

# 4

## Thermodynamics

This chapter is concerned with thermodynamics. As with all the chapters in Part II, there are several sections: overview, several specific technical topics, illustrative open-ended problems, and open-ended problems. The purpose of the first section is to introduce the reader to the subject of thermodynamics. As one might suppose, a comprehensive treatment is not provided although numerous references are included. The several technical topics followed by three open-ended problems; the authors' solution (there may be other solutions) is also provided. The last section contains 39 problems; *no* solutions are provided here.

### 4.1 Overview

This overview section is concerned—as can be noted from its title—with thermodynamics. As one might suppose, it was not possible to address all topics directly or indirectly related to thermodynamics. However, additional details may be obtained from either the references provided at the end of this Overview section and/or at the end of the chapter.

Note: Those readers already familiar with the details associated with this subject may choose to bypass this Overview.

Thermodynamics was once defined as “the science that deals with the intertransformation of heat and work”. The fundamental principles of thermodynamics are contained in the first, second, and third laws of thermodynamics. These principles have been defined as “pure” or “theoretical” thermodynamics. These laws were developed and extensively tested in the latter half of the 19<sup>th</sup> century and are essentially based on experience. (The third law was developed later in the 20<sup>th</sup> century).

Practically all thermodynamics, in the ordinary meaning of the term, is “applied thermodynamics” in that it is essentially the application of these three laws, coupled with certain facts and principles of mathematics, physics, and chemistry, to problems in chemical engineering. The fundamental laws are of such generality that it is not surprising that these laws find application in other disciplines, including physics, chemistry, plus environmental and mechanical engineering.

As described in the previous chapter, the first law of thermodynamics is a conservation law for energy transformations. Regardless of the types of energy involved in processes—thermal, mechanical, electrical, elastic, magnetic, etc.—the change in energy of the system is equal to the difference between energy input and energy output. The first law also allows free “convertibility” from one form of energy to another, as long as the overall energy quantity is conserved. Thus, this law places no restriction on the conversion of work into heat, or on its counterpart—the conversion of heat into work.

The brief discussion of energy-conversion devices above leads to an important second-law consideration—i.e., that energy has quality as well as quantity. Because work is 100% convertible to heat, whereas the reverse situation is not true, work is a more valuable form of energy than heat. Although it is not as obvious, it can also be shown through the second-law principles and arguments that heat has *quality* in terms of its temperature. The higher the temperature at which heat transfer occurs, the greater the potential for energy transformation into work. Thus, thermal energy stored at higher temperatures is generally more useful to society than that available at lower temperatures. While there is an immense quantity of energy stored in the oceans and the earth’s core, for example, its present availability to society for performing useful tasks is essentially nonexistent. Theodore et al [1] also provided a qualitative review of the second law.

The choice of topics to be reviewed in this chapter was initially an area of concern. After some deliberation, it was decided to provide an introduction to four areas that many have included (at one time or another) in this broad engineering subject. These are detailed below:

1. Enthalpy Effects
2. Second Law Calculations
3. Phase Equilibrium
4. Chemical Reaction Equilibrium

The reader should note that the bulk of the material in this chapter has been drawn from L. Theodore and J. Reynolds, *Thermodynamics*, A Theodore Tutorial, originally published by the USEPA/APTI, RTP, NC in 1991 [2].

## 4.2 Enthalpy Effects

There are many different types of enthalpy effects; these include:

1. sensible (temperature);
2. latent (phase);
3. dilution (with water), e.g., HCl with H<sub>2</sub>O;
4. solution (nonaqueous), e.g., HCl with a solvent other than H<sub>2</sub>O; and
5. reaction (chemical).

This section is only concerned with effects (1) and (5). Details on effects (2–4) are available in the literature [1–3].

### 4.2.1 Sensible Enthalpy Effects

Sensible enthalpy effects are associated with temperature. There are methods that can be employed to calculate these changes. These methods include the use of:

1. enthalpy values;
2. average heat capacity values; and
3. heat capacity as a function of temperature.

Detailed calculations on methods (1–3) are provided by Theodore, et al [1,2]. Two expressions for heat capacity are considered in topic (3) employing  $a, b, c$  constants and  $\alpha, \beta, \gamma$  constants.

If enthalpy values are available, the enthalpy change is given by

$$\Delta h = h_2 - h_1; \text{ mass basis} \quad (4.1)$$

$$\Delta H = H_2 - H_1; \text{ mole basis} \quad (4.2)$$

If average molar heat capacity data are available,

$$\Delta H = \overline{C_p} \Delta T \quad (4.3)$$

where  $\overline{C_p}$  = average molar value of  $C_p$  in the temperature range  $\Delta T$ . Average molar heat capacity data are provided in the literature [1–5].

A more rigorous approach to enthalpy calculations can be provided if heat capacity variation with temperature is available. If the heat capacity is a function of the temperature, the enthalpy change is written in differential form:

$$dH = C_p dT \quad (4.4)$$

If the temperature variation of the heat capacity is given by

$$C_p = a + \beta T + \gamma T^2 \quad (4.5)$$

Equation (4.4) may be integrated directly between some reference or standard temperature ( $T_0$ ) and the final temperature ( $T_1$ ).

$$\Delta H = H_1 - H_0 \quad (4.6)$$

$$\Delta H = \alpha(T_1 - T_0) + (\beta/2)(T_1^2 - T_0^2) + (\gamma/3)(T_1^3 - T_0^3) \quad (4.7)$$

Equation (4.4) may also be integrated if the heat capacity is a function of temperature of the form:

$$C_p = a + bT + cT^{-2} \quad (4.8)$$

The enthalpy change is then given by

$$\Delta H = a(T_1 - T_0) + (b/2)(T_1^2 - T_0^2) + c(T_1^{-1} - T_0^{-1}) \quad (4.9)$$

Tabulated values of  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $a$ ,  $b$ ,  $c$  for a host of compounds (including some chlorinated organics) are available in the literature [2].

### 4.2.2 Chemical Reaction Enthalpy Effects

The equivalence of mass and energy needs to be addressed qualitatively. This relationship is only important in nuclear reactions, the details of which are beyond the scope of both this chapter and this text. The energy-related effects discussed here arise because of the rearrangement of electrons outside the nucleus of the atom. However, it is the nucleus of the atom that undergoes rearrangement in a nuclear reaction, releasing a significant quantity of energy; this process occurs with a minuscule loss of mass. The classic Einstein equation relates energy to mass, as provided in Equation (4.10).

$$\Delta E = (\Delta m)c^2 \quad (4.10)$$

where  $\Delta E$  = change in energy

$\Delta m$  = decrease in mass

$c$  = velocity of light

The standard enthalpy (heat) of reduction can be calculated from standard enthalpy of formation data. To simplify the presentation that follows, examine the authors' favorite equation:



If the above reaction is assumed to occur at a standard (or reference) state, the standard enthalpy of reaction,  $\Delta H^0$ , is given by

$$\Delta H^0 = c(\Delta H_f^0)_C + d(\Delta H_f^0)_D - a(\Delta H_f^0)_A - b(\Delta H_f^0)_B \quad (4.12)$$

where  $(\Delta H_f^0)_i$  = standard enthalpy of formation of species  $i$ .

Thus, the (standard) enthalpy of a reaction is obtained by taking the difference between the (standard) enthalpy of formation of products and reactants. If the (standard) enthalpy of reaction or formation is negative (exothermic), as is the case with most combustion reactions, then energy is liberated due to the chemical reaction. Energy is absorbed and  $\Delta H^0$  is positive (endothermic).

Tables of enthalpies of formation and reaction are available in the literature (particularly thermodynamics text/reference books) for a wide variety of compounds. [1] It is important to note that these are valueless unless the stoichiometric equation and the state of the reactants and products are included.

Theodore, et al [1,2] provide equations to describe the effect of temperature on the enthalpy of reaction. For heat capacity data in  $\alpha$ ,  $\beta$ ,  $\gamma$  form:

$$\Delta H_T^0 = \Delta H_{298}^0 + \Delta\alpha(T - 298) + \left(\frac{1}{2}\right)\Delta\beta(T^2 - 298^2) + \left(\frac{1}{3}\right)\Delta\gamma(T^3 - 298^3) \quad (4.13)$$

For the reaction presented in Equation (4.11):

$$\begin{aligned} \Delta\alpha &= c\alpha_C + d\alpha_D - a\alpha_A - b\alpha_B \\ \Delta\beta &= c\beta_C + d\beta_D - a\beta_A - b\beta_B \\ \Delta\gamma &= c\gamma_C + d\gamma_D - a\gamma_A - b\gamma_B \end{aligned} \quad (4.14)$$

For heat capacity in  $a$ ,  $b$ ,  $c$  form,

$$\Delta H_T^0 = \Delta H_{298}^0 + \Delta a(T - 298) + \left(\frac{1}{2}\right)\Delta b(T^2 - 298^2) + \Delta c(T^{-1} - 298^{-1}) \quad (4.15)$$

### 4.3 Second Law Calculations [2]

The law of conservation of energy has already been defined as the *first law of thermodynamics*. Its application allows calculations of energy relationships associated with all kinds of processes. The “limiting” law is called the *second law of thermodynamics* (SLT). Applications involve calculations for maximum power output from a power plant and equilibrium yields in chemical reactions. In principle, this law states that water cannot flow uphill and heat cannot flow from a cold to a hot body of its own accord. Other defining statements for this law that have appeared in the literature are provided below:

1. Any process, the sole net result of which is the transfer of heat from a lower temperature level to a higher one is impossible.

2. No apparatus, equipment, or process can operate in such a way that its only effect (on system and surroundings) is to convert heat absorbed completely into work.
3. It is impossible to convert the heat taken into a system completely into work in a cyclical process.

The second law also serves to define another important thermodynamics function called *entropy*. It is normally designated as  $S$ . The change in  $S$  for a *reversible adiabatic process* is always zero:

$$\Delta S = 0 \quad (4.16)$$

For liquids and solids, the entropy change for a system undergoing a temperature change from  $T_1$  to  $T_2$  is given by

$$\Delta S = C_p \ln(T_2 / T_1); C_p = \text{constant} \quad (4.17)$$

The entropy change of an ideal gas undergoing a physical change of state from  $P_1$  to  $P_2$  at a constant temperature  $T$  is given by

$$\Delta S_T = R \ln(P_1 / P_2); \text{ Btu / lbmol}^\circ\text{R} \quad (4.18)$$

The entropy change of one mole of an ideal gas undergoing a physical change of state from  $T_1$  to  $T_2$  at a constant pressure is given by

$$\Delta S_p = C_p \ln(T_2 / T_1); C_p (\text{gas}) = \text{constant} \quad (4.19)$$

Correspondingly, the entropy change for an ideal gas undergoing a physical change from  $(P_1, T_1)$  to  $(P_2, T_2)$  is

$$\Delta S = R \ln(P_1 / P_2) + C_p \ln(T_2 / T_1) \quad (4.20)$$

Some fundamental facts relative to the entropy concept are discussed below. The entropy change of a system may be positive (+), negative (-), or zero (0); the entropy change of the surroundings during this process may likewise be positive, negative, or zero. *However*, note that the total entropy change,  $\Delta S_T$ , must be equal to or greater than zero:

$$\Delta S_T \geq 0 \quad (4.21)$$

The equality sign applies if the change occurs *reversibly* and *adiabatically*.

Second law calculations will be revisited in Chapter 6 and in Part III, Chapter 27, Heat Transfer Term Projects.

The *third law of thermodynamics* is concerned with the absolute values of entropy. By definition; the entropy of all pure crystalline materials at absolute zero temperature is exactly zero. Note however, that chemical engineers are usually concerned with *changes* in thermodynamic properties, including entropy.

## 4.4 Phase Equilibrium

Relationships governing the equilibrium distribution of a substance between two phases, particularly gas and liquid phases, are the principal subject matter of phase-equilibrium thermodynamics. These relationships form the basis of calculational procedures that are employed in the design and the prediction of the performance of several mass transfer equipment and processes [6].

The most important equilibrium phase relationship is that between a liquid and a vapor. Raoult's and Henry's Laws theoretically describe liquid-vapor behavior and, under certain conditions, are applicable in practice. Raoult's Law is sometimes useful for mixtures of components of similar structure. It states that the partial pressure of any component in the vapor phase is equal to the product of the vapor pressure of the pure component and the mole fraction of that component in the liquid:

$$p_i = p'_i x_i \quad (4.22)$$

where  $p_i$  = partial pressure of component  $i$  in the vapor  
 $p'_i$  = vapor pressure of pure  $i$  at the same temperature  
 $x_i$  = mole fraction of component  $i$  in the liquid

This expression may be applied to all components. If the gas phase is ideal, this equation becomes

$$y_i = (p'_i / P) x_i \quad (4.23)$$

where  $y_i$  = mole fraction of component  $i$  in the vapor  
 $P$  = total system pressure

Unfortunately, relatively few mixtures follow Raoult's law. Henry's law is a more empirical relation used for representing data for many systems:



$$p_i = H_i x_i \quad (4.24)$$

where  $H_i$  = Henry's law constant for component  $i$  (in units of pressure)  
 If the gas behaves ideally, the above equation may be written as

$$y_i = m_i x_i \quad (4.25)$$

where  $m_i$  = constant (dimensionless)

In some engineering applications, mixtures of condensable vapors and noncondensable gases must be handled. A common example is water vapor and air; a mixture of organic vapors and air is another such example that often appears in air pollution applications. Condensers can be used to control organic emissions to the atmosphere by lowering the temperature of the gaseous stream, although an increase in pressure will produce the same result. The calculation for this is often accomplished using the *phase equilibrium constant*  $K$ . This constant has been referred to in industry as a *phase componential split factor* since it provides the ratio of the mole fractions of a component in the two equilibrium phases. The defining equation is

$$K_i = y_i / x_i \quad (4.26)$$

where  $K_i$  = phase equilibrium constant for component  $i$  (dimensionless).

As a first approximation,  $K_i$  is generally treated as a function only of the temperature and pressure. For ideal gas conditions,  $K_i$  may be approximated by

$$K_i = p'_i / P \quad (4.27)$$

where  $p'_i$  is the vapor pressure.

Many of the phase equilibrium calculations involve hydrocarbons. Fortunately, most hydrocarbons approach ideal gas behavior over a fairly wide range of temperatures and pressures. Values for  $K_i$  for a large number of hydrocarbons are provided in two DePriester nomographs, which are available in the literature. These two nomographs or charts were originally developed by DePriester in 1953 [8]. Additional details are provided in Problem 3 in the next section.

The aforementioned DePriester charts are a valuable source of vapor-liquid equilibrium data for many hydrocarbons that approach ideal behavior. However, it should be noted that the DePriester chart data are based on

experimental data. The fact that these compounds approach ideal behavior allows the data to be presented in a simple form, i.e., as a function solely of temperature and pressure.

Although Raoult's law was included in the early analysis, non-ideal deviations can be accounted for by two theoretical models that have been verified by rather extensive experimental data. The two models are:

1. Wilson's method [9]
2. NRTL model [10]

Additional details are available in the literature [1].

## 4.5 Chemical Reaction Equilibrium

With regard to chemical reactions, two important questions are of concern to the engineer: (1) how *far* will the reaction go; and (2) how *fast* will the reaction go? Chemical thermodynamics provides the answer to the first question; however, it tells nothing about the second. Reaction rates fall within the domain of chemical reaction kinetics. To illustrate the difference and importance of both questions in an engineering analysis of a chemical reaction, consider the following process: Substance A, which costs 1 cent/ton, can be converted to B, which is worth 1 million dollars/mg, by the reaction  $A \rightarrow B$ . Chemical thermodynamics will provide information on the maximum amount of B that can be formed. If 99.99% of A can be converted to B, the reaction would then *appear* to be economically feasible, from a *thermodynamic* point of view. However, a *kinetic* analysis might indicate that the reaction is so slow that, for all practical purposes, its rate is vanishingly small. For example, it might take  $10^6$  years to obtain a 10<sup>-6</sup>% conversion of A. The reaction is then economically unfeasible. Thus, it can be seen that both equilibrium and kinetic effects must be considered in an overall engineering analysis of a chemical reaction [2]. This topic receives treatment in Chapter 8.

A rigorous, detailed presentation of this equilibrium topic is beyond the scope of this chapter and this text. However, superficial treatment is presented to provide at least a qualitative introduction to chemical reaction equilibrium. As will be shown in Chapter 8, if a chemical reaction is conducted in which reactants go to products, the products will be formed at a rate governed (in part) by the concentration of the reactants and conditions such as temperature and pressure. Eventually, as the reactants form

products and the products react to form reactants, the *net* rate of reaction must equal zero. At this point, equilibrium will have been achieved.

Chemical reaction equilibrium calculations are structured around a thermodynamic term referred to as *free energy*,  $G$ . This so called energy is a thermodynamic property that cannot be easily defined without some basic grounding in thermodynamics. No attempt will be made to define it here, and the interested reader is directed to the literature [2] for further development of this term. Note that free energy has the same units as enthalpy, and may be used on a mole or total mass basis.

Consider the *equilibrium* reaction:



For this reaction

$$\Delta G_{298}^0 = c(\Delta G_f^0)_C + d(\Delta G_f^0)_D - a(\Delta G_f^0)_A - b(\Delta G_f^0)_B \quad (4.29)$$

The standard free energy of reaction  $\Delta G^0$  may be calculated from standard free energy of formulation data, in a manner similar to that for the standard enthalpy of reaction. The following equation is used to calculate the *chemical reaction equilibrium constant*  $K$  at a temperature  $T$ :

$$\Delta G_T^0 = -RT \ln(K) \quad (4.30)$$

The effect of temperature on the standard free energy of reaction,  $\Delta G_T^0$ , and the chemical reaction equilibrium constant,  $K$ , is available in the literature [1–4] and has been developed in a manner similar to that presented earlier for the effect of temperature on the enthalpy of reaction. Once the chemical reaction equilibrium constant (for a particular reaction) has been determined, one can proceed to estimate the quantities of the participating species at equilibrium [1–4].

A detailed and expanded treatment of thermodynamics is available in the following four references.

1. L. Theodore, F. Ricci, and T. VanVliet, *Thermodynamics for the Practicing Engineer*, John Wiley & Sons, Hoboken, NJ, 2009 [1].
2. J. Smith, H VanNess, and M. Abbott, *Chemical Engineering Thermodynamics*, 6<sup>th</sup> edition, McGraw-Hill, New York City, NY, 2001 [2].

3. D. Green and R. Perry (editors), *Perry's Chemical Engineers' Handbook*, 8<sup>th</sup> edition, McGraw-Hill, New York City, NY, 2008 [5].
4. L. Theodore, *Chemical Engineering: The Essential Reference*, McGraw-Hill, New York City, NY, 2014 [11].

## 4.6 Illustrative Open-Ended Problems

This and the last Section provide open-ended problems. However, solutions *are* provided for the three problems in this Section in order for the reader to hopefully obtain a better understanding of these problems, which differ from the traditional problems/illustrative examples. The first problem is relatively straightforward while the third (and last problem) is somewhat more complex. Note that solutions are not provided for the 39 open-ended problems in the next Section.

**Problem 1:** Define vaporization and discuss its importance to the chemical engineer.

**Solution:** At any one temperature, all molecules move with an average velocity that is independent of state or structure. The temperature at which a phase change occurs can be determined by an energy balance. At the temperature where the energy of any molecule is sufficient to overcome the attractive forces of its neighbors, it will change from a condensed phase to a vapor phase. The phenomenon is the same whether the condensed phase is liquid or solid. When a solid vaporizes, the term *sublimation* (rather than vaporization) is used to describe the phenomenon.

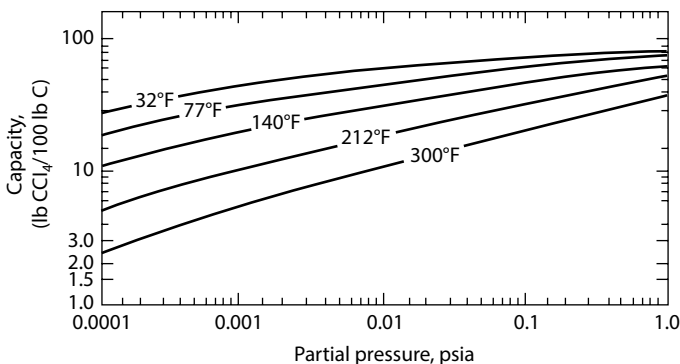
There is a wide distribution of energies among molecules at any one temperature. Hence, if one considers the external surface of a condensed phase as a location from which molecules can escape, some molecules will always have sufficient energy to overcome the attractive forces of their neighbors. If the movement is not constrained, these molecules will move (or escape) into the vapor; this process is defined as *evaporation*. Since the molecules on the surface of a condensed phase are attracted inward on only three sides, it is reasonable to postulate that all the escaping molecules originate at the interphase.

**Problem 2:** This open-ended problem is concerned with a discussion of vapor-solid equilibria. The relation at constant temperature between the amount of substance adsorbed by an adsorbent (solid) and the equilibrium partial pressure or concentration is called the *adsorption isotherm*. The adsorption isotherm is the most important and by far the most often used of the various equilibria data.

Most available data on adsorption systems are determined at equilibrium conditions. *Adsorption equilibrium* is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are leaving. An adsorbent is then said to be “saturated with vapors” and can adsorb no more vapors. Equilibrium determines the maximum amount of vapor that may be adsorbed on the solid at a given set of operating conditions. Although a number of variables affect adsorption, the two most important ones in determining equilibrium for a given system are temperature and pressure. Three types of equilibrium graphs and/or data are used to describe adsorption systems: *isotherm* at constant temperature, *isobar* at constant pressure, and *isostere* at constant amount of vapors adsorbed.

The most common and useful adsorption equilibrium data is the adsorption isotherm. The isotherm is a plot of the adsorbent capacity vs the partial pressure of the adsorbate at a constant temperature. Adsorbent capacity is usually given in weight percent, usually expressed as grams of adsorbate per 100 g of adsorbent. Figure 4.1 shows a typical example of an adsorption isotherm for carbon tetrachloride on activated carbon. Graphs of this type are used to estimate the size of adsorption systems. Attempts have been made to develop generalized equations that can predict adsorption equilibrium from physical data. This is very difficult because adsorption isotherms take many shapes depending on the atomic forces involved. Isotherms may be concave upward, concave downward, or “S” shaped. To date, most of the theories agree with data only for specific adsorbate-systems and are valid over limited concentration ranges.

Although this problem is concerned with isotherms, two additional adsorption equilibrium relationships are the aforementioned isostere and the isobar. The isostere is usually provided as a plot of the  $\ln p$  vs



**Figure 4.1** Adsorption isotherms for carbon tetrachloride on activated carbon.

$1/T$  at a constant amount of vapor adsorbed. Adsorption isostere lines are usually straight for most adsorbate-adsorbent systems. The isostere is important in that the slope of the isostere (approximately) corresponds to the heat of adsorption. The isobar is a plot of the amount of vapors adsorbed vs. temperature at a constant partial pressure. However, the adsorption isotherm is by far the most commonly used equilibrium relationship.

Relative to the isotherm, develop two equations that have been employed to describe vapor-solid adsorption equilibria data.

Comment: Refer to the work of Theodore [11] and Theodore and Ricci [12].

Solution: Several models have been proposed to describe the aforementioned vapor-solid equilibrium phenomena. Two such models are described below to represent the variation of the amount of adsorption per unit area or unit mass with partial pressure.

Freundlich proposed the equation:

$$Y = kp^{1/n} \quad (4.31)$$

where  $Y$  is the weight or volume of gas (or vapor) adsorbed per unit area or unit mass of adsorbent and  $p$  is the equilibrium partial pressure. The  $k$  and  $n$  terms are the empirical constants dependent on the nature of solid and adsorbate, and on the temperature. Equation (4.31) may be rewritten as follows. Taking logarithms of both sides,

$$\log Y = \log k + \left(\frac{1}{n}\right) \log p \quad (4.32)$$

If  $\log Y$  is now plotted against  $\log p$ , a straight line should result with slope equal to  $1/n$  and an ordinate intercept equal to  $\log k$ . Although the requirements of the equations are met satisfactorily at lower pressures, the experimental points curve away from the straight line at higher pressures, indicating that this equation does not have general applicability in reproducing adsorption of gases (or vapors) by solids.

A much better equation for isotherms was deduced by Langmuir from theoretical considerations. The final form is given as

$$Y = \frac{ap}{1+bp} \quad (4.33)$$

which can be rewritten as

$$\frac{p}{Y} = \frac{1}{a} + \left(\frac{b}{a}\right)p \quad (4.34)$$

Since  $a$  and  $b$  are constants, a plot of  $p/Y$  vs.  $p$  should yield a straight line with slope equal to  $b/a$  and an ordinate intercept equal to  $1/a$ .

Other models of potential interest include those developed by Brunauer, Emmett, and Taylor [13], Polyani [14] and Dubinin and coworkers [15–16]

**Problem 3:** Discuss the applicability of the DePriester charts and how the information provided by the charts can be converted to a more useful form.

**Comment:** Refer to literature [1–3] for additional details.

**Solution:** One possible approach to representing the DePriester charts in equation form for the various components ( $I$ ) is to evaluate the A, B, C, D, E coefficients in the equation [17].

$$K(I) = A(I) + B(I) * T + C(I) * T^2 + D(I) * T^3 + E(I) * T^3 \quad (4.35)$$

This equation provides the variation of  $K$  with  $T$ . The effect of  $P$  on  $K$  may be approximated by

$$K(I)_p = K(I)_{p_0} (p_0 / p); p_0 = 1 \text{ atm} \quad (4.36)$$

Numerical values for the five coefficients for a variety of compounds have been developed by Theodore [17].

Another approach is to express the relationship as

$$K(T)' = A(I) + B(I) * T + C(I) * T^2 \quad (4.37)$$

Values of A, B, and C are also provided by Theodore [17] in tabular form.

It is important to note that the DePriester charts discussed earlier are based on the assumption of ideal gas behavior. This assumption is generally not valid for most mixtures containing inorganic components. No simple and reliable method is available for estimating  $K$  for both inorganics and organics in an inorganic-organic mixture.

## 4.7 Open-Ended Problems

This last Section of the chapter contains open-ended problems as they relate to thermodynamics. No detailed and/or specific solution is provided; that task is left to the reader, noting that each problem has either a unique solution or a number of solutions or (in some cases) no solution at all. These are characteristics of open-ended problems described earlier.

There are comments associated with some, but not all, of the problems. The comments are included to assist the reader while attempting to solve the problems. However, it is recommended that the solution to each problem should initially be attempted *without* the assistance of the comments.

There are 39 open-ended problems in this section. As stated above, if difficulty is encountered in solving any particular problem, the reader should next refer to the comment, if any is provided with the problem. The reader should also note that the more difficult problems are generally located at or near the end of the section.

1. Describe the early history associated with thermodynamics.
2. Discuss the recent advances in thermodynamics.
3. Select a refereed, published article on thermodynamics from the literature and provide a review.
4. Develop an original problem in thermodynamics that would be suitable as an illustrative example in a book.
5. Prepare a list of the various books which have been written on thermodynamics. Select the three best and justify your answer. Also select the three weakest books and justify your answer.
6. Provide your interpretation of the principle of corresponding states.
7. Describe the role critical properties play in non-ideal gas behavior calculations.
8. Provide a layman's definition of a reversible process.
9. Is it possible to circumvent the second law?  
Comment: Carefully review the various definitions provided in the literature for the second law.
10. Some individuals have claimed (and several books have been written) that Earth and the humans that inhabit Earth are all doomed. The basis of their argument is that the entropy of the universe is constantly on the rise so that a time will come when there will be no useful energy



available for doing useful work. Discuss the pros and cons of this argument.

Comment: Consider how long will it take for Earth to reach a state when there will be no useful energy available.

11. One of the authors once requested on an examination that the student provide a layman's definition and explanation of the second law. Provide your answer.
12. One of the authors once requested on an examination that the student provide a layman's definition and explanation of entropy. Provide your answer.
13. One of the authors once requested on an examination that the student provide a layman's definition and explanation of exergy. Provide your answer.
14. Describe the difference between entropy and exergy. How are they similar? Which approach better describes the second law?
15. Define the following terms:
  - Ideal work
  - Lost work
  - Minimum work
  - Maximum work

Also discuss how these terms are related.
16. Define and discuss the third law of thermodynamics in both technical and layman terms.
17. Describe the various methods available in the literature for predicting heat capacity values (as opposed to obtaining values experimentally).  
Comment: Check both the internet and the literature.
18. Describe the various methods available in the literature for predicting standard enthalpy of reaction values (including combustion).
19. Describe the various methods available in the literature for predicting normal boiling point.
20. It has been proposed to use the sensible heat from the flue gas of a combustion device to reduce the energy needs of the combustion process. Discuss the advantages and disadvantages of the proposal.  
Comment: The total energy content of the gas should be taken into consideration based on the mass involved.
21. Refer to saturated steam-ice data. Generate an equation describing the specific volume of ice and steam as a function of temperature and pressure.

22. Refer to saturated steam-ice data. Generate an equation describing the specific volume of ice and steam as a function of enthalpy and pressure.
23. Refer saturated steam-ice data. Generate an equation describing the specific volume of ice and steam as a function of entropy and pressure.
24. Convert enthalpy-concentration data for  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  at various temperatures into equation form.  
Comment: Refer to the literature [1–3] for data.
25. Convert enthalpy-concentration data for  $\text{NaOH-H}_2\text{O}$  at various temperatures into equation form.  
Comment: Refer to the literature [1–3] for data.
26. Obtain enthalpy of mixing at infinite dilution data for various gases and solids dissolved in a variety of liquids (not only water).
27. Can the standard enthalpy of reaction ever be positive? Explain.  
Comment: Carefully review the definition of the standard enthalpy of reaction.
28. Describe the effect of pressure on the enthalpy of reaction.  
Comment: Is this effect important in most real-world applications?
29. Define and explain relative volatility in layman terms.
30. Outline the various procedures available to calculate the phase equilibrium constant, and comment on their advantages and disadvantages.
31. Develop another law that combines/integrates the features of both Henry's and Raoult's laws.  
Comment: Carefully review both laws.
32. Develop another method to produce vapor-liquid equilibrium in nonideal solutions.
33. Describe the *Wilson method* employed for vapor-liquid equilibrium in layman terms [9].
34. Describe the *NRTL method* employed for vapor-liquid equilibrium in layman terms [10].
35. Discuss the differences between the Wilson and NRTL methods for describing vapor-liquid equilibrium.
36. Develop another method that combines the features of both the NRTL and Wilson methods to describe non-ideal phase equilibria.  
Comment: Refer to the literature [2, 9–11].

37. Define and describe the chemical reaction equilibrium constant and the standard free energy.
38. Discuss the differences and the relationship between the free energy and the standard free energy.
39. Outline the various procedures available to calculate the chemical reaction equilibrium constant, and comment on their advantages and disadvantages.

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