



高等学校教材

# Physical Properties of Petroleum Reservoir

油层物理学

李爱芬 张志英 主编

中国石油大学出版社

# Reservoir



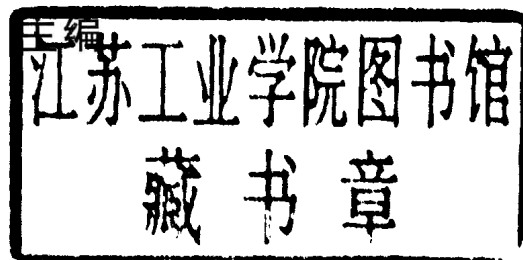
TEACHING MATERIALS FOR COLLEGE STUDENTS

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# PREFACE

This book presents basic concepts, theories and laboratory procedures as related to the reservoir fluids and the porous rock properties and their interactions. The properties of the reservoir rocks and reservoir fluids govern the rates of fluid flow and therefore affect the oil or gas recovery from petroleum reservoirs. Profound understanding of the rock and fluid properties will help the petroleum engineers understand the phenomena occurring in the reservoir during the petroleum production, which are fundamental to engineering analyses of petroleum reservoirs.

Chapter 1 introduces the composition of reservoir fluids, the phase behavior of reservoir fluid and the properties of oil, gas and water. Chapter 2 presents the very important rock properties for petroleum engineering: porosity and permeability. Fluid saturation and rock compressibility are also discussed. The definitions as well as the determination methods are presented in this chapter. Chapter 3 deals with the surface properties of reservoir rock and fluid system. It discusses the interfacial tension, capillary pressure, relative permeability, etc. Chapter 4 introduces the factors which affect the oil recovery during production. The commonly used EOR methods in petroleum industry are included in this chapter too. Exercises and vocabulary are also prepared in this book.

Although this book was primarily organized and prepared for use as a textbook, it also will serve as a reference book for petroleum engineers.

This book is rewritten based on the teaching materials written by Zhang Zhiying in 2004. Through several years applying and consummating, and by referring to many books published in petroleum field, the new book is completed. Chapters 1 and 3 are written by Li Aifen, Chapters 2 and 4 are written by Zhang Zhiying, and the whole book is checked by Li Aifen.

The authors are indebted to Mr. Lei Zhanxiang, who prepared the vocabulary for this book, and also indebted to many authors who have contributed to the petroleum literature in various publications. The authors are also grateful to all the people who give kind help in preparing this book.

**Li Aifen**  
**Zhang Zhiying**

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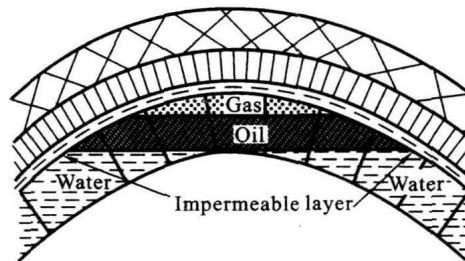
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# Chapter 1

# Properties of Reservoir Fluids

A reservoir is a porous and permeable subsurface formation containing reservoir fluids. It is bounded by a barrier of impermeable rock and often by an aquifer barrier, and characterized by only one natural pressure system (Figure 1.1). The reservoir fluids refer to the crude oil, natural gas and water contained in the pores or interstices of the reservoir rocks.



**Figure 1.1** Cross-section of a typical hydrocarbon reservoir.

The crude oil and natural gas are both complex mixtures of various hydrocarbons. The reservoir fluids we encounter are usually under high pressure and high temperature. At the same time, the crude oil usually contains a large amount of dissolved gas, thus the physical properties of the reservoir fluids are quite different from those of the fluids at the surface. The composition of the petroleum fluids is the internal factor affecting their PVT properties, while the pressure and temperature are the external factors.

In this chapter, the change in phase behavior caused by the changes in the temperature and pressure will be discussed together with the solution of gas in oil and separation of gas from oil. The elemental properties of petroleum fluids (oil, water and gas) will be discussed also.

## SECTION 1 PHASE BEHAVIOR OF HYDROCARBON SYSTEM

Petroleum is a mixture of naturally occurring hydrocarbons and nonhydrocarbons which may

exist in the solid, liquid or gaseous states, depending upon the conditions of pressure and temperature to which it is subjected. Virtually all petroleum is produced from the earth in either liquid or gaseous form, and commonly, these materials are referred to as either crude oil or natural gas, depending upon the state of the hydrocarbon mixture.

## 1 Chemical Composition, Commercial Properties of Petroleum and Its Classification

### 1.1 Chemical Composition of Petroleum

The petroleum compounds that consist of only hydrogen and carbon are known as hydrocarbons. The hydrocarbons we usually encounter in reservoirs include alkanes, cycloalkanes and aromatic hydrocarbons. The alkanes are the main components of petroleum, and have the general formula  $C_nH_{2n+2}$ . These alkanes are also called paraffin hydrocarbons. Petroleum engineers normally call these paraffins.

When the mixture contains mainly small molecules ( $C_1 - C_4$ ), it is a gas at normal temperature and pressure. When the mixture contains larger molecules ( $C_5 - C_{16}$ ), it is a liquid at normal conditions. The mixture is a solid when the  $C_{16+}$  plus are the main components at normal conditions.

Petroleum also contains compounds in which sulfur, oxygen, and/or nitrogen atoms are combined with carbon and hydrogen. These elements usually are combined with the complex ring structures that make up the large molecules of petroleum. Table 1.1.1 gives the main compounds of nonhydrocarbons. Although the quantities of these nonhydrocarbons are very small, they exert great influences on some of the properties of petroleum, such as color, specific gravity, viscosity and interfacial tension.

**Table 1.1.1** Main compounds of nonhydrocarbons.

Compounds	Components	Note
Oxygen compounds	Phenol, naphthenic acid, etc.	
Sulfur compounds	Mercaptans, alkyl sulfides, thiophene, etc.	
Nitrogen compounds	Pyridine, pyrrole, etc.	
Large molecules	Resins and asphaltenes	Surfactant

### 1.2 Commercial Properties of Petroleum

Commercial properties of a petroleum liquid is determined by its composition and can be determined quickly through measurement of the following physical characteristics: specific gravity, viscosity, freezing point, asphalt content, sulfur content, resins content, asphaltenes content and distilled fractions of petroleum. Table 1.1.2 gives the typical properties of crude oils from some oil fields in China.

Table 1.1.2 Properties of some crude oils.

Properties	Specific gravity ( $D_4^{20}$ )	Dynamic viscosity ( $\text{cm}^2/\text{s}$ )		Freezing point ( $^{\circ}\text{C}$ )	Wax content (%)	Resins content (%)	Asphaltenes content (%)	Sulfur content (%)	Residuum (%)	Boiling point ( $^{\circ}\text{C}$ )	Distilled fractions (weight percent)	
		50 $^{\circ}\text{C}$	70 $^{\circ}\text{C}$								<200 $^{\circ}\text{C}$	<300 $^{\circ}\text{C}$
Crude oils												
Daqing	0.875 3	17.40	—	24	28.6	13.3	—	0.15	2.5	88	14	28
Shengli	0.884 5	37.69	17.95	33	17.9	18.3	3.1	0.47	5.5	79.5	9	20
Gudao	0.954 7	427.5	157.5	-12	0	27.5	6.6	2.25	8.95	15.8	1.9	11.2
Dagang	0.917 4	51.97	25.55	-12	6.17	13.98	6.27	0.13	4.81	97	4.0	20.5
Kelamayi	0.869 9	19.23	—	-50	2.04	12.6	0.01	0.13	3.7	58	18	35
Yumen	0.853 0	12.9	—	-15.5	8.3	22.6	—	—	—	—	—	—
Jiangnan	0.974 4	—	62.2	21	3.8	51	9.6	11.8	9.5	89	5	21.8
Liaohu	0.903 7	37.4	—	-7	4.73	17.6	0.15	0.26	6.4	—	—	—
Chuanzhong	0.839 4	12.3	—	30	18.1	3.4	—	—	—	—	—	—
Renqiu	0.889 3	63.5	—	33	22.6	20.7	—	2.35	—	14.8	—	—

$D_4^{20}$  refers to the ratio of the density of crude oil at one atmospheric pressure and 20  $^{\circ}\text{C}$  to the density of water at one atmospheric pressure and 4  $^{\circ}\text{C}$ .

### 1.3 Classification of Petroleum

The specific gravity of crude oil will increase with the molecular size. Usually the oil reservoir and gas reservoir can be classified according to the specific gravity of crude oil and natural gas at surface conditions (Tables 1.1.3 and 1.1.4).

**Table 1.1.3** Classification of oil reservoir.

Specific gravity	0.60 – 0.70	0.71 – 0.80	0.81 – 0.94	> 0.94
Types of oil reservoirs	Condensate oil	Critical oil	Normal oil	Heavy oil

**Table 1.1.4** Classification of gas reservoir.

Specific gravity	0.60 – 0.70	0.71 – 0.80	> 0.80
Types of gas reservoirs	Dry gas	Condensate gas	Wet gas

## 2 Basic Concepts in Study of Phase Behavior

Oil and gas are naturally existing hydrocarbon mixtures, and quite complex in chemical composition which exist at high temperatures and pressures in the reservoir. On production and capture of hydrocarbons at surface, the temperature and pressure of the mixture are reduced. The state of the hydrocarbon mixture at the surface conditions depends upon the composition of the hydrocarbon fluid as it is produced from the well and upon the pressure and temperature at which it is captured. Furthermore, the fluid remaining in the reservoir at any stage of depletion undergoes physical changes as the pressure is reduced by producing quantities of oil and gas from the reservoir. It is necessary to study the physical properties of these naturally existing hydrocarbons and in particular, their variation with pressure and temperature.

### 2.1 Definitions

Before we examine the effect of temperature and pressure on hydrocarbon systems, we will first define some terms:

**System.** Amount of substances within given boundaries under specific conditions composed of a number of components. Everything within the boundaries is part of the system and that existing outside the boundaries is not part of the system. If anything moves across the boundaries, then the system will have changed.

**Phase.** This term defines any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces. A phase can consist of several components. The phases can interchange in a system depending on its temperature and pressure.

**Components.** The substances present in the system, such as methane, ethane, propane, butane, etc. in the petroleum.

**Composition.** The components and their relative quantities of a system, expressed in percentage.

**Equilibrium.** When a system is in equilibrium, then no changes take place with respect to time in the measurable physical properties of the separate phases.

The physical behavior of hydrocarbons when pressure and temperature changes can be explained in relation to the behavior of the individual molecules making up the system. Temperature, pressure and intermolecular forces are important aspects of physical behavior.

The **temperature** is an indication of the kinetic energy of the molecules. It is a physical measure of the average kinetic energy of the molecules. The kinetic energy increases as heat is added. This increase in kinetic energy causes an increase in the motion of the molecules which also results in the molecules moving further apart.

The **pressure** reflects the frequency of the collision of the molecules on the walls of its container. As more molecules are forced closer together, the pressure increases.

Intermolecular forces are the attractive and repulsive forces between molecules. They are affected by the distance between the molecules. The attractive forces increase as the distance between the molecules decreases until however the electronic field of the molecules overlap, and then further decrease in distance causes a repulsive force, which increases as the molecules are forced closer together.

The molecules in gases are widely spaced and attractive forces exist between the molecules, whereas for liquids where the molecules are closer together there is a repelling force which causes the liquid to resist further compression.

The phase behavior of a system is dependent not only on its composition, but also on the temperature and pressure conditions.

## 2.2 Phase Diagram

For a constant-composition system, its phase behavior is a function of the pressure ( $p$ ), temperature ( $T$ ) and specific volume ( $V$ ). The diagram which shows the conditions of temperature and pressure for which different phases exist is the **phase diagram**.

Phase diagrams are useful ways of presenting the behavior of a system. They are usually plots of pressure versus volume ( $p$ - $V$  diagram), or pressure versus temperature ( $p$ - $T$  diagram).  $p$ - $T$  diagram is the most often used one in petroleum industry.

## 3 Phase Diagrams of One-, Two- and Multicomponent System

The hydrocarbon fluids of interest in reservoir systems are composed of many components. However, in understanding the phase behavior of these systems it is convenient to examine first on

the behavior of single- and two-component systems.

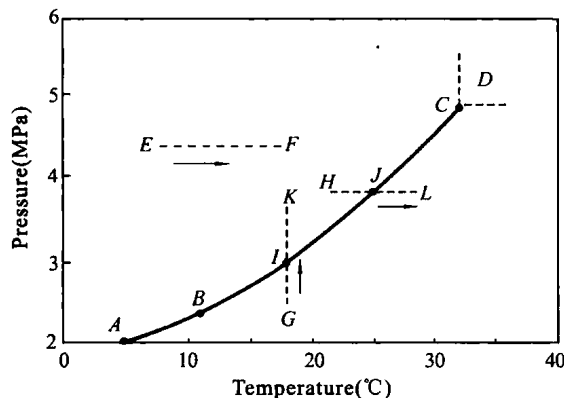
The physical properties of a single-component hydrocarbon and its behavior when it subjected to changes in pressure and temperature are qualitatively similar to those of more complex system. It is convenient, therefore, to introduce the basic definitions and to review the concepts of thermodynamics in terms of a single hydrocarbon.

We will first consider systems which consist of a single, pure substance. After a careful examination of the phase behavior of a pure substance, we will discuss the behavior of systems which contain two or more components and point out the differences between multicomponent behavior and pure substance behavior.

### 3.1 Phase Behavior of One-component System

#### 3.1.1 $p$ - $T$ diagram for one-component system

Pressure-temperature diagram is a graph of pressure plotted against temperature showing the conditions under which the various phases of a substance will be present. Figure 1.1.1 shows the phase diagram for ethane.



**Figure 1.1.1** Pressure-temperature diagram for ethane.

The curve plotted is a vapor-pressure line. At the conditions of pressure and temperature specified by the curve, two phases, liquid and vapor, coexist in equilibrium.

The point C, at which the vapor-pressure curve terminates, is called the critical point. The temperature and pressure represented by this point are called the critical temperature,  $T_c$ , and the critical pressure,  $p_c$ . For a single-component system, the critical point has the highest values of pressure and temperature at which two phases can coexist in equilibrium.

Pressure-temperature points which lie above this line indicate conditions at which the substance is a liquid. Similarly, points below the vapor-pressure line represent conditions at which the substance is a gas.

At conditions indicated by point E, the substance is a liquid. As temperature is increased to point F, the substance is still a liquid at constant pressure.

Consider a process starting at point *G* at which ethane is a gas. Temperature is held constant, and pressure is increased to point *I*. At this point, liquid begins to form, gas and liquid coexist. When the pressure is further increased to point *K*, ethane is in the liquid state. Point *I* is called the **dew point**. Dew point is then defined as the point at which only a small drop of liquid exists.

Now consider the process of decreasing pressure at constant temperature. See line *KIG* in Figure 1.1.1. At point *K*, the substance is a liquid. As pressure is decreased to point *I*, a few molecules will leave the liquid and form a small bubble of gas. This point is called the **bubble point**. It is defined as the point at which a small gas bubble exists. When the pressure is reduced to point *G*, the substance comes to the gas region.

When the temperature increases from point *H* to point *J* at constant pressure, the vaporization of ethane can be observed, the point *J* is called the bubble point. While the temperature decreases from point *L* to point *J*, the condensation of liquid from the ethane gas can be observed, point *J* is the dew point. Therefore, for a pure substance at a certain temperature, the bubble point coincides with the dew point on the vapor-pressure line. The vapor-pressure line is the locus of both the bubble points and the dew points.

The following characteristics can be observed from the  $p$ - $T$  phase diagram of a pure substance:

(1) It is a single line—the vapor-pressure line. It is the locus of both the bubble points and the dew points of the pure substance.

(2) The phase diagram is divided into three regions: gas region, liquid region and two-phase region.

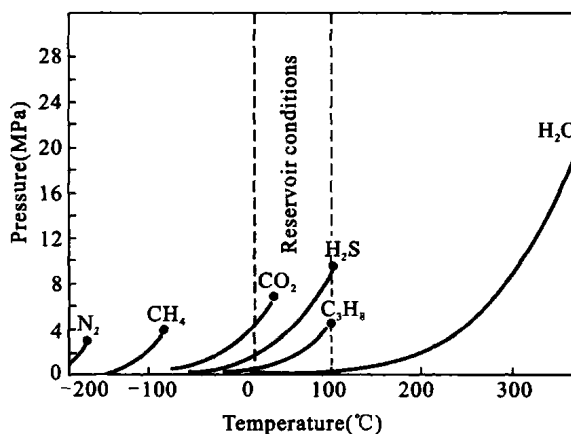
(3) The critical point has the highest pressure and highest temperature at which gas and liquid can coexist in equilibrium.

Figure 1.1.2 shows the phase diagram for several pure substances. They are all single lines. The region between the two dashed lines indicates the normal reservoir conditions. It can be observed that the critical points of propane and carbon dioxide fall in this region, while the critical points of methane and nitrogen locate are far from this region. That is why the propane and carbon dioxide are usually selected for miscible flooding.

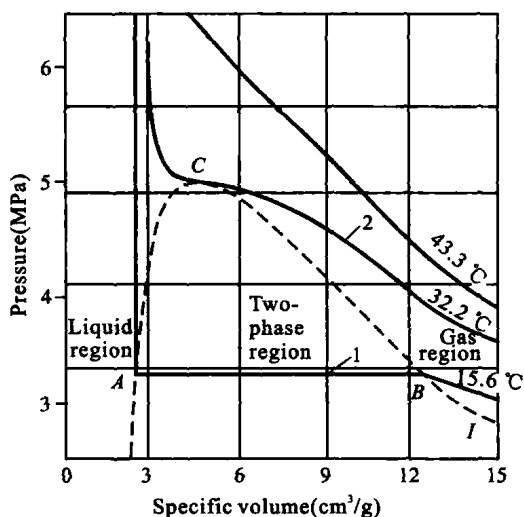
### 3.1.2 Pressure-volume diagram for a pure substance

The process described in Figure 1.1.1 may be presented in the form of a pressure-volume diagram. Figure 1.1.3 shows the  $p$ - $V$  diagram for ethane.

Let's examine the isothermal process indicated by line 1 (15.6 °C). At initial conditions (point *I*), ethane exists as a gas. When the gas volume is decreased at constant temperature, gas pressure will increase until it reaches point *B* on the diagram, where liquid begins to condense. This is the dew point. As the volume of the system is decreased further, more liquid condenses, while the pressure remains constant. This condensation process is represented by the horizontal line *BA*. It is the conditions at which the liquid phase and the gas phase coexist. At point *A*, traces of gas remain and the bubble point is encountered. From this point on, a small decrease in volume will result in a sharp rise in pressure. This behavior evidently reflects the low compressibility of the liquid phase.



**Figure 1.1.2** Phase diagram for several gases.



**Figure 1.1.3**  $p$ - $V$  diagram for ethane.

Other curves of equal temperatures are also shown on this figure. The dashed curve connecting the dew points is called the dew-point curve (line  $BC$ ). Similarly, the dashed curve connecting the bubble points is called the bubble-point curve (line  $AC$ ). Notice that as the temperature increases, the length of the straight line portion of the isotherm decreases, until it eventually vanishes at critical point  $C$ . The bubble point and the dew point join at the critical point  $C$ . The area within the dashed line indicates conditions at which liquid and gas coexist. Often this area is called the saturation envelope.

Above the critical temperature ( $p$ - $V$  line of  $43.3\text{ }^{\circ}\text{C}$ ), the  $p$ - $V$  behavior line shows no abrupt change and simply shows an expansion of the substance and no phase change. This fluid is called a super critical fluid.

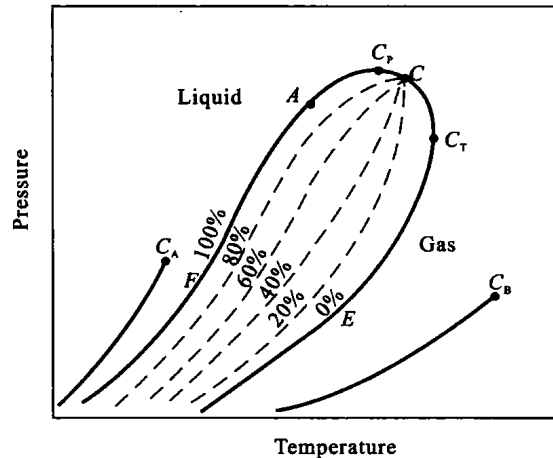
### 3.2 Phase Behavior of Two-component System

Next we will examine the phase behavior of mixtures of two components. The petroleum



engineer does not normally work with two-component systems. Usually mixtures consisting of many components are encountered. However, it is instructive to observe the differences in phase behavior between two-component mixtures and pure substances. These differences are amplified in multicomponent mixtures.

Figure 1.1.4 shows the typical shape of the phase diagram for a mixture of two components. The behavior of a mixture of two components is not as simple as that of a pure substance:



**Figure 1.1.4** Phase diagram for a two-component system.

(1) Instead of a single line for a pure substance, it is an envelope for a two-component system. The line  $FC$  is the **bubble-point line**, and the line  $EC$  is the **dew-point line**. The region bounded by the bubble-point line and the dew-point line is the **two-phase region**. Above and to the left of the bubble-point line is the liquid region, wherein the mixture exists as a **liquid**. Below and to the right of the dew-point line is the gas region, wherein the mixture exists as a **gas**.

(2) The critical point is no longer the highest pressure point, or even the highest temperature point. The definition of the critical point as applied to a pure substance is no long applicable for a two-component mixture. The **critical point** for a two-component system is defined as the point at which the bubble-point line and the dew-point line join. At this point, all the intensive properties of gas and liquid phases, such as viscosity, density, surface tension, etc., become identical.

The behavior of ethane-n-heptane mixtures is shown in Figure 1.1.5. On the left of the figure, terminating at point  $C$ , is the vapor-pressure curve of pure ethane, and on the extreme right of the figure, terminating at point  $C_7$ , is the vapor-pressure curve for pure n-heptane. Between the vapor-pressure curves of the pure constituents lie the phase diagrams of the various binary mixtures of the ethane-n-heptane system. The dashed curve is the locus of critical point for the ethane-n-heptane system.

Figure 1.1.6 presents the vapor-pressure curves of several paraffin hydrocarbons together with the critical loci of various binary mixtures of these hydrocarbons.

Comparing these phase diagrams (Figures 1.1.5 and 1.1.6), it is noted that:

(1) The phase envelope for a mixture lies between the vapor-pressure curves of the two pure