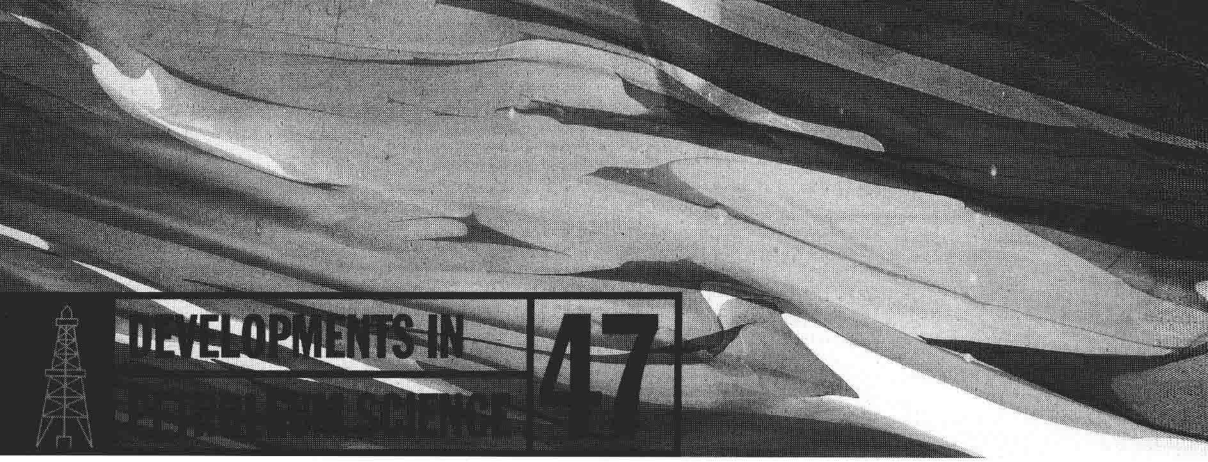
DEVELOPMENTS IN
PETROLEUM SCIENCE
47

PVT AND PHASE BEHAVIOUR OF PETROLEUM RESERVOIR FLUIDS

Ali Danesh

ELSEVIER



DEVELOPMENTS IN PETROLEUM SCIENCE 47

PVT AND PHASE BEHAVIOUR OF PETROLEUM RESERVOIR FLUIDS

ALI DANESH
Department of Petroleum Engineering
Heriot Watt University
Edinburgh, Scotland

ELSEVIER
Amsterdam – Lausanne – New York – Oxford – Shannon – Singapore – Tokyo

ELSEVIER SCIENCE B.V.
Sara Burgerhartstraat [illegible]
P.O. Box 2[illegible]000 AE Amsterdam, The Netherlands

© 1998 Elsevier Science B.V. All rights reserved.

This work is protected under copyright by Elsevier Science, and the following terms and conditions apply to its use:

Photocopying
Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier Science Global Rights Department, PO Box 800, Oxford OX5 1DX, UK; phone: (+44) 1865 843830, fax: (+44) 1865 853333, e-mail: permissions@elsevier.co.uk. You may also contact Global Rights directly through Elsevier□s home page (http://www.elsevier.nl), by selecting 'Obtaining Permissions□.

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 207 631 5555; fax: (+44) 207 631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works
Tables of contents may be reproduced for internal circulation, but permission of Elsevier Science is required for external resale or distribution of such material.
Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage
Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.
Address permissions requests to: Elsevier Science Global Rights Department, at the mail, fax and e-mail addresses noted above.

Notice
No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 1998
Second impression 2001

Library of Congress Cataloging in Publication Data
A catalog record from the Library of Congress has been applied for.

ISBN: 0 444 82196 1

∞ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).
Printed in The Netherlands.

DEVELOPMENTS IN

Volumes 1-5, 7, 10, 11, 13, 14, 16, 17, 21, 22, 23-27, 29, 31 are out of print.

6	*Fundamentals of Numerical Reservoir Simulation*
8	*Fundamentals of Reservoir Engineering*
9	*Compaction and Fluid Migration*
12	*Fundamentals of Fractured Reservoir Engineering*
15a	*Fundamentals of Well-log Interpretation,* ***1.*** *The acquisition of logging data*
15b	*Fundamentals of Well-log Interpretation,* ***2.*** *The interpretation of logging data*
18a	*Production and Transport of Oil and Gas,* ***A.*** *Flow mechanics and production*
18b	*Production and Transport of Oil and Gas,* ***B.*** *Gathering and Transport*
19a	*Surface Operations in Petroleum Production, I*
19b	*Surface Operations in Petroleum Production, II*
20	*Geology in Petroleum Production*
28	*Well Cementing*
30	*Carbonate Reservoir Characterization: A Geologic-Engineering Analysis, Part I*
32	*Fluid Mechanics for Petroleum Engineers*
33	*Petroleum Related Rock Mechanics*
34	*A Practical Companion to Reservoir Stimulation*
35	*Hydrocarbon Migration Systems Analysis*
36	*The Practice of Reservoir Engineering*
37	*Thermal Properties and Temperature related Behavior of Rock/fluid Systems*
38	*Studies in Abnormal Pressures*
39	*Microbial Enhancement of Oil Recovery – Recent Advances – Proceedings of the 1992 International Conference on Microbial Enhanced Oil Recovery*
40a	*Asphaltenes and Asphalts, I*
41	*Subsidence due to Fluid Withdrawal*
42	*Casing Design – Theory and Practice*
43	*Tracers in the Oil Field*
44	*Carbonate Reservoir Characterization: A Geologic-Engineering Analysis, Part II*
45	*Thermal Modeling of Petroleum Generation: Theory and Applications*
46	*Hydrocarbon Exploration and Production*
47	*PVT and Phase Behaviour of Petroleum Reservoir Fluids*

PREFACE

Reliable measurement and prediction of phase behaviour and properties of petroleum reservoir fluids are essential in designing optimum recovery processes and enhancing hydrocarbon production. This book explains relevant fundamentals and presents practical methods of determining required properties for engineering applications by judicious review of established practices and recent advances.

Although the emphasis is on the application of PVT and phase behaviour data to engineering problems, experimental methods are reviewed and their limitations are identified. This should provide the reader with a more thorough understanding of the subject and a realistic evaluation of measured and predicted results.

The book is based on the material developed over many years as lecture notes in courses presented to staff in gas and oil industry, and postgraduate students of petroleum engineering. It covers various aspects of the subject, hence can be tailored for different audience. The first two chapters along with selected sections from chapters 3 and 5 can serve as the subject matter of an introductory course, whereas the rest would be of more interest to practising engineers and postgraduate students. Ample examples are included to illustrate the subject, and further exercises are given in each chapter. Graphical methods and simple correlations amenable to hand calculations are still used in the industry, hence they are included in this book. The emphasis, however, is on the more advanced compositional approaches which are attaining wider application in industry as high computational capabilities are becoming readily available.

I would like to thank Professor DH Tehrani for reviewing the manuscript and valuable suggestions stemming from his vast industrial experience . Also, I am grateful to Professors M. Michelsen and C. Whitson for their helpful comments on sections of the book. Much of the material in this book is based on the author's experience gained through conducting research sponsored by the petroleum industry, at Heriot-Watt University. I am indebted to the sponsors, my students and colleagues for their contributions that made this book possible. In particular, I would acknowledge valuable contributions of Professor AC Todd, Mr F Goozalpour, Dr DH Xu, Mr K Movaghar Nezhad and Dr D Avolonitis. My son Amir cheerfully helped me in preparing the book graphics.

NOMENCLATURE

a	attractive term parameter of equation of state
A	dimensionless attractive term parameter of equation of state
b	repulsive term(co-volume) parameter of equation of state
B	dimensionless repulsive term parameter of equation of state
B_g	gas formation volume factor
B_o	oil formation volume factor
B_t	total formation volume factor
C_g	gas isothermal compressibility coefficient
C_o	oil isothermal compressibility coefficient
f	fugacity
G	Gibbs energy
h	height
$\bar{h}$	molar enthalpy
H	total enthalpy
H_i	Henry's constant
h_i	partial molar enthalpy
k	permeability
k_{ij}	binary interaction parameter
k_{rg}	gas relative permeability
k_{ro}	oil relative permeability
K	equilibrium ratio
K_w	Watson characterisation factor
m	slope in α correlation with temperature
M	molecular weight (molar mass)
n	mole or carbon number
N	number of components
N_p	number of pseudo-components
P	pressure
P_a	atmospheric pressure
P_b	bubble point pressure
P_k	convergence pressure
P_σ	parachor
P^s	vapour pressure
R	universal gas constant
R_s	gas in solution
S	specific gravity, relative density at 288 K (60 °F)
T	temperature
T_b	normal boiling point temperature
$\bar{u}$	molar internal energy
v	molar volume
$\bar{v}$	velocity
V	volume
x_i	mole fraction
y_i	mole fraction in vapour phase
z_i	mole fraction
Z	compressibility factor
Z_{RA}	Rackett compressibility factor

GREEK LETTERS

α	temperature dependency coefficient of attractive term
β	mean value parameter of Γ distribution function
ε_i	activity
ϕ	fugacity coefficient
γ	parameter of Γ distribution function
η	calculated critical compressibility factor
κ	total number of phases
μ	chemical potential
ρ	mass density
ρ_M	molar density
σ	interfacial tension
τ	lowest molecular weight in Γ distribution function
ω	acentric factor
Ω	EOS parameter coefficient
Θ	activity coefficient
$\hbar$	any phase

ACRONYMS

bbl	barrel
BIP	binary interaction parameter
CCE	constant composition expansion
CGR	condensate to gas volumetric ratio
CVD	constant volume depletion
DL	differential liberation
EOS	equation(s) of state
GOR	gas to oil volumetric ratio (sc)
GLR	gas to liquid volumetric ratio (sc)
GPA	Gas Processors Association
GPM	gallon of liquid per thousand cubic feet of gas (sc)
IFT	interfacial tension
MMP	minimum miscibility pressure
MME	minimum miscibility enrichment
PNA	paraffins-naphthenes-aromatics
PR	Peng-Robinson EOS
PT	Patel-Teja EOS
sc	standard conditions
SCF	standard cubic feet
SRK	Soave-Redlich-Kwong EOS
STB	stock tank barrel
SW	Schmidt-Wenzel EOS
TBP	true boiling point temperature
VPT	Valderrama-Patel-Teja EOS
ZJRK	Zudkevitch-Joffe-Redlich-Kwong EOS

SUPERSCRIPTS

F	feed, mixture
h	hydrocarbon phase
L	liquid phase
o	reference state
s	saturation
V	vapour phase
W	water phase

SUBSCRIPTS

b	base or bubble point
c	critical point
d	differential liberation process
g	gas
h	hydrocarbon
o	oil
r	reduced property = value/value at critical point
s	salt
w	water

CONTENTS

1

PHASE BEHAVIOUR FUNDAMENTALS

Petroleum reservoir fluids are composed mainly of hydrocarbon constituents. Water is also present in gas and oil reservoirs in an interstitial form. The influence of water on the phase behaviour and properties of hydrocarbon fluids in most cases is of a minor consideration. The phase behaviour of oil and gas, therefore, is generally treated independent of the water phase, unless water-hydrocarbon solid structures, known as hydrates, are formed.

The behaviour of a hydrocarbon mixture at reservoir and surface conditions is determined by its chemical composition and the prevailing temperature and pressure. This behaviour is of a prime consideration in the development and management of reservoirs, affecting all aspects of petroleum exploration and production.

Although a reservoir fluid may be composed of many thousands of compounds, the phase behaviour fundamentals can be explained by examining the behaviour of pure and simple multicomponent mixtures. The behaviour of all real reservoir fluids basically follows the same principle, but to facilitate the application of the technology in the industry, reservoir fluids have been classified into various groups such as the dry gas, wet gas, gas condensate, volatile oil and black oil.

1.1 RESERVOIR FLUID COMPOSITION

There are various hypotheses regarding the formation of petroleum from organic materials. These views suggest that the composition of a reservoir fluid depends on the depositional environment of the formation, its geological maturity, and the migration path from the source to trap rocks [1]. Reservoir gasses are mainly composed of hydrocarbon molecules of small and medium sizes and some light non-hydrocarbon compounds such as nitrogen and carbon dioxide, whereas oils are predominantly composed of heavier compounds.

Fluids advancing into a trapping reservoir may be of different compositions due to being generated at different times and environments. Hence, lateral and vertical compositional variations within a reservoir will be expected during the early reservoir life. Reservoir fluids are generally considered to have attained equilibrium at maturity due to molecular diffusion and mixing over geological times. However, there are ample evidences of reservoirs still maintaining significant compositional variations, particularly laterally as the diffusive mixing may require many tens of million years to eliminate compositional heterogenuities [2]. Furthermore, the pressure and the temperature increase with depth for a fluid column in a reservoir. This can also result in compositional grading with depth. For operational purposes, this behaviour is of considerable interest for near critical fluids, and oils containing high concentrations of asphaltic material. The compositional grading and its estimation based on thermodynamic concepts will be discussed in Section 5.3.

The crude oil composition is of major consideration in petroleum refining. A number of comprehensive research projects sponsored by the American Petroleum Institute have investigated crude oil constituents and identified petroleum compounds. API-6 studied the composition of a single crude oil for 40 years. The sulphur, nitrogen and organometallic compounds of crude oil samples were investigated in projects API-48, API-52 and API-56 respectively. API-60 studied petroleum heavy ends. Nelson [3] gives a review of petroleum chemistry and test methods used in the refining industry.

Highly detailed information on the constituents composing a reservoir fluid is not of very much use in exploration and production processes. Reservoir fluids are commonly identified by their constituents individually to pentanes, and heavier compounds are reported as groups composed mostly of components with equal number of carbons such as C_6's, C_7's, C_8's. All the compounds forming each single carbon number group do not necessarily possess the same number of carbons as will be discussed in Section 6.1. The most common method of describing the heavy fraction is to lump all the compounds heavier than C_6 and report it as C_{7+}.

Hydrocarbon compounds can be expressed by the general formula of $C_nH_{2n+\xi}$ with some sulphur, nitrogen, oxygen and minor metallic elements mostly present in heavy fractions. Hydrocarbon compounds are classified according to their structures, which determine the value of ξ. The major classes are paraffins (alkanes), olefins (alkenes), naphthenes, and aromatics. The paraffin series are composed of saturated hydrocarbon straight chains with $\xi=2$. Light paraffins in reservoir fluids are sometimes identified and reported as those with a single hydrocarbon chain, as normal, and others with branched chain hydrocarbons, as iso. The olefin series ($\xi=0$) have unsaturated straight chains and are not usually found in reservoir fluids due to their unstable nature. The naphthenes are cyclic compounds composed of saturated ring(s) with $\xi=0$. The aromatics ($\xi=-6$) are unsaturated cyclic compounds. Naphthenes and aromatics form a major part of C_6-C_{11} groups and some of them such as methyl-cyclo-pentane, benzene, toluene and xylene are often individually identified in the extended analysis of reservoir fluids. For example, the structural formulas of the above groups of hydrocarbons with six carbons are shown in Figure 1.1.

As reservoir hydrocarbon liquids may be composed of many thousand components, they cannot all be identified and measured. However, the concentration of hydrocarbon components belonging to the same structural class are occasionally measured and reported as groups, particularly for gas condensate fluids. The test to measure the concentration of **p**araffins, **n**aphthenes, and **a**romatics as groups is commonly referred to as the PNA test [4]. Further information on the structure of reservoir fluid compounds and their labelling according to the IUPAC system can be found in [5]. The compositional analysis of reservoir fluids and their characterisation will be discussed in Chapter 6.

Nitrogen, oxygen and sulphur are found in light and heavy fractions of reservoir fluids. Gas reservoirs containing predominantly N2, H2S, or CO2 have also been discovered. Polycyclic hydrocarbons with fused rings which are more abundant in heavier fractions may contain N, S, and O. These compounds such as carboids, carbenes, asphaltenes and resins are identified by their solubility, or lack of it, in different solvents [6]. The polar nature of these compounds can affect the properties of reservoir fluids, particularly the rock-fluid behaviour, disproportionally higher than their concentrations [7]. These heavy compounds may be present in colloidal suspension in the reservoir oil and precipitate out of solution by changes in the pressure, temperature or compositions occurring during production.

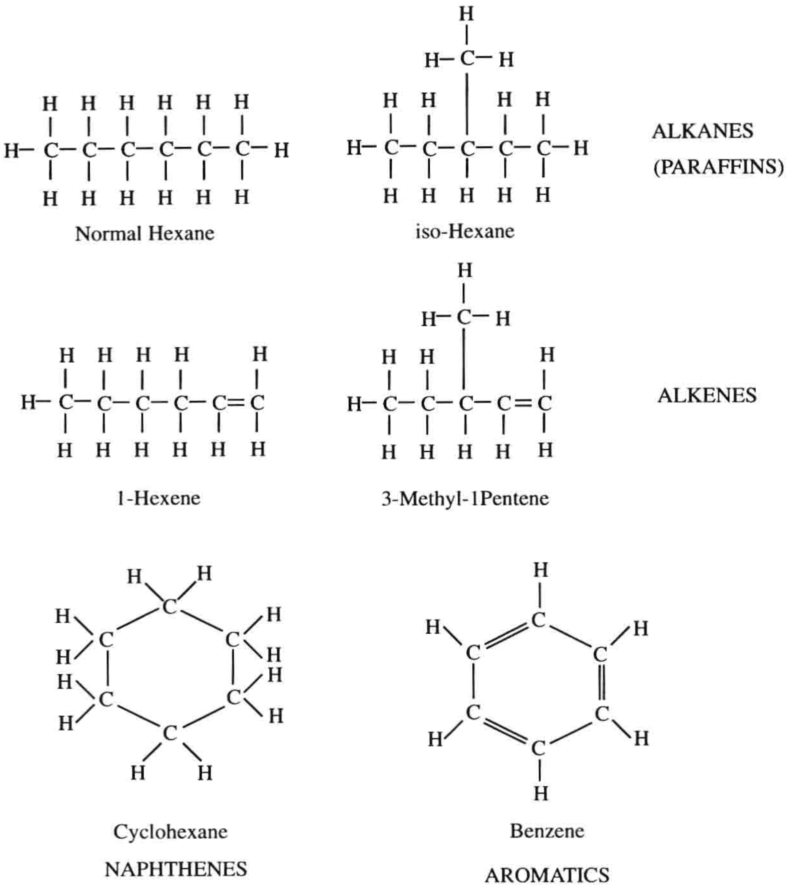


Figure 1.1. Structural formula of various groups of hydrocarbons with six carbons.

1.2 PHASE BEHAVIOUR

Reservoir hydrocarbons exist as vapour, liquid or solid phases. A phase is defined as a part of a system which is physically distinct from other parts by definite boundaries. A reservoir oil (liquid phase) may form gas (vapour phase) during depletion. The evolved gas initially remains dispersed in the oil phase before forming large mobile clusters, but the mixture is considered as a two-phase system in both cases. The formation or disappearance of a phase, or variations in properties of a phase in a multi-phase system are rate phenomena. The subject of phase behaviour, however, focuses only on the state of equilibrium, where no changes will occur with time if the system is left at the prevailing constant pressure and temperature. A system reaches equilibrium when it attains its minimum energy level, as will be discussed in Chapter 3. The assumption of equilibrium between fluid phases in contact in a reservoir, in most cases, is valid in engineering applications. Fluids at equilibrium are also referred to as saturated fluids.

The state of a phase is fully defined when its composition, temperature and pressure are specified. All the intensive properties for such a phase at the prevailing conditions are fixed and identifiable. The intensive properties are those which do not depend on the amount of material (contrary to the extensive properties), such as the density and the specific heat. The term property throughout this book refers to intensive properties.

At equilibrium, a system may form of a number of co-exiting phases, with all the fluid constituents present in all the equilibrated phases. The number of independent variables to define such a system is determined by the Gibbs *phase rule* described as follows.

A phase composed of N components is fully defined by its number of moles plus two thermodynamic functions, commonly temperature and pressure, that is, by N+2 variables. The intensive properties are, however, determined by only N+1 variables as the concentration of components are not all independent, but constrained by,

$$\sum_{1}^{N} x_i = 1 \tag{1.1}$$

where, x_i is the mole fraction of component i. Thus, for a system with κ phases, the total number of variables are equal to $\kappa(N+1)$. However, the temperature, pressure, and chemical potential of each component throughout all phases should be uniform at equilibrium conditions, as will be described in Chapter 3. This imposes $(N+2)(\kappa-1)$ constraints. Hence, the number of independent variables, or so-called the degrees of freedom, F, necessary to define a multiphase system is given by,:

$$F = \kappa(N+1)-(N+2)(\kappa-1) = N - \kappa + 2 \tag{1.2}$$

For a single-component (pure) system, the degrees of freedom is equal to three minus the number of phases. The state of the equilibrium of a vapour-liquid mixture of a pure fluid, therefore, can be determined by identifying either its pressure or its temperature.

Pure Compound

The phase behaviour of a pure compound is shown by the pressure-temperature diagram in Figure 1.2. All the conditions at which the vapour and liquid phases can coexist at equilibrium are shown by the line AC. Any fluid at any other pressure-temperature conditions, is unsaturated single phase as required by the phase rule. The fluid above and to the left of the line is referred to as a compressed or under saturated liquid, whereas that below and to the right of the line is called a superheated vapour or gas.

The line AC is commonly known as the vapour pressure curve, as it shows the pressure exerted by the vapour coexisting with its liquid at any temperature. The temperature corresponding to the atmospheric pressure is called the *normal boiling point* or simply the boiling point of the compound. The boiling point, T_b, of some compounds found in reservoir fluids are given in Table A.1 in Appendix A. Figure 1.3 shows the logarithm of vapour pressure plotted against an arbitrary temperature scale for some compounds. The scale, which is an adjusted reciprocal of the absolute temperature, has been selected so that the vapour pressures of water and most hydrocarbons can be exhibited by straight lines. This plot is known as the Cox chart. A pure substance cannot exist as liquid at a temperature above its critical temperature. Hence the vapour pressure values at temperatures above the critical temperatures, shown by ⊗ in Figure 1.3, are not real, but simply extrapolated values.

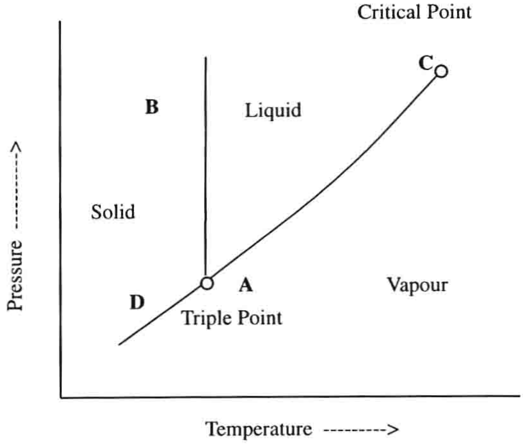


Figure 1.2. Pressure-temperature diagram of pure substance.

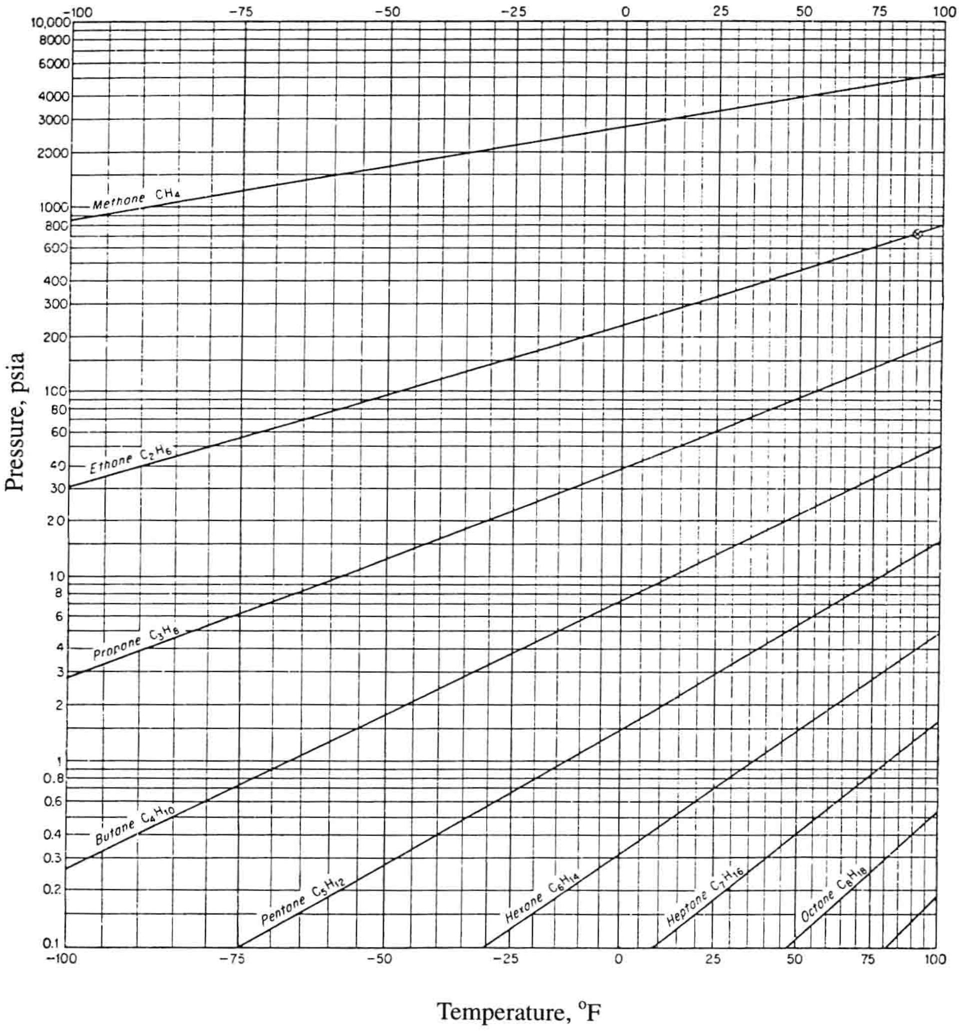
The line AB on Figure 1.2 is the solid-liquid equilibrium line, which is also known as the melting point curve. The intersection of the vapour-liquid and liquid-solid lines is the triple point. It is the only point where the three phases can coexist for a pure system.

The line AD is the solid-vapour equilibrium line or the sublimation curve. The solid carbon dioxide (dry ice) vaporising into its gaseous form is a common example of this region of the phase behaviour diagram.

The variation of saturated fluid density with temperature for a pure compound is shown in Figure 1.5. The densities of vapour and liquid phases approach each other as the temperature increases. They become equal at conditions known as the *critical point*. All the differences between the phases are reduced as the system approaches the critical point. Indeed, *the phases become the same and indistinguishable at the critical point.*

Figure 1.4 shows the variation of saturated fluid density with temperature for a number of pure hydrocarbons . All the compounds show a similar trend, that is, the vapour and liquid densities become equal at the critical point. Other properties also show the same trend. The critical temperature, T_c, and the critical pressure, P_c, are the maximum temperature and pressure at which a *pure compound* can form coexisting phases.

The terms vapour and liquid are referred to the less and the more dense phases of a fluid at equilibrium. Hence, a pure compound at a temperature above its critical value cannot be called either liquid or vapour. The continuity of vapour and liquid is schematically shown in Figure 1.6. The density at each point is shown by the shading intensity, where the darker shading corresponds to a higher density. The discontinuity across the vapour-pressure curve becomes less significant as the temperature increases and vanishes above the critical point. The superheated vapour E can be changed gradually to the compressed liquid F, through an arbitrary path EGF, without any abrupt phase change.



K=(°F+459.67)/1.8 MPa=0.006895 psia

Figure 1.3. Vapour pressure of normal paraffins. McGraw-Hill Companies Copyright. Reproduced from [8] with permission.