

Introduction

NOMENCLATURE

API	API gravity
A%	Percent of aromatics in a petroleum fraction
D	Diffusion coefficient
CH	Carbon-to-hydrogen weight ratio
d	Liquid density at 20°C and 1 atm
K_W	Watson K factor
k	Thermal conductivity
K_i	Equilibrium ratio of component i in a mixture
\log_{10}	Logarithm of base 10
\ln	Logarithm of base e
M	Molecular weight
N_{\min}	Minimum number of theoretical plates in a distillation column
N%	Percent of naphthenes in a petroleum fraction
n	Sodium D line refractive index of liquid at 20°C and 1 atm, dimensionless
n	Number of moles
P	Pressure
P_c	Critical pressure
P^{sat}	Vapor (saturation) pressure
P%	Percent of paraffins in a petroleum fraction
R	Universal gas constant
R_i	Refractivity intercept
SG	Specific gravity at 15.5°C (60°F)
SUS	Saybolt Universal Seconds (unit of viscosity)
S%	Weight % of sulfur in a petroleum fraction
T	Temperature
T_b	Boiling point
T_c	Critical temperature
T_F	Flash point
T_P	Pour point
T_M	Melting (freezing point) point
V	Volume
x_m	Mole fraction of a component in a mixture
x_v	Volume fraction of a component in a mixture
x_w	Weight fraction of a component in a mixture
y	Mole fraction of a component in a vapor phase

Greek Letters

α	Relative volatility
φ	Fugacity coefficient
ω	Acentric factor
σ	Surface tension
ρ	Density at temperature T and pressure P
μ	Viscosity
ν	Kinematic viscosity

Acronyms

API-TDB	American Petroleum Institute–Technical Data Book
bbbl	Barrel
GOR	Gas-to-oil ratio
IUPAC	International Union of Pure and Applied Chemistry
PNA	Paraffin, naphthene, aromatic content of a petroleum fraction
SC	Standard conditions
scf	Standard cubic feet
stb	Stock tank barrel
STO	Stock tank oil
STP	Standard temperature and pressure

IN THIS INTRODUCTORY CHAPTER, first the nature of petroleum fluids, hydrocarbon types, reservoir fluids, crude oils, natural gases, and petroleum fractions are introduced and then types and importance of characterization and physical properties are discussed. Application of materials covered in the book in various parts of the petroleum industry or academia as well as organization of the book are then reviewed followed by specific features of the book and introduction of some other related books. Finally, units and the conversion factors for those parameters used in this book are given at the end of the chapter.

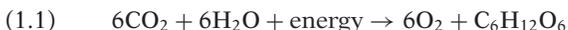
1.1 NATURE OF PETROLEUM FLUIDS

Petroleum is one of the most important substances consumed by man at present time. It is used as a main source of energy for industry, heating, and transportation and it also provides the raw materials for the petrochemical plants to produce polymers, plastics, and many other products. The word *petroleum*, derived from the Latin words *petra* and *oleum*, means literally *rock oil* and a special type of oil called *oleum* [1]. Petroleum is a complex mixture of hydrocarbons that occur in the sedimentary rocks in the form of gases (natural

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gas), liquids (crude oil), semisolids (bitumen), or solids (wax or asphaltite). Liquid fuels are normally produced from liquid hydrocarbons, although conversion of nonliquid hydrocarbons such as coal, oil shale, and natural gas to liquid fuels is being investigated. In this book, only petroleum hydrocarbons in the form of gas or liquid, simply called *petroleum fluids*, are considered. Liquid petroleum is also simply called *oil*. Hydrocarbon gases in a reservoir are called a *natural gas* or simply a *gas*. An underground reservoir that contains hydrocarbons is called *petroleum reservoir* and its hydrocarbon contents that can be recovered through a producing well is called *reservoir fluid*. Reservoir fluids in the reservoirs are usually in contact with water in porous media conditions and because they are lighter than water, they stay above the water level under natural conditions.

Although petroleum has been known for many centuries, the first oil-producing well was discovered in 1859 by E.L. Drake in the state of Pennsylvania and that marked the birth of modern petroleum technology and refining. The main elements of petroleum are carbon (C) and hydrogen (H) and some small quantities of sulfur (S), nitrogen (N), and oxygen (O). There are several theories on the formation of petroleum. It is generally believed that petroleum is derived from aquatic plants and animals through conversion of organic compounds into hydrocarbons. These animals and plants under aquatic conditions have converted inorganic compounds dissolved in water (such as carbon dioxide) to organic compounds through the energy provided by the sun. An example of such reactions is shown below:



in which $\text{C}_6\text{H}_{12}\text{O}_6$ is an organic compound called carbohydrate. In some cases organic compounds exist in an aquatic environment. For example, the Nile river in Egypt and the Uruguay river contain considerable amounts of organic materials. This might be the reason that most oil reservoirs are located near the sea. The organic compounds formed may be decomposed into hydrocarbons under certain conditions.



in which n , x , y , and z are integer numbers and $y\text{CH}_z$ is the closed formula for the produced hydrocarbon compound. Another theory suggests that the inorganic compound calcium carbonate (CaCO_3) with alkali metal can be converted to calcium carbide (CaC_2), and then calcium carbide with water (H_2O) can be converted to acetylene (C_2H_2). Finally, acetylene can be converted to petroleum [1]. Conversion of organic matters into petroleum is called *maturation*. The most important factors in the conversion of organic compounds to petroleum hydrocarbons are (1) heat and pressure, (2) radioactive rays, such as gamma rays, and (3) catalytic reactions. Vanadium- and nickel-type catalysts are the most effective catalysts in the formation of petroleum. For this reason some of these metals may be found in small quantities in petroleum fluids. The role of radioactive materials in the formation of hydrocarbons can be best observed through radioactive bombardment of fatty acids (RCOOH) that form paraffin hydrocarbons. Occasionally traces of radioactive materials such as uranium and potassium can also be found in petroleum. In summary, the following steps are required for the formation of hydrocarbons: (1) a source of organic material, (2) a process to convert

organic compounds into petroleum, and (3) a sealed reservoir space to store the hydrocarbons produced. The conditions required for the process of conversion of organic compounds into petroleum as shown through Eq. (1.2) are (1) geologic time of about 1 million years, (2) maximum pressure of about 17 MPa (2500 psi), and (3) temperature not exceeding 100–120°C (~210–250°F). If a leak occurred sometime in the past, the exploration well will encounter only small amounts of residual hydrocarbons. In some cases bacteria may have biodegraded the oil, destroying light hydrocarbons. An example of such a case would be the large heavy oil accumulations in Venezuela. The hydrocarbons generated gradually migrate from the original beds to more porous rocks, such as sandstone, and form a petroleum *reservoir*. A series of reservoirs within a common rock is called an *oil field*. Petroleum is a mixture of hundreds of different identifiable hydrocarbons, which are discussed in the next section. Once petroleum is accumulated in a reservoir or in various sediments, hydrocarbon compounds may be converted from one form to another with time and varying geological conditions. This process is called *in-situ alteration*, and examples of chemical alteration are thermal maturation and microbial degradation of the reservoir oil. Examples of physical alteration of petroleum are the preferential loss of low-boiling constituents by the diffusion or addition of new materials to the oil in place from a source outside the reservoir [1]. The main difference between various oils from different fields around the world is the difference in their composition of hydrocarbon compounds. Two oils with exactly the same composition have identical physical properties under the same conditions [2].

A good review of statistical data on the amount of oil and gas reservoirs, their production, processing, and consumption is usually reported yearly by the *Oil and Gas Journal* (OGJ). An annual refinery survey by OGJ is usually published in December of each year. OGJ also publishes a forecast and review report in January and a midyear forecast report in July of each year. In 2000 it was reported that total proven oil reserves is estimated at 1016 billion bbl (1.016×10^{12} bbl), which for a typical oil is equivalent to approximately 1.39×10^{11} tons. The rate of oil production was about 64.6 million bbl/d (~3.23 billion ton/year) through more than 900 000 producing wells and some 750 refineries [3, 4]. These numbers vary from one source to another. For example, Energy Information Administration of US Department of Energy reports world oil reserves as of January 1, 2003 as 1213.112 billion bbl according to OGJ and 1034.673 billion bbl according to *World Oil* (www.eia.doe.gov/emeu/iea). According to the OGJ worldwide production reports (*Oil and Gas Journal*, Dec. 22, 2003, p. 44), world oil reserves estimates changed from 999.78 in 1995 to 1265.811 billion bbl on January 1, 2004. For the same period world gas reserves estimates changed from 4.98×10^{15} scf to 6.0683×10^{15} scf. In 2003 oil consumption was about 75 billion bbl/day, and it is expected that it will increase to more than 110 million bbl/day by the year 2020. This means that with existing production rates and reserves, it will take nearly 40 years for the world's oil to end. Oil reserves life (reserves-to-production ratio) in some selected countries is given by OGJ (Dec. 22, 2003, p. 45). According to 2003 production rates, reserves life is 6.1 years in UK, 10.9 years in US, 20 years in Russia, 5.5 years in Canada, 84 years in Saudi Arabia, 143 years in Kuwait, and 247 years

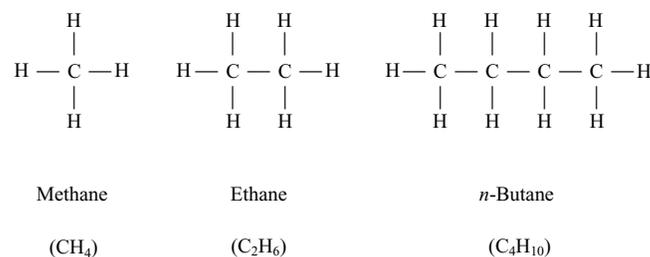
in Iraq. As in January 1, 2002, the total number of world oil wells was 830 689, excluding shut or service wells (OGJ, Dec. 22, 2003). Estimates of world oil reserves in 1967 were at 418 billion and in 1987 were at 896 billion bbl, which shows an increase of 114% in this period [5]. Two-thirds of these reserves are in the Middle East, although this portion depends on the type of oil considered. Although some people believe the Middle East has a little more than half of world oil reserves, it is believed that many undiscovered oil reservoirs exist offshore under the sea, and with increase in use of the other sources of energy, such as natural gas or coal, and through energy conservation, oil production may well continue to the end of the century. January 2000, the total amount of gas reserves was about 5.15×10^{15} scf, and its production in 1999 was about 200×10^9 scf/d (5.66×10^9 sm³/d) through some 1500 gas plants [3]. In January 2004, according to OGJ (Dec. 22, 2003, p. 44), world natural gas reserves stood at 6.068×10^{15} scf (6068.302 trillion scf). This shows that existing gas reserves may last for some 70 years. Estimated natural gas reserves in 1975 were at 2.5×10^{15} scf (7.08×10^{13} sm³), that is, about 50% of current reserves [6]. In the United States, consumption of oil and gas in 1998 was about 65% of total energy consumption. Crude oil demand in the United State in 1998 was about 15 million bbl/d, that is, about 23% of total world crude production [3]. Worldwide consumption of natural gas as a clean fuel is on the rise, and attempts are underway to expand the transfer of natural gas through pipelines as well as its conversion to liquid fuels such as gasoline. The world energy consumption is distributed as 35% through oil, 31% through coal, and 23% through natural gas. Nearly 11% of total world energy is produced through nuclear and hydroelectric sources [1].

1.1.1 Hydrocarbons

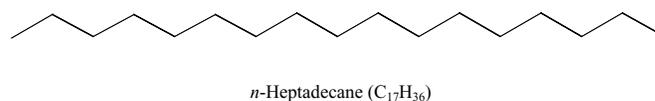
In early days of chemistry science, chemical compounds were divided into two groups: inorganic and organic, depending on their original source. Inorganic compounds were obtained from minerals, while organic compounds were obtained from living organisms and contained carbon. However, now organic compounds can be produced in the laboratory. Those organic compounds that contain only elements of carbon (C) and hydrogen (H) are called *hydrocarbons*, and they form the largest group of organic compounds. There might be as many as several thousand different hydrocarbon compounds in petroleum reservoir fluids. Hydrocarbon compounds have a general closed formula of C_xH_y , where x and y are integer numbers. The lightest hydrocarbon is methane (CH_4), which is the main component in a natural gas. Methane is from a group of hydrocarbons called *paraffins*. Generally, hydrocarbons are divided into four groups: (1) paraffins, (2) olefins, (3) naphthenes, and (4) aromatics. Paraffins, olefins, and naphthenes are sometime called *aliphatic* versus aromatic compounds. The International Union of Pure and Applied Chemistry (IUPAC) is a nongovernment organization that provides standard names, nomenclature, and symbols for different chemical compounds that are widely used [7]. The relationship between the various hydrocarbon constituents of crude oils is hydrogen addition or hydrogen loss. Such

interconversion schemes may occur during the formation, maturation, and *in-situ* alteration of petroleum.

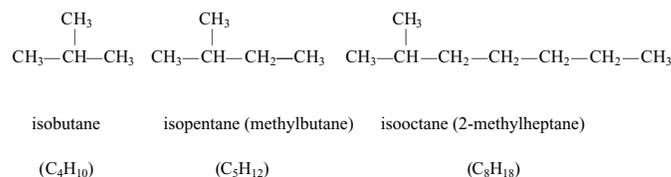
Paraffins are also called alkanes and have the general formula of C_nH_{2n+2} , where n is the number of carbon atoms. Paraffins are divided into two groups of normal and isoparaffins. Normal paraffins or normal alkanes are simply written as *n*-paraffins or *n*-alkanes and they are open, straight-chain saturated hydrocarbons. Paraffins are the largest series of hydrocarbons and begin with methane (CH_4), which is also represented by C_1 . Three *n*-alkanes, methane (C_1), ethane (C_2), and *n*-butane (C_4), are shown below:



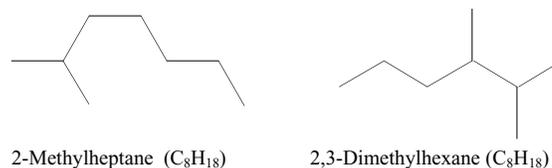
The open formula for *n*- C_4 can also be shown as $CH_3-CH_2-CH_2-CH_3$ and for simplicity in drawing, usually the CH_3 and CH_2 groups are not written and only the carbon-carbon bonds are drawn. For example, for a *n*-alkane compound of *n*-heptadecane with the formula of $C_{17}H_{36}$, the structure can also be shown as follows:



The second group of paraffins is called *isoparaffins*; these are branched-type hydrocarbons and begin with isobutane (methylpropane), which has the same closed formula as *n*-butane (C_4H_{10}). Compounds of different structures but the same closed formula are called *isomers*. Three branched or isoparaffin compounds are shown below:



In the case of isooctane, if the methyl group (CH_3) is attached to another carbon, then we have another compound (i.e., 3-methylheptane). It is also possible to have more than one branch of CH_3 group, for example, 2,3-dimethylhexane and 2-methylheptane, which are simply shown as following:



Numbers refer to carbon numbers where the methyl group is attached. For example, 1 refers to the first carbon either

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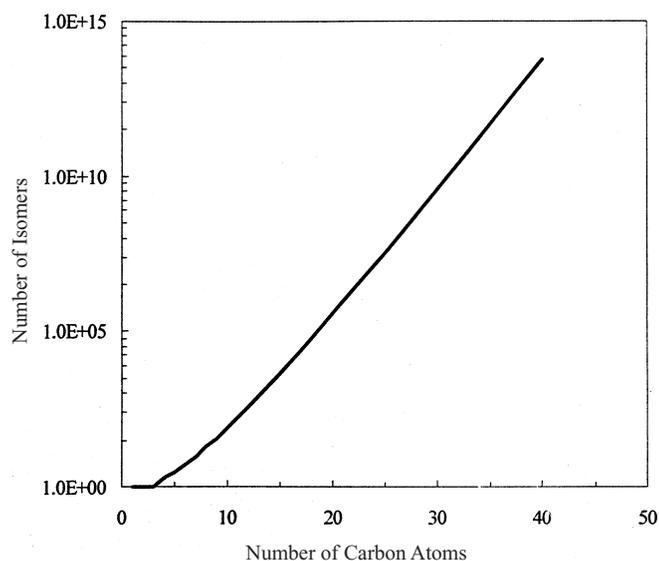


FIG. 1.1—Number of possible alkane isomers.

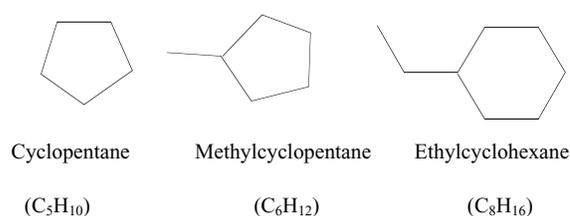
from the right or from the left. There are 2 isomers for butane and 3 for pentane, but there are 5 isomers for hexane, 9 for heptane, 18 for octane (C_8H_{18}), and 35 for nonane. Similarly, dodecane ($C_{12}H_{26}$) has 355, while octadecane ($C_{18}H_{38}$) has 60 523 and C_{40} has 62×10^{12} isomers [1, 8, 9]. The number of isomers rapidly increases with the number of carbon atoms in a molecule because of the rapidly rising number of their possible structural arrangements as shown in Fig. 1.1. For the paraffins in the range of C_5 – C_{12} , the number of isomers is more than 600 although only about 200–400 of them have been identified in petroleum mixtures [10]. Isomers have different physical properties. The same increase in number of isomers with molecular weight applies to other hydrocarbon series. As an example, the total number of hydrocarbons (from different groups) having 20 carbon atoms is more than 300 000 [10]!

Under standard conditions (SC) of $20^\circ C$ and 1 atm, the first four members of the alkane series (methane, ethane, propane, and butane) are in gaseous form, while from C_5H_{12} (pentane) to n -hexadecane ($C_{16}H_{36}$) they are liquids, and from n -heptadecane ($C_{17}H_{38}$) the compounds exist as waxlike solids at this standard temperature and pressure. Paraffins from C_1 to C_{40} usually appear in crude oil and represent up to 20% of crude by volume. Since paraffins are fully saturated (no double bond), they are stable and remain unchanged over long periods of geological time.

Olefins are another series of noncyclic hydrocarbons but they are unsaturated and have at least one double bond between carbon–carbon atoms. Compounds with one double bond are called monoolefins or alkenes, such as ethene (also named ethylene: $CH_2=CH_2$) and propene or propylene ($CH_2=CH-CH_3$). Besides *structural isomerism* connected with the location of double bond, there is another type of isomerism called *geometric isomerism*, which indicates the way atoms are oriented in space. The configurations are differentiated in their names by the prefixes *cis*- and *trans*- such as *cis*- and *trans*-2-butene. Monoolefins have a general formula of C_nH_{2n} . If there are two double bonds, the olefin is called *diolefin* (or diene), such as butadiene ($CH_2=CH-CH=CH_2$).

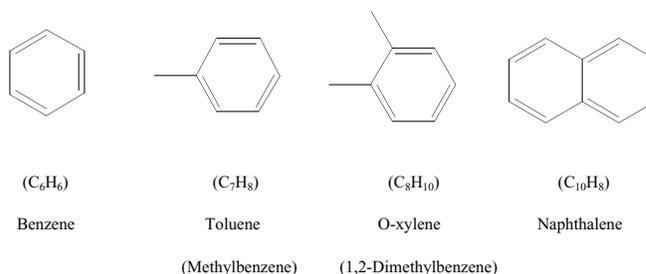
Unsaturated compounds are more reactive than saturated hydrocarbons (without double bond). Olefins are uncommon in crude oils due to their reactivity with hydrogen that makes them saturated; however, they can be produced in refineries through cracking reactions. Olefins are valuable products of refineries and are used as the feed for petrochemical plants to produce polymers such as polyethylene. Similarly compounds with triple bonds such as acetylene ($CH\equiv CH$) are not found in crude oils because of their tendency to become saturated [2].

Naphthenes or cycloalkanes are ring or cyclic saturated hydrocarbons with the general formula of C_nH_{2n} . Cyclopentane (C_5H_{10}), cyclohexane (C_6H_{12}), and their derivatives such as n -alkylcyclopentanes are normally found in crude oils. Three types of naphthenic compounds are shown below:



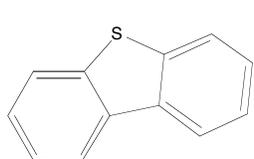
If there is only one alkyl group from n -paraffins (i.e., methyl, ethyl, propyl, n -butyl, ...) attached to a cyclopentane hydrocarbon, the series is called *n-alkylcyclopentanes*, such as the two hydrocarbons shown above where on each junction of the ring there is a CH_2 group except on the alkyl group juncture where there is only a CH group. For simplicity in drawing, these groups are not shown. Similarly there is a homologous naphthenic series of *n-alkylcyclohexanes* with only one saturated ring of cyclohexane, such as ethylcyclohexane shown above. Naphthenic hydrocarbons with only one ring are also called *monocycloparaffins* or *mononaphthenes*. In heavier oils, saturated multirings attached to each other called *polycycloparaffins* or *polynaphthenes* may also be available. Thermodynamic studies show that naphthene rings with five and six carbon atoms are the most stable naphthenic hydrocarbons. The content of cycloparaffins in petroleum may vary up to 60%. Generally, any petroleum mixture that has hydrocarbon compounds with five carbon atoms also contains naphthenic compounds.

Aromatics are an important series of hydrocarbons found in almost every petroleum mixture from any part of the world. Aromatics are cyclic but unsaturated hydrocarbons that begin with benzene molecule (C_6H_6) and contain carbon–carbon double bonds. The name aromatic refers to the fact that such hydrocarbons commonly have fragrant odors. Four different aromatic compounds are shown below:

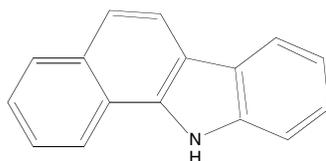


In the above structures, on each junction on the benzene ring where there are three bonds, there is only a group of CH, while at the junction with an alkyl group (i.e., toluene) there is only a C atom. Although benzene has three carbon-carbon double bonds, it has a unique arrangement of electrons that allows benzene to be relatively unreactive. Benzene is, however, known to be a cancer-inducing compound [2]. For this reason, the amount of benzene allowed in petroleum products such as gasoline or fuel oil is limited by government regulations in many countries. Under SC, benzene, toluene, and xylene are in liquid form while naphthalene is in a solid state. Some of the common aromatics found in petroleum and crude oils are benzene and its derivatives with attached methyl, ethyl, propyl, or higher alkyl groups. This series of aromatics is called *alkylbenzenes* and compounds in this homologous group of hydrocarbons have a general formula of C_nH_{2n-6} (where $n \geq 6$). Generally, aromatic series with only one benzene ring are also called *monoaromatics* (MA) or mononuclear aromatics. Naphthalene and its derivatives, which have only two unsaturated rings, are sometime called diaromatics. Crude oils and reservoir fluids all contain aromatic compounds. However, heavy petroleum fractions and residues contain multi-unsaturated rings with many benzene and naphthalene rings attached to each other. Such aromatics (which under SC are in solid form) are also called *polyaromatics* (PA) or polynuclear aromatics (PNA). In this book terms of mono and polyaromatics are used. Usually, heavy crude oils contain more aromatics than do light crudes. The amount of aromatics in coal liquids is usually high and could reach as high as 98% by volume. It is common to have compounds with naphthenic and aromatic rings side by side, especially in heavy fractions. Monoaromatics with one naphthenic ring have the formula of C_nH_{2n-8} and with two naphthenic rings the formula is C_nH_{2n-8} . There are many combinations of alkyl-naphthenoaromatics [1, 7].

Normally, high-molecular-weight polyaromatics contain several *heteroatoms* such as sulfur (S), nitrogen (N), or oxygen (O) but the compound is still called an aromatic hydrocarbon. Two types of these compounds are shown below [1]:



Dibenzothiophene

Benzocarbazole ($C_{16}H_{11}N$)

Except for the atoms S and N, which are specified in the above structures, on other junctions on each ring there is either a CH group or a carbon atom. Such heteroatoms in multiring aromatics are commonly found in asphaltene compounds as shown in Fig. 1.2, where for simplicity, C and H atoms are not shown on the rings.

Sulfur is the most important heteroatom in petroleum and it can be found in cyclic as well as noncyclic compounds such as mercaptanes ($R-S-H$) and sulfides ($R-S-R'$), where R and R' are alkyl groups. Sulfur in natural gas is usually found in the form of hydrogen sulfide (H_2S). Some natural gases

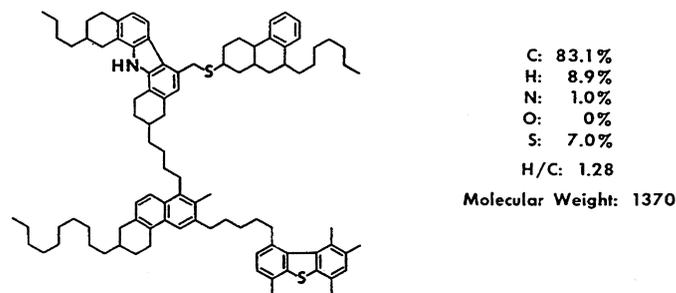


FIG. 1.2—An example of asphaltene molecule. Reprinted from Ref. [1], p. 463, by courtesy of Marcel Dekker, Inc.

contain H_2S as high as 30% by volume. The amount of sulfur in a crude may vary from 0.05 to 6% by weight. In Chapter 3, further discussion on the sulfur contents of petroleum fractions and crude oils will be presented. The presence of sulfur in finished petroleum products is harmful, for example, the presence of sulfur in gasoline can promote corrosion of engine parts. Amounts of nitrogen and oxygen in crude oils are usually less than the amount of sulfur by weight. In general for petroleum oils, it appears that the compositions of elements vary within fairly narrow limits; on a weight basis they are [1]

Carbon (C), 83.0–87.0%
 Hydrogen (H), 10.0–14.0%
 Nitrogen (N), 0.1–2.0%
 Oxygen (O), 0.05–1.5%
 Sulfur (S), 0.05–6.0%
 Metals (Nickel, Vanadium, and Copper), <1000 ppm (0.1%)

Generally, in heavier oils (lower API gravity, defined by Eq. (2.4)) proportions of carbon, sulfur, nitrogen, and oxygen elements increase but the amount of hydrogen and the overall quality decrease. Further information and discussion about the chemistry of petroleum and the type of compounds found in petroleum fractions are given by Speight [1]. Physical properties of some selected pure hydrocarbons from different homologous groups commonly found in petroleum fluids are given in Chapter 2. Vanadium concentrations of above 2 ppm in fuel oils can lead to severe corrosion in turbine blades and deterioration of refractory in furnaces. Ni, Va, and Cu can also severely affect the activities of catalysts and result in lower products. The metallic content may be reduced by solvent extraction with organic solvents. Organometallic compounds are precipitated with the asphaltenes and residues.

1.1.2 Reservoir Fluids and Crude Oil

The word *fluid* refers to a pure substance or a mixture of compounds that are in the form of gas, liquid, or both a mixture of liquid and gas (vapor). *Reservoir fluid* is a term used for the mixture of hydrocarbons in the reservoir or the stream leaving a producing well. Three factors determine if a reservoir fluid is in the form of gas, liquid, or a mixture of gas and liquid. These factors are (1) composition of reservoir fluid, (2) temperature, and (3) pressure. The most important characteristic of a reservoir fluid in addition to specific gravity (or API gravity) is its gas-to-oil ratio (GOR), which represents the amount of gas

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TABLE 1.1—Types and characteristics of various reservoir fluids.

Reservoir fluid type	GOR, scf/stb	CH ₄ , mol%	C ₆₊ , mol%	API gravity of STO ^a
Black oil	<1000	≤50	≥30	<40
Volatile oil	1000–3000	50–70	10–30	40–45
Gas condensate	3000–50 000	70–85	3–10	≥45
Wet gas	≥50 000	≥75	<3	>50
Dry gas	≥10 0000	≥90	<1	No liquid

^aAPI gravity of stock tank oil (STO) produced at the surface facilities at standard conditions (289 K and 1 atm).

produced at SC in standard cubic feet (scf) to the amount of liquid oil produced at the SC in stock tank barrel (stb). Other units of GOR are discussed in Section 1.7.23 and its calculation is discussed in Chapter 9. Generally, reservoir fluids are categorized into four or five types (their characteristics are given in Table 1.1). These five fluids in the direction of increasing GOR are black oil, volatile oil, gas condensate, wet gas, and dry gas.

If a gas after surface separator, under SC, does not produce any liquid oil, it is called *dry gas*. A natural gas that after production at the surface facilities can produce a little liquid oil is called *wet gas*. The word wet does not mean that the gas is wet with water, but refers to the hydrocarbon liquids that condense at surface conditions. In dry gases no liquid hydrocarbon is formed at the surface conditions. However, both dry and wet gases are in the category of natural gases. Volatile oils have also been called *high-shrinkage crude oil* and *near-critical oils*, since the reservoir temperature and pressure are very close to the critical point of such oils, but the critical temperature is always greater than the reservoir temperature [11]. Gases and gas condensate fluids have critical temperatures less than the reservoir temperature. Black oils contain heavier compounds and therefore the API gravity of stock tank oil is generally lower than 40 and the GOR is less than 1000 scf/stb. The specifications given in Table 1.1 for various reservoir fluids, especially at the boundaries between different types, are arbitrary and vary from one source to another [9, 11]. It is possible to have a reservoir fluid type that has

properties outside the corresponding limits mentioned earlier. Determination of a type of reservoir fluid by the above rule of thumb based on the GOR, API gravity of stock tank oil, or its color is not possible for all fluids. A more accurate method of determining the type of a reservoir fluid is based on the phase behavior calculations, its critical point, and shape of the phase diagram which will be discussed in Chapters 5 and 9. In general, oils produced from wet gas, gas condensate, volatile oil, and black oil increase in specific gravity (decrease in API gravity and quality) in the same order. Here quality of oil indicates lower carbon, sulfur, nitrogen, and metal contents which correspond to higher heating value. Liquids from black oils are viscous and black in color, while the liquids from gas condensates or wet gases are clear and colorless. Volatile oils produce fluids brown with some red/green color liquid. Wet gas contains less methane than a dry gas does, but a larger fraction of C₂–C₆ components. Obviously the main difference between these reservoir fluids is their respective composition. An example of composition of different reservoir fluids is given in Table 1.2.

In Table 1.2, C₇₊ refers to all hydrocarbons having seven or higher carbon atoms and is called heptane-plus fraction, while C₆ refers to a group of all hydrocarbons with six carbon atoms (hexanes) that exist in the fluid. M₇₊ and SG₇₊ are the molecular weight and specific gravity at 15.5°C (60°F) for the C₇₊ fraction of the mixture, respectively. It should be realized that molecular weight and specific gravity of the whole reservoir fluid are less than the corresponding values for the

TABLE 1.2—Composition (mol%) and properties of various reservoir fluids and a crude oil.

Component	Dry gas ^a	Wet gas ^b	Gas condensate ^c	Volatile oil ^d	Black oil ^e	Crude oil ^f
CO ₂	3.70	0.00	0.18	1.19	0.09	0.00
N ₂	0.30	0.00	0.13	0.51	2.09	0.00
H ₂ S	0.00	0.00	0.00	0.00	1.89	0.00
C ₁	96.00	82.28	61.92	45.21	29.18	0.00
C ₂	0.00	9.52	14.08	7.09	13.60	0.19
C ₃	0.00	4.64	8.35	4.61	9.20	1.88
<i>i</i> C ₄	0.00	0.64	0.97	1.69	0.95	0.62
<i>n</i> C ₄	0.00	0.96	3.41	2.81	4.30	3.92
<i>i</i> C ₅	0.00	0.35	0.84	1.55	1.38	2.11
<i>n</i> C ₅	0.00	0.29	1.48	2.01	2.60	4.46
C ₆	0.00	0.29	1.79	4.42	4.32	8.59
C ₇₊	0.00	1.01	6.85	28.91	30.40	78.23
Total	100.00	100.00	100.00	100.00	100.00	100.00
GOR (scf/stb)	...	69917	4428	1011	855	...
M ₇₊	...	113	143	190	209.8	266
SG ₇₊ (at 15.5°C)	...	0.794	0.795	0.8142	0.844	0.895
API ₇₊	...	46.7	46.5	42.1	36.1	26.6

^aGas sample from Salt Lake, Utah [12].

^bWet gas data from McCain [11].

^cGas condensate sample from Samson County, Texas (M. B. Standing, personal notes, Department of Petroleum Engineering, Norwegian Institute of Technology, Trondheim, Norway, 1974).

^dVolatile oil sample from Raleigh Field, Smith County, Mississippi (M. B. Standing, personal notes, Department of Petroleum Engineering, Norwegian Institute of Technology, Trondheim, Norway, 1974).

^eBlack oil sample from M. Ghuraiba, M.Sc. Thesis, Kuwait University, Kuwait, 2000.

^fA crude oil sample produced at stock tank conditions.

heptane-plus fraction. For example, for the crude oil sample in Table 1.2, the specific gravity of the whole crude oil is 0.871 or API gravity of 31. Details of such calculations are discussed in Chapter 4. These compositions have been determined from recombination of the compositions of corresponding separator gas and stock tank liquid, which have been measured through analytical tools (i.e., gas chromatography, mass spectrometry, etc.). Composition of reservoir fluids varies with the reservoir pressure and reservoir depth. Generally in a producing oil field, the sulfur and amount of heavy compounds increase versus production time [10]. However, it is important to note that within an oil field, the concentration of light hydrocarbons and the API gravity of the reservoir fluid increase with the reservoir depth, while its sulfur and C_{7+} contents decrease with the depth [1]. The lumped C_{7+} fraction in fact is a mixture of a very large number of hydrocarbons, up to C_{40} or higher. As an example the number of pure hydrocarbons from C_5 to C_9 detected by chromatography tools in a crude oil from North Sea reservoir fluids was 70 compounds. Detailed composition of various reservoir fluids from the North Sea fields is provided by Pedersen *et al.* [13]. As shown in Chapter 9, using the knowledge of the composition of a reservoir fluid, one can determine a pressure–temperature (*PT*) diagram of the fluid. And on the basis of the temperature and pressure of the reservoir, the exact type of the reservoir fluid can be determined from the *PT* diagram.

Reservoir fluids from a producing well are conducted to two- or three-stage separators which reduce the pressure and temperature of the stream to atmospheric pressure and temperature. The liquid leaving the last stage is called *stock tank oil* (STO) and the gas released in various stages is called *associated gas*. The liquid oil after necessary field processing is called *crude oil*. The main factor in operation and design of an oil–gas separator is to find the optimum operating conditions of temperature and pressure so that the amount of produced liquid (oil) is maximized. Such conditions can be determined through phase behavior calculations, which are discussed in detail in Chapter 9. Reservoir fluids from producing wells are mixed with free water. The water is separated through gravitational separators based on the difference between densities of water and oil. Remaining water from the crude can be removed through dehydration processes. Another surface operation is the desalting process that is necessary to remove the salt content of crude oils. Separation of oil, gas, and water from each other and removal of water and salt from oil and any other process that occurs at the surface are called *surface production operations* [14].

The crude oil produced from the atmospheric separator has a composition different from the reservoir fluid from a producing well. The light gases are separated and usually crude oils have almost no methane and a small C_2 – C_3 content while the C_{7+} content is higher than the original reservoir fluid. As an example, the composition of a crude oil produced through a three-stage separator from a reservoir fluid is also given in Table 1.2. Actually this crude is produced from a black oil reservoir fluid (composition given in Table 1.2). Two important characteristics of a crude that determine its quality are the API gravity (specific gravity) and the sulfur content. Generally, a crude with the API gravity of less than 20 ($SG > 0.934$) is called *heavy crude* and with API gravity of greater than 40 ($SG < 0.825$) is called *light crude* [1, 9]. Similarly, if the sulfur

content of a crude is less than 0.5 wt% it is called a sweet oil. It should be realized that these ranges for the gravity and sulfur content are relative and may vary from one source to another. For example, Favennec [15] classifies heavy crude as those with API less than 22 and light crude having API above 33. Further classification of crude oils will be discussed in Chapter 4.

1.1.3 Petroleum Fractions and Products

A crude oil produced after necessary field processing and surface operations is transferred to a refinery where it is processed and converted into various useful products. The refining process has evolved from simple batch distillation in the late nineteenth century to today's complex processes through modern refineries. Refining processes can be generally divided into three major types: (1) separation, (2) conversion, and (3) finishing. Separation is a physical process where compounds are separated by different techniques. The most important *separation* process is distillation that occurs in a distillation column; compounds are separated based on the difference in their boiling points. Other major physical separation processes are absorption, stripping, and extraction. In a gas plant of a refinery that produces light gases, the heavy hydrocarbons (C_5 and heavier) in the gas mixture are separated through their absorption by a liquid oil solvent. The solvent is then regenerated in a stripping unit. The *conversion* process consists of chemical changes that occur with hydrocarbons in reactors. The purpose of such reactions is to convert hydrocarbon compounds from one type to another. The most important reaction in modern refineries is the cracking in which heavy hydrocarbons are converted to lighter and more valuable hydrocarbons. Catalytic cracking and thermal cracking are commonly used for this purpose. Other types of reactions such as isomerization or *alkylation* are used to produce high octane number gasoline. *Finishing* is the purification of various product streams by processes such as desulfurization or acid treatment of petroleum fractions to remove impurities from the product or to stabilize it.

After the desalting process in a refinery, the crude oil enters the atmospheric distillation column, where compounds are separated according to their boiling points. Hydrocarbons in a crude have boiling points ranging from -160°C (boiling point of methane) to more than 600°C (1100°F), which is the boiling point of heavy compounds in the crude oil. However, the carbon–carbon bond in hydrocarbons breaks down at temperatures around 350°C (660°F). This process is called *cracking* and it is undesirable during the distillation process since it changes the structure of hydrocarbons. For this reason, compounds having boiling points above 350°C ($660+^\circ\text{F}$) called residuum are removed from the bottom of atmospheric distillation column and sent to a vacuum distillation column. The pressure in a vacuum distillation column is about 50–100 mm Hg, where hydrocarbons are boiled at much lower temperatures. Since distillation cannot completely separate the compounds, there is no pure hydrocarbon as a product of a distillation column. A group of hydrocarbons can be separated through distillation according to the boiling point of the lightest and heaviest compounds in the mixtures. The lightest product of an atmospheric column is a mixture of methane and ethane (but mainly ethane) that has the boiling

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TABLE 1.3—Some petroleum fractions produced from distillation columns.

Petroleum fraction	Approximate hydrocarbon range	Approximate boiling range	
		°C	°F
Light gases	C ₂ –C ₄	–90 to 1	–130–30
Gasoline (light and heavy)	C ₄ –C ₁₀	–1–200	30–390
Naphthas (light and heavy)	C ₄ –C ₁₁	–1–205	30–400
Jet fuel	C ₉ –C ₁₄	150–255	300–490
Kerosene	C ₁₁ –C ₁₄	205–255	400–490
Diesel fuel	C ₁₁ –C ₁₆	205–290	400–550
Light gas oil	C ₁₄ –C ₁₈	255–315	490–600
Heavy gas oil	C ₁₈ –C ₂₈	315–425	600–800
Wax	C ₁₈ –C ₃₆	315–500	600–930
Lubricating oil	>C ₂₅	>400	>750
Vacuum gas oil	C ₂₈ –C ₅₅	425–600	800–1100
Residuum	>C ₅₅	>600	>1100

Information given in this table is obtained from different sources [1, 18, 19].

range of –180 to –80°C (–260 to –40°F), which corresponds to the boiling point of methane and ethane. This mixture, which is in the form of gas and is known as fuel gas, is actually a *petroleum fraction*. In fact, during distillation a crude is converted into a series of petroleum fractions where each one is a mixture of a limited number of hydrocarbons with a specific range of boiling point. Fractions with a wider range of boiling points contain greater numbers of hydrocarbons. All fractions from a distillation column have a known boiling range, except the residuum for which the upper boiling point is usually not known. The boiling point of the heaviest component in a crude oil is not really known, but it is quite high. The problem of the nature and properties of the heaviest compounds in crude oils and petroleum residuum is still under investigation by researchers [16, 17]. Theoretically, it can be assumed that the boiling point of the heaviest component in a crude oil is infinity. Atmospheric residue has compounds with carbon number greater than 25, while vacuum residue has compounds with carbon number greater than 50 ($M > 800$). Some of the petroleum fractions produced from distillation columns with their boiling point ranges and applications are given in Table 1.3. The boiling point and equivalent carbon number ranges given in this table are approximate and they may vary according to the desired specific product. For example, the light gases fraction is mainly a mixture of ethane, propane, and butane; however, some heavier compounds (C₅₊) may exist in this fraction. The fraction is further fractionated to obtain ethane (a fuel gas) and propane and butane (petroleum gases). The petroleum gases are liquefied to get liquefied petroleum gas (LPG) used for home cooking purposes. In addition the isobutane may be separated for the gas mixture to be used for improving vapor pressure characteristics (volatility) of gasoline in cold weathers. These fractions may go through further processes to produce desired products. For example, gas oil may go through a cracking process to obtain more gasoline. Since distillation is not a perfect separation process, the initial and final boiling points for each fraction are not exact and especially the end points are approximate values. Fractions may be classified as narrow or wide depending on their boiling point range. As an example, the composition of an Alaska crude oil for various products is given in Table 1.4 and is graphically shown in Fig. 1.3. The weight and volume percentages for the products are near each other. More than 50% of the crude is processed in vacuum distillation unit. The vacuum residuum is mainly resin and asphaltene-type compounds composed of high

molecular weight multiring aromatics. The vacuum residuum may be mixed with lighter products to produce a more valuable blend.

Distillation of a crude oil can also be performed in the laboratory to divide the mixture into many narrow boiling point range fractions with a boiling range of about 10°C. Such narrow range fractions are sometimes referred to as *petroleum cuts*. When boiling points of all the cuts in a crude are known, then the boiling point distribution (distillation curve) of the

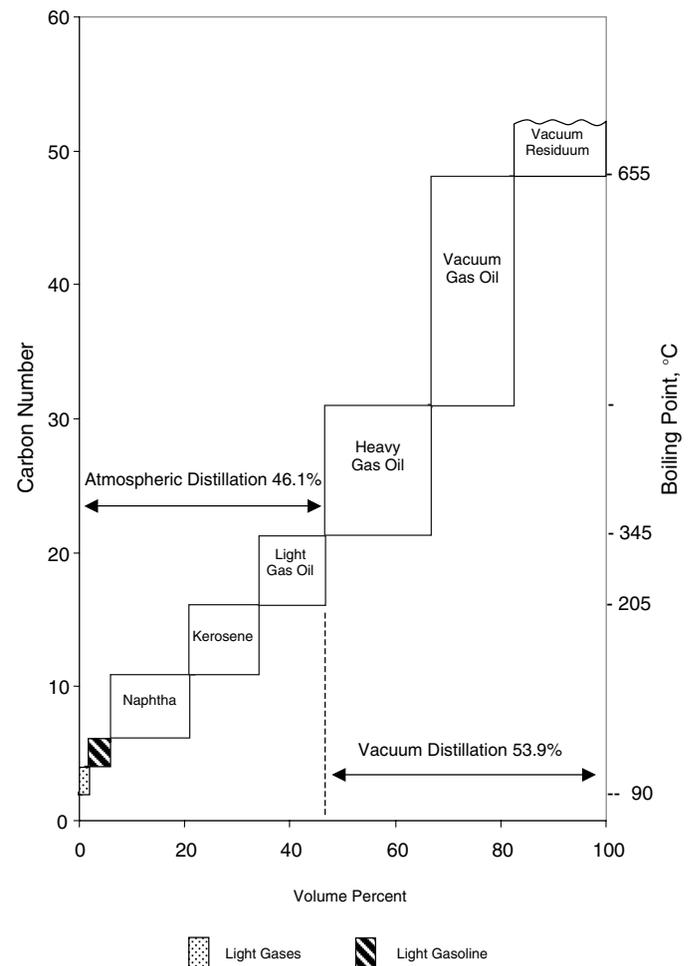


FIG. 1.3—Products and composition of Alaska crude oil.

TABLE 1.4—Products and composition of alaska crude oil.

Petroleum fraction	Approximate hydrocarbon range	Approximate boiling range ^a		vol%	wt%
		°C	°F		
Atmospheric distillation					
Light gases	C ₂ –C ₄	–90 to 1	–130–30	1.2	0.7
Light gasoline	C ₄ –C ₇	–1–83	30–180	4.3	3.5
Naphthas	C ₇ –C ₁₁	83–205	180–400	16.0	14.1
Kerosene	C ₁₁ –C ₁₆	205–275	400–525	12.1	11.4
Light gas oil (LGO)	C ₁₆ –C ₂₁	275–345	525–650	12.5	12.2
Sum	C ₂ –C ₂₁	–90–345	–130–650	46.1	41.9
Vacuum distillation (VD)					
Heavy gas oil (HGO)	C ₂₁ –C ₃₁	345–455	650–850	20.4	21.0
Vacuum gas oil (VGO)	C ₃₁ –C ₄₈	455–655	850–1050	15.5	16.8
Residuum	>C ₄₈	655+	1050+	18.0	20.3
Sum	C ₂₁ –C ₄₈₊	345–655+	650–1050	53.9	58.1
Total Crude	C ₂ –C ₄₈₊	–90–655+	650 to 1050+	100.0	100.0

Information given in this table has been extracted from Ref. [19].

^aBoiling ranges are interconverted to the nearest 5°C (°F).

whole crude can be obtained. Such distillation data and their uses will be discussed in Chapters 3 and 4. In a petroleum cut, hydrocarbons of various types are lumped together in four groups of paraffins (P), olefins (O), naphthenes (N), and aromatics (A). For olefin-free petroleum cuts the composition is represented by the PNA content. If the composition of a hydrocarbon mixture is known the mixture is called a *defined mixture*, while a petroleum fraction that has an unknown composition is called an *undefined fraction*.

As mentioned earlier, the petroleum fractions presented in Table 1.3 are not the final products of a refinery. They go through further physicochemical and finishing processes to get the characteristics set by the market and government regulations. After these processes, the petroleum fractions presented in Table 1.3 are converted to *petroleum products*. The terms petroleum fraction, petroleum cut, and petroleum product are usually used incorrectly, while one should realize that petroleum fractions are products of distillation columns in a refinery before being converted to final products. Petroleum cuts may have very narrow boiling range which may be produced in a laboratory during distillation of a crude. In general the petroleum products can be divided into two groups: (1) fuel products and (2) nonfuel products. The major *fuel petroleum products* are as follows:

1. Liquefied petroleum gases (LPG) that are mainly used for domestic heating and cooking (50%), industrial fuel (clean fuel requirement) (15%), steam cracking feed stock (25%), and as a motor fuel for spark ignition engines (10%). The world production in 1995 was 160 million ton per year ($\cong 5$ million bbl/d) [20]. LPG is basically a mixture of propane and butane.
2. Gasoline is perhaps one of the most important products of a refinery. It contains hydrocarbons from C₄ to C₁₁ (molecular weight of about 100–110). It is used as a fuel for cars. Its main characteristics are antiknock (octane number), volatility (distillation data and vapor pressure), stability, and density. The main evolution in gasoline production has been the use of unleaded gasoline in the world and the use of *reformulated gasoline* (RFG) in the United States. The RFG has less butane, less aromatics, and more oxygenates. The sulfur content of gasoline should not exceed 0.03% by weight. Further properties and characteristics of gasoline

will be discussed in Chapter 3. The U.S. gasoline demand in 1964 was 4.4 million bbl/d and has increased from 7.2 to 8.0 million bbl/d in a period of 7 years from 1991 to 1998 [6, 20]. In 1990, gasoline was about a third of refinery products in the United States.

3. Kerosene and jet fuel are mainly used for lighting and jet engines, respectively. The main characteristics are sulfur content, cold resistance (for jet fuel), density, and ignition quality.
4. Diesel and heating oil are used for motor fuel and domestic purposes. The main characteristics are ignition (for diesel oil), volatility, viscosity, cold resistance, density, sulfur content (corrosion effects), and flash point (safety factor).
5. Residual fuel oil is used for industrial fuel, for thermal production of electricity, and as motor fuel (low speed diesel engines). Its main characteristics are viscosity (good atomization for burners), sulfur content (corrosion), stability (no decantation separation), cold resistance, and flash point for safety.

The major *nonfuel petroleum products* are [18] as follows:

1. Solvents are light petroleum cuts in the C₄–C₁₄ range and have numerous applications in industry and agriculture. As an example of solvents, white spirits which have boiling points between 135 and 205°C are used as paint thinners. The main characteristics of solvents are volatility, purity, odor, and toxicity. Benzene, toluene, and xylenes are used as solvents for glues and adhesives and as a chemical for petrochemical industries.
2. Naphthas constitute a special category of petroleum solvents whose boiling points correspond to the class of white spirits. They can be classified beside solvents since they are mainly used as raw materials for petrochemicals and as the feeds to steam crackers. Naphthas are thus industrial intermediates and not consumer products. Consequently, naphthas are not subject to government specifications but only to commercial specifications.
3. Lubricants are composed of a main base stock and additives to give proper characteristics. One of the most important characteristics of lubricants is their viscosity and viscosity index (change of viscosity with temperature). Usually aromatics are eliminated from lubricants to improve

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their viscosity index. Lubricants have structure similar to isoparaffinic compounds. Additives used for lubricants are viscosity index additives such as polyacrylates and olefin polymers, antiwear additives (i.e., fatty esters), antioxidants (i.e., alkylated aromatic amines), corrosion inhibitors (i.e., fatty acids), and antifoaming agents (i.e., polydimethylsiloxanes). Lubricating greases are another class of lubricants that are semisolid. The properties of lubricants that should be known are viscosity index, aniline point (indication of aromatic content), volatility, and carbon residue.

4. Petroleum waxes are of two types: the paraffin waxes in petroleum distillates and the microcrystalline waxes in petroleum residua. In some countries such as France, paraffin waxes are simply called paraffins. Paraffin waxes are high melting point materials used to improve the oil's pour point and are produced during dewaxing of vacuum distillates. Paraffin waxes are mainly straight chain alkanes (C_{18} – C_{36}) with a very small proportion of isoalkanes and cycloalkanes. Their freezing point is between 30 and 70°C and the average molecular weight is around 350. When present, aromatics appear only in trace quantities. Waxes from petroleum residua (microcrystalline form) are less defined aliphatic mixtures of *n*-alkanes, isoalkanes, and cycloalkanes in various proportions. Their average molecular weights are between 600 and 800, carbon number range is alkanes C_{30} – C_{60} , and the freezing point range is 60–90°C [13]. Paraffin waxes (when completely dearomatized) have applications in the food industry and food packaging. They are also used in the production of candles, polishes, cosmetics, and coatings [18]. Waxes at ordinary temperature of 25°C are in solid states although they contain some hydrocarbons in liquid form. When melted they have relatively low viscosity.
5. Asphalt is another major petroleum product that is produced from vacuum distillation residues. Asphalts contain nonvolatile high molecular weight polar aromatic compounds, such as asphaltenes (molecular weights of several thousands) and cannot be distilled even under very high vacuum conditions. In some countries asphalt is called bitumen, although some suggest these two are different petroleum products. Liquid asphaltic materials are intended for easy applications to roads. Asphalt and bitumen are from a category of products called hydrocarbon binders. Major properties to determine the quality of asphalt are flash point (for safety), composition (wax content), viscosity and softening point, weathering, density or specific gravity, and stability or chemical resistance.
6. There are some other products such as white oils (used in pharmaceuticals or in the food industry), aromatic extracts (used in the paint industry or the manufacture of plastics), and coke (as a fuel or to produce carbon electrodes for aluminum refining). Petroleum cokes generally have boiling points above 1100+°C (~2000+°F), molecular weight of above 2500+, and carbon number of above 200+. Aromatic extracts are black materials, composed essentially of condensed polynuclear aromatics and of heterocyclic nitrogen and/or sulfur compounds. Because of this highly aromatic structure, the extracts have good solvent power.

Further information on technology, properties, and testing methods of fuels and lubricants is given in Ref. [21].

In general, more than 2000 petroleum products within some 20 categories are produced in refineries in the United States [1, 19]. Blending techniques are used to produce some of these products or to improve their quality. The product specifications must satisfy customers' requirements for good performance and government regulations for safety and environment protection. To be able to plan refinery operations, the availability of a set of product quality prediction methods is therefore very important.

There are a number of international organizations that are known as standard organizations that recommend specific characteristics or standard measuring techniques for various petroleum products through their regular publications. Some of these organizations in different countries that are known with their abbreviations are as follows:

1. ASTM (American Society for Testing and Materials) in the United States
2. ISO (International Organization for Standardization), which is at the international level
3. IP (Institute of Petroleum) in the United Kingdom
4. API (American Petroleum Institute) in the United States
5. AFNOR (Association Francaise de Normalisation), an official standard organization in France
6. Deutsche Institut fur Normung (DIN) in Germany
7. Japan Institute of Standards (JIS) in Japan

ASTM is composed of several committees in which the *D-02 committee* is responsible for petroleum products and lubricants, and for this reason its test methods for petroleum materials are designated by the prefix D. For example, the test method ASTM D 2267 provides a standard procedure to determine the benzene content of gasoline [22]. In France this test method is designated by EN 238, which are documented in AFNOR information document M 15-023. Most standard test methods in different countries are very similar in practice and follow ASTM methods but they are designated by different codes. For example the international standard ISO 6743/0, accepted as the French standard NF T 60-162, treats all the petroleum lubricants, industrial oils, and related products. The abbreviation NF is used for the French standard, while EN is used for European standard methods [18].

Government regulations to protect the environment or to save energy, in many cases, rely on the recommendations of official standard organizations. For example, in France, AFNOR gives specifications and requirements for various petroleum products. For diesel fuels it recommends (after 1996) that the sulfur content should not exceed 0.05 wt% and the flash point should not be less than 55°C [18].

1.2 TYPES AND IMPORTANCE OF PHYSICAL PROPERTIES

On the basis of the production and refining processes described above it may be said that the petroleum industry is involved with many types of equipment for production, transportation, and storage of intermediate or final petroleum products. Some of the most important units are listed below.

1. Gravity decanter (to separate oil and water)
2. Separators to separate oil and gas
3. Pumps, compressors, pipes, and valves

4. Storage tanks
5. Distillation, absorption, and stripping columns
6. Boilers, evaporators, condensers, and heat exchangers
7. Flashers (to separate light gases from a liquid)
8. Mixers and agitators
9. Reactors (fixed and fluidized beds)
10. Online analyzers (to monitor the composition)
11. Flow and liquid level measurement devices
12. Control units and control valves

The above list shows some, but not all, of the units involved in the petroleum industry. Optimum design and operation of such units as well as manufacture of products to meet market demands and government regulations require a complete knowledge of properties and characteristics for hydrocarbons, petroleum fractions/products, crude oils, and reservoir fluids. Some of the most important characteristics and properties of these fluids are listed below with some examples for their applications. They are divided into two groups of temperature-independent parameters and temperature-dependent properties. The *temperature-independent properties* and parameters are as follows:

1. *Specific gravity* (SG) or *density* (d) at SC. These parameters are temperature-dependent; however, specific gravity at 15.5°C and 1 atm and density at 20°C and 1 atm used in petroleum characterization are included in this category of temperature-independent properties. The specific gravity is also presented in terms of *API gravity*. It is a useful parameter to characterize petroleum fluids, to determine composition (PNA) and the quality of a fuel (i.e., sulfur content), and to estimate other properties such as critical constants, density at various temperatures, viscosity, or thermal conductivity [23, 24]. In addition to its direct use for size calculations (i.e., pumps, valves, tanks, and pipes), it is also needed in design and operation of equipments such as gravity decanters.
2. *Boiling point* (T_b) or distillation curves such as the true boiling point curve of petroleum fractions. It is used to determine volatility and to estimate characterization parameters such as average boiling point, molecular weight, composition, and many physical properties (i.e., critical constants, vapor pressure, thermal properties, transport properties) [23–25].
3. *Molecular weight* (M) is used to convert molar quantities into mass basis needed for practical applications. Thermodynamic relations always produce molar quantities (i.e., molar density), while in practice mass specific values (i.e., absolute density) are needed. Molecular weight is also used to characterize oils, to predict composition and quality of oils, and to predict physical properties such as viscosity [26–30].
4. *Refractive index* (n) at some reference conditions (i.e., 20°C and 1 atm) is another useful characterization parameter to estimate the composition and quality of petroleum fractions. It is also used to estimate other physical properties such as molecular weight, equation of state parameters, the critical constants, or transport properties of hydrocarbon systems [30, 31].
5. Defined characterization parameters such as Watson K , *carbon-to-hydrogen weight ratio*, (CH weight ratio), *refractivity intercept* (R_i), and *viscosity gravity constant* (VGC)

to determine the quality and composition of petroleum fractions [27–29].

6. Composition of petroleum fractions in terms of wt% of paraffins (P%), naphthenes (N%), aromatics (A%), and sulfur content (S%) are important to determine the quality of a petroleum fraction as well as to estimate physical properties through pseudocomponent methods [31–34]. Composition of other constituents such as *asphaltene* and *resin* components are quite important for heavy oils to determine possibility of solid-phase deposition, a major problem in the production, refining, and transportation of oil [35].
7. *Pour point* (T_p), and *melting point* (T_M) have limited uses in wax and paraffinic heavy oils to determine the degree of solidification and the wax content as well as minimum temperature required to ensure fluidity of the oil.
8. *Aniline point* to determine a rough estimate of aromatic content of oils.
9. *Flash point* (T_F) is a very useful property for the safety of handling volatile fuels and petroleum products especially in summer seasons.
10. *Critical temperature* (T_c), *critical pressure* (P_c), and *critical volume* (V_c) known as critical constants or critical properties are used to estimate various physical and thermodynamic properties through equations of state or generalized correlations [36].
11. *Acentric factor* (ω) is another parameter that is needed together with critical properties to estimate physical and thermodynamic properties through equations of state [36].

The above properties are mainly used to characterize the oil or to estimate the physical and thermodynamic properties which are all *temperature-dependent*. Some of the most important properties are listed as follows:

1. *Density* (ρ) as a function of temperature and pressure is perhaps the most important physical property for petroleum fluids (vapor or liquid forms). It has great application in both petroleum production and processing as well as its transportation and storage. It is used in the calculations related to sizing of pipes, valves, and storage tanks, power required by pumps and compressors, and flow-measuring devices. It is also used in reservoir simulation to estimate the amount of oil and gas in a reservoir, as well as the amount of their production at various reservoir conditions. In addition density is used in the calculation of equilibrium ratios (for phase behavior calculations) as well as other properties, such as transport properties.
2. *Vapor pressure* (P^{vap}) is a measure of volatility and it is used in phase equilibrium calculations, such as flash, bubble point, or dew point pressure calculations, in order to determine the state of the fluid in a reservoir or to separate vapor from liquid. It is needed in calculation of equilibrium ratios for operation and design of distillation, absorber, and stripping columns in refineries. It is also needed in determination of the amount of hydrocarbon losses from storage facilities and their presence in air. Vapor pressure is the property that represents ignition characteristics of fuels. For example, the *Reid vapor pressure* (RVP) and boiling range of gasoline govern ease of starting engine, engine warm-up, rate of acceleration, mileage economy, and tendency toward vapor lock [19].

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3. *Heat capacity* (C_p) of a fluid is needed in design and operation of heat transfer units such as heat exchangers.
4. *Enthalpy* (H) of a fluid is needed in energy balance calculations, heat requirements needed in design and operation of distillation, absorption, stripping columns, and reactors.
5. *Heat of vaporization* (ΔH_{vap}) is needed in calculation of heat requirements in design and operation of reboilers or condensers.
6. *Heats of formation* (ΔH_f), *combustion* (ΔH_c), and *reaction* (ΔH_r) are used in calculation of heating values of fuels and the heat required/generated in reactors and furnaces in refineries. Such information is essential in design and operations of burners, furnaces, and chemical reactors. These properties together with the *Gibbs free energy* are used in calculation of equilibrium constants in chemical reactions to determine the optimum operating conditions in reactors for best conversion of feed stocks into the products.
7. *Viscosity* (μ) is another useful property in petroleum production, refining, and transportation. It is used in reservoir simulators to estimate the rate of oil or gas flow and their production. It is needed in calculation of power required in mixers or to transfer a fluid, the amount of pressure drop in a pipe or column, flow measurement devices, and design and operation of oil/water separators [37, 38].
8. *Thermal conductivity* (k) is needed for design and operation of heat transfer units such as condensers, heat exchangers, as well as chemical reactors [39].
9. *Diffusivity* or *diffusion coefficient* (D) is used in calculation of mass transfer rates and it is a useful property in design and operation of reactors in refineries where feed and products diffuse in catalyst pores. In petroleum production, a gas injection technique is used in improved oil recovery where a gas diffuses into oil under reservoir conditions; therefore, diffusion coefficient is also required in reservoir simulation and modeling [37, 40–42].
10. *Surface tension* (σ) or *interfacial tension* (IFT) is used mainly by the reservoir engineers in calculation of capillary pressure and rate of oil production and is needed in reservoir simulators [37]. In refineries, IFT is a useful parameter to determine foaming characteristics of oils and the possibility of having such problems in distillation, absorption, or stripping columns [43]. It is also needed in calculation of the rate of oil dispersion on seawater surface polluted by an oil spill [44].
11. *Equilibrium ratios* (K_i) and *fugacity coefficients* (ϕ_i) are the most important thermodynamic properties in all phase behavior calculations. These calculations include vapor–liquid equilibria, bubble and dew point pressure, pressure–temperature phase diagram, and GOR. Such calculations are important in design and operation of distillation, absorption and stripping units, gas-processing units, gas–oil separators at production fields, and to determine the type of a reservoir fluid [45, 46].

Generally, the first set of properties introduced above (temperature-independent) are the basic parameters that are used to estimate physical and thermodynamic properties given in the second set (temperature-dependent). Properties

such as density, boiling point, molecular weight, and refractive index are called *physical properties*. Properties such as enthalpy, heat capacity, heat of vaporization, equilibrium ratios, and fugacity are called *thermodynamic properties*. Viscosity, thermal conductivity, diffusion coefficient, and surface tension are in the category of physical properties but they are also called *transport properties*. In general all the thermodynamic and physical properties are called *thermophysical properties*. But they are commonly referred to as physical properties or simply *properties*, which is used in the title of this book.

A property of a system depends on the thermodynamic state of the system that is determined by its temperature, pressure, and composition. A process to experimentally determine various properties for all the industrially important materials, especially complex mixtures such as crude oils or petroleum products, would be prohibitive in both cost and time, indeed it could probably never be completed. For these reasons accurate methods for the estimation of these properties are becoming increasingly important. In some references the term property prediction is used instead of property estimation; however, in this book as generally adopted by most scientists both terms are used for the same purpose.

1.3 IMPORTANCE OF PETROLEUM FLUIDS CHARACTERIZATION

In the previous section, various basic characteristic parameters for petroleum fractions and crude oils were introduced. These properties are important in design and operation of almost every piece of equipment in the petroleum industry. Thermodynamic and physical properties of fluids are generally calculated through standard methods such as corresponding state correlations or equations of state and other pressure–volume–temperature (PVT) relations. These correlations and methods have a generally acceptable degree of accuracy provided accurate input parameters are used. When using cubic equation of state to estimate a thermodynamic property such as absolute density for a fluid at a known temperature and pressure, the critical temperature (T_c), critical pressure (P_c), acentric factor (ω), and molecular weight (M) of the system are required. For most pure compounds and hydrocarbons these properties are known and reported in various handbooks [36, 47–50]. If the system is a mixture such as a crude oil or a petroleum fraction then the pseudocritical properties are needed for the calculation of physical properties. The pseudocritical properties cannot be measured but have to be calculated through the composition of the mixture. Laboratory reports usually contain certain measured properties such as distillation curve (i.e., ASTM D 2887) and the API gravity or specific gravity of the fraction. However, in some cases viscosity at a certain temperature, the percent of paraffin, olefin, naphthene, and aromatic hydrocarbon groups, and sulfur content of the fraction are measured and reported. Petroleum fractions are mixtures of many compounds in which the specific gravity can be directly measured for the mixture, but the average boiling point cannot be measured. Calculation of average boiling point from distillation data, conversion of various distillation curves from one type to another, estimation of molecular weight, and the PNA composition of fractions are the initial steps in characterization of

petroleum fractions [25, 46, 47]. Estimation of other basic parameters introduced in Section 1.2, such as asphaltenes and sulfur contents, CH, flash and pour points, aniline point, refractive index and density at SC, pseudocritical properties, and acentric factor, are also considered as parts of characterization of petroleum fractions [24, 28, 29, 51–53]. Some of these properties such as the critical constants and acentric factor are not even known for some heavy pure hydrocarbons and should be estimated from available properties. Therefore characterization methods also apply to pure hydrocarbons [33]. Through characterization, one can estimate the basic parameters needed for the estimation of various physical and thermodynamic properties as well as to determine the composition and quality of petroleum fractions from available properties easily measurable in a laboratory.

For crude oils and reservoir fluids, the basic laboratory data are usually presented in the form of the composition of hydrocarbons up to hexanes and the heptane-plus fraction (C_{7+}), with its molecular weight and specific gravity as shown in Table 1.2. In some cases laboratory data on a reservoir fluid is presented in terms of the composition of single carbon numbers or simulated distillation data where weight fraction of cuts with known boiling point ranges are given. Certainly because of the wide range of compounds existing in a crude oil or a reservoir fluid (i.e., black oil), an average value for a physical property such as boiling point for the whole mixture has little significant application and meaning. Characterization of a crude oil deals with use of such laboratory data to present the mixture in terms of a defined or a continuous mixture. One commonly used characterization technique for the crudes or reservoir fluids is to represent the hydrocarbon-plus fraction (C_{7+}) in terms of several narrow-boiling-range cuts called *pseudocomponents* (or *pseudofractions*) with known composition and characterization parameters such as, boiling point, molecular weight, and specific gravity [45, 54, 55]. Each pseudocomponent is treated as a petroleum fraction. Therefore, characterization of crude oils and reservoir fluids require characterization of petroleum fractions, which in turn require pure hydrocarbon characterization and properties [56]. It is for this reason that properties of pure hydrocarbon compounds and hydrocarbon characterization methods are first presented in Chapter 2, the characterization of petroleum fractions is discussed in Chapter 3, and finally methods of characterization of crude oils are presented in Chapter 4. Once characterization of a petroleum fraction or a crude oil is done, then a physical property of the fluid can be estimated through an appropriate procedure. In summary, characterization of a petroleum fraction or a crude oil is a technique that through available laboratory data one can calculate basic parameters necessary to determine the quality and properties of the fluid.

Characterization of petroleum fractions, crude oils, and reservoir fluids is a state-of-the-art calculation and plays an important role in accurate estimation of physical properties of these complex mixtures. Watson, Nelson, and Murphy of Universal Oil Products (UOP) in the mid 1930s proposed initial characterization methods for petroleum fractions [57]. They introduced a characterization parameter known as Watson or UOP characterization factor, K_W , which has been used extensively in characterization methods developed in the following years. There are many characterization methods

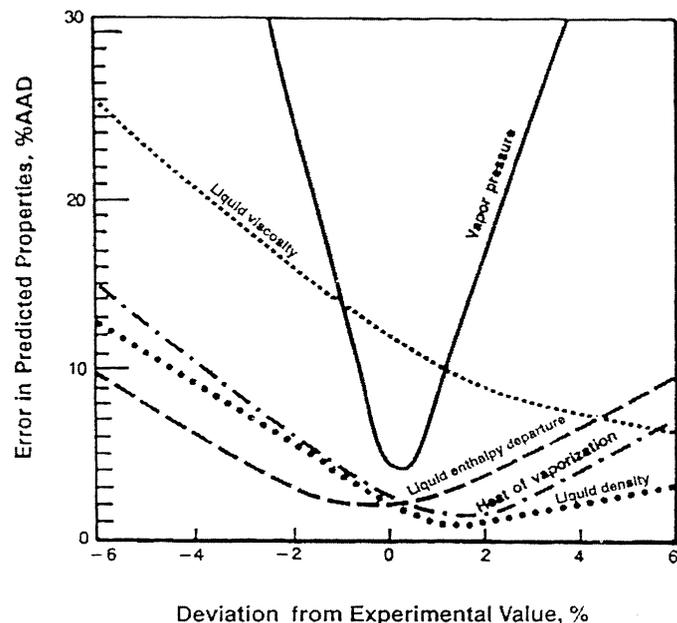


FIG. 1.4—Influence of error in critical temperature on errors in predicted physical properties of toluene. Taken from Ref. [58] with permission.

suggested in the literature or in process simulators and each method generates different characterization parameters that in turn would result different estimated final physical property with subsequent impact in design and operation of related units. To decide which method of characterization and what input parameters (where there is a choice) should be chosen depends very much on the user's knowledge and experience in this important area.

To show how important the role of characterization is in the design and operation of units, errors in the prediction of various physical properties of toluene through a modified BWR equation of state versus errors introduced to actual critical temperature (T_c) are shown in Fig. 1.4 [58]. In this figure, errors in the prediction of vapor pressure, liquid viscosity, vapor viscosity, enthalpy, heat of vaporization, and liquid density are calculated versus different values of critical temperature while other input parameters (i.e., critical pressure, acentric factor, etc.) were kept constant. In the use of the equation of state if the actual (experimental) value of the critical temperature is used, errors in values of predicted properties are generally within 1–3% of experimental values; however, as higher error is introduced to the critical temperature the error in the calculated property increases to a much higher magnitude. For example, when the error in the value of the critical temperature is zero (actual value of T_c), predicted vapor pressure has about 3% error from the experimental value, but when the error in T_c increases to 1, 3, or 5%, error in the predicted vapor pressure increases approximately to 8, 20, and 40%, respectively. Therefore, one can realize that 5% error in an input property for an equation of state does not necessarily reflect the same error in a calculated physical property but can be propagated into much higher errors, while the predictive equation is relatively accurate if actual input parameters are used. Similar results are observed for other physical

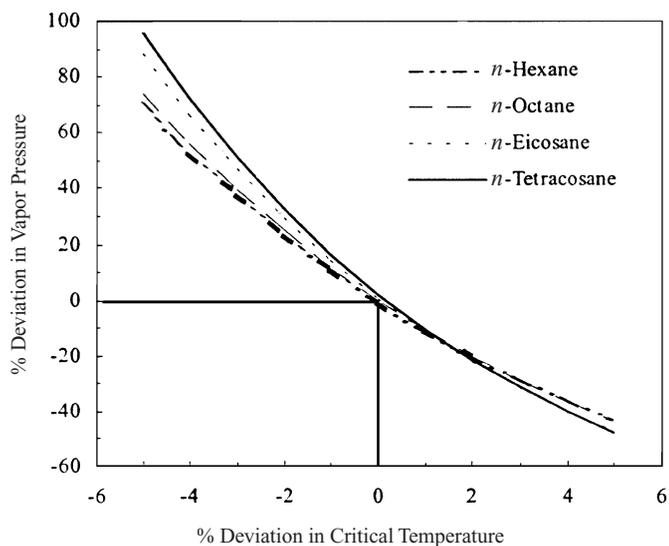


FIG. 1.5—Influence of error in critical temperature on errors of predicted vapor pressure from Lee–Kesler method.

properties and with other correlations for the estimation of physical properties [59]. Effect of the error in the critical temperature on the vapor pressure of different compounds predicted from the Lee–Kesler method (see Section 7.3.2) is shown in Fig. 1.5. When the actual critical temperature is used, the error in the predicted vapor pressure is almost negligible; however, if the critical temperature is under-predicted by 5%, the error in the vapor pressure increases by 60–80% for the various compounds evaluated.

As shown in Chapter 6, vapor pressure is one of the key parameters in the calculation of equilibrium ratios (K_i) and subsequent relative volatility (α_{12}), which is defined in a binary system of components 1 and 2 as follows:

$$(1.3) \quad K_1 = \frac{y_1}{x_1}$$

$$(1.4) \quad \alpha_{12} = \frac{K_1}{K_2} = \frac{y_1}{x_1} \times \frac{x_2}{y_2}$$

where x_1 and x_2 are the mole fractions of components 1 and 2 in the liquid phase, respectively. Similarly y_1 and y_2 are the mole fractions in the vapor phase for components 1 and 2, respectively. For an ideal binary system at low pressure, the equilibrium ratio K_i is directly proportional to the vapor pressure as will be seen in Chapter 6.

The most important aspect in the design and operation of distillation columns is the number or trays needed to make a specific separation for specific feed and products. It has been shown that a small error in the value of relative volatility could lead to a much greater error in the calculation of number of trays and the length of a distillation column [60]. The minimum number of trays required in a distillation column can be calculated from the knowledge of relative volatility through the *Fenske Equation* given below [61].

$$(1.5) \quad N_{\min} = \frac{\ln[x_D(1-x_B)/x_B(1-x_D)]}{\ln(\alpha_{12})} - 1$$

where N_{\min} is the minimum number of plates, and x_D and x_B are the mole fraction of the light component in the distillate (top) and bottom products, respectively. Equation (1.5) is developed for a binary mixture; however, a similar equation has been developed for multicomponent mixtures [61]. For different values of α , errors calculated for the minimum number of trays versus errors introduced in the value of α through Eq. (1.5) are shown in Fig. 1.6. As is shown in this figure, a –5% error in the value of α when its value is 1.1 can generate an error of more than 100% in the calculation of minimum number of trays. It can be imagined that the error in the actual number of trays would be even higher than 100%. In addition, the calculated numbers of trays are theoretical and when converted to real number of trays through overall column efficiency, the error may increase to several hundred percent. The approach of building the column higher to have a safe design is quite expensive.

As an example, a distillation column of diameter 4.5 m and height 85 m has an investment cost of approximately \$4 million (€4.5 million) as stated by Dohrn and Pfohl [60]. Error in the calculation of relative volatility, α , could have been caused by the error in calculation of vapor pressure, which itself could have been caused by a small error in an input parameter such as critical temperature [58, 59]. Therefore, from this simple analysis one can realize the extreme cost and loss in the investment that can be caused by a small error in the estimation of critical temperature. Similar other examples have been given in the literature [62]. Nowadays, investment in refineries or their upgrading costs billions of dollars. For example, for a typical refinery of 160 000 bbl/d (8 million tons/year) capacity, the cost of construction in Europe is about \$2 billion [18]. This is equivalent to refining cost of \$7.5/bbl while this number for refineries of 1980s was about \$2/bbl. In addition to the extra cost of investment, inappropriate design of units can cause extra operating costs and shorten the plant life as well as produce products that do not match the original design specifications. The use of a proper characterization method to calculate more accurate

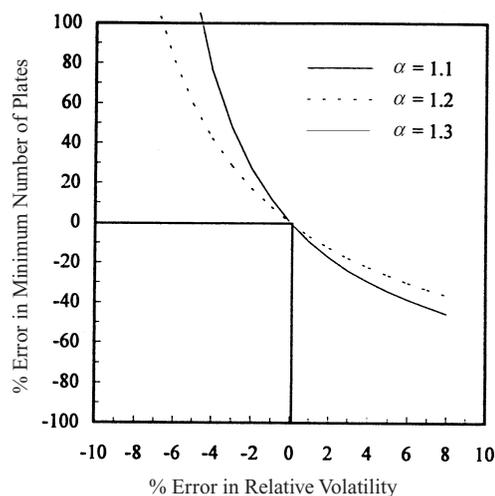


FIG. 1.6—Effect of error in the relative volatility on the error of minimum number of plates of a distillation column.

properties of petroleum fractions can save a large portion of such huge additional investment and operating costs.

1.4 ORGANIZATION OF THE BOOK

As the title of the book portrays and was discussed in Sections 1.2 and 1.3, the book presents methods of characterization and estimation of thermophysical properties of hydrocarbons, defined mixtures, undefined petroleum fractions, crude oils, and reservoir fluids. The entire book is written in nine chapters in a way such that in general every chapter requires materials presented in previous chapters. In addition there is an appendix and an index. Chapter 1 gives a general introduction to the subject from basic definition of various terms, the nature of petroleum, its formation and composition, types of petroleum mixtures, and the importance of characterization and property prediction to specific features of the book and its application in the petroleum industry and academia. Because of the importance of units in property calculations, the last section of Chapter 1 deals with unit conversion factors especially between SI and English units for the parameters used in the book. Chapter 2 is devoted to properties and characterization of pure hydrocarbons from C_1 to C_{22} from different hydrocarbon groups, especially from homologous groups commonly found in petroleum fluids. Properties of some nonhydrocarbons found with petroleum fluids such as H_2O , H_2S , CO_2 , and N_2 are also given. Basic parameters are defined at the beginning of the chapter, followed by characterization of pure hydrocarbons. Predictive methods for various properties of pure hydrocarbons are presented and compared with each other. A discussion is given on the state-of-the-arts development of predictive methods. The procedures presented in this chapter are essential for characterization of petroleum fractions and crude oils discussed in Chapters 3 and 4.

Chapter 3 discusses various characterization methods for petroleum fractions and petroleum products. Characterization parameters are introduced and analytical instruments in laboratory are discussed. In this chapter one can use minimum laboratory data to characterize petroleum fractions and to determine the quality of petroleum products. Estimation of some basic properties such as molecular weight, molecular-type composition, sulfur content, flash, pour point and freezing points, critical constants, and acentric factor for petroleum fractions are presented in this chapter. A theoretical discussion on development of characterization methods and generation of predictive correlations from experimental data is also presented. Methods of Chapter 3 are extended to Chapter 4 for the characterization of various reservoir fluids and crude oils. Chapters 2–4 are perhaps the most important chapters in this book, as the methods presented in these chapters influence the entire field of physical properties in the remaining chapters.

In Chapter 5, PVT relations, equations of state, and corresponding state correlations are presented [31, 63–65]. The use of the velocity of light and sound in developing equations of state is also presented [31, 66–68]. Equations of state and corresponding state correlations are powerful tools in the estimation of volumetric, physical, transport, and thermodynamic properties [64, 65, 69]. Procedures outlined

in Chapter 5 will be used in the prediction of physical properties discussed in the follow-up chapters. Fundamental thermodynamic relations for calculation of thermodynamic properties are presented in Chapter 6. The last three chapters of the book show applications of methods presented in Chapters 2–6 for calculation of various physical, thermodynamic, and transport properties. Methods of calculation and estimation of density and vapor pressure are given in Chapter 7. Thermal properties such as heat capacity, enthalpy, heat of vaporization, heats of combustion and reaction, and the heating value of fuels are also discussed in Chapter 7. Predictive methods for transport properties namely viscosity, thermal conductivity, diffusivity, and surface tension are given in Chapter 8 [30, 31, 42, 43, 69, 70]. Finally, phase equilibrium calculations, estimation of equilibrium ratios, GOR, calculation of pressure–temperature (PT) diagrams, solid formations, the conditions at which asphaltene, wax, and hydrate are formed, as well as their preventive methods are discussed in Chapter 9.

The book is written according to the standards set by ASTM for its publication. Every chapter begins with a general introduction to the chapter. Since in the following chapters for most properties several predictive methods are presented, a section on conclusion and recommendations is added at the end of the chapter. Practical problems as examples are presented and solved for each property discussed in each chapter. Finally, the chapter ends by a set of exercise problems followed by a citation section for the references used in the chapter.

The Appendix gives a summary of definitions of terms and properties used in this manual according to the ASTM dictionary as well as the Greek letters used in this manual. Finally the book ends with an index to provide a quick guide to find specific subjects.

1.5 SPECIFIC FEATURES OF THIS MANUAL

In this part several existing books in the area of characterization and physical properties of petroleum fractions are introduced and their differences with the current book are discussed. Then some special features of this book are presented.

1.5.1 Introduction of Some Existing Books

There are several books available that deal with physical properties of petroleum fractions and hydrocarbon systems. The most comprehensive and widely used book is the *API Technical Data Book—Petroleum Refining* [47]. It is a book with 15 chapters in three volumes, and the first edition appeared in mid 1960s. Every 5 years since, some chapters of the book have been revised and updated. The project has been conducted at the Pennsylvania State University and the sixth edition was published in 1997. It contains a data bank on properties of pure hydrocarbons, chapters on characterization of petroleum fractions, thermodynamic and transport properties of liquid and gaseous hydrocarbons, their mixtures, and undefined petroleum fractions. For each property, one predictive method that has been approved and selected

by the API-TDB committees as the best available method is presented. This book will be referred as *API-TDB* throughout this book.

Another important book in this area is *The Properties of Gases and Liquids* that was originally written by Reid and Sherwood in 1950s and it has been revised and updated nearly every decade. The fifth and latest edition was published in November 2000 [36] by three authors different from the original two authors. The book has been an excellent reference for students and practical engineers in the industry over the past five decades. It discusses various methods for prediction of properties of pure hydrocarbons as well as nonhydrocarbons and their defined mixtures. However, it does not treat undefined petroleum fractions, crude oils, and reservoir fluids. Most of the methods for properties of pure compounds require the chemical structure of compounds (i.e., group contribution techniques). The book compares various methods and gives its recommendations for each method.

There are several other books in the area of properties of oils that document empirically developed predictive methods, among them is the book *Properties of Oils and Natural Gases*, by Pedersen *et al.* [13]. The book mainly treats reservoir fluids, especially gas condensates from North Sea, and it is mainly a useful reference for reservoir engineers. Books by McCain [11], Ahmed [71], Whitson [45], and Danesh [72] are all written by reservoir engineers and contain information mainly for phase behavior calculations needed in petroleum production and reservoir simulators. However, they contain some useful information on methods of prediction of some physical properties of petroleum fractions. Another good reference book was written by Tsonopoulos *et al.* [73] on thermodynamic and transport properties of coal liquids in the mid 1980s. Although there are many similarities between coal liquids and petroleum fractions, the book does not consider crude oils and reservoir fluids. But it provides some useful correlations for properties of coal liquids. The book by Wauquier [18] on petroleum refining has several useful chapters on characterization and physical properties of petroleum fractions and finished products. It also provides the test methods according to European standards. Some organizations' Web sites also provide information on fluid physical properties. A good example of such online information is provided by National Institute of Standards (<http://webbook.nist.gov>) which gives molecular weight, names, formulas, structure, and some data on various compounds [74].

1.5.2 Special Features of the Book

This book has objectives and aims that are different from the books mentioned in Section 1.5.1. The main objective of this book has been to provide a quick reference in the area of petroleum characterization and properties of various petroleum fluids for the people who work in the petroleum industry and research centers, especially in petroleum processing (*downstream*), petroleum production (*upstream*), and related industries. One special characteristic of the book is its discussion on development of various methods which would help the users of process/reservoir simulators to become familiar with the nature of characterization and property estimation methods for petroleum fractions. This would in turn help them to choose the proper predictive method among the

many methods available in a process simulator. However, the book has been written in a language that is understandable to undergraduate and graduate students in all areas of engineering and science. It contains practical solved problems as well as exercise problems so that the book would be suitable as a text for educational purposes.

Special features of this book are Chapters 2, 3, and 4 that deal with the characterization of hydrocarbons, petroleum fractions, and crude oils and their impact on the entire field of property prediction methods. It discusses both light as well as heavy fractions and presents methods of prediction of the important characteristics of petroleum products from minimum laboratory data and easily measurable parameters. It presents several characterization methods developed in recent years and not documented in existing references. The book also presents various predictive methods, including the most accurate and widely used method for each property and discusses points of strength, weaknesses, and limitations. Recommended methods are based on the generality, simplicity, accuracy, and availability of input parameters. This is another special feature of the book. In Chapters 5 and 6 it discusses equations of state based on the velocity of sound and light and how these two measurable properties can be used to predict thermodynamic and volumetric properties of fluids, especially heavy compounds and their mixtures [31, 63, 66–68]. Significant attention is given throughout the book on how to estimate properties of heavy hydrocarbons, petroleum fractions, crude oils, and reservoir fluids. Most of the methods developed by Riazi and coworkers [23, 24, 26–33, 51–56, 63, 65–70], which have been in use by the petroleum industry [47, 75–82], are documented in this book. In addition, a new experimental technique to measure diffusion coefficients in reservoir fluids under reservoir conditions is presented in Chapter 8 [42]. In Chapter 9 some new methods for determination of onset of solid formation are introduced. Reported experimental data on characteristics and properties of various oils from different parts of the world are included in various chapters for direct evaluations and testing of methods. Although both gases and liquids are treated in the book, emphasis is on the liquid fractions. Generally, the methods of estimation of properties of gases are more accurate than those for liquid systems. Most of the methods presented in the book are supported by some scientific basis and they are not simply empirical correlations derived from a certain group of data. This widens the application of the methods presented in the book to different types of oils. However, all basic parameters and necessary engineering concepts are defined in a way that is understandable for those nonengineer scientists who are working in the petroleum or related industry. Nearly all methods are expressed through mathematical relations so they are convenient for computer applications; however, most of them are simple such that the properties can be calculated by hand calculators for a quick estimate whenever applicable special methods are given for coal liquid fractions. This is another unique feature of this book.

1.6 APPLICATIONS OF THE BOOK

The information that is presented in the book may be applied and used in all areas of the petroleum industries: production,

processing, and transportation. It can also be used as a textbook for educational purposes. Some of the applications of the materials covered in the book were discussed in Sections 1.2 and 1.3. The applications and uses of the book may be summarized as follows.

1.6.1 Applications in Petroleum Processing (Downstream)

Engineers, scientists, and operators working in various sectors of petroleum processing and refining or related industries can use the entire material discussed in the book. It helps laboratory people in refineries to measure useful properties and to test the reliability of their measurements. The book should be useful for engineers and researchers to analyze experimental data and develop their own predictive methods. It is also intended to help people who are involved with development of computer softwares and process simulators for design and operation of units and equipments in petroleum refineries. Another objective was to help users of such simulators to be able to select an appropriate predictive method for a particular application based on available data on the fraction.

1.6.2 Applications in Petroleum Production (Upstream)

Reservoir, chemical, and mechanical engineers may use the book in reservoir simulators, design and operation of surface separators in production fields, and feasibility studies for enhanced oil recovery projects, such as gas injection projects. Another application of the book by reservoir engineers is to simulate laboratory data on PVT experiments for the reservoir fluids, determination of the nature and type of reservoir fluids, and calculation of the initial amounts of oil and gas in the reservoir. Reservoir engineers may also use Chapter 9 to determine the conditions that a solid may form, amount of solid formation, and method of its prevention during production. Practically all chapters of the book should be useful for reservoir engineers.

1.6.3 Applications in Academia

Although the original goal and aim in writing this book was to prepare a reference manual for the industry, laboratories, and research institutions in the area of petroleum, it has been written in a way such that it can also be used as a textbook for educational purposes. It can be used as a text for an elective course for either undergraduate (senior level) or graduate level. Students from chemical, petroleum, and mechanical engineering fields as well as from chemistry and physics can take the course and understand the contents of the book. However, it should not be hard for students from other fields of engineering and science to use this book. The book may also be used to conduct short courses in the petroleum industry.

1.6.4 Other Applications

There are several other areas in which the book can be used. One may use this book to determine the quality of crude oils, petroleum fuels, and products for marketing and government

organizations that set the standards for such materials. As an example, the amount of sulfur or aromatic contents of a fuel can be estimated through minimum laboratory data to check if they meet the market demand or government regulations for environmental protection. This book can be used to determine properties of crude oil, its products, and natural gases that are needed for transportation and storage. Examples of such properties are density, boiling point, flash and pour points, sulfur content, vapor pressure, and viscosity.

The book can also be used to determine the properties of oils for clean-up operations where there is an oil spill on seawater. To simulate the fate of an oil spill and the rate of its disappearance at least the following properties are needed in order to use appropriate simulators [44, 83–85]:

- Characterization of petroleum fractions (Chapter 3)
- Pour point (Chapter 3)
- Characterization of crude oil (Chapter 4)
- Solubility parameter (Chapters 4, 6, and 9)
- Density (Chapters 5 and 7)
- Vapor pressure (Chapter 7)
- Viscosity, diffusion coefficient, and surface tension (Chapter 8)

Accurate prediction of the fate of a crude oil spill depends on the characterization technique used to estimate the physical properties. For example, to estimate how much of the initial oil would be vaporized after a certain time, accurate values of the diffusion coefficient, vapor pressure, and molecular weight are needed in addition to an appropriate characterization method to split the crude into several pseudocomponents [83].

1.7 DEFINITION OF UNITS AND THE CONVERSION FACTORS

An estimated physical property is valuable only if it is expressed in an appropriate unit. The most advanced process simulators and the most sophisticated design approaches fail to perform properly if appropriate units are not used. This is particularly important for the case of estimation of physical properties through various correlations or reporting the experimental data. Much of the confusion with reported experimental data arises from ambiguity in their units. If a density is reported without indicating the temperature at which the density has been measured, this value has no use. In this part basic units for properties used in the book are defined and conversion factors between the most commonly used units are given for each property. Finally some units specifically used in the petroleum industry are introduced. Interested readers may also find other information on units from online sources (for example, <http://physics.nist.gov/cuu/contents/index.html>).

1.7.1 Importance and Types of Units

The petroleum industry and its research began and grew mainly in the United States during the last century. The relations developed in the 1930s, 1940s, and 1950s were mainly graphical. The best example of such methods is the Winn nomogram developed in the late 1950s [86]. However, with the

birth of the computer and its expansion, more analytical methods in the form of equations were developed in the 1960s and mainly in the 1970s and 1980s. Nearly all correlations and graphical methods that were developed until the early 1980s are in English units. However, starting from the 1980s many books and handbooks appeared in the SI units (from Le Systeme International d'Unites). The general trend is to unify all engineering books and documents in SI units to be used by the international community. However, many books, reports, handbooks, and equations and figures in various publications are still in English units. The United States and United Kingdom both officially use the English system of units. Therefore, it is essential that engineers be familiar with both unit systems of English and SI. The other unit system that is sometimes used for some properties is the cgs (centimeter, gram, second) unit, which is derived from the SI unit.

Since the book is prepared for an international audience, the primary unit system used for equations, tables, and figures is the SI; however, it has been tried to present equivalent of numbers and values of properties in both SI and English units. There are some figures that are taken from other references in the literature and are in English units and they have been presented in their original form. There are some special units that are commonly used to express some special properties. For example, viscosity is usually expressed in centipoise (cp), kinematic viscosity in centistoke (cSt), density in g/cm^3 , specific gravity (SG) at standard temperature of 60°F, or the GOR in scf/stb. For such properties, these primary units have been used throughout the book, while their respective equivalent values in SI are also presented.

1.7.2 Fundamental Units and Prefixes

Generally there are four fundamental quantities of length (L), mass (M), time (t), and temperature (T) and when their units are known, units of all other derived quantities can be determined. In the SI system, units of length, mass, and temperature are meter (m), kilogram (kg), and Kelvin (K), respectively. In English units these dimensions have the units of foot (ft), pound mass (lb_m), and degrees Rankine ($^{\circ}\text{R}$), respectively. The unit of time in all unit systems is the second (s), although in English unit, hour (h) is also used for the unit of time. From these units, unit of any other quantity in SI is known. For example the unit of force is SI is $\text{kg}\cdot\text{m}/\text{s}^2$ which is called *Newton* (N) and as a result the unit of pressure must be N/m^2 or *Pascal* (Pa). Since 1 Pa is a very small quantity, larger units such as kPa (1000 Pa) or mega Pascal (MPa) are commonly used. The standard prefixes in SI units are as follows:

Giga (G) = 10^9
 Mega (M) = 10^6
 Kilo (k) = 10^3
 Hecto (h) = 10^2
 Deka (da) = 10^1
 Deci (d) = 10^{-1}
 Centi (c) = 10^{-2}
 Milli (m) = 10^{-3}
 Micro (μ) = 10^{-6}
 Nano (n) = 10^{-9}

As an example 1 000 000 Pa can be expressed as 1 MPa. These prefixes are not used in conjunction with the English units. However, in the English system of units when volumetric quantities of gases are presented in large numbers, usually every 1000 units is expressed by one prefix of M. For example, 2000 scf of gas is expressed as 2 Mscf and similarly 2 000 000 scf is written as 2 MMscf. Other symbols usually used to express large quantities are b for billion (1000 million or 10^9) and tr for trillion (one million millions or 10^{12}).

1.7.3 Units of Mass

The mass is shown by m and its unit in SI is kg (kilogram), in cgs is g (gram), and in the English unit system is lb_m (pound-mass). On many occasions the subscript m is dropped for lb when it is referred to mass. In the English unit system, units of ounce (oz) and grains are also used for mass units smaller than a pound. For larger values of mass, unit of *ton* is used, which is defined in three forms of long, short, and metric. Generally the term ton is applied to the metric ton (1000 kg). The conversion factors are as follows:

$$\begin{aligned} 1 \text{ kg} &= 1000 \text{ g} = 2.204634 \text{ lb} = 35.27392 \text{ oz} \\ 1 \text{ lb} &= 0.45359 \text{ kg} = 453.59 \text{ g} = 16 \text{ oz} = 7000 \text{ grain} \\ 1 \text{ g} &= 0.001 \text{ kg} = 0.002204634 \text{ lb} = 15.4324 \text{ grain} \\ 1 \text{ ton (metric)} &= 1000 \text{ kg} = 2204.634 \text{ lb} \\ 1 \text{ ton (short)} &= 2000 \text{ lb} = 907.18 \text{ kg} \\ 1 \text{ ton (long)} &= 2240 \text{ lb} = 1016 \text{ kg} = 1.12 \text{ ton (short)} \\ &= 1.1016 \text{ ton (metric)} \end{aligned}$$

1.7.4 Units of Length

The unit of length in SI is meter (m), in cgs is centimeter (cm), and in English unit system is foot (ft). Smaller values of length in English system are presented in inch (in.). The conversion factors are as follows:

$$\begin{aligned} 1 \text{ m} &= 100 \text{ cm} = 10^{-3} \text{ km} = 1000 \text{ mm} = 10^6 \text{ microns } (\mu\text{m}) \\ &= 10^{10} \text{ angstroms } (\text{\AA}) = 3.28084 \text{ ft} = 39.37008 \text{ in.} \\ &= 1.0936 \text{ yd (yard)} \\ 1 \text{ ft} &= 12 \text{ in.} = 0.3048 \text{ m} = 30.48 \text{ cm} = 304.8 \text{ mm} \\ &= 3.048 \times 10^{-4} \text{ km} = 1/3 \text{ yd} \\ 1 \text{ cm} &= 10^{-2} \text{ m} = 10^{-5} \text{ km} = 10 \text{ mm} = 0.0328084 \text{ ft} \\ &= 0.393701 \text{ in.} \\ 1 \text{ km} &= 1000 \text{ m} = 3280.48 \text{ ft} = 3.93658 \times 10^4 \text{ in.} \\ 1 \text{ in.} &= 2.54 \text{ cm} = 0.0833333 \text{ ft} = 0.0254 \text{ m} = 2.54 \times 10^{-5} \text{ km} \\ 1 \text{ mile} &= 1609.3 \text{ m} = 1.609 \text{ km} = 5279.8 \text{ ft} \end{aligned}$$

1.7.5 Units of Time

The unit of time in all major systems is the second (s); however, for large values of time other units such as minute (min), hour (h), day (d), and sometimes even year (year) are used

appropriately. The conversion factors among these units are as follows:

$$\begin{aligned} 1 \text{ year} &= 365 \text{ d} = 8760 \text{ h} = 5.256 \times 10^5 \text{ min} = 3.1536 \times 10^7 \text{ s} \\ 1 \text{ d} &= 2.743973 \times 10^{-3} \text{ year} = 24 \text{ h} = 1440 \text{ min} = 8.64 \times 10^4 \text{ s} \\ 1 \text{ h} &= 1.14155 \times 10^{-4} \text{ year} = 4.16667 \times 10^{-2} \text{ d} \\ &= 60 \text{ min} = 3600 \text{ s} \\ 1 \text{ min} &= 1.89934 \times 10^{-6} \text{ year} = 6.94444 \times 10^{-4} \text{ d} \\ &= 1.66667 \times 10^{-2} \text{ h} = 60 \text{ s} \\ 1 \text{ s} &= 3.17098 \times 10^{-8} \text{ year} = 1.157407 \times 10^{-5} \text{ d} \\ &= 2.77777 \times 10^{-4} \text{ h} = 1.66667 \times 10^{-2} \text{ min} \end{aligned}$$

1.7.6 Units of Force

As mentioned above, the unit of force in the SI system is Newton (N) and in the English unit system is pound-force (lb_f). 1 lb_f is equivalent to the weight of a mass of 1 lb_m at the sea level where the acceleration of gravity is 32.174 ft/s^2 (9.807 m/s^2). In the cgs system, the unit of force is dyne (dyn). Another unit for the force in the metric system is kg_f , which is equivalent to the weight of a mass of 1 kg at the sea level. The conversion factors are as follows:

$$\begin{aligned} 1 \text{ N} &= 1 \text{ kg} \cdot \text{m/s}^2 = 10^5 \text{ dyn} = 0.2248 \text{ lb}_f = 1.01968 \times 10^{-1} \text{ kg}_f \\ 1 \text{ lb}_f &= 4.4482 \text{ N} = 0.45359 \text{ kg}_f \\ 1 \text{ kg}_f &= 9.807 \text{ N} = 2.204634 \text{ lb}_f \\ 1 \text{ dyn} &= 10^{-5} \text{ N} = 2.248 \times 10^{-6} \text{ lb}_f \end{aligned}$$

1.7.7 Units of Moles

Another unit to present amount of matter especially in engineering calculations is *mole* (mol), which is defined as the ratio of mass (m) to molecular weight (M).

$$(1.6) \quad n = \frac{m}{M}$$

In SI system the unit of mole is kmol, where m in the above equation is in kg. In the English system, the unit of mol is lbmol. In the cgs system, the unit of mol is gmol, which is usually written as mol. For example, for methane (molecular weight 16.04) 1 mol of the gas has mass of 16.04 g. One mole of any substance contains 6.02×10^{23} number of molecules (Avogadro's number). The conversion factors between various units of moles are the same as given for the mass in Section 1.7.3.

$$\begin{aligned} 1 \text{ kmol} &= 1000 \text{ mol} = 2.204634 \text{ lbmol} \\ 1 \text{ lbmol} &= 0.45359 \text{ kmol} = 453.59 \text{ mol} \\ 1 \text{ mol} &= 0.001 \text{ kmol} = 0.002204634 \text{ lbmol} \end{aligned}$$

1.7.8 Units of Molecular Weight

Molecular weight or molar mass shown by M is a number that 1 mol of any substance has equivalent mass of M g. In the SI system the unit of M is kg/kmol and in the English system the unit is lb/lbmol, while in the cgs system the unit of M is g/mol. Molecular weight is represented by the same number in all unit systems regardless of the system used. As an example, methane has the molecular weight of 16 g/mol, 16 lb/lbmol, and 16 kg/kmol in the unit systems of cgs, SI, and English, respectively. For this reason, in many cases the

unit for the molecular weight is not mentioned; however, one must realize that it is not a dimensionless parameter. Most recent compilations of molar masses are provided by Coplen [87].

1.7.9 Units of Pressure

Pressure is the force exerted by a fluid per unit area; therefore, in the SI system it has the unit of N/m^2 , which is called Pascal (Pa), and in the English system has the unit of lb_f/ft^2 (psf) or $\text{lb}_f/\text{in.}^2$ (psi). Other units commonly used for the pressure are the *bar* (bar) and *standard atmosphere* (atm). Pressure may also be expressed in terms of mm Hg. In this book units of MPa, kPa, bar, atm, or psi are commonly used for pressure. The conversion factors are given as follows:

$$\begin{aligned} 1 \text{ atm} &= 1.01325 \text{ bar} = 101\,325 \text{ Pa} = 101.325 \text{ kPa} \\ &= 0.101325 \text{ MPa} = 14.696 \text{ psi} \\ 1 \text{ atm} &= 1.0322 \text{ kg}_f/\text{cm}^2 = 760 \text{ mm Hg (torr)} = 29.921 \text{ in. Hg} \\ &= 10.333 \text{ m H}_2\text{O (4}^\circ\text{C)} \\ 1 \text{ bar} &= 0.98692 \text{ atm} = 1 \times 10^5 \text{ Pa} = 100 \text{ kPa} \\ &= 0.1 \text{ MPa} = 14.5038 \text{ psi} \\ 1 \text{ Pa} &= 1 \times 10^{-3} \text{ kPa} = 1 \times 10^{-6} \text{ MPa} = 9.8692 \times 10^{-6} \text{ atm} \\ &= 1 \times 10^{-5} \text{ bar} = 1.45037 \times 10^{-4} \text{ psi} \\ 1 \text{ psi} &= 6.804573 \times 10^{-2} \text{ atm} = 6.89474 \times 10^{-2} \text{ bar} \\ &= 6.89474 \times 10^{-3} \text{ MPa} \\ 1 \text{ psf} &= 144 \text{ psi} = 9.79858 \text{ atm} = 9.92843 \text{ bar} = 0.99285 \text{ MPa} \\ 1 \text{ kg}_f/\text{cm}^2 &= 0.96784 \text{ atm} = 0.98067 \text{ bar} = 14.223 \text{ psi} \end{aligned}$$

The actual pressure of a fluid is the *absolute pressure*, which is measured relative to vacuum. However, some pressure measurement devices are calibrated to read zero in the atmosphere and they show the difference between the absolute and atmospheric pressure. This difference is called *gage pressure*. Normally "a" is used to indicate the absolute value (i.e., psia, bara) and "g" is used to show the gage pressure (i.e., psig). However, for absolute pressure very often "a" is dropped from the unit (i.e., psi, atm, bar). Another unit for the pressure is *vacuum pressure* that is defined for pressure below atmospheric pressure. Relations between these units are as follows:

$$(1.7) \quad P_{\text{gage}} = P_{\text{abs}} - P_{\text{atm}}$$

$$(1.8) \quad P_{\text{abs}} = P_{\text{atm}} - P_{\text{vac}}$$

Generally gage pressure unit is used to express pressures above the atmospheric pressures and vacuum pressure unit is used for pressures below atmospheric and may be expressed in various units (i.e., mm Hg, psi).

1.7.10 Units of Temperature

Temperature (T) is the most important parameter affecting properties of fluids and it is represented in Centigrade ($^\circ\text{C}$) and Kelvin (K) in the SI system and in Fahrenheit ($^\circ\text{F}$) and degrees Rankine ($^\circ\text{R}$) in the English unit system. Temperature in most equations is in absolute degrees of Kelvin or Rankine. However, according to the definition of Kelvin and degrees Rankine where there is a temperature difference (ΔT), unit of $^\circ\text{C}$ is the same as K and $^\circ\text{F}$ is the same as $^\circ\text{R}$. These

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temperature units are related through the following relations:

$$(1.9) \quad T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

$$(1.10) \quad T(^{\circ}\text{R}) = T(^{\circ}\text{F}) + 459.67$$

$$(1.11) \quad \Delta T(\text{K}) = \Delta T(^{\circ}\text{C})$$

$$(1.12) \quad \Delta T(^{\circ}\text{R}) = \Delta T(^{\circ}\text{F})$$

$$(1.13) \quad T(^{\circ}\text{R}) = 1.8T(\text{K})$$

$$(1.14) \quad T(^{\circ}\text{F}) = 1.8T(^{\circ}\text{C}) + 32$$

As an example, absolute temperature of 100 K is equivalent to 1.8×100 or 180°R . Therefore, the conversion factors between K and $^{\circ}\text{R}$ are as follows:

$$1 \text{ K} = 1.8^{\circ}\text{R} \text{ (for absolute temperature } T \text{ and the temperature difference, } \Delta T)$$

$$1^{\circ}\text{C} = 1.8^{\circ}\text{F} \text{ (only for the temperature difference, } \Delta T)$$

1.7.11 Units of Volume, Specific Volume, and Molar Volume—The Standard Conditions

Volume (V) has the dimension of cubic length (L^3) and thus in SI has the unit of m^3 and in English its unit is cubic feet (cf or ft^3). Some units particularly used for liquids in the SI system are liter (L), cm^3 (cc), or milliliter (mL) and in English units are gallon (in U.S. or Imperial) and barrel (bbl). Volume of one unit mass of a fluid is called specific volume and the volume of 1 mol of a fluid is called molar volume. Some of the conversion factors are as follows.

$$1 \text{ m}^3 = 10^6 \text{ cm}^3 = 1000 \text{ L} = 35.315 \text{ ft}^3 = 264.18 \text{ gallon (U.S.)} \\ = 35.316 \text{ ft}^3 = 6.29 \text{ bbl}$$

$$1 \text{ ft}^3 = 2.8316 \times 10^{-2} \text{ m}^3 = 28.316 \text{ L} = 7.4805 \text{ gallon (U.S.)}$$

$$1 \text{ bbl} = 42 \text{ gallon (U.S.)} = 158.98 \text{ L} = 34.973 \text{ gallon (Imperial)}$$

$$1 \text{ gallon (U.S.)} = 0.8327 \text{ gallon (Imperial)} \\ = 0.023809 \text{ bbl} = 3.7853 \text{ L}$$

$$1 \text{ mL} = 1 \text{ cm}^3 = 10^{-3} \text{ L} = 10^{-6} \text{ m}^3 = 0.061024 \text{ in.}^3$$

For the molar volumes some of the conversion factors are given as follows:

$$1 \text{ m}^3/\text{kmol} = 1 \text{ L/mol} = 0.001 \text{ m}^3/\text{mol} = 1000 \text{ cm}^3/\text{mol} \\ = 16.019 \text{ ft}^3/\text{lbmol}$$

$$1 \text{ ft}^3/\text{lbmol} = 6.24259 \times 10^{-2} \text{ m}^3/\text{kmol} \\ = 6.24259 \times 10^{-5} \text{ m}^3/\text{mol} = 62.4259 \text{ cm}^3/\text{mol}$$

$$1 \text{ cm}^3/\text{mol} = 1 \text{ mL/mol} = 1 \text{ L/kmol} = 0.001 \text{ m}^3/\text{kmol} \\ = 1.6019 \times 10^{-2} \text{ ft}^3/\text{lbmol}$$

It should be noted that the same conversion factors apply to specific volumes. For example,

$$1 \text{ ft}^3/\text{lb} = 6.24259 \times 10^{-2} \text{ m}^3/\text{kg} = 62.4259 \text{ cm}^3/\text{g}$$

Since volume and specific or molar volumes depend on temperature and pressure of the system, values of volume in any unit system are meaningless if the conditions are not specified. This is particularly important for gases in which both temperature and pressure strongly influence the volume. For

this reason, to express amount of gases in terms of volume, normally some SC are defined. The SC in the metric SI units are 0°C and 1 atm and in the English system are 60°F and 1 atm. Under these conditions molar volume of any gas is equivalent to 22.4 L/mol (in SI) and 379 scf/lbmol (in English units). In reservoir engineering calculations and petroleum industry in general, the SC in the SI units are also set at 60°F (15.5°C or 289 K) and 1 atm. The choice of standard temperature and pressure (STP) varies from one source to another. In this book when the standard T and P are not specified the STP refers to 289 K and 1 atm, which is equivalent to the STP in English unit system rather than SI system (273 K and 1 atm). However, for liquid systems the volume is less affected by pressure and for this reason specification of temperature alone is sufficient.

1.7.12 Units of Volumetric and Mass Flow Rates

Most processes in the petroleum industry are continuous and usually the volume or mass quantities are expressed in the form of rate defined as volume or mass per unit time. One particular volumetric flow rate used for liquids in the English system is gallon (U.S.) per minute and is known as GPM. Some of the conversion factors for these quantities are

$$1 \text{ m}^3/\text{s} = 1 \times 10^3 \text{ L/s} = 1.5851 \times 10^4 \text{ GPM} \\ = 5.4345 \times 10^5 \text{ bbl/d} = 1.27133 \times 10^5 \text{ ft}^3/\text{h}$$

$$1 \text{ ft}^3/\text{h} = 7.86558 \times 10^{-4} \text{ m}^3/\text{s} = 0.12468 \text{ GPM} \\ = 4.27466 \text{ bbl/d}$$

$$1 \text{ GPM} = 2.228 \times 10^{-3} \text{ ft}^3/\text{s} = 8.0205 \text{ m}^3/\text{h} = 34.285 \text{ bbl/d}$$

$$1 \text{ bbl/d} = 2.9167 \times 10^{-2} \text{ GPM} = 1.8401 \times 10^{-4} \text{ m}^3/\text{s} \\ = 0.23394 \text{ ft}^3/\text{h}$$

The conversion factors for the mass rates are as follows:

$$1 \text{ kg/s} = 7.93656 \times 10^3 \text{ lb/h} = 3.5136 \times 10^7 \text{ ton/year}$$

$$1 \text{ lb/s} = 1.63295 \times 10^3 \text{ kg/h} = 39.1908 \text{ ton/d}$$

The same conversion factors apply to molar rates.

1.7.13 Units of Density and Molar Density

Density shown by d or ρ is defined as mass per unit volume and it is reciprocal of specific volume. The conversion factors can be obtained from reversing those of specific volume in Section 1.7.11.

$$1 \text{ kg/m}^3 = 6.24259 \times 10^{-2} \text{ lb/ft}^3 = 1 \times 10^{-3} \text{ g/cm}^3 \\ = 8.3455 \times 10^{-3} \text{ lb/gal}$$

$$1 \text{ lb/ft}^3 = 16.019 \text{ kg/m}^3 = 1.6019 \times 10^{-2} \text{ g/cm}^3 \\ = 0.13368 \text{ lb/gal}$$

$$1 \text{ g/cm}^3 = 1 \text{ kg/L} = 10^3 \text{ kg/m}^3 = 62.4259 \text{ lb/ft}^3 \\ = 8.3455 \text{ lb/gal}$$

$$1 \text{ lb/gal} = 1.19825 \times 10^2 \text{ kg/m}^3 = 7.4803 \text{ lb/ft}^3 \\ = 0.119825 \text{ g/cm}^3$$

Density may also be presented in terms of number of moles per unit volume, which is called *molar density* and is reciprocal of molar volume. It can be obtained by dividing absolute density to molecular weight. The conversion factors for molar density are exactly the same as those for the absolute density (i.e., $1 \text{ mol/cm}^3 = 62.4259 \text{ lbmol/ft}^3$). In practical calculations

the conversion factors may be simplified without major error in the calculations. For example, 62.4 instead of 62.4259 or 7.48 instead of 7.4803 are used in practical calculations. In expressing values of densities, similar to specific volumes, the SC must be specified. Generally densities of liquid hydrocarbons are reported either in the form of specific gravity at 15.5°C (60°F) or the absolute density at 20°C and 1 atm in g/cm³.

1.7.14 Units of Specific Gravity

For liquid systems, the specific gravity (SG) is defined as the ratio of density of a liquid to that of water, and therefore, it is a dimensionless quantity. However, the temperature at which specific gravity is reported should be specified. The specific gravity is also called *relative density* versus absolute density. For liquid petroleum fractions and crude oils, densities of both the oil and water are expressed at the SC of 60°F (15.5°C) and 1 atm, and they are usually indicated as SG at 60°F/60°F or simply SG at 60°F. Another unit for the specific gravity of liquid hydrocarbons is defined by the American Petroleum Institute (API) and is called *API degree* and is defined in terms of SG at 60°F (API = 141.5/SG - 131.5). For gases, the specific gravity is defined as the ratio of density of the gas to that of the air at the SC, which is equivalent to the ratio of molecular weights. Further discussion on specific gravity, definitions, and methods of calculation are given in Chapter 2 (Section 2.1.3).

1.7.15 Units of Composition

Composition is the most important characteristic of homogeneous mixtures in which two or more components are uniformly mixed in a single phase. Because of the nature of petroleum fluids, accurate knowledge of composition is important. Generally composition is expressed as percentage (%) or as fraction (percent/100) in terms of weight, mole, and volume. Density of the components (or pseudocomponents) constituting a mixture is required to convert composition from weight basis to volume basis or vice versa. Similarly conversion of composition from mole basis to weight basis or vice versa requires molecular weight of the constituting components (or pseudocomponents). Mole, weight, and volume fractions are shown by x_m , x_w , and x_v , respectively. Mole, weight, and volume percentages are shown by mol%, wt%, and vol%, respectively. Some references use mol/mol, wt/wt, and vol/vol to express fractional compositions. For normalized compositions, the sum of fractions for all components in a mixture is 1 ($\sum x_i = 1$) and the sum of all percentages is 100. If the molecular weights of all components in a mixture are the same, then the mole fraction and weight fraction are identical. Similarly, if the density (or specific gravity) of all components is the same, the weight and volume fractions are identical. The formula to calculate weight fraction from mole fraction is given as

$$(1.15) \quad x_{wi} = \frac{x_{mi} M_i}{\sum_{i=1}^N x_{mi} M_i}$$

where N is the total number of components, M_i is the molecular weight, and x_{wi} and x_{mi} are the weight and mole fractions of component i , respectively. The conversion from weight to

volume fraction can be obtained from the following equation:

$$(1.16) \quad x_{vi} = \frac{x_{wi}/SG_i}{\sum_{i=1}^N x_{wi}/SG_i}$$

in which x_{vi} is the volume fraction and SG_i is the specific gravity of component i . In Eq. (1.16) density (d) can also be used instead of specific gravity. If mole and weight fractions are multiplied by 100, then composition is calculated on the percentage basis. In a similar way the conversion of composition from volume to weight and then to mole fraction can be obtained by reversing the above equations. The composition of a component in a liquid mixture may also be presented by its molar density, units of which were discussed in Section 1.7.13. Generally, a solution with solute molarity of 1 has 1 mol of solute per 1 L of solution (1 mol/L). Through use of both molecular weight of solute and density of solution one can obtain weight fraction from molarity. Another unit to express concentration of a solute in a liquid solution is *molality*. A solution with molality of 1 has 1 mol of solute per 1 kg of liquid solvent.

Another unit for the composition in small quantities is the ppm (*part per million*), which is defined as the ratio of unit weight (or volume) of a component to 10⁶ units of weight or volume for the whole mixture. Therefore, ppm can be presented in terms of both volume or weight. Usually in gases the ppm is presented in terms of volume and in liquids it is expressed in terms of weight. When ppm is presented in terms of weight, its relation with wt% is 1 ppm = 10⁻⁴ wt%. For example, the maximum allowable concentration of H₂S in air for prolonged exposure is 10 ppm or 0.001 wt%. There is another smaller unit defined as *part per billion* known as ppb (1 ppm = 1000 ppb). In the United States a gas is considered "sweet" if the amount of its H₂S content is no more than one quarter grain per 100 scf of gas. This is almost equivalent to 4 × 10⁻⁴ mol fraction [88]. This is in turn equivalent to 4 ppm on the gas volume basis. Gas composition may also be represented in terms of partial pressure where sum of all partial pressures is equivalent to the total pressure.

In general, the composition of gases is presented in volume or mole fractions, while the liquid composition may be presented in any form of weight, mole, or volume. For gases at low pressures (≤ 1 atm where a gas may be considered an ideal gas) mole fraction and volume fractions are the same. However, generally under any conditions, volume and mole fractions are considered the same for gases and vapor mixtures. For narrow boiling range petroleum fractions with compositions presented in terms of PNA percentages, it is assumed that densities and molecular weights for all three representative pseudocomponents are nearly the same. Therefore, with a good degree of approximation, it is assumed that the PNA composition in all three unit systems are the same and for this reason on many occasions the PNA composition is represented only in terms of percentage (%) or fraction without indicating their weight or volume basis. However, this is not the case for the crude or reservoir fluid compositions where the composition is presented in terms of boiling point (or carbon number) and not in the form of molecular type. The following example shows conversion of composition from one type to another for a crude sample.

TABLE 1.5—Conversion of composition of a crude oil sample from mole to weight and volume percent.

Component	mol%	Molecular weight (M)	Specific gravity (SG)	wt%	vol%
C ₂	0.19	30.07	0.356	0.03	0.06
C ₃	1.88	44.10	0.508	0.37	0.64
iC ₄	0.62	58.12	0.563	0.16	0.25
nC ₄	3.92	58.12	0.584	1.02	1.52
iC ₅	2.11	72.15	0.625	0.68	0.95
nC ₅	4.46	72.15	0.631	1.44	1.98
C ₆ (fraction)	8.59	82.00 ^a	0.690	3.15	3.97
C ₇₊ (fraction)	78.23	266.00	0.895	93.15	90.63
Sum	100.00			100.00	100.00

^aThis is molecular weight of C₆ hydrocarbon group and should not be mistaken with M of nC₆ which is 86.2.

Example 1.1—The composition of a Middle East crude oil is given in Table 1.5 in terms of mol% with known molecular weight and specific gravity for each component/pseudocomponent. Calculate the composition of the crude in both wt% and vol%.

Solution—In this table values of molecular weight and specific gravity for pure compounds are obtained from Chapter 2 (Table 2.1), while for the C₆ group, values are taken from Chapter 4 and for the C₇₊ fraction, values are given by the laboratory. Conversion calculations are based on Eqs. (1.15) and (1.16) on the percentage basis and the results are also given in Table 1.5. In this calculation it is seen that in terms of wt% and vol%, heavier compounds (i.e., C₇₊) have higher values than in terms of mol%. ♦

1.7.16 Units of Energy and Specific Energy

Energy in various forms (i.e., heat, work) has the unit of Joule (1 J = 1 N · m) in the SI and ft · lb_f in the English system. Values of heat are also presented in terms of calorie (in SI) and BTU (British Thermal Unit) in the English system. There are two types of joules: absolute joules and international joules, where 1 Joule (int.) = 1.0002 Joule (abs.). In this book only absolute joules is used and it is designated by J. There are also two types of calories: thermochemical and International Steam Tables, where 1 cal (international steam tables) = 1.0007 cal (thermochemical) as defined in the API-TDB [47]. In this book cal refers to the international steam tables unless otherwise is specified. In the cgs system the unit of energy is dyn-cm, which is also called erg. The unit of power in the SI system is J/s or watt (W). Therefore, kW·h equivalent to 3600 kJ is also a unit for the energy. The product of pressure and volume (PV) may also present the unit of energy. Some of the conversion factors for the units of energy are given as follows:

$$\begin{aligned}
 1 \text{ J} &= 1 \text{ N} \cdot \text{m} = 10^{-3} \text{ kJ} = 10^7 \text{ erg} = 0.23885 \text{ cal} \\
 &= 9.4783 \times 10^{-4} \text{ Btu} = 2.778 \times 10^{-7} \text{ kW} \cdot \text{h} \\
 1 \text{ J} &= 3.725 \times 10^{-7} \text{ hp} \cdot \text{h} = 0.73756 \text{ ft} \cdot \text{lb}_f = 9.869 \text{ L} \cdot \text{atm} \\
 1 \text{ cal (International Tables)} &= 3.9683 \times 10^{-3} \text{ Btu} = 4.187 \text{ J} \\
 &= 3.088 \text{ ft} \cdot \text{lb}_f = 1.1630 \times 10^{-6} \text{ kW} \cdot \text{h} \\
 1 \text{ cal (thermochemical)} &= 1 \text{ cal} = 3.9657 \times 10^{-3} \text{ Btu} \\
 &= 4.184 \text{ J} = 3.086 \text{ ft} \cdot \text{lb}_f = 1.1622 \times 10^{-6} \text{ kW} \cdot \text{h} \\
 1 \text{ Btu} &= 1055 \text{ J} = 251.99 \text{ cal} = 778.16 \text{ ft} \cdot \text{lb}_f \\
 &= 2.9307 \times 10^{-4} \text{ kW} \cdot \text{h} \\
 1 \text{ ft} \cdot \text{lb}_f &= 1.3558 \text{ J} = 0.32384 \text{ cal} = 1.2851 \times 10^{-3} \text{ Btu} \\
 &= 3.766 \times 10^{-7} \text{ kW} \cdot \text{h}
 \end{aligned}$$

$$1 \text{ kW} \cdot \text{h} = 3600 \text{ kJ} = 3412.2 \text{ Btu} = 2.655 \times 10^6 \text{ ft} \cdot \text{lb}_f$$

Energy per unit mass is called *specific energy* that may be used to present properties such as specific enthalpy, specific internal energy, specific heats of reaction, and combustion or the heating values of fuels. Some of the conversion factors are given below.

$$\begin{aligned}
 1 \text{ J/g} &= 10^3 \text{ J/kg} = 1 \text{ kJ/kg} = 0.42993 \text{ Btu/lb} \\
 1 \text{ Btu/lb} &= 2.326 \text{ J/g} = 0.55556 \text{ cal/g}
 \end{aligned}$$

The same conversion factors apply to the units of molar energy such as molar enthalpy.

1.7.17 Units of Specific Energy per Degrees

Properties such as heat capacity have the unit of specific energy per degrees. The conversion factors are as follows:

$$\begin{aligned}
 1 \frac{\text{J}}{\text{g} \cdot \text{C}} &= 1 \times 10^{-3} \frac{\text{J}}{\text{kg} \cdot \text{C}} = 1 \frac{\text{kJ}}{\text{kg} \cdot \text{C}} = 0.23885 \frac{\text{Btu}}{\text{lb} \cdot \text{F}} \\
 1 \frac{\text{cal}}{\text{g} \cdot \text{C}} &= 1 \frac{\text{Btu}}{\text{lb} \cdot \text{F}} = 4.1867 \frac{\text{J}}{\text{g} \cdot \text{C}}
 \end{aligned}$$

As mentioned in Section 1.7.13, for the difference in temperature (ΔT), units of °C and K are the same. Therefore, the units of heat capacity may also be represented in terms of specific energy per Kelvin or degrees Rankine (i.e., 1 $\frac{\text{Btu}}{\text{lb} \cdot \text{F}} = 1 \frac{\text{Btu}}{\text{lb} \cdot \text{R}} = 1 \frac{\text{cal}}{\text{g} \cdot \text{C}} = 1 \frac{\text{cal}}{\text{g} \cdot \text{K}}$). The same conversion factors apply to units of molar energy per degrees such as molar heat capacity.

Another parameter which has the unit of molar energy per degrees is the universal *gas constant* (R) used in thermodynamic relations and equations of state. However, the unit of temperature for this parameter is the absolute temperature (K or °R), and °C or °F may never be used in this case. Similar conversion factors as those used for the heat capacity given above also apply to the units of gas constants in terms of molar energy per absolute degrees.

$$\begin{aligned}
 1 \frac{\text{Btu}}{\text{lbmol} \cdot \text{R}} &= 1 \frac{\text{cal}}{\text{mol} \cdot \text{K}} = 1.0007 \frac{\text{cal(thermochemical)}}{\text{mol} \cdot \text{K}} \\
 &= 4.1867 \times 10^3 \frac{\text{J}}{\text{kmol} \cdot \text{K}}
 \end{aligned}$$

Numerical values of the gas constant are given in Section 1.7.24.

1.7.18 Units of Viscosity and Kinematic Viscosity

Viscosity (absolute viscosity) shown by μ is a property that characterizes the fluidity of fluids and it has the dimension of mass per length per time ($M/L \cdot t$). If the relation between dimensions of force (F) and mass (M) is used ($F = M \cdot L \cdot t^{-2}$), then absolute viscosity finds the dimension of $F \cdot t \cdot L^{-2}$ which is the same as dimension for the product of pressure and time. Therefore, in the SI system the unit of viscosity is $\text{Pa} \cdot \text{s}$ ($\text{N} \cdot \text{m}^{-2} \cdot \text{s}$). In the cgs system the unit of viscosity is in $\text{g}/\text{cm} \cdot \text{s}$ that is called *poise* (p) and its hundredth is called centipoise (cp), which is equivalent to $\text{mPa} \cdot \text{s}$ ($\text{mPa} \cdot \text{s}$). The conversion factors in various units are given below.

$$\begin{aligned} 1 \text{ cp} &= 1.02 \times 10^{-4} \text{ kg}_f \cdot \text{s}/\text{m}^2 = 1 \times 10^{-3} \text{ Pa} \cdot \text{s} = 1 \text{ mPa} \cdot \text{s} \\ &= 10^{-2} \text{ p} = 2.089 \times 10^{-5} \text{ lb}_f \cdot \text{s}/\text{ft}^2 = 2.419 \text{ lb}/\text{h} \cdot \text{ft} \\ &= 3.6 \text{ kg}/\text{h} \cdot \text{m} \end{aligned}$$

$$1 \text{ Pa} \cdot \text{s} = 1 \text{ kg}/\text{m} \cdot \text{s} = 1000 \text{ cp} = 0.67194 \text{ lb}/\text{ft} \cdot \text{s}$$

$$1 \text{ lb}/\text{h} \cdot \text{ft} = 8.634 \times 10^{-6} \text{ lb}_f \cdot \text{s}/\text{ft}^2 = 0.4134 \text{ cp} = 1.488 \text{ kg}/\text{h} \cdot \text{m}$$

$$1 \text{ kg}_f \cdot \text{s}/\text{m}^2 = 9.804 \times 10^3 \text{ cp} = 9.804 \text{ Pa} \cdot \text{s} = 0.20476 \text{ lb}_f \cdot \text{s}/\text{ft}^2$$

$$1 \text{ lb}_f \cdot \text{s}/\text{ft}^2 = 4.788 \times 10^4 \text{ cp} = 4.884 \text{ kg}_f \cdot \text{s}/\text{m}^2$$

The ratio of viscosity to density is known as *kinematic viscosity* (ν) and has the dimension of L/t^2 . In the cgs system, the unit of kinematic viscosity is cm^2/s also called *stoke* (St) and its hundredth is centistoke (cSt). The conversion factors are given below.

$$1 \text{ ft}^2/\text{h} = 2.778 \times 10^{-4} \text{ ft}^2/\text{s} = 0.0929 \text{ m}^2/\text{h} = 25.81 \text{ cSt}$$

$$1 \text{ ft}^2/\text{s} = 9.29 \times 10^4 \text{ cSt} = 334.5 \text{ m}^2/\text{h}$$

$$\begin{aligned} 1 \text{ cSt} &= 10^{-2} \text{ St} = 10^{-6} \text{ m}^2/\text{s} = 1 \text{ mm}^2/\text{s} = 3.875 \times 10^{-2} \text{ ft}^2/\text{h} \\ &= 1.076 \times 10^{-5} \text{ ft}^2/\text{s} \end{aligned}$$

$$1 \text{ m}^2/\text{s} = 10^4 \text{ St} = 10^6 \text{ cSt} = 3.875 \times 10^4 \text{ ft}^2/\text{h}$$

Another unit to express kinematic viscosity of liquids is *Saybolt universal seconds* (SUS), which is the unit for the Saybolt universal viscosity (ASTM D 88). Definition of viscosity gravity constant (VGC) is based on SUS unit for the viscosity at two reference temperatures of 100 and 210°F (37.8 and 98.9 °C). The VGC is used in Chapter 3 to estimate the composition of heavy petroleum fractions. The relation between SUS and cSt is a function of temperature and it is given in the API TDB [47]. The analytical relations to convert cSt to SUS are given below [47].

$$\begin{aligned} \text{SUS}_{\text{eq}} &= 4.6324\nu_T \\ &+ \frac{[1.0 + 0.03264\nu_T]}{[(3930.2 + 262.7\nu_T + 23.97\nu_T^2 + 1.646\nu_T^3) \times 10^{-5}]} \end{aligned} \quad (1.17)$$

where ν_T is the kinematic viscosity at temperature T in cSt. The SUS_{eq} calculated from this relation is converted to the SUS_T at the desired temperature of T through the following relation.

$$\text{SUS}_T = [1 + 1.098 \times 10^{-4}(T - 311)]\text{SUS}_{\text{eq}} \quad (1.18)$$

where T is the temperature in kelvin (K). For conversion of cSt to SUS at the reference temperature of 311 K (100°F), only Eq. (1.17) is needed. Equation (1.18) is the correction term for temperatures other than 100°F. For kinematic viscosities greater than 70 cSt, Eqs. (1.17) and (1.18) can be

simplified to the following form at the temperatures of 311 (100°F) and 372 K, (210°F) respectively [1].

$$\text{SUS}_{100\text{F}} = 4.632\nu_{100\text{F}} \quad \nu_{100\text{F}} \geq 75 \text{ cSt} \quad (1.19)$$

$$\text{SUS}_{210\text{F}} = 4.664\nu_{210\text{F}} \quad \nu_{210\text{F}} \geq 75 \text{ cSt} \quad (1.20)$$

where $\nu_{100\text{F}}$ is the kinematic viscosity at 100°F (311 K) in cSt. As an example, a petroleum fraction with kinematic viscosity of 5 cSt at 311 K has an equivalent Saybolt Universal Viscosity of 42.4 SUS as calculated from Eq. (1.17).

Another unit for the viscosity is SFS (Saybolt foural seconds) expressed for Saybolt foural viscosity, which is measured in a way similar to Saybolt universal viscosity but measured by a larger orifice (ASTM D 88). The conversion from cSt to SFS is expressed through the following equations at two reference temperatures of 122°F (323 K) and 210°F (372 K) [47].

$$\text{SFS}_{122\text{F}} = 0.4717\nu_{122\text{F}} + \frac{13924}{\nu_{122\text{F}}^2 - 72.59\nu_{122\text{F}} + 6816} \quad (1.21)$$

$$\text{SFS}_{210\text{F}} = 0.4792\nu_{210\text{F}} + \frac{5610}{\nu_{210\text{F}}^2 + 2130} \quad (1.22)$$

For conversion of Saybolt foural viscosity (SFS) to kinematic viscosity (cSt.), the above equations should be used in reverse or to use tabulated values given by API-TDB [47]. As an example, an oil with Saybolt foural viscosity of 450 SFS at 210°F has a kinematic viscosity of 940 cSt. Generally, viscosity of highly viscous oils is presented by SUS or SFS units.

1.7.19 Units of Thermal Conductivity

Thermal conductivity (k) as discussed in Chapter 8 represents amount of heat passing through a unit area of a medium for one unit of temperature gradient (temperature difference per unit length). Therefore, it has the dimension of energy per time per area per temperature gradient. In the SI units it is expressed in $\text{J}/\text{s} \cdot \text{m} \cdot \text{K}$. Since thermal conductivity is defined based on a temperature difference (ΔT), the unit of °C may also be used instead of K. Because J/s is defined as watt (W), the unit of thermal conductivity in the SI system is usually written as $\text{W}/\text{m} \cdot \text{K}$. In the English system, the unit of thermal conductivity is $\frac{\text{Btu}}{\text{ft} \cdot \text{h} \cdot ^\circ\text{F}}$ and in some references is written as $\frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}/\text{ft}}$, which is the ratio of heat flux to the temperature gradient. The conversion factors between various units are given below.

$$\begin{aligned} 1 \text{ W}/\text{m} \cdot \text{K} (\text{J}/\text{s} \cdot \text{m} \cdot ^\circ\text{C}) &= 0.5778 \text{ Btu}/\text{ft} \cdot \text{h} \cdot ^\circ\text{F} \\ &= 1.605 \times 10^{-4} \text{ Btu}/\text{ft} \cdot \text{s} \cdot ^\circ\text{F} \\ &= 0.8593 \text{ kcal}/\text{h} \cdot \text{m} \cdot ^\circ\text{C} \end{aligned}$$

$$1 \text{ Btu}/\text{ft} \cdot \text{h} \cdot ^\circ\text{F} = 1.7307 \text{ W}/\text{m} \cdot \text{K}$$

$$1 \text{ cal}/\text{cm} \cdot \text{s} \cdot ^\circ\text{C} = 242.07 \text{ Btu}/\text{ft} \cdot \text{h} \cdot ^\circ\text{F} = 418.95 \text{ W}/\text{m} \cdot \text{K}$$

1.7.20 Units of Diffusion Coefficients

Diffusion coefficient or diffusivity represents the amount of mass diffused in a medium per unit area per unit time per unit concentration gradient. As shown in Chapter 8, it has the same dimension as the kinematic viscosity, which is

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squared length per time (L^2/t). Usually it is expressed in cm^2/s .

$$1 \text{ cm}^2/\text{s} = 10^{-4} \text{ m}^2/\text{s} = 9.29 \times 10^{-6} \text{ ft}^2/\text{s} = 3.3445 \times 10^{-4} \text{ ft}^2/\text{h}$$

1.7.21 Units of Surface Tension

Surface tension or interfacial tension (σ) as described in Section 8.6 (Chapter 8) has the unit of energy (work) per unit area and the SI unit of surface tension is $\text{J}/\text{m}^2 = \text{N}/\text{m}$. Since N/m is a large unit the values of surface tension are expressed in milli- N/m (mN/m) which is the same as the cgs unit of surface tension (dyn/cm). The conversion factors for this property are as follows:

$$\begin{aligned} 1 \text{ dyn}/\text{cm} &= 1 \text{ erg}/\text{cm}^2 = 10^{-3} \text{ J}/\text{m}^2 = 1 \text{ mJ}/\text{m}^2 \\ &= 10^{-3} \text{ N}/\text{m} = 1 \text{ mN}/\text{m} \end{aligned}$$

1.7.22 Units of Solubility Parameter

Prediction of solubility parameter (δ) for petroleum fractions and crude oil is discussed in Chapters 4 and 10 and it has the unit of $(\text{energy}/\text{volume})^{0.5}$. The traditional unit of δ is in $(\text{cal}/\text{cm}^3)^{0.5}$. Another form of the unit for the solubility parameter is $(\text{pressure})^{0.5}$. Some conversion factors are given below.

$$\begin{aligned} 1 (\text{cal}_{\text{th}}/\text{cm}^3)^{0.5} &= 2.0455 (\text{J}/\text{cm}^3)^{0.5} = 2.0455 (\text{MPa})^{0.5} \\ &= 2.0455 \times 10^3 (\text{J}/\text{m}^3)^{0.5} \\ &= 2.0455 \times 10^3 (\text{Pa})^{0.5} = 10.6004 (\text{Btu}/\text{ft}^3)^{0.5} \\ &= 31.6228 (\text{kcal}_{\text{th}}/\text{m}^3)^{0.5} \\ &= 6.4259 (\text{atm})^{0.5} = 2.05283 (\text{ft} \cdot \text{lb}_f/\text{ft}^3)^{0.5} \\ 1 (\text{MPa})^{0.5} &= 0.4889 (\text{cal}_{\text{th}}/\text{cm}^3)^{0.5} = 1 (\text{J}/\text{cm}^3)^{0.5} = 10^3 (\text{Pa})^{0.5} \end{aligned}$$

Values of surface tension in the literature are usually expressed in $(\text{cal}/\text{cm}^3)^{0.5}$ where cal represents thermochemical unit of calories.

1.7.23 Units of Gas-to-Oil Ratio

Gas-to-oil ratio is an important parameter in determining the type of a reservoir fluid and in setting the optimum operating conditions in the surface separators at the production field (Chapter 9, Section 9.2.1). In some references such as the API-TDB [47], this parameter is called *gas-to-liquid ratio* and is shown by GLR. GOR represents the ratio of volume of gas to the volume of liquid oil from a separator under the SC of 289 K and 101.3 kPa (60°F and 14.7 psia) for both the gas and liquid. Units of volume were discussed in Section 1.7.13. Three types of units are commonly used: the oilfield, the metric, and the English units.

- Oilfield units: standard cubic feet (scf) is used for the volume of gas, and *stock tank barrels* (stb) is used for the volume of oil. Therefore, GOR has the unit of scf/stb.
- Metric units: standard cubic meters (sm^3) is used for the gas, and stock tank cubic meters (stm^3) unit is used for the oil. The volume of liquid oil produced is usually presented under the stock tank conditions, which are 60°F (15.5°C) and 1 atm. Therefore, GOR unit in this system is sm^3/stm^3 .
- English unit: scf is used for the gas, and *sock tank cubic feet* (stft^3) is used for the liquid volume. Thus the GOR has the

units of scf/stft^3 . This unit is exactly the same as sm^3/stm^3 in the SI unit.

The conversion factors between these three units for the GOR (GLR) are given as follows:

$$\begin{aligned} 1 \text{ scf}/\text{stb} &= 0.1781 \text{ scf}/\text{stft}^3 = 0.1781 \text{ sm}^3/\text{stm}^3 \\ 1 \text{ sm}^3/\text{stm}^3 &= 1 \text{ scf}/\text{stft}^3 = 5.615 \text{ scf}/\text{stb} \end{aligned}$$

1.7.24 Values of Universal Constants

1.7.24.1 Gas Constant

The universal gas constant shown by R is used in equations of state and thermodynamic relations in Chapters 5, 6, 8, and 10. It has the unit of energy per mole per absolute degrees. As discussed in Section 1.7.17, its dimension is similar to that of molar heat capacity. The value of R in the SI unit is $8314 \text{ J}/\text{kmol} \cdot \text{K}$. The energy dimension may also be expressed as the product of pressure and volume (PV), which is useful for application in the equations of state. Value of R in terms of energy unit is more useful in the calculation of thermodynamic properties such as heat capacity or enthalpy. Values of this parameter in several other units are given as follows.

$$\begin{aligned} R &= 8.314 \text{ J}/\text{mol} \cdot \text{K} = 8314 \text{ J}/\text{kmol} \cdot \text{K} = 8.314 \text{ m}^3 \text{ Pa}/\text{mol} \cdot \text{K} \\ &= 83.14 \text{ cm}^3 \text{ bar}/\text{mol} \cdot \text{K} \\ &= 82.06 \text{ cm}^3 \cdot \text{atm}/\text{mol} \cdot \text{K} = 1.987 \text{ cal}_{\text{th}}/\text{mol} \cdot \text{K} \\ &= 1.986 \text{ cal}/\text{mol} \cdot \text{K} = 1.986 \text{ Btu}/\text{lbmol} \cdot \text{R} \\ &= 0.7302 \text{ ft}^3 \cdot \text{atm}/\text{lbmol} \cdot \text{R} = 10.73 \text{ ft}^3 \cdot \text{psia}/\text{lbmol} \cdot \text{R} \\ &= 1545 \text{ ft} \cdot \text{lb}_f/\text{lbmol} \cdot \text{R} \end{aligned}$$

1.7.24.2 Other Numerical Constants

The Avogadro number is the number of molecules in 1 mol of a substance.

$$N_A = \text{Avogadro number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

For example 1 mol of methane (16 g) consists of 6.022×10^{23} molecules. Other constants are

$$\text{Boltzman constant} = k_B = R/N_A = 1.381 \times 10^{-23} \text{ J}/\text{K}.$$

$$\text{Planck constant} = h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}.$$

$$\text{Speed of light in vacuum} = c = 2.998 \times 10^8 \text{ m}/\text{s}.$$

Numerical constants

$$\pi = 3.14159265$$

$$e = 2.718281828$$

$$\ln x = \log_{10} x / \log_{10} e = 2.30258509 \log_{10} x.$$

1.7.25 Special Units for the Rates and Amounts of Oil and Gas

Amounts of oil and gas are usually expressed in volumetric quantities. In the petroleum industry the common unit for volume of oil is barrel (bbl) and for the gas is standard cubic feet (scf) both at the conditions of 60°F (15.5°C) and 1 atm. The production rate for the crude is expressed in bbl/d and for the gas in scf/d.

In some cases, amount of crude oil is expressed in the metric ton. Conversion from volume to weight or vice versa requires density or specific gravity (API) of the oil. For a light

Saudi Arabian crude of 35.5 API (SG = 0.847), the following conversion factors apply between weight and volume of crudes and the rates:

$$\begin{aligned} 1 \text{ ton} &\cong 7.33 \text{ bbl} = 308 \text{ gallon (U.S.)} & 1 \text{ bbl} &\cong 0.136 \text{ ton} \\ 1 \text{ bbl/d} &\cong 50 \text{ ton/year} \end{aligned}$$

For a Middle East crude of API 30, 1 ton \cong 7.19 bbl (1 bbl \cong 0.139 ton).

Another way of expressing quantities of various sources of energy is through their heating values. For example, by burning 1×10^6 tons of a crude oil, the same amount of energy can be produced that is produced through burning 1.5×10^9 tons of coal. Of course this value very much depends on the type of crude and the coal. Therefore, such evaluations and comparisons are approximate. In summary, 1 million tons of a typical crude oil is equivalent to other forms of energy:

$$\begin{aligned} 1 \times 10^6 \text{ tons of crude oil} &\cong 1.111 \times 10^9 \text{ sm}^3 (39.2 \times 10^9 \text{ scf}) \\ &\quad \text{of natural gas} \\ &\cong 1.5 \times 10^6 \text{ tons of coal} \\ &\cong 12 \times 10^9 \text{ kW} \cdot \text{h of electricity} \end{aligned}$$

The \cong sign indicates the approximate values, as they depend on the type of oil or gas. For a typical crude, the heating value is approximately 10 500 cal/g (18 900 Btu/lb) and for the natural gas is about 1000 Btu/scf (37.235×10^3 kJ/sm³). Approximately 1 million tons of a typical crude oil can produce an energy equivalent to 4×10^9 kW · h of electricity through a typical power plant. In 1987 the total nuclear energy produced in the world was equivalent to 404×10^6 tons of crude oil based on the energy produced [5]. In the same year the total hydroelectric energy was equivalent to 523.9×10^6 tons of crude oil. In 1987 the total coal reserves in the world were estimated at 1026×10^9 tons, while the total oil reserves were about 122×10^9 tons. However, from the energy point of view the total coal reserves are equivalent to only 0.68×10^9 tons of crude oil. The subject of heating values will be discussed further in Chapter 7 (see Section 7.4.4).

Unit conversion is an important art in engineering calculations and as was stated before with the knowledge of the definition of some basic units for only a few fundamental quantities (energy, length, mass, time, and temperature), the unit for every other property can be obtained. The basic idea in the unit conversion is that a value of a parameter remains the same when it is multiplied by a factor of unity in a way that the initial units are eliminated and the desired units are kept. The following examples demonstrate how a unit can be converted to another unit system without the use of tabulated conversion factors.

Example 1.2—The molar heating value of methane is 802 kJ/mol. Calculate the heating value of methane in the units of cal/g and Btu/lb. The molecular weight of methane is 16.0.

Solution—In this calculation a practicing engineer has to remember the following basic conversion factors: 1 lb = 453.6 g, 1 cal = 4.187 J, and 1 Btu = 252 cal. The value of molecular weight indicates that 1 mol = 16 g. In the conversion process the initial unit is multiplied by a series of known conversion

factors with ratios of unity as follows:

$$\begin{aligned} 802 \frac{\text{kJ}}{\text{mol}} &= \left(802 \frac{\text{kJ}}{\text{mol}} \right) \times \left| \frac{\text{mol}}{16 \text{ g}} \right| \times \left| \frac{1000 \text{ J}}{\text{kJ}} \right| \times \left| \frac{\text{cal}}{4.187 \text{ J}} \right| \\ &= \left(\frac{802 \times 1000}{16 \times 4.187} \right) [\text{cal/g}] = 11971.58 \text{ cal/g} \end{aligned}$$

The conversion to the English unit is performed in a similar way:

$$\begin{aligned} 11971.58 \text{ cal/g} &= (11971.58 \text{ cal/g}) \times \left| \frac{453.6 \text{ g}}{\text{lb}} \right| \times \left| \frac{\text{Btu}}{252 \text{ cal}} \right| \\ &= \left(\frac{11971.58 \times 453.6}{252} \right) [\text{Btu/lb}] \\ &= 21549.2 \text{ Btu/lb} \end{aligned}$$

In the above calculations all the ratio of terms inside the || sign have values of unity. ♦

Example 1.3—Thermal conductivity of a kerosene sample at 60°C is 0.07 Btu/h · ft · °F. What is the value of thermal conductivity in mW/mK from the following procedures:

1. Use of appropriate conversion factor in Section 1.7.19.
2. Direct calculation with use of conversion factors for fundamental dimensions.

Solution—

1. In Section 1.7.19 the conversion factor between SI and English units is given as:

1 W/mK = 0.5778 Btu/ft · h · °F. With the knowledge that W = 1000 mW, the conversion is carried as:

$$\begin{aligned} 0.07 \text{ Btu/h} \cdot \text{ft} \cdot ^\circ\text{F} &= \left(0.07 \left| \frac{\text{Btu}}{\text{h} \cdot \text{ft} \cdot ^\circ\text{F}} \right| \right) \times \left| \frac{1000 \text{ mW}}{\text{W}} \right| \\ &\quad \times \left| \frac{\text{W/mK}}{0.5778 \text{ Btu/h} \cdot \text{ft} \cdot ^\circ\text{F}} \right| = 121.1 \text{ mW/mK} \end{aligned}$$

2. The conversion can be carried out without use of the conversion tables if a practicing engineer is familiar with the basic definitions and conversion factors. These are 1 W = 1 J/s, 1 W = 1000 mW, 1 cal = 4.187 J, 1 Btu = 251.99 cal, 1 h = 3600 s, 1 ft = 0.3048 m, 1 K = 1°C = 1.8°F (for the temperature difference). It should be noted that thermal conductivity is defined based on temperature difference.

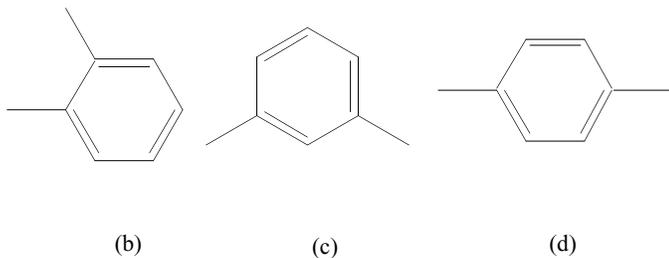
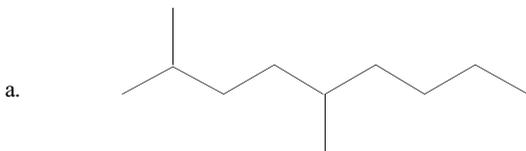
0.07 Btu/h · ft · °F

$$\begin{aligned} &= \left[0.07 \left| \frac{\text{Btu}}{\text{h} \cdot \text{ft} \cdot ^\circ\text{F}} \right| \right] \times \left| \frac{251.99 \text{ cal}}{\text{Btu}} \right| \times \left| \frac{4.187 \text{ J}}{\text{cal}} \right| \times \left| \frac{\text{h}}{3600 \text{ s}} \right| \\ &\quad \times \left| \frac{\text{W}}{\text{J/s}} \right| \times \left| \frac{1000 \text{ mW}}{\text{W}} \right| \times \left| \frac{\text{ft}}{0.3048 \text{ m}} \right| \times \left| \frac{1.8^\circ\text{F}}{^\circ\text{C}} \right| \times \left| \frac{^\circ\text{C}}{\text{K}} \right| \\ &= \left| \frac{0.07 \times 251.99 \times 4.187 \times 1000 \times 1.8}{3600 \times 0.3048} \right| \times \left| \frac{\text{mW}}{\text{m} \cdot \text{K}} \right| \\ &= 121.18 \text{ mW/mK} \end{aligned}$$

Examples 1.2 and 1.3 show that with the knowledge of only very few conversion factors and basic definitions of fundamental units, one can obtain the conversion factor between any two unit systems for any property without use of a reference conversion table.

1.8 PROBLEMS

- 1.1. State one theory for the formation of petroleum and give names of the hydrocarbon groups in a crude oil. What are the most important heteroatoms and their concentration level in a crude oil?
- 1.2. The following compounds are generally found in the analysis of a crude oil: ethane, propane, isobutane, *n*-butane, isopentane, *n*-pentane, 2,2-dimethylbutane, cyclopentane, cyclohexane, *n*-hexane, 2-methylpentane, 3-methylpentane, benzene, methylcyclopentane, 1,1-dimethylcyclopentane, and hydrocarbons from C₇ and heavier grouped as C₇₊.
 - a. For each compound, draw the chemical structure and give the formula. Also indicate the name of hydrocarbon group that each compound belongs to.
 - b. From the above list give the compounds that possibly exist in a gasoline fraction.
- 1.3. Give the names of *n*-C₂₀, *n*-C₃₀, *n*-C₄₀, and three isomers of *n*-heptane according to the IUPAC system.
- 1.4. List the 10 most important physical properties of crude and its products that are required in both the design and operation of an atmospheric distillation column.
- 1.5. What thermodynamic and physical properties of gas and/or liquid fluids are required for the following two cases?
 - a. Design and operation of an absorption column with chemical reaction [40, 89].
 - b. Reservoir simulation [37].
- 1.6. What is the characterization of petroleum fractions, crude oils, and reservoir fluids? Explain their differences.
- 1.7. Give the names of the following compounds according to the IUPAC system.



- 1.8. From an appropriate reference find the following data in recent years.
 - a. What is the distribution of refineries in different parts of the world (North America, South America, Western

- Europe, Africa, Middle East, Eastern Europe and Former Soviet Union, and Asia Pacific)?
- b. Where is the location of the biggest refinery in the world and what is its capacity in bbl/d?
- c. What is the history of the rate of production of gasoline, distillate, and residual from refineries in the world and the United States for the last decade?
- 1.9. Characteristics of three reservoir fluids are given below. For each case determine the type of the reservoir fluid using the rule of thumb.
 - a. GOR = 20 scf/stb
 - b. GOR = 150 000 scf/stb
 - c. CH₄ mol% = 70, API gravity of STO = 40
- 1.10. GOR of a reservoir fluid is 800 scf/stb. Assume the molecular weight of the stock tank oil is 260 and its specific gravity is 0.87.
 - a. Calculate the GOR in sm³/stm³ and the mole fraction of gases in the fluid.
 - b. Derive a general mathematical relation to calculate GOR from mole fraction of dissolved gas (*x*_A) through STO gravity (SG) and oil molecular weight (*M*). Calculate *x*_A using the developed relation.
- 1.11. The total LPG production in 1995 was 160 million tons/year. If the specific gravity of the liquid is assumed to be 0.55, what is the production rate in bbl/d?
- 1.12. A C₇₊ fraction of a crude oil has the following composition in wt%. The molecular weight and specific gravity of each pseudocomponent are also given below. Calculate the composition of crude in terms of vol% and mol%.

Pseudocomponent	wt%	<i>M</i>	SG
C ₇₊ (1)	17.3	110	0.750
C ₇₊ (2)	23.6	168	0.810
C ₇₊ (3)	31.8	263	0.862
C ₇₊ (4)	16.0	402	0.903
C ₇₊ (5)	11.3	608	0.949
Total C ₇₊	100		

- 1.13. It is assumed that a practicing engineer remembers the following fundamental unit conversion factors without a reference.
 - 1 ft = 0.3048 m = 12 in.
 - 1 atm = 101.3 kPa = 14.7 psi
 - 1 K = 1.8°R
 - 1 Btu = 252 cal
 - 1 cal = 4.18 J
 - 1 kg = 2.2 lb
 - g* = 9.8 m/s²
 - 1 lbmol = 379 scf
 - Molecular weight of methane = 16 g/mol
 Calculate the following conversion factors using the above fundamental units.
 - a. The value of gas constant is 1.987 cal/mol · K. What is its value in psi · ft³/lbmol · R?
 - b. Pressure of 5000 psig to atm
 - c. 1 kg_f/cm² to kPa
 - d. 1 Btu/lb · °F to J/kg · K
 - e. 1 Btu/lbmol to cal/g
 - f. 1000 scf of methane gas to lbmol
 - g. 1 MMM scf of methane to kg

- h. 1 cp to lb/ft.h
 - i. 1 Pa · s to cp
 - j. 1 g/cm³ to lb/ft³
- 1.14. A crude oil has API gravity of 24. What is its density in g/cm³, lb/ft³, kg/L, kg/m³?
- 1.15. Convert the following units for the viscosity.
- a. Crude viscosity of 45 SUS (or SSU) at 60°C (140°F) to cSt.
 - b. Viscosity of 50 SFS at 99°C (210°F) to cSt.
 - c. Viscosity of 100 cSt at 38°C (100°F) to SUS
 - d. Viscosity of 10 cSt at 99°C (210°F) to SUS
- 1.16. For each ton of a typical crude oil give the equivalent estimates in the following terms:
- a. Volume of crude in bbl.
 - b. Tons of equivalent coal.
 - c. Standard cubic feet (scf) and sm³ of natural gas.
- 1.17. In terms of equivalent energy values, compare existing reserves for three major fossil types and nonrenewable sources of energy: oil, natural gas, and coal by calculating
- a. the ratio of existing world total gas reserves to the world total oil reserves.
 - b. the ratio of existing world total coal reserves to the world total oil reserves.
 - c. the percent share of amount of each energy source in total reserves of all three sources.

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