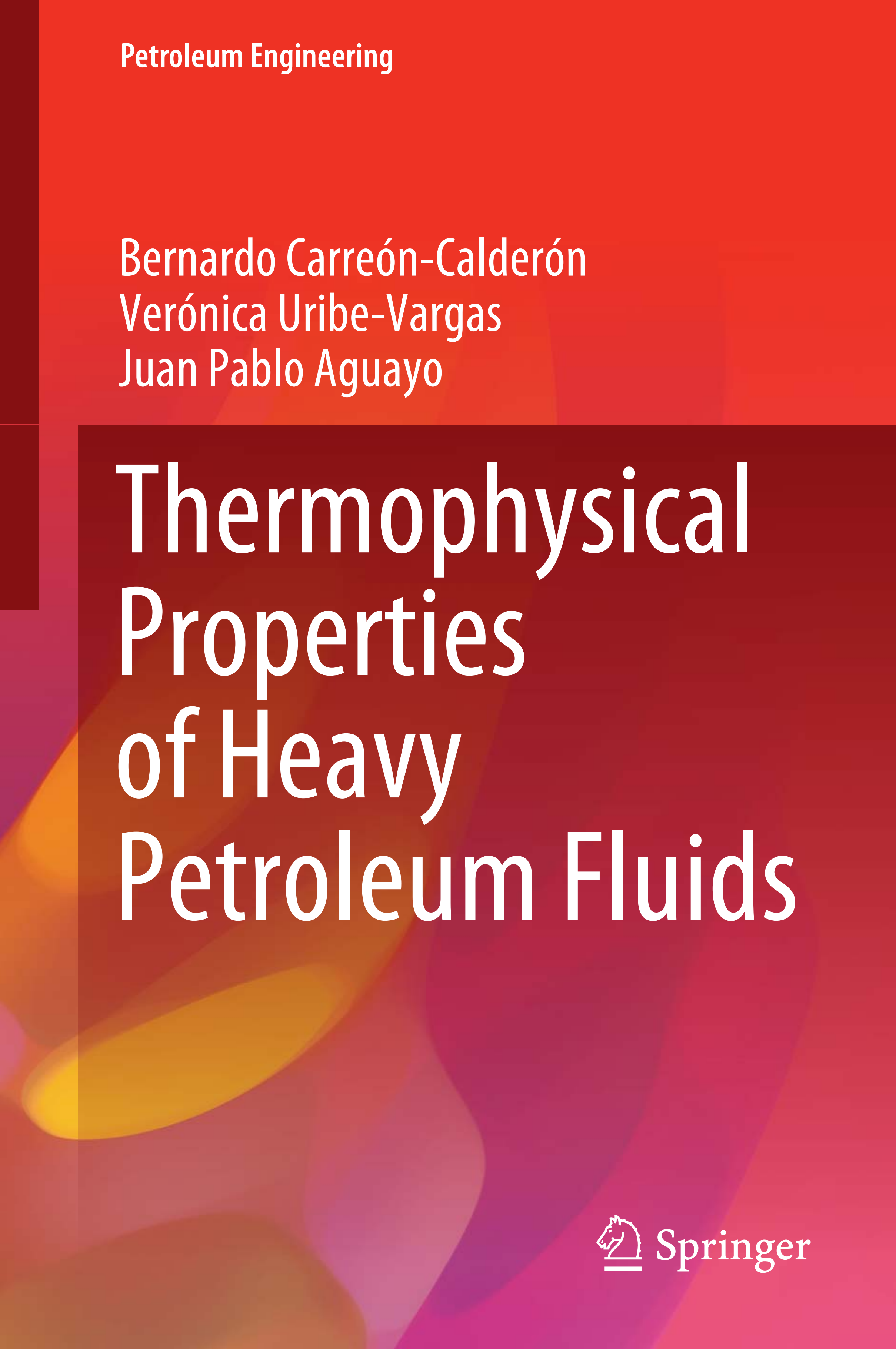

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Bernardo Carreón-Calderón
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Thermophysical Properties of Heavy Petroleum Fluids

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To my wife, Rosalba, and to my children,
Bernardo and Berenice
The reason for being and existing

—Bernardo Carreón-Calderón

To my husband, Manuel and to my two
children, Andrew and Atenea
For their unconditional love

—Verónica Uribe-Vargas

To my parents, José and Gloria, to my wife,
Leticia, and to my son, Fernando.
For the example you have given me.

—Juan Pablo Aguayo

Preface

The main purpose of writing this book is to present new approaches for studying thermophysical properties of petroleum in general and heavy petroleum in particular. Unlike the most books on these topics, this book provides an understanding description of conceptual and mathematical tools for the estimation of such properties, where, whenever possible, adjustments of the model parameters to experimental information is left as the last option. Thus, this book is an ambitious attempt to apply the physical chemistry concepts to property estimation of heavy petroleum fluids predictively. Rheology is an exception to this effort; however, heavy petroleum rheology is analyzed, considering the complex non-Newtonian response that heavy petroleum may present.

The overall approach here is based on theoretical developments, which are contrasted against reported experimental observations, covering the physical aspects encountered within some of the main applications in the exploitation, transportation and processing of heavy petroleum. The book is intended to be comprehensible to readers who have some previous knowledge of fundamentals of physical chemistry (thermodynamics and transport properties), and of organic-petroleum chemistry (terminology) as well as significant mathematical background (differential and integral calculus, and tensorial notation). This book is a compendium which is accessible to engineers and researchers, graduate and postgraduate students devoted to the study of petroleum physical chemistry.

In view of the modest size of the book, it is not possible to cover all possible topics and approaches that can be addressed about heavy petroleum fluids. Therefore, the choice of the topics reflects the experience and prejudgments of the authors. However, authors consider that even though they cannot claim that the issue has been entirely addressed in this book, they believe that some of its contents are considerably addressed here for investigation purposes and future developments.

Mexico City, Mexico
July 2020

Bernardo Carreón-Calderón
Verónica Uribe-Vargas
Juan Pablo Aguayo

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Contents

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Chapter 1
Introduction

List of Abbreviations

DOE	United States Department of Energy
UNITAR	International Group of the United Nations

Thermophysical properties of fluids are of great significance in design and operation of facilities for the exploitation, transportation and processing of petroleum fluids. The thermophysical term implies two types of physical properties: thermodynamic and transport properties. The former have their origin in the study of processes at equilibrium by the area of physics known as Thermodynamics, whereas the latter have their origins in the study of processes of non-equilibrium by the area of physics known as Transport Phenomena. The thermodynamic properties govern the feasibility for a given process to be realizable, while the transport properties determine either the size or the needed time for a given process to occur. Thus, the necessity of accurate and reliable methodologies for estimating thermodynamic and transport properties of petroleum fluids over a wide range of conditions is recognizable. Chronologically, thermodynamic properties should be analyzed before transport properties, because it does not make any sense to determine sizes and times, if such processes are not feasible. This is the treatment that will be given to the study of thermophysical properties of heavy petroleum fluids in this book: first, the thermodynamic properties from their fundamental concepts to applications will be addressed in depth, then the probably most important transport property will be addressed: the viscosity.

1.1 Characteristics of Heavy Petroleum

People are familiar with the terms oil and crude oil, which encompass most hydrocarbon mixtures at liquid state. In the oil industry, the conventional oils are those crude oils characterized by its low viscosity, which allows them to be recovered

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by conventional process. In recent decades, the discovery of high quality (conventional) oil has declined, and as consequence heavy oils and bitumen have begun to be exploited, becoming important resources of crude oils. Bitumens have a higher production and processing cost than conventional crude oils, but they are found with greater abundance [1].

1.1.1 Physical Analysis

The international definition of heavy oil was first discussed at the World Petroleum Congress in 1980; the United States Department of Energy (DOE) continued the work through UNITAR (an international group of the United Nations): Heavy crude oil is described as dead oil (oil without gas) with a density below 21° API and its viscosity is between 100 and 10,000 centipoise (cP) at reservoir temperature. The World Petroleum Congress subsequently adopted the definition of UNITAR, in 1987, with minor modifications. Later, Venezuela added its own definition of extra heavy oil, such as a crude oil that is below 10° API, with a viscosity of less than 10,000 mPa s. In contrast, Canadian heavy oil, which is obtained from the oil sands or carbonates, has an API gravity less than 10° and a viscosity greater than 10,000 mPa s at reservoir conditions. It is the most viscous hydrocarbon and is practically a solid at room temperature, now recognized worldwide as bitumen [2]. Figure 1.1 shows the classification of heavy, extra-heavy, and bitumen oils based on their viscosity.

The presence of light hydrocarbons or other kind of volatile chemical components may be extremely scarce in all these oils irrespective of the used classification to appoint them. Hence, in this book, the designation heavy petroleum fluids or petroleum fluids in general will refer to mixtures formed by oils according to the above conventional meanings and other identifiable components, such as light

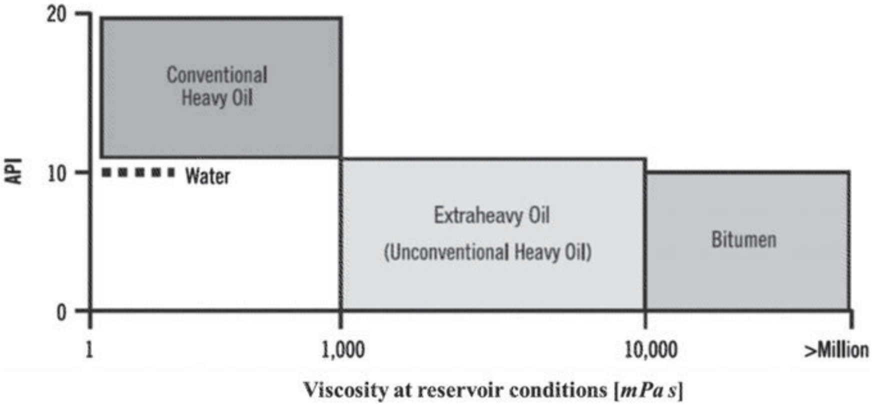

Fig. 1.1 Heavy oil and bitumen definition [2]

alkanes, cycloalkanes, and aromatic components, carbon dioxide, hydrogen sulfide, nitrogen, and water, either they are in the oils naturally or they are added as a part of some kind industrial process.

The other important definition for crude oils is related to the sulfur content: if the crude oil has more than 0.5 wt% sulfur, it is called sour; while for less than 0.5 wt% it called sweet. This distinction between sour and sweet crude oil was originated with the refinery practices employed during most of the twentieth century. At that time, sweet crude oils did not require the removal of sulfur when used for the manufacture of transport fuels. However, since the 1990s, stricter restrictions on the sulfur content of manufactured fuels have made sulfur content important [1].

1.1.2 Chemical Analysis

Heavy oils generally have relatively low proportions of volatile components with low molecular weights and fairly high proportions of lower volatility components with high molecular weights. The high molecular weight fraction of heavy oils is composed of a complex variety of different molecular and chemical types, a mixture of components (not necessarily only paraffins or asphaltenes) with high melting points and high pour points that greatly contribute to the properties of heavy oil. This contributes to its low mobility compared to conventional crude oil [3].

The main components of oil are hydrocarbons, hydrogen and carbon components that show a great variation in their molecular structure. They are generally divided into, paraffins and isoparffins, naphthenic and aromatic. The simplest hydrocarbons are a large group of chain-shaped molecules known as paraffins. Methane (CH_4) is the simplest of all hydrocarbons, and the main component in a natural gas. A paraffinic component consists of hydrocarbon segments of type C, CH, CH_2 or CH_3. Carbon atoms are connected by simple bonds. The paraffins are divided into normal paraffins (n-paraffins) and iso-paraffins (i-paraffins). In an n-paraffin, carbon atoms form linear chains, while an i-paraffin contains at least one side chain. Paraffins are also known as alkanes. Naphthenes: these components are similar to paraffins in that they are formed by the same types of hydrocarbon segments, but they contain one or more cyclic structures. The segments in the ring structures (for example, CH_2) are connected by simple bonds. Most naphthenic ring structures contain six carbon atoms, but naphthenic components with five or seven carbon atoms connected in ring structures are also common in oilfield fluids; naphthenes are also called cycloalkanes. And finally, the aromatic components are like naphthenes, aromatics in which they contain one or more cyclic structures, but carbon atoms in an aromatic component are connected by double bonds. Benzene (C_6H_6), is the simplest aromatic component. Polycyclic aromatic components with two or more ring structures are also found in oilfield fluids.

The percentage of paraffinic as one (P), naphthenic (N) and aromatic (A) components in a reservoir fluid is often called PNA distribution. Petroleum field fluids may also contain inorganic components, of which nitrogen (N_2), carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are the most common. Water (H_2O) is another important component of reservoir fluids. Since water has a limited miscibility with hydrocarbons, most of the water in a reservoir is usually in a separate water zone located below the gas and oil zones [4].

1.1.3 Modelling

According to a recent survey about industrial requirements for thermodynamics and transport properties [5], there is still a necessity for reliable thermodynamic and transport property models for a wide range of systems and industries such as chemical, agrochemical, pharmaceutical, power generation, exploration and production, among others. Some conclusions from this survey are: there is still the necessity for models from a single framework, that cover all conditions of interest; the framework should be generalized so that simple equations of state can be derived for nonpolar, polar, associating, and high boiling substances and their mixtures, with sufficient accuracy for industrial purposes. The number of available models should be reduced by recommending either a unique model or a small number of models; there is a lack of models for larger molecules and complex molecules such as polar and associating ones. Besides, there is a necessity to improve the stability test, the most time-consuming element of the multiphase calculations. The simultaneous description of different thermodynamic properties as well as phase and chemical equilibrium types is of great importance. Thus, there is a necessity for combined models for predicting thermodynamic and transport properties. Finally, there is a necessity for models for predicting properties, especially transport properties of complex molecules or products. Most of these necessities are addressed in this book for the specific case of heavy petroleum fluids.

1.1.3.1 State of Art

Together with the components mentioned in the previous paragraph, in order to perform the modeling of the crude oils, they are separated into identifiable components with a number less than 7 carbons, the components with more than 7 carbons are called the heptane fraction plus (C_{7+}). On these fractions falls the responsibility of the difficulty of modeling in the thermodynamic characterization of petroleum fluids, especially when molecular structures are required [6]. Therefore, a convenient set of components and unidentifiable fractions is needed for the thermodynamic characterization of petroleum [5, 7]. An important aspect is that the components that make up the fractions do not have to be neither real nor present in the mixture. They can be well defined or constructed individual molecules [8–10].

The characterization of unidentifiable petroleum fractions, fractions of unknown composition, implies the use of measurable properties to calculate basic parameters required by state equations or similar expressions. In the case of the cubic state equations, the required parameters are the critical properties and the acentric factor. Therefore, several sets of correlations have been developed to estimate these basic parameters from measurable properties such as molecular weight and liquid density. From the point of view of calculations, a given unidentifiable fraction of oil is considered as a pure hypothetical component in this approach, the above, it allows to calculate the chemical and physical properties with greater precision. However, more computation time and experimental data are required. On the other hand, when unidentifiable oil fractions are treated mathematically as individual components, some volume properties are used to estimate the missing ones. One of the disadvantages of this approach is the use of specific correlations, which are limited to certain conditions and types of oil. This has resulted in different sets of correlations [11, 12]. Therefore, thermodynamic characterization also involves the selection of models and procedures to estimate the volume properties of unidentifiable oil fractions [13, 14]. Attempts have been made to combine the advantages of characterization at the molecular level with the use of unidentifiable fractions as individual components for the concept of group contribution [15, 16]. There, the chemical and physical properties are written in terms of functional groups (CH_3-, $-CH_2-$, etc.) either by correlations [17, 18] or by trial and error procedure [19]. In the latter case, a suggested chemical structure is adjusted so that the available experimental information matches the calculations. These procedures require much less experimental information than characterization at the molecular level. For example, molecular weight, density, true boiling point and the number of hydrocarbon families are commonly needed [20].

In addition to correlations, more rigorous approaches, such as molecular reconstructions, have been suggested. Although these methods differ from each other in the techniques used, they all seek to construct representative molecule mixtures from partial experimental data [7–9, 21]. The objective is that the physical and chemical properties of the actual mixtures, unidentifiable petroleum fractions, can be reproduced using those constructed; good results have been obtained in the case of heavy petroleum fractions [10]. A possible disadvantage of molecular reconstruction methods is that tens, hundreds, or even thousands of molecules are considered necessary. In fact, a rigorous chemical structure and composition may be required for petroleum refining purposes, but a detailed characterization is not necessary for oil production computations because the only properties required are bulk properties such as density, viscosity, etc. In the context of molecular reconstruction methods, the use of group contribution methods to estimate the physical and chemical properties of the properties of pure components may, in principle, give better results than correlations based on massive properties because molecular interactions they are inherently taken into account [22]. Therefore, the use of these methods has already been suggested to estimate the properties of the individual components of the heavy oil fractions [23]. Particular, the Joback-Reid [24] and Marrero-Gani [25] methods to estimate the Critical properties have been used for extremely heavy hydrocarbon mixtures, such as vacuum tower bottoms [26]. In addition, group contribution methods have been developed not only to estimate the critical properties of individual molecules, but also to estimate the parameters used in cubic equations of state, such as the parameters of binary interaction belonging to the classical mixing rule; [27, 28]. Between a characterization at the molecular level, and the use of unidentifiable petroleum fractions as hypothetical individual components, we have the representation by using of the group contribution concept. In this type of methods, the characterization consists not only in determining the volume properties, but also in determining the functional groups, which are structural units that form molecules, so that a volume property can be adjusted. Using these calculated molecular structures, it is possible to employ methods that require molecular structures to calculate other volume properties such as surface tension, solubility [15, 16] and so on. Typically, these methods require fewer input data than molecular reconstruction methods: true boiling point analysis (TBP) or the paraffin-naphthenic-aromatic (PNA) analysis is generally enough. In these methods, a molecular pseudostructure, a set of non-integer functional groups, is calculated for each family of PNA components, that is, from three to one pseudostructures are calculated for each fraction of indefinite oil [17–19, 29].

In this book, the chemical pseudostructure concept will be used widely. In Chap. 2, fundamental concepts of the Classical Thermodynamics will be introduced and analyzed from the fundamental relationships and concepts to the equilibria criteria in terms of pressure, temperature, and composition for multiphase and multicomponent systems. Although the focus is on heavy petroleum fluids, the issues are addressed in a general way, so that they are valid and can be used as starting point for studying systems formed by any kind fluid. Once equilibrium criteria are given, then mathematical expressions that connects pressure, volume and composition of fluids are required, the so-called equations of state. In Chaps. 3 and 4, Cubic Equations of State ($CEoS$) and the Perturbed-Chain-Statistical-Associating-Fluid-Theory equation of state ($PC-SAFT$) are presented in a general form, pointing out strengths and weaknesses for being applied to heavy petroleum fluids. The main emphasis in Chap. 3 will be on EoS/G^E mixing rules, which allows us to extend the prediction capabilities and applicability of $CEoS$ to more complex phase equilibriums, such as those in the presence of mixtures formed by asymmetric components (solvents and heavy oil). Regardless of the equation or the mixing rule, a finite number of components is required for equations of state to be used; however, petroleum is a mixture that shows a continuous distribution concerning its properties, that is, an infinite number of components forms petroleum mixtures. Thus, to turn oil into a mixture of discrete and finite number of components (pseudocomponents) that can be handled by equations of state, it is necessary to make use of distribution functions for random variables. This issue will be addressed in Chap. 5. All concepts and theoretical tools that are developed in Chaps. from 2 to 5 will be applied to real phase equilibrium problems involving heavy petroleum fluids in Chap. 6. First, numerical algorithms for such problems are derived and explained, including phase stability analysis. Then phase equilibriums of heavy petroleum fluids in the presence of gases, light hydrocarbons, water, and asphaltenes are determined and compared with experimental data. The chemical equilibrium is undertaken using the same approach in Chap. 7, but in less detail because experimental information is less abundant. Finally, in Chap. 8, methods are shown and analyzed in order to study viscosity from a Newtonian and non-Newtonian standpoint, considering also other non-Newtonian features that have an impact on the flow response and its modeling.

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Chapter 2

Fundamental Concepts of Thermodynamics

List of Abbreviations

Nomenclature

A	Helmholtz free energy
f	Homogeneous function
$f(x, y)$	Legendre transformation
g	Function equivalent
G	Gibbs free energy
H	Enthalpy
n_i	Number of moles
P	Absolute pressure
P^0	Reference pressure
Q	Thermal energy
R	The universal gas constant
S	Entropy
T	Temperature
U	Internal energy
V	Total volume
W	Work
Z	Compressibility factor
α_j	Phase fraction
δ_{jk}	Kronecker delta
η	Order of homogeneity
λ	Number that increases the mass of the system
μ_i	Chemical potential
σ	Phases number

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Superscripts

~	Molar
0	Pure component
E	Excess property
hg	Hypothetical ideal gas
ig	Ideal gas
is	Ideal solution
R	Real

Subscripts

i	Each component
j	Subsystem

As part of the classical thermodynamics, the study of physical and chemical equilibrium starts with the fundamental laws of nature known as the first and the second laws of thermodynamics. These laws were initially stated as postulates; however, they have been verified by experience so that they have achieved the condition of axioms or laws. In what follows, the basic framework of these laws is outlined so that fundamental concepts and equations are available for the phase and chemical equilibriums involving heavy petroleum fluids to be addressed in following chapters. More detailed discussion about the topics that will be presented here can be found in specialized textbooks [1, 2].

2.1 The First Law of Thermodynamics

The first law of thermodynamics, which is also known as the energy conservation law, states that:

> Energy is not destroyed or created, but it can only be transformed from one type of energy to another.

The mathematical expression of the first law depends on the types of energy that are involved in a given transformation or change. In the case of physical or chemical equilibrium between phases, kinetic and potential energies are usually disregarded; hence, for a system where no mass is exchanged through its boundaries (closed system), the first law of thermodynamic is

$$dU = dQ - dW \tag{2.1}$$

where the internal energy U refers to the energy that the system has by itself. When the system consists of molecules, U refers to the energy that the molecules possess due to their translational, vibrational and rotational movements within the system. On the other hand, Q and W are the thermal energy and macroscopic work exchanged with the surroundings through the boundaries that set the limits of the system. Q and W are functions of the path followed by the system from one thermodynamic state to another, whereas U is a function of state; that is, its value depends only on the state of the system, and not on the path followed to reach it. A thermodynamic state of a given system is found when each of its properties have definite values.

2.2 The Second Law of Thermodynamics

The first law expresses that the energy of the universe remains constant regardless of the changes occurring within the universe itself. However, there is no restrictions from the first law associated with the way or direction for such changes to occur, and consequently, for the corresponding energy and work exchanges. It is the second law of thermodynamics precisely, which provides criteria to establish the direction of natural changes within the universe.

The natural observations that served as starting point to establish the second law are based on the study of the so-called thermal machines, which are machines that transform thermal energy to macroscopic work from cyclic processes. However, the postulates and conclusions from the second law are valid for any type of process or system. The performance of the thermal machines, on which the second law is based, are:

> It is not possible to transform completely the thermal energy absorbed from the surroundings by the system into work performed on the surroundings by the system.
>
> A system in a cyclic process needs at least two reservoirs of thermal energy at two different temperatures to perform work on the surroundings.

The previous observations led to the Clausius inequality o mathematical expression of the second law of thermodynamics for closed systems:

$$dS \geq \frac{dQ}{T} \tag{2.2}$$

which states that, for closed systems subjected to natural or spontaneous processes, the ratio of the change of thermal energy dQ to the absolute temperature T is lesser than or equal to the function of state called entropy S. According to the second law, for an isolated system ($dQ = 0$ and $dW = 0$) undergoing an irreversible transformation ($>$), the transformation will occur in natural way or spontaneously as long as the entropy of the system increases, that is, if $dS > 0$. On the other hand, if the isolated system undergoes a reversible transformation ($=$), the second law establishes that the entropy of the system remains constant. As observed, the second law is connected with the concept of irreversible and reversible transformations. During irreversible transformations, systems and their surroundings undergo permanent changes, while, during reversible transformations, systems and their surroundings can be restored to their original states. Therefore, reversible transformations are not natural processes, but ideal ones. Natural transformations are always irreversible processes.

2.3 Fundamental Expressions of Thermodynamics

Mathematical expressions for calculating and studying thermodynamic properties, and physical and chemical equilibriums between phases are obtained from the fundamental expression of thermodynamics. The fundamental expression arises from combining the first and second laws.

The fundamental expression for closed systems arises from replacing dQ in the second law with the first law, that is,

$$dU \leq TdS - PdV \tag{2.3}$$

where the expansion-compression work is the only one considered here ($dW = PdV$). P and V symbolize the absolute pressure and the total volume of the system, respectively. As can be observed, Eq. (2.3) has the mathematic form of the total differential of U with S and V as independent variables; therefore, from the definition of total differential of any function, we have that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{2.4}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \tag{2.5}$$

The simplicity of these partial derivatives suggests that S and V are the natural variables of U. Although Eq. (2.3) is general and valid for any closed system, it has one inconvenient for its practical use: S appears as independent variable. V can be measured or determined experimentally; however, it is not possible to determine S from experiments directly. Therefore, it is desirable to express the fundamental expression in terms of accessible variables such as pressure, temperature and volume only.

From the mathematical point of view, the Legendre transformation allows functions to be expressed in terms of their partial derivatives rather than their independent variables. In the case of the fundamental expression, it seems convenient because, according to Eqs. (2.4) and (2.5), the partial derivatives of the function U are equal to measurable variables: temperature and pressure.

The Legendre transformation of any function $f(x, y)$ is a function g equivalent to $f(x, y)$, where one independent variable is replaced by the corresponding partial derivative. Hence, to obtain g, it is necessary first to establish the partial derivatives of $f(x, y)$ from the definition of total differential

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = pdx + qdy \tag{2.6}$$

If the independent variable x is replaced by p then the Legendre transformation is

$$g(x, y) = f(x, y) - xp \tag{2.7}$$

Although $g(x, y)$ appears to be function of x and y, it can be shown that $g(x, y)$ is function of p and y actually, because

$$dg = df - xdp - pdx = qdy - xdp \tag{2.8}$$

As mentioned before, it is desirable to choose accessible experimental variables as independent ones for the fundamental inequality. If S is intended to be changed as independent variable, then, according to the Legendre transformation as expressed by Eq. (2.7), we can use the partial derivative given by Eq. (2.4) in order to change S for T as independent variable. Therefore, the Legendre transformation of U, which is symbolized by A, is

$$A \equiv g(T, V) = U - S\left(\frac{\partial U}{\partial S}\right)_V = U - ST \tag{2.9}$$

The energy A defines the Helmholtz free energy, which allows the fundamental expression of thermodynamics to be written as

$$dA \leq -SdT - PdV \tag{2.10}$$

From which and the from definition of total differential again, we found that

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{2.11}$$

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \tag{2.12}$$

On the other hand, we may prefer pressure rather than volume as independent variable in the Legendre transformation given by Eq. (2.9). This can be carried out as illustrated above, but now the Legendre transformation of A is symbolized by G and is determined as

$$G \equiv g(T, P) = A - V\left(\frac{\partial A}{\partial V}\right)_T = U - ST + VP \tag{2.13}$$

The energy G is the Gibbs free energy and allows the fundamental expression of thermodynamics to be written as function of T and P as follows:

$$dG \leq -SdT + VdP \tag{2.14}$$

where the corresponding partial derivatives are

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{2.15}$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{2.16}$$

Finally, it is worth introducing the so-called enthalpy H, because of its significance for the energy exchange in chemical reactions and processes at constant pressure. H may be seen as the Legendre transformation of U, where V is replaced by P as independent variable by means of the partial derivative given by Eq. (2.5), as follows:

$$H(S, P) = U - V\left(\frac{\partial U}{\partial V}\right)_S = U + PV \tag{2.17}$$

From which and from the fundamental expression, we arrive at

$$dH \leq TdS + VdP \tag{2.18}$$

whose associated partial derivatives are

$$\left(\frac{\partial H}{\partial S}\right)_P = T \tag{2.19}$$

and

$$\left(\frac{\partial H}{\partial P}\right)_S = V \tag{2.20}$$

U, A, G, and H are known as thermodynamic potentials because their variations from one state of the system to another establish the corresponding energetic exchanges and whether such exchanges will occur spontaneously or not.

In the study of phase and chemical equilibriums, it is important the tendency of systems to exchange both energy and mass with their surroundings. This implies that the fundamental expressions described above have to be generalized for open systems. By definition, an open system can exchange both mass and energy with its surroundings. Mathematically, this means that U depends not only on S and V, but also on the number of moles n_i of each component i in the system, that is, we have that

$$U = U(S, V, n_1, n_2, \ldots, n_C) \tag{2.21}$$

Therefore, its total differential is

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{C} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j,}\, j\neq i} dS \tag{2.22}$$

Substitution of Eqs. (2.4) and (2.5) leads to

$$dU \leq TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i \tag{2.23}$$

In which, the so-called chemical potential μ_i has been defined as

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j,}\, j\neq i} \tag{2.24}$$

Analogously, the fundamental expression for open systems can be written now in terms of A, G, and H in the following ways

$$dA \leq -SdT - PdV + \sum_{i=1}^{C} \mu_i dn_i \tag{2.25}$$

$$dG \leq -SdT + VdP + \sum_{i=1}^{C} \mu_i dn_i \tag{2.26}$$

$$dH \leq TdS + VdP + \sum_{i=1}^{C} \mu_i dn_i \tag{2.27}$$

Because A, G, and H are equivalent functions to U, the changes of U with respect to n_i must be the same for all the thermodynamic potentials. Hence, μ_i can be defined from any thermodynamic potential

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j,}j\neq i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j,}j\neq i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j,}j\neq i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j,}j\neq i} \tag{2.28}$$

One of the most outstanding characteristics of all previous expressions is that they are only combinations of properties of state; therefore, they can be applied to any state of the system regardless of the path followed to reach a given thermodynamic state. Because temperature, pressure and volume are in practice the available properties that are measured and controlled, Eqs. (2.25) and (2.26) form of basis for phase and chemical equilibrium problems to be addressed.

2.4 Spontaneity and Equilibrium Criteria

In thermodynamics, the system is at equilibrium when there is not tendency to change on macroscopic scale. This means that even though molecules inside the system exchange energy and momentum with each other at molecular level, the average value of all these exchanges remains unaltered.

The spontaneity and equilibrium criteria establish whether a system suffers a spontaneous (natural) transformation or it remains at thermodynamic equilibrium, respectively. These criteria are based on the definition of irreversible and reversible processes. The irreversible ones involve the presence of finite and measurable driving forces for changes of state to occur. The change continues until the driving forces vanish achieving thus an equilibrium state. This final equilibrium state can also be reached by means of a reversible process; however, in this case, driving forces are infinitely small so that the system is always at equilibrium state with its surroundings. In other words, the reversible processes are theoretical simplifications of the natural or irreversible processes. Although the reversible process are ideal transformations, they are important because the mass and energy exchanges associated with them are always extremes (maxima or minima) in comparison with those present in irreversible transformations. Besides, from the mathematical point of view, reversible processes are simpler to outline and to solve than irreversible ones. For these reasons, reversible processes are a common starting point to analyze the natural transformations.

The first criterion of spontaneity and equilibrium arises from the second law applied to isolated system ($dQ = 0$). According to Eq. (2.2), this implies that

$$dS \geq 0 \tag{2.29}$$

Table. 2.1 Spontaneity and equilibrium criteria for closed systems

Conditions	Spontaneity	Equilibrium
$dQ = 0$ and $dW = 0$	$dS > 0$	$dS = 0$
$dT = 0$ and $dP = 0$	$dG < 0$	$dG = 0$
$dT = 0$ and $dV = 0$	$dA < 0$	$dA = 0$
$dS = 0$ and $dV = 0$	$dU < 0$	$dU = 0$
$dS = 0$ and $dP = 0$	$dH < 0$	$dH = 0$

From this expression, it is concluded that the entropy of the system increases ($dS > 0$) during a natural or irreversible transformation, whereas it remains constant ($dS = 0$) during reversible one. The former case corresponds to the spontaneity criterion, while the latter corresponds to the equilibrium criterion for isolated systems.

When temperature and pressure are set as independent variables during a given transformation, then, as explained in the previous section, G plays the role of S to find the corresponding spontaneity and equilibrium criteria. Thus, for transformations at constant pressure and temperature, Eq. (2.14) reduces to

$$dG \leq 0 \tag{2.30}$$

In this case, we have that G of the system decreases ($dG < 0$) during natural transformations, whereas it remains constant ($dG = 0$) during reversible ones. The former case corresponds to the spontaneity criterion, while the latter corresponds to the equilibrium one. As observed from these two examples, the criteria rely on the conditions under which the transformation occur. In Table 2.1, the spontaneity and equilibrium criteria for closed systems are summarized.

When the criteria from Table 2.1 are applied to a system formed by σ subsystems as depicted in Fig. 2.1, more practical spontaneity and equilibrium criteria are found. For instance, if the whole system undergoes a transformation keeping constant volume and temperature, then the following general criterion is fulfilled.

$$dA \leq 0 \tag{2.31}$$

Now, if temperature is held constant and the volume V_j is allow to change during the process for each subsystem j forming the whole system, then Eq. (2.10) applied to each subsystem becomes

$$dA_j \leq -P_j dV_j \tag{2.32}$$

Combination of the two above expressions turns out to be

$$dA = \sum_{j=1}^{\sigma} dA_j \leq -\sum_{j=1}^{\sigma} P_j dV_j = -P_k dV_k - \sum_{j=1}^{\sigma} \left(1 - \delta_{jk}\right) P_j dV_j \leq 0 \tag{2.33}$$

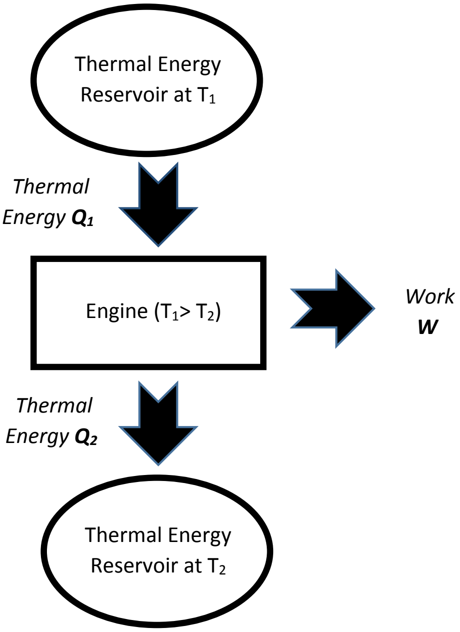

Fig. 2.1 Schematic representation of thermal machines

δ_{jk} is the kronecker delta and takes values of either one or zero according to

$$\delta_{jk} = \begin{cases} 1;\ j = k \\ 0;\ j \neq k \end{cases} \tag{2.34}$$

On the other hand, if the subsystem k suffers a volume expansion ($dV_k > 0$) at the expense of the remaining systems j, which therefore suffer a volume compression $\left(dV_j < 0\right)$ as illustrated in Fig. 2.1 again, then we have that

$$dV_k = -\sum_{j=1}^{\sigma}\left(1 - \delta_{jk}\right)dV_j \tag{2.35}$$

Using this Eq. (2.33) transforms into

$$\sum_{j=1}^{\sigma}\left(1 - \delta_{jk}\right)\left(P_k - P_j\right)dV_j \leq 0 \tag{2.36}$$

As all subsystems j are compressed, from the above expression, it is concluded that the following condition must be satisfied

$$P_k - P_j \geq 0 \tag{2.37}$$