P. TAUSK

CALCULATION OF PROPERTIES
USING CORRESPONDING-STATE METHODS

CHEMICAL ENGINEERING MONOGRAPHS

Edited by Professor S. W. CHURCHILL, Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pa. 19104, U.S.A.

CALCULATION OF PROPERTIES USING CORRESPONDING-STATE METHODS

ZDENĚK ŠTĚRBÁČEK
Research Center, Spolana, Neratovice, Czechoslovakia

BOHUSLAV BISKUP
CHEPOS, Chemical and Food Machinery Works, Brno, Design and Construction Division, Prague, Czechoslovakia

PETR TAUSK
Center for Scientific and Technical Information, Prague, Czechoslovakia

此为试读，需要完整PDF请访问：www.ertongbook.com

Preface

In the present world, where information is taking the dominant role in all branches of science, engineering and economy, there is an ever-increasing demand for data. However, real data originating from experiments are not always at hand. What is more, provision of data in this way only is rather time-consuming, not always economical or feasible, and in some cases this method of data provision could even retard the actual progress of process technology or equipment development.

Fluids form common substrates in many chemical engineering operations and processes. Fluid mixtures result as the outcome of chemical reactions and such mixtures must be efficiently separated into final products. To design chemical reactors and separation equipment efficiently, we must have data on fluid properties in a wide range of temperatures and pressures.

At the time of writing this preface, eighteen years have elapsed since the appearance of the first book in Czech (1961) on the possibilities of predicting physical properties of fluids using the corresponding state methods (B 17). At that time, we encountered third parameters for the first time, and relatively complicated relations for mixtures were formulated. A review of basic publications on this theme covered something of the order of one hundred papers.

The present manual contains complicated calculation procedures, not solvable without the use of computers, based on many sophisticated equations of state having defined applications, which have been devised since. The number of references is also a rough measure of the extent of increase of the subject treated.

We are presenting this selection of computation methods, which must necessarily be incomplete, as a manual of recommended calculation procedures enabling the prediction of fluid properties using methods based on the macroscopic theorem of corresponding states, i.e. on critical properties and on third parameters. Data and relationships have been converted to SI units.

We wish to express our thanks to Dr. G. B. Lawson of Unilever, Colworth House, Dr. G. A. Davies of the Department of Chemical Engineering, University of Manchester Institute of Science and Technology, and to Dr. J. D. Jenkins of the Department of Chemical Engineering, University of Aston, Birmingham, U. K., for their assistance in preparing this English translation. Our thanks are due to all who supplied extensive material in the form of reprints and communic-

5

ations, especially for the bulk of work developed in the institutions of Professor G. Thodos and Professor D. S. Viswanath.

Contents

INTRODUCTION

Definition of the Critical State

Most physical systems exert characteristic phenomena when approaching some defined critical point, and such phenomena are termed critical. Many critical points exist, as given in (S7). The most familiar of this entire set is the critical point for the transition of the liquid phase into vapour and vice versa.

The general definition of the critical state of a pure substance may be stated as follows: *the critical point is a limiting point marking the disappearance of a defined state.* It defines the maximum attainable temperature on the coexistence curve of the states, and the coexistence curve encloses the region in which liquid and
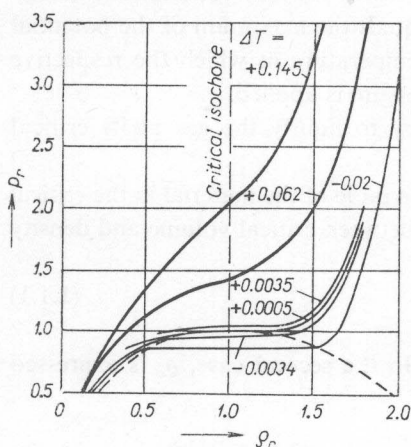
Fig. 1.1 Shape of isotherms in the critical region.

vapour phases coexist. Density at this point is termed critical density and denoted by ϱ_c. Isotherms are horizontal within the coexistence curve, i.e. the coefficient of compressibility is infinite (cf. Fig. 1.1). In this region, gravity forces alone suffice to bring about substantial density gradients.

Throughout this work, critical properties defined in this way for the critical point between the vapour and liquid phases will be used as the basic parameters

for determining properties of materials which are important in the chemical process industries. Such properties are divided into the state, transport and thermodynamic categories, depending on their origin and/or application. Although substantial efforts have been made to determine values experimentally, data are incomplete and we still need methods enabling their prediction or generalisation for many chemical engineering calculations. The theorem of corresponding states, based on the critical constants, is one way. To distinguish this theorem from the theorem based on molecular properties, we denote it as the macroscopic theorem of corresponding states (TCS).

The purpose of this work is to present in the form of a manual, rather than as a monograph, a survey of methods available to practising engineers for the prediction of basic chemical engineering properties using this theorem. We are fully aware of its limitations, but we do consider it to be a valuable working tool for several years to come. The work makes no attempt to review the physicochemical background of the theorem, such a discussion being outside the scope of this treatment.

To summarize, let us define the basic three critical constants in the critical region.

Critical temperature T_c is the temperature at which the molecular kinetic energy of the translational motion of the molecules equals the maximum of the potential energy of attraction. This is the maximum temperature at which the respective gas can be liquified, no matter how great a pressure is applied.

Critical pressure p_c is the pressure necessary to liquify the gas at its critical state temperature.

Critical volume v_c is the volume occupied by a mole of the material in the critical (at T_c and p_c). The following relation is valid between critical volume and density

$$\varrho_c = \frac{M}{v_c} \qquad \text{or} \qquad \varrho_c = v_c^{-1} \tag{1.1.1}$$

where M is the molecular mass (g . mol^{-1}). In the second case, ϱ_c is expressed in mol . cm^{-3}.

FUNDAMENTALS

2.1 Reduced equations of state

The calculation equations and relations given subsequently are based on the so-called *macroscopic theorem of corresponding states* which has been basically defined by van der Waals (W1). According to his definition, substances at equal reduced temperature and pressure have equal reduced volume. The quantities used in this case for the reduction of the equation of state (for making the parameters dimensionless) are phenomenological macroscopic parameters, viz. the critical temperature, pressure or volume. This distinguishes the macroscopic theorem from the statistical-mechanical theorem, where the parameters of the Lennard-Jones $12-6$ potential are generally used for reduction.

There is an empirical relationship between both theorems, and we shall make use of it without going any deeper into the details. The analogies are discussed in (B25, F7, H4, L4, S29) and (S30). For our purpose we use the *van der Waals definition* in the form

$$z = f(T_r, p_r) \tag{2.1.1}$$

where $T_r = T/T_c$, $p_r = p/p_c$. This is the simplest form of the 2-parameter reduced equation of state which can be used under several restrictions to describe the mutual relationship between pressure, volume and temperature $(p-v-T)$ of an ideal fluid.

This relation can be actually formulated in two ways: (a) by methods based on *generalized equations of state*, based, for example, on the theorem of corresponding states (TCS); (b) by means of the *equations of state*. Up to the present time, about hundred equations of state are known, containing 2 to 40 parameters, coefficients or constants. Both the parameters and the constants follow generally from experimental data and are therefore characteristic of the compounds for which they have been determined. On the other hand, practically all are related to the critical constants. Let us take as an example the well known *van der Waals equation of state*

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{2.1.2}$$

The coefficients a and b, are dependent on the given substance. Introducing the relations which follow from the condition of existence of an inflexion point at the critical point;

$$\left(\frac{\partial p}{\partial v}\right)_{T=T_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_c} = 0 \tag{2.1.3}$$

we obtain:

$$a = 27R^2 T_c^2/64 p_c \tag{2.1.3a}$$
$$b = RT_c/8 p_c \tag{2.1.3b}$$

and a formal relation for the universal gas constant

$$R = 8 p_c v_c/3 T_c \tag{2.1.3c}$$

we get

$$\left(p_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r \tag{2.1.4}$$

On comparing Eqs. (2.1.2) and (2.1.4) we see that the coefficients a and b, previously dependent on the specific substance, have been eliminated from the relation and substituted by more easily accessible and more general constants T_c, p_c, v_c. This form of the equation of state is called *the reduced or generalized form*. Its main advantage is its general validity for more than a single substance. As shown by Othmer (O4), there is a defined relationship between these relations and the equations of state reduced by means of the properties of a reference substance, which can be regarded as a special form of the TCS.

Equations of state with 2 parameters

The *van der Waals equation* which has been already discussed is a classical example of a 2-parameter equation of state. On an intuitive basis, separate correction terms have been introduced into the simple equation of state of an ideal gas accounting for the repulsive and attractive forces between molecules. After some trend towards equations of state with several parameters in the past $10-15$ years, a revival of interest in the simpler and physically better understandable equations of state has been observed lately (R19). It is, however, generally known, that the simple equations of state do not explain adequately the $p-v-T$ relationship for fluids at high pressures, diluted quantum gases and fluids with pronounced polar, dipole or multipole effects. The conditions of validity of these simple equations of state are as follows:

(i) spherical or symmetrical shape of molecules;

(ii) sufficiently high temperatures, ensuring the validity of the laws of the classical statistical mechanics;

14

(iii) the potential energy must be a general function of the partition distance and of both characteristic parameters;

(iv) intermolecular degrees of freedom must be independent of the molecular volume.

Basic equations of state of the 2-parameter TCS

The main advantage of the *van der Waals equation of state* (Eq. 2.1.2) or (2.1.4) lies in its simplicity. It describes, with reasonable conformity to experimental data, the isotherms up to $p_r = 1.0$ for slightly supercritical temperatures. When the temperature is increased to approximately $T_r = 2.2$, the deviations from measured values are still acceptable for pressures up to $p_r = 8.0$. The equation can be used below the critical point for describing the behaviour of gases, but not of liquids.

The *Berthelot equation* (B12) is an early modification of the van der Waals equation of state. Temperature is introduced into the term correcting for the forces of attraction:

$$\left(p_r + \frac{3}{T_r v_r^2}\right)(3v_r - 1) = 8T_r \tag{2.1.5}$$

Shah and Thodos (S10) compared the 2-parameter equations of state using $p - v - T$ data for argon. It followed that a worse fit of experimental data is obtained when using Eq. (2.1.5) instead of (2.1.4).

The *Dieterici equation* (D6) is an empirical exponential equation of state given by:

$$p_r = \frac{T_r \exp(2)}{(2v_r - 1)} \exp\left(-\frac{2}{T_r v_r}\right) \tag{2.1.6}$$

The isotherms calculated from Eq. (2.1.6) are by no means better than those obtained from Eq. (2.1.4) in the high pressure region; in the low pressure region, values from Eq. (2.1.4) are definitely better. The differences increase with increasing pressure. Eq. (2.1.6) cannot be used for the liquid phase as well, owing to its empirical nature. At volumes lower than b, the calculated pressures become negative, which is naturally a physical nonsense.

The *Redlich and Kwong* (RK) equation (R8) is one of the most frequently used equations of state employing 2 parameters (T_c and p_c) only.

$$\left(p_r + \frac{3.8464}{T_r^{0.5} v_r (v_r + 0.26)}\right)(v_r - 0.26) = 2.999 T_r \tag{2.1.7}$$

According to the authors of the equation, it gives good results in the supercritical region at broad range of pressures. The obvious conclusion resulting from an inspection of the equation is that at high pressures the volume is approximately constant and equal to $0.26v_c$ and independent of temperature. This equation has

15

been constructed to meet the condition $b \doteq 0.26v_c$ and it gives more probable values at higher pressures.

The constants a and b in the *RK* equation of state in non-reduced form are functions of temperature, and reduced relations have been suggested to formulate this dependence:

$$a_r = \frac{a}{a_c} = \frac{a p_c}{0.043316 R^2 T_c^{2.5}} =$$

$$= 1 - 0.008\,63 T_r^2 - 48.1 \left(-\frac{(T_r - 90)^2}{600}\right) - 31.0 \exp\left(-\frac{(T_r - 125)^2}{400}\right) \quad (2.1.8a)$$

$$b_r = \frac{b}{b_c} = \frac{b p_c}{0.0867 R T_c} = \exp\left(-\frac{(T_r - 1)^2}{7500}\right) - 0.2 \exp\left(-\frac{(T_r - 75)^2}{800}\right) +$$

$$+ 0.125 \left(-\frac{(T_r - 150)^2}{1400}\right) \quad (2.1.8b)$$

As can be seen from Eq. (2.1.8a, b), the constants in the original *RK* equation follow from

$$a = \Omega_a R^2 T_c^{2.5}/p_c; \qquad b = \Omega_b R T_c/p_c$$

and $\Omega_a = 0.043316$, $\Omega_b = 0.0867$. As shown recently by Simonet and Beher (S8), the constants are a function of the temperature, in agreement with Eqs. (2.1.8a, b) and of a third parameter ω (cf. p. 24). Using experimental data on *n*-alkanes ($n_C \in \langle 1, 16\rangle$) *iso*-alkanes ($n_C = 4,5$) benzene, SO_2, H_2S, CO_2, N_2 and cyclohexane, they obtained:

$$\Omega_{ab} = \frac{\Omega_a}{\Omega_b} = \Omega_{ab}^{(0)} + \omega \Omega_{ab}^{(1)} \quad (2.1.8c)$$

where

$$\Omega_{ab}^{(0)} = 0.513\,07$$

$$\Omega_{ab}^{(1)} = -0.821\,66 + 0.8934 T_r^{-1}$$

$$\Omega_b = \Omega_b^{(0)} + \Omega_b^{(1)} |T_r - 1| + \Omega_b^{(2)} |T_r - 1|^2$$

$$\Omega_b^{(0)} = 0.0826 - 0.0122\omega$$

$$\Omega_b^{(1)} = 0.0220 - 0.0127\omega$$

$$\Omega_b^{(2)} = -0.0072 - 0.029\,05\omega$$

and mean errors amount to $0.94 - 8.37\%$.

16