

1

Introduction

With thermodynamics, one can calculate almost everything crudely; with kinetic theory, one can calculate fewer things, but more accurately; and with statistical mechanics, one can calculate almost nothing exactly.

Eugene Wigner

The range and scope of thermodynamics is implied in Wigner's epigrammatic quote above, except for the fact that there are a great many phenomena for which thermodynamics can provide quite accurate calculations. Chemical engineering is to a large extent based on thermodynamic calculations applied to practical systems. The phase rule is indispensable to metallurgists, geologists, geochemists, crystallographers, mineralogists, and chemical engineers. Although students sometimes come away with the notion that thermodynamics is remote and abstract, it is actually the most practical of subjects. Part of what we endeavor to do in this book is to illustrate that practicality, the tie to everyday life and utility.

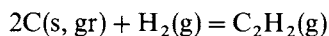
Thermodynamics comprises a field of knowledge that is fundamental and applicable to a vast area of human experience. It is a study of the interactions between two or more bodies, the interactions being described in terms of the basic concepts of heat and work. These concepts are deduced from *experience*, and it is this experience that leads to statements of the first and second laws of thermodynamics. The first law leads to the definition of the energy function, and the second law leads to the definition of the entropy function. With the experimental establishment of these laws, thermodynamics gives an elegant and exact method of studying and determining the properties of natural systems.

The branch of thermodynamics known as the thermodynamics of reversible processes is actually a study of thermodynamic systems at equilibrium, and it is this branch that is so important in the application of thermodynamics to chemical systems. Starting from the fundamental conditions of equilibrium based on the second law, more-practical conditions,

2 Introduction

expressed in terms of experimentally measurable quantities, have been developed. The application of the thermodynamics of chemical systems thus leads to the determination of the equilibrium properties of macroscopic systems as observed in nature (regardless of the complexity of the systems), to possible limitations, and to the determination of the dependence of the equilibrium properties with changes of the values of various independent variables, such as pressure, temperature, or composition.

Since thermodynamics deals with systems at equilibrium, time is not a thermodynamic coordinate. One can calculate, for example, that if benzene(ℓ) were in equilibrium with hydrogen(g) and carbon(s) at 298.15 K, then there would be very little benzene present since the equilibrium constant for the formation of benzene is 1.67×10^{-22} . The equilibrium constant for the formation of diamond(s) from carbon(s, graphite) at 298.15 K is 0.310; that is, graphite is more stable than diamond. As a final example, the equilibrium constant for the following reaction at 298.15 K is 2.24×10^{-37} :



People do not give away their diamonds or worry about benzene or ethyne spontaneously decomposing, since these substances are *not* in equilibrium with their starting materials. A specific catalyst or infinite time might be required to attain equilibrium conditions.

After the appendices we provide a selected bibliography of general references and data compilations. All cited references appear in the list of general references.

1.1 The language of thermodynamics

In thermodynamics terms mean exactly what we define them to mean.

The exact use of language is particularly important in this subject, since calculations and interpretations are directly tied to precisely defined changes of state *and* the way in which those changes of state occur. So, in this introductory chapter the language of thermodynamics is presented.

First, we speak of a *system* and its *surroundings*. The system is any region of matter that we wish to discuss or investigate. The surroundings comprise all other matter in the world or universe that can have an effect on or interact with the system. Thermodynamics, then, is a study of the interaction between a system and its surroundings. These definitions are very broad and allow a great deal of choice concerning the system and its surroundings. The important point is that for any thermodynamic problem we must rigorously define the system with which we are dealing and apply any limitations to the surroundings that appear to be necessary. What we shall consider to be the system and the surroundings is our choice, but it is imperative that we consciously make this choice. As an example, we may be interested in the chemical substances taking part in a chemical reaction. These substances

1.1 The language of thermodynamics

3

would have to be in a container of some kind. Certainly, the substances taking part in the reaction would comprise at least part of the system, but it is our choice whether we consider the container to be part of the system or part of the surroundings. Although the surroundings were defined generally as all other matter in the world or universe, in all practical cases they are limited in extent. Those parts of the universe that have no or only an insignificant effect on the system are excluded, and only those of the surroundings that actually interact with the system need to be considered. In many experimental studies the surroundings that interact with the system are actually designed for the purpose of controlling the system and making measurements on it.

For any thermodynamic system there is always a *boundary*, sometimes called an *envelope*, which separates the system and the surroundings. The only interactions considered in thermodynamics between a system and its surroundings are those that occur across this boundary. Because of this, it is as important to define the boundary and its properties as it is to define the system and the surroundings themselves. The boundary may be real or hypothetical, but it is considered to have certain properties. It may be rigid, so that the volume of the system remains constant, or it may be nonrigid, so that the volume of the system can change. Similarly, the boundary may be adiabatic or diathermic. The boundary may be semipermeable, under which condition it would be permeable to certain substances but not permeable to others. In actual cases the properties of the boundary are determined by the properties of the system and by our design of the surroundings. In simplified, idealized cases we may endow the boundary with whatever properties we choose. A clear definition of the system and of the boundary that separates the system from its surroundings is extremely important in the solution of many thermodynamic problems.

In addition to the general concept of a system, we define different types of systems. An *isolated system* is one that is surrounded by an envelope of such nature that *no interaction whatsoever* can take place between the system and the surroundings. The system is completely isolated from the surroundings. A *closed system* is one in which *no matter* is allowed to transfer across the boundary; that is, no matter can enter or leave the system. In contrast to a closed system we have an *open system*, in which matter can be transferred across the boundary, so that the mass of a system may be varied. (Flow systems are also open systems, but are excluded in this definition because only equilibrium systems are considered in this book.)

The *state* of the system is defined in terms of certain state variables. The state of the system is then fixed by assigning definite values to sufficient variables, chosen to be independent, so that the values of all other variables are fixed. The number of independent variables depends in general upon the problem at hand and upon the system with which we are dealing. The

4 Introduction

determination of this number and the type of variables required for the definition of the state of the system is discussed in Chapter 5. When the values of the independent variables that define the state of the system are changed, we speak of a *change of state* of the system. Here we are concerned with the values of the dependent variables, as well as those of the independent variables, at the initial and final states of the system, and not with the way in which the values of the independent variables are changed between the two states. When it is necessary to consider the way in which the values of the independent variables are changed, we speak of the *path*. In a graphical representation the path is any line connecting the two points that depict the two states. The term *process* encompasses both the change of state and the path.

1.2 Thermodynamic properties of systems

We have implied in Section 1.1 that certain properties of a thermodynamic system can be used as mathematical variables. Several independent and different classifications of these variables may be made. In the first place there are many variables that can be evaluated by experimental measurement. Such quantities are the temperature, pressure, volume, the amount of substance of the components (i.e., the mole numbers), and the position of the system in some potential field. There are other properties or variables of a thermodynamic system that can be evaluated only by means of mathematical calculations in terms of the measurable variables. Such quantities may be called *derived* quantities. Of the many variables, those that can be measured experimentally as well as those that must be calculated, some will be considered as *independent* and the others are *dependent*. The choice of which variables are independent for a given thermodynamic problem is rather arbitrary and a matter of convenience, dictated somewhat by the system itself.

Finally, the thermodynamic properties of a system considered as variables may be classified as either *intensive* or *extensive* variables. The distinction between these two types of variables is best understood in terms of an operation. We consider a system in some fixed state and divide this system into two or more parts without changing any other properties of the system. Those variables whose value remains the same in this operation are called intensive variables. Such variables are the temperature, pressure, concentration variables, and specific and molar quantities. Those variables whose values are changed because of the operation are known as extensive variables. Such variables are the volume and the amount of substance (number of moles) of the components forming the system.

1.3 Notation

In this book we use SI units and IUPAC symbolism and terminology as far as possible. The complete set of notation used in this book is given before this chapter. For clarity and consistency we have made some choices of notation that differ from IUPAC recommendations. Notation is defined where first introduced. Amongst other exceptions is the use of the phrase ‘amount of substance’ for the variable n , which has been traditionally called the ‘number of moles’ or, as we most frequently call it, the ‘mole numbers.’

Some basic reference tables are given in the appendices.

2

Temperature, heat, work, energy, and enthalpy

In this chapter we briefly review the ideas and equations relating to the important concepts of temperature, heat, work, energy, and enthalpy.

2.1 Temperature

The concept of temperature can be defined operationally; that is, in terms of a set of operations or conditions that define the concept. To define a temperature scale operationally we need: (1) one particular pure or defined substance; (2) a specific property of that substance that changes with a naive sense of ‘degree of hotness’ (i.e., temperature); (3) an equation relating temperature to the specific property; (4) a sufficient number of fixed points (defined as reproducible temperatures) to evaluate the constants in the equation in (3); and (5) the assignment of numerical values to the fixed points. Historically, many different choices have been made with respect to the five conditions listed above, and this, of course, has resulted in many temperature scales.

The ideal gas temperature scale is of especial interest, since it can be directly related to the thermodynamic temperature scale (see Sect. 3.7). The typical constant-volume gas thermometer conforms to the thermodynamic temperature scale within about 0.01 K or less at agreed fixed points such as the triple point of oxygen and the freezing points of metals such as silver and gold. The thermodynamic temperature scale requires only one fixed point and is independent of the nature of the substance used in the defining Carnot cycle. This is the triple point of water, which has an *assigned* value of 273.16 K with the use of a gas thermometer as the instrument of measurement.

The International Practical Temperature Scale of 1968 (IPTS-68) is currently the internationally accepted method of measuring temperature reproducibly. A standard platinum resistance thermometer is the transfer medium that is used over most of the range of practical thermometry.

Interpolation formulas and a defined set of fixed points are used to establish the scale. IPTS-68 is due to be replaced in 1990 or 1991.

The *zeroth law of thermodynamics* is in essence the basis of all thermometric measurements. It states that, if a body *A* has the same temperature as the bodies *B* and *C*, then the temperature of *B* and *C* must be the same. One way of doing this is to calibrate a given thermometer against a standard thermometer. The given thermometer may then be used to determine the temperature of some system of interest. The conclusion is made that the temperature of the system of interest is the same as that of any other system with the same reading as the standard thermometer. Since a thermometer in effect measures only its own temperature, great care must be used in assuring thermal equilibrium between the thermometer and the system to be measured.

2.2 Heat and heat capacity

It is observed experimentally that, when two bodies having different temperatures are brought into contact with each other for a sufficient length of time, the temperatures of the two bodies approach each other. Moreover, when we form the contact between the two bodies by means of walls constructed of different materials and otherwise isolate the bodies from the surroundings, the rate at which the two temperatures approach each other depends upon the material used as the wall. Walls that permit a rather rapid rate of temperature change are called *diathermic* walls, and those that permit only a very slow rate are called *adiabatic* walls. The rate would be zero for an ideal adiabatic wall. In thermodynamics we make use of the concept of *ideal adiabatic walls*, although no such walls actually exist.

We describe the phenomenon that the temperatures of the two bodies placed in diathermic contact with each other approach the same value by saying that 'heat' has transferred from one body to another. *This is the only concept of heat that is used in this book.* It is based on the observation of a particular phenomenon, the behavior of two bodies having different temperatures when they are placed in thermal contact with each other.

One way to obtain a quantitative definition of a unit of heat is to choose a particular substance as a standard substance and define a quantity of heat in terms of the temperature change of a definite quantity of the substance. Thus, we can define a quantity of heat, Q , by the equation

$$Q = C(t_2 - t_1) \quad (2.1)$$

where t_2 is the final temperature and t_1 is the initial temperature. The proportionality constant, C , is called the *heat capacity* of the particular quantity of the substance. For the present we will disregard the dependence of C on pressure and volume. Experimental studies have shown that C is an extensive quantity, so that it may be written as mc , where m represents the

8 *Temperature, heat, work, energy, and enthalpy*

number of units of mass of the standard substance used and c represents the *specific heat capacity*. The unit of heat is then defined by assigning an arbitrary value to c . A positive value is assigned to c so that the quantity of heat absorbed during an increase of temperature is positive.

The calorie was originally based on 1 g of water. For the purposes of a more exact definition it has been superseded by the joule, so that

$$\text{cal} = \text{cal}_{\text{th}} \equiv 4.184 \text{ joules} \equiv 4.184 \text{ J}$$

by international convention. It is called the ‘thermodynamic’ calorie. (Many authors omit the subscript ‘th.’)

Measurements of the heat capacity of all substances have shown that the heat capacity is actually a function of temperature. Therefore, Equation (2.1) must be given as

$$Q = \int_{t_1}^{t_2} C \, dT = m \int_{t_1}^{t_2} c \, dT \quad (2.2)$$

where t_2 represents the final temperature and t_1 the initial temperature. If the numerical value of Q is positive, then heat is absorbed by the substance; if it is negative, then heat is emitted by the substance.

The quantity of heat absorbed or emitted by a system for a given change of state depends not only upon the change of temperature, but also upon changes in the values of other independent variables. Here we consider closed systems (those of constant mass) and only either changes in the values of the temperature and pressure or changes in the values of temperature and volume. Differential expressions for the quantity of heat can be written either as

$$dQ = M(T, P) \, dT + N(T, P) \, dP \quad (2.3)$$

or

$$dQ = K(T, V) \, dT + L(T, V) \, dV \quad (2.4)$$

where $M(T, P)$ and $N(T, P)$ represent functions of the temperature and pressure, and $K(T, V)$ and $L(T, V)$ represent functions of the temperature and volume. Experiment shows that these differential expressions for the heat effect are inexact. The symbol δ is used to distinguish between inexact (δ) and exact (d) differential quantities. *The quantity of heat absorbed by the system for a given change of state thus depends upon the path that is followed from the initial state to the final state.* The symbol Q represents a quantity of heat, taken as *positive* for heat *absorbed* by the system from the surroundings. It may be measured experimentally or determined from the line integral of appropriate inexact differential expressions represented by the symbol δQ , such as Equation (2.3) or (2.4).

A general definition of the heat capacity is given by the equation

$$C = \frac{dQ}{dt} = \frac{dQ}{dT} \quad (2.5)$$

where dQ represents the infinitesimal quantity of heat absorbed by a system for a differential increase, dt or dT , in the temperature of the system. However, dQ is an inexact differential quantity and its value is determined only when the path is stated. By relating Equation (2.5) with Equations (2.3) and (2.4) for the systems discussed, we find that $M(T, P)$ is the heat capacity of the system at constant pressure, C_p , and $K(T, V)$ is the heat capacity of the system at constant volume, C_v . Equations (2.3) and (2.4) may then be written as

$$dQ = C_p dT + N(T, P) dP \quad (2.6)$$

and

$$dQ = C_v dT + L(T, V) dv \quad (2.7)$$

The heat capacities in Equations (2.1) and (2.2) are also dependent on pressure and volume.

Heat capacities are not limited to those at constant volume and constant pressure. In some cases values must be assigned to other independent variables in addition to the temperature and pressure, or temperature and volume, in order to define the state of the system. For these cases additional terms must be added to Equations (2.3) and (2.4). The heat capacities are then defined at constant values of these variables in addition to the pressure or volume. In all cases the defining equation for the heat capacity is Equation (2.5) with the provision that the path followed for the change in temperature must be given.

When the heat capacity of a system is known as a function of the temperature, the heat absorbed by the system for a given temperature change can be calculated by integration of Equation (2.5). The integral is a line integral and the path for integration must be known.

2.3 Work

The concept of work is developed here from an operational point of view. Mechanical work is discussed first, and then the concept is expanded to more-general interactions. Observation shows that there are actions that, when acting on a body cause a change in the velocity of the body. Such actions are called *forces*. The relation between the force and the change of velocity is expressed by Newton's second law of motion:

$$\mathbf{F} = m \frac{d\mathbf{v}}{dt} \quad (2.8)$$

10 *Temperature, heat, work, energy, and enthalpy*

for nonrelativistic velocities, where \mathbf{F} represents the force and m the mass of the body. Here t refers to time. The unit of force, the newton (N), is defined in terms of this relation for which m is one kilogram and dv/dt is one meter per second. The differential quantity of work dW , done by a force in operating on a body over a differential displacement, ds , is given by the scalar product of the force and the differential of the displacement, so

$$dW = F \cos \alpha ds \quad (2.9)$$

The symbols F and s here refer to scalar rather than vector quantities, and α is the angle between the direction of the force and the direction of the displacement. The unit of work is the joule.

This basic mechanical concept of work must be extended when it is applied in thermodynamics. We are concerned with the interaction of a system and its surroundings across the boundary that separates them. Both the system and the surroundings may exert forces on the boundary, and it is the action of these forces resulting in a displacement of the boundary that constitutes work. The language used to describe the interaction in terms of work must be developed and used with great care.

Because the change of the volume of a system is so important in the application of thermodynamics to chemical systems, the expansion of a gas is used as an example. Consider a known quantity of gas confined in a frictionless piston-and-cylinder, as illustrated in Figure 2.1. The cylinder is fixed in position relative to the Earth. The piston has a mass m and can move in the direction of the gravitational field of the Earth. There is also a known external force, F_e , exerted on the upper surface of the piston. We

Figure 2.1. Piston-and-cylinder arrangement.

