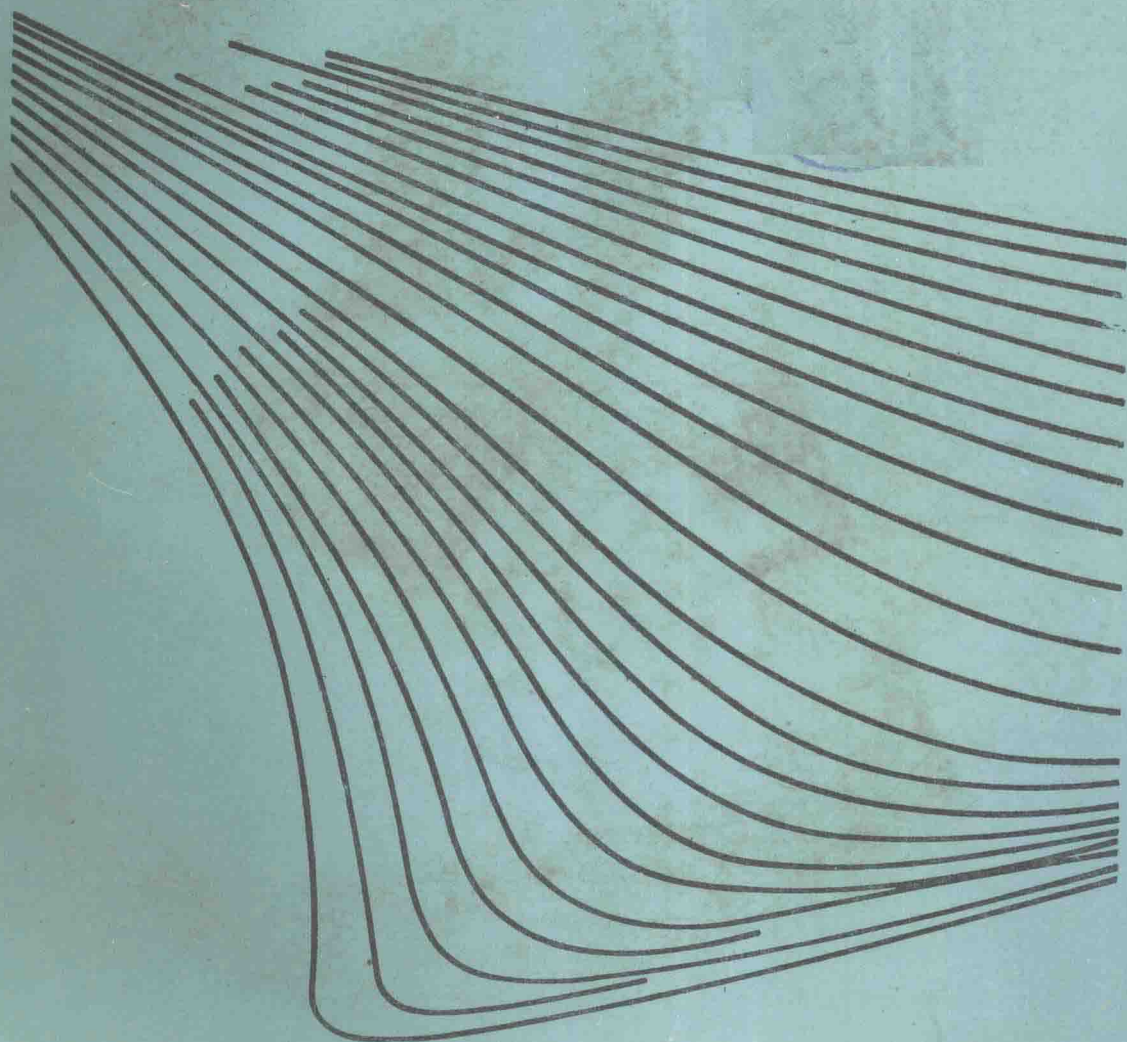# APPLIED HYDROCARBON THERMODYNAMICS

## VOLUME 1

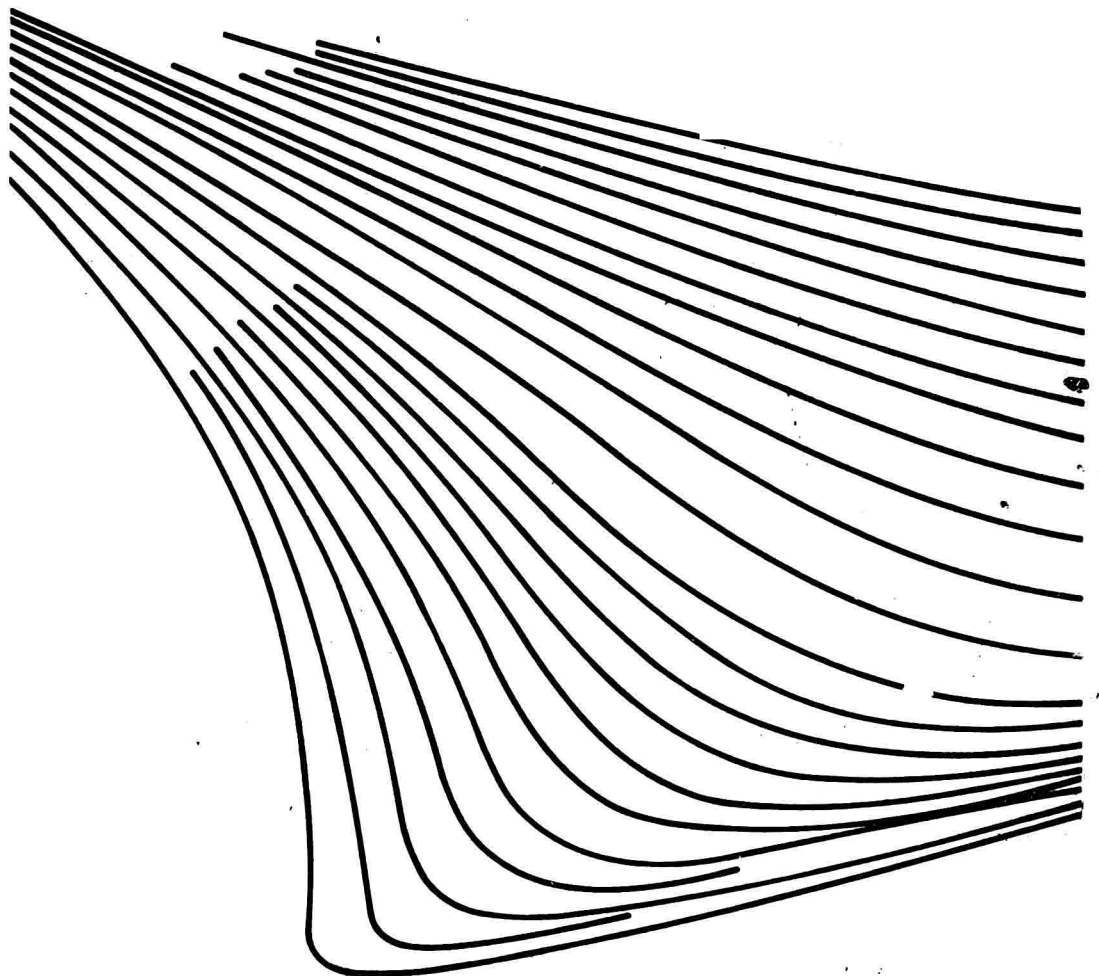### SECOND EDITION

## WAYNE C. EDMISTER
## BYUNG IK LEE

# APPLIED HYDROCARBON THERMODYNAMICS

## VOLUME 1

### SECOND EDITION

## WAYNE C. EDMISTER
## BYUNG IK LEE

# APPLIED
# HYDROCARBON
# THERMODYNAMICS
## VOLUME 1, SECOND EDITION

# Forewo

Although much has been published on theoretical thermodynamics, there has always been a shortage of material dealing with practical application of these theoretical principles. The first edition of this book finally filled the need for a single source of practical information—a source that was understandable yet consistent with theory—converting the theoretical equations into working equations so process engineers could use them.

The second edition of *Applied Hydrocarbon Thermodynamics, Volume 1,* is now before you. Professor Wayne C. Edmister and Dr. Byung Ik Lee have completely rewritten the material and have added much new, needed information. In doing so, they have managed the exceptional feat of adhering to the original purpose of this volume and at the same time making it more useful to the student as well as to the practicing engineer. Many new concepts and technical details have been added. These will be very helpful to the reader.

Prof. Edmister and Dr. Lee first present the fundamentals for both homogeneous and heterogeneous closed systems. Early in the book they formulate the basic laws and equations which are expanded to form the basis of the latter part of the book.

The authors lead the reader very carefully and thoroughly, through much helpful and needed information and methods, which include the following: equations of state and derived formulae for thermodynamic properties predictions; PVT data correlations and corresponding states methods, physical and thermal properties and coefficients for 214 substances; pressure-enthalpy and specific volume charts for hydrocarbons; vapor-liquid equilibria K-value charts; thermal expansion and measurement standards for petroleum fractions.

Professor Edmister and Dr. Lee are well qualified to prepare such a wealth of material for engineers and students. Together they bring extensive experience in developing engineering design methods, data correlations, and other translations of complex theoretical relations into simple working data and equations.

As a reader, you will recognize immediately that the authors draw heavily on their respective talents in the fields of engineering design, research, and teaching in presenting these data with crystal clarity.

John J. McKetta
Chairman
Editorial Committee
*Hydrocarbon Processing*
Houston, Texas

# Preface

The first edition of *Applied Hydrocarbon Thermodynamics* originated as a series of papers in *Hydrocarbon Processing* magazine, and was more of a reference book than a textbook. During the past two decades, the development of increasingly sophisticated computer technology and software has greatly affected engineering problem solving techniques and mathematics. Thus, the first edition of this book became obsolete.

When Gulf Publishing Company asked me to revise and update it, I agreed, providing a suitable, younger coauthor was found; and Byung Ik Lee agreed to join me in this project. Born and educated in Korea, B.I. came to Oklahoma State University from Seoul National University with a bachelor's degree in chemical engineering, and, after completing his master's program, did his doctoral dissertation under my advisement, receiving his Ph.D. in 1971. We both left Stillwater that year—to partial retirement with consulting and lecturing for me, and to an industrial career for B.I. at Mobil Research and Development Corporation. Dr. Lee is responsible for technical data compilation and correlation. He is well qualified to collaborate on this project, to which he gave much time and energy.

In planning this second edition, we decided that revision alone would not be sufficient; a major rewriting was necessary, with changes in format to include more textbook type material, such as theory and equation development, while keeping the emphasis on applications. The objectives of this edition are identical to those of the first edition—to provide thermodynamic tools for process calculations. Some of the original material has been retained with the new. Thanks to my coauthor, many new concepts and technical details have been added.

Thermodynamic relationships and coefficients required for preparing computer programs are in the ten chapters that follow. For convenience, summaries of equations are included at the ends of Chapters 2, 3, 5 and 6.

Chapter 1 reviews the basic concepts and the terminology of thermodynamics.

Chapter 2 covers the fundamentals for homogeneous closed systems, presenting the basic equations for the thermodynamic properties of pure substances and constant composition systems by formulating from the first and second laws of thermodynamics the equations that relate the internal energy, enthalpy, Gibbs free energy, Helmholtz free energy, entropy, and fugacity as functions of the pressure-volume-temperature data of a system.

Chapter 3 covers the fundamentals for heterogeneous closed systems, in which individual components may move across phase boundaries; the constraint equations required to define phase equilibrium are given. Included are solution theories and derivations of expressions for component fugacity as a function of pressure, volume, temperature, and composition.

Chapter 4 reviews *P-V-T* data and correlations, with discussions of important characteristics of the *P-V-T* plots, and the development of equations of state and the corresponding states principle methods of correlation.

Chapter 5 presents the equations of state that are widely used in thermodynamic applications to hydrocarbon processing problems. The most widely used cubic equations are emphasized in this presentation, in which important thermodynamic functions are derived from the equations of state.

Chapter 6 presents the very useful corresponding states methods by equations, charts, and tabulations. Also included are virial equations and expressions for predicting the molar volumes of saturated liquids.

Chapter 7 presents tables of pure component physical constants that are needed as coefficients in equations for various properties for hydrocarbons and related compounds. Also, equations and charts of vapor pressures for these hydrocarbons and related substances are given, as are similar charts for the vapor pressures of narrow cut petroleum fractions.

Chapter 8 presents thre f thermodynamic properties graphs: pressure-enthalpy for nine hydrocarbons and two related compounds, s| )lume charts of eight hydro- carbons, and charts for est he thermal expansion of pe- troleum fractions. Also, p measurement standards are included. All of the char chapter are from previous publications, the pressur y charts being from Star- ling's book, and the speci ne and petroleum expansion factor charts from the first edition of this book. These items are still of value, no significant improvement having been made since their previous publication.

Chapter 9 describes vapor-liquid equilibrium processes and presents methods for making equilibrium flash vaporization calculations.

Chapter 10 presents the relationship between fugacity and the vapor-liquid equilibrium distribution ratio ($K$-value) relationships. It gives several charts to show the development of $K$-charts and working charts for manual calculations.

The appendices give numerical values for conversion of units and methods for solving cubic equations.

Computer methods of applying thermodynamics will be presented in Volume II of this second edition.

*Wayne C. Edmister*
*San Rafael, California*

# Contents

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# *1*

# *Introduction*

## Scope of This Book

A systematic presentation of thermodynamic tools (charts, tables, and equations) for solving process engineering problems is the objective of this book. Sufficient theory and mathematical derivations are included to show the basis for and preparation of these tools. Also included are the numerical methods used in the computer applications, which have become the predominant route in using thermodynamic methods since the first edition of this book in 1961.

This book is mainly intended for hydrocarbon systems. However, the tools are, in principle, applicable to other systems, provided that the basic assumptions remain valid. No attempt has been made to make this book a comprehensive treatise of thermodynamics. For a detailed discussion of fundamental laws, proofs of theorems, and rigorous development of equations, the readers are referred to many fine textbooks and reference books, some of which are listed at the end of this chapter. It should be pointed out, however, that a good effort has been made to cover most of the basic and working equations that are widely used in the applications of thermodynamics to hydrocarbon systems.

## Overview of Thermodynamics

Over the past three centuries thermodynamics has evolved to a science of studying the changes in the properties of substances, particularly of fluids, with changes in conditions, i.e., temperature, pressure, phase condition and composition. But its original aim was, as the word origin of "thermo-dynamics" implies, to study the relation between heat and work. The study was primarily motivated by the human interest in extracting useful work from heat. The "work" has been long recognized as a form of energy

transfer resulting from mechanical motion, such as piston movement, even before the concept of "energy" was clearly understood. Although the word "energy" was first used by Thomas Young in the early nineteenth century, the concept of energy had been introduced in the middle of the seventeenth century in the field of mechanics. This was to rationalize the "conservation of energy" between the energy associated with the gravitation and the energy associated with the velocity, i.e., between the potential energy and the kinetic energy in modern terms. But the inclusion of heat into this concept turned out to be an extremely difficult and controversial task in the history of thermodynamics development.

## Heat and Temperature

In science today, it is common knowledge that heat is another form of energy in transit as a result of a temperature difference, just as work is a form of energy in transit resulting from mechanical motion. But it took more than two centuries to recognize that heat is also a mode of energy transfer, as is work. The first scientific attempt to understand the heat may go back as early as 1592, when Galileo invented the "thermoscope," the precursor of the thermometer. Since then, many individuals contributed to the development of a better thermometer and to the accumulation of better knowledge on heat and temperature. For instance, the Tuscany Grand Duke Ferdinand II developed a thermometer in 1641 using alcohol in a sealed glass tube, and in 1764 Joseph Black first drew the distinction between heat and temperature. Nevertheless, heat was not correctly understood until the 1840's, when Joule proved the equivalence of heat to energy or work, thus finally putting an end to all the imperfect heat theories that had preceded. The most notable and long-lived heat theory prior to the

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Joule's experiments was the "Caloric Theory," which assumed the heat to be a fluid called "caloric." This theory correctly recognized certain characteristics of heat, but it fell short of identifying the heat as energy in transit.

Joule, and others in the later years, conducted a series of careful experiments to show that if the same amount of energy is transferred to a fixed amount of water, the temperature rise of the water is the same regardless of the form of energy delivered; i.e., regardless whether the energy is transferred as a form of electrical energy, mechanical energy (work), heat, or any combination of them. As in Joule's experiments, it is necessary to define a "system" (the fixed amount of water in Joule's case) to conduct a thermodynamic study or experiment.

The definitions of systems and other important terminology of thermodynamics are discussed later.

## Energy Conservation

The temperature rise in the fixed amount of water of Joule's experiments is an indication of the "internal energy" increase of the system. The energy of a system associated with its molecular and atomic structures and also with its molecular motions and interactions is called the internal energy of the system to distinguish it from the potential and kinetic energies, which are called the external energy of the system. The implication of Joule's experiments is that the energy added to (or extracted from) a system from (or to) surroundings in the form of work or heat appears as an increase (or decrease) in the internal energy of the system in the absence of any changes in the external energy, i.e., the total energy of the system and surroundings is conserved.

This principle of energy conservation is called the first law of thermodynamics. In short, the first law has resulted from the recognition of the equivalence between heat and work and from the concept of internal energy and its relation to the heat and work. Even though this law contradicts Einstein's equation of mass-energy conversion ($E = mc^2$), it still forms the fundamental basis of thermodynamics. Incidentally, the conversion of mass to energy has no effect on thermodynamics or its applications as long as there are no nuclear reactions involved. Therefore, the first law remains completely valid for hydrocarbon systems that do not involve any nuclear reactions.

## Heat and Work

Because work and heat are equivalent, their quantity can be measured by the same yardstick. But traditionally, work has been measured in terms of ft-lb$_f$ (foot-pounds force) or J (joule), whereas heat has been measured in terms of Btu (British thermal unit) or cal (calorie). Although both thermal units, Btu and calorie, were precisely defined, their

values were subject to slight variations depending on the accuracy of measurement techniques used. Therefore, the thermal units have been redefined in terms of energy unit as one Btu being equivalent to 778.17 ft-lb$_f$, and one calorie being equivalent to 4.184 J.

The equivalence of heat to work, however, does not necessarily mean that one Btu of heat can be always completely converted to 778.17 ft-lb$_f$ of work, although the reverse is true. For instance, if 778.17 ft-lb$_f$ of energy is added as work to a fixed amount of water as in Joule's experiments, it would increase the internal energy by one Btu, raising the water temperature from its original temperature $T_1$ to a higher temperature $T_2$. By lowering the temperature of the water from $T_2$ to $T_1$, one can recover one Btu of energy as heat, but not 778.17 ft-lb$_f$ of energy as work. At best, a rather small portion of the energy can be recovered as work if a proper device such as heat engine is used.

## Degradation of Energy

Many careful experimental observations have revealed that heat can not be fully converted to work regardless of process or device used, whereas mechanical and electrical work and the external energy which is collectively called mechanical energy can be, in principle, fully converted from one form to others. These observations clearly indicate that the conversion of mechanical energy to heat results in a degradation of energy. In addition to being of a degraded form of energy, heat has another unique characteristic, in that it always flows from a higher temperature to a lower one, never in reverse direction spontaneously. This phenomenon was recognized by Carnot as early as 1824 (even before the establishment of the first law), when he claimed that heat could not be converted to work without the existence of a temperature difference.

Carnot's claim was further expanded upon by Kelvin and later by Clausius in 1850 to become one of the most important principles in thermodynamics, the "second law of thermodynamics." The second law imposes restriction on the direction of actual processes (refer to the definition of process given in the following section). Such restriction may be stated in many different ways. Clausius stated, in effect, that *it is impossible to construct a cyclic process whose only effect is to transfer heat from a temperature to a higher temperature.* Another similar statement made by Kelvin and Planck is: *it is impossible to construct a cyclic process whose only effect is to absorb heat at a temperature and convert it completely to work.* The second law may be even more concisely stated as: *all spontaneous processes are irreversible.* Such irreversible processes always involve a degradation of energy, such as the conversion of work to heat, isothermal expansion of ideal gas, ideal mixing of two unlike gases, etc.

Clearly, the internal energy of expanded gas is less available for work (or in more degraded form) than the gas before the expansion at the same temperature, noting that the internal energy of the ideal gas remains the same during the isothermal expansion. The mixing process of two unlike gases also represents a degradation of energy, because the work that would be required to separate the gases into two pure gases can not be recovered by remixing. All the processes involving energy degradation are more or less irreversible depending on the extent of the degradation of energy. The irreversibility, if made less and less, would eventually approach the ideal limit of reversibility, which accompanies no energy degradation. The definition of reversibility is also given in the next section along with other definitions. The concept of reversibility and that of entropy provide the basis for expressing the second law of thermodynamics quantitatively. The concept of entropy is described in the next chapter.

## Classical vs. Statistical Interpretation

All the thermodynamic concepts mentioned above were based on the "macroscopic" observations of bulk systems. The concepts, on the other hand, may also be developed from the statistical interpretation of the behavior of "microscopic" particles contained in the bulk system. The macroscopic approach to the thermodynamic concepts is often identified as "classical thermodynamics" in contrast to "statistical thermodynamics," which resulted from the microscopic approach. In statistical thermodynamics the entropy is directly related to probability under the postulate that all spontaneous changes proceed toward the most probable state, i.e., towards the maximum probability. In fact the entropy can be shown from statistical approach to be a measure of the distribution of internal energy of a system at equilibrium conditions.

The underlying idea of statistical thermodynamics is to calculate or predict the properties of a bulk system from the characteristics of the individual particles constituting the system using suitable statistical averaging techniques. It should, however, be emphasized that because of the nature of statistics this method is valid only for a system containing a large number of molecules just as is classical thermodynamics, but it is not a great disadvantage because all industrially important processes contain enormous numbers of molecules. Statistical thermodynamics, as established by such renowned scientists as Bernoulli, Maxwell, Boltzmann and Gibbs, provides better insights into the behavior of thermodynamic properties, but it does not alter the basic principles laid down by classical thermodynamics. As statistical thermodynamics is beyond the scope of this book, those interested in the statistical mechanical approach are referred to Andrews (1) and Hill (6).

## Other Postulates

In addition to the first and the second law, there are many other important postulates that resulted either directly or by deduction from experimental observations. The most accepted postulate in and outside of thermodynamics is the conservation of mass. Again, Einstein's relation of $E = mc^2$ is an exception to this. Because Einstein's relation describes the interconversion of mass and energy, it is obvious that the mass and energy together are conserved regardless of the relation. Nevertheless, for the hydrocarbon systems considered in this book the mass and energy conservations are separately valid.

As reviewed earlier, the first and second laws also belong to the postulates obtained from experimental observations, but they have gained the status of "law" because of their practical and traditional importance in the development of thermodynamics. Although there is a third law of thermodynamics, which postulates that the entropy of a perfect crystalline substance is zero at absolute zero temperature, the first and the second laws plus the conservation of mass are the dominating postulates in thermodynamics. In essence this book is based on these three laws together with a few other postulates which will be brought up in the appropriate chapters as needed.

### Review of Terminology

#### System and Surroundings

Thermodynamic studies or experiments are generally focused on an arbitrarily chosen portion of universe. This portion is called a "system," while the rest is called "surroundings." The system surface, real or imaginary, is called a "boundary." A system is called a "closed system" if it does not exchange matter with the surroundings, and an "open system" if it exchanges matter with the surroundings. Both systems may exchange energy with the surroundings. If a system does not exchange matter nor energy with the surroundings, it is called "isolated." The isolated system, however, will not be discussed in this book. The closed system, which is of major interest in this book, is of two types—a *homogeneous* closed system if it contains a single phase, and a *heterogeneous* closed system if it contains more than one phase. A "phase" is a term used in physics for the homogeneous portion of matter.

#### Intensive and Extensive Properties

The thermodynamic properties of a system are classified into two types—"intensive" and "extensive" properties. Intensive properties are those properties that are independent of the size of the system, i.e., of the amount of the substance in the system, such as temperature, pressure etc..

On the other hand, extensive properties are those dependent upon the amount of the substances, such as volume, enthalpy, entropy, etc.. It is important to note that the extensive properties per unit mass or mole, such as specific volume or molar enthalpy, are intensive properties, because these properties are no longer dependent upon the size of the system.

### State Functions

Properties for which the change in state is dependent only on the initial and final states of the system are called "state functions" or "state variables." A change in a state function is in no way dependent upon the method or path followed in going from one state to another. It is this path-independent characteristic of the state functions that makes it possible to quantify the changes of a system.

### Equilibrium State

Equilibrium has been defined as a "state of rest." Within the scope of this book, this means that changes in all properties of fluids eventually cease when there is no external addition or removal of energy. Experiments have shown this to be the case. This eventual state is called the "equilibrium state," in which no further change or, more precisely, no net flux will take place unless one or more properties of the system is altered. In this book, the "state of equilibrium" concept is crucial to the development of the equations for applying thermodynamics to fluid processes. A more quantitative description of the equilibrium state is considered in Chapter 3.

### Thermodynamic Process

A system changes until it reaches its equilibrium state. Any change of a system is called a thermodynamic "process," which may occur with no restrictions or under any arbitrarily prescribed conditions. The following processes are of general interest in thermodynamic study of a system:

1. Adiabatic—no heat added to or removed from system
2. Isothermal—constant temperature
3. Isobaric—constant pressure
4. Isochoric—constant volume
5. Isenthalpic—constant enthalpy
6. Isentropic—constant entropy

### Reversibility

A process is called "reversible," if it proceeds through a series of equilibrium states in such a way that the work done by forward change along a path is identical to the work attained from a backward change along the same path. All real processes are "irreversible" with varying degrees of departure from a reversible one. The reversible process is of an ideal limit that can be approached, but never attained in reality. Thus, the reversible process provides the efficiency standard for all irreversible processes. A more quantitive description of a reversible process is given in Chapter 2.

### Thermodynamic Quantities

The five fundamental quantities used in the scientific world are length, mass, time, force, and temperature. However, in thermodynamics the derived quantities—volume (cube of length), pressure (force per unit area) and mole (molecular mass)—are more frequently used than the corresponding primative quantities of length, force, and mass. Temperature is used as a primary quantity, but time is not a factor in calculating property changes between two equilibrium states, a principle objective of this book. Indeed, the pressure, volume, and temperature play important roles in defining thermodynamic systems, as is shown in the following chapters.

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# 2

# *Homogeneous Closed Systems*

## Introduction

The basic terminologies and the quantity units to be used in this book were briefly described in the previous chapter, where it was pointed out that the thermodynamic systems considered in this chapter and throughout this book are assumed to be in equilibrium states. The main objective of this chapter is to express the most widely used thermodynamic properties of homogeneous closed systems, more specifically of pure or constant composition fluids, as a function of pressure, volume, and temperature (P-V-T) data. This chapter achieves the objective by:

1. Reviewing the first and the second laws of thermodynamics to derive from the laws the fundamental equation (Equation 2.5) that involves the five basic thermodynamic functions (pressure, volume, temperature, internal energy and entropy) of a system.
2. Defining three additional state functions (enthalpy, Helmholtz free energy, and Gibbs free energy) and fugacity.
3. Expressing the internal energy, entropy, enthalpy, heat capacities, Helmholz and Gibbs free energies, and fugacity as a function of P-V-T and ideal gas state property data.
4. Summarizing at the end of this chapter all the important definitions and equations derived in this chapter.

The fundamentals for a heterogeneous closed system and for a homogeneous open system are reviewed separately in Chapter 3.

## First Law of Thermodynamics

The first law of thermodynamics is a generalization of "conservation of energy," i.e., the total energy change of a system is same as that of the surroundings. The total energy of a system may consist of various forms of energy depending on the system under consideration. For most systems, including those of hydrocarbons, it is sufficient to account only for the internal energy, kinetic energy, and potential energy. No other forms of energy, such as nuclear, electro-magnetic, surface energy, etc., will be considered here or elsewhere in this book. In the absence of potential and kinetic energy changes, the change in internal energy of a system is

$$\Delta U = Q + W \tag{2.1}$$

where:  $Q$ = heat; energy transferred as a result of a temperature difference between system and surroundings. By convention $Q$ is positive when heat is added to the system, and negative when heat is removed from the system.

$W$ = work; energy transferred resulting from the movement of the system boundary. By convention, $W$ is positive when work is done on the system, and negative when work is done by the system.

The above definitions clearly indicate that $Q$ and $W$ are not properties of system, but a form of energy in transit between the system and surroundings. Their individual quantities are dependent upon the path followed. However, the sum of the two quantities ($Q$ and $W$) is independent of the path followed, and is identical to the change in internal energy of the system, in the absence of any changes in

other forms of energy, as represented by Equation 2.1. Thus, the internal energy is a state function, which depends only on the initial and final states of the system. Because of this important characteristic, the internal energy change is quantitatively definable, as is shown in the following sections. For mathematical treatment it is more convenient to express Equation 2.1 in differential form as follows:

$$dU = dQ + dW \qquad (2.2)$$

where   $dU$ = infinitesimal change in internal energy.
    $dQ$ = infinitesimal quantity of heat added to the system.
    $dW$ = infinitisimal quantity of work done on the system.

Note that $dQ$ and $dW$ are not exact differentials, because $Q$ and $W$ are not state functions. Again the sum, $dQ + dW$, remains the same regardless of the path the change followed and regardless of the extent of irreversibility of the change. A reversible path is certainly one of the infinite number of possible paths along which the system would undergo a change. By choosing a reversible path and also introducing the concept of entropy, one can transform Equation 2.2 to an equation that involves only state functions of the system. As mentioned earlier $dQ$ and $dW$ are not system properties nor state functions. Such a transformation is important because it incorporates the second law of thermodynamics into the equation, thus making the resultant equation amenable to thermodynamic treatment as discussed below.

### Second Law of Thermodynamics

As described above and also in Chapter 1, the concepts of reversibility and entropy provide the basis for incorporating the second law of thermodynamics into Equation 2.2.

*Reversible work:* Let $dW$ in Equation 2.2 represent the infinitesimal quantity of work done on a system of a gas confined in a cylinder having a frictionless and weightless piston, and $dX$ be the infinitesimal displacement, through which the force $F$ acts. Then, $dW = -F\,dX$. If the piston cross-sectional area is $A$, $dX = dV/A$, where $V$ stands for the volume inside the cylinder occupied by the gas. From the definition of pressure, $F = PA$, thus

$$dW = -F\,dX = -P_{ex}A\,dV/A = -P_{ex}dV$$

In the above equation the subscript "ex" was used to distinguish the external pressure from the pressure exerted by the system on the piston. When the frictionless and weightless piston moves reversibly, the external pressure $P_{ex}$ may be represented by the system pressure $P$ acting on

the piston. In this reversible process $dW$ can be described in terms of the system properties, $P$ and $V$:

$$dW = -P\,dV \qquad (2.3)$$

*Concept of entropy:* The necessity and convenience of defining the entropy stemmed from the study of cyclic processes of heat engine. For a reversible cyclic process, $Q_1/T_1$ and $Q_2/T_2$ (where $Q_1$ is heat absorbed at temperature $T_1$ and $Q_2$ is heat rejected at $T_2$) were found to be identical and independent of the path the process followed, i.e., the $Q/T$'s were dependent only on the initial and final states. The entropy of a system, customarily denoted by $S$, has been defined so that its differential change is equal to $dQ/T$, when all changes of the system take place reversibly, that is,

$$dQ = T\,dS \qquad (2.4)$$

Thus, the entropy is by definition a state function as is the internal energy. This is an important characteristic of entropy as will be shown in the following few chapters. As is obvious from the defining equation, the entropy change of a system would be zero for an adiabatic and reversible process. For an irreversible process, involving energy degradation, $dQ < T\,dS$.

### Thermodynamic Functions

Combining Equations 2.2, 2.3, and 2.4 gives

$$dU = T\,dS - P\,dV \qquad (2.5)$$

This equation by itself is fully capable of describing the change of a homogeneous closed system. However, along the course of development of thermodynamics it has been found more convenient to define three additional functions to describe the system change.
By definition,

| | | |
|---|---|---|
| Enthalpy | $H = U + PV$ | (2.6) |
| Helmholtz free energy | $A = U - TS$ | (2.7) |
| Gibbs free energy | $G = H - TS$ | (2.8) |

From Equations 2.2 and 2.3 and the relationship of $d(PV) = P\,dV + V\,dP$,

$$dU = dQ - d(PV) + V\,dP$$

or

$$d(U + PV) = dQ + V\,dP$$

Combining the above equation with Equation 2.6 at constant pressure gives,

$$dH = dQ$$

The above equality indicates that the heat added to, or extracted from, a system at constant pressure is equal to the enthalpy change of the system. This is the basic idea behind the definition of enthalpy. The convenience of defining enthalpy becomes evident also when dealing with flow processes where $U$ and $PV$ appear together. The Gibbs free energy is most conveniently utilized in phase and/or chemical equilibrium calculations as shown in Chapter 3 and also in the chemical equilibria chapter in Volume 2. From an engineering application point of view, the Helmholtz free energy is not so useful as the Gibbs free energy, but is given here to show its interrelationship with other thermodynamic functions.

Because thermodynamics is only capable of describing the changes of system properties, it is more convenient to express the three defined functions in differential forms. Equation 2.5 provides the basis for deriving the differential equations of the three functions.
Differentiating Equations 2.6 and 2.7, and combining with Equation 2.5 gives

$$dH = T\,dS + V\,dP, \tag{2.9}$$

$$dA = -S\,dT - P\,dV \tag{2.10}$$

Differentiating Equation 2.8 and combining with Equation 2.9 gives

$$dG = -S\,dT + V\,dP \tag{2.11}$$

Now the change in $U$, $H$, $A$, or $G$ between any two states can, in principle, be calculated by integrating the appropriate differential equation, 2.5, 2.9, 2.10, or 2.11.

From a mathematical point of view, the integration of the right-hand side of each expression requires a functional relationship among $P$, $V$, $T$ and $S$. For instance, in order to integrate Equation 2.11, $S$ and $V$ should be expressed as functions of $T$ and $P$.

$$S = S(T, P) \tag{2.12}$$

$$V = V(T, P) \tag{2.13}$$

Then, the integration will result in $G$ as a function of $T$ and $P$, as follows.

$$G = G(T, P) \tag{2.14}$$

In fact, it has been found from experimental observations that the volume $V$ is fixed if $T$ and $P$ are fixed for a homogeneous closed system, and so is the internal energy $U$. Furthermore, as obvious from the defining equations (Equations 2.5 through 2.8), $S$, $H$, $A$, and $G$ of the system are also fixed if $T$ and $P$ are fixed. Actually, it does not have to be the temperature and the pressure that are to be fixed. Any two of the eight state variables appearing in the aforementioned four differential equations (Equations 2.5, 2.9 through 2.11) can fully define all other variables for a homogeneous closed system, thus fixing the entire system (for a heterogeneous closed system refer to "phase rules" in Chapter 3.). Yet, the temperature and pressure are the two most familiar properties among the eight, and their relation to volume has been of particular interest in the physical world.

The relation of $V$ to $T$ and $P$ (Equation 2.13), known as P-V-T relation, may be found by experimental measurements. As a matter of fact, many P-V-T experiments have been made in the past century for a variety of substances including hydrocarbons. Because the P-V-T data are abundant and easy to measure with high accuracy, all other properties that are more difficult to measure are commonly related to P-V-T data. The derivations of the relationships follow.

### Maxwell Relations

The following mathematical manipulation is to obtain an expression relating $S$, $T$, $P$, and $V$, and subsequently to demonstrate the usefulness of Maxwell relations in understanding how the eight state variables are related to each other.

Applying the chain rule to Equation 2.14 for total differential gives

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \tag{2.15}$$

Comparing like terms in Equations 2.11 and 2.15 results in

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{2.16}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{2.17}$$

Differentiating Equation 2.16 with respect to $P$, at constant $T$, gives

$$\frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_P\right]_T = -\left(\frac{\partial S}{\partial P}\right)_T \tag{2.18}$$

Differentiating Equation 2.17 with respect to $T$, at constant $P$, gives

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left(\frac{\partial V}{\partial T}\right)_P \qquad (2.19)$$

Because the order of differentiation is immaterial, the left-hand sides of Equations 2.18 and 2.19 are identical, thus resulting in

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \qquad (2.20)$$

Equation 2.20 is one of the four Maxwell relations and relates $S$ to $T$ and $P$, provided that the P-V-T relationship is known. A more convenient way of deriving Maxwell relations is to apply Green's theorem directly to the differential Equations 2.5, 2.9, 2.10, and 2.11. In fact, Equations 2.10 through 2.20 constitute a proof of Green's theorem which states that if

$$dZ = M\,dX + N\,dY \qquad (2.21)$$

is exact, then

$$\left(\frac{\partial N}{\partial X}\right)_Y = \left(\frac{\partial M}{\partial Y}\right)_X \qquad (2.22)$$

The three remaining Maxwell relations can be found by applying this theorem to Equations 2.5, 2.8 and 2.10. From Equation 2.5,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (2.23)$$

From Equation 2.8,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad (2.24)$$

From Equation 2.10,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (2.25)$$

Equations 2.23 and 2.24 are of little practical value because they involve an isentropic (constant entropy) condition that is practically impossible to duplicate experimentally and also awkward to compute. Their derivations are included here for completeness of the Maxwell relations, however. The other two Maxwell relations, i.e. Equations 2.20 and 2.25, are very useful in relating the thermodynamic functions $U$, $H$, $S$, $A$, and $G$ of a system to $T$, $P$, and/or $V$ of the same system.

Because $T$ and $P$, being intensive properties, are the dominant variables in the physical world, it is a common practice to relate the five thermodynamic functions directly to $T$ and $P$ or indirectly to $T$ and $V$, with $V$ as a function of $T$ and $P$. This is to evaluate the effects of temperature and pressure (or temperature and volume) on the thermodynamic functions.

Equation 2.20 is used to relate the functions to $T$ and $P$, and Equation 2.25 is used for relating the functions to $T$ and $V$. It is, however, not necessary to relate each of the five functions individually to $T$ and $P$ (or $T$ and $V$). Only two functions, i.e., $S$ plus either $U$ or $H$ need to be related to $T$ and $P$ (or $T$ and $V$). For convenience, the enthalpy, in addition to the entropy, are chosen here to express the property dependence on $T$ and $P$, and $U$ and $S$ are chosen for the property dependence on $T$ and $V$. Then, the other three functions $U$ (or $H$), $A$, and $G$ are automatically related to $T$ and $P$ (or $T$ and $V$) via the defining Equations 2.6 through 2.8.

It is also important to recognize that the use of Maxwell relations for relating $H$ and $S$ to $T$ and $P$ (or $U$ and $S$ to $T$ and $V$) inevitably involves an integration which, in turn, requires a reference property (integration constant). In general, the ideal gas property is used as the reference as will be shown in the next few sections. Therefore the ideal gas P-V-T relationships will be first reviewed for the subsequent use of the relationships in deriving the expressions for real fluid properties.

## Ideal Gas Behavior

An ideal gas is an imaginary gas that obeys the following P-V-T relation for all temperatures and pressures:

$$V = RT/P \ (\text{or } Z = PV/RT = 1.0) \qquad (2.26)$$

Real gases do not obey this relationship except at very low pressures, i.e., the compressibility factor, $Z$, varies with $T$ and $P$ for real gases, except at very low pressure and/or high temperature.

Differentiating Equation 2.26 with respect to $T$, at constant $P$, gives

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \qquad (2.27)$$

Combining Equations 2.26 and 2.27 and rearranging, results in

$$V - T\left(\frac{\partial V}{\partial T}\right)_P = 0 \qquad (2.28)$$

Differentiating Equation 2.27 with respect to $T$, at constant $P$, gives

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0 \qquad (2.29)$$

Rearranging Equation 2.26 as $P = RT/V$ and differentiating with respect to $T$, at constant $V$, and combining the resulting equation with Equation 2.26 gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad (2.30)$$

The above ideal gas P-V-T relationships will be used to derive the expressions for the effects of temperature and pressure (or temperature and volume) on the thermodynamic properties of real fluids.

### Properties as Functions of $T$ and $P$

Expressions for describing the effects of temperature and pressure on the thermodynamic functions are derived by starting with $H$ and $S$ expressions together with Equation 2.20 of Maxwell relations. Derivations of equations for thermodynamic functions as functions of $T$ and $P$ are presented here.

### Enthalpy, $H(T,P)$

A general form of enthalpy expression is obtained by defining $H$ as a function of $T$ and $P$, and writing the functional relationship in total differential form, as follows:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (2.31)$$

It should be remembered that any of eight variables $(U,H,S,A,G,P,V,T)$ can be fully defined by any two other variables.

The temperature and pressure derivatives of $H$ in Equation 2.31 will be found next. The isobaric effect of temperature on the enthalpy, $(\partial H/\partial T)_P$, is, by definition, the heat capacity at constant pressure, i.e.

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad (2.32)$$

The isothermal effect of pressure on the enthalpy is obtained by combining Equation 2.9, at constant $T$, with the Maxwell relation given as Equation 2.20:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] \qquad (2.33)$$

Combining Equations 2.31, 2.32, and 2.33 gives

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad (2.34)$$

Expressing $C_P$ and $V$ as functions of $T$ and $P$, and integration of Equation 2.34 from one state $(T_1,P_1)$ to another state $(T_2,P_2)$ would give the enthalpy difference between these two states. Although such an integration is possible, it is more practical to calculate the enthalpy difference from the isothermal form of Equation 2.34, or the differential form of Equation 2.33 as given below.

$$\left\{dH = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP\right\}_T \qquad (2.35)$$

Calculation of $H$ at any $T$ and $P$, by integrating Equation 2.35, would require $V$ as a function $T$ and $P$ and a known $H$ as a reference. Generally, the ideal gas state enthalpy, $H^*$, at the same temperature as $H$ is chosen as the reference, because it is dependent only on temperature, and the $H^*$ data are readily available from the ideal gas state heat capacities which are abundant and relatively easy to obtain with good accuracy.

A state function is independent of the path followed. Therefore, any arbitrarily chosen path may be followed in the integration of any state function, such as Equation 2.35. A widely used path is to integrate from $P_o$(reference pressure) to $P = 0$ along ideal gas state path at given temperature $T$, and then to integrate isothermally from $P = 0$ to $P$ along real path. When the function becomes infinite at $P = 0$ upon integration, an additional manipulation is necessary, as is shown later in the derivation of entropy expression.

Integrating Equation 2.35 from $P_o$ to $P$, at constant $T$, gives

$$H - H^* = \int_{P_o}^{0} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$
$$(ideal)$$
$$+ \int_{0}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$
$$(real)$$

The first right-hand side term vanishes, because the integrant is zero for an ideal gas from Equation 2.28. Thus,