

The Properties of Petroleum Fluids

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Preface

There is quite a change from the second edition of *The Properties of Petroleum Fluids* to this third edition. There are many more gas condensate fields in the petroleum industry today than when the second edition was prepared, so two chapters describing gas condensates have been added. For completeness, a chapter on volatile oils has also been added. The previous chapter 1 has been divided into two chapters; one is a brief review of organic chemistry, and the other specifically addresses the components of petroleum, its origin, and a method of determining its composition. The Phase Behavior chapter has been simplified, and the Properties of Oilfield Waters chapter has been extended.

In order to include this information, several chapters of the second edition have been removed. These include chapters on equations of state, gas-liquid equilibria, and equation-of-state calculations. The information in these chapters has been amplified and will appear in another book.

The word *petroleum* in most English-language dictionaries contains the word *liquid* in its definition. This is *not* the way this word is used in this book!

Petroleum is a naturally occurring mixture of predominately organic chemicals. Petroleum can exist in a petroleum reservoir as a *liquid*; during production some of the petroleum is converted to gas, either in the reservoir or on the trip to the surface. This liquid is often referred to as oil. Or petroleum can exist in a reservoir as a gas; during production some of this is converted to liquid, either in the reservoir or on the trip to the surface. This liquid should be called *condensate*. So, the word petroleum as used here (and in the petroleum industry) can either be a liquid or a gas or both.

It is interesting that approximately one-half of the petroleum liquid reported as oil production in the United States is really condensate.

This book will use the terminology *molecular weight* to describe this physical property due to common usage in the petroleum industry. Apparently, chemists have decided that *molar mass* is better terminology for this property.

The author had two uses in mind when preparing this book. First and most important, the book was designed to be used as a textbook in an early course in petroleum engineering. This will prepare students for the various applications of fluid properties that will occur throughout their undergraduate studies. Second, the book can be used by practicing petroleum engineers as a reference for determining values and uses of fluid properties required in their work.

Accordingly, there are some sections in this that which may be of use to a practicing petroleum engineer but are not especially necessary for an undergraduate petroleum engineering student. These sections are generally located at the ends of

various chapters. An instructor using this book as a textbook may decide to skip some of these sections in order to have time to fully explore the more important material.

For instance, the last couple of sections in chapter 2 and the last three sections in chapter 5, starting with Heating Value, may be deleted from the undergraduate program. Also, the last three sections of chapter 7, starting with Other Uses of G_{av} ; the last three sections of chapter 10, starting with Coefficient of Isobaric Thermal Expansion of a Liquid; and the last two sections of chapter 14 may be left out of undergraduate studies. Also, if time is still short, chapter 15 may be skipped in its entirety; many petroleum engineers go through an entire career without encountering a volatile oil.

I am indebted to Nancy Luedke for creating many of the figures in the book. She does superb work, and working with her is a pleasure. Mary Lu Epps made many useful contributions, from messing with the stupid computer to reading some of the text and providing useful comments. Thank you, Mary Lu.

A number of people struggled with the text, especially with the many equations. These include Kathy Beladi, Carol Mumford, Kate Brady, and Alexis N'zoane. Thank you for your patience and your excellent results. The people with the publisher did a great job with the equations.

Dr. Peter Valko of Texas A&M University participated in either preparing or evaluating virtually all of the correlation equations presented here. Thank you, Peter!

A Brief Review of Organic Chemistry

Petroleum engineers spend their professional lives working with mixtures of organic chemicals. Thus there needs to be an understanding of the different types of organic compounds that make up the petroleum mixtures. The nomenclatures, the relationships one to another, the degrees of volatility, and the degrees of chemical reactivity are all important. Therefore, the study of the properties of petroleum reservoir fluids begins with a review of the behaviors of the compounds that make up these naturally occurring petroleum mixtures (i.e., a brief study of organic chemistry).

Organic Chemistry

Organic chemistry is the chemistry of compounds of *carbon*. The misleading name *organic* is a relic of days when chemical compounds were divided into two classes, *inorganic* and *organic*, depending on their source. Inorganic compounds were obtained from minerals. Organic compounds were obtained from material produced by living organisms.

However, organic compounds now can be produced in the laboratory, so this definition has lost some of its significance. Nevertheless, the term *organic* is still pertinent because the chemistry of carbon compounds is more important to everyday life than that of any other atom.

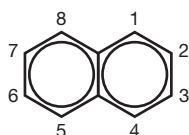
The compounds derived from organic sources have one thing in common: all contain the element carbon. Today most compounds of carbon are synthesized rather than obtained from plant and animal sources. Organic compounds are usually synthesized from other organic compounds, although making organics from inorganic substances such as carbonates or cyanides is possible.

Two of the major sources of organic material from which organic compounds can be obtained are petroleum and coal. Both of these sources are organic in the old sense because both are products of the alteration of the chemical compounds from animals and plants. Chemicals from these sources are used as building blocks for the more complicated organic compounds so important to civilization today.

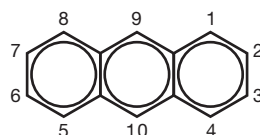
The main reason that there is an entire branch of chemistry centered on carbon is the strength of carbon-to-carbon bonds, which makes long chains and rings of carbon atoms possible.

Fused rings in aromatic hydrocarbons

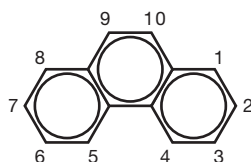
A wide range of aromatic compounds have benzene rings with common ortho positions (i.e., sharing two carbon atoms). These are called *fused rings* (also sometimes called *condensed rings*). Several of the simpler fused aromatics are shown below. Note the numbering of the carbon atoms for the purpose of locating substituent groups. Fused aromatics have the general formula $C_{4r+2}H_{2r+4}$ for rings without substituents, where r = number of rings.



naphthalene



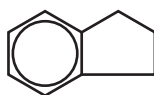
anthracene



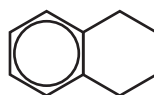
phenanthrene

Cycloalkanoaromatics

Many of the large molecules found in petroleum are fused rings consisting of cycloparaffins and aromatics. These compounds are called *cycloalkanoaromatics* or *naphtheno-aromatics*. The two smallest compounds of this class are lindane and tetrahydronaphthalene (tetralin).



lindane

tetralin
(tetrahydronaphthalene)

For a pure substance, the critical temperature may be defined as the temperature above which the gas cannot be liquefied, regardless of the pressure applied. Similarly, the critical pressure of a pure substance is defined as the pressure above which liquid and gas cannot coexist, regardless of the temperature. These definitions of critical properties are invalid for systems with more than one component.

The normal boiling point. The temperature on the vapor-pressure line at atmospheric pressure is called the *normal boiling point* or *normal boiling point temperature*, T_B ; it is also sometimes referred to as *boiling point*. The boiling point temperature is a good indicator of the *volatility* of a substance. The word *normal* in this instance indicates that the temperature is determined on the vapor pressure at *atmospheric pressure*.

The triple point. Point T on the vapor-pressure line is called the *triple point*. This point represents the one set of pressure-temperature conditions at which solid, liquid, and gas coexist under equilibrium conditions.

The sublimation-pressure line. At temperatures below the triple-point temperature, the extension of the vapor-pressure line divides the conditions for which the substance is solid from the conditions for which the substance is gas. This line is also called the *sublimation-pressure line*. This line extends to a temperature of absolute zero and a pressure of absolute zero.

The melting point line. The *melting point line* is the nearly vertical line extending above the triple point. This line separates conditions for which the substance will be a solid from conditions for which the substance will be a liquid. Pressure-temperature points that fall exactly on this line indicate a two-phase system—in this case, coexistence of solid and liquid. Phase diagrams for some pure materials show other lines within the solid region, indicating changes of phase of the solid brought about by changes in crystalline structure. The upper limit of the melting point line has not been observed experimentally for any pure substance.

Use of phase diagrams

In order to gain a better understanding of the usefulness of phase diagrams, consider a cylinder in which temperature can be controlled and volume varied by injection or removal of mercury as shown in figure 3-2 (mercury is used since it acts like a piston that will not leak).

Constant temperature

Figure 3-2A shows that a pure substance has been trapped in the cylinder at pressure p_1 and at some temperature between the critical temperature and the triple point of the substance. The temperature will be held constant and the volume increased by removing mercury, thereby causing pressure to decrease. The removal of mercury simply represents the movement of a non-leaking piston.

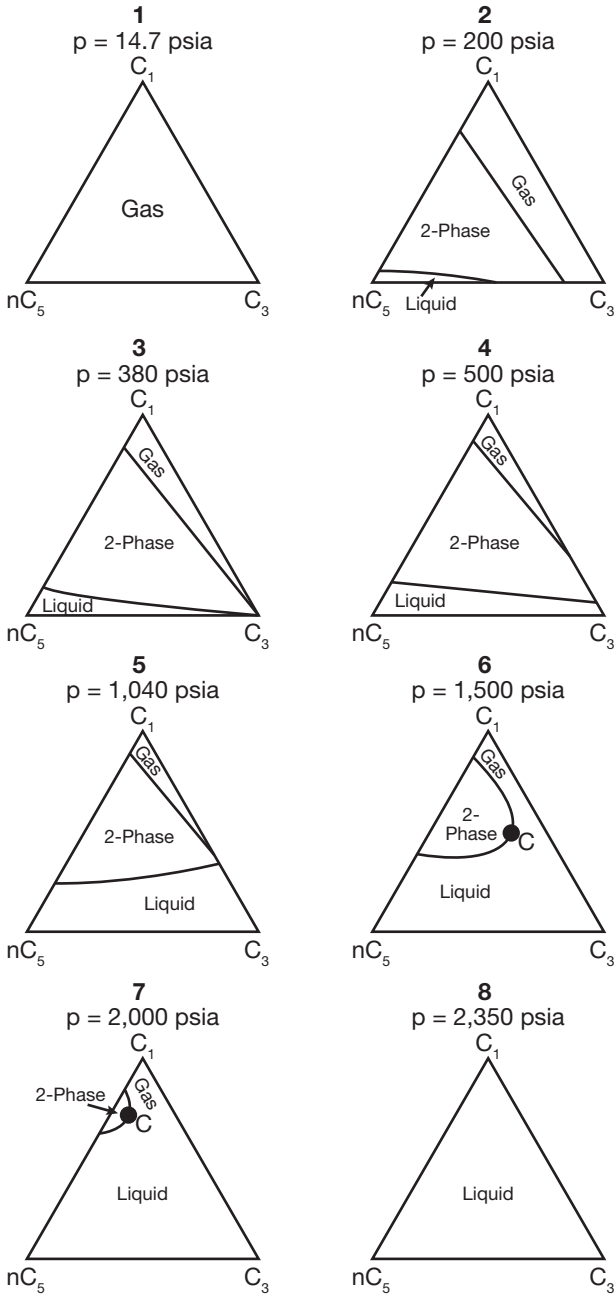


Fig. 3-24. Ternary phase diagrams of mixtures of methane, propane, and n-pentane at 160°F and various pressures, showing typical changes in shapes of the diagrams as pressure is changed (diagram numbers correspond to the numbered points on figure 3-25)

Typical gas condensate phase diagram

The two-phase region in the phase diagram of a typical gas condensate is somewhat smaller in temperature than for oils, and the critical point is further down the left side of the two-phase region. Also, the iso-vol lines with lower liquid volumes are much more widely spaced than they are for the oils. These changes are a result of gas condensates containing far fewer heavy components than the oils.

The phase diagram of a gas condensate has a critical temperature less than reservoir temperature and a cricondentherm greater than reservoir temperature (see fig. 4-4). Initially, the gas condensate is totally gas in the reservoir (point 1). As reservoir pressure decreases, gas condensate exhibits a dewpoint (point 2). As pressure is reduced, liquid condenses from the gas to form a free liquid in the reservoir, a retrograde condensate. This condensate normally will not flow to the wellbores and thus cannot be produced by primary production.

Often the initial pressure of a gas condensate reservoir is equal to the dewpoint pressure of the gas. This implies that there is an oil zone in the reservoir, a volatile oil often with very small volume.

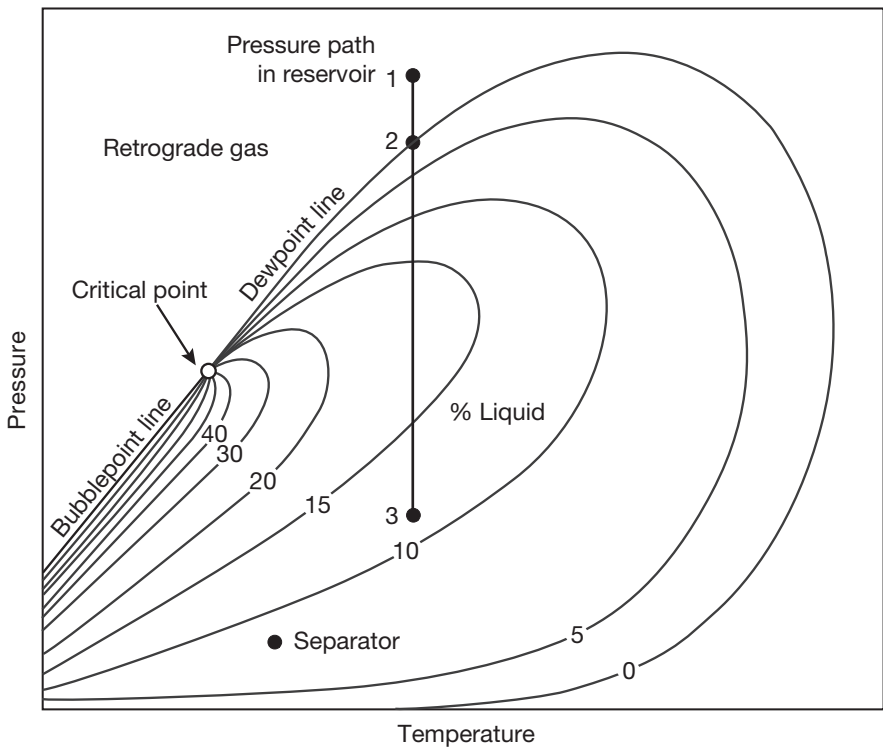


Fig. 4-4. Phase diagram of a typical gas condensate with line of isothermal reduction of reservoir pressure, line 123, and surface separator conditions