Technical Data Book: Chapter 4—Critical Properties

API TECHNICAL REPORT TDB-4
FIRST EDITION, JANUARY 2026



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Table of Contents

Page

4-0 Introduction 1

Figure 4-0.1 – Pressure Temperature Diagram for a Mixture of Constant Composition Near the Critical Point 2

Figure 4-0.2 – Critical Locus for the Ethane-n-Heptane System and Envelopes for Three Binary Mixtures (26) 4

Figure 4-0.3 – Critical Locus for the Methane–n-Decane System (52) 7

Figure 4-0.4 – Critical Locus for the Ethyne-Ethene (Acetylene-Ethylene) System and Envelopes for Four Binary Mixtures [9] 8

Figure 4-0.5 – P-T Critical Loci of Binaries Containing a Common Component and a Representative from a Homologous Series 12

Figure 4-0.6 – Excess Critical Temperature vs Composition for Representative Binary Systems 13

Figure 4-0.7 – The Effect of Relative Size and Absolute Molecular Weight on Excess Functions 14

Figure 4-0.8 – Excess Critical Pressure vs Composition for Representative Binary Systems 15

Table 4-0.9 – Computer Methods 16

4A Critical Properties of Pure Hydrocarbons 17

Procedure 4A1.1 – Group Contribution Method for Calculating the Critical Temperature, Pressure and Volume of a Pure Hydrocarbon 17

Table 4A1.2 – Group Increments for Equations 4A1.1-1 through 4A1.1-3 22

Procedure 4A2.1 – Equation for Calculating the Critical Temperature of a Pure Hydrocarbon 24

Table 4A2.2 – Values of Coefficients for Equation 4A2.1-1 for Calculating the Critical Temperature of a Pure Hydrocarbon 25

Procedure 4A3.1 – Equation for Calculating the Critical Volume of a Pure Hydrocarbon 26

4B Critical Properties of Defined Mixtures 28

Procedure 4B1.1 – Method for the Critical Temperature of a Mixture of Defined Composition 28

Procedure 4B2.1 – Method for the Critical Pressure of a Mixture of Defined Composition 32

Figure 4B2.2 – Critical Pressures of Binary Systems Containing Methane 37

Figure 4B2.3 – Critical Pressures of Binary Systems Containing Carbon Dioxide 38

Figure 4B2.4 – Critical Pressures of Binary Systems Containing Hydrogen Sulfide 39

Procedure 4B3.1 – Method for the Critical Volume of a Mixture of Defined Composition 42

Procedure 4B4.1 – Computer Method for Critical Properties of a Mixture of Defined Composition 46

Figure 4B4.1-1 – Critical Locus for Ethene-Ethyne System 55

Figure 4B4.1-2 – Critical Locus for n-Octane–Benzene System 56
Figure 4B4.1-3 – Excess Critical Temperature 57
Figure 4B4.1-4 – Excess Critical Pressure 58
Figure 4B4.1-5 – Excess Critical Volume.....59
4C Critical Properties of Natural Gases 60
Figure 4C1.1 – True Critical Temperature of Natural Gas Mixtures 60
4D Critical Properties of Petroleum Fractions 64
Procedure 4D1.1 – Method for the Critical Temperature of Petroleum Fractions 64
Figure 4D2.1 – True Critical Pressures of Petroleum Fractions 66
washingonProcedure 4D3.1 – Method for the Pseudocritical Temperature of Petroleum Fractions 69
Figure 4D3.2 –Pseudocritical Temperature of Petroleum Fractions 71
Procedure 4D3.3 – True and Pseudocritical Temperatures of Mixtures Containing both Identified Hydrocarbons and Petroleum Fractions 72
Procedure 4D4.1 – Method for the Pseudocritical Pressure of Petroleum Fractions 76
Figure 4D4.2 – Pseudocritical Pressure of Petroleum Fractions 78
Procedure 4D4.3 – True and Pseudocritical Pressures of Mixtures Containing both Identified Hydrocarbons and Petroleum Fractions 79
Figure 4D4.4 – True Critical Pressures of Petroleum Fractions 81
Bibliography 82

SCOPE

Technical Report TDB-4 provides methods for estimating both the true critical and pseudocritical properties of pure components, petroleum fractions and mixtures that are common in refinery applications. Both computer algorithms and figures are presented for estimation of these properties. An estimate of the accuracy and range of application for each method is presented.

Any references to other chapters within this document refer to the corresponding Technical Data Book chapter, which is published as API Technical Report TDB-x, where x is the chapter number.

4-0 Introduction

The actual experimental or true critical temperature and pressure of pure compounds and of mixtures are of importance in determining existing phase conditions and permissible operating ranges of reactors and mass transfer equipment such as distillation columns and extractors. Critical properties of pure compounds are also essential to calculate pseudocritical properties used throughout the *Technical Data Book* in the theorem of corresponding states (54) for the estimation of thermodynamic and volumetric properties of mixtures. A pseudocritical or molar average property is a calculated value that cannot be measured under any circumstances.

Critical temperatures, pressures, and compressibility factors for pure hydrocarbons and a number of nonhydrocarbons are given in the pure component properties tables.

The Critical State of Mixtures and the Two-Phase Envelope: The conditions of equilibrium for coexisting vapor and liquid phases of a pure substance are defined on a pressure-temperature diagram by the vapor pressure curve. This curve starts at the triple point, where vapor, liquid and solid phases are in equilibrium, and ends at the critical point. As the critical point is approached by the coexisting phases, their properties approach each other until they become identical at the critical temperature and pressure, where a single homogeneous phase is present.

In the case of homogeneous mixtures of liquids, vaporization at a constant pressure takes place over a range of temperatures instead of at the single temperature associated with the vapor pressure of pure substances. Consequently, the vaporization of multicomponent liquids requires two curves on the pressure temperature diagram to define the boiling characteristics instead of a single vapor pressure curve. To illustrate, Figure 4-0.1 shows a part of a pressure temperature diagram for a hypothetical liquid mixture. In this diagram, the two-phase region is enclosed by the envelope LP_MCT_MV which consists of the “bubble-point” curve, LP_MC, and the “dew-point” curve, VT_MC. Their common point, C, is the critical point at which the coexisting liquid and vapor become a single homogeneous phase.

The significance of the bubble-point and dew-point curves may be demonstrated by following either an isobaric or an isothermal path across the envelope so that both bubble-point and dew-point curves are crossed.