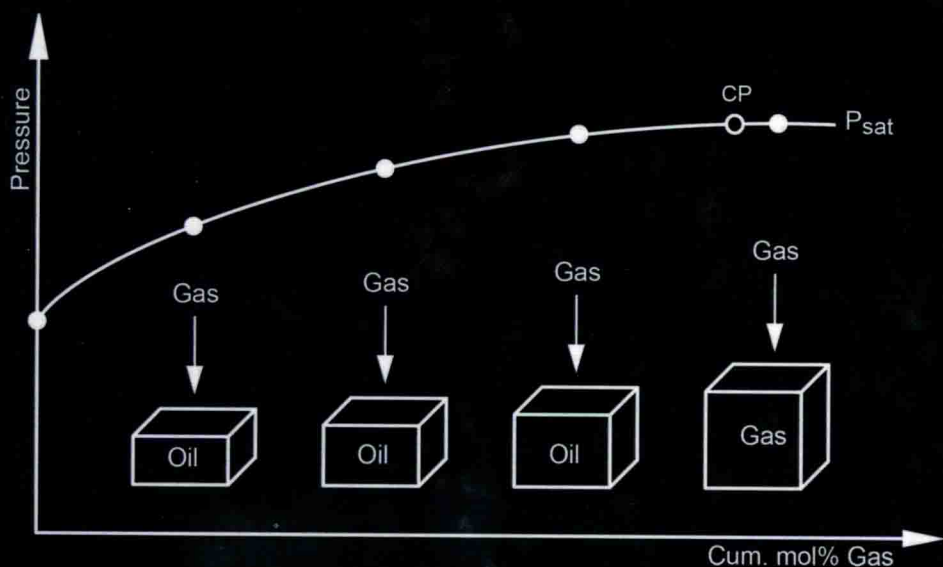


SECOND EDITION

Phase Behavior of Petroleum Reservoir Fluids



Karen Schou Pedersen
Peter L. Christensen
Jawad Azeem Shaikh



CRC Press
Taylor & Francis Group

SECOND EDITION

Phase Behavior of Petroleum Reservoir Fluids

**Karen Schou Pedersen
Peter L. Christensen
Jawad Azeem Shaikh**



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2015 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper
Version Date: 20141008

International Standard Book Number-13: 978-1-4398-5223-1 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

SECOND EDITION

**Phase Behavior
of Petroleum
Reservoir Fluids**

Preface

The techniques of oil and gas recovery are under constant development. This is followed by an increased demand to the accuracy of PVT simulation results. High quality simulation results are dependent on accurate fluid compositions and PVT data. We wanted to cover experimental procedures in more detail in the second edition than in the first edition, so we asked our colleague, Jawad Azeem Shaikh, to be a coauthor. Jawad has 12 years of experience from a commercial PVT laboratory, and his experience includes sampling, compositional analyses, and measurements of both routine and EOR PVT data. Chapters 2 and 3 provide a comprehensive review of experimental procedures used to provide compositional data and PVT data.

The oil industry sees the PC-SAFT equation as a possible alternative or replacement of cubic equations. The PC-SAFT equation is introduced in Chapter 4, and Chapter 5 on fluid characterization includes a section on the characterization of the PC-SAFT equation. Chapter 7 shows simulation results for PVT data obtained with the PC-SAFT equation.

Chapter 9 on regression has a section on how to recreate the original reservoir fluid composition from a depleted gas condensate reservoir fluid sample. Chapter 12 on asphaltenes includes a section on how to simulate the location of a possible asphaltene tar mat.

We have, since the first edition was published, had the opportunity to analyze numerous EOR PVT data and have used this experience to make a thorough update of Chapter 15 on MMP calculations.

All other chapters are updated with new data material and new references.

Karen Schou Pedersen
Peter Lindskou Christensen
Jawad Azeem Shaikh

Authors

Karen Schou Pedersen holds a PhD in liquid physics from the Department of Physical Chemistry at the Technical University of Denmark. She has worked as a research associate at the Physics Department at Edinburgh University and at the nuclear research center, Institut Laue-Langevin, in Grenoble. She has been the managing director of Calsep A/S since 1984 and has been responsible for several R & D projects within reservoir fluid modeling and flow assurance. She is the author of more than 50 publications on oil and gas properties.

Peter Lindskou Christensen holds a PhD from the Department of Chemical Engineering at the Technical University of Denmark. He started his career in oil and gas technology at the Risø National Laboratories in Denmark focusing on studies in the fields of reservoir simulation and PVT. He has been an Associate Professor at the Technical University of Denmark and lectured in thermodynamics, unit operations and oil and gas technology. He is currently a senior principal consultant at Calsep A/S.

Jawad Azeem Shaikh holds an MSc in petroleum technology from the University of Pune in India. He has been the regional manager and principal consultant of Calsep FZ-LLC in Dubai since 2009 and has been responsible for the project including lab coordination, designing of Enhanced Oil Recovery studies, and Equation of State modeling work of oil and gas properties. Before joining the Calsep, he was an advanced studies supervisor for Core Laboratories International B.V. His major job functions at Core Laboratories included technical support to field engineers to carry out bottom hole and separator sampling as well as project coordination and data evaluation in PVT, Compositional, and Enhanced Oil Recovery projects. He has authored several papers and articles on sampling, PVT lab work, and on oil and gas properties.

Contents

Preface.....xi

Authors.....xiii

Chapter 1 Petroleum Reservoir Fluids 1

1.1 Reservoir Fluid Constituents 1

1.2 Properties of Reservoir Fluid Constituents 1

1.3 Phase Envelopes 6

1.4 Classification of Petroleum Reservoir Fluids 7

References 11

Chapter 2 Sampling, Quality Control, and Compositional Analyses 13

2.1 Fluid Sampling 13

2.2 Quality Control of Fluid Samples 16

2.2.1 Bottom Hole/Wellhead Samples..... 16

2.2.2 Separator Samples 17

2.2.2.1 Quality Control of Separator Gas 18

2.2.2.2 QC of Separator Liquid 19

2.3 Compositional Analyses..... 21

2.3.1 Gas Chromatography 21

2.3.1.1 Preparation Oil Mixtures 21

2.3.1.2 Preparation Gas Condensate Mixtures..... 23

2.3.1.3 Gas Chromatograph 23

2.3.2 TBP Analysis..... 30

2.3.2.1 Molecular Weight from Freezing Point Depression..... 33

2.4 Reservoir Fluid Composition from Bottom Hole Sample 34

2.5 Reservoir Fluid Composition from Separator Samples..... 36

2.6 Mud-Contaminated Samples..... 42

References 46

Chapter 3 PVT Experiments..... 47

3.1 Routine PVT Experiments..... 49

3.1.1 Constant-Mass Expansion Experiment 49

3.1.1.1 Oil Mixtures..... 49

3.1.1.2 Gas Condensate Mixtures..... 51

3.1.1.3 Dry Gases 53

3.1.2 Differential Liberation Experiment 56

3.1.3 Constant-Volume Depletion Experiment 60

3.1.4 Separator Test..... 63

3.1.5 Viscosity Experiment..... 66

3.2 EOR PVT Experiments 67

3.2.1 Solubility Swelling Test 67

3.2.2	Equilibrium Contact Experiment	72
3.2.3	Multi-Contact Experiment.....	72
3.2.4	Slim Tube Experiment.....	74
3.2.5	Gas Revaporization Experiment.....	80
	References	81
Chapter 4	Equations of State.....	83
4.1	van der Waals Equation	83
4.2	Redlich–Kwong Equation.....	86
4.3	Soave–Redlich–Kwong Equation.....	87
4.4	Peng–Robinson Equation	91
4.5	Peneloux Volume Correction	92
4.6	Other Cubic Equations of State	95
4.7	Equilibrium Calculations.....	96
4.8	Nonclassical Mixing Rules.....	97
4.9	PC-SAFT Equation	97
4.10	Other Equations of State.....	102
	References	103
Chapter 5	C₇₊ Characterization.....	105
5.1	Classes of Components.....	105
5.1.1	Defined Components to C ₆	105
5.1.2	C ₇₊ Fractions.....	107
5.1.3	Plus Fraction.....	110
5.2	Binary Interaction Coefficients	117
5.3	Lumping	117
5.4	Delumping	121
5.5	Mixing of Multiple Fluids	122
5.6	Characterizing of Multiple Compositions to the Same Pseudocomponents..	125
5.7	Heavy Oil Compositions.....	127
5.7.1	Heavy Oil Reservoir Fluid Compositions	128
5.7.2	Characterization of Heavy Oil Mixture	128
5.8	PC-SAFT Characterization Procedure.....	134
	References	137
Chapter 6	Flash and Phase Envelope Calculations	139
6.1	Pure Component Vapor Pressures from Cubic Equations of State	140
6.2	Mixture Saturation Points from Cubic Equations of State.....	142
6.3	Flash Calculations	144
6.3.1	Stability Analysis.....	144
6.3.2	Solving the Flash Equations	149
6.3.3	Multiphase PT-Flash.....	150
6.3.4	Three Phase PT-Flash with a Pure Water Phase	155
6.3.5	Other Flash Specifications.....	157
6.4	Phase Envelope Calculations.....	158
6.5	Phase Identification	162
	References	163

Chapter 7	PVT Simulation	165
7.1	Constant Mass Expansion	165
7.2	Constant Volume Depletion	169
7.3	Differential Liberation	172
7.4	Separator Test	174
7.5	Solubility Swelling Test	176
7.6	PVT Simulations with PC-SAFT EoS	181
7.7	What to Expect from a PVT Simulation	184
	References	186
Chapter 8	Physical Properties	187
8.1	Density	187
8.2	Enthalpy	188
8.3	Internal Energy	189
8.4	Entropy	189
8.5	Heat Capacity	190
8.6	Joule–Thomson Coefficient	190
8.7	Velocity of Sound	190
8.8	Example Calculations	190
	References	195
Chapter 9	Regression to Experimental PVT Data	197
9.1	Shortcomings of Parameter Regression	197
9.2	Volume Translation Parameter	198
9.3	T_c , P_c , and Acentric Factor of C_{7+} Fractions	198
9.4	Regressing on Coefficients in Property Correlations	199
9.5	Object Functions and Weight Factors	199
9.6	Example of Regression for Gas Condensate	200
9.7	Tuning on Single Pseudocomponent Properties	206
9.8	Near-Critical Fluids	208
9.9	Fluids Characterized to the Same Pseudocomponents	212
9.10	PVT Data with Gas Injection	216
9.11	Original Reservoir Fluid Composition from Depleted Sample	221
9.11.1	Numerical Example	227
9.11.2	Depleted Oil and Shale Reservoir Fluid Samples	229
	References	231
Chapter 10	Transport Properties	233
10.1	Viscosity	233
10.1.1	Corresponding States Viscosity Models	233
10.1.2	Adaptation of Corresponding States Viscosity Model to Heavy Oils	242
10.1.3	Lohrenz–Bray–Clark Method	243
10.1.4	Other Viscosity Models	245
10.1.5	Viscosity Data and Simulation Results	247
10.2	Thermal Conductivity	252
10.2.1	Data and Simulation Results for Thermal Conductivity	260

10.3 Gas/Oil Surface Tension.....	260
10.3.1 Models for Interfacial Tension	262
10.3.2 Data and Simulation Results for Interfacial Tensions.....	265
10.4 Diffusion Coefficients.....	265
References	267
Chapter 11 Wax Formation.....	269
11.1 Experimental Studies of Wax Precipitation.....	269
11.2 Thermodynamic Description of Melting of a Pure Component.....	277
11.3 Modeling of Wax Precipitation.....	282
11.3.1 Activity Coefficient Approach	283
11.3.2 Ideal Solid Solution Wax Models.....	286
11.4 Wax PT Flash Calculations.....	291
11.5 Viscosity of Oil–Wax Suspensions	291
11.6 Wax Inhibitors	294
References	296
Chapter 12 Asphaltenes	299
12.1 Experimental Techniques for Studying Asphaltene Precipitation.....	303
12.1.1 Quantification of Amount of Asphaltenes	303
12.1.2 Detection of Asphaltene Onset Points	303
12.1.2.1 Gravimetric Technique.....	303
12.1.2.2 Acoustic Resonance Technique.....	303
12.1.2.3 Light-Scattering Technique.....	304
12.1.2.4 Filtration and Other Experimental Techniques.....	304
12.1.3 Experimental Data for Asphaltene Onset Pressures	304
12.2 Asphaltene Models	306
12.2.1 Models Based on Cubic Equation of State	307
12.2.2 Polymer Solution Models.....	312
12.2.3 Thermodynamic–Colloidal Model.....	313
12.2.4 PC-SAFT Model.....	314
12.2.5 Other Asphaltene Models	315
12.3 Asphaltene Tar Mat Calculation.....	317
References	319
Chapter 13 Gas Hydrates	323
13.1 Types of Hydrates	323
13.2 Modeling of Hydrate Formation.....	327
13.3 Hydrate Inhibitors.....	332
13.4 Hydrate Simulation Results	333
13.5 Hydrate P/T Flash Calculations.....	340
13.5.1 Hydrate Fugacities.....	340
13.5.2 Flash Simulation Technique.....	342
References	344
Chapter 14 Compositional Variations with Depth.....	347
14.1 Theory of Isothermal Reservoir	347
14.1.1 Depth Gradient Calculations for Isothermal Reservoirs	349

14.2 Theory of Non-isothermal Reservoir	357
14.2.1 Absolute Enthalpies	364
14.2.2 Examples: Calculations on Reservoir Fluids	364
References	370
Chapter 15 Minimum Miscibility Pressure	373
15.1 Three-Component Mixtures	373
15.2 MMP of Multicomponent Mixtures	379
15.2.1 First Contact MMP	379
15.2.2 Tie Line Approach	379
15.2.3 Immiscible Systems	386
15.2.4 Cell-to-Cell Simulation	389
References	392
Chapter 16 Formation Water and Hydrate Inhibitors	395
16.1 Hydrocarbon–Water Phase Equilibrium Models	395
16.1.1 Approach of Kabadi and Danner	398
16.1.2 Asymmetric Mixing Rules	401
16.1.3 Huron and Vidal Mixing Rule	402
16.1.4 Phase Equilibria for Hydrocarbon–Salt Water	407
16.1.5 Association Models	410
16.2 Experimental Hydrocarbon–Water Phase Equilibrium Data	410
16.3 Water Properties	415
16.3.1 Viscosity of Water–Inhibitor Mixtures	417
16.3.2 Properties of Salt Water	417
16.3.3 Oil–Water Emulsion Viscosities	418
16.4 Phase Envelopes of Hydrocarbon–Aqueous Mixtures	418
References	420
Chapter 17 Scale Precipitation	423
17.1 Criteria for Salt Precipitation	423
17.2 Equilibrium Constants	425
17.3 Activity Coefficients	428
17.4 Solution Procedure	436
17.5 Example Calculations	437
References	439
Appendix A Fundamentals on Phase Equilibrium	441
A.1 First and Second Laws of Thermodynamics	441
A.2 Fundamental Thermodynamic Relations	441
A.3 Phase Equilibrium	442
A.4 Fugacities and Fugacity Coefficients	443
Index	447

1 Petroleum Reservoir Fluids

1.1 RESERVOIR FLUID CONSTITUENTS

Petroleum reservoir fluids are multicomponent mixtures consisting primarily of hydrocarbons. Methane (CH_4) is the simplest of all hydrocarbons, and also the most common component in petroleum reservoir fluids. Because methane contains one carbon atom, it is often referred to as C_1 . Similarly, the term C_2 is used for ethane (C_2H_6), C_3 for propane (C_3H_8), and so on. Hydrocarbons with seven and more carbon atoms are called C_{7+} components, and the entity of all C_{7+} components is called the C_{7+} fraction. Petroleum reservoir fluids may contain hydrocarbons as heavy as C_{200} . A particular C_{7+} component will belong to one of the following component classes:

Paraffins: A paraffinic compound consists of hydrocarbon segments of the type C , CH , CH_2 , or CH_3 . The carbon atoms are connected by single bonds. Paraffins are divided into normal paraffins (*n*-paraffins) and iso-paraffins (*i*-paraffins). In an *n*-paraffin, the carbon atoms form straight chains, whereas an *i*-paraffin contains at least one side chain. Paraffins are sometimes also referred to as *alkanes*. Figure 1.1 shows the structure of methane (C_1), ethane (C_2), and *n*-hexane (C_6), which are all examples of paraffinic compounds.

Naphthenes: These compounds are similar to paraffins in the sense that they are built of the same types of hydrocarbon segments, but they differ from paraffins in that they contain one or more cyclic structures. The segments in the ring structures (e.g., CH_2) are connected by single bonds. Most naphthenic ring structures contain six carbon atoms, but naphthenic compounds with either five or seven carbon atoms connected in ring structures are also common in petroleum reservoir fluids. Naphthenes are also called *cycloalkanes*. Cyclohexane and methyl cyclopentane shown in Figure 1.1 are examples of naphthenic components.

Aromatics: Similar to naphthenes, aromatics contain one or more cyclic structures, but the carbon atoms in an aromatic compound are connected by aromatic double bonds. Benzene (C_6H_6), the simplest aromatic component, is shown in Figure 1.1. Polycyclic aromatic compounds with two or more ring structures are also found in petroleum reservoir fluids. An example of the latter type of components is naphthalene (C_{10}H_8), whose structure is also shown in Figure 1.1.

The percentage of paraffinic (P), naphthenic (N), and aromatic (A) components in a reservoir fluid is often referred to as the PNA distribution.

Petroleum reservoir fluids may also contain inorganic compounds, of which nitrogen (N_2), carbon dioxide (CO_2), and hydrogen sulfide (H_2S) are the most common. Water (H_2O) is another important constituent of reservoir fluids. As water has limited miscibility with hydrocarbons, most of the water in a reservoir is usually found in a separate water zone located beneath the gas and oil zones.

1.2 PROPERTIES OF RESERVOIR FLUID CONSTITUENTS

Table 1.1 shows selected physical properties of some constituents found in naturally occurring oil and gas mixtures. By comparing, for example, the normal boiling points, it is evident that hydrocarbons in petroleum reservoir fluids cover a wide range of component properties. At atmospheric pressure, pure methane will be in gaseous form at temperatures above the normal boiling point of

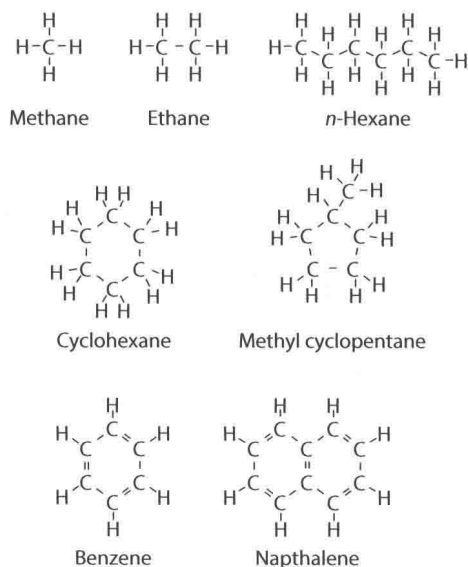


FIGURE 1.1 Molecular structures of some petroleum reservoir fluid constituents.

–161.6°C, whereas at the same pressure the temperature must be raised to 218.0°C before naphthalene evaporates. The properties of hydrocarbons with the same number of carbon atoms may also differ substantially. *n*-Hexane (nC_6), methyl cyclopentane ($m\text{-}cC_5$), and benzene all contain six carbon atoms. However, the properties of these three components are quite different. For example, it may be seen from Table 1.1 that the density of nC_6 at atmospheric conditions is lower than that of $m\text{-}cC_5$, although the density of $m\text{-}cC_5$ is lower than that of benzene. This suggests that densities of components with the same carbon number will increase in the order $P \rightarrow N \rightarrow A$. It is rare to see a measured PNA distribution and, in the absence of experimental information about the predominant molecular structures, the trend in component densities may be used to give an idea about the distribution of P, N, and A components in a given C_{7+} fraction.

The pure component vapor pressures and critical points (CPs) are essential in calculations of component and mixture properties. The pure component vapor pressures are experimentally determined by measuring the corresponding values of temperature (T) and pressure (P) at which the substance undergoes a transition from liquid to gas. Figure 1.2 shows the vapor pressure curves of methane and benzene, both of which are common constituents of oil and gas mixtures. The vapor pressure curve ends at the CP, above which no liquid-to-gas phase transition can take place. The CP of methane is –82.6°C and 46.0 bar and that of benzene 289°C and 48.9 bar. The temperature at CP is called T_C and the pressure P_C .

As illustrated in the right-hand-side plot in Figure 1.3, the phase behavior of a pure component at a given temperature, T_1 , may be studied by placing a fixed amount of this component in a cell at temperature T_1 . The cell volume may be varied by moving the piston up and down. At position A, the cell contents are in the gaseous state. If the piston is moved downward, the volume will decrease and the pressure increases. At position B, a liquid phase starts to form. By moving the piston further downward, the volume will further decrease, but the pressure remains constant until all gas is converted into liquid. This happens at position C. A further decrease in the cell volume will result in a rapidly increasing pressure. The left-hand-side curve in Figure 1.3 illustrates the phase changes when crossing a vapor pressure curve. A pure component can only exist in the form of two phases in equilibrium right at the vapor pressure curve. When the vapor pressure curve is reached, a conversion from either gas to liquid or liquid to gas will start. This phase transition is associated with volumetric changes at constant T and P . At the point B, the component is said to

TABLE 1.1
Physical Properties of Common Petroleum Reservoir Fluid Constituents

Component	Formula	Molecular Weight (g/mol)	Melting Point (°C)	Normal Boiling Point (°C)	Critical Temperature (°C)	Critical Pressure (bar)	Acentric Factor	Density (g/cm ³) at 1 atm and 20°C
Inorganics								
Nitrogen	N ₂	28.013	-209.9	-195.8	147.0	33.9	0.040	—
Carbon dioxide	CO ₂	44.010	-56.6	-78.5	31.1	73.8	0.225	—
Hydrogen sulfide	H ₂ S	34.080	-83.6	59.7	100.1	89.4	0.100	—
				Paraffins				
Methane	CH ₄	16.043	-182.5	-161.6	82.6	46.0	0.008	—
Ethane	C ₂ H ₆	30.070	-183.3	-87.6	32.3	48.8	0.098	—
Propane	C ₃ H ₈	44.094	-187.7	-42.1	96.7	42.5	0.152	—
Iso-butane	C ₄ H ₁₀	58.124	-159.6	-11.8	135.0	36.5	0.176	—
n-Butane	C ₄ H ₁₀	58.124	-138.4	-0.5	152.1	38.0	0.193	—
Iso-pentane	C ₅ H ₁₂	72.151	-159.9	27.9	187.3	33.8	0.227	0.620
n-Pentane	C ₅ H ₁₂	72.151	-129.8	36.1	196.4	33.7	0.251	0.626
n-Hexane	C ₆ H ₁₄	86.178	-95.1	68.8	234.3	29.7	0.296	0.659
Iso-octane	C ₈ H ₁₈	114.232	-109.2	117.7	286.5	24.8	0.378	0.702 (16°C)
n-Decane	C ₁₀ H ₂₂	142.286	-29.7	174.2	344.6	21.2	0.489	0.730
				Naphthenes				
Cyclopentane	C ₅ H ₁₀	70.135	-93.9	49.3	238.6	45.1	0.196	0.745
Methyl cyclopentane	C ₆ H ₁₂	84.162	-142.5	71.9	259.6	37.8	0.231	0.754 (16°C)
Cyclohexane	C ₆ H ₁₂	84.162	6.5	80.7	280.4	40.7	0.212	0.779
				Aromatics				
Benzene	C ₆ H ₆	78.114	5.6	80.1	289.0	48.9	0.212	0.885 (16°C)
Toluene	C ₇ H ₈	92.141	-95.2	110.7	318.7	41.0	0.263	0.867
o-Xylene	C ₈ H ₁₀	106.168	-25.2	144.5	357.2	37.3	0.310	0.880
Naphthalene	C ₁₀ H ₈	128.174	80.4	218.0	475.3	40.5	0.302	0.971 (90°C)

Source: Data from Reid, R.C., Prausnitz, J.M., and Sherwood, T.K. *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1977.

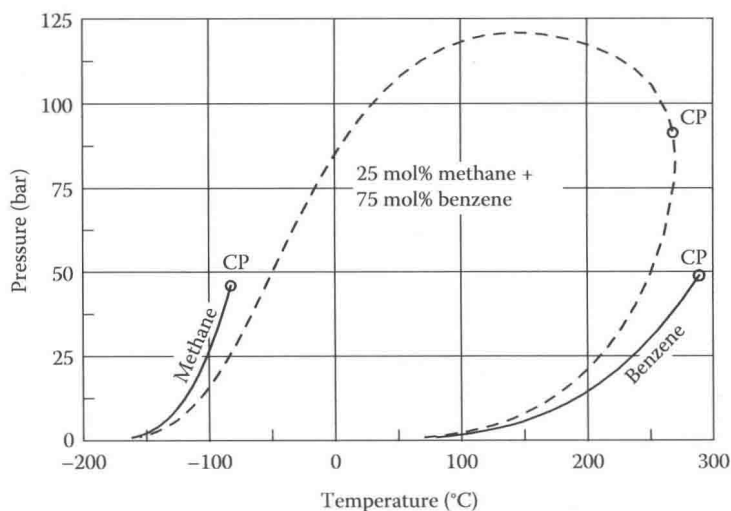


FIGURE 1.2 Vapor pressure curves of methane and benzene (full-drawn line). Phase envelope (dashed line) of a mixture of 25 mol% methane and 75 mol% benzene calculated using the Soave–Redlich–Kwong equation of state as presented in Chapter 4. Abbreviation: CP, critical point.

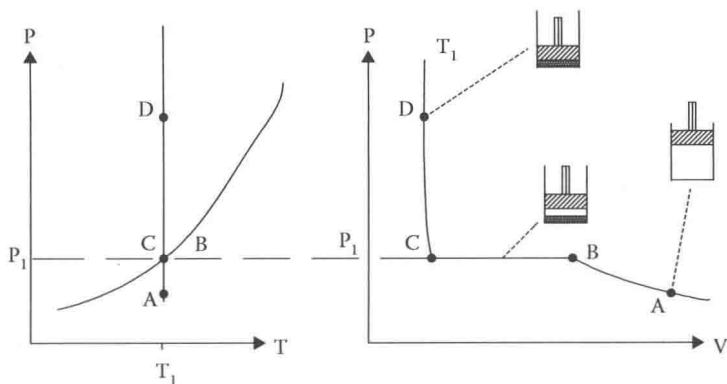


FIGURE 1.3 Pure component phase behavior in PT and PV diagrams.

be at its dew point or in the form of a saturated gas. At position C, the component is at its bubble point or in the form of a saturated liquid. At position A, the state is undersaturated gas, and at D it is undersaturated liquid.

Another important property is the acentric factor, ω , as defined by Pitzer (1955):

$$\omega = -1 - \log_{10} \left(\frac{P_r^{\text{sat}}}{P_c} \right)_{T=0.7T_c} \quad (1.1)$$

where P^{sat} stands for vapor pressure (or saturation pressure). The idea behind this definition is outlined in Figure 1.4. A plot of the logarithm of the reduced pure component vapor pressure, $P_r^{\text{sat}} = P^{\text{sat}}/P_c$, against the reciprocal of the reduced temperature, $T_r = T/T_c$, will for most pure substances give an approximately straight line. Figure 1.4 shows plots of $\log_{10} P_r^{\text{sat}}$ versus $1/T_r$ for argon (Ar) and *n*-decane (*n*C₁₀). For $T_r = 0.7$ ($1/T_r = 1.43$), $\log_{10} P_r^{\text{sat}} = -1.0$ for argon and -1.489 for *n*C₁₀. Argon is used as a reference and assigned an acentric factor of 0. In general, the acentric factor of a component equals $(\log_{10} P_r^{\text{sat}})_{T_r=0.7}$ for argon and $-(\log_{10} P_r^{\text{sat}})_{T_r=0.7}$ for the actual substance.

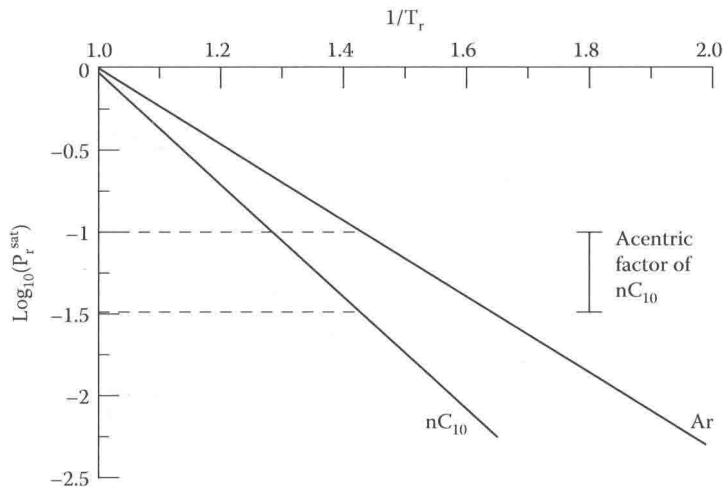


FIGURE 1.4 Acentric factor of nC_{10} from vapor pressure curves of Ar and nC_{10} . Abbreviations: P_r^{sat} , reduced saturation point (P^{sat}/P_c); T_r , reduced temperature (T/T_c).

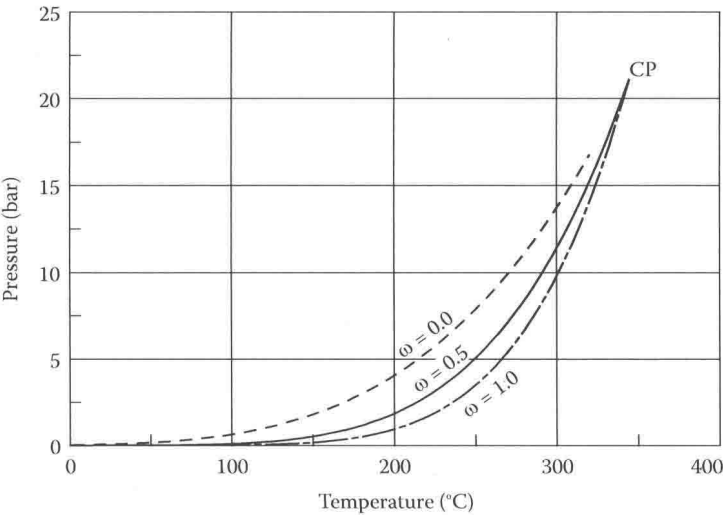


FIGURE 1.5 Vapor pressure curves of component with same T_c and P_c as nC_{10} and acentric factors of 0.0, 0.5, and 1.0.

With this definition, the acentric factor of nC_{10} equals $[-1 - (-1.489)] = 0.489$, which is consistent with the acentric factor given for nC_{10} in Table 1.1.

The acentric factor has got its name because the acentric factor of n -paraffins increases with carbon number. Methane (C_1) has an acentric factor of 0.008, ethane (C_2) 0.098, propane (C_3) 0.152, and so on. With increasing carbon number molecules of this component class get more elongated (less spherical) with increasing carbon number. More fundamentally, the acentric factor can be seen as a measure of the curvature of the pure component vapor pressure curve. Figure 1.5 shows the vapor pressure curves of three hypothetical substances, all having the same critical temperature and pressure as nC_{10} (344.5°C and 21.1 bar), whereas the acentric factors are 0.0, 0.5, and 1.0, respectively (the acentric factor of nC_{10} is 0.489). With the CP locked, the vapor pressure curves are bound to end at the same point, whereas the bend on the curve is determined by the acentric factor.

For an acentric factor of 1.0, the vapor pressure curve is relatively flat at low temperatures and then increases steeply when approaching the critical temperature. If the acentric factor is lower, a more even increase is seen in vapor pressure with temperature. The vapor pressure curves in Figure 1.5 have been calculated using the Peng–Robinson equation of state presented in Chapter 4.

1.3 PHASE ENVELOPES

Petroleum reservoir fluids are multicomponent mixtures; therefore, it is of much interest to find a mixture equivalent of the pure component vapor pressure curve. With two or more components present, the two-phase region is not restricted to a single line in a PT diagram. As is illustrated in Figure 1.2 for a mixture of 25 mol% methane and 75 mol% benzene, the two-phase region for a mixture forms a closed area in P and T. The line surrounding this area is called the *phase envelope*.

Figure 1.6 shows the phase envelope for a natural gas mixture with the composition given in Table 1.2. The phase envelope consists of a dew point branch and a bubble point branch meeting at the CP of the mixture CP. On the dew point branch, the mixture is in gaseous form and in equilibrium with an incipient amount of liquid. Under these conditions, the gas (or vapor) is said to be saturated. At higher temperatures and the same pressure, there is no liquid present. By contrast, the gas may take up liquid components without liquid precipitation taking place. The gas is therefore said to be undersaturated. On the bubble point branch, the mixture is in liquid form and in equilibrium with an incipient amount of gas, and the liquid is said to be saturated. At lower temperatures and the same pressure, the liquid (or oil) is undersaturated. At the CP, two identical phases are in equilibrium, both having a composition equal to the overall composition. At temperatures close to the critical temperature and pressures above the critical pressure, there is only one phase present, but it can be difficult to tell whether it is a gas or a liquid. The term *super-critical fluid* is often used. Phase identification in the super-critical region is discussed in more detail in Chapter 6. The highest pressure at which two phases can exist is called the *cricondenbar* and the highest temperature with two phases present is called the *cricondentherm*.

The phenomenon called *retrograde condensation* is illustrated in Figure 1.6 as a dashed vertical line at $T = -30^{\circ}\text{C}$. At this temperature, the mixture is in gaseous form at pressures above the upper dew point pressure, that is, at pressures above approximately 75 bar. At lower pressures, the mixture will split into two phases, a gas and a liquid. Liquid formation taking place as the result of falling

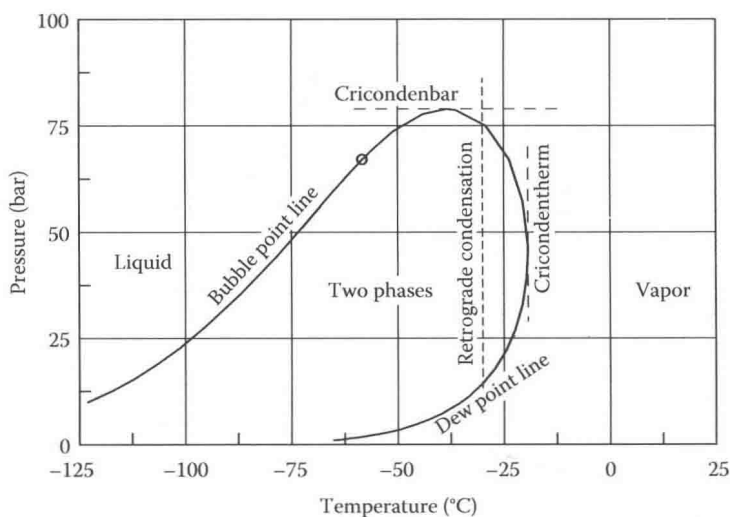


FIGURE 1.6 Phase envelope of natural gas in Table 1.2. CP stands for critical point. The phase envelope has been calculated using the Soave–Redlich–Kwong equation of state as presented in Chapter 4.