

Chapter 2

Volumetric and Phase Behavior of Oil and Gas Systems

2.1 Introduction

Petroleum reservoir fluids are naturally occurring mixtures of natural gas and crude oil that exist in the reservoir at elevated temperatures and pressures. Reservoir-fluid compositions typically include hundreds or thousands of hydrocarbons and a few nonhydrocarbons, such as nitrogen, CO₂, and hydrogen sulfide. The physical properties of these mixtures depend primarily on composition and temperature and pressure conditions. Reservoir temperature can usually be assumed to be constant in a given reservoir or to be a weak function of depth. As oil and gas are produced, reservoir pressure decreases and the remaining hydrocarbon mixtures change in composition, volumetric properties, and phase behavior. Gas injection also may change reservoir-fluid composition and properties. Katz and Williams¹ give an excellent review of reservoir fluids and their general behavior under different operating conditions.

The hydrocarbon phases and connate water sharing the pore volume (PV) in a reservoir are in thermodynamic equilibrium. Strictly speaking, hydrocarbons and water should be treated simultaneously in phase-behavior calculations. At typical reservoir conditions, the effect of connate water on hydrocarbon phase behavior can usually be neglected. Water can, however, affect the total-system phase behavior (for example, when hydrates form from natural-gas/water mixtures).

This chapter covers only two-phase, vapor/liquid phase behavior. Chap. 8 briefly covers three- and four-phase systems (vapor/liquid/liquid and vapor/liquid/liquid/solids) for low-temperature CO₂/oil and rich-gas/oil mixtures, and Chap. 9 gives the behavior of vapor and solids related to hydrates.

Sec. 2.1 introduces the composition of petroleum reservoir fluids and emphasizes their chemical complexity. Because reservoir fluids are made up of many components, a detailed quantitative analysis is difficult to perform. Organic compounds found in reservoir fluids are expressed by a general formula that classifies even high-molecular-weight compounds containing sulfur, nitrogen, and oxygen. This chapter also gives a historical review of the American Petroleum Inst. (API)-supported projects that defined many of the compounds known today.

Simple one- and two-component phase behavior can be helpful in describing the effects of pressure, temperature, and composition on the reservoir-fluid phase behavior. Sec. 2.2 presents pressure/temperature (p - T), pressure/volume (p - V), and pressure/composition (p - x) phase diagrams of simple systems. The behavior of these idealized systems is qualitatively similar to the behavior of complex reservoir fluids, as Sec. 2.3 shows.

Retrograde condensation is perhaps the most unusual phase behavior that petroleum reservoir fluids exhibit.* Sec. 2.4 discusses the definition of retrograde condensation and the effect of retrograde condensation on the behavior of gas-condensate reservoirs.

Petroleum reservoir fluids can be divided into five general categories, in increasing order of chemical complexity: dry gas, wet gas, gas condensate, volatile oil, and black oil. However, the phase behaviors of gas condensates and volatile oils are considerably more complex than those of black oils. The component distribution in a reservoir fluid, not simply the number of components, determines how close a fluid is to a critical state. Complex phase behavior is typically associated with systems that are “near critical”: systems that usually contain 10 to 15 mol% of components that are heptanes and heavier (C₇₊).

Since the early 1930's, experimental data have been measured on fluids of each type listed above. Sec. 2.5 defines each fluid type by its p - T diagram. Also, general characteristics of reservoir fluids are summarized in terms of composition and surface properties, such as GOR and stock-tank-oil gravity.

2.2 Reservoir-Fluid Composition

The nature and composition of a reservoir fluid depends somewhat on the depositional environment of the formation from which the fluid is produced. Geologic maturation also influences reservoir-fluid composition. Several theories offer explanations for the origin and formation of petroleum over geologic time; no single theory suffices to explain how oil and gas were formed in all reservoirs. One theory portrays reservoirs as giant high-temperature/high-pressure reactors with catalytic rock surfaces that slowly convert deposited organic matter into oil and gas. Other theories hypothesize that oil and gas were formed from bacterial action on deposited organic matter. Other investigators maintain that oil and gas may be formed in the same geologic formation but that each fluid migrates to “traps” at different elevations because of fluid-density differences and gravity forces.

Crude oil and natural gas are composed of many chemical compounds with a wide range of molecular weights. Some estimates²⁻⁴ suggest that perhaps 3,000 organic compounds can exist in a single

*Historically, retrograde condensation has been considered the most complex phase-behavior phenomenon observed by reservoir fluids. Perhaps equally intriguing are the phenomena of strong compositional gradients, the condensing/vaporizing miscible mechanism (Chap. 8), asphaltene precipitation, and low-temperature, multiphase CO₂ behavior.

TABLE 2.1—COMPOSITION AND PROPERTIES OF SEVERAL RESERVOIR FLUIDS

Component	Composition (mol%)					
	Dry Gas	Wet Gas	Gas		Volatile Oil	Black Oil
			Condensate	Near-Critical Oil		
CO ₂	0.10	1.41	2.37	1.30	0.93	0.02
N ₂	2.07	0.25	0.31	0.56	0.21	0.34
C ₁	86.12	92.46	73.19	69.44	58.77	34.62
C ₂	5.91	3.18	7.80	7.88	7.57	4.11
C ₃	3.58	1.01	3.55	4.26	4.09	1.01
<i>i</i> -C ₄	1.72	0.28	0.71	0.89	0.91	0.76
<i>n</i> -C ₄		0.24	1.45	2.14	2.09	0.49
<i>i</i> -C ₅	0.50	0.13	0.64	0.90	0.77	0.43
<i>n</i> -C ₅		0.08	0.68	1.13	1.15	0.21
C _{6(s)}		0.14	1.09	1.46	1.75	1.61
C ₇₊		0.82	8.21	10.04	21.76	56.40
Properties						
<i>M</i> _{C₇₊}		130	184	219	228	274
<i>γ</i> _{C₇₊}		0.763	0.816	0.839	0.858	0.920
<i>K</i> _{wC₇}		12.00	11.95	11.98	11.83	11.47
GOR, scf/STB	∞	105,000	5,450	3,650	1,490	300
OGR, STB/MMscf	0	10	180	275		
<i>γ</i> _{API}		57	49	45	38	24
<i>γ</i> _g		0.61	0.70	0.71	0.70	0.63
<i>p</i> _{sat} , psia		3,430	6,560	7,015	5,420	2,810
<i>B</i> _{sat} , ft ³ /scf or bbl/STB		0.0051	0.0039	2.78	1.73	1.16
<i>ρ</i> _{sat} , lbm/ft ³		9.61	26.7	30.7	38.2	51.4

reservoir fluid. The lighter and simpler compounds are produced as natural gas after surface separation, whereas the heavier and more complex compounds form crude oil at stock-tank conditions. **Table 2.1** gives typical oilfield molar compositions for reservoir mixtures. The heavier components are usually lumped into a “plus” fraction instead of being identified individually. Chap. 5 discusses methods of quantifying and characterizing the components that make up the plus fraction—usually heptanes-plus.

Natural gas is composed mainly of low-molecular-weight alkanes (methane through butanes), CO₂, hydrogen sulfide, nitrogen, and, in some cases, lesser quantities of helium, hydrogen, CO, and carbonyl sulfide.⁵ Most crude oils are composed mainly of hydrocarbons (hydrogen and carbon compounds). The broad spectrum of organic compounds found in petroleum during the formation of crude oil also includes sulfur, nitrogen, oxygen, and trace metals. Tars and asphalts are solid or semisolid mixtures that include bitumen, pitch, waxes, and resins. These high-molecular-weight complex colloidal suspensions exhibit non-Newtonian rheology.

The temperature and pressure gradients in a formation may cause reservoir-fluid properties to vary as a function of depth. “Compositional grading” is the continual change of composition as a function of depth.⁶⁻⁸ In compositional grading, reservoir temperature may be near the critical temperature of reservoir fluid(s) at certain depths in the reservoir. Physically, the thermodynamic forces of individual components in a near-critical mixture are of the same order of magnitude as gravity forces that tend to separate the lighter from the heavier components. The result can be a transition from an undersaturated gas condensate at the highest elevation to an undersaturated oil at the lowest elevation, with or without a visible phase transition from gas to oil (gas/oil contact).

In petroleum refining, crude oil is often categorized according to its base and the hydrocarbon series (paraffin, naphthene, or aromatic) it contains in the highest concentration. **Figs. 2.1 and 2.2**⁹ illustrate the types and relative amounts of hydrocarbon series that can be found in typical petroleum-refinery products. Nelson³ gives a full account of basic hydrocarbon chemistry and test methods that

have been used for many years to determine petroleum composition and inspection properties for refining purposes. The more common test methods include paraffin, naphthene, and aromatic; saturates, aromatics, resins, and asphaltenes; and Strieter (asphaltenes, resins, and oils) analyses; oil gravity in °API; Reid vapor pressure; true-boiling-point distillation; flash, fire, cloud, and pour points; color; and Saybolt and Furol viscosities. Chap. 5 discusses some of these methods that are used in petroleum engineering.

The empirical formula C_{*n*}H_{2*n*}+*h*S_{*a*}N_{*b*}O_{*c*} can be used to classify nearly all compounds found in crude oil. The largest portion of crude oil is composed of hydrocarbons with carbon number, *n*, ranging from 1 to about 60, and *h* numbers ranging from *h* = +2 for low-molecular-weight paraffin hydrocarbons to *h* = −20 for high-molecular-weight organic compounds (e.g., polycyclic aromatic hydrocarbons). Occasionally, sulfur, nitrogen, and oxygen substitutions occur in high-molecular-weight organic compounds, with *a*, *b*, and *c* usually ranging from 1 to 3.^{2,10}

Over the past 60 years, petroleum chemists have identified hundreds of the complex organic compounds found in petroleum. Beginning in 1927, Rossini and others^{11,12} conducted a lengthy investigation of the composition of petroleum [API Research Project 6 (API 6)] to develop and improve petroleum-refining processes. It took API 6 investigators almost 40 years to elucidate the composition of a single midcontinent crude oil from Well No. 6 in South Ponca City, Oklahoma.

Because compounds with carbon numbers > 12 could not be isolated from crude oils, during 1940–66, API Research Project 42 focused on synthesizing and characterizing model hydrocarbons with high molecular weights. These model compounds were used for identifying compounds that could not be isolated from crude oil. A crude oil compound with analytical responses that matched those of a synthesized model compound was inferred to have a similar chemical structure.

Other API projects¹³ followed API 6, and increasingly more complex petroleum compounds were identified. API 48 focused on sulfur compounds, API 52 on nitrogen compounds, and API 56 on or-

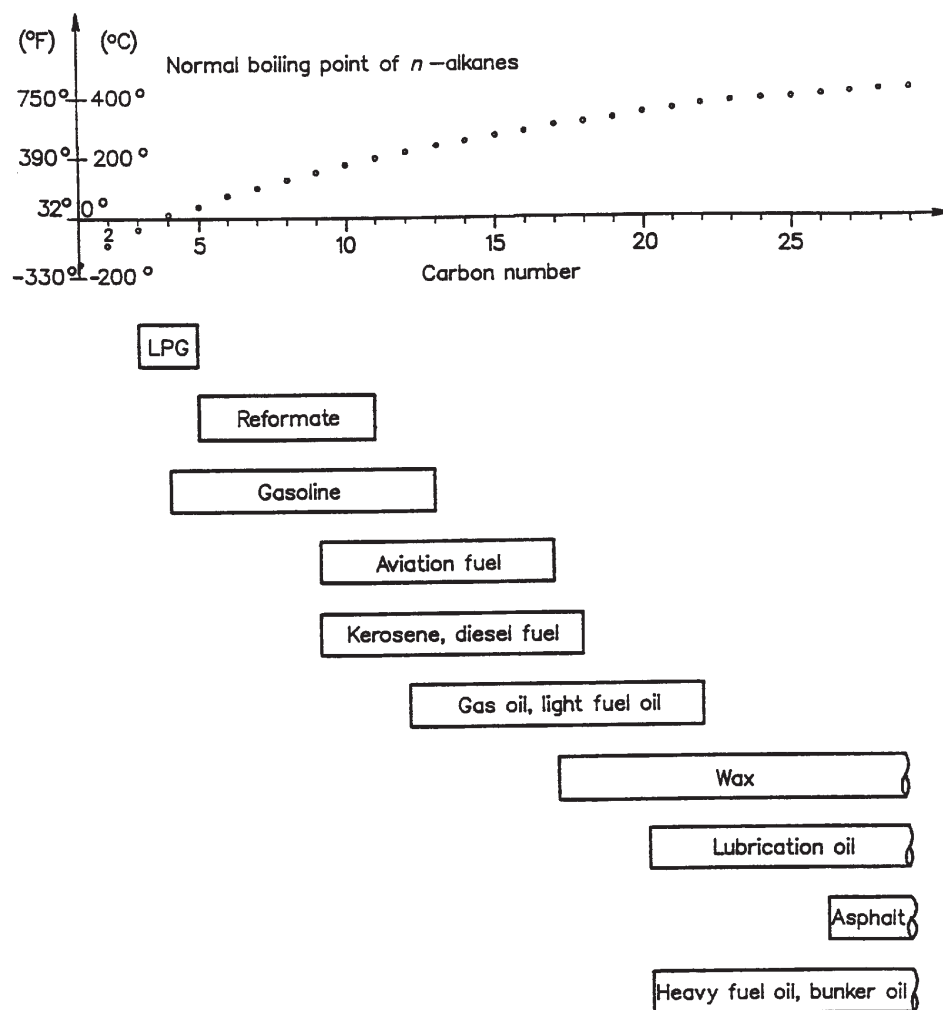


Fig. 2.1—Petroleum products identified according to carbon number.

ganometallic compounds. API 60 extended the work of API 6 to include petroleum heavy ends.

In 1975, API stopped sponsoring basic research into the composition of petroleum. From 1975 to 1982, the petroleum engineering industry made additional advances in analytical techniques mainly because of the synfuels effort. The most sophisticated analytical techniques now in use include highly selective solvent extraction¹⁴⁻¹⁶; simulated distillation; gel permeation, high-performance liquid,¹⁷ and supercritical chromatography¹⁸; and mass infrared,¹³ ¹³C nuclear magnetic resonance,¹⁹ and Fourier-transform infrared spectroscopy. The American Chemical Soc. Div. of Petroleum Chemistry provides a comprehensive review of this area of research every 2 to 3 years.

Table 2.2²⁰ shows an example of a crude-oil distillate classified by *h* number (in the general formula $C_nH_{2n+h}S_aN_bO_c$) and probable structural type, which determines the range of possible *n* numbers. Within and across each hydrocarbon class, many isomers share *h* and *n* numbers. The alkane (paraffin) series (*h* = 2) has completely saturated hydrocarbon chains that are chemically very stable. The alkene (olefin) and alkyne (acetylene) series (*h* = 0 and *h* = -2) are composed of unsaturated, straight-chain hydrocarbons. Because alkenes and alkynes are reactive, they are not usually found in naturally occurring petroleum deposits.

The naphthene series (*h* = 0), saturated-ring or cyclic compounds, are found in nearly all crudes. The aromatic or "benzene" series (*h* = -6) are unsaturated cyclic compounds. Low-boiling-point aromatics, which are also reactive, are found in relatively low concentrations in crude oil. Heavier crude oils are characterized by unsaturated polycyclic aromatic hydrocarbons with increasingly negative *h* num-

bers. As molecular weight increases, these compounds assume varying degrees of fused-ring saturation, with occasional hydrocarbon side chains. Sulfur, nitrogen, and oxygen can be substituted in the fused hydrocarbon rings to form heterocyclics or can occupy various positions on side chains.²¹ Metals, such as nickel and vanadium, can form organometallic compounds (porphyrins) in crude oil.^{2,10}

Asphalts, bitumens, and tars are complex colloidal mixtures of carboids, carbenes, asphaltenes, and maltenes (resins and oils). Micellar structures of carboids, carbenes, and asphaltenes are formed by aromatic polycondensation reactions and are maintained in colloidal suspension by the maltenes. These fractions are separated according to their solubility or lack of solubility in certain low-molecular-weight solvents, such as propane, pentane, *n*-hexane, and carbon disulfide.

Fig. 2.3¹⁶ shows a hypothetical chemical structure of an asphaltene. The bracket around the structure implies that the structure is repeated three times. Although asphalt mixtures are complex in composition and rheology, they follow certain molecular-weight distributions that can be characterized as discussed in Chap. 5.

Understanding the nature of asphaltenes is important in petroleum engineering because, even in low concentrations, asphaltenes can markedly affect reservoir-fluid phase behavior.²² Because asphaltenes are polar and hydrogen bonding, they alter reservoir wettability by adsorbing onto the rock surface.²³ This alteration of reservoir wettability may affect capillary pressure, relative-permeability relations, residual oil saturations, waterflood behavior, dispersion, and electrical properties. Figs. 2.2 and 2.3 vividly show that the composition of crude oil is considerably more complex than the C_nH_{2n+2} straight-chain models commonly thought of as "oil." This complexity

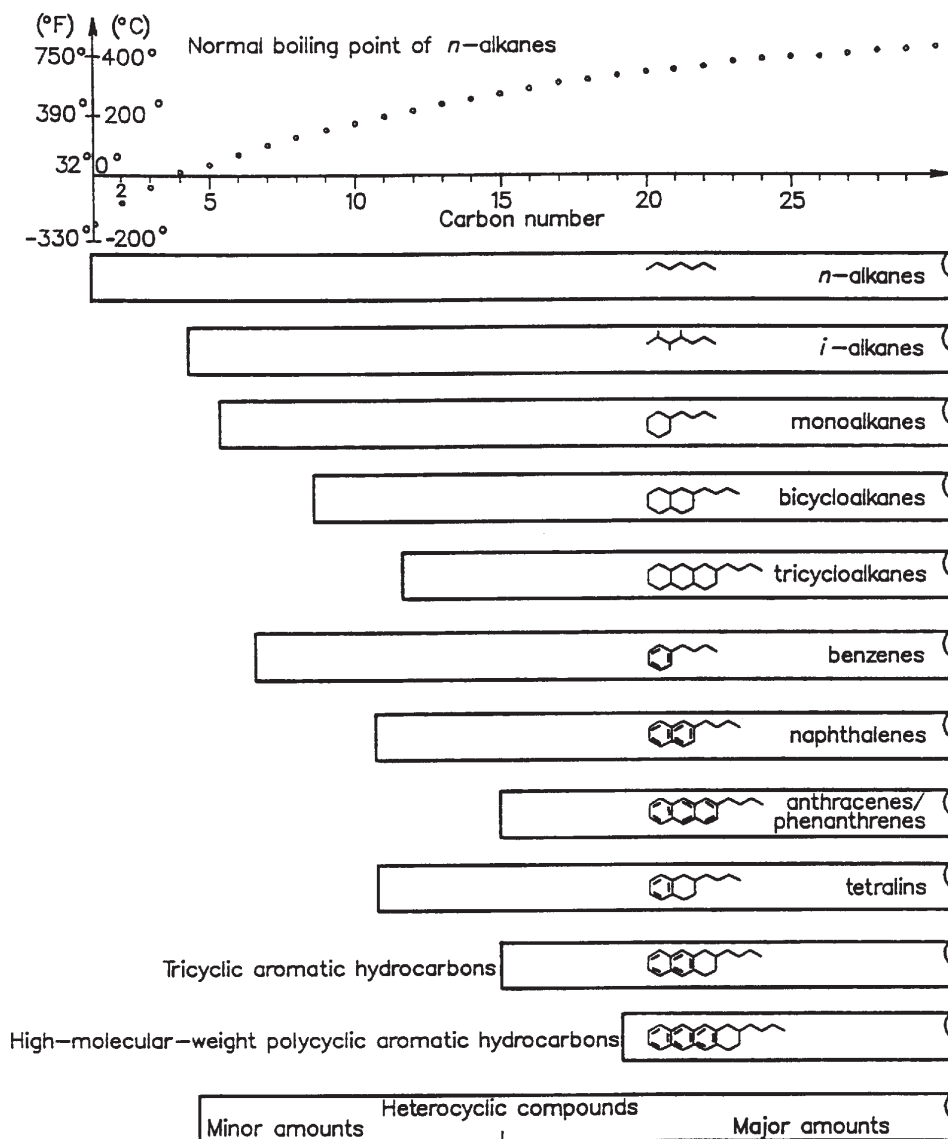


Fig. 2.2—Summary of hydrocarbons to be expected in crude-oil fractions (from Neumann *et al.*⁹).

should be borne in mind when modeling the phase behavior of complex reservoir fluids, particularly in gas-injection projects.^{23,24}

2.3 Phase Diagrams for Simple Systems

The dependence of volumetric and phase behavior on temperature, pressure, and composition is similar for simple (two- and three-component) and complex (multicomponent) systems. Traditionally, the introduction to phase behavior of complex reservoir fluids starts with a description of the vapor-pressure and volumetric behavior of single components. The introduction then proceeds to the behavior of two- and three-component systems, and finally to the behavior of complex multicomponent systems. Part of the rationale for this procession lies in the Gibbs phase rule.^{25,26}

The Gibbs phase rule states that the number of intensive variables (i.e., degrees of freedom), F , that must be specified to determine the thermodynamic state of equilibrium for a mixture containing n components distributed in P phases (gas, liquid, and/or solid), is

$$F = n - P + 2. \quad (2.1)$$

Intensive (thermodynamic) variables, such as temperature, pressure, and density, do not depend on the amount of material in the system. Extensive variables, such as flow rate, total mass, or liquid volume, depend on the extent of the system.

To attain equilibrium requires that no net interphase mass transfer can occur. Thus, the temperatures and pressures of the coexisting

phases must be the same and the chemical potentials of each component in each phase must be equal. A more stringent definition of phase equilibrium includes other forces in addition to chemical potential (e.g., gravity and capillarity).

On the basis of Eq. 2.1, for a two-phase, single-component system, $F = 1$ and only temperature or pressure needs to be specified to determine the thermodynamic state of the system. For a two-phase, two-component system, $F = 2$ and both temperature and pressure need to be specified to define the thermodynamic state of the mixture. Two-phase binary systems allow one to focus on the effect of temperature and pressure on the composition and the relative amounts of each of the two phases, regardless of the composition of the overall mixture.

The Gibbs phase rule implies that as the number of components increases to n in a two-phase mixture, $n - 2$ composition variables must be specified in addition to temperature and pressure. If more than two phases are present, then $n - P$ variables must be specified in addition to temperature and pressure. Because reservoir fluids comprise many components, the number of variables that must be defined to determine the state of a reservoir fluid is conceptually unmanageable. Therefore, simple systems are often used to model the basic volumetric and phase behavior of crude oil mixtures.

Note that the phase rule must be modified if other potential fields are considered. For example, if the force of gravity is considered, as

TABLE 2.2—DISTRIBUTION OF *h* SERIES FROM 698 TO 995°F DISTILLATE OF SWAN HILLS CRUDE OIL (Ref. 20)

Mass <i>h</i> Series	Probable Type
– 12	Naphthalenes
– 14	Naphthenonaphthalenes and/or biphenyls
– 16	Dinaphthenaphthalenes and/or naphthenobiphenyls
– 18	Trinaphthenaphthalenes and/or dinaphthenobiphenyls
– 20	Tetranaphthenaphthalenes and/or trinaphthenobiphenyls
– 22	Pentanaphthenaphthalenes and/or tetranaphthenobiphenyls
– 24	Hexanaphthenaphthalenes and/or pentanaphthenobiphenyls
– 26	Heptanaphthenaphthalenes and/or hexanaphthenobiphenyls
– 28	Octanaphthenaphthalenes and/or heptanaphthenobiphenyls
– 4S	Tricyclic sulfides
– 6S	Tetracyclic sulfides
– 8S	Pentacyclic sulfides
– 10S	Hexacyclic sulfides
– 8S	Thiaindanes/thiatetralins
– 10S	Naphthenothiaindanes/thiatetralins
– 12S	Dinaphthenothiaindanes/thiatetralins
– 14S	Trinaphthenothiaindanes/thiatetralins
– 10S	Benzothiophenes
– 12S	Naphthenobenzothiophenes

is done when calculating compositional variation with depth, the phase rule is $F = n - P + 3$.⁷

2.3.1 Single-Component Systems. The p - T curve shown in Fig. 2.4 is a portion of the vapor-pressure curve for a typical hydrocarbon compound. Above and to the left of the curve, the hydrocarbon behaves as a liquid; below and to the right, the hydrocarbon behaves as a vapor. Saturated liquid and vapor coexist at every point along the vapor-pressure curve. The curve ends at the critical temperature and critical pressure of the hydrocarbon (the “critical point”). Fig. 2.5 shows a 3D PVT diagram of a pure compound.

The critical temperature of a single component defines the temperature above which any gas/liquid mixture cannot coexist, regardless of pressure. Similarly, the critical pressure defines the pressure above which liquid and vapor cannot coexist, regardless of temperature. Along the vapor-pressure curve, two phases coexist in equilibrium. At the critical point, the vapor and liquid phases can no longer be distinguished, and their intensive properties are identical.

For a multicomponent system, the definition of the critical point is also based on a temperature and pressure at which the vapor and liquid phases are indistinguishable. However, for a single-component system, the two-phase region terminates at the critical point. In a multicomponent system, the two-phase region can extend beyond the system’s critical point (i.e., at temperatures greater than the critical temperature and pressures greater than the critical pressure).

Fig. 2.6²⁷ illustrates the continuity of gas and liquid phases for pure components. In this figure, the darker shading corresponds to higher density. A sharp contrast in phase densities is readily apparent along the vapor-pressure curve. As temperature increases along the vapor-pressure curve, the discontinuity becomes harder to discern, until finally, at the critical point, the contrast in shading is hardly noticeable. Qualitatively, the behavior described by the shading in Fig. 2.6 is the same for multicomponent mixtures in the undersaturated region.

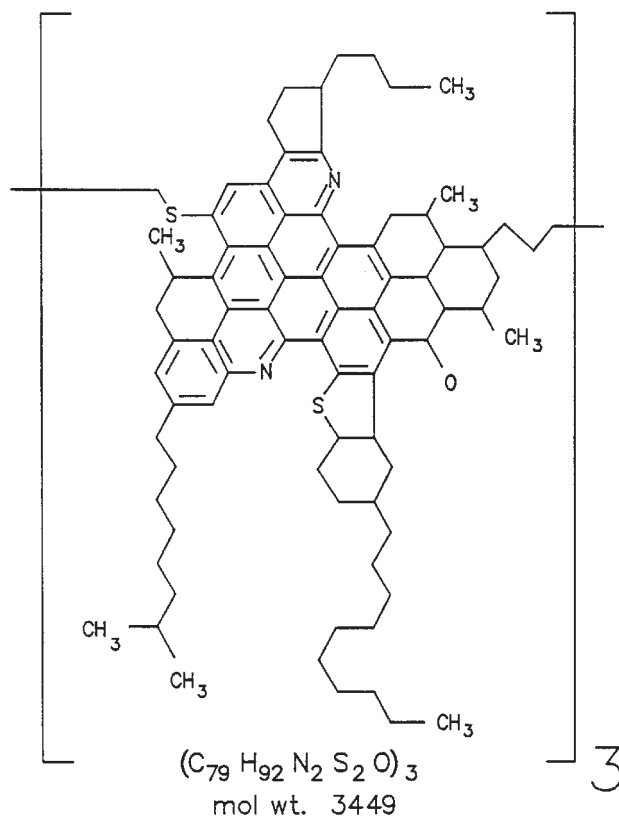


Fig. 2.3—Hypothetical structure of a petroleum asphaltene (after Speight and Moschopedis¹⁴).

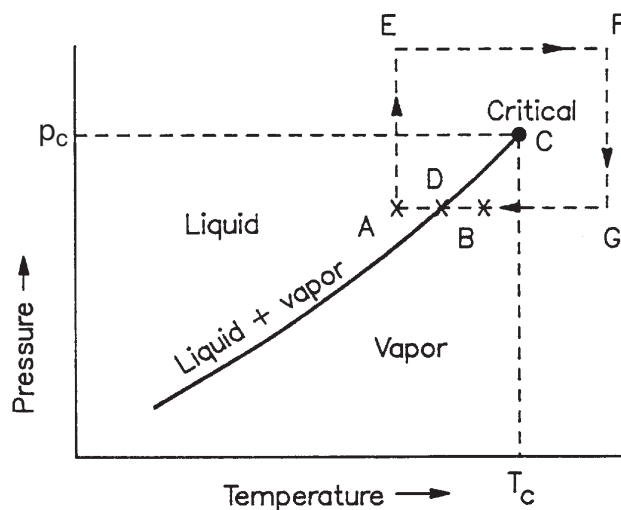


Fig. 2.4— p - T diagram for a single component in the region of vapor/liquid behavior near the critical point (p_c = critical pressure and T_c = critical temperature).

Phase changes do not have to take place abruptly if certain temperature and pressure paths are followed. A process can start as a saturated liquid and end as a saturated vapor, with no abrupt change in phase. The path D–A–E–F–G–B–D in Fig. 2.4 is an example of a process that changes phases without crossing the vapor-pressure curve. Pure components actually exist as a saturated “liquid” and “vapor” only along the vapor-pressure curve. At other pressures and temperatures, the component only *behaves* “liquid-like” or “vapor-like,” depending on the location of the system temperature and pressure relative to the system’s critical point. Katz²⁸ suggested calling a pure substance “single-phase fluid” at pressures greater than the critical pressure. Strictly speaking, the terms liquid-like and vapor-like should be used to describe undersaturated fluids.

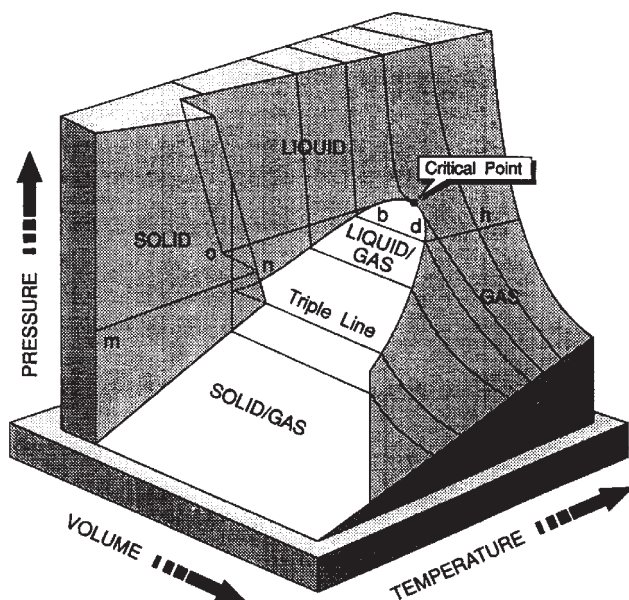


Fig. 2.5—Three-dimensional schematic of the PVT surface of a pure compound (source unknown).

Fig. 2.7²⁶ shows a p - V diagram for ethane. The area enclosed by the saturation envelope represents the two-phase region. The area to the left of the envelope is the liquid-like region, and the area to the right is the vapor-like region. Point C represents the critical point. The saturation curve to the left of the critical point (from Point A to Point C) defines the bubblepoint curve, along which the com-

ponent is a saturated liquid. Similarly, the saturation curve to the right of the critical point (Point B to Point C) defines the dewpoint curve, along which the component is a saturated vapor.

For any temperature less than the critical temperature, successive decreases in volume will elevate the pressure of the vapor until the “dewpoint” (vapor pressure) is reached (Point B on Fig. 2.7). At these conditions, the component is a saturated vapor in equilibrium with an infinitesimal amount of saturated liquid. Further decreases in the volume at constant temperature will result in proportionate increases in the amount of saturated liquid condensed, but the pressure does not change (i.e., the system pressure remains equal to the vapor pressure). While more liquid is being formed, the total volume (at Point D) is being reduced. However, the densities and other intensive properties of the saturated vapor and saturated liquid remain constant as a consequence of the Gibbs phase rule.

A simple mass balance further shows that the ratio of liquid to vapor equals the ratio of Curve B–D to Curve D–A. Further decreases in volume will condense more liquid until the bubblepoint is reached. At the bubblepoint, the system is 100% saturated liquid in equilibrium with an infinitesimal amount of saturated vapor. Further decreases in volume beyond the bubblepoint are accompanied by a large increase in pressure because the liquid is only slightly compressible. This is indicated by the nearly vertical isotherms on the left side of Fig. 2.7. In the undersaturated vapor region on the right side of the diagram, a large change in volume reduces pressure only slightly because the vapor is highly compressible.

2.3.2 Two-Component Systems. Two-component systems are slightly more complex than single-component systems because both temperature and pressure affect phase behavior in the saturated region. Two important differences between single- and two-component systems exist. The saturated p - T projection is represented by a phase envelope rather than by a vapor-pressure curve, and the criti-

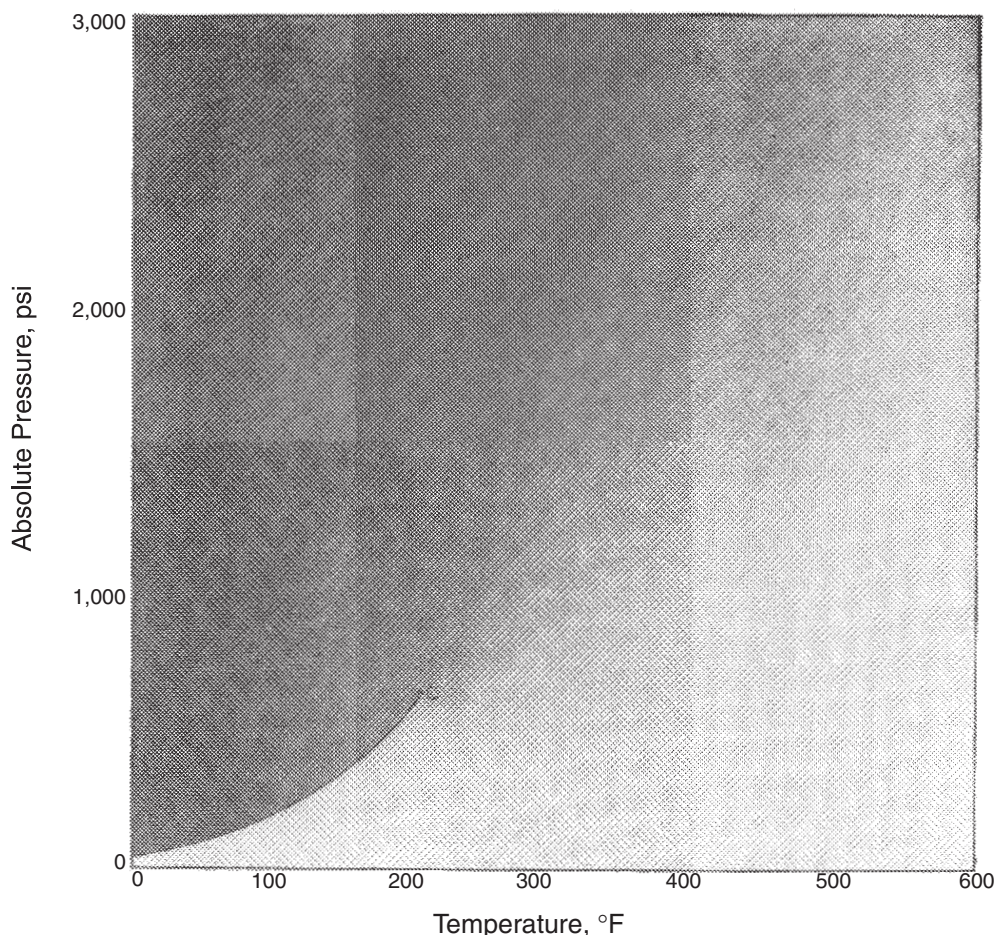


Fig. 2.6—Continuity of vapor and liquid states for a single component along the vapor-pressure curve and at supercritical conditions (after Katz and Kurata²⁷).

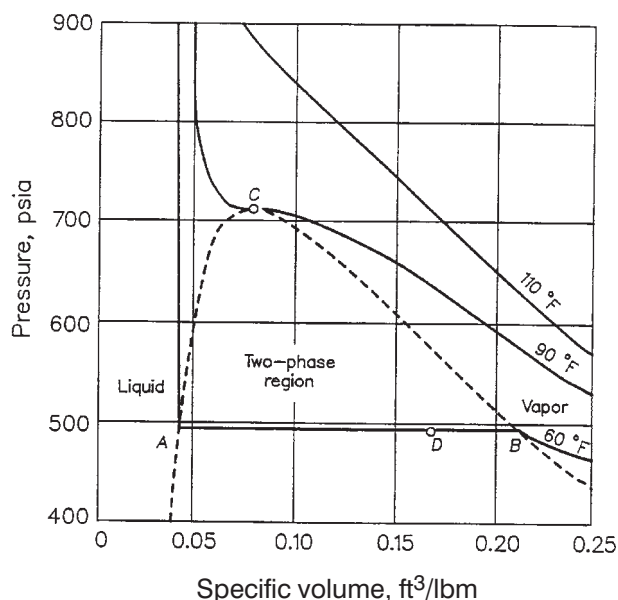


Fig. 2.7— p - V diagram for ethane at three temperatures (from Standing²⁶).

cal temperature and critical pressure no longer define the extent of the two-phase, vapor/liquid region. Fig. 2.8²⁹ compares the p - T and p - V behavior of pure compounds and mixtures.

Fig. 2.9²⁶ is a p - T projection of the ethane/ n -heptane system for a fixed composition. For a single-component system, the dew- and bubblepoint curves are one in the same; i.e., they coincide with the vapor-pressure curve. In a binary (or other multicomponent) system, the dew- and bubblepoint curves no longer coincide, and a phase envelope results instead of a vapor-pressure curve. To the left of the phase envelope, the mixture behaves liquid-like, and to the right it behaves vapor-like.

For binary or other multicomponent systems, the critical temperature and pressure are defined as the point where the dew- and bubblepoint curves intersect. At this point, the equilibrium phases are physically indistinguishable. Also, in contrast to the single-component system, two phases can exist at temperatures and pressures greater than the critical temperature and pressure. The highest temperature at which two phases can coexist in equilibrium is defined as the cricondentherm (Tangent b-b in Fig. 2.9). Similarly, the highest pressure at which two phases can coexist is defined as the cricondenbar (Tangent a-a).

In the single-phase region, vapor and liquid are distinguished only by their densities and other physical properties. The region just beyond the critical point of a mixture has often been called the “supercritical” or “dense-fluid” region. Here, the fluid is considered to be neither gas nor liquid because the fluid properties are not strictly liquid-like or vapor-like.

Kay³⁰ measured the phase behavior of the binary ethane/ n -heptane system for several compositions, as Fig. 2.10 shows. On the left side of this figure, the curve terminating at Point C is the vapor pressure of pure ethane; the curve on the right, terminating at Point C7, is the vapor pressure of pure n -heptane. Points C1 through C3 are the critical points of ethane/ n -heptane mixtures at different compositions. The dashed line represents the locus of critical points for the infinite number of possible ethane/ n -heptane mixtures. Each mixture composition has its own p - T phase envelope.

The three compositions shown, which are 90.22, 50.25, and 9.78 wt% ethane, represent a system that is mainly ethane, a system that is one-half ethane and one-half n -heptane (by weight), and a system that is mainly n -heptane, respectively. Several interesting features of binary and multicomponent systems can be studied from these three mixtures. As composition changes, the location of the critical point and the shape of the p - T phase diagram also change.

Note that the critical pressures of many (but not all) mixtures are higher than the critical pressures of the components composing the

mixture. With a mixture composed mainly of ethane, the critical point lies to the left of the cricondentherm. Such a system is analogous to a reservoir gas-condensate system. As the percentage of ethane in the mixture increases further, the critical point of the system approaches that of pure ethane.

The critical point for the mixture composed mostly of n -heptane lies below the cricondenbar. This system is analogous to a reservoir black-oil system. As the percentage of n -heptane increases, the critical point of the mixture approaches that of pure n -heptane. With equal percentages of ethane and n -heptane, the critical pressure is close to the cricondenbar of ethane and n -heptane. As the concentration of each component becomes similar, the two-phase region becomes larger.

Other binaries provide additional insight into the effect of widely differing boiling points of the components making up the system. Fig. 2.11³¹ shows the vapor pressure of several hydrocarbons and the critical loci of their binary mixtures with methane. As the boiling points of the methane/hydrocarbon binary become more dissimilar, the two-phase region becomes larger and the critical pressure increases. For binaries with components that have similar molecular structures, the loci of critical points are relatively flat.

2.3.3 Multicomponent Systems. Phase diagrams for naturally occurring reservoir fluids are similar to those for binary mixtures. Fig. 2.12⁵ is the first p - T phase diagram measured for a complex gas-condensate system. This p - T diagram is particularly useful because it exhibits oil-like to gas-like behavior over a range of typical reservoir temperatures, from 80 to 240°F. Katz and coworkers³² used a glass-windowed cell to measure the distribution of gas and liquid phases throughout the two-phase region and near the mixture's critical point. Fig. 2.13⁵ shows isotherms of volume percent vs. pressure that were measured to determine the two-phase boundary and the volume-percent quality lines in the p - T diagram in Fig. 2.12.

2.4 Retrograde Condensation

Kurata and Katz³³ give the most concise and relevant discussion of retrograde phenomena related to petroleum engineering. In 1892, Kuenen³⁴ used the term “retrograde condensation” to describe the anomalous behavior of a mixture that forms a liquid by an isothermal decrease in pressure or by an isobaric increase in temperature. Conversely, “retrograde vaporization” can be used to describe the formation of vapor by an isothermal increase in pressure or by an isobaric decrease in temperature. Neither form of retrograde behavior occurs in single-component systems.

Fig. 2.14 is a constant-composition p - T projection of a multicomponent system. The diagram shows lines of constant liquid volume percent (quality). Although total composition is fixed, the respective compositions of saturated vapor and liquid phases change along the quality lines. The bubblepoint curve represents the locus of 100% liquid, and the dewpoint curve represents the locus of 0% liquid. The bubble- and dewpoint curves meet at the mixture critical point. Lines of constant quality also converge at the mixture critical point. The regions of retrograde behavior are defined by the lines of constant quality that exhibit a maximum with respect to temperature or pressure. Fig. 2.14 shows that for retrograde phenomena to occur, the temperature must be between the critical temperature and the cricondentherm. Fig. 2.15³⁵ illustrates the liquid volumetric behavior of a lean gas-condensate system measured by Eilerts *et al.*³⁵⁻³⁷

Fig. 2.12 shows the p - T diagram of a reservoir mixture that would be considered a gas condensate if it had been discovered at a reservoir temperature of, for example, 200°F and an initial pressure of 2,700 psia. For these initial conditions, if reservoir pressure drops below 2,560 psia from depletion, the dewpoint will be passed and a liquid phase will develop in the reservoir. Liquid dropout will continue to increase until the pressure reaches 2,300 psia, when a maximum of 25 vol% liquid will have accumulated. According to Fig. 2.12, further pressure reduction will revaporize most of the condensed liquid.

These comments assume that the overall composition of the reservoir mixture remains constant during depletion, a reasonable assumption in the context of this general discussion. In reality, howev-

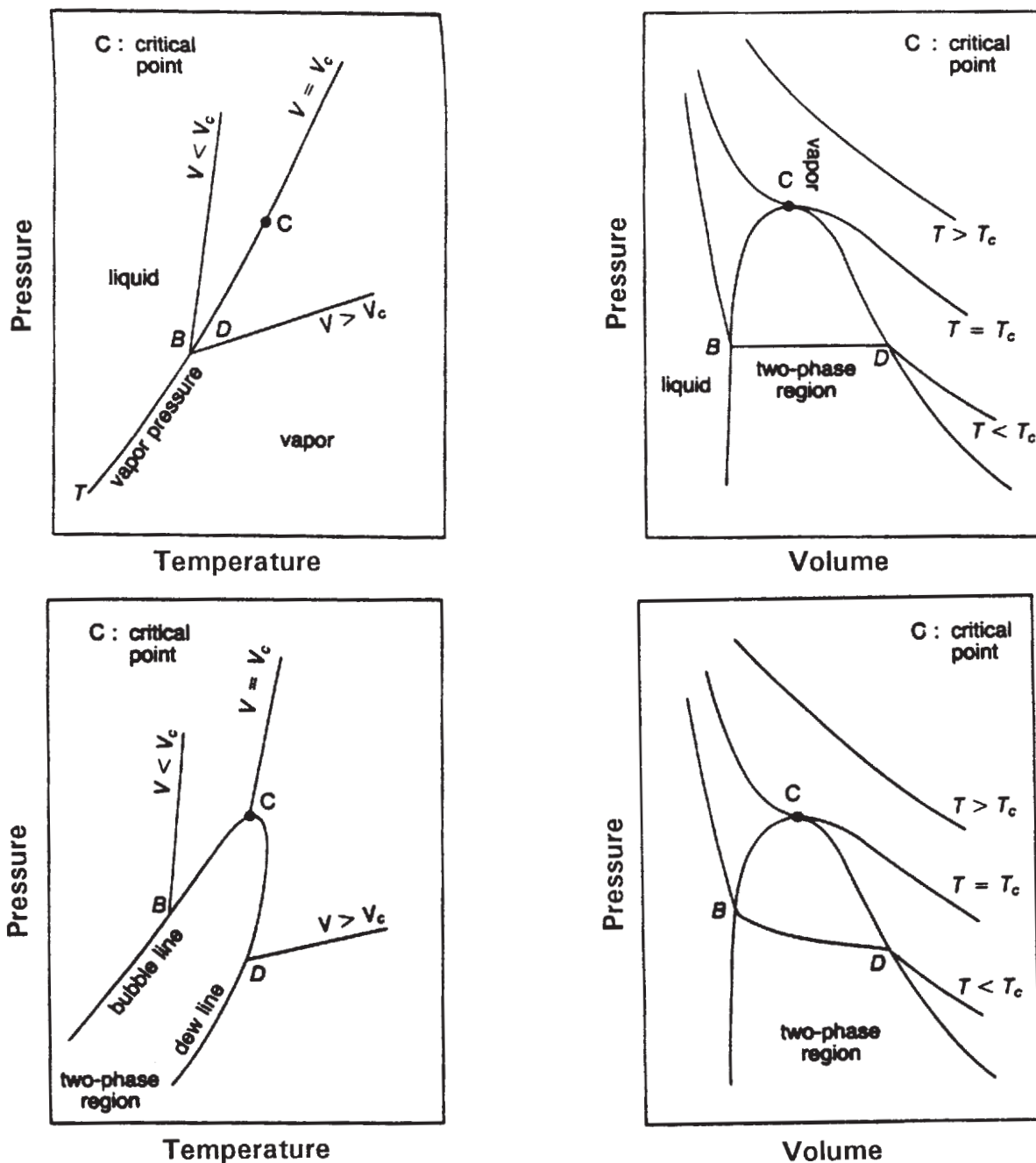


Fig. 2.8—Qualitative p - T and p - V plots for pure fluids and mixtures; V_c = critical volume (after Edmister and Lee²⁹).

er, the behavior of liquid dropout and revaporization differs from that suggested by constant-composition analysis. The retrograde liquid saturation is usually less than the saturation needed to mobilize the liquid phase. Because the heavier components in the original mixture constitute most of the (immobile) condensate saturation, the overall molecular weight of the remaining reservoir fluid increases during depletion. The phase envelope for this heavier reservoir mixture is pushed down and to the right of the original phase diagram (Fig. 2.16); the critical point is shifted to the right toward a higher temperature. It is not unusual that a retrograde-condensate mixture under depletion will reach a condition where the overall composition would exhibit a bubblepoint pressure if the reservoir were repressured (i.e., the overall mixture critical temperature becomes greater than the reservoir temperature). This change in overall reservoir composition results in less revaporization at lower pressures. Fig. 2.17 shows the difference between constant-composition and “depletion” liquid-dropout curves.

2.5 Classification of Oilfield Systems

One might assume that the name used to identify a reservoir fluid should not influence how the fluid is treated as long as its physical properties are correctly defined. In theory this is true, but in practice we are usually required to define petroleum reservoir fluids as either “oil” or “gas.” For example, regulatory bodies require the definition of reservoir fluid for well spacing and determining allowable production rates and field-development strategy (e.g., unitization).

The classification of a reservoir fluid as dry gas, wet gas, gas condensate, volatile oil, or black oil is determined (1) by the location of the reservoir temperature with respect to the critical temperature and the cricondentherm and (2) by the location of the first-stage separator temperature and pressure with respect to the phase diagram of the reservoir fluid. Fig. 2.18 illustrates how four types of depletion reservoirs for the same hydrocarbon system are defined by the location of the initial reservoir temperature and pressure.

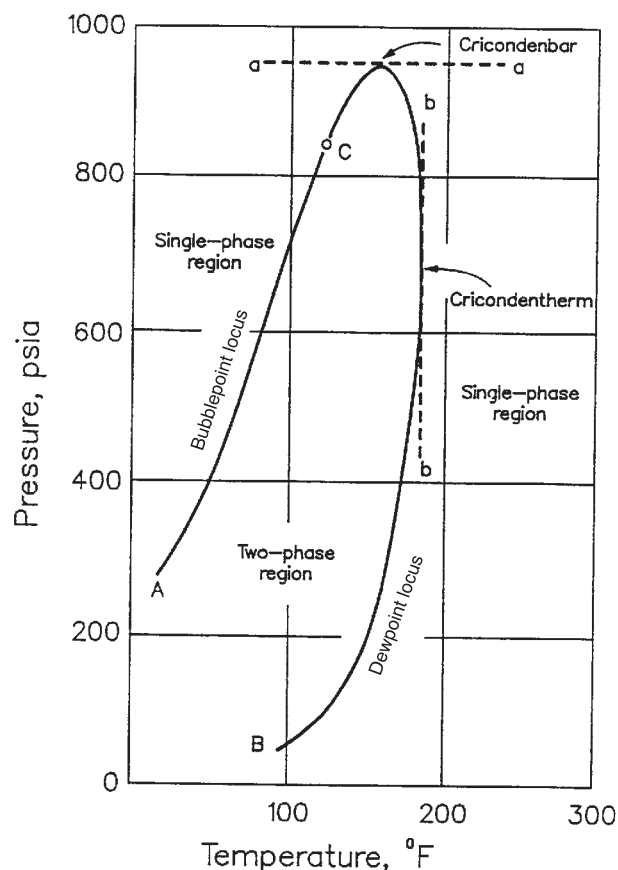


Fig. 2.9— p - T diagram for a C_2/n - C_7 mixture with 96.83 mol% ethane (from Standing²⁶).

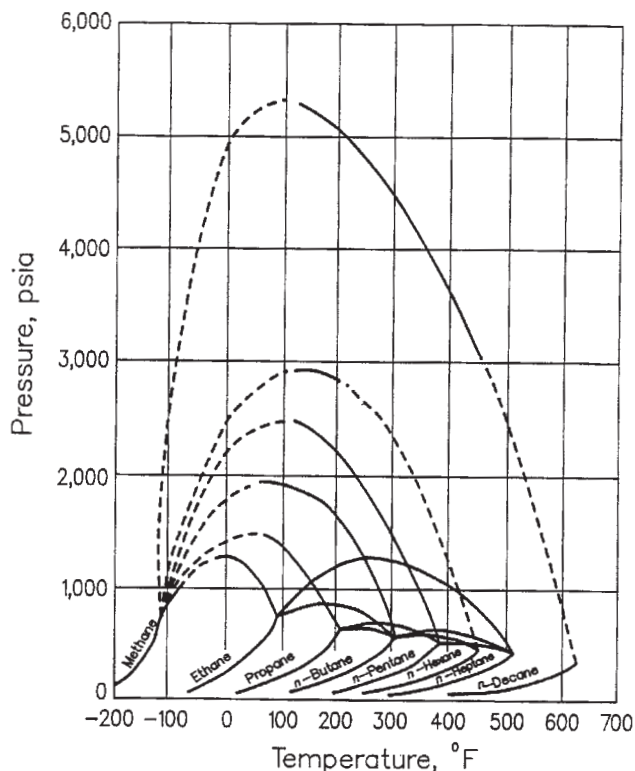


Fig. 2.11— p - T diagram for various hydrocarbon binaries illustrating the effects of molecular-weight differences on critical-point loci (after Brown *et al.*³¹).

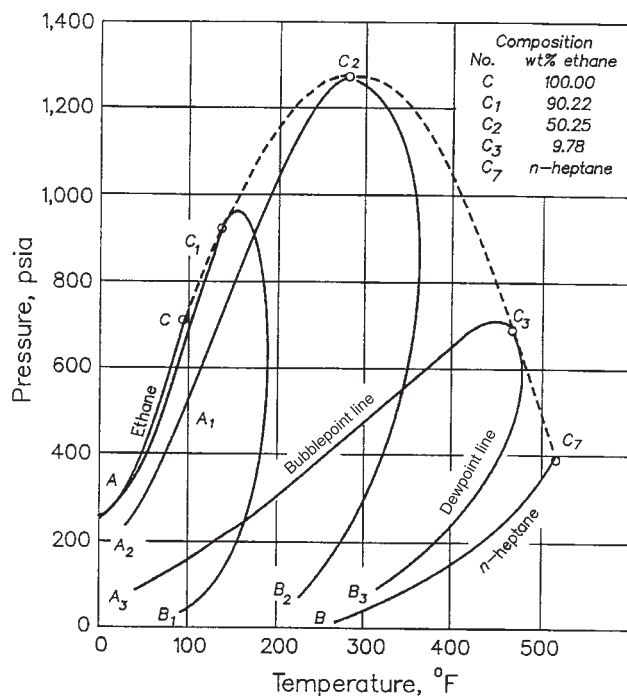


Fig. 2.10— p - T diagram for the C_2/n - C_7 system at various concentrations of C_2 (after Kay³⁰).

A reservoir fluid is classified as dry gas when the reservoir temperature is greater than the cricondetherm and surface/transport conditions are outside the two-phase envelope; as wet gas when the reservoir temperature is greater than the cricondetherm but the surface conditions are in the two-phase region; as gas condensate when the reservoir temperature is less than the cricondetherm and greater than the critical temperature; and as an oil (volatile or black oil) when the reservoir temperature is less than the mixture critical temperature.

For a given reservoir temperature and pressure, Fig. 2.19³⁸ shows the spectrum of reservoir fluids from wet gas to black oil expressed in terms of surface GOR's and oil/gas ratios (OGR's). A more quantitative classification is also given in Fig. 2.19 in terms of molar composition, by use of a ternary diagram. In the near-critical region, gas condensates have a C_{7+} concentration less than ≈ 12.5 mol% and volatile oils fall between 12.5 to 17.5 mol% C_{7+} .

Retrograde gas-condensate reservoirs^{26,39} typically exhibit GOR's between 3,000 and 150,000 scf/STB (OGR's from about 350 to 5 STB/MMscf) and liquid gravities between 40 and 60°API. The color of stock-tank liquid is expected to lighten from volatile-oil to gas-condensate systems, although light volatile oils may be yellowish or water-white and some condensate liquids can be dark brown

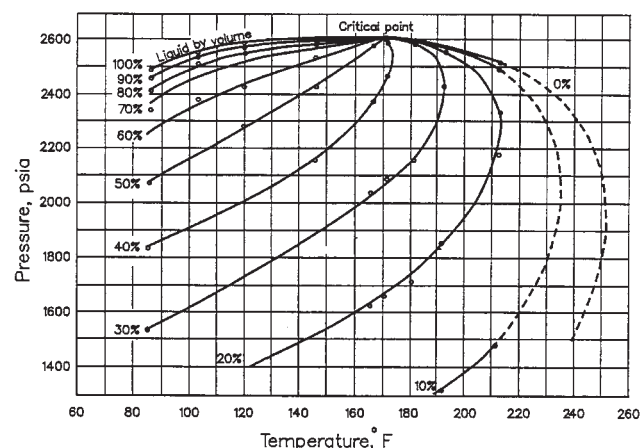


Fig. 2.12— p - T diagram for a gas-condensate system (after Katz *et al.*⁵).

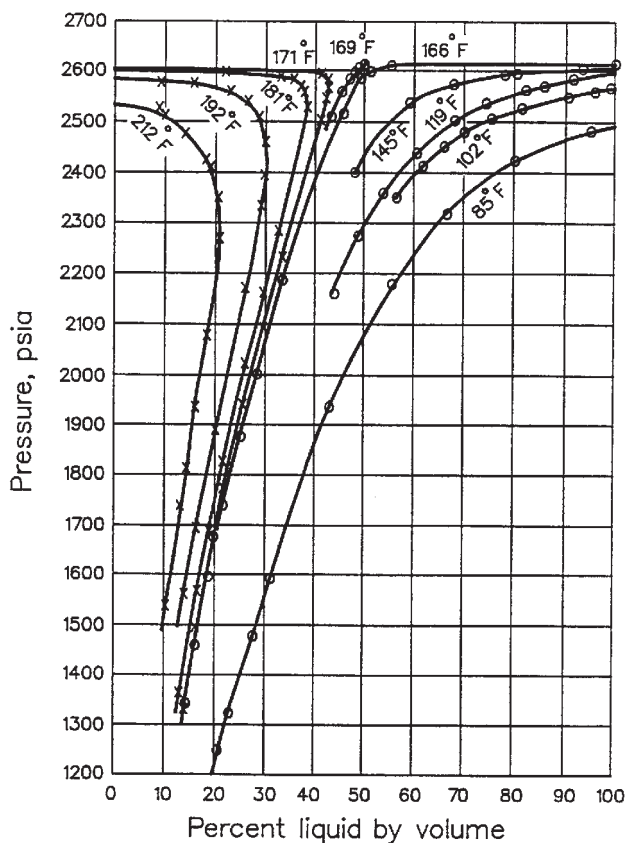


Fig. 2.13—Volume isotherms for the gas-condensate p - T diagram in Fig. 2.12 (after Katz *et al.*⁵)

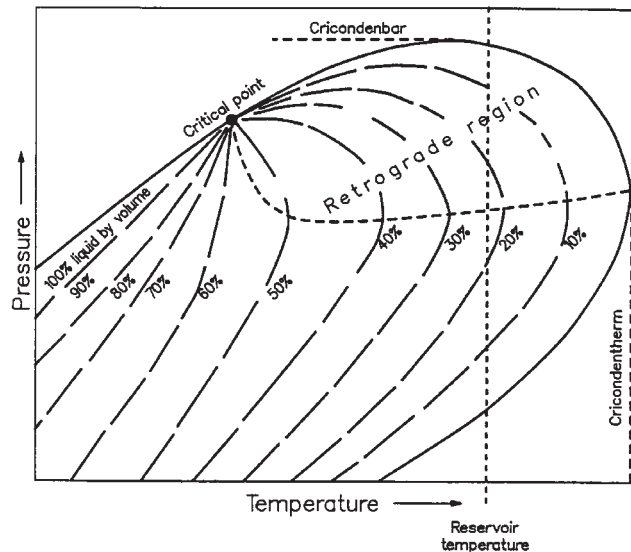


Fig. 2.14—Hypothetical p - T diagram for a gas condensate showing the isothermal retrograde region.

or even black. Color has not been a reliable means of differentiating clearly between gas condensates and volatile oils, but in general, dark colors indicate the presence of heavy hydrocarbons.

In some cases, for condensate recovery from a surface process facility, the reservoir fluid is mistakenly interpreted to be a gas condensate. Strictly speaking, the definition of a gas condensate depends only on reservoir temperature. The definition of a reservoir fluid as wet or dry gas depends on conditions at the surface. This makes differentiation between dry and wet gas difficult because any gas can conceivably be cooled enough to condense a liquid phase.

The classification of a fluid as an oil is unambiguous because the only requirement is that the reservoir temperature be less than the

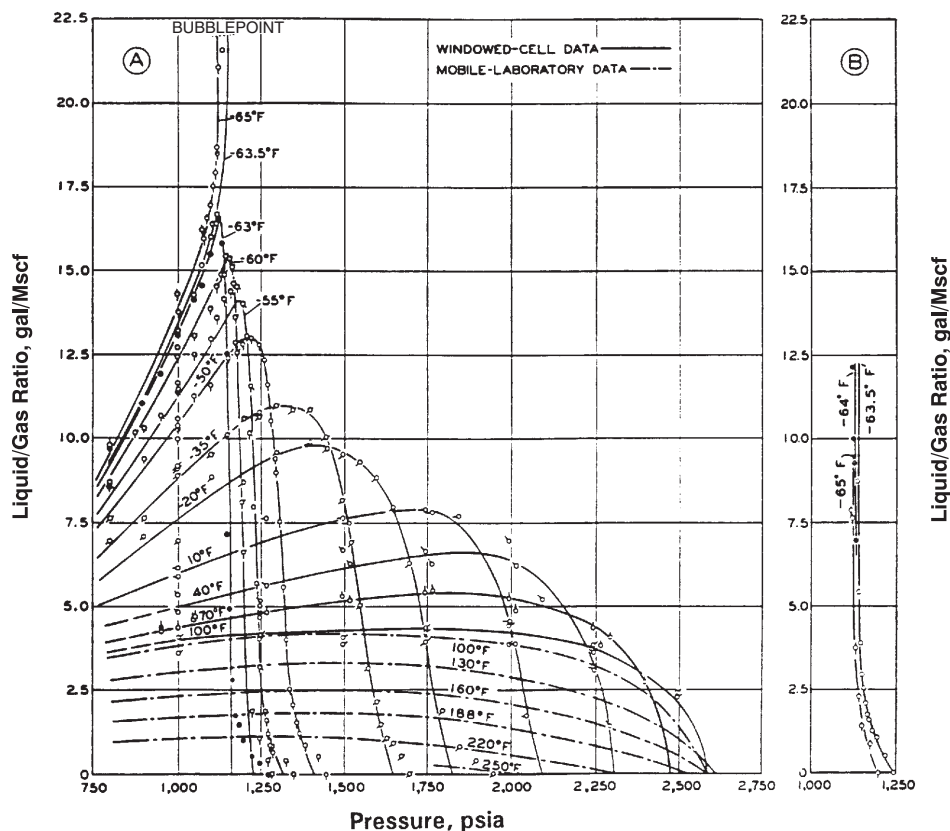


Fig. 2.15—Liquid volume (expressed as a liquid/gas ratio) behavior for a lean-gas-condensate system (from Eilerts *et al.*³⁵).

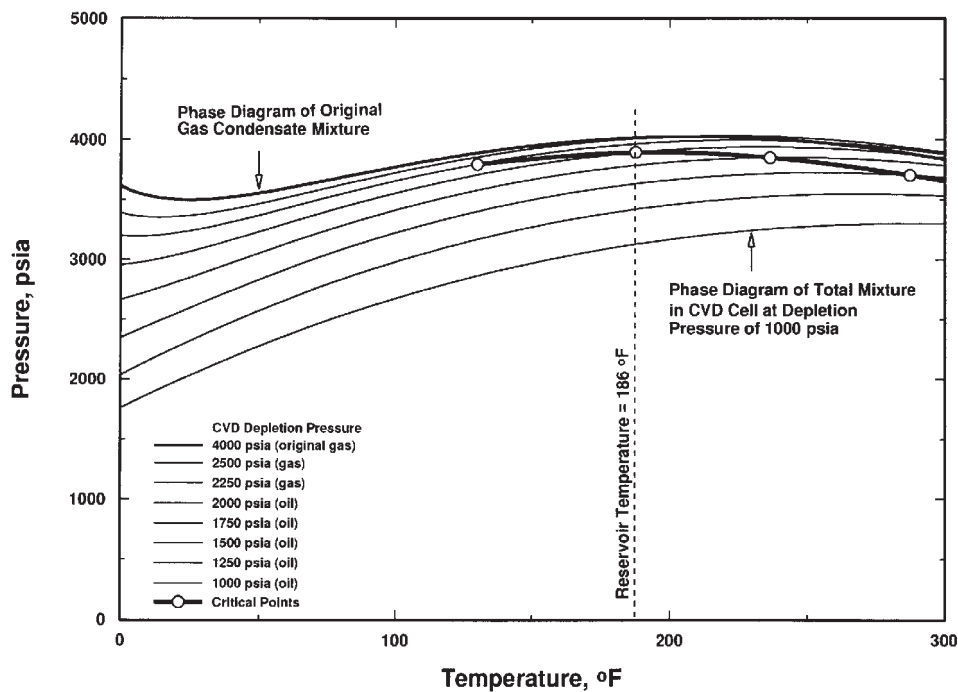


Fig. 2.16—Change in phase envelope during the depletion of a gas condensate.

critical temperature. However, the distinction between a black oil and a volatile oil is more arbitrary. Generally speaking, a volatile oil is a mixture with a relatively high solution gas/oil ratio. Volatile oils exhibit large changes in properties when pressure is reduced only somewhat below the bubblepoint. In an extreme case, the oil volume may shrink from 100 to 50% with a reduction in pressure of only 100 psi below the bubblepoint. Black-oil properties, on the other hand, exhibit gradual changes, with nearly linear pressure dependence below the bubblepoint.

Volatile oils typically yield stock-tank-oil gravities greater than 35°API, surface GOR's between 1,000 and 3,000 scf/STB, and FVF's (see Formation Volume Factors in Chap. 6) greater than ≈ 1.5 RB/STB. Solution gas released from a volatile oil contains significant quantities of stock-tank liquid (condensate) when this gas is produced to the surface. Solution gas from black oils is usually considered "dry," yielding insignificant stock-tank liquids when produced to surface conditions.

For engineering calculations, the liquid content of released solution gas is perhaps the most important distinction between volatile oils and black oils. This difference is also the basis for the modification of standard black-oil PVT properties discussed in Chap. 7. A reasonable engineering distinction between black oils and volatile oils can be made on the basis of simple reservoir material-balance calculations. If the total surface oil and gas recoveries calculated by a reservoir material balance with the standard black-oil PVT formulation are sufficiently close to the recoveries calculated by a compositional material balance, the oil can probably be considered a black oil (see Chap. 7). If calculated oil recoveries are significantly different, the reservoir mixture should be treated as a volatile oil by use of a compositional approach or the modified black-oil PVT properties outlined in Chap. 7. Several researchers^{40,41} have shown that a compositional material balance for depletion of volatile-oil reservoirs may predict from two to four times the surface liquid re-

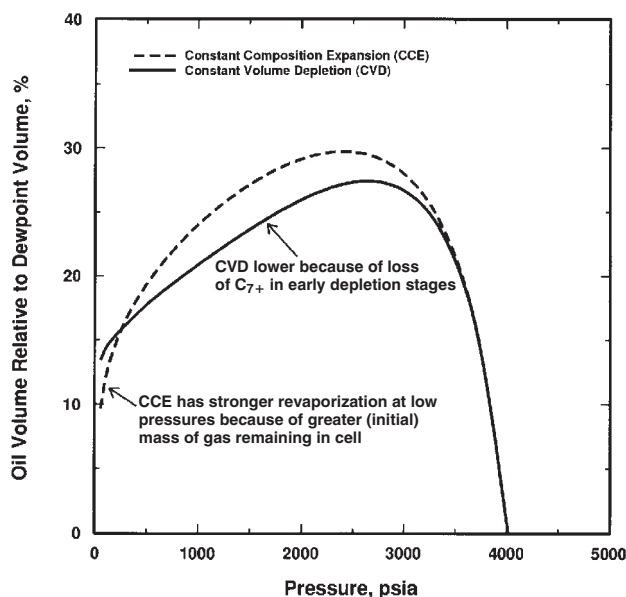


Fig. 2.17—Retrograde volumes for constant-composition and constant-volume depletion experiments.

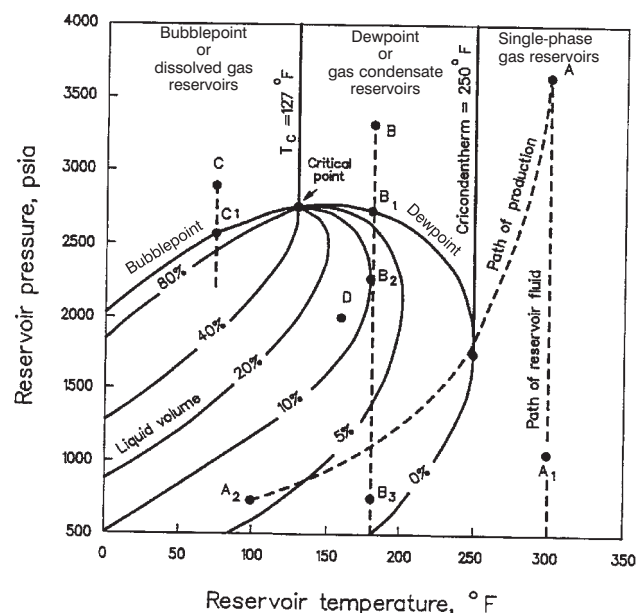


Fig. 2.18— p - T diagram of a reservoir fluid illustrating different types of depletion reservoirs.

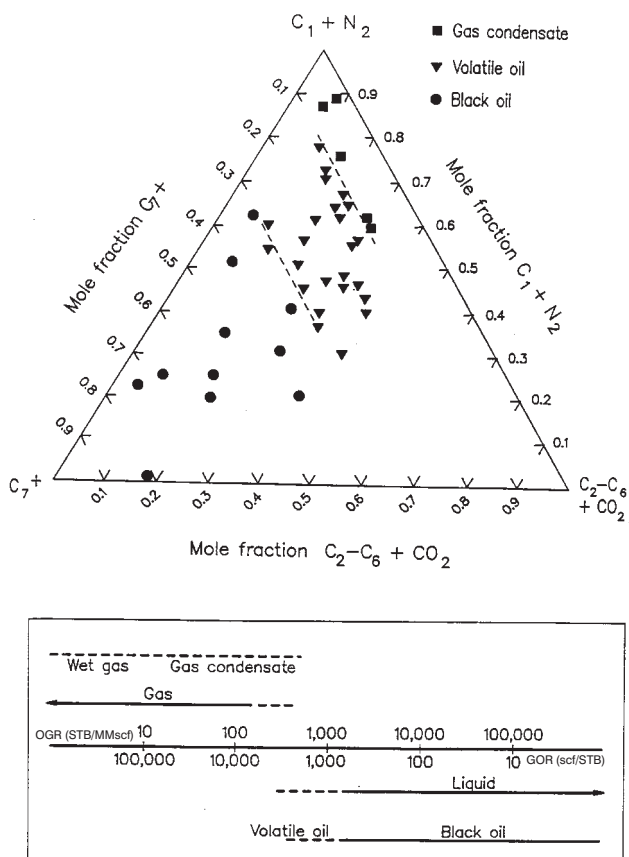


Fig. 2.19—Spectrum of reservoir fluids in order of increasing chemical complexity from wet gas to black oil (from Cronquist³⁸).

covery predicted by conventional material balances that are based on the standard black-oil PVT formulation.

Fluid samples obtained from a new field discovery may be instrumental in defining the existence of an overlying gas cap or an underlying oil rim. Referring to Fig. 2.20, if the initial reservoir pressure equals the measured bubblepoint pressure of a bottomhole or recombined sample, the oil is probably saturated at initial reservoir conditions. This implies that an equilibrium gas cap could exist at some higher elevation. Likewise, if the initial reservoir pressure is the same as the measured dewpoint pressure of a reservoir gas sam-

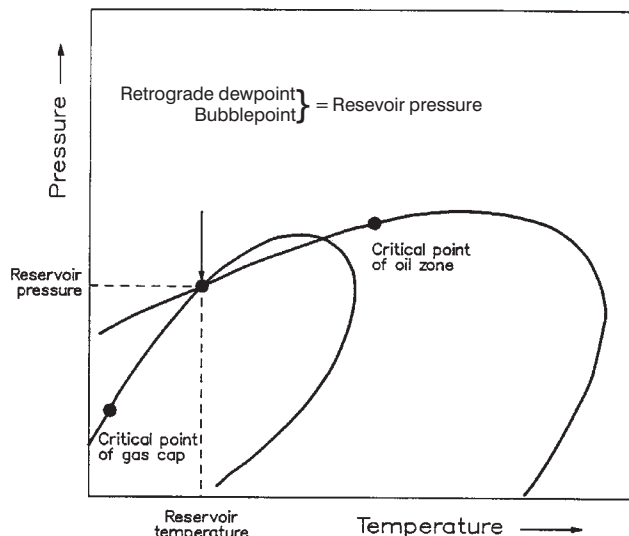


Fig. 2.20— p - T phase diagram of a gas-cap fluid in equilibrium with an underlying saturated oil.

ple, the gas is probably saturated at initial reservoir conditions, and an equilibrium oil could exist at some lower elevation.

Discovery of a saturated reservoir fluid will usually require further field delineation to substantiate the presence of a second equilibrium phase above or below the tested interval. This may entail running a repeat-formation-tester tool to determine the fluid-pressure gradient as a function of depth, or a new well may be required up dip or down dip to the discovery well. Representative samples of saturated fluids may be difficult to obtain during a production test.⁴² Standing²⁶ discusses the situation of an undersaturated gas condensate sampled during a test where bottomhole flowing pressure drops below the dewpoint pressure. The produced fluid, which is not representative of the original reservoir fluid, may have a dewpoint equal to initial reservoir pressure. This situation would incorrectly imply that the reservoir is saturated at initial conditions and that an underlying oil rim may exist.

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SI Metric Conversion Factors

$^{\circ}\text{API}$	$141.5/(131.5 + ^{\circ}\text{API})$	$= \text{g/cm}^3$
bbl	$\times 1.589\,873$	$\text{E} - 01 = \text{m}^3$
ft^3	$\times 2.831\,685$	$\text{E} - 02 = \text{m}^3$
$^{\circ}\text{F}$	$(^{\circ}\text{F} - 32)/1.8$	$= ^{\circ}\text{C}$
gal	$\times 3.785\,412$	$\text{E} - 03 = \text{m}^3$
lbm	$\times 4.535\,924$	$\text{E} - 01 = \text{kg}$
psi	$\times 6.894\,757$	$\text{E} + 00 = \text{kPa}$