

10.41 Refrigerant 134a enters the compressor of a vapor-compression heat pump at 15 lbf/in.², 0°F and is compressed adiabatically to 160 lbf/in.², 160°F. Liquid enters the expansion valve at 160 lbf/in.², 95°F. At the valve exit, the pressure is 15 lbf/in.²

- (a) Determine the isentropic compressor efficiency.
 - (b) Determine the coefficient of performance.
 - (c) Perform a full exergy accounting of the compressor power input, in Btu per lb of refrigerant flowing. Discuss.

Let $T_0 = 480^\circ\text{R}$.

10.42 A geothermal heat pump operating at steady state with Refrigerant-22 as the working fluid is shown schematically in Fig. P10.42. The heat pump uses 55°F water from wells as the thermal source. Operating data are shown on the figure for a day in which the outside air temperature is 20°F. Assume adiabatic operation of the compressor. For the heat pump, determine

- (a) the volumetric flow rate of heated air to the house, in ft^3/min .
 - (b) the isentropic compressor efficiency.
 - (c) the compressor power, in horsepower.
 - (d) the coefficient of performance.
 - (e) the volumetric flow rate of water from the geothermal wells, in gal/min .

For $T_0 = 20^\circ\text{F}$, perform a full exergy accounting of the compressor power input, and devise and evaluate a second law efficiency for the heat pump system.

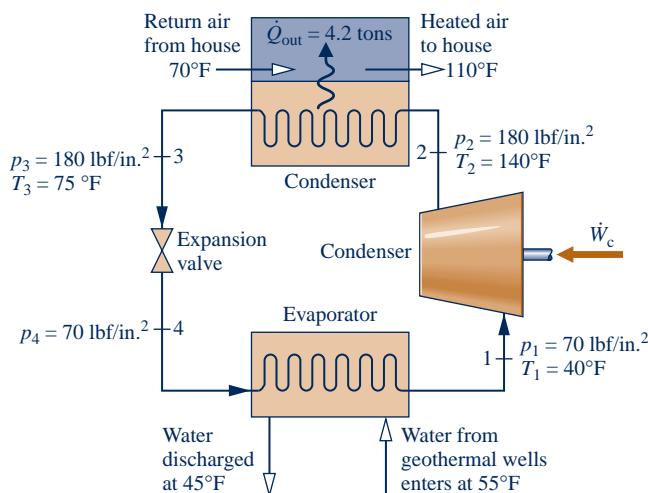


Fig. P10.42

Gas Refrigeration Systems

10.43 Air enters the compressor of an ideal Brayton refrigeration cycle at 100 kPa, 300 K. The compressor pressure ratio is 3.75, and the temperature at the turbine inlet is 350 K. Determine the

- (a) net work input, per unit mass of air flow, in kJ/kg.
 - (b) refrigeration capacity, per unit mass of air flow, in kJ/kg.
 - (c) coefficient of performance.
 - (d) coefficient of performance of a Carnot refrigeration cycle operating between thermal reservoirs at $T_C = 300$ K and $T_H = 350$ K, respectively.

10.44 Air enters the compressor of a Brayton refrigeration cycle at 100 kPa, 270 K. The compressor pressure ratio is 3, and the temperature at the turbine inlet is 315 K. The compressor and turbine have isentropic efficiencies of 82% and 85%, respectively. Determine the

- (a) net work input, per unit mass of air flow, in kJ/kg.
 (b) exergy accounting of the net power input, in kJ per kg of air flowing. Discuss.

Let $T_0 = 315$ K.

10.45 Plot the quantities calculated in parts (a) through (c) of Problem 10.43 versus the compressor pressure ratio ranging from 3 to 6. Repeat for compressor and turbine isentropic efficiencies of 90%, 85%, and 80%.

10.46 An ideal Brayton refrigeration cycle has a compressor pressure ratio of 6. At the compressor inlet, the pressure and temperature of the entering air are 20 lbf/in^2 and 460°R . The temperature at the inlet of the turbine is 700°R . For a refrigerating capacity of 15 tons, determine

- (a) the mass flow rate, in lb/min.
 - (b) the net power input, in Btu/min.
 - (c) the coefficient of performance.

10.47 Reconsider Problem 10.46, but include in the analysis that the compressor and turbine have isentropic efficiencies of 78% and 92%, respectively.

10.48 The table below provides steady-state operating data for an ideal Brayton refrigeration cycle with air as the working fluid. The principal states are numbered as in Fig. 10.15. The volumetric flow rate at the turbine inlet is $0.4 \text{ m}^3/\text{s}$. Sketch the $T-s$ diagram for the cycle and determine the

- (a) specific enthalpy, in kJ/kg, at the turbine exit.
 - (b) mass flow rate, in kg/s.
 - (c) net power input, in kW.
 - (d) refrigeration capacity, in kW.
 - (e) coefficient of performance.

State	p (kPa)	T (K)	h (kJ/kg)	p_r
1	140	270	270.11	0.9590
2	420	—	370.10	2.877
3	420	320	320.29	1.7375
4	140	—	?	—

10.49 Air enters the compressor of a Brayton refrigeration cycle at 100 kPa, 260 K, and is compressed adiabatically to 300 kPa. Air enters the turbine at 300 kPa, 300 K, and expands adiabatically to 100 kPa. For the cycle

- (a) determine the net work per unit mass of air flow, in kJ/kg, and the coefficient of performance if the compressor and turbine isentropic efficiencies are both 100%.

(b) plot the net work per unit mass of air flow, in kJ/kg, and the coefficient of performance for equal compressor and turbine isentropic efficiencies ranging from 80 to 100%.

10.50 The Brayton refrigeration cycle of Problem 10.43 is modified by the introduction of a regenerative heat exchanger. In the modified cycle, compressed air enters the regenerative heat exchanger at 350 K and is cooled

to 320 K before entering the turbine. Determine, for the modified cycle,

- the lowest temperature, in K.
- the net work input per unit mass of air flow, in kJ/kg.
- the refrigeration capacity, per unit mass of air flow, in kJ/kg.
- the coefficient of performance.

10.51 Reconsider Problem 10.50, but include in the analysis that the compressor and turbine have isentropic efficiencies of 85 and 88% respectively. Answer the same questions as in Problem 10.50.

10.52 Plot the quantities calculated in parts (a) through (d) of Problem 10.50 versus the compressor pressure ratio ranging from 4 to 7. Repeat for equal compressor and turbine isentropic efficiencies of 95%, 90%, and 80%.

10.53 Consider a Brayton refrigeration cycle with a regenerative heat exchanger. Air enters the compressor at 480°R, 15 lbf/in.² and is compressed isentropically to 40 lbf/in.² Compressed air enters the regenerative heat exchanger at 540°R and is cooled to 480°R before entering the turbine. The expansion through the turbine is isentropic. If the refrigeration capacity is 15 tons, calculate

- the volumetric flow rate at the compressor inlet, in ft³/min.
- the coefficient of performance.

10.54 Reconsider Problem 10.53, but include in the analysis that the compressor and turbine each have isentropic efficiencies of 88%. Answer the same questions for the modified cycle as in Problem 10.53.

10.55 Air at 2 bar, 380 K is extracted from a main jet engine compressor for cabin cooling. The extracted air enters a heat exchanger where it is cooled at constant pressure to 320 K through heat transfer with the ambient. It then expands adiabatically to 0.95 bar through a turbine and is discharged into the cabin. The turbine has an isentropic efficiency of 75%. If the mass flow rate of the air is 1.0 kg/s, determine

- the power developed by the turbine, in kW.
- the rate of heat transfer from the air to the ambient, in kW.

10.56 Air at 32 lbf/in.², 680°R is extracted from a main jet engine compressor for cabin cooling. The extracted air enters a heat exchanger where it is cooled at constant pressure to 600°R through heat transfer with the ambient. It then expands adiabatically to 14 lbf/in.² through a turbine and is discharged into the cabin at 500°R with a mass flow rate of 200 lb/min. Determine

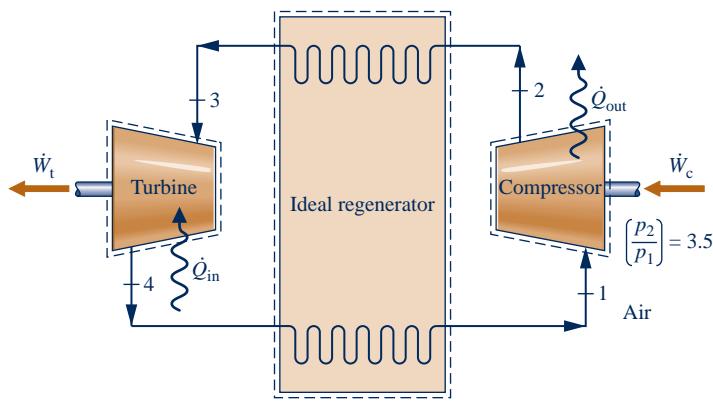
- the power developed by the turbine, in horsepower.
- the isentropic turbine efficiency.
- the rate of heat transfer from the air to the ambient, in Btu/min.

10.57 Air within a piston–cylinder assembly undergoes a *Stirling refrigeration cycle*, which is the reverse of the Stirling power cycle introduced in Sec. 9.8.4. At the beginning of the isothermal compression, the pressure and temperature are 100 kPa and 350 K, respectively. The compression ratio is 7, and the temperature during the isothermal expansion is 150 K. Determine the

- heat transfer for the isothermal compression, in kJ per kg of air.
- net work for the cycle, in kJ per kg of air.
- coefficient of performance.

10.58 Air undergoes an *Ericsson refrigeration cycle*, which is the reverse of the Ericsson power cycle introduced in Sec. 9.8.4. Figure P10.58 provides data for the cycle operating at steady state. Sketch the *p–v* diagram for the cycle and determine the

- heat transfer for the isothermal expansion, per unit mass of air flow, in kJ/kg.
- net work, per unit mass of air flow, in kJ/kg.
- coefficient of performance.



State	p (kPa)	T (K)
1	100	310
2	350	310
3	350	270
4	100	270

Fig. P10.58

► DESIGN & OPEN-ENDED PROBLEMS: EXPLORING ENGINEERING PRACTICE

10.1D Children may wonder how a household refrigerator works to keep food cold in a warm kitchen. Prepare a 20-minute presentation suitable for an elementary school science class to explain the principles of operation of a refrigerator. Include instructional aids to enhance your presentation.

10.2D The object of this project is to select a compact thermoelectric refrigerator to be shared by you and at least

two other students living in the same residence as you do. Survey the other students to determine their needs in order to size the unit. Critically evaluate competing brands. What type and number of thermoelectric modules are used in the unit selected, and what is its power requirement? Summarize your findings in a memorandum.

10.3D In cases involving cardiac arrest, stroke, heart attack, and hyperthermia, hospital medical staff must move quickly to

reduce the patient's body temperature by several degrees. A system for this purpose featuring a disposable plastic *body suit* is described in BIOCONNECTIONS in Sec. 4.9.1. Conduct a search of the patent literature for alternative ways to achieve cooling of medically distressed individuals. Consider patents both granted and pending. Critically evaluate two different methods found in your search relative to each other and the body suit approach. Write a report including at least three references.

10.4D Identify and visit a local facility that uses cold thermal storage. Conduct a forensic study to determine if the cold storage system is well-suited for the given application today. Consider costs, effectiveness in providing the desired cooling, contribution to global climate change, and other pertinent issues. If the cold storage system is well suited for the application, document that. If the cold storage system is not well suited, recommend system upgrades or an alternative approach for obtaining the desired cooling. Prepare a PowerPoint presentation of your findings.

10.5D A vertical, closed-loop *geothermal* heat pump is under consideration for a new 50,000-ft² school building. The design capacity is 100 tons for both heating and cooling. The local water table is 150 ft, and the ground water temperature is 55°F. Specify a ground source heat pump as well as the number and depth of wells for this application and develop a layout of vertical wells and piping required by the system.

10.6D Investigate the economic feasibility of using a waste heat-recovery heat pump for domestic water heating that employs ventilation air being discharged from a dwelling as the source. Assume typical hot water use of a family of four living in a 2200-ft² single-family dwelling in your locale. Write a report of your findings.

10.7D Food poisoning is on the rise and can be fatal. Many of those affected have eaten recently at a restaurant, café, or fast-food outlet serving food that has not been cooled properly by the food supplier or restaurant food-handlers. To be safe, foods should not be allowed to remain in the temperature range where bacteria most quickly multiply. Standard refrigerators typically do not have the ability to provide the rapid cooling needed to ensure dangerous levels of bacteria are not attained. A food processing company supplying a wide range of fish products to restaurants has requested your project group to provide advice on how to achieve best cooling practices in its factory. In particular, you are asked to consider applicable health regulations, suitable equipment, typical operating costs, and other pertinent issues. A written report providing your recommendations is required, including an annotated list of food-cooling *Dos and Don'ts* for restaurants supplied by the company with fish.

10.8D According to researchers, advances in *nanomaterial* fabrication are leading to development of tiny thermoelectric modules that could be used in various applications, including integrating nanoscale cooling devices within the uniforms of firefighters, emergency workers, and military personnel; embedding thermoelectric modules in facades of a building; and using thermoelectric modules to recover waste heat in automobiles. Research two applications for this technology proposed within the past five years. Investigate the technical

readiness and economic feasibility for each concept. Report your findings in an executive summary and a PowerPoint presentation with at least three references.

10.9D In *induced hypothermia*, the temperature of a particular organ, such as the heart, is lowered to reduce the metabolic rate during surgery. Cooling is achieved by circulating blood through a heat exchanger outside the body. When the cooled blood is reintroduced through blood vessels in the organ, it cools the organ to the desired temperature. Develop the preliminary design of a vapor-compression refrigeration system to cool blood during heart surgery. Determine the necessary temperature requirements and specify a refrigerant, operating pressures and temperatures for the working fluid, and the refrigeration capacity.

10.10D A vapor-compression refrigeration system operating continuously is being considered to provide a minimum of 80 tons of refrigeration for an industrial refrigerator maintaining a space at 2°C. The surroundings to which the system rejects energy by heat transfer reach a maximum temperature of 40°C. For effective heat transfer, the system requires a temperature difference of at least 20°C between the condensing refrigerant and surroundings and between the vaporizing refrigerant and refrigerated space. The project manager wishes to install a system that minimizes the annual cost for electricity (monthly electricity cost is fixed at 5.692 cents for the first 250 kW · h and 6.006 cents for any usage above 250 kW · h). You are asked to evaluate two alternative designs: a standard vapor-compression refrigeration cycle and a vapor-compression refrigeration cycle that employs a power-recovery turbine in lieu of an expansion valve. For each alternative, consider three refrigerants: ammonia, Refrigerant 22, and Refrigerant 134a. Based on electricity cost, recommend the better choice between the two alternatives and a suitable refrigerant. Other than electricity cost, what additional factors should the manager consider in making a final selection? Prepare a written report including results, conclusions, and recommendations.

10.11D High-performance aircraft increasingly feature electronics that assist flight crews in performing their duties and reducing their fatigue. While these electronic devices improve aircraft performance, they also add greatly to the *thermal load* that must be managed within the aircraft. Cooling technologies currently used on aircraft are approaching their limits and other means are being considered, including vapor-compression refrigeration systems. However, unlike cooling systems used on earth, systems employed on aircraft must meet rapidly changing conditions. For instance, as onboard electronic devices switch on and off, the energy they emit by heat transfer alters the thermal load; additionally, the temperature of the air outside the aircraft into which such waste heat is discarded changes with altitude and flight speed. Accordingly, for vapor-compression systems to be practical for aircraft use, engineers must determine if the systems can quickly adapt to rapidly changing thermal loads and temperatures. The object of this project is to develop the preliminary design of a bench-top laboratory set-up with which to evaluate the performance of a vapor-compression refrigeration system subject to broadly variable thermal inputs and changing ambient conditions. Document your design in a report having at least three references.



Systems often involve *mixtures* of several different entities; mixture rules for gases are provided in Sec. 11.8. Image Source/Getty Images, Inc.

ENGINEERING CONTEXT As seen in previous chapters, application of thermodynamic principles to engineering systems requires data for specific internal energy, enthalpy, entropy, and other properties. The objective of this chapter is to introduce thermodynamic relations that allow u , h , s , and other thermodynamic properties of simple compressible systems to be evaluated from data that are more readily measured. Primary emphasis is on systems involving a single chemical species such as water or a mixture such as air. An introduction to general property relations for mixtures and solutions is also included.

Means are available for determining pressure, temperature, volume, and mass experimentally. In addition, the relationships between the specific heats c_v and c_p and temperature at relatively low pressure are accessible experimentally. Values for certain other thermodynamic properties also can be measured without great difficulty. However, specific internal energy, enthalpy, and entropy are among those properties that are not easily obtained experimentally, so we resort to computational procedures to determine values for these.



11

Thermodynamic Relations

► LEARNING OUTCOMES

When you complete your study of this chapter, you will be able to...

- ▶ calculate $p-v-T$ data using equations of state involving two or more constants.
- ▶ demonstrate understanding of exact differentials involving properties and utilize the property relations developed from the exact differentials summarized in Table 11.1.
- ▶ evaluate Δu , Δh , and Δs , using the Clapeyron equation when considering phase change, and using equations of state and specific heat relations when considering single phases.
- ▶ demonstrate understanding of how tables of thermodynamic properties are constructed.
- ▶ evaluate Δh and Δs using generalized enthalpy and entropy departure charts.
- ▶ utilize mixture rules, such as Kay's Rule, to relate pressure, volume, and temperature of mixtures.
- ▶ apply thermodynamic relations to multicomponent systems.

11.1

Using Equations of State**equations of state****TAKE NOTE...**

Using the generalized compressibility chart, virial equations of state and the ideal gas model are introduced in Chap. 3. See Secs. 3.11 and 3.12.

An essential ingredient for the calculation of properties such as the specific internal energy, enthalpy, and entropy of a substance is an accurate representation of the relationship among pressure, specific volume, and temperature. The $p-v-T$ relationship can be expressed alternatively: There are *tabular* representations, as exemplified by the steam tables. The relationship also can be expressed *graphically*, as in the $p-v-T$ surface and compressibility factor charts. *Analytical* formulations, called **equations of state**, constitute a third general way of expressing the $p-v-T$ relationship. Computer software such as *Interactive Thermodynamics: IT* also can be used to retrieve $p-v-T$ data.

The virial equation and the ideal gas equation are examples of analytical equations of state introduced in previous sections of the book. Analytical formulations of the $p-v-T$ relationship are particularly convenient for performing the mathematical operations required to calculate u , h , s , and other thermodynamic properties. The object of the present section is to expand on the discussion of $p-v-T$ relations for simple compressible substances presented in Chap. 3 by introducing some commonly used equations of state.

11.1.1 • Getting Started

Recall from Sec. 3.11 that the **virial equation of state** can be derived from the principles of statistical mechanics to relate the $p-v-T$ behavior of a gas to the forces between molecules. In one form, the compressibility factor Z is expanded in inverse powers of specific volume as

$$Z = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \dots \quad (11.1)$$

virial equation

The coefficients B , C , D , etc. are called, respectively, the second, third, fourth, etc. virial coefficients. Each virial coefficient is a function of temperature alone. In principle, the virial coefficients are calculable if a suitable model for describing the forces of interaction between the molecules of the gas under consideration is known. Future advances in refining the theory of molecular interactions may allow the virial coefficients to be predicted with considerable accuracy from the fundamental properties of the molecules involved. However, at present, just the first few coefficients can be calculated and only for gases consisting of relatively simple molecules. Equation 11.1 also can be used in an empirical fashion in which the coefficients become parameters whose magnitudes are determined by fitting $p-v-T$ data in particular realms of interest. Only a few coefficients can be found this way, and the result is a *truncated* equation valid only for certain states.

In the limiting case where the gas molecules are assumed not to interact in any way, the second, third, and higher terms of Eq. 11.1 vanish and the equation reduces to $Z = 1$. Since $Z = p\bar{v}/\bar{R}T$, this gives the ideal gas equation of state $p\bar{v} = \bar{R}/T$. The ideal gas equation of state provides an acceptable approximation at many states, including but not limited to states where the pressure is low relative to the critical pressure and/or the temperature is high relative to the critical temperature of the substance under consideration. At many other states, however, the ideal gas equation of state provides a poor approximation.

Over 100 equations of state have been developed in an attempt to improve on the ideal gas equation of state and yet avoid the complexities inherent in a full virial series. In general, these equations exhibit little in the way of fundamental physical significance and are mainly empirical in character. Most are developed

for gases, but some describe the $p-v-T$ behavior of the liquid phase, at least qualitatively. Every equation of state is restricted to particular states. This realm of applicability is often indicated by giving an interval of pressure, or density, where the equation can be expected to represent the $p-v-T$ behavior faithfully. When it is not stated, the realm of applicability of a given equation can be approximated by expressing the equation in terms of the compressibility factor Z and the reduced properties p_R , T_R , v'_R and superimposing the result on a generalized compressibility chart or comparing with tabulated compressibility data obtained from the literature.

11.1.2 • Two-Constant Equations of State

Equations of state can be classified by the number of adjustable constants they include. Let us consider some of the more commonly used equations of state in order of increasing complexity, beginning with two-constant equations of state.

van der Waals Equation

An improvement over the ideal gas equation of state based on elementary molecular arguments was suggested in 1873 by van der Waals, who noted that gas molecules actually occupy more than the negligibly small volume presumed by the ideal gas model and also exert long-range attractive forces on one another. Thus, not all of the volume of a container would be available to the gas molecules, and the force they exert on the container wall would be reduced because of the attractive forces that exist between molecules. Based on these elementary molecular arguments, the **van der Waals equation of state** is

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

(11.2) van der Waals equation

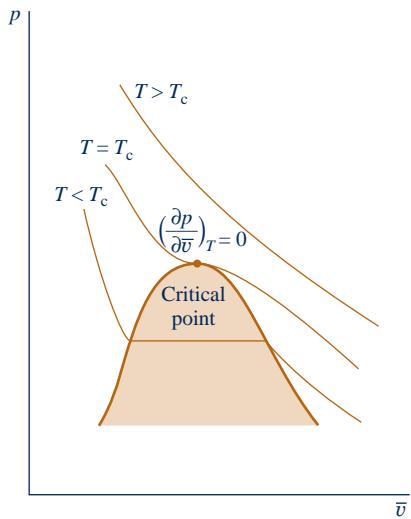
The constant b is intended to account for the finite volume occupied by the molecules, the term a/\bar{v}^2 accounts for the forces of attraction between molecules, and \bar{R} is the universal gas constant. Note that when a and b are set to zero, the ideal gas equation of state results.

The van der Waals equation gives pressure as a function of temperature and specific volume and thus is *explicit* in pressure. Since the equation can be solved for temperature as a function of pressure and specific volume, it is also explicit in temperature. However, the equation is cubic in specific volume, so it cannot generally be solved for specific volume in terms of temperature and pressure. The van der Waals equation is *not* explicit in specific volume.

EVALUATING a AND b . The van der Waals equation is a *two-constant* equation of state. For a specified substance, values for the constants a and b can be found by fitting the equation to $p-v-T$ data. With this approach several sets of constants might be required to cover all states of interest. Alternatively, a single set of constants for the van der Waals equation can be determined by noting that the critical isotherm passes through a point of inflection at the critical point, and the slope is zero there. Expressed mathematically, these conditions are, respectively

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0, \quad \left(\frac{\partial p}{\partial v}\right)_T = 0 \quad (\text{critical point}) \quad (11.3)$$

Although less overall accuracy normally results when the constants a and b are determined using critical point behavior than when they are determined



by fitting $p-v-T$ data in a particular region of interest, the advantage of this approach is that the van der Waals constants can be expressed in terms of the critical pressure p_c and critical temperature T_c , as demonstrated next.

For the van der Waals equation at the critical point

$$p_c = \frac{\bar{R}T_c}{\bar{v}_c - b} - \frac{a}{\bar{v}_c^2}$$

Applying Eqs. 11.3 with the van der Waals equation gives

$$\begin{aligned}\left(\frac{\partial^2 p}{\partial v^2}\right)_T &= \frac{2\bar{R}T_c}{(\bar{v}_c - b)^3} - \frac{6a}{\bar{v}_c^4} = 0 \\ \left(\frac{\partial p}{\partial v}\right)_T &= -\frac{\bar{R}T_c}{(\bar{v}_c - b)^2} + \frac{2a}{\bar{v}_c^3} = 0\end{aligned}$$

Solving the foregoing three equations for a , b , and \bar{v}_c in terms of the critical pressure and critical temperature

$$a = \frac{27}{64} \frac{\bar{R}^2 T_c^2}{p_c} \quad (11.4a)$$

$$b = \frac{\bar{R}T_c}{8p_c} \quad (11.4b)$$

$$\bar{v}_c = \frac{3}{8} \frac{\bar{R}T_c}{p_c} \quad (11.4c)$$

Values of the van der Waals constants a and b determined from Eqs. 11.4a and 11.4b for several common substances are given in Table A-24 for pressure in bar, specific volume in m^3/kmol , and temperature in K. Values of a and b for the same substances are given in Table A-24E for pressure in atm, specific volume in ft^3/lkmol , and temperature in $^{\circ}\text{R}$.

GENERALIZED FORM. Introducing the compressibility factor $Z = p\bar{v}/\bar{R}T$, the reduced temperature $T_R = T/T_c$, the pseudoreduced specific volume $v'_R = p_c\bar{v}/\bar{R}T_c$, and the foregoing expressions for a and b , the van der Waals equation can be written in terms of Z , v'_R , and T_R as

$$Z = \frac{v'_R}{v'_R - 1/8} - \frac{27/64}{T_R v'_R} \quad (11.5)$$

or alternatively in terms of Z , T_R , and p_R as

$$Z^3 - \left(\frac{p_R}{8T_R} + 1\right)Z^2 + \left(\frac{27p_R}{64T_R^2}\right)Z - \frac{27p_R^2}{512T_R^3} = 0 \quad (11.6)$$

The details of these developments are left as exercises. Equation 11.5 can be evaluated for specified values of v'_R and T_R and the resultant Z values located on a generalized compressibility chart to show approximately where the equation performs satisfactorily. A similar approach can be taken with Eq. 11.6.

The compressibility factor at the critical point yielded by the van der Waals equation is determined from Eq. 11.4c as

$$Z_c = \frac{p_c \bar{v}_c}{\bar{R}T_c} = 0.375$$

Actually, Z_c varies from about 0.23 to 0.33 for most substances (see Tables A-1). Accordingly, with the set of constants given by Eqs. 11.4, the van der Waals equation is inaccurate in the vicinity of the critical point. Further study would show inaccuracy in other regions as well, so this equation is not suitable for many thermodynamic evaluations. The van der Waals equation is of interest to us primarily because it is

the simplest model that accounts for the departure of actual gas behavior from the ideal gas equation of state.

Redlich–Kwong Equation

Three other two-constant equations of state that have been widely used are the Berthelot, Dieterici, and Redlich–Kwong equations. The **Redlich–Kwong equation**, considered by many to be the best of the two-constant equations of state, is

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v} + b)T^{1/2}} \quad (11.7)$$

Redlich–Kwong equation

This equation, proposed in 1949, is mainly empirical in nature, with no rigorous justification in terms of molecular arguments. The Redlich–Kwong equation is explicit in pressure but not in specific volume or temperature. Like the van der Waals equation, the Redlich–Kwong equation is cubic in specific volume.

Although the Redlich–Kwong equation is somewhat more difficult to manipulate mathematically than the van der Waals equation, it is more accurate, particularly at higher pressures. The two-constant Redlich–Kwong equation performs better than some equations of state having several adjustable constants; still, two-constant equations of state tend to be limited in accuracy as pressure (or density) increases. Increased accuracy at such states normally requires equations with a greater number of adjustable constants. Modified forms of the Redlich–Kwong equation have been proposed to achieve improved accuracy.

EVALUATING a AND b . As for the van der Waals equation, the constants a and b in Eq. 11.7 can be determined for a specified substance by fitting the equation to p – v – T data, with several sets of constants required to represent accurately all states of interest. Alternatively, a single set of constants in terms of the critical pressure and critical temperature can be evaluated using Eqs. 11.3, as for the van der Waals equation. The result is

$$a = a' \frac{\bar{R}^2 T_c^{5/2}}{p_c} \quad \text{and} \quad b = b' \frac{\bar{R} T_c}{p_c} \quad (11.8)$$

where $a' = 0.42748$ and $b' = 0.08664$. Evaluation of these constants is left as an exercise. Values of the Redlich–Kwong constants a and b determined from Eqs. 11.8 for several common substances are given in Table A-24 for pressure in bar, specific volume in m^3/kmol , and temperature in K. Values of a and b for the same substances are given in Table A-24E for pressure in atm, specific volume in ft^3/lbmol , and temperature in $^{\circ}\text{R}$.

GENERALIZED FORM. Introducing the compressibility factor Z , the reduced temperature T_R , the pseudoreduced specific volume v'_R , and the foregoing expressions for a and b , the Redlich–Kwong equation can be written as

$$Z = \frac{v'_R}{v'_R - b'} - \frac{a'}{(v'_R + b')T_R^{3/2}} \quad (11.9)$$

Equation 11.9 can be evaluated at specified values of v'_R and T_R and the resultant Z values located on a generalized compressibility chart to show the regions where the equation performs satisfactorily. With the constants given by Eqs. 11.8, the compressibility factor at the critical point yielded by the Redlich–Kwong equation is $Z_c = 0.333$, which is at the high end of the range of values for most substances, indicating that inaccuracy in the vicinity of the critical point should be expected.

In Example 11.1, the pressure of a gas is determined using three equations of state and the generalized compressibility chart. The results are compared.

EXAMPLE 11.1

Comparing Equations of State

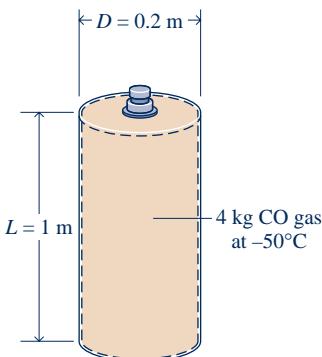
A cylindrical tank containing 4.0 kg of carbon monoxide gas at -50°C has an inner diameter of 0.2 m and a length of 1 m. Determine the pressure, in bar, exerted by the gas using (a) the generalized compressibility chart, (b) the ideal gas equation of state, (c) the van der Waals equation of state, (d) the Redlich–Kwong equation of state. Compare the results obtained.

SOLUTION

Known: A cylindrical tank of known dimensions contains 4.0 kg of CO gas at -50°C .

Find: Determine the pressure exerted by the gas using four alternative methods.

Schematic and Given Data:



Engineering Model:

1. As shown in the accompanying figure, the closed system is taken as the gas.
2. The system is at equilibrium.

Fig. E11.1

Analysis: The molar specific volume of the gas is required in each part of the solution. Let us begin by evaluating it. The volume occupied by the gas is

$$V = \left(\frac{\pi D^2}{4}\right)L = \frac{\pi(0.2 \text{ m})^2(1.0 \text{ m})}{4} = 0.0314 \text{ m}^3$$

The molar specific volume is then

$$\bar{v} = Mv = M\left(\frac{V}{m}\right) = \left(28 \frac{\text{kg}}{\text{kmol}}\right)\left(\frac{0.0314 \text{ m}^3}{4.0 \text{ kg}}\right) = 0.2198 \frac{\text{m}^3}{\text{kmol}}$$

(a) From Table A-1 for CO, $T_c = 133 \text{ K}$, $p_c = 35 \text{ bar}$. Thus, the reduced temperature T_R and pseudoreduced specific volume v'_R are, respectively

$$T_R = \frac{223 \text{ K}}{133 \text{ K}} = 1.68$$

$$v'_R = \frac{\bar{v}p_c}{RT_c} = \frac{(0.2198 \text{ m}^3/\text{kmol})(35 \times 10^5 \text{ N/m}^2)}{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(133 \text{ K})} = 0.696$$

Turning to Fig. A-2, $Z \approx 0.9$. Solving $Z = p\bar{v}/\bar{R}T$ for pressure and inserting known values

$$p = \frac{Z\bar{R}T}{\bar{v}} = \frac{0.9(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(223 \text{ K})}{(0.2198 \text{ m}^3/\text{kmol})} \left| \frac{1 \text{ bar}}{10^5 \text{ N/m}^2} \right| = 75.9 \text{ bar}$$

(b) The ideal gas equation of state gives

$$p = \frac{\bar{R}T}{\bar{v}} = \frac{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(223 \text{ K})}{(0.2198 \text{ m}^3/\text{kmol})} \left| \frac{1 \text{ bar}}{10^5 \text{ N/m}^2} \right| = 84.4 \text{ bar}$$

(c) For carbon monoxide, the van der Waals constants a and b given by Eqs. 11.4 can be read directly from Table A-24. Thus

$$a = 1.474 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2 \quad \text{and} \quad b = 0.0395 \frac{\text{m}^3}{\text{kmol}}$$

Substituting into Eq. 11.2

$$\begin{aligned} p &= \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2} \\ &= \frac{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(223 \text{ K})}{(0.2198 - 0.0395)(\text{m}^3/\text{kmol})} \left| \frac{1 \text{ bar}}{10^5 \text{ N/m}^2} \right| - \frac{1.474 \text{ bar}(\text{m}^3/\text{kmol})^2}{(0.2198 \text{ m}^3/\text{kmol})^2} \\ &= 72.3 \text{ bar} \end{aligned}$$

Alternatively, the values for ν'_R and T_R obtained in the solution of part (a) can be substituted into Eq. 11.5, giving $Z = 0.86$. Then, with $p = Z\bar{R}T/\bar{v}$, $p = 72.5$ bar. The slight difference is attributed to roundoff.

(d) For carbon monoxide, the Redlich–Kwong constants given by Eqs. 11.8 can be read directly from Table A-24. Thus

$$a = \frac{17.22 \text{ bar}(\text{m}^6)(\text{K})^{1/2}}{(\text{kmol})^2} \quad \text{and} \quad b = 0.02737 \text{ m}^3/\text{kmol}$$

Substituting into Eq. 11.7

$$\begin{aligned} p &= \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v} + b)T^{1/2}} \\ &= \frac{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(223 \text{ K})}{(0.2198 - 0.02737) \text{ m}^3/\text{kmol}} \left| \frac{1 \text{ bar}}{10^5 \text{ N/m}^2} \right| - \frac{17.22 \text{ bar}}{(0.2198)(0.24717)(223)^{1/2}} \\ &= 75.1 \text{ bar} \end{aligned}$$

Alternatively, the values for ν'_R and T_R obtained in the solution of part (a) can be substituted into Eq. 11.9, giving $Z = 0.89$. Then, with $p = Z\bar{R}T/\bar{v}$, $p = 75.1$ bar. In comparison to the value of part (a), the ideal gas equation of state predicts a pressure that is 11% higher and the van der Waals equation gives a value that is 5% lower. The Redlich–Kwong value is about 1% less than the value obtained using the compressibility chart.

Skills Developed

Ability to...

- determine pressure using the compressibility chart, ideal gas model, and the van der Waals and Redlich–Kwong equations of state.
- perform unit conversions correctly.

QuickQUIZ

Using the given temperature and the pressure value determined in part (a), check the value of Z using Fig. A-2. **Ans.** $Z \approx 0.9$.

11.1.3 Multiconstant Equations of State

To fit the p – v – T data of gases over a wide range of states, Beattie and Bridgeman proposed in 1928 a pressure-explicit equation involving five constants in addition to the gas constant. The **Beattie–Bridgeman equation** can be expressed in a truncated virial form as

$$p = \frac{\bar{R}T}{\bar{v}} + \frac{\beta}{\bar{v}^2} + \frac{\gamma}{\bar{v}^3} + \frac{\delta}{\bar{v}^4} \quad (11.10)$$

Beattie–Bridgeman equation

where

$$\begin{aligned} \beta &= B\bar{R}T - A - c\bar{R}/T^2 \\ \gamma &= -Bb\bar{R}T + Aa - Bc\bar{R}/T^2 \\ \delta &= Bbc\bar{R}/T^2 \end{aligned} \quad (11.11)$$

The five constants a , b , c , A , and B appearing in these equations are determined by curve fitting to experimental data.

Benedict, Webb, and Rubin extended the Beattie–Bridgeman equation of state to cover a broader range of states. The resulting equation, involving eight constants in addition to the gas constant, has been particularly successful in predicting the p – v – T behavior of *light hydrocarbons*. The **Benedict–Webb–Rubin equation** is

Benedict–Webb–Rubin equation

$$p = \frac{\bar{R}T}{\bar{v}} + \left(B\bar{R}T - A - \frac{C}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{(b\bar{R}T - a)}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) \exp\left(-\frac{\gamma}{\bar{v}^2}\right) \quad (11.12)$$

Values of the constants appearing in Eq. 11.12 for five common substances are given in Table A-24 for pressure in bar, specific volume in m^3/kmol , and temperature in K. Values of the constants for the same substances are given in Table A-24E for pressure in atm, specific volume in ft^3/lbmol , and temperature in $^{\circ}\text{R}$. Because Eq. 11.12 has been so successful, its realm of applicability has been extended by introducing additional constants.

Equations 11.10 and 11.12 are merely representative of multiconstant equations of state. Many other multiconstant equations have been proposed. With high-speed computers, equations having 50 or more constants have been developed for representing the p – v – T behavior of different substances.

11.2 Important Mathematical Relations

TAKE NOTE...

The state principle for simple systems is introduced in Sec. 3.1.

exact differential

Values of two independent intensive properties are sufficient to fix the intensive state of a simple compressible system of specified mass and composition—for instance, temperature and specific volume (see Sec. 3.1). All other intensive properties can be determined as functions of the two independent properties: $p = p(T, v)$, $u = u(T, v)$, $h = h(T, v)$, and so on. These are all functions of two independent variables of the form $z = z(x, y)$, with x and y being the independent variables. It might also be recalled that the differential of every property is *exact* (Sec. 2.2.1). The differentials of nonproperties such as work and heat are *inexact*. Let us review briefly some concepts from calculus about functions of two independent variables and their differentials.

The **exact differential** of a function z , continuous in the variables x and y , is

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (11.13a)$$

This can be expressed alternatively as

$$dz = M dx + N dy \quad (11.13b)$$

where $M = (\partial z / \partial x)_y$ and $N = (\partial z / \partial y)_x$. The coefficient M is the partial derivative of z with respect to x (the variable y being held constant). Similarly, N is the partial derivative of z with respect to y (the variable x being held constant).

If the coefficients M and N have continuous first partial derivatives, the order in which a second partial derivative of the function z is taken is immaterial. That is

$$\frac{\partial}{\partial y} \left[\left(\frac{\partial z}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial x} \left[\left(\frac{\partial z}{\partial y} \right)_x \right]_y \quad (11.14a)$$

or

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad (11.14b)$$

test for exactness

which can be called the **test for exactness**, as discussed next.

In words, Eqs. 11.14 indicate that the mixed second partial derivatives of the function z are equal. The relationship in Eqs. 11.14 is both a necessary and sufficient condition for the *exactness* of a differential expression, and it may therefore be used as a test for exactness. When an expression such as $M dx + N dy$ does not meet this test, no function z exists whose differential is equal to this expression. In thermodynamics, Eq. 11.14 is not generally used to test exactness but rather to develop additional property relations. This is illustrated in Sec. 11.3 to follow.

Two other relations among partial derivatives are listed next for which applications are found in subsequent sections of this chapter. These are

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \quad (11.15)$$

and

$$\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -1 \quad (11.16)$$

► FOR EXAMPLE consider the three quantities x , y , and z , any two of which may be selected as the independent variables. Thus, we can write $x = x(y, z)$ and $y = y(x, z)$. The differentials of these functions are, respectively

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \text{and} \quad dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

Eliminating dy between these two equations results in

$$\left[1 - \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z\right] dx = \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \quad (11.17)$$

Since x and z can be varied independently, let us hold z constant and vary x . That is, let $dz = 0$ and $dx \neq 0$. It then follows from Eq. 11.17 that the coefficient of dx must vanish, so Eq. 11.15 must be satisfied. Similarly, when $dx = 0$ and $dz \neq 0$, the coefficient of dz in Eq. 11.17 must vanish. Introducing Eq. 11.15 into the resulting expression and rearranging gives Eq. 11.16. The details are left as an exercise. ◀◀◀◀◀

APPLICATION. An equation of state $p = p(T, v)$ provides a specific example of a function of two independent variables. The partial derivatives $(\partial p/\partial T)_v$ and $(\partial p/\partial v)_T$ of $p(T, v)$ are important for subsequent discussions. The quantity $(\partial p/\partial T)_v$ is the partial derivative of p with respect to T (the variable v being held constant). This partial derivative represents the slope at a point on a line of constant specific volume (isometric) projected onto the $p-T$ plane. Similarly, the partial derivative $(\partial p/\partial v)_T$ is the partial derivative of p with respect to v (the variable T being held constant). This partial derivative represents the slope at a point on a line of constant temperature (isotherm) projected on the $p-v$ plane. The partial derivatives $(\partial p/\partial T)_v$ and $(\partial p/\partial v)_T$ are themselves intensive properties because they have unique values at each state.

The $p-v-T$ surfaces given in Figs. 3.1 and 3.2 are graphical representations of functions of the form $p = p(v, T)$. Figure 11.1 shows the liquid, vapor, and two-phase regions of a $p-v-T$ surface projected onto the $p-v$ and $p-T$ planes. Referring first to Fig. 11.1a, note that several isotherms are sketched. In the single-phase regions, the partial derivative $(\partial p/\partial v)_T$ giving the slope is negative at each state along an isotherm except at the critical point, where the partial derivative vanishes. Since the isotherms are horizontal in the two-phase liquid-vapor region, the partial derivative $(\partial p/\partial v)_T$ vanishes there as well. For these states, pressure is independent of specific volume and is a function of temperature only: $p = p_{\text{sat}}(T)$.

Figure 11.1b shows the liquid and vapor regions with several isometrics (constant specific volume lines) superimposed. In the single-phase regions, the isometrics are

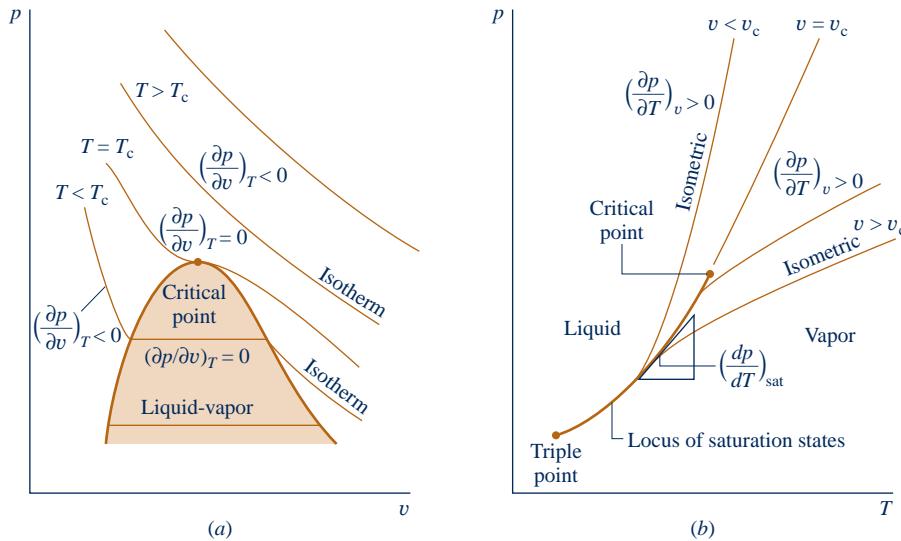


Fig. 11.1 Diagrams used to discuss $(\partial p / \partial v)_T$ and $(\partial p / \partial T)_v$. (a) p - v diagram. (b) Phase diagram.

nearly straight or are slightly curved and the partial derivative $(\partial p / \partial T)_v$ is positive at each state along the curves. For the two-phase liquid–vapor states corresponding to a specified value of temperature, the pressure is independent of specific volume and is determined by the temperature only. Hence, the slopes of isometrics passing through the two-phase states corresponding to a specified temperature are all equal, being given by the slope of the saturation curve at that temperature, denoted simply as $(dp/dT)_{\text{sat}}$. For these two-phase states, $(\partial p / \partial T)_v = (dp/dT)_{\text{sat}}$.

In this section, important aspects of functions of two variables have been introduced. The following example illustrates some of these ideas using the van der Waals equation of state.

EXAMPLE 11.2

Applying Mathematical Relations

For the van der Waals equation of state, (a) determine an expression for the exact differential dp , (b) show that the mixed second partial derivatives of the result obtained in part (a) are equal, and (c) develop an expression for the partial derivative $(\partial v / \partial T)_p$.

SOLUTION

Known: The equation of state is the van der Waals equation.

Find: Determine the differential dp , show that the mixed second partial derivatives of dp are equal, and develop an expression for $(\partial v / \partial T)_p$.

Analysis:

(a) By definition, the differential of a function $p = p(T, v)$ is

$$dp = \left(\frac{\partial p}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial v} \right)_T dv$$

The partial derivatives appearing in this expression obtained from the van der Waals equation expressed as $p = RT/(v - b) - a/v^2$ are

$$M = \left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v - b}, \quad N = \left(\frac{\partial p}{\partial v} \right)_T = -\frac{RT}{(v - b)^2} + \frac{2a}{v^3}$$

Accordingly, the differential takes the form

$$dp = \left(\frac{R}{v - b} \right) dT + \left[\frac{-RT}{(v - b)^2} + \frac{2a}{v^3} \right] dv$$

(b) Calculating the mixed second partial derivatives

$$\begin{aligned} \left(\frac{\partial M}{\partial v} \right)_T &= \frac{\partial}{\partial v} \left[\left(\frac{\partial p}{\partial T} \right)_v \right]_T = -\frac{R}{(v - b)^2} \\ \left(\frac{\partial N}{\partial T} \right)_v &= \frac{\partial}{\partial T} \left[\left(\frac{\partial p}{\partial v} \right)_T \right]_v = -\frac{R}{(v - b)^2} \end{aligned}$$

Thus, the mixed second partial derivatives are equal, as expected.

(c) An expression for $(\partial v / \partial T)_p$ can be derived using Eqs. 11.15 and 11.16. Thus, with $x = p$, $y = v$, and $z = T$, Eq. 11.16 gives

$$\left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial T}{\partial p} \right)_v = -1$$

or

$$\left(\frac{\partial v}{\partial T} \right)_p = -\frac{1}{(\partial p / \partial v)_T (\partial T / \partial p)_v}$$

Then, with $x = T$, $y = p$, and $z = v$, Eq. 11.15 gives

$$\left(\frac{\partial T}{\partial p} \right)_v = \frac{1}{(\partial p / \partial T)_v}$$

Combining these results

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{(\partial p / \partial T)_v}{(\partial p / \partial v)_T}$$

The numerator and denominator of this expression have been evaluated in part (a), so

$$① \quad \left(\frac{\partial v}{\partial T} \right)_p = -\frac{R/(v - b)}{[-RT/(v - b)^2 + 2a/v^3]}$$

which is the desired result.

- ① Since the van der Waals equation is cubic in specific volume, it can be solved for $v(T, p)$ at only certain states. Part (c) shows how the partial derivative $(\partial v / \partial T)_p$ can be evaluated at states where it exists.

Skills Developed

Ability to...

- use Eqs. 11.15 and 11.16 together with the van der Waals equation of state to develop a thermodynamic property relation.

QuickQUIZ

Using the results obtained, develop an expression for

$$\left(\frac{\partial v}{\partial T} \right)_p$$

11.3

Developing Property Relations

In this section, several important property relations are developed, including the expressions known as the *Maxwell* relations. The concept of a *fundamental thermodynamic function* is also introduced. These results, which are important for subsequent discussions, are obtained for simple compressible systems of fixed chemical composition using the concept of an exact differential.

11.3.1 ↗ Principal Exact Differentials

The principal results of this section are obtained using Eqs. 11.18, 11.19, 11.22, and 11.23. The first two of these equations are derived in Sec. 6.3, where they are referred to as the *T ds equations*. For present purposes, it is convenient to express them as

$$du = T ds - p dv \quad (11.18)$$

$$dh = T ds + v dp \quad (11.19)$$

The other two equations used to obtain the results of this section involve, respectively, the specific **Helmholtz function** ψ defined by

Helmholtz function

$$\psi = u - Ts \quad (11.20)$$

and the specific **Gibbs function** g defined by

Gibbs function

$$g = h - Ts \quad (11.21)$$

The Helmholtz and Gibbs functions are properties because each is defined in terms of properties. From inspection of Eqs. 11.20 and 11.21, the units of ψ and g are the same as those of u and h . These two new properties are introduced solely because they contribute to the present discussion, and no physical significance need be attached to them at this point.

Forming the differential $d\psi$

$$d\psi = du - d(Ts) = du - T ds - s dT$$

Substituting Eq. 11.18 into this gives

$$d\psi = -p dv - s dT \quad (11.22)$$

Similarly, forming the differential dg

$$dg = dh - d(Ts) = dh - T ds - s dT$$

Substituting Eq. 11.19 into this gives

$$dg = v dp - s dT \quad (11.23)$$

11.3.2 ↗ Property Relations from Exact Differentials

The four differential equations introduced above, Eqs. 11.18, 11.19, 11.22, and 11.23, provide the basis for several important property relations. Since only properties are involved, each is an exact differential exhibiting the general form $dz = M dx + N dy$ considered in Sec. 11.2. Underlying these exact differentials are, respectively, functions of the form $u(s, v)$, $h(s, p)$, $\psi(v, T)$, and $g(T, p)$. Let us consider these functions in the order given.

The differential of the function $u = u(s, v)$ is

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

By comparison with Eq. 11.18, we conclude that

$$T = \left(\frac{\partial u}{\partial s} \right)_v \quad (11.24)$$

$$-p = \left(\frac{\partial u}{\partial v} \right)_s \quad (11.25)$$

The differential of the function $h = h(s, p)$ is

$$dh = \left(\frac{\partial h}{\partial s} \right)_p ds + \left(\frac{\partial h}{\partial p} \right)_s dp$$

By comparison with Eq. 11.19, we conclude that

$$T = \left(\frac{\partial h}{\partial s} \right)_p \quad (11.26)$$

$$\nu = \left(\frac{\partial h}{\partial p} \right)_s \quad (11.27)$$

Similarly, the coefficients $-p$ and $-s$ of Eq. 11.22 are partial derivatives of $\psi(v, T)$

$$-p = \left(\frac{\partial \psi}{\partial v} \right)_T \quad (11.28)$$

$$-s = \left(\frac{\partial \psi}{\partial T} \right)_v \quad (11.29)$$

and the coefficients ν and $-s$ of Eq. 11.23 are partial derivatives of $g(T, p)$

$$\nu = \left(\frac{\partial g}{\partial p} \right)_T \quad (11.30)$$

$$-s = \left(\frac{\partial g}{\partial T} \right)_p \quad (11.31)$$

As each of the four differentials introduced above is exact, the second mixed partial derivatives are equal. Thus, in Eq. 11.18, T plays the role of M in Eq. 11.14b and $-p$ plays the role of N in Eq. 11.14b, so

$$\left(\frac{\partial T}{\partial v} \right)_s = -\left(\frac{\partial p}{\partial s} \right)_v \quad (11.32)$$

In Eq. 11.19, T and ν play the roles of M and N in Eq. 11.14b, respectively. Thus

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial \nu}{\partial s} \right)_p \quad (11.33)$$

Similarly, from Eqs. 11.22 and 11.23 follow

$$\left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial s}{\partial \nu} \right)_T \quad (11.34)$$

$$\left(\frac{\partial \nu}{\partial T} \right)_p = -\left(\frac{\partial s}{\partial p} \right)_T \quad (11.35)$$

TABLE 11.1**Summary of Property Relations from Exact Differentials**

Basic relations:

from $u = u(s, v)$ from $h = h(s, p)$

$$T = \left(\frac{\partial u}{\partial s} \right)_v \quad (11.24)$$

$$T = \left(\frac{\partial h}{\partial s} \right)_p \quad (11.26)$$

$$-p = \left(\frac{\partial u}{\partial v} \right)_s \quad (11.25)$$

$$v = \left(\frac{\partial h}{\partial p} \right)_s \quad (11.27)$$

from $\psi = \psi(v, T)$ from $g = g(T, p)$

$$-p = \left(\frac{\partial \psi}{\partial v} \right)_T \quad (11.28)$$

$$v = \left(\frac{\partial g}{\partial p} \right)_T \quad (11.30)$$

$$-s = \left(\frac{\partial \psi}{\partial T} \right)_v \quad (11.29)$$

$$-s = \left(\frac{\partial g}{\partial T} \right)_p \quad (11.31)$$

Maxwell relations:

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v \quad (11.32)$$

$$\left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T \quad (11.34)$$

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \quad (11.33)$$

$$\left(\frac{\partial v}{\partial T} \right)_p = - \left(\frac{\partial s}{\partial p} \right)_T \quad (11.35)$$

Additional relations:

$$\left(\frac{\partial u}{\partial s} \right)_v = \left(\frac{\partial h}{\partial s} \right)_p$$

$$\left(\frac{\partial u}{\partial v} \right)_s = \left(\frac{\partial \psi}{\partial v} \right)_T \quad (11.36)$$

$$\left(\frac{\partial h}{\partial p} \right)_s = \left(\frac{\partial g}{\partial p} \right)_T$$

$$\left(\frac{\partial \psi}{\partial T} \right)_v = \left(\frac{\partial g}{\partial T} \right)_p$$

Maxwell relationsEquations 11.32 through 11.35 are known as the **Maxwell relations**.Since each of the properties T, p, v, s appears on the left side of two of the eight equations, Eqs. 11.24 through 11.31, four additional property relations can be obtained by equating such expressions. They are

$$\begin{aligned} \left(\frac{\partial u}{\partial s} \right)_v &= \left(\frac{\partial h}{\partial s} \right)_p, & \left(\frac{\partial u}{\partial v} \right)_s &= \left(\frac{\partial \psi}{\partial v} \right)_T \\ \left(\frac{\partial h}{\partial p} \right)_s &= \left(\frac{\partial g}{\partial p} \right)_T, & \left(\frac{\partial \psi}{\partial T} \right)_v &= \left(\frac{\partial g}{\partial T} \right)_p \end{aligned} \quad (11.36)$$

Equations 11.24 through 11.36, which are listed in Table 11.1 for ease of reference, are 16 property relations obtained from Eqs. 11.18, 11.19, 11.22, and 11.23, using the concept of an exact differential. Since Eqs. 11.19, 11.22, and 11.23 can themselves be derived from Eq. 11.18, the important role of the first $T dS$ equation in developing property relations is apparent.

The utility of these 16 property relations is demonstrated in subsequent sections of this chapter. However, to give a specific illustration at this point, suppose the partial derivative $(\partial s/\partial v)_T$ involving entropy is required for a certain purpose. The Maxwell relation Eq. 11.34 would allow the derivative to be determined by evaluating the partial derivative $(\partial p/\partial T)_v$, which can be obtained using $p-v-T$ data only. Further elaboration is provided in Example 11.3.

► ► ► ► **EXAMPLE 11.3**

Applying the Maxwell Relations

Evaluate the partial derivative $(\partial s/\partial v)_T$ for water vapor at a state fixed by a temperature of 240°C and a specific volume of 0.4646 m³/kg. (a) Use the Redlich–Kwong equation of state and an appropriate Maxwell relation. (b) Check the value obtained using steam table data.

SOLUTION

Known: The system consists of a fixed amount of water vapor at 240°C and 0.4646 m³/kg.

Find: Determine the partial derivative $(\partial s/\partial v)_T$ employing the Redlich–Kwong equation of state, together with a Maxwell relation. Check the value obtained using steam table data.

Engineering Model:

1. The system consists of a fixed amount of water at a known equilibrium state.
2. Accurate values for $(\partial s/\partial T)_v$ in the neighborhood of the given state can be determined from the Redlich–Kwong equation of state.

Analysis:

(a) The Maxwell relation given by Eq. 11.34 allows $(\partial s/\partial v)_T$ to be determined from the p – v – T relationship. That is

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

The partial derivative $(\partial p/\partial T)_v$ obtained from the Redlich–Kwong equation, Eq. 11.7, is

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{\bar{v} - b} + \frac{a}{2\bar{v}(\bar{v} + b)T^{3/2}}$$

At the specified state, the temperature is 513 K and the specific volume on a molar basis is

$$\bar{v} = 0.4646 \frac{\text{m}^3}{\text{kg}} \left(\frac{18.02 \text{ kg}}{\text{kmol}} \right) = 8.372 \frac{\text{m}^3}{\text{kmol}}$$

From Table A-24

$$a = 142.59 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2 (\text{K})^{1/2}, \quad b = 0.0211 \frac{\text{m}^3}{\text{kmol}}$$

Substituting values into the expression for $(\partial p/\partial T)_v$

$$\begin{aligned} \left(\frac{\partial p}{\partial T}\right)_v &= \frac{\left(8314 \frac{\text{N} \cdot \text{m}}{\text{kmol} \cdot \text{K}}\right)}{(8.372 - 0.0211) \frac{\text{m}^3}{\text{kmol}}} + \frac{142.59 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2 (\text{K})^{1/2}}{2 \left(8.372 \frac{\text{m}^2}{\text{kmol}} \right) \left(8.3931 \frac{\text{m}^3}{\text{kmol}} \right) (513 \text{ K})^{3/2}} \left| \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right| \\ &= \left(1004.3 \frac{\text{N} \cdot \text{m}}{\text{m}^3 \cdot \text{K}} \right) \left| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right| \\ &= 1.0043 \frac{\text{kJ}}{\text{m}^3 \cdot \text{K}} \end{aligned}$$

Accordingly

$$\left(\frac{\partial s}{\partial v}\right)_T = 1.0043 \frac{\text{kJ}}{\text{m}^3 \cdot \text{K}}$$

(b) A value for $(\partial s/\partial v)_T$ can be estimated using a graphical approach with steam table data, as follows: At 240°C, Table A-4 provides the values for specific entropy s and specific volume v tabulated below

$T = 240^{\circ}\text{C}$		
p (bar)	s (kJ/kg · K)	v (m ³ /kg)
1.0	7.9949	2.359
1.5	7.8052	1.570
3.0	7.4774	0.781
5.0	7.2307	0.4646
7.0	7.0641	0.3292
10.0	6.8817	0.2275

With the values for s and v listed in the table, the plot in Fig. E11.3a giving s versus v can be prepared. Note that a line representing the tangent to the curve at the given state is shown on the plot. The pressure at this state is 5 bar. The slope of the tangent is $(\partial s / \partial v)_T \approx 1.0 \text{ kJ/m}^3 \cdot \text{K}$. Thus, the value of $(\partial s / \partial v)_T$ obtained using the Redlich–Kwong equation agrees closely with the result determined graphically using steam table data.

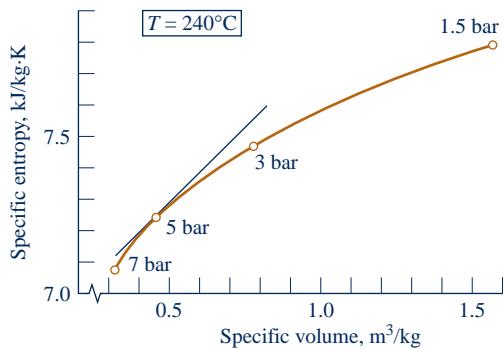


Fig. E11.3a

Alternative Solution: Alternatively, the partial derivative $(\partial s / \partial v)_T$ can be estimated using numerical methods and computer-generated data. The following *IT* code illustrates one way the partial derivative, denoted dsdv , can be estimated:

```

v = 0.4646 // m3/kg
T = 240 // °C
v2 = v + dv
v1 = v - dv
dv = 0.2
v2 = v_PT ("Water/Steam", p2, T)
v1 = v_PT ("Water/Steam", p1, T)
s2 = s_PT ("Water/Steam", p2, T)
s1 = s_PT ("Water/Steam", p1, T)
dsdv = (s2 - s1)/(v2 - v1)

```

Using the **Explore** button, sweep dv from 0.0001 to 0.2 in steps of 0.001. Then, using the **Graph** button, the following graph can be constructed:

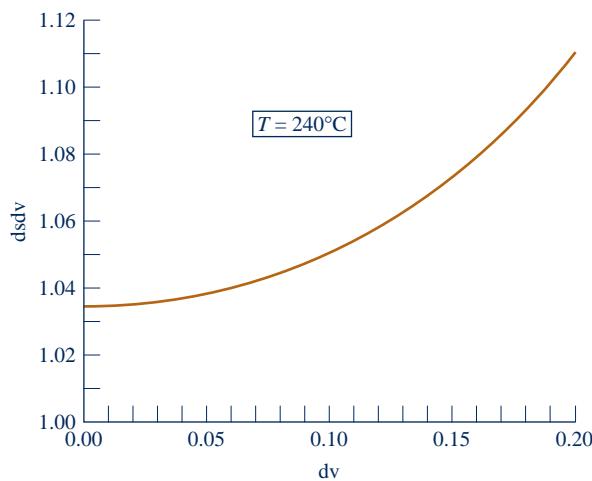


Fig. E11.3b

- From the computer data, the y-intercept of the graph is

$$\textcircled{1} \quad \left(\frac{\partial s}{\partial v} \right)_T = \lim_{\Delta v \rightarrow 0} \left(\frac{\Delta s}{\Delta v} \right)_T \approx 1.033 \frac{\text{kJ}}{\text{m}^3 \cdot \text{K}}$$

This answer is an estimate because it relies on a numerical approximation of the partial derivative based on the equation of state that underlies the *steam tables*. The values obtained using the Redlich–Kwong equation of state and the graphical method using steam table data agree with this result.

- 1 It is left as an exercise to show that, in accordance with Eq. 11.34, the value of $(\partial p/\partial T)_v$, estimated by a procedure like the one used for $(\partial s/\partial v)_T$ agrees with the value given here.

QuickQUIZ

QUIZ For steam at $T = 240^\circ\text{C}$, $v = 0.4646 \text{ m}^3/\text{kg}$, $p = 5 \text{ bar}$, calculate the value of the compressibility factor Z . **Ans.** 0.981.



Skills Developed

Ability to

- apply a Maxwell relation to evaluate a thermodynamic quantity.
 - apply the Redlich-Kwong equation.
 - perform a comparison with data from the steam table using graphical and computer-based methods.

11.3.3 Fundamental Thermodynamic Functions

A *fundamental thermodynamic function* provides a complete description of the thermodynamic state. In the case of a pure substance with two independent properties, the **fundamental thermodynamic function** can take one of the following four forms:

$$\begin{aligned} u &= u(s, v) \\ h &= h(s, p) \\ \psi &= \psi(T, v) \\ g &= g(T, p) \end{aligned}$$

(11.37)

fundamental thermodynamic function

Of the four fundamental functions listed in Eqs. 11.37, the Helmholtz function ψ and the Gibbs function g have the greatest importance for subsequent discussions (see Sec. 11.6.2). Accordingly, let us discuss the fundamental function concept with reference to ψ and g .

In principle, all properties of interest can be determined from a fundamental thermodynamic function by differentiation and combination.

► **FOR EXAMPLE** consider a fundamental function of the form $\psi(T, v)$. The properties v and T , being the independent variables, are specified to fix the state. The pressure p at this state can be determined from Eq. 11.28 by differentiation of $\psi(T, v)$. Similarly, the specific entropy s at the state can be found from Eq. 11.29 by differentiation. By definition, $\psi = u - Ts$, so the specific internal energy is obtained as

$$u = \psi + Ts$$

With u , p , and v known, the specific enthalpy can be found from the definition $h = u + pv$. Similarly, the specific Gibbs function is found from the definition, $g = h - Ts$. The specific heat c_v can be determined by further differentiation, $c_v = (\partial u / \partial T)_v$. Other properties can be calculated with similar operations.

► **FOR EXAMPLE** consider a fundamental function of the form $g(T, p)$. The properties T and p are specified to fix the state. The specific volume and specific entropy at this state can be determined by differentiation from Eqs. 11.30 and 11.31, respectively. By definition, $g = h - Ts$, so the specific enthalpy is obtained as

$$h = g + Ts$$

With h , p , and v known, the specific internal energy can be found from $u = h - pv$. The specific heat c_p can be determined by further differentiation, $c_p = (\partial h / \partial T)_p$. Other properties can be calculated with similar operations. ◀◀◀◀◀

Like considerations apply for functions of the form $u(s, v)$ and $h(s, p)$, as can readily be verified. Note that a Mollier diagram provides a graphical representation of the fundamental function $h(s, p)$.

11.4 Evaluating Changes in Entropy, Internal Energy, and Enthalpy

With the introduction of the Maxwell relations, we are in a position to develop thermodynamic relations that allow changes in entropy, internal energy, and enthalpy to be evaluated from measured property data. The presentation begins by considering relations applicable to phase changes and then turns to relations for use in single-phase regions.

11.4.1 Considering Phase Change

The objective of this section is to develop relations for evaluating the changes in specific entropy, internal energy, and enthalpy accompanying a change of phase at fixed temperature and pressure. A principal role is played by the *Clapeyron equation*, which allows the change in enthalpy during vaporization, sublimation, or melting at a constant temperature to be evaluated from pressure-specific volume–temperature data pertaining to the phase change. Thus, the present discussion provides important examples of how p – v – T measurements can lead to the determination of other property changes, namely Δs , Δu , and Δh for a change of phase.

Consider a change in phase from saturated liquid to saturated vapor at fixed temperature. For an isothermal phase change, pressure also remains constant, so Eq. 11.19 reduces to

$$dh = T ds$$

Integration of this expression gives

$$s_g - s_f = \frac{h_g - h_f}{T} \quad (11.38)$$

Hence, the change in specific entropy accompanying a phase change from saturated liquid to saturated vapor at temperature T can be determined from the temperature and the change in specific enthalpy.

The change in specific internal energy during the phase change can be determined using the definition $h = u + pv$.

$$u_g - u_f = h_g - h_f - p(v_g - v_f) \quad (11.39)$$

Thus, the change in specific internal energy accompanying a phase change at temperature T can be determined from the temperature and the changes in specific volume and enthalpy.

CLAPEYRON EQUATION. The change in specific enthalpy required by Eqs. 11.38 and 11.39 can be obtained using the Clapeyron equation. To derive the Clapeyron equation, begin with the Maxwell relation

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad (11.34)$$

During a phase change at fixed temperature, the pressure is independent of specific volume and is determined by temperature alone. Thus, the quantity $(\partial p/\partial T)_v$ is determined by the temperature and can be represented as

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{\text{sat}}$$

where "sat" indicates that the derivative is the slope of the saturation pressure–temperature curve at the point determined by the temperature held constant during the phase change (Sec. 11.2). Combining the last two equations gives

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{dp}{dT}\right)_{\text{sat}}$$

Since the right side of this equation is fixed when the temperature is specified, the equation can be integrated to give

$$s_g - s_f = \left(\frac{dp}{dT}\right)_{\text{sat}} (v_g - v_f)$$

Introducing Eq. 11.38 into this expression results in the **Clapeyron equation**

Clapeyron equation

$$\left(\frac{dp}{dT}\right)_{\text{sat}} = \frac{h_g - h_f}{T(v_g - v_f)} \quad (11.40)$$

Equation 11.40 allows $(h_g - h_f)$ to be evaluated using only p – v – T data pertaining to the phase change. In instances when the enthalpy change is also measured, the Clapeyron equation can be used to check the consistency of the data. Once the specific enthalpy change is determined, the corresponding changes in specific entropy and specific internal energy can be found from Eqs. 11.38 and 11.39, respectively.

Equations 11.38, 11.39, and 11.40 also can be written for sublimation or melting occurring at constant temperature and pressure. In particular, the Clapeyron equation would take the form

$$\left(\frac{dp}{dT}\right)_{\text{sat}} = \frac{h'' - h'}{T(v'' - v')} \quad (11.41)$$

where " and ' denote the respective phases, and $(dp/dT)_{\text{sat}}$ is the slope of the relevant saturation pressure–temperature curve.

The Clapeyron equation shows that the slope of a saturation line on a phase diagram depends on the signs of the specific volume and enthalpy changes accompanying the phase change. In most cases, when a phase change takes place with an increase in specific enthalpy, the specific volume also increases, and $(dp/dT)_{\text{sat}}$ is positive. However, in the case of the melting of ice and a few other substances, the specific volume decreases on melting. The slope of the saturated solid–liquid curve for these few substances is negative, as pointed out in Sec. 3.2.2 in the discussion of phase diagrams.

An approximate form of Eq. 11.40 can be derived when the following two idealizations are justified: (1) v_f is negligible in comparison to v_g , and (2) the pressure is low enough that v_g can be evaluated from the ideal gas equation of state as $v_g = RT/p$. With these, Eq. 11.40 becomes

$$\left(\frac{dp}{dT}\right)_{\text{sat}} = \frac{h_g - h_f}{RT^2/p}$$

which can be rearranged to read

$$\left(\frac{d \ln p}{dT}\right)_{\text{sat}} = \frac{h_g - h_f}{RT^2} \quad (11.42)$$

Equation 11.42 is called the **Clausius–Clapeyron equation**. A similar expression applies for the case of sublimation.

Clausius–Clapeyron equation

The use of the Clapeyron equation in any of the foregoing forms requires an accurate representation for the relevant saturation pressure–temperature curve. This must not only depict the pressure–temperature variation accurately but also enable accurate values of the derivative $(dp/dT)_{\text{sat}}$ to be determined. Analytical representations in the form of equations are commonly used. Different equations for different portions of the pressure–temperature curves may be required. These equations can involve several constants. One form that is used for the vapor-pressure curves is the four-constant equation

$$\ln p_{\text{sat}} = A + \frac{B}{T} + C \ln T + DT$$

in which the constants A, B, C, D are determined empirically.

The use of the Clapeyron equation for evaluating changes in specific entropy, internal energy, and enthalpy accompanying a phase change at fixed T and p is illustrated in the next example.

EXAMPLE 11.4

Applying the Clapeyron Equation

Using p – v – T data for saturated water, calculate at 100°C (a) $h_g - h_f$, (b) $u_g - u_f$, (c) $s_g - s_f$. Compare with the respective steam table value.

SOLUTION

Known: The system consists of a unit mass of saturated water at 100°C.

Find: Using saturation data, determine at 100°C the change on vaporization of the specific enthalpy, specific internal energy, and specific entropy, and compare with the respective steam table value.

Analysis: For comparison, Table A-2 gives at 100°C, $h_g - h_f = 2257.0 \text{ kJ/kg}$, $u_g - u_f = 2087.6 \text{ kJ/kg}$, $s_g - s_f = 6.048 \text{ kJ/kg} \cdot \text{K}$.

(a) The value of $h_g - h_f$ can be determined from the Clapeyron equation, Eq. 11.40, expressed as

$$h_g - h_f = T(v_g - v_f) \left(\frac{dp}{dT} \right)_{\text{sat}}$$

This equation requires a value for the slope $(dp/dT)_{\text{sat}}$ of the saturation pressure–temperature curve at the specified temperature.

The required value for $(dp/dT)_{\text{sat}}$ at 100°C can be estimated graphically as follows. Using saturation pressure–temperature data from the steam tables, the accompanying plot can be prepared. Note that a line drawn tangent to the curve at 100°C is shown on the plot. The slope of this tangent line is about $3570 \text{ N/m}^2 \cdot \text{K}$. Accordingly, at 100°C

$$\left(\frac{dp}{dT} \right)_{\text{sat}} \approx 3570 \frac{\text{N}}{\text{m}^2 \cdot \text{K}}$$

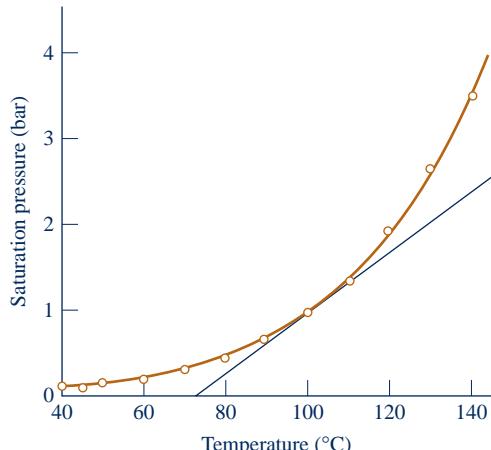


Fig. E11.4

Inserting property data from Table A-2 into the equation for $h_g - h_f$ gives

$$h_g - h_f = (373.15 \text{ K})(1.673 - 1.0435 \times 10^{-3}) \left(\frac{\text{m}^3}{\text{kg}} \right) \left(3570 \frac{\text{N}}{\text{m}^2 \cdot \text{K}} \right) \left| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right| \\ = 2227 \text{ kJ/kg}$$

This value is about 1% less than the value read from the steam tables.

- 1 Alternatively, the derivative $(dp/dT)_{\text{sat}}$ can be estimated using numerical methods and computer-generated data. The following *IT* code illustrates *one way* the derivative, denoted $d\text{pdT}$, can be estimated:

```
T = 100 // °C
dT = 0.001
T1 = T - dT
T2 = T + dT
p1 = Psat ("Water/Steam", T1) // bar
p2 = Psat ("Water/Steam", T2) // bar
dpdT = ((p2 - p1) / (T2 - T1)) * 100000
```

Using the **Explore** button, sweep dT from 0.001 to 0.01 in steps of 0.001. Then, reading the limiting value from the computer data

$$\left(\frac{dp}{dT} \right)_{\text{sat}} \approx 3616 \frac{\text{N}}{\text{m}^2 \cdot \text{K}}$$

When this value is used in the above expression for $h_g - h_f$, the result is $h_g - h_f = 2256 \text{ kJ/kg}$, which agrees closely with the value read from the steam tables.

- (b) With Eq. 11.39

$$u_g - u_f = h_g - h_f - p_{\text{sat}}(v_g - v_f)$$

Inserting the *IT* result for $(h_g - h_f)$ from part (a) together with saturation data at 100°C from Table A-2

$$u_g - u_f = 2256 \frac{\text{kJ}}{\text{kg}} - \left(1.014 \times 10^5 \frac{\text{N}}{\text{m}^2} \right) \left(1.672 \frac{\text{m}^3}{\text{kg}} \right) \left| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right| \\ = 2086.5 \frac{\text{kJ}}{\text{kg}}$$

which also agrees closely with the value from the steam tables.

- (c) With Eq. 11.38 and the *IT* result for $(h_g - h_f)$ from part (a)

$$s_g - s_f = \frac{h_g - h_f}{T} = \frac{2256 \text{ kJ/kg}}{373.15 \text{ K}} = 6.046 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

which again agrees closely with the steam table value.

- 1 Also, $(dp/dT)_{\text{sat}}$ might be obtained by differentiating an analytical expression for the vapor pressure curve, as discussed on page 650.

Skills Developed

Ability to...

- use the Clapeyron Equation with $p-v-T$ data for saturated water to evaluate, u_{fg} , h_{fg} , and s_{fg} .
- use graphical and computer-based methods to evaluate thermodynamic property data and relations.

QuickQUIZ

Use the *IT* result $(dp/dT)_{\text{sat}} = 3616 \text{ N/m}^2 \cdot \text{K}$ to extrapolate the saturation pressure, in bar, at 105°C. **Ans.** 1.195 bar.

11.4.2 Considering Single-Phase Regions

The objective of the present section is to derive expressions for evaluating Δs , Δu , and Δh between states in single-phase regions. These expressions require both $p-v-T$ data and appropriate specific heat data. Since single-phase regions are under present

consideration, any two of the properties pressure, specific volume, and temperature can be regarded as the independent properties that fix the state. Two convenient choices are T, v and T, p .

T AND v AS INDEPENDENT PROPERTIES. With temperature and specific volume as the independent properties that fix the state, the specific entropy can be regarded as a function of the form $s = s(T, v)$. The differential of this function is

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

The partial derivative $(\partial s/\partial v)_T$ appearing in this expression can be replaced using the Maxwell relation, Eq. 11.34, giving

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial T} \right)_v dv \quad (11.43)$$

The specific internal energy also can be regarded as a function of T and v : $u = u(T, v)$. The differential of this function is

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

With $c_v = (\partial u/\partial T)_v$

$$du = c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \quad (11.44)$$

Substituting Eqs. 11.43 and 11.44 into $du = T ds - p dv$ and collecting terms results in

$$\left[\left(\frac{\partial u}{\partial v} \right)_T + p - T \left(\frac{\partial p}{\partial T} \right)_v \right] dv = \left[T \left(\frac{\partial s}{\partial T} \right)_v - c_v \right] dT \quad (11.45)$$

Since specific volume and temperature can be varied independently, let us hold specific volume constant and vary temperature. That is, let $dv = 0$ and $dT \neq 0$. It then follows from Eq. 11.45 that

$$\left(\frac{\partial s}{\partial T} \right)_v = \frac{c_v}{T} \quad (11.46)$$

Similarly, suppose that $dT = 0$ and $dv \neq 0$. It then follows that

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p \quad (11.47)$$

Equations 11.46 and 11.47 are additional examples of useful thermodynamic property relations.

TAKE NOTE...

Here we demonstrate that the specific internal energy of a gas whose equation of state is

$$pv = RT$$

depends on temperature alone, thereby confirming a claim made in Sec. 3.12.2.

► **FOR EXAMPLE** Equation 11.47, which expresses the dependence of the specific internal energy on specific volume at fixed temperature, allows us to demonstrate that the internal energy of a gas whose equation of state is $pv = RT$ depends on temperature alone, a result first discussed in Sec. 3.12.2. Equation 11.47 requires the partial derivative $(\partial p/\partial T)_v$. If $p = RT/v$, the derivative is $(\partial p/\partial T)_v = R/v$. Introducing this, Eq. 11.47 gives

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p = T \left(\frac{R}{v} \right) - p = p - p = 0$$

This demonstrates that when $pv = RT$, the specific internal energy is independent of specific volume and depends on temperature alone. ▲ ▲ ▲ ▲ ▲

Continuing the discussion, when Eq. 11.46 is inserted in Eq. 11.43, the following expression results.

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T} \right)_v dv \quad (11.48)$$

Inserting Eq. 11.47 into Eq. 11.44 gives

$$du = c_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv \quad (11.49)$$

Observe that the right sides of Eqs. 11.48 and 11.49 are expressed solely in terms of p , v , T , and c_v .

Changes in specific entropy and internal energy between two states are determined by integration of Eqs. 11.48 and 11.49, respectively.

$$s_2 - s_1 = \int_1^2 \frac{c_v}{T} dT + \int_1^2 \left(\frac{\partial p}{\partial T} \right)_v dv \quad (11.50)$$

$$u_2 - u_1 = \int_1^2 c_v dT + \int_1^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv \quad (11.51)$$

To integrate the first term on the right of each of these expressions, the variation of c_v with temperature at one fixed specific volume (isometric) is required. Integration of the second term requires knowledge of the $p-v-T$ relation at the states of interest. An equation of state explicit in pressure would be particularly convenient for evaluating the integrals involving $(\partial p/\partial T)_v$. The accuracy of the resulting specific entropy and internal energy changes would depend on the accuracy of this derivative. In cases where the integrands of Eqs. 11.50 and 11.51 are too complicated to be integrated in closed form they may be evaluated numerically. Whether closed-form or numerical integration is used, attention must be given to the path of integration.

► FOR EXAMPLE let us consider the evaluation of Eq. 11.51. Referring to Fig. 11.2, if the specific heat c_v is known as a function of temperature along the isometric (constant specific volume) passing through the states x and y , one possible path of integration for determining the change in specific internal energy between states 1 and 2 is 1-x-y-2. The integration would be performed in three steps. Since temperature is constant from state 1 to state x , the first integral of Eq. 11.51 vanishes, so

$$u_x - u_1 = \int_{v_1}^{v_x} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv$$

From state x to y , the specific volume is constant and c_v is known as a function of temperature only, so

$$u_y - u_x = \int_{T_x}^{T_y} c_v dT$$

where $T_x = T_1$ and $T_y = T_2$. From state y to state 2, the temperature is constant once again, and

$$u_2 - u_y = \int_{v_y=v_x}^{v_2} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv$$

When these are added, the result is the change in specific internal energy between states 1 and 2. ▲ ▲ ▲ ▲ ▲

T AND p AS INDEPENDENT PROPERTIES. In this section a presentation parallel to that considered above is provided for the choice of temperature and pressure as the independent properties.

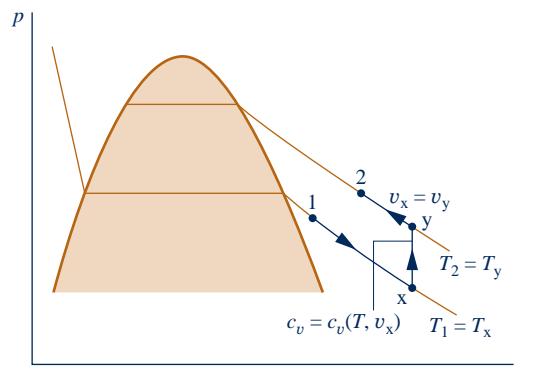


Fig. 11.2 Integration path between two vapor states.

With this choice for the independent properties, the specific entropy can be regarded as a function of the form $s = s(T, p)$. The differential of this function is

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp$$

The partial derivative $(\partial s/\partial p)_T$ appearing in this expression can be replaced using the Maxwell relation, Eq. 11.35, giving

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT - \left(\frac{\partial v}{\partial T} \right)_p dp \quad (11.52)$$

The specific enthalpy also can be regarded as a function of T and p : $h = h(T, p)$. The differential of this function is

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp$$

With $c_p = (\partial h/\partial T)_p$

$$dh = c_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp \quad (11.53)$$

Substituting Eqs. 11.52 and 11.53 into $dh = T ds + v dp$ and collecting terms results in

$$\left[\left(\frac{\partial h}{\partial p} \right)_T + T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dp = \left[T \left(\frac{\partial s}{\partial T} \right)_p - c_p \right] dT \quad (11.54)$$

Since pressure and temperature can be varied independently, let us hold pressure constant and vary temperature. That is, let $dp = 0$ and $dT \neq 0$. It then follows from Eq. 11.54 that

$$\left(\frac{\partial s}{\partial T} \right)_p = \frac{c_p}{T} \quad (11.55)$$

Similarly, when $dT = 0$ and $dp \neq 0$, Eq. 11.54 gives

$$\left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p \quad (11.56)$$

Equations 11.55 and 11.56, like Eqs. 11.46 and 11.47, are useful thermodynamic property relations.

When Eq. 11.55 is inserted in Eq. 11.52, the following equation results:

$$ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_p dp \quad (11.57)$$

Introducing Eq. 11.56 into Eq. 11.53 gives

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (11.58)$$

Observe that the right sides of Eqs. 11.57 and 11.58 are expressed solely in terms of p , v , T , and c_p .

Changes in specific entropy and enthalpy between two states are found by integrating Eqs. 11.57 and 11.58, respectively

$$s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT - \int_1^2 \left(\frac{\partial v}{\partial T} \right)_p dp \quad (11.59)$$

$$h_2 - h_1 = \int_1^2 c_p dT + \int_1^2 \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (11.60)$$

To integrate the first term on the right of each of these expressions, the variation of c_p with temperature at one fixed pressure (isobar) is required. Integration of the second term requires knowledge of the $p-v-T$ behavior at the states of interest. An equation of state explicit in v would be particularly convenient for evaluating the integrals involving $(\partial v / \partial T)_p$. The accuracy of the resulting specific entropy and enthalpy changes would depend on the accuracy of this derivative.

Changes in specific enthalpy and internal energy are related through $h = u + pv$ by

$$h_2 - h_1 = (u_2 - u_1) + (p_2 v_2 - p_1 v_1) \quad (11.61)$$

Hence, only one of Δh and Δu need be found by integration. Then, the other can be evaluated from Eq. 11.61. Which of the two property changes is found by integration depends on the information available. Δh would be found using Eq. 11.60 when an equation of state explicit in v and c_p as a function of temperature at some fixed pressure are known. Δu would be found from Eq. 11.51 when an equation of state explicit in p and c_v as a function of temperature at some specific volume are known. Such issues are considered in Example 11.5.

EXAMPLE 11.5

Evaluating Δs , Δu , and Δh of a Gas

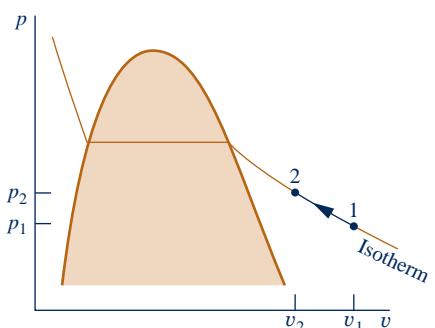
Using the Redlich-Kwong equation of state, develop expressions for the changes in specific entropy, internal energy, and enthalpy of a gas between two states where the temperature is the same, $T_1 = T_2$, and the pressures are p_1 and p_2 , respectively.

SOLUTION

Known: Two states of a unit mass of a gas as the system are fixed by p_1 and T_1 at state 1 and p_2 , $T_2 (= T_1)$ at state 2.

Find: Determine the changes in specific entropy, internal energy, and enthalpy between these two states.

Schematic and Given Data:



Engineering Model: The Redlich-Kwong equation of state represents the $p-v-T$ behavior at these states and yields accurate values for $(\partial p / \partial T)_v$.

Fig. E11.5

Analysis: The Redlich-Kwong equation of state is explicit in pressure, so Eqs. 11.50 and 11.51 are selected for determining $s_2 - s_1$ and $u_2 - u_1$. Since $T_1 = T_2$, an isothermal path of integration between the two states is convenient. Thus, these equations reduce to give

$$s_2 - s_1 = \int_1^2 \left(\frac{\partial p}{\partial T} \right)_v dv$$

$$u_2 - u_1 = \int_1^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv$$

The limits for each of the foregoing integrals are the specific volumes v_1 and v_2 at the two states under consideration. Using p_1 , p_2 , and the known temperature, these specific volumes would be determined from the Redlich–Kwong equation of state. Since this equation is not explicit in specific volume, the use of an equation solver such as *Interactive Thermodynamics: IT* is recommended.

The above integrals involve the partial derivative $(\partial p/\partial T)_v$, which can be determined from the Redlich–Kwong equation of state as

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b} + \frac{a}{2v(v + b)T^{3/2}}$$

Inserting this into the expression for $(s_2 - s_1)$ gives

$$\begin{aligned} s_2 - s_1 &= \int_{v_1}^{v_2} \left[\frac{R}{v - b} + \frac{a}{2v(v + b)T^{3/2}} \right] dv \\ &= \int_{v_1}^{v_2} \left[\frac{R}{v - b} + \frac{a}{2bT^{3/2}} \left(\frac{1}{v} - \frac{1}{v + b} \right) \right] dv \\ &= R \ln \left(\frac{v_2 - b}{v_1 - b} \right) + \frac{a}{2bT^{3/2}} \left[\ln \left(\frac{v_2}{v_1} \right) - \ln \left(\frac{v_2 + b}{v_1 + b} \right) \right] \\ &= R \ln \left(\frac{v_2 - b}{v_1 - b} \right) + \frac{a}{2bT^{3/2}} \ln \left[\frac{v_2(v_1 + b)}{v_1(v_2 + b)} \right] \end{aligned}$$

With the Redlich–Kwong equation, the integrand of the expression for $(u_2 - u_1)$ becomes

$$\begin{aligned} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] &= T \left[\frac{R}{v - b} + \frac{a}{2v(v + b)T^{3/2}} \right] - \left[\frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}} \right] \\ &= \frac{3a}{2v(v + b)T^{1/2}} \end{aligned}$$

Accordingly

$$\begin{aligned} u_2 - u_1 &= \int_{v_1}^{v_2} \frac{3a}{2v(v + b)T^{1/2}} dv = \frac{3a}{2bT^{1/2}} \int_{v_1}^{v_2} \left(\frac{1}{v} - \frac{1}{v + b} \right) dv \\ &= \frac{3a}{2bT^{1/2}} \left[\ln \frac{v_2}{v_1} - \ln \left(\frac{v_2 + b}{v_1 + b} \right) \right] = \frac{3a}{2bT^{1/2}} \ln \left[\frac{v_2(v_1 + b)}{v_1(v_2 + b)} \right] \end{aligned}$$

Finally, $(h_2 - h_1)$ would be determined using Eq. 11.61 together with the known values of $(u_2 - u_1)$, p_1 , v_1 , p_2 , and v_2 .

Skills Developed

Ability to...

- perform differentiations and integrations required to evaluate Δu and Δs using the two-constant Redlich–Kwong equation of state.

QuickQUIZ

Using results obtained, develop expressions for Δu and Δs of an ideal gas. **Ans.** $\Delta u = 0$, $\Delta s = R \ln (v_2/v_1)$.

11.5 Other Thermodynamic Relations

The presentation to this point has been directed mainly at developing thermodynamic relations that allow changes in u , h , and s to be evaluated from measured property data. The objective of the present section is to introduce several other thermodynamic relations that are useful for thermodynamic analysis. Each of the properties considered has a common attribute: it is defined in terms of a partial derivative of some other property. The specific heats c_v and c_p are examples of this type of property.

11.5.1 • Volume Expansivity, Isothermal and Isentropic Compressibility

In single-phase regions, pressure and temperature are independent, and we can think of the specific volume as being a function of these two, $v = v(T, p)$. The differential of such a function is

$$dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp$$

Two thermodynamic properties related to the partial derivatives appearing in this differential are the **volume expansivity** β , also called the *coefficient of volume expansion*

volume expansivity

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p \quad (11.62)$$

and the **isothermal compressibility** κ

isothermal compressibility

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T \quad (11.63)$$

By inspection, the unit for β is seen to be the reciprocal of that for temperature and the unit for κ is the reciprocal of that for pressure. The volume expansivity is an indication of the change in volume that occurs when temperature changes while pressure remains constant. The isothermal compressibility is an indication of the change in volume that takes place when pressure changes while temperature remains constant. The value of κ is positive for all substances in all phases.

The volume expansivity and isothermal compressibility are thermodynamic properties, and like specific volume are functions of T and p . Values for β and κ are provided in compilations of engineering data. Table 11.2 gives values of these properties for liquid water at a pressure of 1 atm versus temperature. For a pressure of 1 atm, water has a *state of maximum density* at about 4°C. At this state, the value of β is zero.

The **isentropic compressibility** α is an indication of the change in volume that occurs when pressure changes while entropy remains constant:

isentropic compressibility

$$\alpha = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_s \quad (11.64)$$

The unit for α is the reciprocal of that for pressure.

TABLE 11.2

Volume Expansivity β and Isothermal Compressibility κ of Liquid Water at 1 atm Versus Temperature

T (°C)	Density (kg/m ³)	$\beta \times 10^6$ (K ⁻¹)	$\kappa \times 10^6$ (bar) ⁻¹
0	999.84	-68.14	50.89
10	999.70	87.90	47.81
20	998.21	206.6	45.90
30	995.65	303.1	44.77
40	992.22	385.4	44.24
50	988.04	457.8	44.18

velocity of sound

The isentropic compressibility is related to the speed at which sound travels in a substance, and such speed measurements can be used to determine α . In Sec. 9.12.2, the **velocity of sound**, or *sonic velocity*, is introduced as

$$c = \sqrt{-v^2 \left(\frac{\partial p}{\partial v} \right)_s} \quad (9.36b)$$

The relationship of the isentropic compressibility and the velocity of sound can be obtained using the relation between partial derivatives expressed by Eq. 11.15. Identifying p with x , v with y , and s with z , we have

$$\left(\frac{\partial p}{\partial v} \right)_s = \frac{1}{(\partial v / \partial p)_s}$$

With this, the previous two equations can be combined to give

$$c = \sqrt{v/\alpha} \quad (11.65)$$

The details are left as an exercise.

TAKE NOTE...

Through the Mach number, the sonic velocity c plays an important role in analyzing flow in nozzles and diffusers. See Sec. 9.13.

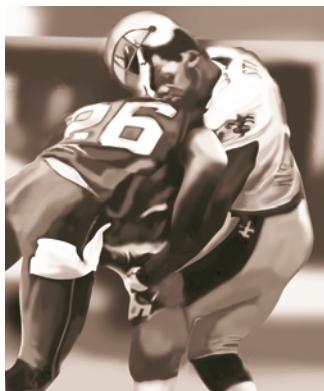


BIOCONNECTIONS The propagation of elastic waves, such as sound waves, has important implications related to injury in living things. During impact such as a collision in a sporting event (see accompanying figure), elastic waves are created that cause some bodily material to move relative to the rest of the body. The waves can propagate at supersonic, transonic, or subsonic speeds depending on the nature of the impact, and the resulting trauma can cause serious damage. The waves may be focused into a small area, causing localized damage, or they may be reflected at the boundary of organs and cause more widespread damage.

An example of the focusing of waves occurs in some head injuries. An impact to the skull causes flexural and compression waves to move along the curved surface and arrive at the far side of the skull simultaneously. Waves also propagate through the softer brain tissue. Consequently, concussions, skull fractures, and other injuries can appear at locations away from the site of the original impact.

Central to an understanding of traumatic injury is data on speed of sound and other elastic characteristics of organs and tissues. For humans the speed of sound varies widely, from approximately 30–45 m/s in spongy lung tissue to about 1600 m/s in muscle and 3500 m/s in bone. Because the speed of sound in the lungs is relatively low, impacts such as in automobile collisions or even air-bag deployment can set up waves that propagate supersonically. Medical personnel responding to traumas are trained to check for lung injuries.

The study of wave phenomena in the body constitutes an important area in the field of biomechanics.



11.5.2 Relations Involving Specific Heats

In this section, general relations are obtained for the difference between specific heats ($c_p - c_v$) and the ratio of specific heats c_p/c_v .

EVALUATING ($c_p - c_v$). An expression for the difference between c_p and c_v can be obtained by equating the two differentials for entropy given by Eqs. 11.48 and 11.57 and rearranging to obtain

$$(c_p - c_v) dT = T \left(\frac{\partial p}{\partial T} \right)_v dv + T \left(\frac{\partial v}{\partial T} \right)_p dp$$

Considering the equation of state $p = p(T, v)$, the differential dp can be expressed as

$$dp = \left(\frac{\partial p}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial v} \right)_T dv$$

Eliminating dp between the last two equations and collecting terms gives

$$\left[(c_p - c_v) - T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v \right] dT = T \left[\left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial v} \right)_T + \left(\frac{\partial p}{\partial T} \right)_v \right] dv$$

Since temperature and specific volume can be varied independently, the coefficients of the differentials in this expression must vanish, so

$$c_p - c_v = T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v \quad (11.66)$$

$$\left(\frac{\partial p}{\partial T} \right)_v = - \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial v} \right)_T \quad (11.67)$$

Introducing Eq. 11.67 into Eq. 11.66 gives

$$c_p - c_v = -T \left(\frac{\partial v}{\partial T} \right)_p^2 \left(\frac{\partial p}{\partial v} \right)_T \quad (11.68)$$

This equation allows c_v to be calculated from observed values of c_p knowing only $p-v-T$ data, or c_p to be calculated from observed values of c_v .

► FOR EXAMPLE for the special case of an ideal gas, Eq. 11.68 reduces to Eq. 3.44: $c_p(T) = c_v(T) + R$, as can readily be shown. ◀◀◀◀◀

The right side of Eq. 11.68 can be expressed in terms of the volume expansivity β and the isothermal compressibility κ . Introducing Eqs. 11.62 and 11.63, we get

$$c_p - c_v = v \frac{T\beta^2}{\kappa} \quad (11.69)$$

In developing this result, the relationship between partial derivatives expressed by Eq. 11.15 has been used.

Several important conclusions about the specific heats c_p and c_v can be drawn from Eq. 11.69.

► FOR EXAMPLE since the factor β^2 cannot be negative and κ is positive for all substances in all phases, the value of c_p is always greater than, or equal to, c_v . The specific heats are equal when $\beta = 0$, as occurs in the case of water at 1 atmosphere and 4°C, where water is at its state of maximum density. The two specific heats also become equal as the temperature approaches absolute zero. For some liquids and solids at certain states, c_p and c_v differ only slightly. For this reason, tables often give the specific heat of a liquid or solid without specifying whether it is c_p or c_v . The data reported are normally c_p values, since these are more easily determined for liquids and solids. ◀◀◀◀◀

EVALUATING c_p/c_v . Next, let us obtain expressions for the ratio of specific heats, k . Employing Eq. 11.16, we can rewrite Eqs. 11.46 and 11.55, respectively, as

$$\frac{c_v}{T} = \left(\frac{\partial s}{\partial T} \right)_v = \frac{-1}{(\partial v/\partial s)_T (\partial T/\partial v)_s}$$

$$\frac{c_p}{T} = \left(\frac{\partial s}{\partial T} \right)_p = \frac{-1}{(\partial p/\partial s)_T (\partial T/\partial p)_s}$$

Forming the ratio of these equations gives

$$\frac{c_p}{c_v} = \frac{(\partial v/\partial s)_T (\partial T/\partial v)_s}{(\partial p/\partial s)_T (\partial T/\partial p)_s} \quad (11.70)$$

Since $(\partial s/\partial p)_T = 1/(\partial p/\partial s)_T$ and $(\partial p/\partial T)_s = 1/(\partial T/\partial p)_s$, Eq. 11.70 can be expressed as

$$\frac{c_p}{c_v} = \left[\left(\frac{\partial v}{\partial s} \right)_T \left(\frac{\partial s}{\partial p} \right)_T \right] \left[\left(\frac{\partial p}{\partial T} \right)_s \left(\frac{\partial T}{\partial v} \right)_s \right] \quad (11.71)$$

Finally, the chain rule from calculus allows us to write $(\partial v/\partial p)_T = (\partial v/\partial s)_T (\partial s/\partial p)_T$ and $(\partial p/\partial v)_s = (\partial p/\partial T)_s (\partial T/\partial v)_s$, so Eq. 11.71 becomes

$$k = \frac{c_p}{c_v} = \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial v} \right)_s \quad (11.72)$$

This can be expressed alternatively in terms of the isothermal and isentropic compressibilities as

$$k = \frac{\kappa}{\alpha} \quad (11.73)$$

Solving Eq. 11.72 for $(\partial p/\partial v)_s$ and substituting the resulting expression into Eq. 9.36b gives the following relationship involving the velocity of sound c and the specific heat ratio k

$$c = \sqrt{-k v^2 (\partial p/\partial v)_T} \quad (11.74)$$

Equation 11.74 can be used to determine c knowing the specific heat ratio and $p-v-T$ data, or to evaluate k knowing c and $(\partial p/\partial v)_T$.

► FOR EXAMPLE in the special case of an ideal gas, Eq. 11.74 reduces to give Eq. 9.37 (Sec. 9.12.2):

$$c = \sqrt{kRT} \quad (\text{ideal gas}) \quad (9.37)$$

as can easily be verified. ◀ ◀ ◀ ◀ ◀

In the next example we illustrate the use of specific heat relations introduced above.

EXAMPLE 11.6 ►

Using Specific Heat Relations

For liquid water at 1 atm and 20°C, estimate **(a)** the percent error in c_v that would result if it were assumed that $c_p = c_v$, **(b)** the velocity of sound, in m/s.

SOLUTION

Known: The system consists of a fixed amount of liquid water at 1 atm and 20°C.

Find: Estimate the percent error in c_v that would result if c_v were approximated by c_p , and the velocity of sound, in m/s.

Analysis:

(a) Equation 11.69 gives the difference between c_p and c_v . Table 11.2 provides the required values for the volume expansivity β , the isothermal compressibility κ , and the specific volume. Thus

$$\begin{aligned} c_p - c_v &= v \frac{T\beta^2}{\kappa} \\ &= \left(\frac{1}{998.21 \text{ kg/m}^3} \right) (293 \text{ K}) \left(\frac{206.6 \times 10^{-6}}{\text{K}} \right)^2 \left(\frac{\text{bar}}{45.90 \times 10^{-6}} \right) \\ &= \left(272.96 \times 10^{-6} \frac{\text{bar} \cdot \text{m}^3}{\text{kg} \cdot \text{K}} \right) \left| \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right| \left| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right| \\ &= 0.027 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{aligned}$$

- ① Interpolating in Table A-19 at 20°C gives $c_p = 4.188 \text{ kJ/kg} \cdot \text{K}$. Thus, the value of c_v is

$$c_v = 4.188 - 0.027 = 4.161 \text{ kJ/kg} \cdot \text{K}$$

Using these values, the percent error in approximating c_v by c_p is

$$② \quad \left(\frac{c_p - c_v}{c_v} \right) (100) = \left(\frac{0.027}{4.161} \right) (100) = 0.6\%$$

(b) The velocity of sound at this state can be determined using Eq. 11.65. The required value for the isentropic compressibility α is calculable in terms of the specific heat ratio k and the isothermal compressibility κ . With Eq. 11.73, $\alpha = \kappa/k$. Inserting this into Eq. 11.65 results in the following expression for the velocity of sound

$$c = \sqrt{\frac{k\nu}{\kappa}}$$

The values of ν and κ required by this expression are the same as used in part (a). Also, with the values of c_p and c_v from part (a), the specific heat ratio is $k = 1.006$. Accordingly

$$③ \quad c = \sqrt{\frac{(1.006)(10^6) \text{ bar}}{(998.21 \text{ kg/m}^3)(45.90)}} \left| \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right| \left| \frac{1 \text{ kg} \cdot \text{m/s}^2}{1 \text{ N}} \right| = 1482 \text{ m/s}$$

- ① Consistent with the discussion of Sec. 3.10.1, we take c_p at 1 atm and 20°C as the saturated liquid value at 20°C.
- ② The result of part (a) shows that for liquid water at the given state, c_p and c_v are closely equal.
- ③ For comparison, the velocity of sound in air at 1 atm, 20°C is about 343 m/s, which can be checked using Eq. 9.37.

**Skills Developed**

Ability to...

- apply specific heat relations to liquid water.
- evaluate velocity of sound for liquid water.

QuickQUIZ

A submarine moves at a speed of 20 knots (1 knot = 1.852 km/h). Using the sonic velocity calculated in part (b), estimate the Mach number of the vessel relative to the water. **Ans.** 0.0069.

11.5.3 Joule-Thomson Coefficient

The value of the specific heat c_p can be determined from $p-v-T$ data and the Joule-Thomson coefficient. The **Joule-Thomson coefficient** μ_J is defined as

Joule-Thomson coefficient

$$\mu_J = \left(\frac{\partial T}{\partial p} \right)_h \quad (11.75)$$

Like other partial differential coefficients introduced in this section, the Joule–Thomson coefficient is defined in terms of thermodynamic properties only and thus is itself a property. The units of μ_J are those of temperature divided by pressure.

A relationship between the specific heat c_p and the Joule–Thomson coefficient μ_J can be established by using Eq. 11.16 to write

$$\left(\frac{\partial T}{\partial p}\right)_h \left(\frac{\partial p}{\partial h}\right)_T \left(\frac{\partial h}{\partial T}\right)_p = -1$$

The first factor in this expression is the Joule–Thomson coefficient and the third is c_p . Thus

$$c_p = \frac{-1}{\mu_J (\partial p / \partial h)_T}$$

With $(\partial h / \partial p)_T = 1 / (\partial p / \partial h)_T$ from Eq. 11.15, this can be written as

$$c_p = -\frac{1}{\mu_J} \left(\frac{\partial h}{\partial p}\right)_T \quad (11.76)$$

The partial derivative $(\partial h / \partial p)_T$, called the *constant-temperature coefficient*, can be eliminated from Eq. 11.76 by use of Eq. 11.56. The following expression results:

$$c_p = \frac{1}{\mu_J} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] \quad (11.77)$$

Equation 11.77 allows the value of c_p at a state to be determined using p – v – T data and the value of the Joule–Thomson coefficient at that state. Let us consider next how the Joule–Thomson coefficient can be found experimentally.

EXPERIMENTAL EVALUATION. The Joule–Thomson coefficient can be evaluated experimentally using an apparatus like that pictured in Fig. 11.3. Consider first Fig. 11.3a, which shows a porous plug through which a gas (or liquid) may pass. During operation at steady state, the gas enters the apparatus at a specified temperature T_1 and pressure p_1 and expands through the plug to a lower pressure p_2 , which is controlled by an outlet valve. The temperature T_2 at the exit is measured. The apparatus is designed

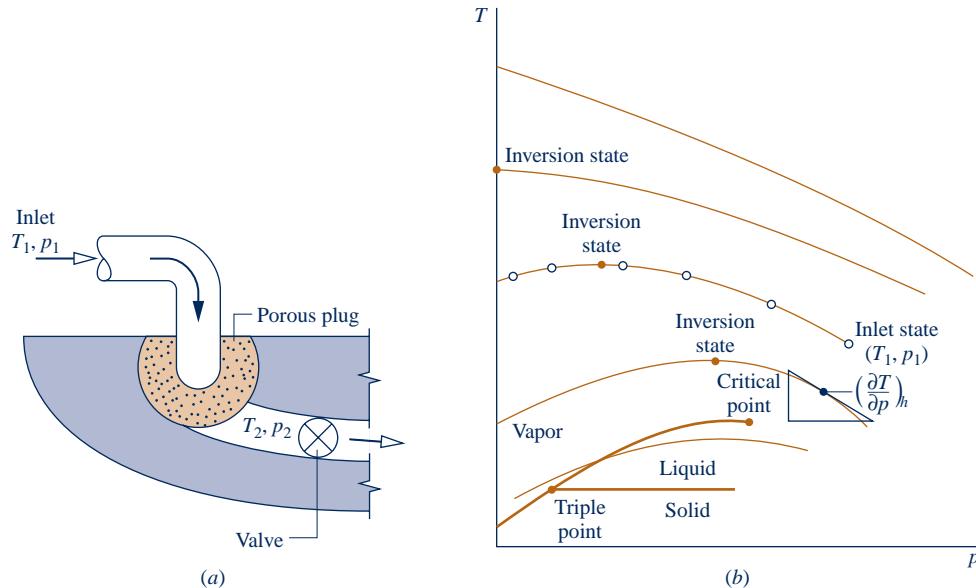


Fig. 11.3 Joule–Thomson expansion. (a) Apparatus. (b) Isenthalpics on a T – p diagram.

so that the gas undergoes a *throttling* process (Sec. 4.10) as it expands from 1 to 2. Accordingly, the exit state fixed by p_2 and T_2 has the same value for the specific enthalpy as at the inlet, $h_2 = h_1$. By progressively lowering the outlet pressure, a finite sequence of such exit states can be visited, as indicated on Fig. 11.3b. A curve may be drawn through the set of data points. Such a curve is called an isenthalpic (constant enthalpy) curve. An isenthalpic curve is the locus of all points representing equilibrium states of the same specific enthalpy.

The slope of an isenthalpic curve at any state is the Joule–Thomson coefficient at that state. The slope may be positive, negative, or zero in value. States where the coefficient has a zero value are called **inversion states**. Notice that not all lines of constant h have an inversion state. The uppermost curve of Fig. 11.3b, for example, always has a negative slope. Throttling a gas from an initial state on this curve would result in an increase in temperature. However, for isenthalpic curves having an inversion state, the temperature at the exit of the apparatus may be greater than, equal to, or less than the initial temperature, depending on the exit pressure specified. For states to the right of an inversion state, the value of the Joule–Thomson coefficient is negative. For these states, the temperature increases as the pressure at the exit of the apparatus decreases. At states to the left of an inversion state, the value of the Joule–Thomson coefficient is positive. For these states, the temperature decreases as the pressure at the exit of the device decreases. This can be used to advantage in systems designed to *liquefy gases*.

Inversion states



Small Power Plants Pack Punch

An innovation in power systems moving from concept to reality promises to help keep computer networks humming, hospital operating rooms lit, and shopping centers thriving. Called *distributed generation systems*, compact power plants provide electricity for small loads or are linked for larger applications. With distributed generation, consumers hope to avoid unpredictable price swings and brownouts.

Distributed generation includes a broad range of technologies that provide relatively small levels of power at sites close to users, including but not limited to internal combustion engines, micro-turbines, fuel cells, and photovoltaic systems.

Although the cost per kilowatt-hour may be higher with distributed generation, some customers are willing to pay more to gain control over their electric supply. Computer networks and hospitals need high reliability, since even short disruptions can be disastrous. Businesses such as shopping centers also must avoid costly service interruptions. With distributed generation, the needed reliability is provided by modular units that can be combined with power management and energy storage systems to ensure quality power is available when needed.

11.6 Constructing Tables of Thermodynamic Properties

The objective of this section is to utilize the thermodynamic relations introduced thus far to describe how tables of thermodynamic properties can be constructed. The characteristics of the tables under consideration are embodied in the tables for water and the refrigerants presented in the Appendix. The methods introduced in this section are extended in Chap. 13 for the analysis of reactive systems, such as gas turbine and vapor power systems involving combustion. The methods of this section also provide the basis for computer retrieval of thermodynamic property data.

Two different approaches for constructing property tables are considered:

- The presentation of Sec. 11.6.1 employs the methods introduced in Sec. 11.4 for assigning specific enthalpy, specific internal energy, and specific entropy to states of pure, simple compressible substances using p – v – T data, together with a limited amount of specific heat data. The principal mathematical operation of this approach is *integration*.

- The approach of Sec. 11.6.2 utilizes the fundamental thermodynamic function concept introduced in Sec. 11.3.3. Once such a function has been constructed, the principal mathematical operation required to determine all other properties is *differentiation*.

11.6.1 • Developing Tables by Integration Using p - v - T and Specific Heat Data

In principle, all properties of present interest can be determined using

$$\begin{aligned} c_p &= c_{p0}(T) \\ p &= p(v, T), \quad v = v(p, T) \end{aligned} \quad (11.78)$$

In Eqs. 11.78, $c_{p0}(T)$ is the specific heat c_p for the substance under consideration extrapolated to zero pressure. This function might be determined from data obtained calorimetrically or from spectroscopic data, using equations supplied by statistical mechanics. Specific heat expressions for several gases are given in Tables A-21. The expressions $p(v, T)$ and $v(p, T)$ represent functions that describe the saturation pressure-temperature curves, as well as the p - v - T relations for the single-phase regions. These functions may be tabular, graphical, or analytical in character. Whatever their forms, however, the functions must not only represent the p - v - T data accurately but also yield accurate values for derivatives such as $(\partial v / \partial T)_p$ and $(dp/dT)_{\text{sat}}$.

Figure 11.4 shows eight states of a substance. Let us consider how values can be assigned to specific enthalpy and specific entropy at these states. The same procedures can be used to assign property values at other states of interest. Note that when h has been assigned to a state, the specific internal energy at that state can be found from $u = h - pv$.

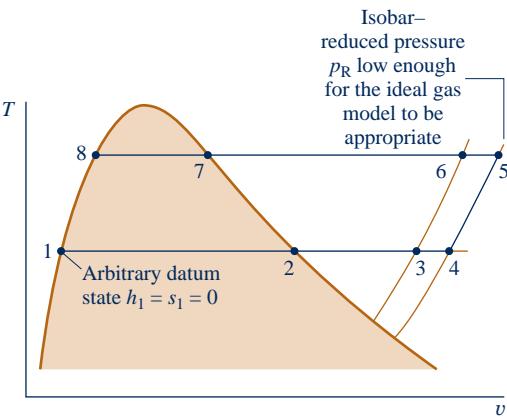


Fig. 11.4 T - v diagram used to discuss how h and s can be assigned to liquid and vapor states.

- Let the state denoted by 1 on Fig. 11.4 be selected as the datum state for enthalpy and entropy. Any value can be assigned to h and s at this state, but a value of zero would be usual. It should be noted that the use of an arbitrary datum state and arbitrary reference values for specific enthalpy and specific entropy suffices only for evaluations involving differences in property values between states of the same composition, for then datums cancel.

- Once a value is assigned to enthalpy at state 1, the enthalpy at the saturated vapor state, state 2, can be determined using the Clapeyron equation, Eq. 11.40

$$h_2 - h_1 = T_1(v_2 - v_1) \left(\frac{dp}{dT} \right)_{\text{sat}}$$

where the derivative $(dp/dT)_{\text{sat}}$ and the specific volumes v_1 and v_2 are obtained from appropriate representations of the p - v - T data for the substance under consideration. The specific entropy at state 2 is found using Eq. 11.38 in the form

$$s_2 - s_1 = \frac{h_2 - h_1}{T_1}$$

- Proceeding at constant temperature from state 2 to state 3, the entropy and enthalpy are found by means of Eqs. 11.59 and 11.60, respectively. Since temperature is fixed, these equations reduce to give

$$s_3 - s_2 = - \int_{p_2}^{p_3} \left(\frac{\partial v}{\partial T} \right)_p dp \quad \text{and} \quad h_3 - h_2 = \int_{p_2}^{p_3} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$

With the same procedure, s_4 and h_4 can be determined.

- The isobar (constant-pressure line) passing through state 4 is assumed to be at a low enough pressure for the ideal gas model to be appropriate. Accordingly, to evaluate s and h at states such as 5 on this isobar, the only required information would be $c_{p0}(T)$ and the temperatures at these states. Thus, since pressure is fixed, Eqs. 11.59 and 11.60 give, respectively

$$s_5 - s_4 = \int_{T_4}^{T_5} c_{p0} \frac{dT}{T} \quad \text{and} \quad h_5 - h_4 = \int_{T_4}^{T_5} c_{p0} dT$$

- Specific entropy and enthalpy values at states 6 and 7 are found from those at state 5 by the same procedure used in assigning values at states 3 and 4 from those at state 2. Finally, s_8 and h_8 are obtained from the values at state 7 using the Clapeyron equation.

11.6.2 Developing Tables by Differentiating a Fundamental Thermodynamic Function

Property tables also can be developed using a fundamental thermodynamic function. It is convenient for this purpose to select the independent variables of the fundamental function from among pressure, specific volume (density), and temperature. This indicates the use of the Helmholtz function $\psi(T, v)$ or the Gibbs function $g(T, p)$. The properties of water tabulated in Tables A-2 through A-6 have been calculated using the Helmholtz function. Fundamental thermodynamic functions also have been employed successfully to evaluate the properties of other substances in the Appendix tables.

The development of a fundamental thermodynamic function requires considerable mathematical manipulation and numerical evaluation. Prior to the advent of high-speed computers, the evaluation of properties by this means was not feasible, and the approach described in Sec. 11.6.1 was used exclusively. The fundamental function approach involves three steps:

1. The first step is the selection of a functional form in terms of the appropriate pair of independent properties and a set of adjustable coefficients, which may number 50 or more. The functional form is specified on the basis of both theoretical and practical considerations.
2. Next, the coefficients in the fundamental function are determined by requiring that a set of carefully selected property values and/or observed conditions be satisfied in a least-squares sense. This generally involves the use of property data requiring the assumed functional form to be differentiated one or more times, such as $p-v-T$ and specific heat data.
3. When all coefficients have been evaluated, the function is carefully tested for accuracy by using it to evaluate properties for which accepted values are known. These may include properties requiring differentiation of the fundamental function two or more times. For example, velocity of sound and Joule–Thomson data might be used.

This procedure for developing a fundamental thermodynamic function is not routine and can be accomplished only with a computer. However, once a suitable fundamental function is established, extreme accuracy in and consistency among the thermodynamic properties is possible.

The form of the Helmholtz function used in constructing the steam tables from which Tables A-2 through A-6 have been extracted is

$$\psi(\rho, T) = \psi_0(T) + RT[\ln \rho + \rho Q(\rho, \tau)] \quad (11.79)$$

where ψ_0 and Q are given as the sums listed in Table 11.3. The independent variables are density and temperature. The variable τ denotes $1000/T$. Values for pressure, specific

TABLE 11.3**Fundamental Equation Used to Construct the Steam Tables^{a,b}**

$$\psi = \psi_0(T) + RT[\ln \rho + \rho Q(\rho, \tau)] \quad (1)$$

where

$$\psi_0 = \sum_{i=1}^6 C_i/\tau^{i-1} + C_7 \ln T + C_8 \ln T/\tau \quad (2)$$

and

$$Q = (\tau - \tau_c) \sum_{j=1}^7 (\tau - \tau_{aj})^{j-2} \left[\sum_{i=1}^8 A_{ij}(\rho - \rho_{aj})^{i-1} + e^{-E\rho} \sum_{i=9}^{10} A_{ij}\rho^{i-9} \right] \quad (3)$$

In (1), (2), and (3), T denotes temperature on the Kelvin scale, τ denotes $1000/T$, ρ denotes density in g/cm^3 , $R = 4.6151 \text{ bar} \cdot \text{cm}^3/\text{g} \cdot \text{K}$ or $0.46151 \text{ J/g} \cdot \text{K}$, $\tau_c = 1000/T_c = 1.544912$, $E = 4.8$, and

$$\begin{aligned} \tau_{aj} &= \tau_c(j=1) & \rho_{aj} &= 0.634(j=1) \\ &= 2.5(j>1) & &= 1.0(j>1) \end{aligned}$$

The coefficients for ψ_0 in J/g are given as follows:

$$\begin{array}{lll} C_1 = 1857.065 & C_4 = 36.6649 & C_7 = 46.0 \\ C_2 = 3229.12 & C_5 = -20.5516 & C_8 = -1011.249 \\ C_3 = -419.465 & C_6 = 4.85233 & \end{array}$$

Values for the coefficients A_{ij} are listed in the original source.^a

^aJ. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York, 1969.

^bAlso see L. Haar, J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables*, Hemisphere, Washington, D.C., 1984.

The properties of water are determined in this reference using a different functional form for the Helmholtz function than given by Eqs. (1)–(3).

internal energy, and specific entropy can be determined by differentiation of Eq. 11.79. Values for the specific enthalpy and Gibbs function are found from $h = u + pv$ and $g = \psi + pv$, respectively. The specific heat c_v is evaluated by further differentiation, $c_v = (\partial u / \partial T)_v$. With similar operations, other properties can be evaluated. Property values for water calculated from Eq. 11.79 are in excellent agreement with experimental data over a wide range of conditions.



ENERGY & ENVIRONMENT Due to the phase-out of chlorine-containing CFC refrigerants because of ozone layer and global climate change concerns, new substances and mixtures with no chlorine have been developed in recent years as possible alternatives (see Sec. 10.3). This has led to significant research efforts to provide the necessary thermodynamic property data for analysis and design.

The National Institute of Standards and Technology (NIST) has led governmental efforts to provide accurate data. Specifically, data have been developed for high-accuracy $p-v-T$ equations of state from which fundamental thermodynamic functions can be obtained. The equations are carefully validated using data for velocity of sound, Joule–Thomson coefficient, saturation pressure–temperature relations, and specific heats. Such data were used to calculate the property values in Tables A-7 to A-18 in the Appendix. NIST has developed REFPROP, a computer data base that is the current standard for refrigerant and refrigerant mixture properties.

Example 11.7 illustrates the use of a fundamental function to determine thermodynamic properties for computer evaluation and to develop tables.

►►►► **EXAMPLE 11.7**

Determining Properties Using a Fundamental Function

The following expression for the Helmholtz function has been used to determine the properties of water:

$$\psi(\rho, T) = \psi_0(T) + RT[\ln \rho + \rho Q(\rho, \tau)]$$

where ρ denotes density and τ denotes $1000/T$. The functions ψ_0 and Q are sums involving the indicated independent variables and a number of adjustable constants (see Table 11.3). Obtain expressions for (a) pressure, (b) specific entropy, and (c) specific internal energy resulting from this fundamental thermodynamic function.

SOLUTION

Known: An expression for the Helmholtz function ψ is given.

Find: Determine the expressions for pressure, specific entropy, and specific internal energy that result from this fundamental thermodynamic function.

Analysis: The expressions developed below for p , s , and u require only the functions $\psi_0(T)$ and $Q(\rho, \tau)$. Once these functions are determined, p , s , and u can each be determined as a function of density and temperature using elementary mathematical operations.

(a) When expressed in terms of density instead of specific volume, Eq. 11.28 becomes

$$p = \rho^2 \left(\frac{\partial \psi}{\partial \rho} \right)_T$$

as can easily be verified. When T is held constant τ is also constant. Accordingly, the following is obtained on differentiation of the given function:

$$\left(\frac{\partial \psi}{\partial \rho} \right)_T = RT \left[\frac{1}{\rho} + Q(\rho, \tau) + \rho \left(\frac{\partial Q}{\partial \rho} \right)_\tau \right]$$

Combining these equations gives an expression for pressure

$$p = \rho RT \left[1 + \rho Q + \rho^2 \left(\frac{\partial Q}{\partial \rho} \right)_\tau \right] \quad (a)$$

(b) From Eq. 11.29

$$s = - \left(\frac{\partial \psi}{\partial T} \right)_\rho$$

Differentiation of the given expression for ψ yields

$$\begin{aligned} \left(\frac{\partial \psi}{\partial T} \right)_\rho &= \frac{d\psi_0}{dT} + \left[R(\ln \rho + \rho Q) + RT\rho \left(\frac{\partial Q}{\partial \tau} \right)_\rho \frac{d\tau}{dT} \right] \\ &= \frac{d\psi_0}{dT} + \left[R(\ln \rho + \rho Q) + RT\rho \left(\frac{\partial Q}{\partial \tau} \right)_\rho \left(-\frac{1000}{T^2} \right) \right] \\ &= \frac{d\psi_0}{dT} + R \left[\ln \rho + \rho Q - \rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho \right] \end{aligned}$$

Combining results gives

$$s = - \frac{d\psi_0}{dT} - R \left[\ln \rho + \rho Q - \rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho \right] \quad (b)$$

(c) By definition, $\psi = u - Ts$. Thus, $u = \psi + Ts$. Introducing the given expression for ψ together with the expression for s from part (b) results in

$$\begin{aligned} u &= [\psi_0 + RT(\ln \rho + \rho Q)] + T \left\{ - \frac{d\psi_0}{dT} - R \left[\ln \rho + \rho Q - \rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho \right] \right\} \\ &= \psi_0 - T \frac{d\psi_0}{dT} + RT\rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho \end{aligned}$$

- This can be written more compactly by noting that

$$T \frac{d\psi_0}{dT} = T \frac{d\psi_0}{d\tau} \frac{d\tau}{dT} = T \frac{d\psi_0}{d\tau} \left(-\frac{1000}{T^2} \right) = -\tau \frac{d\psi_0}{d\tau}$$

Thus,

$$\psi_0 - T \frac{d\psi_0}{dT} = \psi_0 + \tau \frac{d\psi_0}{d\tau} = \frac{d(\psi_0 \tau)}{d\tau}$$

Finally, the expression for u becomes

$$u = \frac{d(\psi_0 \tau)}{d\tau} + RT\rho\tau \left(\frac{\partial Q}{\partial \tau} \right)_p \quad (c)$$

Skills Developed

Ability to...

- derive expressions for pressure, specific entropy, and specific internal energy based on a fundamental thermodynamic function.

QuickQUIZ

Using results obtained, how can an expression be developed for h ? **Ans.** $h = u + p/\rho$. Substitute Eq. (c) for u and Eq. (a) for p and collect terms.

11.7

Generalized Charts for Enthalpy and Entropy

TAKE NOTE...

Generalized compressibility charts are provided in Appendix figures A-1, A-2, and A-3. See Example 3.7 for an application.

Generalized charts giving the compressibility factor Z in terms of the reduced properties p_R , T_R , and v'_R are introduced in Sec. 3.11. With such charts, estimates of $p-v-T$ data can be obtained rapidly knowing only the critical pressure and critical temperature for the substance of interest. The objective of the present section is to introduce generalized charts that allow changes in enthalpy and entropy to be estimated.

Generalized Enthalpy Departure Chart

The change in specific enthalpy of a gas (or liquid) between two states fixed by temperature and pressure can be evaluated using the identity

$$h(T_2, p_2) - h(T_1, p_1) = [h^*(T_2) - h^*(T_1)] + \underline{\{[h(T_2, p_2) - h^*(T_2)] - [h(T_1, p_1) - h^*(T_1)]\}} \quad (11.80)$$

The term $[h(T, p) - h^*(T)]$ denotes the specific enthalpy of the substance relative to that of its ideal gas model when both are at the same temperature. The superscript * is used in this section to identify ideal gas property values. Thus, Eq. 11.80 indicates that the change in specific enthalpy between the two states equals the enthalpy change determined using the ideal gas model plus a correction that accounts for the departure from ideal gas behavior. The correction is shown underlined in Eq. 11.80. The ideal gas term can be evaluated using methods introduced in Chap. 3. Next, we show how the correction term is evaluated in terms of the *enthalpy departure*.

DEVELOPING THE ENTHALPY DEPARTURE. The variation of enthalpy with pressure at fixed temperature is given by Eq. 11.56 as

$$\left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p$$

Integrating from pressure p' to pressure p at fixed temperature T

$$h(T, p) - h(T, p') = \int_{p'}^p \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$

This equation is not altered fundamentally by adding and subtracting $h^*(T)$ on the left side. That is

$$[h(T, p) - h^*(T)] - [h(T, p') - h^*(T)] = \int_{p'}^p \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (11.81)$$

As pressure tends to zero at fixed temperature, the enthalpy of the substance approaches that of its ideal gas model. Accordingly, as p' tends to zero

$$\lim_{p' \rightarrow 0} [h(T, p') - h^*(T)] = 0$$

In this limit, the following expression is obtained from Eq. 11.81 for the specific enthalpy of a substance relative to that of its ideal gas model when both are at the same temperature:

$$h(T, p) - h^*(T) = \int_0^p \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (11.82)$$

This also can be thought of as the change in enthalpy as the pressure is increased from zero to the given pressure while temperature is held constant. Using p - v - T data only, Eq. 11.82 can be evaluated at states 1 and 2 and thus the correction term of Eq. 11.80 evaluated. Let us consider next how this procedure can be conducted in terms of compressibility factor data and the reduced properties T_R and p_R .

The integral of Eq. 11.82 can be expressed in terms of the compressibility factor Z and the reduced properties T_R and p_R as follows. Solving $Z = pv/RT$ gives

$$v = \frac{ZRT}{p}$$

On differentiation

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{RZ}{p} + \frac{RT}{p} \left(\frac{\partial Z}{\partial T} \right)_p$$

With the previous two expressions, the integrand of Eq. 11.82 becomes

$$v - T \left(\frac{\partial v}{\partial T} \right)_p = \frac{ZRT}{p} - T \left[\frac{RZ}{p} + \frac{RT}{p} \left(\frac{\partial Z}{\partial T} \right)_p \right] = -\frac{RT^2}{p} \left(\frac{\partial Z}{\partial T} \right)_p \quad (11.83)$$

Equation 11.83 can be written in terms of reduced properties as

$$v - T \left(\frac{\partial v}{\partial T} \right)_p = -\frac{RT_c}{p_c} \cdot \frac{T_R^2}{p_R} \left(\frac{\partial Z}{\partial T_R} \right)_{p_R}$$

Introducing this into Eq. 11.82 gives on rearrangement

$$\frac{h^*(T) - h(T, p)}{RT_c} = T_R^2 \int_0^{p_R} \left(\frac{\partial Z}{\partial T_R} \right)_{p_R} \frac{dp_R}{p_R}$$

Or, on a per mole basis, the **enthalpy departure** is

enthalpy departure

$$\frac{\bar{h}^*(T) - \bar{h}(T, p)}{RT_c} = T_R^2 \int_0^{p_R} \left(\frac{\partial Z}{\partial T_R} \right)_{p_R} \frac{dp_R}{p_R} \quad (11.84)$$

The right side of Eq. 11.84 depends only on the reduced temperature T_R and reduced pressure p_R . Accordingly, the quantity $(\bar{h}^* - \bar{h})/RT_c$, the enthalpy departure, is a function only of these two reduced properties. Using a generalized equation of state giving Z as a function of T_R and p_R , the enthalpy departure can readily be evaluated with a computer. Tabular representations are also found in the literature. Alternatively, the graphical representation provided in Fig. A-4 can be employed.

EVALUATING ENTHALPY CHANGE. The change in specific enthalpy between two states can be evaluated by expressing Eq. 11.80 in terms of the enthalpy departure as

$$\bar{h}_2 - \bar{h}_1 = \underline{\bar{h}_2^* - \bar{h}_1^*} - \underline{\bar{R}T_c} \left[\left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_2 - \left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_1 \right] \quad (11.85)$$

The first underlined term in Eq. 11.85 represents the change in specific enthalpy between the two states assuming ideal gas behavior. The second underlined term is the correction that must be applied to the ideal gas value for the enthalpy change to obtain the actual value for the enthalpy change. Referring to the engineering literature, the quantity $(\bar{h}^* - \bar{h})/\bar{R}T_c$ at states 1 and 2 can be calculated with an equation giving $Z(T_R, p_R)$ or obtained from tables. This quantity also can be evaluated at state 1 from the generalized enthalpy departure chart, Fig. A-4, using the reduced temperature T_{R1} and reduced pressure p_{R1} corresponding to the temperature T_1 and pressure p_1 at the initial state, respectively. Similarly, $(\bar{h}^* - \bar{h})/\bar{R}T_c$ at state 2 can be evaluated from Fig. A-4 using T_{R2} and p_{R2} . The use of Eq. 11.85 is illustrated in the next example.

EXAMPLE 11.8

Using the Generalized Enthalpy Departure Chart

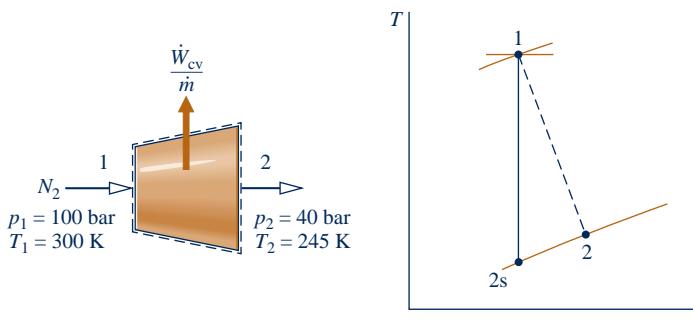
Nitrogen enters a turbine operating at steady state at 100 bar and 300 K and exits at 40 bar and 245 K. Using the enthalpy departure chart, determine the work developed, in kJ per kg of nitrogen flowing, if heat transfer with the surroundings can be ignored. Changes in kinetic and potential energy from inlet to exit also can be neglected.

SOLUTION

Known: A turbine operating at steady state has nitrogen entering at 100 bar and 300 K and exiting at 40 bar and 245 K.

Find: Using the enthalpy departure chart, determine the work developed.

Schematic and Given Data:



Engineering Model:

1. The control volume shown on the accompanying figure operates at steady state.
2. There is no significant heat transfer between the control volume and its surroundings.
3. Changes in kinetic and potential energy between inlet and exit can be neglected.
4. Equilibrium property relations apply at the inlet and exit.

Fig. E11.8

Analysis: The mass and energy rate balances reduce at steady state to give

$$0 = \frac{\dot{Q}_{cv}}{\dot{m}} - \frac{\dot{W}_{cv}}{\dot{m}} + \left[h_1 - h_2 + \frac{V_1^2 - V_2^2}{2} + g(z_1 - z_2) \right]$$

where \dot{m} is the mass flow rate. Dropping the heat transfer term by assumption 2 and the kinetic and potential energy terms by assumption 3 gives on rearrangement

$$\frac{\dot{W}_{cv}}{\dot{m}} = h_1 - h_2$$

The term $h_1 - h_2$ can be evaluated as follows:

$$h_1 - h_2 = \frac{1}{M} \left\{ \bar{h}_1^* - \bar{h}_2^* - \bar{R}T_c \left[\left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_1 - \left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_2 \right] \right\}$$

In this expression, M is the molecular weight of nitrogen and the other terms have the same significance as in Eq. 11.85.

With specific enthalpy values from Table A-23 at $T_1 = 300$ K and $T_2 = 245$ K, respectively

$$\bar{h}_1^* - \bar{h}_2^* = 8723 - 7121 = 1602 \text{ kJ/kmol}$$

The terms $(\bar{h}^* - \bar{h})/\bar{R}T_c$ at states 1 and 2 required by the above expression for $h_1 - h_2$ can be determined from Fig. A-4. First, the reduced temperature and reduced pressure at the inlet and exit must be determined. From Tables A-1, $T_c = 126$ K, $p_c = 33.9$ bar. Thus, at the inlet

$$T_{R1} = \frac{300}{126} = 2.38, \quad p_{R1} = \frac{100}{33.9} = 2.95$$

At the exit

$$T_{R2} = \frac{245}{126} = 1.94, \quad p_{R2} = \frac{40}{33.9} = 1.18$$

By inspection of Fig. A-4

$$① \quad \left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_1 \approx 0.5, \quad \left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_2 \approx 0.31$$

Substituting values

$$\dot{W}_{cv} = \frac{1}{\dot{m}} \left[1602 \frac{\text{kJ}}{\text{kmol}} - \left(8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \right) (126 \text{ K})(0.5 - 0.31) \right] = 50.1 \text{ kJ/kg}$$

- ① Due to inaccuracy in reading values from a graph such as Fig. A-4, we cannot expect extreme accuracy in the final calculated result.

Skills Developed

Ability to...

- use data from the generalized enthalpy departure chart to calculate the change in enthalpy of nitrogen.

QuickQUIZ

Determine the work developed, in kJ per kg of nitrogen flowing, assuming the ideal gas model. Ans. 57.2 kJ/kg.

Generalized Entropy Departure Chart

A generalized chart that allows changes in specific entropy to be evaluated can be developed in a similar manner to the generalized enthalpy departure chart introduced earlier in this section. The difference in specific entropy between states 1 and 2 of a gas (or liquid) can be expressed as the identity

$$s(T_2, p_2) - s(T_1, p_1) = s^*(T_2, p_2) - s^*(T_1, p_1) + \{ [s(T_2, p_2) - s^*(T_2, p_2)] - [s(T_1, p_1) - s^*(T_1, p_1)] \} \quad (11.86)$$

where $[s(T, p) - s^*(T, p)]$ denotes the specific entropy of the substance relative to that of its ideal gas model when both are at the same temperature and pressure. Equation 11.86 indicates that the change in specific entropy between the two states equals the entropy change determined using the ideal gas model plus a correction (shown underlined) that accounts for the departure from ideal gas behavior. The ideal gas term can be evaluated using methods introduced in Sec. 6.5. Let us consider next how the correction term is evaluated in terms of the *entropy departure*.

DEVELOPING THE ENTROPY DEPARTURE. The following Maxwell relation gives the variation of entropy with pressure at fixed temperature:

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad (11.35)$$

Integrating from pressure p' to pressure p at fixed temperature T gives

$$s(T, p) - s(T, p') = - \int_{p'}^p \left(\frac{\partial v}{\partial T}\right)_p dp \quad (11.87)$$

For an ideal gas, $v = RT/p$, so $(\partial v/\partial T)_p = R/p$. Using this in Eq. 11.87, the change in specific entropy assuming ideal gas behavior is

$$s^*(T, p) - s^*(T, p') = - \int_{p'}^p \frac{R}{p} dp \quad (11.88)$$

Subtracting Eq. 11.88 from Eq. 11.87 gives

$$[s(T, p) - s^*(T, p)] - [s(T, p') - s^*(T, p')] = \int_{p'}^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p \right] dp \quad (11.89)$$

Since the properties of a substance tend to merge into those of its ideal gas model as pressure tends to zero at fixed temperature, we have

$$\lim_{p' \rightarrow 0} [s(T, p') - s^*(T, p')] = 0$$

Thus, in the limit as p' tends to zero, Eq. 11.89 becomes

$$s(T, p) - s^*(T, p) = \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p \right] dp \quad (11.90)$$

Using $p-v-T$ data only, Eq. 11.90 can be evaluated at states 1 and 2 and thus the correction term of Eq. 11.86 evaluated.

Equation 11.90 can be expressed in terms of the compressibility factor Z and the reduced properties T_R and p_R . The result, on a per mole basis, is the **entropy departure**

$$\frac{\bar{s}^*(T, p) - \bar{s}(T, p)}{\bar{R}} = \frac{\bar{h}^*(T) - \bar{h}(T, p)}{\bar{R}T_R T_c} + \int_0^{p_R} (Z - 1) \frac{dp_R}{p_R} \quad (11.91)$$

The right side of Eq. 11.91 depends only on the reduced temperature T_R and reduced pressure p_R . Accordingly, the quantity $(\bar{s}^* - \bar{s})/\bar{R}$, the entropy departure, is a function only of these two reduced properties. As for the enthalpy departure, the entropy departure can be evaluated with a computer using a generalized equation of state giving Z as a function of T_R and p_R . Alternatively, tabular data from the literature or the graphical representation provided in Fig. A-5 can be employed.

EVALUATING ENTROPY CHANGE. The change in specific entropy between two states can be evaluated by expressing Eq. 11.86 in terms of the entropy departure as

$$\underline{\bar{s}_2 - \bar{s}_1} = \underline{\bar{s}_2^* - \bar{s}_1^*} - \bar{R} \left[\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_2 - \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_1 \right] \quad (11.92)$$

The first underlined term in Eq. 11.92 represents the change in specific entropy between the two states assuming ideal gas behavior. The second underlined term is the correction that must be applied to the ideal gas value for entropy change to obtain the actual value for the entropy change. The quantity $(\bar{s}^* - \bar{s})_1/\bar{R}$ appearing in Eq. 11.92 can be evaluated from the generalized entropy departure chart, Fig. A-5, using the reduced temperature T_{R1} and reduced pressure p_{R1} corresponding to the temperature T_1 and pressure p_1 at the initial state, respectively. Similarly, $(\bar{s}^* - \bar{s})_2/\bar{R}$

can be evaluated from Fig. A-5 using T_{R2} and p_{R2} . The use of Eq. 11.92 is illustrated in the next example.

►►►► EXAMPLE 11.9 ►

Using the Generalized Entropy Departure Chart

For the case of Example 11.8, determine **(a)** the rate of entropy production, in $\text{kJ/kg} \cdot \text{K}$, and **(b)** the isentropic turbine efficiency.

SOLUTION

Known: A turbine operating at steady state has nitrogen entering at 100 bar and 300 K and exiting at 40 bar and 245 K.

Find: Determine the rate of entropy production, in $\text{kJ/kg} \cdot \text{K}$, and the isentropic turbine efficiency.

Schematic and Given Data: See Fig. E11.8.

Engineering Model: See Example 11.8.

Analysis:

(a) At steady state, the control volume form of the entropy rate equation reduces to give

$$\frac{\dot{\sigma}_{cv}}{\dot{m}} = s_2 - s_1$$

The change in specific entropy required by this expression can be written as

$$s_2 - s_1 = \frac{1}{M} \left\{ \bar{s}_2^* - \bar{s}_1^* - \bar{R} \left[\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_2 - \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_1 \right] \right\}$$

where M is the molecular weight of nitrogen and the other terms have the same significance as in Eq. 11.92.

The change in specific entropy $\bar{s}_2^* - \bar{s}_1^*$ can be evaluated using

$$\bar{s}_2^* - \bar{s}_1^* = \bar{s}^\circ(T_2) - \bar{s}^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1}$$

With values from Table A-23

$$\bar{s}_2^* - \bar{s}_1^* = 185.775 - 191.682 - 8.314 \ln \frac{40}{100} = 1.711 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}}$$

The terms $(\bar{s}^* - \bar{s})/\bar{R}$ at the inlet and exit can be determined from Fig. A-5. Using the reduced temperature and reduced pressure values calculated in the solution to Example 11.8, inspection of Fig. A-5 gives

$$\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_1 \approx 0.21, \quad \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_2 \approx 0.14$$

Substituting values

$$\begin{aligned} \frac{\dot{\sigma}_{cv}}{\dot{m}} &= \frac{1}{(28 \text{ kg/kmol})} \left[1.711 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} - 8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} (0.14 - 0.21) \right] \\ &= 0.082 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{aligned}$$

(b) The isentropic turbine efficiency is defined in Sec. 6.12 as

$$\eta_t = \frac{(\dot{W}_{cv}/\dot{m})}{(\dot{W}_{cv}/\dot{m})_s}$$

where the denominator is the work that would be developed by the turbine if the nitrogen expanded isentropically from the specified inlet state to the specified exit pressure. Thus, it is necessary to fix the state, call it 2s, at the turbine exit for an expansion in which there is no change in specific entropy from inlet to exit. With $(\bar{s}_{2s} - \bar{s}_1) = 0$ and procedures similar to those used in part (a)

$$0 = \bar{s}_{2s}^* - \bar{s}_1^* - \bar{R} \left[\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_{2s} - \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_1 \right]$$

$$0 = \left[\bar{s}^\circ(T_{2s}) - \bar{s}^\circ(T_1) - \bar{R} \ln \left(\frac{p_2}{p_1} \right) \right] - \bar{R} \left[\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_{2s} - \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_1 \right]$$

Using values from part (a), the last equation becomes

$$0 = \bar{s}^\circ(T_{2s}) - 191.682 - 8.314 \ln \frac{40}{100} - \bar{R} \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_{2s} + 1.746$$

or

$$\bar{s}^\circ(T_{2s}) - \bar{R} \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_{2s} = 182.3$$

The temperature T_{2s} can be determined in an iterative procedure using \bar{s}° data from Table A-23 and $(\bar{s}^* - \bar{s})/\bar{R}$ from Fig. A-5 as follows: First, a value for the temperature T_{2s} is assumed. The corresponding value of \bar{s}° can then be obtained from Table A-23. The reduced temperature $(T_R)_{2s} = T_{2s}/T_c$, together with $p_{R2} = 1.18$, allows a value for $(\bar{s}^* - \bar{s})/\bar{R}$ to be obtained from Fig. A-5. The procedure continues until agreement with the value on the right side of the above equation is obtained. Using this procedure, T_{2s} is found to be closely 228 K.

With the temperature T_{2s} known, the work that would be developed by the turbine if the nitrogen expanded isentropically from the specified inlet state to the specified exit pressure can be evaluated from

$$\left(\frac{\dot{W}_{cv}}{\dot{m}} \right)_s = h_1 - h_{2s}$$

$$= \frac{1}{M} \left\{ (\bar{h}_1^* - \bar{h}_{2s}^*) - \bar{R} T_c \left[\left(\frac{\bar{h}^* - \bar{h}}{\bar{R} T_c} \right)_1 - \left(\frac{\bar{h}^* - \bar{h}}{\bar{R} T_c} \right)_{2s} \right] \right\}$$

From Table A-23, $\bar{h}_{2s}^* = 6654 \text{ kJ/kmol}$. From Fig. A-4 at $p_{R2} = 1.18$ and $(T_R)_{2s} = 228/126 = 1.81$

$$\left(\frac{\bar{h}^* - \bar{h}}{\bar{R} T_c} \right)_{2s} \approx 0.36$$

Values for the other terms in the expression for $(\dot{W}_{cv}/\dot{m})_s$ are obtained in the solution to Example 11.8. Finally

$$\left(\frac{\dot{W}_{cv}}{\dot{m}} \right)_s = \frac{1}{28} [8723 - 6654 - (8.314)(126)(0.5 - 0.36)] = 68.66 \text{ kJ/kg}$$

With the work value from Example 11.8, the turbine efficiency is

$$① \quad \eta_t = \frac{(\dot{W}_{cv}/\dot{m})}{(\dot{W}_{cv}/\dot{m})_s} = \frac{50.1}{68.66} = 0.73 (73\%)$$

- ① We cannot expect extreme accuracy when reading data from a generalized chart such as Fig. A-5, which affects the final calculated result.

Skills Developed

Ability to...

- use data from the generalized entropy departure chart to calculate the entropy production.
- use data from the generalized enthalpy and entropy departure charts to calculate isentropic turbine efficiency.
- use an iterative procedure to calculate the temperature at the end of an isentropic process using data from the generalized entropy departure chart.

QuickQUIZ

Determine the rate of entropy production, in kJ/K per kg of nitrogen flowing, assuming the ideal gas model. **Ans.** 0.061 kJ/kg · K.

11.8 *p*-*v*-*T* Relations for Gas Mixtures

Many systems of interest involve mixtures of two or more components. The principles of thermodynamics introduced thus far *are* applicable to systems involving mixtures, but to apply such principles requires that mixture properties be evaluated.

Since an unlimited variety of mixtures can be formed from a given set of pure components by varying the relative amounts present, the properties of mixtures are available in tabular, graphical, or equation forms only in particular cases such as air. Generally, special means are required for determining mixture properties.

In this section, methods for evaluating the *p*-*v*-*T* relations for pure components introduced in previous sections of the book are adapted to obtain plausible estimates for gas mixtures. In Sec. 11.9 some general aspects of property evaluation for multi-component systems are introduced.

To evaluate the properties of a mixture requires knowledge of the composition. The composition can be described by giving the *number of moles* (kmol or lbmol) of each component present. The total number of moles, n , is the sum of the number of moles of each of the components

$$n = n_1 + n_2 + \cdots + n_j = \sum_{i=1}^j n_i \quad (11.93)$$

The *relative amounts* of the components present can be described in terms of *mole fractions*. The mole fraction y_i of component i is defined as

$$y_i = \frac{n_i}{n} \quad (11.94)$$

Dividing each term of Eq. 11.93 by the total number of moles and using Eq. 11.94

$$1 = \sum_{i=1}^j y_i \quad (11.95)$$

That is, the sum of the mole fractions of all components present is equal to unity.

Most techniques for estimating mixture properties are empirical in character and are not derived from fundamental principles. The realm of validity of any particular technique can be established only by comparing predicted property values with empirical data. The brief discussion to follow is intended only to show how certain of the procedures for evaluating the *p*-*v*-*T* relations of pure components introduced previously can be extended to gas mixtures.

MIXTURE EQUATION OF STATE. One way the *p*-*v*-*T* relation for a gas mixture can be estimated is by applying to the overall mixture an equation of state such as introduced in Sec. 11.1. The constants appearing in the equation selected would be *mixture values* determined with empirical combining rules developed for the equation. For example, mixture values of the constants a and b for use in the van der Waals and Redlich-Kwong equations would be obtained using relations of the form

$$a = \left(\sum_{i=1}^j y_i a_i^{1/2} \right)^2, \quad b = \left(\sum_{i=1}^j y_i b_i \right) \quad (11.96)$$

where a_i and b_i are the values of the constants for component i and y_i is the mole fraction. Combination rules for obtaining mixture values for the constants in other equations of state also have been suggested.

KAY'S RULE. The *principle of corresponding states* method for single components introduced in Sec. 3.11.3 can be extended to mixtures by regarding the mixture as if it were a single pure component having critical properties calculated by one of several mixture rules. Perhaps the simplest of these, requiring only the determination of a mole fraction averaged critical temperature T_c and critical pressure p_c , is **Kay's rule**

TAKE NOTE...

The special case of *ideal gas mixtures* is considered in Secs. 12.1–12.4, with applications to *psychrometrics* in the second part of Chap. 12 and reacting mixtures in Chaps. 13 and 14.

$$T_c = \sum_{i=1}^j y_i T_{c,i}, \quad p_c = \sum_{i=1}^j y_i p_{c,i} \quad (11.97)$$

where $T_{c,i}$, $p_{c,i}$, and y_i are the critical temperature, critical pressure, and mole fraction of component i , respectively. Using T_c and p_c , the mixture compressibility factor Z is obtained as for a single pure component. The unknown quantity from among the pressure p , volume V , temperature T , and total number of moles n of the gas mixture can then be obtained by solving

$$Z = \frac{pV}{n\bar{R}T} \quad (11.98)$$

Mixture values for T_c and p_c also can be used to enter the generalized enthalpy departure and entropy departure charts introduced in Sec. 11.7.

additive pressure rule

ADDITIONAL PRESSURE RULE. Additional means for estimating $p-v-T$ relations for mixtures are provided by empirical mixture rules, of which several are found in the engineering literature. Among these are the *additive pressure* and *additive volume* rules. According to the **additive pressure rule**, the pressure of a gas mixture occupying volume V at temperature T is expressible as a sum of pressures exerted by the individual components:

$$p = p_1 + p_2 + p_3 + \dots]_{T,V} \quad (11.99a)$$

where the pressures p_1 , p_2 , etc. are evaluated by considering the respective components to be at the volume and temperature of the mixture. These pressures would be determined using tabular or graphical $p-v-T$ data or a suitable equation of state.

An alternative expression of the additive pressure rule in terms of compressibility factors can be obtained. Since component i is considered to be at the volume and temperature of the mixture, the compressibility factor Z_i for this component is $Z_i = p_i V / n \bar{R} T$, so the pressure p_i is

$$p_i = \frac{Z_i n_i \bar{R} T}{V}$$

Similarly, for the mixture

$$p = \frac{Z n \bar{R} T}{V}$$

Substituting these expressions into Eq. 11.99a and reducing gives the following relationship between the compressibility factors for the mixture Z and the mixture components Z_i

$$Z = \sum_{i=1}^j y_i Z_i]_{T,V} \quad (11.99b)$$

The compressibility factors Z_i are determined assuming that component i occupies the entire volume of the mixture at the temperature T .

additive volume rule

ADDITIONAL VOLUME RULE. The underlying assumption of the **additive volume rule** is that the volume V of a gas mixture at temperature T and pressure p is expressible as the sum of volumes occupied by the individual components:

$$V = V_1 + V_2 + V_3 + \dots]_{p,T} \quad (11.100a)$$

where the volumes V_1 , V_2 , etc. are evaluated by considering the respective components to be at the pressure and temperature of the mixture. These volumes would be determined from tabular or graphical $p-v-T$ data or a suitable equation of state.

An alternative expression of the additive volume rule in terms of compressibility factors can be obtained. Since component i is considered to be at the pressure and temperature of the mixture, the compressibility factor Z_i for this component is $Z_i = pV_i/n_i\bar{R}T$, so the volume V_i is

$$V_i = \frac{Z_i n_i \bar{R} T}{p}$$

Similarly, for the mixture

$$V = \frac{Z n \bar{R} T}{p}$$

Substituting these expressions into Eq. 11.100a and reducing gives

$$Z = \sum_{i=1}^j y_i Z_i]_{p,T} \quad (11.100b)$$

The compressibility factors Z_i are determined assuming that component i exists at the temperature T and pressure p of the mixture.

The next example illustrates alternative means for estimating the pressure of a gas mixture.

EXAMPLE 11.10

Estimating Mixture Pressure by Alternative Means

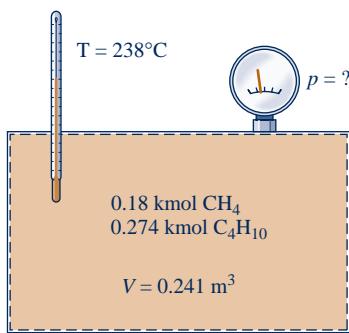
A mixture consisting of 0.18 kmol of methane (CH_4) and 0.274 kmol of butane (C_4H_{10}) occupies a volume of 0.241 m^3 at a temperature of 238°C . The experimental value for the pressure is 68.9 bar. Calculate the pressure, in bar, exerted by the mixture by using (a) the ideal gas equation of state, (b) Kay's rule together with the generalized compressibility chart, (c) the van der Waals equation, and (d) the rule of additive pressures employing the generalized compressibility chart. Compare the calculated values with the known experimental value.

SOLUTION

Known: A mixture of two specified hydrocarbons with known molar amounts occupies a known volume at a specified temperature.

Find: Determine the pressure, in bar, using four alternative methods, and compare the results with the experimental value.

Schematic and Given Data:



Engineering Model: As shown in the accompanying figure, the system is the mixture.

Fig. E11.10

Analysis: The total number of moles of mixture n is

$$n = 0.18 + 0.274 = 0.454 \text{ kmol}$$

Thus, the mole fractions of the methane and butane are, respectively

$$y_1 = 0.396 \quad \text{and} \quad y_2 = 0.604$$

The specific volume of the mixture on a molar basis is

$$\bar{v} = \frac{0.241 \text{ m}^3}{(0.18 + 0.274) \text{ kmol}} = 0.531 \frac{\text{m}^3}{\text{kmol}}$$

(a) Substituting values into the ideal gas equation of state

$$\begin{aligned} p &= \frac{\bar{R}T}{\bar{v}} = \frac{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(511 \text{ K})}{(0.531 \text{ m}^3/\text{kmol})} \left| \frac{1 \text{ bar}}{10^5 \text{ N/m}^2} \right| \\ &= 80.01 \text{ bar} \end{aligned}$$

(b) To apply Kay's rule, the critical temperature and pressure for each component are required. From Table A-1, for methane

$$T_{c1} = 191 \text{ K}, \quad p_{c1} = 46.4 \text{ bar}$$

and for butane

$$T_{c2} = 425 \text{ K}, \quad p_{c2} = 38.0 \text{ bar}$$

Thus, with Eqs. 11.97

$$T_c = y_1 T_{c1} + y_2 T_{c2} = (0.396)(191) + (0.604)(425) = 332.3 \text{ K}$$

$$p_c = y_1 p_{c1} + y_2 p_{c2} = (0.396)(46.4) + (0.604)(38.0) = 41.33 \text{ bar}$$

Treating the mixture as a pure component having the above values for the critical temperature and pressure, the following reduced properties are determined for the mixture:

$$\begin{aligned} T_R &= \frac{T}{T_c} = \frac{511}{332.3} = 1.54 \\ v'_R &= \frac{\bar{v} p_c}{\bar{R} T_c} = \frac{(0.531)(41.33)|10^5|}{(8314)(332.3)} \\ &= 0.794 \end{aligned}$$

Turning to Fig. A-2, $Z \approx 0.88$. The mixture pressure is then found from

$$\begin{aligned} p &= \frac{Z n \bar{R} T}{V} = Z \frac{\bar{R} T}{\bar{v}} = 0.88 \frac{(8314)(511)}{(0.531)|10^5|} \\ &= 70.4 \text{ bar} \end{aligned}$$

(c) Mixture values for the van der Waals constants can be obtained using Eqs. 11.96. This requires values of the van der Waals constants for each of the two mixture components. Table A-24 gives the following values for methane:

$$a_1 = 2.293 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2, \quad b_1 = 0.0428 \frac{\text{m}^3}{\text{kmol}}$$

Similarly, from Table A-24 for butane

$$a_2 = 13.86 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2, \quad b_2 = 0.1162 \frac{\text{m}^3}{\text{kmol}}$$

Then, the first of Eqs. 11.96 gives a mixture value for the constant a as

$$\begin{aligned} a &= (y_1 a_1^{1/2} + y_2 a_2^{1/2})^2 = [0.396(2.293)^{1/2} + 0.604(13.86)^{1/2}]^2 \\ &= 8.113 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2 \end{aligned}$$

Substituting into the second of Eqs. 11.96 gives a mixture value for the constant b

$$\begin{aligned} b &= y_1 b_1 + y_2 b_2 = (0.396)(0.0428) + (0.604)(0.1162) \\ &= 0.087 \frac{\text{m}^3}{\text{kmol}} \end{aligned}$$

Inserting the mixture values for a and b into the van der Waals equation together with known data

$$\begin{aligned} p &= \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2} \\ &= \frac{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(511 \text{ K})}{(0.531 - 0.087)(\text{m}^3/\text{kmol})} \left| \frac{1 \text{ bar}}{10^5 \text{ N/m}^2} \right| - \frac{8.113 \text{ bar} (\text{m}^3/\text{kmol})^2}{(0.531 \text{ m}^3/\text{kmol})^2} \\ &= 66.91 \text{ bar} \end{aligned}$$

(d) To apply the additive pressure rule with the generalized compressibility chart requires that the compressibility factor for each component be determined assuming that the component occupies the entire volume at the mixture temperature. With this assumption, the following reduced properties are obtained for methane

$$\begin{aligned} T_{R1} &= \frac{T}{T_{c1}} = \frac{511}{191} = 2.69 \\ v'_{R1} &= \frac{\bar{v}_1 p_{c1}}{\bar{R} T_{c1}} = \frac{(0.241 \text{ m}^3/0.18 \text{ kmol})(46.4 \text{ bar})}{(8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K})(191 \text{ K})} \left| \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right| = 3.91 \end{aligned}$$

With these reduced properties, Fig. A-2 gives $Z_1 \approx 1.0$.

Similarly, for butane

$$\begin{aligned} T_{R2} &= \frac{T}{T_{c2}} = \frac{511}{425} = 1.2 \\ v'_{R2} &= \frac{\bar{v}_2 p_{c2}}{\bar{R} T_{c2}} = \frac{(0.88)(38)|10^5|}{(8314)(425)} = 0.95 \end{aligned}$$

From Fig. A-2, $Z_2 \approx 0.8$.

The compressibility factor for the mixture determined from Eq. 11.99b is

$$Z = y_1 Z_1 + y_2 Z_2 = (0.396)(1.0) + (0.604)(0.8) = 0.88.$$

Accordingly, the same value for pressure as determined in part (b) using Kay's rule results: $p = 70.4$ bar.

In this particular example, the ideal gas equation of state gives a value for pressure that exceeds the experimental value by nearly 16%. Kay's rule and the rule of additive pressures give pressure values about 3% greater than the experimental value. The van der Waals equation with mixture values for the constants gives a pressure value about 3% less than the experimental value.

Skills Developed

Ability to...

- calculate the pressure of a gas mixture using four alternative methods.

QuickQUIZ

Convert the mixture analysis from a molar basis to a mass fraction basis. **Ans.** Methane: 0.153, Butane: 0.847.

11.9

Analyzing Multicomponent Systems

In the preceding section we considered means for evaluating the $p-v-T$ relation of gas mixtures by extending methods developed for pure components. The current section is devoted to the development of some general aspects of the properties of systems with two or more components. Primary emphasis is on the case of *gas mixtures*, but the methods developed also apply to *solutions*. When liquids and solids are under consideration, the term **solution** is sometimes used in place of mixture. The present discussion is limited to nonreacting mixtures or solutions in a single phase. The effects of chemical reactions and equilibrium between different phases are taken up in Chaps. 13 and 14.

To describe multicomponent systems, composition must be included in our thermodynamic relations. This leads to the definition and development of several new concepts, including the *partial molal property*, the *chemical potential*, and the *fugacity*.

TAKE NOTE...

Section 11.9 may be deferred until Secs. 12.1–12.4 have been studied.

solution

11.9.1 Partial Molal Properties

In the present discussion we introduce the concept of a *partial molal* property and illustrate its use. This concept plays an important role in subsequent discussions of multicomponent systems.

DEFINING PARTIAL MOLAL PROPERTIES. Any extensive thermodynamic property X of a single-phase, single-component system is a function of two independent intensive properties and the size of the system. Selecting temperature and pressure as the independent properties and the number of moles n as the measure of size, we have $X = X(T, p, n)$. For a single-phase, *multicomponent* system, the extensive property X must then be a function of temperature, pressure, and the number of moles of each component present, $X = X(T, p, n_1, n_2, \dots, n_j)$.

If each mole number is increased by a factor α , the size of the system increases by the same factor, and so does the value of the extensive property X . That is

$$\alpha X(T, p, n_1, n_2, \dots, n_j) = X(T, p, \alpha n_1, \alpha n_2, \dots, \alpha n_j)$$

Differentiating with respect to α while holding temperature, pressure, and the mole numbers fixed and using the chain rule on the right side gives

$$X = \frac{\partial X}{\partial(\alpha n_1)} n_1 + \frac{\partial X}{\partial(\alpha n_2)} n_2 + \dots + \frac{\partial X}{\partial(\alpha n_j)} n_j$$

This equation holds for all values of α . In particular, it holds for $\alpha = 1$. Setting $\alpha = 1$

$$X = \sum_{i=1}^j n_i \left. \frac{\partial X}{\partial n_i} \right|_{T, p, n_l} \quad (11.101)$$

where the subscript n_l denotes that all n 's except n_i are held fixed during differentiation.

partial molal property

The **partial molal property** \bar{X}_i is by definition

$$\bar{X}_i = \left. \frac{\partial X}{\partial n_i} \right|_{T, p, n_l} \quad (11.102)$$

The partial molal property \bar{X}_i is a property of the mixture and not simply a property of component i , for \bar{X}_i depends in general on temperature, pressure, *and* mixture composition: $\bar{X}_i(T, p, n_1, n_2, \dots, n_j)$. Partial molal properties are intensive properties of the mixture.

Introducing Eq. 11.102, Eq. 11.101 becomes

$$X = \sum_{i=1}^j n_i \bar{X}_i \quad (11.103)$$

This equation shows that the extensive property X can be expressed as a weighted sum of the partial molal properties \bar{X}_i .

Selecting the extensive property X in Eq. 11.103 to be volume, internal energy, enthalpy, and entropy, respectively, gives

$$V = \sum_{i=1}^j n_i \bar{V}_i, \quad U = \sum_{i=1}^j n_i \bar{U}_i, \quad H = \sum_{i=1}^j n_i \bar{H}_i, \quad S = \sum_{i=1}^j n_i \bar{S}_i \quad (11.104)$$

where \bar{V}_i , \bar{U}_i , \bar{H}_i , \bar{S}_i denote the partial molal volume, internal energy, enthalpy, and entropy. Similar expressions can be written for the Gibbs function G and the Helmholtz function Ψ . Moreover, the relations between these extensive properties: $H = U + pV$, $G = H - TS$, $\Psi = U - TS$ can be differentiated with respect to n_i while holding temperature, pressure, and the remaining n 's constant to produce corresponding relations

among partial molal properties: $\bar{H}_i = \overline{U}_i + p\bar{V}_i$, $\bar{G}_i = \bar{H}_i - T\bar{S}_i$, $\bar{\Psi}_i = \overline{U}_i - T\bar{S}_i$, where \bar{G}_i and $\bar{\Psi}_i$ are the partial molal Gibbs function and Helmholtz function, respectively. Several additional relations involving partial molal properties are developed later in this section.

EVALUATING PARTIAL MOLAL PROPERTIES. Partial molal properties can be evaluated by several methods, including the following:

- If the property X can be measured, \bar{X}_i can be found by extrapolating a plot giving $(\Delta X / \Delta n_i)_{T, p, n_l}$ versus Δn_i . That is

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i} \right)_{T, p, n_l} = \lim_{\Delta n_i \rightarrow 0} \left(\frac{\Delta X}{\Delta n_i} \right)_{T, p, n_l}$$

- If an expression for X in terms of its independent variables is known, \bar{X}_i can be evaluated by differentiation. The derivative can be determined analytically if the function is expressed analytically or found numerically if the function is in tabular form.
- When suitable data are available, a simple graphical procedure known as the **method of intercepts** can be used to evaluate partial molal properties. In principle, the method can be applied for any extensive property. To introduce this method, let us consider the volume of a system consisting of two components, A and B. For this system, Eq. 11.103 takes the form

$$V = n_A \bar{V}_A + n_B \bar{V}_B$$

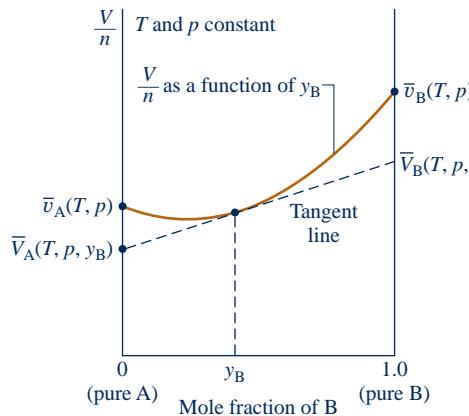
where \bar{V}_A and \bar{V}_B are the partial molal volumes of A and B, respectively. Dividing by the number of moles of mixture n

$$\frac{V}{n} = y_A \bar{V}_A + y_B \bar{V}_B$$

where y_A and y_B denote the mole fractions of A and B, respectively. Since $y_A + y_B = 1$, this becomes

$$\frac{V}{n} = (1 - y_B) \bar{V}_A + y_B \bar{V}_B = \bar{V}_A + y_B (\bar{V}_B - \bar{V}_A)$$

This equation provides the basis for the method of intercepts. For example, refer to Fig. 11.5, in which V/n is plotted as a function of y_B at constant T and p . At a specified value for y_B , a tangent to the curve is shown on the figure. When extrapolated, the tangent line intersects the axis on the left at \bar{v}_A and the axis on the right at \bar{v}_B . These values for the partial molal volumes correspond to the particular specifications for T , p , and y_B . At fixed temperature and pressure, \bar{V}_A and \bar{V}_B vary with y_B and are not equal to the molar specific volumes of *pure* A and *pure* B, denoted on the figure as \bar{v}_A and \bar{v}_B , respectively. The values of \bar{v}_A and \bar{v}_B are fixed by temperature and pressure only.



method of intercepts

Fig. 11.5 Illustration of the evaluation of partial molal volumes by the method of intercepts.

EXTENSIVE PROPERTY CHANGES ON MIXING. Let us conclude the present discussion by evaluating the change in volume on mixing of pure components at the same temperature and pressure, a result for which an application is given in the discussion of Eq. 11.135. The total volume of the pure components before mixing is

$$V_{\text{components}} = \sum_{i=1}^j n_i \bar{v}_i$$

where \bar{v}_i is the molar specific volume of pure component i . The volume of the mixture is

$$V_{\text{mixture}} = \sum_{i=1}^j n_i \bar{V}_i$$

where \bar{V}_i is the partial molal volume of component i in the mixture. The volume change on mixing is

$$\Delta V_{\text{mixing}} = V_{\text{mixture}} - V_{\text{components}} = \sum_{i=1}^j n_i \bar{V}_i - \sum_{i=1}^j n_i \bar{v}_i$$

or

$$\Delta V_{\text{mixing}} = \sum_{i=1}^j n_i (\bar{V}_i - \bar{v}_i) \quad (11.105)$$

Similar results can be obtained for other extensive properties, for example,

$$\begin{aligned} \Delta U_{\text{mixing}} &= \sum_{i=1}^j n_i (\bar{U}_i - \bar{u}_i) \\ \Delta H_{\text{mixing}} &= \sum_{i=1}^j n_i (\bar{H}_i - \bar{h}_i) \\ \Delta S_{\text{mixing}} &= \sum_{i=1}^j n_i (\bar{S}_i - \bar{s}_i) \end{aligned} \quad (11.106)$$

In Eqs. 11.106, \bar{u}_i , \bar{h}_i , and \bar{s}_i denote the molar internal energy, enthalpy, and entropy of pure component i , respectively. The symbols \bar{U}_i , \bar{H}_i , and \bar{S}_i denote the respective partial molal properties.

11.9.2 Chemical Potential

chemical potential

Of the partial molal properties, the partial molal Gibbs function is particularly useful in describing the behavior of mixtures and solutions. This quantity plays a central role in the criteria for both chemical and phase equilibrium (Chap. 14). Because of its importance in the study of multicomponent systems, the partial molal Gibbs function of component i is given a special name and symbol. It is called the **chemical potential** of component i and symbolized by μ_i

$$\mu_i = \bar{G}_i = \left. \frac{\partial G}{\partial n_i} \right|_{T, p, n_l} \quad (11.107)$$

Like temperature and pressure, the chemical potential μ_i is an *intensive* property.

Applying Eq. 11.103 together with Eq. 11.107, the following expression can be written:

$$G = \sum_{i=1}^j n_i \mu_i \quad (11.108)$$

Expressions for the internal energy, enthalpy, and Helmholtz function can be obtained from Eq. 11.108, using the definitions $H = U + pV$, $G = H - TS$, and $\Psi = U - TS$. They are

$$\begin{aligned} U &= TS - pV + \sum_{i=1}^j n_i \mu_i \\ H &= TS + \sum_{i=1}^j n_i \mu_i \\ \Psi &= -pV + \sum_{i=1}^j n_i \mu_i \end{aligned} \quad (11.109)$$

Other useful relations can be obtained as well. Forming the differential of $G(T, p, n_1, n_2, \dots, n_j)$

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T,n} dp + \left(\frac{\partial G}{\partial T} \right)_{p,n} dT + \sum_{i=1}^j \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_i} dn_i \quad (11.110)$$

The subscripts n in the first two terms indicate that all n 's are held fixed during differentiation. Since this implies fixed composition, it follows from Eqs. 11.30 and 11.31 (Sec. 11.3.2) that

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,n} \quad \text{and} \quad -S = \left(\frac{\partial G}{\partial T} \right)_{p,n} \quad (11.111)$$

With Eqs. 11.107 and 11.111, Eq. 11.110 becomes

$$dG = V dp - S dT + \sum_{i=1}^j \mu_i dn_i \quad (11.112)$$

which for a multicomponent system is the counterpart of Eq. 11.23.

Another expression for dG is obtained by forming the differential of Eq. 11.108. That is

$$dG = \sum_{i=1}^j n_i d\mu_i + \sum_{i=1}^j \mu_i dn_i$$

Combining this equation with Eq. 11.112 gives the **Gibbs–Duhem equation**

Gibbs–Duhem equation

$$\sum_{i=1}^j n_i d\mu_i = V dp - S dT \quad (11.113)$$

11.9.3 • Fundamental Thermodynamic Functions for Multicomponent Systems

A *fundamental thermodynamic function* provides a complete description of the thermodynamic state of a system. In principle, all properties of interest can be determined from such a function by differentiation and/or combination. Reviewing the developments of Sec. 11.9.2, we see that a function $G(T, p, n_1, n_2, \dots, n_j)$ is a fundamental thermodynamic function for a multicomponent system.

Functions of the form $U(S, V, n_1, n_2, \dots, n_j)$, $H(S, p, n_1, n_2, \dots, n_j)$, and $\Psi(T, V, n_1, n_2, \dots, n_j)$ also can serve as fundamental thermodynamic functions for multicomponent systems. To demonstrate this, first form the differential of each of Eqs. 11.109 and use the Gibbs–Duhem equation, Eq. 11.113, to reduce the resultant expressions to obtain

$$dU = T dS - p dV + \sum_{i=1}^j \mu_i dn_i \quad (11.114a)$$

$$dH = T dS + V dp + \sum_{i=1}^j \mu_i dn_i \quad (11.114b)$$

$$d\Psi = -p dV - S dT + \sum_{i=1}^j \mu_i dn_i \quad (11.114c)$$

For multicomponent systems, these are the counterparts of Eqs. 11.18, 11.19, and 11.22, respectively.

The differential of $U(S, V, n_1, n_2, \dots, n_j)$ is

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n} dV + \sum_{i=1}^j \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_l} dn_i$$

Comparing this expression term by term with Eq. 11.114a, we have

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, n}, \quad -p = \left(\frac{\partial U}{\partial V} \right)_{S, n}, \quad \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_l} \quad (11.115a)$$

That is, the temperature, pressure, and chemical potentials can be obtained by differentiation of $U(S, V, n_1, n_2, \dots, n_j)$. The first two of Eqs. 11.115a are the counterparts of Eqs. 11.24 and 11.25.

A similar procedure using a function of the form $H(S, p, n_1, n_2, \dots, n_j)$ together with Eq. 11.114b gives

$$T = \left(\frac{\partial H}{\partial S} \right)_{p, n}, \quad V = \left(\frac{\partial H}{\partial p} \right)_{S, n}, \quad \mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S, p, n_l} \quad (11.115b)$$

where the first two of these are the counterparts of Eqs. 11.26 and 11.27. Finally, with $\Psi(S, V, n_1, n_2, \dots, n_j)$ and Eq. 11.114c

$$-p = \left(\frac{\partial \Psi}{\partial V} \right)_{T, n}, \quad -S = \left(\frac{\partial \Psi}{\partial T} \right)_{V, n}, \quad \mu_i = \left(\frac{\partial \Psi}{\partial n_i} \right)_{T, V, n_l} \quad (11.115c)$$

The first two of these are the counterparts of Eqs. 11.28 and 11.29. With each choice of fundamental function, the remaining extensive properties can be found by combination using the definitions $H = U + pV$, $G = H - TS$, $\Psi = U - TS$.

The foregoing discussion of fundamental thermodynamic functions has led to several property relations for multicomponent systems that correspond to relations obtained previously. In addition, counterparts of the Maxwell relations can be obtained by equating mixed second partial derivatives. For example, the first two terms on the right of Eq. 11.112 give

$$\left(\frac{\partial V}{\partial T} \right)_{p, n} = -\left(\frac{\partial S}{\partial p} \right)_{T, n} \quad (11.116)$$

which corresponds to Eq. 11.35. Numerous relationships involving chemical potentials can be derived similarly by equating mixed second partial derivatives. An important example from Eq. 11.112 is

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T, n} = \left(\frac{\partial V}{\partial n_i} \right)_{T, p, n_l}$$

Recognizing the right side of this equation as the partial molal volume, we have

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T, n} = \bar{V}_i \quad (11.117)$$

This relationship is applied in the development of Eqs. 11.126.

The present discussion concludes by listing four different expressions derived above for the chemical potential in terms of other properties. In the order obtained, they are

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_l} = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_l} = \left(\frac{\partial H}{\partial n_i} \right)_{S, p, n_l} = \left(\frac{\partial \Psi}{\partial n_i} \right)_{T, V, n_l} \quad (11.118)$$

Only the first of these partial derivatives is a partial molal property, however, for the term *partial molal* applies only to partial derivatives where the independent

variables are temperature, pressure, and the number of moles of each component present.

11.9.4 • Fugacity

The chemical potential plays an important role in describing multicomponent systems. In some instances, however, it is more convenient to work in terms of a related property, the fugacity. The fugacity is introduced in the present discussion.

Single-Component Systems

Let us begin by taking up the case of a system consisting of a single component. For this case, Eq. 11.108 reduces to give

$$G = n\mu \quad \text{or} \quad \mu = \frac{G}{n} = \bar{g}$$

That is, for a pure component the chemical potential equals the Gibbs function per mole. With this equation, Eq. 11.30 written on a per mole basis becomes

$$\left. \frac{\partial \mu}{\partial p} \right)_T = \bar{v} \quad (11.119)$$

For the special case of an ideal gas, $\bar{v} = \bar{R}T/p$, and Eq. 11.119 assumes the form

$$\left. \frac{\partial \mu^*}{\partial p} \right)_T = \frac{\bar{R}T}{p}$$

where the asterisk denotes ideal gas. Integrating at constant temperature

$$\mu^* = \bar{R}T \ln p + C(T) \quad (11.120)$$

where $C(T)$ is a function of integration. Since the pressure p can take on values from zero to plus infinity, the $\ln p$ term of this expression, and thus the chemical potential, has an inconvenient range of values from minus infinity to plus infinity. Equation 11.120 also shows that the chemical potential can be determined only to within an arbitrary constant.

INTRODUCING FUGACITY. Because of the above considerations, it is advantageous for many types of thermodynamic analyses to use fugacity in place of the chemical potential, for it is a well-behaved function that can be more conveniently evaluated. We introduce the **fugacity** f by the expression

$$\mu = \bar{R}T \ln f + C(T) \quad (11.121)$$

fugacity

Comparing Eq. 11.121 with Eq. 11.120, the fugacity is seen to play the same role in the general case as pressure plays in the ideal gas case. Fugacity has the same units as pressure.

Substituting Eq. 11.121 into Eq. 11.119 gives

$$\bar{R}T \left(\frac{\partial \ln f}{\partial p} \right)_T = \bar{v} \quad (11.122)$$

Integration of Eq. 11.122 while holding temperature constant can determine the fugacity only to within a constant term. However, since ideal gas behavior is approached as pressure tends to zero, the constant term can be fixed by requiring that the fugacity of a pure component equals the pressure in the limit of zero pressure. That is

$$\lim_{p \rightarrow 0} \frac{f}{p} = 1 \quad (11.123)$$

Equations 11.122 and 11.123 then completely determine the fugacity function.

EVALUATING FUGACITY. Let us consider next how the fugacity can be evaluated. With $Z = p\bar{v}/\bar{R}T$, Eq. 11.122 becomes

$$\bar{R}T \left(\frac{\partial \ln f}{\partial p} \right)_T = \frac{\bar{R}TZ}{p}$$

or

$$\left(\frac{\partial \ln f}{\partial p} \right)_T = \frac{Z}{p}$$

Subtracting $1/p$ from both sides and integrating from pressure p' to pressure p at fixed temperature T

$$[\ln f - \ln p]_{p'}^p = \int_{p'}^p (Z - 1)d \ln p$$

or

$$\left[\ln \frac{f}{p} \right]_{p'}^p = \int_{p'}^p (Z - 1)d \ln p$$

Taking the limit as p' tends to zero and applying Eq. 11.123 results in

$$\ln \frac{f}{p} = \int_0^p (Z - 1)d \ln p$$

When expressed in terms of the reduced pressure, $p_R = p/p_c$, the above equation is

$$\ln \frac{f}{p} = \int_0^{p_R} (Z - 1)d \ln p_R \quad (11.124)$$

Since the compressibility factor Z depends on the reduced temperature T_R and reduced pressure p_R , it follows that the right side of Eq. 11.124 depends on these properties only. Accordingly, the quantity $\ln f/p$ is a function only of these two reduced properties. Using a generalized equation of state giving Z as a function of T_R and p_R , $\ln f/p$ can readily be evaluated with a computer. Tabular representations are also found in the literature. Alternatively, the graphical representation presented in Fig. A-6 can be employed.

► **FOR EXAMPLE** to illustrate the use of Fig. A-6, consider two states of water vapor at the same temperature, 400°C. At state 1 the pressure is 200 bar, and at state 2 the pressure is 240 bar. The change in the chemical potential between these states can be determined using Eq. 11.121 as

$$\mu_2 - \mu_1 = \bar{R}T \ln \frac{f_2}{f_1} = \bar{R}T \ln \left(\frac{f_2}{f_1} \frac{p_2}{p_1} \frac{p_1}{f_1} \right)$$

Using the critical temperature and pressure of water from Table A-1, at state 1 $p_{R1} = 0.91$, $T_{R1} = 1.04$, and at state 2 $p_{R2} = 1.09$, $T_{R2} = 1.04$. By inspection of Fig. A-6, $f_1/p_1 = 0.755$ and $f_2/p_2 = 0.7$. Inserting values in the above equation

$$\mu_2 - \mu_1 = (8.314)(673.15) \ln \left[(0.7) \left(\frac{240}{200} \right) \left(\frac{1}{0.755} \right) \right] = 597 \text{ kJ/kmol}$$

For a pure component, the chemical potential equals the Gibbs function per mole, $\bar{g} = \bar{h} - T\bar{s}$. Since the temperature is the same at states 1 and 2, the change in the chemical potential can be expressed as $\mu_2 - \mu_1 = \bar{h}_2 - \bar{h}_1 - T(\bar{s}_2 - \bar{s}_1)$. Using steam table data, the value obtained with this expression is 597 kJ/kmol, which agrees with the value determined from the generalized fugacity coefficient chart. ◀◀◀◀◀

Multicomponent Systems

The fugacity of a component i in a mixture can be defined by a procedure that parallels the definition for a pure component. For a pure component, the development

begins with Eq. 11.119, and the fugacity is introduced by Eq. 11.121. These are then used to write the pair of equations, Eqs. 11.122 and 11.123, from which the fugacity can be evaluated. For a mixture, the development begins with Eq. 11.117, the counterpart of Eq. 11.119, and the fugacity \bar{f}_i of component i is introduced by

$$\mu_i = \bar{R}T \ln \bar{f}_i + C_i(T) \quad (11.125)$$

which parallels Eq. 11.121. The pair of equations that allow the **fugacity of a mixture component**, \bar{f}_i , to be evaluated are

$$\bar{R}T \left(\frac{\partial \ln \bar{f}_i}{\partial p} \right)_{T,n} = \bar{V}_i \quad (11.126a)$$

$$\lim_{p \rightarrow 0} \left(\frac{\bar{f}_i}{y_i p} \right) = 1 \quad (11.126b)$$

fugacity of a mixture component

The symbol \bar{f}_i denotes the fugacity of component i in the *mixture* and should be carefully distinguished in the presentation to follow from f_i , which denotes the fugacity of *pure* i .

DISCUSSION. Referring to Eq. 11.126b, note that in the ideal gas limit the fugacity \bar{f}_i is not required to equal the pressure p as for the case of a pure component, but to equal the quantity $y_i p$. To see that this is the appropriate limiting quantity, consider a system consisting of a mixture of gases occupying a volume V at pressure p and temperature T . If the overall mixture behaves as an ideal gas, we can write

$$p = \frac{n\bar{R}T}{V} \quad (11.127)$$

where n is the total number of moles of mixture. Recalling from Sec. 3.12.3 that an ideal gas can be regarded as composed of molecules that exert negligible forces on one another and whose volume is negligible relative to the total volume, we can think of each component i as behaving as if it were an ideal gas alone at the temperature T and volume V . Thus, the pressure exerted by component i would not be the mixture pressure p but the pressure p_i given by

$$p_i = \frac{n_i \bar{R}T}{V} \quad (11.128)$$

where n_i is the number of moles of component i . Dividing Eq. 11.128 by Eq. 11.127

$$\frac{p_i}{p} = \frac{n_i \bar{R}T/V}{n \bar{R}T/V} = \frac{n_i}{n} = y_i$$

On rearrangement

$$p_i = y_i p \quad (11.129)$$

Accordingly, the quantity $y_i p$ appearing in Eq. 11.126b corresponds to the pressure p_i . Summing both sides of Eq. 11.129, we obtain

$$\sum_{i=1}^j p_i = \sum_{i=1}^j y_i p = p \sum_{i=1}^j y_i$$

Or, since the sum of the mole fractions equals unity

$$p = \sum_{i=1}^j p_i \quad (11.130)$$

In words, Eq. 11.130 states that the sum of the pressures p_i equals the mixture pressure. This gives rise to the designation *partial pressure* for p_i . With this background, we now see that Eq. 11.126b requires the fugacity of component i to approach the partial pressure of component i as pressure p tends to zero. Comparing Eqs. 11.130

and 11.99a, we also see that the *additive pressure rule* is exact for ideal gas mixtures. This special case is considered further in Sec. 12.2 under the heading *Dalton model*.

EVALUATING FUGACITY IN A MIXTURE. Let us consider next how the fugacity of component i in a mixture can be expressed in terms of quantities that can be evaluated. For a pure component i , Eq. 11.122 gives

$$\bar{R}T \left(\frac{\partial \ln f_i}{\partial p} \right)_T = \bar{v}_i \quad (11.131)$$

where \bar{v}_i is the molar specific volume of pure i . Subtracting Eq. 11.131 from Eq. 11.126a

$$\bar{R}T \left[\frac{\partial \ln (\bar{f}_i/f_i)}{\partial p} \right]_{T,n} = \bar{V}_i - \bar{v}_i \quad (11.132)$$

Integrating from pressure p' to pressure p at fixed temperature and mixture composition

$$\bar{R}T \left[\ln \left(\frac{\bar{f}_i}{f_i} \right) \right]_{p'}^p = \int_{p'}^p (\bar{V}_i - \bar{v}_i) dp$$

In the limit as p' tends to zero, this becomes

$$\bar{R}T \left[\ln \left(\frac{\bar{f}_i}{f_i} \right) - \lim_{p' \rightarrow 0} \ln \left(\frac{\bar{f}_i}{f_i} \right) \right] = \int_0^p (\bar{V}_i - \bar{v}_i) dp$$

Since $f_i \rightarrow p'$ and $\bar{f}_i \rightarrow y_i p'$ as pressure p' tends to zero

$$\lim_{p' \rightarrow 0} \ln \left(\frac{\bar{f}_i}{f_i} \right) \rightarrow \ln \left(\frac{y_i p'}{p'} \right) = \ln y_i$$

Therefore, we can write

$$\bar{R}T \left[\ln \left(\frac{\bar{f}_i}{f_i} \right) - \ln y_i \right] = \int_0^p (\bar{V}_i - \bar{v}_i) dp$$

or

$$\bar{R}T \ln \left(\frac{\bar{f}_i}{y_i f_i} \right) = \int_0^p (\bar{V}_i - \bar{v}_i) dp \quad (11.133)$$

in which \bar{f}_i is the fugacity of component i at pressure p in a mixture of given composition at a given temperature, and f_i is the fugacity of pure i at the same temperature and pressure. Equation 11.133 expresses the relation between \bar{f}_i and f_i in terms of the difference between \bar{V}_i and \bar{v}_i , a measurable quantity.

11.9.5 Ideal Solution

ideal solution

The task of evaluating the fugacities of the components in a mixture is considerably simplified when the mixture can be modeled as an ideal solution. An **ideal solution** is a mixture for which

$$\bar{f}_i = y_i f_i \quad (\text{ideal solution}) \quad (11.134)$$

Lewis–Randall rule

Equation 11.134, known as the **Lewis–Randall rule**, states that the fugacity of each component in an ideal solution is equal to the product of its mole fraction and the fugacity of the pure component at the same temperature, pressure, and state of aggregation (gas, liquid, or solid) as the mixture. Many gaseous mixtures at low to moderate pressures are adequately modeled by the Lewis–Randall rule. The ideal gas mixtures

considered in Chap. 12 are an important special class of such mixtures. Some liquid solutions also can be modeled with the Lewis–Randall rule.

As consequences of the definition of an ideal solution, the following characteristics are exhibited:

- Introducing Eq. 11.134 into Eq. 11.132, the left side vanishes, giving $\bar{V}_i - \bar{v}_i = 0$, or

$$\bar{V}_i = \bar{v}_i \quad (11.135)$$

Thus, the partial molal volume of each component in an ideal solution is equal to the molar specific volume of the corresponding pure component at the same temperature and pressure. When Eq. 11.135 is introduced in Eq. 11.105, it can be concluded that there is no volume change on mixing pure components to form an ideal solution.

With Eq. 11.135, the volume of an ideal solution is

$$V = \sum_{i=1}^j n_i \bar{V}_i = \sum_{i=1}^j n_i \bar{v}_i = \sum_{i=1}^j V_i \quad (\text{ideal solution}) \quad (11.136)$$

where V_i is the volume that pure component i would occupy when at the temperature and pressure of the mixture. Comparing Eqs. 11.136 and 11.100a, the *additive volume rule* is seen to be exact for ideal solutions.

- It also can be shown that the partial molal internal energy of each component in an ideal solution is equal to the molar internal energy of the corresponding pure component at the same temperature and pressure. A similar result applies for enthalpy. In symbols

$$\bar{U}_i = \bar{u}_i, \quad \bar{H}_i = \bar{h}_i \quad (11.137)$$

With these expressions, it can be concluded from Eqs. 11.106 that there is no change in internal energy or enthalpy on mixing pure components to form an ideal solution.

With Eqs. 11.137, the internal energy and enthalpy of an ideal solution are

$$U = \sum_{i=1}^j n_i \bar{u}_i \quad \text{and} \quad H = \sum_{i=1}^j n_i \bar{h}_i \quad (\text{ideal solution}) \quad (11.138)$$

where \bar{u}_i and \bar{h}_i denote, respectively, the molar internal energy and enthalpy of pure component i at the temperature and pressure of the mixture.

Although there is no change in V , U , or H on mixing pure components to form an ideal solution, we expect an entropy increase to result from the *adiabatic* mixing of different pure components because such a process is irreversible: The separation of the mixture into the pure components would never occur spontaneously. The entropy change on adiabatic mixing is considered further for the special case of ideal gas mixtures in Sec. 12.4.2.

The Lewis–Randall rule requires that the fugacity of mixture component i be evaluated in terms of the fugacity of pure component i at the same temperature and pressure as the mixture and in the *same state of aggregation*. For example, if the mixture were a gas at T, p , then f_i would be determined for pure i at T, p and as a gas. However, at certain temperatures and pressures of interest a component of a gaseous mixture may, as a pure substance, be a liquid or solid. An example is an air–water vapor mixture at 20°C (68°F) and 1 atm. At this temperature and pressure, water exists not as a vapor but as a liquid. Although not considered here, means have been developed that allow the ideal solution model to be useful in such cases.

11.9.6 Chemical Potential for Ideal Solutions

The discussion of multicomponent systems concludes with the introduction of expressions for evaluating the chemical potential for ideal solutions used in Sec. 14.3.3.

Consider a reference state where component i of a multicomponent system is pure at the temperature T of the system and a reference-state pressure p_{ref} . The difference in the chemical potential of i between a specified state of the multicomponent system and the reference state is obtained with Eq. 11.125 as

$$\mu_i - \mu_i^\circ = \bar{R}T \ln \frac{\bar{f}_i}{f_i^\circ} \quad (11.139)$$

activity

where the superscript \circ denotes property values at the reference state. The fugacity ratio appearing in the logarithmic term is known as the **activity**, a_i , of component i in the mixture. That is

$$a_i = \frac{\bar{f}_i}{f_i^\circ} \quad (11.140)$$

For subsequent applications, it suffices to consider the case of gaseous mixtures. For gaseous mixtures, p_{ref} is specified as 1 atm, so μ_i° and f_i° in Eq. 11.140 are, respectively, the chemical potential and fugacity of pure i at temperature T and 1 atm.

Since the chemical potential of a pure component equals the Gibbs function per mole, Eq. 11.139 can be written as

$$\mu_i = \bar{g}_i^\circ + \bar{R}T \ln a_i \quad (11.141)$$

where \bar{g}_i° is the Gibbs function per mole of pure component i evaluated at temperature T and 1 atm: $\bar{g}_i^\circ = \bar{g}_i(T, 1 \text{ atm})$.

For an ideal solution, the Lewis–Randall rule applies and the activity is

$$a_i = \frac{y_i f_i}{f_i^\circ} \quad (11.142)$$

where f_i is the fugacity of pure component i at temperature T and pressure p . Introducing Eq. 11.142 into Eq. 11.141

$$\mu_i = \bar{g}_i^\circ + \bar{R}T \ln \frac{y_i f_i}{f_i^\circ}$$

or

$$\mu_i = \bar{g}_i^\circ + \bar{R}T \ln \left[\left(\frac{f_i}{p} \right) \left(\frac{p_{\text{ref}}}{f_i^\circ} \right) \frac{y_i p}{p_{\text{ref}}} \right] \quad (\text{ideal solution}) \quad (11.143)$$

In principle, the ratios of fugacity to pressure shown underlined in this equation can be evaluated from Eq. 11.124 or the generalized fugacity chart, Fig. A-6, developed from it. If component i behaves as an ideal gas at both T, p and T, p_{ref} , we have $f_i/p = f_i^\circ/p_{\text{ref}} = 1$; Eq. 11.143 then reduces to

$$\mu_i = \bar{g}_i^\circ + \bar{R}T \ln \frac{y_i p}{p_{\text{ref}}} \quad (\text{ideal gas}) \quad (11.144)$$

► CHAPTER SUMMARY AND STUDY GUIDE

In this chapter, we introduce thermodynamic relations that allow u , h , and s as well as other properties of simple compressible systems to be evaluated using property data that are more readily measured. The emphasis is on systems involving a single chemical species such as water or a mixture such as air. An intro-

duction to general property relations for mixtures and solutions is also included.

Equations of state relating p , v , and T are considered, including the virial equation and examples of two-constant and multi-constant equations. Several important property relations based

on the mathematical characteristics of exact differentials are developed, including the Maxwell relations. The concept of a fundamental thermodynamic function is discussed. Means for evaluating changes in specific internal energy, enthalpy, and entropy are developed and applied to phase change and to single-phase processes. Property relations are introduced involving the volume expansivity, isothermal and isentropic compressibilities, velocity of sound, specific heats and specific heat ratio, and the Joule–Thomson coefficient.

Additionally, we describe how tables of thermodynamic properties are constructed using the property relations and methods developed in this chapter. Such procedures also provide the basis for data retrieval by computer software. Also described are means for using the generalized enthalpy and entropy departure charts and the generalized fugacity coefficient chart to evaluate enthalpy, entropy, and fugacity, respectively.

We also consider $p-v-T$ relations for gas mixtures of known composition, including Kay's rule. The chapter concludes with a discussion of property relations for multicomponent systems, including partial molal properties, chemical potential, fugacity, and activity. Ideal solutions and the Lewis–Randall rule are introduced as a part of that presentation.

The following checklist provides a study guide for this chapter. When your study of the text and end-of-chapter exercises has been completed you should be able to write out the meanings of the terms listed in the margins throughout the chapter and understand each of the related concepts. The subset of key

concepts listed below is particularly important. Additionally, for systems involving a single species you should be able to

- ▶ calculate $p-v-T$ data using equations of state such as the Redlich–Kwong and Benedict–Webb–Rubin equations.
- ▶ use the 16 property relations summarized in Table 11.1 and explain how the relations are obtained.
- ▶ evaluate Δs , Δu , and Δh , using the Clapeyron equation when considering phase change, and using equations of state and specific heat relations when considering single phases.
- ▶ use the property relations introduced in Sec. 11.5, such as those involving the specific heats, the volume expansivity, and the Joule–Thomson coefficient.
- ▶ explain how tables of thermodynamic properties, such as Tables A-2 through A-18, are constructed.
- ▶ use the generalized enthalpy and entropy departure charts, Figs. A-4 and A-5, to evaluate Δh and Δs .

For a *gas mixture* of known composition, you should be able to

- ▶ apply the methods introduced in Sec. 11.8 for relating pressure, specific volume, and temperature—Kay's rule, for example.

For *multicomponent systems*, you should be able to

- ▶ evaluate extensive properties in terms of the respective partial molal properties.
- ▶ evaluate partial molal volumes using the *method of intercepts*.
- ▶ evaluate fugacity using data from the generalized fugacity coefficient chart, Fig. A-6.
- ▶ apply the ideal solution model.

► KEY ENGINEERING CONCEPTS

equation of state, p. 632
exact differential, p. 638
test for exactness, p. 638
Helmholtz function, p. 642
Gibbs function, p. 642
Maxwell relations, p. 644

fundamental thermodynamic function, p. 647
Clapeyron equation, p. 649
Joule–Thomson coefficient, p. 661
enthalpy departure, p. 669
entropy departure, p. 672

Kay's rule, p. 675
method of intercepts, p. 681
chemical potential, p. 682
fugacity, p. 685
Lewis–Randall rule, p. 688

► KEY EQUATIONS

Equations of State

$Z = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \dots$	(11.1) p. 632	Virial equation of state
$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$	(11.2) p. 633	van der Waals equation of state
$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v} + b)T^{1/2}}$	(11.7) p. 635	Redlich–Kwong equation of state

Mathematical Relations for Properties

$\frac{\partial}{\partial y} \left[\left(\frac{\partial z}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial x} \left[\left(\frac{\partial z}{\partial y} \right)_x \right]_y$ $\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$	(11.14a) p. 638 (11.14b) p. 638	Test for exactness
$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1$ $\left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z = -1$	(11.15) p. 639 (11.16) p. 639	Important relations among partial derivatives of properties
Table 11.1	(11.24–11.36) p. 644	Summary of property relations from exact differentials

Expressions for Δu , Δh , and Δs

$\left(\frac{dp}{dT} \right)_{\text{sat}} = \frac{h_g - h_f}{T(v_g - v_f)}$	(11.40) p. 649	Clapeyron equation
$s_2 - s_1 = \int_1^2 \frac{c_v}{T} dT + \int_1^2 \left(\frac{\partial p}{\partial T} \right)_v dv$ $u_2 - u_1 = \int_1^2 c_v dT + \int_1^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv$	(11.50) p. 653 (11.51) p. 653	Expressions for changes in s and u with T and v as independent variables
$s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT - \int_1^2 \left(\frac{\partial v}{\partial T} \right)_p dp$ $h_2 - h_1 = \int_1^2 c_p dT + \int_1^2 \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$	(11.59) p. 654 (11.60) p. 655	Expressions for changes in s and h with T and p as independent variables
$\bar{h}_2 - \bar{h}_1 = \bar{h}_2^* - \bar{h}_1^* - \bar{R}T_c \left[\left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_2 - \left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_1 \right]$ $\bar{s}_2 - \bar{s}_1 = \bar{s}_2^* - \bar{s}_1^* - \bar{R} \left[\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_2 - \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}} \right)_1 \right]$	(11.85) p. 670 (11.92) p. 672	Evaluating enthalpy and entropy changes in terms of generalized enthalpy and entropy departures and data from Figs. A-4 and A-5, respectively

Additional Thermodynamic Relations

$\psi = u - Ts$	(11.20) p. 642	Helmholtz function
$g = h - Ts$	(11.21) p. 642	Gibbs function
$c = \sqrt{-v^2 \left(\frac{\partial p}{\partial v} \right)_s} = \sqrt{-kv^2 \left(\frac{\partial p}{\partial v} \right)_T}$	(9.36b) p. 658 (11.74) p. 660	Expressions for velocity of sound
$\mu_J = \left(\frac{\partial T}{\partial p} \right)_h$	(11.75) p. 661	Joule–Thomson coefficient

Properties of Multicomponent Mixtures

$T_c = \sum_{i=1}^j y_i T_{c,i}, \quad p_c = \sum_{i=1}^j y_i p_{c,i}$	(11.97) p. 676	Kay's rule for critical temperature and pressure of mixtures
$\bar{X}_i = \left(\frac{\partial X}{\partial n_i} \right)_{T,p,n_l}$	(11.102) p. 680	Partial molal property \bar{X}_i and its relation to extensive property X
$X = \sum_{i=1}^j n_i \bar{X}_i$	(11.103) p. 680	X as a weighted sum of partial molal properties
$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_l}$	(11.107) p. 682	Chemical potential of species i in a mixture
$\bar{R}T \left(\frac{\partial \ln f}{\partial p} \right)_T = \bar{v}$	(11.122) p. 685	Expressions for evaluating fugacity of a single-component system
$\lim_{p \rightarrow 0} \frac{f}{p} = 1$	(11.123) p. 685	
$\bar{R}T \left(\frac{\partial \ln \bar{f}_i}{\partial p} \right)_{T,n} = \bar{V}_i$	(11.126a) p. 687	Expressions for evaluating fugacity of mixture component i
$\lim_{p \rightarrow 0} \left(\frac{\bar{f}_i}{y_i p} \right) = 1$	(11.126b) p. 687	
$\bar{f}_i = y_i f_i$	(11.134) p. 688	Lewis–Randall rule for ideal solutions
$\mu_i = \bar{g}_i^\circ + \bar{R}T \ln \frac{y_i p}{p_{ref}}$	(11.144) p. 690	Chemical potential of component i in an ideal gas mixture

► EXERCISES: THINGS ENGINEERS THINK ABOUT

1. What is an advantage of using the Redlich–Kwong equation of state in the generalized form given by Eq. 11.9 instead of Eq. 11.7? A disadvantage?
2. To determine the specific volume of superheated water vapor at a known pressure and temperature, when would you use each of the following: the *steam tables*, the generalized compressibility chart, an equation of state, the ideal gas model?
3. If the function $p = p(T, v)$ is an equation of state, is $(\partial p / \partial T)_v$ a property? What are the independent variables of $(\partial p / \partial T)_v$?
4. In the expression $(\partial u / \partial T)_v$, what does the subscript v signify?
5. Explain how a Mollier diagram provides a graphical representation of the fundamental function $h(s, p)$.
6. How is the Clapeyron equation used?
7. For a gas whose equation of state is $p\bar{v} = \bar{R}T$, are the specific heats \bar{c}_p and \bar{c}_v necessarily functions of temperature alone?
8. Referring to the phase diagram for water (Fig. 3.5), explain why ice melts under the blade of an ice skate?
9. Can you devise a way to determine the specific heat \bar{c}_p of a gas by *direct* measurement? *Indirectly*, using other measured data?
10. For an ideal gas, what is the value of the Joule–Thomson coefficient?
11. At what states is the entropy departure negligible? The fugacity coefficient, f/p , closely equal to unity?
12. In Eq. 11.107, what do the subscripts T , p , and n_l signify? What does i denote?
13. How does Eq. 11.108 reduce for a system consisting of a pure substance? Repeat for an ideal gas mixture.
14. If two different liquids of known volumes are mixed, is the final volume *necessarily* equal to the sum of the original volumes?
15. For a *binary* solution at temperature T and pressure p , how would you determine the specific heat \bar{c}_p ? Repeat for an ideal solution and for an ideal gas mixture.

► PROBLEMS: DEVELOPING ENGINEERING SKILLS

Using Equations of State

11.1 Owing to safety requirements, the pressure within a 19.3 ft³ cylinder should not exceed 52 atm. Check the pressure within the cylinder if filled with 100 lb of CO₂ maintained at 212°F using the

- (a) van der Waals equation.
- (b) compressibility chart.
- (c) ideal gas equation of state.

11.2 Ten pounds mass of propane have a volume of 2 ft³ and a pressure of 600 lbf/in.² Determine the temperature, in °R, using the

- (a) van der Waals equation.
- (b) compressibility chart.
- (c) ideal gas equation of state.
- (d) propane tables.

11.3 The pressure within a 23.3-m³ tank should not exceed 105 bar. Check the pressure within the tank if filled with 1000 kg of water vapor maintained at 360°C using the

- (a) ideal gas equation of state.
- (b) van der Waals equation.
- (c) Redlich–Kwong equation.
- (d) compressibility chart.
- (e) steam tables.

11.4 Estimate the pressure of water vapor at a temperature of 500°C and a density of 24 kg/m³ using the

- (a) steam tables.
- (b) compressibility chart.
- (c) Redlich–Kwong equation.
- (d) van der Waals equation.
- (e) ideal gas equation of state.

11.5 Methane gas flows through a pipeline with a volumetric flow rate of 11 ft³/s at a pressure of 183 atm and a temperature of 56°F. Determine the mass flow rate, in lb/s, using the

- (a) ideal gas equation of state.
- (b) van der Waals equation.
- (c) compressibility chart.

11.6 Determine the specific volume of water vapor at 20 MPa and 400°C, in m³/kg, using the

- (a) steam tables.
- (b) compressibility chart.
- (c) Redlich–Kwong equation.
- (d) van der Waals equation.
- (e) ideal gas equation of state.

11.7 A vessel whose volume is 1 m³ contains 4 kmol of methane at 100°C. Owing to safety requirements, the pressure of the methane should not exceed 12 MPa. Check the pressure using the

- (a) ideal gas equation of state.
- (b) Redlich–Kwong equation.
- (c) Benedict–Webb–Rubin equation.

11.8 Methane gas at 100 atm and –18°C is stored in a 10-m³ tank. Determine the mass of methane contained in the tank, in kg, using the

- (a) ideal gas equation of state.
- (b) van der Waals equation.
- (c) Benedict–Webb–Rubin equation.

11.9 Using the Benedict–Webb–Rubin equation of state, determine the volume, in m³, occupied by 165 kg of methane at a pressure of 200 atm and temperature of 400 K. Compare with the results obtained using the ideal gas equation of state and the generalized compressibility chart.

11.10 A rigid tank contains 1 kg of oxygen (O₂) at p₁ = 40 bar, T₁ = 180 K. The gas is cooled until the temperature drops to 150 K. Determine the volume of the tank, in m³, and the final pressure, in bar, using the

- (a) ideal gas equation of state.
- (b) Redlich–Kwong equation.
- (c) compressibility chart.

11.11 One pound mass of air initially occupying a volume of 0.4 ft³ at a pressure of 1000 lbf/in.² expands in a piston–cylinder assembly isothermally and without irreversibilities until the volume is 2 ft³. Using the Redlich–Kwong equation of state, determine the

- (a) temperature, in °R.
- (b) final pressure, in lbf/in.²
- (c) work developed in the process, in Btu.

11.12 Water vapor initially at 240°C, 1 MPa expands in a piston–cylinder assembly isothermally and without internal irreversibilities to a final pressure of 0.1 MPa. Evaluate the work done, in kJ/kg. Use a truncated virial equation of state with the form

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2}$$

where B and C are evaluated from steam table data at 240°C and pressures ranging from 0 to 1 MPa.

11.13 Referring to the virial series, Eqs. 3.30 and 3.31, show that $\hat{B} = B/\bar{R}T$, $\hat{C} = (C - B^2)/\bar{R}^2T^2$.

11.14 Express Eq. 11.5, the van der Waals equation, in terms of the compressibility factor Z

- (a) as a virial series in v'_R. [Hint: Expand the (v'_R – 1/8)⁻¹ term of Eq. 11.5 in a series.]
- (b) as a virial series in p_R.
- (c) Dropping terms involving (p_R)² and higher in the virial series of part (b), obtain the following approximate form:

$$Z = 1 + \left(\frac{1}{8} - \frac{27/64}{T_R} \right) \frac{p_R}{T_R}$$

(d) Compare the compressibility factors determined from the equation of part (c) with tabulated compressibility factors from the literature for $0 < p_R < 0.6$ and each of $T_R = 1.0, 1.2, 1.4, 1.6, 1.8, 2.0$. Comment on the realm of validity of the approximate form.

11.15 The Berthelot equation of state has the form

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{T\bar{v}^2}$$

(a) Using Eqs. 11.3, show that

$$a = \frac{27}{64} \frac{\bar{R}^2 T_c^3}{p_c}, \quad b = \frac{1}{8} \frac{\bar{R} T_c}{T_c^2}$$

(b) Express the equation in terms of the compressibility factor Z , the reduced temperature T_R , and the pseudoreduced specific volume, v'_R .

11.16 The Beattie–Bridgeman equation of state can be expressed as

$$p = \frac{RT(1-\varepsilon)(v+B)}{v^2} - \frac{A}{v^2}$$

where

$$A = A_0 \left(1 - \frac{a}{v}\right), \quad B = B_0 \left(1 - \frac{b}{v}\right)$$

$$\varepsilon = \frac{c}{vT^3}$$

and A_0 , B_0 , a , b , and c are constants. Express this equation of state in terms of the reduced pressure, p_R , reduced temperature, T_R , pseudoreduced specific volume, v'_R , and appropriate dimensionless constants.

11.17 The Dieterici equation of state is

$$p = \left(\frac{RT}{v-b}\right) \exp\left(\frac{-a}{RTv}\right)$$

(a) Using Eqs. 11.3, show that

$$a = \frac{4R^2 T_c^2}{p_c e^2}, \quad b = \frac{RT_c}{p_c e^2}$$

(b) Show that the equation of state can be expressed in terms of compressibility chart variables as

$$Z = \left(\frac{v'_R}{v'_R - 1/e^2}\right) \exp\left(\frac{-4}{T_R v'_R e^2}\right)$$

(c) Convert the result of part (b) to a virial series in v'_R . (*Hint:* Expand the $(v'_R - 1/e^2)^{-1}$ term in a series. Also expand the exponential term in a series.)

11.18 The Peng–Robinson equation of state has the form

$$p = \frac{RT}{v-b} - \frac{a}{v^2 - c^2}$$

Using Eqs. 11.3, evaluate the constants a , b , c in terms of the critical pressure p_c , critical temperature T_c , and critical compressibility factor Z_c .

11.19 The p – v – T relation for chlorofluorinated hydrocarbons can be described by the Carnahan–Starling–De Santis equation of state

$$\frac{p\bar{v}}{\bar{R}T} = \frac{1 + \beta + \beta^2 - \beta^3}{(1 + \beta)^3} - \frac{a}{\bar{R}T(\bar{v} + b)}$$

where $\beta = b/4\bar{v}$, $a = a_0 \exp(a_1 T + a_2 T^2)$, and $b = b_0 + b_1 T + b_2 T^2$. For Refrigerants 12 and 13, the required coefficients for T in K, a in J · L/(mol)², and b in L/mol are given in Table P11.19. Specify which of the two refrigerants would allow the smaller amount of mass to be stored in a 10-m³ vessel at 0.2 MPa, 80°C.

Using Relations from Exact Differentials

11.20 The differential of pressure obtained from a certain equation of state is given by one of the following expressions. Determine the equation of state.

$$dp = \frac{2(v-b)}{RT} dv + \frac{(v-b)^2}{RT^2} dT$$

$$dp = -\frac{RT}{(v-b)^2} dv + \frac{R}{v-b} dT$$

11.21 Introducing $\delta Q_{\text{int}}^{\text{rev}} = T dS$ into Eq. 6.8 gives

$$\delta Q_{\text{int}}^{\text{rev}} = dU + p dV$$

Using this expression together with the test for exactness, demonstrate that $Q_{\text{int}}^{\text{rev}}$ is not a property.

11.22 Show that Eq. 11.16 is satisfied by an equation of state with the form $p = [RT/(v-b)] + a$.

11.23 For the functions $x = x(y, w)$, $y = y(z, w)$, $z = z(x, w)$, demonstrate that

$$\left. \frac{\partial x}{\partial y} \right|_w \left. \frac{\partial y}{\partial z} \right|_w \left. \frac{\partial z}{\partial x} \right|_w = 1$$

11.24 Using Eq. 11.35, check the consistency of

(a) the steam tables at 2 MPa, 400°C.

(b) the Refrigerant 134a tables at 2 bar, 50°C.

11.25 Using Eq. 11.35, check the consistency of

(a) the steam tables at 100 lbf/in.², 600°F.

(b) the Refrigerant 134a tables at 40 lbf/in.², 100°F.

11.26 At a pressure of 1 atm, liquid water has a state of maximum density at about 4°C. What can be concluded about $(\partial s/\partial p)_T$ at

(a) 3°C?

(b) 4°C?

(c) 5°C?

11.27 A gas enters a compressor operating at steady state and is compressed isentropically. Does the specific enthalpy increase or decrease as the gas passes from the inlet to the exit?

11.28 Show that T , p , h , ψ , and g can each be determined from a fundamental thermodynamic function of the form $u = u(s, v)$.



	$a_0 \times 10^{-3}$	$a_1 \times 10^3$	$a_2 \times 10^6$	b_0	$b_1 \times 10^4$	$b_2 \times 10^8$
R-12	3.52412	-2.77230	-0.67318	0.15376	-1.84195	-5.03644
R-13	2.29813	-3.41828	-1.52430	0.12814	-1.84474	-10.7951

Table P11.19

11.29 Evaluate p , s , u , h , c_v , and c_p for a substance for which the Helmholtz function has the form

$$\psi = -RT \ln \frac{v}{v'} - cT' \left[1 - \frac{T}{T'} + \frac{T}{T'} \ln \frac{T}{T'} \right]$$

where v' and T' denote specific volume and temperature, respectively, at a reference state, and c is a constant.

11.30 The Mollier diagram provides a graphical representation of the fundamental thermodynamic function $h = h(s, p)$. Show that at any state fixed by s and p the properties T , v , u , ψ , and g can be evaluated using data obtained from the diagram.

11.31 Derive the relation $c_p = -T(\partial^2 g / \partial T^2)_p$.

Evaluating Δs , Δu , and Δh

11.32 Using p - v - T data for saturated ammonia from Table A-13E, calculate at 20°F

- (a) $h_g - h_f$
- (b) $u_g - u_f$
- (c) $s_g - s_f$

Compare with values obtained from Table A-13E.

11.33 Using p - v - T data for saturated water from the steam tables, calculate at 50°C

- (a) $h_g - h_f$
- (b) $u_g - u_f$
- (c) $s_g - s_f$

Compare with values obtained from the steam tables.

11.34 Using h_{fg} , v_{fg} , and p_{sat} at 10°F from the Refrigerant 134a tables, estimate the saturation pressure at 20°F. Comment on the accuracy of your estimate.

11.35 Using h_{fg} , v_{fg} , and p_{sat} at 26°C from the ammonia tables, estimate the saturation pressure at 30°C. Comment on the accuracy of your estimate.

11.36 Using triple-point data for water from Table A-6E, estimate the saturation pressure at -40°F. Compare with the value listed in Table A-6E.

11.37 At 0°C, the specific volumes of saturated solid water (ice) and saturated liquid water are, respectively, $v_i = 1.0911 \times 10^{-3} \text{ m}^3/\text{kg}$ and $v_f = 1.0002 \times 10^{-3} \text{ m}^3/\text{kg}$, and the change in specific enthalpy on melting is $h_{if} = 333.4 \text{ kJ/kg}$. Calculate the melting temperature of ice at (a) 250 bar, (b) 500 bar. Locate your answers on a sketch of the p - T diagram for water.

11.38 The line representing the two-phase solid-liquid region on the phase diagram slopes to the left for substances that expand on freezing and to the right for substances that contract on freezing (Sec. 3.2.2). Verify this for the cases of lead that contracts on freezing and bismuth that expands on freezing.

11.39 Consider a four-legged chair at rest on an ice rink. The total mass of the chair and a person sitting on it is 80 kg. If the ice temperature is -2°C, determine the minimum total area, in cm^2 , the tips of the chair legs can have before the ice in contact with the legs would melt. Use data from Problem 11.37 and let the local acceleration of gravity be 9.8 m/s^2 .

11.40 Over a certain temperature interval, the saturation pressure-temperature curve of a substance is represented by an equation of the form $\ln p_{sat} = A - B/T$, where A and B are empirically determined constants.

(a) Obtain expressions for $h_g - h_f$ and $s_g - s_f$ in terms of p - v - T data and the constant B .

(b) Using the results of part (a), calculate $h_g - h_f$ and $s_g - s_f$ for water vapor at 25°C and compare with steam table data.



11.41 Using data for water from Table A-2, determine the constants A and B to give the best fit in a least-squares sense to the saturation pressure in the interval from 20 to 30°C by the equation $\ln p_{sat} = A - B/T$. Using this equation, determine dp_{sat}/dT at 25°C. Calculate $h_g - h_f$ at 25°C and compare with the steam table value.

11.42 Over limited intervals of temperature, the saturation pressure-temperature curve for two-phase liquid-vapor states can be represented by an equation of the form $\ln p_{sat} = A - B/T$, where A and B are constants. Derive the following expression relating any three states on such a portion of the curve:

$$\frac{P_{sat,3}}{P_{sat,1}} = \left(\frac{P_{sat,2}}{P_{sat,1}} \right)^\tau$$

where $\tau = T_2(T_3 - T_1)/T_3(T_2 - T_1)$.

11.43 Use the result of Problem 11.42 to determine

(a) the saturation pressure at 30°C using saturation pressure-temperature data at 20 and 40°C from Table A-2. Compare with the table value for saturation pressure at 30°C.

(b) the saturation temperature at 0.006 MPa using saturation pressure-temperature data at 20 to 40°C from Table A-2. Compare with the saturation temperature at 0.006 MPa given in Table A-3.

11.44 Complete the following exercises dealing with slopes:

(a) At the triple point of water, evaluate the ratio of the slope of the vaporization line to the slope of the sublimation line. Use steam table data to obtain a numerical value for the ratio.

(b) Consider the superheated vapor region of a temperature-entropy diagram. Show that the slope of a constant specific volume line is greater than the slope of a constant pressure line through the same state.

(c) An enthalpy-entropy diagram (Mollier diagram) is often used in analyzing steam turbines. Obtain an expression for the slope of a constant-pressure line on such a diagram in terms of p - v - T data only.

(d) A pressure-enthalpy diagram is often used in the refrigeration industry. Obtain an expression for the slope of an isentropic line on such a diagram in terms of p - v - T data only.

11.45 Using only p - v - T data from the ammonia tables, evaluate the changes in specific enthalpy and entropy for a process from 70 lbf/in.², 40°F to 14 lbf/in.², 40°F. Compare with the table values.



11.46 One kmol of argon at 300 K is initially confined to one side of a rigid, insulated container divided into equal volumes of 0.2 m³ by a partition. The other side is initially evacuated. The partition is removed and the argon expands to fill the

entire container. Using the van der Waals equation of state, determine the final temperature of the argon, in K. Repeat using the ideal gas equation of state.

11.47 Obtain the relationship between c_p and c_v for a gas that obeys the equation of state $p(v - b) = RT$.

11.48 The $p-v-T$ relation for a certain gas is represented closely by $v = RT/p + B - A/RT$, where R is the gas constant and A and B are constants. Determine expressions for the changes in specific enthalpy, internal energy, and entropy, $[h(p_2, T) - h(p_1, T)]$, $[u(p_2, T) - u(p_1, T)]$, and $[s(p_2, T) - s(p_1, T)]$, respectively.

11.49 Develop expressions for the specific enthalpy, internal energy, and entropy changes $[h(v_2, T) - h(v_1, T)]$, $[u(v_2, T) - u(v_1, T)]$, $[s(v_2, T) - s(v_1, T)]$, using the

- (a) van der Waals equation of state.
- (b) Redlich-Kwong equation of state.

11.50 At certain states, the $p-v-T$ data of a gas can be expressed as $Z = 1 - Ap/T^4$, where Z is the compressibility factor and A is a constant.

- (a) Obtain an expression for $(\partial p/\partial T)_v$ in terms of p , T , A , and the gas constant R .
- (b) Obtain an expression for the change in specific entropy, $[s(p_2, T) - s(p_1, T)]$.
- (c) Obtain an expression for the change in specific enthalpy, $[h(p_2, T) - h(p_1, T)]$.

11.51 For a gas whose $p-v-T$ behavior is described by $Z = 1 + Bp/RT$, where B is a function of temperature, derive expressions for the specific enthalpy, internal energy, and entropy changes, $[h(p_2, T) - h(p_1, T)]$, $[u(p_2, T) - u(p_1, T)]$, and $[s(p_2, T) - s(p_1, T)]$.

11.52 For a gas whose $p-v-T$ behavior is described by $Z = 1 + B/v + C/v^2$, where B and C are functions of temperature, derive an expression for the specific entropy change, $[s(v_2, T) - s(v_1, T)]$.

Using Other Thermodynamic Relations

11.53 The volume of a 1-kg copper sphere is not allowed to vary by more than 0.1%. If the pressure exerted on the sphere is increased from 10 bar while the temperature remains constant at 300 K, determine the maximum allowed pressure, in bar. Average values of ρ , β , and κ are 8888 kg/m^3 , $49.2 \times 10^{-6} (\text{K})^{-1}$, and $0.776 \times 10^{-11} \text{ m}^2/\text{N}$ respectively.

11.54 The volume of a 1-lb copper sphere is not allowed to vary by more than 0.1%. If the pressure exerted on the sphere is increased from 1 atm while the temperature remains constant at 80°F, determine the maximum allowed pressure, in atm. Average values of ρ , β , and κ are 555 lb/ft^3 , $2.75 \times 10^{-5} (\text{°R})^{-1}$, and $3.72 \times 10^{-10} \text{ ft}^2/\text{lbf}$, respectively.

11.55 Develop expressions for the volume expansivity β and the isothermal compressibility κ for

- (a) an ideal gas.
- (b) a gas whose equation of state is $p(v - b) = RT$.
- (c) a gas obeying the van der Waals equation.

11.56 Derive expressions for the volume expansivity β and the isothermal compressibility κ in terms of T , p , Z , and the first

partial derivatives of Z . For gas states with $p_R < 3$, $T_R < 2$, determine the sign of κ . Discuss.

11.57 Show that the isothermal compressibility κ is always greater than or equal to the isentropic compressibility α .

11.58 Prove that $(\partial \beta / \partial p)_T = -(\partial \kappa / \partial T)_p$.

11.59 For aluminum at 0°C, $\rho = 2700 \text{ kg/m}^3$, $\beta = 71.4 \times 10^{-8} (\text{K})^{-1}$, $\kappa = 1.34 \times 10^{-13} \text{ m}^2/\text{N}$, and $c_p = 0.9211 \text{ kJ/kg} \cdot \text{K}$. Determine the percent error in c_v that would result if it were assumed that $c_p = c_v$.

11.60 Estimate the temperature rise, in °C, of mercury, initially at 0°C and 1 bar if its pressure were raised to 1000 bar isentropically. For mercury at 0°C, $c_p = 28.0 \text{ kJ/kmol} \cdot \text{K}$, $\bar{v} = 0.0147 \text{ m}^3/\text{kmol}$, and $\beta = 17.8 \times 10^{-5} (\text{K})^{-1}$.

11.61 At certain states, the $p-v-T$ data for a particular gas can be represented as $Z = 1 - Ap/T^4$, where Z is the compressibility factor and A is a constant. Obtain an expression for the specific heat c_p in terms of the gas constant R , specific heat ratio k , and Z . Verify that your expression reduces to Eq. 3.47a when $Z = 1$.

11.62 For a gas obeying the van der Waals equation of state,

- (a) show that $(\partial c_v / \partial v)_T = 0$.
- (b) develop an expression for $c_p - c_v$.
- (c) develop expressions for $[u(T_2, v_2) - u(T_1, v_1)]$ and $[s(T_2, v_2) - s(T_1, v_1)]$.
- (d) complete the Δu and Δs evaluations if $c_v = a + bT$, where a and b are constants.

11.63 If the value of the specific heat c_v of air is 0.1965 Btu/lb · °R at $T_1 = 1000^\circ\text{F}$, $v_1 = 36.8 \text{ ft}^3/\text{lb}$, determine the value of c_v at $T_2 = 1000^\circ\text{F}$, $v_2 = 0.0555 \text{ ft}^3/\text{lb}$. Assume that air obeys the Berthelot equation of state

$$p = \frac{RT}{v - b} - \frac{a}{Tv^2}$$

where

$$a = \frac{27}{64} \frac{R^2 T_c^3}{p_c}, \quad b = \frac{1}{8} \frac{RT_c}{p_c}$$

11.64 Show that the specific heat ratio k can be expressed as $k = c_p \kappa / (c_p \kappa - T v \beta^2)$. Using this expression together with data from the steam tables, evaluate k for water vapor at 200 lbf/in.², 500°F.

11.65 For liquid water at 40°C, 1 atm estimate

- (a) c_v , in $\text{kJ/kg} \cdot \text{K}$.
- (b) the velocity of sound, in m/s.

Use Data from Table 11.2, as required.

11.66 Using steam table data, estimate the velocity of sound in liquid water at (a) 20°C, 50 bar, (b) 50°F, 1500 lbf/in.²

11.67 At a certain location in a *wind tunnel*, a stream of air is at 500°F, 1 atm and has a velocity of 2115 ft/s. Determine the Mach number at this location.

11.68 For a gas obeying the equation of state $p(v - b) = RT$, where b is a positive constant, can the temperature be reduced in a Joule-Thomson expansion?

11.69 A gas is described by $v = RT/p - A/T + B$, where A and B are constants. For the gas

- obtain an expression for the temperatures at the Joule–Thomson inversion states.
- obtain an expression for $c_p - c_v$.

11.70 Determine the *maximum* Joule–Thomson inversion temperature in terms of the critical temperature T_c predicted by the

- van der Waals equation.
- Redlich–Kwong equation.
- Dieterici equation given in Problem 11.17.

11.71 Derive an equation for the Joule–Thomson coefficient as a function of T and v for a gas that obeys the van der Waals equation of state and whose specific heat c_v is given by $c_v = A + BT + CT^2$, where A , B , C are constants. Evaluate the temperatures at the *inversion* states in terms of R , v , and the van der Waals constants a and b .

11.72 Show that Eq. 11.77 can be written as

$$\mu_J = \frac{T^2}{c_p} \left(\frac{\partial(v/T)}{\partial T} \right)_p$$

- Using this result, obtain an expression for the Joule–Thomson coefficient for a gas obeying the equation of state

$$v = \frac{RT}{p} - \frac{Ap}{T^2}$$

where A is a constant.

- Using the result of part (a), determine c_p , in $\text{kJ/kg} \cdot \text{K}$, for CO_2 at 400 K, 1 atm, where $\mu_J = 0.57 \text{ K/atm}$. For CO_2 , $A = 2.78 \times 10^{-3} \text{ m}^5 \cdot \text{K}^2/\text{kg} \cdot \text{N}$.

Developing Property Data

11.73 If the specific heat c_v of a gas obeying the van der Waals equation is given at a particular pressure, p' , by $c_v = A + BT$, where A and B are constants, develop an expression for the change in specific entropy between any two states 1 and 2: $[s(T_2, p_2) - s(T_1, p_1)]$.

11.74 For air, write a computer program that evaluates the change in specific enthalpy from a state where the temperature is 25°C and the pressure is 1 atm to a state where the temperature is T and the pressure is p . Use the van der Waals equation of state and account for the variation of the ideal gas specific heat as in Table A-21.

11.75 Using the Redlich–Kwong equation of state, determine the changes in specific enthalpy, in kJ/kmol , and entropy, in $\text{kJ/kmol} \cdot \text{K}$, for ethylene between 400 K, 1 bar and 400 K, 100 bar.

11.76 Using the Benedict–Webb–Rubin equation of state together with a specific heat relation from Table A-21, determine the change in specific enthalpy, in kJ/kmol , for methane between 300 K, 1 atm and 400 K, 200 atm.

11.77 A certain pure, simple compressible substance has the following property relations. The p – v – T relationship in the vapor phase is

$$v = \frac{RT}{p} - \frac{Bp}{T^2}$$

where v is in ft^3/lb , T is in $^\circ\text{R}$, p is in lbf/ft^2 , $R = 50 \text{ ft} \cdot \text{lbf}/\text{lb} \cdot ^\circ\text{R}$, and $B = 100 \text{ ft}^5 \cdot (^\circ\text{R})^2/\text{lb} \cdot \text{lbf}$. The saturation pressure, in lbf/ft^2 , is described by

$$\ln p_{\text{sat}} = 12 - \frac{2400}{T}$$

The Joule–Thomson coefficient at 10 lbf/in^2 , 200°F is $0.004^\circ\text{R} \cdot \text{ft}^2/\text{lbf}$. The ideal gas specific heat c_{p0} is constant over the temperature range 0 to 300°F.

- Complete the accompanying table of property values

T	p	v_f	v_g	h_f	h_g	s_f	s_g
0°F		0.03		0		0.000	
100°F		0.03					

for p in lbf/in^2 , v in ft^3/lb , h in Btu/lb , and s in $\text{Btu}/\text{lb} \cdot ^\circ\text{R}$.

- Evaluate v , h , s at the state fixed by 15 lbf/in^2 , 300°F.

11.78 In Table A-2, at temperatures up to 50°C, the values of u_f and h_f differ in most cases by 0.01 kJ/kg. Yet at each of these temperatures the product $p_{\text{sat}}v_f$ is small enough to be neglected and the table values of u_f and h_f should be the same. In a memorandum, provide a plausible explanation.

Using Enthalpy and Entropy Departures

11.79 Beginning with Eq. 11.90, derive Eq. 11.91.

11.80 Derive an expression giving

- the internal energy of a substance relative to that of its ideal gas model at the same temperature: $[u(T, v) - u^*(T)]$.
- the entropy of a substance relative to that of its ideal gas model at the same temperature and specific volume: $[s(T, v) - s^*(T, v)]$.

11.81 Derive expressions for the enthalpy and entropy departures using an equation of state with the form $Z = 1 + Bp_R$, where B is a function of the reduced temperature, T_R .

11.82 The following expression for the enthalpy departure is convenient for use with equations of state that are explicit in pressure:

$$\frac{\bar{h}^*(T) - \bar{h}(T, \bar{v})}{\bar{R}T_c} = T_R \left[1 - Z - \frac{1}{\bar{R}T} \int_{\infty}^{\bar{v}} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] d\bar{v} \right]$$

- Derive this expression.

(b) Using the given expression, evaluate the enthalpy departure for a gas obeying the Redlich–Kwong equation of state.

(c) Using the result of part (b), determine the change in specific enthalpy, in kJ/kmol , for CO_2 undergoing an isothermal process at 300 K from 50 to 20 bar.

11.83 Using the equation of state of Problem 11.14 (c), evaluate v and c_p for water vapor at 550°C, 20 MPa and compare with data from Table A-4 and Fig. 3.9, respectively. Discuss.

11.84 Ethylene at 67°C, 10 bar enters a compressor operating at steady state and is compressed isothermally without internal irreversibilities to 100 bar. Kinetic and potential energy changes are negligible. Evaluate in kJ per kg of ethylene flowing through the compressor

- the work required.
- the heat transfer.

11.85 Methane at 27°C, 10 MPa enters a turbine operating at steady state, expands adiabatically through a 5 : 1 pressure ratio, and exits at -48°C. Kinetic and potential energy effects are negligible. If $\bar{c}_{po} = 35 \text{ kJ/kmol} \cdot \text{K}$, determine the work developed per kg of methane flowing through the turbine. Compare with the value obtained using the ideal gas model.

11.86 Nitrogen (N_2) enters a compressor operating at steady state at 1.5 MPa, 300 K and exits at 8 MPa, 500 K. If the work input is 240 kJ per kg of nitrogen flowing, determine the heat transfer, in kJ per kg of nitrogen flowing. Ignore kinetic and potential energy effects.

11.87 Oxygen (O_2) enters a control volume operating at steady state with a mass flow rate of 9 kg/min at 100 bar, 287 K and is compressed adiabatically to 150 bar, 400 K. Determine the power required, in kW, and the rate of entropy production, in kW/K. Ignore kinetic and potential energy effects.

11.88 Argon gas enters a turbine operating at steady state at 100 bar, 325 K and expands adiabatically to 40 bar, 235 K with no significant changes in kinetic or potential energy. Determine

- (a) the work developed, in kJ per kg of argon flowing through the turbine.
- (b) the amount of entropy produced, in kJ/K per kg of argon flowing.

11.89 Oxygen (O_2) undergoes a throttling process from 100 bar, 300 K to 20 bar. Determine the temperature after throttling, in K, and compare with the value obtained using the ideal gas model.

11.90 Water vapor enters a turbine operating at steady state at 30 MPa, 600°C and expands adiabatically to 6 MPa with no significant change in kinetic or potential energy. If the isentropic turbine efficiency is 80%, determine the work developed, in kJ per kg of steam flowing, using the generalized property charts. Compare with the result obtained using steam table data. Discuss.

11.91 Oxygen (O_2) enters a nozzle operating at steady state at 60 bar, 300 K, 1 m/s and expands isentropically to 30 bar. Determine the velocity at the nozzle exit, in m/s.

11.92 A quantity of nitrogen gas in a piston-cylinder assembly undergoes a process at a constant pressure of 80 bar from 220 to 300 K. Determine the work and heat transfer for the process, each in kJ per kmol of nitrogen.

11.93 A closed, rigid, insulated vessel having a volume of 0.142 m³ contains oxygen (O_2) initially at 100 bar, 7°C. The oxygen is stirred by a paddle wheel until the pressure becomes 150 bar. Determine the

- (a) final temperature, in °C.
- (b) work, in kJ.
- (c) amount of exergy destroyed in the process, in kJ.

Let $T_0 = 7^\circ\text{C}$.

Evaluating p - v - T for Gas Mixtures

11.94 A preliminary design calls for a 1 kmol mixture of CO_2 and C_2H_6 (ethane) to occupy a volume of 0.15 m³ at a temperature of 400 K. The mole fraction of CO_2 is 0.3.

Owing to safety requirements, the pressure should not exceed 180 bar. Check the pressure using

- (a) the ideal gas equation of state.
- (b) Kay's rule together with the generalized compressibility chart.
- (c) the additive pressure rule together with the generalized compressibility chart.

Compare and discuss these results.

11.95 A gaseous mixture with a molar composition of 60% CO and 40% H_2 enters a turbine operating at steady state at 300°F, 2000 lbf/in.² and exits at 212°F, 1 atm with a volumetric flow rate of 20,000 ft³/min. Estimate the volumetric flow rate at the turbine inlet, in ft³/min, using Kay's rule. What value would result from using the ideal gas model? Discuss.

11.96 A 0.1-m³ cylinder contains a gaseous mixture with a molar composition of 97% CO and 3% CO_2 initially at 138 bar. Due to a leak, the pressure of the mixture drops to 129 bar while the temperature remains constant at 30°C. Using Kay's rule, estimate the amount of mixture, in kmol, that leaks from the cylinder.

11.97 A gaseous mixture consisting of 0.75 kmol of hydrogen (H_2) and 0.25 kmol of nitrogen (N_2) occupies 0.085 m³ at 25°C. Estimate the pressure, in bar, using

- (a) the ideal gas equation of state.
- (b) Kay's rule together with the generalized compressibility chart.
- (c) the van der Waals equation together with mixture values for the constants a and b .
- (d) the rule of additive pressure together with the generalized compressibility chart.

11.98 A gaseous mixture of 0.5 lbmol of methane and 0.5 lbmol of propane occupies a volume of 7.65 ft³ at a temperature of 194°F. Estimate the pressure using the following procedures and compare each estimate with the measured value of pressure, 50 atm:

- (a) the ideal gas equation of state.
- (b) Kay's rule together with the generalized compressibility chart.
- (c) the van der Waals equation together with mixture values for the constants a and b .
- (d) the rule of additive pressures together with the van der Waals equation.
- (e) the rule of additive pressures together with the generalized compressibility chart.
- (f) the rule of additive volumes together with the van der Waals equation.

11.99 One lbmol of a gaseous mixture occupies a volume of 1.78 ft³ at 212°F. The mixture consists of 69.5% carbon dioxide and 30.5% ethylene (C_2H_4) on a molar basis. Estimate the mixture pressure, in atm, using

- (a) the ideal gas equation of state.
- (b) Kay's rule together with the generalized compressibility chart.
- (c) the additive pressure rule together with the generalized compressibility chart.
- (d) the van der Waals equation together with mixture values for the constants a and b .

11.100 Air having an approximate molar composition of 79% N₂ and 21% O₂ fills a 0.36-m³ vessel. The mass of mixture is 100 kg. The measured pressure and temperature are 101 bar and 180 K, respectively. Compare the measured pressure with the pressure predicted using

- (a) the ideal gas equation of state.
- (b) Kay's rule.
- (c) the additive pressure rule with the Redlich-Kwong equation.
- (d) the additive volume rule with the Redlich-Kwong equation.

11.101 A gaseous mixture consisting of 50% argon and 50% nitrogen (molar basis) is contained in a closed tank at 20 atm, -140°F. Estimate the specific volume, in ft³/lb, using

- (a) the ideal gas equation of state.
- (b) Kay's rule together with the generalized compressibility chart.
- (c) the Redlich-Kwong equation with mixture values for *a* and *b*.
- (d) the additive volume rule together with the generalized compressibility chart.

11.102 Using the Carnahan-Starling-DeSantis equation of state introduced in Problem 11.19, together with the following expressions for the mixture values of *a* and *b*:

$$\begin{aligned} a &= y_1^2 a_1 + 2y_1 y_2 (1 - f_{12}) (a_1 a_2)^{1/2} + y_2^2 a_2 \\ b &= y_1 b_1 + y_2 b_2 \end{aligned}$$

where *f*₁₂ is an empirical *interaction* parameter, determine the pressure, in kPa, at *v* = 0.005 m³/kg, *T* = 180°C for a mixture of Refrigerants 12 and 13, in which Refrigerant 12 is 40% by mass. For a mixture of Refrigerants 12 and 13, *f*₁₂ = 0.035.

11.103 A rigid vessel initially contains carbon dioxide gas at 32°C and pressure *p*. Ethylene gas is allowed to flow into the tank until a mixture consisting of 20% carbon dioxide and 80% ethylene (molar basis) exists within the tank at a temperature of 43°C and a pressure of 110 bar. Determine the pressure *p*, in bar, using Kay's rule together with the generalized compressibility chart.

11.104 Two tanks having equal volumes are connected by a valve. One tank contains carbon dioxide gas at 100°F and pressure *p*. The other tank contains ethylene gas at 100°F and 1480 lbf/in.² The valve is opened and the gases mix, eventually attaining equilibrium at 100°F and pressure *p'* with a composition of 20% carbon dioxide and 80% ethylene (molar basis). Using Kay's rule and the generalized compressibility chart, determine in lbf/in.²

- (a) the initial pressure of the carbon dioxide, *p*.
- (b) the final pressure of the mixture, *p'*.

Analyzing Multicomponent Systems

11.105 A binary solution at 25°C consists of 59 kg of ethyl alcohol (C₂H₅OH) and 41 kg of water. The respective partial molal volumes are 0.0573 and 0.0172 m³/kmol. Determine the total volume, in m³. Compare with the volume calculated using the molar specific volumes of the pure components, each a liquid at 25°C, in the place of the partial molal volumes.

11.106 The following data are for a binary solution of ethane (C₂H₆) and pentane (C₅H₁₂) at a certain temperature and pressure:

mole fraction of ethane	0.2	0.3	0.4	0.5	0.6	0.7	0.8
volume (in m ³) per kmol of solution	0.119	0.116	0.112	0.109	0.107	0.107	0.11

Estimate

- (a) the specific volumes of pure ethane and pure pentane, each in m³/kmol.
- (b) the partial molal volumes of ethane and pentane for an equimolar solution, each in m³/kmol.

11.107 The following data are for a binary mixture of carbon dioxide and methane at a certain temperature and pressure:

mole fraction of methane	0.000	0.204	0.406	0.606	0.847	1.000
volume (in ft ³) per lbmol of mixture	1.506	3.011	3.540	3.892	4.149	4.277

Estimate

- (a) the specific volumes of pure carbon dioxide and pure methane, each in ft³/lbmol.
- (b) the partial molal volumes of carbon dioxide and methane for an equimolar mixture, each in ft³/lbmol.

11.108 Using *p-v-T* data from the steam tables, determine the fugacity of water as a saturated vapor at (a) 280°C, (b) 500°F. Compare with the values obtained from the generalized fugacity chart.

11.109 Determine the fugacity, in atm, for

- (a) butane at 555 K, 150 bar.
- (b) methane at 120°F, 800 lbf/in.²
- (c) benzene at 890°R, 135 atm.

11.110 Using the equation of state of Problem 11.14 (c), evaluate the fugacity of ammonia at 750 K, 100 atm and compare with the value obtained from Fig. A-6.

11.111 Using tabulated compressibility factor data from the literature, evaluate *f/p* at *T*_R = 1.40 and *p*_R = 2.0. Compare with the value obtained from Fig. A-6.

11.112 Consider the truncated virial expansion

$$Z = 1 + \hat{B}(T_R)p_R + \hat{C}(T_R)p_R^2 + \hat{D}(T_R)p_R^3$$

(a) Using tabulated compressibility factor data from the literature, evaluate the coefficients *B*, *C*, and *D* for 0 < *p*_R < 1.0 and each of *T*_R = 1.0, 1.2, 1.4, 1.6, 1.8, 2.0.

(b) Obtain an expression for ln (*f/p*) in terms of *T*_R and *p*_R. Using the coefficients of part (a), evaluate *f/p* at selected states and compare with tabulated values from the literature.

11.113 Derive the following approximation for the fugacity of a liquid at temperature *T* and pressure *p*:

$$f(T, p) \approx f_{\text{sat}}^L(T) \exp \left\{ \frac{v_f(T)}{RT} [p - p_{\text{sat}}(T)] \right\}$$

where *f*_{sat}^L(*T*) is the fugacity of the saturated liquid at temperature *T*. For what range of pressures might the approximation *f*(*T, p*) ≈ *f*_{sat}^L(*T*) apply?

11.114 Beginning with Eq. 11.122,

- (a) evaluate $\ln f$ for a gas obeying the Redlich–Kwong equation of state.
 (b) Using the result of part (a), evaluate the fugacity, in bar, for Refrigerant 134a at 90°C, 10 bar. Compare with the fugacity value obtained from the generalized fugacity chart.



11.115 Consider a one-inlet, one-exit control volume at steady state through which the flow is internally reversible and isothermal. Show that the work per unit of mass flowing can be expressed in terms of the fugacity f as

$$\left(\frac{\dot{W}_{cv}}{\dot{m}}\right)_{rev} = -RT \ln\left(\frac{f_2}{f_1}\right) + \frac{V_1^2 - V_2^2}{2} + g(z_1 - z_2)$$

11.116 Methane expands isothermally and without irreversibilities through a turbine operating at steady state, entering at 60 atm, 77°F and exiting at 1 atm. Using data from the generalized fugacity chart, determine the work developed, in Btu per lb of methane flowing. Ignore kinetic and potential energy effects.

11.117 Propane (C_3H_8) enters a turbine operating at steady state at 100 bar, 400 K and expands isothermally without irreversibilities to 10 bar. There are no significant changes in kinetic or potential energy. Using data from the generalized fugacity chart, determine the power developed, in kW, for a mass flow rate of 50 kg/min.

11.118 Ethane (C_2H_6) is compressed isothermally without irreversibilities at a temperature of 320 K from 5 to 40 bar. Using data from the generalized fugacity and enthalpy departure charts, determine the work of compression and the heat transfer, each in kJ per kg of ethane flowing. Assume steady-state operation and neglect kinetic and potential energy effects.

11.119 Methane enters a turbine operating at steady state at 100 bar, 275 K and expands isothermally without irreversibilities to 15 bar. There are no significant changes in kinetic or potential energy. Using data from the generalized fugacity and enthalpy departure charts, determine the power developed and heat transfer, each in kW, for a mass flow rate of 0.5 kg/s.

11.120 Methane flows isothermally and without irreversibilities through a horizontal pipe operating at steady state, entering at 50 bar, 300 K, 10 m/s and exiting at 40 bar. Using data from the generalized fugacity chart, determine the velocity at the exit, in m/s.

11.121 Determine the fugacity, in atm, for pure ethane at 310 K, 20.4 atm and as a component with a mole fraction of 0.35 in an ideal solution at the same temperature and pressure.

11.122 Denoting the *solvent* and *solute* in a dilute binary liquid solution at temperature T and pressure p by the subscripts 1 and 2, respectively, show that if the fugacity of the solute is proportional to its mole fraction in the solution: $\bar{f}_2 = ky_2$, where k is a constant (*Henry's rule*), then the fugacity of the solvent is $\bar{f}_1 = y_1 f_1$, where y_1 is the solvent mole fraction and f_1 is the fugacity of pure 1 at T, p .

11.123 A tank contains 310 kg of a gaseous mixture of 70% ethane and 30% nitrogen (molar basis) at 311 K and 170 atm. Determine the volume of the tank, in m^3 , using data from the generalized compressibility chart together with (a)

Kay's rule, (b) the ideal solution model. Compare with the measured tank volume of 1 m^3 .

11.124 A tank contains a mixture of 75% argon and 25% ethylene on a molar basis at 77°F, 81.42 atm. For 157 lb of mixture, estimate the tank volume, in ft^3 , using

- (a) the ideal gas equation of state.
 (b) Kay's rule together with data from the generalized compressibility chart.
 (c) the ideal solution model together with data from the generalized compressibility chart.

11.125 A tank contains a mixture of 70% ethane and 30% nitrogen (N_2) on a molar basis at 400 K, 200 atm. For 2130 kg of mixture, estimate the tank volume, in m^3 , using

- (a) the ideal gas equation of state.
 (b) Kay's rule together with data from the generalized compressibility chart.
 (c) the ideal solution model together with data from the generalized compressibility chart.

11.126 An equimolar mixture of O_2 and N_2 enters a compressor operating at steady state at 10 bar, 220 K with a mass flow rate of 1 kg/s. The mixture exits at 60 bar, 400 K with no significant change in kinetic or potential energy. Stray heat transfer from the compressor can be ignored. Determine for the compressor

- (a) the power required, in kW.
 (b) the rate of entropy production, in kW/K.

Assume the mixture is modeled as an ideal solution. For the pure components:

	10 bar, 220 K		60 bar, 400 K	
	h (kJ/kg)	s (kJ/kg · K)	h (kJ/kg)	s (kJ/kg · K)
Oxygen	195.6	5.521	358.2	5.601
Nitrogen	224.1	5.826	409.8	5.911

11.127 A gaseous mixture with a molar analysis of 70% CH_4 and 30% N_2 , enters a compressor operating at steady state at 10 bar, 250 K and a molar flow rate of 6 kmol/h. The mixture exits the compressor at 100 bar. During compression, the temperature of the mixture departs from 250 K by no more than 0.1 K. The power required by the compressor is reported to be 6 kW. Can this value be correct? Explain. Ignore kinetic and potential energy effects. Assume the mixture is modeled as an ideal solution. For the pure components at 250 K:

	h (kJ/kg)		s (kJ/kg · K)	
	10 bar	100 bar	10 bar	100 bar
Methane	506.0	358.6	10.003	8.3716
Nitrogen	256.18	229.68	5.962	5.188

11.128 The departure of a binary solution from ideal solution behavior is gauged by the *activity coefficient*, $\gamma_i = a_i/y_i$, where a_i is the activity of component i and y_i is its mole fraction in the solution ($i = 1, 2$). Introducing Eq. 11.140, the activity coefficient can be expressed alternatively as $\gamma_i = \bar{f}_i/y_i f_i^\circ$. Using this expression together with the *Gibbs–Duhem* equation, derive the following relation among the activity coefficients and the mole fractions for a solution at temperature T and pressure p :

$$\left(y_1 \frac{\partial \ln \gamma_1}{\partial y_1}\right)_{p,T} = \left(y_2 \frac{\partial \ln \gamma_2}{\partial y_2}\right)_{p,T}$$

How might this expression be used?

► DESIGN & OPEN-ENDED PROBLEMS: EXPLORING ENGINEERING PRACTICE

11.1D Design a laboratory flask for containing up to 10 kmol of mercury vapor at pressures up to 3 MPa, and temperatures from 900 to 1000 K. Consider the health and safety of the technicians who would be working with such a mercury vapor-filled container. Use a $p-v-T$ relation for mercury vapor obtained from the literature, including appropriate property software. Write a report including at least three references.

11.2D The $p-h$ diagram (Sec. 10.2.4) used in the refrigeration engineering field has specific enthalpy and the natural logarithm of pressure as coordinates. Inspection of such a diagram suggests that in portions of the vapor region constant-entropy lines are nearly linear, and thus the relation between h , $\ln p$ and s might be expressible there as

$$h(s, p) = (As + B) \ln p + (Cs + D)$$

Investigate the viability of this expression for pressure ranging up to 10 bar, using data for Refrigerant 134a. Summarize your conclusions in a memorandum.

11.3D Compressed natural gas (CNG) is being used as a fuel to replace gasoline for automobile engines. Aluminum cylinders wrapped in a fibrous composite can provide lightweight, economical, and safe on-board storage. The storage vessels should hold enough CNG for 100 to 125 miles of urban travel, at storage pressures up to 3000 lbf/in.², and with a maximum total mass of 150 lb. Adhering to applicable U.S. Department of Transportation standards, specify both the size and number of cylinders that would meet the above design constraints.

11.4D A portable refrigeration machine requiring no external power supply and using carbon dioxide at its *triple point* is described in U.S. Patent No. 4,096,707. Estimate the cost of the initial carbon dioxide charge required by such a machine to maintain a 6 ft by 8 ft by 15 ft cargo container at 35°F for up to 24 hours, if the container is fabricated from sheet metal covered with a 1-in. layer of polystyrene. Would you recommend the use of such a refrigeration machine? Report your findings in a PowerPoint presentation.

11.5D A power plant located at a river's mouth where freshwater river currents meet saltwater ocean tides can generate electricity by exploiting the difference in composition of the freshwater and saltwater. The technology for generating power is called *reverse electrodialysis*. While only small-scale demonstration power plants using reverse electrodialysis have been developed thus far, some observers have high expectations for the approach. Investigate the technical readiness and economic feasibility of this renewable power source for providing 3%, or more, of annual U.S. electricity by 2030. Present your conclusions in a report, including a discussion of potential adverse environmental effects of such power plants and at least three references.

11.6D During a phase change from liquid to vapor at fixed pressure, the temperature of a binary *nonazeotropic* solution such as an ammonia–water solution increases rather than remains constant as for a pure substance. This attribute is exploited in both the *Kalina* power cycle and in the *Lorenz* refrigeration cycle. Write a report assessing the status of

technologies based on these cycles. Discuss the principal advantages of using binary nonazeotropic solutions. What are some of the main design issues related to their use in power and refrigeration systems?

11.7D The following data are known for a 100-ton ammonia–water absorption system like the one shown in Fig. 10.12. The pump is to handle 570 lb of strong solution per minute. The generator conditions are 175 lbf/in.², 220°F. The absorber is at 29 lbf/in.² with strong solution exiting at 80°F. For the evaporator, the pressure is 30 lbf/in.² and the exit temperature is 10°F. Specify the type and size, in horsepower, of the pump required. Present your findings in a memorandum.

11.8D The *Servel* refrigerator works on an absorption principle and requires no moving parts. An energy input by heat transfer is used to drive the cycle, and the refrigerant circulates due to its natural buoyancy. This type of refrigerator is commonly employed in mobile applications, such as recreational vehicles. Liquid propane is burned to provide the required energy input during mobile operation, and electric power is used when the vehicle is parked and can be connected to an electrical outlet. Investigate the principles of operation of commercially available Servel-type systems, and study their feasibility for solar-activated operation. Consider applications in remote locations where electricity or gas is not available. Write a report summarizing your findings.

11.9D In the experiment for the *regelation* of ice, a small-diameter wire weighted at each end is draped over a block of ice. The loaded wire is observed to cut slowly through the ice without leaving a trace. In one such set of experiments, a weighted 1.00-mm-diameter wire is reported to have passed through 0°C ice at a rate of 54 mm/h. Perform the regelation experiment and propose a plausible explanation for this phenomenon.

11.10D Figure P11.10D shows the schematic of a hydraulic accumulator in the form of a cylindrical pressure vessel with a piston separating a hydraulic fluid from a charge of nitrogen gas. The device has been proposed as a means for storing some of the exergy of a decelerating vehicle as it comes to rest. The exergy is stored by compressing the nitrogen. When the vehicle accelerates again, the gas expands and returns some exergy to the hydraulic fluid which is in communication with the vehicle's drive train, thereby assisting the vehicle to accelerate. In a proposal for one such device, the nitrogen operates in the range 50–150 bar and 200–350 K. Develop a thermodynamic model of the accumulator and use the model to assess its suitability for vehicle deceleration/acceleration.

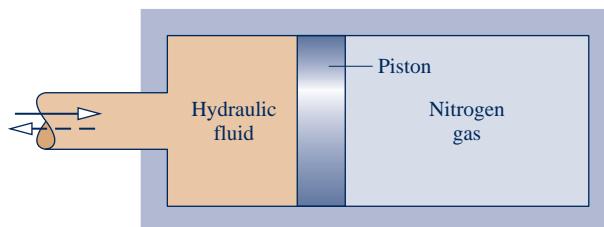


Fig. P11.10D



Library stacks require careful temperature and humidity control using *air-conditioning processes* considered in Sec. 12.8. © GreHinsdale Corbis RF/Age Fotostock America, Inc.

ENGINEERING CONTEXT Many systems of interest involve gas mixtures of two or more components. To apply the principles of thermodynamics introduced thus far to these systems requires that we evaluate properties of the mixtures. Means are available for determining the properties of mixtures from the mixture composition and the properties of the individual pure components from which the mixtures are formed. Methods for this purpose are discussed both in Chap. 11 and in the present chapter.

The **objective** of the present chapter is to study mixtures where the overall mixture and each of its components can be modeled as ideal gases. General ideal gas mixture considerations are provided in the first part of the chapter. Understanding the behavior of ideal gas mixtures of dry air and water vapor is prerequisite to considering air-conditioning processes in the second part of the chapter, which is identified by the heading, *Psychrometric Applications*. In those processes, we sometimes must consider the presence of liquid water as well. We will also need to know how to handle ideal gas mixtures when we study the subjects of combustion and chemical equilibrium in Chaps. 13 and 14, respectively.



12

Ideal Gas Mixture and Psychrometric Applications

► LEARNING OUTCOMES

When you complete your study of this chapter, you will be able to...

- ▶ describe ideal gas mixture composition in terms of mass fractions or mole fractions.
- ▶ use the *Dalton model* to relate pressure, volume, and temperature and to calculate changes in U , H , and S for ideal gas mixtures.
- ▶ apply mass, energy, and entropy balances to systems involving ideal gas mixtures, including mixing processes.
- ▶ demonstrate understanding of psychrometric terminology, including humidity ratio, relative humidity, mixture enthalpy, and dew point temperature.
- ▶ use the psychrometric chart to represent common air-conditioning processes and to retrieve data.
- ▶ apply mass, energy, and entropy balances to analyze air-conditioning processes and cooling towers.

Ideal Gas Mixtures: General Considerations

TAKE NOTE...

- In Secs. 12.1–12.3, we introduce mixture concepts required for study of psychometrics in the second part of this chapter and combustion in Chap. 13.
- In Sec. 12.4, we extend the discussion of mixtures and provide several solved examples illustrating important types of mixture applications. For economy of effort, some readers may elect to defer Sec. 12.4 and proceed directly to content having more immediate interest for them: psychometrics beginning in Sec. 12.5 or combustion beginning in Sec. 13.1.

mass fractions

gravimetric analysis

mole fractions

12.1 Describing Mixture Composition

To specify the state of a mixture requires the composition and the values of two independent intensive properties such as temperature and pressure. The object of the present section is to consider ways for describing mixture composition. In subsequent sections, we show how mixture properties other than composition can be evaluated.

Consider a closed system consisting of a gaseous mixture of two or more components. The composition of the mixture can be described by giving the *mass* or the *number of moles* of each component present. With Eq. 1.8, the mass, the number of moles, and the molecular weight of a component i are related by

$$n_i = \frac{m_i}{M_i} \quad (12.1)$$

where m_i is the mass, n_i is the number of moles, and M_i is the molecular weight of component i , respectively. When m_i is expressed in terms of the kilogram, n_i is in kmol. When m_i is in terms of the pound mass, n_i is in lbmol. However, any unit of mass can be used in this relationship.

The total mass of the mixture, m , is the sum of the masses of its components

$$m = m_1 + m_2 + \cdots + m_j = \sum_{i=1}^j m_i \quad (12.2)$$

The *relative* amounts of the components present in the mixture can be specified in terms of **mass fractions**. The mass fraction mf_i of component i is defined as

$$mf_i = \frac{m_i}{m} \quad (12.3)$$

A listing of the mass fractions of the components of a mixture is sometimes referred to as a **gravimetric analysis**.

Dividing each term of Eq. 12.2 by the total mass of mixture m and using Eq. 12.3

$$1 = \sum_{i=1}^j mf_i \quad (12.4)$$

That is, the sum of the mass fractions of all the components in a mixture is equal to unity.

The total number of moles in a mixture, n , is the sum of the number of moles of each of its components

$$n = n_1 + n_2 + \cdots + n_j = \sum_{i=1}^j n_i \quad (12.5)$$

The *relative* amounts of the components present in the mixture also can be described in terms of **mole fractions**. The mole fraction y_i of component i is defined as

$$y_i = \frac{n_i}{n} \quad (12.6)$$

A listing of the mole fractions of the components of a mixture may be called a **molar analysis**. An analysis of a mixture in terms of mole fractions is also called a **volumetric analysis**.

Dividing each term of Eq. 12.5 by the total number of moles of mixture n and using Eq. 12.6

$$1 = \sum_{i=1}^j y_i \quad (12.7)$$

That is, the sum of the mole fractions of all the components in a mixture is equal to unity.

The **apparent (or average) molecular weight** of the mixture, M , is defined as the ratio of the total mass of the mixture, m , to the total number of moles of mixture, n

$$M = \frac{m}{n} \quad (12.8)$$

Equation 12.8 can be expressed in a convenient alternative form. With Eq. 12.2, it becomes

$$M = \frac{m_1 + m_2 + \dots + m_j}{n}$$

Introducing $m_i = n_i M_i$ from Eq. 12.1

$$M = \frac{n_1 M_1 + n_2 M_2 + \dots + n_j M_j}{n}$$

Finally, with Eq. 12.6, the apparent molecular weight of the mixture can be calculated as a mole-fraction average of the component molecular weights

$$M = \sum_{i=1}^j y_i M_i \quad (12.9)$$

► FOR EXAMPLE consider the case of air. A sample of *atmospheric air* contains several gaseous components including water vapor and contaminants such as dust, pollen, and pollutants. The term **dry air** refers only to the gaseous components when all water vapor and contaminants have been removed. The molar analysis of a typical sample of dry air is given in Table 12.1. Selecting molecular weights for nitrogen, oxygen, argon, and carbon dioxide from Table A-1, and neglecting the trace substances neon, helium, etc., the apparent molecular weight of dry air obtained from Eq. 12.9 is

$$\begin{aligned} M &\approx 0.7808(28.02) + 0.2095(32.00) + 0.0093(39.94) + 0.0003(44.01) \\ &= 28.97 \text{ kg/kmol} = 28.97 \text{ lb/lbmol} \end{aligned}$$

This value, which is the entry for air in Tables A-1, would not be altered significantly if the trace substances were also included in the calculation. ▲ ▲ ▲ ▲ ▲

molar analysis

volumetric analysis

apparent molecular weight

TABLE 12.1

Approximate Composition of Dry Air

Component	Mole Fraction (%)
Nitrogen	78.08
Oxygen	20.95
Argon	0.93
Carbon dioxide	0.03
Neon, helium, methane, and others	0.01

dry air

Next, we consider two examples illustrating, respectively, the conversion from an analysis in terms of mole fractions to an analysis in terms of mass fractions, and conversely.

EXAMPLE 12.1 ►

Converting Mole Fractions to Mass Fractions

The molar analysis of the gaseous products of combustion of a certain hydrocarbon fuel is CO₂, 0.08; H₂O, 0.11; O₂, 0.07; N₂, 0.74. **(a)** Determine the apparent molecular weight of the mixture. **(b)** Determine the composition in terms of mass fractions (gravimetric analysis).

SOLUTION

Known: The molar analysis of the gaseous products of combustion of a hydrocarbon fuel is given.

Find: Determine (a) the apparent molecular weight of the mixture, (b) the composition in terms of mass fractions.

Analysis:

(a) Using Eq. 12.9 and molecular weights (rounded) from Table A-1

$$\begin{aligned} M &= 0.08(44) + 0.11(18) + 0.07(32) + 0.74(28) \\ &= 28.46 \text{ kg/kmol} = 28.46 \text{ lb/lbmol} \end{aligned}$$

(b) Equations 12.1, 12.3, and 12.6 are the key relations required to determine the composition in terms of mass fractions.

① Although the actual amount of mixture is not known, the calculations can be based on any convenient amount. Let us base the solution on 1 kmol of mixture. Then, with Eq. 12.6 the amount n_i of each component present in kmol is numerically equal to the mole fraction, as listed in column (ii) of the accompanying table. Column (iii) of the table gives the respective molecular weights of the components.

Column (iv) of the table gives the mass m_i of each component, in kg per kmol of mixture, obtained with Eq. 12.1 in the form $m_i = M_i n_i$. The values of column (iv) are obtained by multiplying each value of column (ii) by the corresponding value of column (iii). The sum of the values in column (iv) is the mass of the mixture: kg of mixture per kmol of mixture. Note that this sum is just the apparent mixture molecular weight determined in part (a). Finally, using Eq. 12.3, column (v) gives the mass fractions as a percentage. The values of column (v) are obtained by dividing the values of column (iv) by the column (iv) total and multiplying by 100.

(i) Component	(ii)* n_i	×	(iii) M_i	=	(iv)** m_i	(v) $mf_i\%$
CO ₂	0.08	×	44	=	3.52	12.37
H ₂ O	0.11	×	18	=	1.98	6.96
O ₂	0.07	×	32	=	2.24	7.87
N ₂	0.74	×	28	=	20.72	72.80
	1.00				28.46	100.00

*Entries in this column have units of kmol per kmol of mixture. For example, the first entry is 0.08 kmol of CO₂ per kmol of mixture.

**Entries in this column have units of kg per kmol of mixture. For example, the first entry is 3.52 kg of CO₂ per kmol of mixture. The column sum, 28.46, has units of kg of mixture per kmol of mixture.

Skills Developed

Ability to...

- calculate the apparent molecular weight with known mole fractions.
- determine the gravimetric analysis given the molar analysis.

① If the solution to part (b) were conducted on the basis of some other assumed amount of mixture—for example, 100 kmol or 100 lbmol—the same result for the mass fractions would be obtained, as can be verified.

QuickQUIZ

Determine the mass, in kg, of CO₂ in 0.5 kmol of mixture.

Ans. 1.76 kg.

EXAMPLE 12.2**Converting Mass Fractions to Mole Fractions**

A gas mixture has the following composition in terms of mass fractions: H₂, 0.10; N₂, 0.60; CO₂, 0.30. Determine **(a)** the composition in terms of mole fractions and **(b)** the apparent molecular weight of the mixture.

SOLUTION

Known: The gravimetric analysis of a gas mixture is known.

Find: Determine the analysis of the mixture in terms of mole fractions (molar analysis) and the apparent molecular weight of the mixture.

Analysis:

(a) Equations 12.1, 12.3, and 12.6 are the key relations required to determine the composition in terms of mole fractions.

Although the actual amount of mixture is not known, the calculation can be based on any convenient amount. Let us base the solution on 100 kg. Then, with Eq. 12.3, the amount m_i of each component present, in kg, is equal to the mass fraction multiplied by 100 kg. The values are listed in column (ii) of the accompanying table. Column (iii) of the table gives the respective molecular weights of the components.

Column (iv) of the table gives the amount n_i of each component, in kmol per 100 kg of mixture, obtained using Eq. 12.1. The values of column (iv) are obtained by dividing each value of column (ii) by the corresponding value of column (iii). The sum of the values of column (iv) is the total amount of mixture, in kmol per 100 kg of mixture. Finally, using Eq. 12.6, column (v) gives the mole fractions as a percentage. The values of column (v) are obtained by dividing the values of column (iv) by the column (iv) total and multiplying by 100.

②	(i) Component	(ii)* m_i	÷	(iii) M_i	=	(iv)** n_i	(v) y_i %
	H ₂	10	÷	2	=	5.00	63.9
	N ₂	60	÷	28	=	2.14	27.4
	CO ₂	30	÷	44	=	0.68	8.7
		100				7.82	100.0

*Entries in this column have units of kg per 100 kg of mixture. For example, the first entry is 10 kg of H₂ per 100 kg of mixture.

**Entries in this column have units of kmol per 100 kg of mixture. For example, the first entry is 5.00 kmol of H₂ per 100 kg of mixture. The column sum, 7.82, has units of kmol of mixture per 100 kg of mixture.

(b) The apparent molecular weight of the mixture can be found by using Eq. 12.9 and the calculated mole fractions. The value can be determined alternatively by using the column (iv) total giving the total amount of mixture in kmol per 100 kg of mixture. Thus, with Eq. 12.8

$$M = \frac{m}{n} = \frac{100 \text{ kg}}{7.82 \text{ kmol}} = 12.79 \frac{\text{kg}}{\text{kmol}} = 12.79 \frac{\text{lb}}{\text{lbfmol}}$$

- If the solution to part (a) were conducted on the basis of some other assumed amount of mixture, the same result for the mass fractions would be obtained, as can be verified.
- Although H₂ has the smallest mass fraction, its mole fraction is the largest.

Skills Developed

Ability to...

determine the molar analysis given the gravimetric analysis.

QuickQUIZ

How many kmol of H₂ would be present in 200 kg of mixture?

Ans. 10 kmol.

12.2

Relating p , V , and T for Ideal Gas Mixtures¹

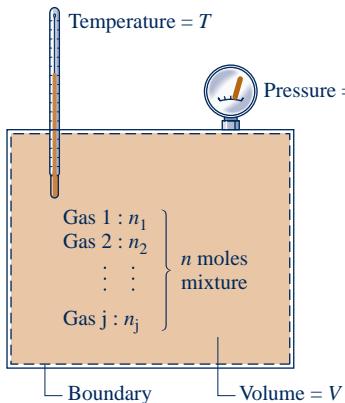


Fig. 12.1 Mixture of several gases.

Dalton model

partial pressure

The definitions given in Sec. 12.1 apply generally to mixtures. In the present section we are concerned only with *ideal gas* mixtures and introduce a model commonly used in conjunction with this idealization: the *Dalton model*.

Consider a system consisting of a number of gases contained within a closed vessel of volume V as shown in Fig. 12.1. The temperature of the gas mixture is T and the pressure is p . The overall mixture is considered an ideal gas, so p , V , T , and the total number of moles of mixture n are related by the ideal gas equation of state

$$p = n \frac{\bar{R}T}{V} \quad (12.10)$$

With reference to this system let us consider the Dalton model.

The Dalton model is consistent with the concept of an ideal gas as being made up of molecules that exert negligible forces on one another and whose volume is negligible relative to the volume occupied by the gas (Sec. 3.12.3). In the absence of significant intermolecular forces, the behavior of each component is unaffected by the presence of the other components. Moreover, if the volume occupied by the molecules is a very small fraction of the total volume, the molecules of each gas present may be regarded as free to roam throughout the full volume. In keeping with this simple picture, the **Dalton model** assumes that each mixture component behaves as an ideal gas as if it were *alone at the temperature T and volume V of the mixture*.

It follows from the Dalton model that the individual components would not exert the mixture pressure p but rather a *partial pressure*. As shown below, the sum of the partial pressures equals the mixture pressure. The **partial pressure** of component i , p_i , is the pressure that n_i moles of component i would exert if the component were alone in the volume V at the mixture temperature T . The partial pressure can be evaluated using the ideal gas equation of state

$$p_i = \frac{n_i \bar{R}T}{V} \quad (12.11)$$

Dividing Eq. 12.11 by Eq. 12.10

$$\frac{p_i}{p} = \frac{n_i \bar{R}T/V}{n \bar{R}T/V} = \frac{n_i}{n} = y_i$$

Thus, the partial pressure of component i can be evaluated in terms of its mole fraction y_i and the mixture pressure p

$$p_i = y_i p \quad (12.12)$$

To show that the sum of partial pressures equals the mixture pressure, sum both sides of Eq. 12.12 to obtain

$$\sum_{i=1}^j p_i = \sum_{i=1}^j y_i p = p \sum_{i=1}^j y_i$$

Since the sum of the mole fractions is unity (Eq. 12.7), this becomes

$$p = \sum_{i=1}^j p_i \quad (12.13)$$

The Dalton model is a special case of the *additive pressure* rule for relating the pressure, specific volume, and temperature of gas mixtures introduced in Sec. 11.8.

¹The concept of an ideal gas mixture is a special case of the *ideal solution* concept introduced in Sec. 11.9.5.

Among numerous other mixture rules found in the engineering literature is the *Amagat model* considered in the box that follows.

Introducing the Amagat Model

The underlying assumption of the *Amagat model* is that each mixture component behaves as an ideal gas as if it existed separately at the pressure p and temperature T of the mixture.

The volume that n_i moles of component i would occupy if the component existed at p and T is called the *partial volume*, V_i , of component i . As shown below, the sum of the partial volumes equals the total volume. The partial volume can be evaluated using the ideal gas equation of state

$$V_i = \frac{n_i \bar{R} T}{p} \quad (12.14)$$

Dividing Eq. 12.14 by the total volume V

$$\frac{V_i}{V} = \frac{n_i \bar{R} T / p}{n \bar{R} T / p} = \frac{n_i}{n} = y_i$$

Thus, the partial volume of component i also can be evaluated in terms of its mole fraction y_i and the total volume

$$V_i = y_i V \quad (12.15)$$

This relationship between volume fraction and mole fraction underlies the use of the term *volumetric analysis* as signifying an analysis of a mixture in terms of mole fractions.

To show that the sum of partial volumes equals the total volume, sum both sides of Eq. 12.15 to obtain

$$\sum_{i=1}^j V_i = \sum_{i=1}^j y_i V = V \sum_{i=1}^j y_i$$

Since the sum of the mole fractions equals unity, this becomes

$$V = \sum_{i=1}^j V_i \quad (12.16)$$

Finally, note that the Amagat model is a special case of the *additive volume model* introduced in Sec. 11.8.

12.3

Evaluating U , H , S , and Specific Heats

To apply the conservation of energy principle to a system involving an ideal gas mixture requires evaluation of the internal energy, enthalpy, or specific heats of the mixture at various states. Similarly, to conduct an analysis using the second law normally requires the entropy of the mixture. The objective of the present section is to develop means to evaluate these properties for ideal gas mixtures.

12.3.1 • Evaluating U and H

Consider a closed system consisting of an ideal gas mixture. Extensive properties of the mixture, such as U , H , or S , can be found by adding the contribution of each component *at the condition at which the component exists in the mixture*. Let us apply this model to internal energy and enthalpy.

Since the internal energy and enthalpy of ideal gases are functions of temperature only, the values of these properties for each component present in the mixture are determined by the mixture temperature alone. Accordingly

$$U = U_1 + U_2 + \cdots + U_j = \sum_{i=1}^j U_i \quad (12.17)$$

$$H = H_1 + H_2 + \cdots + H_j = \sum_{i=1}^j H_i \quad (12.18)$$

where U_i and H_i are the internal energy and enthalpy, respectively, of component i evaluated at the mixture temperature.

Equations 12.17 and 12.18 can be rewritten on a molar basis as

$$n\bar{u} = n_1\bar{u}_1 + n_2\bar{u}_2 + \cdots + n_j\bar{u}_j = \sum_{i=1}^j n_i\bar{u}_i \quad (12.19)$$

and

$$n\bar{h} = n_1\bar{h}_1 + n_2\bar{h}_2 + \cdots + n_j\bar{h}_j = \sum_{i=1}^j n_i\bar{h}_i \quad (12.20)$$

where \bar{u} and \bar{h} are the specific internal energy and enthalpy of the *mixture* per mole of mixture, and \bar{u}_i and \bar{h}_i are the specific internal energy and enthalpy of *component* i per mole of i . Dividing by the total number of moles of mixture, n , gives expressions for the specific internal energy and enthalpy of the mixture per mole of mixture, respectively

$$\bar{u} = \sum_{i=1}^j y_i\bar{u}_i \quad (12.21)$$

$$\bar{h} = \sum_{i=1}^j y_i\bar{h}_i \quad (12.22)$$

Each of the molar internal energy and enthalpy terms appearing in Eqs. 12.19 through 12.22 is evaluated at the mixture temperature only.

12.3.2 Evaluating c_v and c_p

Differentiation of Eqs. 12.21 and 12.22 with respect to temperature results, respectively, in the following expressions for the specific heats \bar{c}_v and \bar{c}_p of the mixture on a molar basis

$$\bar{c}_v = \sum_{i=1}^j y_i\bar{c}_{v,i} \quad (12.23)$$

$$\bar{c}_p = \sum_{i=1}^j y_i\bar{c}_{p,i} \quad (12.24)$$

That is, the mixture specific heats \bar{c}_p and \bar{c}_v are mole-fraction averages of the respective component specific heats. The specific heat ratio for the mixture is $k = \bar{c}_p/\bar{c}_v$.

12.3.3 Evaluating S

The entropy of a mixture can be found, as for U and H , by adding the contribution of each component at the condition at which the component exists in the mixture.

The entropy of an ideal gas depends on two properties, not on temperature alone as for internal energy and enthalpy. Accordingly, for the mixture

$$S = S_1 + S_2 + \cdots + S_j = \sum_{i=1}^j S_i \quad (12.25)$$

where S_i is the entropy of component i evaluated at the mixture temperature T and partial pressure p_i (or at temperature T and total volume V).

Equation 12.25 can be written on a molar basis as

$$n\bar{s} = n_1\bar{s}_1 + n_2\bar{s}_2 + \cdots + n_j\bar{s}_j = \sum_{i=1}^j n_i\bar{s}_i \quad (12.26)$$

where \bar{s} is the entropy of the *mixture* per mole of mixture and \bar{s}_i is the entropy of component i per mole of i . Dividing by the total number of moles of mixture, n , gives an expression for the entropy of the mixture per mole of mixture

$$\bar{s} = \sum_{i=1}^j y_i\bar{s}_i \quad (12.27)$$

In subsequent applications, the specific entropies \bar{s}_i of Eqs. 12.26 and 12.27 are evaluated at the mixture temperature T and the partial pressure p_i .

12.3.4 Working on a Mass Basis

In cases where it is convenient to work on a mass basis, the foregoing expressions are written with the mass of the mixture, m , and the mass of component i in the mixture, m_i , replacing, respectively, the number of moles of mixture, n , and the number of moles of component i , n_i . Similarly, the mass fraction of component i , mf_i , replaces the mole fraction, y_i . All specific internal energies, enthalpies, and entropies are evaluated on a unit mass basis rather than on a per mole basis as above. To illustrate, Table 12.2

TABLE 12.2

Property Relations on a Mass Basis for Binary Ideal Gas Mixtures

Notation: m_1 = mass of gas 1, M_1 = molecular weight of gas 1
 m_2 = mass of gas 2, M_2 = molecular weight of gas 2
 m = mixture mass = $m_1 + m_2$, $mf_1 = (m_1/m)$, $mf_2 = (m_2/m)$
 T = mixture temperature, p = mixture pressure, V = mixture volume

Equation of state:

$$p = m(\bar{R}/M)T/V \quad (a)$$

where $M = (y_1 M_1 + y_2 M_2)$ and the mole fractions y_1 and y_2 are given by

$$y_1 = n_1/(n_1 + n_2), y_2 = n_2/(n_1 + n_2) \quad (b)$$

where $n_1 = m_1/M_1$ and $n_2 = m_2/M_2$.

Partial pressures: $p_1 = y_1 p$, $p_2 = y_2 p$ (c)

Properties on a mass basis:

$$\text{Mixture enthalpy: } H = m_1 h_1(T) + m_2 h_2(T) \quad (d)$$

$$\text{Mixture internal energy: } U = m_1 u_1(T) + m_2 u_2(T) \quad (e)$$

$$\begin{aligned} \text{Mixture specific heats: } c_p &= (m_1/m)c_{p1}(T) + (m_2/m)c_{p2}(T) \\ &= (mf_1)c_{p1}(T) + (mf_2)c_{p2}(T) \end{aligned} \quad (f)$$

$$\begin{aligned} c_v &= (m_1/m)c_{v1}(T) + (m_2/m)c_{v2}(T) \\ &= (mf_1)c_{v1}(T) + (mf_2)c_{v2}(T) \end{aligned} \quad (g)$$

$$\text{Mixture entropy: } S = m_1 s_1(T, p_1) + m_2 s_2(T, p_2) \quad (h)$$

provides property relations on a mass basis for *binary* mixtures. These relations are applicable, in particular, to *moist* air, introduced in Sec. 12.5.

By using the molecular weight of the mixture or of component *i*, as appropriate, data can be converted from a mass basis to a molar basis, or conversely, with relations of the form

$$\bar{u} = Mu, \quad \bar{h} = Mh, \quad \bar{c}_p = Mc_p, \quad \bar{c}_v = Mc_v, \quad \bar{s} = Ms \quad (12.28)$$

for the mixture, and

$$\bar{u}_i = M_i u_i, \quad \bar{h}_i = M_i h_i, \quad \bar{c}_{p,i} = M_i c_{p,i}, \quad \bar{c}_{v,i} = M_i c_{v,i}, \quad \bar{s}_i = M_i s_i \quad (12.29)$$

for component *i*.

12.4 Analyzing Systems Involving Mixtures

To perform thermodynamic analyses of systems involving *nonreacting* ideal gas mixtures requires no new fundamental principles. The conservation of mass and energy principles and the second law of thermodynamics are applicable in the forms previously introduced. The only new aspect is the proper evaluation of the required property data for the mixtures involved. This is illustrated in the present section, which deals with two classes of problems involving mixtures: In Sec. 12.4.1 the mixture is already formed, and we study processes in which there is no change in composition. Section 12.4.2 considers the formation of mixtures from individual components that are initially separate.

12.4.1 Mixture Processes at Constant Composition

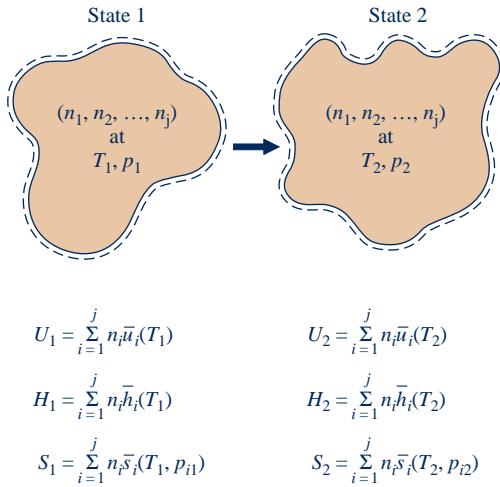


Fig. 12.2 Process of an ideal gas mixture.

In the present section we are concerned with the case of ideal gas mixtures undergoing processes during which the composition remains constant. The number of moles of each component present, and thus the total number of moles of mixture, remain the same throughout the process. This case is shown schematically in Fig. 12.2, which is labeled with expressions for *U*, *H*, and *S* of a mixture at the initial and final states of a process undergone by the mixture. In accordance with the discussion of Sec. 12.3, the specific internal energies and enthalpies of the components are evaluated at the temperature of the mixture. The specific entropy of each component is evaluated at the mixture temperature and the partial pressure of the component in the mixture.

The changes in the internal energy and enthalpy of the mixture during the process are given, respectively, by

$$U_2 - U_1 = \sum_{i=1}^j n_i [\bar{u}_i(T_2) - \bar{u}_i(T_1)] \quad (12.30)$$

$$H_2 - H_1 = \sum_{i=1}^j n_i [\bar{h}_i(T_2) - \bar{h}_i(T_1)] \quad (12.31)$$

where *T*₁ and *T*₂ denote the temperature at the initial and final states. Dividing by the number of moles of mixture, *n*, expressions for the change in internal energy and enthalpy of the mixture per mole of mixture result

$$\Delta \bar{u} = \sum_{i=1}^j y_i [\bar{u}_i(T_2) - \bar{u}_i(T_1)] \quad (12.32)$$

$$\Delta \bar{h} = \sum_{i=1}^j y_i [\bar{h}_i(T_2) - \bar{h}_i(T_1)] \quad (12.33)$$

Similarly, the change in entropy for the mixture is

$$S_2 - S_1 = \sum_{i=1}^j n_i [\bar{s}_i(T_2, p_{i2}) - \bar{s}_i(T_1, p_{i1})] \quad (12.34)$$

where p_{i1} and p_{i2} denote, respectively, the initial and final partial pressures of component i . Dividing by the total moles of mixture, Eq. 12.34 becomes

$$\Delta \bar{s} = \sum_{i=1}^j y_i [\bar{s}_i(T_2, p_{i2}) - \bar{s}_i(T_1, p_{i1})] \quad (12.35)$$

Companion expressions for Eqs. 12.30 through 12.35 on a mass basis also can be written. This is left as an exercise.

The foregoing expressions giving the changes in internal energy, enthalpy, and entropy of the mixture are written in terms of the respective property changes of the components. Accordingly, different datums might be used to assign specific enthalpy values to the various components because the datums would cancel when the component enthalpy changes are calculated. Similar remarks apply to the cases of internal energy and entropy.

Using Ideal Gas Tables

For several common gases modeled as ideal gases, the quantities \bar{u}_i and \bar{h}_i appearing in the foregoing expressions can be evaluated as functions of temperature only from Tables A-22 and A-23. Table A-22 for air gives these quantities on a *mass* basis. Table A-23 gives them on a *molar* basis.

The ideal gas tables also can be used to evaluate the entropy change. The change in specific entropy of component i required by Eqs. 12.34 and 12.35 can be determined with Eq. 6.20b as

$$\Delta \bar{s}_i = \bar{s}_i^\circ(T_2) - \bar{s}_i^\circ(T_1) - \bar{R} \ln \frac{p_{i2}}{p_{i1}}$$

Since the mixture composition remains constant, the ratio of the partial pressures in this expression is the same as the ratio of the mixture pressures, as can be shown by using Eq. 12.12 to write

$$\frac{p_{i2}}{p_{i1}} = \frac{y_i p_2}{y_i p_1} = \frac{p_2}{p_1}$$

Accordingly, when the composition is constant, the change in the specific entropy of component i is simply

$$\Delta \bar{s}_i = \bar{s}_i^\circ(T_2) - \bar{s}_i^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1} \quad (12.36)$$

where p_1 and p_2 denote, respectively, the initial and final *mixture* pressures. The terms \bar{s}_i° of Eq. 12.36 can be obtained as functions of temperature for several common gases from Table A-23. Table A-22 for air gives s° versus temperature.

TAKE NOTE...

When mixture composition remains constant, a ratio of partial pressures, p_{i2}/p_{i1} , equals the ratio of mixture pressures, p_2/p_1 .

Assuming Constant Specific Heats

When the component specific heats $\bar{c}_{v,i}$ and $\bar{c}_{p,i}$ are taken as constants, the specific internal energy, enthalpy, and entropy changes of the mixture and the components of the mixture are given by

$$\Delta \bar{u} = \bar{c}_v(T_2 - T_1), \quad \Delta \bar{u}_i = \bar{c}_{v,i}(T_2 - T_1) \quad (12.37)$$

$$\Delta \bar{h} = \bar{c}_p(T_2 - T_1), \quad \Delta \bar{h}_i = \bar{c}_{p,i}(T_2 - T_1) \quad (12.38)$$

$$\Delta \bar{s} = \bar{c}_p \ln \frac{T_2}{T_1} - \bar{R} \ln \frac{p_2}{p_1}, \quad \Delta \bar{s}_i = \bar{c}_{p,i} \ln \frac{T_2}{T_1} - \bar{R} \ln \frac{p_2}{p_1} \quad (12.39)$$

where the mixture specific heats \bar{c}_v and \bar{c}_p are evaluated from Eqs. 12.23 and 12.24, respectively, using data from Tables A-20 or the literature, as required.

The expression for $\Delta\bar{u}$ can be obtained formally by substituting the above expression for $\Delta\bar{u}_i$ into Eq. 12.32 and using Eq. 12.23 to simplify the result. Similarly, the expressions for $\Delta\bar{h}$ and $\Delta\bar{s}$ can be obtained by inserting $\Delta\bar{h}_i$ and $\Delta\bar{s}_i$ into Eqs. 12.33 and 12.35, respectively, and using Eq. 12.24 to simplify. In the equations for entropy change, the ratio of mixture pressures replaces the ratio of partial pressures as discussed above. Similar expressions can be written for the mixture specific internal energy, enthalpy, and entropy changes on a mass basis. This is left as an exercise.

Using Computer Software

The changes in internal energy, enthalpy, and entropy required in Eqs. 12.32, 12.33, and 12.35, respectively, also can be evaluated using computer software. *Interactive Thermodynamics: IT* provides data for a large number of gases modeled as ideal gases, and its use is illustrated in Example 12.4 below.

The next example illustrates the use of ideal gas mixture relations for analyzing a compression process.

EXAMPLE 12.3

Analyzing an Ideal Gas Mixture Undergoing Compression

A mixture of 0.3 lb of carbon dioxide and 0.2 lb of nitrogen is compressed from $p_1 = 1 \text{ atm}$, $T_1 = 540^\circ\text{R}$ to $p_2 = 3 \text{ atm}$ in a polytropic process for which $n = 1.25$. Determine (a) the final temperature, in $^\circ\text{R}$, (b) the work, in Btu, (c) the heat transfer, in Btu, (d) the change in entropy of the mixture, in $\text{Btu}/^\circ\text{R}$.

SOLUTION

Known: A mixture of 0.3 lb of CO_2 and 0.2 lb of N_2 is compressed in a polytropic process for which $n = 1.25$. At the initial state, $p_1 = 1 \text{ atm}$, $T_1 = 540^\circ\text{R}$. At the final state, $p_2 = 3 \text{ atm}$.

Find: Determine the final temperature, in $^\circ\text{R}$, the work, in Btu, the heat transfer, in Btu, and the entropy change of the mixture in, $\text{Btu}/^\circ\text{R}$.

Schematic and Given Data:

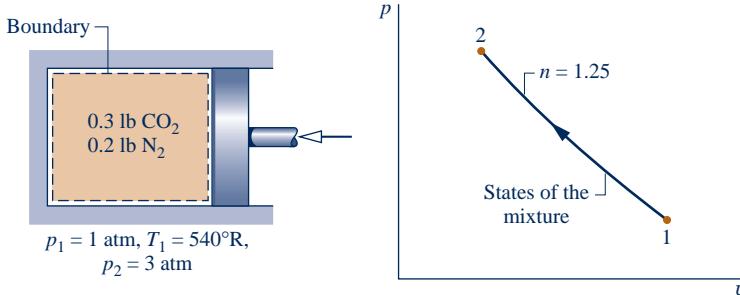


Fig. E12.3

Engineering Model:

- As shown in the accompanying figure, the system is the mixture of CO_2 and N_2 . The mixture composition remains constant during the compression.
- The Dalton model applies: Each mixture component behaves as if it were an ideal gas occupying the entire system volume at the mixture temperature. The overall mixture acts as an ideal gas.
- The compression process is a polytropic process for which $n = 1.25$.
- The changes in kinetic and potential energy between the initial and final states can be ignored.

Analysis:

(a) For an ideal gas, the temperatures and pressures at the end states of a polytropic process are related by Eq. 3.56

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{(n-1)/n}$$

Inserting values

$$T_2 = 540 \left(\frac{3}{1} \right)^{0.2} = 673^\circ\text{R}$$

(b) The work for the compression process is given by

$$W = \int_1^2 p dV$$

Introducing $pV^n = \text{constant}$ and performing the integration

$$W = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

With the ideal gas equation of state, this reduces to

$$W = \frac{m(\bar{R}/M)(T_2 - T_1)}{1 - n}$$

The mass of the mixture is $m = 0.3 + 0.2 = 0.5$ lb. The apparent molecular weight of the mixture can be calculated using $M = m/n$, where n is the total number of moles of mixture. With Eq. 12.1, the numbers of moles of CO₂ and N₂ are, respectively

$$n_{\text{CO}_2} = \frac{0.3}{44} = 0.0068 \text{ lbmol}, \quad n_{\text{N}_2} = \frac{0.2}{28} = 0.0071 \text{ lbmol}$$

The total number of moles of mixture is then $n = 0.0139$ lbmol. The apparent molecular weight of the mixture is $M = 0.5/0.0139 = 35.97$.

Calculating the work

$$W = \frac{(0.5 \text{ lb}) \left(\frac{1545 \text{ ft} \cdot \text{lbf}}{35.97 \text{ lb} \cdot {}^\circ\text{R}} \right) (673^\circ\text{R} - 540^\circ\text{R})}{1 - 1.25} \left| \frac{1 \text{ Btu}}{778 \text{ ft} \cdot \text{lbf}} \right| \\ = -14.69 \text{ Btu}$$

where the minus sign indicates that work is done on the mixture, as expected.

(c) With assumption 4, the closed system energy balance can be placed in the form

$$Q = \Delta U + W$$

where ΔU is the change in internal energy of the mixture.

The change in internal energy of the mixture equals the sum of the internal energy changes of the components. With Eq. 12.30

$$\textcircled{1} \quad \Delta U = n_{\text{CO}_2} [\bar{u}_{\text{CO}_2}(T_2) - \bar{u}_{\text{CO}_2}(T_1)] + n_{\text{N}_2} [\bar{u}_{\text{N}_2}(T_2) - \bar{u}_{\text{N}_2}(T_1)]$$

This form is convenient because Table A-23E gives internal energy values for N₂ and CO₂, respectively, on a molar basis. With values from this table

$$\begin{aligned} \Delta U &= (0.0068)(3954 - 2984) + (0.0071)(3340 - 2678) \\ &= 11.3 \text{ Btu} \end{aligned}$$

Inserting values for ΔU and W into the expression for Q

$$Q = +11.3 - 14.69 = -3.39 \text{ Btu}$$

where the minus sign signifies a heat transfer from the system.

- (d) The change in entropy of the mixture equals the sum of the entropy changes of the components. With Eq. 12.34

$$\Delta S = n_{\text{CO}_2} \Delta \bar{s}_{\text{CO}_2} + n_{\text{N}_2} \Delta \bar{s}_{\text{N}_2}$$

where $\Delta \bar{s}_{\text{N}_2}$ and $\Delta \bar{s}_{\text{CO}_2}$ are evaluated using Eq. 12.36 and values of \bar{s}° for N₂ and CO₂ from Table A-23E. That is

2

$$\begin{aligned}\Delta S &= 0.0068 \left(53.123 - 51.082 - 1.986 \ln \frac{3}{1} \right) \\ &\quad + 0.0071 \left(47.313 - 45.781 - 1.986 \ln \frac{3}{1} \right) \\ &= -0.0056 \text{ Btu}/^\circ\text{R}\end{aligned}$$

Entropy decreases in the process because entropy is transferred from the system accompanying heat transfer.

- In view of the relatively small temperature change, the changes in the internal energy and entropy of the mixture can be evaluated alternatively using the constant specific heat relations, Eqs. 12.37 and 12.39, respectively. In these equations, \bar{c}_v and \bar{c}_p are specific heats for the mixture determined using Eqs. 12.23 and 12.24 together with appropriate specific heat values for the components chosen from Table A-20E.
- Since the composition remains constant, the ratio of partial pressures equals the ratio of mixture pressures, so Eq. 12.36 can be used to evaluate the component specific entropy changes required here.

Skills Developed

Ability to...

- analyze a polytropic process of a closed system for a mixture of ideal gases.
- apply ideal gas mixture principles.
- determine changes in internal energy and entropy for ideal gas mixtures using tabular data.

QuickQUIZ

Recalling that polytropic processes are internally reversible, determine for the system the amount of entropy transfer accompanying heat transfer, in Btu/°R. **Ans.** $-0.0056 \text{ Btu}/^\circ\text{R}$.

The next example illustrates the application of ideal gas mixture principles for the analysis of a mixture expanding isentropically through a nozzle. The solution features the use of table data and *IT* as an alternative.

EXAMPLE 12.4

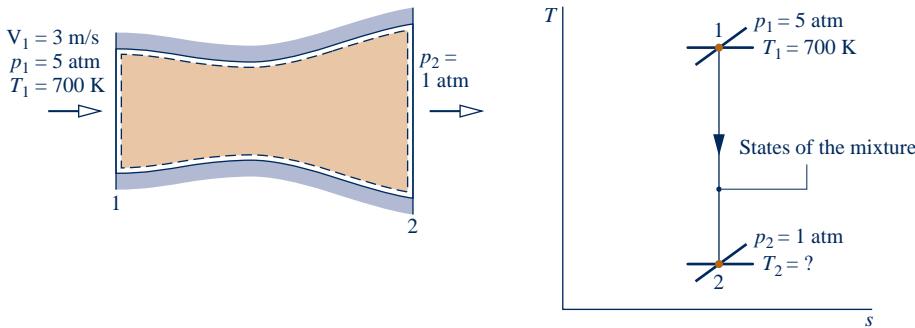
Considering an Ideal Gas Mixture Expanding Isentropically Through a Nozzle

A gas mixture consisting of CO₂ and O₂ with mole fractions 0.8 and 0.2, respectively, expands isentropically and at steady state through a nozzle from 700 K, 5 atm, 3 m/s to an exit pressure of 1 atm. Determine (a) the temperature at the nozzle exit, in K, (b) the entropy changes of the CO₂ and O₂ from inlet to exit, in kJ/kmol · K, (c) the exit velocity, in m/s.

SOLUTION

Known: A gas mixture consisting of CO₂ and O₂ in specified proportions expands isentropically through a nozzle from specified inlet conditions to a given exit pressure.

Find: Determine the temperature at the nozzle exit, in K, the entropy changes of the CO₂ and O₂ from inlet to exit, in kJ/kmol · K, and the exit velocity, in m/s.

Schematic and Given Data:**Fig. E12.4****Engineering Model:**

1. The control volume shown by the dashed line on the accompanying figure operates at steady state.
2. The mixture composition remains constant as the mixture expands isentropically through the nozzle.
3. The Dalton model applies: The overall mixture and each mixture component act as ideal gases. The state of each component is defined by the temperature and the partial pressure of the component.
4. The change in potential energy between inlet and exit can be ignored.

Analysis:

(a) The temperature at the exit can be determined using the fact that the expansion occurs isentropically: $\bar{s}_2 - \bar{s}_1 = 0$. As there is no change in the specific entropy of the *mixture* between inlet and exit, Eq. 12.35 can be used to write

$$\bar{s}_2 - \bar{s}_1 = y_{O_2} \Delta \bar{s}_{O_2} + y_{CO_2} \Delta \bar{s}_{CO_2} = 0 \quad (\text{a})$$

Since composition remains constant, the ratio of partial pressures equals the ratio of mixture pressures. Accordingly, the change in specific entropy of each component can be determined using Eq. 12.36. Equation (a) then becomes

$$y_{O_2} \left[\bar{s}_{O_2}^{\circ}(T_2) - \bar{s}_{O_2}^{\circ}(T_1) - \bar{R} \ln \frac{p_2}{p_1} \right] + y_{CO_2} \left[\bar{s}_{CO_2}^{\circ}(T_2) - \bar{s}_{CO_2}^{\circ}(T_1) - \bar{R} \ln \frac{p_2}{p_1} \right] = 0$$

On rearrangement

$$y_{O_2} \bar{s}_{O_2}^{\circ}(T_2) + y_{CO_2} \bar{s}_{CO_2}^{\circ}(T_2) = y_{O_2} \bar{s}_{O_2}^{\circ}(T_1) + y_{CO_2} \bar{s}_{CO_2}^{\circ}(T_1) + (y_{O_2} + y_{CO_2}) \bar{R} \ln \frac{p_2}{p_1}$$

The sum of mole fractions equals unity, so the coefficient of the last term on the right side is $(y_{O_2} + y_{CO_2}) = 1$.

Introducing given data, and values of \bar{s}° for O_2 and CO_2 at $T_1 = 700 \text{ K}$ from Table A-23

$$0.2 \bar{s}_{O_2}^{\circ}(T_2) + 0.8 \bar{s}_{CO_2}^{\circ}(T_2) = 0.2(231.358) + 0.8(250.663) + 8.314 \ln \frac{1}{5}$$

or

$$0.2 \bar{s}_{O_2}^{\circ}(T_2) + 0.8 \bar{s}_{CO_2}^{\circ}(T_2) = 233.42 \text{ kJ/kmol} \cdot \text{K}$$

To determine the temperature T_2 requires an iterative approach with the above equation: A final temperature T_2 is assumed, and the \bar{s}° values for O_2 and CO_2 are found from Table A-23. If these two values do not satisfy the equation, another temperature is assumed. The procedure continues until the desired agreement is attained. In the present case

$$\text{at } T = 510 \text{ K: } 0.2(221.206) + 0.8(235.700) = 232.80$$

$$\text{at } T = 520 \text{ K: } 0.2(221.812) + 0.8(236.575) = 233.62$$

Linear interpolation between these values gives $T_2 = 5176 \text{ K}$.

Alternative Solution:

Alternatively, the following *IT* program can be used to evaluate T_2 without resorting to iteration with table data. In the program, y_{O_2} denotes the mole fraction of O_2 , p_{1,O_2} denotes the partial pressure of O_2 at state 1, s_{1,O_2} denotes the entropy per mole of O_2 at state 1, and so on.

```

T1 = 700 // K
p1 = 5 // bar
p2 = 1 // bar
yO2 = 0.2
yCO2 = 0.8
p1_O2 = yO2 * p1
p1_CO2 = yCO2 * p1
p2_O2 = yO2 * p2
p2_CO2 = yCO2 * p2
s1_O2 = s_TP ("O2",T1,p1_O2)
s1_CO2 = s_TP ("CO2",T1,p1_CO2)
s2_O2 = s_TP ("O2",T2,p2_O2)
s2_CO2 = s_TP ("CO2",T2,p2_CO2)
// When expressed in terms of these quantities, Eq. (a) takes the form
yO2 * (s2_O2 - s1_O2) + yCO2 * (s2_CO2 - s1_CO2) = 0

```

Using the **Solve** button, the result is $T_2 = 517.6$ K, which agrees with the value obtained using table data. Note that *IT* provides the value of specific entropy for each component directly and does not return \bar{s}° of the ideal gas tables.

1 (b) The change in the specific entropy for each of the components can be determined using Eq. 12.36. For O_2

$$\Delta \bar{s}_{O_2} = \bar{s}_{O_2}^\circ(T_2) - \bar{s}_{O_2}^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1}$$

Inserting \bar{s}° values for O_2 from Table A-23 at $T_1 = 700$ K and $T_2 = 517.6$ K

$$\Delta \bar{s}_{O_2} = 221.667 - 231.358 - 8.314 \ln(0.2) = 3.69 \text{ kJ/kmol} \cdot \text{K}$$

Similarly, with CO_2 data from Table A-23

$$\begin{aligned} \Delta \bar{s}_{CO_2} &= \bar{s}_{CO_2}^\circ(T_2) - \bar{s}_{CO_2}^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1} \\ &= 236.365 - 250.663 - 8.314 \ln(0.2) \\ &= -0.92 \text{ kJ/kmol} \cdot \text{K} \end{aligned}$$

2 (c) Reducing the energy rate balance for the one-inlet, one-exit control volume at steady state

$$0 = h_1 - h_2 + \frac{V_1^2 - V_2^2}{2}$$

where h_1 and h_2 are the enthalpy of the mixture, per unit mass of mixture, at the inlet and exit, respectively. Solving for V_2

$$V_2 = \sqrt{V_1^2 + 2(h_1 - h_2)}$$

The term $(h_1 - h_2)$ in the expression for V_2 can be evaluated as

$$h_1 - h_2 = \frac{\bar{h}_1 - \bar{h}_2}{M} = \frac{1}{M} [y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2} + y_{CO_2}(\bar{h}_1 - \bar{h}_2)_{CO_2}]$$

where M is the apparent molecular weight of mixture, and the molar specific enthalpies of O_2 and CO_2 are from Table A-23. With Eq. 12.9, the apparent molecular weight of the mixture is

$$M = 0.8(44) + 0.2(32) = 41.6 \text{ kg/kmol}$$

Then, with enthalpy values at $T_1 = 700$ K and $T_2 = 517.6$ K from Table A-23

$$\begin{aligned} h_1 - h_2 &= \frac{1}{41.6} [0.2(21,184 - 15,320) + 0.8(27,125 - 18,468)] \\ &= 194.7 \text{ kJ/kg} \end{aligned}$$

Finally,

$$③ V_2 = \sqrt{\left(3 \frac{m}{s}\right)^2 + 2\left(194.7 \frac{kJ}{kg}\right) \left|\frac{1 \text{ kg} \cdot \text{m/s}^2}{1 \text{ N}}\right| \left|\frac{10^3 \text{ N} \cdot \text{m}}{1 \text{ kJ}}\right|} = 624 \text{ m/s}$$

- ① Parts (b) and (c) can be solved alternatively using *IT*. These parts also can be solved using a constant c_p together with Eqs. 12.38 and 12.39. Inspection of Table A-20 shows that the specific heats of CO_2 and O_2 increase only slightly with temperature over the interval from 518 to 700 K, and so suitable constant values of c_p for the components and the overall mixture can be readily determined. These alternative solutions are left as exercises.
- ② Each component experiences an entropy change as it passes from inlet to exit. The increase in entropy of the oxygen and the decrease in entropy of the carbon dioxide are due to entropy transfer accompanying heat transfer from the CO_2 to the O_2 as they expand through the nozzle. However, as indicated by Eq. (a), there is no change in the entropy of the *mixture* as it expands through the nozzle.
- ③ Note the use of unit conversion factors in the calculation of V_2 .

QuickQUIZ

What would be the exit velocity, in m/s, if the isentropic nozzle efficiency were 90%? **Ans.** 592 m/s.



Skills Developed

Ability to...

- analyze the isentropic expansion of an ideal gas mixture flowing through a nozzle.
- apply ideal gas mixture principles together with mass and energy balances to calculate the exit velocity of a nozzle.
- determine the exit temperature for a given inlet state and a given exit pressure using tabular data and alternatively using *IT*.

12.4.2 Mixing of Ideal Gases

Thus far, we have considered only mixtures that have already been formed. Now let us take up cases where ideal gas mixtures are formed by mixing gases that are initially separate. Such mixing is irreversible because the mixture forms spontaneously, and a work input from the surroundings would be required to separate the gases and return them to their respective initial states. In this section, the irreversibility of mixing is demonstrated through calculations of the entropy production.

Three factors contribute to the production of entropy in mixing processes:

1. The gases are initially at different temperatures.
2. The gases are initially at different pressures.
3. The gases are distinguishable from one another.

Entropy is produced when any of these factors is present during a mixing process. This is illustrated in the next example, where different gases, initially at different temperatures and pressures, are mixed.

EXAMPLE 12.5

Investigating Adiabatic Mixing of Gases at Constant Total Volume

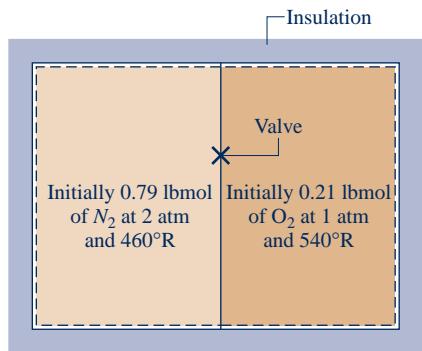
Two rigid, insulated tanks are interconnected by a valve. Initially 0.79 lbmol of nitrogen at 2 atm and 460°R fills one tank. The other tank contains 0.21 lbmol of oxygen at 1 atm and 540°R. The valve is opened and the gases are allowed to mix until a final equilibrium state is attained. During this process, there are no heat or work interactions between the tank contents and the surroundings. Determine (a) the final temperature of the mixture, in °R, (b) the final pressure of the mixture, in atm, (c) the amount of entropy produced in the mixing process, in Btu/°R.

SOLUTION

Known: Nitrogen and oxygen, initially separate at different temperatures and pressures, are allowed to mix without heat or work interactions with the surroundings until a final equilibrium state is attained.

Find: Determine the final temperature of the mixture, in °R, the final pressure of the mixture, in atm, and the amount of entropy produced in the mixing process, in Btu/°R.

Schematic and Given Data:



Engineering Model:

1. The system is taken to be the nitrogen and the oxygen together.
2. When separate, each of the gases behaves as an ideal gas.
3. The final mixture acts as an ideal gas and the Dalton model applies: Each mixture component occupies the total volume and exhibits the mixture temperature.
4. No heat or work interactions occur with the surroundings, and there are no changes in kinetic and potential energy.

Fig. E12.5

Analysis:

(a) The final temperature of the mixture can be determined from an energy balance. With assumption 4, the closed system energy balance reduces to

$$\Delta U = \dot{Q}^0 - \dot{W}^0 \quad \text{or} \quad U_2 - U_1 = 0$$

The initial internal energy of the system, U_1 , equals the sum of the internal energies of the two gases when separate

$$U_1 = n_{N_2}\bar{u}_{N_2}(T_{N_2}) + n_{O_2}\bar{u}_{O_2}(T_{O_2})$$

where $T_{N_2} = 460^\circ\text{R}$ is the initial temperature of the nitrogen and $T_{O_2} = 540^\circ\text{R}$ is the initial temperature of the oxygen. The final internal energy of the system, U_2 , equals the sum of the internal energies of the two gases evaluated at the final mixture temperature T_2

$$U_2 = n_{N_2}\bar{u}_{N_2}(T_2) + n_{O_2}\bar{u}_{O_2}(T_2)$$

Collecting the last three equations

$$n_{N_2}[\bar{u}_{N_2}(T_2) - \bar{u}_{N_2}(T_{N_2})] + n_{O_2}[\bar{u}_{O_2}(T_2) - \bar{u}_{O_2}(T_{O_2})] = 0$$

The temperature T_2 can be determined using specific internal energy data from Table A-23E and an iterative procedure like that employed in part (a) of Example 12.4. However, since the specific heats of N_2 and O_2 vary little over the temperature interval from 460 to 540°R , the solution can be conducted accurately on the basis of constant specific heats. Hence, the foregoing equation becomes

$$n_{N_2}\bar{c}_{v,N_2}(T_2 - T_{N_2}) + n_{O_2}\bar{c}_{v,O_2}(T_2 - T_{O_2}) = 0$$

Solving for T_2

$$T_2 = \frac{n_{N_2}\bar{c}_{v,N_2}T_{N_2} + n_{O_2}\bar{c}_{v,O_2}T_{O_2}}{n_{N_2}\bar{c}_{v,N_2} + n_{O_2}\bar{c}_{v,O_2}}$$

Selecting c_v values for N_2 and O_2 from Table A-20E at the average of the initial temperatures of the gases, 500°R , and using the respective molecular weights to convert to a molar basis

$$\begin{aligned} \bar{c}_{v,N_2} &= \left(28.01 \frac{\text{lb}}{\text{lbmol}}\right) \left(0.177 \frac{\text{Btu}}{\text{lb} \cdot {}^\circ\text{R}}\right) = 4.96 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}} \\ \bar{c}_{v,O_2} &= \left(32.0 \frac{\text{lb}}{\text{lbmol}}\right) \left(0.156 \frac{\text{Btu}}{\text{lb} \cdot {}^\circ\text{R}}\right) = 4.99 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}} \end{aligned}$$

Substituting values into the expression for T_2

$$T_2 = \frac{(0.79 \text{ lbmol})\left(4.96 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}}\right)(460^\circ\text{R}) + (0.21 \text{ lbmol})\left(4.99 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}}\right)(540^\circ\text{R})}{(0.79 \text{ lbmol})\left(4.96 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}}\right) + (0.21 \text{ lbmol})\left(4.99 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}}\right)}$$

$$= 477^\circ\text{R}$$

(b) The final mixture pressure p_2 can be determined using the ideal gas equation of state, $p_2 = n\bar{R}T_2/V$, where n is the total number of moles of mixture and V is the total volume occupied by the mixture. The volume V is the sum of the volumes of the two tanks, obtained with the ideal gas equation of state as follows

$$V = \frac{n_{\text{N}_2}\bar{R}T_{\text{N}_2}}{p_{\text{N}_2}} + \frac{n_{\text{O}_2}\bar{R}T_{\text{O}_2}}{p_{\text{O}_2}}$$

where $p_{\text{N}_2} = 2 \text{ atm}$ is the initial pressure of the nitrogen and $p_{\text{O}_2} = 1 \text{ atm}$ is the initial pressure of the oxygen. Combining results and reducing

$$p_2 = \frac{(n_{\text{N}_2} + n_{\text{O}_2})T_2}{\left(\frac{n_{\text{N}_2}T_{\text{N}_2}}{p_{\text{N}_2}} + \frac{n_{\text{O}_2}T_{\text{O}_2}}{p_{\text{O}_2}}\right)}$$

Substituting values

$$p_2 = \frac{(1.0 \text{ lbmol})(477^\circ\text{R})}{\left[\frac{(0.79 \text{ lbmol})(460^\circ\text{R})}{2 \text{ atm}} + \frac{(0.21 \text{ lbmol})(540^\circ\text{R})}{1 \text{ atm}}\right]}$$

$$= 1.62 \text{ atm}$$

(c) Reducing the closed system form of the entropy balance

$$S_2 - S_1 = \int_V^2 \left(\cancel{\frac{\delta Q}{T}} \right)_b^0 + \sigma$$

where the entropy transfer term drops out for the adiabatic mixing process. The initial entropy of the system, S_1 , is the sum of the entropies of the gases at the respective initial states

$$S_1 = n_{\text{N}_2}\bar{s}_{\text{N}_2}(T_{\text{N}_2}, p_{\text{N}_2}) + n_{\text{O}_2}\bar{s}_{\text{O}_2}(T_{\text{O}_2}, p_{\text{O}_2})$$

The final entropy of the system, S_2 , is the sum of the entropies of the individual components, each evaluated at the final mixture temperature and the partial pressure of the component in the mixture

$$S_2 = n_{\text{N}_2}\bar{s}_{\text{N}_2}(T_2, y_{\text{N}_2}p_2) + n_{\text{O}_2}\bar{s}_{\text{O}_2}(T_2, y_{\text{O}_2}p_2)$$

Collecting the last three equations

$$\sigma = n_{\text{N}_2}[\bar{s}_{\text{N}_2}(T_2, y_{\text{N}_2}p_2) - \bar{s}_{\text{N}_2}(T_{\text{N}_2}, p_{\text{N}_2})] \\ + n_{\text{O}_2}[\bar{s}_{\text{O}_2}(T_2, y_{\text{O}_2}p_2) - \bar{s}_{\text{O}_2}(T_{\text{O}_2}, p_{\text{O}_2})]$$

Evaluating the change in specific entropy of each gas in terms of a constant specific heat \bar{c}_p , this becomes

$$\sigma = n_{\text{N}_2} \left(\bar{c}_{p,\text{N}_2} \ln \frac{T_2}{T_{\text{N}_2}} - \bar{R} \ln \frac{y_{\text{N}_2}p_2}{p_{\text{N}_2}} \right) \\ + n_{\text{O}_2} \left(\bar{c}_{p,\text{O}_2} \ln \frac{T_2}{T_{\text{O}_2}} - \bar{R} \ln \frac{y_{\text{O}_2}p_2}{p_{\text{O}_2}} \right)$$

The required values for \bar{c}_p can be found by adding \bar{R} to the \bar{c}_v values found previously (Eq. 3.45)

$$\bar{c}_{p,\text{N}_2} = 6.95 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}}, \quad \bar{c}_{p,\text{O}_2} = 6.98 \frac{\text{Btu}}{\text{lbmol} \cdot {}^\circ\text{R}}$$

Since the total number of moles of mixture $n = 0.79 + 0.21 = 1.0$, the mole fractions of the two gases are $y_{N_2} = 0.79$ and $y_{O_2} = 0.21$.

Substituting values into the expression for σ gives

$$\begin{aligned}\sigma &= 0.79 \text{ lbmol} \left[6.95 \frac{\text{Btu}}{\text{lbfmol} \cdot ^\circ\text{R}} \ln \left(\frac{477^\circ\text{R}}{460^\circ\text{R}} \right) - 1.986 \frac{\text{Btu}}{\text{lbfmol} \cdot ^\circ\text{R}} \ln \left(\frac{(0.79)(1.62 \text{ atm})}{2 \text{ atm}} \right) \right] \\ &\quad + 0.21 \text{ lbmol} \left[6.98 \frac{\text{Btu}}{\text{lbfmol} \cdot ^\circ\text{R}} \ln \left(\frac{477^\circ\text{R}}{540^\circ\text{R}} \right) - 1.986 \frac{\text{Btu}}{\text{lbfmol} \cdot ^\circ\text{R}} \ln \left(\frac{(0.21)(1.62 \text{ atm})}{1 \text{ atm}} \right) \right]\end{aligned}$$

$$\textcircled{1} = 1.168 \text{ Btu}/^\circ\text{R}$$

- 1** Entropy is produced when different gases, initially at different temperatures and pressures, are allowed to mix.

QuickQUIZ

Determine the total volume of the final mixture, in ft^3 .

Ans. 215 ft^3 .

Skills Developed

Ability to...

- analyze the adiabatic mixing of two ideal gases at constant total volume.
- apply energy and entropy balances to the mixing of two gases.
- apply ideal gas mixture principles assuming constant specific heats.

In the next example, we consider a control volume at steady state where two incoming streams form a mixture. A single stream exits.

EXAMPLE 12.6

Analyzing Adiabatic Mixing of Two Streams

At steady state, $100 \text{ m}^3/\text{min}$ of dry air at 32°C and 1 bar is mixed adiabatically with a stream of oxygen (O_2) at 127°C and 1 bar to form a mixed stream at 47°C and 1 bar. Kinetic and potential energy effects can be ignored. Determine **(a)** the mass flow rates of the dry air and oxygen, in kg/min , **(b)** the mole fractions of the dry air and oxygen in the exiting mixture, and **(c)** the time rate of entropy production, in $\text{kJ}/\text{K} \cdot \text{min}$.

SOLUTION

Known: At steady state, $100 \text{ m}^3/\text{min}$ of dry air at 32°C and 1 bar is mixed adiabatically with an oxygen stream at 127°C and 1 bar to form a mixed stream at 47°C and 1 bar.

Find: Determine the mass flow rates of the dry air and oxygen, in kg/min , the mole fractions of the dry air and oxygen in the exiting mixture, and the time rate of entropy production, in $\text{kJ}/\text{K} \cdot \text{min}$.

Schematic and Given Data:

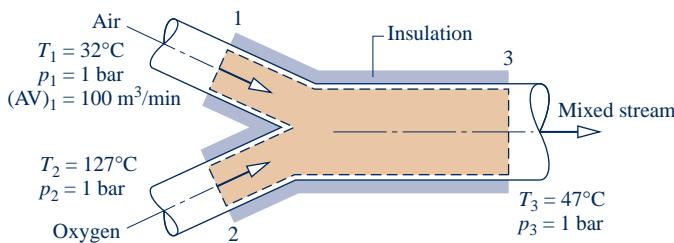


Fig. E12.6

Engineering Model:

1. The control volume identified by the dashed line on the accompanying figure operates at steady state.
2. No heat transfer occurs with the surroundings.

- 3. Kinetic and potential energy effects can be ignored, and $\dot{W}_{cv} = 0$.
- 4. The entering gases can be regarded as ideal gases. The exiting mixture can be regarded as an ideal gas mixture adhering to the Dalton model.
- 5. The dry air is treated as a pure component.

Analysis:

- (a) The mass flow rate of the dry air entering the control volume can be determined from the given volumetric flow rate (AV)₁

$$\dot{m}_{a1} = \frac{(AV)_1}{v_{a1}}$$

where v_{a1} is the specific volume of the air at 1. Using the ideal gas equation of state

$$v_{a1} = \frac{(\bar{R}/M_a)T_1}{p_1} = \frac{\left(\frac{8314 \text{ N} \cdot \text{m}}{28.97 \text{ kg} \cdot \text{K}}\right)(305 \text{ K})}{10^5 \text{ N/m}^2} = 0.875 \frac{\text{m}^3}{\text{kg}}$$

The mass flow rate of the dry air is then

$$\dot{m}_{a1} = \frac{100 \text{ m}^3/\text{min}}{0.875 \text{ m}^3/\text{kg}} = 114.29 \frac{\text{kg}}{\text{min}}$$

The mass flow rate of the oxygen can be determined using mass and energy rate balances. At steady state, the amounts of dry air and oxygen contained within the control volume do not vary. Thus, for each component individually it is necessary for the incoming and outgoing mass flow rates to be equal. That is

$$\dot{m}_{a1} = \dot{m}_{a3} \quad (\text{dry air})$$

$$\dot{m}_{o2} = \dot{m}_{o3} \quad (\text{oxygen})$$

Using assumptions 1–3 together with the foregoing mass flow rate relations, the energy rate balance reduces to

$$0 = \dot{m}_a h_a(T_1) + \dot{m}_o h_o(T_2) - [\dot{m}_a h_a(T_3) + \dot{m}_o h_o(T_3)]$$

where \dot{m}_a and \dot{m}_o denote the mass flow rates of the dry air and oxygen, respectively. The enthalpy of the mixture at the exit is evaluated by summing the contributions of the air and oxygen, each at the mixture temperature. Solving for \dot{m}_o

$$\dot{m}_o = \dot{m}_a \left[\frac{h_a(T_3) - h_a(T_1)}{h_o(T_2) - h_o(T_3)} \right]$$

The specific enthalpies can be obtained from Tables A-22 and A-23. Since Table A-23 gives enthalpy values on a molar basis, the molecular weight of oxygen is introduced into the denominator to convert the molar enthalpy values to a mass basis

$$\begin{aligned} \dot{m}_o &= \frac{(114.29 \text{ kg/min})(320.29 \text{ kJ/kg} - 305.22 \text{ kJ/kg})}{\left(\frac{1}{32 \text{ kg/kmol}}\right)(11,711 \text{ kJ/kmol} - 9,325 \text{ kJ/kmol})} \\ &= 23.1 \frac{\text{kg}}{\text{min}} \end{aligned}$$

(b) To obtain the mole fractions of the dry air and oxygen in the exiting mixture, first convert the mass flow rates to molar flow rates using the respective molecular weights

$$\dot{n}_a = \frac{\dot{m}_a}{M_a} = \frac{114.29 \text{ kg/min}}{28.97 \text{ kg/kmol}} = 3.95 \text{ kmol/min}$$

$$\dot{n}_o = \frac{\dot{m}_o}{M_o} = \frac{23.1 \text{ kg/min}}{32 \text{ kg/kmol}} = 0.72 \text{ kmol/min}$$

where \dot{n} denotes molar flow rate. The molar flow rate of the mixture \dot{n} is the sum

$$\dot{n} = \dot{n}_a + \dot{n}_o = 3.95 + 0.72 = 4.67 \text{ kmol/min}$$

The mole fractions of the air and oxygen in the exiting mixture are, respectively

$$① \quad y_a = \frac{\dot{n}_a}{\dot{n}} = \frac{3.95}{4.67} = 0.846 \quad \text{and} \quad y_o = \frac{\dot{n}_o}{\dot{n}} = \frac{0.72}{4.67} = 0.154$$

(c) For the control volume at steady state, the entropy rate balance reduces to

$$0 = \dot{m}_a s_a(T_1, p_1) + \dot{m}_o s_o(T_2, p_2) - [\dot{m}_a s_a(T_3, y_a p_3) + \dot{m}_o s_o(T_3, y_o p_3)] + \dot{\sigma}$$

The specific entropy of each component in the exiting ideal gas mixture is evaluated at its partial pressure in the mixture and at the mixture temperature. Solving for $\dot{\sigma}$

$$\dot{\sigma} = \dot{m}_a [s_a(T_3, y_a p_3) - s_a(T_1, p_1)] + \dot{m}_o [s_o(T_3, y_o p_3) - s_o(T_2, p_2)]$$

Since $p_1 = p_3$, the specific entropy change of the dry air is

$$\begin{aligned} s_a(T_3, y_a p_3) - s_a(T_1, p_1) &= s_a^{\circ}(T_3) - s_a^{\circ}(T_1) - \frac{\bar{R}}{M_a} \ln \frac{y_a p_3}{p_1} \\ &= s_a^{\circ}(T_3) - s_a^{\circ}(T_1) - \frac{\bar{R}}{M_a} \ln y_a \end{aligned}$$

The s_a° terms are evaluated from Table A-22. Similarly, since $p_2 = p_3$, the specific entropy change of the oxygen is

$$s_o(T_3, y_o p_3) - s_o(T_2, p_2) = \frac{1}{M_o} [\bar{s}_o^{\circ}(T_3) - \bar{s}_o^{\circ}(T_2) - \bar{R} \ln y_o]$$

The \bar{s}_o° terms are evaluated from Table A-23. Note the use of the molecular weights M_a and M_o in the last two equations to obtain the respective entropy changes on a mass basis.

The expression for the rate of entropy production becomes

$$\dot{\sigma} = \dot{m}_a \left[s_a^{\circ}(T_3) - s_a^{\circ}(T_1) - \frac{\bar{R}}{M_a} \ln y_a \right] + \frac{\dot{m}_o}{M_o} [\bar{s}_o^{\circ}(T_3) - \bar{s}_o^{\circ}(T_2) - \bar{R} \ln y_o]$$

Substituting values

$$\begin{aligned} ② \quad \dot{\sigma} &= \left(114.29 \frac{\text{kg}}{\text{min}} \right) \left[1.7669 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} - 1.71865 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} - \left(\frac{8.314}{28.97} \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right) \ln 0.846 \right] \\ &\quad + \left(\frac{23.1 \text{ kg/min}}{32 \text{ kg/kmol}} \right) \left[207.112 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} - 213.765 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} - \left(\frac{8.314}{28.97} \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \right) \ln 0.154 \right] \\ &= 17.42 \frac{\text{kJ}}{\text{K} \cdot \text{min}} \end{aligned}$$

- ① This calculation is based on dry air modeled as a pure component (assumption 5). However, since O₂ is a component of dry air (Table 12.1), the *actual* mole fraction of O₂ in the exiting mixture is greater than given here.
- ② Entropy is produced when different gases, initially at different temperatures, are allowed to mix.

Skills Developed

Ability to...

- analyze the adiabatic mixing of two ideal gas streams at steady state.
- apply ideal mixture principles together with mass, energy, and entropy rate balances.

QuickQUIZ

What are the mass fractions of air and oxygen in the exiting mixture? **Ans.** $m_{\text{air}} = 0.832$, $m_{\text{O}_2} = 0.168$.



BIO CONNECTIONS Does spending time inside a building cause you to sneeze, cough, or develop a headache? If so, the culprit could be the ambient air.

The term *sick building syndrome* (SBS) describes a condition where indoor air quality leads to acute health problems and comfort issues for building occupants. Effects of SBS are often linked to the amount of time an occupant spends within the space; yet while the specific cause and illness are frequently unidentifiable, symptoms typically subside after the occupant leaves the building. If the symptoms persist even after leaving the space and are diagnosed as a specific illness attributed to an airborne contaminant, the term *building-related illness* is a more accurate descriptor.

The U.S. Environmental Protection Agency (EPA) recently conducted a study of 100 domestic office buildings, the largest study of its kind. The results agree with most previous findings that relate lower ventilation rates per person within office buildings to higher rates of SBS symptom reporting. Building codes and guidelines in the U.S. generally recommend ventilation rates within office buildings in the range of 15–20 ft³/min per occupant. Some of the spaces studied had ventilation rates below the guidelines.

Careful design is needed to ensure that air distribution systems deliver acceptable ventilation for each space. Inadequate system installation and improper maintenance also can give rise to indoor air quality problems, even when appropriate standards have been applied in the design. The EPA study found this to be the case with the systems of many buildings in the study group. Also, testing and balancing of the installed systems were never conducted in several of the buildings to ensure that systems were operating according to design intent.

Indoor air quality continues to be a significant concern for both building occupants and engineers who design and operate building air delivery systems.

Psychrometric Applications

The remainder of this chapter is concerned with the study of systems involving mixtures of dry air and water vapor. A condensed water phase also may be present. Knowledge of the behavior of such systems is essential for the analysis and design of air-conditioning devices, cooling towers, and industrial processes requiring close control of the vapor content in air. The study of systems involving dry air and water is known as **psychrometrics**.

psychrometrics

12.5

Introducing Psychrometric Principles

The object of the present section is to introduce some important definitions and principles used in the study of systems involving dry air and water.

12.5.1 • Moist Air

The term **moist air** refers to a mixture of dry air and water vapor in which the dry air is treated as if it were a pure component. As can be verified by reference to appropriate property data, the overall mixture and each mixture component behave as ideal gases at the states under present consideration. Accordingly, for the applications to be considered, the ideal gas mixture concepts introduced previously apply directly.

In particular, the Dalton model and the relations provided in Table 12.2 are applicable to moist air mixtures. Simply by identifying gas 1 with dry air, denoted by the subscript a, and gas 2 with water vapor, denoted by the subscript v, the table gives a useful set of moist air property relations. Referring to Fig. 12.3, let's verify this point by obtaining a sampling of moist air relations and relating them to entries in Table 12.2.

moist air

TAKE NOTE...

Moist air is a *binary* mixture of dry air and water vapor, and the property relations of Table 12.2 apply.

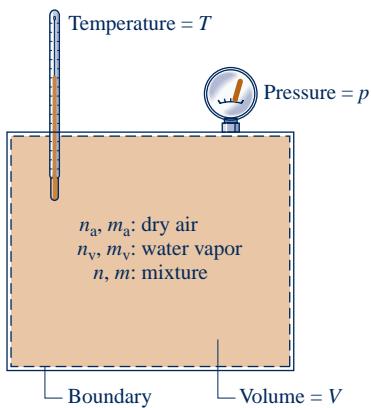


Fig. 12.3 Mixture of dry air and water vapor.

Shown in Fig. 12.3—a special case of Fig. 12.1—is a closed system consisting of moist air occupying a volume V at mixture pressure p and mixture temperature T . The overall mixture is assumed to obey the ideal gas equation of state. Thus

$$p = \frac{n\bar{R}T}{V} = \frac{m(\bar{R}/M)T}{V} \quad (12.40)$$

where n , m , and M denote the moles, mass, and molecular weight of the mixture, respectively, and $n = m/M$.

Each mixture component is considered to act as if it existed alone in the volume V at the mixture temperature T while exerting a part of the pressure. The mixture pressure is the sum of the partial pressures of the dry air and the water vapor: $p = p_a + p_v$. That is, the Dalton model applies.

Using the ideal gas equation of state, the partial pressures p_a and p_v of the dry air and water vapor are, respectively

$$p_a = \frac{n_a\bar{R}T}{V} = \frac{m_a(\bar{R}/M_a)T}{V}, \quad p_v = \frac{n_v\bar{R}T}{V} = \frac{m_v(\bar{R}/M_v)T}{V} \quad (12.41a)$$

where n_a and n_v denote the moles of dry air and water vapor, respectively; m_a , m_v , M_a , and M_v are the respective masses and molecular weights. The amount of water vapor present is normally much less than the amount of dry air. Accordingly, the values of n_v , m_v , and p_v are small relative to the corresponding values of n_a , m_a , and p_a .

Forming ratios with Eqs. 12.40 and 12.41a, we get the following alternative expressions for p_a and p_v

$$p_a = y_a p, \quad p_v = y_v p \quad (12.41b)$$

where y_a and y_v are the mole fractions of the dry air and water vapor, respectively. These moist air expressions conform to Eqs. (c) in Table 12.2.

A typical state of water vapor in moist air is shown in Fig. 12.4. At this state, fixed by the partial pressure p_v and the mixture temperature T , the vapor is superheated. When the partial pressure of the water vapor corresponds to the saturation pressure of water at the mixture temperature, p_g of Fig. 12.4, the mixture is said to be **saturated air**. **Saturated air** is a mixture of dry air and saturated water vapor. The amount of water vapor in moist air varies from zero in dry air to a maximum, depending on the pressure and temperature, when the mixture is saturated.

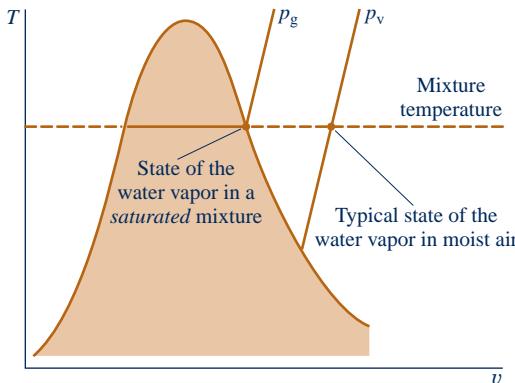


Fig. 12.4 T-v diagram for water vapor in an air-water mixture.

saturated air

12.5.2 • Humidity Ratio, Relative Humidity, Mixture Enthalpy, and Mixture Entropy

A given moist air sample can be described in a number of ways. The mixture can be described in terms of the moles of dry air and water vapor present or in terms of the respective mole fractions. Alternatively, the mass of dry air and water vapor, or the respective mass fractions, can be specified. The composition also can be indicated by means of the **humidity ratio** ω , defined as the ratio of the mass of the water vapor to the mass of dry air

$$\omega = \frac{m_v}{m_a} \quad (12.42)$$

humidity ratio

The humidity ratio is sometimes referred to as the *specific humidity*.

The humidity ratio can be expressed in terms of partial pressures and molecular weights by solving Eqs. 12.41a for m_a and m_v , respectively, and substituting the resulting expressions into Eq. 12.42 to obtain

$$\omega = \frac{m_v}{m_a} = \frac{M_v p_v V / \bar{R}T}{M_a p_a V / \bar{R}T} = \frac{M_v p_v}{M_a p_a}$$

Introducing $p_a = p - p_v$ and noting that the ratio of the molecular weight of water to that of dry air, M_v/M_a , is approximately 0.622, this expression can be written as

$$\omega = 0.622 \frac{p_v}{p - p_v} \quad (12.43)$$

Moist air also can be described in terms of the *relative humidity* ϕ , defined as the ratio of the mole fraction of water vapor y_v in a given moist air sample to the mole fraction $y_{v,\text{sat}}$ in a saturated moist air sample at the same mixture temperature and pressure:

$$\phi = \left(\frac{y_v}{y_{v,\text{sat}}} \right)_{T,p}$$

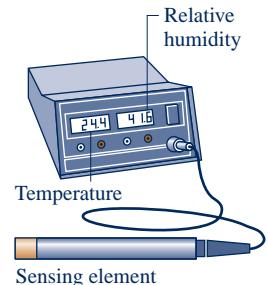
Since $p_v = y_v p$ and $p_g = y_{v,\text{sat}} p$, the **relative humidity** can be expressed as

relative humidity

$$\phi = \left(\frac{p_v}{p_g} \right)_{T,p} \quad (12.44)$$

The pressures in this expression for the relative humidity are labeled on Fig. 12.4.

The humidity ratio and relative humidity can be measured. For laboratory measurements of humidity ratio, a *hygrometer* can be used in which a moist air sample is exposed to suitable chemicals until the moisture present is absorbed. The amount of water vapor is determined by weighing the chemicals. Continuous recording of the relative humidity can be accomplished by means of transducers consisting of resistance- or capacitance-type sensors whose electrical characteristics change with relative humidity.



Evaluating H , U , and S for Moist Air

The values of H , U , and S for moist air modeled as an ideal gas mixture can be found by adding the contribution of each component at the condition at which the component exists in the mixture. For example, the enthalpy H of a given moist air sample is

$$H = H_a + H_v = m_a h_a + m_v h_v \quad (12.45)$$

This moist air expression conforms to Eq. (d) in Table 12.2.

Dividing by m_a and introducing the humidity ratio gives the **mixture enthalpy per unit mass of dry air**

mixture enthalpy

$$\frac{H}{m_a} = h_a + \frac{m_v}{m_a} h_v = h_a + \omega h_v \quad (12.46)$$

The enthalpies of the dry air and water vapor appearing in Eq. 12.46 are evaluated at the mixture temperature. An approach similar to that for enthalpy also applies to the evaluation of the internal energy of moist air.

Reference to steam table data or a Mollier diagram for water shows that the enthalpy of superheated water vapor at *low vapor pressures* is very closely given by the saturated vapor value corresponding to the given temperature. Hence, the enthalpy of the water vapor h_v in Eq. 12.46 can be taken as h_g at the mixture temperature. That is

$$h_v \approx h_g(T) \quad (12.47)$$

Equation 12.47 is used in the remainder of the chapter. Enthalpy data for water vapor as an ideal gas from Table A-23 are *not used* for h_v because the enthalpy datum of the ideal gas tables differs from that of the steam tables. These different datums can lead to error when studying systems that contain both water vapor and a liquid or solid phase of water. The enthalpy of dry air, h_a , can be obtained from the appropriate ideal gas table, Table A-22 or Table A-22E, however, because air is a gas at all states under present consideration and is closely modeled as an ideal gas at these states.

mixture entropy

In accord with Eq. (h) in Table 12.2, the moist air **mixture entropy** has two contributions: water vapor and dry air. The contribution of each component is determined at the mixture temperature and the partial pressure of the component in the mixture. Using Eq. 6.18 and referring to Fig. 12.4 for the states, the specific entropy of the water vapor is given by $s_v(T, p_v) = s_g(T) - R \ln p_v/p_g$, where s_g is the specific entropy of saturated vapor at temperature T . Observe that the ratio of pressures, p_v/p_g , can be replaced by the relative humidity ϕ , giving an alternative expression.

Using Computer Software

Property functions for moist air are listed under the **Properties** menu of *Interactive Thermodynamics: IT*. Functions are included for humidity ratio, relative humidity, specific enthalpy and entropy as well as other psychrometric properties introduced later. The methods used for evaluating these functions correspond to the methods discussed in this chapter, and the values returned by the computer software agree closely with those obtained by hand calculations with table data. The use of *IT* for psychrometric evaluations is illustrated in examples later in the chapter.



BIO CONNECTIONS Medical practitioners and their patients have long noticed that influenza cases peak during winter. Speculation about the cause ranged widely, including the possibility that people spend more time indoors in winter and thus transmit the flu virus more easily, or that the peak might be related to less sunlight exposure during winter, perhaps affecting human immune responses.

Since air is drier in winter, others suspected a link between relative humidity and influenza virus survival and transmission. In a 2007 study, using influenza-infected guinea pigs in climate-controlled habitats, researchers investigated the effects of variable habitat temperature and humidity on the aerosol spread of influenza virus. The study showed there were more infections when it was colder and drier, but relative humidity was a relatively weak variable in explaining findings. This prompted researchers to look for a better rationale.

When data from the 2007 study were reanalyzed, a significant correlation was found between humidity ratio and influenza. Unlike relative humidity, humidity ratio measures the actual amount of moisture present in air. When humidity ratio is low, as in peak winter flu months, the virus survives longer and transmission rates increase, researchers say. These findings strongly point to the value of humidifying indoor air in winter, particularly in high-risk places such as nursing homes.

12.5.3 Modeling Moist Air in Equilibrium with Liquid Water

Thus far, our study of psychometrics has been conducted as an application of the ideal gas mixture principles introduced in the first part of this chapter. However, many systems of interest are composed of a mixture of dry air and water vapor in contact with a liquid (or solid) water phase. To study these systems requires additional considerations.

Shown in Fig. 12.5 is a vessel containing liquid water, above which is a mixture of water vapor and dry air. If no interactions with the surroundings are allowed, liquid will evaporate until eventually the gas phase becomes saturated and the system attains an equilibrium state. For many engineering applications, systems consisting of moist air in *equilibrium* with a liquid water phase can be described simply and accurately with the following idealizations:

- ▶ The dry air and water vapor behave as independent ideal gases.
- ▶ The equilibrium between the liquid phase and the water vapor is not significantly disturbed by the presence of the air.
- ▶ The partial pressure of the water vapor equals the saturation pressure of water corresponding to the temperature of the mixture: $p_v = p_g(T)$.

Similar considerations apply for systems consisting of moist air in equilibrium with a solid water phase. The presence of the air actually alters the partial pressure of the vapor from the saturation pressure by a small amount whose magnitude is calculated in Sec. 14.6.

12.5.4 Evaluating the Dew Point Temperature

A significant aspect of the behavior of moist air is that partial condensation of the water vapor can occur when the temperature is reduced. This type of phenomenon is commonly encountered in the condensation of vapor on windowpanes and on pipes carrying cold water. The formation of dew on grass is another familiar example.

To study such condensation, consider a closed system consisting of a sample of moist air that is cooled at *constant* pressure, as shown in Fig. 12.6. The property diagram given on this figure locates states of the water vapor. Initially, the water vapor is superheated at state 1. In the first part of the cooling process, both the system pressure *and* the composition of the moist air remain constant. Accordingly, since $p_v = y_v p$, the *partial pressure* of the water vapor remains constant, and the water vapor cools at constant p_v from state 1 to state d, called the *dew point*. The saturation temperature corresponding to p_v is called the **dew point temperature**. This temperature is labeled on Fig. 12.6.

In the next part of the cooling process, the system cools *below* the dew point temperature and some of the water vapor initially present condenses. At the final state, the system consists of a gas phase of dry air and water vapor in equilibrium with a liquid water phase. In accord with the discussion of Sec. 12.5.3, the vapor that remains is saturated vapor at the final temperature, state 2 of Fig. 12.6, with a partial pressure equal to the saturation pressure p_{g2} corresponding to this temperature. The condensate is saturated liquid at the final temperature: state 3 of Fig. 12.6.

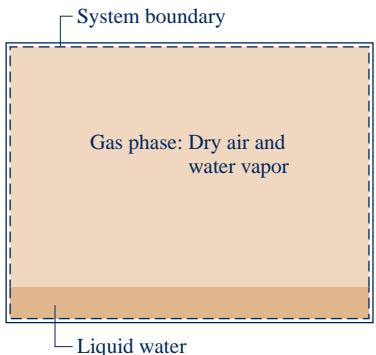


Fig. 12.5 System consisting of moist air in contact with liquid water.

12.5.4 Evaluating the Dew Point Temperature

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dew point temperature

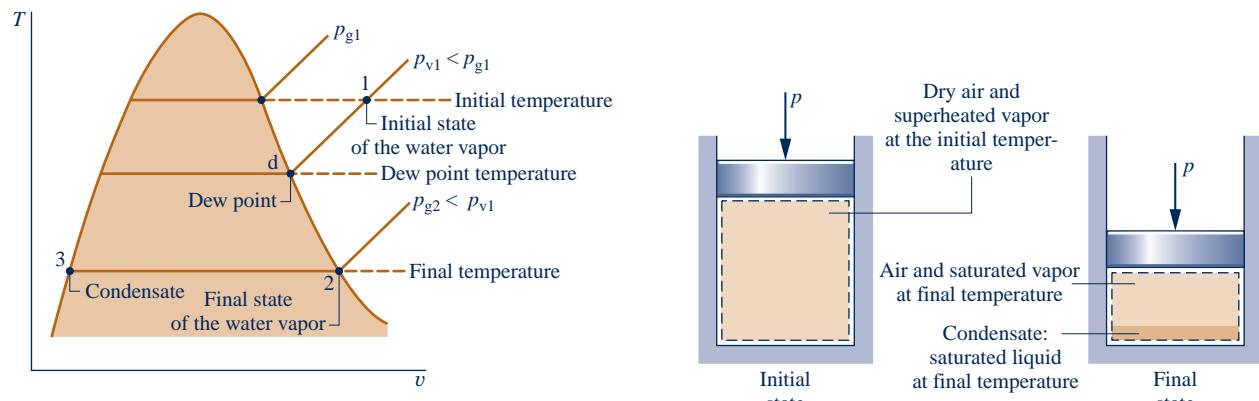


Fig. 12.6 States of water for moist air cooled at constant mixture pressure.

Referring again to Fig. 12.6, note that the partial pressure of the water vapor at the final state, p_{g2} , is less than the initial value, p_{v1} . Owing to condensation, the partial pressure decreases because the amount of water vapor present at the final state is less than at the initial state. Since the amount of dry air is unchanged, the mole fraction of water vapor in the moist air also decreases.

In the next two examples, we illustrate the use of psychrometric properties introduced thus far. The examples consider, respectively, cooling moist air at constant pressure and at constant volume.

EXAMPLE 12.7

Cooling Moist Air at Constant Pressure

A 1-lb sample of moist air initially at 70°F, 14.7 lbf/in.², and 70% relative humidity is cooled to 40°F while keeping the pressure constant. Determine (a) the initial humidity ratio, (b) the dew point temperature, in °F, and (c) the amount of water vapor that condenses, in lb.

SOLUTION

Known: A 1-lb sample of moist air is cooled at a constant mixture pressure of 14.7 lbf/in.² from 70 to 40°F. The initial relative humidity is 70%.

Find: Determine the initial humidity ratio, the dew point temperature, in °F, and the amount of water vapor that condenses, in lb.

Schematic and Given Data:

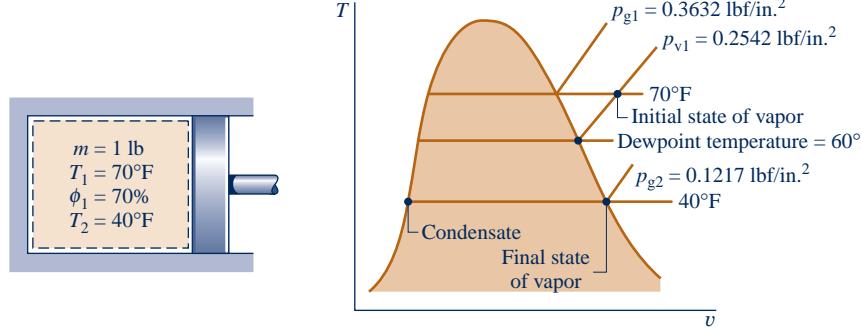


Fig. E12.7

Engineering Model:

1. The 1-lb sample of moist air is taken as the closed system. The system pressure remains constant at 14.7 lbf/in.²
2. The gas phase can be treated as an ideal gas mixture. The Dalton model applies: Each mixture component acts as an ideal gas existing alone in the volume occupied by the gas phase at the mixture temperature.
3. When a liquid water phase is present, the water vapor exists as a saturated vapor at the system temperature. The liquid present is a saturated liquid at the system temperature.

Analysis:

- (a) The initial humidity ratio can be evaluated from Eq. 12.43. This requires the partial pressure of the water vapor, p_{v1} , which can be found from the given relative humidity and p_g from Table A-2E at 70°F as follows

$$p_{v1} = \phi p_g = (0.7) \left(0.3632 \frac{\text{lbf}}{\text{in.}^2} \right) = 0.2542 \frac{\text{lbf}}{\text{in.}^2}$$

Inserting values in Eq. 12.43

$$\omega_1 = 0.622 \left(\frac{0.2542}{14.7 - 0.2542} \right) = 0.011 \frac{\text{lb (vapor)}}{\text{lb (dry air)}}$$

(b) The dew point temperature is the saturation temperature corresponding to the partial pressure, p_{v1} . Interpolation in Table A-2E gives $T = 60^\circ\text{F}$. The dew point temperature is labeled on the accompanying property diagram.

(c) The amount of condensate, m_w , equals the difference between the initial amount of water vapor in the sample, m_{v1} , and the final amount of water vapor, m_{v2} . That is

$$m_w = m_{v1} - m_{v2}$$

To evaluate m_{v1} , note that the system initially consists of 1 lb of dry air and water vapor, so $1 \text{ lb} = m_a + m_{v1}$, where m_a is the mass of dry air present in the sample. Since $\omega_1 = m_{v1}/m_a$, $m_a = m_{v1}/\omega_1$. With this we get

$$1 \text{ lb} = \frac{m_{v1}}{\omega_1} + m_{v1} = m_{v1} \left(\frac{1}{\omega_1} + 1 \right)$$

Solving for m_{v1}

$$m_{v1} = \frac{1 \text{ lb}}{(1/\omega_1) + 1}$$

Inserting the value of ω_1 determined in part (a)

$$m_{v1} = \frac{1 \text{ lb}}{(1/0.011) + 1} = 0.0109 \text{ lb (vapor)}$$

① The mass of dry air present is then $m_a = 1 - 0.0109 = 0.9891 \text{ lb (dry air)}$.

Next, let us evaluate m_{v2} . With assumption 3, the partial pressure of the water vapor remaining in the system at the final state is the saturation pressure corresponding to 40°F : $p_g = 0.1217 \text{ lbf/in}^2$. Accordingly, the humidity ratio after cooling is found from Eq. 12.43 as

$$\omega_2 = 0.622 \left(\frac{0.1217}{14.7 - 0.1217} \right) = 0.0052 \frac{\text{lb (vapor)}}{\text{lb (dry air)}}$$

The mass of the water vapor present at the final state is then

$$m_{v2} = \omega_2 m_a = (0.0052)(0.9891) = 0.0051 \text{ lb (vapor)}$$

Finally, the amount of water vapor that condenses is

$$m_w = m_{v1} - m_{v2} = 0.0109 - 0.0051 = 0.0058 \text{ lb (condensate)}$$

- ① The amount of water vapor present in a typical moist air mixture is considerably less than the amount of dry air present.

Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- demonstrate understanding of the dew point temperature and the formation of liquid condensate when pressure is constant.
- retrieve property data for water.

QuickQUIZ

Determine the quality of the two-phase, liquid-vapor mixture and the relative humidity of the gas phase at the final state. Ans. 47%, 100%.

EXAMPLE 12.8

Cooling Moist Air at Constant Volume

An air-water vapor mixture is contained in a rigid, closed vessel with a volume of 35 m^3 at 1.5 bar, 120°C , and $\phi = 10\%$. The mixture is cooled at constant volume until its temperature is reduced to 22°C . Determine (a) the dew point temperature corresponding to the initial state, in $^\circ\text{C}$, (b) the temperature at which condensation actually begins, in $^\circ\text{C}$, and (c) the amount of water condensed, in kg.

SOLUTION

Known: A rigid, closed tank with a volume of 35 m^3 containing moist air initially at 1.5 bar, 120°C , and $\phi = 10\%$ is cooled to 22°C .

Find: Determine the dew point temperature at the initial state, in $^\circ\text{C}$, the temperature at which condensation actually begins, in $^\circ\text{C}$, and the amount of water condensed, in kg.

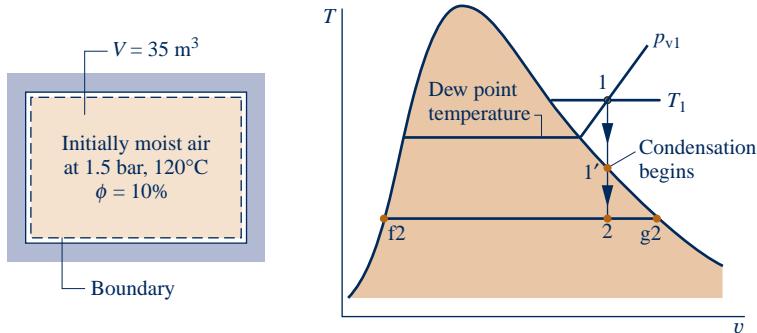
Schematic and Given Data:

Fig. E12.8

Engineering Model:

1. The contents of the tank are taken as a closed system. The system volume remains constant.
2. The gas phase can be treated as an ideal gas mixture. The Dalton model applies: Each mixture component acts as an ideal gas existing alone in the volume occupied by the gas phase at the mixture temperature.
3. When a liquid water phase is present, the water vapor exists as a saturated vapor at the system temperature. The liquid is a saturated liquid at the system temperature.

Analysis:

(a) The dew point temperature at the initial state is the saturation temperature corresponding to the partial pressure p_{v1} . With the given relative humidity and the saturation pressure at 120°C from Table A-2

$$p_{v1} = \phi_1 p_{g1} = (0.10)(1.985) = 0.1985 \text{ bar}$$

Interpolating in Table A-2 gives the dew point temperature as 60°C , which is the temperature condensation would begin if the moist air were cooled at *constant pressure*.

(b) Whether the water exists as a vapor only, or as liquid *and* vapor, it occupies the full volume, which remains constant. Accordingly, since the total mass of the water present is also constant, the water undergoes the constant specific volume process illustrated on the accompanying T - v diagram. In the process from state 1 to state 1', the water exists as a vapor only. For the process from state 1' to state 2, the water exists as a two-phase liquid-vapor mixture. Note that pressure does not remain constant during the cooling process from state 1 to state 2.

State 1' on the T - v diagram denotes the state where the water vapor first becomes saturated. The saturation temperature at this state is denoted as T' . Cooling to a temperature less than T' results in condensation of some of the water vapor present. Since state 1' is a saturated vapor state, the temperature T' can be found by interpolating in Table A-2 with the specific volume of the water at this state. The specific volume of the vapor at state 1' equals the specific volume of the vapor at state 1, which can be evaluated from the ideal gas equation

$$\begin{aligned} v_{v1} &= \frac{(\bar{R}/M_v)T_1}{p_{v1}} = \left(\frac{8314}{18} \frac{\text{N} \cdot \text{m}}{\text{kg} \cdot \text{K}} \right) \left(\frac{393 \text{ K}}{0.1985 \times 10^5 \text{ N/m}^2} \right) \\ &= 9.145 \frac{\text{m}^3}{\text{kg}} \end{aligned}$$

① Interpolation in Table A-2 with $v_{v1} = v_g$ gives $T' = 56^\circ\text{C}$. This is the temperature at which condensation begins.

(c) The amount of condensate equals the difference between the initial and final amounts of water vapor present. The mass of the water vapor present initially is

$$m_{v1} = \frac{V}{v_{v1}} = \frac{35 \text{ m}^3}{9.145 \text{ m}^3/\text{kg}} = 3.827 \text{ kg}$$

The mass of water vapor present finally can be determined from the *quality*. At the final state, the water forms a two-phase liquid–vapor mixture having a specific volume of $9.145 \text{ m}^3/\text{kg}$. Using this specific volume value, the quality x_2 of the liquid–vapor mixture can be found as

$$x_2 = \frac{v_{v2} - v_{f2}}{v_{g2} - v_{f2}} = \frac{9.145 - 1.0022 \times 10^{-3}}{51.447 - 1.0022 \times 10^{-3}} = 0.178$$

where v_{f2} and v_{g2} are the saturated liquid and saturated vapor specific volumes at $T_2 = 22^\circ\text{C}$, respectively.

Using the quality together with the known total amount of water present, 3.827 kg, the mass of the water vapor contained in the system at the final state is

$$m_{v2} = (0.178)(3.827) = 0.681 \text{ kg}$$

The mass of the condensate, m_{w2} , is then

$$m_{w2} = m_{v1} - m_{v2} = 3.827 - 0.681 = 3.146 \text{ kg}$$

- ① When a moist air mixture is cooled at constant mixture volume, the temperature at which condensation begins is not the dew point temperature corresponding to the initial state. In this case, condensation begins at 56°C , but the dew point temperature at the initial state, determined in part (a), is 60°C .



Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- demonstrate understanding of the onset of condensation when cooling moist air at constant volume.
- retrieve property data for water.

QuickQUIZ

Determine the humidity ratio at the initial state and the amount of dry air present, in kg. **Ans.** 0.0949, 40.389 kg.

No additional fundamental concepts are required for the study of closed systems involving mixtures of dry air and water vapor. Example 12.9, which builds on Example 12.8, brings out some special features of the use of conservation of mass and conservation of energy in analyzing this kind of system. Similar considerations can be used to study other closed systems involving moist air.

EXAMPLE 12.9

Evaluating Heat Transfer for Moist Air Cooling at Constant Volume

An air–water vapor mixture is contained in a rigid, closed vessel with a volume of 35 m^3 at 1.5 bar, 120°C , and $\phi = 10\%$. The mixture is cooled until its temperature is reduced to 22°C . Determine the heat transfer during the process, in kJ.

SOLUTION

Known: A rigid, closed tank with a volume of 35 m^3 containing moist air initially at 1.5 bar, 120°C , and $\phi = 10\%$ is cooled to 22°C .

Find: Determine the heat transfer for the process, in kJ.

Schematic and Given Data: See the figure for Example 12.8.

Engineering Model:

1. The contents of the tank are taken as a closed system. The system volume remains constant.
2. The gas phase can be treated as an ideal gas mixture. The Dalton model applies: Each component acts as an ideal gas existing alone in the volume occupied by the gas phase at the mixture temperature.

3. When a liquid water phase is present, the water vapor exists as a saturated vapor and the liquid is a saturated liquid, each at the system temperature.
4. There is no work during the cooling process and no change in kinetic or potential energy.

Analysis: Reduction of the closed system energy balance using assumption 4 results in

$$\Delta U = Q - W^0$$

or

$$Q = U_2 - U_1$$

where

$$U_1 = m_a u_{a1} + m_{v1} u_{v1} = m_a u_{a1} + m_{v1} u_{g1}$$

and

$$U_2 = m_a u_{a2} + m_{v2} u_{v2} + m_{w2} u_{w2} = m_a u_{a2} + m_{v2} u_{g2} + m_{w2} u_{f2}$$

In these equations, the subscripts a, v, and w denote, respectively, dry air, water vapor, and liquid water. The specific internal energy of the water vapor at the initial state can be approximated as the saturated vapor value at T_1 . At the final state, the water vapor is assumed to exist as a saturated vapor, so its specific internal energy is u_g at T_2 . The liquid water at the final state is saturated, so its specific internal energy is u_f at T_2 .

Collecting the last three equations

$$① \quad Q = \underline{m_a(u_{a2} - u_{a1})} + \underline{m_{v2}u_{g2}} + \underline{m_{w2}u_{f2}} - \underline{m_{v1}u_{g1}}$$

The mass of dry air, m_a , can be found using the ideal gas equation of state together with the partial pressure of the dry air at the initial state obtained using $p_{v1} = 0.1985$ bar from the solution to Example 12.8 as follows:

$$m_a = \frac{p_{a1}V}{(\bar{R}/M_a)T_1} = \frac{[(1.5 - 0.1985) \times 10^5 \text{ N/m}^2](35 \text{ m}^3)}{(8314/28.97 \text{ N} \cdot \text{m/kg} \cdot \text{K})(393 \text{ K})} \\ = 40.389 \text{ kg}$$

Then, evaluating internal energies of dry air and water from Tables A-22 and A-2, respectively

$$Q = 40.389(210.49 - 281.1) + 0.681(2405.7) + 3.146(92.32) - 3.827(2529.3) \\ = -2851.87 + 1638.28 + 290.44 - 9679.63 = -10,603 \text{ kJ}$$

The values for m_{v1} , m_{v2} , and m_{w2} are from the solution to Example 12.8.

- 1 The first underlined term in this equation for Q is evaluated with specific internal energies from the ideal gas table for air, Table A-22. Steam table data are used to evaluate the second underlined term. The different datums for internal energy underlying these tables cancel because each of these two terms involves internal energy *differences*. Since the specific heat c_{va} for dry air varies only slightly over the interval from 120 to 22°C (Table A-20), the specific internal energy change of the dry air could be evaluated alternatively using a constant c_{va} value. See the QuickQuiz that follows.

Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply the energy balance to the cooling of moist air at constant volume.
- retrieve property data for water.

QuickQUIZ

Calculate the change in internal energy of the *dry air*, in kJ, assuming a constant specific heat c_{va} interpolated from Table A-20 at the average of the initial and final temperatures. **Ans.** -2854 kJ.

12.5.5 Evaluating Humidity Ratio Using the Adiabatic-Saturation Temperature

The humidity ratio ω of an air–water vapor mixture can be determined, in principle, knowing the values of three mixture properties: the pressure p , the temperature T , and the **adiabatic-saturation temperature** T_{as} introduced in this section. The relationship among these mixture properties is obtained by applying conservation of mass and conservation of energy to an *adiabatic saturator* (see box).

Equations 12.48 and 12.49 give the humidity ratio ω in terms of the adiabatic-saturation temperature and other quantities:

$$\omega = \frac{h_a(T_{as}) - h_a(T) + \omega' [h_g(T_{as}) - h_f(T_{as})]}{h_g(T) - h_f(T_{as})} \quad (12.48)$$

adiabatic-saturation temperature

where h_f and h_g denote the enthalpies of saturated liquid water and saturated water vapor, respectively, obtained from the steam tables at the indicated temperatures. The enthalpies of the dry air h_a can be obtained from the ideal gas table for air. Alternatively, $h_a(T_{as}) - h_a(T) = c_{pa}(T_{as} - T)$, where c_{pa} is an appropriate constant value for the specific heat of dry air. The humidity ratio ω' appearing in Eq. 12.48 is

$$\omega' = 0.622 \frac{p_g(T_{as})}{p - p_g(T_{as})} \quad (12.49)$$

where $p_g(T_{as})$ is the saturation pressure at the adiabatic-saturation temperature and p is the mixture pressure.

Modeling an Adiabatic Saturator

Figure 12.7 shows the schematic and process representations of an adiabatic saturator, which is a two-inlet, single-exit device through which moist air passes. The device is assumed to operate at steady state and without significant heat transfer with its surroundings. An air–water vapor mixture of *unknown* humidity ratio ω enters the adiabatic saturator at a known pressure p and temperature T . As the mixture passes through the device, it comes into contact with a pool of water. If the entering mixture is not saturated ($\phi < 100\%$), some of the water would evaporate. The energy required to evaporate the water would come from the moist air, so the mixture temperature would decrease as the air passes through the duct. For a sufficiently long duct, the mixture would be saturated as it exits ($\phi = 100\%$). Since a saturated mixture would be achieved without heat transfer with the surroundings, the temperature of the exiting mixture is the *adiabatic-saturation temperature*. As indicated on Fig. 12.7, a steady flow of makeup water at temperature T_{as} is added at the same rate at which water is evaporated. The pressure of the mixture is assumed to remain constant as it passes through the device.

Equation 12.48 giving the humidity ratio ω of the entering moist air in terms of p , T , and T_{as} can be obtained by applying conservation of mass and conservation of energy to the adiabatic saturator, as follows:

At steady state, the mass flow rate of the dry air entering the device, \dot{m}_a , must equal the mass flow rate of the dry air exiting. The mass flow rate of the makeup water is the difference between the exiting and entering vapor flow rates denoted by \dot{m}_v and \dot{m}'_v , respectively. These flow rates are labeled on Fig. 12.7a. At steady state, the energy rate balance reduces to

$$(\dot{m}_a h_a + \dot{m}_v h_v)_{\text{moist air entering}} + [(\dot{m}'_v - \dot{m}_v) h_w]_{\text{makeup water}} = (\dot{m}_a h_a + \dot{m}'_v h_v)_{\text{moist air exiting}}$$

Several assumptions underlie this expression: Each of the two moist air streams is modeled as an ideal gas mixture of dry air and water vapor. Heat transfer with the surroundings

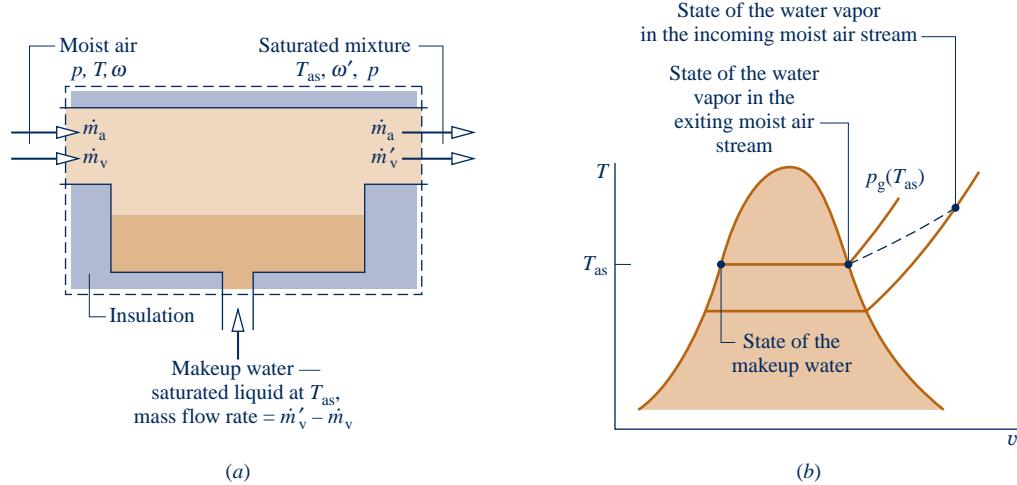


Fig. 12.7 Adiabatic saturator. (a) Schematic. (b) Process representation.

TAKE NOTE...

Although derived with reference to the adiabatic saturator in Fig. 12.7, the relationship provided by Eq. 12.48 applies generally to moist air mixtures and is not restricted to this type of system or even to control volumes. The relationship allows the humidity ratio ω to be determined for any moist air mixture for which the pressure p , temperature T , and adiabatic-saturation temperature T_{as} are known.

is assumed to be negligible. There is no work \dot{W}_{cv} , and changes in kinetic and potential energy are ignored.

Dividing by the mass flow rate of the dry air, \dot{m}_a , the energy rate balance can be written on the basis of a unit mass of dry air passing through the device as

$$(h_a + \omega h_g)_{\text{moist air entering}} + [(\omega' - \omega)h_f]_{\text{makeup water}} = (h_a + \omega' h_g)_{\text{moist air exiting}} \quad (12.50)$$

where $\omega = \dot{m}_v/\dot{m}_a$ and $\omega' = \dot{m}'_v/\dot{m}_a$.

For the exiting saturated mixture, the partial pressure of the water vapor is the saturation pressure corresponding to the adiabatic-saturation temperature, $p_g(T_{as})$. Accordingly, the humidity ratio ω' can be evaluated knowing T_{as} and the mixture pressure p , as indicated by Eq. 12.49. In writing Eq. 12.50, the specific enthalpy of the entering water vapor has been evaluated as that of saturated water vapor at the temperature of the incoming mixture, in accordance with Eq. 12.47. Since the exiting mixture is saturated, the enthalpy of the water vapor at the exit is given by the saturated vapor value at T_{as} . The enthalpy of the makeup water is evaluated as that of saturated liquid at T_{as} .

When Eq. 12.50 is solved for ω , Eq. 12.48 results. The details of the solution are left as an exercise.

12.6

Psychrometers: Measuring the Wet-Bulb and Dry-Bulb Temperatures

For moist air mixtures in the normal pressure and temperature ranges of psychrometrics, the readily-measured wet-bulb temperature is an important parameter.

The **wet-bulb temperature** is read from a wet-bulb thermometer, which is an ordinary liquid-in-glass thermometer whose bulb is enclosed by a wick moistened with water. The term **dry-bulb temperature** refers simply to the temperature that would be measured by a thermometer placed in the mixture. Often a wet-bulb thermometer is mounted together with a dry-bulb thermometer to form an instrument called a **psychrometer**.

The psychrometer of Fig. 12.8a is whirled in the air whose wet- and dry-bulb temperatures are to be determined. This induces air flow over the two thermometers. For the psychrometer of Fig. 12.8b, the air flow is induced by a battery-operated fan.

wet-bulb temperature

dry-bulb temperature

psychrometer

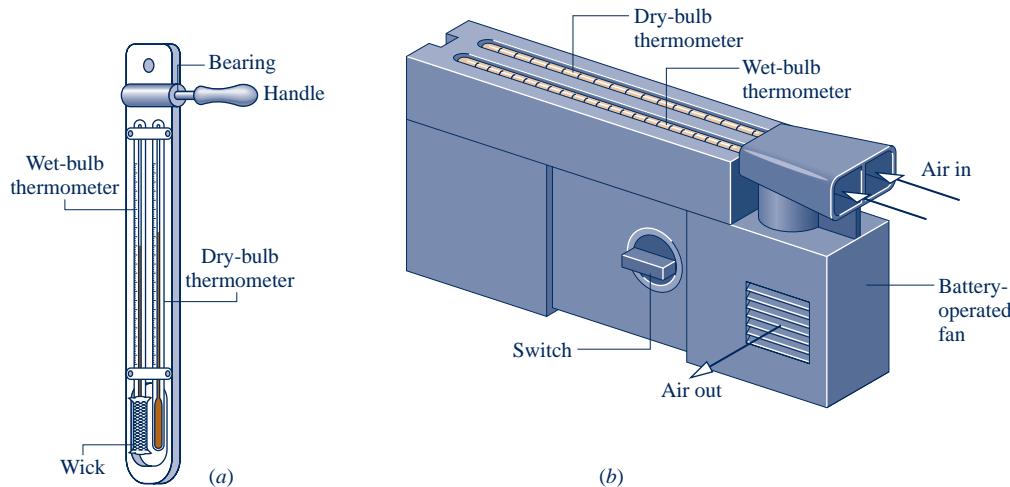


Fig. 12.8 Psychrometers. (a) Sling psychrometer. (b) Aspirating psychrometer.

In each type of psychrometer, if the surrounding air is not saturated, water in the wick of the wet-bulb thermometer evaporates and the temperature of the remaining water falls below the dry-bulb temperature. Eventually a steady-state condition is attained by the wet-bulb thermometer. The wet- and dry-bulb temperatures are then read from the respective thermometers. The wet-bulb temperature depends on the rates of heat and mass transfer between the moistened wick and the air. Since these depend in turn on the geometry of the thermometer, air velocity, supply water temperature, and other factors, the wet-bulb temperature is not a mixture property.

For moist air mixtures in the normal pressure and temperature ranges of psychrometric applications, the adiabatic saturation temperature introduced in Sec. 12.5.5 is closely approximated by the wet-bulb temperature. Accordingly, the humidity ratio for any such mixture can be calculated by using the wet-bulb temperature in Eqs. 12.48 and 12.49 in place of the adiabatic-saturation temperature. Close agreement between the adiabatic-saturation and wet-bulb temperatures is not generally found for moist air departing from normal psychrometric conditions.

TAKE NOTE...

The humidity ratio for moist air mixtures considered in this book can be calculated by using the wet-bulb temperature in Eqs. 12.48 and 12.49 in place of the adiabatic saturation temperature.



BIO CONNECTIONS The *National Weather Service* is finding better ways to help measure our misery during cold snaps so we can avoid weather dangers. The wind chill index, for many years based on a single 1945 study, has been upgraded using new physiological data and computer modeling to better reflect the perils of cold winds and freezing temperatures.

The new wind chill index is a standardized “temperature” that accounts for both the actual air temperature and the wind speed. The formula on which it is based uses measurements of skin tissue thermal resistance and computer models of the wind patterns over the human face, together with principles of heat transfer. Using the new index, an air temperature of 5°F and a wind speed of 25 miles per hour correspond to a wind chill temperature of -40°F . The old index assigned a wind chill of only -20°F to the same conditions. With the new information, people are better armed to avoid exposure that can lead to such serious medical problems as frostbite.

The improved measure was developed by universities, international scientific societies, and government in an effort that led to the new standard being adopted in the United States. Further upgrades are in the works to include the amount of cloud cover in the formula, since solar radiation is also an important factor in how cold it feels.

12.7

Psychrometric Charts

psychrometric chart

Graphical representations of several important properties of moist air are provided by **psychrometric charts**. The main features of one form of chart are shown in Fig. 12.9. Complete charts in SI and English units are given in Figs. A-9 and A-9E. These charts are constructed for a mixture pressure of 1 atm, but charts for other mixture pressures are also available. When the mixture pressure differs only slightly from 1 atm, Figs. A-9 remain sufficiently accurate for engineering analyses. In this text, such differences are ignored.

Let us consider several features of the psychrometric chart:

- Referring to Fig. 12.9, note that the abscissa gives the dry-bulb temperature and the ordinate provides the humidity ratio. For charts in SI, the temperature is in °C and ω is expressed in kg, or g, of water vapor per kg of dry air. Charts in English units give temperature in °F and ω in lb, or grains, of water vapor per lb of dry air, where 1 lb = 7000 grains.
- Equation 12.43 shows that for fixed mixture pressure there is a direct correspondence between the partial pressure of the water vapor and the humidity ratio. Accordingly, the vapor pressure also can be shown on the ordinate, as illustrated on Fig. 12.9.
- Curves of constant relative humidity are shown on psychrometric charts. On Fig. 12.9, curves labeled $\phi = 100, 50$, and 10% are indicated. Since the dew point is the state where the mixture becomes saturated when cooled at constant vapor pressure, the dew point temperature corresponding to a given moist air state can be determined by following a line of constant ω (constant p_v) to the saturation line, $\phi = 100\%$. The dew point temperature and dry-bulb temperature are identical for states on the saturation curve.
- Psychrometric charts also give values of the mixture enthalpy per unit mass of dry air in the mixture: $h_a + \omega h_v$. In Figs. A-9 and A-9E, the mixture enthalpy has units of kJ per kg of dry air and Btu per lb of dry air, respectively. The numerical values provided on these charts are determined relative to the following *special* reference states and reference values. In Fig. A-9, the enthalpy of the dry air h_a is determined relative to a zero value at 0°C, and not 0 K as in Table A-22. Accordingly, in place of Eq. 3.49 used to develop the enthalpy data of Tables A-22, the following expression is employed to evaluate the enthalpy of the dry air for use on the psychrometric chart:

$$h_a = \int_{273.15 \text{ K}}^T c_{pa} dT = c_{pa} T (\text{°C}) \quad (12.51)$$

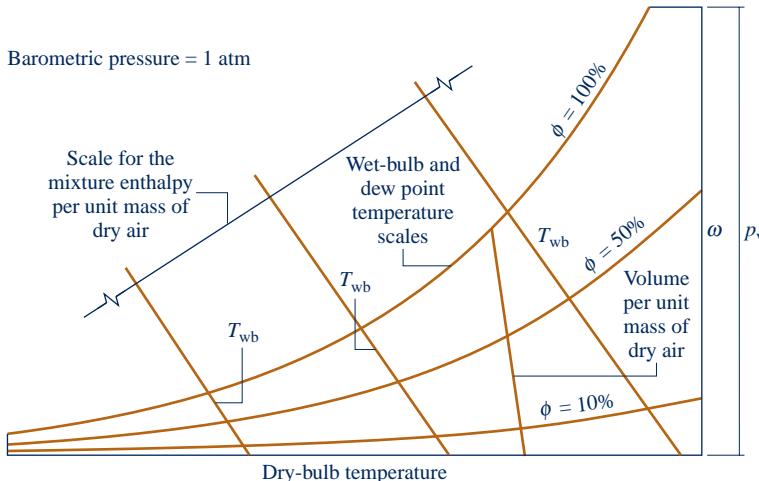


Fig. 12.9 Psychrometric chart.

where c_{pa} is a constant value for the specific heat c_p of dry air and $T(^{\circ}\text{C})$ denotes the temperature in $^{\circ}\text{C}$. For the chart in English units, Fig. A-9E, h_a is determined relative to a datum of 0°F , using $h_a = c_{pa} T(^{\circ}\text{F})$, where $T(^{\circ}\text{F})$ denotes the temperature in $^{\circ}\text{F}$. In the temperature ranges of Figs. A-9 and A-9E, c_{pa} can be taken as $1.005 \text{ kJ/kg} \cdot \text{K}$ and $0.24 \text{ Btu/lb} \cdot ^{\circ}\text{R}$, respectively. On Figs. A-9 the enthalpy of the water vapor h_v is evaluated as h_g at the dry-bulb temperature of the mixture from Table A-2 or A-2E, as appropriate.

- ▶ Another important parameter on psychrometer charts is the wet-bulb temperature. As illustrated by Figs. A-9, constant T_{wb} lines run from the upper left to the lower right of the chart. The relationship between the wet-bulb temperature and other chart quantities is provided by Eq. 12.48. The wet-bulb temperature can be used in this equation in place of the adiabatic-saturation temperature for the states of moist air located on Figs. A-9.
- ▶ Lines of constant wet-bulb temperature are approximately lines of constant mixture enthalpy per unit mass of dry air. This feature can be brought out by study of the energy balance for the adiabatic saturator, Eq. 12.50. Since the contribution of the energy entering the adiabatic saturator with the makeup water is normally much smaller than that of the moist air, the enthalpy of the entering moist air is very nearly equal to the enthalpy of the saturated mixture exiting. Accordingly, all states with the same value of the wet-bulb temperature (adiabatic-saturation temperature) have nearly the same value for the mixture enthalpy per unit mass of dry air. Although Figs. A-9 ignore this slight effect, some psychrometric charts are drawn to show the departure of lines of constant wet-bulb temperature from lines of constant mixture enthalpy.
- ▶ As shown on Fig. 12.9, psychrometric charts also provide lines representing volume per unit mass of dry air, V/m_a . Figures A-9 and A-9E give this quantity in units of m^3/kg and ft^3/lb , respectively. These specific volume lines can be interpreted as giving the volume of dry air or of water vapor, per unit mass of dry air, since each mixture component is considered to fill the entire volume.

The psychrometric chart is easily used.

▶ **FOR EXAMPLE** a psychrometer indicates that in a classroom the dry-bulb temperature is 68°F and the wet-bulb temperature is 60°F . Locating the mixture state on Fig. A-9E corresponding to the intersection of these temperatures, we read $\omega = 0.0092 \text{ lb(vapor)}/\text{lb(dry air)}$ and $\phi = 63\%$. ▶▶▶▶▶

12.8 Analyzing Air-Conditioning Processes

The purpose of the present section is to study typical air-conditioning processes using the psychrometric principles developed in this chapter. Specific illustrations are provided in the form of solved examples involving control volumes at steady state. In each example, the methodology introduced in Sec. 12.8.1 is employed to arrive at the solution.

To reinforce principles developed in this chapter, the psychrometric parameters required by these examples are determined in most cases using tabular data from Appendix tables. Where a full psychrometric chart solution is not also provided, we recommend the example be solved using the chart, checking results with values from the solution presented.

12.8.1 Applying Mass and Energy Balances to Air-Conditioning Systems

The object of this section is to illustrate the use of the conservation of mass and conservation of energy principles in analyzing systems involving mixtures of dry air and water vapor in which a condensed water phase may be present. The same basic

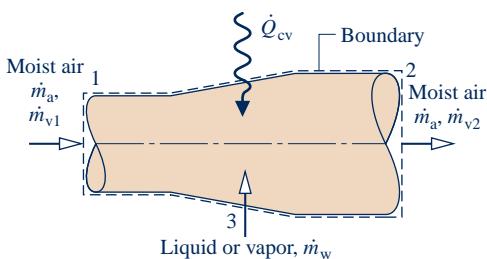


Fig. 12.10 System for conditioning moist air.

solution approach that has been used in thermodynamic analyses considered thus far is applicable. The only new aspect is the use of the special vocabulary and parameters of psychometrics.

Systems that accomplish air-conditioning processes such as heating, cooling, humidification, or dehumidification are normally analyzed on a control volume basis. To consider a typical analysis, refer to Fig. 12.10, which shows a two-inlet, single-exit control volume at steady state. A moist air stream enters at 1, a moist air stream exits at 2, and a water-only stream enters (or exits) at 3. The water-only stream may be a liquid or a vapor. Heat transfer at the rate \dot{Q}_{cv} can occur between the control volume and its surroundings. Depending on the application, the value of \dot{Q}_{cv} might be positive, negative, or zero.

Mass Balance

At steady state, the amounts of dry air and water vapor contained within the control volume cannot vary. Thus, for each component individually it is necessary for the total incoming and outgoing mass flow rates to be equal. That is

$$\begin{aligned}\dot{m}_{a1} &= \dot{m}_{a2} && (\text{dry air}) \\ \dot{m}_{v1} + \dot{m}_w &= \dot{m}_{v2} && (\text{water})\end{aligned}$$

For simplicity, the constant mass flow rate of the dry air is denoted by \dot{m}_a . The mass flow rates of the water vapor can be expressed conveniently in terms of humidity ratios as $\dot{m}_{v1} = \omega_1 \dot{m}_a$ and $\dot{m}_{v2} = \omega_2 \dot{m}_a$. With these expressions, the mass balance for water becomes

$$\dot{m}_w = \dot{m}_a(\omega_2 - \omega_1) \quad (\text{water}) \quad (12.52)$$

When water is added at 3, ω_2 is greater than ω_1 .

TAKE NOTE...

As indicated by the developments of Sec. 12.8.1, several simplifying assumptions are made when analyzing air-conditioning systems considered in Examples 12.10–12.14 to follow. They include:

- The control volume is at steady-state.
- Moist air streams are ideal gas mixtures of dry air and water vapor adhering to the Dalton model.
- Flow is one-dimensional where mass crosses the boundary of the control volume, and the effects of kinetic and potential energy at these locations are neglected.
- The only work is flow work (Sec. 4.4.2) where mass crosses the boundary of the control volume.

Energy Balance

Assuming $\dot{W}_{cv} = 0$ and ignoring all kinetic and potential energy effects, the energy rate balance reduces at steady state to

$$0 = \dot{Q}_{cv} + (\dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1}) + \dot{m}_w h_w - (\dot{m}_a h_{a2} + \dot{m}_{v2} h_{v2}) \quad (12.53)$$

In this equation, the entering and exiting moist air streams are regarded as ideal gas mixtures of dry air and water vapor.

Equation 12.53 can be cast into a form that is particularly convenient for the analysis of air-conditioning systems. First, with Eq. 12.47 the enthalpies of the entering and exiting water vapor can be evaluated as the saturated vapor enthalpies corresponding to the temperatures T_1 and T_2 , respectively, giving

$$0 = \dot{Q}_{cv} + (\dot{m}_a h_{a1} + \dot{m}_{v1} h_{g1}) + \dot{m}_w h_w - (\dot{m}_a h_{a2} + \dot{m}_{v2} h_{g2})$$

Then, with $\dot{m}_{v1} = \omega_1 \dot{m}_a$ and $\dot{m}_{v2} = \omega_2 \dot{m}_a$, the equation can be expressed as

$$0 = \dot{Q}_{cv} + \dot{m}_a(h_{a1} + \omega_1 h_{g1}) + \dot{m}_w h_w - \dot{m}_a(h_{a2} + \omega_2 h_{g2}) \quad (12.54)$$

Finally, introducing Eq. 12.52, the energy rate balance becomes

$$0 = \dot{Q}_{cv} + \dot{m}_a[(h_{a1} - h_{a2}) + \underline{\omega_1 h_{g1}} + (\omega_2 - \omega_1)h_w - \underline{\omega_2 h_{g2}}] \quad (12.55)$$

The first underlined term of Eq. 12.55 can be evaluated from Tables A-22 giving the ideal gas properties of air. Alternatively, since relatively small temperature differences are normally encountered in the class of systems under present consideration, this term can be evaluated as $h_{a1} - h_{a2} = c_{pa}(T_1 - T_2)$, where c_{pa} is a constant value for the specific heat of dry air. The second underlined term of Eq. 12.55 can be evaluated using steam table data together with known values for ω_1 and ω_2 . As illustrated in discussions to follow, Eq. 12.55 also can be evaluated using the psychometric chart or IT.

12.8.2 Conditioning Moist Air at Constant Composition

Building air-conditioning systems frequently heat or cool a moist air stream with no change in the amount of water vapor present. In such cases the humidity ratio ω remains constant, while relative humidity and other moist air parameters vary. Example 12.10 gives an elementary illustration using the methodology of Sec. 12.8.1.

EXAMPLE 12.10

Heating Moist Air in a Duct

Moist air enters a duct at 10°C, 80% relative humidity, and a volumetric flow rate of 150 m³/min. The mixture is heated as it flows through the duct and exits at 30°C. No moisture is added or removed, and the mixture pressure remains approximately constant at 1 bar. For steady-state operation, determine (a) the rate of heat transfer, in kJ/min, and (b) the relative humidity at the exit. Changes in kinetic and potential energy can be ignored.

SOLUTION

Known: Moist air that enters a duct at 10°C and $\phi = 80\%$ with a volumetric flow rate of 150 m³/min is heated at constant pressure and exits at 30°C. No moisture is added or removed.

Find: Determine the rate of heat transfer, in kJ/min, and the relative humidity at the exit.

Schematic and Given Data:

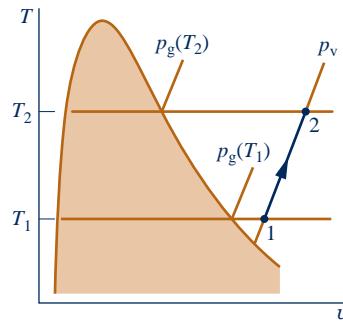
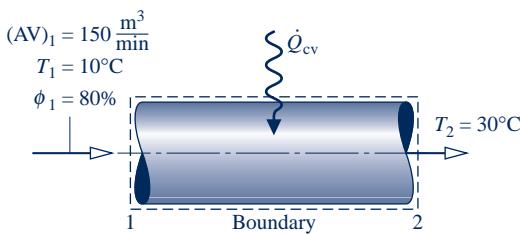


Fig. E12.10a

Engineering Model:

- The control volume shown in the accompanying figure operates at steady state.
- The changes in kinetic and potential energy between inlet and exit can be ignored and $\dot{W}_{cv} = 0$.
- The entering and exiting moist air streams are regarded as ideal gas mixtures adhering to the Dalton model.

Analysis:

(a) The heat transfer rate \dot{Q}_{cv} can be determined from the mass and energy rate balances. At steady state, the amounts of dry air and water vapor contained within the control volume cannot vary. Thus, for each component individually it is necessary for the incoming and outgoing mass flow rates to be equal. That is

$$\begin{aligned}\dot{m}_{a1} &= \dot{m}_{a2} && (\text{dry air}) \\ \dot{m}_{v1} &= \dot{m}_{v2} && (\text{water vapor})\end{aligned}$$

For simplicity, the constant mass flow rates of the dry air and water vapor are denoted, respectively, by \dot{m}_a and \dot{m}_v . From these considerations, it can be concluded that the humidity ratio is the same at the inlet and exit: $\omega_1 = \omega_2$.

The steady-state form of the energy rate balance reduces with assumption 2 to

$$0 = \dot{Q}_{cv} - \dot{W}_{cv}^0 + (\dot{m}_a h_{a1} + \dot{m}_v h_{v1}) - (\dot{m}_a h_{a2} + \dot{m}_v h_{v2})$$

In writing this equation, the incoming and outgoing moist air streams are regarded as ideal gas mixtures of dry air and water vapor.

Solving for \dot{Q}_{cv}

$$\dot{Q}_{cv} = \dot{m}_a(h_{a2} - h_{a1}) + \dot{m}_v(h_{v2} - h_{v1})$$

Noting that $\dot{m}_v = \omega \dot{m}_a$, where ω is the humidity ratio, the expression for \dot{Q}_{cv} can be written in the form

$$\textcircled{1} \quad \dot{Q}_{cv} = \dot{m}_a[(h_{a2} - h_{a1}) + \omega(h_{v2} - h_{v1})] \quad (\text{a})$$

To evaluate \dot{Q}_{cv} from this expression requires the specific enthalpies of the dry air and water vapor at the inlet and exit, the mass flow rate of the dry air, and the humidity ratio.

The specific enthalpies of the dry air are obtained from Table A-22 at the inlet and exit temperatures T_1 and T_2 , respectively: $h_{a1} = 283.1 \text{ kJ/kg}$, $h_{a2} = 303.2 \text{ kJ/kg}$. The specific enthalpies of the water vapor are found using $h_v \approx h_g$ and data from Table A-2 at T_1 and T_2 , respectively: $h_{g1} = 2519.8 \text{ kJ/kg}$, $h_{g2} = 2556.3 \text{ kJ/kg}$.

The mass flow rate of the dry air can be determined from the volumetric flow rate at the inlet (AV)₁

$$\dot{m}_a = \frac{(\text{AV})_1}{v_{a1}}$$

In this equation, v_{a1} is the specific volume of the dry air evaluated at T_1 and the partial pressure of the dry air p_{a1} . Using the ideal gas equation of state

$$v_{a1} = \frac{(\bar{R}/M)T_1}{p_{a1}}$$

The partial pressure p_{a1} can be determined from the mixture pressure p and the partial pressure of the water vapor p_{v1} : $p_{a1} = p - p_{v1}$. To find p_{v1} , use the given inlet relative humidity and the saturation pressure at 10°C from Table A-2

$$p_{v1} = \phi_1 p_{g1} = (0.8)(0.01228 \text{ bar}) = 0.0098 \text{ bar}$$

Since the mixture pressure is 1 bar, it follows that $p_{a1} = 0.9902 \text{ bar}$. The specific volume of the dry air is then

$$v_{a1} = \frac{\left(\frac{8314 \text{ N} \cdot \text{m}}{28.97 \text{ kg} \cdot \text{K}}\right)(283 \text{ K})}{(0.9902 \times 10^5 \text{ N/m}^2)} = 0.82 \text{ m}^3/\text{kg}$$

Using this value, the mass flow rate of the dry air is

$$\dot{m}_a = \frac{150 \text{ m}^3/\text{min}}{0.82 \text{ m}^3/\text{kg}} = 182.9 \text{ kg/min}$$

The humidity ratio ω can be found from

$$\begin{aligned} \omega &= 0.622 \left(\frac{p_{v1}}{p - p_{v1}} \right) = 0.622 \left(\frac{0.0098}{1 - 0.0098} \right) \\ &= 0.00616 \frac{\text{kg (vapor)}}{\text{kg (dry air)}} \end{aligned}$$

Finally, substituting values into Eq. (a) we get

$$\begin{aligned} \dot{Q}_{cv} &= 182.9[(303.2 - 283.1) + (0.00616)(2556.3 - 2519.8)] \\ &= 3717 \text{ kJ/min} \end{aligned}$$

(b) The states of the water vapor at the duct inlet and exit are located on the accompanying $T-v$ diagram. Since the composition of the moist air and the mixture pressure remain constant, the partial pressure of the water vapor at the exit equals the partial pressure of the water vapor at the inlet: $p_{v2} = p_{v1} = 0.0098 \text{ bar}$. The relative humidity at the exit is then

$$\textcircled{2} \quad \phi_2 = \frac{p_{v2}}{p_{g2}} = \frac{0.0098}{0.04246} = 0.231(23.1\%)$$

where p_{g2} is from Table A-2 at 30°C.

Alternative Psychrometric Chart Solution: Let us consider an alternative solution using the psychrometric chart. As shown on the sketch of the psychrometric chart, Fig. E12.10b, the state of the moist air at the inlet is defined by $\phi_1 = 80\%$ and a dry-bulb temperature of 10°C. From the solution to part (a), we know that the humidity ratio has the same value at the exit as at the inlet. Accordingly, the state of the moist air at the exit is fixed by

$\omega_2 = \omega_1$ and a dry-bulb temperature of 30°C. By inspection of Fig. A-9, the relative humidity at the duct exit is about 23%, and thus in agreement with the result of part (b).

The rate of heat transfer can be evaluated from the psychrometric chart using the following expression obtained by rearranging Eq. (a) of part (a) to read

$$\dot{Q}_{cv} = \dot{m}_a [(h_a + \omega h_v)_2 - (h_a + \omega h_v)_1] \quad (\text{b})$$

To evaluate \dot{Q}_{cv} from this expression requires values for the mixture enthalpy per unit mass of dry air ($h_a + \omega h_v$) at the inlet and exit. These can be determined by inspection of the psychrometric chart, Fig. A-9, as $(h_a + \omega h_v)_1 = 25.7 \text{ kJ/kg(dry air)}$, $(h_a + \omega h_v)_2 = 45.9 \text{ kJ/kg(dry air)}$.

Using the specific volume value v_{a1} at the inlet state read from the chart together with the given volumetric flow rate at the inlet, the mass flow rate of the dry air is found as

$$\dot{m}_a = \frac{150 \text{ m}^3/\text{min}}{0.81 \text{ m}^3/\text{kg(dry air)}} = 185 \frac{\text{kg(dry air)}}{\text{min}}$$

Substituting values into the energy rate balance, Eq. (b), we get

$$\begin{aligned} \dot{Q}_{cv} &= 185 \frac{\text{kg(dry air)}}{\text{min}} (45.9 - 25.7) \frac{\text{kJ}}{\text{kg(dry air)}} \\ &= 3737 \frac{\text{kJ}}{\text{min}} \end{aligned}$$

which agrees closely with the result obtained in part (a), as expected.

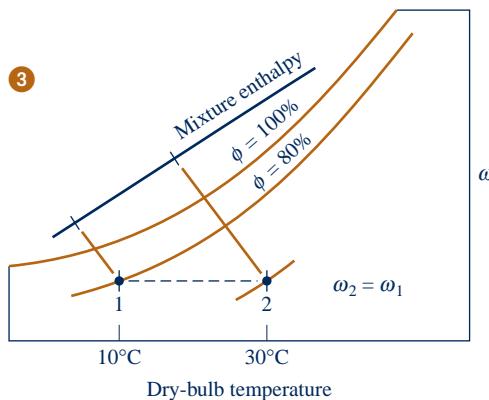


Fig. E12.10b

- ① The first underlined term in this equation for \dot{Q}_{cv} is evaluated with specific enthalpies from the ideal gas table for air, Table A-22. Steam table data are used to evaluate the second underlined term. Note that the different datums for enthalpy underlying these tables cancel because each of the two terms involves enthalpy *differences* only. Since the specific heat c_{pa} for dry air varies only slightly over the interval from 10 to 30°C (Table A-20), the specific enthalpy change of the dry air could be evaluated alternatively with $c_{pa} = 1.005 \text{ kJ/kg} \cdot \text{K}$.
- ② No water is added or removed as the moist air passes through the duct at constant pressure; accordingly, the humidity ratio ω and the partial pressures p_v and p_a remain constant. However, because the saturation pressure increases as the temperature increases from inlet to exit, the *relative humidity* decreases: $\phi_2 < \phi_1$.
- ③ The mixture pressure, 1 bar, differs slightly from the pressure used to construct the psychrometric chart, 1 atm. This difference is ignored.

Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply mass and energy balances for heating at constant composition in a control volume at steady state.
- retrieve necessary property data.

QuickQUIZ

Using the psychrometric chart, what is the dew point temperature, in °C, for the moist air entering? At the exit? Ans. $\approx 7^\circ\text{C}$, same.

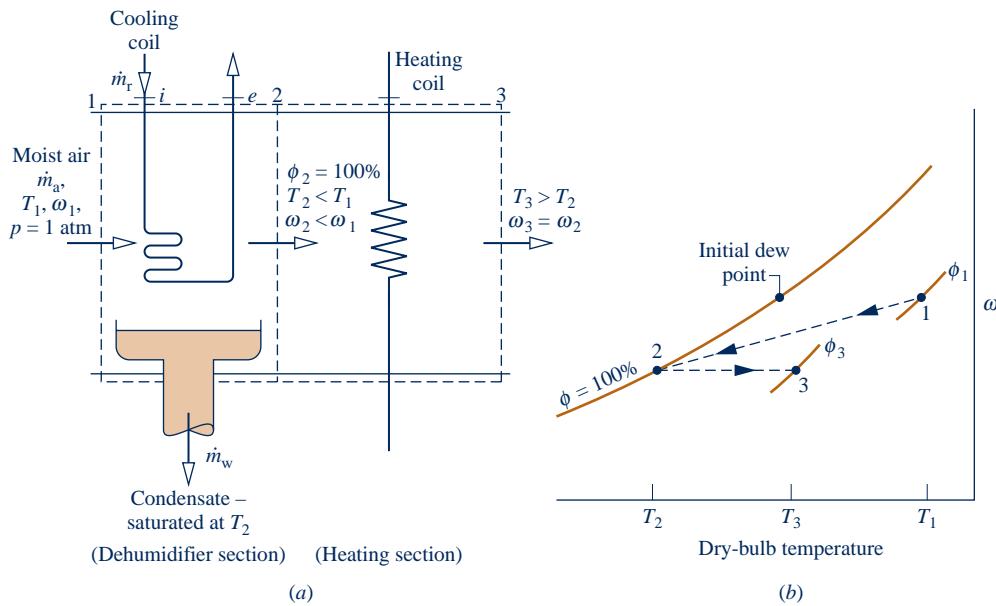


Fig. 12.11 Dehumidification. (a) Equipment schematic. (b) Psychrometric chart representation.

12.8.3 Dehumidification

TAKE NOTE...

A dashed line on a property diagram signals only that a process has occurred between initial and final equilibrium states, and does not define a path for the process.

When a moist air stream is cooled at constant mixture pressure to a temperature below its dew point temperature, some condensation of the water vapor initially present will occur. Figure 12.11 shows the schematic of a dehumidifier using this principle. Moist air enters at state 1 and flows across a cooling coil through which a refrigerant or chilled water circulates. Some of the water vapor initially present in the moist air condenses, and a saturated moist air mixture exits the dehumidifier section at state 2. Although water condenses at various temperatures, the condensed water is assumed to be cooled to T_2 before it exits the dehumidifier. Since the moist air leaving the humidifier is saturated at a temperature lower than the temperature of the moist air entering, the moist air stream at state 2 might be uncomfortable for direct use in occupied spaces. However, by passing the stream through a following heating section, it can be brought to a condition—state 3—most occupants would regard as comfortable.

Let us sketch the procedure for evaluating the rates at which condensate exits and refrigerant circulates. This requires the use of mass and energy rate balances for the dehumidifier section. They are developed next.

Mass Balance

The mass flow rate of the condensate \dot{m}_w can be related to the mass flow rate of the dry air \dot{m}_a by applying conservation of mass separately for the dry air and water passing through the dehumidifier section. At steady state

$$\begin{aligned}\dot{m}_{a1} &= \dot{m}_{a2} && (\text{dry air}) \\ \dot{m}_{v1} &= \dot{m}_w + \dot{m}_{v2} && (\text{water})\end{aligned}$$

The common mass flow rate of the dry air is denoted as \dot{m}_a . Solving for the mass flow rate of the condensate

$$\dot{m}_w = \dot{m}_{v1} - \dot{m}_{v2}$$

Introducing $\dot{m}_{v1} = \omega_1 \dot{m}_a$ and $\dot{m}_{v2} = \omega_2 \dot{m}_a$, the amount of water condensed per unit mass of dry air passing through the device is

$$\frac{\dot{m}_w}{\dot{m}_a} = \omega_1 - \omega_2$$

This expression requires the humidity ratios ω_1 and ω_2 . Because no moisture is added or removed in the heating section, it can be concluded from conservation of mass that $\omega_2 = \omega_3$, so ω_3 can be used in the above equation in place of ω_2 .

Energy Balance

The mass flow rate of the refrigerant through the cooling coil \dot{m}_r can be related to the mass flow rate of the dry air \dot{m}_a by means of an energy rate balance applied to the dehumidifier section. With $\dot{W}_{cv} = 0$, negligible heat transfer with the surroundings, and no significant kinetic and potential energy changes, the energy rate balance reduces at steady state to

$$0 = \dot{m}_r(h_i - h_e) + (\dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1}) - \dot{m}_w h_w - (\dot{m}_a h_{a2} + \dot{m}_{v2} h_{v2})$$

where h_i and h_e denote the specific enthalpy values of the refrigerant entering and exiting the dehumidifier section, respectively. Introducing $\dot{m}_{v1} = \omega_1 \dot{m}_a$, $\dot{m}_{v2} = \omega_2 \dot{m}_a$, and $\dot{m}_w = (\omega_1 - \omega_2) \dot{m}_a$

$$0 = \dot{m}_r(h_i - h_e) + \dot{m}_a[(h_{a1} - h_{a2}) + \omega_1 h_{g1} - \omega_2 h_{g2} - (\omega_1 - \omega_2)h_{f2}]$$

where the specific enthalpies of the water vapor at 1 and 2 are evaluated at the saturated vapor values corresponding to T_1 and T_2 , respectively. Since the condensate is assumed to exit as a saturated liquid at T_2 , $h_w = h_{f2}$. Solving for the refrigerant mass flow rate per unit mass of dry air flowing through the device

$$\frac{\dot{m}_r}{\dot{m}_a} = \frac{(h_{a1} - h_{a2}) + \omega_1 h_{g1} - \omega_2 h_{g2} - (\omega_1 - \omega_2)h_{f2}}{h_e - h_i}$$

The accompanying psychrometric chart, Fig. 12.11b, illustrates important features of the processes involved. As indicated by the chart, the moist air first cools from state 1, where the temperature is T_1 and the humidity ratio is ω_1 , to state 2, where the mixture is saturated ($\phi_2 = 100\%$), the temperature is $T_2 < T_1$, and the humidity ratio is $\omega_2 < \omega_1$. During the subsequent heating process, the humidity ratio remains constant, $\omega_2 = \omega_3$, and the temperature increases to T_3 . Since all states visited are not equilibrium states, these processes are indicated on the psychrometric chart by dashed lines.

The example that follows provides an illustration involving dehumidification where one of the objectives is the refrigerating capacity of the cooling coil.

EXAMPLE 12.11

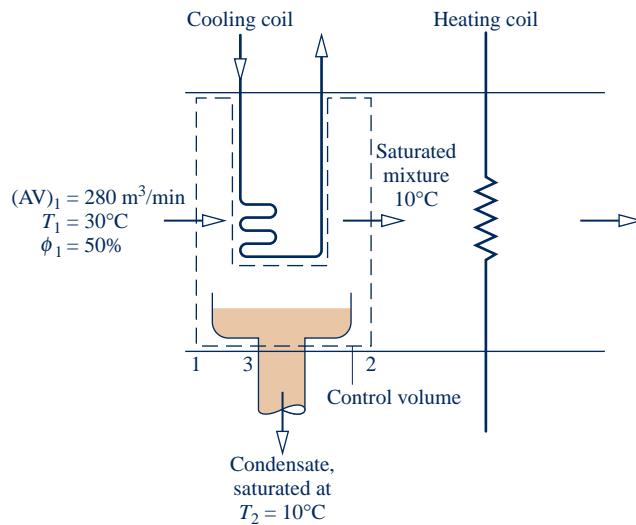
Assessing Dehumidifier Performance

Moist air at 30°C and 50% relative humidity enters a dehumidifier operating at steady state with a volumetric flow rate of 280 m³/min. The moist air passes over a cooling coil and water vapor condenses. Condensate exits the dehumidifier saturated at 10°C. Saturated moist air exits in a separate stream at the same temperature. There is no significant loss of energy by heat transfer to the surroundings and pressure remains constant at 1.013 bar. Determine (a) the mass flow rate of the dry air, in kg/min, (b) the rate at which water is condensed, in kg per kg of dry air flowing through the control volume, and (c) the required refrigerating capacity, in tons.

SOLUTION

Known: Moist air enters a dehumidifier at 30°C and 50% relative humidity with a volumetric flow rate of 280 m³/min. Condensate and moist air exit in separate streams at 10°C.

Determine: Find the mass flow rate of the dry air, in kg/min, the rate at which water is condensed, in kg per kg of dry air, and the required refrigerating capacity, in tons.

Schematic and Given Data:**Fig. E12.11a****Analysis:**

(a) At steady state, the mass flow rates of the dry air entering and exiting are equal. The common mass flow rate of the dry air can be determined from the volumetric flow rate at the inlet

$$\dot{m}_a = \frac{(AV)_1}{v_{a1}}$$

The specific volume of the dry air at inlet 1, v_{a1} , can be evaluated using the ideal gas equation of state, so

$$\dot{m}_a = \frac{(AV)_1}{(\bar{R}/M_a)(T_1/p_{a1})}$$

The partial pressure of the dry air p_{a1} can be determined from $p_{a1} = p_1 - p_{v1}$. Using the relative humidity at the inlet ϕ_1 and the saturation pressure at 30°C from Table A-2

$$p_{v1} = \phi_1 p_{g1} = (0.5)(0.04246) = 0.02123 \text{ bar}$$

Thus, $p_{a1} = 1.013 - 0.02123 = 0.99177$ bar. Inserting values into the expression for \dot{m}_a gives

$$\dot{m}_a = \frac{(280 \text{ m}^3/\text{min})(0.99177 \times 10^5 \text{ N/m}^2)}{(8314/28.97 \text{ N} \cdot \text{m/kg} \cdot \text{K})(303 \text{ K})} = 319.35 \text{ kg/min}$$

(b) Conservation of mass for the water requires $\dot{m}_{v1} = \dot{m}_{v2} + \dot{m}_w$. With $\dot{m}_{v1} = \omega_1 \dot{m}_a$ and $\dot{m}_{v2} = \omega_2 \dot{m}_a$, the rate at which water is condensed per unit mass of dry air is

$$\frac{\dot{m}_w}{\dot{m}_a} = \omega_1 - \omega_2$$

The humidity ratios ω_1 and ω_2 can be evaluated using Eq. 12.43. Thus, ω_1 is

$$\omega_1 = 0.662 \left(\frac{p_{v1}}{p_1 - p_{v1}} \right) = 0.622 \left(\frac{0.02123}{0.99177} \right) = 0.0133 \frac{\text{kg(vapor)}}{\text{kg(dry air)}}$$

Since the moist air is saturated at 10°C, p_{v2} equals the saturation pressure at 10°C: $p_g = 0.01228$ bar from Table A-2. Equation 12.43 then gives $\omega_2 = 0.0076 \text{ kg(vapor)/kg(dry air)}$. With these values for ω_1 and ω_2

$$\frac{\dot{m}_w}{\dot{m}_a} = 0.0133 - 0.0076 = 0.0057 \frac{\text{kg(condensate)}}{\text{kg(dry air)}}$$

Engineering Model:

1. The control volume shown in the accompanying figure operates at steady state. Changes in kinetic and potential energy can be neglected, and $\dot{W}_{cv} = 0$.
2. There is no significant heat transfer to the surroundings.
3. The pressure remains constant throughout at 1.013 bar.
4. At location 2, the moist air is saturated. The condensate exits at location 3 as a saturated liquid at temperature T_2 .
5. The moist air streams are regarded as ideal gas mixtures adhering to the Dalton model.

(c) The rate of heat transfer \dot{Q}_{cv} between the moist air stream and the refrigerant coil can be determined using an energy rate balance. With assumptions 1 and 2, the steady-state form of the energy rate balance reduces to

$$0 = \dot{Q}_{cv} + (\dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1}) - \dot{m}_w h_w - (\dot{m}_a h_{a2} + \dot{m}_{v2} h_{v2}) \quad (a)$$

With $\dot{m}_{v1} = \omega_1 \dot{m}_a$, $\dot{m}_{v2} = \omega_2 \dot{m}_a$, and $\dot{m}_w = (\omega_1 - \omega_2) \dot{m}_a$, this becomes

$$\dot{Q}_{cv} = \dot{m}_a [(h_{a2} - h_{a1}) - \omega_1 h_{g1} + \omega_2 h_{g2} + (\omega_1 - \omega_2) h_f] \quad (b)$$

which agrees with Eq. 12.55. In Eq. (b), the specific enthalpies of the water vapor at 1 and 2 are evaluated at the saturated vapor values corresponding to T_1 and T_2 , respectively, and the specific enthalpy of the exiting condensate is evaluated as h_f at T_2 . Selecting enthalpies from Tables A-2 and A-22, as appropriate, Eq. (b) reads

$$\begin{aligned} \dot{Q}_{cv} &= (319.35)[(283.1 - 303.2) - 0.0133(2556.3) + 0.0076(2519.8) + 0.0057(42.01)] \\ &= -11,084 \text{ kJ/min} \end{aligned}$$

Since 1 ton of refrigeration equals a heat transfer rate of 211 kJ/min (Sec. 10.2.1), the required refrigerating capacity is 52.5 tons.

Alternative Psychrometric Chart Solution: Let us consider an alternative solution using the psychrometric chart. As shown on the sketch of the psychrometric chart, Fig. E12.11b, the state of the moist air at the inlet 1 is defined by $\phi = 50\%$ and a dry-bulb temperature of 30°C . At 2, the moist air is saturated at 10°C . Rearranging Eq. (a), we get

$$\dot{Q}_{cv} = \dot{m}_a [(\underline{h_a + \omega h_v})_2 - (\underline{h_a + \omega h_v})_1 + (\omega_1 - \omega_2) h_w] \quad (c)$$

The underlined terms and humidity ratios, ω_1 and ω_2 , can be read directly from the chart. The mass flow rate of the dry air can be determined using the volumetric flow rate at the inlet and v_{a1} read from the chart. The specific enthalpy h_w is obtained (as above) from Table A-2: h_f at T_2 . The details are left as an exercise.

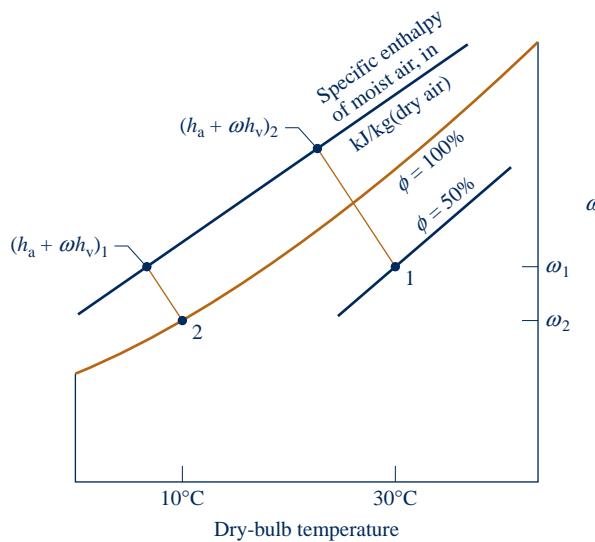


Fig. E12.11b



Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply mass and energy balances for a dehumidification process in a control volume at steady state.
- retrieve property data for dry air and water.
- apply the psychrometric chart.

QuickQUIZ

Using the psychrometric chart, determine the wet-bulb temperature of the moist air entering the dehumidifier, in $^\circ\text{C}$. Ans. $\approx 22^\circ\text{C}$.

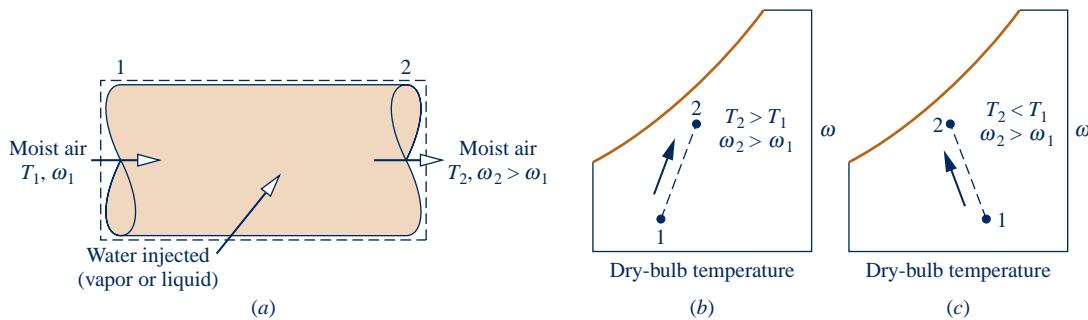


Fig. 12.12 Humidification. (a) Control volume. (b) Steam injected. (c) Liquid injected.

12.8.4 • Humidification

It is often necessary to increase the moisture content of the air circulated through occupied spaces. One way to accomplish this is to inject steam. Alternatively, liquid water can be sprayed into the air. Both cases are shown schematically in Fig. 12.12a. The temperature of the moist air as it exits the humidifier depends on the condition of the water introduced. When relatively high-temperature steam is injected, both the humidity ratio and the dry-bulb temperature are increased. This is illustrated by the accompanying psychrometric chart of Fig. 12.12b. If liquid water is injected instead of steam, the moist air may exit the humidifier with a *lower* temperature than at the inlet. This is illustrated in Fig. 12.12c. The example to follow illustrates the case of steam injection. The case of liquid water injection is considered further in the next section.

EXAMPLE 12.12 ▶

Analyzing a Steam-Spray Humidifier

Moist air with a temperature of 22°C and a wet-bulb temperature of 9°C enters a steam-spray humidifier. The mass flow rate of the dry air is 90 kg/min. Saturated water vapor at 110°C is injected into the mixture at a rate of 52 kg/h. There is no heat transfer with the surroundings, and the pressure is constant throughout at 1 bar. Using the psychrometric chart, determine at the exit (a) the humidity ratio and (b) the temperature, in °C.

SOLUTION

Known: Moist air enters a humidifier at a temperature of 22°C and a wet-bulb temperature of 9°C. The mass flow rate of the dry air is 90 kg/min. Saturated water vapor at 110°C is injected into the mixture at a rate of 52 kg/h.

Find: Using the psychrometric chart, determine at the exit the humidity ratio and the temperature, in °C.

Schematic and Given Data:

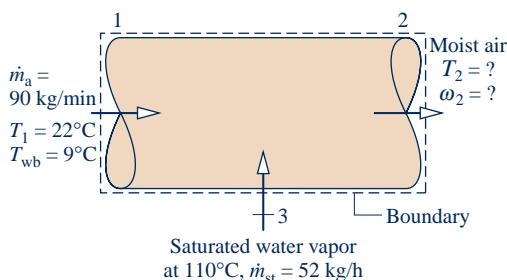


Fig. E12.12a

Engineering Model:

1. The control volume shown in the accompanying figure operates at steady state. Changes in kinetic and potential energy can be neglected and $W_{cv} = 0$.
2. There is no heat transfer with the surroundings.
3. The pressure remains constant throughout at 1 bar. Figure A-9 remains valid at this pressure.
4. The moist air streams are regarded as ideal gas mixtures adhering to the Dalton model.

Analysis:

(a) The humidity ratio at the exit ω_2 can be found from mass rate balances on the dry air and water individually. Thus

$$\begin{aligned}\dot{m}_{a1} &= \dot{m}_{a2} && (\text{dry air}) \\ \dot{m}_{v1} + \dot{m}_{st} &= \dot{m}_{v2} && (\text{water})\end{aligned}$$

With $\dot{m}_{v1} = \omega_1 \dot{m}_a$, and $\dot{m}_{v2} = \omega_2 \dot{m}_a$, where \dot{m}_a is the mass flow rate of the air, the second of these becomes

$$\omega_2 = \omega_1 + \frac{\dot{m}_{st}}{\dot{m}_a}$$

Using the inlet dry-bulb temperature, 22°C, and the inlet wet-bulb temperature, 9°C, the value of the humidity ratio ω_1 can be found by inspection of the psychrometric chart, Fig. A-9. The result is $\omega_1 = 0.002 \text{ kg (vapor)/kg(dry air)}$. This value should be verified as an exercise. Inserting values into the expression for ω_2

$$\omega_2 = 0.002 + \frac{(52 \text{ kg/h})|1 \text{ h}/60 \text{ min}|}{90 \text{ kg/min}} = 0.0116 \frac{\text{kg(vapor)}}{\text{kg(dry air)}}$$

(b) The temperature at the exit can be determined using an energy rate balance. With assumptions 1 and 2, the steady-state form of the energy rate balance reduces to a special case of Eq. 12.55. Namely

$$0 = h_{a1} - h_{a2} + \omega_1 h_{g1} + (\omega_2 - \omega_1) h_{g3} - \omega_2 h_{g2} \quad (\text{a})$$

In writing this, the specific enthalpies of the water vapor at 1 and 2 are evaluated as the respective saturated vapor values, and h_{g3} denotes the enthalpy of the saturated vapor injected into the moist air.

Equation (a) can be rearranged in the following form suitable for use with the psychrometric chart.

$$(h_a + \omega h_g)_2 = (h_a + \omega h_g)_1 + (\omega_2 - \omega_1) h_{g3} \quad (\text{b})$$

As shown on the sketch of the psychrometric chart, Fig. E12.12b, the first term on the right of Eq. (b) can be obtained from Fig. A-9 at the inlet state, defined by the intersection of the inlet dry-bulb temperature, 22°C, and the inlet wet-bulb temperature, 9°C; the value is 27.2 kJ/kg(dry air). The second term on the right can be evaluated using the known humidity ratios ω_1 and ω_2 and h_{g3} from Table A-2: 2691.5 kJ/kg(vapor). The value of the second term of Eq. (b) is 25.8 kJ/kg(dry air). The state at the exit is then fixed by ω_2 and $(h_a + \omega h_g)_2 = 53 \text{ kJ/kg(dry air)}$, calculated from the two values just determined. Finally, the temperature at the exit can be read directly from the chart. The result is $T_2 \approx 23.5^\circ\text{C}$.

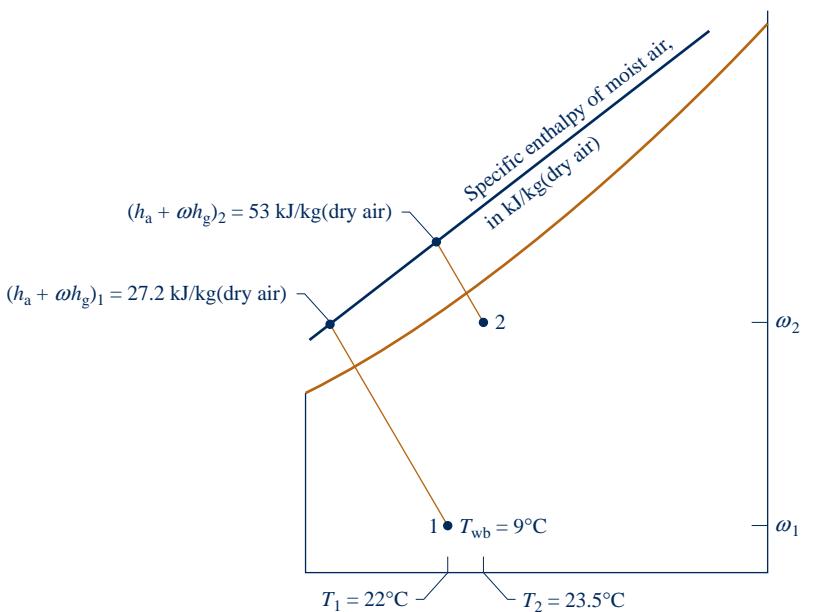


Fig. E12.12b

Alternative IT Solution:

(2) The following program allows T_2 to be determined using IT, where \dot{m}_a is denoted as `mdata`, \dot{m}_{st} is denoted as `mdotst`, $w1$ and $w2$ denote ω_1 and ω_2 , respectively, and so on.

```

// Given data
T1 = 22 // °C
Twb1 = 9 // °C
mdota = 90 // kg/min
p = 1 // bar
Tst = 110 // °C
mdotst = (52 / 60) // converting kg/h to kg/min
// Evaluate humidity ratios
w1 = w_TTwb (T1,Twb1,p)
w2 = w1 + (mdotst / mdota)
// Denoting the enthalpy of moist air at state 1 by
// h1, etc., the energy balance, Eq. (a), becomes
o = h1 - h2 + (w2 - w1)*hst
// Evaluate enthalpies
h1 = ha_Tw(T1,w1)
h2 = ha_Tw(T2,w2)
hst = hsat_Px("Water/Steam",psat,1)
psat = Psat_T("Water/Steam ",Tst)

```

Using the **Solve** button, the result is $T_2 = 23.4^\circ\text{C}$, which agrees closely with the values obtained above, as expected.

- 1 A solution of Eq. (b) using data from Tables A-2 and A-22 requires an iterative (trial) procedure. The result is $T_2 = 24^\circ\text{C}$, as can be verified.
- 2 Note the use of special *Moist Air* functions listed in the **Properties** menu of *IT*.

Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply mass and energy balances for a spray humidification process in a control volume at steady state.
- retrieve necessary property data using the psychrometric chart.
- apply *IT* for psychrometric analysis.

QuickQUIZ

Using the psychrometric chart, what is the relative humidity at the exit? **Ans.** $\approx 63\%$.

12.8.5 • Evaporative Cooling

Cooling in hot, relatively dry climates can be accomplished by *evaporative cooling*. This involves either spraying liquid water into air or forcing air through a soaked pad that is kept replenished with water, as shown in Fig. 12.13. Owing to the low humidity of the moist air entering at state 1, part of the injected water evaporates. The energy for evaporation is provided by the air stream, which is reduced in temperature and exits at state 2 with a lower temperature than the entering stream. Because the incoming air is relatively dry, the additional moisture carried by the exiting moist air stream is normally beneficial.

For negligible heat transfer with the surroundings, no work \dot{W}_{cv} , and no significant changes in kinetic and potential energy, the steady-state forms of the mass and energy rate balances reduce for the control volume of Fig. 12.13a to this special case of Eq. 12.55:

$$(h_{a2} + \underline{\omega_2 h_{g2}}) = (\underline{\omega_2 - \omega_1})h_f + (h_{a1} + \omega_1 h_{g1})$$

TAKE NOTE...

Evaporative cooling takes place at a nearly constant wet-bulb temperature.

where h_f denotes the specific enthalpy of the liquid stream entering the control volume. All the injected water is assumed to evaporate into the moist air stream. The underlined term accounts for the energy carried in with the injected liquid water. This term is normally much smaller in magnitude than either of the two moist air enthalpy terms. Accordingly, the enthalpy of the moist air varies only slightly, as illustrated on the psychrometric chart of Fig. 12.13b. Recalling that lines of constant

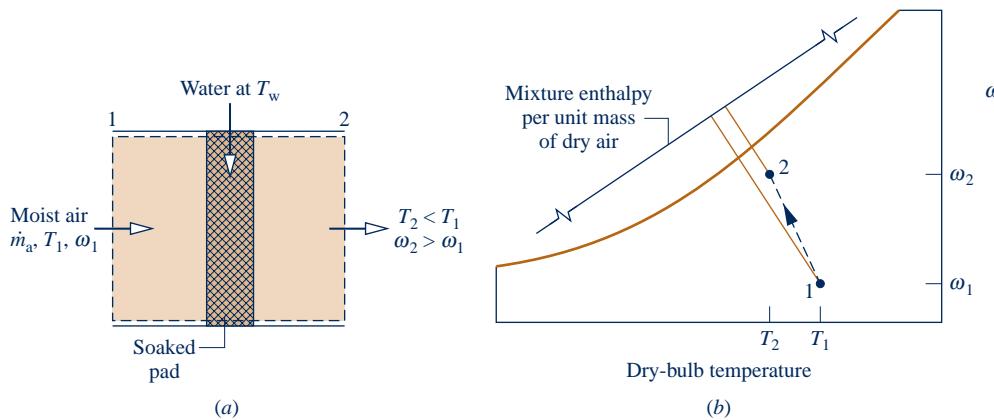


Fig. 12.13 Evaporative cooling. (a) Equipment schematic. (b) Psychrometric chart representation.

mixture enthalpy are closely lines of constant wet-bulb temperature (Sec. 12.7), it follows that evaporative cooling takes place at a nearly constant wet-bulb temperature.

In the next example, we consider the analysis of an evaporative cooler.

EXAMPLE 12.13

Considering an Evaporative Cooler

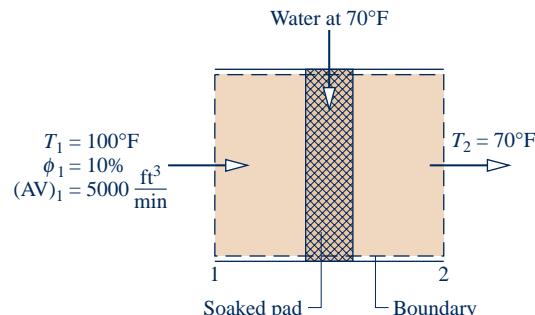
Air at 100°F and 10% relative humidity enters an evaporative cooler with a volumetric flow rate of 5000 ft³/min. Moist air exits the cooler at 70°F. Water is added to the soaked pad of the cooler as a liquid at 70°F and evaporates fully into the moist air. There is no heat transfer with the surroundings and the pressure is constant throughout at 1 atm. Determine (a) the mass flow rate of the water to the soaked pad, in lb/h, and (b) the relative humidity of the moist air at the exit to the evaporative cooler.

SOLUTION

Known: Air at 100°F and $\phi = 10\%$ enters an evaporative cooler with a volumetric flow rate of 5000 ft³/min. Moist air exits the cooler at 70°F. Water is added to the soaked pad of the cooler at 70°F.

Find: Determine the mass flow rate of the water to the soaked pad, in lb/h, and the relative humidity of the moist air at the exit of the cooler.

Schematic and Given Data:



Engineering Model:

1. The control volume shown in the accompanying figure operates at steady state. Changes in kinetic and potential energy can be neglected and $\dot{W}_{cv} = 0$.
2. There is no heat transfer with the surroundings.
3. The water added to the soaked pad enters as a liquid and evaporates fully into the moist air.
4. The pressure remains constant throughout at 1 atm.
5. The moist air streams are regarded as ideal gas mixtures adhering to the Dalton model.

Fig. E12.13

Analysis:

(a) Applying conservation of mass to the dry air and water individually as in previous examples gives

$$\dot{m}_w = \dot{m}_a(\omega_2 - \omega_1)$$

where \dot{m}_w is the mass flow rate of the water to the soaked pad. To find \dot{m}_w requires ω_1 , \dot{m}_a , and ω_2 . These will now be evaluated in turn.

The humidity ratio ω_1 can be found from Eq. 12.43, which requires p_{v1} , the partial pressure of the moist air entering the control volume. Using the given relative humidity ϕ_1 and p_g at T_1 from Table A-2E, we have $p_{v1} = \phi_1 p_{g1} = 0.095 \text{ lbf/in.}^2$. With this, $\omega_1 = 0.00405 \text{ lb(vapor)/lb(dry air)}$.

The mass flow rate of the dry air \dot{m}_a can be found as in previous examples using the volumetric flow rate and specific volume of the dry air. Thus

$$\dot{m}_a = \frac{(AV)_1}{v_{a1}}$$

The specific volume of the dry air can be evaluated from the ideal gas equation of state. The result is $v_{a1} = 14.2 \text{ ft}^3/\text{lb}$ (dry air). Inserting values, the mass flow rate of the dry air is

$$\dot{m}_a = \frac{5000 \text{ ft}^3/\text{min}}{14.2 \text{ ft}^3/\text{lb(dry air)}} = 352.1 \frac{\text{lb(dry air)}}{\text{min}}$$

To find the humidity ratio ω_2 , reduce the steady-state forms of the mass and energy rate balances using assumption 1 to obtain

$$0 = (\dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1}) + \dot{m}_w h_w - (\dot{m}_a h_{a2} + \dot{m}_{v2} h_{v2})$$

With the same reasoning as in previous examples, this can be expressed as the following special form of Eq. 12.55:

$$0 = (h_a + \omega h_g)_1 + (\underline{\omega_2 - \omega_1}) h_f - (h_a + \omega h_g)_2 \quad (\text{a})$$

where h_f denotes the specific enthalpy of the water entering the control volume at 70°F. Solving for ω_2

$$\textcircled{1} \quad \omega_2 = \frac{h_{a1} - h_{a2} + \omega_1(h_{g1} - h_f)}{h_{g2} - h_f} = \frac{c_{pa}(T_1 - T_2) + \omega_1(h_{g1} - h_f)}{h_{g2} - h_f}$$

where $c_{pa} = 0.24 \text{ Btu/lb} \cdot ^\circ\text{R}$. With h_f , h_{g1} , and h_{g2} from Table A-2E

$$\begin{aligned} \omega_2 &= \frac{0.24(100 - 70) + 0.00405(1105 - 38.1)}{(1092 - 38.1)} \\ &= 0.0109 \frac{\text{lb(vapor)}}{\text{lb(dry air)}} \end{aligned}$$

Substituting values for \dot{m}_a , ω_1 , and ω_2 into the expression for \dot{m}_w

$$\begin{aligned} \dot{m}_w &= \left[352.1 \frac{\text{lb(dry air)}}{\text{min}} \left| \frac{60 \text{ min}}{1 \text{ h}} \right| \right] (0.0109 - 0.00405) \frac{\text{lb(water)}}{\text{lb(dry air)}} \\ &= 144.7 \frac{\text{lb(water)}}{\text{h}} \end{aligned}$$

(b) The relative humidity of the moist air at the exit can be determined using Eq. 12.44. The partial pressure of the water vapor required by this expression can be found by solving Eq. 12.43 to obtain

$$p_{v2} = \frac{\omega_2 p}{\omega_2 + 0.622}$$

Inserting values

$$p_{v2} = \frac{(0.0109)(14.696 \text{ lbf/in.}^2)}{(0.0109 + 0.622)} = 0.253 \text{ lbf/in.}^2$$

At 70°F, the saturation pressure is 0.3632 lbf/in.² Thus, the relative humidity at the exit is

$$\phi_2 = \frac{0.253}{0.3632} = 0.697(69.7\%)$$

Alternative Psychrometric Chart Solution: Since the underlined term in Eq. (a) is much smaller than either of the moist air enthalpies, the enthalpy of the moist air remains nearly constant, and thus evaporative cooling takes place at a nearly constant wet-bulb temperature. See Fig. 12.13b and the accompanying discussion. Using this approach with the psychrometric chart, Fig. A-9E, determine humidity ratio and relative humidity at the exit, and compare with the previously determined values. The details are left as an exercise.

- ① A constant value of the specific heat c_{pa} has been used here to evaluate the term $(h_{a1} - h_{a2})$. As shown in previous examples, this term can be evaluated alternatively using the ideal gas table for air.

Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply mass and energy balances for an evaporative cooling process in a control volume at steady state.
- retrieve property data for dry air and water.

QuickQUIZ

Using steam table data, what is the dew point temperature at the exit, in °F? **Ans.** 59.6°F.

12.8.6 Adiabatic Mixing of Two Moist Air Streams

A common process in air-conditioning systems is the mixing of moist air streams, as shown in Fig. 12.14. The objective of the thermodynamic analysis of such a process is normally to fix the flow rate and state of the exiting stream for specified flow rates and states of each of the two inlet streams. The case of adiabatic mixing is governed by Eqs. 12.56 to follow.

The mass rate balances for the dry air and water vapor at steady state are, respectively,

$$\begin{aligned}\dot{m}_{a1} + \dot{m}_{a2} &= \dot{m}_{a3} && \text{(dry air)} \\ \dot{m}_{v1} + \dot{m}_{v2} &= \dot{m}_{v3} && \text{(water vapor)}\end{aligned}\tag{12.56a}$$

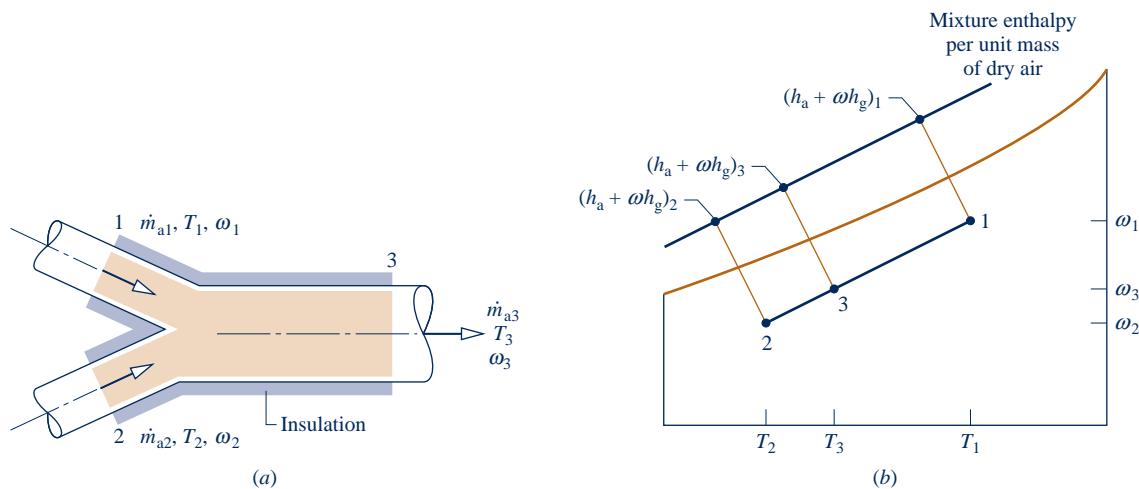


Fig. 12.14 Adiabatic mixing of two moist air streams. (a) Equipment representation. (b) Psychrometric chart representation.

With $\dot{m}_v = \omega \dot{m}_a$, the water vapor mass balance becomes

$$\omega_1 \dot{m}_{a1} + \omega_2 \dot{m}_{a2} = \omega_3 \dot{m}_{a3} \quad (\text{water vapor}) \quad (12.56\text{b})$$

Assuming $\dot{Q}_{cv} = \dot{W}_{cv} = 0$ and ignoring the effects of kinetic and potential energy, the energy rate balance at steady state reduces to

$$\dot{m}_{a1}(h_{a1} + \omega_1 h_{g1}) + \dot{m}_{a2}(h_{a2} + \omega_2 h_{g2}) = \dot{m}_{a3}(h_{a3} + \omega_3 h_{g3}) \quad (12.56\text{c})$$

where the enthalpies of the entering and exiting water vapor are evaluated as the saturated vapor values at the respective dry-bulb temperatures.

If the inlet flow rates and states are known, Eqs. 12.56 are three equations in three unknowns: \dot{m}_{a3} , ω_3 , and $(h_{a3} + \omega_3 h_{g3})$. The solution of these equations is illustrated by Example 12.14.

Let us also consider how Eqs. 12.56 can be solved *geometrically* with the psychrometric chart: Using Eq. 12.56a to eliminate \dot{m}_{a3} , the mass flow rate of dry air at 3, from Eqs. 12.56b and 12.56c, we get

$$\frac{\dot{m}_{a1}}{\dot{m}_{a2}} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3} = \frac{(h_{a3} + \omega_3 h_{g3}) - (h_{a2} + \omega_2 h_{g2})}{(h_{a1} + \omega_1 h_{g1}) - (h_{a3} + \omega_3 h_{g3})} \quad (12.57)$$

From the relations of Eqs. 12.57, we conclude that on a psychrometric chart state 3 of the mixture lies on a straight line connecting states 1 and 2 of the two streams before mixing (see end-of-chapter Prob. 12.93). This is shown in Fig. 12.14b.

EXAMPLE 12.14

Analyzing Adiabatic Mixing of Two Moist Air Streams

A stream consisting of $142 \text{ m}^3/\text{min}$ of moist air at a temperature of 5°C and a humidity ratio of $0.002 \text{ kg(vapor)}/\text{kg(dry air)}$ is mixed adiabatically with a second stream consisting of $425 \text{ m}^3/\text{min}$ of moist air at 24°C and 50% relative humidity. The pressure is constant throughout at 1 bar. Determine (a) the humidity ratio and (b) the temperature of the exiting mixed stream, in $^\circ\text{C}$.

SOLUTION

Known: A moist air stream at 5°C , $\omega = 0.002 \text{ kg(vapor)}/\text{kg(dry air)}$, and a volumetric flow rate of $142 \text{ m}^3/\text{min}$ is mixed adiabatically with a stream consisting of $425 \text{ m}^3/\text{min}$ of moist air at 24°C and $\phi = 50\%$.

Find: Determine the humidity ratio and the temperature, in $^\circ\text{C}$, of the mixed stream exiting the control volume.

Schematic and Given Data:

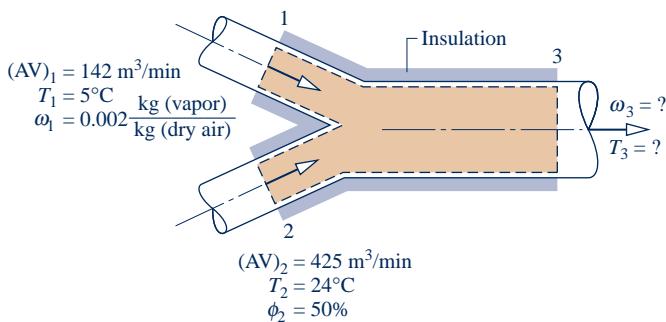


Fig. E12.14

Analysis:

- (a) The humidity ratio ω_3 can be found by means of mass rate balances for the dry air and water vapor, respectively

Engineering Model:

- The control volume shown in the accompanying figure operates at steady state. Changes in kinetic and potential energy can be neglected and $\dot{W}_{cv} = 0$.
- There is no heat transfer with the surroundings.
- The pressure remains constant throughout at 1 bar.
- The moist air streams are regarded as ideal gas mixtures adhering to the Dalton model.

$$\begin{aligned}\dot{m}_{a1} + \dot{m}_{a2} &= \dot{m}_{a3} && \text{(dry air)} \\ \dot{m}_{v1} + \dot{m}_{v2} &= \dot{m}_{v3} && \text{(water vapor)}\end{aligned}$$

With $\dot{m}_{v1} = \omega_1 \dot{m}_{a1}$, $\dot{m}_{v2} = \omega_2 \dot{m}_{a2}$, and $\dot{m}_{v3} = \omega_3 \dot{m}_{a3}$, the second of these balances becomes (Eq. 12.56b)

$$\omega_1 \dot{m}_{a1} + \omega_2 \dot{m}_{a2} = \omega_3 \dot{m}_{a3}$$

Solving

$$\omega_3 = \frac{\omega_1 \dot{m}_{a1} + \omega_2 \dot{m}_{a2}}{\dot{m}_{a3}}$$

Since $\dot{m}_{a3} = \dot{m}_{a1} + \dot{m}_{a2}$, this can be expressed as

$$\omega_3 = \frac{\omega_1 \dot{m}_{a1} + \omega_2 \dot{m}_{a2}}{\dot{m}_{a1} + \dot{m}_{a2}}$$

To determine ω_3 requires values for ω_2 , \dot{m}_{a1} , and \dot{m}_{a2} . The mass flow rates of the dry air, \dot{m}_{a1} and \dot{m}_{a2} , can be found as in previous examples using the given volumetric flow rates

$$\dot{m}_{a1} = \frac{(AV)_1}{v_{a1}}, \quad \dot{m}_{a2} = \frac{(AV)_2}{v_{a2}}$$

The values of v_{a1} , v_{a2} , and ω_2 are readily found from the psychrometric chart, Fig. A-9. Thus, at $\omega_1 = 0.002$ and $T_1 = 5^\circ\text{C}$, $v_{a1} = 0.79 \text{ m}^3/\text{kg(dry air)}$. At $\phi_2 = 50\%$ and $T_2 = 24^\circ\text{C}$, $v_{a2} = 0.855 \text{ m}^3/\text{kg(dry air)}$ and $\omega_2 = 0.0094$. The mass flow rates of the dry air are then $\dot{m}_{a1} = 180 \text{ kg(dry air)/min}$ and $\dot{m}_{a2} = 497 \text{ kg(dry air)/min}$. Inserting values into the expression for ω_3

$$\omega_3 = \frac{(0.002)(180) + (0.0094)(497)}{180 + 497} = 0.0074 \frac{\text{kg(vapor)}}{\text{kg(dry air)}}$$

(b) The temperature T_3 of the exiting mixed stream can be found from an energy rate balance. Reduction of the energy rate balance using assumptions 1 and 2 gives (Eq. 12.56c)

$$\dot{m}_{a1}(h_a + \omega h_g)_1 + \dot{m}_{a2}(h_a + \omega h_g)_2 = \dot{m}_{a3}(h_a + \omega h_g)_3 \quad (\text{a})$$

Solving

$$(h_a + \omega h_g)_3 = \frac{\dot{m}_{a1}(h_a + \omega h_g)_1 + \dot{m}_{a2}(h_a + \omega h_g)_2}{\dot{m}_{a1} + \dot{m}_{a2}} \quad (\text{b})$$

With $(h_a + \omega h_g)_1 = 10 \text{ kJ/kg(dry air)}$ and $(h_a + \omega h_g)_2 = 47.8 \text{ kJ/kg(dry air)}$ from Fig. A-9 and other known values

$$(h_a + \omega h_g)_3 = \frac{180(10) + 497(47.8)}{180 + 497} = 37.7 \frac{\text{kJ}}{\text{kg(dry air)}}$$

① This value for the enthalpy of the moist air at the exit, together with the previously determined value for ω_3 , fixes the state of the exiting moist air. From inspection of Fig. A-9, $T_3 = 19^\circ\text{C}$.

Alternative Solutions:

The use of the psychrometric chart facilitates the solution for T_3 . Without the chart, an iterative solution of Eq. (b) using data from Tables A-2 and A-22 could be used. Alternatively, T_3 can be determined using the following *IT* program, where ϕ_2 is denoted as phi2, the volumetric flow rates at 1 and 2 are denoted as AV1 and AV2, respectively, and so on.

```
// Given data
T1 = 5 // °C
w1 = 0.002 // kg(vapor) / kg(dry air)
AV1 = 142 // m³/min
T2 = 24 // °C
phi2 = 0.5
AV2 = 425 // m³/min
p = 1 // bar
```

```

// Mass balances for water vapor and dry air:
w1 * mdot1 + w2 * mdot2 = w3 * mdot3
mdot1 + mdot2 = mdot3
// Evaluate mass flow rates of dry air
mdot1 = AV1 / va1
② va1 = va_Tw(T1, w1, p)
mdot2 = AV2 / va2
va2 = va_Tphi(T2, phi2, p)

// Determine w2
w2 = w_Tphi(T2, phi2, p)
// The energy balance, Eq. (a), reads
mdot1 * h1 + mdot2 * h2 = mdot3 * h3
h1 = ha_Tw(T1, w1)
h2 = ha_Tphi(T2, phi2, p)
h3 = ha_Tw(T3, w3)

```

Using the **Solve** button, the result is $T_3 = 19.01^\circ\text{C}$ and $w_3 = 0.00745 \text{ kg(vapor)}/\text{kg (dry air)}$, which agree with the psychrometric chart solution.

- ① A solution using the geometric approach based on Eqs. 12.57 is left as an exercise.
- ② Note the use here of special *Moist Air* functions listed in the **Properties** menu of *IT*.

Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply mass and energy balances for an adiabatic mixing process of two moist air streams in a control volume at steady state.
- retrieve property data for moist air using the psychrometric chart.
- apply *IT* for psychrometric analysis.

QuickQUIZ

Using the psychrometric chart, what is the relative humidity at the exit? **Ans.** $\approx 53\%$.

12.9 Cooling Towers

Power plants invariably discharge considerable energy to their surroundings by heat transfer (Chap. 8). Although water drawn from a nearby river or lake can be employed to carry away this energy, cooling towers provide an alternative in locations where sufficient cooling water cannot be obtained from natural sources or where concerns for the environment place a limit on the temperature at which cooling water can be returned to the surroundings. Cooling towers also are frequently employed to provide chilled water for applications other than those involving power plants.

Cooling towers can operate by *natural* or *forced* convection. Also they may be *counterflow*, *cross-flow*, or a combination of these. A schematic diagram of a forced-convection, counterflow cooling tower is shown in Fig. 12.15. The warm water to be cooled enters at 1 and is sprayed from the top of the tower. The falling water usually passes through a series of baffles intended to keep it broken up into fine drops to promote evaporation. Atmospheric air drawn in at 3 by the fan flows upward, counter to the direction of the falling water droplets. As the two streams interact, a fraction of the entering liquid water stream evaporates into the moist air, which exits at 4 with a greater humidity ratio than the incoming moist air at 3, while liquid water exits at 2 with a lower temperature than the water entering at 1. Since some of the incoming water is evaporated into the moist air stream, an equivalent amount of

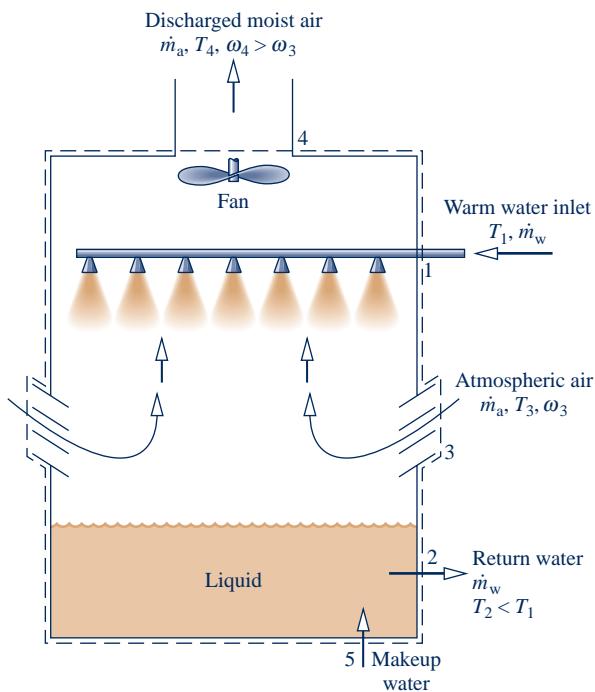


Fig. 12.15 Schematic of a cooling tower.

makeup water is added at 5 so that the return mass flow rate of the cool water equals the mass flow rate of the warm water entering at 1.

For operation at steady state, mass balances for the dry air and water and an energy balance on the overall cooling tower provide information about cooling tower performance. In applying the energy balance, heat transfer with the surroundings is usually neglected. The power input to the fan of forced-convection towers also may be negligible relative to other energy rates involved. The example to follow illustrates the analysis of a cooling tower using conservation of mass and energy together with property data for the dry air and water.

►►► EXAMPLE 12.15 ►

Determining Mass Flow Rates for a Power Plant Cooling Tower

Water exiting the condenser of a power plant at 38°C enters a cooling tower with a mass flow rate of $4.5 \times 10^7 \text{ kg/h}$. A stream of cooled water is returned to the condenser from a cooling tower with a temperature of 30°C and the same flow rate. Makeup water is added in a separate stream at 20°C . Atmospheric air enters the cooling tower at 25°C and 35% relative humidity. Moist air exits the tower at 35°C and 90% relative humidity. Determine the mass flow rates of the dry air and the makeup water, in kg/h. The cooling tower operates at steady state. Heat transfer with the surroundings and the fan power can each be neglected, as can changes in kinetic and potential energy. The pressure remains constant throughout at 1 atm.

SOLUTION

Known: A liquid water stream enters a cooling tower from a condenser at 38°C with a known mass flow rate. A stream of cooled water is returned to the condenser at 30°C and the same flow rate. Makeup water is added at 20°C . Atmospheric air enters the tower at 25°C and $\phi = 35\%$. Moist air exits the tower at 35°C and $\phi = 90\%$.

Find: Determine the mass flow rates of the dry air and the makeup water, in kg/h.

Schematic and Given Data:

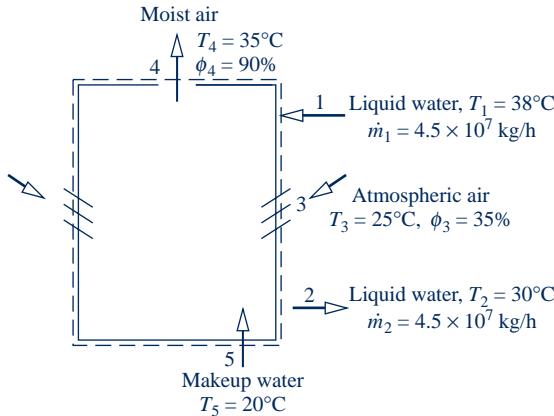


Fig. E12.15

Analysis: The required mass flow rates can be found from mass and energy rate balances. Mass balances for the dry air and water individually reduce at steady state to

$$\begin{aligned} \dot{m}_{a3} &= \dot{m}_{a4} && \text{(dry air)} \\ \dot{m}_1 + \dot{m}_5 + \dot{m}_{v3} &= \dot{m}_2 + \dot{m}_{v4} && \text{(water)} \end{aligned}$$

The common mass flow rate of the dry air is denoted as \dot{m}_a . Since $\dot{m}_1 = \dot{m}_2$, the second of these equations becomes

$$\dot{m}_5 = \dot{m}_{v4} - \dot{m}_{v3}$$

With $\dot{m}_{v3} = \omega_3 \dot{m}_a$ and $\dot{m}_{v4} = \omega_4 \dot{m}_a$

$$\dot{m}_5 = \dot{m}_a (\omega_4 - \omega_3)$$

Accordingly, the two required mass flow rates, \dot{m}_a and \dot{m}_5 , are related by this equation. Another equation relating the flow rates is provided by the energy rate balance.

Reducing the energy rate balance with assumption 1 results in

$$0 = \dot{m}_1 h_{w1} + (\dot{m}_a h_{a3} + \dot{m}_{v3} h_{g3}) + \dot{m}_5 h_{w5} - \dot{m}_2 h_{w2} - (\dot{m}_a h_{a4} + \dot{m}_{v4} h_{g4})$$

Evaluating the enthalpies of the water vapor as the saturated vapor values at the respective temperatures and the enthalpy of each liquid stream as the saturated liquid enthalpy at each respective temperature, the energy rate equation becomes

$$0 = \dot{m}_1 h_{f1} + (\dot{m}_a h_{a3} + \dot{m}_{v3} h_{g3}) + \dot{m}_5 h_{f5} - \dot{m}_2 h_{f2} - (\dot{m}_a h_{a4} + \dot{m}_{v4} h_{g4})$$

Introducing $\dot{m}_1 = \dot{m}_2$, $\dot{m}_5 = \dot{m}_a(\omega_4 - \omega_3)$, $\dot{m}_{v3} = \omega_3 \dot{m}_a$, and $\dot{m}_{v4} = \omega_4 \dot{m}_a$ and solving for \dot{m}_a

$$\dot{m}_a = \frac{\dot{m}_1 (h_{f1} - h_{f2})}{h_{a4} - h_{a3} + \omega_4 h_{g4} - \omega_3 h_{g3} - (\omega_4 - \omega_3) h_{f5}} \quad (\text{a})$$

The humidity ratios ω_3 and ω_4 required by this expression can be determined from Eq. 12.43, using the partial pressure of the water vapor obtained with the respective relative humidity. Thus, $\omega_3 = 0.00688 \text{ kg(vapor)/kg(dry air)}$ and $\omega_4 = 0.0327 \text{ kg(vapor)/kg(dry air)}$.

With enthalpies from Tables A-2 and A-22, as appropriate, and the known values for ω_3 , ω_4 , and \dot{m}_1 , the expression for \dot{m}_a becomes

$$\begin{aligned} \dot{m}_a &= \frac{(4.5 \times 10^7)(159.21 - 125.79)}{(308.2 - 298.2) + (0.0327)(2565.3) - (0.00688)(2547.2) - (0.0258)(83.96)} \\ &= 2.03 \times 10^7 \text{ kg/h} \end{aligned}$$

Finally, inserting known values into the expression for \dot{m}_5 results in

$$\dot{m}_5 = (2.03 \times 10^7)(0.0327 - 0.00688) = 5.24 \times 10^5 \text{ kg/h}$$

Engineering Model:

1. The control volume shown in the accompanying figure operates at steady state. Heat transfer with the surroundings can be neglected, as can changes in kinetic and potential energy; also $\dot{W}_{cv} = 0$.
2. To evaluate specific enthalpies, each liquid stream is regarded as a saturated liquid at the corresponding specified temperature.
3. The moist air streams are regarded as ideal gas mixtures adhering to the Dalton model.
4. The pressure is constant throughout at 1 atm.

- Alternative Psychrometric Chart Solution:** Equation (a) can be rearranged to read

$$\dot{m}_a = \frac{\dot{m}_1(h_{f1} - h_{f2})}{(h_{a4} + \omega_4 h_{g4}) - (h_{a3} + \omega_3 h_{g3}) - (\omega_4 - \omega_3)h_{f5}}$$

- The specific enthalpy terms h_{f1} , h_{f2} , and h_{f5} are obtained from Table A-2, as above. The underlined terms and ω_3 and ω_4 can be obtained by inspection of a psychrometric chart from the engineering literature providing data at states 3 and 4. Figure A-9 does not suffice in this application at state 4. The details are left as an exercise.



Skills Developed

Ability to...

- apply psychrometric terminology and principles.
- apply mass and energy balances for a cooling tower process in a control volume at steady state.
- retrieve property data for dry air and water.

QuickQUIZ

Using steam table data, determine the partial pressure of the water vapor in the entering moist air stream, p_{v3} , in bar. **Ans.** 0.0111 bar.

► CHAPTER SUMMARY AND STUDY GUIDE

In this chapter we have applied the principles of thermodynamics to systems involving ideal gas mixtures, including the special case of *psychrometric* applications involving air–water vapor mixtures, possibly in the presence of liquid water. Both closed system and control volume applications are presented.

The first part of the chapter deals with general ideal gas mixture considerations and begins by describing mixture composition in terms of the mass fractions or mole fractions. The Dalton model, which brings in the partial pressure concept, is then introduced for the p – v – T relation of ideal gas mixtures.

Means are also introduced for evaluating the enthalpy, internal energy, and entropy of a mixture by adding the contribution of each component at its condition in the mixture. Applications are considered where ideal gas mixtures undergo processes at constant composition as well as where ideal gas mixtures are formed from their component gases.

In the second part of the chapter, we study *psychrometrics*. Special terms commonly used in psychrometrics are introduced, including moist air, humidity ratio, relative humidity, mixture enthalpy, and the dew point, dry-bulb, and wet-bulb temperatures. The *psychrometric chart*, which gives a graphical representation of important moist air properties, is introduced. The principles of conservation of mass and energy are formulated in terms of psychrometric quantities, and typical air-conditioning applications are considered, including dehumidification and humidification, evaporative cooling, and mix-

ing of moist air streams. A discussion of cooling towers is also provided.

The following list provides a study guide for this chapter. When your study of the text and end-of-chapter exercises has been completed, you should be able to

- ▶ write out the meanings of the terms listed in the margin throughout the chapter and understand each of the related concepts. The subset of key concepts listed below is particularly important.
- ▶ describe mixture composition in terms of mass fractions or mole fractions.
- ▶ relate pressure, volume, and temperature of ideal gas mixtures using the Dalton model, and evaluate U , H , c_v , c_p , and S of ideal gas mixtures in terms of the mixture composition and the respective contribution of each component.
- ▶ apply the conservation of mass and energy principles and the second law of thermodynamics to systems involving ideal gas mixtures.

For psychrometric applications, you should be able to

- ▶ evaluate the humidity ratio, relative humidity, mixture enthalpy, and dew point temperature.
- ▶ use the psychrometric chart.
- ▶ apply the conservation of mass and energy principles and the second law of thermodynamics to analyze air-conditioning processes and cooling towers.

► KEY ENGINEERING CONCEPTS

mass fraction, p. 706

gravimetric analysis, p. 706

mole fraction, p. 706

molar (volumetric) analysis, p. 707

apparent molecular weight, p. 707

Dalton model, p. 710

partial pressure, p. 710

psychrometrics, p. 727

moist air, p. 727

humidity ratio, p. 728

relative humidity, p. 729

mixture enthalpy, p. 729

dew point temperature, p. 731

dry-bulb temperature, p. 738

wet-bulb temperature, p. 738

psychrometric chart, p. 740

► KEY EQUATIONS

Ideal Gas Mixtures: General Considerations

$mf_i = m_i/m$	(12.3) p. 706	Analysis in terms of mass fractions
$1 = \sum_{i=1}^j mf_i$	(12.4) p. 706	
$y_i = n_i/n$	(12.6) p. 706	Analysis in terms of mole fractions
$1 = \sum_{i=1}^j y_i$	(12.7) p. 707	
$M = \sum_{i=1}^j y_i M_i$	(12.9) p. 707	Apparent molecular weight
$p_i = y_i p$	(12.12) p. 710	Partial pressure of component i and relation to mixture pressure p
$p = \sum_{i=1}^j p_i$	(12.13) p. 710	
$\bar{u} = \sum_{i=1}^j y_i \bar{u}_i$	(12.21) p. 712	Internal energy, enthalpy, and entropy per mole of mixture. \bar{u}_i and \bar{h}_i evaluated at mixture temperature T . \bar{s}_i evaluated at T and partial pressure p_i .
$\bar{h} = \sum_{i=1}^j y_i \bar{h}_i$	(12.22) p. 712	
$\bar{s} = \sum_{i=1}^j y_i \bar{s}_i$	(12.27) p. 713	
$\bar{c}_v = \sum_{i=1}^j y_i \bar{c}_{v,i}$	(12.23) p. 712	Mixture specific heats on a molar basis
$\bar{c}_p = \sum_{i=1}^j y_i \bar{c}_{p,i}$	(12.24) p. 712	

Psychrometric Applications

$\omega = \frac{m_v}{m_a} = 0.622 \frac{p_v}{p - p_v}$	(12.42, 12.43) p. 729	Humidity ratio
$\phi = \left(\frac{p_v}{p_g} \right)_{T,p}$	(12.44) p. 729	Relative humidity
$\frac{H}{m_a} = h_a + \omega h_v$	(12.46) p. 729	Mixture enthalpy per unit mass of dry air

► EXERCISES: THINGS ENGINEERS THINK ABOUT

- In an *equimolar* mixture of O₂ and N₂, are the mass fractions equal? Explain.
- If two different ideal gases mix spontaneously, is the process irreversible? Explain.
- Which component of the fuel-air mixture in a cylinder of an automobile engine would have the greater mass fraction?
- A rigid, insulated container is divided into two compartments by a partition, and each compartment contains air at the

- same temperature and pressure. If the partition is removed is entropy produced within the container? Explain.
5. Which do you think is most closely related to human comfort, the humidity ratio or the relative humidity? Explain.
 6. How do you explain the different rates of evaporation from a dish of water in winter and summer?
 7. Can the dry-bulb and wet-bulb temperatures be equal? Explain.
 8. How do you explain the water dripping from the tailpipe of an automobile on a cold morning?
 9. Would you recommend an evaporative cooling system for use in Florida? In Arizona? Explain.
 10. During winter, why do eyeglasses fog up when the wearer enters a warm building?

11. Does operating a car's air-conditioning system affect its fuel economy? Explain.
12. What is a *food dehydrator* and when might you use one?
13. What is meant by a *zero-energy building*?
14. What is the difference between a *steam sauna* and a *steam room*?
15. Your local weather report gives the temperature, relative humidity, and dew point. When planning summertime outdoor activities, are these equally important? Explain.
16. Under what conditions would frost accumulate on the interior of a car's windshield?

► PROBLEMS: DEVELOPING ENGINEERING SKILLS

Determining Mixture Composition

12.1 The analysis on a mass basis of an ideal gas mixture at 50°F, 25 lbf/in.² is 60% CO₂, 25% SO₂, and 15% N₂. Determine
 (a) the analysis in terms of mole fractions.
 (b) the apparent molecular weight of the mixture.
 (c) the partial pressure of each component, in lbf/in.².
 (d) the volume occupied by 20 lb of the mixture, in ft³.

12.2 The molar analysis of a gas mixture at 30°C, 2 bar is 40% N₂, 50% CO₂, and 10% CH₄. Determine
 (a) the analysis in terms of mass fractions.
 (b) the partial pressure of each component, in bar.
 (c) the volume occupied by 10 kg of mixture, in m³.

12.3 The analysis on a molar basis of a gas mixture at 50°F, 1 atm is 20% Ar, 35% CO₂, and 45% O₂. Determine
 (a) the analysis in terms of mass fractions.
 (b) the partial pressure of each component, in lbf/in.².
 (c) the volume occupied by 10 lb of mixture, in ft³.

12.4 The molar analysis of a gas mixture at 25°C, 0.1 MPa is 60% N₂, 30% CO₂, and 10% O₂. Determine
 (a) the analysis in terms of mass fractions.
 (b) the partial pressure of each component, in MPa.
 (c) the volume occupied by 50 kg of the mixture, in m³.

12.5 The analysis on a mass basis of an ideal gas mixture at 30°F, 15 lbf/in.² is 55% CO₂, 30% CO, and 15% O₂. Determine
 (a) the analysis in terms of mole fractions.
 (b) the apparent molecular weight of the mixture.
 (c) the partial pressure of each component, in lbf/in.².
 (d) the volume occupied by 10 lb of the mixture, in ft³.

12.6 Natural gas at 23°C, 1 bar enters a furnace with the following molar analysis: 40% propane (C₃H₈), 40% ethane (C₂H₆), 20% methane (CH₄). Determine
 (a) the analysis in terms of mass fractions.
 (b) the partial pressure of each component, in bar.
 (c) the mass flow rate, in kg/s, for a volumetric flow rate of 20 m³/s.

12.7 A rigid vessel having a volume of 3 m³ initially contains a mixture at 21°C, 1 bar consisting of 79% N₂ and 21% O₂ on a molar basis. Helium is allowed to flow into the vessel until the pressure is 2 bar. If the final temperature of the mixture within the vessel is 27°C, determine the mass, in kg, of each component present.

12.8 Nitrogen (N₂) at 150 kPa, 40°C occupies a closed, rigid container having a volume of 1 m³. If 2 kg of oxygen (O₂) is added to the container, what is the molar analysis of the resulting mixture? If the temperature remains constant, what is the pressure of the mixture, in kPa?

12.9 A flue gas in which the mole fraction of H₂S is 0.002 enters a *scrubber* operating at steady state at 200°F, 1 atm and a volumetric flow rate of 20,000 ft³/h. If the scrubber removes 92% (molar basis) of the entering H₂S, determine the rate at which H₂S is removed, in lb/h. Comment on why H₂S should be removed from the gas stream.

12.10 A gas mixture with a molar analysis of 20% C₃H₈ (propane) and 80% air enters a control volume operating at steady state at location 1 with a mass flow rate of 5 kg/min, as shown in Fig. P12.10. Air enters as a separate stream at 2 and dilutes the mixture. A single stream exits with a mole fraction of propane of 3%. Assuming air has a molar analysis of 21% O₂ and 79% N₂, determine
 (a) the molar flow rate of the entering air at 2, in kmol/min.
 (b) the mass flow rate of oxygen in the exiting stream, in kg/min.

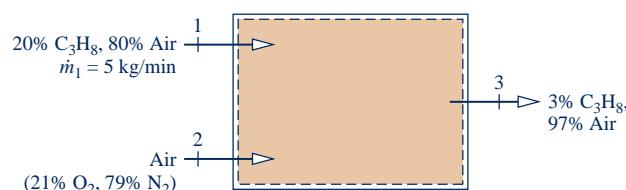


Fig. P12.10

Considering Constant-Composition Processes

12.11 A gas mixture in a piston–cylinder assembly consists of 2 lb of N₂ and 3 lb of He. Determine

- (a) the composition in terms of mass fractions.
- (b) the composition in terms of mole fractions.
- (c) the heat transfer, in Btu, required to increase the mixture temperature from 70 to 150°F, while keeping the pressure constant.
- (d) the change in entropy of the mixture for the process of part (c), in Btu/°R.

For parts (c) and (d), use the ideal gas model with constant specific heats.

12.12 Two kg of a mixture having an analysis on a mass basis of 30% N₂, 40% CO₂, 30% O₂ is compressed adiabatically from 1 bar, 300 K to 4 bar, 500 K. Determine

- (a) the work, in kJ.
- (b) the amount of entropy produced, in kJ/K.

12.13 As illustrated in Fig. P12.13, an ideal gas mixture in a piston–cylinder assembly has a molar analysis of 30% carbon dioxide (CO₂) and 70% nitrogen (N₂). The mixture is cooled at constant pressure from 425 to 325 K. Assuming constant specific heats evaluated at 375 K, determine the heat transfer and the work, each in kJ per kg of mixture.

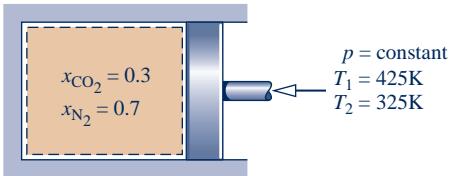


Fig. P12.13

12.14 A mixture consisting of 0.6 lbmol of N₂ and 0.4 lbmol of O₂ is compressed isothermally at 1000°F from 1 to 3 atm. During the process, there is energy transfer by heat from the mixture to the surroundings, which are at 40°F. For the mixture, determine

- (a) the work, in Btu.
- (b) the heat transfer, in Btu.
- (c) the amount of entropy produced, in Btu/°R.

For an enlarged system that includes the mixture and enough of its immediate surroundings that heat transfer occurs at 40°F, determine the amount of entropy produced, in Btu/°R. Discuss.

12.15 A mixture consisting of 2.8 kg of N₂ and 3.2 kg of O₂ is compressed from 1 bar, 300 K to 2 bar, 600 K. During the process there is heat transfer from the mixture to the surroundings, which are at 27°C. The work done on the mixture is claimed to be 2300 kJ. Can this value be correct?

12.16 A mixture having a molar analysis of 50% CO₂, 33.3% CO, and 16.7% O₂ enters a compressor operating at steady state at 37°C, 1 bar, 40 m/s with a mass flow rate of 1 kg/s and exits at 237°C, 30 m/s. The rate of heat transfer from the compressor to its surroundings is 5% of the power input.

(a) Neglecting potential energy effects, determine the power input to the compressor, in kW.

(b) If the compression is polytropic, evaluate the polytropic exponent *n* and the exit pressure, in bar.

12.17 A mixture of 5 kg of H₂ and 4 kg of O₂ is compressed in a piston–cylinder assembly in a polytropic process for which *n* = 1.6. The temperature increases from 40 to 250°C. Using constant values for the specific heats, determine

- (a) the heat transfer, in kJ.
- (b) the entropy change, in kJ/K.

12.18 A gas turbine receives a mixture having the following molar analysis: 10% CO₂, 19% H₂O, 71% N₂ at 720 K, 0.35 MPa and a volumetric flow rate of 3.2 m³/s. The mixture exits the turbine at 380 K, 0.11 MPa. For adiabatic operation with negligible kinetic and potential energy effects, determine the power developed at steady state, in kW.

12.19 A gas mixture at 1500 K with the molar analysis 10% CO₂, 20% H₂O, 70% N₂ enters a waste-heat boiler operating at steady state, and exits the boiler at 600 K. A separate stream of saturated liquid water enters at 25 bar and exits as saturated vapor with a negligible pressure drop. Ignoring stray heat transfer and kinetic and potential energy changes, determine the mass flow rate of the exiting saturated vapor, in kg per kmol of gas mixture.

12.20 An equimolar mixture of helium and carbon dioxide enters an insulated nozzle at 260°F, 5 atm, 100 ft/s and expands isentropically to a pressure of 3.24 atm. Determine the temperature, in °F, and the velocity, in ft/s, at the nozzle exit. Neglect potential energy effects.

12.21 An equimolar mixture of helium (He) and carbon dioxide (CO₂) enters an insulated nozzle at 260°F, 5 atm, 100 ft/s and expands isentropically to a velocity of 1110 ft/s. Determine the temperature, in °F, and the pressure, in atm, at the nozzle exit. Neglect potential energy effects.

12.22 A gas mixture having a molar analysis of 60% O₂ and 40% N₂ enters an insulated compressor operating at steady state at 1 bar, 20°C with a mass flow rate of 0.5 kg/s and is compressed to 5.4 bar. Kinetic and potential energy effects are negligible. For an isentropic compressor efficiency of 78%, determine

- (a) the temperature at the exit, in °C.
- (b) the power required, in kW.
- (c) the rate of entropy production, in kW/K.

12.23 A mixture having a molar analysis of 60% N₂, 17% CO₂, and 17% H₂O enters a turbine at 1000 K, 8 bar, with a mass flow rate of 2 kg/s and expands isentropically to a pressure of 1 bar. Ignoring kinetic and potential energy effects, determine for steady-state operation

- (a) the temperature at the exit, in K.
- (b) the power developed by the turbine, in kW.

12.24 A mixture having a molar analysis of 60% N₂ and 40% CO₂ enters an insulated compressor operating at steady state at 1 bar, 30°C with a mass flow rate of 1 kg/s and is compressed to 3 bar, 147°C. Neglecting kinetic and potential energy effects, determine

- (a) the power required, in kW.
 (b) the isentropic compressor efficiency.
 (c) the rate of exergy destruction, in kW, for $T_0 = 300\text{ K}$.

12.25 An equimolar mixture of N_2 and CO_2 enters a heat exchanger at -40°F , 500 lbf/in.² and exits at 500°F , 500 lbf/in.² The heat exchanger operates at steady state, and kinetic and potential energy effects are negligible.

- (a) Using the ideal gas mixture concepts of the present chapter, determine the rate of heat transfer to the mixture, in Btu per lbmol of mixture flowing.
 (b) Compare with the value of the heat transfer determined using the generalized enthalpy chart (Fig. A-4), together with Kay's rule (see Sec. 11.8).

12.26 Natural gas having a molar analysis of 60% methane (CH_4) and 40% ethane (C_2H_6) enters a compressor at 340 K , 6 bar and is compressed isothermally without internal irreversibilities to 20 bar. The compressor operates at steady state, and kinetic and potential energy effects are negligible.

- (a) Assuming ideal gas behavior, determine for the compressor the work and heat transfer, each in kJ per kmol of mixture flowing.
 (b) Compare with the values for work and heat transfer, respectively, determined assuming ideal solution behavior (Sec. 11.9.5). For the pure components at 340 K :

	<i>h</i> (kJ/kg)		<i>s</i> (kJ/kg · K)	
	6 bar	20 bar	6 bar	20 bar
Methane	715.33	704.40	10.9763	10.3275
Ethane	462.39	439.13	7.3493	6.9680

Forming Mixtures

12.27 One kilogram of argon at 27°C , 1 bar is contained in a rigid tank connected by a valve to another rigid tank containing 0.8 kg of O_2 at 127°C , 5 bar. The valve is opened, and the gases are allowed to mix, achieving an equilibrium state at 87°C . Determine

- (a) the volume of each tank, in m^3 .
 (b) the final pressure, in bar.
 (c) the heat transfer to or from the gases during the process, in kJ.
 (d) the entropy change of each gas, in kJ/K .

12.28 Using the ideal gas model with constant specific heats, determine the mixture temperature, in K, for each of two cases:

- (a) Initially, 0.6 kmol of O_2 at 500 K is separated by a partition from 0.4 kmol of H_2 at 300 K in a rigid insulated vessel. The partition is removed and the gases mix to obtain a final equilibrium state.
 (b) Oxygen (O_2) at 500 K and a molar flow rate of 0.6 kmol/s enters an insulated control volume operating at steady state and mixes with H_2 entering as a separate stream at 300 K and a molar flow rate of 0.4 kmol/s. A single mixed stream exits. Kinetic and potential energy effects can be ignored.

12.29 A system consists initially of n_A moles of gas A at pressure p and temperature T and n_B moles of gas B separate

from gas A but at the same pressure and temperature. The gases are allowed to mix with no heat or work interactions with the surroundings. The final equilibrium pressure and temperature are p and T , respectively, and the mixing occurs with no change in total volume.

- (a) Assuming ideal gas behavior, obtain an expression for the entropy produced in terms of \bar{R} , n_A , and n_B .
 (b) Using the result of part (a), demonstrate that the entropy produced has a positive value.
 (c) Would entropy be produced when samples of the *same* gas at the *same* temperature and pressure mix? Explain.

12.30 Determine the amount of entropy produced, in $\text{Btu}/^\circ\text{R}$, when 1 lb of H_2 at 70°F , 1 atm is allowed to mix adiabatically to a final equilibrium state with 20 lb of (a) CO_2 and (b) H_2 , initially at the same temperature and pressure.

12.31 Two kg of N_2 at 450 K , 7 bar is contained in a rigid tank connected by a valve to another rigid tank holding 1 kg of O_2 at 300 K , 3 bar. The valve is opened and gases are allowed to mix, achieving an equilibrium state at 370 K . Determine

- (a) the volume of each tank, in m^3 .
 (b) the final pressure, in bar.
 (c) the heat transfer to or from the gases during the process, in kJ.
 (d) the entropy change of each gas, in kJ/K .

12.32 An insulated tank having a total volume of 60 ft^3 is divided into two compartments. Initially one compartment having a volume of 20 ft^3 contains 4 lb of carbon monoxide (CO) at 500°F and the other contains 0.8 lb of helium (He) at 60°F . The gases are allowed to mix until an equilibrium state is attained. Determine

- (a) the final temperature, in $^\circ\text{F}$.
 (b) the final pressure, in lbf/in.²
 (c) the exergy destruction, in Btu, for $T_0 = 60^\circ\text{F}$.

12.33 A rigid insulated tank has two compartments. Initially one compartment is filled with 2.0 lbmol of argon at 150°F , 50 lbf/in.² and the other is filled with 0.7 lbmol of helium at 0°F , 15 lbf/in.² The gases are allowed to mix until an equilibrium state is attained. Determine

- (a) the final temperature, in $^\circ\text{F}$.
 (b) the final pressure, in atm.
 (c) the amount of entropy produced, in $\text{Btu}/^\circ\text{R}$.

12.34 A rigid insulated tank has two compartments. Initially one contains 0.5 kmol of carbon dioxide (CO_2) at 27°C , 2 bar and the other contains 1 kmol of oxygen (O_2) at 152°C , 5 bar. The gases are allowed to mix while 500 kJ of energy are added by electrical work. Determine

- (a) the final temperature, in $^\circ\text{C}$.
 (b) the final pressure, in bar.
 (c) the change in exergy, in kJ, for $T_0 = 20^\circ\text{C}$.
 (d) the exergy destruction, in kJ.

12.35 Air at 40°C , 1 atm and a volumetric flow rate of $50\text{ m}^3/\text{min}$ enters an insulated control volume operating at steady state and mixes with helium entering as a separate stream at 100°C , 1 atm and a volumetric flow rate of $20\text{ m}^3/\text{min}$. A single mixed

stream exits at 1 atm. Ignoring kinetic and potential energy effects, determine for the control volume

- the temperature of the exiting mixture, in °C.
- the rate of entropy production, in kW/K.

12.36 Argon (Ar), at 300 K, 1 bar with a mass flow rate of 1 kg/s enters the insulated mixing chamber shown in Fig. P12.36 and mixes with carbon dioxide (CO_2) entering as a separate stream at 575 K, 1 bar with a mass flow rate of 0.5 kg/s. The mixture exits at 1 bar. Assume ideal gas behavior with $k = 1.67$ for Ar and $k = 1.25$ for CO_2 . For steady-state operation, determine

- the molar analysis of the exiting mixture.
- the temperature of the exiting mixture, in K.
- the rate of entropy production, in kW/K.

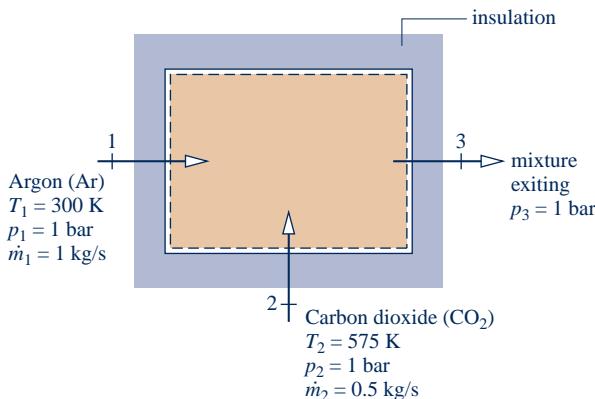


Fig. P12.36

12.37 Nitrogen (N_2) at 120°F, 20 lbf/in.² and a volumetric flow rate of 300 ft³/min enters an insulated control volume operating at steady state and mixes with oxygen (O_2) entering as a separate stream at 200°F, 20 lbf/in.² and a mass flow rate of 50 lb/min. A single mixed stream exits at 17 lbf/in.² Kinetic and potential energy effects can be ignored. Using the ideal gas model with constant specific heats, determine for the control volume

- the temperature of the exiting mixture, in °F.
- the rate of exergy destruction, in Btu/min, for $T_0 = 40^\circ\text{F}$.

12.38 Air at 77°C, 1 bar, and a molar flow rate of 0.1 kmol/s enters an insulated mixing chamber operating at steady state and mixes with water vapor entering at 277°C, 1 bar, and a molar flow rate of 0.3 kmol/s. The mixture exits at 1 bar. Kinetic and potential energy effects can be ignored. For the chamber, determine

- the temperature of the exiting mixture, in °C.
- the rate of entropy production, in kW/K.

12.39 A gas mixture required in an industrial process is prepared by first allowing carbon monoxide (CO) at 80°F, 18 lbf/in.² to enter an insulated mixing chamber operating at steady state and mix with argon (Ar) entering at 380°F, 18 lbf/in.² The mixture exits the chamber at 140°F, 16 lbf/in.² and is then allowed to expand in a throttling process through a valve to 14.7 lbf/in.² Determine

- the mass and molar analyses of the mixture.
- the temperature of the mixture at the exit of the valve, in °F.
- the rates of exergy destruction for the mixing chamber and the valve, each in Btu per lb of mixture, for $T_0 = 40^\circ\text{F}$.

Kinetic and potential energy effects can be ignored.

12.40 Helium at 400 K, 1 bar enters an insulated mixing chamber operating at steady state, where it mixes with argon entering at 300 K, 1 bar. The mixture exits at a pressure of 1 bar. If the argon mass flow rate is x times that of helium, plot versus x

- the exit temperature, in K.
- the rate of exergy destruction within the chamber, in kJ per kg of helium entering.

Kinetic and potential energy effects can be ignored. Let $T_0 = 300$ K.

12.41 Hydrogen (H_2) at 77°C, 4 bar enters an insulated chamber at steady state, where it mixes with nitrogen (N_2) entering as a separate stream at 277°C, 4 bar. The mixture exits at 3.8 bar with the molar analysis 75% H_2 , 25% N_2 . Kinetic and potential energy effects can be ignored. Determine

- the temperature of the exiting mixture, in °C.
- the rate at which entropy is produced, in kJ/K per kmol of mixture exiting.

12.42 An insulated, rigid tank initially contains 1 kmol of argon (Ar) at 300 K, 1 bar. The tank is connected by a valve to a large vessel containing nitrogen (N_2) at 500 K, 4 bar. A quantity of nitrogen flows into the tank, forming an argon-nitrogen mixture at temperature T and pressure p . Plot T , in K, and p , in bar, versus the amount of N_2 within the tank, in kmol.

12.43 A stream of oxygen (O_2) at 100°F, 2 atm enters an insulated chamber at steady state with a mass flow rate of 1 lb/min and mixes with a stream of air entering separately at 200°F, 1.5 atm with a mass flow rate of 2 lb/min. The mixture exits at a pressure of 1 atm. Kinetic and potential energy effects can be ignored. On the basis of constant specific heats, determine

- the temperature of the exiting mixture, in °F.
- the rate of exergy destruction, in Btu/min, for $T_0 = 40^\circ\text{F}$.

12.44 A device is being designed to separate into components a natural gas consisting of CH_4 and C_2H_6 in which the mole fraction of C_2H_6 , denoted by y , may vary from 0.05 to 0.50. The device will receive natural gas at 20°C, 1 atm with a volumetric flow rate of 100 m³/s. Separate streams of CH_4 and C_2H_6 will exit, each at 20°C, 1 atm. Heat transfer between the device and its surroundings occurs at 20°C. Ignoring kinetic and potential energy effects, plot versus y the minimum theoretical work input required at steady state, in kW.

Exploring Psychrometric Principles

12.45 A water pipe at 5°C runs above ground between two buildings. The surrounding air is at 35°C. What is the maximum relative humidity the air can have before condensation occurs on the pipe?



Fig. P12.47

12.46 The inside temperature of a wall in a dwelling is 16°C. If the air in the room is at 21°C, what is the maximum relative humidity the air can have before condensation occurs on the wall?

12.47 A lecture hall having a volume of 10^6 ft^3 contains air at 80°F, 1 atm, and a humidity ratio of 0.01 lb of water vapor per lb of dry air. Determine

- the relative humidity.
- the dew point temperature, in °F.
- the mass of water vapor contained in the room, in lb.

12.48 A large room contains moist air at 30°C, 102 kPa. The partial pressure of water vapor is 1.5 kPa. Determine

- the relative humidity.
- the humidity ratio, in kg(vapor) per kg(dry air).
- the dew point temperature, in °C.
- the mass of dry air, in kg, if the mass of water vapor is 10 kg.

12.49 To what temperature, in °C, must moist air with a humidity ratio of 5×10^{-3} kg(vapor) per kg(dry air) be cooled at a constant pressure of 2 bar to become saturated moist air?

12.50 A fixed amount of moist air initially at 1 bar and a relative humidity of 60% is compressed isothermally until condensation of water begins. Determine the pressure of the mixture at the onset of condensation, in bar. Repeat if the initial relative humidity is 90%.

12.51 As shown in Fig. P12.51, moist air at 30°C, 2 bar, and 50% relative humidity enters a heat exchanger operating at

steady state with a mass flow rate of 600 kg/h and is cooled at constant pressure to 20°C. Ignoring kinetic and potential energy effects, determine the rate of heat transfer from the moist air stream, in kJ/h.



Fig. P12.51

12.52 One pound of moist air initially at 80°F, 1 atm, 50% relative humidity is compressed isothermally to 3 atm. If condensation occurs, determine the amount of water condensed, in lb. If there is no condensation, determine the final relative humidity.

12.53 A vessel whose volume is 0.5 m^3 initially contains dry air at 0.2 MPa and 20°C. Water is added to the vessel until the air is saturated at 20°C. Determine the

- mass of water added, in kg.
- final pressure in the vessel, in bar.

12.54 Wet grain at 20°C containing 40% moisture by mass enters a dryer operating at steady state. Dry air enters the dryer at 90°C, 1 atm at a rate of 15 kg per kg of wet grain entering. Moist air exits the dryer at 38°C, 1 atm, and 52% relative humidity. For the grain exiting the dryer, determine the percent moisture by mass.

12.55 Figure P12.55 shows a spray dryer operating at steady state. The mixture of liquid water and suspended solid particles entering through the spray head contains 30% solid matter by mass. Dry air enters at 177°C, 1 atm, and moist air exits at 85°C, 1 atm, and 21% relative humidity with a volumetric flow rate of 310 m³/min. The dried particles exit separately. Determine

- (a) the volumetric flow rate of the entering dry air, in m³/min.
- (b) the rate that dried particles exit, in kg/min.

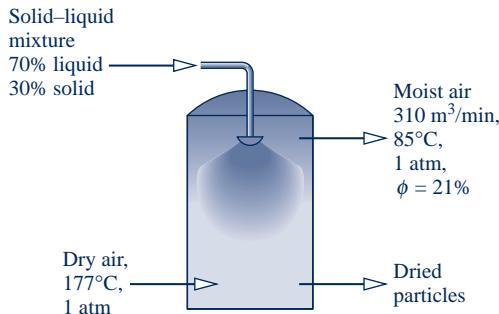


Fig. P12.55

12.56 A mixture of nitrogen and water vapor at 200°F, 1 atm has the molar analysis 80% N₂, 20% water vapor. If the mixture is cooled at constant pressure, determine the temperature, in °F, at which water vapor begins to condense.

12.57 A system consisting initially of 0.5 m³ of air at 35°C, 1 bar, and 70% relative humidity is cooled at constant pressure to 29°C. Determine the work and heat transfer for the process, each in kJ.

12.58 Moist air initially at 125°C, 4 bar, and 50% relative humidity is contained in a 2.5-m³ closed, rigid tank. The tank contents are cooled. Determine the heat transfer, in kJ, if the final temperature in the tank is (a) 110°C, (b) 30°C.

12.59 A closed, rigid tank initially contains 0.5 m³ of moist air in equilibrium with 0.1 m³ of liquid water at 80°C and 0.1 MPa. If the tank contents are heated to 200°C, determine

- (a) the final pressure, in MPa.
- (b) the heat transfer, in kJ.

12.60 A closed, rigid cylindrical tank having a height of 6 ft and a diameter of 2 ft initially contains air at 300°F, 80 lbf/in.², and 10% relative humidity. If the tank contents are cooled to 170°F, determine

- (a) if condensation occurs.
- (b) the final pressure, in lbf/in.²
- (c) the heat transfer, in Btu.
- (d) the change in entropy, in Btu/°R.

12.61 Gaseous combustion products with the molar analysis of 15% CO₂, 25% H₂O, 60% N₂ enter an engine's exhaust pipe at 1100°F, 1 atm and are cooled as they pass through the pipe, to 125°F, 1 atm. Determine the heat transfer at steady state, in Btu per lb of entering mixture.

12.62 Air at 60°F, 14.7 lbf/in.², and 75% relative humidity enters an insulated compressor operating at steady state and

is compressed to 100 lbf/in.² The isentropic compressor efficiency is η_c .

- (a) For $\eta_c = 0.8$, determine the temperature, in °R, of the exiting air, and the work input required and the exergy destruction, each in Btu per lb of dry air flowing. Let $T_0 = 520^\circ\text{R}$.
- (b) Plot each of the quantities determined in part (a) versus η_c ranging from 0.7 to 1.0.

12.63 Air at 35°C, 3 bar, 30% relative humidity, and a velocity of 50 m/s expands isentropically through a nozzle. Determine the lowest exit pressure, in bar, that can be attained without condensation. For this exit pressure, determine the exit velocity, in m/s. The nozzle operates at steady state and without significant potential energy effects.

12.64 A closed, rigid tank having a volume of 1 m³ contains a mixture of carbon dioxide (CO₂) and water vapor at 75°C. The respective masses are 12.3 kg of carbon dioxide and 0.05 kg of water vapor. If the tank contents are cooled to 20°C, determine the heat transfer, in kJ, assuming ideal gas behavior.

12.65 Gaseous combustion products at 800°F, 1 atm and a volumetric flow rate of 5 ft³/s enter a counterflow heat exchanger operating at steady state and exit at 200°F. The molar analysis of the products is 7.1% CO₂, 4.3% O₂, 14.3% H₂O, 74.3% N₂. A separate moist-air stream enters the heat exchanger at 60°F, 1 atm, and 30% relative humidity and exits at 100°F. Determine the mass flow rate of the entering moist-air stream, in lb/s. The pressure drops of the two streams can be ignored, as can stray heat transfer and kinetic and potential energy effects.

12.66 Air enters a compressor operating at steady state at 50°C, 0.9 bar, 70% relative humidity with a volumetric flow rate of 0.8 m³/s. The moist air exits the compressor at 195°C, 1.5 bar. Assuming the compressor is well insulated, determine

- (a) the relative humidity at the exit.
- (b) the power input, in kW.
- (c) the rate of entropy production, in kW/K.

12.67 Moist air enters a control volume operating at steady state with a volumetric flow rate of 3500 ft³/min. The moist air enters at 120°F, 1.2 atm, and 75% relative humidity. Heat transfer occurs through a surface maintained at 50°F. Saturated moist air and condensate exit the control volume, each at 68°F. Assuming $\dot{W}_{cv} = 0$, and kinetic and potential energy effects are negligible, determine

- (a) the mass flow rate of condensate, in lb/min.
- (b) the rate of heat transfer, in Btu/min.
- (c) the rate of entropy production, in Btu/°R · min.
- (d) the rate of exergy destruction, in Btu/min, for $T_0 = 50^\circ\text{F}$.

12.68 Moist air at 15°C, 1.3 atm, 63% relative humidity and a volumetric flow rate of 770 m³/h enters a control volume at steady state and flows along a surface maintained at 187°C, through which heat transfer occurs. Liquid water at 15°C is injected at a rate of 7 kg/h and evaporates into the flowing stream. For the control volume, $\dot{W}_{cv} = 0$, and kinetic and potential energy effects are negligible. If moist air exits at 45°C, 1.3 atm, determine

- (a) the rate of heat transfer, in kW.
- (b) the rate of entropy production, in kW/K.



12.69 Using Eq. 12.48, determine the humidity ratio and relative humidity for each case below.

- (a) The dry-bulb and wet-bulb temperatures in a conference room at 1 atm are 24 and 16°C, respectively.
- (b) The dry-bulb and wet-bulb temperatures in a factory space at 1 atm are 75 and 60°F, respectively.
- (c) Repeat parts (a) and (b) using the psychrometric chart.
- (d) Repeat parts (a) and (b) using *Interactive Thermodynamics: IT*.



12.70 Using the psychrometric chart, Fig. A-9, determine

- (a) the relative humidity, the humidity ratio, and the specific enthalpy of the mixture, in kJ per kg of dry air, corresponding to dry-bulb and wet-bulb temperatures of 30 and 25°C, respectively.
- (b) the humidity ratio, mixture specific enthalpy, and wet-bulb temperature corresponding to a dry-bulb temperature of 30°C and 60% relative humidity.
- (c) the dew point temperature corresponding to dry-bulb and wet-bulb temperatures of 30 and 20°C, respectively.
- (d) Repeat parts (a)–(c) using *Interactive Thermodynamics: IT*.

12.71 Using the psychrometric chart, Fig. A-9E, determine

- (a) the dew point temperature corresponding to dry-bulb and wet-bulb temperatures of 80 and 70°F, respectively.
- (b) the humidity ratio, the specific enthalpy of the mixture, in Btu per lb of dry air, and the wet-bulb temperature corresponding to a dry-bulb temperature of 80°F and 70% relative humidity.
- (c) the relative humidity, humidity ratio, and mixture specific enthalpy corresponding to dry-bulb and wet-bulb temperatures of 80 and 65°F, respectively.
- (d) Repeat parts (a)–(c) using *Interactive Thermodynamics: IT*.



12.72 A fixed amount of air initially at 52°C, 1 atm, and 10% relative humidity is cooled at constant pressure to 15°C. Using the psychrometric chart, determine whether condensation occurs. If so, evaluate the amount of water condensed, in kg per kg of dry air. If there is no condensation, determine the relative humidity at the final state.

12.73 A fan within an insulated duct delivers moist air at the duct exit at 35°C, 50% relative humidity, and a volumetric flow rate of 0.4 m³/s. At steady state, the power input to the fan is 1.7 kW. The pressure in the duct is nearly 1 atm throughout. Using the psychrometric chart, determine the temperature, in °C, and relative humidity at the duct inlet.

12.74 The mixture enthalpy per unit mass of dry air, in kJ/kg(a), represented on Fig. A-9 can be approximated closely from the expression

$$\frac{H}{m_a} = 1.005 T(\text{°C}) + \omega[2501.7 + 1.82 T(\text{°C})]$$

When using Fig. A-9E, the corresponding expression, in Btu/lb(a), is

$$\frac{H}{m_a} = 0.24 T(\text{°F}) + \omega[1061 + 0.444 T(\text{°F})]$$

Noting all significant assumptions, develop the above expressions.

Considering Air-Conditioning Applications

12.75 Each case listed gives the dry-bulb temperature and relative humidity of the moist-air stream entering an air-conditioning system: (a) 30°C, 40%, (b) 17°C, 60%, (c) 25°C, 70%, (d) 15°C, 40%, (e) 27°C, 30%. The condition of the moist-air stream exiting the system must satisfy these constraints: 22 ≤ $T_{\text{db}} \leq 27^\circ\text{C}$, 40 ≤ $\phi \leq 60\%$. In each case, develop a schematic of equipment and processes from Sec. 12.8 that would achieve the desired result. Sketch the processes on a psychrometric chart.

12.76 Moist air enters an air-conditioning system as shown in Fig. 12.11 at 26°C, $\phi = 80\%$ and a volumetric flow rate of 0.47 m³/s. At the exit of the heating section the moist air is at 26°C, $\phi = 50\%$. For operation at steady state, and neglecting kinetic and potential energy effects, determine

- (a) the rate energy is removed by heat transfer in the dehumidifier section, in tons.
- (b) the rate energy is added by heat transfer in the heating section, in kW.

12.77 Air at 1 atm with dry-bulb and wet-bulb temperatures of 82 and 68°F, respectively, enters a duct with a mass flow rate of 10 lb/min and is cooled at essentially constant pressure to 62°F. For steady-state operation and negligible kinetic and potential energy effects, determine

- (a) the relative humidity at the duct inlet.
- (b) the rate of heat transfer, in Btu/min.
- (c) Check your answers using data from the psychrometric chart.
- (d) Check your answers using *Interactive Thermodynamics: IT*.



12.78 Air at 35°C, 1 atm, and 50% relative humidity enters a dehumidifier operating at steady state. Saturated moist air and condensate exit in separate streams, each at 15°C. Neglecting kinetic and potential energy effects, determine

- (a) the heat transfer from the moist air, in kJ per kg of dry air.
- (b) the amount of water condensed, in kg per kg of dry air.
- (c) Check your answers using data from the psychrometric chart.
- (d) Check your answers using *Interactive Thermodynamics: IT*.



12.79 Air at 80°F, 1 atm, and 70% relative humidity enters a dehumidifier operating at steady state with a mass flow rate of 1 lb/s. Saturated moist air and condensate exit in separate streams, each at 50°F. Neglecting kinetic and potential energy effects, determine

- (a) the rate of heat transfer from the moist air, in tons.
- (b) the rate water is condensed, in lb/s.
- (c) Check your answers using data from the psychrometric chart.
- (d) Check your answers using *Interactive Thermodynamics: IT*.



12.80 Moist air at 28°C, 1 bar, and 50% relative humidity flows through a duct operating at steady state. The air is cooled at essentially constant pressure and exits at 20°C. Determine the heat transfer rate, in kJ per kg of dry air flowing, and the relative humidity at the exit.

12.81 An air conditioner operating at steady state takes in moist air at 28°C, 1 bar, and 70% relative humidity. The moist air first passes over a cooling coil in the dehumidifier unit and

some water vapor is condensed. The rate of heat transfer between the moist air and the cooling coil is 11 tons. Saturated moist air and condensate streams exit the dehumidifier unit at the same temperature. The moist air then passes through a heating unit, exiting at 24°C , 1 bar, and 40% relative humidity. Neglecting kinetic and potential energy effects, determine

- the temperature of the moist air exiting the dehumidifier unit, in $^{\circ}\text{C}$.
- the volumetric flow rate of the air entering the air conditioner, in m^3/min .
- the rate water is condensed, in kg/min .
- the rate of heat transfer to the air passing through the heating unit, in kW .

12.82 Figure P12.82 shows a compressor followed by an aftercooler. Atmospheric air at 14.7 lbf/in.^2 , 90°F , and 75% relative humidity enters the compressor with a volumetric flow rate of $100 \text{ ft}^3/\text{min}$. The compressor power input is 15 hp. The moist air exiting the compressor at 100 lbf/in.^2 , 400°F flows through the aftercooler, where it is cooled at constant pressure, exiting saturated at 100°F . Condensate also exits the aftercooler at 100°F . For steady-state operation and negligible kinetic and potential energy effects, determine

- the rate of heat transfer from the compressor to its surroundings, in Btu/min .
- the mass flow rate of the condensate, in lb/min .
- the rate of heat transfer from the moist air to the refrigerant circulating in the cooling coil, in tons of refrigeration.

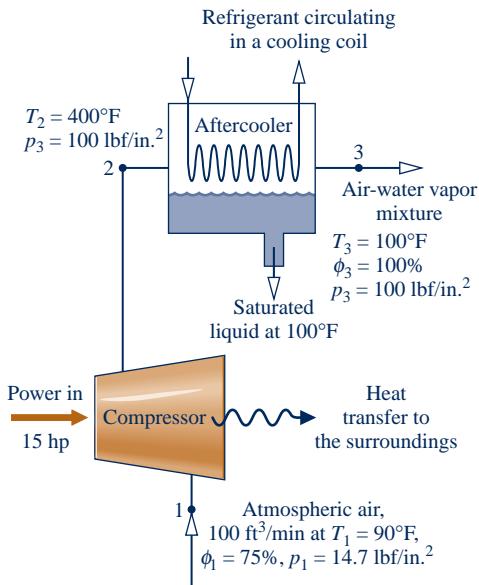


Fig. P12.82

12.83 Outside air at 50°F , 1 atm, and 40% relative humidity enters an air-conditioning device operating at steady state. Liquid water is injected at 45°F and a moist air stream exits with a volumetric flow rate of $1000 \text{ ft}^3/\text{min}$ at 90°F , 1 atm and a relative humidity of 40%. Neglecting kinetic and potential energy effects, determine

- the rate water is injected, in lb/min .
- the rate of heat transfer to the moist air, in Btu/h .

12.84 An air-conditioning system consists of a spray section followed by a reheat. Moist air at 32°C and $\phi = 77\%$ enters the system and passes through a water spray, leaving the spray section cooled and saturated with water. The moist air is then heated to 25°C and $\phi = 45\%$ with no change in the amount of water vapor present. For operation at steady state, determine

- the temperature of the moist air leaving the spray section, in $^{\circ}\text{C}$.
 - the change in the amount of water vapor contained in the moist air passing through the system, in kg per kg of dry air.
- Locate the principal states on a psychrometric chart.

12.85 Moist air at 95°F , 1 atm, and a relative humidity of 30% enters a steam-spray humidification device operating at steady state with a volumetric flow rate of $5700 \text{ ft}^3/\text{min}$. Saturated water vapor at 230°F is sprayed into the moist air, which then exits the device at a relative humidity of 50%. Heat transfer between the device and its surroundings can be ignored, as can kinetic and potential energy effects. Determine

- the temperature of the exiting moist air stream, in $^{\circ}\text{F}$.
- the rate at which steam is injected, in lb/min .

12.86 For the steam-spray humidifier in Problem 12.85, determine the exergy destruction rate, in Btu/min . Let $T_0 = 95^{\circ}\text{F}$.

12.87 Outside air at 50°F , 1 atm, and 40% relative humidity enters an air conditioner operating at steady state with a mass flow rate of 3.3 lb/s . The air is first heated at essentially constant pressure to 90°F . Liquid water at 60°F is then injected, bringing the air to 70°F , 1 atm. Determine

- the rate of heat transfer to the air passing through the heating section, in Btu/s .
- the rate water is injected, in lb/s .
- the relative humidity at the exit of the humidification section.

Kinetic and potential energy effects can be ignored.

12.88 Moist air at 27°C , 1 atm, and 50% relative humidity enters an evaporative cooling unit operating at steady state consisting of a heating section followed by a soaked pad evaporative cooler operating adiabatically. The air passing through the heating section is heated to 45°C . Next, the air passes through a soaked pad exiting with 50% relative humidity. Using data from the psychrometric chart, determine

- the humidity ratio of the entering moist air mixture, in $\text{kg}(\text{vapor})$ per $\text{kg}(\text{dry air})$.
- the rate of heat transfer to the moist air passing through the heating section, in kJ per kg of mixture.
- the humidity ratio and temperature, in $^{\circ}\text{C}$, at the exit of the evaporative cooling section.

12.89 In an industrial dryer operating at steady state, atmospheric air at 80°F , 1 atm, and 65% relative humidity is first heated to 280°F at constant pressure. The heated air is then allowed to pass over the materials being dried, exiting the dryer at 150°F , 1 atm, and 30% relative humidity. If moisture is to be removed from the materials at a rate of 2700 lb/h , determine

- the mass flow rate of dry air required, in lb/h .
- the rate of heat transfer to the air as it passes through the heating section, in Btu/h .

Neglect kinetic and potential energy effects.

12.90 At steady state, moist air is to be supplied to a classroom at a specified volumetric flow rate and temperature T . Air is removed from the classroom in a separate stream at a temperature of 27°C and 50% relative humidity. Moisture is added to the air in the room from the occupants at a rate of 4.5 kg/h. The moisture can be regarded as saturated vapor at 33°C . Heat transfer into the occupied space from all sources is estimated to occur at a rate of 34,000 kJ/h. The pressure remains uniform at 1 atm.

- (a) For a supply air volumetric flow rate of $40 \text{ m}^3/\text{min}$, determine the supply air temperature T , in $^\circ\text{C}$, and the relative humidity.
 (b) Plot the supply air temperature, in $^\circ\text{C}$, and relative humidity, each versus the supply air volumetric flow rate ranging from 35 to $90 \text{ m}^3/\text{min}$.



12.91 At steady state, a device for heating and humidifying air has $250 \text{ ft}^3/\text{min}$ of air at 40°F , 1 atm, and 80% relative humidity entering at one location, $1000 \text{ ft}^3/\text{min}$ of air at 60°F , 1 atm, and 80% relative humidity entering at another location, and liquid water injected at 55°F . A single moist air stream exits at 85°F , 1 atm, and 35% relative humidity. Determine

- (a) the rate of heat transfer to the device, in Btu/min.
 (b) the rate at which liquid water is injected, in lb/min.

Neglect kinetic and potential energy effects.

12.92 Air at 35°C , 1 bar, and 10% relative humidity enters an evaporative cooler operating at steady state. The volumetric flow rate of the incoming air is $50 \text{ m}^3/\text{min}$. Liquid water at 20°C enters the cooler and fully evaporates. Moist air exits the cooler at 25°C , 1 bar. If there is no significant heat transfer between the device and its surroundings, determine

- (a) the rate at which liquid enters, in kg/min.
 (b) the relative humidity at the exit.
 (c) the rate of exergy destruction, in kJ/min, for $T_0 = 20^\circ\text{C}$.

Neglect kinetic and potential energy effects.

12.93 Using Eqs. 12.56, show that

$$\frac{\dot{m}_{a1}}{\dot{m}_{a2}} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3} = \frac{(h_{a3} + \omega_3 h_{g3}) - (h_{a2} + \omega_2 h_{g2})}{(h_{a1} + \omega_1 h_{g1}) - (h_{a3} + \omega_3 h_{g3})}$$

Employ this relation to demonstrate on a psychrometric chart that state 3 of the mixture lies on a straight line connecting the initial states of the two streams before mixing.

12.94 For the adiabatic mixing process in Example 12.14, plot the exit temperature, in $^\circ\text{C}$, versus the volumetric flow rate of stream 2 ranging from 0 to $1400 \text{ m}^3/\text{min}$. Discuss the plot as $(AV)_2$ goes to zero and as $(AV)_2$ becomes large.

12.95 A stream consisting of $35 \text{ m}^3/\text{min}$ of moist air at 14°C , 1 atm, 80% relative humidity mixes adiabatically with a stream consisting of $80 \text{ m}^3/\text{min}$ of moist air at 40°C , 1 atm, 40% relative humidity, giving a single mixed stream at 1 atm. Using the psychrometric chart together with the procedure of Problem 12.93, determine the relative humidity and temperature, in $^\circ\text{C}$, of the exiting stream.

12.96 At steady state, a stream of air at 60°F , 1 atm, 30% relative humidity is mixed adiabatically with a stream of air at 90°F , 1 atm, 70% relative humidity. The mass flow rate of the higher-temperature stream is twice that of the other stream. A single mixed stream exits at 1 atm. Using the result of Problem 12.74, determine for the exiting stream

- (a) the temperature, in $^\circ\text{F}$.
 (b) the relative humidity.

Neglect kinetic and potential energy effects.

12.97 At steady state, moist air at 42°C , 1 atm, 30% relative humidity is mixed adiabatically with a second moist air stream entering at 1 atm. The mass flow rates of the two streams are the same. A single mixed stream exits at 29°C , 1 atm, 40% relative humidity with a mass flow rate of 2 kg/s . Kinetic and potential energy effects are negligible. For the second entering moist air stream, determine, using data from the psychrometric chart,

- (a) the relative humidity.
 (b) the temperature, in $^\circ\text{C}$.

12.98 Figure P12.98 shows two options for conditioning atmospheric air at steady state. In each case, air enters at 15°C , 1 atm, and 20% relative humidity with a volumetric flow rate of $150 \text{ m}^3/\text{min}$ and exits at 30°C , 1 atm, and 40%

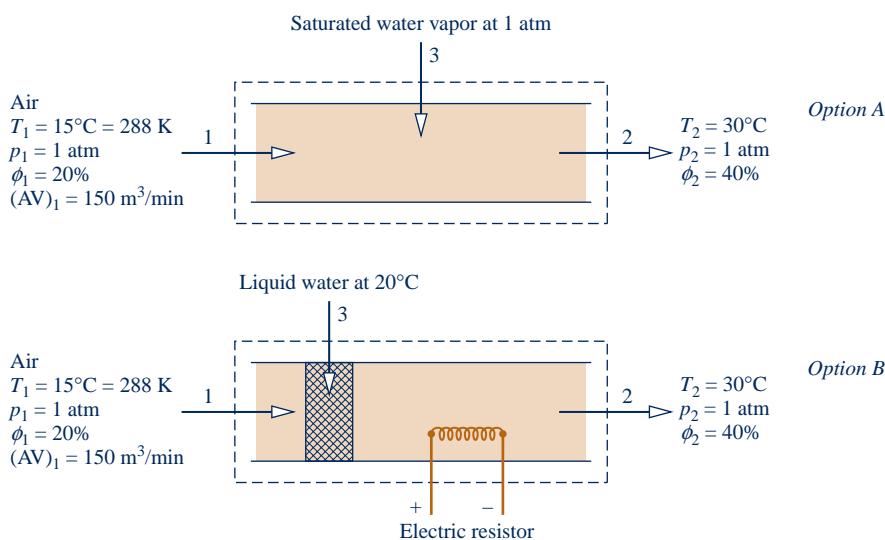


Fig. P12.98

relative humidity. One method conditions the air by injecting saturated water vapor at 1 atm. The other method allows the entering air to pass through a soaked pad replenished by liquid water entering at 20°C. The moist air stream is then heated by an electric resistor. For $T_0 = 288$ K, which of the two options is preferable from the standpoint of having less exergy destruction? Discuss.

- 12.99** Air at 30°C, 1 bar, 50% relative humidity enters an insulated chamber operating at steady state with a mass flow rate of 3 kg/min and mixes with a saturated moist air stream entering at 5°C, 1 bar with a mass flow rate of 5 kg/min. A single mixed stream exits at 1 bar. Determine

- the relative humidity and temperature, in °C, of the exiting stream.
- the rate of exergy destruction, in kW, for $T_0 = 20^\circ\text{C}$.

Neglect kinetic and potential energy effects.

- 12.100** Moist air enters a dehumidifier at 80°F, 1 atm, and $\phi = 60\%$ and exits at 58°F, 1 atm, and $\phi = 90\%$ with a volumetric flow rate of 10,000 ft³/min. The stream then mixes adiabatically with a moist air stream at 95°F, 1 atm, and $\phi = 47\%$ having a volumetric flow rate of 2000 ft³/min. A single moist-air stream exits the mixing chamber. Stray heat transfer and kinetic and potential energy effects can be ignored. Determine at steady state

- the rate water is removed from the moist air passing through the dehumidifier, in lb/h.
- the temperature, in °F, and the relative humidity of the moist air at the mixing chamber exit.

- 12.101** A stream of air (stream 1) at 60°F, 1 atm, 30% relative humidity is mixed adiabatically with a stream of air (stream 2) at 90°F, 1 atm, 80% relative humidity. A single stream (stream 3) exits the mixing chamber at temperature T_3 and 1 atm. Assume steady state and ignore kinetic and potential energy effects. Letting r denote the ratio of dry air mass flow rates $\dot{m}_{\text{a1}}/\dot{m}_{\text{a2}}$

- determine T_3 , in °F, for $r = 2$.
- plot T_3 , in °F, versus r ranging from 0 to 10.

- 12.102** Figure P12.102 shows the adiabatic mixing of two moist-air streams at steady state. Kinetic and potential energy effects are negligible. Determine the rate of exergy destruction, in Btu/min, for $T_0 = 95^\circ\text{F}$.

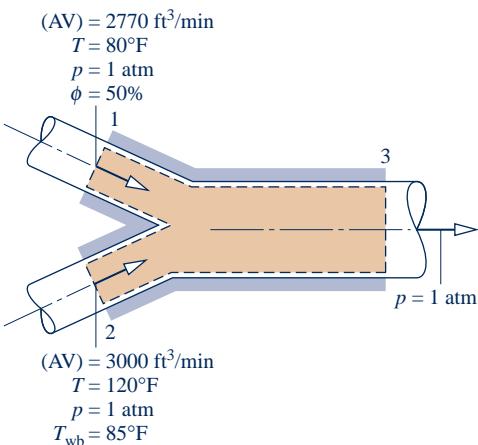


Fig. P12.102

Analyzing Cooling Towers

- 12.103** In the condenser of a power plant, energy is discharged by heat transfer at a rate of 836 MW to cooling water that exits the condenser at 40°C into a cooling tower. Cooled water at 20°C is returned to the condenser. Atmospheric air enters the tower at 25°C, 1 atm, 35% relative humidity. Moist air exits at 35°C, 1 atm, 90% relative humidity. Makeup water is supplied at 20°C. For operation at steady state, determine the mass flow rate, in kg/s, of

- the entering atmospheric air.
- the makeup water.

Ignore kinetic and potential energy effects.

- 12.104** Liquid water at 100°F enters a cooling tower operating at steady state, and cooled water exits the tower at 80°F. Data for the various streams entering and exiting the tower are shown in Fig. P12.104. No makeup water is provided. Determine

- the mass flow rate of the entering atmospheric air, in lb/h.
- the rate at which water evaporates, in lb/h.
- the mass flow rate of the exiting liquid stream, in lb/h.

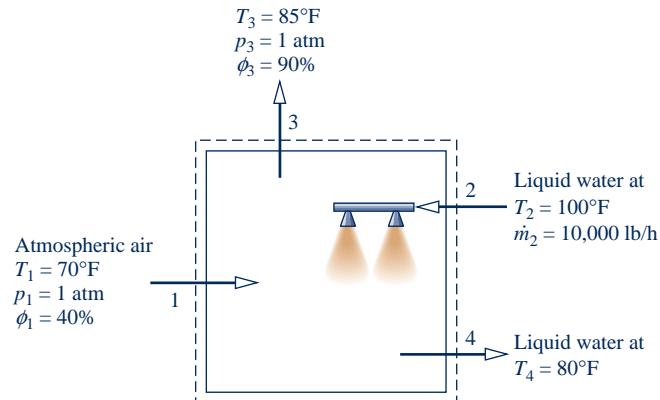


Fig. P12.104

- 12.105** Liquid water at 130°F and a mass flow rate of 10⁵ lb/h enters a cooling tower operating at steady state. Liquid water exits the tower at 70°F. No makeup water is provided. Atmospheric air enters at 1 atm with a dry-bulb temperature of 50°F and a wet-bulb temperature of 35°F. Saturated air exits at 120°F, 1 atm. Ignoring kinetic and potential energy effects, determine the mass flow rate of the cooled water stream exiting the tower, in lb/h.

- 12.106** Liquid water at 100°F and a volumetric flow rate of 200 gal/min enters a cooling tower operating at steady state. Atmospheric air enters at 1 atm with a dry-bulb temperature of 80°F and a wet-bulb temperature of 60°F. Moist air exits the cooling tower at 90°F and 90% relative humidity. Makeup water is provided at 80°F. Plot the mass flow rates of the dry air and makeup water, each in lb/min, versus return water temperature ranging from 80 to 100°F. Ignore kinetic and potential energy effects.

- 12.107** Liquid water enters a cooling tower operating at steady state at 40°C with a mass flow rate of 10⁵ kg/h. Cooled water at 25°C exits the cooling tower at the same mass flow rate.

Makeup water is supplied at 23°C. Atmospheric air enters the tower at 30°C, 1 bar, 35% relative humidity. A saturated moist air stream exits at 34°C, 1 bar. Determine

- the mass flow rates of the dry air and makeup water, each in kg/h.
- the rate of exergy destruction within the cooling tower, in kW, for $T_0 = 23^\circ\text{C}$.

Ignore kinetic and potential energy effects.

12.108 Liquid water at 110°F and a volumetric flow rate of 250 ft³/min enters a cooling tower operating at steady state.

Cooled water exits the cooling tower at 88°F. Atmospheric air enters the tower at 80°F, 1 atm, 40% relative humidity, and saturated moist air at 105°F, 1 atm exits the cooling tower. Determine

- the mass flow rates of the dry air and the cooled water, each in lb/min.
- the rate of exergy destruction within the cooling tower, in Btu/s, for $T_0 = 77^\circ\text{F}$.

Ignore kinetic and potential energy effects.

► DESIGN & OPEN-ENDED PROBLEMS: EXPLORING ENGINEERING PRACTICE

12.1D About half the air we breathe on some airplanes is fresh air, and the rest is recirculated. Investigate typical equipment schematics for providing a blend of fresh and recirculated filtered air to the passenger cabins of commercial airplanes. What types of filters are used and how do they work? Write a report including at least three references.

12.2D Identify a campus, commercial, or other building in your locale with an air-conditioning system installed 20 or more years ago. Critically evaluate the efficacy of the system in terms of comfort level provided, operating costs, maintenance costs, global warming potential of the refrigerant used, and other pertinent issues. On this basis, recommend specific system upgrades or a full system replacement, as warranted. Present your findings in a PowerPoint presentation.

12.3D Study the air-conditioning system for one of the classrooms you frequent where occupant comfort is unsatisfactory and describe the system in detail, including the control strategy used. Propose modifications aimed at improving occupant satisfaction, including a new heating, ventilation, and air conditioning (HVAC) system for the room, if warranted. Compare the proposed and existing systems in terms of occupant comfort, potential impact on productivity, and energy requirements. Detail your findings in an executive summary and PowerPoint presentation.

12.4D Critically evaluate a cooling tower on your campus, or nearby, in terms of effectiveness in providing the required range of cooled water, operating costs, maintenance costs, and other relevant issues. If warranted, recommend cost-effective upgrades of the existing cooling tower or alternative cooling technologies to achieve the desired level of performance, including options for minimizing water loss. Present your findings in a report including at least three references.

12.5D Using methods in the most current *ASHRAE Handbook of HVAC Applications*, estimate the rate of evaporation from the surface of an Olympic-size swimming pool. The swimming hall is maintained at 30°C with a dew point temperature of 21°C. Based on your estimate, determine the load in kW, that the added moisture places on the air-conditioning system. Write a memorandum that summarizes your analysis and include at least three references.

12.6D Write a report explaining the way the human body regulates its temperature, both under cold and hot climate conditions. Based on these *thermoregulation* mechanisms,

discuss designs of *personal protective clothing* for fire fighters and other first responders. How are such clothing systems designed to provide protection against chemical or biological agents while maintaining sufficient thermal comfort to allow for strenuous physical activity? Include in your report at least three references.

12.7D Tunnel-type spray coolers are used to cool vegetables. In one application, tomatoes on a 4-ft-wide conveyor belt pass under a 34°F water spray and cool from 70 to 40°F. The water is collected in a reservoir below and recirculated through the evaporator of an ammonia refrigeration unit. Recommend the length of the tunnel and the conveyor speed. Estimate the number of tomatoes that can be cooled in an hour with your design. Write a report including sample calculations and at least three references.

12.8D Nearly 20 years ago, eight scientists entered Biosphere 2, located in Oracle, Arizona, for a planned two-year period of isolation. The three-acre biosphere had several ecosystems, including a desert, tropical rain forest, grassland, and saltwater wetlands. It also included species of plants and microorganisms intended to sustain the ecosystems. According to plan, the scientists would produce their own food using intensive organic farming, fish farmed in ponds, and a few barnyard animals. Occupants also would breathe oxygen produced by the plants and drink water cleansed by natural processes. Sunlight and a natural gas-fueled generator were to meet all energy needs. Numerous difficulties were encountered with the ecosystems and by the scientists, including insufficient oxygen, hunger and loss of body weight, and animosities among individuals. Study the record of Biosphere 2 for lessons that would substantially assist in designing a self-sustaining enclosed biosphere for human habitation on Mars. Present your results in a report including at least three references.

12.9D In a 2007 study using influenza-infected guinea pigs in climate-controlled habitats, researchers investigated the aerosol transmission of influenza virus while varying the temperature and humidity within the habitats. The research showed there were more infections when it was colder and drier, and based on this work a significant correlation was found between humidity ratio and influenza. (See BIOCONNECTIONS on p. 730) For the aerosol transmission experiments, guinea pigs were housed within cabinets like the one shown in Figure P12.9D. Each cabinet is fitted with a dedicated compressed-air



Fig. P12.9D

line and an associated compressed-air dryer that provides precise and rapid control for the cabinet's humidity injection and dehumidification systems. A condensate recirculator collects and recycles the condensate that forms in the base of the chamber and provides continuous, clean, filtered water to the cabinet's humidity injection system. The cabinets were placed within an isolated room with an ambient temperature of approximately 20°C. Experimenters say ambient temperatures in excess of 25°C can result in chamber failure. The objective of this project is to specify the heating, ventilation, and air conditioning (HVAC) system for the room housing the cabinets, assuming the room encompasses 500 ft² and houses five environmental cabinets with up to eight guinea pigs per cabinet. Each cabinet delivers a maximum heat transfer rate of 4000 Btu/h to the room. Document your design in a report including a minimum of three references that substantiate assumptions made during the design process.

12.10D Building energy use is significant in the United States, consuming about 70% of all electricity generated. An increase in electricity use of about 50% is expected by the end of the current decade. In response to the adverse impact that buildings have on energy use and the environment, in 1998 the U.S. Green Building Council developed LEED® (Leadership in Energy and Environmental Design), a certification system aimed at improving the performance of buildings across several measures, including energy and water use, greenhouse gas emission, and indoor environmental quality. Thousands of buildings throughout the world have now gained LEED®

certification. Identify a newly constructed LEED®-certified building on your campus or in a nearby locale. Determine the level of LEED® certification the building achieves: certified, silver, gold, or platinum. Prepare a summary of the building's design, focusing on elements incorporated to improve building energy and environmental performance and associated costs. Present your findings in a written report including at least three references.

12.11D In 2010, the U.S. Department of Energy focused its research agenda on innovative technologies to provide energy-efficient cooling for buildings and reduce greenhouse gas emissions. Key agenda items include developing the following:

1. Cooling systems using refrigerants with *global warming potential* less than or equal to 1
2. Air conditioning systems for warm and humid climates that increase the coefficient of performance of *ventilation air cooling* by 50% or more, based on current technology
3. Hot-climate vapor-compression air-conditioning systems that condition recirculated air while increasing the coefficient of performance by 50% or more, based on current technology

For one such project supported by the Department of Energy, prepare a report that summarizes the project goals and objectives, research plan, and expected outcomes. Also critically evaluate the feasibility of incorporating the resulting technology into existing cooling systems.

12.12D An air-handling system is being designed for a 40 ft \times 40 ft \times 8 ft biological research facility that houses 3000 laboratory mice. The indoor conditions must be maintained at 75°F, 60% relative humidity when the outdoor air conditions are 90°F, 70% relative humidity. Develop a preliminary design of an air conditioning and distribution system that satisfies National Institute of Health (NIH) standards for animal facilities. Assume a *biological safety level of one* (BSL-1), and that two thirds of the floor space is devoted to animal care. Since an interruption in ventilation or air conditioning could place the laboratory animals under stress and compromise the research under way in the facility, account for *redundancy* in your design.

12.13D Adequate levels of ventilation reduce the likelihood of *sick building syndrome*. (See BIOCONNECTIONS on p. 727.) The outdoor air used for ventilation must be conditioned, and this requires energy. Consider the air-handling system for the commercial building illustrated in Figure P12.13D, consisting of ducting, two dampers labeled A and B, a vapor-compression dehumidifier, and a heater. The system supplies 25 m³/s of conditioned air at 20°C and a relative humidity of 55% to maintain the interior space at 25°C and a relative humidity of

50%. The recirculated air has the same conditions as the air in the interior space. A minimum of 5 m³/s of outdoor air is required to provide adequate ventilation. Dampers A and B can be set to provide alternative operating modes to maintain required ventilation rates. On a given summer day when the outside air dry-bulb temperature and relative humidity are 25°C and 60%, respectively, which of the following three operating modes is best from the standpoint of minimizing the total heat transfer of energy *from* the conditioned air *to* the cooling coil and *to* the conditioned air *from* the heating coil?

1. Dampers A and B closed.
2. Damper A open and damper B closed with outside air contributing one-quarter of the total supply air.
3. Dampers A and B open. One-quarter of the conditioned air comes from outside air and one-third of the recirculated air bypasses the dehumidifier via open damper B; the rest flows through damper A.

Present your recommendation together with your reasoning in a PowerPoint presentation suitable for your class. Additionally, in an accompanying memorandum, provide well-documented sample calculations in support of your recommendation.

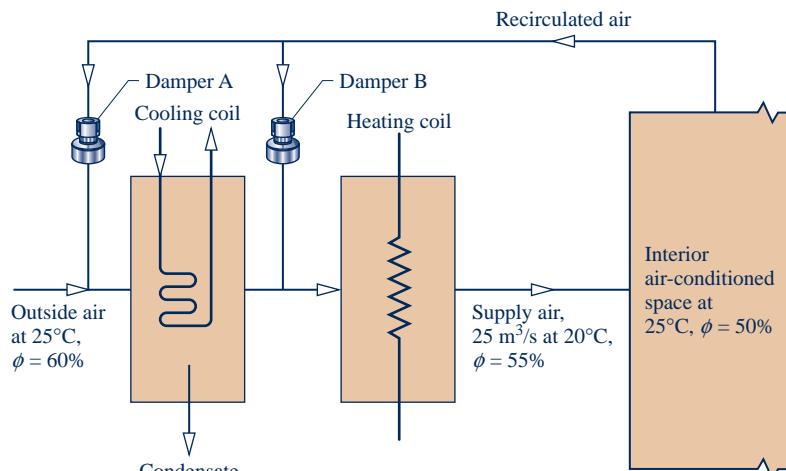


Fig. P12.13D



Combustion fundamentals are introduced in Sec. 13.1. © Digital Vision/Age Fotostock America, Inc.

ENGINEERING CONTEXT The **objective** of this chapter is to study systems involving chemical reactions. Since the *combustion* of hydrocarbon fuels occurs in most power-producing devices (Chaps. 8 and 9), combustion is emphasized.

The thermodynamic analysis of reacting systems is primarily an extension of principles introduced thus far. The concepts applied in the *first part* of the chapter dealing with combustion fundamentals remain the same: conservation of mass, conservation of energy, and the second law. It is necessary, though, to modify the methods used to evaluate specific enthalpy, internal energy, and entropy, by accounting for changing chemical composition. Only the manner in which these properties are evaluated represents a departure from previous practice, for once appropriate values are determined they are used as in earlier chapters in the energy and entropy balances for the system under consideration. In the *second part* of the chapter, the exergy concept of Chap. 7 is extended by introducing chemical exergy.

The principles developed in this chapter allow the equilibrium composition of a mixture of chemical substances to be determined. This topic is studied in Chap. 14. The subject of *dissociation* is also deferred until then. Prediction of *reaction rates* is not within the scope of classical thermodynamics, so the topic of chemical kinetics, which deals with reaction rates, is not discussed in this text.

13

Reacting Mixtures and Combustion

► LEARNING OUTCOMES

When you complete your study of this chapter, you will be able to...

- ▶ demonstrate understanding of key concepts, including complete combustion, theoretical air, enthalpy of formation, and adiabatic flame temperature.
- ▶ determine balanced reaction equations for combustion of hydrocarbon fuels.
- ▶ apply mass, energy, and entropy balances to closed systems and control volumes involving chemical reactions.
- ▶ perform exergy analyses, including chemical exergy and the evaluation of exergetic efficiencies.

Combustion Fundamentals

reactants
products

complete combustion

stoichiometric coefficients

13.1

Introducing Combustion

When a chemical reaction occurs, the bonds within molecules of the **reactants** are broken, and atoms and electrons rearrange to form **products**. In combustion reactions, rapid oxidation of combustible elements of the fuel results in energy release as combustion products are formed. The three major combustible chemical elements in most common fuels are carbon, hydrogen, and sulfur. Sulfur is usually a relatively unimportant contributor to the energy released, but it can be a significant cause of pollution and corrosion problems. Combustion is **complete** when all the carbon present in the fuel is burned to carbon dioxide, all the hydrogen is burned to water, all the sulfur is burned to sulfur dioxide, and all other combustible elements are fully oxidized. When these conditions are not fulfilled, combustion is *incomplete*.

In this chapter, we deal with combustion reactions expressed by chemical equations of the form



or



When dealing with chemical reactions, it is necessary to remember that mass is conserved, so the mass of the products equals the mass of the reactants. The total mass of each chemical *element* must be the same on both sides of the equation, even though the elements exist in different chemical compounds in the reactants and products. However, the number of moles of products may differ from the number of moles of reactants.

► FOR EXAMPLE consider the complete combustion of hydrogen with oxygen



In this case, the reactants are hydrogen and oxygen. Hydrogen is the fuel and oxygen is the oxidizer. Water is the only product of the reaction. The numerical coefficients in the equation, which precede the chemical symbols to give equal amounts of each chemical element on both sides of the equation, are called **stoichiometric coefficients**. In words, Eq. 13.1 states



or in English units



Note that the total numbers of moles on the left and right sides of Eq. 13.1 are not equal. However, because mass is conserved, the total mass of reactants must equal the total mass of products. Since 1 kmol of H₂ equals 2 kg, $\frac{1}{2}$ kmol of O₂ equals 16 kg, and 1 kmol of H₂O equals 18 kg, Eq. 13.1 can be interpreted as stating



or in English units



In the remainder of this section, consideration is given to the makeup of the fuel, oxidizer, and combustion products typically involved in engineering combustion applications.

13.1.1 Fuels

A *fuel* is simply a combustible substance. In this chapter emphasis is on hydrocarbon fuels, which contain hydrogen and carbon. Sulfur and other chemical substances also may be present. Hydrocarbon fuels can exist as liquids, gases, and solids.

Liquid hydrocarbon fuels are commonly derived from crude oil through distillation and cracking processes. Examples are gasoline, diesel fuel, kerosene, and other types of fuel oils. Most liquid fuels are mixtures of hydrocarbons for which compositions are usually given in terms of mass fractions. For simplicity in combustion calculations, gasoline is often modeled as octane, C_8H_{18} , and diesel fuel as dodecane, $C_{12}H_{26}$.

Gaseous hydrocarbon fuels are obtained from natural gas wells or are produced in certain chemical processes. Natural gas normally consists of several different hydrocarbons, with the major constituent being methane, CH_4 . The compositions of gaseous fuels are usually given in terms of mole fractions. Both gaseous and liquid hydrocarbon fuels can be synthesized from coal, oil shale, and tar sands.

Coal is a familiar solid fuel. Its composition varies considerably with the location from which it is mined. For combustion calculations, the composition of coal is usually expressed as an ultimate analysis. The **ultimate analysis** gives the composition on a *mass basis* in terms of the relative amounts of chemical elements (carbon, sulfur, hydrogen, nitrogen, oxygen) and ash.

ultimate analysis

13.1.2 Modeling Combustion Air

Oxygen is required in every combustion reaction. Pure oxygen is used only in special applications such as cutting and welding. In most combustion applications, air provides the needed oxygen. The composition of a typical sample of dry air is given in Table 12.1. For the combustion calculations of this book, however, the following model is used for simplicity:

- ▶ All components of dry air other than oxygen are lumped together with nitrogen. Accordingly, air is considered to be 21% oxygen and 79% nitrogen on a molar basis. With this idealization the molar ratio of the nitrogen to the oxygen is $0.79/0.21 = 3.76$. When air supplies the oxygen in a combustion reaction, therefore, every mole of oxygen is accompanied by 3.76 moles of nitrogen.
- ▶ We also assume that the nitrogen present in the combustion air does *not* undergo chemical reaction. That is, nitrogen is regarded as inert. The nitrogen in the products is at the same temperature as the other products, however. Accordingly, nitrogen undergoes a change of state if the products are at a temperature other than the reactant air temperature. If a high enough product temperature is attained, nitrogen can form compounds such as nitric oxide and nitrogen dioxide. Even trace amounts of oxides of nitrogen appearing in the exhaust of internal combustion engines can be a source of air pollution.

TAKE NOTE...

In this model, air is assumed to contain no water vapor. When moist air is involved in combustion, the water vapor present must be considered in writing the combustion equation.

Air–Fuel Ratio

Two parameters that are frequently used to quantify the amounts of fuel and air in a particular combustion process are the air–fuel ratio and its reciprocal, the fuel–air ratio. The **air–fuel ratio** is simply the ratio of the amount of air in a reaction to the amount of fuel. The ratio can be written on a molar basis (moles of air divided by moles of fuel) or on a mass basis (mass of air divided by mass of fuel). Conversion between these values is accomplished using the molecular weights of the air, M_{air} , and fuel, M_{fuel} ,

$$\begin{aligned}\frac{\text{mass of air}}{\text{mass of fuel}} &= \frac{\text{moles of air} \times M_{air}}{\text{moles of fuel} \times M_{fuel}} \\ &= \frac{\text{moles of air}}{\text{moles of fuel}} \left(\frac{M_{air}}{M_{fuel}} \right)\end{aligned}$$

air–fuel ratio

or

$$AF = \overline{AF} \left(\frac{M_{\text{air}}}{M_{\text{fuel}}} \right) \quad (13.2)$$

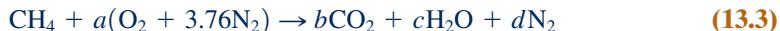
where \overline{AF} is the air–fuel ratio on a molar basis and AF is the ratio on a mass basis. For the combustion calculations of this book the molecular weight of air is taken as 28.97. Tables A-1 provide the molecular weights of several important hydrocarbons. Since AF is a ratio, it has the same value whether the quantities of air and fuel are expressed in SI units or English units.

Theoretical Air

theoretical air

The minimum amount of air that supplies sufficient oxygen for the complete combustion of all the carbon, hydrogen, and sulfur present in the fuel is called the **theoretical amount of air**. For complete combustion with the theoretical amount of air, the products consist of carbon dioxide, water, sulfur dioxide, the nitrogen accompanying the oxygen in the air, and any nitrogen contained in the fuel. No free oxygen appears in the products.

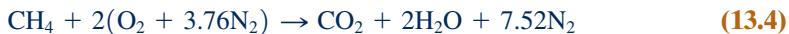
► FOR EXAMPLE let us determine the theoretical amount of air for the complete combustion of methane. For this reaction, the products contain only carbon dioxide, water, and nitrogen. The reaction is



where a , b , c , and d represent the numbers of moles of oxygen, carbon dioxide, water, and nitrogen. In writing the left side of Eq. 13.3, 3.76 moles of nitrogen are considered to accompany each mole of oxygen. Applying the conservation of mass principle to the carbon, hydrogen, oxygen, and nitrogen, respectively, results in four equations among the four unknowns

$$\begin{aligned} \text{C:} \quad b &= 1 \\ \text{H:} \quad 2c &= 4 \\ \text{O:} \quad 2b + c &= 2a \\ \text{N:} \quad d &= 3.76a \end{aligned}$$

Solving these equations, the *balanced* chemical equation is



The coefficient 2 before the term $(\text{O}_2 + 3.76\text{N}_2)$ in Eq. 13.4 is the number of moles of *oxygen* in the combustion air, per mole of fuel, and *not* the amount of air. The amount of combustion air is 2 moles of oxygen *plus* 2×3.76 moles of nitrogen, giving a total of 9.52 moles of air per mole of fuel. Thus, for the reaction given by Eq. 13.4 the air–fuel ratio on a molar basis is 9.52. To calculate the air–fuel ratio on a mass basis, use Eq. 13.2 to write

$$AF = \overline{AF} \left(\frac{M_{\text{air}}}{M_{\text{fuel}}} \right) = 9.52 \left(\frac{28.97}{16.04} \right) = 17.19 \blacktriangleleft \blacktriangleleft \blacktriangleleft \blacktriangleleft \blacktriangleleft$$

percent of theoretical air

percent excess air

Normally the amount of air supplied is either greater or less than the theoretical amount. The amount of air actually supplied is commonly expressed in terms of the **percent of theoretical air**. For example, 150% of theoretical air means that the air actually supplied is 1.5 times the theoretical amount of air. The amount of air supplied can be expressed alternatively as a **percent excess air** or a **percent deficiency** of air. Thus, 150% of theoretical air is equivalent to 50% excess air, and 80% of theoretical air is the same as a 20% deficiency of air.

► **FOR EXAMPLE** consider the *complete* combustion of methane with 150% theoretical air (50% excess air). The balanced chemical reaction equation is



In this equation, the amount of air per mole of fuel is 1.5 times the theoretical amount determined by Eq. 13.4. Accordingly, the air-fuel ratio is 1.5 times the air-fuel ratio determined for Eq. 13.4. Since complete combustion is assumed, the products contain only carbon dioxide, water, nitrogen, and oxygen. The excess air supplied appears in the products as uncombined oxygen and a greater amount of nitrogen than in Eq. 13.4, based on the theoretical amount of air. ◀◀◀◀◀

The **equivalence ratio** is the ratio of the actual fuel-air ratio to the fuel-air ratio for complete combustion with the theoretical amount of air. The reactants are said to form a *lean* mixture when the equivalence ratio is less than unity. When the ratio is greater than unity, the reactants are said to form a *rich* mixture.

equivalence ratio

In Example 13.1, we use conservation of mass to obtain balanced chemical reactions. The air-fuel ratio for each of the reactions is also calculated.

►►►► EXAMPLE 13.1 ►

Determining the Air–Fuel Ratio for Complete Combustion of Octane

Determine the air–fuel ratio on both a molar and mass basis for the complete combustion of octane, C_8H_{18} , with (a) the theoretical amount of air, (b) 150% theoretical air (50% excess air).

SOLUTION

Known: Octane, C_8H_{18} , is burned completely with (a) the theoretical amount of air, (b) 150% theoretical air.

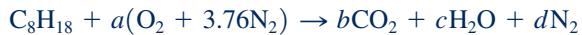
Find: Determine the air–fuel ratio on a molar and a mass basis.

Engineering Model:

1. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen.
2. The nitrogen is inert.
3. Combustion is complete.

Analysis:

(a) For complete combustion of C_8H_{18} with the theoretical amount of air, the products contain carbon dioxide, water, and nitrogen only. That is



Applying the conservation of mass principle to the carbon, hydrogen, oxygen, and nitrogen, respectively, gives

$$\begin{aligned} \text{C:} \quad b &= 8 \\ \text{H:} \quad 2c &= 18 \\ \text{O:} \quad 2b + c &= 2a \\ \text{N:} \quad d &= 3.76a \end{aligned}$$

Solving these equations, $a = 12.5$, $b = 8$, $c = 9$, $d = 47$. The balanced chemical equation is



The air–fuel ratio on a molar basis is

$$\overline{AF} = \frac{12.5 + 12.5(3.76)}{1} = \frac{12.5(4.76)}{1} = 59.5 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

- The air-fuel ratio expressed on a mass basis is

$$AF = \left[59.5 \frac{\text{kmol (air)}}{\text{kmol (fuel)}} \right] \left[\frac{28.97 \frac{\text{kg (air)}}{\text{kmol (air)}}}{114.22 \frac{\text{kg (fuel)}}{\text{kmol (fuel)}}} \right] = 15.1 \frac{\text{kg (air)}}{\text{kg (fuel)}}$$

- (b) For 150% theoretical air, the chemical equation for complete combustion takes the form



Applying conservation of mass

$$\begin{aligned} \text{C:} \quad b &= 8 \\ \text{H:} \quad 2c &= 18 \\ \text{O:} \quad 2b + c + 2e &= (1.5)(12.5)(2) \\ \text{N:} \quad d &= (1.5)(12.5)(3.76) \end{aligned}$$

Solving this set of equations, $b = 8$, $c = 9$, $d = 70.5$, $e = 6.25$, giving a balanced chemical equation



The air-fuel ratio on a molar basis is

$$\overline{AF} = \frac{18.75(4.76)}{1} = 89.25 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

On a mass basis, the air-fuel ratio is 22.6 kg (air)/kg (fuel), as can be verified.

- 1 When complete combustion occurs with *excess air*, oxygen appears in the products, in addition to carbon dioxide, water, and nitrogen.

Skills Developed

Ability to...

- balance a chemical reaction equation for complete combustion with theoretical air and with excess air.
- apply definitions of air-fuel ratio on mass and molar bases.

QuickQUIZ

For the condition in part (b), determine the *equivalence ratio*.

Ans. 0.67.

13.1.3 Determining Products of Combustion

In each of the illustrations given above, complete combustion is assumed. For a hydrocarbon fuel, this means that the only allowed products are CO_2 , H_2O , and N_2 , with O_2 also present when excess air is supplied. If the fuel is specified and combustion is complete, the respective amounts of the products can be determined by applying the conservation of mass principle to the chemical equation. The procedure for obtaining the balanced reaction equation of an *actual* reaction where combustion is incomplete is not always so straightforward.

Combustion is the result of a series of very complicated and rapid chemical reactions, and the products formed depend on many factors. When fuel is burned in the cylinder of an internal combustion engine, the products of the reaction vary with the temperature and pressure in the cylinder. In combustion equipment of all kinds, the degree of mixing of the fuel and air is a controlling factor in the reactions that occur once the fuel and air mixture is ignited. Although the amount of air supplied in an actual combustion process may exceed the theoretical amount, it is not uncommon for some carbon monoxide and unburned oxygen to appear in the products. This can be due to incomplete mixing, insufficient time for complete combustion, and other factors. When the amount of air supplied is less than the theoretical amount of air, the products

TAKE NOTE...

In *actual* combustion processes, the products of combustion and their relative amounts can be determined only through measurement.

may include both CO_2 and CO , and there also may be unburned fuel in the products. Unlike the complete combustion cases considered above, the products of combustion of an actual combustion process and their relative amounts can be determined only by *measurement*.

Among several devices for measuring the composition of products of combustion are the *Orsat analyzer*, *gas chromatograph*, *infrared analyzer*, and *flame ionization detector*. Data from these devices can be used to determine the mole fractions of the gaseous products of combustion. The analyses are often reported on a “dry” basis. In a **dry product analysis**, the mole fractions are given for all gaseous products *except* the water vapor. In Examples 13.2 and 13.3, we show how analyses of the products of combustion on a dry basis can be used to determine the balanced chemical reaction equations.

Since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapor in the gaseous products of combustion can be significant. If the gaseous products of combustion are cooled at constant mixture pressure, the *dew point temperature* is reached when water vapor begins to condense. Since water deposited on duct work, mufflers, and other metal parts can cause corrosion, knowledge of the dew point temperature is important. Determination of the dew point temperature is illustrated in Example 13.2, which also features a dry product analysis.

dry product analysis

TAKE NOTE...

For cooling of combustion products at constant pressure, the *dew point temperature* marks the onset of condensation of water vapor present in the products. See Sec. 12.5.4 to review this concept.

EXAMPLE 13.2

Using a Dry Product Analysis for Combustion of Methane

Methane, CH_4 , is burned with dry air. The molar analysis of the products on a dry basis is CO_2 , 9.7%; CO , 0.5%; O_2 , 2.95%; and N_2 , 86.85%. Determine (a) the air–fuel ratio on both a molar and a mass basis, (b) the percent theoretical air, (c) the dew point temperature of the products, in °F, if the mixture were cooled at 1 atm.

SOLUTION

Known: Methane is burned with dry air. The molar analysis of the products on a dry basis is provided.

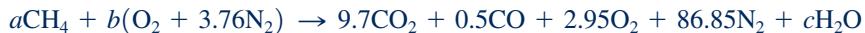
Find: Determine (a) the air–fuel ratio on both a molar and a mass basis, (b) the percent theoretical air, and (c) the dew point temperature of the products, in °F, if cooled at 1 atm.

Engineering Model:

1. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
2. The products form an ideal gas mixture and the dew point temperature of the mixture is conceptualized as in Sec. 12.5.4.

Analysis:

- 1 (a) The solution is conveniently conducted on the basis of 100 lbmol of dry products. The chemical equation then reads



In addition to the assumed 100 lbmol of dry products, water must be included as a product.

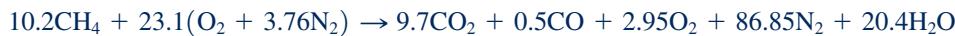
Applying conservation of mass to carbon, hydrogen, and oxygen, respectively

$$\text{C:} \quad 9.7 + 0.5 = a$$

$$\text{H:} \quad 2c = 4a$$

$$\text{O:} \quad (9.7)(2) + 0.5 + 2(2.95) + c = 2b$$

- 2 Solving this set of equations gives $a = 10.2$, $b = 23.1$, $c = 20.4$. The balanced chemical equation is



- On a molar basis, the air–fuel ratio is

$$\overline{AF} = \frac{23.1(4.76)}{10.2} = 10.78 \frac{\text{lbmol (air)}}{\text{lbmol (fuel)}}$$

On a mass basis

$$AF = (10.78) \left(\frac{28.97}{16.04} \right) = 19.47 \frac{\text{lb (air)}}{\text{lb (fuel)}}$$

- (b) The balanced chemical equation for the *complete combustion* of methane with the *theoretical amount* of air is



The theoretical air–fuel ratio on a molar basis is

$$(\overline{AF})_{\text{theo}} = \frac{2(4.76)}{1} = 9.52 \frac{\text{lbmol (air)}}{\text{lbmol (fuel)}}$$

The percent theoretical air is then found from

$$\begin{aligned} \% \text{ theoretical air} &= \frac{(\overline{AF})}{(\overline{AF})_{\text{theo}}} \\ &= \frac{10.78 \text{ lbmol (air)/lbmol (fuel)}}{9.52 \text{ lbmol (air)/lbmol (fuel)}} = 1.13 (113\%) \end{aligned}$$

- (c) To determine the dew point temperature requires the partial pressure of the water vapor p_v . The partial pressure p_v is found from $p_v = y_v p$, where y_v is the mole fraction of the water vapor in the combustion products and p is 1 atm.

Referring to the balanced chemical equation of part (a), the mole fraction of the water vapor is

$$y_v = \frac{20.4}{100 + 20.4} = 0.169$$

- ③ Thus, $p_v = 0.169 \text{ atm} = 2.484 \text{ lbf/in.}^2$ Interpolating in Table A-2E, $T = 134^\circ\text{F}$.

- The solution could be obtained on the basis of any assumed amount of dry products—for example, 1 lbmol. With some other assumed amount, the values of the coefficients of the balanced chemical equation would differ from those obtained in the solution, but the air–fuel ratio, the value for the percent of theoretical air, and the dew point temperature would be unchanged.
- The three unknown coefficients, a , b , and c , are evaluated here by application of conservation of mass to carbon, hydrogen, and oxygen. As a check, note that the nitrogen also balances

$$\text{N: } b(3.76) = 86.85$$

This confirms the accuracy of both the given product analysis and the calculations conducted to determine the unknown coefficients.

- If the products of combustion were cooled at constant pressure below the dew point temperature of 134°F , some condensation of the water vapor would occur.

Skills Developed

Ability to...

- balance a chemical reaction equation for incomplete combustion given the analysis of dry products of combustion.
- apply definitions of air–fuel ratio on mass and molar bases as well as percent theoretical air.
- determine the dew point temperature of combustion products.

QuickQUIZ

Recalculate the dew point temperature as in part (c) if the air supply were *moist* air, including 3.53 kmol of additional water vapor.

Ans. 139°F .

In Example 13.3, a fuel mixture having a known molar analysis is burned with air, giving products with a known dry analysis.

EXAMPLE 13.3**Burning Natural Gas with Excess Air**

A natural gas has the following molar analysis: CH₄, 80.62%; C₂H₆, 5.41%; C₃H₈, 1.87%; C₄H₁₀, 1.60%; N₂, 10.50%. The gas is burned with dry air, giving products having a molar analysis on a dry basis: CO₂, 7.8%; CO, 0.2%; O₂, 7%; N₂, 85%. **(a)** Determine the air-fuel ratio on a molar basis. **(b)** Assuming ideal gas behavior for the fuel mixture, determine the amount of products in kmol that would be formed from 100 m³ of fuel mixture at 300 K and 1 bar. **(c)** Determine the percent of theoretical air.

SOLUTION

Known: A natural gas with a specified molar analysis burns with dry air, giving products having a known molar analysis on a dry basis.

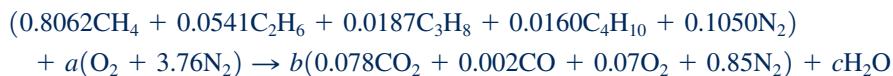
Find: Determine the air-fuel ratio on a molar basis, the amount of products in kmol that would be formed from 100 m³ of natural gas at 300 K and 1 bar, and the percent of theoretical air.

Engineering Model:

1. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
2. The fuel mixture can be modeled as an ideal gas.

Analysis:

(a) The solution can be conducted on the basis of an assumed amount of fuel mixture or on the basis of an assumed amount of dry products. Let us illustrate the first procedure, basing the solution on 1 kmol of fuel mixture. The chemical equation then takes the form



The products consist of b kmol of dry products and c kmol of water vapor, each per kmol of fuel mixture. Applying conservation of mass to carbon

$$b(0.078 + 0.002) = 0.8062 + 2(0.0541) + 3(0.0187) + 4(0.0160)$$

Solving gives $b = 12.931$. Conservation of mass for hydrogen results in

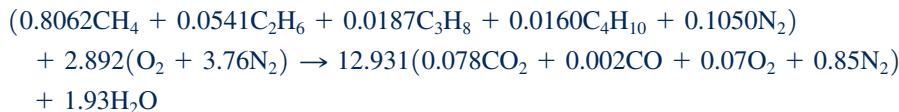
$$2c = 4(0.8062) + 6(0.0541) + 8(0.0187) + 10(0.0160)$$

which gives $c = 1.93$. The unknown coefficient a can be found from either an oxygen balance or a nitrogen balance. Applying conservation of mass to oxygen

$$12.931[2(0.078) + 0.002 + 2(0.07)] + 1.93 = 2a$$

① giving $a = 2.892$.

The balanced chemical equation is then



The air-fuel ratio on a molar basis is

$$\overline{AF} = \frac{(2.892)(4.76)}{1} = 13.77 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

(b) By inspection of the chemical reaction equation, the total amount of products is $b + c = 12.931 + 1.93 = 14.861$ kmol of products per kmol of fuel. The amount of fuel in kmol, n_F , present in 100 m³ of fuel mixture

- at 300 K and 1 bar can be determined from the ideal gas equation of state as

$$n_F = \frac{pV}{RT}$$

$$= \frac{(10^5 \text{ N/m}^2)(100 \text{ m}^3)}{(8314 \text{ N} \cdot \text{m/kmol} \cdot \text{K})(300 \text{ K})} = 4.01 \text{ kmol (fuel)}$$

Accordingly, the amount of product mixture that would be formed from 100 m³ of fuel mixture is (14.861)(4.01) = 59.59 kmol of product gas.

- (c) The balanced chemical equation for the complete combustion of the fuel mixture with the *theoretical amount* of air is



The theoretical air–fuel ratio on a molar basis is

$$(\overline{AF})_{\text{theo}} = \frac{2(4.76)}{1} = 9.52 \frac{\text{kmol (air)}}{\text{kmol (fuel)}}$$

The percent theoretical air is then

$$\% \text{ theoretical air} = \frac{13.77 \text{ kmol (air)/kmol (fuel)}}{9.52 \text{ kmol (air)/kmol (fuel)}} = 1.45 (145\%)$$

- 1 A check on both the accuracy of the given molar analyses and the calculations conducted to determine the unknown coefficients is obtained by applying conservation of mass to nitrogen. The amount of nitrogen in the reactants is

$$0.105 + (3.76)(2.892) = 10.98 \text{ kmol/kmol of fuel}$$

The amount of nitrogen in the products is (0.85)(12.931) = 10.99 kmol/kmol of fuel. The difference can be attributed to round-off.

Skills Developed

Ability to...

- balance a chemical reaction equation for incomplete combustion of a fuel mixture given the analysis of dry products of combustion.
- apply the definition of air-fuel ratio on a molar basis as well as percent theoretical air.

QuickQUIZ

Determine the mole fractions of the products of combustion.

Ans. $y_{\text{CO}_2} = 0.0679$, $y_{\text{CO}} = 0.0017$, $y_{\text{O}_2} = 0.0609$, $y_{\text{N}_2} = 0.7396$, $y_{\text{H}_2\text{O}} = 0.1299$.

13.1.4 Energy and Entropy Balances for Reacting Systems

Thus far our study of reacting systems has involved only the conservation of mass principle. A more complete understanding of reacting systems requires application of the first and second laws of thermodynamics. For these applications, energy and entropy balances play important roles, respectively. Energy balances for reacting systems are developed and applied in Secs. 13.2 and 13.3; entropy balances for reacting systems are the subject of Sec. 13.5. To apply such balances, it is necessary to take special care in how internal energy, enthalpy, and entropy are evaluated.

For the energy and entropy balances of this chapter, combustion air and (normally) products of combustion are modeled as ideal gas mixtures. Accordingly, ideal gas mixture principles introduced in the first part of Chap. 12 play a role. For ease of reference, Table 13.1 summarizes ideal gas mixture relations introduced in Chap. 12 that are used in this chapter.

TABLE 13.1**Internal Energy, Enthalpy, and Entropy for Ideal Gas Mixtures**

Notation: n_i = moles of gas i , y_i = mole fraction of gas i

T = mixture temperature, p = mixture pressure

$p_i = y_i p$ = partial pressure of gas i

\bar{u}_i = specific internal energy of gas i , per mole of i

\bar{h}_i = specific enthalpy of gas i , per mole of i

\bar{s}_i = specific entropy of gas i , per mole of i

Mixture internal energy:

$$U = n_1 \bar{u}_1 + n_2 \bar{u}_2 + \cdots + n_j \bar{u}_j = \sum_{i=1}^j n_i \bar{u}_i(T) \quad (12.19)$$

Mixture enthalpy:

$$H = n_1 \bar{h}_1 + n_2 \bar{h}_2 + \cdots + n_j \bar{h}_j = \sum_{i=1}^j n_i \bar{h}_i(T) \quad (12.20)$$

Mixture entropy:

$$S = n_1 \bar{s}_1 + n_2 \bar{s}_2 + \cdots + n_j \bar{s}_j = \sum_{i=1}^j n_i \bar{s}_i(T, p_i) \quad (12.26)$$

► With Eq. 6.18:

$$\begin{aligned} \bar{s}_i(T, p_i) &= \bar{s}_i(T, p) - \bar{R} \ln \frac{p_i}{p} \\ &= \bar{s}_i(T, p) - \bar{R} \ln y_i \end{aligned} \quad (a)$$

► With Eq. 6.18 and $p_{\text{ref}} = 1 \text{ atm}$:

$$\begin{aligned} \bar{s}_i(T, p_i) &= \bar{s}_i(T, p_{\text{ref}}) - \bar{R} \ln \frac{p_i}{p_{\text{ref}}} \\ &= \bar{s}_i^\circ(T) - \bar{R} \ln \frac{y_i p}{p_{\text{ref}}} \end{aligned} \quad (b)^1$$

where \bar{s}_i° is obtained from Table A-23 and A-23E, as appropriate.

¹Equation (b) corresponds to Eq. 13.23.

13.2**Conservation of Energy—Reacting Systems**

The objective of the present section is to illustrate the application of the conservation of energy principle to reacting systems. The forms of the conservation of energy principle introduced previously remain valid whether or not a chemical reaction occurs within the system. However, the methods used for evaluating the properties of reacting systems differ somewhat from the practices used to this point.

13.2.1 Evaluating Enthalpy for Reacting Systems

In most tables of thermodynamic properties used thus far, values for the specific internal energy, enthalpy, and entropy are given relative to some arbitrary datum state where the enthalpy (or alternatively the internal energy) and entropy are set to zero. This approach is satisfactory for evaluations involving *differences* in property values between states of the same composition, for then arbitrary datums cancel. However,

TAKE NOTE...

When applying energy and entropy balances to reacting systems, it is necessary to take special care in how internal energy, enthalpy, and entropy are evaluated.

standard reference state**enthalpy of formation**

when a chemical reaction occurs, reactants disappear and products are formed, so differences cannot be calculated for all substances involved. For reacting systems, it is necessary to evaluate h , u , and s in such a way that there are no subsequent ambiguities or inconsistencies in evaluating properties. In this section, we will consider how this is accomplished for h and u . The case of entropy is handled differently and is taken up in Sec. 13.5.

An enthalpy datum for the study of reacting systems can be established by assigning arbitrarily a value of zero to the enthalpy of the *stable elements* at a state called the **standard reference state** and defined by $T_{\text{ref}} = 298.15 \text{ K}$ (25°C) and $p_{\text{ref}} = 1 \text{ atm}$. In English units the temperature at the standard reference state is closely 537°R (77°F). Note that only *stable* elements are assigned a value of zero enthalpy at the standard state. The term stable simply means that the particular element is in a chemically stable form. For example, at the standard state the stable forms of hydrogen, oxygen, and nitrogen are H_2 , O_2 , and N_2 and not the monatomic H , O , and N . No ambiguities or conflicts result with this choice of datum.

ENTHALPY OF FORMATION. Using the datum introduced above, enthalpy values can be assigned to *compounds* for use in the study of reacting systems. The enthalpy of a compound at the standard state equals its *enthalpy of formation*, symbolized \bar{h}_f° . The **enthalpy of formation** is the energy released or absorbed when the compound is formed from its elements, the compound and elements all being at T_{ref} and p_{ref} . The enthalpy of formation is usually determined by application of procedures from statistical thermodynamics using observed spectroscopic data.

The enthalpy of formation also can be found in principle by measuring the heat transfer in a reaction in which the compound is formed from the elements.

► **FOR EXAMPLE** consider the simple reactor shown in Fig. 13.1, in which carbon and oxygen each enter at T_{ref} and p_{ref} and react completely at steady state to form carbon dioxide at the same temperature and pressure. Carbon dioxide is *formed* from carbon and oxygen according to



This reaction is *exothermic*, so for the carbon dioxide to exit at the same temperature as the entering elements, there would be a heat transfer from the reactor to its surroundings. The rate of heat transfer and the enthalpies of the incoming and exiting streams are related by the energy rate balance

$$0 = \dot{Q}_{\text{cv}} + \dot{m}_{\text{C}}h_{\text{C}} + \dot{m}_{\text{O}_2}h_{\text{O}_2} - \dot{m}_{\text{CO}_2}h_{\text{CO}_2}$$

where \dot{m} and h denote, respectively, mass flow rate and specific enthalpy. In writing this equation, we have assumed no work \dot{W}_{cv} and negligible effects of kinetic and potential energy. For enthalpies on a molar basis, the energy rate balance appears as

$$0 = \dot{Q}_{\text{cv}} + \dot{n}_{\text{C}}\bar{h}_{\text{C}} + \dot{n}_{\text{O}_2}\bar{h}_{\text{O}_2} - \dot{n}_{\text{CO}_2}\bar{h}_{\text{CO}_2}$$

where \dot{n} and \bar{h} denote, respectively, the molar flow rate and specific enthalpy per mole. Solving for the specific enthalpy of carbon dioxide and noting from Eq. 13.6 that all molar flow rates are equal

$$\bar{h}_{\text{CO}_2} = \frac{\dot{Q}_{\text{cv}}}{\dot{n}_{\text{CO}_2}} + \frac{\dot{n}_{\text{C}}}{\dot{n}_{\text{CO}_2}}\bar{h}_{\text{C}} + \frac{\dot{n}_{\text{O}_2}}{\dot{n}_{\text{CO}_2}}\bar{h}_{\text{O}_2} = \frac{\dot{Q}_{\text{cv}}}{\dot{n}_{\text{CO}_2}} + \bar{h}_{\text{C}} + \bar{h}_{\text{O}_2} \quad (13.7)$$

Since carbon and oxygen are stable elements at the standard state, $\bar{h}_{\text{C}} = \bar{h}_{\text{O}_2} = 0$, and Eq. 13.7 becomes

$$\bar{h}_{\text{CO}_2} = \frac{\dot{Q}_{\text{cv}}}{\dot{n}_{\text{CO}_2}} \quad (13.8)$$

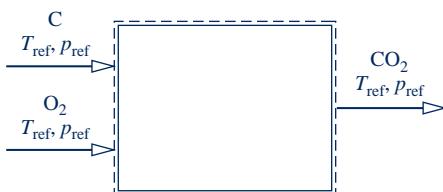


Fig. 13.1 Reactor used to discuss the enthalpy of formation concept.

Accordingly, the value assigned to the specific enthalpy of carbon dioxide at the standard state, the enthalpy of formation, equals the heat transfer,

per mole of CO₂, between the reactor and its surroundings. If the heat transfer could be measured accurately, it would be found to equal -393,520 kJ per kmol of carbon dioxide formed (-169,300 Btu per lbmol of CO₂ formed). ◀◀◀◀◀

Tables A-25 and A-25E give values of the enthalpy of formation for several compounds in units of kJ/kmol and Btu/lbmol, respectively. In this text, the superscript ° is used to denote properties at 1 atm. For the case of the enthalpy of formation, the reference temperature T_{ref} is also intended by this symbol. The values of \bar{h}_f° listed in Tables A-25 and A-25E for CO₂ correspond to those given in the previous example.

The sign associated with the enthalpy of formation values appearing in Tables A-25 corresponds to the sign convention for heat transfer. If there is heat transfer *from* a reactor in which a compound is formed from its elements (an *exothermic* reaction as in the previous example), the enthalpy of formation has a negative sign. If a heat transfer *to* the reactor is required (an *endothermic* reaction), the enthalpy of formation is positive.

Evaluating Enthalpy

The specific enthalpy of a compound at a state other than the standard state is found by adding the specific enthalpy change $\Delta\bar{h}$ between the standard state and the state of interest to the enthalpy of formation

$$\bar{h}(T, p) = \bar{h}_f^\circ + [\bar{h}(T, p) - \bar{h}(T_{\text{ref}}, p_{\text{ref}})] = \bar{h}_f^\circ + \Delta\bar{h} \quad (13.9)$$

That is, the enthalpy of a compound is composed of \bar{h}_f° , associated with the formation of the compound from its elements, and $\Delta\bar{h}$, associated with a change of state at constant composition. An arbitrary choice of datum can be used to determine $\Delta\bar{h}$, since it is a *difference* at constant composition. Accordingly, $\Delta\bar{h}$ can be evaluated from tabular sources such as the steam tables, the ideal gas tables when appropriate, and so on. Note that as a consequence of the enthalpy datum adopted for the stable elements, the specific enthalpy determined from Eq. 13.9 is often negative.

Tables A-25 provide two values of the enthalpy of formation of water: $\bar{h}_f^\circ(1)$, $\bar{h}_f^\circ(g)$. The first is for liquid water and the second is for water vapor. Under equilibrium conditions, water exists only as a liquid at 25°C (77°F) and 1 atm. The vapor value listed is for a *hypothetical* ideal gas state in which water is a vapor at 25°C (77°F) and 1 atm. The difference between the two enthalpy of formation values is given closely by the enthalpy of vaporization \bar{h}_{fg} at T_{ref} . That is,

$$\bar{h}_f^\circ(g) - \bar{h}_f^\circ(1) \approx \bar{h}_{fg}(25^\circ\text{C}) \quad (13.10)$$

Similar considerations apply to other substances for which liquid and vapor values for \bar{h}_f° are listed in Tables A-25.

TAKE NOTE...

When applying Eq. 13.9 to water vapor, we use the vapor value of the enthalpy of formation of water, $\bar{h}_f^\circ(g)$, from Tables A-25 together with $\Delta\bar{h}$ for water vapor from Tables A-23.

13.2.2 Energy Balances for Reacting Systems

Several considerations enter when writing energy balances for systems involving combustion. Some of these apply generally, without regard for whether combustion takes place. For example, it is necessary to consider if significant work and heat transfers take place and if the respective values are known or unknown. Also, the effects of kinetic and potential energy must be assessed. Other considerations are related directly to the occurrence of combustion. For example, it is important to know the state of the fuel before combustion occurs. Whether the fuel is a liquid, a gas, or a solid is important. It is also necessary to consider whether the fuel is premixed with the combustion air or the fuel and air enter a reactor separately.

The state of the combustion products also must be assessed. For instance, the presence of water vapor should be noted, for some of the water present will condense if the products are cooled sufficiently. The energy balance must then be written to account for the presence of water in the products as both a liquid and a vapor. For cooling of combustion products at constant pressure, the dew point temperature method of Example 13.2 is used to determine the temperature at the onset of condensation.

Analyzing Control Volumes at Steady State

To illustrate the many considerations involved when writing energy balances for reacting systems, we consider special cases of broad interest, highlighting the underlying assumptions. Let us begin by considering the steady-state reactor shown in Fig. 13.2, in which a hydrocarbon fuel C_aH_b burns completely with the theoretical amount of air according to



The fuel enters the reactor in a stream separate from the combustion air, which is regarded as an ideal gas mixture. The products of combustion also are assumed to form an ideal gas mixture. Kinetic and potential energy effects are ignored.

With the foregoing idealizations, the mass and energy rate balances for the two-inlet, single-exit reactor can be used to obtain the following equation on a *per mole of fuel basis*:

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \underbrace{\left[a\bar{h}_{CO_2} + \frac{b}{2}\bar{h}_{H_2O} + \left(a + \frac{b}{4}\right)3.76\bar{h}_{N_2}\right]}_{-\bar{h}_F} - \underbrace{\left[\left(a + \frac{b}{4}\right)\bar{h}_{O_2} + \left(a + \frac{b}{4}\right)3.76\bar{h}_{N_2}\right]}_{-\bar{h}_R} \quad (13.12a)$$

where \dot{n}_F denotes the molar flow rate of the fuel. Note that each coefficient on the right side of this equation is the same as the coefficient of the corresponding substance in the reaction equation.

The first underlined term on the right side of Eq. 13.12a is the enthalpy of the exiting gaseous products of combustion *per mole of fuel*. The second underlined term on the right side is the enthalpy of the combustion air *per mole of fuel*. In accord with Table 13.1, the enthalpies of the combustion products and the air have been evaluated by adding the contribution of each component present in the respective ideal gas mixtures. The symbol \bar{h}_F denotes the molar enthalpy of the fuel.

Equation 13.12a can be expressed more concisely as

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \bar{h}_P - \bar{h}_R \quad (13.12b)$$

where \bar{h}_P and \bar{h}_R denote, respectively, the enthalpies of the products and reactants per mole of fuel.

EVALUATING ENTHALPY TERMS. Once the energy balance has been written, the next step is to evaluate the individual enthalpy terms. Since each component of

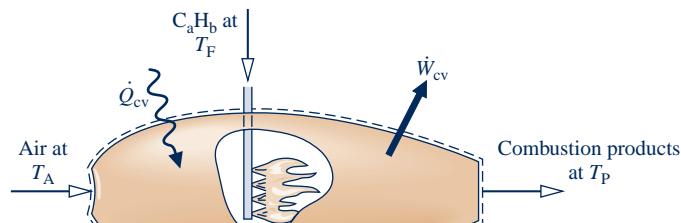


Fig. 13.2 Reactor at steady state.

the combustion products is assumed to behave as an ideal gas, its contribution to the enthalpy of the products depends solely on the temperature of the products, T_p . Accordingly, for each component of the products, Eq. 13.9 takes the form

$$\bar{h} = \bar{h}_f^\circ + [\bar{h}(T_p) - \bar{h}(T_{ref})] \quad (13.13)$$

In Eq. 13.13, \bar{h}_f° is the enthalpy of formation from Table A-25 or A-25E, as appropriate. The second term accounts for the change in enthalpy from the temperature T_{ref} to the temperature T_p . For several common gases, this term can be evaluated from tabulated values of enthalpy versus temperature in Tables A-23 and A-23E, as appropriate. Alternatively, the term can be obtained by integration of the ideal gas specific heat \bar{c}_p obtained from Tables A-21 or some other source of data.

A similar approach is employed to evaluate the enthalpies of the oxygen and nitrogen in the combustion air. For these

$$\bar{h} = \bar{h}_f^\circ + [\bar{h}(T_A) - \bar{h}(T_{ref})] \quad (13.14)$$

where T_A is the temperature of the air entering the reactor. Note that the enthalpy of formation for oxygen and nitrogen is zero by definition and thus drops out of Eq. 13.14 as indicated.

The evaluation of the enthalpy of the fuel is also based on Eq. 13.9. If the fuel can be modeled as an ideal gas, the fuel enthalpy is obtained using an expression of the same form as Eq. 13.13, with the temperature of the incoming fuel replacing T_p .

With the foregoing considerations, Eq. 13.12a takes the form

$$\begin{aligned} \frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} &= a(\bar{h}_f^\circ + \Delta\bar{h})_{CO_2} + \frac{b}{2}(\bar{h}_f^\circ + \Delta\bar{h})_{H_2O} + \left(a + \frac{b}{4}\right)3.76(\bar{h}_f^\circ + \Delta\bar{h})_{N_2} \\ &- (\bar{h}_f^\circ + \Delta\bar{h})_F - \left(a + \frac{b}{4}\right)(\bar{h}_f^\circ + \Delta\bar{h})_{O_2} - \left(a + \frac{b}{4}\right)3.76(\bar{h}_f^\circ + \Delta\bar{h})_{N_2} \end{aligned} \quad (13.15a)$$

The terms set to zero in this expression are the enthalpies of formation of oxygen and nitrogen.

Equation 13.15a can be written more concisely as

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \sum_P n_e (\bar{h}_f^\circ + \Delta\bar{h})_e - \sum_R n_i (\bar{h}_f^\circ + \Delta\bar{h})_i \quad (13.15b)$$

where i denotes the incoming fuel and air streams and e the exiting combustion products.

Although Eqs. 13.15 have been developed with reference to the reaction of Eq. 13.11, equations having the same general forms would be obtained for other combustion reactions.

In Examples 13.4 and 13.5, the energy balance is applied together with tabular property data to analyze control volumes at steady state involving combustion. Example 13.4 involves a reciprocating internal combustion engine while Example 13.5 involves a simple gas turbine power plant.

TAKE NOTE...

The coefficients n_i and n_e of Eq. 13.15b correspond to the respective coefficients of the reaction equation giving the moles of reactants and products per mole of fuel, respectively.

EXAMPLE 13.4

Analyzing an Internal Combustion Engine Fueled with Liquid Octane

Liquid octane enters an internal combustion engine operating at steady state with a mass flow rate of 0.004 lb/s and is mixed with the theoretical amount of air. The fuel and air enter the engine at 77°F and 1 atm. The mixture burns completely and combustion products leave the engine at 1140°F. The engine develops a power output of 50 horsepower. Determine the rate of heat transfer from the engine, in Btu/s, neglecting kinetic and potential energy effects.

SOLUTION

Known: Liquid octane and the theoretical amount of air enter an internal combustion engine operating at steady state in separate streams at 77°F, 1 atm. Combustion is complete and the products exit at 1140°F. The power developed by the engine and fuel mass flow rate are specified.

Find: Determine the rate of heat transfer from the engine, in Btu/s.

Schematic and Given Data:

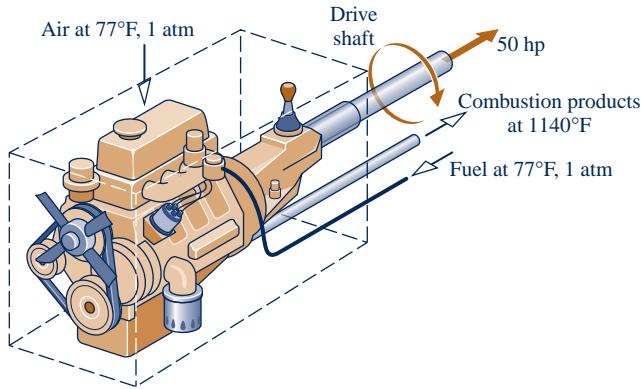


Fig. E13.4

Analysis: The balanced chemical equation for complete combustion with the theoretical amount of air is obtained from the solution to Example 13.1 as



The energy rate balance reduces, with assumptions 1–3, to give

$$\begin{aligned} \frac{\dot{Q}_{cv}}{\dot{n}_F} &= \frac{\dot{W}_{cv}}{\dot{n}_F} + \bar{h}_P - \bar{h}_R \\ &= \frac{\dot{W}_{cv}}{\dot{n}_F} + \{8[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{CO}_2} + 9[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{H}_2\text{O(g)}} + 47[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{N}_2}\} \\ &\quad - \{[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{C}_8\text{H}_{18(l)}} + 12.5[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{O}_2} + 47[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{N}_2}\} \end{aligned} \quad (1)$$

where each coefficient is the same as the corresponding term of the balanced chemical equation and Eq. 13.9 has been used to evaluate enthalpy terms. The enthalpy of formation terms for oxygen and nitrogen are zero; and $\Delta\bar{h} = 0$ for each of the reactants because the fuel and combustion air enter at 77°F.

With the enthalpy of formation for $\text{C}_8\text{H}_{18(l)}$ from Table A-25E

$$\bar{h}_R = (\bar{h}_f^\circ)_{\text{C}_8\text{H}_{18(l)}} = -107,530 \text{ Btu/lbmol(fuel)}$$

With enthalpy of formation values for CO_2 and $\text{H}_2\text{O(g)}$ from Table A-25E, and enthalpy values for N_2 , H_2O , and CO_2 from Table A-23E

$$\begin{aligned} \bar{h}_P &= 8[-169,300 + (15,829 - 4027.5)] + 9[-104,040 + (13,494.4 - 4258)] \\ &\quad + 47[11,409.7 - 3729.5] \\ &= -1,752,251 \text{ Btu/lbmol(fuel)} \end{aligned}$$

Using the molecular weight of the fuel from Table A-1E, the molar flow rate of the fuel is

$$\dot{n}_F = \frac{0.004 \text{ lb(fuel)}/\text{s}}{114.22 \text{ lb(fuel)}/\text{lbtmol(fuel)}} = 3.5 \times 10^{-5} \text{ lbmol(fuel)}/\text{s}$$

Engineering Model:

1. The control volume identified by a dashed line on the accompanying figure operates at steady state.
2. Kinetic and potential energy effects can be ignored.
3. The combustion air and the products of combustion each form ideal gas mixtures.
4. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen. The nitrogen is inert and combustion is complete.

Inserting values into the expression for the rate of heat transfer

$$\begin{aligned}\dot{Q}_{cv} &= \dot{W}_{cv} + \dot{n}_F(\bar{h}_P - \bar{h}_R) \\ &= (50 \text{ hp}) \left| \frac{2545 \text{ Btu/h}}{1 \text{ hp}} \right| \left| \frac{1 \text{ h}}{3600 \text{ s}} \right| \\ &\quad + \left[3.5 \times 10^{-5} \frac{\text{lbmol(fuel)}}{\text{s}} \right] [-1,752,251 - (-107,530)] \frac{\text{Btu}}{\text{lbmol(fuel)}} \\ &= -22.22 \text{ Btu/s}\end{aligned}$$

- ① These expressions correspond to Eqs. 13.12b and 13.15b, respectively.



Skills Developed

Ability to...

- balance a chemical reaction equation for complete combustion of octane with theoretical air.
- apply the control volume energy balance to a reacting system.
- evaluate enthalpy values appropriately.

QuickQUIZ

If the density of octane is 5.88 lb/gal, how many gallons of fuel would be used in 2 h of continuous operation of the engine? **Ans.** 4.9 gal.

EXAMPLE 13.5

Analyzing a Gas Turbine Fueled with Methane

Methane (CH_4) at 25°C , enters the combustor of a simple open gas turbine power plant and burns completely with 400% of theoretical air entering the compressor at 25°C , 1 atm. Products of combustion exit the turbine at 730 K, 1 atm. The rate of heat transfer from the power plant is estimated as 3% of the net power developed. Determine the net power developed, in MW, if the fuel mass flow rate is 20 kg/min. For the entering air and exiting combustion products, kinetic and potential energy effects are negligible.

SOLUTION

Known: Steady-state operating data are provided for a simple gas turbine power plant.

Find: The net power developed, in MW, for a given fuel mass flow rate.

Schematic and Given Data:

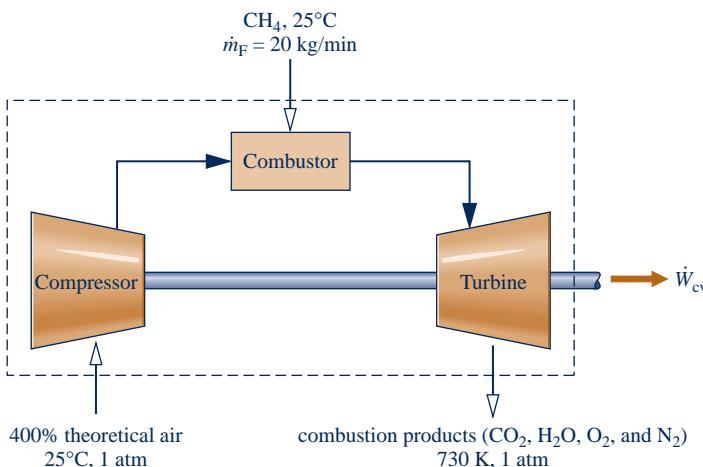


Fig. E13.5

Analysis: The balanced chemical equation for complete combustion of methane with the theoretical amount of air is given by Eq. 13.4



Engineering Model:

1. The control volume identified by a dashed line on the accompanying figure operates at steady state.
2. Kinetic and potential energy effects can be ignored where mass enters and exits the control volume.
3. The ideal gas model is applicable to the fuel; the combustion air and the products of combustion each form ideal gas mixtures.
4. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert. Combustion is complete.

For combustion of fuel with 400% theoretical air



Applying conservation of mass to carbon, hydrogen, oxygen, and nitrogen, respectively

$$\begin{aligned} \text{C:} \quad & 1 = a \\ \text{H:} \quad & 4 = 2b \\ \text{O:} \quad & (4.0)(2)(2) = 2a + b + 2c \\ \text{N:} \quad & (4.0)(2)(3.76)(2) = 2d \end{aligned}$$

Solving these equations, $a = 1$, $b = 2$, $c = 6$, $d = 30.08$.

The balanced chemical equation for complete combustion of the fuel with 400% of theoretical air is



The energy rate balance reduces, with assumptions 1–3, to give

$$1 \quad 0 = \frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} + \bar{h}_R - \bar{h}_P$$

Since the rate of heat transfer from the power plant is 3% of the net power developed, we have $\dot{Q}_{cv} = -0.03\dot{W}_{cv}$. Accordingly, the energy rate balance becomes

$$\frac{1.03\dot{W}_{cv}}{\dot{n}_F} = \bar{h}_R - \bar{h}_P$$

Evaluating terms, we get

$$\begin{aligned} \frac{1.03\dot{W}_{cv}}{\dot{n}_F} &= \{[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{CH}_4}^0 + 8[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{O}_2}^0 + 30.08[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{N}_2}^0\} \\ &\quad - \{[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{CO}_2} + 2[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{H}_2\text{O(g)}} + 6[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{O}_2} + 30.08[\bar{h}_f^\circ + \Delta\bar{h}]_{\text{N}_2}\} \end{aligned}$$

where each coefficient is the same as the corresponding term of the balanced chemical equation and Eq. 13.9 has been used to evaluate enthalpy terms. The enthalpy of formation terms for oxygen and nitrogen are zero; and $\Delta\bar{h} = 0$ for each of the reactants because the fuel and combustion air enter at 25°C.

With the enthalpy of formation for $\text{CH}_4(\text{g})$ from Table A-25

$$2 \quad \bar{h}_R = (\bar{h}_f^\circ)_{\text{CH}_4(\text{g})} = -74,850 \text{ kJ/kmol(fuel)}$$

With enthalpy of formation values for CO_2 and $\text{H}_2\text{O(g)}$ from Table A-25, and enthalpy values for CO_2 , H_2O , O_2 , and N_2 at 730 K and 298 K from Table A-23

$$\begin{aligned} \bar{h}_P &= [-393,520 + 28,622 - 9,364] + 2[-241,820 + 25,218 - 9,904] \\ &\quad + 6[22,177 - 8,682] + 30.08[21,529 - 8,669] \\ \bar{h}_P &= -359,475 \text{ kJ/kmol(fuel)} \end{aligned}$$

Using the molecular weight of methane from Table A-1, the molar flow rate of the fuel is

$$\dot{n}_F = \frac{\dot{m}_F}{M_F} = \frac{20 \text{ kg(fuel)}/\text{min}}{16.04 \text{ kg(fuel)}/\text{kmol(fuel)}} \left| \frac{1 \text{ min}}{60 \text{ s}} \right| = 0.02078 \text{ kmol(fuel)}/\text{s}$$

Inserting values into the expression for the power

$$\begin{aligned} \dot{W}_{cv} &= \frac{\dot{n}_F(\bar{h}_R - \bar{h}_P)}{1.03} \\ \dot{W}_{cv} &= \frac{\left(0.02078 \frac{\text{kmol(fuel)}}{\text{s}}\right) [-74,850 - (-359,475)] \frac{\text{kJ}}{\text{kmol(fuel)}}}{1.03} \left| \frac{1 \text{ MW}}{10^3 \frac{\text{kJ}}{\text{s}}} \right| = 5.74 \text{ MW} \end{aligned}$$

The positive sign indicates power is *from* the control volume.

- 1 This expression corresponds to Eq. 13.12b.
- 2 In the combustor, fuel is injected into air at a pressure greater than 1 atm because combustion air pressure has been increased in passing through the compressor. Still, since ideal gas behavior is assumed for the fuel, the fuel enthalpy is determined only by its temperature, 25°C.

QuickQUIZ

Determine the net power developed, in MW, if the rate of heat transfer from the power plant is 10% of the net power developed.

Ans. 5.38 MW.



Skills Developed

Ability to...

- balance a chemical reaction equation for complete combustion of methane with 400% of theoretical air.
- apply the control volume energy balance to a reacting system.
- evaluate enthalpy values appropriately.

Analyzing Closed Systems

Let us consider next a closed system involving a combustion process. In the absence of kinetic and potential energy effects, the appropriate form of the energy balance is

$$U_P - U_R = Q - W$$

where U_R denotes the internal energy of the reactants and U_P denotes the internal energy of the products.

If the reactants and products form ideal gas mixtures, the energy balance can be expressed as

$$\sum_P n \bar{u} - \sum_R n \bar{u} = Q - W \quad (13.16)$$

where the coefficients n on the left side are the coefficients of the reaction equation giving the moles of each reactant or product.

Since each component of the reactants and products behaves as an ideal gas, the respective specific internal energies of Eq. 13.16 can be evaluated as $\bar{u} = \bar{h} - \bar{R}T$, so the equation becomes

$$Q - W = \sum_P n(\bar{h} - \bar{R}T_P) - \sum_R n(\bar{h} - \bar{R}T_R) \quad (13.17a)$$

where T_P and T_R denote the temperature of the products and reactants, respectively. With expressions of the form of Eq. 13.13 for each of the reactants and products, Eq. 13.17a can be written alternatively as

$$\begin{aligned} Q - W &= \sum_P n(\bar{h}_f^o + \Delta\bar{h} - \bar{R}T_P) - \sum_R n(\bar{h}_f^o + \Delta\bar{h} - \bar{R}T_R) \\ &= \sum_P n(\bar{h}_f^o + \Delta\bar{h}) - \sum_R n(\bar{h}_f^o + \Delta\bar{h}) - \bar{R}T_P \sum_P n + \bar{R}T_R \sum_R n \end{aligned} \quad (13.17b)$$

The enthalpy of formation terms are obtained from Table A-25 or Table A-25E. The $\Delta\bar{h}$ terms are evaluated from Table A-23 or Table A-23E.

The foregoing concepts are illustrated in Example 13.6, where a gaseous mixture burns in a closed, rigid container.

EXAMPLE 13.6**Analyzing Combustion of Methane with Oxygen at Constant Volume**

A mixture of 1 kmol of gaseous methane and 2 kmol of oxygen initially at 25°C and 1 atm burns completely in a closed, rigid container. Heat transfer occurs until the products are cooled to 900 K. If the reactants and products each form ideal gas mixtures, determine (a) the amount of heat transfer, in kJ, and (b) the final pressure, in atm.

SOLUTION

Known: A mixture of gaseous methane and oxygen, initially at 25°C and 1 atm, burns completely within a closed rigid container. The products are cooled to 900 K.

Find: Determine the amount of heat transfer, in kJ, and the final pressure of the combustion products, in atm.

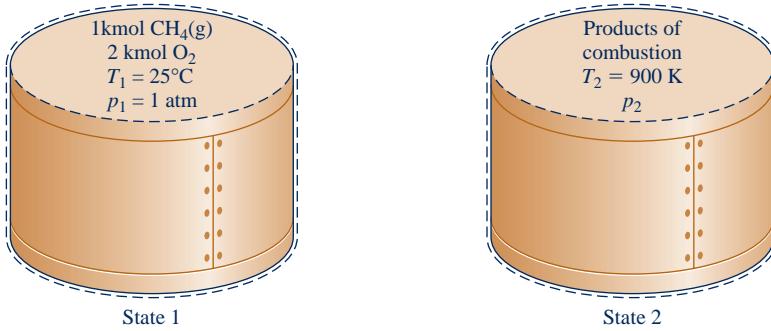
Schematic and Given Data:

Fig. E13.6

Engineering Model:

1. The contents of the closed, rigid container are taken as the system.
2. Kinetic and potential energy effects are absent, and $W = 0$.
3. Combustion is complete.
4. The initial mixture and the products of combustion each form ideal gas mixtures.
5. The initial and final states are equilibrium states.

Analysis: The chemical reaction equation for the complete combustion of methane with oxygen is



(a) With assumptions 2 and 3, the closed system energy balance takes the form

$$U_P - U_R = Q - W^0$$

or

$$Q = U_P - U_R = (\bar{u}_{\text{CO}_2} + 2\bar{u}_{\text{H}_2\text{O}(g)}) - (\bar{u}_{\text{CH}_4(g)} + 2\bar{u}_{\text{O}_2})$$

Each coefficient in this equation is the same as the corresponding term of the balanced chemical equation.

Since each reactant and product behaves as an ideal gas, the respective specific internal energies can be evaluated as $\bar{u} = \bar{h} - \bar{RT}$. The energy balance then becomes

$$Q = [1(\bar{h}_{\text{CO}_2} - \bar{RT}_2) + 2(\bar{h}_{\text{H}_2\text{O}(g)} - \bar{RT}_2)] - [1(\bar{h}_{\text{CH}_4(g)} - \bar{RT}_1) + 2(\bar{h}_{\text{O}_2} - \bar{RT}_1)]$$

where T_1 and T_2 denote, respectively, the initial and final temperatures. Collecting like terms

$$Q = (\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}(g)} - \bar{h}_{\text{CH}_4(g)} - 2\bar{h}_{\text{O}_2}) + 3\bar{R}(T_1 - T_2)$$

The specific enthalpies are evaluated in terms of the respective enthalpies of formation to give

$$\begin{aligned} ① \quad Q &= [(\bar{h}_f^\circ + \Delta\bar{h})_{\text{CO}_2} + 2(\bar{h}_f^\circ + \Delta\bar{h})_{\text{H}_2\text{O}(g)} \\ &\quad - (\bar{h}_f^\circ + \Delta\bar{h})_{\text{CH}_4(g)}^0 - 2(\bar{h}_f^\circ + \Delta\bar{h})_{\text{O}_2}^0] + 3\bar{R}(T_1 - T_2) \end{aligned}$$

Since the methane and oxygen are initially at 25°C. $\Delta\bar{h} = 0$ for each of these reactants. Also, $\bar{h}_f^\circ = 0$ for oxygen.

With enthalpy of formation values for CO₂, H₂O(g) and CH₄(g) from Table A-25 and enthalpy values for H₂O and CO₂ from Table A-23

$$\begin{aligned} Q &= [-393,520 + (37,405 - 9364)] + 2[-241,820 + (31,828 - 9904)] \\ &\quad - (-74,850) + 3(8.314)(298 - 900) \\ &= -745,436 \text{ kJ} \end{aligned}$$

(b) By assumption 4, the initial mixture and the products of combustion each form ideal gas mixtures. Thus, for the reactants

$$p_1 V = n_R \bar{R} T_1$$

where n_R is the total number of moles of reactants and p_1 is the initial pressure. Similarly, for the products

$$p_2 V = n_P \bar{R} T_2$$

where n_P is the total number of moles of products and p_2 is the final pressure.

Since $n_R = n_P = 3$ and volume is constant, these equations combine to give

$$p_2 = \frac{T_2}{T_1} p_1 = \left(\frac{900 \text{ K}}{298 \text{ K}} \right) (1 \text{ atm}) = 3.02 \text{ atm}$$

① This expression corresponds to Eq. 13.17b.



Skills Developed

Ability to...

- apply the closed system energy balance to a reacting system.
- evaluate property data appropriately.
- apply the ideal gas equation of state.

QuickQUIZ

Calculate the volume of the system, in m³. Ans. 73.36 m³.

13.2.3 Enthalpy of Combustion and Heating Values

Although the enthalpy of formation concept underlies the formulations of the energy balances for reactive systems presented thus far, the enthalpy of formation of fuels is not always tabulated.

► **FOR EXAMPLE** fuel oil and coal are normally composed of several individual chemical substances, the relative amounts of which may vary considerably, depending on the source. Owing to the wide variation in composition that these fuels can exhibit, we do not find their enthalpies of formation listed in Tables A-25 or similar compilations of thermophysical data. ◀◀◀◀◀

In many cases of practical interest, however, the *enthalpy of combustion*, which is accessible experimentally, can be used to conduct an energy analysis when enthalpy of formation data are lacking.

The **enthalpy of combustion** \bar{h}_{RP} is defined as the difference between the enthalpy of the products and the enthalpy of the reactants when *complete* combustion occurs at a *given temperature and pressure*. That is

$$\bar{h}_{RP} = \sum_{\text{P}} n_e \bar{h}_e - \sum_{\text{R}} n_i \bar{h}_i \quad (13.18)$$

where the n 's correspond to the respective coefficients of the reaction equation giving the moles of reactants and products per mole of fuel. When the enthalpy of combustion is expressed on a unit mass of fuel basis, it is designated h_{RP} . Tabulated values are usually given at the standard temperature T_{ref} and pressure p_{ref} introduced in Sec. 13.2.1. The symbol \bar{h}_{RP}° or h_{RP}° is used for data at this temperature and pressure.

The *heating value* of a fuel is a positive number equal to the magnitude of the enthalpy of combustion. Two heating values are recognized by name: the **higher heating value** (HHV) and the **lower heating value** (LHV). The higher heating value is obtained when all the water formed by combustion is a liquid; the lower heating value

enthalpy of combustion

higher and lower heating values

is obtained when all the water formed by combustion is a vapor. The higher heating value exceeds the lower heating value by the energy that would be released were all water in the products condensed to liquid. Values for the HHV and LHV also depend on whether the fuel is a liquid or a gas. Heating value data for several hydrocarbons are provided in Tables A-25.

The calculation of the enthalpy of combustion, and the associated heating value, using table data is illustrated in the next example.

EXAMPLE 13.7 ▶

Calculating Enthalpy of Combustion of Methane

Calculate the enthalpy of combustion of gaseous methane, in kJ per kg of fuel, (a) at 25°C, 1 atm with liquid water in the products, (b) at 25°C, 1 atm with water vapor in the products. (c) Repeat part (b) at 1000 K, 1 atm.

SOLUTION

Known: The fuel is gaseous methane.

Find: Determine the enthalpy of combustion, in kJ per kg of fuel, (a) at 25°C, 1 atm with liquid water in the products, (b) at 25°C, 1 atm with water vapor in the products, (c) at 1000 K, 1 atm with water vapor in the products.

Engineering Model:

1. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
2. Combustion is complete, and both reactants and products are at the same temperature and pressure.
3. The ideal gas model applies for methane, the combustion air, and the gaseous products of combustion.

Analysis: The combustion equation is obtained from Eq. 13.4



Using Eq. 13.9 in Eq. 13.18, the enthalpy of combustion is

$$\bar{h}_{RP} = \sum_P n_e (\bar{h}_f^\circ + \Delta\bar{h})_e - \sum_R n_i (\bar{h}_f^\circ + \Delta\bar{h})_i$$

Introducing the coefficients of the combustion equation and evaluating the specific enthalpies in terms of the respective enthalpies of formation

$$\begin{aligned}\bar{h}_{RP} &= \bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}} - \bar{h}_{\text{CH}_4(\text{g})} - 2\bar{h}_{\text{O}_2} \\ &= (\bar{h}_f^\circ + \Delta\bar{h})_{\text{CO}_2} + 2(\bar{h}_f^\circ + \Delta\bar{h})_{\text{H}_2\text{O}} - (\bar{h}_f^\circ + \Delta\bar{h})_{\text{CH}_4(\text{g})} - 2(\bar{h}_f^\circ + \Delta\bar{h})_{\text{O}_2}\end{aligned}$$

For nitrogen, the enthalpy terms of the reactants and products cancel. Also, the enthalpy of formation of oxygen is zero by definition. On rearrangement, the enthalpy of combustion expression becomes

$$\begin{aligned}\bar{h}_{RP} &= (\bar{h}_f^\circ)_{\text{CO}_2} + 2(\bar{h}_f^\circ)_{\text{H}_2\text{O}} - (\bar{h}_f^\circ)_{\text{CH}_4(\text{g})} + [(\Delta\bar{h})_{\text{CO}_2} + 2(\Delta\bar{h})_{\text{H}_2\text{O}} - (\Delta\bar{h})_{\text{CH}_4(\text{g})} - 2(\Delta\bar{h})_{\text{O}_2}] \\ &= \bar{h}_{RP}^\circ + [(\Delta\bar{h})_{\text{CO}_2} + 2(\Delta\bar{h})_{\text{H}_2\text{O}} - (\Delta\bar{h})_{\text{CH}_4(\text{g})} - 2(\Delta\bar{h})_{\text{O}_2}]\end{aligned}\quad (1)$$

The values for \bar{h}_{RP}° and $(\Delta\bar{h})_{\text{H}_2\text{O}}$ depend on whether the water in the products is a liquid or a vapor.

(a) Since the reactants and products are at 25°C, 1 atm in this case, the $\Delta\bar{h}$ terms drop out of Eq. (1) giving the expression for \bar{h}_{RP} . Thus, for liquid water in the products, the enthalpy of combustion is

$$\bar{h}_{RP}^\circ = (\bar{h}_f^\circ)_{\text{CO}_2} + 2(\bar{h}_f^\circ)_{\text{H}_2\text{O(l)}} - (\bar{h}_f^\circ)_{\text{CH}_4(\text{g})}$$

With enthalpy of formation values from Table A-25

$$\bar{h}_{RP}^\circ = -393,520 + 2(-285,830) - (-74,850) = -890,330 \text{ kJ/kmol(fuel)}$$

Dividing by the molecular weight of methane places this result on a unit mass of fuel basis

$$h_{RP}^{\circ} = \frac{-890,330 \text{ kJ/kmol (fuel)}}{16.04 \text{ kg (fuel)/kmol (fuel)}} = -55,507 \text{ kJ/kg (fuel)}$$

The magnitude of this value agrees with the higher heating value of methane given in Table A-25.

(b) As in part (a), the $\Delta\bar{h}$ terms drop out of the expression for \bar{h}_{RP} , Eq. (1), which for water vapor in the products reduces to \bar{h}_{RP}° , where

$$\bar{h}_{RP}^{\circ} = (\bar{h}_f^{\circ})_{CO_2} + 2(\bar{h}_f^{\circ})_{H_2O(g)} - (\bar{h}_f^{\circ})_{CH_4(g)}$$

With enthalpy of formation values from Table A-25

$$\bar{h}_{RP}^{\circ} = -393,520 + 2(-241,820) - (-74,850) = -802,310 \text{ kJ/kmol (fuel)}$$

On a unit of mass of fuel basis, the enthalpy of combustion for this case is

$$h_{RP}^{\circ} = \frac{-802,310}{16.04} = -50,019 \text{ kJ/kg (fuel)}$$

The magnitude of this value agrees with the lower heating value of methane given in Table A-25.

(c) For the case where the reactants and products are at 1000 K, 1 atm, the term \bar{h}_{RP}° in Eq. (1) giving the expression for \bar{h}_{RP} has the value determined in part (b): $\bar{h}_{RP}^{\circ} = -802,310 \text{ kJ/kmol (fuel)}$, and the $\Delta\bar{h}$ terms for O₂, H₂O(g), and CO₂ can be evaluated using specific enthalpies at 298 and 1000 K from Table A-23. The results are

$$\begin{aligned} (\Delta\bar{h})_{O_2} &= 31,389 - 8682 = 22,707 \text{ kJ/kmol} \\ (\Delta\bar{h})_{H_2O(g)} &= 35,882 - 9904 = 25,978 \text{ kJ/kmol} \\ (\Delta\bar{h})_{CO_2} &= 42,769 - 9364 = 33,405 \text{ kJ/kmol} \end{aligned}$$

For methane, the \bar{c}_p expression of Table A-21 can be used to obtain

$$\begin{aligned} \text{① } (\Delta\bar{h})_{CH_4(g)} &= \int_{298}^{1000} \bar{c}_p dT \\ &= \bar{R} \left(3.826T - \frac{3.979}{10^3} \frac{T^2}{2} + \frac{24.558}{10^6} \frac{T^3}{3} - \frac{22.733}{10^9} \frac{T^4}{4} + \frac{6.963}{10^{12}} \frac{T^5}{5} \right)_{298}^{1000} \\ &= 38,189 \text{ kJ/kmol (fuel)} \end{aligned}$$

Substituting values into the expression for the enthalpy of combustion, Eq. (1), we get

$$\begin{aligned} \bar{h}_{RP} &= -802,310 + [33,405 + 2(25,978) - 38,189 - 2(22,707)] \\ &= -800,522 \text{ kJ/kmol (fuel)} \end{aligned}$$

On a unit mass basis

$$\text{② } h_{RP} = \frac{-800,552}{16.04} = -49,910 \text{ kJ/kg (fuel)}$$

1 Using *Interactive Thermodynamics: IT*, we get 38,180 kJ/kmol (fuel).

2 Comparing the values of parts (b) and (c), the enthalpy of combustion of methane is seen to vary little with temperature. The same is true for many hydrocarbon fuels. This fact is sometimes used to simplify combustion calculations.

Skills Developed

Ability to...

- calculate the enthalpy of combustion at standard temperature and pressure.
- calculate the enthalpy of combustion at an elevated temperature and standard pressure.

QuickQUIZ

What is the lower heating value of methane, in kJ/kg (fuel) at 25°C, 1 atm? **Ans.** 50,020 kJ/kg (Table A-25).

Evaluating Enthalpy of Combustion by Calorimetry

When enthalpy of formation data are available for *all* the reactants and products, the enthalpy of combustion can be calculated directly from Eq. 13.18, as illustrated in Example 13.7. Otherwise, it must be obtained experimentally using devices known as *calorimeters*. Both constant-volume (bomb calorimeters) and flow-through devices are employed for this purpose. Consider as an illustration a reactor operating at steady state in which the fuel is burned completely with air. For the products to be returned to the same temperature as the reactants, a heat transfer from the reactor would be required. From an energy rate balance, the required heat transfer is

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} = \sum_P n_e \bar{h}_e - \sum_R n_i \bar{h}_i \quad (13.19)$$

where the symbols have the same significance as in previous discussions. The heat transfer per mole of fuel, \dot{Q}_{cv}/\dot{n}_F , would be determined from measured data. Comparing Eq. 13.19 with the defining equation, Eq. 13.18, we have $\bar{h}_{RP} = \dot{Q}_{cv}/\dot{n}_F$. In accord with the usual sign convention for heat transfer, the enthalpy of combustion would be negative.

As noted previously, the enthalpy of combustion can be used for energy analyses of reacting systems.

► FOR EXAMPLE consider a control volume at steady state in which a fuel oil reacts completely with air. The energy rate balance is given by Eq. 13.15b

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \sum_P n_e (\bar{h}_f^\circ + \Delta \bar{h})_e - \sum_R n_i (\bar{h}_f^\circ + \Delta \bar{h})_i$$

All symbols have the same significance as in previous discussions. This equation can be rearranged to read

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \underbrace{\sum_P n_e (\bar{h}_f^\circ)_e - \sum_R n_i (\bar{h}_f^\circ)_i}_{\text{Enthalpy of combustion}} + \sum_P n_e (\Delta \bar{h})_e - \sum_R n_i (\Delta \bar{h})_i$$

For a complete reaction, the underlined term is just the enthalpy of combustion \bar{h}_{RP}° , at T_{ref} and p_{ref} . Thus, the equation becomes

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \bar{h}_{RP}^\circ + \sum_P n_e (\Delta \bar{h})_e - \sum_R n_i (\Delta \bar{h})_i \quad (13.20)$$

The right side of Eq. 13.20 can be evaluated with an experimentally determined value for \bar{h}_{RP}° and $\Delta \bar{h}$ values for the reactants and products determined as discussed previously. ▲ ▲ ▲ ▲ ▲

13.3

Determining the Adiabatic Flame Temperature

Let us reconsider the reactor at steady state pictured in Fig. 13.2. In the absence of work \dot{W}_{cv} and appreciable kinetic and potential energy effects, the energy liberated on combustion is transferred from the reactor in two ways only: by energy accompanying the exiting combustion products and by heat transfer to the surroundings. The smaller the heat transfer, the greater the energy carried out with the combustion products and thus the greater the temperature of the products. The temperature that would be achieved by the products in the limit of adiabatic operation of the reactor is called the **adiabatic flame temperature** or **adiabatic combustion** temperature.

The adiabatic flame temperature can be determined by use of the conservation of mass and conservation of energy principles. To illustrate the procedure, let us suppose that the combustion air and the combustion products each form ideal gas mixtures.

Then, with the other assumptions stated previously, the energy rate balance on a per mole of fuel basis, Eq. 13.12b, reduces to the form $\bar{h}_P = \bar{h}_R$ —that is

$$\sum_P n_e \bar{h}_e = \sum_R n_i \bar{h}_i \quad (13.21a)$$

where i denotes the incoming fuel and air streams and e the exiting combustion products. With this expression, the adiabatic flame temperature can be determined using table data or computer software, as follows.

13.3.1 • Using Table Data

When using Eq. 13.9 with table data to evaluate enthalpy terms, Eq. 13.21a takes the form

$$\sum_P n_e (\bar{h}_f^\circ + \Delta \bar{h})_e = \sum_R n_i (\bar{h}_f^\circ + \Delta \bar{h})_i$$

or

$$\sum_P n_e (\Delta \bar{h})_e = \sum_R n_i (\Delta \bar{h})_i + \sum_R n_i \bar{h}_{fi}^\circ - \sum_P n_e \bar{h}_{fe}^\circ \quad (13.21b)$$

The n 's are obtained on a per mole of fuel basis from the balanced chemical reaction equation. The enthalpies of formation of the reactants and products are obtained from Table A-25 or A-25E. Enthalpy of combustion data might be employed in situations where the enthalpy of formation for the fuel is not available. Knowing the states of the reactants as they enter the reactor, the $\Delta \bar{h}$ terms for the reactants can be evaluated as discussed previously. Thus, all terms on the right side of Eq. 13.21b can be evaluated. The terms $(\Delta \bar{h})_e$ on the left side account for the changes in enthalpy of the products from T_{ref} to the unknown adiabatic flame temperature. Since the unknown temperature appears in each term of the sum on the left side of the equation, determination of the adiabatic flame temperature requires *iteration*: A temperature for the products is assumed and used to evaluate the left side of Eq. 13.21b. The value obtained is compared with the previously determined value for the right side of the equation. The procedure continues until satisfactory agreement is attained. Example 13.8 gives an illustration.

13.3.2 • Using Computer Software

Thus far we have emphasized the use of Eq. 13.9 together with table data when evaluating the specific enthalpies required by energy balances for reacting systems. Such enthalpy values also can be retrieved using *Interactive Thermodynamics: IT*. With *IT*, the quantities on the right side of Eq. 13.9 are evaluated by software, and \bar{h} data are returned *directly*.

► **FOR EXAMPLE** consider CO₂ at 500 K modeled as an ideal gas. The specific enthalpy is obtained from *IT* as follows:

$$T = 500 // K$$

$$h = h_T("CO_2", T)$$

Choosing K for the temperature unit and moles for the amount under the **Units** menu, *IT* returns $h = -3.852 \times 10^5$ kJ/kmol.

This value agrees with the value calculated from Eq. 13.9 using enthalpy data for CO₂ from Table A-23, as follows

$$\begin{aligned} \bar{h} &= \bar{h}_f^\circ + [\bar{h}(500 \text{ K}) - \bar{h}(298 \text{ K})] \\ &= -393,520 + [17,678 - 9364] \\ &= -3.852 \times 10^5 \text{ kJ/kmol} \end{aligned}$$

TAKE NOTE...

The adiabatic flame temperature can be determined iteratively using table data or *IT*. See Example 13.8.

As suggested by this discussion, *IT* is also useful for analyzing reacting systems. In particular, the equation solver and property retrieval features of *IT* allow the adiabatic flame temperature to be determined without the iteration required when using table data.

In Example 13.8, we show how the adiabatic flame temperature can be determined iteratively using table data or *Interactive Thermodynamics: IT*.

EXAMPLE 13.8

Determining the Adiabatic Flame Temperature for Complete Combustion of Liquid Octane

Liquid octane at 25°C, 1 atm enters a well-insulated reactor and reacts with air entering at the same temperature and pressure. For steady-state operation and negligible effects of kinetic and potential energy, determine the temperature of the combustion products for complete combustion with (a) the theoretical amount of air, (b) 400% theoretical air.

SOLUTION

Known: Liquid octane and air, each at 25°C and 1 atm, burn completely within a well-insulated reactor operating at steady state.

Find: Determine the temperature of the combustion products for (a) the theoretical amount of air and (b) 400% theoretical air.

Schematic and Given Data:

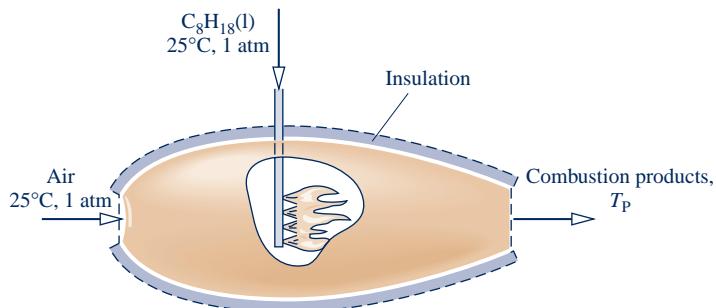


Fig. E13.8

Engineering Model:

- The control volume indicated on the accompanying figure by a dashed line operates at steady state.
- For the control volume, $\dot{Q}_{cv} = 0$, $\dot{W}_{cv} = 0$, and kinetic and potential effects are negligible.
- The combustion air and the products of combustion each form ideal gas mixtures.
- Combustion is complete.
- Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.

Analysis: At steady state, the control volume energy rate balance Eq. 13.12b reduces with assumptions 2 and 3 to give Eq. 13.21a

$$\sum_{\text{P}} n_e \bar{h}_e = \sum_{\text{R}} n_i \bar{h}_i \quad (1)$$

When Eq. 13.9 and table data are used to evaluate the enthalpy terms, Eq. (1) is written as

$$\sum_{\text{P}} n_e (\bar{h}_f^\circ + \Delta \bar{h})_e = \sum_{\text{R}} n_i (\bar{h}_f^\circ + \Delta \bar{h})_i$$

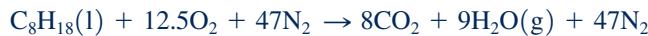
On rearrangement, this becomes

$$\sum_{\text{P}} n_e (\Delta \bar{h})_e = \sum_{\text{R}} n_i (\Delta \bar{h})_i + \sum_{\text{R}} n_i \bar{h}_{fi}^\circ - \sum_{\text{P}} n_e \bar{h}_{fe}^\circ$$

which corresponds to Eq. 13.21b. Since the reactants enter at 25°C, the $(\Delta\bar{h})_i$ terms on the right side vanish, and the energy rate equation becomes

$$\sum_{\text{P}} n_e (\Delta\bar{h})_e = \sum_{\text{R}} n_i \bar{h}_{\text{f}}^{\circ} - \sum_{\text{P}} n_e \bar{h}_{\text{f}}^{\circ} \quad (2)$$

(a) For combustion of liquid octane with the theoretical amount of air, the chemical equation is



Introducing the coefficients of this equation, Eq. (2) takes the form

$$\begin{aligned} 8(\Delta\bar{h})_{\text{CO}_2} + 9(\Delta\bar{h})_{\text{H}_2\text{O}(\text{g})} + 47(\Delta\bar{h})_{\text{N}_2} \\ = [(\bar{h}_{\text{f}}^{\circ})_{\text{C}_8\text{H}_{18}(\text{l})} + 12.5(\bar{h}_{\text{f}}^{\circ})_{\text{O}_2} + 47(\bar{h}_{\text{f}}^{\circ})_{\text{N}_2}] \\ - [8(\bar{h}_{\text{f}}^{\circ})_{\text{CO}_2} + 9(\bar{h}_{\text{f}}^{\circ})_{\text{H}_2\text{O}(\text{g})} + 47(\bar{h}_{\text{f}}^{\circ})_{\text{N}_2}] \end{aligned}$$

The right side of the above equation can be evaluated with enthalpy of formation data from Table A-25, giving

$$8(\Delta\bar{h})_{\text{CO}_2} + 9(\Delta\bar{h})_{\text{H}_2\text{O}(\text{g})} + 47(\Delta\bar{h})_{\text{N}_2} = 5,074,630 \text{ kJ/kmol(fuel)}$$

Each $\Delta\bar{h}$ term on the left side of this equation depends on the temperature of the products, T_{P} . This temperature can be determined by an iterative procedure.

The following table gives a summary of the iterative procedure for three trial values of T_{P} . Since the summation of the enthalpies of the products equals 5,074,630 kJ/kmol, the actual value of T_{P} is in the interval from 2350 to 2400 K. Interpolation between these temperatures gives $T_{\text{P}} = 2395$ K.

T_{P}	2500 K	2400 K	2350 K
$8(\Delta\bar{h})_{\text{CO}_2}$	975,408	926,304	901,816
$9(\Delta\bar{h})_{\text{H}_2\text{O}(\text{g})}$	890,676	842,436	818,478
$47(\Delta\bar{h})_{\text{N}_2}$	3,492,664	3,320,597	3,234,869
$\sum_{\text{P}} n_e (\Delta\bar{h})_e$	5,358,748	5,089,337	4,955,163

Alternative Solution:

The following *IT* code can be used as an alternative to iteration with table data, where hN_2R and hN_2P denote the enthalpy of N_2 in the reactants and products, respectively, and so on. In the **Units** menu, select temperature in K and amount of substance in moles.

```

TR = 25 + 273.15 // K
// Evaluate reactant and product enthalpies, hR and hP, respectively
hR = hC8H18 + 12.5 * hO2_R + 47 * hN2_R
hP = 8 * hCO2_P + 9 * hH2O_P + 47 * hN2_P
hC8H18 = -249910 // kj/kmol (value from Table A-25)
hO2_R = h_T("O2",TR)
hN2_R = h_T("N2",TR)
hCO2_P = h_T("CO2",TP)
hH2O_P = h_T("H2O",TP)
hN2_P = h_T("N2",TP)
// Energy balance
hP = hR

```

Using the **Solve** button, the result is $\text{TP} = 2394$ K, which agrees closely with the result obtained above.

(b) For complete combustion of liquid octane with 400% theoretical air, the chemical equation is



The energy rate balance, Eq. (2), reduces for this case to

$$8(\bar{\Delta h})_{CO_2} + 9(\bar{\Delta h})_{H_2O(g)} + 37.5(\bar{\Delta h})_{O_2} + 188(\bar{\Delta h})_{N_2} = 5,074,630 \text{ kJ/kmol (fuel)}$$

- 1 Observe that the right side has the same value as in part (a). Proceeding iteratively as above, the temperature of the products is $T_p = 962 \text{ K}$. The use of IT to solve part (b) is left as an exercise.

- 1 The temperature determined in part (b) is considerably lower than the value found in part (a). This shows that once enough oxygen has been provided for complete combustion, bringing in more air dilutes the combustion products, lowering their temperature.

Skills Developed

Ability to...

- apply the control volume energy balance to calculate the adiabatic flame temperature.
- evaluate enthalpy values appropriately.

QuickQUIZ

If octane gas entered instead of liquid octane, would the adiabatic flame temperature increase, decrease, or stay the same? **Ans.** Increase.

13.3.3 Closing Comments

For a specified fuel and specified temperature and pressure of the reactants, the *maximum* adiabatic flame temperature is for complete combustion with the theoretical amount of air. The measured value of the temperature of the combustion products may be several hundred degrees below the calculated maximum adiabatic flame temperature, however, for several reasons:

- Once adequate oxygen has been provided to permit complete combustion, bringing in more air dilutes the combustion products, lowering their temperature.
- Incomplete combustion also tends to reduce the temperature of the products, and combustion is seldom complete (see Sec. 14.4).
- Heat losses can be reduced but not altogether eliminated.
- As a result of the high temperatures achieved, some of the combustion products may dissociate. Endothermic dissociation reactions lower the product temperature. The effect of dissociation on the adiabatic flame temperature is considered in Sec. 14.4.

13.4 Fuel Cells

fuel cell

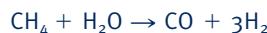
A **fuel cell** is an *electrochemical* device in which fuel and an oxidizer (normally oxygen from air) undergo a chemical reaction, providing electrical current to an external circuit and producing products. The fuel and oxidizer react catalytically in stages on separate electrodes: the anode and the cathode. An electrolyte separating the two electrodes allows passage of ions formed by reaction. Depending on the type of fuel cell, the ions may be positively or negatively charged. Individual fuel cells are connected in parallel or series to form fuel cell *stacks* to provide the desired level of power output.

With today's technology, the preferred fuel for oxidation at the fuel cell anode is hydrogen because of its exceptional ability to produce electrons when suitable catalysts are used, while producing no harmful emissions from the fuel cell itself. Depending on the type of fuel cell, methanol (CH_3OH) and carbon monoxide (CO) can be oxidized at the anode in some applications, but often with performance penalties.

Since hydrogen is not naturally occurring, it must be produced. Production methods include electrolysis of water (see Sec. 2.7) and chemically reforming hydrogen-bearing fuels, predominantly hydrocarbons. See the following box.

Hydrogen Production by Reforming of Hydrocarbons

Reforming reactions to produce hydrogen include endothermic *steam reforming* of hydrocarbons. For example, steam reforming of methane takes the form



This often is accompanied by the exothermic *water-gas shift* reaction



to produce additional hydrogen and eliminate from the hydrogen stream carbon monoxide, which poisons platinum catalysts used to promote reaction rates in some fuel cells. Other reforming techniques include dry reforming (carbon dioxide reforming) of hydrocarbons, partial oxidation of hydrocarbons, pyrolysis (thermal cracking) of hydrocarbons, and steam reforming of alcohols.

TAKE NOTE...

As discussed in the *Horizons* in Sec. 5.3.3, hydrogen production by electrolysis of water and by reforming of hydrocarbons are each burdened by the second law. Significant exergy destruction is observed with each method of production.

Hydrocarbon reforming can occur either separately or within the fuel cell (depending on type). When hydrogen is produced by reforming fuel separately from the fuel cell itself, this is known as *external reforming*. If not fed directly from the reformer to a fuel cell, hydrogen can be stored as a compressed gas, a cryogenic liquid, or atoms absorbed within metallic structures, and then provided to fuel cells from storage, when required. *Internal reforming* refers to applications where hydrogen production by reforming fuel is integrated within the fuel cell. Owing to limitations of current technology, internal reforming is feasible only in fuel cells operating at temperatures above about 600°C.

Rates of reaction in fuel cells are limited by the time it takes for diffusion of chemical species through the electrodes and the electrolyte and by the speed of the chemical reactions themselves. The reaction in a fuel cell is *not* a combustion process. These features result in fuel cell internal irreversibilities that are inherently less significant than those encountered in power systems employing combustion. Thus, fuel cells have the *potential* of providing more power from a given supply of fuel and oxidizer than conventional internal combustion engines and gas turbines.

Fuel cells do not operate as thermodynamic power cycles, and thus the notion of a limiting thermal efficiency imposed by the second law is not applicable. However, as for all power systems, the power provided by fuel cell *systems* is eroded by inefficiencies in auxiliary equipment. For fuel cells this includes heat exchangers, compressors, and humidifiers. Irreversibilities and losses inherent in hydrogen production also can be greater than those seen in production of more conventional fuels.

In comparison to reciprocating internal combustion engines and gas turbines that incorporate combustion, fuel cells typically produce relatively few damaging emissions as they develop power. Still, such emissions accompany production of fuels consumed by fuel cells as well as the manufacture of fuel cells and their supporting components. See *Horizons*, Sec. 5.3.3 for additional discussion.

Despite potential thermodynamic advantages, widespread fuel cell use has not occurred thus far owing primarily to cost. Table 13.2 summarizes the most promising fuel cell technologies currently under investigation. Included are potential applications and other characteristics.

Cooperative efforts by government and industry have fostered advances in both proton exchange membrane fuel cells and solid oxide fuel cells, which appear to provide the greatest range of potential applications in transportation, portable power, and stationary power. The proton exchange membrane fuel cell and the solid oxide fuel cell are discussed next.

TABLE 13.2**Characteristics of Major Fuel Cell Types**

	Proton Exchange Membrane Fuel Cell (PEMFC)	Phosphoric Acid Fuel Cell (PAFC)	Molten Carbonate Fuel Cell (MCFC)	Solid Oxide Fuel Cell (SOFC)
Transportation application	Automotive power	Large vehicle power	None	Vehicle auxiliary power Heavy vehicle propulsion
Other applications	Portable power Small-scale stationary power	On-site cogeneration Electric power generation	On-site cogeneration Electric power generation	On-site cogeneration Electric power generation
Electrolyte	Ion exchange membrane	Liquid phosphoric acid	Liquid molten carbonate	Solid oxide ceramic
Charge carrier	H ⁺	H ⁺	CO ₃ ²⁻	O ⁼
Operating temperature	60–80°C	150–220°C	600–700°C	600–1000°C
Fuel oxidized at anode	H ₂ or methanol	H ₂	H ₂	H ₂ or CO
Fuel reforming	External	External	Internal or external	Internal or external
Fuels typically used for internal reforming	None	None	CO Light hydrocarbons (e.g., methane, propane) Methanol	Light hydrocarbons (e.g., methane, propane) Synthetic diesel and gasoline

Sources: *Fuel Cell Handbook*, Seventh Edition, 2004, EG&G Technical Services, Inc., DOE Contract No. DE-AM26-99FT40575. Larminie, J., and Dicks, A., 2000, *Fuel Cell Systems Explained*, John Wiley & Sons, Ltd., Chichester, West Sussex, England.

13.4.1 Proton Exchange Membrane Fuel Cell

The fuel cells shown in Fig. 13.3 are *proton exchange membrane fuel cells* (PEMFCs). At the anode, hydrogen ions (H⁺) and electrons (e⁻) are produced. At the cathode, oxygen, hydrogen ions, and electrons react to produce water.

► The fuel cell shown schematically in Fig. 13.3a operates with hydrogen (H₂) as the fuel and oxygen (O₂) as the oxidizer. The reactions at these electrodes and the *overall* cell reaction are labeled on the figure. The only products of this fuel cell are water, power generated, and waste heat.

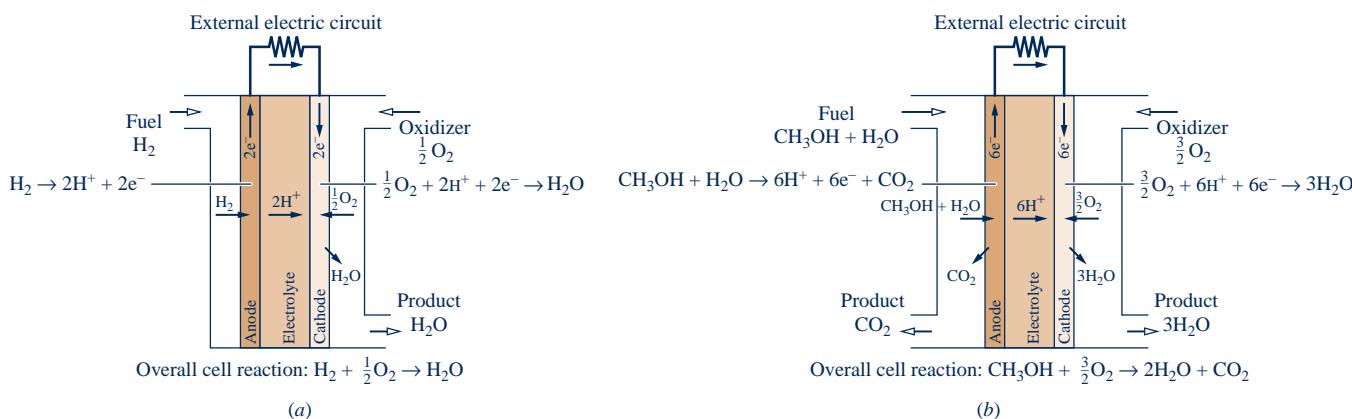


Fig. 13.3 Proton exchange membrane fuel cell. (a) Hydrogen fueled. (b) Humidified-methanol fueled.



Goodbye Batteries, Hello Fuel Cells?

Power needs of cellular phones, laptops, and other portable electronic devices are increasing so rapidly that the battery industry is struggling to keep up. Some observers say that today's batteries won't be able to provide enough power, are too heavy, and don't last long enough to meet the needs of quickly evolving electronics. Pocket-size fuel cells might prove to be a viable alternative.

To meet consumer needs, companies are rushing to develop small fuel cells that provide as much, or more, power on a single charge than conventional batteries, and can be charged instantly just by adding more fuel.

Battery companies are fighting back with a new generation of batteries. One of these, the lithium-ion battery, is already used in watches, flash cameras, and rechargeable power packs. Lithium-ion batteries provide several times the output of similar-size alkaline batteries and can be recharged numerous times.

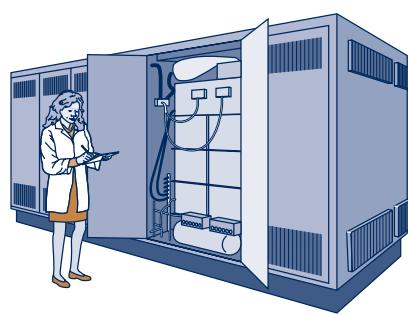
To compete, fuel cells must prove themselves as reliable and versatile as batteries, and stakes are high in the consumer electronics market. Still, many think fuel cells for portable electronics will be the first fuel cells most of us will actually use because of strong consumer demand for cost-competitive, longer-lasting, instantly rechargeable power.

- The fuel cell shown schematically in Fig. 13.3b operates with humidified methanol ($\text{CH}_3\text{OH} + \text{H}_2\text{O}$) as the fuel and oxygen (O_2) as the oxidizer. This type of PEMFC is a *direct-methanol fuel cell*. The reactions at these electrodes and the *overall* cell reaction are labeled on the figure. The only products of this fuel cell are water, carbon dioxide, power generated, and waste heat.

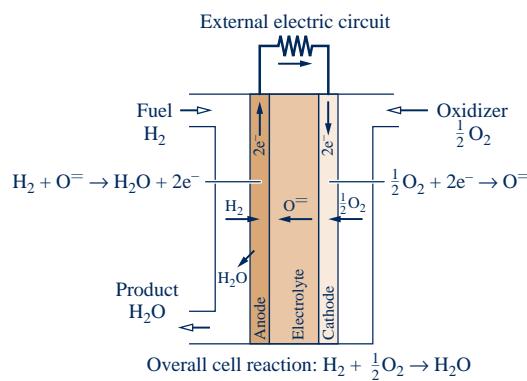
For PEMFCs, charge-carrying hydrogen ions are conducted through the electrolytic membrane. For acceptable ion conductivity, high membrane water content is required. This requirement restricts the fuel cell to operating below the boiling point of water, so PEMFCs typically operate at temperatures in the range 60–80°C. Cooling is generally needed to maintain the fuel cell at the operating temperature.

Owing to the relatively low-temperature operation of proton exchange membrane fuel cells, hydrogen derived from hydrocarbon feedstock must be produced using external reforming, while costly platinum catalysts are required at both the anode and cathode to increase ionization reaction rates. Due to extremely slow reaction rate at the anode, the direct-methanol fuel cell requires almost ten times as much platinum catalyst as the hydrogen-fueled PEMFC to improve anode reaction rate. Catalytic activity is more important in lower-temperature fuel cells because rates of reaction at the anode and cathode tend to decrease with decreasing temperature.

Automakers are introducing hydrogen-powered proton exchange membrane fuel cell vehicles. Fuel cell vehicles are undergoing large-scale market testing (United States) and are being offered by limited lease (Japan). Both hydrogen-fueled PEMFCs and direct-methanol fuel cells have potential to replace batteries in portable devices such as cellular phones, laptop computers, and video players (see *Horizons*, above). Hurdles to wider deployment of PEMFCs include extending stack life, simplifying system integration, and reducing costs.



(a)



(b)

Fig. 13.4 Solid oxide fuel cell. (a) Module. (b) Schematic.

13.4.2 Solid Oxide Fuel Cell

For scale, Fig. 13.4a shows a *solid oxide* fuel cell (SOFC) module. The fuel cell schematic shown in Fig. 13.4b operates with hydrogen (H_2) as the fuel and oxygen (O_2) as the oxidizer. At the anode, water (H_2O) and electrons (e^-) are produced. At the cathode, oxygen reacts with electrons (e^-) to produce oxygen ions ($O^{=}$) that migrate through the electrolyte to the anode. The reactions at these electrodes and the *overall* cell reaction are labeled on the figure. The only products of this fuel cell are water, power generated, and waste heat.

For SOFCs, an alternative fuel to hydrogen is carbon monoxide (CO) that produces carbon dioxide (CO_2) and electrons (e^-) during oxidation at the anode. The cathode reaction is the same as that in Fig. 13.4(b). Due to their high-temperature operation, solid oxide fuel cells can incorporate internal reforming of various hydrocarbon fuels to produce hydrogen and/or carbon monoxide at the anode.

Since waste heat is produced at relatively high temperature, solid oxide fuel cells can be used for cogeneration of power and process heat or steam. SOFCs also can be used for distributed (decentralized) power generation and for fuel cell–microturbine hybrids. These technologies are in the proof-of-concept testing and demonstration phases of development. Such applications are very attractive because they achieve objectives without using highly irreversible combustion.

For instance, a solid oxide fuel cell replaces the combustor in the gas turbine shown in the fuel cell–microturbine schematic in Fig. 13.5. The fuel cell produces electric power while its high-temperature exhaust expands through the microturbine, producing shaft power \dot{W}_{net} . By producing power electrically *and* mechanically without combustion, fuel cell–microturbine hybrids have the potential of significantly improving effectiveness of fuel utilization over that achievable with comparable conventional gas turbine technology *and* with fewer harmful emissions.

13.5 Absolute Entropy and the Third Law of Thermodynamics

Thus far our analyses of reacting systems have been conducted using the conservation of mass and conservation of energy principles. In the present section some of the implications of the second law of thermodynamics for reacting systems are

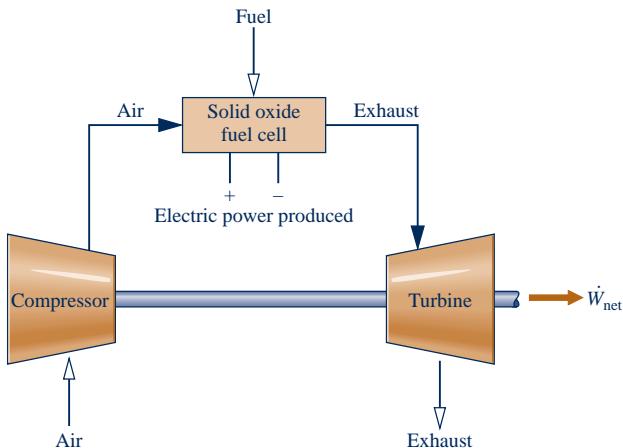


Fig. 13.5 Solid oxide fuel cell–microturbine hybrid.

considered. The discussion continues in the second part of this chapter dealing with the exergy concept, and in the next chapter where the subject of chemical equilibrium is taken up.

13.5.1 Evaluating Entropy for Reacting Systems

The property entropy plays an important part in quantitative evaluations using the second law of thermodynamics. When reacting systems are under consideration, the same problem arises for entropy as for enthalpy and internal energy: A common datum must be used to assign entropy values for each substance involved in the reaction. This is accomplished using the *third law* of thermodynamics and the *absolute entropy* concept.

The **third law** deals with the entropy of substances at the absolute zero of temperature. Based on empirical evidence, this law states that the entropy of a pure crystalline substance is zero at the absolute zero of temperature, 0 K or 0°R. Substances not having a pure crystalline structure at absolute zero have a nonzero value of entropy at absolute zero. The experimental evidence on which the third law is based is obtained primarily from studies of chemical reactions at low temperatures and specific heat measurements at temperatures approaching absolute zero.

third law of thermodynamics

ABSOLUTE ENTROPY. For present considerations, the importance of the third law is that it provides a datum relative to which the entropy of each substance participating in a reaction can be evaluated so that no ambiguities or conflicts arise. The entropy relative to this datum is called the **absolute entropy**. The change in entropy of a substance between absolute zero and any given state can be determined from precise measurements of energy transfers and specific heat data or from procedures based on statistical thermodynamics and observed molecular data.

absolute entropy

Tables A-25 and A-25E give the value of the absolute entropy for selected substances at the standard reference state, $T_{\text{ref}} = 298.15 \text{ K}$, $p_{\text{ref}} = 1 \text{ atm}$, in units of $\text{kJ}/\text{kmol} \cdot \text{K}$ and $\text{Btu}/\text{lbmol} \cdot {}^{\circ}\text{R}$, respectively. Two values of absolute entropy for water are provided. One is for liquid water and the other is for water vapor. As for the case of the enthalpy of formation of water considered in Sec. 13.2.1, the vapor value listed is for a *hypothetical* ideal gas state in which water is a vapor at 25°C (77°F) and $p_{\text{ref}} = 1 \text{ atm}$.

Tables A-23 and A-23E give tabulations of absolute entropy versus temperature at a pressure of 1 atm for selected gases. In these tables, the absolute entropy at 1 atm and temperature T is designated $\bar{s}^\circ(T)$, and ideal gas behavior is assumed for the gases.

USING ABSOLUTE ENTROPY. When the absolute entropy is known at the standard state, the specific entropy at any other state can be found by adding the specific entropy change between the two states to the absolute entropy at the standard state. Similarly, when the absolute entropy is known at the pressure p_{ref} and temperature T , the absolute entropy at the same temperature and any pressure p can be found from

$$\bar{s}(T, p) = \bar{s}(T, p_{\text{ref}}) + [\bar{s}(T, p) - \bar{s}(T, p_{\text{ref}})]$$

For the ideal gases listed in Tables A-23, the first term on the right side of this equation is $\bar{s}^\circ(T)$, and the second term on the right can be evaluated using Eq. 6.18. Collecting results, we get

$$\bar{s}(T, p) = \bar{s}^\circ(T) - \bar{R} \ln \frac{p}{p_{\text{ref}}} \quad (\text{ideal gas}) \quad (13.22)$$

To reiterate, $\bar{s}^\circ(T)$ is the absolute entropy at temperature T and pressure $p_{\text{ref}} = 1 \text{ atm}$.

The entropy of the i th component of an ideal gas mixture is evaluated at the mixture temperature T and the *partial* pressure p_i : $\bar{s}_i(T, p_i)$. The partial pressure is given

by $p_i = y_i p$, where y_i is the mole fraction of component i and p is the mixture pressure. Thus, Eq. 13.22 takes the form

$$\bar{s}_i(T, p_i) = \bar{s}_i^\circ(T) - \bar{R} \ln \frac{p_i}{p_{\text{ref}}}$$

or

$$\bar{s}_i(T, p_i) = \bar{s}_i^\circ(T) - \bar{R} \ln \frac{y_i p}{p_{\text{ref}}} \quad \left(\begin{array}{l} \text{component } i \text{ of an} \\ \text{ideal gas mixture} \end{array} \right) \quad (13.23)$$

where $\bar{s}_i^\circ(T)$ is the absolute entropy of component i at temperature T and $p_{\text{ref}} = 1 \text{ atm}$. Equation 13.23 corresponds to Eq. (b) of Table 13.1.

Finally, note that *Interactive Thermodynamics (IT)* returns absolute entropy directly and does not use the special function \bar{s}° .

13.5.2 Entropy Balances for Reacting Systems

Many of the considerations that enter when energy balances are written for reacting systems also apply to entropy balances. The writing of entropy balances for reacting systems will be illustrated by referring to special cases of broad interest.

CONTROL VOLUMES AT STEADY STATE. Let us begin by reconsidering the steady-state reactor of Fig. 13.2, for which the combustion reaction is given by Eq. 13.11. The combustion air and the products of combustion are each assumed to form ideal gas mixtures, and thus Eq. 12.26 from Table 13.1 for mixture entropy is applicable to them. The entropy rate balance for the two-inlet, single-exit reactor can be expressed on a *per mole of fuel* basis as

$$0 = \sum_i \underline{\frac{\dot{Q}_j/T_j}{\dot{n}_F}} + \bar{s}_F + \underline{\left[\left(a + \frac{b}{4} \right) \bar{s}_{O_2} + \left(a + \frac{b}{4} \right) 3.76 \bar{s}_{N_2} \right]} - \underline{\left[a \bar{s}_{CO_2} + \frac{b}{2} \bar{s}_{H_2O} + \left(a + \frac{b}{4} \right) 3.76 \bar{s}_{N_2} \right]} + \underline{\frac{\dot{\sigma}_{cv}}{\dot{n}_F}} \quad (13.24)$$

where \dot{n}_F is the molar flow rate of the fuel and the coefficients appearing in the underlined terms are the same as those for the corresponding substances in the reaction equation.

All entropy terms of Eq. 13.24 are absolute entropies. The first underlined term on the right side of Eq. 13.24 is the entropy of the combustion air *per mole of fuel*. The second underlined term is the entropy of the exiting combustion products *per mole of fuel*. In accord with Table 13.1, the entropies of the air and combustion products are evaluated by adding the contribution of each component present in the respective gas mixtures. For instance, the specific entropy of a substance in the combustion products is evaluated from Eq. 13.23 using the temperature of the combustion products and the partial pressure of the substance in the combustion product mixture. Such considerations are illustrated in Example 13.9.

EXAMPLE 13.9

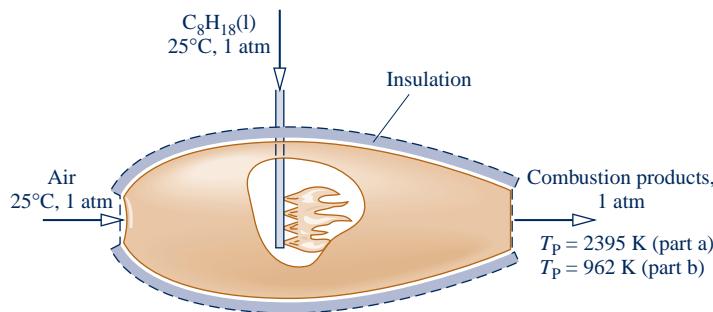
Evaluating Entropy Production for a Reactor Fueled by Liquid Octane

Liquid octane at 25°C , 1 atm enters a well-insulated reactor and reacts with air entering at the same temperature and pressure. The products of combustion exit at 1 atm pressure. For steady-state operation and negligible effects of kinetic and potential energy, determine the rate of entropy production, in kJ/K per kmol of fuel, for complete combustion with (a) the theoretical amount of air, (b) 400% theoretical air.

SOLUTION

Known: Liquid octane and air, each at 25°C and 1 atm, burn completely within a well-insulated reactor operating at steady state. The products of combustion exit at 1 atm pressure.

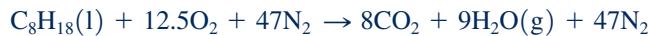
Find: Determine the rate of entropy production, in kJ/K per kmol of fuel, for combustion with (a) the theoretical amount of air, (b) 400% theoretical air.

Schematic and Given Data:**Fig. E13.9****Engineering Model:**

- The control volume shown on the accompanying figure by a dashed line operates at steady state and without heat transfer with its surroundings.
- Combustion is complete. Each mole of oxygen in the combustion air is accompanied by 3.76 moles of nitrogen, which is inert.
- The combustion air can be modeled as an ideal gas mixture, as can the products of combustion.
- The reactants enter at 25°C, 1 atm. The products exit at a pressure of 1 atm.

Analysis: The temperature of the exiting products of combustion T_p was evaluated in Example 13.8 for each of the two cases. For combustion with the theoretical amount of air, $T_p = 2395$ K. For complete combustion with 400% theoretical air, $T_p = 962$ K.

(a) For combustion of liquid octane with the theoretical amount of air, the chemical equation is



With assumptions 1 and 3, the entropy rate balance on a per mole of fuel basis, Eq. 13.24, takes the form

$$0 = \sum_j \frac{\dot{Q}_j}{\dot{n}_F}^0 + \bar{s}_F + (12.5\bar{s}_{\text{O}_2} + 47\bar{s}_{\text{N}_2}) - (8\bar{s}_{\text{CO}_2} + 9\bar{s}_{\text{H}_2\text{O(g)}} + 47\bar{s}_{\text{N}_2}) + \frac{\dot{\sigma}_{cv}}{\dot{n}_F}$$

or on rearrangement

$$\frac{\dot{\sigma}_{cv}}{\dot{n}_F} = (8\bar{s}_{\text{CO}_2} + 9\bar{s}_{\text{H}_2\text{O(g)}} + 47\bar{s}_{\text{N}_2}) - \bar{s}_F - (12.5\bar{s}_{\text{O}_2} + 47\bar{s}_{\text{N}_2}) \quad (1)$$

Each coefficient of this equation is the same as for the corresponding term of the balanced chemical equation.

The fuel enters the reactor separately at T_{ref} , p_{ref} . The absolute entropy of liquid octane required by the entropy balance is obtained from Table A-25 as 360.79 kJ/kmol · K.

The oxygen and nitrogen in the combustion air enter the reactor as components of an ideal gas mixture at T_{ref} , p_{ref} . With Eq. 13.23 and absolute entropy data from Table A-23

$$\begin{aligned} \bar{s}_{\text{O}_2} &= \bar{s}_{\text{O}_2}^\circ(T_{ref}) - \bar{R} \ln \frac{y_{\text{O}_2} p_{ref}}{p_{ref}} \\ &= 205.03 - 8.314 \ln 0.21 = 218.01 \text{ kJ/kmol} \cdot \text{K} \\ \bar{s}_{\text{N}_2} &= \bar{s}_{\text{N}_2}^\circ(T_{ref}) - \bar{R} \ln \frac{y_{\text{N}_2} p_{ref}}{p_{ref}} \\ &= 191.5 - 8.314 \ln 0.79 = 193.46 \text{ kJ/kmol} \cdot \text{K} \end{aligned}$$

The product gas exits as an ideal gas mixture at 1 atm, 2395 K with the following composition: $y_{CO_2} = 8/64 = 0.125$, $y_{H_2O(g)} = 9/64 = 0.1406$, $y_{N_2} = 47/64 = 0.7344$. With Eq. 13.23 and absolute entropy data at 2395 K from Tables A-23

$$\begin{aligned}\bar{s}_{CO_2} &= \bar{s}_{CO_2}^\circ - \bar{R} \ln y_{CO_2} \\ &= 320.173 - 8.314 \ln 0.125 = 337.46 \text{ kJ/kmol} \cdot \text{K} \\ \bar{s}_{H_2O} &= 273.986 - 8.314 \ln 0.1406 = 290.30 \text{ kJ/kmol} \cdot \text{K} \\ \bar{s}_{N_2} &= 258.503 - 8.314 \ln 0.7344 = 261.07 \text{ kJ/kmol} \cdot \text{K}\end{aligned}$$

Inserting values into Eq. (1), the expression for the rate of entropy production, we get

$$\begin{aligned}\frac{\dot{\sigma}_{cv}}{\dot{n}_F} &= 8(337.46) + 9(290.30) + 47(261.07) \\ &\quad - 360.79 - 12.5(218.01) - 47(193.46) \\ &= 5404 \text{ kJ/kmol (octane)} \cdot \text{K}\end{aligned}$$

Alternative Solution:

As an alternative, the following *IT* code can be used to determine the entropy production per mole of fuel entering, where sigma denotes $\dot{\sigma}_{cv}/\dot{n}_F$, and s_{N2_R} and s_{N2_P} denote the entropy of N_2 in the reactants and products, respectively, and so on. In the **Units** menu, select temperature in K, pressure in bar, and amount of substance in moles.

```
TR = 25 + 273.15 // K
p = 1.01325 // bar
TP = 2394 // K (Value from the IT alternative solution of Example 13.8)

// Determine the partial pressures
pO2_R = 0.21 * p
pN2_R = 0.79 * p
pCO2_P = (8/64) * p
pH2O_P = (9/64) * p
pN2_P = (47/64) * p

// Evaluate the absolute entropies
sC8H18 = 360.79 // kJ/kmol · K (from Table A-25)
sO2_R = s_TP("O2", TR, pO2_R)
sN2_R = s_TP("N2", TR, pN2_R)
① sCO2_P = s_TP("CO2", TP, pCO2_P)
sH2O_P = s_TP("H2O", TP, pH2O_P)
sN2_P = s_TP("N2", TP, pN2_P)

// Evaluate the reactant and product entropies, sR and sP, respectively
sR = sC8H18 + 12.5 * sO2_R + 47 * sN2_R
sR = 8 * sCO2_P + 9 * sH2O_P + 47 * sN2_P

// Entropy balance, Eq. (1)
sigma = sP - sR
```

Using the **Solve** button, the result is $\sigma = 5404 \text{ kJ/kmol (octane)} \cdot \text{K}$, which agrees with the result obtained above.

(b) The complete combustion of liquid octane with 400% theoretical air is described by the following chemical equation:



The entropy rate balance on a per mole of fuel basis takes the form

$$\frac{\dot{\sigma}_{cv}}{\dot{n}_F} = (8\bar{s}_{CO_2} + 9\bar{s}_{H_2O(g)} + 37.5\bar{s}_{O_2} + 188\bar{s}_{N_2}) - \bar{s}_F - (50\bar{s}_{O_2} + 188\bar{s}_{N_2})$$

The specific entropies of the reactants have the same values as in part (a). The product gas exits as an ideal gas mixture at 1 atm, 962 K with the following composition: $y_{CO_2} = 8/242.5 = 0.033$, $y_{H_2O(g)} = 9/242.5 = 0.0371$, $y_{O_2} = 37.5/242.5 = 0.1546$, $y_{N_2} = 0.7753$. With the same approach as in part (a)

$$\begin{aligned}\bar{s}_{\text{CO}_2} &= 267.12 - 8.314 \ln 0.033 = 295.481 \text{ kJ/kmol} \cdot \text{K} \\ \bar{s}_{\text{H}_2\text{O}} &= 231.01 - 8.314 \ln 0.0371 = 258.397 \text{ kJ/kmol} \cdot \text{K} \\ \bar{s}_{\text{O}_2} &= 242.12 - 8.314 \ln 0.1546 = 257.642 \text{ kJ/kmol} \cdot \text{K} \\ \bar{s}_{\text{N}_2} &= 226.795 - 8.314 \ln 0.7753 = 228.911 \text{ kJ/kmol} \cdot \text{K}\end{aligned}$$

Inserting values into the expression for the rate of entropy production

$$\begin{aligned}\frac{\dot{\sigma}_{\text{cv}}}{n_F} &= 8(295.481) + 9(258.397) + 37.5(257.642) + 188(228.911) \\ &\quad - 360.79 - 50(218.01) - 188(193.46) \\ &= 9754 \text{ kJ/kmol (octane)} \cdot \text{K}\end{aligned}$$

The use of *IT* to solve part (b) is left as an exercise.

- 1 For several gases modeled as ideal gases, *IT* directly returns the absolute entropies required by entropy balances for reacting systems. The entropy data obtained from *IT* agree with values calculated from Eq. 13.23 using table data.
- 2 Although the rates of entropy production calculated in this example are positive, as required by the second law, this does not mean that the proposed reactions necessarily would occur, for the results are based on the assumption of *complete* combustion. The possibility of achieving complete combustion with specified reactants at a given temperature and pressure can be investigated with the methods of Chap. 14, dealing with chemical equilibrium. For further discussion, see Sec. 14.4.1.



Skills Developed

Ability to...

- apply the control volume entropy balance to a reacting system.
- evaluate entropy values appropriately based on absolute entropies.

QuickQUIZ

How do combustion product temperature and rate of entropy production vary, respectively, as percent excess air increases? Assume complete combustion. **Ans.** Decrease, increase.

CLOSED SYSTEMS. Next consider an entropy balance for a process of a closed system during which a chemical reaction occurs

$$S_P - S_R = \int \left(\frac{\delta Q}{T} \right)_b + \sigma \quad (13.25)$$

S_R and S_P denote, respectively, the entropy of the reactants and the entropy of the products.

When the reactants and products form ideal gas mixtures, the entropy balance can be expressed on a *per mole of fuel* basis as

$$\sum_P n \bar{s} - \sum_R n \bar{s} = \frac{1}{n_F} \int \left(\frac{\delta Q}{T} \right)_b + \frac{\sigma}{n_F} \quad (13.26)$$

where the coefficients n on the left are the coefficients of the reaction equation giving the moles of each reactant or product *per mole of fuel*. The entropy terms of Eq. 13.26 are evaluated from Eq. 13.23 using the temperature and partial pressures of the reactants or products, as appropriate. In any such application, the fuel is mixed with the oxidizer, so this must be taken into account when determining the partial pressures of the reactants.

Example 13.10 provides an illustration of the evaluation of entropy change for combustion at constant volume.

EXAMPLE 13.10**Determining Entropy Change for Combustion of Gaseous Methane with Oxygen at Constant Volume**

Determine the change in entropy of the system of Example 13.6 in kJ/K.

SOLUTION

Known: A mixture of gaseous methane and oxygen, initially at 25°C and 1 atm, burns completely within a closed rigid container. The products are cooled to 900 K, 3.02 atm.

Find: Determine the change in entropy for the process in kJ/K.

Schematic and Given Data: See Fig. E13.6.

Engineering Model:

1. The contents of the container are taken as the system.
2. The initial mixture can be modeled as an ideal gas mixture, as can the products of combustion.
3. Combustion is complete.

Analysis: The chemical equation for the complete combustion of methane with oxygen is



The change in entropy for the process of the closed system is $\Delta S = S_p - S_R$, where S_R and S_p denote, respectively, the initial and final entropies of the system. Since the initial mixture forms an ideal gas mixture (assumption 2), the entropy of the reactants can be expressed as the sum of the contributions of the components, each evaluated at the mixture temperature and the partial pressure of the component. That is

$$S_R = \bar{s}_{\text{CH}_4}(T_1, y_{\text{CH}_4}p_1) + 2\bar{s}_{\text{O}_2}(T_1, y_{\text{O}_2}p_1)$$

where $y_{\text{CH}_4} = 1/3$ and $y_{\text{O}_2} = 2/3$ denote, respectively, the mole fractions of the methane and oxygen in the initial mixture. Similarly, since the products of combustion form an ideal gas mixture (assumption 2)

$$S_p = \bar{s}_{\text{CO}_2}(T_2, y_{\text{CO}_2}p_2) + 2\bar{s}_{\text{H}_2\text{O}}(T_2, y_{\text{H}_2\text{O}}p_2)$$

where $y_{\text{CO}_2} = 1/3$ and $y_{\text{H}_2\text{O}} = 2/3$ denote, respectively, the mole fractions of the carbon dioxide and water vapor in the products of combustion. In these equations, p_1 and p_2 denote the pressure at the initial and final states, respectively.

The specific entropies required to determine S_R can be calculated from Eq. 13.23. Since $T_1 = T_{\text{ref}}$ and $p_1 = p_{\text{ref}}$, absolute entropy data from Table A-25 can be used as follows

$$\begin{aligned}\bar{s}_{\text{CH}_4}(T_1, y_{\text{CH}_4}p_1) &= \bar{s}_{\text{CH}_4}^{\circ}(T_{\text{ref}}) - \bar{R} \ln \frac{y_{\text{CH}_4}p_{\text{ref}}}{p_{\text{ref}}} \\ &= 186.16 - 8.314 \ln \frac{1}{3} = 195.294 \text{ kJ/kmol} \cdot \text{K}\end{aligned}$$

Similarly

$$\begin{aligned}\bar{s}_{\text{O}_2}(T_1, y_{\text{O}_2}p_1) &= \bar{s}_{\text{O}_2}^{\circ}(T_{\text{ref}}) - \bar{R} \ln \frac{y_{\text{O}_2}p_{\text{ref}}}{p_{\text{ref}}} \\ &= 205.03 - 8.314 \ln \frac{2}{3} = 208.401 \text{ kJ/kmol} \cdot \text{K}\end{aligned}$$

At the final state, the products are at $T_2 = 900 \text{ K}$ and $p_2 = 3.02 \text{ atm}$. With Eq. 13.23 and absolute entropy data from Tables A-23

$$\begin{aligned}\bar{s}_{\text{CO}_2}(T_2, y_{\text{CO}_2}p_2) &= \bar{s}_{\text{CO}_2}^{\circ}(T_2) - \bar{R} \ln \frac{y_{\text{CO}_2}p_2}{p_{\text{ref}}} \\ &= 263.559 - 8.314 \ln \frac{(1/3)(3.02)}{1} = 263.504 \text{ kJ/kmol} \cdot \text{K}\end{aligned}$$

$$\begin{aligned}\bar{s}_{\text{H}_2\text{O}}(T_2, y_{\text{H}_2\text{O}} p_2) &= \bar{s}_{\text{H}_2\text{O}}^{\circ}(T_2) - \bar{R} \ln \frac{y_{\text{H}_2\text{O}} p_2}{p_{\text{ref}}} \\ &= 228.321 - 8.314 \ln \frac{(2/3)(3.02)}{1} = 222.503 \text{ kJ/kmol} \cdot \text{K}\end{aligned}$$

Finally, the entropy change for the process is

$$\begin{aligned}\Delta S &= S_{\text{P}} - S_{\text{R}} \\ &= [263.504 + 2(222.503)] - [195.294 + 2(208.401)] \\ &= 96.414 \text{ kJ/K}\end{aligned}$$

Skills Developed

Ability to...

- apply the closed system entropy balance to a reacting system.
- evaluate entropy values appropriately based on absolute entropies.

QuickQUIZ

Applying the entropy balance, Eq. 13.25, is σ greater than, less than, or equal to ΔS ? **Ans.** Greater than.

13.5.3 Evaluating Gibbs Function for Reacting Systems

The thermodynamic property known as the Gibbs function plays a role in the second part of this chapter dealing with exergy analysis. The *specific Gibbs function* \bar{g} , introduced in Sec. 11.3, is

$$\bar{g} = \bar{h} - T\bar{s} \quad (13.27)$$

The procedure followed in setting a datum for the Gibbs function closely parallels that used in defining the enthalpy of formation: To each stable element at the standard state is assigned a zero value of the Gibbs function. The **Gibbs function of formation** of a compound, \bar{g}_f° , equals the change in the Gibbs function for the reaction in which the compound is formed from its elements, the compound and the elements all being at $T_{\text{ref}} = 25^\circ\text{C}$ (77°F) and $p_{\text{ref}} = 1 \text{ atm}$. Tables A-25 and A-25E give the Gibbs function of formation, \bar{g}_f° , for selected substances.

Gibbs function of formation

The Gibbs function at a state other than the standard state is found by adding to the Gibbs function of formation the change in the specific Gibbs function $\Delta\bar{g}$ between the standard state and the state of interest

$$\bar{g}(T, p) = \bar{g}_f^{\circ} + [\bar{g}(T, p) - \bar{g}(T_{\text{ref}}, p_{\text{ref}})] = \bar{g}_f^{\circ} + \Delta\bar{g} \quad (13.28a)$$

With Eq. 13.27, $\Delta\bar{g}$ can be written as

$$\Delta\bar{g} = [\bar{h}(T, p) - \bar{h}(T_{\text{ref}}, p_{\text{ref}})] - [T\bar{s}(T, p) - T_{\text{ref}}\bar{s}(T_{\text{ref}}, p_{\text{ref}})] \quad (13.28b)$$

The Gibbs function of component i in an ideal gas mixture is evaluated at the *partial pressure* of component i and the mixture temperature.

The procedure for determining the Gibbs function of formation is illustrated in the next example.

TAKE NOTE...

Gibbs function is introduced here because it contributes to subsequent developments of this chapter.

Gibbs function is a property because it is defined in terms of properties. Like enthalpy, introduced as a combination of properties in Sec. 3.6.1, Gibbs function has no physical significance—in general.

EXAMPLE 13.11

Determining the Gibbs Function of Formation for Methane

Determine the Gibbs function of formation of methane at the standard state, 25°C and 1 atm , in kJ/kmol , and compare with the value given in Table A-25.

SOLUTION

Known: The compound is methane.

Find: Determine the Gibbs function of formation at the standard state, in kJ/kmol, and compare with the Table A-25 value.

Assumptions: In the formation of methane from carbon and hydrogen (H_2), the carbon and hydrogen are each initially at 25°C and 1 atm. The methane formed is also at 25°C and 1 atm.

Analysis: Methane is formed from carbon and hydrogen according to $C + 2H_2 \rightarrow CH_4$. The change in the Gibbs function for this reaction is

$$\begin{aligned}\bar{g}_P - \bar{g}_R &= (\bar{h} - T\bar{s})_{CH_4} - (\bar{h} - T\bar{s})_C - 2(\bar{h} - T\bar{s})_{H_2} \\ &= (\bar{h}_{CH_4} - \bar{h}_C - 2\bar{h}_{H_2}) - T(\bar{s}_{CH_4} - \bar{s}_C - 2\bar{s}_{H_2})\end{aligned}\quad (1)$$

where \bar{g}_P and \bar{g}_R denote, respectively, the Gibbs functions of the products and reactants, each per kmol of methane.

In the present case, all substances are at the same temperature and pressure, 25°C and 1 atm, which correspond to the standard reference state values. At the standard reference state, the enthalpies and Gibbs functions for carbon and hydrogen are zero by definition. Thus, in Eq. (1), $\bar{g}_R = \bar{h}_C = \bar{h}_{H_2} = 0$. Also, $\bar{g}_P = (\bar{g}_f)_{CH_4}$. Eq. (1) then reads

$$(\bar{g}_f)_{CH_4} = (\bar{h}_f)_{CH_4} - T_{ref}(\bar{s}_{CH_4}^o - \bar{s}_C^o - 2\bar{s}_{H_2}^o) \quad (2)$$

where all properties are at T_{ref} , p_{ref} . With enthalpy of formation and absolute entropy data from Table A-25, Eq. (2) gives

$$(\bar{g}_f)_{CH_4} = -74,850 - 298.15[186.16 - 5.74 - 2(130.57)] = -50,783 \text{ kJ/kmol}$$

The slight difference between the calculated value for the Gibbs function of formation of methane and the value from Table A-25 can be attributed to round-off.

 **Skills Developed**

Ability to...

- apply the definition of Gibbs function of formation to calculate \bar{g}_f^o .

QuickQUIZ

Using the method applied in the example, calculate \bar{g}_f^o for monatomic oxygen at the standard state, in kJ/kmol. Begin by writing $\frac{1}{2}O_2 \rightarrow O$. **Ans.** 231,750 kJ/kmol, which agrees with Table A-25.

Chemical Exergy

The objective of this part of the chapter is to extend the exergy concept introduced in Chap. 7 to include chemical exergy. Several important exergy aspects are listed in Sec. 7.3.1. We suggest you review this material before continuing the current discussion.

A key aspect carried from Chap. 7 is that exergy is a measure of the departure of the state of a system from that of a thermodynamic model of the Earth and its atmosphere called the *exergy reference environment*, or simply the *environment*. In the current discussion, the departure of the system state from the environment centers on the respective temperature, pressure, and composition, for composition now plays a key role. If one or more of system temperature, pressure, and composition differs from that of the environment, the system has exergy.

Exergy is the *maximum* theoretical work obtainable from an overall system of system plus environment as the system passes from a specified state to equilibrium with the environment. Alternatively, exergy is the *minimum* theoretical work *input* required to form the system from the environment and bring it to the specified state.

For conceptual and computational ease, we think of the system passing to equilibrium with the environment in two steps. With this approach, exergy is the sum of two contributions: *thermomechanical*, developed in Chap. 7, and *chemical*, developed in this chapter.

TABLE 13.3**Set of Substances Represented by $C_aH_bO_c$**

	C	H₂	C_aH_b	CO	CO_2	H_2O(liq.)
a	1	0	a	1	1	0
b	0	2	b	0	0	2
c	0	0	0	1	2	1

TABLE 13.4**Exergy Reference Environment Used in Sec. 13.6**Gas phase at $T_0 = 298.15\text{ K}$ (25°C), $p_0 = 1\text{ atm}$

Component	$y^e(\%)$
N_2	75.67
O_2	20.35
$H_2O(g)$	3.12
CO_2	0.03
Other	0.83

13.6**Conceptualizing Chemical Exergy**

In this section, we consider a thought experiment to bring out important aspects of chemical exergy. This involves

- a set of substances represented by $C_aH_bO_c$ (see Table 13.3),
- an *environment* modeling Earth's atmosphere (see Table 13.4), and
- an *overall system* including a control volume (see Fig. 13.6).

Referring to Table 13.4, the exergy reference environment considered in the present discussion is an ideal gas mixture modeling the Earth's atmosphere. T_0 and p_0 denote the temperature and pressure of the environment, respectively. The composition of the environment is given in terms of mole fractions denoted by y^e , where superscript e is used to signal the mole fraction of an environmental component. The values of these mole fractions, and the values of T_0 and p_0 , are specified and remain unchanged throughout the development to follow. The gas mixture modeling the atmosphere adheres to the Dalton model (Sec. 12.2).

Considering Fig. 13.6, a substance represented by $C_aH_bO_c$ enters the control volume at T_0, p_0 . Depending on the particular substance, compounds present in the environment enter (O_2) and exit (CO_2 and $H_2O(g)$) at T_0 and their respective partial pressures in the environment. All substances enter and exit with negligible effects of motion and gravity. Heat transfer between the control volume and environment occurs only at temperature T_0 . The control volume operates at steady state, and the ideal gas model applies to all gases. Finally, for the overall system whose boundary is denoted by the dotted line, total volume is constant and there is no heat transfer across the boundary.

Next, we apply conservation of mass, an energy balance, and an entropy balance to the control volume of Fig. 13.6 with the objective of determining the maximum theoretical work per mole of substance $C_aH_bO_c$ entering—namely, the maximum theoretical value of \dot{W}_{cv}/\dot{n}_F . This value is the molar chemical exergy of the substance. The chemical exergy is given by

$$\bar{e}^{ch} = \left[\bar{h}_F + \left(a + \frac{b}{4} - \frac{c}{2} \right) \bar{h}_{O_2} - a \bar{h}_{CO_2} - \frac{b}{2} \bar{h}_{H_2O} \right] - T_0 \left[\bar{s}_F + \left(a + \frac{b}{4} - \frac{c}{2} \right) \bar{s}_{O_2} - a \bar{s}_{CO_2} - \frac{b}{2} \bar{s}_{H_2O} \right] \quad (13.29)$$

where the superscript ch is used to distinguish this contribution to the exergy magnitude from the thermomechanical exergy introduced in Chap. 7. The subscript F

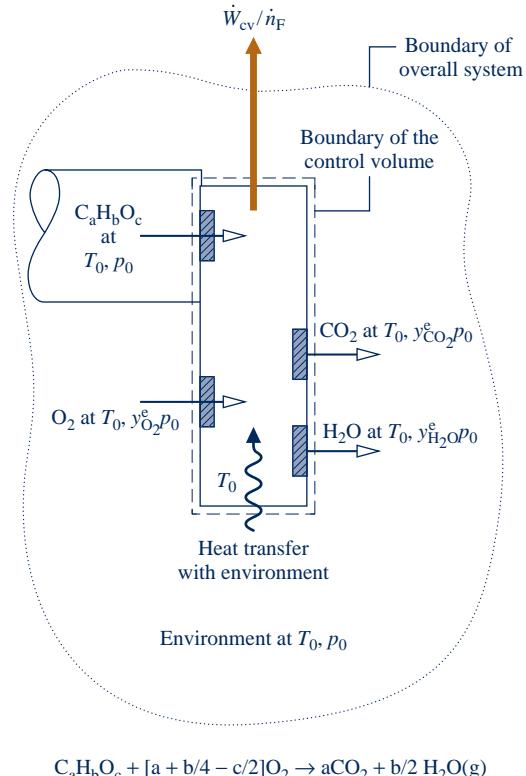


Fig. 13.6 Illustration used to conceptualize chemical exergy.

denotes the substance represented by $C_aH_bO_c$. The other molar enthalpies and entropies appearing in Eq. 13.29 refer to the substances entering and exiting the control volume, each evaluated at the state at which it enters or exits. See the following box for the derivation of Eq. 13.29.

Evaluating Chemical Exergy

Although chemical reaction does not occur in every case we will be considering, conservation of mass is accounted for generally by the following expression



which assumes that when reaction occurs, the reaction is complete.

For steady-state operation, the energy rate balance for the control volume of Fig. 13.6 reduces to give

$$\frac{\dot{W}_{cv}}{\dot{n}_F} = \frac{\dot{Q}_{cv}}{\dot{n}_F} + \bar{h}_F + \left(a + \frac{b}{4} - \frac{c}{2}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O} \quad (13.31)$$

where the subscript F denotes a substance represented by $C_aH_bO_c$ (Table 13.3). Since the control volume is at steady state, its volume does not change with time, so no portion of \dot{W}_{cv}/\dot{n}_F is required to displace the environment. Thus, in keeping with all specified idealizations, Eq. 13.31 also gives the work developed by the overall system of control volume plus environment whose boundary is denoted on Fig. 13.6 by a dotted line. The potential for such work is the difference in composition between substance $C_aH_bO_c$ and the environment.

Heat transfer is assumed to occur with environment only at temperature T_o . An entropy balance for the control volume takes the form

$$0 = \frac{\dot{Q}_{cv}/\dot{n}_F}{T_o} + \bar{s}_F + \left(a + \frac{b}{4} - \frac{c}{2}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O} + \frac{\dot{\sigma}_{cv}}{\dot{n}_F} \quad (13.32)$$

Eliminating the heat transfer rate between Eqs. 13.31 and 13.32 gives

$$\begin{aligned} \frac{\dot{W}_{cv}}{\dot{n}_F} &= \left[\bar{h}_F + \left(a + \frac{b}{4} - \frac{c}{2}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O} \right] \\ &\quad - T_o \left[\bar{s}_F + \left(a + \frac{b}{4} - \frac{c}{2}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O} \right] - T_o \frac{\dot{\sigma}_{cv}}{\dot{n}_F} \end{aligned} \quad (13.33)$$

In Eq. 13.33, the specific enthalpy h_F and specific entropy s_F are evaluated at T_o and p_o . Since the ideal gas model applies to the environment (Table 13.4), the specific enthalpies of the first underlined term of Eq. 13.33 are determined knowing only the temperature T_o . Further, the specific entropy of each substance of the second underlined term is determined by temperature T_o and the partial pressure in the environment of that substance. Accordingly, since the environment is specified, all enthalpy and entropy terms of Eq. 13.33 are known and independent of the nature of the processes occurring within the control volume.

The term $T_o\dot{\sigma}_{cv}$ depends explicitly on the nature of such processes, however. In accordance with the second law, $T_o\dot{\sigma}_{cv}$ is positive whenever irreversibilities are present, vanishes in the limiting case of no irreversibilities, and is never negative. The *maximum theoretical value* for the work developed is obtained when no irreversibilities are present. Setting $T_o\dot{\sigma}_{cv}$ to zero in Eq. 13.33, yields the expression for *chemical exergy* given by Eq. 13.29.

TAKE NOTE...

Observe that the approach used here to evaluate chemical exergy parallels those used in Secs. 7.3 and 7.5 to evaluate exergy of a system and flow exergy. In each case, energy and entropy balances are applied to evaluate maximum theoretical work in the limit as entropy production tends to zero.

13.6.1 Working Equations for Chemical Exergy

For computational convenience, the chemical exergy given by Eq. 13.29 is written as Eqs. 13.35 and 13.36. The first of these is obtained by recasting the specific entropies of O₂, CO₂, and H₂O using the following equation obtained by application of Eq. (a) of Table 13.1:

$$\bar{s}_i(T_0, y_i^e p_0) = \bar{s}_i(T_0, p_0) - \bar{R} \ln y_i^e \quad (13.34)$$

The first term on the right is the absolute entropy at T_0 and p_0 , and y_i^e is the mole fraction of component i in the environment.

Applying Eq. 13.34, Eq. 13.29 becomes

$$\begin{aligned} \bar{e}^{ch} = & \left[\bar{h}_F + \left(a + \frac{b}{4} - \frac{c}{2} \right) \bar{h}_{O_2} - a \bar{h}_{CO_2} - \frac{b}{2} \bar{h}_{H_2O(g)} \right] (T_0, p_0) \\ & - T_0 \left[\bar{s}_F + \left(a + \frac{b}{4} - \frac{c}{2} \right) \bar{s}_{O_2} - a \bar{s}_{CO_2} - \frac{b}{2} \bar{s}_{H_2O(g)} \right] (T_0, p_0) \\ & + \bar{R} T_0 \ln \left[\frac{(y_{O_2}^e)^{a+b/4-c/2}}{(y_{CO_2}^e)^a (y_{H_2O}^e)^{b/2}} \right] \end{aligned} \quad (13.35)$$

where the notation (T_0, p_0) signals that the specific enthalpy and entropy terms of Eq. 13.35 are each evaluated at T_0 and p_0 , although T_0 suffices for the enthalpy of substances modeled as ideal gases.

Recognizing the Gibbs function in Eq. 13.35— $\bar{g}_F = \bar{h}_F - T_0 \bar{s}_F$, for instance—Eq. 13.35 can be expressed alternatively in terms of the Gibbs functions of the several substances as

$$\begin{aligned} \bar{e}^{ch} = & \left[\bar{g}_F + \left(a + \frac{b}{4} - \frac{c}{2} \right) \bar{g}_{O_2} - a \bar{g}_{CO_2} - \frac{b}{2} \bar{g}_{H_2O(g)} \right] (T_0, p_0) \\ & + \bar{R} T_0 \ln \left[\frac{(y_{O_2}^e)^{a+b/4-c/2}}{(y_{CO_2}^e)^a (y_{H_2O}^e)^{b/2}} \right] \end{aligned} \quad (13.36)$$

The logarithmic term common to Eqs. 13.35 and 13.36 typically contributes only a few percent to the chemical exergy magnitude. Other observations follow:

- ▶ The specific Gibbs functions of Eq. 13.36 are evaluated at the temperature T_0 and pressure p_0 of the environment. These terms can be determined with Eq. 13.28a as

$$\bar{g}(T_0, p_0) = \bar{g}_f^\circ + [\bar{g}(T_0, p_0) - \bar{g}(T_{ref}, p_{ref})] \quad (13.37)$$

where \bar{g}_f° is the Gibbs function of formation and $T_{ref} = 25^\circ\text{C}$ (77°F), $p_{ref} = 1 \text{ atm}$.

- ▶ For the *special case* where T_0 and p_0 are the same as T_{ref} and p_{ref} , respectively, the second term on the right of Eq. 13.37 vanishes and the specific Gibbs function is just the Gibbs function of formation. That is, the Gibbs function values of Eq. 13.36 can be simply read from Tables A-25 or similar compilations.
- ▶ Finally, note that the underlined term of Eq. 13.36 can be written more compactly as $-\Delta G$: the negative of the change in Gibbs function for the reaction, Eq. 13.30, regarding each substance as separate at temperature T_0 and pressure p_0 .

13.6.2 Evaluating Chemical Exergy for Several Cases

Cases of practical interest corresponding to selected values of a , b , and c in the representation C_aH_bO_c can be obtained from Eq. 13.36. For example, $a = 8$, $b = 18$, $c = 0$

corresponds to octane, C₈H₁₈. An application of Eq. 13.36 to evaluate the chemical exergy of octane is provided in Example 13.12. Further special cases follow:

- Consider the case of pure carbon monoxide at T₀, p₀. For CO we have a = 1, b = 0, c = 1. Accordingly, Eq. 13.30 reads CO + ½O₂ → CO₂, and the chemical exergy obtained from Eq. 13.36 is

$$\bar{e}_{CO}^{ch} = [\bar{g}_{CO} + \frac{1}{2}\bar{g}_{O_2} - \bar{g}_{CO_2}](T_0, p_0) + \bar{R}T_0 \ln \left[\frac{(y_{CO}^e)^{1/2}}{y_{CO_2}^e} \right] \quad (13.38)$$

If carbon monoxide is not pure but a component of an ideal gas mixture at T₀, p₀, each component *i* of the mixture enters the control volume of Fig. 13.6 at temperature T₀ and the respective partial pressure y_{*i*}p₀. The contribution of carbon monoxide to the chemical exergy of the mixture, per mole of CO, is then given by Eq. 13.38, but with the mole fraction of carbon monoxide in the mixture, y_{CO}, appearing in the numerator of the logarithmic term that then reads ln[y_{CO}(y_{O₂}^e)^{1/2}/y_{CO₂}^e]. This becomes important when evaluating the exergy of combustion products involving carbon monoxide.

- Consider the case of pure water at T₀ and p₀. Water is a liquid when at T₀, p₀, but is a vapor within the environment of Table 13.4. Thus water enters the control volume of Fig. 13.6 as a liquid and exits as a vapor at T₀, y_{H₂O}^ep₀, with *no chemical reaction required*. In this case, a = 0, b = 2, and c = 1. Equation 13.36 gives the chemical exergy as

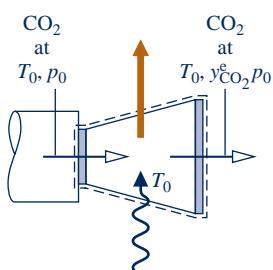
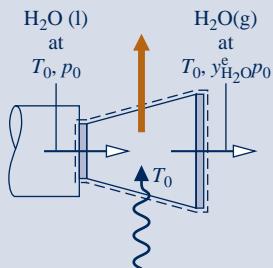
$$\bar{e}_{H_2O}^{ch} = [\bar{g}_{H_2O(l)} - \bar{g}_{H_2O(g)}](T_0, p_0) + \bar{R}T_0 \ln \left(\frac{1}{y_{H_2O}^e} \right) \quad (13.39)$$

- Consider the case of pure carbon dioxide at T₀, p₀. Like water, carbon dioxide is present within the environment and thus requires no chemical reaction to evaluate its chemical exergy. With a = 1, b = 0, c = 2, Eq. 13.36 gives the chemical exergy simply in terms of a logarithmic expression of the form

$$\bar{e}^{ch} = \bar{R}T_0 \ln \left(\frac{1}{y_{CO_2}^e} \right) \quad (13.40)$$

TAKE NOTE...

For liquid water, we think only of the work that could be developed as water expands through a turbine, or comparable device, from pressure p₀ to the partial pressure of the water vapor in the environment:



Provided the appropriate mole fraction y^e is used, Eq. 13.40 also applies to other substances that are gases in the environment, in particular to O₂ and N₂. Moreover, Eqs. 13.39 and 13.40 reveal that a chemical reaction does not always play a part when conceptualizing chemical exergy. In the cases of liquid water, CO₂, O₂, N₂, and other gases present in the environment, we think of the work that could be done as the particular substance passes by *diffusion* from the dead state, where its pressure is p₀, to the environment, where its pressure is the partial pressure, y_{*i*}p₀.

- Finally, for an ideal gas mixture at T₀, p₀ consisting *only* of substances present as gases in the environment, the chemical exergy is obtained by summing the contributions of each of the components. The result, per mole of mixture, is

$$\bar{e}^{ch} = \bar{R}T_0 \sum_{i=1}^j y_i \ln \left(\frac{y_i}{y_i^e} \right) \quad (13.41a)$$

where y_{*i*} and y_{*i*}^e denote, respectively, the mole fraction of component *i* in the mixture at T₀, p₀ and in the environment.

Expressing the logarithmic term as $(\ln(1/y_i^e) + \ln y_i)$ and introducing a relation like Eq. 13.40 for each gas i , Eq. 13.41a can be written alternatively as

$$\bar{e}^{ch} = \sum_{i=1}^j y_i \bar{e}_i^{ch} + \bar{R}T_0 \sum_{i=1}^j y_i \ln y_i \quad (13.41b)$$

The development of Eqs. 13.41a and 13.41b is left as an exercise.

13.6.3 Closing Comments

The approach introduced in this section for conceptualizing the chemical exergy of the set of substances represented by $C_aH_bO_c$ can also be applied, in principle, for other substances. In any such application, the chemical exergy is the maximum theoretical work that could be developed by a control volume like that considered in Fig. 13.6 where the substance of interest enters the control volume at T_0, p_0 and reacts completely with environmental components to produce environmental components. All participating environmental components enter and exit the control volume at their conditions within the environment. By describing the environment appropriately, this approach can be applied to many substances of practical interest.¹

13.7 Standard Chemical Exergy

While the approach used in Sec. 13.6 for conceptualizing chemical exergy can be applied to many substances of practical interest, complications are soon encountered. For one thing, the environment generally must be extended; the simple environment of Table 13.4 no longer suffices. In applications involving coal, for example, sulfur dioxide or some other sulfur-bearing compound must appear among the environmental components. Furthermore, once the environment is determined, a series of calculations are required to obtain exergy values for the substances of interest. These complexities can be sidestepped by using a table of *standard chemical exergies*.

Standard chemical exergy values are based on a standard exergy reference environment exhibiting standard values of the environmental temperature T_0 and pressure p_0 such as 298.15 K (536.67°R) and 1 atm, respectively. The exergy reference environment also consists of a set of reference substances with standard concentrations reflecting as closely as possible the chemical makeup of the natural environment. To exclude the possibility of developing work from interactions among parts of the environment, these reference substances must be in equilibrium mutually.

The reference substances generally fall into three groups: gaseous components of the atmosphere, solid substances from the Earth's crust, and ionic and nonionic substances from the oceans. A common feature of standard exergy reference environments is a gas phase, intended to represent air, that includes N_2 , O_2 , CO_2 , $H_2O(g)$, and other gases. The i th gas present in this gas phase is assumed to be at temperature T_0 and the partial pressure $p_i^e = y_i^e p_0$.

Two standard exergy reference environments are considered in this book, called *Model I* and *Model II*. For each of these models, Table A-26 gives values of the standard chemical exergy for several substances, in units of kJ/kmol, together with a brief description of the underlying rationale. The methods employed to determine the tabulated standard chemical exergy values are detailed in the references accompanying the tables. Only one of the two models should be used in a particular analysis.

The use of a table of standard chemical exergies often simplifies the application of exergy principles. However, the term "standard" is somewhat misleading, for there is no one specification of the environment that suffices for *all* applications. Still, chemical exergies calculated relative to alternative specifications of the environment are generally in good agreement. For a broad range of engineering applications, the

TAKE NOTE...

Equation 13.41b is also applicable for mixtures containing gases other than those present in the reference environment, for example gaseous fuels.

Moreover, this equation can be applied to mixtures that do not adhere to the ideal gas model. In all such applications, the terms \bar{e}_i^{ch} may be selected from a table of standard chemical exergies, introduced in Sec. 13.7 to follow.

standard chemical exergy

TAKE NOTE...

Standard exergy Model II is commonly used in practice. Model I is provided to show that other standard reference environments can at least be imagined.

¹For further discussion see M. J. Moran, *Availability Analysis: A Guide to Efficient Energy Use*, ASME Press, New York, 1989, pp. 169–170.

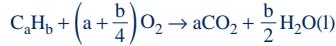
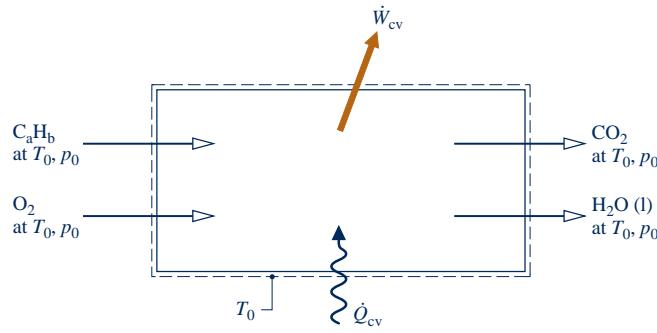


Fig. 13.7 Reactor used to introduce the standard chemical exergy of C_aH_b .

convenience of using standard values generally outweighs the slight lack of accuracy that might result. In particular, the effect of slight variations in the values of T_0 and p_0 about their standard values normally can be neglected.

13.7.1 Standard Chemical Exergy of a Hydrocarbon: C_aH_b

In principle, the standard chemical exergy of a substance *not* present in the environment can be evaluated by considering a reaction of the substance with other substances for which the chemical exergies *are known*.

To illustrate this for the case of a pure hydrocarbon fuel C_aH_b at T_0, p_0 , refer to the control volume at steady state shown in Fig. 13.7 where the fuel reacts completely with oxygen to form carbon dioxide and *liquid* water. All substances are assumed to enter and exit at T_0, p_0 and heat transfer occurs only at temperature T_0 .

Assuming no irreversibilities, an exergy rate balance for the control volume reads

$$0 = \sum_j \left[1 - \frac{T_0}{T_j} \right]^0 \left(\frac{\dot{Q}_j}{\dot{n}_F} \right) - \left(\frac{\dot{W}_{cv}}{\dot{n}_F} \right)_{int_{rev}} + \bar{e}_F^{ch} + \left(a + \frac{b}{4} \right) \bar{e}_{O_2}^{ch} - a \bar{e}_{CO_2}^{ch} - \left(\frac{b}{2} \right) \bar{e}_{H_2O(l)}^{ch} - \dot{E}_d^0$$

where the subscript F denotes C_aH_b . Solving for the chemical exergy e_F^{ch} , we get

$$\bar{e}_F^{ch} = \left(\frac{\dot{W}_{cv}}{\dot{n}_F} \right)_{int_{rev}} + a \bar{e}_{CO_2}^{ch} + \left(\frac{b}{2} \right) \bar{e}_{H_2O(l)}^{ch} - \left(a + \frac{b}{4} \right) \bar{e}_{O_2}^{ch} \quad (13.42)$$

Applying energy and entropy balances to the control volume, as in the development in the box on p. 818, we get

$$\begin{aligned} \left(\frac{\dot{W}_{cv}}{\dot{n}_F} \right)_{int_{rev}} &= \left[\bar{h}_F + \left(a + \frac{b}{4} \right) \bar{h}_{O_2} - a \bar{h}_{CO_2} - \frac{b}{2} \bar{h}_{H_2O(l)} \right] (T_0, p_0) \\ &\quad - T_0 \left[\bar{s}_F + \left(a + \frac{b}{4} \right) \bar{s}_{O_2} - a \bar{s}_{CO_2} - \frac{b}{2} \bar{s}_{H_2O(l)} \right] (T_0, p_0) \end{aligned} \quad (13.43)$$

The underlined term in Eq. 13.43 is recognized from Sec. 13.2.3 as the molar higher heating value \overline{HHV} (T_0, p_0). Substituting Eq. 13.43 into Eq. 13.42, we obtain

$$\begin{aligned} \bar{e}_F^{ch} &= \overline{HHV}(T_0, p_0) - T_0 \left[\bar{s}_F + \left(a + \frac{b}{4} \right) \bar{s}_{O_2} - a \bar{s}_{CO_2} - \frac{b}{2} \bar{s}_{H_2O(l)} \right] (T_0, p_0) \\ &\quad + a \bar{e}_{CO_2}^{ch} + \left(\frac{b}{2} \right) \bar{e}_{H_2O(l)}^{ch} - \left(a + \frac{b}{4} \right) \bar{e}_{O_2}^{ch} \end{aligned} \quad (13.44a)$$

Equations 13.42 and 13.43 can be expressed alternatively in terms of molar Gibbs functions as follows

$$\bar{e}_F^{ch} = \left[\bar{g}_F + \left(a + \frac{b}{4} \right) \bar{g}_{O_2} - a \bar{g}_{CO_2} - \frac{b}{2} \bar{g}_{H_2O(l)} \right] (T_0, p_0) \\ + a \bar{e}_{CO_2} + \left(\frac{b}{2} \right) \bar{e}_{H_2O(l)} - \left(a + \frac{b}{4} \right) \bar{e}_{O_2} \quad (13.44b)$$

With Eqs. 13.44, the standard chemical exergy of the hydrocarbon C_aH_b can be calculated using the standard chemical exergies of O_2 , CO_2 , and $H_2O(l)$, together with selected property data: the higher heating value and absolute entropies, or Gibbs functions.

► **FOR EXAMPLE** consider the case of methane, CH_4 , and $T_0 = 298.15\text{ K}$ (25°C), $p_0 = 1\text{ atm}$. For this application we can use Gibbs function data directly from Table A-25, and standard chemical exergies for CO_2 , $H_2O(l)$, and O_2 from Table A-26 (Model II), since each source corresponds to 298.15 K , 1 atm . With $a = 1$, $b = 4$, Eq. 13.44b gives $831,680\text{ kJ/kmol}$. This agrees with the value listed for methane in Table A-26 for Model II. ◀◀◀◀◀

We conclude the present discussion by noting special aspects of Eqs. 13.44:

- First, Eq. 13.44a requires the higher heating value and the absolute entropy \bar{s}_F . When data from property compilations are lacking for these quantities, as in the cases of coal, char, and fuel oil, the approach of Eq. 13.44a can be invoked using a *measured* or *estimated* heating value and an *estimated* value of the absolute entropy \bar{s}_F determined with procedures discussed in the literature.²
- Next, note that the first term of Eq. 13.44b can be written more compactly as $-\Delta G$: the negative of the change in Gibbs function for the reaction.
- Finally, note that only the underlined terms of Eqs. 13.44 require chemical exergy data relative to the model selected for the exergy reference environment.

In Example 13.12 we compare the use of Eq. 13.36 and Eq. 13.44b for evaluating the chemical exergy of a pure hydrocarbon fuel.

²See, for example, A. Bejan, G. Tsatsaronis, and M. J. Moran, *Thermal Design and Optimization*, Wiley, New York, 1996, Secs. 3.4.3 and 3.5.4.

►►►► EXAMPLE 13.12 ►.....

Evaluating the Chemical Exergy of Liquid Octane

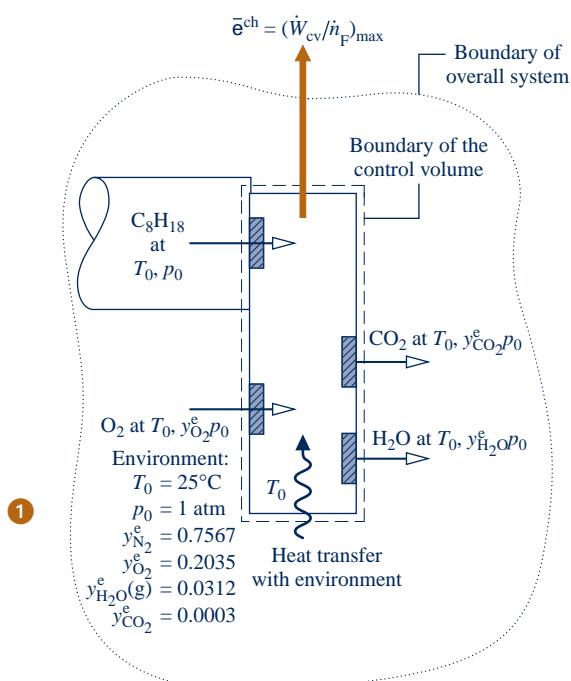
Determine the chemical exergy of liquid octane at 25°C , 1 atm , in kJ/kg . (a) Using Eq. 13.36, evaluate the chemical exergy for an environment corresponding to Table 13.4—namely, a gas phase at 25°C , 1 atm obeying the ideal gas model with the following composition on a molar basis: N_2 , 75.67%; O_2 , 20.35%; H_2O , 3.12%; CO_2 , 0.03%; other, 0.83%. (b) Evaluate the chemical exergy using Eq. 13.44b and standard chemical exergies from Table A-26 (Model II). Compare each calculated exergy value with the standard chemical exergy for liquid octane reported in Table A-26 (Model II).

SOLUTION

Known: The fuel is liquid octane.

Find: Determine the chemical exergy (a) using Eq. 13.36 relative to an environment consisting of a gas phase at 25°C , 1 atm with a specified composition, (b) using Eq. 13.44b and standard chemical exergies. Compare calculated values with the value reported in Table A-26 (Model II).

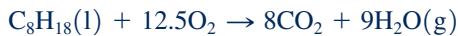
Schematic and Given Data:



Engineering Model: As shown in Fig. E13.12, the environment for part (a) consists of an ideal gas mixture with the molar analysis: N₂, 75.67%; O₂, 20.35%; H₂O, 3.12%; CO₂, 0.03%; other, 0.83%. For part (b), Model II of Table A-26 applies.

Fig. E13.12

Analysis: (a) Since $a = 8$, $b = 18$, $c = 0$, Eq. 13.30 gives the following expression for the complete combustion of liquid octane with O₂



Furthermore, Eq. 13.36 takes the form

$$\begin{aligned} \bar{e}^{\text{ch}} &= [\bar{g}_{\text{C}_8\text{H}_{18(l)}} + 12.5\bar{g}_{\text{O}_2} - 8\bar{g}_{\text{CO}_2} - 9\bar{g}_{\text{H}_2\text{O(g)}}](T_0, p_0) \\ &\quad + \bar{R}T_0 \ln \left[\frac{(y_{O_2}^e)^{12.5}}{(y_{CO_2}^e)^8 (y_{H_2O(g)}^e)^9} \right] \end{aligned}$$

Since $T_0 = T_{\text{ref}}$ and $p_0 = p_{\text{ref}}$, the required specific Gibbs functions are just the Gibbs functions of formation from Table A-25. With the given composition of the environment and data from Table A-25, the above equation gives

$$\begin{aligned} \bar{e}^{\text{ch}} &= [6610 + 12.5(0) - 8(-394,380) - 9(-228,590)] \\ &\quad + 8.314(298.15) \ln \left[\frac{(0.2035)^{12.5}}{(0.0003)^8 (0.0312)^9} \right] \\ &= 5,218,960 + 188,883 = 5,407,843 \text{ kJ/kmol} \end{aligned}$$

2

This value agrees closely with the standard chemical exergy for liquid octane reported in Table A-26 (Model II): 5,413,100 kJ/kmol.

Dividing by the molecular weight, the chemical exergy is obtained on a unit mass basis

$$e^{\text{ch}} = \frac{5,407,843}{114.22} = 47,346 \text{ kJ/kg}$$

(b) Using coefficients from the reaction equation above, Eq. 13.44b reads

$$\begin{aligned} \bar{e}^{\text{ch}} &= [\bar{g}_{\text{C}_8\text{H}_{18(l)}} + 12.5\bar{g}_{\text{O}_2} - 8\bar{g}_{\text{CO}_2} - 9\bar{g}_{\text{H}_2\text{O(l)}}](T_0, p_0) \\ &\quad + 8\bar{e}_{\text{CO}_2}^{\text{ch}} + 9\bar{e}_{\text{H}_2\text{O(l)}}^{\text{ch}} - 12.5\bar{e}_{\text{O}_2}^{\text{ch}} \end{aligned}$$

With data from Table A-25 and Model II of Table A-26, the above equation gives

$$\begin{aligned} \bar{e}^{\text{ch}} &= [6610 + 12.5(0) - 8(-394,380) - 9(-237,180)] \\ &\quad + 8(19,870) + 9(900) - 12.5(3970) \\ &= 5,296,270 + 117,435 = 5,413,705 \text{ kJ/kmol} \end{aligned}$$

- As expected, this agrees closely with the value listed for octane in Table A-26 (Model II): 5,413,100 kJ/kmol. Dividing by the molecular weight, the chemical exergy is obtained on a unit mass basis

$$\bar{e}^{\text{ch}} = \frac{5,413,705}{114.22} = 47,397 \text{ kJ/kg}$$

- The chemical exergies determined with the two approaches used in parts (a) and (b) also closely agree.

- 1 A molar analysis of this environment on a *dry* basis reads: O₂, 21%, N₂, CO₂ and the other dry components: 79%. This is consistent with the dry air analysis used throughout the chapter. The water vapor present in the assumed environment corresponds to the amount of vapor that would be present were the gas phase saturated with water at the specified temperature and pressure.
- 2 The value of the logarithmic term of Eq. 13.36 depends on the composition of the environment. In the present case, this term contributes about 3% to the magnitude of the chemical exergy. The contribution of the logarithmic term is usually small. In such instances, a satisfactory approximation to the chemical exergy can be obtained by omitting the term.

Skills Developed

Ability to...

- calculate the chemical exergy of a hydrocarbon fuel relative to a specified reference environment.
- calculate the chemical exergy of a hydrocarbon fuel based on standard chemical exergies.

QuickQUIZ

Would the higher heating value (HHV) of liquid octane provide a plausible estimate of the chemical exergy in this case? **Ans.** Yes, Table A-25 gives 47,900 kJ/kg, which is approximately 1% greater than values obtained in parts (a) and (b).

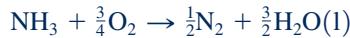
13.7.2 Standard Chemical Exergy of Other Substances

By paralleling the development given in Sec. 13.7.1 leading to Eq. 13.44b, we can in principle determine the standard chemical exergy of any substance not present in the environment. With such a substance playing the role of C_aH_b in the previous development, we consider a reaction of the substance with other substances for which the standard chemical exergies *are known*, and write

$$\bar{e}^{\text{ch}} = -\Delta G + \underbrace{\sum_{\text{P}} n \bar{e}^{\text{ch}}}_{\text{underlined}} - \underbrace{\sum_{\text{R}} n \bar{e}^{\text{ch}}}_{\text{underlined}} \quad (13.45)$$

where ΔG is the change in Gibbs function for the reaction, regarding each substance as separate at temperature T_0 and pressure p_0 . The underlined term corresponds to the underlined term of Eq. 13.44b and is evaluated using the *known* standard chemical exergies, together with the n 's giving the moles of these reactants and products per mole of the substance whose chemical exergy is being evaluated.

► **FOR EXAMPLE** consider the case of ammonia, NH₃, and $T_0 = 298.15 \text{ K}$ (25°C), $p_0 = 1 \text{ atm}$. Letting NH₃ play the role of C_aH_b in the development leading to Eq. 13.44b, we can consider any reaction of NH₃ with other substances for which the standard chemical exergies are known. For the reaction



Eq. 13.45 takes the form

$$\begin{aligned} \bar{e}_{\text{NH}_3}^{\text{ch}} &= [\bar{g}_{\text{NH}_3} + \frac{3}{4}\bar{g}_{\text{O}_2} - \frac{1}{2}\bar{g}_{\text{N}_2} - \frac{3}{2}\bar{g}_{\text{H}_2\text{O(l)}}](T_0, p_0) \\ &\quad + \frac{1}{2}\bar{e}_{\text{N}_2}^{\text{ch}} + \frac{3}{2}\bar{e}_{\text{H}_2\text{O(l)}}^{\text{ch}} - \frac{3}{4}\bar{e}_{\text{O}_2}^{\text{ch}} \end{aligned}$$

Using Gibbs function data from Table A-25, and standard chemical exergies for O₂, N₂, and H₂O(l) from Table A-26 (Model II), $\bar{e}_{\text{NH}_3}^{\text{ch}} = 337,910 \text{ kJ/kmol}$. This agrees closely with the value for ammonia listed in Table A-26 for Model II. ◀◀◀◀◀

13.8 Applying Total Exergy

The exergy associated with a specified state of a system is the sum of two contributions: the thermomechanical contribution introduced in Chap. 7 and the chemical contribution introduced in this chapter. On a unit mass basis, the **total exergy** is

total exergy

$$\underline{e = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz + e^{\text{ch}}} \quad (13.46)$$

where the underlined term is the thermomechanical contribution (Eq. 7.2) and e^{ch} is the chemical contribution evaluated as in Sec. 13.6 or 13.7. Similarly, the **total flow exergy** associated with a specified state is the sum

total flow exergy

$$\underline{e_f = h - h_0 - T_0(s - s_0) + \frac{V^2}{2} + gz + e^{\text{ch}}} \quad (13.47)$$

where the underlined term is the thermomechanical contribution (Eq. 7.14) and e^{ch} is the chemical contribution.

13.8.1 Calculating Total Exergy

Exergy evaluations considered in previous chapters of this book have been alike in this respect: Differences in exergy or flow exergy between states of the same composition have been evaluated. In such cases, the chemical exergy contribution cancels, leaving just the difference in thermomechanical contributions to exergy. However, for many evaluations it is necessary to account explicitly for chemical exergy—for instance, chemical exergy is important when evaluating processes involving combustion.

TAKE NOTE...

To simplify total exergy evaluations, combustion products at the dead state are assumed to contain water only as a vapor.

When using Eqs. 13.46 and 13.47 to evaluate total exergy at a state, we first think of bringing the system from that state to the state where the system is in thermal and mechanical equilibrium with the environment—that is, to the *dead state* where temperature is T_0 and pressure is p_0 . In applications dealing with gas mixtures involving water vapor, such as combustion products of hydrocarbons, some condensation of water vapor to liquid normally will occur in any such process to the dead state. Thus, at the dead state the initial gas mixture consists of a gas phase containing water vapor plus a relatively small amount of liquid water. Still, to simplify total exergy evaluations we will assume at the dead state that all water present in the combustion products of hydrocarbons exists only in vapor form. This *hypothetical* dead state condition suffices for applications considered in this chapter.

In Examples 13.13 and 13.14 to follow, we illustrate the evaluation of total exergy using the principles developed in Sec. 13.6. In Example 13.13, Eq. 13.47 is applied to evaluate the total specific flow exergy of a steam leak.

EXAMPLE 13.13 ▶

Evaluating the Total Flow Exergy of a Steam Leak

Steam at 5 bar, 240°C leaks from a line in a vapor power plant. Evaluate the total flow exergy of the steam, in kJ/kg, relative to an environment consisting of an ideal gas mixture at 25°C, 1 atm in which the mole fraction of water vapor is $y_{\text{H}_2\text{O}}^e = 0.0250$. Neglect the effects of motion and gravity.

SOLUTION

Known: Water vapor at a known state is specified. The environment is also described.

Find: Determine the total flow exergy of the water vapor, in kJ/kg.

Engineering Model:

1. The environment consists of a gas phase at $T_0 = 25^\circ\text{C}$, $p_0 = 1 \text{ atm}$ that obeys the ideal gas model. The mole fraction of water vapor in the environment is 0.0250.
2. Neglect the effects of motion and gravity.

Analysis: With assumption 2, the total specific flow exergy is given by Eq. 13.47 as

$$e_f = \underline{(h - h_0)} - T_0(s - s_0) + e^{\text{ch}}$$

The underlined term is the thermomechanical contribution to the flow exergy, evaluated as in Chap. 7. With data from the steam tables, and noting that water is a liquid at T_0 , p_0

$$\begin{aligned} h - h_0 - T_0(s - s_0) &= (2939.9 - 104.9) - 298(7.2307 - 0.3674) \\ &= 789.7 \text{ kJ/kg} \end{aligned}$$

where h_0 and s_0 are approximated as the saturated liquid values at T_0 .

The chemical exergy contribution to the flow exergy relative to the specified environment is evaluated using Eq. 13.39. With data from Table A-25 and applying the molar mass to convert to a mass basis

$$\begin{aligned} e^{\text{ch}} &= \frac{1}{M} \left\{ [\bar{g}_{\text{H}_2\text{O}(l)} - \bar{g}_{\text{H}_2\text{O}(g)}](T_0, p_0) + \bar{R}T_0 \ln \left(\frac{1}{y_{\text{H}_2\text{O}}^e} \right) \right\} \\ &= \frac{1}{18} \left\{ [-237,180 - (-228,590)] + (8.314)(298) \ln \left(\frac{1}{0.0250} \right) \right\} \\ &= \frac{549.5 \text{ kJ/kmol}}{18 \text{ kg/kmol}} = 30.5 \text{ kJ/kg} \end{aligned}$$

Adding the thermomechanical and chemical contributions, the flow exergy of steam at the specified state is

$$e_f = 789.7 + 30.5 = 820.2 \text{ kJ/kg}$$

In this case, the chemical exergy contributes about 4% to the total flow exergy magnitude.

 **Skills Developed**

Ability to...

- determine the flow exergy, including the chemical exergy contribution, of steam.

QuickQUIZ

If the mass flow rate of the steam leak is 0.07 kg/s, and the flow exergy is valued at \$0.10/kW · h, what is the value of one day's steam loss? **Ans.** \$138/day.

In Example 13.14, the total specific flow exergy of combustion products is evaluated.

 **EXAMPLE 13.14**
Evaluating the Total Flow Exergy of Combustion Products

Methane gas enters a reactor and burns completely with 140% theoretical air. Combustion products exit as a mixture at temperature T and a pressure of 1 atm. For $T = 865$ and 2820°R , evaluate the total specific flow exergy of the combustion products, in Btu per lbmol of fuel. Perform calculations relative to an environment consisting of an ideal gas mixture at 77°F , 1 atm with the molar analysis, $y_{\text{N}_2}^e = 0.7567$, $y_{\text{O}_2}^e = 0.2035$, $y_{\text{H}_2\text{O}}^e = 0.0303$, $y_{\text{CO}_2}^e = 0.0003$.

SOLUTION

Known: Methane gas reacts completely with 140% of the theoretical amount of air. Combustion products exit the reactor at 1 atm and a specified temperature. The environment is also specified.

Find: Determine the total flow exergy of the combustion products, in Btu per lbmol of fuel, for each of two given temperatures.

Engineering Model:

1. The combustion products are modeled as an ideal gas mixture at all states considered.
2. The environment consists of an ideal gas mixture at $T_0 = 77^\circ\text{F}$, $p_0 = 1 \text{ atm}$ with a specified molar analysis.
3. Neglect the effects of motion and gravity.

Analysis: For 140% theoretical air, the reaction equation for complete combustion of methane is



The total specific flow exergy is given by Eq. 13.47, which involves chemical and thermomechanical contributions. Since the combustion products form an ideal gas mixture when at T_0 , p_0 (assumption 1) and each component is present within the environment, the chemical exergy contribution, per mole of fuel, is obtained from the following expression patterned after Eq. 13.41a

$$① \quad \bar{e}^{\text{ch}} = \bar{R}T_0 \left[1 \ln \left(\frac{y_{\text{CO}_2}}{y_{\text{CO}_2}^e} \right) + 2 \ln \left(\frac{y_{\text{H}_2\text{O}}}{y_{\text{H}_2\text{O}}^e} \right) + 10.53 \ln \left(\frac{y_{\text{N}_2}}{y_{\text{N}_2}^e} \right) + 0.8 \ln \left(\frac{y_{\text{O}_2}}{y_{\text{O}_2}^e} \right) \right]$$

From the reaction equation, the mole fractions of the components of the products are $y_{\text{CO}_2} = 0.0698$, $y_{\text{H}_2\text{O}} = 0.1396$, $y_{\text{N}_2} = 0.7348$, $y_{\text{O}_2} = 0.0558$. Substituting these values together with the respective environmental mole fractions, we obtain $\bar{e}^{\text{ch}} = 7637 \text{ Btu per lbmol of fuel}$.

Applying ideal gas mixture principles from Table 13.1, the thermomechanical contribution to the flow exergy, per mole of fuel, is

$$\begin{aligned} \bar{h} - \bar{h}_0 - T_0(\bar{s} - \bar{s}_0) &= [\bar{h}(T) - \bar{h}(T_0) - T_0(\bar{s}^\circ(T) - \bar{s}^\circ(T_0) - \bar{R} \ln(y_{\text{CO}_2} p / y_{\text{CO}_2} p_0))]_{\text{CO}_2} \\ &\quad + 2[\bar{h}(T) - \bar{h}(T_0) - T_0(\bar{s}^\circ(T) - \bar{s}^\circ(T_0) - \bar{R} \ln(y_{\text{H}_2\text{O}} p / y_{\text{H}_2\text{O}} p_0))]_{\text{H}_2\text{O}} \\ &\quad + 10.53[\bar{h}(T) - \bar{h}(T_0) - T_0(\bar{s}^\circ(T) - \bar{s}^\circ(T_0) - \bar{R} \ln(y_{\text{N}_2} p / y_{\text{N}_2} p_0))]_{\text{N}_2} \\ &\quad + 0.8[\bar{h}(T) - \bar{h}(T_0) - T_0(\bar{s}^\circ(T) - \bar{s}^\circ(T_0) - \bar{R} \ln(y_{\text{O}_2} p / y_{\text{O}_2} p_0))]_{\text{O}_2} \end{aligned}$$

Since $p = p_0$, each of the logarithm terms drop out, and with \bar{h} and \bar{s}° data at T_0 from Table A-23E, the thermomechanical contribution reads

$$\begin{aligned} \bar{h} - \bar{h}_0 - T_0(\bar{s} - \bar{s}_0) &= [\bar{h}(T) - 4027.5 - 537(\bar{s}^\circ(T) - 51.032)]_{\text{CO}_2} \\ &\quad + 2[\bar{h}(T) - 4258 - 537(\bar{s}^\circ(T) - 45.079)]_{\text{H}_2\text{O}} \\ &\quad + 10.53[\bar{h}(T) - 3729.5 - 537(\bar{s}^\circ(T) - 45.743)]_{\text{N}_2} \\ &\quad + 0.8[\bar{h}(T) - 3725.1 - 537(\bar{s}^\circ(T) - 48.982)]_{\text{O}_2} \end{aligned}$$

Then, with \bar{h} and \bar{s}° from Table A-23E at $T = 865$ and 2820°R , respectively, the following results are obtained

$$T = 865^\circ\text{R}: \bar{h} - \bar{h}_0 - T_0(\bar{s} - \bar{s}_0) = 7622 \text{ Btu per lbmol of fuel}$$

$$T = 2820^\circ\text{R}: \bar{h} - \bar{h}_0 - T_0(\bar{s} - \bar{s}_0) = 169,319 \text{ Btu per lbmol of fuel}$$

Adding the two contributions, the total specific flow exergy of the combustion products at each of the specified states is

$$② \quad \begin{aligned} T = 865^\circ\text{R}: \bar{e}_f &= 15,259 \text{ Btu per lbmol of fuel} \\ T = 2820^\circ\text{R}: \bar{e}_f &= 176,956 \text{ Btu per lbmol of fuel} \end{aligned}$$

1 This assumes a *hypothetical* dead state condition. Although condensation of some of the water vapor present in the combustion products would occur were the products brought to T_0 , p_0 , we assume for simplicity that all water remains a vapor at the dead state. An exergy evaluation explicitly taking such condensation into

account is considered in Bejan, Tsatsaronis, and Moran, *Thermal Design and Optimization*, p. 129, p. 138.

- ② The chemical contribution to the flow exergy is relatively unimportant in the higher-temperature case, amounting only to about 4% of the flow exergy. Chemical exergy accounts for about half of the exergy in the lower-temperature case, however.



Skills Developed

Ability to...

- determine the flow exergy, including the chemical exergy contribution, of gaseous products of combustion.

QuickQUIZ

If fuel enters with a mass flow rate of 28 lb/h, determine the flow exergy rate of the exiting combustion gases at $T = 2820^{\circ}\text{R}$, in Btu/h and kW. **Ans.** 3.1×10^5 Btu/h, 90.8 kW.

13.8.2 Calculating Exergetic Efficiencies of Reacting Systems

Devices designed to do work by utilization of a combustion process, such as vapor and gas power plants and reciprocating internal combustion engines, invariably have irreversibilities and losses associated with their operation. Accordingly, actual devices produce work equal to only a fraction of the maximum theoretical value that might be obtained. The vapor power plant exergy analysis of Sec. 8.6 and the combined cycle exergy analysis of Example 9.12 provide illustrations.

The performance of devices whose primary function is to do work can be evaluated as the ratio of the actual work developed to the exergy of the fuel consumed in producing that work. This ratio is an *exergetic efficiency*. The relatively low exergetic efficiency exhibited by many common power-producing devices suggests that thermodynamically more thrifty ways of utilizing the fuel to develop power might be possible. However, efforts in this direction must be tempered by the economic imperatives that govern the practical application of all devices. The trade-off between fuel savings and the additional costs required to achieve those savings must be carefully weighed.

The fuel cell provides an illustration of a relatively fuel-efficient device. We noted previously (Sec. 13.4) that the chemical reactions in fuel cells are more controlled than the rapidly occurring, highly irreversible combustion reactions taking place in conventional power-producing systems. In principle, fuel cells can achieve greater exergetic efficiencies than many such devices. Still, relative to conventional power systems, fuel cell systems typically cost more per unit of power generated, and this has limited their deployment.

The examples to follow illustrate the evaluation of an exergetic efficiency for an internal combustion engine and a reactor. In each case, standard chemical exergies are used in the solution.

EXAMPLE 13.15

Evaluating Exergetic Efficiency of an Internal Combustion Engine

Devise and evaluate an exergetic efficiency for the internal combustion engine of Example 13.4. For the fuel, use the standard chemical exergy value from Table A-26 (Model II).

SOLUTION

Known: Liquid octane and the theoretical amount of air enter an internal combustion engine operating at steady state in separate streams at 77°F , 1 atm, and burn completely. The combustion products exit at 1140°F . The power developed by the engine is 50 horsepower, and the fuel mass flow rate is 0.004 lb/s.

Find: Devise and evaluate an exergetic efficiency for the engine using the fuel standard chemical exergy value from Table A-26 (Model II).

Schematic and Given Data: See Fig. E13.4.

Engineering Model:

1. See the assumptions listed in the solution to Example 13.4.
2. The environment corresponds to Model II of Table A-26.
3. The combustion air enters at the condition of the environment.

Analysis: An exergy balance can be used in formulating an exergetic efficiency for the engine: At steady state, the rate at which exergy enters the engine equals the rate at which exergy exits plus the rate at which exergy is destroyed within the engine. As the combustion air enters at the condition of the environment, and thus with zero exergy, exergy enters the engine only with the fuel. Exergy exits the engine accompanying heat and work, and with the products of combustion.

If the power developed is taken to be the *product* of the engine, and the heat transfer and exiting product gas are regarded as *losses*, an exergetic efficiency expression that gauges the extent to which the exergy entering the engine with the fuel is converted to the product is

$$1 \quad \varepsilon = \frac{\dot{W}_{cv}}{\dot{E}_F}$$

where \dot{E}_F denotes the rate at which exergy enters with the fuel.

Since the fuel enters the engine at 77°F and 1 atm, which correspond to the values of T_0 and p_0 of the environment, and kinetic and potential energy effects are negligible, the exergy of the fuel is just the chemical exergy. There is no thermomechanical contribution. Thus, with data from Table A-1 and Table A-26 (Model II)

$$\dot{E}_F = \dot{m}_F e^{ch} = \left(0.004 \frac{\text{lb}}{\text{s}}\right) \left(\frac{5,413,100 \text{ kJ/kmol}}{114.22 \text{ kg/kmol}}\right) \left|\frac{\text{Btu/lb}}{2.326 \text{ kJ/kg}}\right| = 81.5 \frac{\text{Btu}}{\text{s}}$$

The exergetic efficiency is then

$$\varepsilon = \left(\frac{50 \text{ hp}}{81.5 \text{ Btu/s}}\right) \left|\frac{2545 \text{ Btu/h}}{1 \text{ hp}}\right| \left|\frac{1 \text{ h}}{3600 \text{ s}}\right| = 0.434 (43.4\%)$$

- 1 The exergy of exhaust gas and engine coolant of internal combustion engines may be utilizable for various purposes—for instance, additional power might be produced using *bottoming* cycles as considered in Problem 9.12D. In most cases, such additional power would be included in the numerator of the exergetic efficiency expression. Since a greater portion of the entering fuel exergy is utilized in such arrangements, the value of ε would be greater than that evaluated in the solution.

Skills Developed

Ability to...

- devise and evaluate an exergetic efficiency for an internal combustion engine.

QuickQUIZ

Using a rationale paralleling that for the internal combustion engine, devise and evaluate an exergetic efficiency for the gas turbine power plant of Example 13.5. **Ans.** 0.332 (33.2%).

In the next example, we evaluate an exergetic efficiency for a reactor. In this case, the exergy of the combustion products, not power developed, is the valued output.

EXAMPLE 13.16

Evaluating Exergetic Efficiency of a Reactor Fueled by Liquid Octane

For the reactor of Examples 13.8 and 13.9, determine the exergy destruction, in kJ per kmol of fuel, and devise and evaluate an exergetic efficiency. Consider two cases: complete combustion with the theoretical amount of air, and complete combustion with 400% theoretical air. For the fuel, use the standard chemical exergy value from Table A-26 (Model II).

SOLUTION

Known: Liquid octane and air, each at 25°C and 1 atm, burn completely in a well-insulated reactor operating at steady state. The products of combustion exit at 1 atm pressure.

Find: Determine the exergy destruction, in kJ per kmol of fuel, and evaluate an exergetic efficiency for complete combustion with the theoretical amount of air and 400% theoretical air.

Schematic and Given Data: See Fig. E13.9.

Engineering Model:

1. See assumptions listed in Examples 13.8 and 13.9.
2. The environment corresponds to Model II of Table A-26.
3. The combustion air enters at the condition of the environment.

Analysis: An exergy rate balance can be used in formulating an exergetic efficiency: At steady state, the rate at which exergy enters the reactor equals the rate at which exergy exits plus the rate at which exergy is destroyed within the reactor. Since the combustion air enters at the condition of the environment, and thus with zero exergy, exergy enters the reactor only with the fuel. The reactor is well insulated, so there is no exergy transfer accompanying heat transfer. There is also no work \dot{W}_{cv} . Accordingly, exergy exits only with the combustion products, which is the valuable output in this case. The exergy rate balance then reads

$$\dot{E}_F = \dot{E}_{\text{products}} + \dot{E}_d \quad (\text{a})$$

where \dot{E}_F is the rate at which exergy enters with the fuel, $\dot{E}_{\text{products}}$ is the rate at which exergy exits with the combustion products, and \dot{E}_d is the rate of exergy destruction within the reactor.

An exergetic efficiency then takes the form

$$\varepsilon = \frac{\dot{E}_{\text{products}}}{\dot{E}_F} \quad (\text{b})$$

The rate at which exergy exits with the products can be evaluated with the approach used in the solution to Example 13.14. But in the present case effort is saved with the following approach: Using the exergy balance for the reactor, Eq. (a), the exergetic efficiency expression, Eq. (b), can be written alternatively as

$$\varepsilon = \frac{\dot{E}_F - \dot{E}_d}{\dot{E}_F} = 1 - \frac{\dot{E}_d}{\dot{E}_F} \quad (\text{c})$$

The exergy destruction term appearing in Eq. (b) can be found from the relation

$$\frac{\dot{E}_d}{\dot{n}_F} = T_0 \frac{\dot{\sigma}_{cv}}{\dot{n}_F}$$

where T_0 is the temperature of the environment and $\dot{\sigma}_{cv}$ is the rate of entropy production. The rate of entropy production is evaluated in the solution to Example 13.9 for each of the two cases. For the case of complete combustion with the theoretical amount of air

$$\frac{\dot{E}_d}{\dot{n}_F} = (298 \text{ K}) \left(5404 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \right) = 1,610,392 \frac{\text{kJ}}{\text{kmol}}$$

Similarly, for the case of complete combustion with 400% of the theoretical amount of air

$$\frac{\dot{E}_d}{\dot{n}_F} = (298)(9754) = 2,906,692 \frac{\text{kJ}}{\text{kmol}}$$

Since the fuel enters the reactor at 25°C, 1 atm, which correspond to the values of T_0 and p_0 of the environment, and kinetic and potential effects are negligible, the exergy of the fuel is just the standard chemical exergy from Table A-26 (Model II): 5,413,100 kJ/kmol. There is no thermomechanical contribution. Thus, for the case of complete combustion with the theoretical amount of air, Eq. (c) gives

$$\varepsilon = 1 - \frac{1,610,392}{5,413,100} = 0.703 (70.3\%)$$

Similarly, for the case of complete combustion with 400% of the theoretical amount of air, we get

$$\textcircled{1} \quad \varepsilon = 1 - \frac{2,906,692}{5,413,100} = 0.463 \text{ (46.3%)}$$

- 1** The calculated efficiency values show that a substantial portion of the fuel exergy is destroyed in the combustion process. In the case of combustion with the theoretical amount of air, about 30% of the fuel exergy is destroyed. In the excess air case, over 50% of the fuel exergy is destroyed. Further exergy destructions would take place as the hot gases are utilized. It might be evident, therefore, that the overall conversion from fuel input to end use would have a relatively low exergetic efficiency. The vapor power plant exergy analysis of Sec. 8.6 illustrates this point.

Skills Developed

Ability to...

- determine exergy destruction for a reactor.
- devise and evaluate an appropriate exergetic efficiency.

QuickQUIZ

For complete combustion with 300% of theoretical air, would the exergetic efficiency be greater than, or less than, the exergetic efficiency determined for the case of 400% of theoretical air? **Ans.** Greater than.

► CHAPTER SUMMARY AND STUDY GUIDE

In this chapter we have applied the principles of thermodynamics to systems involving chemical reactions, with emphasis on systems involving the combustion of hydrocarbon fuels. We also have extended the notion of exergy to include chemical exergy.

The first part of the chapter begins with a discussion of concepts and terminology related to fuels, combustion air, and products of combustion. The application of energy balances to reacting systems is then considered, including control volumes at steady state and closed systems. To evaluate the specific enthalpies required in such applications, the enthalpy of formation concept is introduced and illustrated. The determination of the adiabatic flame temperature is considered as an application.

The use of the second law of thermodynamics is also discussed. The absolute entropy concept is developed to provide the specific entropies required by entropy balances for systems involving chemical reactions. The related Gibbs function of formation concept is introduced. The first part of the chapter also includes a discussion of fuel cells.

In the second part of the chapter, we extend the exergy concept of Chap. 7 by introducing chemical exergy. The *standard* chemical exergy concept is also discussed. Means are developed and illustrated for evaluating the chemical exergies of hydrocar-

bon fuels and other substances. The presentation concludes with a discussion of exergetic efficiencies of reacting systems.

The following list provides a study guide for this chapter. When your study of the text and end-of-chapter exercises has been completed, you should be able to

- ▶ write out the meaning of the terms listed in the margin throughout the chapter and understand each of the related concepts. The subset of key concepts listed below is particularly important.
- ▶ determine balanced reaction equations for the combustion of hydrocarbon fuels, including complete and incomplete combustion with various percentages of theoretical air.
- ▶ apply energy balances to systems involving chemical reactions, including the evaluation of enthalpy using Eq. 13.9 and the evaluation of the adiabatic flame temperature.
- ▶ apply entropy balances to systems involving chemical reactions, including the evaluation of the entropy produced.
- ▶ evaluate the chemical exergy of hydrocarbon fuels and other substances using Eqs. 13.35 and 13.36, as well as the standard chemical exergy using Eqs. 13.44 and 13.45.
- ▶ evaluate total exergy using Eqs. 3.46 and 3.47.
- ▶ apply exergy analysis, including chemical exergy and the evaluation of exergetic efficiencies.

► KEY ENGINEERING CONCEPTS

complete combustion, p. 778
air-fuel ratio, p. 779
theoretical air, p. 780
percent of theoretical air, p. 780

dry product analysis, p. 783
enthalpy of formation, p. 788
heating values, p. 797
adiabatic flame temperature, p. 800

fuel cell, p. 804
absolute entropy, p. 809
chemical exergy, p. 816
standard chemical exergy, p. 821

► KEY EQUATIONS

$AF = \overline{AF} \left(\frac{M_{\text{air}}}{M_{\text{fuel}}} \right)$	(13.2) p. 780	Relation between air-fuel ratios on mass and molar bases
$\bar{h}(T, p) = \bar{h}_{\text{f}}^{\circ} + [\bar{h}(T, p) - \bar{h}(T_{\text{ref}}, p_{\text{ref}})] = \bar{h}_{\text{f}}^{\circ} + \Delta \bar{h}$	(13.9) p. 789	Evaluating enthalpy at T, p in terms of enthalpy of formation
$\frac{\dot{Q}_{\text{cv}}}{\dot{n}_{\text{F}}} - \frac{\dot{W}_{\text{cv}}}{\dot{n}_{\text{F}}} = \sum_{\text{P}} n_e (\bar{h}_{\text{f}}^{\circ} + \Delta \bar{h})_e - \sum_{\text{R}} n_i (\bar{h}_{\text{f}}^{\circ} + \Delta \bar{h})_i$	(13.15b) p. 791	Energy rate balance for a control volume at steady state per mole of fuel entering
$Q - W = \sum_{\text{P}} n (\bar{h}_{\text{f}}^{\circ} + \Delta \bar{h}) - \sum_{\text{R}} n (\bar{h}_{\text{f}}^{\circ} + \Delta \bar{h}) - \bar{R} T_p \sum_{\text{P}} n + \bar{R} T_R \sum_{\text{R}} n$	(13.17b) p. 795	Closed system energy balance, where reactants and products are each ideal gas mixtures
$\bar{s}(T, p) = \bar{s}^{\circ}(T) - \bar{R} \ln \frac{p}{p_{\text{ref}}}$	(13.22) p. 809	Absolute entropy of an ideal gas (molar basis) at T, p , where $\bar{s}^{\circ}(T)$ is from Tables A-23
$\bar{s}_i(T, p_i) = \bar{s}_i^{\circ}(T) - \bar{R} \ln \frac{y_i P}{p_{\text{ref}}}$	(13.23) p. 810	Absolute entropy for component i of an ideal gas mixture (molar basis) at T, p , where $\bar{s}_i^{\circ}(T)$ is from Tables A-23
$\bar{g}(T, p) = \bar{g}_{\text{f}}^{\circ} + [\bar{g}(T, p) - \bar{g}(T_{\text{ref}}, p_{\text{ref}})] = \bar{g}_{\text{f}}^{\circ} + \Delta \bar{g}$ where $\Delta \bar{g} = [\bar{h}(T, p) - \bar{h}(T_{\text{ref}}, p_{\text{ref}})] - [T \bar{s}(T, p) - T_{\text{ref}} \bar{s}(T_{\text{ref}}, p_{\text{ref}})]$	(13.28a) p. 815 (13.28b) p. 815	Evaluating Gibbs function at T, p in terms of Gibbs function of formation (see Tables A-25 for $\bar{g}_{\text{f}}^{\circ}$ values)
$e_f = h - h_0 - T_0(s - s_0) + \frac{V^2}{2} + gz + e^{ch}$	(13.47) p. 826	Total specific flow exergy including thermomechanical and chemical contributions (see Secs. 13.6 and 13.7 for chemical exergy expressions)

► EXERCISES: THINGS ENGINEERS THINK ABOUT

- If an engine burns *rich*, is the percent of theoretical air greater than 100% or less than 100%?
- When you burn wood in a fireplace, do you contribute to *global* climate change? Explain.
- Why are some *high-efficiency*, residential natural gas furnaces equipped with drain tubes?
- You read that for every gallon of gasoline burned by a car's engine, nearly 20 lb of carbon dioxide is produced. Is this correct? Explain.
- Can coal be converted to a liquid diesel-like fuel? Explain.
- How does the octane rating of gasoline relate to the combustion in a car's engine?
- In K, how close to absolute zero have experimenters reached?
- How is the desired air-fuel ratio maintained in automotive internal combustion engines?
- Does complete combustion of natural gas in *pure* oxygen produce a higher or lower adiabatic flame temperature than complete combustion of natural gas in atmospheric air? Explain.
- What is the difference between *octane rating* and *octane*?
- How do those instant hot and cold packs used by athletes to treat injuries work? For what kinds of injury is each type of pack best suited?
- What is an advantage of using standard chemical exergies? A disadvantage?
- How might an exergetic efficiency be defined for the hybrid power system of Fig. 13.5?
- In the derivation of Eqs. 13.44, we assume the reactor of Fig. 13.7 operates without internal irreversibilities. Is this assumption necessary? Explain.

► PROBLEMS: DEVELOPING ENGINEERING SKILLS

Working with Reaction Equations

13.1 A vessel contains a mixture of 60% O₂ and 40% CO on a mass basis. Determine the percent excess or percent deficiency of oxygen, as appropriate.

13.2 Ten grams of propane (C₃H₈) burns with just enough oxygen (O₂) for complete combustion. Determine the amount of oxygen required and the amount of combustion products formed, each in grams.

13.3 Ethane (C₂H₆) burns completely with the theoretical amount of air. Determine the air-fuel ratio on a (a) molar basis, (b) mass basis.

13.4 A gas turbine burns octane (C₈H₁₈) completely with 400% of theoretical air. Determine the amount of N₂ in the products, in kmol per kmol of fuel.

13.5 One hundred kmol of butane (C₄H₁₀) together with 4000 kmol of air enter a furnace per unit of time. Carbon dioxide, carbon monoxide, and unburned fuel appear in the products of combustion exiting the furnace. Determine the percent excess or percent deficiency of air, whichever is appropriate.

13.6 Propane (C₃H₈) is burned with air. For each case, obtain the balanced reaction equation for complete combustion

- (a) with the theoretical amount of air.
- (b) with 20% excess air.
- (c) with 20% excess air, but only 90% of the propane being consumed in the reaction.

13.7 Butane (C₄H₁₀) burns completely with air. The equivalence ratio is 0.9. Determine

- (a) the balanced reaction equation.
- (b) the percent excess air.

13.8 A natural gas mixture having a molar analysis 60% CH₄, 30% C₂H₆, 10% N₂ is supplied to a furnace like the one shown in Fig. P13.8, where it burns completely with 20% excess air. Determine

- (a) the balanced reaction equation.
- (b) the air-fuel ratio, both on a molar and a mass basis.

13.9 A fuel mixture with the molar analysis 40% CH₃OH, 50% C₂H₅OH, and 10% N₂ burns completely with 33% excess air. Determine

- (a) the balanced reaction equation.
- (b) the air-fuel ratio, both on a molar and mass basis.

13.10 A gas mixture with the molar analysis 25% H₂, 25% CO, 50% O₂ reacts to form products consisting of CO₂, H₂O, and O₂ only. Determine the amount of each product, in kg per kg of mixture.

13.11 A natural gas with the molar analysis 78% CH₄, 13% C₂H₆, 6% C₃H₈, 1.7% C₄H₁₀, 1.3% N₂ burns completely with 40% excess air in a reactor operating at steady state. If the molar flow rate of the fuel is 0.5 kmol/h, determine the molar flow rate of the air, in kmol/h.

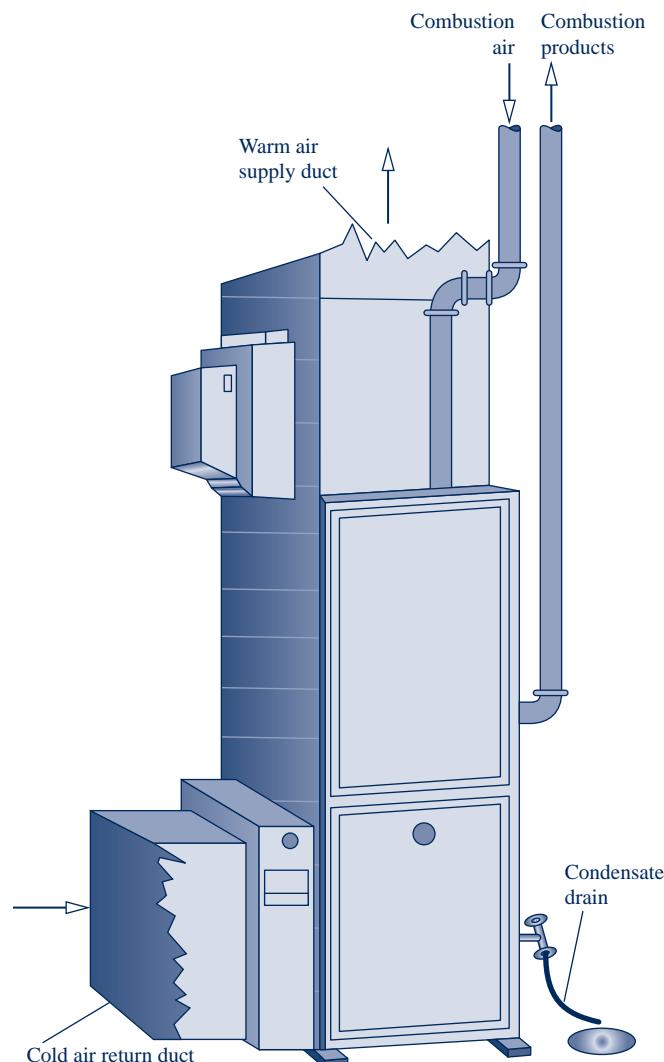


Fig. P13.8

13.12 A natural gas fuel mixture has the molar analysis shown below. Determine the molar analysis of the products for complete combustion with 70% excess dry air.

Fuel	CH ₄	H ₂	NH ₃
y _i	25%	30%	45%

13.13 Coal with the mass analysis 77.54% C, 4.28% H, 1.46% S, 7.72% O, 1.34% N, 7.66% noncombustible ash burns completely with 120% of theoretical air. Determine

- (a) the balanced reaction equation.
- (b) the amount of SO₂ produced, in kg per kg of coal.

13.14 A coal sample has a mass analysis of 80.4% carbon, 3.9% hydrogen (H), 5.0% oxygen (O), 1.1% nitrogen (N), 1.1% sulfur, and the rest is noncombustible ash. For complete combustion with 120% of the theoretical amount of air, determine the air-fuel ratio on a mass basis.

13.15 A sample of dried feedlot manure is being tested for use as a fuel. The mass analysis of the sample is 42.7% carbon, 5.5% hydrogen (H), 31.3% oxygen (O), 2.4% nitrogen (N), 0.3% sulfur, and 17.8% noncombustible ash. The sample is burned completely with 120% of theoretical air. Determine

- the balanced reaction equation.
- the air-fuel ratio on a mass basis.

13.16 A sample of dried Appanoose County coal has a mass analysis of 71.1% carbon, 5.1% hydrogen (H), 9.0% oxygen (O), 1.4% nitrogen (N_2), 5.8% sulfur, and the rest noncombustible ash. For complete combustion with the theoretical amount of air, determine

- the amount of SO_2 produced, in kg per kg of coal.
- the air-fuel ratio on a mass basis.

13.17 Octane (C_8H_{18}) burns completely with 120% of theoretical air. Determine

- the air-fuel ratio on a molar and mass basis.
- the dew point temperature of the combustion products, in $^{\circ}C$, when cooled at 1 atm.

13.18 Butane (C_4H_{10}) burns completely with 150% of theoretical air. If the combustion products are cooled at 1 atm to temperature T , plot the amount of water vapor condensed, in kmol per kmol of fuel, versus T ranging from 20 to $60^{\circ}C$.

13.19 Ethylene (C_2H_4) burns completely with air and the combustion products are cooled to temperature T at 1 atm. The air-fuel ratio on a mass basis is AF .

- Determine for $AF = 15$ and $T = 70^{\circ}F$, the percent excess air and the amount of water vapor condensed, in lb per lbmol of fuel.

- Plot the amount of water vapor condensed, in lb per lbmol of fuel, versus T ranging from 70 to $100^{\circ}F$, for $AF = 15, 20, 25, 30$.

13.20 A gaseous fuel mixture with a specified molar analysis burns completely with moist air to form gaseous products as shown in Fig. P13.20. Determine the dew point temperature of the products, in $^{\circ}C$.

13.21 The gas driven off when low-grade coal is burned with insufficient air for complete combustion is known as *producer gas*. A particular producer gas has the following volumetric

analysis: 3.8% CH_4 , 0.1% C_2H_6 , 4.8% CO_2 , 11.7% H_2 , 0.6% O_2 , 23.2% CO , and the remainder N_2 . Determine, for complete combustion with the theoretical amount of air

- the molar analysis of the dry products of combustion.
- the amount of water vapor condensed, in lbmol/lbmol of producer gas, if the products are cooled to $70^{\circ}F$ at a constant pressure of 1 atm.

13.22 Acetylene (C_2H_2) enters a torch and burns completely with 110% of theoretical air entering at $74^{\circ}F$, 1 atm, 50% relative humidity. Obtain the balanced reaction equation, and determine the dew point temperature of the products, in $^{\circ}F$, at 1 atm.

13.23 Butane (C_4H_{10}) burns completely with 160% of theoretical air at $20^{\circ}C$, 1 atm, and 90% relative humidity. Determine

- the balanced reaction equation.
- the dew point temperature, in $^{\circ}C$, of the products, when cooled at 1 atm.

13.24 Ethane (C_2H_6) enters a furnace and burns completely with 130% of theoretical air entering at $25^{\circ}C$, 85 kPa, 50% relative humidity. Determine

- the balanced reaction equation.
- the dew point temperature of the combustion products, in $^{\circ}C$, at 85 kPa.

13.25 Propane (C_3H_8) burns completely with the theoretical amount of air at $60^{\circ}F$, 1 atm, 90% relative humidity. Determine

- the balanced reaction equation.
- the dew point temperature of the combustion products at 1 atm.
- the amount of water condensed, in lbmol per lbmol of fuel, if the combustion products are cooled to $75^{\circ}F$, at 1 atm.

13.26 A liquid fuel mixture that is 40% octane (C_8H_{18}) and 60% decane ($C_{10}H_{22}$) by mass is burned completely with 10% excess air at $25^{\circ}C$, 1 atm, 80% relative humidity.

- Determine the equivalent hydrocarbon composition, C_aH_b , of a fuel that would have the same carbon-hydrogen ratio on a mass basis as the fuel mixture.

- If the combustion products are cooled to $25^{\circ}C$ at a pressure of 1 atm, determine the amount of water vapor that condenses, in kg per kg of fuel mixture.

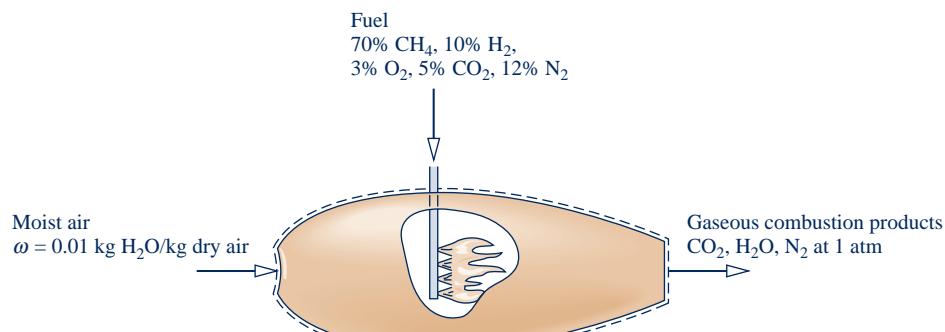


Fig. P13.20

13.27 Hydrogen (H_2) enters a combustion chamber with a mass flow rate of 5 lb/h and burns with air entering at 85°F, 1 atm with a volumetric flow rate of 75 ft³/min. Determine the percent of theoretical air used.

13.28 Methyl alcohol (CH_3OH) burns with 200% theoretical air, yielding CO_2 , H_2O , O_2 , and N_2 . Determine the

- (a) balanced reaction equation.
- (b) air-fuel ratio on a mass basis.
- (c) molar analysis of the products.

13.29 Octane (C_8H_{18}) is burned with 20% excess air, yielding CO_2 , CO , O_2 , H_2O , and N_2 only. If 5% of the dry products (molar basis) is O_2 , determine

- (a) the balanced reaction equation.
- (b) the analysis of the products on a dry molar basis.

13.30 Hexane (C_6H_{14}) burns with dry air to give products with the dry molar analysis 8.5% CO_2 , 5.2% CO , 3% O_2 , 83.3% N_2 . Determine

- (a) the balanced reaction equation.
- (b) the percent of theoretical air.
- (c) the dew point temperature, in °C, of the products at 1 atm.

13.31 The components of the exhaust gas of a spark-ignition engine using a fuel mixture represented as C_8H_{17} have a dry molar analysis of 8.7% CO_2 , 8.9% CO , 0.3% O_2 , 3.7% H_2 , 0.3% CH_4 , and 78.1% N_2 . Determine the equivalence ratio.

13.32 The combustion of a hydrocarbon fuel, represented as C_4H_b , results in products with the dry molar analysis 11% CO_2 , 0.5% CO , 2% CH_4 , 1.5% H_2 , 6% O_2 , and 79% N_2 . Determine the air-fuel ratio on (a) a molar basis, (b) a mass basis.

13.33 Decane ($\text{C}_{10}\text{H}_{22}$) burns completely in dry air. The air-fuel ratio on a mass basis is 33. Determine the

- (a) analysis of the products on a dry molar basis.
- (b) percent of theoretical air.

13.34 Butane (C_4H_{10}) burns with air, giving products having the dry molar analysis 11.0% CO_2 , 1.0% CO , 3.5% O_2 , 84.5% N_2 . Determine

- (a) the percent theoretical air.
- (b) the dew point temperature of the combustion products, in °C, at 1 bar.

13.35 A natural gas with the volumetric analysis 97.3% CH_4 , 2.3% CO_2 , 0.4% N_2 is burned with air in a furnace to give products having a dry molar analysis of 9.20% CO_2 , 3.84% O_2 , 0.64% CO , and the remainder N_2 . Determine

- (a) the percent theoretical air.
- (b) the dew point temperature, in °F, of the combustion products at 1 atm.

13.36 A fuel oil having an analysis on a mass basis of 85.7% C, 14.2% H, 0.1% inert matter burns with air to give products with a dry molar analysis of 12.29% CO_2 , 3.76% O_2 , 83.95% N_2 . Determine the air-fuel ratio on a mass basis.

13.37 Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) burns with air. The product gas is analyzed and the laboratory report gives only the following percentages on a dry molar basis: 6.9% CO_2 , 1.4% CO , 0.5%

$\text{C}_2\text{H}_5\text{OH}$. Assuming the remaining components consist of O_2 and N_2 , determine

- (a) the percentages of O_2 and N_2 in the dry molar analysis.
- (b) the percent excess air.

13.38 A fuel oil with the mass analysis 87% C, 11% H, 1.4% S, 0.6% inert matter burns with 120% of theoretical air. The hydrogen and sulfur are completely oxidized, but 95% of the carbon is oxidized to CO_2 and the remainder to CO .

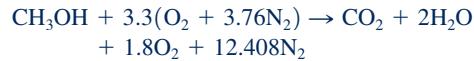
- (a) Determine the balanced reaction equation.
- (b) For the CO and SO_2 , determine the amount, in kmol per 10⁶ kmol of combustion products (that is, the amount in *parts per million*).

13.39 Pentane (C_5H_{12}) burns with air so that a fraction x of the carbon is converted to CO_2 . The remaining carbon appears as CO . There is no free O_2 in the products. Develop plots of the air-fuel ratio and the percent of theoretical air versus x , for x ranging from zero to unity.

13.40 For each of the following mixtures, determine the equivalence ratio and indicate if the mixture is lean or rich:

- (a) 1 kmol of butane (C_4H_{10}) and 32 kmol of air.
- (b) 1 lb of propane (C_3H_8) and 14.5 lb of air.

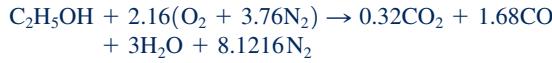
13.41 Methyl alcohol (CH_3OH) burns in dry air according to the reaction



Determine the

- (a) air-fuel ratio on a mass basis.
- (b) equivalence ratio.
- (c) percent excess air.

13.42 Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) burns in dry air according to the reaction



Determine the

- (a) air-fuel ratio on a mass basis.
- (b) equivalence ratio.
- (c) percent theoretical air.

13.43 Octane (C_8H_{18}) enters an engine and burns with air to give products with the dry molar analysis of CO_2 , 10.5%; CO , 5.8%; CH_4 , 0.9%; H_2 , 2.6%; O_2 , 0.3%; N_2 , 79.9%. Determine the equivalence ratio.

13.44 Methane (CH_4) burns with air to form products consisting of CO_2 , CO , H_2O , and N_2 only. If the equivalence ratio is 1.25, determine the balanced reaction equation.

Applying the First Law to Reacting Systems

13.45 Liquid octane (C_8H_{18}) at 77°F, 1 atm enters a combustion chamber operating at steady state and burns completely with 50% excess dry air entering at 120°F, 1 atm. The products exit at 1060°F, 1 atm. Determine the rate of heat transfer between the combustion chamber and its surroundings, in

Btu per lbmol of fuel entering. Kinetic and potential energy effects are negligible.

13.46 Propane (C_3H_8) at 298 K, 1 atm, enters a combustion chamber operating at steady state with a molar flow rate of 0.7 kmol/s and burns completely with 200% of theoretical air entering at 298 K, 1 atm. Kinetic and potential energy effects are negligible. If the combustion products exit at 560 K, 1 atm, determine the rate of heat transfer for the combustion chamber, in kW. Repeat for an exit temperature of 298 K.

13.47 Methane (CH_4) at 25°C, 1 atm enters a furnace operating at steady state and burns completely with 140% of theoretical air entering at 400 K, 1 atm. The products of combustion exit at 700 K, 1 atm. Kinetic and potential energy effects are negligible. If the rate of heat transfer from the furnace to the surroundings is 400 kW, determine the mass flow rate of methane, in kg/s.

13.48 Methane gas (CH_4) at 25°C, 1 atm enters a steam generator operating at steady state. The methane burns completely with 140% of theoretical air entering at 127°C, 1 atm. Products of combustion exit at 427°C, 1 atm. In a separate stream, saturated liquid water enters at 8 MPa and exits as superheated vapor at 480°C with a negligible pressure drop. If the vapor mass flow rate is 3.7×10^5 kg/h, determine the volumetric flow rate of the methane, in m^3/h .

13.49 Liquid ethanol (C_2H_5OH) at 77°F, 1 atm enters a combustion chamber operating at steady state and burns completely with dry air entering at 340°F, 1 atm. The fuel flow rate is 50 lb/s, and the equivalence ratio is 0.8. Products of combustion exit at 2000°F, 1 atm. Ignoring kinetic and potential energy effects, determine

- the air-fuel ratio on a mass basis.
- the rate of heat transfer, in Btu/s.

13.50 Octane gas (C_8H_{18}) at 25°C, 1 atm enters a combustion chamber operating at steady state and burns with 120% theoretical air entering at 25°C, 1 atm. The combustion products exit at 1200 K and include only CO_2 , H_2O , O_2 , and N_2 . If the rate of heat transfer from the combustion chamber to the surroundings is 2500 kW, determine the mass flow rate of the fuel, in kg/s.

13.51 Liquid propane (C_3H_8) at 25°C, 1 atm, enters a well-insulated reactor operating at steady state. Air enters at the same temperature and pressure. For liquid propane, $\bar{h}_f^\circ = -118,900$ kJ/kmol. Determine the temperature of the combustion products, in K, for complete combustion with

- the theoretical amount of air.
- 300% of theoretical air.

13.52 The energy required to vaporize the working fluid passing through the boiler of a simple vapor power plant is provided by the complete combustion of methane with 110% of theoretical air. The fuel and air enter in separate streams at 25°C, 1 atm. Products of combustion exit the stack at 150°C, 1 atm. Plot the mass flow rate of fuel required, in kg/h per MW of power developed by the plant versus the plant thermal efficiency, η . Consider η in the range 30–40%. Kinetic and potential energy effects are negligible.

13.53 Methane (CH_4) at 25°C, enters the combustor of a simple open gas turbine power plant and burns completely with 400% of theoretical air entering the compressor at 25°C, 1 atm. Products of combustion exit the turbine at 577°C, 1 atm. The rate of heat transfer from the gas turbine is estimated as 10% of the net power developed. Determine the net power output, in MW, if the fuel mass flow rate is 1200 kg/h. Kinetic and potential energy effects are negligible.

13.54 Octane gas C_8H_{18} at 25°C enters a jet engine and burns completely with 300% of theoretical air entering at 25°C, 1 atm with a volumetric flow rate of $42 \text{ m}^3/\text{s}$. Products of combustion exit at 990 K, 1 atm. If the fuel and air enter with negligible velocities, determine the *thrust* produced by the engine in kN.

13.55 Figure P13.55 provides data for a boiler and air preheater operating at steady state. Methane (CH_4) entering the boiler at 25°C, 1 atm is burned completely with 170% of theoretical air. Ignoring stray heat transfer and kinetic and potential energy effects, determine the temperature, in °C, of the combustion air entering the boiler from the preheater.

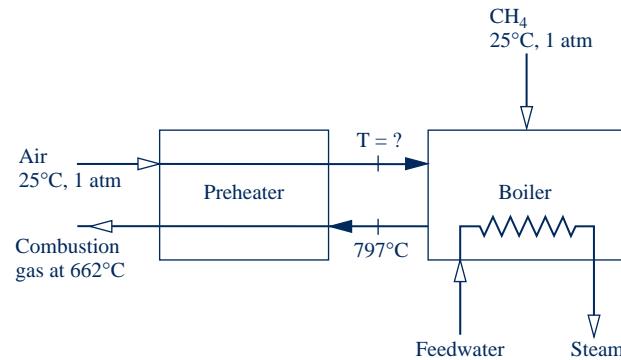


Fig. P13.55

13.56 One lbmol of octane gas (C_8H_{18}) reacts with the theoretical amount of air in a closed, rigid tank. Initially, the reactants are at 77°F, 1 atm. After complete combustion, the pressure in the tank is 3.98 atm. Determine the heat transfer, in Btu.

13.57 A closed, rigid vessel initially contains a gaseous mixture at 25°C, 1 atm with the molar analysis of 20% ethane (C_2H_6), 80% oxygen (O_2). The initial mixture contains one kmol of ethane. Complete combustion occurs, and the products are cooled to 25°C. Determine the heat transfer, in kJ, and the final pressure, in atm.

13.58 A closed, rigid vessel initially contains a gaseous mixture of 1 kmol of pentane (C_5H_{12}) and 150% of theoretical air at 25°C, 1 atm. If the mixture burns completely, determine the heat transfer from the vessel, in kJ, and the final pressure, in atm, for a final temperature of 800 K.

13.59 Calculate the enthalpy of combustion of gaseous pentane (C_5H_{12}), in kJ per kmol of fuel, at 25°C with water vapor in the products.



13.60 Plot the enthalpy of combustion for gaseous propane (C_3H_8), in Btu per lbmol of fuel, at 1 atm versus temperature in the interval 77 to 500°F. Assume water vapor in the products. For propane, let $c_p = 0.41 \text{ Btu/lb} \cdot ^\circ\text{R}$.



13.61 Plot the enthalpy of combustion for gaseous methane (CH_4), in Btu per lbmol of fuel, at 1 atm versus temperature in the interval from 537 to 1800°R. Assume water vapor in the products. For methane, let $\bar{c}_p = 4.52 + 7.37(T/1000) \text{ Btu/lbmol} \cdot ^\circ\text{R}$, where T is in °R.

13.62 For the *producer gas* of Prob. 13.21, determine the enthalpy of combustion, in Btu per lbmol of mixture, at 77°F, 1 atm, assuming water vapor in the products.

13.63 Determine the lower heating value, in kJ per kmol of fuel and in kJ per kg of fuel, at 25°C, 1 atm for

- (a) gaseous ethane (C_2H_6).
- (b) liquid ethanol (C_2H_5OH).
- (c) gaseous propane (C_3H_8).
- (d) liquid octane (C_8H_{18}).

13.64 For a natural gas with a molar analysis of 86.5% CH_4 , 8% C_2H_6 , 2% C_3H_8 , 3.5% N_2 , determine the lower heating value, in kJ per kmol of fuel and in kJ per kg of fuel, at 25°C, 1 atm.

13.65 Liquid octane (C_8H_{18}) at 25°C, 1 atm enters an insulated reactor operating at steady state and burns with 90% of theoretical air at 25°C, 1 atm to form products consisting of CO_2 , CO , H_2O , and N_2 only. Determine the temperature of the exiting products, in K. Compare with the results of Example 13.8 and comment.



13.66 For each of the following fuels, plot the adiabatic flame temperature, in K, versus percent excess air for complete combustion in a combustor operating at steady state. The reactants enter at 25°C, 1 atm.

- (a) carbon.
- (b) hydrogen (H_2).
- (c) liquid octane (C_8H_{18}).



13.67 Propane gas (C_3H_8) at 25°C, 1 atm enters an insulated reactor operating at steady state and burns completely with air entering at 25°C, 1 atm. Plot the adiabatic flame temperature versus percent of theoretical air ranging from 100 to 400%. Why does the adiabatic flame temperature vary with increasing combustion air?



13.68 Hydrogen (H_2) at 77°F, 1 atm enters an insulated reactor operating at steady state and burns completely with $x\%$ of theoretical air entering at 77°F 1 atm. Plot the adiabatic flame temperature for x ranging from 100 to 400%.



13.69 Methane gas (CH_4) at 25°C, 1 atm enters an insulated reactor operating at steady state and burns completely with $x\%$ of theoretical air entering at 25°C, 1 atm. Plot the adiabatic flame temperature for x ranging from 100 to 400%.

13.70 Methane (CH_4) at 25°C, 1 atm enters an insulated reactor operating at steady state and burns with the theoretical amount of air entering at 25°C, 1 atm. The products contain CO_2 , CO , H_2O , O_2 , and N_2 , and exit at 2260 K. Determine the fractions of the entering carbon in the fuel that burn to CO_2 and CO , respectively.

13.71 Ethane (C_2H_6) gas at 77°F, 1 atm enters a well-insulated reactor operating at steady state and burns completely with air entering at 240°F, 1 atm. Determine the temperature of the products, in °F. Neglect kinetic and potential energy effects.

13.72 Liquid methanol (CH_3OH) at 25°C, 1 atm enters an insulated reactor operating at steady state and burns completely with air entering at 100°C, 1 atm. If the combustion products exit at 1256°C, determine the percent excess air used. Neglect kinetic and potential energy effects.

13.73 Methane (CH_4) at 77°F enters the combustor of a gas turbine power plant operating at steady state and burns completely with air entering at 400°F. The temperature of the products of combustion flowing from the combustor to the turbine depends on the percent excess air for combustion. Plot the percent excess air versus combustion product temperatures ranging from 1400 to 1800°F. There is no significant heat transfer between the combustor and its surroundings, and kinetic and potential energy effects can be ignored.

13.74 Air enters the compressor of a simple gas turbine power plant at 70°F, 1 atm, is compressed adiabatically to 40 lbf/in.², and then enters the combustion chamber where it burns completely with propane gas (C_3H_8) entering at 77°F, 40 lbf/in.² and a molar flow rate of 1.7 lbmol/h. The combustion products at 1340°F, 40 lbf/in.² enter the turbine and expand adiabatically to a pressure of 1 atm. The isentropic compressor efficiency is 83.3% and the isentropic turbine efficiency is 90%. Determine at steady state

- (a) the percent of theoretical air required.
- (b) the net power developed, in horsepower.

13.75 A mixture of gaseous octane (C_8H_{18}) and 200% of theoretical air, initially at 25°C, 1 atm, reacts completely in a rigid vessel.

- (a) If the vessel were well-insulated, determine the temperature, in °C, and the pressure, in atm, of the combustion products.
- (b) If the combustion products were cooled at constant volume to 25°C, determine the final pressure, in atm, and the heat transfer, in kJ per kmol of fuel.

13.76 Methane gas (CH_4) reacts completely with the theoretical amount of oxygen (O_2) in a piston-cylinder assembly. Initially, the mixture is at 77°F, 1 atm. If the process occurs at constant pressure and the final volume is 1.9 times the initial volume, determine the work and the heat transfer, each in Btu per lbmol of fuel.

13.77 A 5×10^{-3} kg sample of liquid benzene (C_6H_6) together with 20% excess air, initially at 25°C and 1 atm, reacts completely in a rigid, insulated vessel. Determine the temperature, in °C, and the pressure, in atm, of the combustion products.

Applying the Second Law to Reacting Systems

13.78 Carbon monoxide (CO) at 25°C, 1 atm enters an insulated reactor operating at steady state and reacts completely with the theoretical amount of air entering in a separate stream at 25°C, 1 atm. The products of combustion exit as a mixture at 1 atm. For the reactor, determine the

rate of entropy production, in kJ/K per kmol of CO entering. Neglect kinetic and potential energy effects.

13.79 Methane (CH_4) at 77°F , 1 atm enters an insulated reactor operating at steady state and burns completely with air entering in a separate stream at 77°F , 1 atm. The products of combustion exit as a mixture at 1 atm. For the reactor, determine the rate of entropy production, in Btu/ $^{\circ}\text{R}$ per lbmol of methane entering, for combustion with

- the theoretical amount of air.
- 200% of theoretical air.

Neglect kinetic and potential energy effects.

 **13.80** Carbon monoxide (CO) reacts with water vapor in an insulated reactor operating at steady state to form hydrogen (H_2) and carbon dioxide (CO_2). The products exit as a mixture at 1 atm. For the reactor, determine the rate of entropy production, in kJ/K per kmol of carbon monoxide entering. Neglect kinetic and potential energy effects. Consider two cases:

- The carbon monoxide and water vapor enter the reactor in separate streams, each at 400 K , 1 atm.
- The carbon monoxide and water vapor enter the reactor as a mixture at 400 K , 1 atm.

Explain why the answers in parts (a) and (b) differ.

13.81 A gaseous mixture of butane (C_4H_{10}) and 80% excess air at 25°C , 3 atm enters a reactor. Complete combustion occurs, and the products exit as a mixture at 1200 K , 3 atm. Coolant enters an outer jacket as a saturated liquid and saturated vapor exits at essentially the same pressure. No significant heat transfer occurs from the outer surface of the jacket, and kinetic and potential energy effects are negligible. Determine for the jacketed reactor

- the mass flow rate of the coolant, in kg per kmol of fuel.
- the rate of entropy production, in kJ/K per kmol of fuel.
- the rate of exergy destruction, in kJ per kmol of fuel, for $T_0 = 25^\circ\text{C}$.

Consider each of two coolants: water at 1 bar and ammonia at 10 bar.

 **13.82** Liquid ethanol ($\text{C}_2\text{H}_5\text{OH}$) at 25°C , 1 atm enters a reactor operating at steady state and burns completely with 130% of theoretical air entering in a separate stream at 25°C , 1 atm. Combustion products exit at 227°C , 1 atm. Heat transfer from the reactor takes place at an average surface temperature T_b . For T_b ranging from 25 to 200°C , determine the rate of exergy destruction within the reactor, in kJ per kmol of fuel. Kinetic and potential energy effects are negligible. Let $T_0 = 25^\circ\text{C}$.

 **13.83** A gaseous mixture of ethane (C_2H_6) and the theoretical amount of air at 25°C , 1 atm enters a reactor operating at steady state and burns completely. Combustion products exit at 627°C , 1 atm. Heat transfer from the reactor takes place at an average surface temperature T_b . For T_b ranging from 25 to 600°C , determine the rate of exergy destruction within the reactor, in kJ per kmol of fuel. Kinetic and potential energy effects are negligible. Let $T_0 = 25^\circ\text{C}$.

13.84 Determine the change in the Gibbs function, in kJ per kmol of methane, at 25°C , 1 atm for $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, using

- Gibbs function of formation data.
- enthalpy of formation data, together with absolute entropy data.

13.85 Determine the change in the Gibbs function, in Btu per lbmol of hydrogen, at 77°F , 1 atm for $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(\text{g})$, using

- Gibbs function of formation data.
- enthalpy of formation data, together with absolute entropy data.

13.86 Separate streams of hydrogen (H_2) and oxygen (O_2) at 25°C , 1 atm enter a fuel cell operating at steady state, and liquid water exits at 25°C , 1 atm. The hydrogen flow rate is 2×10^{-4} kmol/s. If the fuel cell operates isothermally at 25°C , determine the maximum theoretical power it can develop and the accompanying rate of heat transfer, each in kW. Kinetic and potential energy effects are negligible.

13.87 Streams of methane (CH_4) and oxygen (O_2), each at 25°C , 1 atm, enter a fuel cell operating at steady state. Streams of carbon dioxide and water exit separately at 25°C , 1 atm. If the fuel cell operates isothermally at 25°C , 1 atm, determine the maximum theoretical work that it can develop, in kJ per kmol of methane. Ignore kinetic and potential energy effects.

 **13.88** Streams of hydrogen (H_2) and oxygen (O_2), each at 1 atm, enter a fuel cell operating at steady state and water vapor exits at 1 atm. If the cell operates isothermally at (a) 300 K , (b) 400 K , and (c) 500 K , determine the maximum theoretical work that can be developed by the cell in each case, in kJ per kmol of hydrogen flowing, and comment. Heat transfer with the surroundings takes place at the cell temperature, and kinetic and potential energy effects can be ignored.

13.89 An inventor has developed a device that at steady state takes in liquid water at 25°C , 1 atm with a mass flow rate of 4 kg/h and produces separate streams of hydrogen (H_2) and oxygen (O_2), each at 25°C , 1 atm. The inventor claims that the device requires an electrical power input of 14.6 kW when operating isothermally at 25°C . Heat transfer with the surroundings occurs, but kinetic and potential energy effects can be ignored. Evaluate the inventor's claim.

13.90 Coal with a mass analysis of 88% C, 6% H, 4% O, 1% N, 1% S burns completely with the theoretical amount of air. Determine

- the amount of SO_2 produced, in kg per kg of coal.
- the air-fuel ratio on a mass basis.
- For environmental reasons, it is desired to separate the SO_2 from the combustion products by supplying the products at 340 K , 1 atm to a device operating isothermally at 340 K . At steady state, a stream of SO_2 and a stream of the remaining gases exit, each at 340 K , 1 atm. If the coal is burned at a rate of 10 kg/s, determine the minimum theoretical power input required by the device, in kW. Heat transfer with the surroundings occurs, but kinetic and potential energy effects can be ignored.

Using Chemical Exergy

13.91 Applying Eq. 13.36 for (a) carbon, (b) hydrogen (H_2), (c) methane, (d) carbon monoxide, (e) nitrogen (N_2), (f) oxygen (O_2), and (g) carbon dioxide, determine the chemical exergy, in kJ/kg, relative to the following environment in which the gas phase obeys the ideal gas model:

Environment		
$T_0 = 298.15 \text{ K (25}^\circ\text{C)}, p_0 = 1 \text{ atm}$		
Gas Phase:	Component	$y^e(\%)$
	N_2	75.67
	O_2	20.35
	$H_2O(g)$	3.12
	CO_2	0.03
	Other	0.83

13.92 The accompanying table shows an environment consisting of a gas phase and a condensed water phase. The gas phase forms an ideal gas mixture.

Environment		
$T_0 = 298.15 \text{ K (25}^\circ\text{C)}, p_0 = 1 \text{ atm}$		
Condensed Phase: $H_2O(l)$ at T_0, p_0		
Gas Phase:	Component	$y^e(\%)$
	N_2	75.67
	O_2	20.35
	$H_2O(g)$	3.12
	CO_2	0.03
	Other	0.83

(a) Show that the chemical exergy of the hydrocarbon C_aH_b can be determined as

$$\bar{e}^{ch} = \left[\bar{g}_F + \left(a + \frac{b}{4} \right) \bar{g}_{O_2} - a \bar{g}_{CO_2} - \frac{b}{2} \bar{g}_{H_2O(l)} \right] + \bar{R} T_0 \ln \left[\frac{(y_{O_2}^e)^{a+b/4}}{(y_{CO_2}^e)^a} \right]$$

(b) Using the result of part (a), repeat parts (a) through (c) of Problem 13.91.

13.93 Justify the use of Eq. 13.36 for liquid methanol, CH_3OH , and liquid ethanol, C_2H_5OH , and apply it to evaluate the chemical exergy, in kJ/kmol, of each substance relative to the environment of Prob. 13.91. Compare with the respective standard chemical exergy values from Table A-26 (Model II).

13.94 Showing all important steps, derive (a) Eqs. 13.41a, b (b) Eqs. 13.44 a, b.

13.95 Using data from Tables A-25 and A-26, together with Eq. 13.44b, determine the standard molar chemical exergy, in kJ/kmol, of propane $C_3H_8(g)$. Compare this value with the standard chemical exergy from Table A-26 (Model II).

13.96 Evaluate the total specific flow exergy of nitrogen (N_2), in Btu/lb, at 200°F , 4 atm. Neglect the effects of motion and gravity. Perform calculations

- (a) relative to the environment of Problem 13.91.
- (b) using data from Table A-26 (Model II).

13.97 Evaluate the total specific flow exergy of water vapor, in kJ/kg, at 200°C , 1 bar. Neglect the effects of motion and gravity. Perform calculations

- (a) relative to the environment of Problem 13.91.
- (b) using data from Table A-26 for each of the models.

13.98 Evaluate the total specific flow exergy of an equimolar mixture of oxygen (O_2) and nitrogen (N_2), in kJ/kg, at 227°C , 1 atm. Neglect the effects of motion and gravity. Perform calculations

- (a) relative to the environment of Problem 13.91.
- (b) using data from Table A-26 (Model II).

13.99 A mixture of methane gas (CH_4) and 150% of theoretical air enters a combustion chamber at 77°F , 1 atm. Determine the total specific flow exergy of the entering mixture, in Btu per lbmol of methane. Ignore the effects of motion and gravity. Perform calculations

- (a) relative to the environment of Problem 13.91.
- (b) using data from Table A-26 (Model II).

13.100 A mixture having an analysis on a molar basis of 85% dry air, 15% CO enters a device at 125°C , 2.1 atm, and a velocity of 250 m/s. If the mass flow rate is 1.0 kg/s, determine the rate exergy enters, in MW. Neglect the effect of gravity. Perform calculations

- (a) relative to the environment of Problem 13.91.
- (b) using data from Table A-26 (Model II).

13.101 The following flow rates in lb/h are reported for the exiting syngas (synthesis gas) stream in a certain process for producing syngas from bituminous coal:

CH_4	429,684 lb/h
CO_2	9,093 lb/h
N_2	3,741 lb/h
H_2	576 lb/h
CO	204 lb/h
H_2O	60 lb/h

If the syngas stream is at 77°F , 1 atm, determine the rate at which exergy exits, in Btu/h. Perform calculations relative to the environment of Problem 13.91. Neglect the effects of motion and gravity.

Exergy Analysis of Reacting and Psychrometric Systems

13.102 Carbon at 25°C , 1 atm enters an insulated reactor operating at steady state and reacts completely with the theoretical amount of air entering separately at 25°C , 1 atm. For the reactor, (a) determine the rate of exergy destruction, in kJ per kmol of carbon, and (b) evaluate an exergetic efficiency. Perform calculations relative to the environment of Problem 13.91. Neglect the effects of motion and gravity.

13.103 Propane gas (C_3H_8) at 25°C , 1 atm and a volumetric flow rate of $0.03 \text{ m}^3/\text{min}$ enters a furnace operating at steady state and burns completely with 200% of theoretical air entering at 25°C , 1 atm. The furnace provides energy by heat transfer at 227°C for an industrial process and combustion products at 277°C , 1 atm for cogeneration of hot water. For the furnace, perform a full exergy accounting, in kJ/min, of the exergy supplied by the fuel. Use standard chemical exergies from Table A-26 (Model II), as required, and ignore the effects of motion and gravity.

13.104 Figure P13.104 shows a coal gasification reactor making use of the *carbon–steam* process. The energy required for the endothermic reaction is supplied by an electrical resistor. The reactor operates at steady state, with no stray heat transfers and negligible effects of motion and gravity. Evaluate in Btu per lbmol of carbon entering

- the required electrical input.
- the exergy entering with the carbon.
- the exergy entering with the steam.
- the exergy exiting with the product gas.
- the exergy destruction within the reactor.

Perform calculations relative to the environment of Problem 13.91.

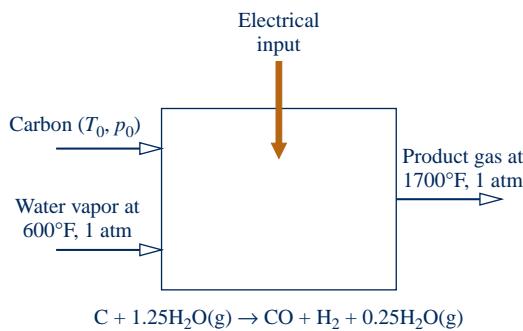


Fig. P13.104

13.105 Carbon monoxide (CO) at 25°C, 1 atm enters an insulated reactor operating at steady state and reacts completely with the theoretical amount of air entering in a separate stream at 25°C, 1 atm. The products exit as a mixture at 1 atm. Determine in kJ per kmol of CO

- the exergy entering with the carbon monoxide.
- the exergy exiting with the products.
- the rate of exergy destruction.

Also, evaluate an exergetic efficiency for the reactor. Perform calculations relative to the environment of Problem 13.91. Neglect the effects of motion and gravity.

13.106 Acetylene gas (C_2H_2) at 77°F, 1 atm enters an insulated reactor operating at steady state and burns completely with 180% of theoretical air, entering in a separate stream at 77°F, 1 atm. The products exit as a mixture at 1 atm. Determine in Btu per lbmol of fuel

- the exergy of the fuel entering the reactor.
- the exergy exiting with the products.
- the rate of exergy destruction.

Also, evaluate an exergetic efficiency for the reactor. Perform calculations relative to the environment of Problem 13.91. Neglect the effects of motion and gravity.

13.107 Liquid octane (C_8H_{18}) at 25°C, 1 atm and a mass flow rate of 0.57 kg/h enters an internal combustion engine operating at steady state. The fuel burns with air entering the engine in a separate stream at 25°C, 1 atm. Combustion products exit at 670 K, 1 atm with a dry molar analysis of 11.4% CO_2 , 2.9% CO, 1.6% O_2 , and 84.1% N_2 . If the engine develops power at the rate of 3 kW, determine

- the rate of heat transfer from the engine, in kW.
- an exergetic efficiency for the engine.

Use the environment of Problem 13.91 and neglect the effects of motion and gravity.

13.108 Figure P13.108 shows a simple vapor power plant. The fuel is methane that enters at 77°F, 1 atm and burns completely with 200% theoretical air entering at 77°F, 1 atm. Steam exits the steam generator at 900°F, 500 lbf/in.². The vapor expands through the turbine and exits at 1 lbf/in.², and

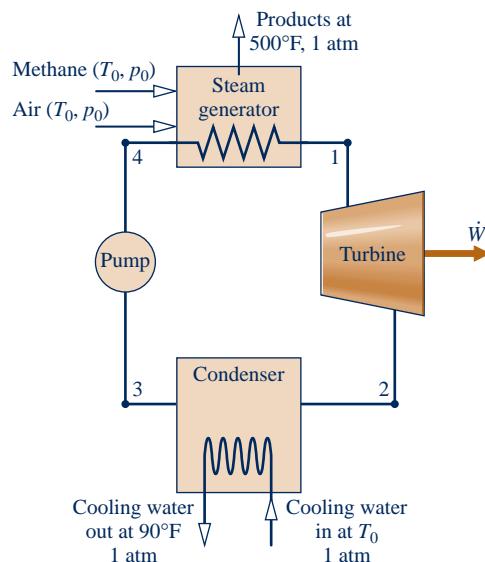
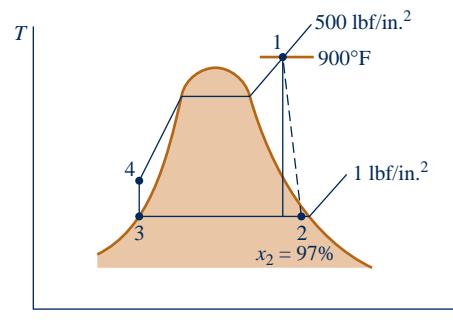


Fig. P13.108



a quality of 97%. At the condenser exit, the pressure is 1 lbf/in.² and the water is a saturated liquid. The plant operates at steady state with no stray heat transfers from any plant component. Pump work and the effects of motion and gravity are negligible. Determine

- the balanced reaction equation.
- the vapor mass flow rate, in lb per lbmol of fuel.
- the cooling water mass flow rate, in lb per lbmol of fuel.
- each of the following, expressed as a percent of the exergy entering the steam generator with the fuel, (i) the exergy exiting with the stack gases, (ii) the exergy destroyed in the steam generator, (iii) the power developed by the turbine, (iv) the exergy destroyed in the turbine, (v) the exergy exiting with the cooling water, (vi) the exergy destroyed in the condenser.

Base exergy values on the environment of Problem 13.91.

13.109 Consider a furnace operating at steady state idealized as shown in Fig. P13.109. The fuel is methane, which enters at 25°C, 1 atm and burns completely with 200% theoretical air entering at the same temperature and pressure. The furnace delivers energy by heat transfer at an average temperature of 227°C. Combustion products at 600 K, 1 atm are provided to the surroundings for cogeneration of steam. There are no stray heat transfers, and the effects of motion and gravity can be ignored. Determine in kJ per kmol of fuel

- the exergy entering the furnace with the fuel.
- the exergy exiting with the products.
- the rate of exergy destruction.

Also, evaluate an exergetic efficiency for the furnace and comment. Perform calculations relative to the environment of Problem 13.91.

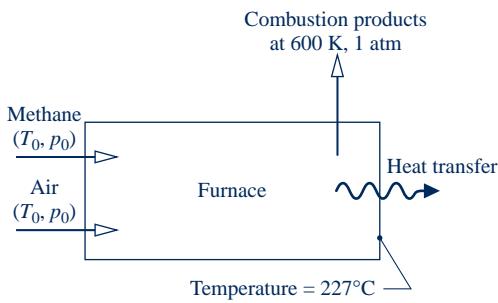


Fig. P13.109

13.110 Coal enters the combustor of a power plant with a mass analysis of 49.8% C, 3.5% H, 6.8% O, 6.4% S, 14.1% H₂O, and 19.4% noncombustible ash. The higher heating value of the coal is measured as 21,220 kJ/kg, and the lower heating value on a dry basis, (LHV)_d, is 20,450 kJ/kg. The following expression can be used to estimate the chemical exergy of the coal, in kJ/kg:

$$e^{\text{ch}} = (\text{LHV})_d \left(1.0438 + 0.0013 \frac{h}{c} + 0.1083 \frac{o}{c} + 0.0549 \frac{n}{c} \right) + 6740s$$

where h/c , o/c , and n/c denote, respectively, the mass ratio of hydrogen to carbon, oxygen to carbon, and nitrogen to carbon, and s is the mass fraction of sulfur in kg per kg of fuel.³ The environment is closely the same as in Problem 13.92, but extended appropriately to account for the presence of sulfur in the coal.

- Using the above expression, calculate the chemical exergy of the coal, in kJ/kg.
- Compare the answer of part (a) with the values that would result by approximating the chemical exergy with each of the measured heating values.
- What data would be required to determine the chemical exergy in this case using the methodology of Sec. 13.6? Discuss.

13.111 For psychrometric applications such as those considered in Chap. 12, the environment often can be modeled simply as an ideal gas mixture of water vapor and dry air at temperature T_0 and pressure p_0 . The composition of the environment is defined by the dry air and water vapor mole fractions y_a^e , y_v^e , respectively.

- Show that relative to such an environment the total specific flow exergy of a moist air stream at temperature T and pressure p with dry air and water vapor mole fractions y_a and y_v , respectively, can be expressed on a molar basis as

$$\bar{e}_f = T_0 \left\{ (y_a \bar{c}_{pa} + y_v \bar{c}_{pv}) \left[\left(\frac{T}{T_0} \right)^{-1} - \ln \left(\frac{T}{T_0} \right) \right] + \bar{R} \ln \left(\frac{p}{p_0} \right) \right\} + \bar{R} T_0 \left[y_a \ln \left(\frac{y_a}{y_a^e} \right) + y_v \ln \left(\frac{y_v}{y_v^e} \right) \right]$$

where \bar{c}_{pa} and \bar{c}_{pv} denote the molar specific heats of dry air and water vapor, respectively. Neglect the effects of motion and gravity.

- Express the result of part (a) on a *per unit mass of dry air basis* as

$$e_f = T_0 \left\{ (c_{pa} + \omega c_{pv}) \left[\frac{T}{T_0} - 1 - \ln \left(\frac{T}{T_0} \right) \right] + (1 + \tilde{\omega}) R_a \ln \left(\frac{p}{p_0} \right) \right\} + R_a T_0 \left\{ (1 + \tilde{\omega}) \ln \left(\frac{1 + \tilde{\omega}^e}{1 + \tilde{\omega}} \right) + \tilde{\omega} \ln \left(\frac{\tilde{\omega}}{\tilde{\omega}^e} \right) \right\}$$

where $R_a = \bar{R}/M_a$ and $\tilde{\omega} = \omega M_a/M_v = y_v/y_a$.

13.112 For each of the following, use the result of Problem 13.111(a) to determine the total specific flow exergy, in kJ/kg, relative to an environment consisting of moist air at 20°C, 1 atm, $\phi = 100\%$

- moist air at 20°C, 1 atm, $\phi = 90\%$.
- moist air at 20°C, 1 atm, $\phi = 50\%$.
- moist air at 20°C, 1 atm, $\phi = 10\%$.

³Moran, *Availability Analysis*, pp. 192–193.

13.113 Using the result of Problem 13.111(b), determine the total specific flow exergy at locations 1, 2, and 3 and the rate of exergy destruction, each in Btu/min, for the device of Problem 12.102. Let the environment be a mixture of dry air and water vapor at 95°F, 1 atm with $y_v^e = 0.022$, $y_a^e = 0.978$. Also, let $c_{pa} = 0.24 \text{ Btu/lb} \cdot ^\circ\text{R}$ and $c_{pv} = 0.44 \text{ Btu/lb} \cdot ^\circ\text{R}$.

13.114 Figure P13.114 provides data for a cooling tower at steady state. Using results from Problem 13.111 as needed, determine the rate of exergy destruction, in Btu/min. Let the environment be a mixture of dry air and water vapor at 90°F, 1 atm with $y_v^e = 0.024$, $y_a^e = 0.976$. Also, let $c_{pa} = 0.24 \text{ Btu/lb} \cdot ^\circ\text{R}$ and $c_{pv} = 0.44 \text{ Btu/lb} \cdot ^\circ\text{R}$.

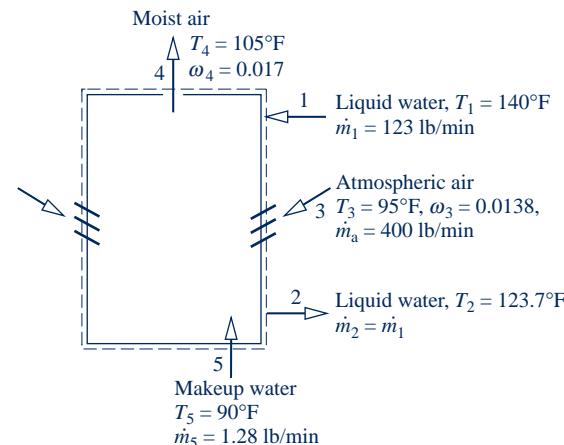


Fig. P13.114

► DESIGN & OPEN-ENDED PROBLEMS: EXPLORING ENGINEERING PRACTICE

13.1D Middle school science students may wonder how gasoline powers their family's car. Prepare a 30-minute presentation suitable for an eighth-grade science class to explain the basic operation of a spark-ignition engine while touching on relevant chemical reactions and emission concerns. Include instructional aids and a group activity to enhance your presentation.

13.2D Complete two of the following and report your findings in a memorandum, including sample calculations, discussion of the modeling used, and references to the technical literature, as appropriate.

(a) Assuming electricity is provided by a coal-fired vapor power plant, determine how much coal, in kg, is saved over the lifetime of a compact fluorescent light bulb in comparison to the coal required to power a comparable incandescent light bulb over the same interval.

(b) When crude oil is brought to earth's surface, it is often accompanied by natural gas, which is commonly *flared*, releasing carbon dioxide to the atmosphere. What are other options for managing such natural gas than flaring it? Rank-order them in terms of economic feasibility.

(c) An advertisement describes a *hydrogen energy station* that produces hydrogen from water using electricity from the grid. The hydrogen is said to be an *emissions-free* fuel for vehicles, emergency back-up power units for buildings, and other applications. Investigate how the hydrogen energy station works and critically evaluate the claims that are made by the manufacturer.

(d) From the engineering literature, obtain the standard chemical exergy, in kJ/kg, for gold and lead. Also, for each determine the current market price, in \$/kg. Investigate the difference between exergetic value and economic value, and on this basis rationalize the chemical exergy and market-price values determined for these commodities.

13.3D Municipal solid waste (MSW), often called garbage or trash, consists of the combined solid waste produced by homes and workplaces. In the United States, a portion of the annual MSW accumulation is burned to generate steam for producing electricity, and heating water and buildings, while

several times as much MSW is buried in *sanitary* landfills. Investigate these two MSW disposal approaches. For each approach, prepare a list of at least three advantages and three disadvantages, together with brief discussions of each advantage and disadvantage. Report your findings in a PowerPoint presentation suitable for a community planning group.

13.4D Mounting evidence suggests that more frequent severe weather events, melting of glaciers and polar icecaps, and other observed changes in nature are linked to emissions from fossil fuel combustion. Researchers have developed detailed computer simulations to predict global weather patterns and investigate the effects of CO₂ and other gaseous emissions on the weather. Investigate the underlying modeling assumptions and characteristics of computer simulations used to predict global weather patterns. Write a report, including at least three references, of your findings.

13.5D Federal and state governmental legislation places restrictions on harmful emissions associated with combustion of fossil fuels in power plants and vehicles. For stationary power plants and for vehicles in your geographic area, identify the restricted emissions, their allowed levels, their associated hazards, and means employed to achieve desired emission levels. Investigate and discuss political, social, economic, and technological issues that influenced adoption of these regulations, and project whether any future adjustments to them might occur. Summarize your findings in a report citing at least three references.

13.6D Many utilities are converting power plants from coal to alternative fuels due to environmental considerations. Conduct a case study of a power plant in your geographic region that has converted or is planning to convert from coal to an alternative fuel. Provide a schematic of the coal-based system and the alternative fuel-based system and describe pertinent features of each. Investigate the advantages of using the new fuel, physical plant changes with associated costs required to accommodate the new fuel, and the impact of the fuel change on system performance and operational cost. Summarize your findings in a PowerPoint presentation suitable for your class.

13.7D A proposed simple gas turbine will produce power at a rate of 500 kW by burning fuel with 200% theoretical air in the combustor. Air temperature and pressure at the compressor inlet are 298 K and 100 kPa, respectively. Fuel enters the combustor at 298 K, while products of combustion consisting of CO₂, H₂O, O₂, and N₂ exit the combustor with no significant change in pressure. Metallurgical considerations require the turbine inlet temperature to be no greater than 1500 K. Products of combustion exit the turbine at 100 kPa. The compressor has an isentropic efficiency of 85%, while the turbine isentropic efficiency is 90%. Three fuels are being considered: methane (CH₄), ethylene (C₂H₄), and ethane (C₂H₆). On the basis of minimal fuel use, recommend a fuel, turbine inlet temperature, and compressor pressure ratio for the gas turbine. Summarize your findings in a report, supported by well-documented sample calculations and a full discussion of the thermodynamic modeling used.

13.8D Fuel cell systems installed as part of a distributed generation network require auxiliary components to support the fuel cell stack. Depending on the type of fuel cell, these components may provide fuel reforming, humidification, and appropriate flows of fuel and oxidizer. Auxiliary components also accommodate heat transfer, power conditioning, and electrical connection. Additionally, the fuel cell system requires various controls. Identify and research a fuel cell system for combined heat and power integrated with a building in your geographic region. Describe each component in the fuel cell system and create a schematic of the system to include fuel cell stack, its auxiliary components, and its integration with the building to provide electricity and heating. Contact the building supervisor to identify any installation, operational, and/or maintenance issues. Estimate total costs (components, installation, and annual fuel and operating costs) for the fuel cell system and compare to the prior system's cost, assuming the same annual electricity and heating requirements. Summarize your findings in a PowerPoint presentation.

13.9D The chemical exergies of common hydrocarbons C_aH_b can be represented in terms of their respective lower heating value, LHV, by an expression of the form

$$\frac{\bar{e}^{ch}}{(LHV)} = c_1 + c_2(b/a) - c_3/a$$

where c_1 , c_2 , and c_3 are constants. Evaluate the constants to obtain an expression applicable to the gaseous hydrocarbons of Table A-26 (Model II).

13.10D Coal gasification is a means for using coal to produce various energy products, usually including electricity. In particular, coal gasification is a key feature of Integrated Gasification Combined Cycle (IGCC) Plants (Sec. 9.10). Evaluate the exergetic efficiencies of the gasifier and synthetic gas (syngas) cleanup units within such an IGCC Plant. Use operating data obtained from the engineering literature for the plant together with standard chemical exergies. In a report, give the exergetic efficiency values you obtain, supported by well-documented sample calculations, a full discussion of the thermodynamic modeling used, and at least three references.

13.11D Coal mining operations in certain regions of the United States have created vast amounts of waste coal known as *culm*. Some power plants have been built near culm banks to generate electricity from this waste resource. Using a gravimetric analysis for culm of 43% carbon, 36% ash, 15% moisture, 3% oxygen, and trace amounts of hydrogen, nitrogen, and sulfur, evaluate its standard chemical exergy relative to the exergy reference of Table A-26, *Model II*. Also determine the standard chemical exergy of anthracite coal. Investigate the advantages and disadvantages of using culm instead of coal in power plants. Write a report summarizing your findings, including a comparison of the chemical exergy values obtained, sample calculations, and at least three references.



In Sec. 14.1, *equilibrium* criteria are introduced. Philip and Karen Smith/Getty Images, Inc.

ENGINEERING CONTEXT The **objective** of the present chapter is to consider the concept of equilibrium in greater depth than has been done thus far. In the first part of the chapter, we develop the fundamental concepts used to study chemical and phase equilibrium. In the second part of the chapter, the study of reacting systems initiated in Chap. 13 is continued with a discussion of *chemical* equilibrium in a single phase. Particular emphasis is placed on the case of reacting ideal gas mixtures. The third part of the chapter concerns *phase* equilibrium. The equilibrium of multicomponent, multiphase, nonreacting systems is considered and the *phase rule* is introduced.



14

Chemical and Phase Equilibrium

► LEARNING OUTCOMES

When you complete your study of this chapter, you will be able to...

- ▶ demonstrate understanding of key concepts related to chemical and phase equilibrium, including criteria for equilibrium, the equilibrium constant, and the Gibbs phase rule.
- ▶ apply the equilibrium constant relationship, Eq. 14.35, to relate pressure, temperature, and equilibrium constant for ideal gas mixtures involving individual and multiple reactions.
- ▶ use chemical equilibrium concepts with the energy balance.
- ▶ determine the equilibrium flame temperature.
- ▶ apply the Gibbs phase rule, Eq. 14.68.

Equilibrium Fundamentals

In this part of the chapter, fundamental concepts are developed that are useful in the study of chemical and phase equilibrium. Among these are equilibrium criteria and the chemical potential concept.

14.1

Introducing Equilibrium Criteria

thermodynamic equilibrium

A system is said to be in **thermodynamic equilibrium** if, when it is isolated from its surroundings, there would be no macroscopically observable changes. An important requirement for equilibrium is that the temperature be uniform throughout the system or each part of the system in thermal contact. If this condition were not met, spontaneous heat transfer from one location to another could occur when the system was isolated. There must also be no unbalanced forces between parts of the system. These conditions ensure that the system is in thermal and mechanical equilibrium, but there is still the possibility that complete equilibrium does not exist. A process might occur involving a chemical reaction, a transfer of mass between phases, or both. The objective of this section is to introduce criteria that can be applied to decide whether a system in a particular state is in equilibrium. These criteria are developed using the conservation of energy principle and the second law of thermodynamics as discussed next.

Consider the case of a simple compressible system of fixed mass for which temperature and pressure are uniform with position throughout. In the absence of overall system motion and ignoring the influence of gravity, the energy balance in differential form (Eq. 2.36) is

$$dU = \delta Q - \delta W$$

If volume change is the only work mode and pressure is uniform with position throughout the system, $\delta W = p dV$. Introducing this in the energy balance and solving for δQ gives

$$\delta Q = dU + p dV$$

Since temperature is uniform with position throughout the system, the entropy balance in differential form (Eq. 6.25) is

$$dS = \frac{\delta Q}{T} + \delta\sigma$$

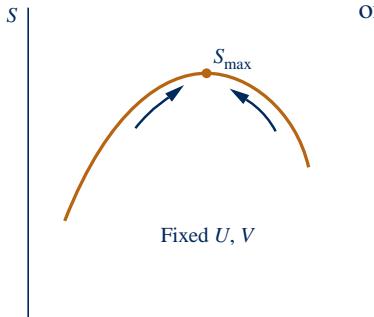
Eliminating δQ between the last two equations

$$T dS - dU - p dV = T \delta\sigma \quad (14.1)$$

Entropy is produced in all actual processes and conserved only in the absence of irreversibilities. Hence, Eq. 14.1 provides a constraint on the direction of processes. The only processes allowed are those for which $\delta\sigma \geq 0$. Thus

$$T dS - dU - p dV \geq 0 \quad (14.2)$$

Equation 14.2 can be used to study equilibrium under various conditions.



► **FOR EXAMPLE** a process taking place in an insulated, constant-volume vessel, where $dU = 0$ and $dV = 0$, must be such that

$$dS]_{U,V} \geq 0 \quad (14.3)$$

Equation 14.3 suggests that changes of state of a closed system at constant internal energy and volume can occur only in the direction of *increasing entropy*. The expression also implies that entropy approaches a *maximum* as a state of equilibrium is approached. This is a special case of the increase of entropy principle introduced in Sec. 6.8.1. ▶▶▶▶▶

An important case for the study of chemical and phase equilibria is one in which temperature and pressure are fixed. For this, it is convenient to employ the **Gibbs function** in extensive form

Gibbs function

$$G = H - TS = U + pV - TS$$

Forming the differential

$$dG = dU + p dV + V dp - T dS - S dT$$

or on rearrangement

$$dG - V dp + S dT = -(T dS - dU - p dV)$$

Except for the minus sign, the right side of this equation is the same as the expression appearing in Eq. 14.2. Accordingly, Eq. 14.2 can be written as

$$dG - V dp + S dT \leq 0 \quad (14.4)$$

where the inequality reverses direction because of the minus sign noted above.

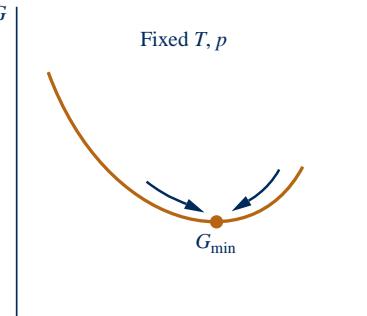
It can be concluded from Eq. 14.4 that any process taking place at a specified temperature and pressure ($dT = 0$ and $dp = 0$) must be such that

$$dG]_{T,p} \leq 0 \quad (14.5)$$

This inequality indicates that the Gibbs function of a system at fixed T and p *decreases* during an irreversible process. Each step of such a process results in a decrease in the Gibbs function of the system and brings the system closer to equilibrium. The equilibrium state is the one having the *minimum* value of the Gibbs function. Therefore, when

$$dG]_{T,p} = 0 \quad (14.6)$$

we have equilibrium. In subsequent discussions, we refer to Eq. 14.6 as the **equilibrium criterion**.



Equation 14.6 provides a relationship among the properties of a system when it is *at* an equilibrium state. The manner in which the equilibrium state is reached is unimportant, however, for once an equilibrium state is obtained, a system exists at a particular T and p and no further spontaneous changes can take place. When applying Eq. 14.6, therefore, we may specify the temperature T and pressure p , but it is unnecessary to require additionally that the system actually achieves equilibrium at fixed T and fixed p .

14.1.1 Chemical Potential and Equilibrium

In the present discussion, the Gibbs function is considered further as a prerequisite for application of the equilibrium criterion $dG]_{T,p} = 0$ introduced above. Let us begin by noting that any *extensive* property of a single-phase, single-component system is a function of two independent intensive properties and the size of the system. Selecting temperature and pressure as the independent properties and the number of moles n as the measure of size, the Gibbs function can be expressed in the form $G = G(T, p, n)$. For a single-phase, **multicomponent system**, G may then be considered a function of temperature, pressure, and the number of moles of each component present, written $G = G(T, p, n_1, n_2, \dots, n_j)$.

multicomponent system

If each mole number is multiplied by α , the size of the system changes by the same factor and so does the value of every extensive property. Thus, for the Gibbs function we may write

$$\alpha G(T, p, n_1, n_2, \dots, n_j) = G(T, p, \alpha n_1, \alpha n_2, \dots, \alpha n_j)$$

Differentiating with respect to α while holding temperature, pressure, and the mole numbers fixed and using the chain rule on the right side gives

$$G = \frac{\partial G}{\partial(\alpha n_1)} n_1 + \frac{\partial G}{\partial(\alpha n_2)} n_2 + \dots + \frac{\partial G}{\partial(\alpha n_j)} n_j$$

This equation holds for all values of α . In particular, it holds for $\alpha = 1$. Setting $\alpha = 1$, the following expression results:

$$G = \sum_{i=1}^j n_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_l} \quad (14.7)$$

TAKE NOTE...

Equations 14.8 and 14.9 correspond to Eqs. 11.107 and 11.108, respectively.

chemical potential

where the subscript n_l denotes that all n 's except n_i are held fixed during differentiation.

The partial derivatives appearing in Eq. 14.7 have such importance for our study of chemical and phase equilibrium that they are given a special name and symbol. The **chemical potential** of component i , symbolized by μ_i , is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_l} \quad (14.8)$$

The chemical potential is an *intensive property*. With Eq. 14.8, Eq. 14.7 becomes

$$G = \sum_{i=1}^j n_i \mu_i \quad (14.9)$$

The equilibrium criterion given by Eq. 14.6 can be written in terms of chemical potentials, providing an expression of fundamental importance for subsequent discussions of equilibrium. Forming the differential of $G(T, p, n_1, \dots, n_j)$ while holding temperature and pressure fixed results in

$$dG]_{T, p} = \sum_{i=1}^j \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_l} dn_i$$

The partial derivatives are recognized from Eq. 14.8 as the chemical potentials, so

$$dG]_{T, p} = \sum_{i=1}^j \mu_i dn_i \quad (14.10)$$

With Eq. 14.10, the equilibrium criterion $dG]_{T, p} = 0$ can be placed in the form

$$\sum_{i=1}^j \mu_i dn_i = 0 \quad (14.11)$$

TAKE NOTE...

Equations 14.10 and 14.11 are special forms of Eqs. 11.112 and 11.113, respectively.

Like Eq. 14.6, from which it is obtained, this equation provides a relationship among properties of a system when the system is *at* an equilibrium state where the temperature is T and the pressure is p . Like Eq. 14.6, this equation applies to a particular state, and the manner in which that state is attained is not important.

14.1.2 Evaluating Chemical Potentials

Means for evaluating the chemical potentials for two cases of interest are introduced in this section: a single phase of a pure substance and an ideal gas mixture.

SINGLE PHASE OF A PURE SUBSTANCE. An elementary case considered later in this chapter is that of equilibrium between two phases involving a pure substance. For a single phase of a pure substance, Eq. 14.9 becomes simply

$$G = n\mu$$

or

$$\mu = \frac{G}{n} = \bar{g} \quad (14.12)$$

That is, the chemical potential is just the Gibbs function per mole.

IDEAL GAS MIXTURE. An important case for the study of chemical equilibrium is that of an ideal gas mixture. The enthalpy and entropy of an ideal gas mixture are given by

$$H = \sum_{i=1}^j n_i \bar{h}_i(T) \quad \text{and} \quad S = \sum_{i=1}^j n_i \bar{s}_i(T, p_i)$$

where $p_i = y_i p$ is the partial pressure of component i . Accordingly, the Gibbs function takes the form

$$\begin{aligned} G &= H - TS = \sum_{i=1}^j n_i \bar{h}_i(T) - T \sum_{i=1}^j n_i \bar{s}_i(T, p_i) \\ &= \sum_{i=1}^j n_i [\bar{h}_i(T) - T \bar{s}_i(T, p_i)] \quad (\text{ideal gas}) \end{aligned} \quad (14.13)$$

Introducing the molar Gibbs function of component i

$$\bar{g}_i(T, p_i) = \bar{h}_i(T) - T \bar{s}_i(T, p_i) \quad (\text{ideal gas}) \quad (14.14)$$

Equation 14.13 can be expressed as

$$G = \sum_{i=1}^j n_i \bar{g}_i(T, p_i) \quad (\text{ideal gas}) \quad (14.15)$$

Comparing Eq. 14.15 to Eq. 14.9 suggests that

$$\mu_i = \bar{g}_i(T, p_i) \quad (\text{ideal gas}) \quad (14.16)$$

That is, the chemical potential of component i in an ideal gas mixture is equal to its Gibbs function per mole of i , evaluated at the mixture temperature and the partial pressure of i in the mixture. Equation 14.16 can be obtained formally by taking the partial derivative of Eq. 14.15 with respect to n_i , holding temperature, pressure, and the remaining n 's constant, and then applying the definition of chemical potential, Eq. 14.8.

The chemical potential of component i in an ideal gas mixture can be expressed in an alternative form that is somewhat more convenient for subsequent applications. Using Eq. 13.23, Eq. 14.14 becomes

$$\begin{aligned} \mu_i &= \bar{h}_i(T) - T \bar{s}_i(T, p_i) \\ &= \bar{h}_i(T) - T \left(\bar{s}_i^\circ(T) - \bar{R} \ln \frac{y_i p}{p_{\text{ref}}} \right) \\ &= \bar{h}_i(T) - T \bar{s}_i^\circ(T) + \bar{R} T \ln \frac{y_i p}{p_{\text{ref}}} \end{aligned}$$

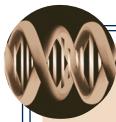
TAKE NOTE...

Expressions for the internal energy, enthalpy, and entropy of ideal gas mixtures are summarized in Table 13.1.

where p_{ref} is 1 atm and y_i is the mole fraction of component i in a mixture at temperature T and pressure p . The last equation can be written compactly as

$$\mu_i = \bar{g}_i^\circ + \bar{R}T \ln \frac{y_i p}{p_{\text{ref}}} \quad (\text{ideal gas}) \quad (14.17)$$

where \bar{g}_i° is the Gibbs function of component i evaluated at temperature T and a pressure of 1 atm. Additional details concerning the chemical potential concept are provided in Sec. 11.9. Equation 14.17 is the same as Eq. 11.144 developed there.



BIO CONNECTIONS The human body, as well as all living things, exist in a type of equilibrium that is considered in biology to be a *dynamic* equilibrium called *homeostasis*. The term refers to the ability of the body to regulate its internal state, such as body temperature, within specific limits necessary for life despite the conditions of the external environment, or the level of exertion (see accompanying figure). Within the body, feedback mechanisms regulate numerous variables that must be kept under control. If this dynamic equilibrium cannot be maintained because of the severe influence of the surroundings, living things can become sick and die.

The numerous control mechanisms in the body are varied, but they share some common elements. Generally, they involve a feedback loop that includes a way to sense a fluctuation of a variable from its desired condition and generate a corrective action to bring the variable back into the desired range. Feedback loops exist within the body at the levels of cells, body fluid systems (such as the circulatory system), tissues, and organs. These feedback loops also interact to maintain homeostasis much as a home thermostat regulates the heating and cooling system in a house. The mechanisms are highly stable as long as the external conditions are not too severe.

An example of the complexity of homeostasis is the way in which the body maintains the levels of glucose in the blood within desired limits. Glucose is an essential “fuel” for the processes within cells. Glucose absorbed by the digestive system from food, or stored as glycogen in the liver, is distributed by the blood stream to the cells. The body senses the level of glucose in the blood and various glands produce hormones to *stimulate* the conversion of glucose from stored glycogen, if needed to supplement food intake, or to *inhibit* the release of glucose, as necessary to maintain the desired levels. Several different hormones and numerous organs within the body are involved. The result is a balance that is highly stable within the limits needed by the body for homeostatic equilibrium.



Chemical Equilibrium

In this part of the chapter, the equilibrium criterion $dG]_{T,p} = 0$ introduced in Sec. 14.1 is used to study the equilibrium of reacting mixtures. The objective is to establish the composition present at equilibrium for a specified temperature and pressure. An important parameter for determining the equilibrium composition is the *equilibrium constant*. The equilibrium constant is introduced and its use illustrated by several solved examples. The discussion is concerned only with equilibrium states of reacting systems, and no information can be deduced about the *rates of reaction*. Whether an equilibrium mixture would form quickly or slowly can be determined only by considering the *chemical kinetics*, a topic that is not treated in this text.

14.2 Equation of Reaction Equilibrium

In Chap. 13 the conservation of mass and conservation of energy principles are applied to reacting systems by assuming that the reactions can occur as written. However, the extent to which a chemical reaction proceeds is limited by many factors. In general, the composition of the products actually formed from a given set of reactants, and the relative amounts of the products, can be determined only from experiment. Knowledge of the composition that would be present were a reaction to proceed to equilibrium is frequently useful, however. The *equation of reaction equilibrium* introduced in the present section provides the basis for determining the equilibrium composition of a reacting mixture.

14.2.1 Introductory Case

Consider a closed system consisting initially of a gaseous mixture of hydrogen and oxygen. A number of reactions might take place, including



Let us consider for illustration purposes only the first of the reactions given above, in which hydrogen and oxygen combine to form water. At equilibrium, the system will consist in general of three components: H_2 , O_2 , and H_2O , for not all of the hydrogen and oxygen initially present need be reacted. Changes in the amounts of these components during each differential step of the reaction leading to the formation of an equilibrium mixture are governed by Eq. 14.18. That is

$$dn_{\text{H}_2} = -dn_{\text{H}_2\text{O}}, \quad dn_{\text{O}_2} = -\frac{1}{2}dn_{\text{H}_2\text{O}} \quad (14.21a)$$

where dn denotes a differential change in the respective component. The minus signs signal that the amounts of hydrogen and oxygen present decrease when the reaction proceeds toward the right. Equations 14.21a can be expressed alternatively as

$$\frac{-dn_{\text{H}_2}}{1} = \frac{-dn_{\text{O}_2}}{\frac{1}{2}} = \frac{dn_{\text{H}_2\text{O}}}{1} \quad (14.21b)$$

which emphasizes that increases and decreases in the components are proportional to the stoichiometric coefficients of Eq. 14.18.

Equilibrium is a condition of *balance*. Accordingly, as suggested by the direction of the arrows in Eq. 14.18, when the system is at equilibrium, the tendency of the hydrogen and oxygen to form water is just balanced by the tendency of water to dissociate into oxygen and hydrogen. The equilibrium criterion $dG]_{T,p} = 0$ can be used to determine the composition at an equilibrium state where the temperature is T and the pressure is p . This requires evaluation of the differential $dG]_{T,p}$ in terms of system properties.

For the present case, Eq. 14.10 giving the difference in the Gibbs function of the mixture between two states having the same temperature and pressure, but compositions that differ infinitesimally, takes the following form:

$$dG]_{T,p} = \mu_{H_2} dn_{H_2} + \mu_{O_2} dn_{O_2} + \mu_{H_2O} dn_{H_2O} \quad (14.22)$$

The changes in the mole numbers are related by Eqs. 14.21. Hence

$$dG]_{T,p} = (-1\mu_{H_2} - \frac{1}{2}\mu_{O_2} + 1\mu_{H_2O}) dn_{H_2O}$$

At equilibrium, $dG]_{T,p} = 0$, so the term in parentheses must be zero. That is

$$-1\mu_{H_2} - \frac{1}{2}\mu_{O_2} + 1\mu_{H_2O} = 0$$

When expressed in a form that resembles Eq. 14.18, this becomes

$$1\mu_{H_2} + \frac{1}{2}\mu_{O_2} = 1\mu_{H_2O} \quad (14.23)$$

Equation 14.23 is the *equation of reaction equilibrium* for the case under consideration. The chemical potentials are functions of temperature, pressure, and composition. Thus, the composition that would be present at equilibrium for a given temperature and pressure can be determined, in principle, by solving this equation. The solution procedure is described in Sec. 14.3.

14.2.2 General Case

The foregoing development can be repeated for reactions involving any number of components. Consider a closed system containing *five* components, A, B, C, D, and E, at a given temperature and pressure, subject to a single chemical reaction of the form



where the ν 's are stoichiometric coefficients. Component E is assumed to be inert and thus does not appear in the reaction equation. As we will see, component E does influence the equilibrium composition even though it is not involved in the chemical reaction. The form of Eq. 14.24 suggests that at equilibrium the tendency of A and B to form C and D is just balanced by the tendency of C and D to form A and B.

The stoichiometric coefficients ν_A , ν_B , ν_C , and ν_D do not correspond to the respective number of moles of the components present. The amounts of the components present are designated n_A , n_B , n_C , n_D , and n_E . However, *changes* in the amounts of the components present do bear a definite relationship to the values of the stoichiometric coefficients. That is

$$\frac{-dn_A}{\nu_A} = \frac{-dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} \quad (14.25a)$$

where the minus signs indicate that A and B would be consumed when C and D are produced. Since E is inert, the amount of this component remains constant, so $dn_E = 0$.

Introducing a proportionality factor $d\varepsilon$, Eqs. 14.25a take the form

$$\frac{-dn_A}{\nu_A} = \frac{-dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} = d\varepsilon$$

from which the following expressions are obtained:

$$\begin{aligned} dn_A &= -\nu_A d\varepsilon, & dn_B &= -\nu_B d\varepsilon \\ dn_C &= \nu_C d\varepsilon, & dn_D &= \nu_D d\varepsilon \end{aligned} \quad (14.25b)$$

For the system under present consideration, Eq. 14.10 takes the form

$$dG]_{T,p} = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D + \mu_E dn_E$$

Introducing Eqs. 14.25b and noting that $dn_E = 0$, this becomes

$$dG]_{T,p} = (-\nu_A \mu_A - \nu_B \mu_B + \nu_C \mu_C + \nu_D \mu_D) d\varepsilon$$

At equilibrium, $dG]_{T,p} = 0$, so the term in parentheses must be zero. That is

$$-\nu_A \mu_A - \nu_B \mu_B + \nu_C \mu_C + \nu_D \mu_D = 0$$

or when written in a form resembling Eq. 14.24

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \quad (14.26)$$

equation of reaction equilibrium

For the present case, Eq. 14.26 is the **equation of reaction equilibrium**. In principle, the composition that would be present at equilibrium for a given temperature and pressure can be determined by solving this equation. The solution procedure is simplified through the *equilibrium constant* concept introduced in the next section.

14.3 Calculating Equilibrium Compositions

The objective of the present section is to show how the equilibrium composition of a system at a specified temperature and pressure can be determined by solving the equation of reaction equilibrium. An important part is played in this by the *equilibrium constant*.

14.3.1 Equilibrium Constant for Ideal Gas Mixtures

The first step in solving the equation of reaction equilibrium, Eq. 14.26, for the equilibrium composition is to introduce expressions for the chemical potentials in terms of temperature, pressure, and composition. For an ideal gas mixture, Eq. 14.17 can be used for this purpose. When this expression is introduced for each of the components A, B, C, and D, Eq. 14.26 becomes

$$\begin{aligned} & \nu_A \left(\bar{g}_A^\circ + \bar{R}T \ln \frac{y_A p}{p_{\text{ref}}} \right) + \nu_B \left(\bar{g}_B^\circ + \bar{R}T \ln \frac{y_B p}{p_{\text{ref}}} \right) \\ &= \nu_C \left(\bar{g}_C^\circ + \bar{R}T \ln \frac{y_C p}{p_{\text{ref}}} \right) + \nu_D \left(\bar{g}_D^\circ + \bar{R}T \ln \frac{y_D p}{p_{\text{ref}}} \right) \end{aligned} \quad (14.27)$$

where \bar{g}_i° is the Gibbs function of component i evaluated at temperature T and the pressure $p_{\text{ref}} = 1 \text{ atm}$. Equation 14.27 is the basic working relation for chemical equilibrium in a mixture of ideal gases. However, subsequent calculations are facilitated if it is written in an alternative form, as follows.

Collect like terms and rearrange Eq. 14.27 as

$$\begin{aligned} & (\nu_C \bar{g}_C^\circ + \nu_D \bar{g}_D^\circ - \nu_A \bar{g}_A^\circ - \nu_B \bar{g}_B^\circ) \\ &= -\bar{R}T \left(\nu_C \ln \frac{y_C p}{p_{\text{ref}}} + \nu_D \ln \frac{y_D p}{p_{\text{ref}}} - \nu_A \ln \frac{y_A p}{p_{\text{ref}}} - \nu_B \ln \frac{y_B p}{p_{\text{ref}}} \right) \end{aligned} \quad (14.28)$$

The term on the left side of Eq. 14.28 can be expressed concisely as ΔG° . That is

$$\Delta G^\circ = \nu_C \bar{g}_C^\circ + \nu_D \bar{g}_D^\circ - \nu_A \bar{g}_A^\circ - \nu_B \bar{g}_B^\circ \quad (14.29a)$$

which is the change in the Gibbs function for the reaction given by Eq. 14.24 if each reactant and product were separate at temperature T and a pressure of 1 atm.

This expression can be written alternatively in terms of specific enthalpies and entropies as

$$\begin{aligned}\Delta G^\circ &= \nu_C(\bar{h}_C - T\bar{s}_C^\circ) + \nu_D(\bar{h}_D - T\bar{s}_D^\circ) - \nu_A(\bar{h}_A - T\bar{s}_A^\circ) - \nu_B(\bar{h}_B - T\bar{s}_B^\circ) \\ &= (\nu_C\bar{h}_C + \nu_D\bar{h}_D - \nu_A\bar{h}_A - \nu_B\bar{h}_B) - T(\nu_C\bar{s}_C^\circ + \nu_D\bar{s}_D^\circ - \nu_A\bar{s}_A^\circ - \nu_B\bar{s}_B^\circ)\end{aligned}\quad (14.29b)$$

Since the enthalpy of an ideal gas depends on temperature only, the \bar{h} 's of Eq. 14.29b are evaluated at temperature T . As indicated by the superscript $^\circ$, each of the entropies is evaluated at temperature T and a pressure of 1 atm.

Introducing Eq. 14.29a into Eq. 14.28 and combining the terms involving logarithms into a single expression gives

$$-\frac{\Delta G^\circ}{RT} = \ln \left[\frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{p}{p_{\text{ref}}} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \right] \quad (14.30)$$

Equation 14.30 is simply the form taken by the equation of reaction equilibrium, Eq. 14.26, for an ideal gas mixture subject to the reaction Eq. 14.24. As illustrated by subsequent examples, similar expressions can be written for other reactions.

Equation 14.30 can be expressed concisely as

$$-\frac{\Delta G^\circ}{RT} = \ln K(T) \quad (14.31)$$

where K is the **equilibrium constant** defined by

$$K(T) = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{p}{p_{\text{ref}}} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \quad (14.32)$$

Given the values of the stoichiometric coefficients, ν_A , ν_B , ν_C , and ν_D and the temperature T , the left side of Eq. 14.31 can be evaluated using either of Eqs. 14.29 together with the appropriate property data. The equation can then be solved for the value of the equilibrium constant K . Accordingly, for selected reactions K can be evaluated and tabulated against temperature. It is common to tabulate $\log_{10}K$ or $\ln K$ versus temperature, however. A tabulation of $\log_{10}K$ values over a range of temperatures for several reactions is provided in Table A-27, which is extracted from a more extensive compilation.

The terms in the numerator and denominator of Eq. 14.32 correspond, respectively, to the products and reactants of the reaction given by Eq. 14.24 as it proceeds from left to right as written. For the *inverse* reaction $\nu_C C + \nu_D D \rightleftharpoons \nu_A A + \nu_B B$, the equilibrium constant takes the form

$$K^* = \frac{y_A^{\nu_A} y_B^{\nu_B}}{y_C^{\nu_C} y_D^{\nu_D}} \left(\frac{p}{p_{\text{ref}}} \right)^{\nu_A + \nu_B - \nu_C - \nu_D} \quad (14.33)$$

Comparing Eqs. 14.32 and 14.33, it follows that the value of K^* is just the reciprocal of K : $K^* = 1/K$. Accordingly,

$$\log_{10}K^* = -\log_{10}K \quad (14.34)$$

Hence, Table A-27 can be used both to evaluate K for the reactions listed proceeding in the direction left to right and to evaluate K^* for the inverse reactions proceeding in the direction right to left.

Example 14.1 illustrates how the $\log_{10}K$ values of Table A-27 are determined. Subsequent examples show how the $\log_{10}K$ values can be used to evaluate equilibrium compositions.

EXAMPLE 14.1**Evaluating the Equilibrium Constant at a Specified Temperature**

Evaluate the equilibrium constant, expressed as $\log_{10}K$, for the reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$ at (a) 298 K and (b) 2000 K. Compare with the value obtained from Table A-27.

SOLUTION

Known: The reaction is $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$.

Find: Determine the equilibrium constant for $T = 298 \text{ K}$ (25°C) and $T = 2000 \text{ K}$.

Engineering Model: The ideal gas model applies.

Analysis: The equilibrium constant requires the evaluation of ΔG° for the reaction. Invoking Eq. 14.29b for this purpose, we have

$$\Delta G^\circ = (\bar{h}_{\text{CO}_2} - \bar{h}_{\text{CO}} - \frac{1}{2}\bar{h}_{\text{O}_2}) - T(\bar{s}_{\text{CO}_2}^\circ - \bar{s}_{\text{CO}}^\circ - \frac{1}{2}\bar{s}_{\text{O}_2}^\circ)$$

where the enthalpies are evaluated at temperature T and the absolute entropies are evaluated at temperature T and a pressure of 1 atm. Using Eq. 13.9, the enthalpies are evaluated in terms of the respective enthalpies of formation, giving

$$\Delta G^\circ = [(\bar{h}_f^\circ)_{\text{CO}_2} - (\bar{h}_f^\circ)_{\text{CO}} - \frac{1}{2}(\bar{h}_f^\circ)_{\text{O}_2}] + [(\Delta\bar{h})_{\text{CO}_2} - (\Delta\bar{h})_{\text{CO}} - \frac{1}{2}(\Delta\bar{h})_{\text{O}_2}] - T(\bar{s}_{\text{CO}_2}^\circ - \bar{s}_{\text{CO}}^\circ - \frac{1}{2}\bar{s}_{\text{O}_2}^\circ)$$

where the $\Delta\bar{h}$ terms account for the change in specific enthalpy from $T_{\text{ref}} = 298 \text{ K}$ to the specified temperature T . The enthalpy of formation of oxygen is zero by definition.

(a) When $T = 298 \text{ K}$, the $\Delta\bar{h}$ terms of the above expression for ΔG° vanish. The required enthalpy of formation and absolute entropy values can be read from Table A-25, giving

$$\begin{aligned}\Delta G^\circ &= [(-393,520) - (-110,530) - \frac{1}{2}(0)] - 298[213.69 - 197.54 - \frac{1}{2}(205.03)] \\ &= -257,253 \text{ kJ/kmol}\end{aligned}$$

With this value for ΔG° , Eq. 14.31 gives

$$\ln K = -\frac{(-257,253 \text{ kJ/kmol})}{(8.314 \text{ kJ/kmol} \cdot \text{K})(298 \text{ K})} = 103.83$$

which corresponds to $\log_{10}K = 45.093$.

Table A-27 gives the logarithm to the base 10 of the equilibrium constant for the inverse reaction: $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$. That is, $\log_{10}K^* = -45.066$. Thus, with Eq. 14.34, $\log_{10}K = 45.066$, which agrees closely with the calculated value.

(b) When $T = 2000 \text{ K}$, the $\Delta\bar{h}$ and \bar{s}° terms for O_2 , CO , and CO_2 required by the above expression for ΔG° are evaluated from Tables A-23. The enthalpy of formation values are the same as in part (a). Thus

$$\begin{aligned}\Delta G^\circ &= [(-393,520) - (-110,530) - \frac{1}{2}(0)] + [(100,804 - 9364) - (65408 - 8669) \\ &\quad - \frac{1}{2}(67,881 - 8682)] - 2000[309.210 - 258.600 - \frac{1}{2}(268.655)] \\ &= -282,990 + 5102 + 167,435 = -110,453 \text{ kJ/kmol}\end{aligned}$$

With this value, Eq. 14.31 gives

$$\ln K = -\frac{(-110,453)}{(8.314)(2000)} = 6.643$$

which corresponds to $\log_{10}K = 2.885$.

At 2000 K, Table A-27 gives $\log_{10}K^* = -2.884$. With Eq. 14.34, $\log_{10}K = 2.884$, which is in agreement with the calculated value.

Using the procedures described above, it is straightforward to determine $\log_{10}K$ versus temperature for each of several specified reactions and tabulate the results as in Table A-27.

QuickQUIZ

If $\ln K = 23.535$ for the given reaction, use Table A-27 to determine T , in K. **Ans.** 1000 K.

Skills Developed

Ability to...

- evaluate $\log_{10}K$ based on Eq. 14.31 and data from Tables A-23 and A-25.
- use the relation of Eq. 14.34 for inverse reactions.

14.3.2 Illustrations of the Calculation of Equilibrium Compositions for Reacting Ideal Gas Mixtures

It is often convenient to express Eq. 14.32 explicitly in terms of the number of moles that would be present at equilibrium. Each mole fraction appearing in the equation has the form $y_i = n_i/n$, where n_i is the amount of component i in the equilibrium mixture and n is the total number of moles of mixture. Hence, Eq. 14.32 can be rewritten as

$$K = \frac{n_C^{\nu_C} n_D^{\nu_D}}{n_A^{\nu_A} n_B^{\nu_B}} \left(\frac{p/p_{\text{ref}}}{n} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \quad (14.35)$$

The value of n must include not only the reacting components A, B, C, and D but also all inert components present. Since inert component E has been assumed present, we would write $n = n_A + n_B + n_C + n_D + n_E$.

Equation 14.35 provides a relationship among the temperature, pressure, and composition of an ideal gas mixture at equilibrium. Accordingly, if any two of temperature, pressure, and composition are known, the third can be found by solving this equation.

► **FOR EXAMPLE** suppose that the temperature T and pressure p are known and the object is the equilibrium composition. With temperature known, the value of K can be obtained from Table A-27. The n 's of the reacting components A, B, C, and D can be expressed in terms of a single unknown variable through application of the conservation of mass principle to the various chemical species present. Then, since the pressure is known, Eq. 14.35 constitutes a single equation in a single unknown, which can be solved using an *equation solver* or iteratively with a hand calculator. ◀◀◀◀◀

In Example 14.2, we apply Eq. 14.35 to study the effect of pressure on the equilibrium composition of a mixture of CO_2 , CO, and O_2 .

EXAMPLE 14.2

Determining Equilibrium Composition Given Temperature and Pressure

One kilomole of carbon monoxide, CO, reacts with $\frac{1}{2}$ kmol of oxygen, O_2 , to form an equilibrium mixture of CO_2 , CO, and O_2 at 2500 K and (a) 1 atm, (b) 10 atm. Determine the equilibrium composition in terms of mole fractions.

SOLUTION

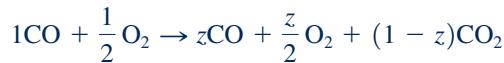
Known: A system initially consisting of 1 kmol of CO and $\frac{1}{2}$ kmol of O_2 reacts to form an equilibrium mixture of CO_2 , CO, and O_2 . The temperature of the mixture is 2500 K and the pressure is (a) 1 atm, (b) 10 atm.

Find: Determine the equilibrium composition in terms of mole fractions.

Engineering Model: The equilibrium mixture is modeled as an ideal gas mixture.

Analysis: Equation 14.35 relates temperature, pressure, and composition for an ideal gas mixture at equilibrium. If any two are known, the third can be determined using this equation. In the present case, T and p are known, and the composition is unknown.

Applying conservation of mass, the overall balanced chemical reaction equation is



where z is the amount of CO, in kmol, present in the equilibrium mixture. Note that $0 \leq z \leq 1$.

The total number of moles n in the equilibrium mixture is

$$n = z + \frac{z}{2} + (1 - z) = \frac{2 + z}{2}$$

Accordingly, the molar analysis of the equilibrium mixture is

$$y_{\text{CO}} = \frac{2z}{2 + z}, \quad y_{\text{O}_2} = \frac{z}{2 + z}, \quad y_{\text{CO}_2} = \frac{2(1 - z)}{2 + z}$$

At equilibrium, the tendency of CO and O₂ to form CO₂ is just balanced by the tendency of CO₂ to form CO and O₂, so we have CO₂ ⇌ CO + ½O₂. Accordingly, Eq. 14.35 takes the form

$$K = \frac{z(z/2)^{1/2}}{(1 - z)} \left[\frac{p/p_{\text{ref}}}{(2 + z)/2} \right]^{1+1/2-1} = \frac{z}{1 - z} \left(\frac{z}{2 + z} \right)^{1/2} \left(\frac{p}{p_{\text{ref}}} \right)^{1/2}$$

At 2500 K, Table A-27 gives log₁₀K = -1.44. Thus, $K = 0.0363$. Inserting this value into the last expression

$$0.0363 = \frac{z}{1 - z} \left(\frac{z}{2 + z} \right)^{1/2} \left(\frac{p}{p_{\text{ref}}} \right)^{1/2} \quad (\text{a})$$

(a) When $p = 1$ atm, Eq. (a) becomes

$$0.0363 = \frac{z}{1 - z} \left(\frac{z}{2 + z} \right)^{1/2}$$

Using an equation solver or iteration with a hand calculator, $z = 0.129$. The equilibrium composition in terms of mole fractions is then

$$y_{\text{CO}} = \frac{2(0.129)}{2.129} = 0.121, \quad y_{\text{O}_2} = \frac{0.129}{2.129} = 0.061, \quad y_{\text{CO}_2} = \frac{2(1 - 0.129)}{2.129} = 0.818$$

(b) When $p = 10$ atm, Eq. (a) becomes

$$0.0363 = \frac{z}{1 - z} \left(\frac{z}{2 + z} \right)^{1/2} (10)^{1/2}$$

- ① Solving, $z = 0.062$. The corresponding equilibrium composition in terms of mole fractions is $y_{\text{CO}} = 0.06$, $y_{\text{O}_2} = 0.03$, $y_{\text{CO}_2} = 0.91$.

- ② Comparing the results of parts (a) and (b) we conclude that the extent to which the reaction proceeds toward completion (the extent to which CO₂ is formed) is increased by increasing the pressure.



Skills Developed

Ability to...

- apply Eq. 14.35 to determine equilibrium composition given temperature and pressure.
- retrieve and use data from Table A-27.

QuickQUIZ

If $z = 0.0478$ (corresponding to $p = 22.4$ atm, $T = 2500$ K), what would be the mole fraction of each constituent of the equilibrium mixture? **Ans.** $y_{\text{CO}} = 0.0467$, $y_{\text{O}_2} = 0.0233$, $y_{\text{CO}_2} = 0.9300$.

In Example 14.3, we determine the temperature of an equilibrium mixture when the pressure and composition are known.

EXAMPLE 14.3 ►

Determining Equilibrium Temperature Given Pressure and Composition

Measurements show that at a temperature T and a pressure of 1 atm, the equilibrium mixture for the system of Example 14.2 has the composition $y_{\text{CO}} = 0.298$, $y_{\text{O}_2} = 0.149$, $y_{\text{CO}_2} = 0.553$. Determine the temperature T of the mixture, in K.

SOLUTION

Known: The pressure and composition of an equilibrium mixture of CO, O₂, and CO₂ are specified.

Find: Determine the temperature of the mixture, in K.

Engineering Model: The mixture can be modeled as an ideal gas mixture.

Analysis: Equation 14.35 relates temperature, pressure, and composition for an ideal gas mixture at equilibrium. If any two are known, the third can be found using this equation. In the present case, composition and pressure are known, and the temperature is the unknown.

Equation 14.35 takes the same form here as in Example 14.2. Thus, when $p = 1 \text{ atm}$, we have

$$K(T) = \frac{z}{1-z} \left(\frac{z}{2+z} \right)^{1/2}$$

where z is the amount of CO, in kmol, present in the equilibrium mixture and T is the temperature of the mixture.

The solution to Example 14.2 gives the following expression for the mole fraction of the CO in the mixture: $y_{\text{CO}} = 2z/(2 + z)$. Since $y_{\text{CO}} = 0.298$, $z = 0.35$.

Inserting this value for z into the expression for the equilibrium constant ① gives $K = 0.2078$. Thus, $\log_{10} K = -0.6824$. Interpolation in Table A-27 then gives $T = 2881 \text{ K}$.

- ① Comparing this example with part (a) of Example 14.2, we conclude that the extent to which the reaction proceeds to completion (the extent to which CO₂ is formed) is decreased by increasing the temperature.

Skills Developed

Ability to...

- apply Eq. 14.35 to determine temperature given pressure and equilibrium composition.
- retrieve and use data from Table A-27.

QuickQUIZ

Determine the temperature, in K, for a pressure of 2 atm if the equilibrium composition were unchanged. **Ans.** $\approx 2970 \text{ K}$.

In Example 14.4, we consider the effect of an inert component on the equilibrium composition.

EXAMPLE 14.4 ►

Considering the Effect on Equilibrium of an Inert Component

One kilomole of carbon monoxide reacts with the theoretical amount of air to form an equilibrium mixture of CO₂, CO, O₂, and N₂ at 2500 K and 1 atm. Determine the equilibrium composition in terms of mole fractions, and compare with the result of Example 14.2.

SOLUTION

Known: A system initially consisting of 1 kmol of CO and the theoretical amount of air reacts to form an equilibrium mixture of CO₂, CO, O₂, and N₂. The temperature and pressure of the mixture are 2500 K and 1 atm.

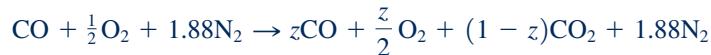
Find: Determine the equilibrium composition in terms of mole fractions, and compare with the result of Example 14.2.

Engineering Model: The equilibrium mixture can be modeled as an ideal gas mixture wherein N₂ is inert.

Analysis: For a *complete reaction* of CO with the theoretical amount of air



Accordingly, the reaction of CO with the theoretical amount of air to form CO₂, CO, O₂, and N₂ is



where z is the amount of CO, in kmol, present in the equilibrium mixture.

The total number of moles n in the equilibrium mixture is

$$n = z + \frac{z}{2} + (1 - z) + 1.88 = \frac{5.76 + z}{2}$$

The composition of the equilibrium mixture in terms of mole fractions is

$$y_{\text{CO}} = \frac{2z}{5.76 + z}, \quad y_{\text{O}_2} = \frac{z}{5.76 + z}, \quad y_{\text{CO}_2} = \frac{2(1 - z)}{5.76 + z}, \quad y_{\text{N}_2} = \frac{3.76}{5.76 + z}$$

At equilibrium we have $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$. So Eq. 14.35 takes the form

$$K = \frac{z(z/2)^{1/2}}{(1 - z)} \left[\frac{p/p_{\text{ref}}}{(5.76 + z)/2} \right]^{1/2}$$

The value of K is the same as in the solution to Example 14.2, $K = 0.0363$. Thus, since $p = 1$ atm, we have

$$0.0363 = \frac{z}{1 - z} \left(\frac{z}{5.76 + z} \right)^{1/2}$$

Solving, $z = 0.175$. The corresponding equilibrium composition is $y_{\text{CO}} = 0.059$, $y_{\text{CO}_2} = 0.278$, $y_{\text{O}_2} = 0.029$, $y_{\text{N}_2} = 0.634$.

Comparing this example with Example 14.2, we conclude that the presence of the inert component nitrogen reduces the extent to which the reaction proceeds toward completion at the specified temperature and pressure (reduces the extent to which CO₂ is formed).

**Skills Developed**

Ability to...

- apply Eq. 14.35 to determine equilibrium composition for given temperature and pressure in the presence of an inert component.
- retrieve and use data from Table A-27.

QuickQUIZ

Determine the amounts, in kmol, of each component of the equilibrium mixture. **Ans.** $n_{\text{CO}} = 0.175$, $n_{\text{O}_2} = 0.0875$, $n_{\text{CO}_2} = 0.8250$, $n_{\text{N}_2} = 1.88$.

In the next example, the equilibrium concepts of this chapter are applied together with the energy balance for reacting systems developed in Chap. 13.

EXAMPLE 14.5**Using Equilibrium Concepts with the Energy Balance**

Carbon dioxide at 25°C, 1 atm enters a reactor operating at steady state and dissociates, giving an equilibrium mixture of CO₂, CO, and O₂ that exits at 3200 K, 1 atm. Determine the heat transfer to the reactor, in kJ per kmol of CO₂ entering. The effects of kinetic and potential energy can be ignored and $\dot{W}_{cv} = 0$.

SOLUTION

Known: Carbon dioxide at 25°C, 1 atm enters a reactor at steady state. An equilibrium mixture of CO₂, CO, and O₂ exits at 3200 K, 1 atm.

Find: Determine the heat transfer to the reactor, in kJ per kmol of CO₂ entering.

Schematic and Given Data:

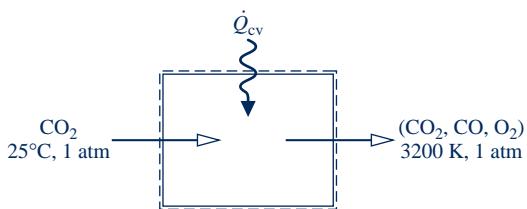


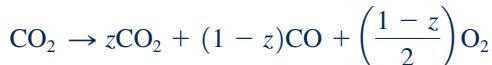
Fig. E14.5

Engineering Model:

1. The control volume shown on the accompanying sketch by a dashed line operates at steady state with $\dot{W}_{cv} = 0$. Kinetic energy and potential energy effects can be ignored.
2. The entering CO₂ is modeled as an ideal gas.
3. The exiting mixture of CO₂, CO, and O₂ is an equilibrium ideal gas mixture.

Analysis: The required heat transfer can be determined from an energy rate balance for the control volume, but first the composition of the exiting equilibrium mixture must be determined.

Applying the conservation of mass principle, the overall dissociation reaction is described by



where z is the amount of CO₂, in kmol, present in the mixture exiting the control volume, per kmol of CO₂ entering. The total number of moles n in the mixture is then

$$n = z + (1 - z) + \left(\frac{1 - z}{2}\right) = \frac{3 - z}{2}$$

The exiting mixture is assumed to be an equilibrium mixture (assumption 3). Thus, for the mixture we have $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$. Equation 14.35 takes the form

$$K = \frac{(1 - z)[(1 - z)/2]^{1/2}}{z} \left[\frac{p/p_{ref}}{(3 - z)/2} \right]^{1+1/2-1}$$

Rearranging and noting that $p = 1$ atm

$$K = \left(\frac{1 - z}{z}\right) \left(\frac{1 - z}{3 - z}\right)^{1/2}$$

At 3200 K, Table A-27 gives $\log_{10}K = -0.189$. Thus, $K = 0.647$, and the equilibrium constant expression becomes

$$0.647 = \left(\frac{1 - z}{z}\right) \left(\frac{1 - z}{3 - z}\right)^{1/2}$$

Solving, $z = 0.422$. The composition of the exiting equilibrium mixture, in kmol per kmol of CO₂ entering, is then 0.422CO₂, 0.578CO, 0.289O₂.

When expressed per kmol of CO₂ entering the control volume, the energy rate balance reduces by assumption 1 to

$$0 = \frac{\dot{Q}_{cv}}{\dot{n}_{\text{CO}_2}} - \frac{\dot{W}_{cv}^0}{\dot{n}_{\text{CO}_2}} + \bar{h}_{\text{CO}_2} - (0.422\bar{h}_{\text{CO}_2} + 0.578\bar{h}_{\text{CO}} + 0.289\bar{h}_{\text{O}_2})$$

Solving for the heat transfer per kmol of CO₂ entering, and evaluating each enthalpy in terms of the respective enthalpy of formation

$$\frac{\dot{Q}_{cv}}{\dot{n}_{\text{CO}_2}} = 0.422(\bar{h}_f^\circ + \Delta\bar{h})_{\text{CO}_2} + 0.578(\bar{h}_f^\circ + \Delta\bar{h})_{\text{CO}} + 0.289(\bar{h}_f^\circ + \Delta\bar{h})_{\text{O}_2} - (\bar{h}_f^\circ + \Delta\bar{h})_{\text{CO}_2}$$

- The enthalpy of formation of O_2 is zero by definition; $\Delta\bar{h}$ for the CO_2 at the inlet vanishes because CO_2 enters at $25^\circ C$.

With enthalpy of formation values from Tables A-25 and $\Delta\bar{h}$ values for O_2 , CO , and CO_2 , from Table A-23

$$\begin{aligned} \frac{\dot{Q}_{cv}}{\dot{n}_{CO_2}} &= 0.422[-393,520 + (174,695 - 9364)] + 0.578[-110,530 + (109,667 - 8669)] \\ &\quad + 0.289(114,809 - 8682) - (-393,520) \\ ① &= 322,385 \text{ kJ/kmol}(CO_2) \end{aligned}$$

- For comparison, let us determine the heat transfer if we assume no dissociation—namely, when CO_2 alone exits the reactor. With data from Table A-23, the heat transfer is

$$\begin{aligned} \frac{\dot{Q}_{cv}}{\dot{n}_{CO_2}} &= \bar{h}_{CO_2}(3200 \text{ K}) - \bar{h}_{CO_2}(298 \text{ K}) \\ &= 174,695 - 9364 = 165,331 \text{ kJ/kmol}(CO_2) \end{aligned}$$

- The value is much less than the value obtained in the solution above because the dissociation of CO_2 requires more energy input (an endothermic reaction).



Skills Developed

Ability to...

- apply Eq. 14.35 together with the energy balance for reacting systems to determine heat transfer for a reactor.
- retrieve and use data from Tables A-23, A-25, and A-27.

QuickQUIZ

Determine the heat transfer rate, in kW, and the molar flow rate of mixture exiting, in kmol/s, for a flow rate of 3.1×10^{-5} kmol/s of CO_2 entering. **Ans.** 10 kW, 4×10^{-5} kmol/s.

14.3.3 Equilibrium Constant for Mixtures and Solutions

The procedures that led to the equilibrium constant for reacting ideal gas mixtures can be followed for the general case of reacting mixtures by using the fugacity and activity concepts introduced in Sec. 11.9. In principle, equilibrium compositions of such mixtures can be determined with an approach paralleling the one for ideal gas mixtures.

Equation 11.141 can be used to evaluate the chemical potentials appearing in the equation of reaction equilibrium (Eq. 14.26). The result is

$$v_A(\bar{g}_A^\circ + \bar{R}T \ln a_A) + v_B(\bar{g}_B^\circ + \bar{R}T \ln a_B) = v_C(\bar{g}_C^\circ + \bar{R}T \ln a_C) + v_D(\bar{g}_D^\circ + \bar{R}T \ln a_D) \quad (14.36)$$

where \bar{g}_i° is the Gibbs function of pure component i at temperature T and the pressure $p_{ref} = 1 \text{ atm}$, and a_i is the *activity* of that component.

Collecting terms and employing Eq. 14.29a, Eq. 14.36 becomes

$$-\frac{\Delta G^\circ}{RT} = \ln \left(\frac{a_C^{v_C} a_D^{v_D}}{a_A^{v_A} a_B^{v_B}} \right) \quad (14.37)$$

This equation can be expressed in the same form as Eq. 14.31 by defining the equilibrium constant as

$$K = \frac{a_C^{v_C} a_D^{v_D}}{a_A^{v_A} a_B^{v_B}} \quad (14.38)$$

TAKE NOTE...

Study of Sec. 14.3.3 requires content from Sec. 11.9

Since Table A-27 and similar compilations are constructed simply by evaluating $-\Delta G^\circ / RT$ for specified reactions at several temperatures, such tables can be employed to evaluate the more general equilibrium constant given by Eq. 14.38. However, before Eq. 14.38 can be used to determine the equilibrium composition for a known value of K , it is necessary to evaluate the activity of the various mixture components. Let us illustrate this for the case of mixtures that can be modeled as *ideal solutions*.

IDEAL SOLUTIONS. For an ideal solution, the activity of component i is given by

$$a_i = \frac{y_i f_i}{f_i^\circ} \quad (11.142)$$

where f_i is the fugacity of pure i at the temperature T and pressure p of the mixture, and f_i° is the fugacity of pure i at temperature T and the pressure p_{ref} . Using this expression to evaluate a_A , a_B , a_C , and a_D , Eq. 14.38 becomes

$$K = \frac{(y_C f_C/f_C^\circ)^{v_C} (y_D f_D/f_D^\circ)^{v_D}}{(y_A f_A/f_A^\circ)^{v_A} (y_B f_B/f_B^\circ)^{v_B}} \quad (14.39a)$$

which can be expressed alternatively as

$$K = \left[\frac{(f_C/p)^{v_C} (f_D/p)^{v_D}}{(f_A/p)^{v_A} (f_B/p)^{v_B}} \right] \left[\frac{(f_A^\circ/p_{\text{ref}})^{v_A} (f_B^\circ/p_{\text{ref}})^{v_B}}{(f_C^\circ/p_{\text{ref}})^{v_C} (f_D^\circ/p_{\text{ref}})^{v_D}} \right] \left[\frac{y_C^{v_C} y_D^{v_D}}{y_A^{v_A} y_B^{v_B}} \left(\frac{p}{p_{\text{ref}}} \right)^{v_C + v_D - v_A - v_B} \right] \quad (14.39b)$$

The ratios of fugacity to pressure in this equation can be evaluated, in principle, from Eq. 11.124 or the generalized fugacity chart, Fig. A-6, developed from it. In the special case when each component behaves as an ideal gas at both T, p and T, p_{ref} , these ratios equal unity and Eq. 14.39b reduces to the underlined term, which is just Eq. 14.32.

Horizons

Methane, Another Greenhouse Gas

While carbon dioxide is often mentioned by the media because of its effect on global climate change, and rightly so, other gases released to the atmosphere also contribute to climate change but get less publicity. In particular, methane, CH_4 , which receives little notice as a greenhouse gas, has a Global Warming Potential of 25, compared to carbon dioxide's GWP of 1 (see Table 10.1).

Sources of methane related to human activity include fossil-fuel (coal, natural gas, and petroleum) production, distribution, combustion, and other uses. Wastewater treatment, landfills, and agriculture, including ruminant animals raised for food, are also human-related sources of methane. Natural sources of methane include wetlands and methane *hydrate* deposits in seafloor sediments.

For decades, the concentration of methane in the atmosphere has increased significantly. But some observers report that the increase has slowed recently and may be ceasing. While this could be only a temporary pause, reasons have been advanced to explain the development. Some say governmental actions aimed at reducing release of methane have begun to show results. Changes in agricultural practices, such as the way rice

is produced, also may be a factor in the reported reduction of methane in the atmosphere.

Another view is that the plateau in atmospheric methane may at least in part be due to chemical equilibrium: Methane released to the atmosphere is balanced by its consumption in the atmosphere. Methane is consumed in the atmosphere principally by its reaction with the hydroxyl radical (OH), which is produced through decomposition of atmospheric ozone by action of solar radiation. For instance, OH reacts with methane to yield water and CH_3 , a methyl radical, according to $\text{CH}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3$. Other reactions follow this, leading eventually to water-soluble products that are *washed out* of the atmosphere by rain and snow.

Understanding the reasons for the apparent slowing rate of growth of methane in the atmosphere will take effort, including quantifying changes in the various sources of methane and pinpointing natural mechanisms by which it is removed from the atmosphere. Better understanding will enable us to craft measures aimed at curbing release of methane, allowing the atmosphere's natural ability to cleanse itself to assist in maintaining a healthier balance.

14.4 Further Examples of the Use of the Equilibrium Constant

Some additional aspects of the use of the equilibrium constant are introduced in this section: the equilibrium flame temperature, the van't Hoff equation, and chemical equilibrium for ionization reactions and simultaneous reactions. To keep the presentation at an introductory level, only the case of ideal gas mixtures is considered.

14.4.1 Determining Equilibrium Flame Temperature

In this section, the effect of incomplete combustion on the adiabatic flame temperature, introduced in Sec. 13.3, is considered using concepts developed in the present chapter. We begin with a review of some ideas related to the adiabatic flame temperature by considering a reactor operating at steady state for which no significant heat transfer with the surroundings takes place.

Let carbon monoxide gas entering at one location react *completely* with the theoretical amount of air entering at another location as follows:

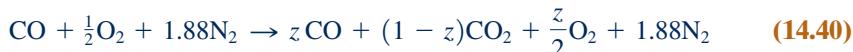


As discussed in Sec. 13.3, the products would exit the reactor at a temperature we have designated the *maximum adiabatic flame temperature*. This temperature can be determined by solving a *single* equation, the energy equation. At such an elevated temperature, however, there would be a tendency for CO₂ to dissociate



Since dissociation requires energy (an endothermic reaction), the temperature of the products would be *less than* the maximum adiabatic temperature found under the assumption of complete combustion.

When dissociation takes place, the gaseous products exiting the reactor would not be CO₂ and N₂, but a mixture of CO₂, CO, O₂, and N₂. The balanced chemical reaction equation would read

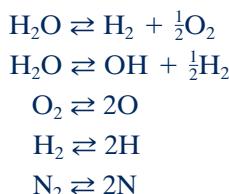


where z is the amount of CO, in kmol, present in the exiting mixture for each kmol of CO entering the reactor.

Accordingly, there are *two* unknowns: z and the temperature of the exiting stream. To solve a problem with two unknowns requires two equations. One is provided by an energy equation. If the exiting gas mixture is in equilibrium, the other equation is provided by the equilibrium constant, Eq. 14.35. The temperature of the products may then be called the **equilibrium flame temperature**. The equilibrium constant used to evaluate the equilibrium flame temperature would be determined with respect to $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$.

equilibrium flame temperature

Although only the dissociation of CO₂ has been discussed, other products of combustion may dissociate, for example



When there are many dissociation reactions, the study of chemical equilibrium is facilitated by the use of computers to solve the *simultaneous* equations that result.

Simultaneous reactions are considered in Sec. 14.4.4. The following example illustrates how the equilibrium flame temperature is determined when one dissociation reaction occurs.

EXAMPLE 14.6 ►

Determining the Equilibrium Flame Temperature

Carbon monoxide at 25°C, 1 atm enters a well-insulated reactor and reacts with the theoretical amount of air entering at the same temperature and pressure. An equilibrium mixture of CO₂, CO, O₂, and N₂ exits the reactor at a pressure of 1 atm. For steady-state operation and negligible effects of kinetic and potential energy, determine the composition and temperature of the exiting mixture in K.

SOLUTION

Known: Carbon monoxide at 25°C, 1 atm reacts with the theoretical amount of air at 25°C, 1 atm to form an equilibrium mixture of CO₂, CO, O₂, and N₂ at temperature T and a pressure of 1 atm.

Find: Determine the composition and temperature of the exiting mixture.

Schematic and Given Data:

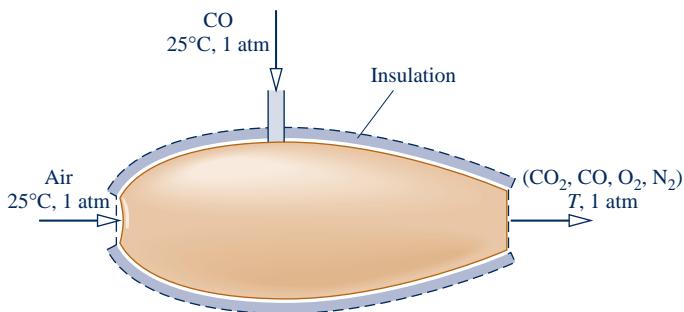
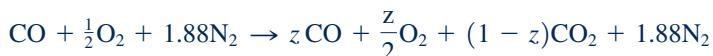


Fig. E14.6

Engineering Model:

- The control volume shown on the accompanying sketch by a dashed line operates at steady state with $\dot{Q}_{cv} = 0$, $\dot{W}_{cv} = 0$, and negligible effects of kinetic and potential energy.
- The entering gases are modeled as ideal gases.
- The exiting mixture is an ideal gas mixture at equilibrium wherein N₂ is inert.

Analysis: The overall reaction is the same as in the solution to Example 14.4



By assumption 3, the exiting mixture is an equilibrium mixture. The equilibrium constant expression developed in the solution to Example 14.4 is

$$K(T) = \frac{z(z/2)^{1/2}}{(1-z)} \left(\frac{p/p_{ref}}{(5.76+z)/2} \right)^{1/2} \quad (\text{a})$$

Since $p = 1$ atm, Eq. (a) reduces to

$$K(T) = \frac{z}{(1-z)} \left(\frac{z}{5.76+z} \right)^{1/2} \quad (\text{b})$$

This equation involves two unknowns: z and the temperature T of the exiting equilibrium mixture.

Another equation involving the two unknowns is obtained from an energy rate balance of the form Eq. 13.12b, which reduces with assumption 1 to

$$\bar{h}_R = \bar{h}_P \quad (\text{c})$$

where

$$\bar{h}_R = (\bar{h}_f + \Delta\bar{h})_{CO} + \frac{1}{2}(\bar{h}_f^0 + \Delta\bar{h})_{O_2} + 1.88(\bar{h}_f^0 + \Delta\bar{h})_{N_2}$$

and

$$\bar{h}_P = z(\bar{h}_f + \Delta\bar{h})_{CO} + \frac{z}{2}(\bar{h}_f^0 + \Delta\bar{h})_{O_2} + (1 - z)(\bar{h}_f + \Delta\bar{h})_{CO_2} + 1.88(\bar{h}_f^0 + \Delta\bar{h})_{N_2}$$

The enthalpy of formation terms set to zero are those for oxygen and nitrogen. Since the reactants enter at 25°C, the corresponding $\Delta\bar{h}$ terms also vanish. Collecting and rearranging, we get

$$\begin{aligned} z(\Delta\bar{h})_{CO} + \frac{z}{2}(\Delta\bar{h})_{O_2} + (1 - z)(\Delta\bar{h})_{CO_2} + 1.88(\Delta\bar{h})_{N_2} \\ + (1 - z)[(\bar{h}_f^0)_{CO_2} - (\bar{h}_f^0)_{CO}] = 0 \end{aligned} \quad (d)$$

Equations (b) and (d) are simultaneous equations involving the unknowns z and T . When solved *iteratively* using *tabular data*, the results are $z = 0.125$ and $T = 2399$ K, as can be verified. The composition of the equilibrium mixture, in kmol per kmol of CO entering the reactor, is then 0.125CO, 0.0625O₂, 0.875CO₂, 1.88N₂.



Skills Developed

Ability to...

- apply Eq. 14.35 together with the energy balance for reacting systems to determine equilibrium flame temperature.
- retrieve and use data from Tables A-23, A-25, and A-27.

QuickQUIZ

If the CO and air each entered at 500°C, would the equilibrium flame temperature increase, decrease, or stay constant? **Ans.** Increase.

As illustrated by Example 14.7, the equation solver and property retrieval features of *Interactive Thermodynamics: IT* allow the equilibrium flame temperature and composition to be determined without the iteration required when using table data.

EXAMPLE 14.7

Determining the Equilibrium Flame Temperature Using Software

Solve Example 14.6 using *Interactive Thermodynamics: IT* and plot equilibrium flame temperature and z , the amount of CO present in the exiting mixture, each versus pressure ranging from 1 to 10 atm.

SOLUTION

Known: See Example 14.6.

Find: Using *IT*, plot the equilibrium flame temperature and the amount of CO present in the exiting mixture of Example 14.6, each versus pressure ranging from 1 to 10 atm.

Engineering Model: See Example 14.6.

Analysis: Equation (a) of Example 14.6 provides the point of departure for the *IT* solution

$$K(T) = \frac{z(z/2)^{1/2}}{(1 - z)} \left[\frac{p/p_{ref}}{(5.76 + z)/2} \right]^{1/2} \quad (a)$$

For a given pressure, this expression involves two unknowns: z and T .

Also, from Example 14.6, we use the energy balance, Eq. (c)

$$\bar{h}_R = \bar{h}_P \quad (c)$$

where

$$\bar{h}_R = (\bar{h}_{CO})_R + \frac{1}{2}(\bar{h}_{O_2})_R + 1.88(\bar{h}_{N_2})_R$$

and

$$\bar{h}_P = z(\bar{h}_{CO})_P + (z/2)(\bar{h}_{O_2})_P + (1 - z)(\bar{h}_{CO_2})_P + 1.88(\bar{h}_{N_2})_P$$

where the subscripts R and P denote reactants and products, respectively, and z denotes the amount of CO in the products, in kmol per kmol of CO entering.

With pressure known, Eqs. (a) and (c) can be solved for T and z using the following IT code. Choosing SI from the **Units** menu and amount of substance in moles, and letting hCO_R denote the specific enthalpy of CO in the reactants, and so on, we have

```
// Given data
TR = 25 + 273.15 // K
p = 1 // atm
pref = 1 // atm

// Evaluating the equilibrium constant using Eq. (a)
K = ((z * (z/2)^0.5) / (1 - z)) * ((p / pref) / ((5.76 + z) / 2))^0.5

// Energy balance: Eq. (c)
hR = hP
hR = hCO_R + (1/2) * hO2_R + 1.88 * hN2_R
hP = z * hCO_P + (z / 2) * hO2_P + (1 - z) * hCO2_P + 1.88 * hN2_P

hCO_R = h_T("CO",TR)
hO2_R = h_T("O2",TR)
hN2_R = h_T("N2",TR)

hCO_P = h_T("CO",T)
hO2_P = h_T("O2",T)
hCO2_P = h_T("CO2",T)
hN2_P = h_T("N2",T)

/* To obtain data for the equilibrium constant use the Look-up Table
option under the Edit menu. Load the file "eqco2.lut". Data for
①  $CO_2 \rightleftharpoons CO + 1/2 O_2$  from Table A-27 are stored in the look-up table
as T in column 1 and  $\log_{10}(K)$  in column 2. To retrieve the data use */
log(K) = lookupvall(eqco2, 1, T,2)
```

Obtain a solution for $p = 1$ using the **Solve** button. To ensure rapid convergence, restrict T and K to positive values, and set a lower limit of 0.001 and an upper limit of 0.999 for z . The results are $T = 2399$ K and $z = 0.1249$, which agree with the values obtained in Example 14.6.

Now, use the **Explore** button and sweep p from 1 to 10 atm in steps of 0.01. Using the **Graph** button, construct the following plots:

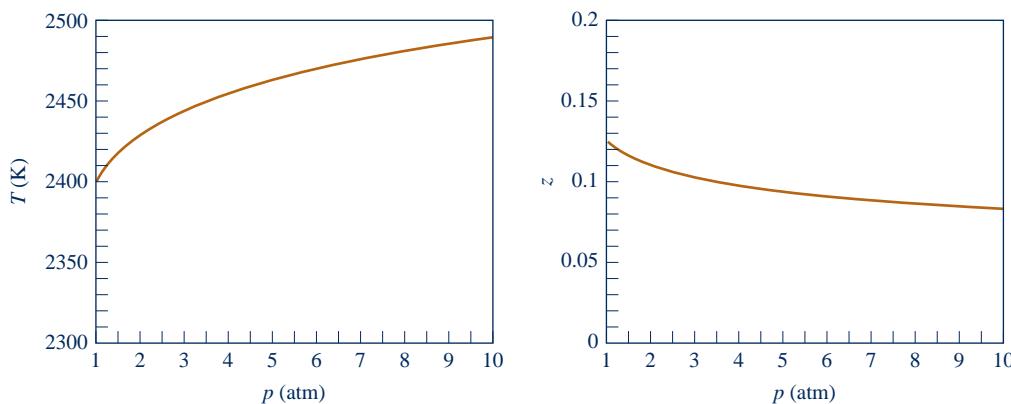


Fig. E14.7

- From Fig. E14.7, we see that as pressure increases more CO is oxidized to CO₂ (z decreases) and temperature increases.

- Similar files are included in *IT* for each of the reactions in Table A-27.

QuickQUIZ

If the CO and air each entered at 500°C, determine the equilibrium flame temperature in K using *Interactive Thermodynamics: IT*.

Ans. 2575.

**Skills Developed****Ability to...**

- apply Eq. 14.35 together with the energy balance for reacting systems to determine equilibrium flame temperature.
- perform equilibrium calculations using *Interactive Thermodynamics: IT*.

14.4.2 Van't Hoff Equation

The dependence of the equilibrium constant on temperature exhibited by the values of Table A-27 follows from Eq. 14.31. An alternative way to express this dependence is given by the van't Hoff equation, Eq. 14.43b.

The development of this equation begins by introducing Eq. 14.29b into Eq. 14.31 to obtain on rearrangement

$$\bar{R}T \ln K = -[(\nu_C \bar{h}_C + \nu_D \bar{h}_D - \nu_A \bar{h}_A - \nu_B \bar{h}_B) - T(\nu_C \bar{s}_C^\circ + \nu_D \bar{s}_D^\circ - \nu_A \bar{s}_A^\circ - \nu_B \bar{s}_B^\circ)] \quad (14.41)$$

Each of the specific enthalpies and entropies in this equation depends on temperature alone. Differentiating with respect to temperature

$$\begin{aligned} \bar{R}T \frac{d \ln K}{dT} + \bar{R} \ln K = & - \left[\nu_C \left(\frac{d \bar{h}_C}{dT} - T \frac{d \bar{s}_C^\circ}{dT} \right) + \nu_D \left(\frac{d \bar{h}_D}{dT} - T \frac{d \bar{s}_D^\circ}{dT} \right) \right. \\ & - \left. \nu_A \left(\frac{d \bar{h}_A}{dT} - T \frac{d \bar{s}_A^\circ}{dT} \right) - \nu_B \left(\frac{d \bar{h}_B}{dT} - T \frac{d \bar{s}_B^\circ}{dT} \right) \right] \\ & + (\nu_C \bar{s}_C^\circ + \nu_D \bar{s}_D^\circ - \nu_A \bar{s}_A^\circ - \nu_B \bar{s}_B^\circ) \end{aligned}$$

From the definition of $\bar{s}^\circ(T)$ (Eq. 6.19), we have $d\bar{s}^\circ/dT = \bar{c}_p/T$. Moreover, $d\bar{h}/dT = \bar{c}_p$. Accordingly, each of the underlined terms in the above equation vanishes identically, leaving

$$\bar{R}T \frac{d \ln K}{dT} + \bar{R} \ln K = (\nu_C \bar{s}_C^\circ + \nu_D \bar{s}_D^\circ - \nu_A \bar{s}_A^\circ - \nu_B \bar{s}_B^\circ) \quad (14.42)$$

Using Eq. 14.41 to evaluate the second term on the left and simplifying the resulting expression, Eq. 14.42 becomes

$$\frac{d \ln K}{dT} = \frac{(\nu_C \bar{h}_C + \nu_D \bar{h}_D - \nu_A \bar{h}_A - \nu_B \bar{h}_B)}{\bar{R}T^2} \quad (14.43a)$$

or, expressed more concisely

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (14.43b) \quad \text{van't Hoff equation}$$

which is the **van't Hoff equation**.

In Eq. 14.43b, ΔH is the *enthalpy of reaction* at temperature T . The van't Hoff equation shows that when ΔH is negative (exothermic reaction), K decreases with temperature, whereas for ΔH positive (endothermic reaction), K increases with temperature.

The enthalpy of reaction ΔH is often very nearly constant over a rather wide interval of temperature. In such cases, Eq. 14.43b can be integrated to yield

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (14.44)$$

where K_1 and K_2 denote the equilibrium constants at temperatures T_1 and T_2 , respectively. This equation shows that $\ln K$ is linear in $1/T$. Accordingly, plots of $\ln K$ versus $1/T$ can be used to determine ΔH from experimental equilibrium composition data. Alternatively, the equilibrium constant can be determined using enthalpy data.

14.4.3 Ionization

The methods developed for determining the equilibrium composition of a reactive ideal gas mixture can be applied to systems involving ionized gases, also known as *plasmas*. In previous sections we considered the chemical equilibrium of systems where dissociation is a factor. For example, the dissociation reaction of diatomic nitrogen



can occur at elevated temperatures. At still higher temperatures, ionization may take place according to



That is, a nitrogen atom loses an electron, yielding a singly ionized nitrogen atom N^+ and a free electron e^- . Further heating can result in the loss of additional electrons until all electrons have been removed from the atom.

For some cases of practical interest, it is reasonable to think of the neutral atoms, positive ions, and electrons as forming an ideal gas mixture. With this idealization, ionization equilibrium can be treated in the same manner as the chemical equilibrium of reacting ideal gas mixtures. The change in the Gibbs function for the equilibrium ionization reaction required to evaluate the ionization-equilibrium constant can be calculated as a function of temperature by using the procedures of statistical thermodynamics. In general, the extent of ionization increases as the temperature is raised and the pressure is lowered.

Example 14.8 illustrates the analysis of ionization equilibrium.

EXAMPLE 14.8

Considering Ionization Equilibrium

Consider an equilibrium mixture at 3600°R consisting of Cs , Cs^+ , and e^- , where Cs denotes neutral cesium atoms, Cs^+ singly ionized cesium ions, and e^- free electrons. The ionization-equilibrium constant at this temperature for



is $K = 15.63$. Determine the pressure, in atmospheres, if the ionization of Cs is 95% complete, and plot percent completion of ionization versus pressure ranging from 0 to 10 atm.

SOLUTION

Known: An equilibrium mixture of Cs , Cs^+ , e^- is at 3600°R. The value of the equilibrium constant at this temperature is known.

Find: Determine the pressure of the mixture if the ionization of Cs is 95% complete. Plot percent completion versus pressure.

Engineering Model: Equilibrium can be treated in this case using ideal gas mixture equilibrium considerations.

Analysis: The ionization of cesium to form a mixture of Cs, Cs⁺, and e⁻ is described by



where z denotes the extent of ionization, ranging from 0 to 1. The total number of moles of mixture n is

$$n = (1 - z) + z + z = 1 + z$$

At equilibrium, we have $\text{Cs} \rightleftharpoons \text{Cs}^+ + e^-$, so Eq. 14.35 takes the form

$$K = \frac{(z)(z)}{(1 - z)} \left[\frac{p/p_{\text{ref}}}{(1 + z)} \right]^{1+1-1} = \left(\frac{z^2}{1 - z^2} \right) \left(\frac{p}{p_{\text{ref}}} \right) \quad (\text{a})$$

Solving for the ratio p/p_{ref} and introducing the known value of K

$$\frac{p}{p_{\text{ref}}} = (15.63) \left(\frac{1 - z^2}{z^2} \right)$$

For $p_{\text{ref}} = 1 \text{ atm}$ and $z = 0.95$ (95%), $p = 1.69 \text{ atm}$. Using an equation-solver and plotting package, the following plot can be constructed:

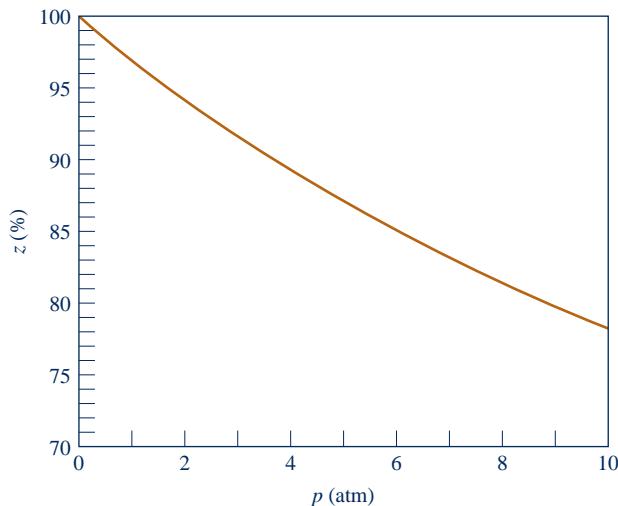


Fig. E14.8



Skills Developed

Ability to...

- apply Eq. 14.35 to determine the extent of ionization of cesium given temperature and pressure.

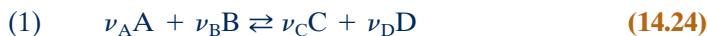
QuickQUIZ

Solving Eq. (a) for z , determine the percent of ionization of

Cs at $T = 2880^\circ\text{R}$ ($K = 0.78$) and $p = 1 \text{ atm}$. **Ans.** 66.2%.

14.4.4 • Simultaneous Reactions

Let us return to the discussion of Sec. 14.2 and consider the possibility of more than one reaction among the substances present within a system. For the present application, the closed system is assumed to contain a mixture of *eight* components A, B, C, D, E, L, M, and N, subject to *two* independent reactions



As in Sec. 14.2, component E is inert. Also, note that component A has been taken as common to both reactions but with a possibly different stoichiometric coefficient ($\nu_{A'}$ is not necessarily equal to ν_A).

The stoichiometric coefficients of the above equations do not correspond to the numbers of moles of the respective components present within the system, but *changes* in the amounts of the components are related to the stoichiometric coefficients by

$$\frac{-dn_A}{\nu_A} = \frac{-dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} \quad (14.25a)$$

following from Eq. 14.24, and

$$\frac{-dn_A}{\nu_{A'}} = \frac{-dn_L}{\nu_L} = \frac{dn_M}{\nu_M} = \frac{dn_N}{\nu_N} \quad (14.47a)$$

following from Eq. 14.46. Introducing a proportionality factor $d\varepsilon_1$, Eqs. 14.25a may be represented by

$$\begin{aligned} dn_A &= -\nu_A d\varepsilon_1, & dn_B &= -\nu_B d\varepsilon_1 \\ dn_C &= \nu_C d\varepsilon_1, & dn_D &= \nu_D d\varepsilon_1 \end{aligned} \quad (14.25b)$$

Similarly, with the proportionality factor $d\varepsilon_2$, Eqs. 14.47a may be represented by

$$\begin{aligned} dn_A &= -\nu_{A'} d\varepsilon_2, & dn_L &= -\nu_L d\varepsilon_2 \\ dn_M &= \nu_M d\varepsilon_2, & dn_N &= \nu_N d\varepsilon_2 \end{aligned} \quad (14.47b)$$

Component A is involved in both reactions, so the total change in A is given by

$$dn_A = -\nu_A d\varepsilon_1 - \nu_{A'} d\varepsilon_2 \quad (14.48)$$

Also, we have $dn_E = 0$ because component E is inert.

For the system under present consideration, Eq. 14.10 is

$$\begin{aligned} dG]_{T,p} &= \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D \\ &\quad + \mu_E dn_E + \mu_L dn_L + \mu_M dn_M + \mu_N dn_N \end{aligned} \quad (14.49)$$

Introducing the above expressions giving the changes in the n 's, this becomes

$$\begin{aligned} dG]_{T,p} &= (-\nu_A \mu_A - \nu_B \mu_B + \nu_C \mu_C + \nu_D \mu_D) d\varepsilon_1 \\ &\quad + (-\nu_{A'} \mu_A - \nu_L \mu_L + \nu_M \mu_M + \nu_N \mu_N) d\varepsilon_2 \end{aligned} \quad (14.50)$$

Since the two reactions are independent, $d\varepsilon_1$ and $d\varepsilon_2$ can be independently varied. Accordingly, when $dG]_{T,p} = 0$, the terms in parentheses must be zero and *two* equations of reaction equilibrium result, one corresponding to each of the foregoing reactions:

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \quad (14.26b)$$

$$\nu_{A'} \mu_A + \nu_L \mu_L = \nu_M \mu_M + \nu_N \mu_N \quad (14.51)$$

The first of these equations is exactly the same as that obtained in Sec. 14.2. For the case of reacting ideal gas mixtures, this equation can be expressed as

$$-\left(\frac{\Delta G^\circ}{RT}\right)_1 = \ln \left[\frac{y_C^{\nu_C} y_D^{\nu_D}}{y_{A'}^{\nu_{A'}} y_B^{\nu_B}} \left(\frac{p}{p_{ref}} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \right] \quad (14.52)$$

Similarly, Eq. 14.51 can be expressed as

$$-\left(\frac{\Delta G^\circ}{RT}\right)_2 = \ln \left[\frac{y_M^{\nu_M} y_N^{\nu_N}}{y_{A'}^{\nu_{A'}} y_L^{\nu_L}} \left(\frac{p}{p_{ref}} \right)^{\nu_M + \nu_N - \nu_{A'} - \nu_L} \right] \quad (14.53)$$

In each of these equations, the ΔG° term is evaluated as the change in Gibbs function for the respective reaction, regarding each reactant and product as separate at temperature T and a pressure of 1 atm.

From Eq. 14.52 follows the equilibrium constant

$$K_1 = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_{A'}^{\nu_{A'}} y_B^{\nu_B}} \left(\frac{p}{p_{ref}} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \quad (14.54)$$

and from Eq. 14.53 follows

$$K_2 = \frac{y_M^{v_M} y_N^{v_N}}{y_A^{v_A} y_L^{v_L}} \left(\frac{p}{P_{\text{ref}}} \right)^{v_M + v_N - v_A - v_L} \quad (14.55)$$

The equilibrium constants K_1 and K_2 can be determined from Table A-27 or a similar compilation. The mole fractions appearing in these expressions must be evaluated by considering *all* the substances present within the system, including the inert substance E. Each mole fraction has the form $y_i = n_i/n$, where n_i is the amount of component i in the equilibrium mixture and

$$n = n_A + n_B + n_C + n_D + n_E + n_L + n_M + n_N \quad (14.56)$$

The n 's appearing in Eq. 14.56 can be expressed in terms of *two* unknown variables through application of the conservation of mass principle to the various chemical species present. Accordingly, for a specified temperature and pressure, Eqs. 14.54 and 14.55 give *two* equations in *two* unknowns. The composition of the system at equilibrium can be determined by solving these equations simultaneously. This procedure is illustrated by Example 14.9.

The procedure discussed in this section can be extended to systems involving several simultaneous independent reactions. The number of simultaneous equilibrium constant expressions that results equals the number of independent reactions. As these equations are nonlinear and require simultaneous solution, the use of a computer is usually required.

►►►► EXAMPLE 14.9 ►.....

Considering Equilibrium with Simultaneous Reactions

As a result of heating, a system consisting initially of 1 kmol of CO_2 , $\frac{1}{2}$ kmol of O_2 , and $\frac{1}{2}$ kmol of N_2 forms an equilibrium mixture of CO_2 , CO , O_2 , N_2 , and NO at 3000 K, 1 atm. Determine the composition of the equilibrium mixture.

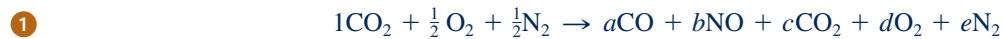
SOLUTION

Known: A system consisting of specified amounts of CO_2 , O_2 , and N_2 is heated to 3000 K, 1 atm, forming an equilibrium mixture of CO_2 , CO , O_2 , N_2 , and NO .

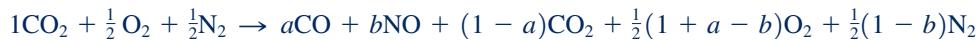
Find: Determine the equilibrium composition.

Engineering Model: The final mixture is an equilibrium mixture of ideal gases.

Analysis: The overall reaction has the form



Applying conservation of mass to carbon, oxygen, and nitrogen, the five unknown coefficients can be expressed in terms of any two of the coefficients. Selecting a and b as the unknowns, the following balanced equation results:



The total number of moles n in the mixture formed by the products is

$$n = a + b + (1-a) + \frac{1}{2}(1+a-b) + \frac{1}{2}(1-b) = \frac{4+a}{2}$$

At equilibrium, two independent reactions relate the components of the product mixture:



For the first of these reactions, the form taken by the equilibrium constant when $p = 1 \text{ atm}$ is

$$K_1 = \frac{a[\frac{1}{2}(1+a-b)]^{1/2}}{(1-a)} \left[\frac{1}{(4+a)/2} \right]^{1+1/2-1} = \frac{a}{1-a} \left(\frac{1+a-b}{4+a} \right)^{1/2}$$

Similarly, the equilibrium constant for the second of the reactions is

$$K_2 = \frac{b}{[\frac{1}{2}(1+a-b)]^{1/2} [\frac{1}{2}(1-b)]^{1/2}} \left[\frac{1}{(4+a)/2} \right]^{1-1/2-1/2} = \frac{2b}{[(1+a-b)(1-b)]^{1/2}}$$

At 3000 K, Table A-27 provides $\log_{10} K_1 = -0.485$ and $\log_{10} K_2 = -0.913$, giving $K_1 = 0.3273$ and $K_2 = 0.1222$. Accordingly, the two equations that must be solved simultaneously for the two unknowns a and b are

$$0.3273 = \frac{a}{1-a} \left(\frac{1+a-b}{4+a} \right)^{1/2}, \quad 0.1222 = \frac{2b}{[(1+a-b)(1-b)]^{1/2}}$$

The solution is $a = 0.3745$, $b = 0.0675$, as can be verified. The composition of the equilibrium mixture, in kmol per kmol of CO_2 present initially, is then 0.3745CO, 0.0675NO, 0.6255 CO_2 , 0.6535O₂, 0.4663N₂.

- ① If high enough temperatures are attained, nitrogen can combine with oxygen to form components such as nitric oxide. Even trace amounts of oxides of nitrogen in products of combustion can be a source of air pollution.

Skills Developed

Ability to...

- apply Eq. 14.35 to determine equilibrium composition given temperature and pressure for two simultaneous equilibrium reactions.
- retrieve and use data from Table A-27.

QuickQUIZ

Determine the mole fractions of the components of the equilibrium mixture. Ans. $y_{\text{CO}} = 0.171$, $y_{\text{NO}} = 0.031$, $y_{\text{CO}_2} = 0.286$, $y_{\text{O}_2} = 0.299$, $y_{\text{N}_2} = 0.213$.

Phase Equilibrium

In this part of the chapter the equilibrium condition $dG]_{T,p} = 0$ introduced in Sec. 14.1 is used to study the equilibrium of multicomponent, multiphase, nonreacting systems. The discussion begins with the elementary case of equilibrium between two phases of a pure substance and then turns to the general case of several components present in several phases.

14.5

Equilibrium between Two Phases of a Pure Substance

Consider the case of a system consisting of two phases of a pure substance at equilibrium. Since the system is at equilibrium, each phase is at the same temperature and pressure. The Gibbs function for the system is

$$G = n' \bar{g}'(T, p) + n'' \bar{g}''(T, p) \quad (14.57)$$

where the primes ' and " denote phases 1 and 2, respectively.

Forming the differential of G at fixed T and p

$$dG]_{T,p} = \bar{g}' dn' + \bar{g}'' dn'' \quad (14.58)$$

Since the total amount of the pure substance remains constant, an increase in the amount present in one of the phases must be compensated by an equivalent decrease

in the amount present in the other phase. Thus, we have $d\bar{n}'' = -d\bar{n}'$, and Eq. 14.58 becomes

$$dG]_{T,p} = (\bar{g}' - \bar{g}'') d\bar{n}'$$

At equilibrium, $dG]_{T,p} = 0$, so

$$\bar{g}' = \bar{g}'' \quad (14.59)$$

At equilibrium, the molar Gibbs functions of the phases are equal.

CLAPEYRON EQUATION. Equation 14.59 can be used to derive the *Clapeyron* equation, obtained by other means in Sec. 11.4. For two phases at equilibrium, variations in pressure are uniquely related to variations in temperature: $p = p_{\text{sat}}(T)$; thus, differentiation of Eq. 14.59 with respect to temperature gives

$$\left. \frac{\partial \bar{g}'}{\partial T} \right)_p + \left. \frac{\partial \bar{g}'}{\partial p} \right)_T \frac{dp_{\text{sat}}}{dT} = \left. \frac{\partial \bar{g}''}{\partial T} \right)_p + \left. \frac{\partial \bar{g}''}{\partial p} \right)_T \frac{dp_{\text{sat}}}{dT}$$

With Eqs. 11.30 and 11.31, this becomes

$$-\bar{s}' + \bar{v}' \frac{dp_{\text{sat}}}{dT} = -\bar{s}'' + \bar{v}'' \frac{dp_{\text{sat}}}{dT}$$

Or on rearrangement

$$\frac{dp_{\text{sat}}}{dT} = \frac{\bar{s}'' - \bar{s}'}{\bar{v}'' - \bar{v}'}$$

This can be expressed alternatively by noting that, with $\bar{g} = \bar{h} - T\bar{s}$, Eq. 14.59 becomes

$$\bar{h}' - T\bar{s}' = \bar{h}'' - T\bar{s}''$$

or

$$\bar{s}'' - \bar{s}' = \frac{\bar{h}'' - \bar{h}'}{T} \quad (14.60)$$

Combining results, the **Clapeyron equation** is obtained

Clapeyron equation

$$\frac{dp_{\text{sat}}}{dT} = \frac{1}{T} \left(\frac{\bar{h}'' - \bar{h}'}{\bar{v}'' - \bar{v}'} \right) \quad (14.61)$$

An application of the Clapeyron equation is provided in Example 11.4.

A special form of Eq. 14.61 for a system at equilibrium consisting of a liquid or solid phase and a vapor phase can be obtained simply. If the specific volume of the liquid or solid, \bar{v}' , is negligible compared with the specific volume of the vapor, \bar{v}'' , and the vapor can be treated as an ideal gas, $\bar{v}'' = \bar{R}T/p_{\text{sat}}$, Eq. 14.61 becomes

$$\frac{dp_{\text{sat}}}{dT} = \frac{\bar{h}'' - \bar{h}'}{\bar{R}T^2/p_{\text{sat}}}$$

or

$$\frac{d \ln p_{\text{sat}}}{dT} = \frac{\bar{h}'' - \bar{h}'}{\bar{R}T^2} \quad (14.62)$$

Clausius–Clapeyron equation

which is the **Clausius–Clapeyron equation**. The similarity in form of Eq. 14.62 and the van't Hoff equation, Eq. 14.43b, may be noted. The van't Hoff equation for chemical equilibrium is the counterpart of the Clausius–Clapeyron equation for phase equilibrium.

TAKE NOTE...

Equations 11.40 and 11.42 are special cases of Eqs. 14.61 and 14.62, respectively.

14.6

Equilibrium of Multicomponent, Multiphase Systems

The equilibrium of systems that may involve several phases, each having a number of components present, is considered in this section. The principal result is the Gibbs phase rule, which summarizes important limitations on multicomponent, multiphase systems at equilibrium.

14.6.1 Chemical Potential and Phase Equilibrium

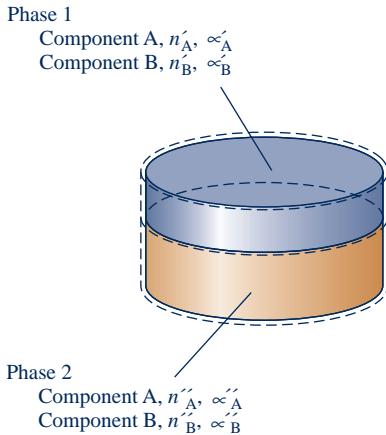


Fig. 14.1 System consisting of two components in two phases.

Figure 14.1 shows a system consisting of *two* components A and B in *two* phases 1 and 2 that are at the same temperature and pressure. Applying Eq. 14.10 to each of the phases

$$\begin{aligned} dG']_{T,p} &= \mu'_A dn'_A + \mu'_B dn'_B \\ dG'']_{T,p} &= \mu''_A dn''_A + \mu''_B dn''_B \end{aligned} \quad (14.63)$$

where as before the primes identify the two phases.

When matter is transferred between the two phases in the absence of chemical reaction, the total amounts of A and B must remain constant. Thus, the increase in the amount present in one of the phases must be compensated by an equivalent decrease in the amount present in the other phase. That is

$$dn'_A = -dn''_A, \quad dn''_B = -dn'_B \quad (14.64)$$

With Eqs. 14.63 and 14.64, the change in the Gibbs function for the system is

$$\begin{aligned} dG]_{T,p} &= dG']_{T,p} + dG'']_{T,p} \\ &= (\mu'_A - \mu''_A) dn'_A + (\mu'_B - \mu''_B) dn''_B \end{aligned} \quad (14.65)$$

Since n'_A and n''_B can be varied independently, it follows that when $dG]_{T,p} = 0$, the terms in parentheses are zero, resulting in

$$\mu'_A = \mu''_A \quad \text{and} \quad \mu'_B = \mu''_B \quad (14.66)$$

At equilibrium, the chemical potential of each component is the same in each phase.

The significance of the chemical potential for phase equilibrium can be brought out simply by reconsidering the system of Fig. 14.1 in the special case when the chemical potential of component B is the same in both phases: $\mu'_B = \mu''_B$. With this constraint, Eq. 14.65 reduces to

$$dG]_{T,p} = (\mu'_A - \mu''_A) dn'_A$$

Any spontaneous process of the system taking place at a fixed temperature and pressure must be such that the Gibbs function decreases: $dG]_{T,p} < 0$. Thus, with the above expression we have

$$(\mu'_A - \mu''_A) dn'_A < 0$$

Accordingly,

- when the chemical potential of A is greater in phase 1 than in phase 2 ($\mu'_A > \mu''_A$), it follows that $dn'_A < 0$. That is, substance A passes from phase 1 to phase 2.
- when the chemical potential of A is greater in phase 2 than in phase 1 ($\mu''_A > \mu'_A$), it follows that $dn'_A > 0$. That is, substance A passes from phase 2 to phase 1.

At equilibrium, the chemical potentials are equal ($\mu'_A = \mu''_A$), and there is no net transfer of A between the phases.

With this reasoning, we see that the chemical potential can be regarded as a measure of the *escaping tendency* of a component. If the chemical potential of a component is not the same in each phase, there will be a tendency for that component to pass from the

phase having the higher chemical potential for that component to the phase having the lower chemical potential. When the chemical potential is the same in both phases, there is no tendency for a net transfer to occur from one phase to the other.

In Example 14.10, we apply phase equilibrium principles to provide a rationale for the model introduced in Sec. 12.5.3 for moist air in contact with liquid water.

EXAMPLE 14.10

Evaluating Equilibrium of Moist Air in Contact with Liquid Water

A closed system at a temperature of 70°F and a pressure of 1 atm consists of a pure liquid water phase in equilibrium with a vapor phase composed of water vapor and dry air. Determine the departure, in percent, of the partial pressure of the water vapor from the saturation pressure of water at 70°F.

SOLUTION

Known: A phase of liquid water only is in equilibrium with *moist air* at 70°F and 1 atm.

Find: Determine the percentage departure of the partial pressure of the water vapor in the moist air from the saturation pressure of water at 70°F.

Schematic and Given Data:

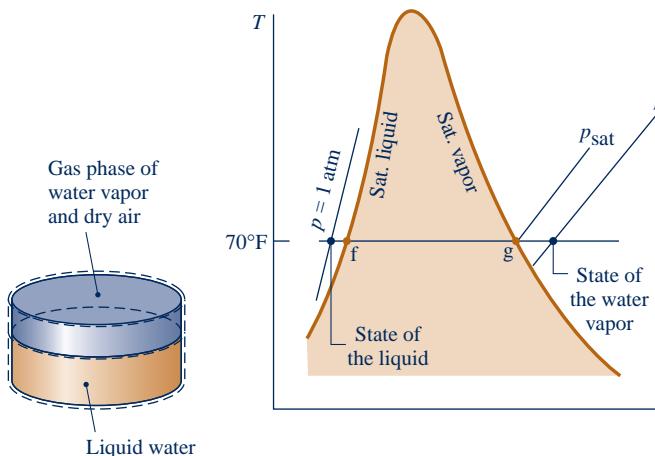


Fig. E14.10

Analysis: For phase equilibrium, the chemical potential of the water must have the same value in both phases: $\mu_1 = \mu_v$, where μ_1 and μ_v denote, respectively, the chemical potentials of the pure liquid water in the liquid phase and the water vapor in the vapor phase.

The chemical potential μ_1 is the Gibbs function per mole of pure liquid water (Eq. 14.12)

$$\mu_1 = \bar{g}(T, p)$$

Since the vapor phase is assumed to form an ideal gas mixture, the chemical potential μ_v equals the Gibbs function per mole evaluated at temperature T and the partial pressure p_v of the water vapor (Eq. 14.16)

$$\mu_v = \bar{g}(T, p_v)$$

For phase equilibrium, $\mu_1 = \mu_v$, or

$$\bar{g}(T, p_v) = \bar{g}(T, p)$$

With $\bar{g} = \bar{h} - T\bar{s}$, this can be expressed alternatively as

$$\bar{h}(T, p_v) - T\bar{s}(T, p_v) = \bar{h}(T, p) - T\bar{s}(T, p)$$

The water vapor is modeled as an ideal gas. Thus, the enthalpy is given closely by the saturated vapor value at temperature T

$$\bar{h}(T, p_v) \approx \bar{h}_g$$

Engineering Model:

1. The gas phase can be modeled as an ideal gas mixture.
2. The liquid phase is pure water only.

- Furthermore, the relationship between the specific entropy of the water vapor and the specific entropy at the corresponding saturated vapor state is

$$\bar{s}(T, p_v) = \bar{s}_g(T) - \bar{R} \ln \frac{p_v}{p_{\text{sat}}}$$

where p_{sat} is the saturation pressure at temperature T (see Sec. 12.5.2 for discussion).

With Eq. 3.13, the enthalpy of the liquid is closely

$$\bar{h}(T, p) \approx \bar{h}_f + \bar{v}_f(p - p_{\text{sat}})$$

where \bar{v}_f and \bar{h}_f are the saturated liquid specific volume and enthalpy at temperature T . Furthermore, with Eq. 6.5

$$\bar{s}(T, p) \approx \bar{s}_f(T)$$

where \bar{s}_f is the saturated liquid specific entropy at temperature T .

Collecting the foregoing expressions, we have

$$\bar{h}_g - T \left(\bar{s}_g - \bar{R} \ln \frac{p_v}{p_{\text{sat}}} \right) = \bar{h}_f + \bar{v}_f(p - p_{\text{sat}}) - T \bar{s}_f$$

or

$$\bar{R} T \ln \frac{p_v}{p_{\text{sat}}} = \bar{v}_f(p - p_{\text{sat}}) - [(h_g - h_f) - T(s_g - s_f)]$$

The underlined term vanishes by Eq. 14.60, leaving

$$\ln \frac{p_v}{p_{\text{sat}}} = \frac{\bar{v}_f(p - p_{\text{sat}})}{\bar{R} T} \quad \text{or} \quad \frac{p_v}{p_{\text{sat}}} = \exp \frac{\bar{v}_f(p - p_{\text{sat}})}{\bar{R} T}$$

With data from Table A-2E at 70°F, $v_f = 0.01605 \text{ ft}^3/\text{lb}$ and $p_{\text{sat}} = 0.3632 \text{ lbf/in.}^2$, we have on a mass basis

$$\begin{aligned} \frac{v_f(p - p_{\text{sat}})}{RT} &= \frac{0.01605 \text{ ft}^3/\text{lb}(14.696 - 0.3632)(\text{lbf/in.}^2)|144 \text{ in.}^2/\text{ft}^2|}{\left(\frac{1545}{18.02} \frac{\text{ft} \cdot \text{lbf}}{\text{lb} \cdot {}^\circ\text{R}}\right)(530^\circ\text{R})} \\ &= 7.29 \times 10^{-4} \end{aligned}$$

Finally

$$\frac{p_v}{p_{\text{sat}}} = \exp(7.29 \times 10^{-4}) = 1.00073$$

When expressed as a percentage, the departure of p_v from p_{sat} is

$$\textcircled{2} \quad \left(\frac{p_v - p_{\text{sat}}}{p_{\text{sat}}} \right)(100) = (1.00073 - 1)(100) = 0.073\%$$

- For phase equilibrium, there would be a small, but finite, concentration of air in the liquid water phase. However, this small amount of dissolved air is ignored in the present development.
- The departure of p_v from p_{sat} is negligible at the specified conditions. This suggests that at normal temperatures and pressures the equilibrium between the liquid water phase and the water vapor is not significantly disturbed by the presence of the dry air. Accordingly, the partial pressure of the water vapor can be taken as equal to the saturation pressure of the water at the system temperature. This model, introduced in Sec. 12.5.3, is used extensively in Chap. 12.

Skills Developed

Ability to...

- apply the concept of phase equilibrium expressed by Eqs. 14.66 to an air-water vapor mixture in equilibrium with liquid water.

QuickQUIZ

Using the methods of Sec. 12.5.2, determine the humidity ratio, ω , of the air–water vapor mixture. Ans. 0.01577 lb(vapor)/lb(dry air).

14.6.2 Gibbs Phase Rule

The requirement for equilibrium of a system consisting of two components and two phases, given by Eqs. 14.66, can be extended with similar reasoning to nonreacting multicomponent, multiphase systems. At equilibrium, the chemical potential of each component must be the same in all phases. For the case of N components that are present in P phases we have, therefore, the following set of $N(P - 1)$ equations:

$$N \left\{ \underbrace{\mu_1^1 = \mu_1^2 = \mu_1^3 = \cdots = \mu_1^P}_{\vdots} \right. \\ \left. \begin{array}{l} \mu_2^1 = \mu_2^2 = \mu_2^3 = \cdots = \mu_2^P \\ \vdots \\ \mu_N^1 = \mu_N^2 = \mu_N^3 = \cdots = \mu_N^P \end{array} \right\}^{P - 1} \quad (14.67)$$

where μ_i^j denotes the chemical potential of the i th component in the j th phase. This set of equations provides the basis for the *Gibbs phase rule*, which allows the determination of the number of *independent intensive* properties that may be arbitrarily specified in order to fix the *intensive* state of the system. The number of independent intensive properties is called the **degrees of freedom** (or the *variance*).

degrees of freedom

Since the chemical potential is an intensive property, its value depends on the relative proportions of the components present and not on the amounts of the components. In other words, in a given phase involving N components at temperature T and pressure p , the chemical potential is determined by the *mole fractions* of the components present and not the respective n 's. However, as the mole fractions add to unity, at most $N - 1$ of the mole fractions can be independent. Thus, for a system involving N components, there are at most $N - 1$ independently variable mole fractions for each phase. For P phases, therefore, there are at most $P(N - 1)$ independently variable mole fractions. In addition, the temperature and pressure, which are the same in each phase, are two further intensive properties, giving a maximum of $P(N - 1) + 2$ independently variable intensive properties for the system. But because of the $N(P - 1)$ equilibrium conditions represented by Eqs. 14.67 among these properties, the number of intensive properties that are freely variable, the degrees of freedom F , is

$$F = [P(N - 1) + 2] - N(P - 1) = 2 + N - P \quad (14.68) \quad \text{Gibbs phase rule}$$

which is the **Gibbs phase rule**.

In Eq. 14.68, F is the number of intensive properties that may be arbitrarily specified and that must be specified to fix the intensive state of a nonreacting system at equilibrium.

► **FOR EXAMPLE** let us apply the Gibbs phase rule to a liquid solution consisting of water and ammonia such as considered in the discussion of absorption refrigeration (Sec. 10.5). This solution involves two components and a single phase: $N = 2$ and $P = 1$. Equation 14.68 then gives $F = 3$, so the intensive state is fixed by giving the values of *three* intensive properties, such as temperature, pressure, and the ammonia (or water) mole fraction. ▲ ▲ ▲ ▲ ▲

The phase rule summarizes important limitations on various types of systems. For example, for a system involving a single component such as water, $N = 1$ and Eq. 14.68 becomes

$$F = 3 - P \quad (14.69)$$

► The minimum number of phases is one, corresponding to $P = 1$. For this case, Eq. 14.69 gives $F = 2$. That is, *two* intensive properties must be specified to fix the intensive

state of the system. This requirement is familiar from our use of the steam tables and similar property tables. To obtain properties of superheated vapor, say, from such tables requires that we give values for *any two* of the tabulated properties, for example, T and p .

- When two phases are present in a system involving a single component, $N = 1$ and $P = 2$. Equation 14.69 then gives $F = 1$. That is, the intensive state is determined by a single intensive property value. For example, the intensive states of the separate phases of an equilibrium mixture of liquid water and water vapor are completely determined by specifying the temperature.
- The minimum allowable value for the degrees of freedom is zero: $F = 0$. For a single-component system, Eq. 14.69 shows that this corresponds to $P = 3$, a three-phase system. Thus, *three* is the maximum number of different phases of a pure component that can coexist in equilibrium. Since there are no degrees of freedom, both temperature and pressure are fixed at equilibrium. For example, there is only a single temperature 0.01°C (32.02°F) and a single pressure 0.6113 kPa (0.006 atm) for which ice, liquid water, and water vapor are in equilibrium.

The phase rule given here must be modified for application to systems in which chemical reactions occur. Furthermore, the system of equations, Eqs. 14.67, giving the requirements for phase equilibrium at a specified temperature and pressure can be expressed alternatively in terms of partial molal Gibbs functions, fugacities, and activities, all of which are introduced in Sec. 11.9. To use any such expression to determine the equilibrium composition of the different phases present within a system at equilibrium requires a model for each phase that allows the relevant quantities—the chemical potentials, fugacities, and so on—to be evaluated for the components present in terms of system properties that can be determined. For example, a gas phase might be modeled as an ideal gas mixture or, at higher pressures, as an ideal solution.

► CHAPTER SUMMARY AND STUDY GUIDE

In this chapter, we have studied chemical equilibrium and phase equilibrium. The chapter opens by developing criteria for equilibrium and introducing the chemical potential. In the second part of the chapter, we study the chemical equilibrium of ideal gas mixtures using the equilibrium constant concept. We also utilize the energy balance and determine the equilibrium flame temperature as an application. The final part of the chapter concerns phase equilibrium, including multicomponent, multiphase systems and the Gibbs phase rule.

The following list provides a study guide for this chapter. When your study of the text and end-of-chapter exercises has been completed, you should be able to

- write out the meaning of the terms listed in the margin throughout the chapter and understand each of the related

concepts. The subset of key concepts listed below is particularly important.

- apply the equilibrium constant relationship, Eq. 14.35, to determine the third quantity when *any two* of temperature, pressure, and equilibrium composition of an ideal gas mixture are known. Special cases include applications with simultaneous reactions and systems involving ionized gases.
- use chemical equilibrium concepts with the energy balance, including determination of the equilibrium flame temperature.
- apply Eq. 14.43b, the van't Hoff equation, to determine the enthalpy of reaction when the equilibrium constant is known, and conversely.
- apply the Gibbs phase rule, Eq. 14.68.

► KEY ENGINEERING CONCEPTS

Gibbs function, p. 849
equilibrium criterion, p. 849
chemical potential, p. 850

equation of reaction equilibrium, p. 855
equilibrium constant, p. 856

equilibrium flame temperature, p. 865
Gibbs phase rule, p. 879

► KEY EQUATIONS

$dG]_{T,p} = 0$	(14.6) p. 849	Equilibrium criterion
$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$	(14.8) p. 850	Chemical potential of component i in a mixture.
$G = \sum_{i=1}^j n_i \bar{g}_i(T, p_i)$ $\mu_i = \bar{g}_i(T, p_i)$ $\mu_i = \bar{g}_i^\circ + RT \ln \frac{y_i p}{p_{\text{ref}}}$	(14.15) p. 851 (14.16) p. 851 (14.17) p. 852	Gibbs function and chemical potential relations for ideal gas mixtures.
$K(T) = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{p}{p_{\text{ref}}} \right)^{\nu_C + \nu_D - \nu_A - \nu_B}$ $K = \frac{n_C^{\nu_C} n_D^{\nu_D}}{n_A^{\nu_A} n_B^{\nu_B}} \left(\frac{p/p_{\text{ref}}}{n} \right)^{\nu_C + \nu_D - \nu_A - \nu_B}$	(14.32) p. 856 (14.35) p. 858	Equilibrium constant expressions for an equilibrium mixture of ideal gases.
$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$	(14.43b) p. 869	van't Hoff equation.
$\bar{g}' = \bar{g}''$ $\mu'_A = \mu''_A \quad \mu'_B = \mu''_B$	(14.59) p. 875 (14.66) p. 876	Phase equilibrium criterion for a pure substance Phase equilibrium criteria for two-component, two-phase systems.
$F = 2 + N - P$	(14.68) p. 879	Gibbs phase rule.

► EXERCISES: THINGS ENGINEERS THINK ABOUT

- Why is using the Gibbs function advantageous when studying chemical and phase equilibrium?
- For Eq. 14.6 to apply at equilibrium, must a system attain equilibrium at fixed T and p ?
- Show that $(dA)_{T,V} = 0$ is a valid equilibrium criterion, where $A = U - TS$ is the *Helmholtz function*.
- A mixture of 1 kmol of CO and $\frac{1}{2}$ kmol of O₂ is held at ambient temperature and pressure. After 100 hours only an insignificant amount of CO₂ has formed. Why?
- Why might oxygen contained in an iron tank be treated as *inert* in a thermodynamic analysis even though iron *oxidizes* in the presence of oxygen?
- For CO₂ + H₂ ⇌ CO + H₂O, how does pressure affect the equilibrium composition?
- For each of the reactions listed in Table A-27, the value of log₁₀ K increases with increasing temperature. What does this imply?
- For each of the reactions listed in Table A-27, the value of the equilibrium constant K at 298 K is relatively small. What does this imply?
- If a system initially containing CO₂ and H₂O were held at fixed T , p , list chemical species that *might* be present at equilibrium.
- Using Eq. 14.12 together with phase equilibrium considerations, suggest how the chemical potential of a mixture component could be evaluated.
- Note 1 of Example 14.10 refers to the small amount of air that would be dissolved in the liquid phase. For equilibrium, what must be true of the chemical potentials of air in the liquid and gas phases?
- Water can exist in a number of different solid phases. Can liquid water, water vapor, and two phases of ice exist in equilibrium?

► PROBLEMS: DEVELOPING ENGINEERING SKILLS

Working with the Equilibrium Constant

14.1 Determine the change in the Gibbs function ΔG° at 25°C in kJ/kmol, for the reaction



using

(a) Gibbs function of formation data.

(b) enthalpy of formation and absolute entropy data.

14.2 Calculate the equilibrium constant, expressed as $\log_{10}K$, for $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ at (a) 500 K, (b) 1800°F. Compare with values from Table A-27.

14.3 Calculate the equilibrium constant, expressed as $\log_{10}K$, for the water-gas shift reaction $\text{CO} + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2 + \text{H}_2$ at (a) 298 K, (b) 1000 K. Compare with values from Table A-27.

14.4 Calculate the equilibrium constant, expressed as $\log_{10}K$, for $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ at (a) 298 K, (b) 3600°F. Compare with values from Table A-27.

14.5 Using data from Table A-27, determine $\log_{10}K$ at 2500 K for

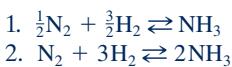
- (a) $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$.
- (b) $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$.
- (c) $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$.



14.6 In Table A-27, $\log_{10}K$ is nearly linear in $1/T$: $\log_{10}K = C_1 + C_2/T$, where C_1 and C_2 are constants. For selected reactions listed in the table

- (a) verify this by plotting $\log_{10}K$ versus $1/T$ for temperature ranging from 2100 to 2500 K.
- (b) evaluate C_1 and C_2 for any pair of adjacent table entries in the temperature range of part (a).

14.7 Determine the relationship between the ideal gas equilibrium constants K_1 and K_2 for the following two alternative ways of expressing the ammonia synthesis reaction:



14.8 Consider the reactions

1. $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$
2. $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$
3. $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$

Show that $K_1 = (K_3/K_2)^{1/2}$.

14.9 Consider the reactions

1. $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$
2. $\text{CO} \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$
3. $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$

(a) Show that $K_1 = K_2/K_3$.

(b) Evaluate $\log_{10}K_1$ at 298 K, 1 atm using the expression from part (a), together with $\log_{10}K$ data from Table A-27.

(c) Check the value for $\log_{10}K_1$ obtained in part (b) by applying Eq. 14.31 to reaction 1.

14.10 Evaluate the equilibrium constant at 2000 K for $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}$. At 2000 K, $\log_{10}K = 7.469$ for $\text{C} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}$, and $\log_{10}K = -3.408$ for $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$.

14.11 For each of the following dissociation reactions, determine the equilibrium compositions:

(a) One kmol of N_2O_4 dissociates to form an equilibrium ideal gas mixture of N_2O_4 and NO_2 at 25°C, 2 atm. For $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, $\Delta G^\circ = 5400 \text{ kJ/kmol}$ at 25°C.

(b) One kmol of CH_4 dissociates to form an equilibrium ideal gas mixture of CH_4 , H_2 , and C at 1000 K, 5 atm. For $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$, $\log_{10}K = 1.011$ at 1000 K.

14.12 Determine the extent to which dissociation occurs in the following cases: One lbmol of H_2O dissociates to form an equilibrium mixture of H_2O , H_2 , and O_2 at 4740°F, 1.25 atm. One lbmol of CO_2 dissociates to form an equilibrium mixture of CO_2 , CO , and O_2 at the same temperature and pressure.

14.13 One lbmol of carbon reacts with 2 lbmol of oxygen (O_2) to form an equilibrium mixture of CO_2 , CO , and O_2 at 4940°F, 1 atm. Determine the equilibrium composition.

14.14 The following exercises involve oxides of nitrogen:



(a) One kmol of N_2O_4 dissociates at 25°C, 1 atm to form an equilibrium ideal gas mixture of N_2O_4 and NO_2 in which the amount of N_2O_4 present is 0.8154 kmol. Determine the amount of N_2O_4 that would be present in an equilibrium mixture at 25°C, 0.5 atm.

(b) A gaseous mixture consisting of 1 kmol of NO , 10 kmol of O_2 , and 40 kmol of N_2 reacts to form an equilibrium ideal gas mixture of NO_2 , NO , and O_2 at 500 K, 0.1 atm. Determine the composition of the equilibrium mixture. For $\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2$, $K = 120$ at 500 K.

(c) An equimolar mixture of O_2 and N_2 reacts to form an equilibrium ideal gas mixture of O_2 , N_2 , and NO . Plot the mole fraction of NO in the equilibrium mixture versus equilibrium temperature ranging from 1200 to 2000 K.

Why are oxides of nitrogen of concern?

14.15 One kmol of CO_2 dissociates to form an equilibrium ideal gas mixture of CO_2 , CO , and O_2 at temperature T and pressure p :



(a) For $T = 3000 \text{ K}$, plot the amount of CO present, in kmol, versus pressure for $1 \leq p \leq 10 \text{ atm}$.

(b) For $p = 1 \text{ atm}$ plot the amount of CO present, in kmol, versus temperature for $2000 \leq T \leq 3500 \text{ K}$.

14.16 One lbmol of H_2O dissociates to form an equilibrium ideal gas mixture of H_2O , H_2 , and O_2 at temperature T and pressure p :



(a) For $T = 5400^\circ\text{R}$, plot the amount of H_2 present, in lbmol, versus pressure ranging from 1 to 10 atm.

(b) For $p = 1 \text{ atm}$, plot the amount of H_2 present, in lbmol, versus temperature ranging from 3600 to 6300°R.

14.17 One lbmol of H_2O together with x lbmol of N_2 (inert) forms an equilibrium mixture at 5400°R, 1 atm consisting of H_2O , H_2 , O_2 , and N_2 . Plot the amount of H_2 present in the equilibrium mixture, in lbmol, versus x ranging from 0 to 2.



14.18 An equimolar mixture of CO and O_2 reacts to form an equilibrium mixture of CO_2 , CO , and O_2 at 3000 K. Determine the effect of pressure on the composition of the



equilibrium mixture. Will lowering the pressure while keeping the temperature fixed increase or decrease the amount of CO_2 present? Explain.

14.19 An equimolar mixture of CO and $\text{H}_2\text{O(g)}$ reacts to form an equilibrium mixture of CO_2 , CO, H_2O , and H_2 at 1727°C , 1 atm.

- (a) Will lowering the temperature increase or decrease the amount of H_2 present? Explain.
- (b) Will decreasing the pressure while keeping the temperature constant increase or decrease the amount of H_2 present? Explain.

14.20 Determine the temperature, in K, at which 9% of diatomic hydrogen (H_2) dissociates into monatomic hydrogen (H) at a pressure of 10 atm. For a greater percentage of H_2 at the same pressure, would the temperature be *higher* or *lower*? Explain.

 **14.21** Two kmol of CO_2 dissociate to form an equilibrium mixture of CO_2 , CO, and O_2 in which 1.8 kmol of CO_2 is present. Plot the temperature of the equilibrium mixture, in K, versus the pressure p for $0.5 \leq p \leq 10$ atm.

 **14.22** One kmol of $\text{H}_2\text{O(g)}$ dissociates to form an equilibrium mixture of $\text{H}_2\text{O(g)}$, H_2 , and O_2 in which the amount of water vapor present is 0.95 kmol. Plot the temperature of the equilibrium mixture, in K, versus the pressure p for $1 \leq p \leq 10$ atm.

 **14.23** A vessel initially containing 1 kmol of $\text{H}_2\text{O(g)}$ and x kmol of N_2 forms an equilibrium mixture at 1 atm consisting of $\text{H}_2\text{O(g)}$, H_2 , O_2 , and N_2 in which 0.5 kmol of $\text{H}_2\text{O(g)}$ is present. Plot x versus the temperature T for $3000 \leq T \leq 3600$ K.

 **14.24** A vessel initially containing 2 lbmol of N_2 and 1 lbmol of O_2 forms an equilibrium mixture at 1 atm consisting of N_2 , O_2 , and NO. Plot the amount of NO formed versus temperature T for $3600 \leq T \leq 6300^\circ\text{R}$.

14.25 A vessel initially containing 1 kmol of CO and 4.76 kmol of dry air forms an equilibrium mixture of CO_2 , CO, O_2 , and N_2 at 3000 K, 1 atm. Determine the equilibrium composition.

14.26 A vessel initially containing 1 kmol of O_2 , 2 kmol of N_2 , and 1 kmol of Ar forms an equilibrium mixture of O_2 , N_2 , NO, and Ar at 2727°C , 1 atm. Determine the equilibrium composition.

14.27 One kmol of CO and 0.5 kmol of O_2 react to form a mixture at temperature T and pressure p consisting of CO_2 , CO, and O_2 . If 0.35 kmol of CO is present in an equilibrium mixture when the pressure is 1 atm, determine the amount of CO present in an equilibrium mixture at the same temperature if the pressure were 10 atm.

14.28 A vessel initially contains 1 kmol of H_2 and 4 kmol of N_2 . An equilibrium mixture of H_2 , H, and N_2 forms at 3000 K, 1 atm. Determine the equilibrium composition. If the pressure were increased while keeping the temperature fixed, would the amount of monatomic hydrogen in the equilibrium mixture increase or decrease? Explain.

14.29 Dry air enters a heat exchanger. An equilibrium mixture of N_2 , O_2 , and NO exits at 3882°F , 1 atm. Determine the mole fraction of NO in the exiting mixture. Will the amount of

NO increase or decrease as temperature decreases at fixed pressure? Explain.

14.30 A gaseous mixture with a molar analysis of 20% CO_2 , 40% CO, and 40% O_2 enters a heat exchanger and is heated at constant pressure. An equilibrium mixture of CO_2 , CO, and O_2 exits at 3000 K, 1.5 bar. Determine the molar analysis of the exiting mixture.

14.31 An ideal gas mixture with the molar analysis 30% CO, 10% CO_2 , 40% H_2O , 20% inert gas enters a reactor operating at steady state. An equilibrium mixture of CO, CO_2 , H_2O , H_2 , and the inert gas exits at 1 atm.

- (a) If the equilibrium mixture exits at 1200 K, determine on a molar basis the ratio of the H_2 in the equilibrium mixture to the H_2O in the entering mixture.

- (b) If the mole fraction of CO present in the equilibrium mixture is 7.5%, determine the temperature of the equilibrium mixture, in K.

14.32 A mixture of 1 kmol CO and 0.5 kmol O_2 in a closed vessel, initially at 1 atm and 300 K, reacts to form an equilibrium mixture of CO_2 , CO, and O_2 at 2500 K. Determine the final pressure, in atm.

14.33 Methane burns with 90% of theoretical air to form an equilibrium mixture of CO_2 , CO, $\text{H}_2\text{O(g)}$, H_2 , and N_2 at 1000 K, 1 atm. Determine the composition of the equilibrium mixture, per kmol of mixture.

14.34 Octane (C_8H_{18}) burns with air to form an equilibrium mixture of CO_2 , H_2 , CO, $\text{H}_2\text{O(g)}$, and N_2 at 1700 K, 1 atm. Determine the composition of the products, in kmol per kmol of fuel, for an equivalence ratio of 1.2.

14.35 Acetylene gas (C_2H_2) at 25°C , 1 atm enters a reactor operating at steady state and burns with 40% excess air entering at 25°C , 1 atm, 80% relative humidity. An equilibrium mixture of CO_2 , H_2O , O_2 , NO, and N_2 exits at 2200 K, 0.9 atm. Determine, per kmol of C_2H_2 entering, the composition of the exiting mixture.

Chemical Equilibrium and the Energy Balance

14.36 Carbon dioxide gas at 25°C , 5.1 atm enters a heat exchanger operating at steady state. An equilibrium mixture of CO_2 , CO, and O_2 exits at 2527°C , 5 atm. Determine, per kmol of CO_2 entering,

- (a) the composition of the exiting mixture.
- (b) the heat transfer to the gas stream, in kJ.

Neglect kinetic and potential energy effects.

14.37 Saturated water vapor at 15 lbf/in^2 enters a heat exchanger operating at steady state. An equilibrium mixture of $\text{H}_2\text{O(g)}$, H_2 , and O_2 exits at 4040°F , 1 atm. Determine, per kmol of steam entering,

- (a) the composition of the exiting mixture.
- (b) the heat transfer to the flowing stream, in Btu.

Neglect kinetic and potential energy effects.

14.38 Carbon at 25°C , 1 atm enters a reactor operating at steady state and burns with oxygen entering at 127°C , 1 atm. The entering streams have equal molar flow rates. An equilibrium

mixture of CO_2 , CO , and O_2 exits at 2727°C , 1 atm. Determine, per kmol of carbon,

- the composition of the exiting mixture.
- the heat transfer between the reactor and its surroundings, in kJ.

Neglect kinetic and potential energy effects.

14.39 An equimolar mixture of carbon monoxide and water vapor at 200°F , 1 atm enters a reactor operating at steady state. An equilibrium mixture of CO_2 , CO , $\text{H}_2\text{O(g)}$, and H_2 exits at 2240°F , 1 atm. Determine the heat transfer between the reactor and its surroundings, in Btu per lbmol of CO entering. Neglect kinetic and potential energy effects.

14.40 Carbon dioxide (CO_2) and oxygen (O_2) in a 1:2 molar ratio enter a reactor operating at steady state in separate streams at 1 atm, 127°C and 1 atm, 277°C , respectively. An equilibrium mixture of CO_2 , CO , and O_2 exits at 1 atm. If the mole fraction of CO in the exiting mixture is 0.1, determine the rate of heat transfer from the reactor, in kJ per kmol of CO_2 entering. Ignore kinetic and potential energy effects.

14.41 Methane gas at 25°C , 1 atm enters a reactor operating at steady state and burns with 80% of theoretical air entering at 227°C , 1 atm. An equilibrium mixture of CO_2 , CO , $\text{H}_2\text{O(g)}$, H_2 , and N_2 exits at 1427°C , 1 atm. Determine, per kmol of methane entering,

- the composition of the exiting mixture.
- the heat transfer between the reactor and its surroundings, in kJ.

Neglect kinetic and potential energy effects.

14.42 Gaseous propane (C_3H_8) at 25°C , 1 atm enters a reactor operating at steady state and burns with 80% of theoretical air entering separately at 25°C , 1 atm. An equilibrium mixture of CO_2 , CO , $\text{H}_2\text{O(g)}$, H_2 , and N_2 exits at 1227°C , 1 atm. Determine the heat transfer between the reactor and its surroundings, in kJ per kmol of propane entering. Neglect kinetic and potential energy effects.

14.43 Gaseous propane (C_3H_8) at 77°F , 1 atm enters a reactor operating at steady state and burns with the theoretical amount of air entering separately at 240°F , 1 atm. An equilibrium mixture of CO_2 , CO , $\text{H}_2\text{O(g)}$, O_2 , and N_2 exits at 3140°F , 1 atm. Determine the heat transfer between the reactor and its surroundings, in Btu per lbmol of propane entering. Neglect kinetic and potential energy effects.

14.44 One kmol of CO_2 in a piston–cylinder assembly, initially at temperature T and 1 atm, is heated at constant pressure until a final state is attained consisting of an equilibrium mixture of CO_2 , CO , and O_2 in which the amount of CO_2 present is 0.422 kmol. Determine the heat transfer and the work, each in kJ, if T is (a) 298 K, (b) 400 K.

14.45 Hydrogen gas (H_2) at 25°C , 1 atm enters an insulated reactor operating at steady state and reacts with 250% excess oxygen entering at 227°C , 1 atm. The products of combustion exit at 1 atm. Determine the temperature of the products, in K, if

- combustion is complete.
- an equilibrium mixture of H_2O , H_2 , and O_2 exits.

Kinetic and potential energy effects are negligible.

14.46 For each case of Problem 14.45, determine the rate of entropy production, in kJ/K per kmol of H_2 entering. What can be concluded about the possibility of achieving complete combustion?

14.47 Hydrogen (H_2) at 25°C , 1 atm enters an insulated reactor operating at steady state and reacts with 100% of theoretical air entering at 25°C , 1 atm. The products of combustion exit at temperature T and 1 atm. Determine T , in K, if

- combustion is complete.
- an equilibrium mixture of H_2O , H_2 , O_2 , and N_2 exits.

14.48 Methane at 77°F , 1 atm enters an insulated reactor operating at steady state and burns with 90% of theoretical air entering separately at 77°F , 1 atm. The products exit at 1 atm as an equilibrium mixture of CO_2 , CO , $\text{H}_2\text{O(g)}$, H_2 and N_2 . Determine the temperature of the exiting products, in $^\circ\text{R}$. Kinetic and potential energy effects are negligible.

14.49 Carbon monoxide at 77°F , 1 atm enters an insulated reactor operating at steady state and burns with air entering at 77°F , 1 atm. The products exit at 1 atm as an equilibrium mixture of CO_2 , CO , O_2 , and N_2 . Determine the temperature of the equilibrium mixture, in $^\circ\text{R}$, if the combustion occurs with

- 80% of theoretical air.
- 100% of theoretical air.

Kinetic and potential energy effects are negligible.

14.50 For each case of Problem 14.49, determine the rate of exergy destruction, in kJ per kmol of CO entering the reactor. Let $T_0 = 537^\circ\text{R}$.

14.51 Carbon monoxide at 25°C , 1 atm enters an insulated reactor operating at steady state and burns with excess oxygen (O_2) entering at 25°C , 1 atm. The products exit at 2950 K , 1 atm as an equilibrium mixture of CO_2 , CO , and O_2 . Determine the percent excess oxygen. Kinetic and potential energy effects are negligible.

14.52 A gaseous mixture of carbon monoxide and the theoretical amount of air at 260°F , 1.5 atm enters an insulated reactor operating at steady state. An equilibrium mixture of CO_2 , CO , O_2 and N_2 exits at 1.5 atm. Determine the temperature of the exiting mixture, in $^\circ\text{R}$. Kinetic and potential energy effects are negligible.

14.53 Methane at 25°C , 1 atm enters an insulated reactor operating at steady state and burns with oxygen entering at 127°C , 1 atm. An equilibrium mixture of CO_2 , CO , O_2 , and $\text{H}_2\text{O(g)}$ exits at 3250 K , 1 atm. Determine the rate at which oxygen enters the reactor, in kmol per kmol of methane. Kinetic and potential energy effects are negligible.

14.54 Methane at 77°F , 1 atm enters an insulated reactor operating at steady state and burns with the theoretical amount of air entering at 77°F , 1 atm. An equilibrium mixture of CO_2 , CO , O_2 , $\text{H}_2\text{O(g)}$, and N_2 exits at 1 atm.

- Determine the temperature of the exiting products, in $^\circ\text{R}$.
- Determine the rate of exergy destruction, in Btu per lbmol of methane entering, for $T_0 = 537^\circ\text{R}$.

Kinetic and potential energy effects are negligible.

14.55 Methane gas at 25°C , 1 atm enters an insulated reactor operating at steady state, where it burns with x times the

theoretical amount of air entering at 25°C, 1 atm. An equilibrium mixture of CO₂, CO, O₂, H₂O, and N₂ exits at 1 atm. For selected values of x ranging from 1 to 4, determine the temperature of the exiting equilibrium mixture, in K. Kinetic and potential energy effects are negligible.

14.56 A mixture consisting of 1 kmol of carbon monoxide (CO), 0.5 kmol of oxygen (O₂), and 1.88 kmol of nitrogen (N₂), initially at 227°C, 1 atm, reacts in a closed, rigid, insulated vessel, forming an equilibrium mixture of CO₂, CO, O₂, and N₂. Determine the final equilibrium pressure, in atm.

14.57 A mixture consisting of 1 kmol of CO and the theoretical amount of air, initially at 60°C, 1 atm, reacts in a closed, rigid, insulated vessel to form an equilibrium mixture. An analysis of the products shows that there are 0.808 kmol of CO₂, 0.192 kmol of CO, and 0.096 kmol of O₂ present. The temperature of the final mixture is measured as 2465°C. Check the consistency of these data.

Using the van't Hoff Equation, Ionization

14.58 Estimate the enthalpy of reaction at 2000 K, in kJ/kmol, for $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ using the van't Hoff equation and equilibrium constant data. Compare with the value obtained for the enthalpy of reaction using enthalpy data.

14.59 Estimate the enthalpy of reaction at 2000 K, in kJ/kmol, for $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$, using the van't Hoff equation and equilibrium constant data. Compare with the value obtained for the enthalpy of reaction using enthalpy data.

14.60 Estimate the equilibrium constant at 2800 K for $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ using the equilibrium constant at 2000 K from Table A-27, together with the van't Hoff equation and enthalpy data. Compare with the value for the equilibrium constant obtained from Table A-27.

14.61 Estimate the equilibrium constant at 2800 K for the reaction $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ using the equilibrium constant at 2500 K from Table A-27, together with the van't Hoff equation and enthalpy data. Compare with the value for the equilibrium constant obtained from Table A-27.

14.62 At 25°C, $\log_{10}K = 8.9$ for $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$. Assuming that the enthalpy of reaction does not vary much with temperature, estimate the value of $\log_{10}K$ at 500°C.

14.63 If the ionization-equilibrium constants for $\text{Cs} \rightleftharpoons \text{Cs}^+ + \text{e}^-$ at 1600 and 2000 K are $K = 0.78$ and $K = 15.63$, respectively, estimate the enthalpy of ionization, in kJ/kmol, at 1800 K using the van't Hoff equation.

14.64 An equilibrium mixture at 2000 K, 1 atm consists of Cs, Cs⁺, and e⁻. Based on 1 kmol of Cs present initially, determine the percent ionization of cesium. At 2000 K, the ionization-equilibrium constant for $\text{Cs} \rightleftharpoons \text{Cs}^+ + \text{e}^-$ is $K = 15.63$.

14.65 An equilibrium mixture at 18,000°R and pressure p consists of Ar, Ar⁺, and e⁻. Based on 1 lbmol of neutral argon present initially, plot the percent ionization of argon versus pressure for $0.01 \leq p \leq 0.05$ atm. At 18,000°R, the ionization-equilibrium constant for $\text{Ar} \rightleftharpoons \text{Ar}^+ + \text{e}^-$ is $K = 4.2 \times 10^{-4}$.

14.66 At 2000 K and pressure p , 1 kmol of Na ionizes to form an equilibrium mixture of Na, Na⁺, and e⁻ in which the

amount of Na present is x kmol. Plot the pressure, in atm, versus x for $0.2 \leq x \leq 0.3$ kmol. At 2000 K, the ionization-equilibrium constant for $\text{Na} \rightleftharpoons \text{Na}^+ + \text{e}^-$ is $K = 0.668$.

14.67 At 12,000 K and 6 atm, 1 kmol of N ionizes to form an equilibrium mixture of N, N⁺, and e⁻ in which the amount of N present is 0.95 kmol. Determine the ionization-equilibrium constant at this temperature for $\text{N} \rightleftharpoons \text{N}^+ + \text{e}^-$.

Considering Simultaneous Reactions

14.68 Carbon dioxide (CO₂), oxygen (O₂), and nitrogen (N₂) enter a reactor operating at steady state with equal molar flow rates. An equilibrium mixture of CO₂, O₂, N₂, CO, and NO exits at 3000 K, 5 atm. Determine the molar analysis of the equilibrium mixture.

14.69 An equimolar mixture of carbon monoxide and water vapor enters a heat exchanger operating at steady state. An equilibrium mixture of CO, CO₂, O₂, H₂O(g), and H₂ exits at 2227°C, 1 atm. Determine the molar analysis of the exiting equilibrium mixture.

14.70 A closed vessel initially contains a gaseous mixture consisting of 3 lbmol of CO₂, 6 lbmol of CO, and 1 lbmol of H₂. An equilibrium mixture at 4220°F, 1 atm is formed containing CO₂, CO, H₂O, H₂, and O₂. Determine the composition of the equilibrium mixture.

14.71 Butane (C₄H₁₀) burns with 100% excess air to form an equilibrium mixture at 1400 K, 20 atm consisting of CO₂, O₂, H₂O(g), N₂, NO, and NO₂. Determine the balanced reaction equation. For $\text{N}_2 + 2\text{O}_2 \rightleftharpoons 2\text{NO}_2$ at 1400 K, $K = 8.4 \times 10^{-10}$.

14.72 One lbmol of H₂O(g) dissociates to form an equilibrium mixture at 5000°R, 1 atm consisting of H₂O(g), H₂, O₂, and OH. Determine the equilibrium composition.

14.73 Steam enters a heat exchanger operating at steady state. An equilibrium mixture of H₂O, H₂, O₂, H, and OH exits at temperature T , 1 atm. Determine the molar analysis of the exiting equilibrium mixture for

- (a) $T = 2800$ K.
- (b) $T = 3000$ K.

Considering Phase Equilibrium

14.74 For a two-phase liquid-vapor mixture of water at 100°C, use tabulated property data to show that the specific Gibbs functions of the saturated liquid and saturated vapor are equal. Repeat for a two-phase liquid-vapor mixture of Refrigerant 134a at 20°C.

14.75 Using the Clapeyron equation, solve the following problems from Chap. 11: (a) 11.32, (b) 11.33, (c) 11.34, (d) 11.35, (e) 11.40.

14.76 A closed system at 20°C, 1 bar consists of a pure liquid water phase in equilibrium with a vapor phase composed of water vapor and dry air. Determine the departure, in percent, of the partial pressure of the water vapor from the saturation pressure of pure water at 20°C.

14.77 Derive an expression for estimating the pressure at which graphite and diamond exist in equilibrium at 25°C in terms of the specific volume, specific Gibbs function, and

isothermal compressibility of each phase at 25°C, 1 atm. Discuss.

14.78 An isolated system has two phases, denoted by A and B, each of which consists of the same two substances, denoted by 1 and 2. Show that necessary conditions for equilibrium are

1. the temperature of each phase is the same, $T_A = T_B$.
2. the pressure of each phase is the same, $p_A = p_B$.
3. the chemical potential of each component has the same value in each phase, $\mu_1^A = \mu_1^B, \mu_2^A = \mu_2^B$.

14.79 An isolated system has two phases, denoted by A and B, each of which consists of the same two substances, denoted by 1 and 2. The phases are separated by a freely moving *thin* wall permeable only by substance 2. Determine the necessary conditions for equilibrium.

14.80 Referring to Problem 14.79, let each phase be a binary mixture of argon and helium and the wall be permeable only to argon. If the phases initially are at the conditions tabulated below, determine the final equilibrium temperature, pressure, and composition in the two phases.

	T(K)	p(MPa)	n(kmol)	y_{Ar}	y_{He}
Phase A	300	0.2	6	0.5	0.5
Phase B	400	0.1	5	0.8	0.2

14.81 Figure P14.81 shows an ideal gas mixture at temperature T and pressure p containing substance k, separated from a gas phase of pure k at temperature T and pressure p' by a semipermeable membrane that allows only k to pass through. Assuming the ideal gas model also applies to the pure gas phase, determine the relationship between p and p' for there to be no net transfer of k through the membrane.

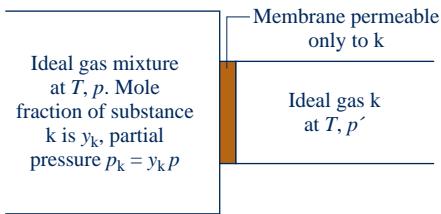


Fig. P14.81

14.82 What is the maximum number of homogeneous phases that can exist at equilibrium for a system involving

- (a) one component?
- (b) two components?
- (c) three components?

14.83 Determine the number of degrees of freedom for systems composed of

- (a) ice and liquid water.
- (b) ice, liquid water, and water vapor.
- (c) liquid water and water vapor.
- (d) water vapor only.
- (e) water vapor and dry air.
- (f) liquid water, water vapor, and dry air.
- (g) ice, water vapor, and dry air.
- (h) N_2 and O_2 at 20°C, 1 atm.
- (i) a liquid phase and a vapor phase, each of which contains ammonia and water.
- (j) liquid mercury, liquid water, and a vapor phase of mercury and water.
- (k) liquid acetone and a vapor phase of acetone and N_2 .

14.84 Develop the *phase rule* for chemically reacting systems.

14.85 Apply the result of Problem 14.84 to determine the number of degrees of freedom for the gas phase reaction:



14.86 For a gas–liquid system in equilibrium at temperature T and pressure p , Raoult's law models the relation between the partial pressure of substance i in the gas phase, p_i , and the mole fraction of substance i in the liquid phase, y_i , as follows:

$$p_i = y_i p_{\text{sat},i}(T)$$

where $p_{\text{sat},i}(T)$ is the saturation pressure of pure i at temperature T . The gas phase is assumed to form an ideal gas mixture; thus, $p_i = x_i p$ where x_i is the mole fraction of i in the gas phase. Apply Raoult's law to the following cases, which are representative of conditions that might be encountered in ammonia–water absorption systems (Sec. 10.5):

- (a) Consider a two-phase, liquid–vapor ammonia–water system in equilibrium at 20°C. The mole fraction of ammonia in the liquid phase is 80%. Determine the pressure, in bar, and the mole fraction of ammonia in the vapor phase.
- (b) Determine the mole fractions of ammonia in the liquid and vapor phases of a two-phase ammonia–water system in equilibrium at 40°C, 12 bar.

► DESIGN & OPEN-ENDED PROBLEMS: EXPLORING ENGINEERING PRACTICE

14.1D Spark-ignition engine exhaust gases contain several air pollutants including the oxides of nitrogen, NO and NO_2 , collectively known as NO_x . Additionally, the exhaust gases may contain carbon monoxide (CO) and unburned or partially burned hydrocarbons (HC). The pollutant amounts actually present depend on engine design and operating conditions, and they typically differ significantly from values calculated on the basis of chemical equilibrium. Discuss both the reasons for these discrepancies and

possible mechanisms by which such pollutants are formed in an actual engine. In a memorandum, summarize your findings and conclusions.

14.2D The Federal Clean Air Act of 1970 and succeeding Clean Air Act Amendments target the oxides of nitrogen NO and NO_2 , collectively known as NO_x , as significant air pollutants. NO_x is formed in combustion via three primary mechanisms: *thermal* NO_x formation, *prompt* NO_x formation, and *fuel* NO_x

formation. Discuss these formation mechanisms, including a discussion of thermal NO_x formation by the *Zeldovich mechanism*. What is the role of NO_x in the formation of ozone? What are some NO_x reduction strategies? Write a report including at least three references.

14.3D Using appropriate software, develop plots giving the variation with equivalence ratio of the equilibrium products of octane–air mixtures at 30 atm and selected temperatures ranging from 1700 to 2800 K. Consider equivalence ratios in the interval from 0.2 to 1.4 and equilibrium products including, but not necessarily limited to, CO_2 , CO , H_2O , O_2 , O , H_2 , N_2 , NO , OH . Under what conditions is the formation of nitric oxide (NO) and carbon monoxide (CO) most significant? Write a report including at least three references.

14.4D The amount of sulfur dioxide (SO_2) present in *off gases* from industrial processes can be reduced by oxidizing the SO_2 to SO_3 at an elevated temperature in a catalytic reactor. The SO_3 can be reacted in turn with water to form sulfuric acid that has economic value. For an off gas at 1 atm having the molar analysis of 12% SO_2 , 8% O_2 , 80% N_2 , estimate the range of temperatures at which a *substantial* conversion of SO_2 to SO_3 might be realized. Report your findings in a PowerPoint presentation suitable for your class. Additionally, in an accompanying memorandum, discuss your modeling assumptions and provide sample calculations.

14.5D A gaseous mixture of hydrogen (H_2) and carbon monoxide (CO) enters a catalytic reactor and a gaseous mixture of methanol (CH_3OH), hydrogen, and carbon monoxide exits. At the preliminary process design stage, plausible estimates are required of the inlet hydrogen mole fraction, y_{H_2} , the temperature of the exiting mixture, T_e , and the pressure of the exiting mixture, p_e , subject to the following four constraints: (1) $0.5 \leq y_{\text{H}_2} \leq 0.75$, (2) $300 \leq T_e \leq 400$ K, (3) $1 \leq p_e \leq 10$ atm, and (4) the exiting mixture contains at least 75% methanol on a molar basis. In a memorandum, provide your estimates together with a discussion of the modeling employed and sample calculations.

14.6D When systems in thermal, mechanical, and chemical equilibrium are *perturbed*, changes within the systems can occur, leading to a new equilibrium state. The effects of perturbing the system considered in developing Eqs. 14.32 and 14.33 can be determined by study of these equations. For example, at fixed pressure and temperature it can be concluded that an increase in the amount of the inert component E would lead to increases in n_C and n_D when $\Delta v = (\nu_C + \nu_D - \nu_A - \nu_B)$ is positive, to decreases in n_C and n_D when Δv is negative, and no change when $\Delta v = 0$.

(a) For a system consisting of NH_3 , N_2 , and H_2 at fixed pressure and temperature, subject to the reaction



investigate the effects, in turn, of additions in the amounts present of NH_3 , H_2 , and N_2 .

(b) For the *general case* of Eqs. 14.32 and 14.33, investigate the effects, in turn, of additions of A, B, C, and D.

Present your findings, together with the modeling assumptions used, in a PowerPoint presentation suitable for your class.

14.7D With reference to the equilibrium constant data of Table A-27:

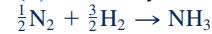
(a) For each of the tabulated reactions plot $\log_{10}K$ versus $1/T$ and determine the slope of the line of best fit. What is the thermodynamic significance of the slope? Check your conclusion about the slope using data from the *JANAF tables*.¹

(b) A text book states that the magnitude of the equilibrium constant often signals the importance of a reaction, and offers this *rule of thumb*: When $K < 10^{-3}$, the extent of the reaction is usually not significant, whereas when $K > 10^3$ the reaction generally proceeds closely to equilibrium. Confirm or deny this rule.

Present your findings and conclusions in a report including at least three references.

14.8D (a) For an equilibrium ideal gas mixture of N_2 , H_2 , and NH_3 , evaluate the equilibrium constant from an expression you derive from the *van't Hoff equation* that requires only standard state enthalpy of formation and Gibbs function of formation data together with suitable analytical expressions in terms of temperature for the ideal gas specific heats of N_2 , H_2 , NH_3 .

(b) For the synthesis of ammonia by



provide a recommendation for the ranges of temperature and pressure for which the mole fraction of ammonia in the mixture is at least 0.5.

Write a report including your derivation, recommendations for the ranges of temperature and pressure, sample calculations, and at least three references.

14.9D U.S. Patent 5,298,233 describes a means for converting industrial wastes to carbon dioxide and water vapor. Hydrogen- and carbon-containing feed, such as organic or inorganic sludge, low-grade fuel oil, or municipal garbage, is introduced into a molten bath consisting of two immiscible molten metal phases. The carbon and hydrogen of the feed are converted, respectively, to dissolved carbon and dissolved hydrogen. The dissolved carbon is oxidized in the first molten metal phase to carbon dioxide, which is released from the bath. The dissolved hydrogen migrates to the second molten metal phase, where it is oxidized to form water vapor, which is also released from the bath. Critically evaluate this technology for waste disposal. Is the technology promising commercially? Compare with alternative waste management practices such as pyrolysis and incineration. Write a report including at least three references.

14.10D Figure P14.10D gives a table of data for a lithium bromide–water absorption refrigeration cycle together with the sketch of a property diagram showing the cycle. The property diagram plots the vapor pressure versus the lithium bromide concentration. Apply the *phase rule* to verify that the numbered states are fixed by the property values provided. What does the *crystallization* line on the equilibrium diagram

¹Stull, D. R., and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37, National Bureau of Standards, Washington, DC, June 1971.

represent, and what is its significance for absorption cycle operation? Locate the numbered states on an enthalpy-concentration diagram for lithium bromide–water solutions obtained from the literature. Finally, develop a sketch of the equipment schematic for this refrigeration cycle. Present your findings in a report including at least three references.

State	Temperature (°F)	Pressure (in. Hg)	$(mf)_{\text{LiBr}}$ (%)
1	115	0.27	63.3
2	104	0.27	59.5
3	167	1.65	59.5
4	192	3.00	59.5
5	215	3.00	64.0
6	135	0.45	64.0
7	120	0.32	63.3

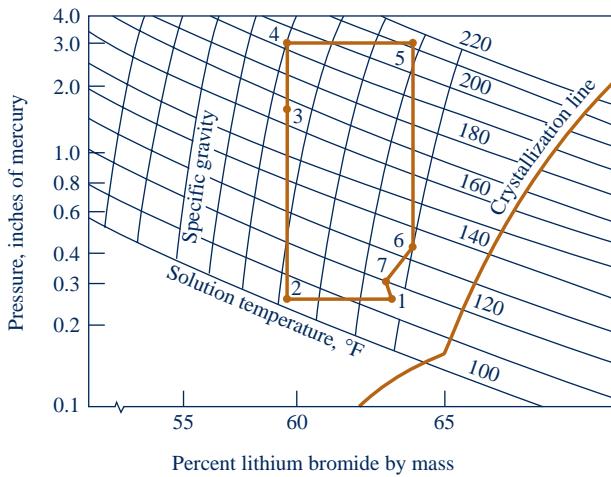


Fig. P14.10D

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TABLE A-1**Atomic or Molecular Weights and Critical Properties of Selected Elements and Compounds**

Substance	Chemical Formula	M (kg/kmol)	T_c (K)	p_c (bar)	Z_c = $\frac{p_c v_c}{R T_c}$
Acetylene	C ₂ H ₂	26.04	309	62.8	0.274
Air (equivalent)	—	28.97	133	37.7	0.284
Ammonia	NH ₃	17.03	406	112.8	0.242
Argon	Ar	39.94	151	48.6	0.290
Benzene	C ₆ H ₆	78.11	563	49.3	0.274
Butane	C ₄ H ₁₀	58.12	425	38.0	0.274
Carbon	C	12.01	—	—	—
Carbon dioxide	CO ₂	44.01	304	73.9	0.276
Carbon monoxide	CO	28.01	133	35.0	0.294
Copper	Cu	63.54	—	—	—
Ethane	C ₂ H ₆	30.07	305	48.8	0.285
Ethanol	C ₂ H ₅ OH	46.07	516	63.8	0.249
Ethylene	C ₂ H ₄	28.05	283	51.2	0.270
Helium	He	4.003	5.2	2.3	0.300
Hydrogen	H ₂	2.016	33.2	13.0	0.304
Methane	CH ₄	16.04	191	46.4	0.290
Methanol	CH ₃ OH	32.04	513	79.5	0.220
Nitrogen	N ₂	28.01	126	33.9	0.291
Octane	C ₈ H ₁₈	114.22	569	24.9	0.258
Oxygen	O ₂	32.00	154	50.5	0.290
Propane	C ₃ H ₈	44.09	370	42.7	0.276
Propylene	C ₃ H ₆	42.08	365	46.2	0.276
Refrigerant 12	CCl ₂ F ₂	120.92	385	41.2	0.278
Refrigerant 22	CHClF ₂	86.48	369	49.8	0.267
Refrigerant 134a	CF ₃ CH ₂ F	102.03	374	40.7	0.260
Sulfur dioxide	SO ₂	64.06	431	78.7	0.268
Water	H ₂ O	18.02	647.3	220.9	0.233

Sources: Adapted from *International Critical Tables* and L. C. Nelson and E. F. Obert, Generalized Compressibility Charts, *Chem. Eng.*, 61: 203 (1954).

TABLE A-2**Properties of Saturated Water (Liquid–Vapor): Temperature Table**

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

Temp. °C	Press. bar	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Temp. °C
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
.01	0.00611	1.0002	206.136	0.00	2375.3	0.01	2501.3	2501.4	0.0000	9.1562
4	0.00813	1.0001	157.232	16.77	2380.9	16.78	2491.9	2508.7	0.0610	9.0514
5	0.00872	1.0001	147.120	20.97	2382.3	20.98	2489.6	2510.6	0.0761	9.0257
6	0.00935	1.0001	137.734	25.19	2383.6	25.20	2487.2	2512.4	0.0912	9.0003
8	0.01072	1.0002	120.917	33.59	2386.4	33.60	2482.5	2516.1	0.1212	8.9501
10	0.01228	1.0004	106.379	42.00	2389.2	42.01	2477.7	2519.8	0.1510	8.9008
11	0.01312	1.0004	99.857	46.20	2390.5	46.20	2475.4	2521.6	0.1658	8.8765
12	0.01402	1.0005	93.784	50.41	2391.9	50.41	2473.0	2523.4	0.1806	8.8524
13	0.01497	1.0007	88.124	54.60	2393.3	54.60	2470.7	2525.3	0.1953	8.8285
14	0.01598	1.0008	82.848	58.79	2394.7	58.80	2468.3	2527.1	0.2099	8.8048
15	0.01705	1.0009	77.926	62.99	2396.1	62.99	2465.9	2528.9	0.2245	8.7814
16	0.01818	1.0011	73.333	67.18	2397.4	67.19	2463.6	2530.8	0.2390	8.7582
17	0.01938	1.0012	69.044	71.38	2398.8	71.38	2461.2	2532.6	0.2535	8.7351
18	0.02064	1.0014	65.038	75.57	2400.2	75.58	2458.8	2534.4	0.2679	8.7123
19	0.02198	1.0016	61.293	79.76	2401.6	79.77	2456.5	2536.2	0.2823	8.6897
20	0.02339	1.0018	57.791	83.95	2402.9	83.96	2454.1	2538.1	0.2966	8.6672
21	0.02487	1.0020	54.514	88.14	2404.3	88.14	2451.8	2539.9	0.3109	8.6450
22	0.02645	1.0022	51.447	92.32	2405.7	92.33	2449.4	2541.7	0.3251	8.6229
23	0.02810	1.0024	48.574	96.51	2407.0	96.52	2447.0	2543.5	0.3393	8.6011
24	0.02985	1.0027	45.883	100.70	2408.4	100.70	2444.7	2545.4	0.3534	8.5794
25	0.03169	1.0029	43.360	104.88	2409.8	104.89	2442.3	2547.2	0.3674	8.5580
26	0.03363	1.0032	40.994	109.06	2411.1	109.07	2439.9	2549.0	0.3814	8.5367
27	0.03567	1.0035	38.774	113.25	2412.5	113.25	2437.6	2550.8	0.3954	8.5156
28	0.03782	1.0037	36.690	117.42	2413.9	117.43	2435.2	2552.6	0.4093	8.4946
29	0.04008	1.0040	34.733	121.60	2415.2	121.61	2432.8	2554.5	0.4231	8.4739
30	0.04246	1.0043	32.894	125.78	2416.6	125.79	2430.5	2556.3	0.4369	8.4533
31	0.04496	1.0046	31.165	129.96	2418.0	129.97	2428.1	2558.1	0.4507	8.4329
32	0.04759	1.0050	29.540	134.14	2419.3	134.15	2425.7	2559.9	0.4644	8.4127
33	0.05034	1.0053	28.011	138.32	2420.7	138.33	2423.4	2561.7	0.4781	8.3927
34	0.05324	1.0056	26.571	142.50	2422.0	142.50	2421.0	2563.5	0.4917	8.3728
35	0.05628	1.0060	25.216	146.67	2423.4	146.68	2418.6	2565.3	0.5053	8.3531
36	0.05947	1.0063	23.940	150.85	2424.7	150.86	2416.2	2567.1	0.5188	8.3336
38	0.06632	1.0071	21.602	159.20	2427.4	159.21	2411.5	2570.7	0.5458	8.2950
40	0.07384	1.0078	19.523	167.56	2430.1	167.57	2406.7	2574.3	0.5725	8.2570
45	0.09593	1.0099	15.258	188.44	2436.8	188.45	2394.8	2583.2	0.6387	8.1648

TABLE A-2

(Continued)

H₂O

		Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Temp. °C
		Sat. Liquid <i>v_f</i> × 10 ³	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
50	.1235	1.0121	12.032	209.32	2443.5	209.33	2382.7	2592.1	.7038	8.0763
55	.1576	1.0146	9.568	230.21	2450.1	230.23	2370.7	2600.9	.7679	7.9913
60	.1994	1.0172	7.671	251.11	2456.6	251.13	2358.5	2609.6	.8312	7.9096
65	.2503	1.0199	6.197	272.02	2463.1	272.06	2346.2	2618.3	.8935	7.8310
70	.3119	1.0228	5.042	292.95	2469.6	292.98	2333.8	2626.8	.9549	7.7553
75	.3858	1.0259	4.131	313.90	2475.9	313.93	2321.4	2635.3	1.0155	7.6824
80	.4739	1.0291	3.407	334.86	2482.2	334.91	2308.8	2643.7	1.0753	7.6122
85	.5783	1.0325	2.828	355.84	2488.4	355.90	2296.0	2651.9	1.1343	7.5445
90	.7014	1.0360	2.361	376.85	2494.5	376.92	2283.2	2660.1	1.1925	7.4791
95	.8455	1.0397	1.982	397.88	2500.6	397.96	2270.2	2668.1	1.2500	7.4159
100	1.014	1.0435	1.673	418.94	2506.5	419.04	2257.0	2676.1	1.3069	7.3549
110	1.433	1.0516	1.210	461.14	2518.1	461.30	2230.2	2691.5	1.4185	7.2387
120	1.985	1.0603	0.8919	503.50	2529.3	503.71	2202.6	2706.3	1.5276	7.1296
130	2.701	1.0697	0.6685	546.02	2539.9	546.31	2174.2	2720.5	1.6344	7.0269
140	3.613	1.0797	0.5089	588.74	2550.0	589.13	2144.7	2733.9	1.7391	6.9299
150	4.758	1.0905	0.3928	631.68	2559.5	632.20	2114.3	2746.5	1.8418	6.8379
160	6.178	1.1020	0.3071	674.86	2568.4	675.55	2082.6	2758.1	1.9427	6.7502
170	7.917	1.1143	0.2428	718.33	2576.5	719.21	2049.5	2768.7	2.0419	6.6663
180	10.02	1.1274	0.1941	762.09	2583.7	763.22	2015.0	2778.2	2.1396	6.5857
190	12.54	1.1414	0.1565	806.19	2590.0	807.62	1978.8	2786.4	2.2359	6.5079
200	15.54	1.1565	0.1274	850.65	2595.3	852.45	1940.7	2793.2	2.3309	6.4323
210	19.06	1.1726	0.1044	895.53	2599.5	897.76	1900.7	2798.5	2.4248	6.3585
220	23.18	1.1900	0.08619	940.87	2602.4	943.62	1858.5	2802.1	2.5178	6.2861
230	27.95	1.2088	0.07158	986.74	2603.9	990.12	1813.8	2804.0	2.6099	6.2146
240	33.44	1.2291	0.05976	1033.2	2604.0	1037.3	1766.5	2803.8	2.7015	6.1437
250	39.73	1.2512	0.05013	1080.4	2602.4	1085.4	1716.2	2801.5	2.7927	6.0730
260	46.88	1.2755	0.04221	1128.4	2599.0	1134.4	1662.5	2796.6	2.8838	6.0019
270	54.99	1.3023	0.03564	1177.4	2593.7	1184.5	1605.2	2789.7	2.9751	5.9301
280	64.12	1.3321	0.03017	1227.5	2586.1	1236.0	1543.6	2779.6	3.0668	5.8571
290	74.36	1.3656	0.02557	1278.9	2576.0	1289.1	1477.1	2766.2	3.1594	5.7821
300	85.81	1.4036	0.02167	1332.0	2563.0	1344.0	1404.9	2749.0	3.2534	5.7045
320	112.7	1.4988	0.01549	1444.6	2525.5	1461.5	1238.6	2700.1	3.4480	5.5362
340	145.9	1.6379	0.01080	1570.3	2464.6	1594.2	1027.9	2622.0	3.6594	5.3357
360	186.5	1.8925	0.006945	1725.2	2351.5	1760.5	720.5	2481.0	3.9147	5.0526
374.14	220.9	3.155	0.003155	2029.6	2029.6	2099.3	0	2099.3	4.4298	374.14

Source: Tables A-2 through A-5 are extracted from J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York, 1969.

TABLE A-3**Properties of Saturated Water (Liquid–Vapor): Pressure Table**

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

Press. bar	Temp. °C	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Press. bar
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
0.04	28.96	1.0040	34.800	121.45	2415.2	121.46	2432.9	2554.4	0.4226	8.4746
0.06	36.16	1.0064	23.739	151.53	2425.0	151.53	2415.9	2567.4	0.5210	8.3304
0.08	41.51	1.0084	18.103	173.87	2432.2	173.88	2403.1	2577.0	0.5926	8.2287
0.10	45.81	1.0102	14.674	191.82	2437.9	191.83	2392.8	2584.7	0.6493	8.1502
0.20	60.06	1.0172	7.649	251.38	2456.7	251.40	2358.3	2609.7	0.8320	7.9085
0.30	69.10	1.0223	5.229	289.20	2468.4	289.23	2336.1	2625.3	0.9439	7.7686
0.40	75.87	1.0265	3.993	317.53	2477.0	317.58	2319.2	2636.8	1.0259	7.6700
0.50	81.33	1.0300	3.240	340.44	2483.9	340.49	2305.4	2645.9	1.0910	7.5939
0.60	85.94	1.0331	2.732	359.79	2489.6	359.86	2293.6	2653.5	1.1453	7.5320
0.70	89.95	1.0360	2.365	376.63	2494.5	376.70	2283.3	2660.0	1.1919	7.4797
0.80	93.50	1.0380	2.087	391.58	2498.8	391.66	2274.1	2665.8	1.2329	7.4346
0.90	96.71	1.0410	1.869	405.06	2502.6	405.15	2265.7	2670.9	1.2695	7.3949
1.00	99.63	1.0432	1.694	417.36	2506.1	417.46	2258.0	2675.5	1.3026	7.3594
1.50	111.4	1.0528	1.159	466.94	2519.7	467.11	2226.5	2693.6	1.4336	7.2233
2.00	120.2	1.0605	0.8857	504.49	2529.5	504.70	2201.9	2706.7	1.5301	7.1271
2.50	127.4	1.0672	0.7187	535.10	2537.2	535.37	2181.5	2716.9	1.6072	7.0527
3.00	133.6	1.0732	0.6058	561.15	2543.6	561.47	2163.8	2725.3	1.6718	6.9919
3.50	138.9	1.0786	0.5243	583.95	2546.9	584.33	2148.1	2732.4	1.7275	6.9405
4.00	143.6	1.0836	0.4625	604.31	2553.6	604.74	2133.8	2738.6	1.7766	6.8959
4.50	147.9	1.0882	0.4140	622.25	2557.6	623.25	2120.7	2743.9	1.8207	6.8565
5.00	151.9	1.0926	0.3749	639.68	2561.2	640.23	2108.5	2748.7	1.8607	6.8212
6.00	158.9	1.1006	0.3157	669.90	2567.4	670.56	2086.3	2756.8	1.9312	6.7600
7.00	165.0	1.1080	0.2729	696.44	2572.5	697.22	2066.3	2763.5	1.9922	6.7080
8.00	170.4	1.1148	0.2404	720.22	2576.8	721.11	2048.0	2769.1	2.0462	6.6628
9.00	175.4	1.1212	0.2150	741.83	2580.5	742.83	2031.1	2773.9	2.0946	6.6226
10.0	179.9	1.1273	0.1944	761.68	2583.6	762.81	2015.3	2778.1	2.1387	6.5863
15.0	198.3	1.1539	0.1318	843.16	2594.5	844.84	1947.3	2792.2	2.3150	6.4448
20.0	212.4	1.1767	0.09963	906.44	2600.3	908.79	1890.7	2799.5	2.4474	6.3409
25.0	224.0	1.1973	0.07998	959.11	2603.1	962.11	1841.0	2803.1	2.5547	6.2575
30.0	233.9	1.2165	0.06668	1004.8	2604.1	1008.4	1795.7	2804.2	2.6457	6.1869
35.0	242.6	1.2347	0.05707	1045.4	2603.7	1049.8	1753.7	2803.4	2.7253	6.1253
40.0	250.4	1.2522	0.04978	1082.3	2602.3	1087.3	1714.1	2801.4	2.7964	6.0701
45.0	257.5	1.2692	0.04406	1116.2	2600.1	1121.9	1676.4	2798.3	2.8610	6.0199
50.0	264.0	1.2859	0.03944	1147.8	2597.1	1154.2	1640.1	2794.3	2.9202	5.9734
60.0	275.6	1.3187	0.03244	1205.4	2589.7	1213.4	1571.0	2784.3	3.0267	5.8892
70.0	285.9	1.3513	0.02737	1257.6	2580.5	1267.0	1505.1	2772.1	3.1211	5.8133
80.0	295.1	1.3842	0.02352	1305.6	2569.8	1316.6	1441.3	2758.0	3.2068	5.7432
90.0	303.4	1.4178	0.02048	1350.5	2557.8	1363.3	1378.9	2742.1	3.2858	5.6772
100.	311.1	1.4524	0.01803	1393.0	2544.4	1407.6	1317.1	2724.7	3.3596	5.6141
110.	318.2	1.4886	0.01599	1433.7	2529.8	1450.1	1255.5	2705.6	3.4295	5.5527

H₂O

TABLE A-3

(Continued)

H₂O

Press. bar	Temp. °C	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Press. bar
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
120.	324.8	1.5267	0.01426	1473.0	2513.7	1491.3	1193.6	2684.9	3.4962	5.4924
130.	330.9	1.5671	0.01278	1511.1	2496.1	1531.5	1130.7	2662.2	3.5606	5.4323
140.	336.8	1.6107	0.01149	1548.6	2476.8	1571.1	1066.5	2637.6	3.6232	5.3717
150.	342.2	1.6581	0.01034	1585.6	2455.5	1610.5	1000.0	2610.5	3.6848	5.3098
160.	347.4	1.7107	0.009306	1622.7	2431.7	1650.1	930.6	2580.6	3.7461	5.2455
170.	352.4	1.7702	0.008364	1660.2	2405.0	1690.3	856.9	2547.2	3.8079	5.1777
180.	357.1	1.8397	0.007489	1698.9	2374.3	1732.0	777.1	2509.1	3.8715	5.1044
190.	361.5	1.9243	0.006657	1739.9	2338.1	1776.5	688.0	2464.5	3.9388	5.0228
200.	365.8	2.036	0.005834	1785.6	2293.0	1826.3	583.4	2409.7	4.0139	4.9269
220.9	374.1	3.155	0.003155	2029.6	2029.6	2099.3	0	2099.3	4.4298	4.4298

TABLE A-4**Properties of Superheated Water Vapor**

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p = 0.06 bar = 0.006 MPa</i> <i>(T_{sat} = 36.16°C)</i>								
<i>p = 0.35 bar = 0.035 MPa</i> <i>(T_{sat} = 72.69°C)</i>								
Sat.	23.739	2425.0	2567.4	8.3304	4.526	2473.0	2631.4	7.7158
80	27.132	2487.3	2650.1	8.5804	4.625	2483.7	2645.6	7.7564
120	30.219	2544.7	2726.0	8.7840	5.163	2542.4	2723.1	7.9644
160	33.302	2602.7	2802.5	8.9693	5.696	2601.2	2800.6	8.1519
200	36.383	2661.4	2879.7	9.1398	6.228	2660.4	2878.4	8.3237
240	39.462	2721.0	2957.8	9.2982	6.758	2720.3	2956.8	8.4828
280	42.540	2781.5	3036.8	9.4464	7.287	2780.9	3036.0	8.6314
320	45.618	2843.0	3116.7	9.5859	7.815	2842.5	3116.1	8.7712
360	48.696	2905.5	3197.7	9.7180	8.344	2905.1	3197.1	8.9034
400	51.774	2969.0	3279.6	9.8435	8.872	2968.6	3279.2	9.0291
440	54.851	3033.5	3362.6	9.9633	9.400	3033.2	3362.2	9.1490
500	59.467	3132.3	3489.1	10.1336	10.192	3132.1	3488.8	9.3194
<i>p = 0.70 bar = 0.07 MPa</i> <i>(T_{sat} = 89.95°C)</i>								
<i>p = 1.0 bar = 0.10 MPa</i> <i>(T_{sat} = 99.63°C)</i>								
Sat.	2.365	2494.5	2660.0	7.4797	1.694	2506.1	2675.5	7.3594
100	2.434	2509.7	2680.0	7.5341	1.696	2506.7	2676.2	7.3614
120	2.571	2539.7	2719.6	7.6375	1.793	2537.3	2716.6	7.4668
160	2.841	2599.4	2798.2	7.8279	1.984	2597.8	2796.2	7.6597
200	3.108	2659.1	2876.7	8.0012	2.172	2658.1	2875.3	7.8343
240	3.374	2719.3	2955.5	8.1611	2.359	2718.5	2954.5	7.9949
280	3.640	2780.2	3035.0	8.3162	2.546	2779.6	3034.2	8.1445
320	3.905	2842.0	3115.3	8.4504	2.732	2841.5	3114.6	8.2849
360	4.170	2904.6	3196.5	8.5828	2.917	2904.2	3195.9	8.4175
400	4.434	2968.2	3278.6	8.7086	3.103	2967.9	3278.2	8.5435
440	4.698	3032.9	3361.8	8.8286	3.288	3032.6	3361.4	8.6636
500	5.095	3131.8	3488.5	8.9991	3.565	3131.6	3488.1	8.8342
<i>p = 1.5 bar = 0.15 MPa</i> <i>(T_{sat} = 111.37°C)</i>								
<i>p = 3.0 bar = 0.30 MPa</i> <i>(T_{sat} = 133.55°C)</i>								
Sat.	1.159	2519.7	2693.6	7.2233	0.606	2543.6	2725.3	6.9919
120	1.188	2533.3	2711.4	7.2693	0.651	2587.1	2782.3	7.1276
160	1.317	2595.2	2792.8	7.4665	0.651	2587.1	2782.3	7.1276
200	1.444	2656.2	2872.9	7.6433	0.716	2650.7	2865.5	7.3115
240	1.570	2717.2	2952.7	7.8052	0.781	2713.1	2947.3	7.4774
280	1.695	2778.6	3032.8	7.9555	0.844	2775.4	3028.6	7.6299
320	1.819	2840.6	3113.5	8.0964	0.907	2838.1	3110.1	7.7722
360	1.943	2903.5	3195.0	8.2293	0.969	2901.4	3192.2	7.9061
400	2.067	2967.3	3277.4	8.3555	1.032	2965.6	3275.0	8.0330
440	2.191	3032.1	3360.7	8.4757	1.094	3030.6	3358.7	8.1538
500	2.376	3131.2	3487.6	8.6466	1.187	3130.0	3486.0	8.3251
600	2.685	3301.7	3704.3	8.9101	1.341	3300.8	3703.2	8.5892

Pressure Conversions:
1 bar = 0.1 MPa
= 10² kPa

H₂O

TABLE A-4

(Continued)

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 5.0 bar = 0.50 MPa</i> <i>(T_{sat} = 151.86°C)</i>								
Sat. 0.3749 2561.2 2748.7 6.8213 0.2729 2572.5 2763.5 6.7080								
180 0.4045	2609.7	2812.0	6.9656	0.2847	2599.8	2799.1	6.7880	
200 0.4249	2642.9	2855.4	7.0592	0.2999	2634.8	2844.8	6.8865	
240 0.4646	2707.6	2939.9	7.2307	0.3292	2701.8	2932.2	7.0641	
280 0.5034	2771.2	3022.9	7.3865	0.3574	2766.9	3017.1	7.2233	
320 0.5416	2834.7	3105.6	7.5308	0.3852	2831.3	3100.9	7.3697	
360 0.5796	2898.7	3188.4	7.6660	0.4126	2895.8	3184.7	7.5063	
400 0.6173	2963.2	3271.9	7.7938	0.4397	2960.9	3268.7	7.6350	
440 0.6548	3028.6	3356.0	7.9152	0.4667	3026.6	3353.3	7.7571	
500 0.7109	3128.4	3483.9	8.0873	0.5070	3126.8	3481.7	7.9299	
600 0.8041	3299.6	3701.7	8.3522	0.5738	3298.5	3700.2	8.1956	
700 0.8969	3477.5	3925.9	8.5952	0.6403	3476.6	3924.8	8.4391	
<i>p = 10.0 bar = 1.0 MPa</i> <i>(T_{sat} = 179.91°C)</i>								
Sat. 0.1944 2583.6 2778.1 6.5865 0.1318 2594.5 2792.2 6.4448								
200 0.2060	2621.9	2827.9	6.6940	0.1325	2598.1	2796.8	6.4546	
240 0.2275	2692.9	2920.4	6.8817	0.1483	2676.9	2899.3	6.6628	
280 0.2480	2760.2	3008.2	7.0465	0.1627	2748.6	2992.7	6.8381	
320 0.2678	2826.1	3093.9	7.1962	0.1765	2817.1	3081.9	6.9938	
360 0.2873	2891.6	3178.9	7.3349	0.1899	2884.4	3169.2	7.1363	
400 0.3066	2957.3	3263.9	7.4651	0.2030	2951.3	3255.8	7.2690	
440 0.3257	3023.6	3349.3	7.5883	0.2160	3018.5	3342.5	7.3940	
500 0.3541	3124.4	3478.5	7.7622	0.2352	3120.3	3473.1	7.5698	
540 0.3729	3192.6	3565.6	7.8720	0.2478	3189.1	3560.9	7.6805	
600 0.4011	3296.8	3697.9	8.0290	0.2668	3293.9	3694.0	7.8385	
640 0.4198	3367.4	3787.2	8.1290	0.2793	3364.8	3783.8	7.9391	
<i>p = 20.0 bar = 2.0 MPa</i> <i>(T_{sat} = 212.42°C)</i>								
Sat. 0.0996 2600.3 2799.5 6.3409 0.0667 2604.1 2804.2 6.1869								
240 0.1085	2659.6	2876.5	6.4952	0.0682	2619.7	2824.3	6.2265	
280 0.1200	2736.4	2976.4	6.6828	0.0771	2709.9	2941.3	6.4462	
320 0.1308	2807.9	3069.5	6.8452	0.0850	2788.4	3043.4	6.6245	
360 0.1411	2877.0	3159.3	6.9917	0.0923	2861.7	3138.7	6.7801	
400 0.1512	2945.2	3247.6	7.1271	0.0994	2932.8	3230.9	6.9212	
440 0.1611	3013.4	3335.5	7.2540	0.1062	3002.9	3321.5	7.0520	
500 0.1757	3116.2	3467.6	7.4317	0.1162	3108.0	3456.5	7.2338	
540 0.1853	3185.6	3556.1	7.5434	0.1227	3178.4	3546.6	7.3474	
600 0.1996	3290.9	3690.1	7.7024	0.1324	3285.0	3682.3	7.5085	
640 0.2091	3362.2	3780.4	7.8035	0.1388	3357.0	3773.5	7.6106	
700 0.2232	3470.9	3917.4	7.9487	0.1484	3466.5	3911.7	7.7571	

TABLE A-4

(Continued)

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 40 bar = 4.0 MPa</i> <i>(T_{sat} = 250.4°C)</i>								
<i>p = 60 bar = 6.0 MPa</i> <i>(T_{sat} = 275.64°C)</i>								
Sat.	0.04978	2602.3	2801.4	6.0701	0.03244	2589.7	2784.3	5.8892
280	0.05546	2680.0	2901.8	6.2568	0.03317	2605.2	2804.2	5.9252
320	0.06199	2767.4	3015.4	6.4553	0.03876	2720.0	2952.6	6.1846
360	0.06788	2845.7	3117.2	6.6215	0.04331	2811.2	3071.1	6.3782
400	0.07341	2919.9	3213.6	6.7690	0.04739	2892.9	3177.2	6.5408
440	0.07872	2992.2	3307.1	6.9041	0.05122	2970.0	3277.3	6.6853
500	0.08643	3099.5	3445.3	7.0901	0.05665	3082.2	3422.2	6.8803
540	0.09145	3171.1	3536.9	7.2056	0.06015	3156.1	3517.0	6.9999
600	0.09885	3279.1	3674.4	7.3688	0.06525	3266.9	3658.4	7.1677
640	0.1037	3351.8	3766.6	7.4720	0.06859	3341.0	3752.6	7.2731
700	0.1110	3462.1	3905.9	7.6198	0.07352	3453.1	3894.1	7.4234
740	0.1157	3536.6	3999.6	7.7141	0.07677	3528.3	3989.2	7.5190
<i>p = 80 bar = 8.0 MPa</i> <i>(T_{sat} = 295.06°C)</i>								
<i>p = 100 bar = 10.0 MPa</i> <i>(T_{sat} = 311.06°C)</i>								
Sat.	0.02352	2569.8	2758.0	5.7432	0.01803	2544.4	2724.7	5.6141
320	0.02682	2662.7	2877.2	5.9489	0.01925	2588.8	2781.3	5.7103
360	0.03089	2772.7	3019.8	6.1819	0.02331	2729.1	2962.1	6.0060
400	0.03432	2863.8	3138.3	6.3634	0.02641	2832.4	3096.5	6.2120
440	0.03742	2946.7	3246.1	6.5190	0.02911	2922.1	3213.2	6.3805
480	0.04034	3025.7	3348.4	6.6586	0.03160	3005.4	3321.4	6.5282
520	0.04313	3102.7	3447.7	6.7871	0.03394	3085.6	3425.1	6.6622
560	0.04582	3178.7	3545.3	6.9072	0.03619	3164.1	3526.0	6.7864
600	0.04845	3254.4	3642.0	7.0206	0.03837	3241.7	3625.3	6.9029
640	0.05102	3330.1	3738.3	7.1283	0.04048	3318.9	3723.7	7.0131
700	0.05481	3443.9	3882.4	7.2812	0.04358	3434.7	3870.5	7.1687
740	0.05729	3520.4	3978.7	7.3782	0.04560	3512.1	3968.1	7.2670
<i>p = 120 bar = 12.0 MPa</i> <i>(T_{sat} = 324.75°C)</i>								
<i>p = 140 bar = 14.0 MPa</i> <i>(T_{sat} = 336.75°C)</i>								
Sat.	0.01426	2513.7	2684.9	5.4924	0.01149	2476.8	2637.6	5.3717
360	0.01811	2678.4	2895.7	5.8361	0.01422	2617.4	2816.5	5.6602
400	0.02108	2798.3	3051.3	6.0747	0.01722	2760.9	3001.9	5.9448
440	0.02355	2896.1	3178.7	6.2586	0.01954	2868.6	3142.2	6.1474
480	0.02576	2984.4	3293.5	6.4154	0.02157	2962.5	3264.5	6.3143
520	0.02781	3068.0	3401.8	6.5555	0.02343	3049.8	3377.8	6.4610
560	0.02977	3149.0	3506.2	6.6840	0.02517	3133.6	3486.0	6.5941
600	0.03164	3228.7	3608.3	6.8037	0.02683	3215.4	3591.1	6.7172
640	0.03345	3307.5	3709.0	6.9164	0.02843	3296.0	3694.1	6.8326
700	0.03610	3425.2	3858.4	7.0749	0.03075	3415.7	3846.2	6.9939
740	0.03781	3503.7	3957.4	7.1746	0.03225	3495.2	3946.7	7.0952

TABLE A-4

(Continued)

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 160 bar = 16.0 MPa</i> <i>(T_{sat} = 347.44°C)</i>								
<i>p = 180 bar = 18.0 MPa</i> <i>(T_{sat} = 357.06°C)</i>								
Sat.	0.00931	2431.7	2580.6	5.2455	0.00749	2374.3	2509.1	5.1044
360	0.01105	2539.0	2715.8	5.4614	0.00809	2418.9	2564.5	5.1922
400	0.01426	2719.4	2947.6	5.8175	0.01190	2672.8	2887.0	5.6887
440	0.01652	2839.4	3103.7	6.0429	0.01414	2808.2	3062.8	5.9428
480	0.01842	2939.7	3234.4	6.2215	0.01596	2915.9	3203.2	6.1345
520	0.02013	3031.1	3353.3	6.3752	0.01757	3011.8	3378.0	6.2960
560	0.02172	3117.8	3465.4	6.5132	0.01904	3101.7	3444.4	6.4392
600	0.02323	3201.8	3573.5	6.6399	0.02042	3188.0	3555.6	6.5696
640	0.02467	3284.2	3678.9	6.7580	0.02174	3272.3	3663.6	6.6905
700	0.02674	3406.0	3833.9	6.9224	0.02362	3396.3	3821.5	6.8580
740	0.02808	3486.7	3935.9	7.0251	0.02483	3478.0	3925.0	6.9623
<i>p = 200 bar = 20.0 MPa</i> <i>(T_{sat} = 365.81°C)</i>								
<i>p = 240 bar = 24.0 MPa</i>								
Sat.	0.00583	2293.0	2409.7	4.9269	0.00673	2477.8	2639.4	5.2393
400	0.00994	2619.3	2818.1	5.5540	0.00929	2700.6	2923.4	5.6506
440	0.01222	2774.9	3019.4	5.8450	0.01100	2838.3	3102.3	5.8950
480	0.01399	2891.2	3170.8	6.0518	0.01241	2950.5	3248.5	6.0842
520	0.01551	2992.0	3302.2	6.2218	0.01366	3051.1	3379.0	6.2448
560	0.01689	3085.2	3423.0	6.3705	0.01481	3145.2	3500.7	6.3875
600	0.01818	3174.0	3537.6	6.5048	0.01588	3235.5	3616.7	6.5174
640	0.01940	3260.2	3648.1	6.6286	0.01739	3366.4	3783.8	6.6947
700	0.02113	3386.4	3809.0	6.7993	0.01835	3451.7	3892.1	6.8038
740	0.02224	3469.3	3914.1	6.9052	0.01974	3578.0	4051.6	6.9567
<i>p = 280 bar = 28.0 MPa</i>								
<i>p = 320 bar = 32.0 MPa</i>								
400	0.00383	2223.5	2330.7	4.7494	0.00236	1980.4	2055.9	4.3239
440	0.00712	2613.2	2812.6	5.4494	0.00544	2509.0	2683.0	5.2327
480	0.00885	2780.8	3028.5	5.7446	0.00722	2718.1	2949.2	5.5968
520	0.01020	2906.8	3192.3	5.9566	0.00853	2860.7	3133.7	5.8357
560	0.01136	3015.7	3333.7	6.1307	0.00963	2979.0	3287.2	6.0246
600	0.01241	3115.6	3463.0	6.2823	0.01061	3085.3	3424.6	6.1858
640	0.01338	3210.3	3584.8	6.4187	0.01150	3184.5	3552.5	6.3290
700	0.01473	3346.1	3758.4	6.6029	0.01273	3325.4	3732.8	6.5203
740	0.01558	3433.9	3870.0	6.7153	0.01350	3415.9	3847.8	6.6361
800	0.01680	3563.1	4033.4	6.8720	0.01460	3548.0	4015.1	6.7966
900	0.01873	3774.3	4298.8	7.1084	0.01633	3762.7	4285.1	7.0372

TABLE A-5**Properties of Compressed Liquid Water**

T °C	v × 10 ³ m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v × 10 ³ m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 25 bar = 2.5 MPa</i> <i>(T_{sat} = 223.99°C)</i>								
<i>p = 50 bar = 5.0 MPa</i> <i>(T_{sat} = 263.99°C)</i>								
20	1.0006	83.80	86.30	.2961	.9995	83.65	88.65	.2956
40	1.0067	167.25	169.77	.5715	1.0056	166.95	171.97	.5705
80	1.0280	334.29	336.86	1.0737	1.0268	333.72	338.85	1.0720
100	1.0423	418.24	420.85	1.3050	1.0410	417.52	422.72	1.3030
140	1.0784	587.82	590.52	1.7369	1.0768	586.76	592.15	1.7343
180	1.1261	761.16	763.97	2.1375	1.1240	759.63	765.25	2.1341
200	1.1555	849.9	852.8	2.3294	1.1530	848.1	853.9	2.3255
220	1.1898	940.7	943.7	2.5174	1.1866	938.4	944.4	2.5128
Sat.	1.1973	959.1	962.1	2.5546	1.2859	1147.8	1154.2	2.9202
<i>p = 75 bar = 7.5 MPa</i> <i>(T_{sat} = 290.59°C)</i>								
<i>p = 100 bar = 10.0 MPa</i> <i>(T_{sat} = 311.06°C)</i>								
20	.9984	83.50	90.99	.2950	.9972	83.36	93.33	.2945
40	1.0045	166.64	174.18	.5696	1.0034	166.35	176.38	.5686
80	1.0256	333.15	340.84	1.0704	1.0245	332.59	342.83	1.0688
100	1.0397	416.81	424.62	1.3011	1.0385	416.12	426.50	1.2992
140	1.0752	585.72	593.78	1.7317	1.0737	584.68	595.42	1.7292
180	1.1219	758.13	766.55	2.1308	1.1199	756.65	767.84	2.1275
220	1.1835	936.2	945.1	2.5083	1.1805	934.1	945.9	2.5039
260	1.2696	1124.4	1134.0	2.8763	1.2645	1121.1	1133.7	2.8699
Sat.	1.3677	1282.0	1292.2	3.1649	1.4524	1393.0	1407.6	3.3596
<i>p = 150 bar = 15.0 MPa</i> <i>(T_{sat} = 342.24°C)</i>								
<i>p = 200 bar = 20.0 MPa</i> <i>(T_{sat} = 365.81°C)</i>								
20	.9950	83.06	97.99	.2934	.9928	82.77	102.62	.2923
40	1.0013	165.76	180.78	.5666	.9992	165.17	185.16	.5646
80	1.0222	331.48	346.81	1.0656	1.0199	330.40	350.80	1.0624
100	1.0361	414.74	430.28	1.2955	1.0337	413.39	434.06	1.2917
140	1.0707	582.66	598.72	1.7242	1.0678	580.69	602.04	1.7193
180	1.1159	753.76	770.50	2.1210	1.1120	750.95	773.20	2.1147
220	1.1748	929.9	947.5	2.4953	1.1693	925.9	949.3	2.4870
260	1.2550	1114.6	1133.4	2.8576	1.2462	1108.6	1133.5	2.8459
300	1.3770	1316.6	1337.3	3.2260	1.3596	1306.1	1333.3	3.2071
Sat.	1.6581	1585.6	1610.5	3.6848	2.036	1785.6	1826.3	4.0139
<i>p = 250 bar = 25 MPa</i>								
<i>p = 300 bar = 30.0 MPa</i>								
20	.9907	82.47	107.24	.2911	.9886	82.17	111.84	.2899
40	.9971	164.60	189.52	.5626	.9951	164.04	193.89	.5607
100	1.0313	412.08	437.85	1.2881	1.0290	410.78	441.66	1.2844
200	1.1344	834.5	862.8	2.2961	1.1302	831.4	865.3	2.2893
300	1.3442	1296.6	1330.2	3.1900	1.3304	1287.9	1327.8	3.1741

Pressure Conversions:
1 bar = 0.1 MPa
= 10² kPa

H₂O

TABLE A-6**Properties of Saturated Water (Solid-Vapor): Temperature Table**

Temp. °C	Pressure kPa	Specific Volume m ³ /kg				Internal Energy kJ/kg				Enthalpy kJ/kg				Entropy kJ/kg · K	
		Sat. Solid $v_i \times 10^3$	Sat. Vapor v_g	Sat. Solid u_i	Sat. Vapor u_{fg}	Sat. Solid h_i	Sat. Vapor h_{fg}	Sat. Solid s_i	Sat. Vapor s_{fg}	Sat. Solid s_i	Sat. Vapor s_{fg}	Subl. s_{fg}	Subl. s_g	Sat. Vapor s_g	
.01	.6113	1.0908	206.1	-333.40	2708.7	2375.3	-333.40	2834.8	2501.4	-1.221	10.378	9.156			
0	.6108	1.0908	206.3	-333.43	2708.8	2375.3	-333.43	2834.8	2501.3	-1.221	10.378	9.157			
-2	.5176	1.0904	241.7	-337.62	2710.2	2372.6	-337.62	2835.3	2497.7	-1.237	10.456	9.219			
-4	.4375	1.0901	283.8	-341.78	2711.6	2369.8	-341.78	2835.7	2494.0	-1.253	10.536	9.283			
-6	.3689	1.0898	334.2	-345.91	2712.9	2367.0	-345.91	2836.2	2490.3	-1.268	10.616	9.348			
-8	.3102	1.0894	394.4	-350.02	2714.2	2364.2	-350.02	2836.6	2486.6	-1.284	10.698	9.414			
-10	.2602	1.0891	466.7	-354.09	2715.5	2361.4	-354.09	2837.0	2482.9	-1.299	10.781	9.481			
-12	.2176	1.0888	553.7	-358.14	2716.8	2358.7	-358.14	2837.3	2479.2	-1.315	10.865	9.550			
-14	.1815	1.0884	658.8	-362.15	2718.0	2355.9	-362.15	2837.6	2475.5	-1.331	10.950	9.619			
-16	.1510	1.0881	786.0	-366.14	2719.2	2353.1	-366.14	2837.9	2471.8	-1.346	11.036	9.690			
-18	.1252	1.0878	940.5	-370.10	2720.4	2350.3	-370.10	2838.2	2468.1	-1.362	11.123	9.762			
-20	.1035	1.0874	1128.6	-374.03	2721.6	2347.5	-374.03	2838.4	2464.3	-1.377	11.212	9.835			
-22	.0853	1.0871	1358.4	-377.93	2722.7	2344.7	-377.93	2838.6	2460.6	-1.393	11.302	9.909			
-24	.0701	1.0868	1640.1	-381.80	2723.7	2342.0	-381.80	2838.7	2456.9	-1.408	11.394	9.985			
-26	.0574	1.0864	1986.4	-385.64	2724.8	2339.2	-385.64	2838.9	2453.2	-1.424	11.486	10.062			
-28	.0469	1.0861	2413.7	-389.45	2725.8	2336.4	-389.45	2839.0	2449.5	-1.439	11.580	10.141			
-30	.0381	1.0858	2943	-393.23	2726.8	2333.6	-393.23	2839.0	2445.8	-1.455	11.676	10.221			
-32	.0309	1.0854	3600	-396.98	2727.8	2330.8	-396.98	2839.1	2442.1	-1.471	11.773	10.303			
-34	.0250	1.0851	4419	-400.71	2728.7	2328.0	-400.71	2839.1	2438.4	-1.486	11.872	10.386			
-36	.0201	1.0848	5444	-404.40	2729.6	2325.2	-404.40	2839.1	2434.7	-1.501	11.972	10.470			
-38	.0161	1.0844	6731	-408.06	2730.5	2322.4	-408.06	2839.0	2430.9	-1.517	12.073	10.556			
-40	.0129	1.0841	8354	-411.70	2731.3	2319.6	-411.70	2838.9	2427.2	-1.532	12.176	10.644			

Source: J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York, 1978.

TABLE A-7

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

Properties of Saturated Refrigerant 22 (Liquid–Vapor): Temperature Table

Temp. °C	Press. bar	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Temp. °C
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Sat. Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
-60	0.3749	0.6833	0.5370	-21.57	203.67	-21.55	245.35	223.81	-0.0964	1.0547
-50	0.6451	0.6966	0.3239	-10.89	207.70	-10.85	239.44	228.60	-0.0474	1.0256
-45	0.8290	0.7037	0.2564	-5.50	209.70	-5.44	236.39	230.95	-0.0235	1.0126
-40	1.0522	0.7109	0.2052	-0.07	211.68	0.00	233.27	233.27	0.0000	1.0005
-36	1.2627	0.7169	0.1730	4.29	213.25	4.38	230.71	235.09	0.0186	0.9914
-32	1.5049	0.7231	0.1468	8.68	214.80	8.79	228.10	236.89	0.0369	0.9828
-30	1.6389	0.7262	0.1355	10.88	215.58	11.00	226.77	237.78	0.0460	0.9787
-28	1.7819	0.7294	0.1252	13.09	216.34	13.22	225.43	238.66	0.0551	0.9746
-26	1.9345	0.7327	0.1159	15.31	217.11	15.45	224.08	239.53	0.0641	0.9707
-22	2.2698	0.7393	0.0997	19.76	218.62	19.92	221.32	241.24	0.0819	0.9631
-20	2.4534	0.7427	0.0926	21.99	219.37	22.17	219.91	242.09	0.0908	0.9595
-18	2.6482	0.7462	0.0861	24.23	220.11	24.43	218.49	242.92	0.0996	0.9559
-16	2.8547	0.7497	0.0802	26.48	220.85	26.69	217.05	243.74	0.1084	0.9525
-14	3.0733	0.7533	0.0748	28.73	221.58	28.97	215.59	244.56	0.1171	0.9490
-12	3.3044	0.7569	0.0698	31.00	222.30	31.25	214.11	245.36	0.1258	0.9457
-10	3.5485	0.7606	0.0652	33.27	223.02	33.54	212.62	246.15	0.1345	0.9424
-8	3.8062	0.7644	0.0610	35.54	223.73	35.83	211.10	246.93	0.1431	0.9392
-6	4.0777	0.7683	0.0571	37.83	224.43	38.14	209.56	247.70	0.1517	0.9361
-4	4.3638	0.7722	0.0535	40.12	225.13	40.46	208.00	248.45	0.1602	0.9330
-2	4.6647	0.7762	0.0501	42.42	225.82	42.78	206.41	249.20	0.1688	0.9300
0	4.9811	0.7803	0.0470	44.73	226.50	45.12	204.81	249.92	0.1773	0.9271
2	5.3133	0.7844	0.0442	47.04	227.17	47.46	203.18	250.64	0.1857	0.9241
4	5.6619	0.7887	0.0415	49.37	227.83	49.82	201.52	251.34	0.1941	0.9213
6	6.0275	0.7930	0.0391	51.71	228.48	52.18	199.84	252.03	0.2025	0.9184
8	6.4105	0.7974	0.0368	54.05	229.13	54.56	198.14	252.70	0.2109	0.9157
10	6.8113	0.8020	0.0346	56.40	229.76	56.95	196.40	253.35	0.2193	0.9129
12	7.2307	0.8066	0.0326	58.77	230.38	59.35	194.64	253.99	0.2276	0.9102
16	8.1268	0.8162	0.0291	63.53	231.59	64.19	191.02	255.21	0.2442	0.9048
20	9.1030	0.8263	0.0259	68.33	232.76	69.09	187.28	256.37	0.2607	0.8996
24	10.164	0.8369	0.0232	73.19	233.87	74.04	183.40	257.44	0.2772	0.8944
28	11.313	0.8480	0.0208	78.09	234.92	79.05	179.37	258.43	0.2936	0.8893
32	12.556	0.8599	0.0186	83.06	235.91	84.14	175.18	259.32	0.3101	0.8842
36	13.897	0.8724	0.0168	88.08	236.83	89.29	170.82	260.11	0.3265	0.8790
40	15.341	0.8858	0.0151	93.18	237.66	94.53	166.25	260.79	0.3429	0.8738
45	17.298	0.9039	0.0132	99.65	238.59	101.21	160.24	261.46	0.3635	0.8672
50	19.433	0.9238	0.0116	106.26	239.34	108.06	153.84	261.90	0.3842	0.8603
60	24.281	0.9705	0.0089	120.00	240.24	122.35	139.61	261.96	0.4264	0.8455

R-22

Source: Tables A-7 through A-9 are calculated based on equations from A. Kamei and S. W. Beyerlein, "A Fundamental Equation for Chlorodifluoromethane (R-22)," *Fluid Phase Equilibria*, Vol. 80, No. 11, 1992, pp. 71–86.

TABLE A-8**Properties of Saturated Refrigerant 22 (Liquid–Vapor): Pressure Table**

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

R-22

Press. bar	Temp. °C	Specific Volume m^3/kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy $kJ/kg \cdot K$		Press. bar
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
0.40	-58.86	0.6847	0.5056	-20.36	204.13	-20.34	244.69	224.36	-0.0907	1.0512
0.50	-54.83	0.6901	0.4107	-16.07	205.76	-16.03	242.33	226.30	-0.0709	1.0391
0.60	-51.40	0.6947	0.3466	-12.39	207.14	-12.35	240.28	227.93	-0.0542	1.0294
0.70	-48.40	0.6989	0.3002	-9.17	208.34	-9.12	238.47	229.35	-0.0397	1.0213
0.80	-45.73	0.7026	0.2650	-6.28	209.41	-6.23	236.84	230.61	-0.0270	1.0144
0.90	-43.30	0.7061	0.2374	-3.66	210.37	-3.60	235.34	231.74	-0.0155	1.0084
1.00	-41.09	0.7093	0.2152	-1.26	211.25	-1.19	233.95	232.77	-0.0051	1.0031
1.25	-36.23	0.7166	0.1746	4.04	213.16	4.13	230.86	234.99	0.0175	0.9919
1.50	-32.08	0.7230	0.1472	8.60	214.77	8.70	228.15	236.86	0.0366	0.9830
1.75	-28.44	0.7287	0.1274	12.61	216.18	12.74	225.73	238.47	0.0531	0.9755
2.00	-25.18	0.7340	0.1123	16.22	217.42	16.37	223.52	239.88	0.0678	0.9691
2.25	-22.22	0.7389	0.1005	19.51	218.53	19.67	221.47	241.15	0.0809	0.9636
2.50	-19.51	0.7436	0.0910	22.54	219.55	22.72	219.57	242.29	0.0930	0.9586
2.75	-17.00	0.7479	0.0831	25.36	220.48	25.56	217.77	243.33	0.1040	0.9542
3.00	-14.66	0.7521	0.0765	27.99	221.34	28.22	216.07	244.29	0.1143	0.9502
3.25	-12.46	0.7561	0.0709	30.47	222.13	30.72	214.46	245.18	0.1238	0.9465
3.50	-10.39	0.7599	0.0661	32.82	222.88	33.09	212.91	246.00	0.1328	0.9431
3.75	-8.43	0.7636	0.0618	35.06	223.58	35.34	211.42	246.77	0.1413	0.9399
4.00	-6.56	0.7672	0.0581	37.18	224.24	37.49	209.99	247.48	0.1493	0.9370
4.25	-4.78	0.7706	0.0548	39.22	224.86	39.55	208.61	248.16	0.1569	0.9342
4.50	-3.08	0.7740	0.0519	41.17	225.45	41.52	207.27	248.80	0.1642	0.9316
4.75	-1.45	0.7773	0.0492	43.05	226.00	43.42	205.98	249.40	0.1711	0.9292
5.00	0.12	0.7805	0.0469	44.86	226.54	45.25	204.71	249.97	0.1777	0.9269
5.25	1.63	0.7836	0.0447	46.61	227.04	47.02	203.48	250.51	0.1841	0.9247
5.50	3.08	0.7867	0.0427	48.30	227.53	48.74	202.28	251.02	0.1903	0.9226
5.75	4.49	0.7897	0.0409	49.94	227.99	50.40	201.11	251.51	0.1962	0.9206
6.00	5.85	0.7927	0.0392	51.53	228.44	52.01	199.97	251.98	0.2019	0.9186
7.00	10.91	0.8041	0.0337	57.48	230.04	58.04	195.60	253.64	0.2231	0.9117
8.00	15.45	0.8149	0.0295	62.88	231.43	63.53	191.52	255.05	0.2419	0.9056
9.00	19.59	0.8252	0.0262	67.84	232.64	68.59	187.67	256.25	0.2591	0.9001
10.00	23.40	0.8352	0.0236	72.46	233.71	73.30	183.99	257.28	0.2748	0.8952
12.00	30.25	0.8546	0.0195	80.87	235.48	81.90	177.04	258.94	0.3029	0.8864
14.00	36.29	0.8734	0.0166	88.45	236.89	89.68	170.49	260.16	0.3277	0.8786
16.00	41.73	0.8919	0.0144	95.41	238.00	96.83	164.21	261.04	0.3500	0.8715
18.00	46.69	0.9104	0.0127	101.87	238.86	103.51	158.13	261.64	0.3705	0.8649
20.00	51.26	0.9291	0.0112	107.95	239.51	109.81	152.17	261.98	0.3895	0.8586
24.00	59.46	0.9677	0.0091	119.24	240.22	121.56	140.43	261.99	0.4241	0.8463

TABLE A-9**Properties of Superheated Refrigerant 22 Vapor**

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p = 0.4 bar = 0.04 MPa</i> <i>(T_{sat} = -58.86°C)</i>								
<i>p = 0.6 bar = 0.06 MPa</i> <i>(T_{sat} = -51.40°C)</i>								
Sat.	0.50559	204.13	224.36	1.0512	0.34656	207.14	227.93	1.0294
-55	0.51532	205.92	226.53	1.0612	0.34895	207.80	228.74	1.0330
-50	0.52787	208.26	229.38	1.0741				
-45	0.54037	210.63	232.24	1.0868	0.35747	210.20	231.65	1.0459
-40	0.55284	213.02	235.13	1.0993	0.36594	212.62	234.58	1.0586
-35	0.56526	215.43	238.05	1.1117	0.37437	215.06	237.52	1.0711
-30	0.57766	217.88	240.99	1.1239	0.38277	217.53	240.49	1.0835
-25	0.59002	220.35	243.95	1.1360	0.39114	220.02	243.49	1.0956
-20	0.60236	222.85	246.95	1.1479	0.39948	222.54	246.51	1.1077
-15	0.61468	225.38	249.97	1.1597	0.40779	225.08	249.55	1.1196
-10	0.62697	227.93	253.01	1.1714	0.41608	227.65	252.62	1.1314
-5	0.63925	230.52	256.09	1.1830	0.42436	230.25	255.71	1.1430
0	0.65151	233.13	259.19	1.1944	0.43261	232.88	258.83	1.1545
<i>p = 0.8 bar = 0.08 MPa</i> <i>(T_{sat} = -45.73°C)</i>								
<i>p = 1.0 bar = 0.10 MPa</i> <i>(T_{sat} = -41.09°C)</i>								
Sat.	0.26503	209.41	230.61	1.0144	0.21518	211.25	232.77	1.0031
-45	0.26597	209.76	231.04	1.0163	0.21633	211.79	233.42	1.0059
-40	0.27245	212.21	234.01	1.0292				
-35	0.27890	214.68	236.99	1.0418	0.22158	214.29	236.44	1.0187
-30	0.28530	217.17	239.99	1.0543	0.22679	216.80	239.48	1.0313
-25	0.29167	219.68	243.02	1.0666	0.23197	219.34	242.54	1.0438
-20	0.29801	222.22	246.06	1.0788	0.23712	221.90	245.61	1.0560
-15	0.30433	224.78	249.13	1.0908	0.24224	224.48	248.70	1.0681
-10	0.31062	227.37	252.22	1.1026	0.24734	227.08	251.82	1.0801
-5	0.31690	229.98	255.34	1.1143	0.25241	229.71	254.95	1.0919
0	0.32315	232.62	258.47	1.1259	0.25747	232.36	258.11	1.1035
5	0.32939	235.29	261.64	1.1374	0.26251	235.04	261.29	1.1151
10	0.33561	237.98	264.83	1.1488	0.26753	237.74	264.50	1.1265
<i>p = 1.5 bar = 0.15 MPa</i> <i>(T_{sat} = -32.08°C)</i>								
<i>p = 2.0 bar = 0.20 MPa</i> <i>(T_{sat} = -25.18°C)</i>								
Sat.	0.14721	214.77	236.86	0.9830	0.11232	217.42	239.88	0.9691
-30	0.14872	215.85	238.16	0.9883	0.11242	217.51	240.00	0.9696
-25	0.15232	218.45	241.30	1.0011				
-20	0.15588	221.07	244.45	1.0137	0.11520	220.19	243.23	0.9825
-15	0.15941	223.70	247.61	1.0260	0.11795	222.88	246.47	0.9952
-10	0.16292	226.35	250.78	1.0382	0.12067	225.58	249.72	1.0076
-5	0.16640	229.02	253.98	1.0502	0.12336	228.30	252.97	1.0199
0	0.16987	231.70	257.18	1.0621	0.12603	231.03	256.23	1.0310
5	0.17331	234.42	260.41	1.0738	0.12868	233.78	259.51	1.0438
10	0.17674	237.15	263.66	1.0854	0.13132	236.54	262.81	1.0555
15	0.18015	239.91	266.93	1.0968	0.13393	239.33	266.12	1.0671
20	0.18355	242.69	270.22	1.1081	0.13653	242.14	269.44	1.0786
25	0.18693	245.49	273.53	1.1193	0.13912	244.97	272.79	1.0899

Pressure Conversions:
1 bar = 0.1 MPa
= 10⁵ Pa
= 10² kPa

TABLE A-9

(Continued)

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 2.5 bar = 0.25 MPa</i> <i>(T_{sat} = -19.51°C)</i>								
<i>p = 3.0 bar = 0.30 MPa</i> <i>(T_{sat} = -14.66°C)</i>								
Sat.	0.09097	219.55	242.29	0.9586	0.07651	221.34	244.29	0.9502
-15	0.09303	222.03	245.29	0.9703				
-10	0.09528	224.79	248.61	0.9831	0.07833	223.96	247.46	0.9623
-5	0.09751	227.55	251.93	0.9956	0.08025	226.78	250.86	0.9751
0	0.09971	230.33	255.26	1.0078	0.08214	229.61	254.25	0.9876
5	0.10189	233.12	258.59	1.0199	0.08400	232.44	257.64	0.9999
10	0.10405	235.92	261.93	1.0318	0.08585	235.28	261.04	1.0120
15	0.10619	238.74	265.29	1.0436	0.08767	238.14	264.44	1.0239
20	0.10831	241.58	268.66	1.0552	0.08949	241.01	267.85	1.0357
25	0.11043	244.44	272.04	1.0666	0.09128	243.89	271.28	1.0472
30	0.11253	247.31	275.44	1.0779	0.09307	246.80	274.72	1.0587
35	0.11461	250.21	278.86	1.0891	0.09484	249.72	278.17	1.0700
40	0.11669	253.13	282.30	1.1002	0.09660	252.66	281.64	1.0811
<i>p = 3.5 bar = 0.35 MPa</i> <i>(T_{sat} = -10.39°C)</i>								
<i>p = 4.0 bar = 0.40 MPa</i> <i>(T_{sat} = -6.56°C)</i>								
Sat.	0.06605	222.88	246.00	0.9431	0.05812	224.24	247.48	0.9370
-10	0.06619	223.10	246.27	0.9441				
-5	0.06789	225.99	249.75	0.9572	0.05860	225.16	248.60	0.9411
0	0.06956	228.86	253.21	0.9700	0.06011	228.09	252.14	0.9542
5	0.07121	231.74	256.67	0.9825	0.06160	231.02	225.66	0.9670
10	0.07284	234.63	260.12	0.9948	0.06306	233.95	259.18	0.9795
15	0.07444	237.52	263.57	1.0069	0.06450	236.89	262.69	0.9918
20	0.07603	240.42	267.03	1.0188	0.06592	239.83	266.19	1.0039
25	0.07760	243.34	270.50	1.0305	0.06733	242.77	269.71	1.0158
30	0.07916	246.27	273.97	1.0421	0.06872	245.73	273.22	1.0274
35	0.08070	249.22	277.46	1.0535	0.07010	248.71	276.75	1.0390
40	0.08224	252.18	280.97	1.0648	0.07146	251.70	280.28	1.0504
45	0.08376	255.17	284.48	1.0759	0.07282	254.70	283.83	1.0616
<i>p = 4.5 bar = 0.45 MPa</i> <i>(T_{sat} = -3.08°C)</i>								
<i>p = 5.0 bar = 0.50 MPa</i> <i>(T_{sat} = 0.12°C)</i>								
Sat.	0.05189	225.45	248.80	0.9316	0.04686	226.54	249.97	0.9269
0	0.05275	227.29	251.03	0.9399				
5	0.05411	230.28	254.63	0.9529	0.04810	229.52	253.57	0.9399
10	0.05545	233.26	258.21	0.9657	0.04934	232.55	257.22	0.9530
15	0.05676	236.24	261.78	0.9782	0.05056	235.57	260.85	0.9657
20	0.05805	239.22	265.34	0.9904	0.05175	238.59	264.47	0.9781
25	0.05933	242.20	268.90	1.0025	0.05293	241.61	268.07	0.9903
30	0.06059	245.19	272.46	1.0143	0.05409	244.63	271.68	1.0023
35	0.06184	248.19	276.02	1.0259	0.05523	247.66	275.28	1.0141
40	0.06308	251.20	279.59	1.0374	0.05636	250.70	278.89	1.0257
45	0.06430	254.23	283.17	1.0488	0.05748	253.76	282.50	1.0371
50	0.06552	257.28	286.76	1.0600	0.05859	256.82	286.12	1.0484
55	0.06672	260.34	290.36	1.0710	0.05969	259.90	289.75	1.0595

TABLE A-9

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 5.5 bar = 0.55 MPa (T _{sat} = 3.08°C)								
<i>p</i> = 6.0 bar = 0.60 MPa (T _{sat} = 5.85°C)								
Sat.	0.04271	227.53	251.02	0.9226	0.03923	228.44	251.98	0.9186
5	0.04317	228.72	252.46	0.9278				
10	0.04433	231.81	256.20	0.9411	0.04015	231.05	255.14	0.9299
15	0.04547	234.89	259.90	0.9540	0.04122	234.18	258.91	0.9431
20	0.04658	237.95	263.57	0.9667	0.04227	237.29	262.65	0.9560
25	0.04768	241.01	267.23	0.9790	0.04330	240.39	266.37	0.9685
30	0.04875	244.07	270.88	0.9912	0.04431	243.49	270.07	0.9808
35	0.04982	247.13	274.53	1.0031	0.04530	246.58	273.76	0.9929
40	0.05086	250.20	278.17	1.0148	0.04628	249.68	277.45	1.0048
45	0.05190	253.27	281.82	1.0264	0.04724	252.78	281.13	1.0164
50	0.05293	256.36	285.47	1.0378	0.04820	255.90	284.82	1.0279
55	0.05394	259.46	289.13	1.0490	0.04914	259.02	288.51	1.0393
60	0.05495	262.58	292.80	1.0601	0.05008	262.15	292.20	1.0504
<i>p</i> = 7.0 bar = 0.70 MPa (T _{sat} = 10.91°C)								
<i>p</i> = 8.0 bar = 0.80 MPa (T _{sat} = 15.45°C)								
Sat.	0.03371	230.04	253.64	0.9117	0.02953	231.43	255.05	0.9056
15	0.03451	232.70	256.86	0.9229				
20	0.03547	235.92	260.75	0.9363	0.03033	234.47	258.74	0.9182
25	0.03639	239.12	264.59	0.9493	0.03118	237.76	262.70	0.9315
30	0.03730	242.29	268.40	0.9619	0.03202	241.04	266.66	0.9448
35	0.03819	245.46	272.19	0.9743	0.03283	244.28	270.54	0.9574
40	0.03906	248.62	275.96	0.9865	0.03363	247.52	274.42	0.9700
45	0.03992	251.78	279.72	0.9984	0.03440	250.74	278.26	0.9821
50	0.04076	254.94	283.48	1.0101	0.03517	253.96	282.10	0.9941
55	0.04160	258.11	287.23	1.0216	0.03592	257.18	285.92	1.0058
60	0.04242	261.29	290.99	1.0330	0.03667	260.40	289.74	1.0174
65	0.04324	264.48	294.75	1.0442	0.03741	263.64	293.56	1.0287
70	0.04405	267.68	298.51	1.0552	0.03814	266.87	297.38	1.0400
<i>p</i> = 9.0 bar = 0.90 MPa (T _{sat} = 19.59°C)								
<i>p</i> = 10.0 bar = 1.00 MPa (T _{sat} = 23.40°C)								
Sat.	0.02623	232.64	256.25	0.9001	0.02358	233.71	257.28	0.8952
20	0.02630	232.92	256.59	0.9013				
30	0.02789	239.73	264.83	0.9289	0.02457	238.34	262.91	0.9139
40	0.02939	246.37	272.82	0.9549	0.02598	245.18	271.17	0.9407
50	0.03082	252.95	280.68	0.9795	0.02732	251.90	279.22	0.9660
60	0.03219	259.49	288.46	1.0033	0.02860	258.56	287.15	0.9902
70	0.03353	266.04	296.21	1.0262	0.02984	265.19	295.03	1.0135
80	0.03483	272.62	303.96	1.0484	0.03104	271.84	302.88	1.0361
90	0.03611	279.23	311.73	1.0701	0.03221	278.52	310.74	1.0580
100	0.03736	285.90	319.53	1.0913	0.03337	285.24	318.61	1.0794
110	0.03860	292.63	327.37	1.1120	0.03450	292.02	326.52	1.1003
120	0.03982	299.42	335.26	1.1323	0.03562	298.85	334.46	1.1207
130	0.04103	306.28	343.21	1.1523	0.03672	305.74	342.46	1.1408
140	0.04223	313.21	351.22	1.1719	0.03781	312.70	350.51	1.1605
150	0.04342	320.21	359.29	1.1912	0.03889	319.74	358.63	1.1790

TABLE A-9

(Continued)

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 12.0 bar = 1.20 MPa</i> <i>(T_{sat} = 30.25°C)</i>								
<i>p = 14.0 bar = 1.40 MPa</i> <i>(T_{sat} = 36.29°C)</i>								
Sat.	0.01955	235.48	258.94	0.8864	0.01662	236.89	260.16	0.8786
40	0.02083	242.63	267.62	0.9146	0.01708	239.78	263.70	0.8900
50	0.02204	249.69	276.14	0.9413	0.01823	247.29	272.81	0.9186
60	0.02319	256.60	284.43	0.9666	0.01929	254.52	281.53	0.9452
70	0.02428	263.44	292.58	0.9907	0.02029	261.60	290.01	0.9703
80	0.02534	270.25	300.66	1.0139	0.02125	268.60	298.34	0.9942
90	0.02636	277.07	308.70	1.0363	0.02217	275.56	306.60	1.0172
100	0.02736	283.90	316.73	1.0582	0.02306	282.52	314.80	1.0395
110	0.02834	290.77	324.78	1.0794	0.02393	289.49	323.00	1.0612
120	0.02930	297.69	332.85	1.1002	0.02478	296.50	331.19	1.0823
130	0.03024	304.65	340.95	1.1205	0.02562	303.55	339.41	1.1029
140	0.03118	311.68	349.09	1.1405	0.02644	310.64	347.65	1.1231
150	0.03210	318.77	357.29	1.1601	0.02725	317.79	355.94	1.1429
160	0.03301	325.92	365.54	1.1793	0.02805	324.99	364.26	1.1624
170	0.03392	333.14	373.84	1.1983	0.02884	332.26	372.64	1.1815
<i>p = 16.0 bar = 1.60 MPa</i> <i>(T_{sat} = 41.73°C)</i>								
<i>p = 18.0 bar = 1.80 MPa</i> <i>(T_{sat} = 46.69°C)</i>								
Sat.	0.01440	238.00	261.04	0.8715	0.01265	238.86	261.64	0.8649
50	0.01533	244.66	269.18	0.8971	0.01301	241.72	265.14	0.8758
60	0.01634	252.29	278.43	0.9252	0.01401	249.86	275.09	0.9061
70	0.01728	259.65	287.30	0.9515	0.01492	257.57	284.43	0.9337
80	0.01817	266.86	295.93	0.9762	0.01576	265.04	293.40	0.9595
90	0.01901	274.00	304.42	0.9999	0.01655	272.37	302.16	0.9839
100	0.01983	281.09	312.82	1.0228	0.01731	279.62	310.77	1.0073
110	0.02062	288.18	321.17	1.0448	0.01804	286.83	319.30	1.0299
120	0.02139	295.28	329.51	1.0663	0.01874	294.04	327.78	1.0517
130	0.02214	302.41	337.84	1.0872	0.01943	301.26	336.24	1.0730
140	0.02288	309.58	346.19	1.1077	0.02011	308.50	344.70	1.0937
150	0.02361	316.79	354.56	1.1277	0.02077	315.78	353.17	1.1139
160	0.02432	324.05	362.97	1.1473	0.02142	323.10	361.66	1.1338
170	0.02503	331.37	371.42	1.1666	0.02207	330.47	370.19	1.1532
<i>p = 20.0 bar = 2.00 MPa</i> <i>(T_{sat} = 51.26°C)</i>								
<i>p = 24.0 bar = 2.4 MPa</i> <i>(T_{sat} = 59.46°C)</i>								
Sat.	0.01124	239.51	261.98	0.8586	0.00907	240.22	261.99	0.8463
60	0.01212	247.20	271.43	0.8873	0.00913	240.78	262.68	0.8484
70	0.01300	255.35	281.36	0.9167	0.01006	250.30	274.43	0.8831
80	0.01381	263.12	290.74	0.9436	0.01085	258.89	284.93	0.9133
90	0.01457	270.67	299.80	0.9689	0.01156	267.01	294.75	0.9407
100	0.01528	278.09	308.65	0.9929	0.01222	274.85	304.18	0.9663
110	0.01596	285.44	317.37	1.0160	0.01284	282.53	313.35	0.9906
120	0.01663	292.76	326.01	1.0383	0.01343	290.11	322.35	1.0137
130	0.01727	300.08	334.61	1.0598	0.01400	297.64	331.25	1.0361
140	0.01789	307.40	343.19	1.0808	0.01456	305.14	340.08	1.0577
150	0.01850	314.75	351.76	1.1013	0.01509	312.64	348.87	1.0787
160	0.01910	322.14	360.34	1.1214	0.01562	320.16	357.64	1.0992
170	0.01969	329.56	368.95	1.1410	0.01613	327.70	366.41	1.1192
180	0.02027	337.03	377.58	1.1603	0.01663	335.27	375.20	1.1388

TABLE A-10

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

Properties of Saturated Refrigerant 134a (Liquid–Vapor): Temperature Table

Temp. °C	Press. bar	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Temp. °C
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Sat. Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
-40	0.5164	0.7055	0.3569	-0.04	204.45	0.00	222.88	222.88	0.0000	0.9560
-36	0.6332	0.7113	0.2947	4.68	206.73	4.73	220.67	225.40	0.0201	0.9506
-32	0.7704	0.7172	0.2451	9.47	209.01	9.52	218.37	227.90	0.0401	0.9456
-28	0.9305	0.7233	0.2052	14.31	211.29	14.37	216.01	230.38	0.0600	0.9411
-26	1.0199	0.7265	0.1882	16.75	212.43	16.82	214.80	231.62	0.0699	0.9390
-24	1.1160	0.7296	0.1728	19.21	213.57	19.29	213.57	232.85	0.0798	0.9370
-22	1.2192	0.7328	0.1590	21.68	214.70	21.77	212.32	234.08	0.0897	0.9351
-20	1.3299	0.7361	0.1464	24.17	215.84	24.26	211.05	235.31	0.0996	0.9332
-18	1.4483	0.7395	0.1350	26.67	216.97	26.77	209.76	236.53	0.1094	0.9315
-16	1.5748	0.7428	0.1247	29.18	218.10	29.30	208.45	237.74	0.1192	0.9298
-12	1.8540	0.7498	0.1068	34.25	220.36	34.39	205.77	240.15	0.1388	0.9267
-8	2.1704	0.7569	0.0919	39.38	222.60	39.54	203.00	242.54	0.1583	0.9239
-4	2.5274	0.7644	0.0794	44.56	224.84	44.75	200.15	244.90	0.1777	0.9213
0	2.9282	0.7721	0.0689	49.79	227.06	50.02	197.21	247.23	0.1970	0.9190
4	3.3765	0.7801	0.0600	55.08	229.27	55.35	194.19	249.53	0.2162	0.9169
8	3.8756	0.7884	0.0525	60.43	231.46	60.73	191.07	251.80	0.2354	0.9150
12	4.4294	0.7971	0.0460	65.83	233.63	66.18	187.85	254.03	0.2545	0.9132
16	5.0416	0.8062	0.0405	71.29	235.78	71.69	184.52	256.22	0.2735	0.9116
20	5.7160	0.8157	0.0358	76.80	237.91	77.26	181.09	258.36	0.2924	0.9102
24	6.4566	0.8257	0.0317	82.37	240.01	82.90	177.55	260.45	0.3113	0.9089
26	6.8530	0.8309	0.0298	85.18	241.05	85.75	175.73	261.48	0.3208	0.9082
28	7.2675	0.8362	0.0281	88.00	242.08	88.61	173.89	262.50	0.3302	0.9076
30	7.7006	0.8417	0.0265	90.84	243.10	91.49	172.00	263.50	0.3396	0.9070
32	8.1528	0.8473	0.0250	93.70	244.12	94.39	170.09	264.48	0.3490	0.9064
34	8.6247	0.8530	0.0236	96.58	245.12	97.31	168.14	265.45	0.3584	0.9058
36	9.1168	0.8590	0.0223	99.47	246.11	100.25	166.15	266.40	0.3678	0.9053
38	9.6298	0.8651	0.0210	102.38	247.09	103.21	164.12	267.33	0.3772	0.9047
40	10.164	0.8714	0.0199	105.30	248.06	106.19	162.05	268.24	0.3866	0.9041
42	10.720	0.8780	0.0188	108.25	249.02	109.19	159.94	269.14	0.3960	0.9035
44	11.299	0.8847	0.0177	111.22	249.96	112.22	157.79	270.01	0.4054	0.9030
48	12.526	0.8989	0.0159	117.22	251.79	118.35	153.33	271.68	0.4243	0.9017
52	13.851	0.9142	0.0142	123.31	253.55	124.58	148.66	273.24	0.4432	0.9004
56	15.278	0.9308	0.0127	129.51	255.23	130.93	143.75	274.68	0.4622	0.8990
60	16.813	0.9488	0.0114	135.82	256.81	137.42	138.57	275.99	0.4814	0.8973
70	21.162	1.0027	0.0086	152.22	260.15	154.34	124.08	278.43	0.5302	0.8918
80	26.324	1.0766	0.0064	169.88	262.14	172.71	106.41	279.12	0.5814	0.8827
90	32.435	1.1949	0.0046	189.82	261.34	193.69	82.63	276.32	0.6380	0.8655
100	39.742	1.5443	0.0027	218.60	248.49	224.74	34.40	259.13	0.7196	0.8117

R-134a

Source: Tables A-10 through A-12 are calculated based on equations from D. P. Wilson and R. S. Basu, "Thermodynamic Properties of a New Stratospherically Safe Working Fluid—Refrigerant 134a," *ASHRAE Trans.*, Vol. 94, Pt. 2, 1988, pp. 2095–2118.

TABLE A-11**Properties of Saturated Refrigerant 134a (Liquid-Vapor): Pressure Table**

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

R-134a

Press. bar	Temp. °C	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Press. bar
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
0.6	-37.07	0.7097	0.3100	3.41	206.12	3.46	221.27	224.72	0.0147	0.9520
0.8	-31.21	0.7184	0.2366	10.41	209.46	10.47	217.92	228.39	0.0440	0.9447
1.0	-26.43	0.7258	0.1917	16.22	212.18	16.29	215.06	231.35	0.0678	0.9395
1.2	-22.36	0.7323	0.1614	21.23	214.50	21.32	212.54	233.86	0.0879	0.9354
1.4	-18.80	0.7381	0.1395	25.66	216.52	25.77	210.27	236.04	0.1055	0.9322
1.6	-15.62	0.7435	0.1229	29.66	218.32	29.78	208.19	237.97	0.1211	0.9295
1.8	-12.73	0.7485	0.1098	33.31	219.94	33.45	206.26	239.71	0.1352	0.9273
2.0	-10.09	0.7532	0.0993	36.69	221.43	36.84	204.46	241.30	0.1481	0.9253
2.4	-5.37	0.7618	0.0834	42.77	224.07	42.95	201.14	244.09	0.1710	0.9222
2.8	-1.23	0.7697	0.0719	48.18	226.38	48.39	198.13	246.52	0.1911	0.9197
3.2	2.48	0.7770	0.0632	53.06	228.43	53.31	195.35	248.66	0.2089	0.9177
3.6	5.84	0.7839	0.0564	57.54	230.28	57.82	192.76	250.58	0.2251	0.9160
4.0	8.93	0.7904	0.0509	61.69	231.97	62.00	190.32	252.32	0.2399	0.9145
5.0	15.74	0.8056	0.0409	70.93	235.64	71.33	184.74	256.07	0.2723	0.9117
6.0	21.58	0.8196	0.0341	78.99	238.74	79.48	179.71	259.19	0.2999	0.9097
7.0	26.72	0.8328	0.0292	86.19	241.42	86.78	175.07	261.85	0.3242	0.9080
8.0	31.33	0.8454	0.0255	92.75	243.78	93.42	170.73	264.15	0.3459	0.9066
9.0	35.53	0.8576	0.0226	98.79	245.88	99.56	166.62	266.18	0.3656	0.9054
10.0	39.39	0.8695	0.0202	104.42	247.77	105.29	162.68	267.97	0.3838	0.9043
12.0	46.32	0.8928	0.0166	114.69	251.03	115.76	155.23	270.99	0.4164	0.9023
14.0	52.43	0.9159	0.0140	123.98	253.74	125.26	148.14	273.40	0.4453	0.9003
16.0	57.92	0.9392	0.0121	132.52	256.00	134.02	141.31	275.33	0.4714	0.8982
18.0	62.91	0.9631	0.0105	140.49	257.88	142.22	134.60	276.83	0.4954	0.8959
20.0	67.49	0.9878	0.0093	148.02	259.41	149.99	127.95	277.94	0.5178	0.8934
25.0	77.59	1.0562	0.0069	165.48	261.84	168.12	111.06	279.17	0.5687	0.8854
30.0	86.22	1.1416	0.0053	181.88	262.16	185.30	92.71	278.01	0.6156	0.8735

TABLE A-12**Properties of Superheated Refrigerant 134a Vapor**

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p = 0.6 bar = 0.06 MPa</i> <i>(T_{sat} = -37.07°C)</i>								
<i>p = 1.0 bar = 0.10 MPa</i> <i>(T_{sat} = -26.43°C)</i>								
Sat.	0.31003	206.12	224.72	0.9520	0.19170	212.18	231.35	0.9395
-20	0.33536	217.86	237.98	1.0062	0.19770	216.77	236.54	0.9602
-10	0.34992	224.97	245.96	1.0371	0.20686	224.01	244.70	0.9918
0	0.36433	232.24	254.10	1.0675	0.21587	231.41	252.99	1.0227
10	0.37861	239.69	262.41	1.0973	0.22473	238.96	261.43	1.0531
20	0.39279	247.32	270.89	1.1267	0.23349	246.67	270.02	1.0829
30	0.40688	255.12	279.53	1.1557	0.24216	254.54	278.76	1.1122
40	0.42091	263.10	288.35	1.1844	0.25076	262.58	287.66	1.1411
50	0.43487	271.25	297.34	1.2126	0.25930	270.79	296.72	1.1696
60	0.44879	279.58	306.51	1.2405	0.26779	279.16	305.94	1.1977
70	0.46266	288.08	315.84	1.2681	0.27623	287.70	315.32	1.2254
80	0.47650	296.75	325.34	1.2954	0.28464	296.40	324.87	1.2528
90	0.49031	305.58	335.00	1.3224	0.29302	305.27	334.57	1.2799
<i>p = 1.4 bar = 0.14 MPa</i> <i>(T_{sat} = -18.80°C)</i>								
<i>p = 1.8 bar = 0.18 MPa</i> <i>(T_{sat} = -12.73°C)</i>								
Sat.	0.13945	216.52	236.04	0.9322	0.10983	219.94	239.71	0.9273
-10	0.14549	223.03	243.40	0.9606	0.11135	222.02	242.06	0.9362
0	0.15219	230.55	251.86	0.9922	0.11678	229.67	250.69	0.9684
10	0.15875	238.21	260.43	1.0230	0.12207	237.44	259.41	0.9998
20	0.16520	246.01	269.13	1.0532	0.12723	245.33	268.23	1.0304
30	0.17155	253.96	277.97	1.0828	0.13230	253.36	277.17	1.0604
40	0.17783	262.06	286.96	1.1120	0.13730	261.53	286.24	1.0898
50	0.18404	270.32	296.09	1.1407	0.14222	269.85	295.45	1.1187
60	0.19020	278.74	305.37	1.1690	0.14710	278.31	304.79	1.1472
70	0.19633	287.32	314.80	1.1969	0.15193	286.93	314.28	1.1753
80	0.20241	296.06	324.39	1.2244	0.15672	295.71	323.92	1.2030
90	0.20846	304.95	334.14	1.2516	0.16148	304.63	333.70	1.2303
100	0.21449	314.01	344.04	1.2785	0.16622	313.72	343.63	1.2573
<i>p = 2.0 bar = 0.20 MPa</i> <i>(T_{sat} = -10.09°C)</i>								
<i>p = 2.4 bar = 0.24 MPa</i> <i>(T_{sat} = -5.37°C)</i>								
Sat.	0.09933	221.43	241.30	0.9253	0.08343	224.07	244.09	0.9222
-10	0.09938	221.50	241.38	0.9256	0.08574	228.31	248.89	0.9399
0	0.10438	229.23	250.10	0.9582	0.08993	236.26	257.84	0.9721
10	0.10922	237.05	258.89	0.9898	0.09399	244.30	266.85	1.0034
20	0.11394	244.99	267.78	1.0206	0.09794	252.45	275.95	1.0339
30	0.11856	253.06	276.77	1.0508	0.10181	260.72	285.16	1.0637
40	0.12311	261.26	285.88	1.0804	0.10562	269.12	294.47	1.0930
50	0.12758	269.61	295.12	1.1094	0.10937	277.67	303.91	1.1218
60	0.13201	278.10	304.50	1.1380	0.11307	286.35	313.49	1.1501
70	0.13639	286.74	314.02	1.1661	0.11674	295.18	323.19	1.1780
80	0.14073	295.53	323.68	1.1939	0.12037	304.15	333.04	1.2055
90	0.14504	304.47	333.48	1.2212	0.12398	313.27	343.03	1.2326

Pressure Conversions:
1 bar = 0.1 MPa
= 10⁵ Pa
= 10² kPa

TABLE A-12

(Continued)

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
<i>p = 2.8 bar = 0.28 MPa</i> <i>(T_{sat} = -1.23°C)</i>								
<i>p = 3.2 bar = 0.32 MPa</i> <i>(T_{sat} = 2.40°C)</i>								
Sat.	0.07193	226.38	246.52	0.9197	0.06322	228.43	248.66	0.9177
0	0.07240	227.37	247.64	0.9238				
10	0.07613	235.44	256.76	0.9566	0.06576	234.61	255.65	0.9427
20	0.07972	243.59	265.91	0.9883	0.06901	242.87	264.95	0.9749
30	0.08320	251.83	275.12	1.0192	0.07214	251.19	274.28	1.0062
40	0.08660	260.17	284.42	1.0494	0.07518	259.61	283.67	1.0367
50	0.08992	268.64	293.81	1.0789	0.07815	268.14	293.15	1.0665
60	0.09319	277.23	303.32	1.1079	0.08106	276.79	302.72	1.0957
70	0.09641	285.96	312.95	1.1364	0.08392	285.56	312.41	1.1243
80	0.09960	294.82	322.71	1.1644	0.08674	294.46	322.22	1.1525
90	0.10275	303.83	332.60	1.1920	0.08953	303.50	332.15	1.1802
100	0.10587	312.98	342.62	1.2193	0.09229	312.68	342.21	1.2076
110	0.10897	322.27	352.78	1.2461	0.09503	322.00	352.40	1.2345
120	0.11205	331.71	363.08	1.2727	0.09774	331.45	362.73	1.2611
<i>p = 4.0 bar = 0.40 MPa</i> <i>(T_{sat} = 8.93°C)</i>								
<i>p = 5.0 bar = 0.50 MPa</i> <i>(T_{sat} = 15.74°C)</i>								
Sat.	0.05089	231.97	252.32	0.9145	0.04086	235.64	256.07	0.9117
10	0.05119	232.87	253.35	0.9182				
20	0.05397	241.37	262.96	0.9515	0.04188	239.40	260.34	0.9264
30	0.05662	249.89	272.54	0.9837	0.04416	248.20	270.28	0.9597
40	0.05917	258.47	282.14	1.0148	0.04633	256.99	280.16	0.9918
50	0.06164	267.13	291.79	1.0452	0.04842	265.83	290.04	1.0229
60	0.06405	275.89	301.51	1.0748	0.05043	274.73	299.95	1.0531
70	0.06641	284.75	311.32	1.1038	0.05240	283.72	309.92	1.0825
80	0.06873	293.73	321.23	1.1322	0.05432	292.80	319.96	1.1114
90	0.07102	302.84	331.25	1.1602	0.05620	302.00	330.10	1.1397
100	0.07327	312.07	341.38	1.1878	0.05805	311.31	340.33	1.1675
110	0.07550	321.44	351.64	1.2149	0.05988	320.74	350.68	1.1949
120	0.07771	330.94	362.03	1.2417	0.06168	330.30	361.14	1.2218
130	0.07991	340.58	372.54	1.2681	0.06347	339.98	371.72	1.2484
140	0.08208	350.35	383.18	1.2941	0.06524	349.79	382.42	1.2746
<i>p = 6.0 bar = 0.60 MPa</i> <i>(T_{sat} = 21.58°C)</i>								
<i>p = 7.0 bar = 0.70 MPa</i> <i>(T_{sat} = 26.72°C)</i>								
Sat.	0.03408	238.74	259.19	0.9097	0.02918	241.42	261.85	0.9080
30	0.03581	246.41	267.89	0.9388	0.02979	244.51	265.37	0.9197
40	0.03774	255.45	278.09	0.9719	0.03157	253.83	275.93	0.9539
50	0.03958	264.48	288.23	1.0037	0.03324	263.08	286.35	0.9867
60	0.04134	273.54	298.35	1.0346	0.03482	272.31	296.69	1.0182
70	0.04304	282.66	308.48	1.0645	0.03634	281.57	307.01	1.0487
80	0.04469	291.86	318.67	1.0938	0.03781	290.88	317.35	1.0784
90	0.04631	301.14	328.93	1.1225	0.03924	300.27	327.74	1.1074
100	0.04790	310.53	339.27	1.1505	0.04064	309.74	338.19	1.1358
110	0.04946	320.03	349.70	1.1781	0.04201	319.31	348.71	1.1637
120	0.05099	329.64	360.24	1.2053	0.04335	328.98	359.33	1.1910
130	0.05251	339.38	370.88	1.2320	0.04468	338.76	370.04	1.2179
140	0.05402	349.23	381.64	1.2584	0.04599	348.66	380.86	1.2444
150	0.05550	359.21	392.52	1.2844	0.04729	358.68	391.79	1.2706
160	0.05698	369.32	403.51	1.3100	0.04857	368.82	402.82	1.2963

TABLE A-12

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 8.0 bar = 0.80 MPa (T _{sat} = 31.33°C)								
Sat. 0.02547 243.78 264.15 0.9066 0.02255 245.88 266.18 0.9054								
40 0.02691	252.13	273.66	0.9374	0.02325	250.32	271.25	0.9217	
50 0.02846	261.62	284.39	0.9711	0.02472	260.09	282.34	0.9566	
60 0.02992	271.04	294.98	1.0034	0.02609	269.72	293.21	0.9897	
70 0.03131	280.45	305.50	1.0345	0.02738	279.30	303.94	1.0214	
80 0.03264	289.89	316.00	1.0647	0.02861	288.87	314.62	1.0521	
90 0.03393	299.37	326.52	1.0940	0.02980	298.46	325.28	1.0819	
100 0.03519	308.93	337.08	1.1227	0.03095	308.11	335.96	1.1109	
110 0.03642	318.57	347.71	1.1508	0.03207	317.82	346.68	1.1392	
120 0.03762	328.31	358.40	1.1784	0.03316	327.62	357.47	1.1670	
130 0.03881	338.14	369.19	1.2055	0.03423	337.52	368.33	1.1943	
140 0.03997	348.09	380.07	1.2321	0.03529	347.51	379.27	1.2211	
150 0.04113	358.15	391.05	1.2584	0.03633	357.61	390.31	1.2475	
160 0.04227	368.32	402.14	1.2843	0.03736	367.82	401.44	1.2735	
170 0.04340	378.61	413.33	1.3098	0.03838	378.14	412.68	1.2992	
180 0.04452	389.02	424.63	1.3351	0.03939	388.57	424.02	1.3245	
<i>p</i> = 10.0 bar = 1.00 MPa (T _{sat} = 39.39°C)								
Sat. 0.02020 247.77 267.97 0.9043 0.01663 251.03 270.99 0.9023								
40 0.02029	248.39	268.68	0.9066					
50 0.02171	258.48	280.19	0.9428	0.01712	254.98	275.52	0.9164	
60 0.02301	268.35	291.36	0.9768	0.01835	265.42	287.44	0.9527	
70 0.02423	278.11	302.34	1.0093	0.01947	275.59	298.96	0.9868	
80 0.02538	287.82	313.20	1.0405	0.02051	285.62	310.24	1.0192	
90 0.02649	297.53	324.01	1.0707	0.02150	295.59	321.39	1.0503	
100 0.02755	307.27	334.82	1.1000	0.02244	305.54	332.47	1.0804	
110 0.02858	317.06	345.65	1.1286	0.02335	315.50	343.52	1.1096	
120 0.02959	326.93	356.52	1.1567	0.02423	325.51	354.58	1.1381	
130 0.03058	336.88	367.46	1.1841	0.02508	335.58	365.68	1.1660	
140 0.03154	346.92	378.46	1.2111	0.02592	345.73	376.83	1.1933	
150 0.03250	357.06	389.56	1.2376	0.02674	355.95	388.04	1.2201	
160 0.03344	367.31	400.74	1.2638	0.02754	366.27	399.33	1.2465	
170 0.03436	377.66	412.02	1.2895	0.02834	376.69	410.70	1.2724	
180 0.03528	388.12	423.40	1.3149	0.02912	387.21	422.16	1.2980	
<i>p</i> = 14.0 bar = 1.40 MPa (T _{sat} = 52.43°C)								
Sat. 0.01405 253.74 273.40 0.9003 0.01208 256.00 275.33 0.8982								
60 0.01495	262.17	283.10	0.9297	0.01233	258.48	278.20	0.9069	
70 0.01603	272.87	295.31	0.9658	0.01340	269.89	291.33	0.9457	
80 0.01701	283.29	307.10	0.9997	0.01435	280.78	303.74	0.9813	
90 0.01792	293.55	318.63	1.0319	0.01521	291.39	315.72	1.0148	
100 0.01878	303.73	330.02	1.0628	0.01601	301.84	327.46	1.0467	
110 0.01960	313.88	341.32	1.0927	0.01677	312.20	339.04	1.0773	
120 0.02039	324.05	352.59	1.1218	0.01750	322.53	350.53	1.1069	
130 0.02115	334.25	363.86	1.1501	0.01820	332.87	361.99	1.1357	
140 0.02189	344.50	375.15	1.1777	0.01887	343.24	373.44	1.1638	
150 0.02262	354.82	386.49	1.2048	0.01953	353.66	384.91	1.1912	
160 0.02333	365.22	397.89	1.2315	0.02017	364.15	396.43	1.2181	
170 0.02403	375.71	409.36	1.2576	0.02080	374.71	407.99	1.2445	
180 0.02472	386.29	420.90	1.2834	0.02142	385.35	419.62	1.2704	
190 0.02541	396.96	432.53	1.3088	0.02203	396.08	431.33	1.2960	
200 0.02608	407.73	444.24	1.3338	0.02263	406.90	443.11	1.3212	

TABLE A-13**Properties of Saturated Ammonia (Liquid–Vapor): Temperature Table**

Pressure Conversions:
1 bar = 0.1 MPa
= 10^2 kPa

Temp. °C	Press. bar	Specific Volume m^3/kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Temp. °C
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
-50	0.4086	1.4245	2.6265	-43.94	1264.99	-43.88	1416.20	1372.32	-0.1922	6.1543
-45	0.5453	1.4367	2.0060	-22.03	1271.19	-21.95	1402.52	1380.57	-0.0951	6.0523
-40	0.7174	1.4493	1.5524	-0.10	1277.20	0.00	1388.56	1388.56	0.0000	5.9557
-36	0.8850	1.4597	1.2757	17.47	1281.87	17.60	1377.17	1394.77	0.0747	5.8819
-32	1.0832	1.4703	1.0561	35.09	1286.41	35.25	1365.55	1400.81	0.1484	5.8111
-30	1.1950	1.4757	0.9634	43.93	1288.63	44.10	1359.65	1403.75	0.1849	5.7767
-28	1.3159	1.4812	0.8803	52.78	1290.82	52.97	1353.68	1406.66	0.2212	5.7430
-26	1.4465	1.4867	0.8056	61.65	1292.97	61.86	1347.65	1409.51	0.2572	5.7100
-22	1.7390	1.4980	0.6780	79.46	1297.18	79.72	1335.36	1415.08	0.3287	5.6457
-20	1.9019	1.5038	0.6233	88.40	1299.23	88.68	1329.10	1417.79	0.3642	5.6144
-18	2.0769	1.5096	0.5739	97.36	1301.25	97.68	1322.77	1420.45	0.3994	5.5837
-16	2.2644	1.5155	0.5291	106.36	1303.23	106.70	1316.35	1423.05	0.4346	5.5536
-14	2.4652	1.5215	0.4885	115.37	1305.17	115.75	1309.86	1425.61	0.4695	5.5239
-12	2.6798	1.5276	0.4516	124.42	1307.08	124.83	1303.28	1428.11	0.5043	5.4948
-10	2.9089	1.5338	0.4180	133.50	1308.95	133.94	1296.61	1430.55	0.5389	5.4662
-8	3.1532	1.5400	0.3874	142.60	1310.78	143.09	1289.86	1432.95	0.5734	5.4380
-6	3.4134	1.5464	0.3595	151.74	1312.57	152.26	1283.02	1435.28	0.6077	5.4103
-4	3.6901	1.5528	0.3340	160.88	1314.32	161.46	1276.10	1437.56	0.6418	5.3831
-2	3.9842	1.5594	0.3106	170.07	1316.04	170.69	1269.08	1439.78	0.6759	5.3562
0	4.2962	1.5660	0.2892	179.29	1317.71	179.96	1261.97	1441.94	0.7097	5.3298
2	4.6270	1.5727	0.2695	188.53	1319.34	189.26	1254.77	1444.03	0.7435	5.3038
4	4.9773	1.5796	0.2514	197.80	1320.92	198.59	1247.48	1446.07	0.7770	5.2781
6	5.3479	1.5866	0.2348	207.10	1322.47	207.95	1240.09	1448.04	0.8105	5.2529
8	5.7395	1.5936	0.2195	216.42	1323.96	217.34	1232.61	1449.94	0.8438	5.2279
10	6.1529	1.6008	0.2054	225.77	1325.42	226.75	1225.03	1451.78	0.8769	5.2033
12	6.5890	1.6081	0.1923	235.14	1326.82	236.20	1217.35	1453.55	0.9099	5.1791
16	7.5324	1.6231	0.1691	253.95	1329.48	255.18	1201.70	1456.87	0.9755	5.1314
20	8.5762	1.6386	0.1492	272.86	1331.94	274.26	1185.64	1459.90	1.0404	5.0849
24	9.7274	1.6547	0.1320	291.84	1334.19	293.45	1169.16	1462.61	1.1048	5.0394
28	10.993	1.6714	0.1172	310.92	1336.20	312.75	1152.24	1465.00	1.1686	4.9948
32	12.380	1.6887	0.1043	330.07	1337.97	332.17	1134.87	1467.03	1.2319	4.9509
36	13.896	1.7068	0.0930	349.32	1339.47	351.69	1117.00	1468.70	1.2946	4.9078
40	15.549	1.7256	0.0831	368.67	1340.70	371.35	1098.62	1469.97	1.3569	4.8652
45	17.819	1.7503	0.0725	393.01	1341.81	396.13	1074.84	1470.96	1.4341	4.8125
50	20.331	1.7765	0.0634	417.56	1342.42	421.17	1050.09	1471.26	1.5109	4.7604

Source: Tables A-13 through A-15 are calculated based on equations from L. Haar and J. S. Gallagher, "Thermodynamic Properties of Ammonia," *J. Phys. Chem. Reference Data*, Vol. 7, 1978, pp. 635–792.

TABLE A-14

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

Properties of Saturated Ammonia (Liquid–Vapor): Pressure Table

Press. bar	Temp. °C	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Press. bar
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	
0.40	-50.36	1.4236	2.6795	-45.52	1264.54	-45.46	1417.18	1371.72	-0.1992	6.1618
0.50	-46.53	1.4330	2.1752	-28.73	1269.31	-28.66	1406.73	1378.07	-0.1245	6.0829
0.60	-43.28	1.4410	1.8345	-14.51	1273.27	-14.42	1397.76	1383.34	-0.0622	6.0186
0.70	-40.46	1.4482	1.5884	-2.11	1276.66	-2.01	1389.85	1387.84	-0.0086	5.9643
0.80	-37.94	1.4546	1.4020	8.93	1279.61	9.04	1382.73	1391.78	0.0386	5.9174
0.90	-35.67	1.4605	1.2559	18.91	1282.24	19.04	1376.23	1395.27	0.0808	5.8760
1.00	-33.60	1.4660	1.1381	28.03	1284.61	28.18	1370.23	1398.41	0.1191	5.8391
1.25	-29.07	1.4782	0.9237	48.03	1289.65	48.22	1356.89	1405.11	0.2018	5.7610
1.50	-25.22	1.4889	0.7787	65.10	1293.80	65.32	1345.28	1410.61	0.2712	5.6973
1.75	-21.86	1.4984	0.6740	80.08	1297.33	80.35	1334.92	1415.27	0.3312	5.6435
2.00	-18.86	1.5071	0.5946	93.50	1300.39	93.80	1325.51	1419.31	0.3843	5.5969
2.25	-16.15	1.5151	0.5323	105.68	1303.08	106.03	1316.83	1422.86	0.4319	5.5558
2.50	-13.67	1.5225	0.4821	116.88	1305.49	117.26	1308.76	1426.03	0.4753	5.5190
2.75	-11.37	1.5295	0.4408	127.26	1307.67	127.68	1301.20	1428.88	0.5152	5.4858
3.00	-9.24	1.5361	0.4061	136.96	1309.65	137.42	1294.05	1431.47	0.5520	5.4554
3.25	-7.24	1.5424	0.3765	146.06	1311.46	146.57	1287.27	1433.84	0.5864	5.4275
3.50	-5.36	1.5484	0.3511	154.66	1313.14	155.20	1280.81	1436.01	0.6186	5.4016
3.75	-3.58	1.5542	0.3289	162.80	1314.68	163.38	1274.64	1438.03	0.6489	5.3774
4.00	-1.90	1.5597	0.3094	170.55	1316.12	171.18	1268.71	1439.89	0.6776	5.3548
4.25	-0.29	1.5650	0.2921	177.96	1317.47	178.62	1263.01	1441.63	0.7048	5.3336
4.50	1.25	1.5702	0.2767	185.04	1318.73	185.75	1257.50	1443.25	0.7308	5.3135
4.75	2.72	1.5752	0.2629	191.84	1319.91	192.59	1252.18	1444.77	0.7555	5.2946
5.00	4.13	1.5800	0.2503	198.39	1321.02	199.18	1247.02	1446.19	0.7791	5.2765
5.25	5.48	1.5847	0.2390	204.69	1322.07	205.52	1242.01	1447.53	0.8018	5.2594
5.50	6.79	1.5893	0.2286	210.78	1323.06	211.65	1237.15	1448.80	0.8236	5.2430
5.75	8.05	1.5938	0.2191	216.66	1324.00	217.58	1232.41	1449.99	0.8446	5.2273
6.00	9.27	1.5982	0.2104	222.37	1324.89	223.32	1227.79	1451.12	0.8649	5.2122
7.00	13.79	1.6148	0.1815	243.56	1328.04	244.69	1210.38	1455.07	0.9394	5.1576
8.00	17.84	1.6302	0.1596	262.64	1330.64	263.95	1194.36	1458.30	1.0054	5.1099
9.00	21.52	1.6446	0.1424	280.05	1332.82	281.53	1179.44	1460.97	1.0649	5.0675
10.00	24.89	1.6584	0.1285	296.10	1334.66	297.76	1165.42	1463.18	1.1191	5.0294
12.00	30.94	1.6841	0.1075	324.99	1337.52	327.01	1139.52	1466.53	1.2152	4.9625
14.00	36.26	1.7080	0.0923	350.58	1339.56	352.97	1115.82	1468.79	1.2987	4.9050
16.00	41.03	1.7306	0.0808	373.69	1340.97	376.46	1093.77	1470.23	1.3729	4.8542
18.00	45.38	1.7522	0.0717	394.85	1341.88	398.00	1073.01	1471.01	1.4399	4.8086
20.00	49.37	1.7731	0.0644	414.44	1342.37	417.99	1053.27	1471.26	1.5012	4.7670

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

TABLE A-15

Properties of Superheated Ammonia Vapor

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
$p = 0.4 \text{ bar} = 0.04 \text{ MPa}$ ($T_{\text{sat}} = -50.36^\circ\text{C}$)								
$p = 0.6 \text{ bar} = 0.06 \text{ MPa}$ ($T_{\text{sat}} = -43.28^\circ\text{C}$)								
Sat.	2.6795	1264.54	1371.72	6.1618	1.8345	1273.27	1383.34	6.0186
-50	2.6841	1265.11	1372.48	6.1652				
-45	2.7481	1273.05	1382.98	6.2118				
-40	2.8118	1281.01	1393.48	6.2573	1.8630	1278.62	1390.40	6.0490
-35	2.8753	1288.96	1403.98	6.3018	1.9061	1286.75	1401.12	6.0946
-30	2.9385	1296.93	1414.47	6.3455	1.9491	1294.88	1411.83	6.1390
-25	3.0015	1304.90	1424.96	6.3882	1.9918	1303.01	1422.52	6.1826
-20	3.0644	1312.88	1435.46	6.4300	2.0343	1311.13	1433.19	6.2251
-15	3.1271	1320.87	1445.95	6.4711	2.0766	1319.25	1443.85	6.2668
-10	3.1896	1328.87	1456.45	6.5114	2.1188	1327.37	1454.50	6.3077
-5	3.2520	1336.88	1466.95	6.5509	2.1609	1335.49	1465.14	6.3478
0	3.3142	1344.90	1477.47	6.5898	2.2028	1343.61	1475.78	6.3871
5	3.3764	1352.95	1488.00	6.6280	2.2446	1351.75	1486.43	6.4257
$p = 0.8 \text{ bar} = 0.08 \text{ MPa}$ ($T_{\text{sat}} = -37.94^\circ\text{C}$)								
$p = 1.0 \text{ bar} = 0.10 \text{ MPa}$ ($T_{\text{sat}} = -33.60^\circ\text{C}$)								
Sat.	1.4021	1279.61	1391.78	5.9174	1.1381	1284.61	1398.41	5.8391
-35	1.4215	1284.51	1398.23	5.9446				
-30	1.4543	1292.81	1409.15	5.9900	1.1573	1290.71	1406.44	5.8723
-25	1.4868	1301.09	1420.04	6.0343	1.1838	1299.15	1417.53	5.9175
-20	1.5192	1309.36	1430.90	6.0777	1.2101	1307.57	1428.58	5.9616
-15	1.5514	1317.61	1441.72	6.1200	1.2362	1315.96	1439.58	6.0046
-10	1.5834	1325.85	1452.53	6.1615	1.2621	1324.33	1450.54	6.0467
-5	1.6153	1334.09	1463.31	6.2021	1.2880	1332.67	1461.47	6.0878
0	1.6471	1342.31	1474.08	6.2419	1.3136	1341.00	1472.37	6.1281
5	1.6788	1350.54	1484.84	6.2809	1.3392	1349.33	1483.25	6.1676
10	1.7103	1358.77	1495.60	6.3192	1.3647	1357.64	1494.11	6.2063
15	1.7418	1367.01	1506.35	6.3568	1.3900	1365.95	1504.96	6.2442
20	1.7732	1375.25	1517.10	6.3939	1.4153	1374.27	1515.80	6.2816
$p = 1.5 \text{ bar} = 0.15 \text{ MPa}$ ($T_{\text{sat}} = -25.22^\circ\text{C}$)								
$p = 2.0 \text{ bar} = 0.20 \text{ MPa}$ ($T_{\text{sat}} = -18.86^\circ\text{C}$)								
Sat.	0.7787	1293.80	1410.61	5.6973	0.59460	1300.39	1419.31	5.5969
-25	0.7795	1294.20	1411.13	5.6994				
-20	0.7978	1303.00	1422.67	5.7454				
-15	0.8158	1311.75	1434.12	5.7902	0.60542	1307.43	1428.51	5.6328
-10	0.8336	1320.44	1445.49	5.8338	0.61926	1316.46	1440.31	5.6781
-5	0.8514	1329.08	1456.79	5.8764	0.63294	1325.41	1452.00	5.7221
0	0.8689	1337.68	1468.02	5.9179	0.64648	1334.29	1463.59	5.7649
5	0.8864	1346.25	1479.20	5.9585	0.65989	1343.11	1475.09	5.8066
10	0.9037	1354.78	1490.34	5.9981	0.67320	1351.87	1486.51	5.8473
15	0.9210	1363.29	1501.44	6.0370	0.68640	1360.59	1497.87	5.8871
20	0.9382	1371.79	1512.51	6.0751	0.69952	1369.28	1509.18	5.9260
25	0.9553	1380.28	1523.56	6.1125	0.71256	1377.93	1520.44	5.9641
30	0.9723	1388.76	1534.60	6.1492	0.72553	1386.56	1531.67	6.0014

TABLE A-15

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 2.5 bar = 0.25 MPa (T _{sat} = -13.67°C)								
<i>p</i> = 3.0 bar = 0.30 MPa (T _{sat} = -9.24°C)								
Sat.	0.48213	1305.49	1426.03	5.5190	0.40607	1309.65	1431.47	5.4554
-10	0.49051	1312.37	1435.00	5.5534				
-5	0.50180	1321.65	1447.10	5.5989	0.41428	1317.80	1442.08	5.4953
0	0.51293	1330.83	1459.06	5.6431	0.42382	1327.28	1454.43	5.5409
5	0.52393	1339.91	1470.89	5.6860	0.43323	1336.64	1466.61	5.5851
10	0.53482	1348.91	1482.61	5.7278	0.44251	1345.89	1478.65	5.6280
15	0.54560	1357.84	1494.25	5.7685	0.45169	1355.05	1490.56	5.6697
20	0.55630	1366.72	1505.80	5.8083	0.46078	1364.13	1502.36	5.7103
25	0.56691	1375.55	1517.28	5.8471	0.46978	1373.14	1514.07	5.7499
30	0.57745	1384.34	1528.70	5.8851	0.47870	1382.09	1525.70	5.7886
35	0.58793	1393.10	1540.08	5.9223	0.48756	1391.00	1537.26	5.8264
40	0.59835	1401.84	1551.42	5.9589	0.49637	1399.86	1548.77	5.8635
45	0.60872	1410.56	1562.74	5.9947	0.50512	1408.70	1560.24	5.8998
<i>p</i> = 3.5 bar = 0.35 MPa (T _{sat} = -5.36°C)								
<i>p</i> = 4.0 bar = 0.40 MPa (T _{sat} = -1.90°C)								
Sat.	0.35108	1313.14	1436.01	5.4016	0.30942	1316.12	1439.89	5.3548
0	0.36011	1323.66	1449.70	5.4522	0.31227	1319.95	1444.86	5.3731
10	0.37654	1342.82	1474.61	5.5417	0.32701	1339.68	1470.49	5.4652
20	0.39251	1361.49	1498.87	5.6259	0.34129	1358.81	1495.33	5.5515
30	0.40814	1379.81	1522.66	5.7057	0.35520	1377.49	1519.57	5.6328
40	0.42350	1397.87	1546.09	5.7818	0.36884	1395.85	1543.38	5.7101
60	0.45363	1433.55	1592.32	5.9249	0.39550	1431.97	1590.17	5.8549
80	0.48320	1469.06	1638.18	6.0586	0.42160	1467.77	1636.41	5.9897
100	0.51240	1504.73	1684.07	6.1850	0.44733	1503.64	1682.58	6.1169
120	0.54136	1540.79	1730.26	6.3056	0.47280	1539.85	1728.97	6.2380
140	0.57013	1577.38	1776.92	6.4213	0.49808	1576.55	1775.79	6.3541
160	0.59876	1614.60	1824.16	6.5330	0.52323	1613.86	1823.16	6.4661
180	0.62728	1652.51	1872.06	6.6411	0.54827	1651.85	1871.16	6.5744
200	0.65572	1691.15	1920.65	6.7460	0.57322	1690.56	1919.85	6.6796
<i>p</i> = 4.5 bar = 0.45 MPa (T _{sat} = 1.25°C)								
<i>p</i> = 5.0 bar = 0.50 MPa (T _{sat} = 4.13°C)								
Sat.	0.27671	1318.73	1443.25	5.3135	0.25034	1321.02	1446.19	5.2765
10	0.28846	1336.48	1466.29	5.3962	0.25757	1333.22	1462.00	5.3330
20	0.30142	1356.09	1491.72	5.4845	0.26949	1353.32	1488.06	5.4234
30	0.31401	1375.15	1516.45	5.5674	0.28103	1372.76	1513.28	5.5080
40	0.32631	1393.80	1540.64	5.6460	0.29227	1391.74	1537.87	5.5878
60	0.35029	1430.37	1588.00	5.7926	0.31410	1428.76	1585.81	5.7362
80	0.37369	1466.47	1634.63	5.9285	0.33535	1465.16	1632.84	5.8733
100	0.39671	1502.55	1681.07	6.0564	0.35621	1501.46	1679.56	6.0020
120	0.41947	1538.91	1727.67	6.1781	0.37681	1537.97	1726.37	6.1242
140	0.44205	1575.73	1774.65	6.2946	0.39722	1574.90	1773.51	6.2412
160	0.46448	1613.13	1822.15	6.4069	0.41749	1612.40	1821.14	6.3537
180	0.48681	1651.20	1870.26	6.5155	0.43765	1650.54	1869.36	6.4626
200	0.50905	1689.97	1919.04	6.6208	0.45771	1689.38	1918.24	6.5681

TABLE A-15

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 5.5 bar = 0.55 MPa (T _{sat} = 6.79°C)					<i>p</i> = 6.0 bar = 0.60 MPa (T _{sat} = 9.27°C)			
Sat.	0.22861	1323.06	1448.80	5.2430	0.21038	1324.89	1451.12	5.2122
10	0.23227	1329.88	1457.63	5.2743	0.21115	1326.47	1453.16	5.2195
20	0.24335	1350.50	1484.34	5.3671	0.22155	1347.62	1480.55	5.3145
30	0.25403	1370.35	1510.07	5.4534	0.23152	1367.90	1506.81	5.4026
40	0.26441	1389.64	1535.07	5.5345	0.24118	1387.52	1532.23	5.4851
50	0.27454	1408.53	1559.53	5.6114	0.25059	1406.67	1557.03	5.5631
60	0.28449	1427.13	1583.60	5.6848	0.25981	1425.49	1581.38	5.6373
80	0.30398	1463.85	1631.04	5.8230	0.27783	1462.52	1629.22	5.7768
100	0.32307	1500.36	1678.05	5.9525	0.29546	1499.25	1676.52	5.9071
120	0.34190	1537.02	1725.07	6.0753	0.31281	1536.07	1723.76	6.0304
140	0.36054	1574.07	1772.37	6.1926	0.32997	1573.24	1771.22	6.1481
160	0.37903	1611.66	1820.13	6.3055	0.34699	1610.92	1819.12	6.2613
180	0.39742	1649.88	1868.46	6.4146	0.36390	1649.22	1867.56	6.3707
200	0.41571	1688.79	1917.43	6.5203	0.38071	1688.20	1916.63	6.4766
<i>p</i> = 7.0 bar = 0.70 MPa (T _{sat} = 13.79°C)					<i>p</i> = 8.0 bar = 0.80 MPa (T _{sat} = 17.84°C)			
Sat.	0.18148	1328.04	1455.07	5.1576	0.15958	1330.64	1458.30	5.1099
20	0.18721	1341.72	1472.77	5.2186	0.16138	1335.59	1464.70	5.1318
30	0.19610	1362.88	1500.15	5.3104	0.16948	1357.71	1493.29	5.2277
40	0.20464	1383.20	1526.45	5.3958	0.17720	1378.77	1520.53	5.3161
50	0.21293	1402.90	1551.95	5.4760	0.18465	1399.05	1546.77	5.3986
60	0.22101	1422.16	1576.87	5.5519	0.19189	1418.77	1572.28	5.4763
80	0.23674	1459.85	1625.56	5.6939	0.20590	1457.14	1621.86	5.6209
100	0.25205	1497.02	1673.46	5.8258	0.21949	1494.77	1670.37	5.7545
120	0.26709	1534.16	1721.12	5.9502	0.23280	1532.24	1718.48	5.8801
140	0.28193	1571.57	1768.92	6.0688	0.24590	1569.89	1766.61	5.9995
160	0.29663	1609.44	1817.08	6.1826	0.25886	1607.96	1815.04	6.1140
180	0.31121	1647.90	1865.75	6.2925	0.27170	1646.57	1863.94	6.2243
200	0.32571	1687.02	1915.01	6.3988	0.28445	1685.83	1913.39	6.3311
<i>p</i> = 9.0 bar = 0.90 MPa (T _{sat} = 21.52°C)					<i>p</i> = 10.0 bar = 1.00 MPa (T _{sat} = 24.89°C)			
Sat.	0.14239	1332.82	1460.97	5.0675	0.12852	1334.66	1463.18	5.0294
30	0.14872	1352.36	1486.20	5.1520	0.13206	1346.82	1478.88	5.0816
40	0.15582	1374.21	1514.45	5.2436	0.13868	1369.52	1508.20	5.1768
50	0.16263	1395.11	1541.47	5.3286	0.14499	1391.07	1536.06	5.2644
60	0.16922	1415.32	1567.61	5.4083	0.15106	1411.79	1562.86	5.3460
80	0.18191	1454.39	1618.11	5.5555	0.16270	1451.60	1614.31	5.4960
100	0.19416	1492.50	1667.24	5.6908	0.17389	1490.20	1664.10	5.6332
120	0.20612	1530.30	1715.81	5.8176	0.18478	1528.35	1713.13	5.7612
140	0.21788	1568.20	1764.29	5.9379	0.19545	1566.51	1761.96	5.8823
160	0.22948	1606.46	1813.00	6.0530	0.20598	1604.97	1810.94	5.9981
180	0.24097	1645.24	1862.12	6.1639	0.21638	1643.91	1860.29	6.1095
200	0.25237	1684.64	1911.77	6.2711	0.22670	1683.44	1910.14	6.2171

TABLE A-15

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 12.0 bar = 1.20 MPa (T _{sat} = 30.94°C)								
Sat. 0.10751 1337.52 1466.53 4.9625 0.09231 1339.56 1468.79 4.9050								
40 0.11287 1359.73 1495.18 5.0553 0.09432 1349.29 1481.33 4.9453								
60 0.12378 1404.54 1553.07 5.2347 0.10423 1396.97 1542.89 5.1360								
80 0.13387 1445.91 1606.56 5.3906 0.11324 1440.06 1598.59 5.2984								
100 0.14347 1485.55 1657.71 5.5315 0.12172 1480.79 1651.20 5.4433								
120 0.15275 1524.41 1707.71 5.6620 0.12986 1520.41 1702.21 5.5765								
140 0.16181 1563.09 1757.26 5.7850 0.13777 1559.63 1752.52 5.7013								
160 0.17072 1601.95 1806.81 5.9021 0.14552 1598.92 1802.65 5.8198								
180 0.17950 1641.23 1856.63 6.0145 0.15315 1638.53 1852.94 5.9333								
200 0.18819 1681.05 1906.87 6.1230 0.16068 1678.64 1903.59 6.0427								
220 0.19680 1721.50 1957.66 6.2282 0.16813 1719.35 1954.73 6.1485								
240 0.20534 1762.63 2009.04 6.3303 0.17551 1760.72 2006.43 6.2513								
260 0.21382 1804.48 2061.06 6.4297 0.18283 1802.78 2058.75 6.3513								
280 0.22225 1847.04 2113.74 6.5267 0.19010 1845.55 2111.69 6.4488								
<i>p</i> = 16.0 bar = 1.60 MPa (T _{sat} = 41.03°C)								
Sat. 0.08079 1340.97 1470.23 4.8542 0.07174 1341.88 1471.01 4.8086								
60 0.08951 1389.06 1532.28 5.0461 0.07801 1380.77 1521.19 4.9627								
80 0.09774 1434.02 1590.40 5.2156 0.08565 1427.79 1581.97 5.1399								
100 0.10539 1475.93 1644.56 5.3648 0.09267 1470.97 1637.78 5.2937								
120 0.11268 1516.34 1696.64 5.5008 0.09931 1512.22 1690.98 5.4326								
140 0.11974 1556.14 1747.72 5.6276 0.10570 1552.61 1742.88 5.5614								
160 0.12663 1595.85 1798.45 5.7475 0.11192 1592.76 1794.23 5.6828								
180 0.13339 1635.81 1849.23 5.8621 0.11801 1633.08 1845.50 5.7985								
200 0.14005 1676.21 1900.29 5.9723 0.12400 1673.78 1896.98 5.9096								
220 0.14663 1717.18 1951.79 6.0789 0.12991 1715.00 1948.83 6.0170								
240 0.15314 1758.79 2003.81 6.1823 0.13574 1756.85 2001.18 6.1210								
260 0.15959 1801.07 2056.42 6.2829 0.14152 1799.35 2054.08 6.2222								
280 0.16599 1844.05 2109.64 6.3809 0.14724 1842.55 2107.58 6.3207								
<i>p</i> = 20.0 bar = 2.00 MPa (T _{sat} = 49.37°C)								
Sat. 0.06445 1342.37 1471.26 4.7670								
60 0.06875 1372.05 1509.54 4.8838								
80 0.07596 1421.36 1573.27 5.0696								
100 0.08248 1465.89 1630.86 5.2283								
120 0.08861 1508.03 1685.24 5.3703								
140 0.09447 1549.03 1737.98 5.5012								
160 0.10016 1589.65 1789.97 5.6241								
180 0.10571 1630.32 1841.74 5.7409								
200 0.11116 1671.33 1893.64 5.8530								
220 0.11652 1712.82 1945.87 5.9611								
240 0.12182 1754.90 1998.54 6.0658								
260 0.12706 1797.63 2051.74 6.1675								
280 0.13224 1841.03 2105.50 6.2665								

TABLE A-16

Properties of Saturated Propane (Liquid–Vapor): Temperature Table											
Temp. °C	Press. bar	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Temp. °C	
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f		
-100	0.02888	1.553	11.27	-128.4	319.5	-128.4	480.4	352.0	-0.634	2.140	-100
-90	0.06426	1.578	5.345	-107.8	329.3	-107.8	471.4	363.6	-0.519	2.055	-90
-80	0.1301	1.605	2.774	-87.0	339.3	-87.0	462.4	375.4	-0.408	1.986	-80
-70	0.2434	1.633	1.551	-65.8	349.5	-65.8	453.1	387.3	-0.301	1.929	-70
-60	0.4261	1.663	0.9234	-44.4	359.9	-44.3	443.5	399.2	-0.198	1.883	-60
-50	0.7046	1.694	0.5793	-22.5	370.4	-22.4	433.6	411.2	-0.098	1.845	-50
-40	1.110	1.728	0.3798	-0.2	381.0	0.0	423.2	423.2	0.000	1.815	-40
-30	1.677	1.763	0.2585	22.6	391.6	22.9	412.1	435.0	0.096	1.791	-30
-20	2.444	1.802	0.1815	45.9	402.4	46.3	400.5	446.8	0.190	1.772	-20
-10	3.451	1.844	0.1309	69.8	413.2	70.4	388.0	458.4	0.282	1.757	-10
0	4.743	1.890	0.09653	94.2	423.8	95.1	374.5	469.6	0.374	1.745	0
4	5.349	1.910	0.08591	104.2	428.1	105.3	368.8	474.1	0.410	1.741	4
8	6.011	1.931	0.07666	114.3	432.3	115.5	362.9	478.4	0.446	1.737	8
12	6.732	1.952	0.06858	124.6	436.5	125.9	356.8	482.7	0.482	1.734	12
16	7.515	1.975	0.06149	135.0	440.7	136.4	350.5	486.9	0.519	1.731	16
20	8.362	1.999	0.05525	145.4	444.8	147.1	343.9	491.0	0.555	1.728	20
24	9.278	2.024	0.04973	156.1	448.9	158.0	337.0	495.0	0.591	1.725	24
28	10.27	2.050	0.04483	166.9	452.9	169.0	329.9	498.9	0.627	1.722	28
32	11.33	2.078	0.04048	177.8	456.7	180.2	322.4	502.6	0.663	1.720	32
36	12.47	2.108	0.03659	188.9	460.6	191.6	314.6	506.2	0.699	1.717	36
40	13.69	2.140	0.03310	200.2	464.3	203.1	306.5	509.6	0.736	1.715	40
44	15.00	2.174	0.02997	211.7	467.9	214.9	298.0	512.9	0.772	1.712	44
48	16.40	2.211	0.02714	223.4	471.4	227.0	288.9	515.9	0.809	1.709	48
52	17.89	2.250	0.02459	235.3	474.6	239.3	279.3	518.6	0.846	1.705	52
56	19.47	2.293	0.02227	247.4	477.7	251.9	269.2	521.1	0.884	1.701	56
60	21.16	2.340	0.02015	259.8	480.6	264.8	258.4	523.2	0.921	1.697	60
65	23.42	2.406	0.01776	275.7	483.6	281.4	243.8	525.2	0.969	1.690	65
70	25.86	2.483	0.01560	292.3	486.1	298.7	227.7	526.4	1.018	1.682	70
75	28.49	2.573	0.01363	309.5	487.8	316.8	209.8	526.6	1.069	1.671	75
80	31.31	2.683	0.01182	327.6	488.2	336.0	189.2	525.2	1.122	1.657	80
85	34.36	2.827	0.01011	347.2	486.9	356.9	164.7	521.6	1.178	1.638	85
90	37.64	3.038	0.008415	369.4	482.2	380.8	133.1	513.9	1.242	1.608	90
95	41.19	3.488	0.006395	399.8	467.4	414.2	79.5	493.7	1.330	1.546	95
96.7	42.48	4.535	0.004535	434.9	434.9	454.2	0.0	457.2	1.437	1.437	96.7

Propane

Source: Tables A-16 through A-18 are calculated based on B. A. Younglove and J. F. Ely, "Thermophysical Properties of Fluids. II. Methane, Ethane, Propane, Isobutane and Normal Butane," *J. Phys. Chem. Ref. Data*, Vol. 16, No. 4, 1987, pp. 577–598.

Pressure Conversions:
1 bar = 0.1 MPa
= 10⁵ Pa

TABLE A-17

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 Pa

Properties of Saturated Propane (Liquid–Vapor): Pressure Table

Press. bar	Temp. °C	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/kg · K		Press. bar	
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f		
0.05	-93.28	1.570	6.752	-114.6	326.0	-114.6	474.4	359.8	-0.556	2.081	0.05
0.10	-83.87	1.594	3.542	-95.1	335.4	-95.1	465.9	370.8	-0.450	2.011	0.10
0.25	-69.55	1.634	1.513	-64.9	350.0	-64.9	452.7	387.8	-0.297	1.927	0.25
0.50	-56.93	1.672	0.7962	-37.7	363.1	-37.6	440.5	402.9	-0.167	1.871	0.50
0.75	-48.68	1.698	0.5467	-19.6	371.8	-19.5	432.3	412.8	-0.085	1.841	0.75
1.00	-42.38	1.719	0.4185	-5.6	378.5	-5.4	425.7	420.3	-0.023	1.822	1.00
2.00	-25.43	1.781	0.2192	33.1	396.6	33.5	406.9	440.4	0.139	1.782	2.00
3.00	-14.16	1.826	0.1496	59.8	408.7	60.3	393.3	453.6	0.244	1.762	3.00
4.00	-5.46	1.865	0.1137	80.8	418.0	81.5	382.0	463.5	0.324	1.751	4.00
5.00	1.74	1.899	0.09172	98.6	425.7	99.5	372.1	471.6	0.389	1.743	5.00
6.00	7.93	1.931	0.07680	114.2	432.2	115.3	363.0	478.3	0.446	1.737	6.00
7.00	13.41	1.960	0.06598	128.2	438.0	129.6	354.6	484.2	0.495	1.733	7.00
8.00	18.33	1.989	0.05776	141.0	443.1	142.6	346.7	489.3	0.540	1.729	8.00
9.00	22.82	2.016	0.05129	152.9	447.6	154.7	339.1	493.8	0.580	1.726	9.00
10.00	26.95	2.043	0.04606	164.0	451.8	166.1	331.8	497.9	0.618	1.723	10.00
11.00	30.80	2.070	0.04174	174.5	455.6	176.8	324.7	501.5	0.652	1.721	11.00
12.00	34.39	2.096	0.03810	184.4	459.1	187.0	317.8	504.8	0.685	1.718	12.00
13.00	37.77	2.122	0.03499	193.9	462.2	196.7	311.0	507.7	0.716	1.716	13.00
14.00	40.97	2.148	0.03231	203.0	465.2	206.0	304.4	510.4	0.745	1.714	14.00
15.00	44.01	2.174	0.02997	211.7	467.9	215.0	297.9	512.9	0.772	1.712	15.00
16.00	46.89	2.200	0.02790	220.1	470.4	223.6	291.4	515.0	0.799	1.710	16.00
17.00	49.65	2.227	0.02606	228.3	472.7	232.0	285.0	517.0	0.824	1.707	17.00
18.00	52.30	2.253	0.02441	236.2	474.9	240.2	278.6	518.8	0.849	1.705	18.00
19.00	54.83	2.280	0.02292	243.8	476.9	248.2	272.2	520.4	0.873	1.703	19.00
20.00	57.27	2.308	0.02157	251.3	478.7	255.9	265.9	521.8	0.896	1.700	20.00
22.00	61.90	2.364	0.01921	265.8	481.7	271.0	253.0	524.0	0.939	1.695	22.00
24.00	66.21	2.424	0.01721	279.7	484.3	285.5	240.1	525.6	0.981	1.688	24.00
26.00	70.27	2.487	0.01549	293.1	486.2	299.6	226.9	526.5	1.021	1.681	26.00
28.00	74.10	2.555	0.01398	306.2	487.5	313.4	213.2	526.6	1.060	1.673	28.00
30.00	77.72	2.630	0.01263	319.2	488.1	327.1	198.9	526.0	1.097	1.664	30.00
35.00	86.01	2.862	0.009771	351.4	486.3	361.4	159.1	520.5	1.190	1.633	35.00
40.00	93.38	3.279	0.007151	387.9	474.7	401.0	102.3	503.3	1.295	1.574	40.00
42.48	96.70	4.535	0.004535	434.9	434.9	454.2	0.0	454.2	1.437	1.437	42.48

Pressure Conversions:
1 bar = 0.1 MPa
= 10^5 kPa

TABLE A-18

Properties of Superheated Propane Vapor

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg · K
$p = 0.05 \text{ bar} = 0.005 \text{ MPa}$ ($T_{\text{sat}} = -93.28^\circ\text{C}$)								
$p = 0.1 \text{ bar} = 0.01 \text{ MPa}$ ($T_{\text{sat}} = -83.87^\circ\text{C}$)								
Sat.	6.752	326.0	359.8	2.081	3.542	367.3	370.8	2.011
-90	6.877	329.4	363.8	2.103	3.617	339.5	375.7	2.037
-80	7.258	339.8	376.1	2.169				
-70	7.639	350.6	388.8	2.233	3.808	350.3	388.4	2.101
-60	8.018	361.8	401.9	2.296	3.999	361.5	401.5	2.164
-50	8.397	373.3	415.3	2.357	4.190	373.1	415.0	2.226
-40	8.776	385.1	429.0	2.418	4.380	385.0	428.8	2.286
-30	9.155	397.4	443.2	2.477	4.570	397.3	443.0	2.346
-20	9.533	410.1	457.8	2.536	4.760	410.0	457.6	2.405
-10	9.911	423.2	472.8	2.594	4.950	423.1	472.6	2.463
0	10.29	436.8	488.2	2.652	5.139	436.7	488.1	2.520
10	10.67	450.8	504.1	2.709	5.329	450.6	503.9	2.578
20	11.05	270.6	520.4	2.765	5.518	465.1	520.3	2.634
$p = 0.5 \text{ bar} = 0.05 \text{ MPa}$ ($T_{\text{sat}} = -56.93^\circ\text{C}$)								
$p = 1.0 \text{ bar} = 0.1 \text{ MPa}$ ($T_{\text{sat}} = -42.38^\circ\text{C}$)								
Sat.	0.796	363.1	402.9	1.871	0.4185	378.5	420.3	1.822
-50	0.824	371.3	412.5	1.914	0.4234	381.5	423.8	1.837
-40	0.863	383.4	426.6	1.976				
-30	0.903	396.0	441.1	2.037	0.4439	394.2	438.6	1.899
-20	0.942	408.8	455.9	2.096	0.4641	407.3	453.7	1.960
-10	0.981	422.1	471.1	2.155	0.4842	420.7	469.1	2.019
0	1.019	435.8	486.7	2.213	0.5040	434.4	484.8	2.078
10	1.058	449.8	502.7	2.271	0.5238	448.6	501.0	2.136
20	1.096	464.3	519.1	2.328	0.5434	463.3	517.6	2.194
30	1.135	479.2	535.9	2.384	0.5629	478.2	534.5	2.251
40	1.173	494.6	553.2	2.440	0.5824	493.7	551.9	2.307
50	1.211	510.4	570.9	2.496	0.6018	509.5	569.7	2.363
60	1.249	526.7	589.1	2.551	0.6211	525.8	587.9	2.419
$p = 2.0 \text{ bar} = 0.2 \text{ MPa}$ ($T_{\text{sat}} = -25.43^\circ\text{C}$)								
$p = 3.0 \text{ bar} = 0.3 \text{ MPa}$ ($T_{\text{sat}} = -14.16^\circ\text{C}$)								
Sat.	0.2192	396.6	440.4	1.782	0.1496	408.7	453.6	1.762
-20	0.2251	404.0	449.0	1.816	0.1527	414.7	460.5	1.789
-10	0.2358	417.7	464.9	1.877				
0	0.2463	431.8	481.1	1.938	0.1602	429.0	477.1	1.851
10	0.2566	446.3	497.6	1.997	0.1674	443.8	494.0	1.912
20	0.2669	461.1	514.5	2.056	0.1746	458.8	511.2	1.971
30	0.2770	476.3	531.7	2.113	0.1816	474.2	528.7	2.030
40	0.2871	491.9	549.3	2.170	0.1885	490.1	546.6	2.088
50	0.2970	507.9	567.3	2.227	0.1954	506.2	564.8	2.145
60	0.3070	524.3	585.7	2.283	0.2022	522.7	583.4	2.202
70	0.3169	541.1	604.5	2.339	0.2090	539.6	602.3	2.258
80	0.3267	558.4	623.7	2.394	0.2157	557.0	621.7	2.314
90	0.3365	576.1	643.4	2.449	0.2223	574.8	641.5	2.369

TABLE A-18

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 4.0 bar = 0.4 MPa (T _{sat} = -5.46°C)								
Sat. 0.1137 418.0 463.5 1.751 0.09172 425.7 471.6 1.743								
0 0.1169	426.1	472.9	1.786	0.09577	438.4	486.3	1.796	
10 0.1227	441.2	490.3	1.848					
20 0.1283	456.6	507.9	1.909	0.1005	454.1	504.3	1.858	
30 0.1338	472.2	525.7	1.969	0.1051	470.0	522.5	1.919	
40 0.1392	488.1	543.8	2.027	0.1096	486.1	540.9	1.979	
50 0.1445	504.4	562.2	2.085	0.1140	502.5	559.5	2.038	
60 0.1498	521.1	581.0	2.143	0.1183	519.4	578.5	2.095	
70 0.1550	538.1	600.1	2.199	0.1226	536.6	597.9	2.153	
80 0.1601	555.7	619.7	2.255	0.1268	554.1	617.5	2.209	
90 0.1652	573.5	639.6	2.311	0.1310	572.1	637.6	2.265	
100 0.1703	591.8	659.9	2.366	0.1351	590.5	658.0	2.321	
110 0.1754	610.4	680.6	2.421	0.1392	609.3	678.9	2.376	
<i>p</i> = 6.0 bar = 0.6 MPa (T _{sat} = 7.93°C)								
Sat. 0.07680 432.2 478.3 1.737 0.06598 438.0 484.2 1.733								
10 0.07769	435.6	482.2	1.751	0.06847	448.8	496.7	1.776	
20 0.08187	451.5	500.6	1.815					
30 0.08588	467.7	519.2	1.877	0.07210	465.2	515.7	1.840	
40 0.08978	484.0	537.9	1.938	0.07558	481.9	534.8	1.901	
50 0.09357	500.7	556.8	1.997	0.07896	498.7	554.0	1.962	
60 0.09729	517.6	576.0	2.056	0.08225	515.9	573.5	2.021	
70 0.1009	535.0	595.5	2.113	0.08547	533.4	593.2	2.079	
80 0.1045	552.7	615.4	2.170	0.08863	551.2	613.2	2.137	
90 0.1081	570.7	635.6	2.227	0.09175	569.4	633.6	2.194	
100 0.1116	589.2	656.2	2.283	0.09482	587.9	654.3	2.250	
110 0.1151	608.0	677.1	2.338	0.09786	606.8	675.3	2.306	
120 0.1185	627.3	698.4	2.393	0.1009	626.2	696.8	2.361	
<i>p</i> = 8.0 bar = 0.8 MPa (T _{sat} = 18.33°C)								
Sat. 0.05776 443.1 489.3 1.729 0.05129 447.2 493.8 1.726								
20 0.05834	445.9	492.6	1.740	0.05355	460.0	508.2	1.774	
30 0.06170	462.7	512.1	1.806					
40 0.06489	479.6	531.5	1.869	0.05653	477.2	528.1	1.839	
50 0.06796	496.7	551.1	1.930	0.05938	494.7	548.1	1.901	
60 0.07094	514.0	570.8	1.990	0.06213	512.2	568.1	1.962	
70 0.07385	531.6	590.7	2.049	0.06479	530.0	588.3	2.022	
80 0.07669	549.6	611.0	2.107	0.06738	548.1	608.7	2.081	
90 0.07948	567.9	631.5	2.165	0.06992	566.5	629.4	2.138	
100 0.08222	586.5	652.3	2.221	0.07241	585.2	650.4	2.195	
110 0.08493	605.6	673.5	2.277	0.07487	604.3	671.7	2.252	
120 0.08761	625.0	695.1	2.333	0.07729	623.7	693.3	2.307	
130 0.09026	644.8	717.0	2.388	0.07969	643.6	715.3	2.363	
140 0.09289	665.0	739.3	2.442	0.08206	663.8	737.7	2.418	

TABLE A-18

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 10.0 bar = 1.0 MPa (T _{sat} = 26.95°C)								
Sat. 0.04606 451.8 497.9 1.723 0.03810 459.1 504.8 1.718								
30 0.04696	457.1	504.1	1.744	0.03957	469.4	516.9	1.757	
40 0.04980	474.8	524.6	1.810					
50 0.05248	492.4	544.9	1.874	0.04204	487.8	538.2	1.824	
60 0.05505	510.2	565.2	1.936	0.04436	506.1	559.3	1.889	
70 0.05752	528.2	585.7	1.997	0.04657	524.4	580.3	1.951	
80 0.05992	546.4	606.3	2.056	0.04869	543.1	601.5	2.012	
90 0.06226	564.9	627.2	2.114	0.05075	561.8	622.7	2.071	
100 0.06456	583.7	648.3	2.172	0.05275	580.9	644.2	2.129	
110 0.06681	603.0	669.8	2.228	0.05470	600.4	666.0	2.187	
120 0.06903	622.6	691.6	2.284	0.05662	620.1	688.0	2.244	
130 0.07122	642.5	713.7	2.340	0.05851	640.1	710.3	2.300	
140 0.07338	662.8	736.2	2.395	0.06037	660.6	733.0	2.355	
<i>p</i> = 14.0 bar = 1.4 MPa (T _{sat} = 40.97°C)								
Sat. 0.03231 465.2 510.4 1.714 0.02790 470.4 515.0 1.710								
50 0.03446	482.6	530.8	1.778	0.02861	476.7	522.5	1.733	
60 0.03664	501.6	552.9	1.845	0.03075	496.6	545.8	1.804	
70 0.03869	520.4	574.6	1.909	0.03270	516.2	568.5	1.871	
80 0.04063	539.4	596.3	1.972	0.03453	535.7	590.9	1.935	
90 0.04249	558.6	618.1	2.033	0.03626	555.2	613.2	1.997	
100 0.04429	577.9	639.9	2.092	0.03792	574.8	635.5	2.058	
110 0.04604	597.5	662.0	2.150	0.03952	594.7	657.9	2.117	
120 0.04774	617.5	684.3	2.208	0.04107	614.8	680.5	2.176	
130 0.04942	637.7	706.9	2.265	0.04259	635.3	703.4	2.233	
140 0.05106	658.3	729.8	2.321	0.04407	656.0	726.5	2.290	
150 0.05268	679.2	753.0	2.376	0.04553	677.1	749.9	2.346	
160 0.05428	700.5	776.5	2.431	0.04696	698.5	773.6	2.401	
<i>p</i> = 18.0 bar = 1.8 MPa (T _{sat} = 52.30°C)								
Sat. 0.02441 474.9 518.8 1.705 0.02157 478.7 521.8 1.700								
60 0.02606	491.1	538.0	1.763	0.02216	484.8	529.1	1.722	
70 0.02798	511.4	561.8	1.834	0.02412	506.3	554.5	1.797	
80 0.02974	531.6	585.1	1.901	0.02585	527.1	578.8	1.867	
90 0.03138	551.5	608.0	1.965	0.02744	547.6	602.5	1.933	
100 0.03293	571.5	630.8	2.027	0.02892	568.1	625.9	1.997	
110 0.03443	591.7	653.7	2.087	0.03033	588.5	649.2	2.059	
120 0.03586	612.1	676.6	2.146	0.03169	609.2	672.6	2.119	
130 0.03726	632.7	699.8	2.204	0.03299	630.0	696.0	2.178	
140 0.03863	653.6	723.1	2.262	0.03426	651.2	719.7	2.236	
150 0.03996	674.8	746.7	2.318	0.03550	672.5	743.5	2.293	
160 0.04127	696.3	770.6	2.374	0.03671	694.2	767.6	2.349	
170 0.04256	718.2	794.8	2.429	0.03790	716.2	792.0	2.404	
180 0.04383	740.4	819.3	2.484	0.03907	738.5	816.6	2.459	

TABLE A-18

(Continued)

<i>T</i> °C	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K	<i>v</i> m ³ /kg	<i>u</i> kJ/kg	<i>h</i> kJ/kg	<i>s</i> kJ/kg · K
<i>p</i> = 22.0 bar = 2.2 MPa (T _{sat} = 61.90°C)								
Sat. 0.01921 481.8 524.0 1.695 0.01721 484.3 525.6 1.688								
70 0.02086	500.5	546.4	1.761	0.01802	493.7	536.9	1.722	
80 0.02261	522.4	572.1	1.834	0.01984	517.0	564.6	1.801	
90 0.02417	543.5	596.7	1.903	0.02141	539.0	590.4	1.873	
100 0.02561	564.5	620.8	1.969	0.02283	560.6	615.4	1.941	
110 0.02697	585.3	644.6	2.032	0.02414	581.9	639.8	2.006	
120 0.02826	606.2	668.4	2.093	0.02538	603.2	664.1	2.068	
130 0.02949	627.3	692.2	2.153	0.02656	624.6	688.3	2.129	
140 0.03069	648.6	716.1	2.211	0.02770	646.0	712.5	2.188	
150 0.03185	670.1	740.2	2.269	0.02880	667.8	736.9	2.247	
160 0.03298	691.9	764.5	2.326	0.02986	689.7	761.4	2.304	
170 0.03409	714.1	789.1	2.382	0.03091	711.9	786.1	2.360	
180 0.03517	736.5	813.9	2.437	0.03193	734.5	811.1	2.416	
<i>p</i> = 26.0 bar = 2.6 MPa (T _{sat} = 70.27°C)								
Sat. 0.01549 486.2 526.5 1.681 0.01263 488.2 526.0 1.664								
80 0.01742	511.0	556.3	1.767	0.01318	495.4	534.9	1.689	
90 0.01903	534.2	583.7	1.844	0.01506	522.8	568.0	1.782	
100 0.02045	556.4	609.6	1.914	0.01654	547.2	596.8	1.860	
110 0.02174	578.3	634.8	1.981	0.01783	570.4	623.9	1.932	
120 0.02294	600.0	659.6	2.045	0.01899	593.0	650.0	1.999	
130 0.02408	621.6	684.2	2.106	0.02007	615.4	675.6	2.063	
140 0.02516	643.4	708.8	2.167	0.02109	637.7	701.0	2.126	
150 0.02621	665.3	733.4	2.226	0.02206	660.1	726.3	2.186	
160 0.02723	687.4	758.2	2.283	0.02300	682.6	751.6	2.245	
170 0.02821	709.9	783.2	2.340	0.02390	705.4	777.1	2.303	
180 0.02918	732.5	808.4	2.397	0.02478	728.3	802.6	2.360	
190 0.03012	755.5	833.8	2.452	0.02563	751.5	828.4	2.417	
<i>p</i> = 35.0 bar = 3.5 MPa (T _{sat} = 86.01°C)								
Sat. 0.00977 486.3 520.5 1.633 0.00715 474.7 503.3 1.574								
90 0.01086	502.4	540.5	1.688	0.00940	512.1	549.7	1.700	
100 0.01270	532.9	577.3	1.788					
110 0.01408	558.9	608.2	1.870	0.01110	544.7	589.1	1.804	
120 0.01526	583.4	636.8	1.944	0.01237	572.1	621.6	1.887	
130 0.01631	607.0	664.1	2.012	0.01344	597.4	651.2	1.962	
140 0.01728	630.2	690.7	2.077	0.01439	621.9	679.5	2.031	
150 0.01819	653.3	717.0	2.140	0.01527	645.9	707.0	2.097	
160 0.01906	676.4	743.1	2.201	0.01609	669.7	734.1	2.160	
170 0.01989	699.6	769.2	2.261	0.01687	693.4	760.9	2.222	
180 0.02068	722.9	795.3	2.319	0.01761	717.3	787.7	2.281	
190 0.02146	746.5	821.6	2.376	0.01833	741.2	814.5	2.340	
200 0.02221	770.3	848.0	2.433	0.01902	765.3	841.4	2.397	

TABLE A-19**Properties of Selected Solids and Liquids: c_p , ρ , and κ**

Substance	Specific Heat, c_p (kJ/kg · K)	Density, ρ (kg/m³)	Thermal Conductivity, κ (W/m · K)
<i>Selected Solids, 300K</i>			
Aluminum	0.903	2700	237
Coal, anthracite	1.260	1350	0.26
Copper	0.385	8930	401
Granite	0.775	2630	2.79
Iron	0.447	7870	80.2
Lead	0.129	11300	35.3
Sand	0.800	1520	0.27
Silver	0.235	10500	429
Soil	1.840	2050	0.52
Steel (AISI 302)	0.480	8060	15.1
Tin	0.227	7310	66.6
<i>Building Materials, 300K</i>			
Brick, common	0.835	1920	0.72
Concrete (stone mix)	0.880	2300	1.4
Glass, plate	0.750	2500	1.4
Hardboard, siding	1.170	640	0.094
Limestone	0.810	2320	2.15
Plywood	1.220	545	0.12
Softwoods (fir, pine)	1.380	510	0.12
<i>Insulating Materials, 300K</i>			
Blanket (glass fiber)	—	16	0.046
Cork	1.800	120	0.039
Duct liner (glass fiber, coated)	0.835	32	0.038
Polystyrene (extruded)	1.210	55	0.027
Vermiculite fill (flakes)	0.835	80	0.068
<i>Saturated Liquids</i>			
Ammonia, 300K	4.818	599.8	0.465
Mercury, 300K	0.139	13529	8.540
Refrigerant 22, 300K	1.267	1183.1	0.085
Refrigerant 134a, 300K	1.434	1199.7	0.081
Unused Engine Oil, 300K	1.909	884.1	0.145
Water, 275K	4.211	999.9	0.574
300K	4.179	996.5	0.613
325K	4.182	987.1	0.645
350K	4.195	973.5	0.668
375K	4.220	956.8	0.681
400K	4.256	937.4	0.688

Sources: Drawn from several sources, these data are only representative. Values can vary depending on temperature, purity, moisture content, and other factors.

TABLE A-20**Ideal Gas Specific Heats of Some Common Gases (kJ/kg · K)**

Temp. K	c_p	c_v	k	c_p	c_v	k	c_p	c_v	k	Temp. K
Air										
Nitrogen, N₂										
250	1.003	0.716	1.401	1.039	0.742	1.400	0.913	0.653	1.398	250
300	1.005	0.718	1.400	1.039	0.743	1.400	0.918	0.658	1.395	300
350	1.008	0.721	1.398	1.041	0.744	1.399	0.928	0.668	1.389	350
400	1.013	0.726	1.395	1.044	0.747	1.397	0.941	0.681	1.382	400
450	1.020	0.733	1.391	1.049	0.752	1.395	0.956	0.696	1.373	450
500	1.029	0.742	1.387	1.056	0.759	1.391	0.972	0.712	1.365	500
550	1.040	0.753	1.381	1.065	0.768	1.387	0.988	0.728	1.358	550
600	1.051	0.764	1.376	1.075	0.778	1.382	1.003	0.743	1.350	600
650	1.063	0.776	1.370	1.086	0.789	1.376	1.017	0.758	1.343	650
700	1.075	0.788	1.364	1.098	0.801	1.371	1.031	0.771	1.337	700
750	1.087	0.800	1.359	1.110	0.813	1.365	1.043	0.783	1.332	750
800	1.099	0.812	1.354	1.121	0.825	1.360	1.054	0.794	1.327	800
900	1.121	0.834	1.344	1.145	0.849	1.349	1.074	0.814	1.319	900
1000	1.142	0.855	1.336	1.167	0.870	1.341	1.090	0.830	1.313	1000
Carbon Dioxide, CO₂										
Carbon Monoxide, CO										
Hydrogen, H₂										
250	0.791	0.602	1.314	1.039	0.743	1.400	14.051	9.927	1.416	250
300	0.846	0.657	1.288	1.040	0.744	1.399	14.307	10.183	1.405	300
350	0.895	0.706	1.268	1.043	0.746	1.398	14.427	10.302	1.400	350
400	0.939	0.750	1.252	1.047	0.751	1.395	14.476	10.352	1.398	400
450	0.978	0.790	1.239	1.054	0.757	1.392	14.501	10.377	1.398	450
500	1.014	0.825	1.229	1.063	0.767	1.387	14.513	10.389	1.397	500
550	1.046	0.857	1.220	1.075	0.778	1.382	14.530	10.405	1.396	550
600	1.075	0.886	1.213	1.087	0.790	1.376	14.546	10.422	1.396	600
650	1.102	0.913	1.207	1.100	0.803	1.370	14.571	10.447	1.395	650
700	1.126	0.937	1.202	1.113	0.816	1.364	14.604	10.480	1.394	700
750	1.148	0.959	1.197	1.126	0.829	1.358	14.645	10.521	1.392	750
800	1.169	0.980	1.193	1.139	0.842	1.353	14.695	10.570	1.390	800
900	1.204	1.015	1.186	1.163	0.866	1.343	14.822	10.698	1.385	900
1000	1.234	1.045	1.181	1.185	0.888	1.335	14.983	10.859	1.380	1000

Source: Adapted from K. Wark, *Thermodynamics*, 4th ed., McGraw-Hill, New York, 1983, as based on "Tables of Thermal Properties of Gases," NBS Circular 564, 1955.

TABLE A-21**Variation of \bar{c}_p with Temperature for Selected Ideal Gases**

$$\frac{\bar{c}_p}{R} = \alpha + \beta T + \gamma T^2 + \delta T^3 + \varepsilon T^4$$

T is in K, equations valid from 300 to 1000 K

Gas	α	$\beta \times 10^3$	$\gamma \times 10^6$	$\delta \times 10^9$	$\varepsilon \times 10^{12}$
CO	3.710	-1.619	3.692	-2.032	0.240
CO ₂	2.401	8.735	-6.607	2.002	0
H ₂	3.057	2.677	-5.810	5.521	-1.812
H ₂ O	4.070	-1.108	4.152	-2.964	0.807
O ₂	3.626	-1.878	7.055	-6.764	2.156
N ₂	3.675	-1.208	2.324	-0.632	-0.226
Air	3.653	-1.337	3.294	-1.913	0.2763
SO ₂	3.267	5.324	0.684	-5.281	2.559
CH ₄	3.826	-3.979	24.558	-22.733	6.963
C ₂ H ₂	1.410	19.057	-24.501	16.391	-4.135
C ₂ H ₄	1.426	11.383	7.989	-16.254	6.749
Monatomic gases ^a	2.5	0	0	0	0

^aFor monatomic gases, such as He, Ne, and Ar, \bar{c}_p is constant over a wide temperature range and is very nearly equal to $5/2 R$.

Source: Adapted from K. Wark, *Thermodynamics*, 4th ed., McGraw-Hill, New York, 1983, as based on NASA SP-273, U.S. Government Printing Office, Washington, DC, 1971.

TABLE A-22**Ideal Gas Properties of Air**

T(K), h and u(kJ/kg), s° (kJ/kg · K)											
when $\Delta s = 0^1$				when $\Delta s = 0$							
T	h	u	s°	p _r	v _r	T	h	u	s°	p _r	v _r
200	199.97	142.56	1.29559	0.3363	1707.	450	451.80	322.62	2.11161	5.775	223.6
210	209.97	149.69	1.34444	0.3987	1512.	460	462.02	329.97	2.13407	6.245	211.4
220	219.97	156.82	1.39105	0.4690	1346.	470	472.24	337.32	2.15604	6.742	200.1
230	230.02	164.00	1.43557	0.5477	1205.	480	482.49	344.70	2.17760	7.268	189.5
240	240.02	171.13	1.47824	0.6355	1084.	490	492.74	352.08	2.19876	7.824	179.7
250	250.05	178.28	1.51917	0.7329	979.	500	503.02	359.49	2.21952	8.411	170.6
260	260.09	185.45	1.55848	0.8405	887.8	510	513.32	366.92	2.23993	9.031	162.1
270	270.11	192.60	1.59634	0.9590	808.0	520	523.63	374.36	2.25997	9.684	154.1
280	280.13	199.75	1.63279	1.0889	738.0	530	533.98	381.84	2.27967	10.37	146.7
285	285.14	203.33	1.65055	1.1584	706.1	540	544.35	389.34	2.29906	11.10	139.7
290	290.16	206.91	1.66802	1.2311	676.1	550	554.74	396.86	2.31809	11.86	133.1
295	295.17	210.49	1.68515	1.3068	647.9	560	565.17	404.42	2.33685	12.66	127.0
300	300.19	214.07	1.70203	1.3860	621.2	570	575.59	411.97	2.35531	13.50	121.2
305	305.22	217.67	1.71865	1.4686	596.0	580	586.04	419.55	2.37348	14.38	115.7
310	310.24	221.25	1.73498	1.5546	572.3	590	596.52	427.15	2.39140	15.31	110.6
315	315.27	224.85	1.75106	1.6442	549.8	600	607.02	434.78	2.40902	16.28	105.8
320	320.29	228.42	1.76690	1.7375	528.6	610	617.53	442.42	2.42644	17.30	101.2
325	325.31	232.02	1.78249	1.8345	508.4	620	628.07	450.09	2.44356	18.36	96.92
330	330.34	235.61	1.79783	1.9352	489.4	630	638.63	457.78	2.46048	19.84	92.84
340	340.42	242.82	1.82790	2.149	454.1	640	649.22	465.50	2.47716	20.64	88.99
350	350.49	250.02	1.85708	2.379	422.2	650	659.84	473.25	2.49364	21.86	85.34
360	360.58	257.24	1.88543	2.626	393.4	660	670.47	481.01	2.50985	23.13	81.89
370	370.67	264.46	1.91313	2.892	367.2	670	681.14	488.81	2.52589	24.46	78.61
380	380.77	271.69	1.94001	3.176	343.4	680	691.82	496.62	2.54175	25.85	75.50
390	390.88	278.93	1.96633	3.481	321.5	690	702.52	504.45	2.55731	27.29	72.56
400	400.98	286.16	1.99194	3.806	301.6	700	713.27	512.33	2.57277	28.80	69.76
410	411.12	293.43	2.01699	4.153	283.3	710	724.04	520.23	2.58810	30.38	67.07
420	421.26	300.69	2.04142	4.522	266.6	720	734.82	528.14	2.60319	32.02	64.53
430	431.43	307.99	2.06533	4.915	251.1	730	745.62	536.07	2.61803	33.72	62.13
440	441.61	315.30	2.08870	5.332	236.8	740	756.44	544.02	2.63280	35.50	59.82

1. p_r and v_r data for use with Eqs. 6.41 and 6.42, respectively.

TABLE A-22

(Continued)

T(K), h and u (kJ/kg), s° (kJ/kg · K)											
when $\Delta s = 0^1$				when $\Delta s = 0$							
T	h	u	s°	p_r	v_f	T	h	u	s°	p_r	v_f
750	767.29	551.99	2.64737	37.35	57.63	1300	1395.97	1022.82	3.27345	330.9	11.275
760	778.18	560.01	2.66176	39.27	55.54	1320	1419.76	1040.88	3.29160	352.5	10.747
770	789.11	568.07	2.67595	41.31	53.39	1340	1443.60	1058.94	3.30959	375.3	10.247
780	800.03	576.12	2.69013	43.35	51.64	1360	1467.49	1077.10	3.32724	399.1	9.780
790	810.99	584.21	2.70400	45.55	49.86	1380	1491.44	1095.26	3.34474	424.2	9.337
800	821.95	592.30	2.71787	47.75	48.08	1400	1515.42	1113.52	3.36200	450.5	8.919
820	843.98	608.59	2.74504	52.59	44.84	1420	1539.44	1131.77	3.37901	478.0	8.526
840	866.08	624.95	2.77170	57.60	41.85	1440	1563.51	1150.13	3.39586	506.9	8.153
860	888.27	641.40	2.79783	63.09	39.12	1460	1587.63	1168.49	3.41247	537.1	7.801
880	910.56	657.95	2.82344	68.98	36.61	1480	1611.79	1186.95	3.42892	568.8	7.468
900	932.93	674.58	2.84856	75.29	34.31	1500	1635.97	1205.41	3.44516	601.9	7.152
920	955.38	691.28	2.87324	82.05	32.18	1520	1660.23	1223.87	3.46120	636.5	6.854
940	977.92	708.08	2.89748	89.28	30.22	1540	1684.51	1242.43	3.47712	672.8	6.569
960	1000.55	725.02	2.92128	97.00	28.40	1560	1708.82	1260.99	3.49276	710.5	6.301
980	1023.25	741.98	2.94468	105.2	26.73	1580	1733.17	1279.65	3.50829	750.0	6.046
1000	1046.04	758.94	2.96770	114.0	25.17	1600	1757.57	1298.30	3.52364	791.2	5.804
1020	1068.89	776.10	2.99034	123.4	23.72	1620	1782.00	1316.96	3.53879	834.1	5.574
1040	1091.85	793.36	3.01260	133.3	22.39	1640	1806.46	1335.72	3.55381	878.9	5.355
1060	1114.86	810.62	3.03449	143.9	21.14	1660	1830.96	1354.48	3.56867	925.6	5.147
1080	1137.89	827.88	3.05608	155.2	19.98	1680	1855.50	1373.24	3.58335	974.2	4.949
1100	1161.07	845.33	3.07732	167.1	18.896	1700	1880.1	1392.7	3.5979	1025	4.761
1120	1184.28	862.79	3.09825	179.7	17.886	1750	1941.6	1439.8	3.6336	1161	4.328
1140	1207.57	880.35	3.11883	193.1	16.946	1800	2003.3	1487.2	3.6684	1310	3.944
1160	1230.92	897.91	3.13916	207.2	16.064	1850	2065.3	1534.9	3.7023	1475	3.601
1180	1254.34	915.57	3.15916	222.2	15.241	1900	2127.4	1582.6	3.7354	1655	3.295
1200	1277.79	933.33	3.17888	238.0	14.470	1950	2189.7	1630.6	3.7677	1852	3.022
1220	1301.31	951.09	3.19834	254.7	13.747	2000	2252.1	1678.7	3.7994	2068	2.776
1240	1324.93	968.95	3.21751	272.3	13.069	2050	2314.6	1726.8	3.8303	2303	2.555
1260	1348.55	986.90	3.23638	290.8	12.435	2100	2377.4	1775.3	3.8605	2559	2.356
1280	1372.24	1004.76	3.25510	310.4	11.835	2150	2440.3	1823.8	3.8901	2837	2.175
						2200	2503.2	1872.4	3.9191	3138	2.012
						2250	2566.4	1921.3	3.9474	3464	1.864

Source: Table A-22 is based on J. H. Keenan and J. Kaye, *Gas Tables*, Wiley, New York, 1945.

TABLE A-23

Ideal Gas Properties of Selected Gases

<i>T(K)</i>	Carbon Dioxide, CO ₂ ($\bar{h}_f^o = -393,520 \text{ kJ/kmol}$)				Carbon Monoxide, CO ($\bar{h}_f^o = -110,530 \text{ kJ/kmol}$)				Water Vapor, H ₂ O ($\bar{h}_f^o = -241,820 \text{ kJ/kmol}$)				Absolute entropy at 1 atm $\bar{s}^o(T)$, in kJ/kmol · K.				Nitrogen, N ₂ ($\bar{h}_f^o = 0 \text{ kJ/kmol}$)			
	<i>h</i>	<i>u</i>	<i>s</i> ^o	<i>h</i>	<i>u</i>	<i>s</i> ^o	<i>h</i>	<i>u</i>	<i>s</i> ^o	<i>h</i>	<i>u</i>	<i>s</i> ^o	<i>h</i>	<i>u</i>	<i>s</i> ^o	<i>h</i>	<i>u</i>	<i>s</i> ^o	<i>h</i>	
0	0	0	0	6,601	4,772	202,966	6,391	4,562	188,683	7,295	5,466	178,576	6,404	4,575	196,171	6,391	4,562	182,638	0	0
220	6,601	4,772	202,966	6,683	5,026	204,464	6,683	4,771	189,980	7,628	5,715	180,054	6,694	4,782	197,461	6,683	4,770	183,938	220	230
230	6,938	5,285	205,920	6,975	5,285	205,920	6,975	4,979	191,221	7,961	5,965	181,471	6,984	4,989	198,696	6,975	4,979	185,480	240	250
240	7,280	5,548	207,337	7,266	5,548	207,337	7,266	5,188	192,411	8,294	6,225	182,831	7,275	5,197	199,885	7,266	5,188	186,370	250	250
250	7,627																			
260	7,979	5,817	208,717	7,558	5,396	193,554	8,627	6,466	184,139	7,566	5,405	201,027	7,558	5,396	187,514	260				
270	8,335	6,091	210,062	7,849	5,604	194,654	8,961	6,716	185,399	7,858	5,613	202,128	7,849	5,604	188,614	270				
280	8,697	6,369	211,376	8,140	5,812	195,173	9,296	6,968	186,616	8,150	5,822	203,191	8,141	5,813	189,673	280				
290	9,063	6,651	212,660	8,432	6,020	196,735	9,631	7,219	187,791	8,443	6,032	204,218	8,432	6,021	190,695	290				
298	9,364	6,885	213,685	8,669	6,190	197,543	9,904	7,425	188,720	8,682	6,203	205,033	8,669	6,190	191,502	298				
300	9,431	6,939	213,915	8,723	6,229	197,723	9,966	7,472	188,928	8,736	6,242	205,213	8,723	6,229	191,682	300				
310	9,807	7,230	215,146	9,014	6,437	198,678	10,302	7,725	190,030	9,030	6,453	206,177	9,016	6,437	192,638	310				
320	10,186	7,526	216,351	9,306	6,645	199,603	10,639	7,978	191,098	9,325	6,664	207,112	9,306	6,645	193,562	320				
330	10,570	7,826	217,534	9,597	6,854	200,500	10,976	8,232	192,136	9,620	6,877	208,020	9,597	6,853	194,459	330				
340	10,959	8,131	218,694	9,889	7,062	201,371	11,314	8,487	193,144	9,916	7,090	208,904	9,888	7,061	195,328	340				
350	11,351	8,439	219,831	10,181	7,271	202,217	11,652	8,742	194,125	10,213	7,303	209,765	10,180	7,270	196,173	350				
360	11,748	8,752	220,948	10,473	7,480	203,040	11,992	8,998	195,081	10,511	7,518	210,604	10,471	7,478	196,995	360				
370	12,148	9,068	222,044	10,765	7,689	203,842	12,331	9,255	196,012	10,809	7,733	211,423	10,763	7,687	197,794	370				
380	12,552	9,392	223,122	11,058	7,899	204,622	12,672	9,513	196,920	11,109	7,949	212,222	11,055	7,895	198,572	380				
390	12,960	9,718	224,182	11,351	8,108	205,383	13,014	9,771	197,807	11,409	8,166	213,002	11,347	8,104	199,331	390				
400	13,372	10,046	225,225	11,644	8,319	206,125	13,356	10,030	198,673	11,711	8,384	213,765	11,640	8,314	200,071	400				
410	13,787	10,378	226,250	11,938	8,529	206,850	13,699	10,290	199,521	12,012	8,603	214,510	11,932	8,523	200,794	410				
420	14,206	10,714	227,258	12,232	8,740	207,549	14,043	10,551	200,350	12,314	8,822	215,241	12,225	8,733	201,499	420				
430	14,628	11,053	228,252	12,526	8,951	208,252	14,388	10,833	201,160	12,618	9,043	215,955	12,518	8,943	202,189	430				
440	15,054	11,393	229,230	12,821	9,163	208,929	14,734	11,075	201,955	12,923	9,264	216,656	12,811	9,153	202,863	440				
450	15,483	11,742	230,194	13,116	9,375	209,593	15,080	11,339	202,734	13,228	9,487	217,342	13,105	9,363	203,523	450				
460	15,916	12,091	231,144	13,412	9,587	210,243	15,428	11,603	203,497	13,535	9,710	218,016	13,399	9,574	204,170	460				
470	16,351	12,444	232,080	13,708	9,800	210,880	15,777	11,869	204,247	13,842	9,935	218,676	13,693	9,786	204,803	470				
480	16,791	12,800	233,004	14,005	10,014	211,504	16,126	12,135	204,982	14,151	10,160	219,326	13,988	9,997	205,424	480				
490	17,232	13,158	233,916	14,302	10,228	212,117	16,477	12,403	205,705	14,460	10,386	219,963	14,285	10,210	206,033	490				
500	17,678	13,521	234,814	14,600	10,443	212,719	16,828	12,671	206,413	14,770	10,614	220,589	14,581	10,423	206,630	500				
510	18,126	13,885	235,700	14,898	10,658	213,310	17,181	12,940	207,112	15,082	10,842	221,206	14,876	10,635	207,216	510				
520	18,576	14,253	236,575	15,197	10,874	213,890	17,534	13,211	207,799	15,395	11,071	221,812	15,172	10,848	207,792	520				
530	19,029	14,622	237,439	15,497	11,090	214,460	17,889	13,482	208,475	15,708	11,301	222,409	15,469	11,062	208,358	530				
540	19,495	14,985	238,292	15,797	11,307	215,020	18,245	13,755	209,139	16,022	11,533	222,997	15,766	11,277	208,914	540				
550	19,945	15,372	239,135	16,097	11,524	215,572	18,601	14,028	209,795	16,338	11,765	223,576	16,064	11,492	209,461	550				
560	20,407	15,751	239,962	16,399	11,743	216,145	18,959	14,303	210,440	16,654	11,998	224,146	16,363	11,707	209,999	560				
570	20,870	16,131	240,789	16,701	11,961	216,649	19,318	14,579	211,075	16,971	12,232	224,708	16,662	11,923	210,528	570				
580	21,337	16,515	241,602	17,003	12,181	217,175	19,678	14,856	211,702	17,290	12,467	225,262	16,962	12,139	211,049	580				
590	21,807	16,902	242,405	17,307	12,401	217,693	20,039	15,134	212,320	17,609	12,703	225,808	17,262	12,356	211,562	590				

Table A-23

Table A-23

(Continued)

$T(K)$	Carbon Dioxide, CO_2 ($\bar{h}_f^\circ = -393.520 \text{ kJ/kmol}$)				Carbon Monoxide, CO ($\bar{h}_f^\circ = -110.530 \text{ kJ/kmol}$)				Water Vapor, H_2O ($\bar{h}_f^\circ = -241.820 \text{ kJ/kmol}$)				Oxygen, O_2 ($\bar{h}_f^\circ = 0 \text{ kJ/kmol}$)				Nitrogen, N_2 ($\bar{h}_f^\circ = 0 \text{ kJ/kmol}$)			
	\bar{h}	\bar{u}	\bar{s}°	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{s}°	$T(K)$			
600	22,280	17,291	243,199	17,611	12,622	218,204	20,402	15,413	212,920	17,929	12,940	226,346	17,563	12,574	212,066	600				
610	22,754	17,683	243,983	17,915	12,843	218,708	20,765	15,693	213,529	18,250	13,178	226,877	17,864	12,792	212,564	610				
620	23,231	18,076	244,758	18,221	13,066	219,205	21,130	15,975	214,122	18,572	13,417	227,400	18,166	13,011	213,055	620				
630	23,709	18,471	245,524	18,527	13,289	219,695	21,495	16,257	214,707	18,895	13,657	227,918	18,468	13,230	213,541	630				
640	24,190	18,869	246,282	18,833	13,512	220,179	21,862	16,541	215,285	19,29	13,898	228,429	18,772	13,450	214,018	640				
650	24,674	19,270	247,032	19,141	13,736	220,656	22,230	16,826	215,856	19,544	14,140	228,932	19,075	13,671	214,489	650				
660	25,160	19,672	247,773	19,449	13,962	221,127	22,600	17,112	216,419	19,870	14,383	229,430	19,380	13,892	214,954	660				
670	25,648	20,078	248,507	19,758	14,187	221,592	22,970	17,399	216,976	20,197	14,626	229,920	19,685	14,114	215,413	670				
680	26,138	20,484	249,233	20,068	14,414	222,052	23,342	17,688	217,527	20,524	14,871	230,405	19,991	14,337	215,866	680				
690	26,631	20,894	249,952	20,378	14,641	222,505	23,714	17,978	218,071	20,854	15,116	230,885	20,297	14,560	216,314	690				
700	27,125	21,305	250,663	20,690	14,870	222,953	24,088	18,268	218,610	21,184	15,364	231,358	20,604	14,784	216,756	700				
710	27,622	21,719	251,368	21,002	15,099	223,396	24,464	18,561	219,142	21,514	15,611	231,827	20,912	15,008	217,192	710				
720	28,121	22,134	252,065	21,315	15,328	223,833	24,840	18,854	219,668	21,845	15,859	232,291	21,220	15,234	217,624	720				
730	28,622	22,552	252,755	21,628	15,558	224,265	25,218	19,148	220,189	22,177	16,107	232,748	21,529	15,460	218,059	730				
740	29,124	22,972	253,439	21,943	15,789	224,692	25,597	19,444	220,707	22,510	16,357	233,201	21,839	15,686	218,472	740				
750	29,629	23,393	254,117	22,258	16,022	225,115	25,977	19,741	221,215	22,844	16,607	233,649	22,149	15,913	218,889	750				
760	30,135	23,817	254,787	22,573	16,255	225,533	26,358	20,039	221,720	23,178	16,859	234,091	22,460	16,141	219,301	760				
770	30,644	24,242	255,452	22,890	16,488	225,947	26,741	20,339	222,221	23,513	17,111	234,528	22,772	16,370	219,709	770				
780	31,154	24,669	256,110	23,208	16,723	226,357	27,125	20,639	222,717	23,850	17,364	234,960	23,085	16,599	220,113	780				
790	31,665	25,097	256,762	23,526	16,957	226,762	27,510	20,941	223,207	24,186	17,618	235,387	23,398	16,830	220,512	790				
800	32,179	25,527	257,408	23,844	17,193	227,162	27,896	21,245	223,693	24,523	17,872	235,810	23,714	17,061	220,907	800				
810	32,694	25,959	258,048	24,164	17,429	227,559	28,284	21,549	224,174	24,861	18,126	236,230	24,027	17,292	221,298	810				
820	33,212	26,394	258,682	24,483	17,665	227,952	28,672	21,855	224,651	25,19	18,382	236,644	24,342	17,524	221,684	820				
830	33,730	26,829	259,311	24,803	17,902	228,339	29,062	22,162	225,123	25,537	18,637	237,055	24,658	17,757	222,067	830				
840	34,251	27,267	259,974	25,124	18,140	228,724	29,454	22,470	225,592	25,877	18,893	237,462	24,974	17,990	222,447	840				
850	34,773	27,706	260,551	25,446	18,379	229,106	29,846	22,779	226,057	26,218	19,150	237,864	25,292	18,224	222,822	850				
860	35,296	28,125	261,164	25,768	18,617	229,482	30,240	23,090	226,517	26,559	19,408	238,264	25,610	18,459	223,194	860				
870	35,821	28,588	261,770	26,091	18,858	229,856	30,635	23,402	226,973	26,899	19,666	238,660	25,928	18,695	223,562	870				
880	36,347	29,031	262,371	26,415	19,099	230,227	31,032	23,745	227,426	27,242	19,925	239,051	26,248	19,931	223,927	880				
890	36,876	29,476	262,968	26,740	19,341	230,593	31,429	24,029	227,875	27,584	20,185	239,439	26,568	19,168	224,288	890				
900	37,405	29,922	263,559	27,066	19,583	230,957	31,828	24,345	228,321	27,928	20,445	239,823	26,890	19,407	224,647	900				
910	37,935	30,369	264,146	27,392	19,826	231,317	32,228	24,662	228,763	28,272	20,706	240,203	27,210	19,644	225,002	910				
920	38,467	30,818	264,728	27,719	20,070	231,674	32,629	24,980	229,202	28,616	20,967	240,580	27,532	19,883	225,353	920				
930	39,000	31,268	265,304	28,046	20,314	232,028	33,032	25,300	229,637	28,960	21,228	240,953	27,854	20,122	225,701	930				
940	39,535	31,719	265,877	28,375	20,559	232,379	33,436	25,621	230,070	29,306	21,491	241,323	28,178	20,362	226,047	940				
950	40,070	32,171	266,444	28,703	20,805	232,727	33,841	25,943	230,499	29,652	21,754	241,689	28,501	20,603	226,389	950				
960	40,607	32,625	267,097	29,033	21,051	233,072	34,247	26,265	230,924	29,999	22,017	242,052	28,826	20,844	226,728	960				
970	41,145	33,081	267,566	29,362	21,298	233,413	34,653	26,588	231,347	30,345	22,280	242,411	29,151	21,086	227,064	970				
980	41,685	33,537	268,119	29,693	21,545	233,752	35,061	26,913	231,767	30,692	22,544	242,768	29,476	21,328	227,398	980				
990	42,226	33,995	268,670	30,024	21,793	234,088	35,472	27,240	232,184	32,240	22,809	243,120	21,571	21,571	227,728	990				

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(Continued)

$T(K)$	Carbon Dioxide, CO_2 ($\bar{h}_f = -393520 \text{ kJ/kmol}$)				Carbon Monoxide, CO ($\bar{h}_f = -410530 \text{ kJ/kmol}$)				Water Vapor, H_2O ($\bar{h}_f = -241820 \text{ kJ/kmol}$)				Oxygen, O_2 ($\bar{h}_f = 0 \text{ kJ/kmol}$)				Nitrogen, N_2 ($\bar{h}_f = 0 \text{ kJ/kmol}$)			
	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	$T(K)$	
1000	42,769	34,455	269,215	30,355	22,041	234,421	35,882	27,568	232,597	31,389	23,075	243,471	30,129	21,815	228,057	1000				
1020	43,859	35,378	270,293	31,020	22,540	235,079	36,709	28,228	233,415	32,088	23,607	244,164	30,784	22,304	228,706	1020				
1040	44,953	36,306	271,354	31,688	23,041	235,728	37,542	28,895	234,223	32,789	24,142	244,844	31,442	22,795	229,344	1040				
1060	46,051	37,238	272,400	32,357	23,544	236,364	38,380	29,567	235,020	33,490	24,677	245,513	32,101	23,288	229,973	1060				
1080	47,153	38,174	273,430	33,029	24,049	236,992	39,223	30,243	235,806	34,194	25,214	246,171	32,762	23,782	230,591	1080				
1100	48,258	39,112	274,445	33,702	24,557	237,609	40,071	30,925	236,584	34,899	25,753	246,818	33,426	24,280	231,199	1100				
1120	49,369	40,057	275,444	34,377	25,065	238,217	40,923	34,611	237,352	35,606	26,294	247,454	34,092	24,780	231,799	1120				
1140	50,484	41,006	276,430	35,054	25,575	238,817	41,780	32,301	238,110	36,314	26,836	248,081	34,760	25,282	232,391	1140				
1160	51,602	41,957	277,403	35,733	26,088	239,407	42,642	32,997	238,859	37,023	27,379	248,698	35,430	25,786	232,973	1160				
1180	52,724	42,933	278,362	36,406	26,602	239,989	43,509	33,698	239,600	37,734	27,923	249,307	36,104	26,291	233,549	1180				
1200	53,848	43,871	279,307	37,095	27,118	240,663	44,380	34,403	240,333	38,447	28,469	249,906	36,777	26,799	234,115	1200				
1220	54,977	44,834	280,238	37,780	27,637	241,128	45,256	35,112	241,057	39,162	29,018	250,497	37,452	27,308	234,673	1220				
1240	56,108	45,799	281,158	38,466	28,426	241,686	46,137	35,827	241,773	39,877	29,568	251,079	38,129	27,819	235,223	1240				
1260	57,244	46,768	282,066	39,154	28,678	242,236	47,022	36,546	242,482	40,594	30,118	251,653	38,807	28,331	235,766	1260				
1280	58,381	47,739	282,962	39,884	29,201	242,780	47,912	37,270	243,183	41,312	30,670	252,219	39,488	28,845	236,302	1280				
1300	59,522	48,713	283,847	40,534	29,725	243,316	48,807	38,000	243,877	42,033	31,224	252,776	40,170	29,361	236,831	1300				
1320	60,666	49,691	284,722	41,266	30,251	243,844	49,707	38,732	244,564	42,753	31,778	253,325	40,853	29,878	237,353	1320				
1340	61,813	50,672	285,586	41,919	30,778	243,366	50,612	39,470	245,243	43,475	32,334	253,868	41,539	30,398	237,867	1340				
1360	62,963	51,656	286,439	42,613	31,306	244,880	51,521	40,213	245,955	44,198	32,891	254,404	42,227	30,919	238,376	1360				
1380	64,116	52,643	287,283	43,309	31,836	245,388	52,434	40,960	246,582	44,923	33,449	254,932	42,915	31,441	238,878	1380				
1400	65,271	53,631	288,106	44,007	32,367	245,889	53,351	41,711	247,241	45,648	34,008	255,454	43,605	31,964	239,375	1400				
1420	66,427	54,621	288,934	44,707	32,900	246,385	54,273	42,466	247,895	46,374	34,567	255,968	44,295	32,489	239,865	1420				
1440	67,586	55,614	289,743	45,408	33,434	246,876	55,198	43,226	248,543	47,102	35,129	256,475	44,988	33,014	240,350	1440				
1460	68,748	56,609	290,542	46,110	33,971	247,360	56,128	43,989	249,185	47,831	35,692	256,978	45,682	33,543	240,827	1460				
1480	69,911	57,606	291,333	46,813	34,508	247,839	57,062	44,756	249,820	48,561	36,256	257,474	46,377	34,071	241,301	1480				
1500	71,078	58,606	292,114	47,517	35,046	248,312	57,999	45,528	250,450	49,292	36,821	257,965	47,073	34,601	241,768	1500				
1520	72,246	59,609	292,888	48,222	35,584	248,778	58,942	46,304	251,074	50,024	37,387	258,450	47,771	35,133	242,228	1520				
1540	73,417	60,613	292,654	48,928	36,124	249,240	59,888	47,084	251,693	50,756	37,952	258,928	48,470	35,665	242,685	1540				
1560	74,590	61,620	294,411	49,635	36,665	249,695	60,838	47,868	252,305	51,490	38,520	259,402	49,168	36,197	243,137	1560				
1580	76,767	62,630	295,161	50,344	37,207	250,147	61,792	48,655	252,912	52,224	39,088	259,870	49,869	36,732	243,585	1580				
1600	76,944	63,741	295,901	51,053	37,750	250,592	62,748	49,445	253,513	52,961	39,658	260,333	50,571	37,268	244,028	1600				
1620	78,123	64,653	296,632	51,763	38,293	251,033	63,709	52,240	254,111	53,696	40,227	260,791	51,275	37,806	244,464	1620				
1640	79,303	65,668	297,356	52,472	38,837	251,470	64,675	51,039	254,703	54,434	40,799	261,242	51,980	38,344	244,896	1640				
1660	80,486	66,592	298,072	53,184	39,382	251,901	65,643	51,841	255,290	55,172	41,370	261,690	52,686	38,884	245,324	1660				
1680	81,670	67,702	298,781	53,895	39,927	252,329	66,614	52,646	255,873	55,912	41,944	262,132	53,393	39,424	245,747	1680				
1700	82,856	68,721	299,482	54,609	40,474	252,751	67,589	53,455	256,450	56,652	42,517	262,571	54,099	39,965	246,166	1700				
1720	84,043	69,742	300,177	55,323	41,023	253,169	68,567	54,267	257,022	57,394	43,093	263,005	54,807	40,507	246,580	1720				
1740	85,231	70,764	300,863	56,039	41,572	253,582	69,550	55,083	257,589	58,136	43,669	263,435	55,516	41,049	246,990	1740				

Table A-23

(Continued)

$T(K)$	Carbon Dioxide, CO_2 ($\bar{h}_f = -393.520 \text{ kJ/kmol}$)				Carbon Monoxide, CO ($\bar{h}_f = -110.530 \text{ kJ/kmol}$)				Water Vapor, H_2O ($\bar{h}_f = -241.820 \text{ kJ/kmol}$)				Oxygen, O_2 ($\bar{h}_f = 0 \text{ kJ/kmol}$)				Nitrogen, N_2 ($\bar{h}_f = 0 \text{ kJ/kmol}$)			
	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	$T(K)$	
1760	86,420	71,787	301,543	56,756	42,123	253,991	70,535	55,902	258,151	58,800	44,247	263,861	56,227	41,594	247,396	1760				
1780	87,612	72,812	302,271	57,473	42,673	254,398	71,523	56,723	258,708	59,624	44,825	264,283	56,938	42,139	247,798	1780				
1800	88,806	73,840	302,884	58,191	43,225	254,797	72,513	57,547	259,262	60,371	45,405	264,701	57,651	42,685	248,195	1800				
1820	90,000	74,868	303,544	58,910	43,778	255,194	73,507	58,375	259,811	61,118	45,986	265,113	58,363	43,231	248,589	1820				
1840	91,196	75,897	304,198	59,629	44,331	255,587	74,506	59,207	260,357	61,866	46,568	265,521	59,075	43,777	248,979	1840				
1860	92,394	76,929	304,845	60,351	44,886	255,976	75,506	60,042	260,898	62,616	47,151	265,925	59,790	44,324	249,365	1860				
1880	93,593	77,962	305,487	61,072	45,441	256,361	76,511	60,880	261,436	63,365	47,734	266,326	60,504	44,873	249,748	1880				
1900	94,793	78,996	306,122	61,794	45,997	256,743	77,517	61,720	261,969	64,116	48,319	266,722	61,220	45,423	250,128	1900				
1920	95,995	80,031	306,751	62,516	46,552	257,122	78,527	62,564	262,497	64,868	48,904	267,115	61,936	45,973	250,502	1920				
1940	97,197	81,067	307,374	63,238	47,108	257,497	79,540	63,411	263,022	65,620	49,490	267,505	62,654	46,524	250,874	1940				
1960	98,401	82,105	307,992	63,961	47,665	257,868	80,555	64,259	263,542	66,374	50,078	267,891	63,381	47,975	251,242	1960				
1980	99,606	83,144	308,604	64,684	48,221	258,236	81,573	65,111	264,059	67,127	50,665	268,275	64,090	47,627	251,607	1980				
2000	100,804	84,185	309,210	65,408	48,780	258,600	82,593	65,965	264,571	67,881	51,253	268,655	64,810	48,181	251,969	2000				
2050	103,835	86,791	310,701	67,224	50,179	259,494	85,156	68,111	265,838	69,772	52,727	269,588	66,612	49,567	252,858	2050				
2100	106,864	89,404	312,160	69,044	51,584	260,370	87,735	70,275	267,081	71,668	54,208	270,504	68,417	50,957	253,726	2100				
2150	109,898	92,023	313,589	70,864	52,988	261,226	90,330	72,454	268,301	73,573	55,697	271,399	70,226	52,351	254,578	2150				
2200	112,939	94,648	314,988	72,688	54,396	262,065	92,940	74,649	269,500	75,484	57,192	272,278	72,040	53,749	255,412	2200				
2250	115,984	97,277	316,356	74,516	55,809	262,887	95,562	76,855	270,679	77,397	58,690	273,136	73,856	55,149	256,227	2250				
2300	119,035	99,912	317,695	76,345	57,222	263,692	98,199	79,076	271,839	79,316	60,193	273,981	75,676	56,553	257,027	2300				
2350	122,091	102,552	319,011	78,178	58,640	264,480	100,846	81,308	272,978	81,243	61,704	274,809	77,496	57,958	257,810	2350				
2400	125,152	105,197	320,302	80,015	60,060	265,253	103,508	83,553	274,098	83,174	63,219	275,625	79,320	59,366	258,580	2400				
2450	128,219	107,849	321,566	81,852	61,482	266,012	106,183	85,811	275,201	85,112	64,742	276,424	81,149	60,779	259,332	2450				
2500	131,290	110,504	322,808	83,692	62,906	266,755	108,868	88,082	276,286	87,057	66,271	277,207	82,981	62,195	260,073	2500				
2550	134,368	113,166	324,026	85,537	64,335	267,485	111,565	90,364	277,354	89,004	67,802	277,979	84,814	63,613	260,799	2550				
2600	137,449	115,832	325,222	87,383	65,766	268,202	114,273	92,656	278,407	90,956	69,339	278,738	86,650	65,033	261,512	2600				
2650	140,533	118,500	326,396	89,230	67,197	268,905	116,91	94,958	279,441	92,916	70,883	279,485	88,488	66,455	262,213	2650				
2700	143,620	121,172	327,549	91,077	68,628	269,596	119,717	97,269	280,462	94,881	72,433	280,219	90,328	67,880	262,902	2700				
2750	146,713	123,849	328,684	92,930	70,066	270,285	122,453	99,588	281,464	96,852	73,987	280,942	92,171	69,306	263,577	2750				
2800	149,808	126,528	329,800	94,784	71,504	270,943	125,198	101,917	282,453	98,826	75,546	281,654	94,014	70,734	264,241	2800				
2850	152,908	129,212	330,896	96,639	72,945	271,602	127,952	104,256	283,429	100,808	77,112	282,357	95,859	72,163	264,895	2850				
2900	156,009	131,898	331,975	98,495	74,383	272,249	130,717	106,605	284,390	102,793	78,682	283,048	97,705	73,593	265,538	2900				
2950	159,117	134,589	333,037	100,352	75,825	272,884	133,486	108,959	285,338	104,785	80,258	283,728	99,556	75,028	266,170	2950				
3000	162,226	137,283	334,084	102,210	77,267	273,508	136,264	111,321	286,273	106,780	81,837	284,399	101,407	76,464	266,793	3000				
3050	165,341	139,982	335,114	104,073	78,715	274,123	139,051	113,692	287,194	108,778	83,419	285,060	103,260	77,902	267,404	3050				
3100	168,456	142,681	336,126	105,939	80,164	274,730	141,846	116,072	288,102	110,784	85,009	285,713	105,115	79,341	268,007	3100				
3150	171,576	145,385	337,124	107,802	81,612	275,326	144,648	118,458	288,999	112,795	86,601	286,355	106,972	80,782	268,601	3150				
3200	174,695	148,089	338,199	109,667	83,061	275,914	147,457	120,851	289,884	114,809	88,203	286,989	108,830	82,224	269,186	3200				
3250	177,822	150,801	339,069	111,534	84,513	276,494	150,272	123,250	290,756	116,827	89,804	287,614	110,690	83,668	269,763	3250				

Source: Table A-23 is based on the JANAF Thermochemical Tables, NSRDS-NBS-37, 1971.

TABLE A-24**Constants for the van der Waals, Redlich–Kwong, and Benedict–Webb–Rubin Equations of State**1. van der Waals and Redlich–Kwong: Constants for pressure in bar, specific volume in m³/kmol, and temperature in K

Substance	van der Waals		Redlich–Kwong	
	a bar $\left(\frac{m^3}{kmol}\right)^2$	b $\frac{m^3}{kmol}$	a bar $\left(\frac{m^3}{kmol}\right)^2 K^{1/2}$	b $\frac{m^3}{kmol}$
Air	1.368	0.0367	15.989	0.02541
Butane (C ₄ H ₁₀)	13.86	0.1162	289.55	0.08060
Carbon dioxide (CO ₂)	3.647	0.0428	64.43	0.02963
Carbon monoxide (CO)	1.474	0.0395	17.22	0.02737
Methane (CH ₄)	2.293	0.0428	32.11	0.02965
Nitrogen (N ₂)	1.366	0.0386	15.53	0.02677
Oxygen (O ₂)	1.369	0.0317	17.22	0.02197
Propane (C ₃ H ₈)	9.349	0.0901	182.23	0.06242
Refrigerant 12	10.49	0.0971	208.59	0.06731
Sulfur dioxide (SO ₂)	6.883	0.0569	144.80	0.03945
Water (H ₂ O)	5.531	0.0305	142.59	0.02111

Source: Calculated from critical data.

2. Benedict–Webb–Rubin: Constants for pressure in bar, specific volume in m³/kmol, and temperature in K

Substance	a	A	b	B	c	C	α	γ
C ₄ H ₁₀	1.9073	10.218	0.039998	0.12436	3.206×10^5	1.006×10^6	1.101×10^{-3}	0.0340
CO ₂	0.1386	2.7737	0.007210	0.04991	1.512×10^4	1.404×10^5	8.47×10^{-5}	0.00539
CO	0.0371	1.3590	0.002632	0.05454	1.054×10^3	8.676×10^3	1.350×10^{-4}	0.0060
CH ₄	0.0501	1.8796	0.003380	0.04260	2.579×10^3	2.287×10^4	1.244×10^{-4}	0.0060
N ₂	0.0254	1.0676	0.002328	0.04074	7.381×10^2	8.166×10^3	1.272×10^{-4}	0.0053

Source: H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing*, 46 (12): 141 (1967).

TABLE A-25**Thermochemical Properties of Selected Substances at 298K and 1 atm**

Substance	Formula	Molar Mass, <i>M</i> (kg/kmol)	Enthalpy of Formation, \bar{h}_f° (kJ/kmol)	Gibbs Function of Formation, \bar{g}° (kJ/kmol)	Absolute Entropy, \bar{s}° (kJ/kmol · K)	Heating Values	
						Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H ₂ (g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N ₂ (g)	28.01	0	0	191.50	—	—
Oxygen	O ₂ (g)	32.00	0	0	205.03	—	—
Carbon monoxide	CO(g)	28.01	-110,530	-137,150	197.54	—	—
Carbon dioxide	CO ₂ (g)	44.01	-393,520	-394,380	213.69	—	—
Water	H ₂ O(g)	18.02	-241,820	-228,590	188.72	—	—
Water	H ₂ O(l)	18.02	-285,830	-237,180	69.95	—	—
Hydrogen peroxide	H ₂ O ₂ (g)	34.02	-136,310	-105,600	232.63	—	—
Ammonia	NH ₃ (g)	17.03	-46,190	-16,590	192.33	—	—
Oxygen	O(g)	16.00	249,170	231,770	160.95	—	—
Hydrogen	H(g)	1.008	218,000	203,290	114.61	—	—
Nitrogen	N(g)	14.01	472,680	455,510	153.19	—	—
Hydroxyl	OH(g)	17.01	39,460	34,280	183.75	—	—
Methane	CH ₄ (g)	16.04	-74,850	-50,790	186.16	55,510	50,020
Acetylene	C ₂ H ₂ (g)	26.04	226,730	209,170	200.85	49,910	48,220
Ethylene	C ₂ H ₄ (g)	28.05	52,280	68,120	219.83	50,300	47,160
Ethane	C ₂ H ₆ (g)	30.07	-84,680	-32,890	229.49	51,870	47,480
Propylene	C ₃ H ₆ (g)	42.08	20,410	62,720	266.94	48,920	45,780
Propane	C ₃ H ₈ (g)	44.09	-103,850	-23,490	269.91	50,350	46,360
Butane	C ₄ H ₁₀ (g)	58.12	-126,150	-15,710	310.03	49,500	45,720
Pentane	C ₅ H ₁₂ (g)	72.15	-146,440	-8,200	348.40	49,010	45,350
Octane	C ₈ H ₁₈ (g)	114.22	-208,450	17,320	463.67	48,260	44,790
Octane	C ₈ H ₁₈ (l)	114.22	-249,910	6,610	360.79	47,900	44,430
Benzene	C ₆ H ₆ (g)	78.11	82,930	129,660	269.20	42,270	40,580
Methanol	CH ₃ OH(g)	32.04	-200,890	-162,140	239.70	23,850	21,110
Methanol	CH ₃ OH(l)	32.04	-238,810	-166,290	126.80	22,670	19,920
Ethanol	C ₂ H ₅ OH(g)	46.07	-235,310	-168,570	282.59	30,590	27,720
Ethanol	C ₂ H ₅ OH(l)	46.07	-277,690	-174,890	160.70	29,670	26,800

Source: Based on JANAF Thermochemical Tables, NSRDS-NBS-37, 1971; *Selected Values of Chemical Thermodynamic Properties*, NBS Tech. Note 270-3, 1968; and API Research Project 44, Carnegie Press, 1953. Heating values calculated.

TABLE A-26**Standard Molar Chemical Exergy, \bar{e}^{ch} (kJ/kmol), of Selected Substances at 298 K and p_0**

Substance	Formula	Model I ^a	Model II ^b
Nitrogen	N ₂ (g)	640	720
Oxygen	O ₂ (g)	3,950	3,970
Carbon dioxide	CO ₂ (g)	14,175	19,870
Water	H ₂ O(g)	8,635	9,500
Water	H ₂ O(l)	45	900
Carbon (graphite)	C(s)	404,590	410,260
Hydrogen	H ₂ (g)	235,250	236,100
Sulfur	S(s)	598,160	609,600
Carbon monoxide	CO(g)	269,410	275,100
Sulfur dioxide	SO ₂ (g)	301,940	313,400
Nitrogen monoxide	NO(g)	88,850	88,900
Nitrogen dioxide	NO ₂ (g)	55,565	55,600
Hydrogen sulfide	H ₂ S(g)	799,890	812,000
Ammonia	NH ₃ (g)	336,685	337,900
Methane	CH ₄ (g)	824,350	831,650
Acetylene	C ₂ H ₂ (g)	—	1,265,800
Ethylene	C ₂ H ₄ (g)	—	1,361,100
Ethane	C ₂ H ₆ (g)	1,482,035	1,495,840
Propylene	C ₃ H ₆ (g)	—	2,003,900
Propane	C ₃ H ₈ (g)	—	2,154,000
Butane	C ₄ H ₁₀ (g)	—	2,805,800
Pentane	C ₅ H ₁₂ (g)	—	3,463,300
Benzene	C ₆ H ₆ (g)	—	3,303,600
Octane	C ₈ H ₁₈ (l)	—	5,413,100
Methanol	CH ₃ OH(g)	715,070	722,300
Methanol	CH ₃ OH(l)	710,745	718,000
Ethanol	C ₂ H ₅ OH(g)	1,348,330	1,363,900
Ethanol	C ₂ H ₅ OH(l)	1,342,085	1,357,700

^aJ. Ahrendts, "Die Exergie Chemisch Reaktionsfähiger Systeme," *VDI-Forschungsheft*, VDI-Verlag, Dusseldorf, 579, 1977. Also see "Reference States," *Energy—The International Journal*, 5: 667–677, 1980. In Model I, $p_0 = 1.019$ atm. This model attempts to impose a criterion that the reference environment be in equilibrium. The reference substances are determined assuming restricted chemical equilibrium for nitric acid and nitrates and unrestricted thermodynamic equilibrium for all other chemical components of the atmosphere, the oceans, and a portion of the Earth's crust. The chemical composition of the gas phase of this model approximates the composition of the natural atmosphere.

^bJ. Szargut, D. R. Morris, and F. R. Steward, *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes*, Hemisphere, New York, 1988. In Model II, $p_0 = 1.0$ atm. In developing this model a reference substance is selected for each chemical element from among substances that contain the element being considered and that are abundantly present in the natural environment, even though the substances are not in completely mutual stable equilibrium. An underlying rationale for this approach is that substances found abundantly in nature have little economic value. On an overall basis, the chemical composition of the exergy reference environment of Model II is closer than Model I to the composition of the natural environment, but the equilibrium criterion is not always satisfied.

TABLE A-27**Logarithms to the Base 10 of the Equilibrium Constant K**

Temp. K	$H_2 \rightleftharpoons 2H$	$\log_{10} K$							Temp. °R
		$O_2 \rightleftharpoons 2O$	$N_2 \rightleftharpoons 2N$	$\frac{1}{2}O_2 + \frac{1}{2}N_2 \rightleftharpoons NO$	$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$	$H_2O \rightleftharpoons OH + \frac{1}{2}H_2$	$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	
298	-71.224	-81.208	-159.600	-15.171	-40.048	-46.054	-45.066	-5.018	537
500	-40.316	-45.880	-92.672	-8.783	-22.886	-26.130	-25.025	-2.139	900
1000	-17.292	-19.614	-43.056	-4.062	-10.062	-11.280	-10.221	-0.159	1800
1200	-13.414	-15.208	-34.754	-3.275	-7.899	-8.811	-7.764	+0.135	2160
1400	-10.630	-12.054	-28.812	-2.712	-6.347	-7.021	-6.014	+0.333	2520
1600	-8.532	-9.684	-24.350	-2.290	-5.180	-5.677	-4.706	+0.474	2880
1700	-7.666	-8.706	-22.512	-2.116	-4.699	-5.124	-4.169	+0.530	3060
1800	-6.896	-7.836	-20.874	-1.962	-4.270	-4.613	-3.693	+0.577	3240
1900	-6.204	-7.058	-19.410	-1.823	-3.886	-4.190	-3.267	+0.619	3420
2000	-5.580	-6.356	-18.092	-1.699	-3.540	-3.776	-2.884	+0.656	3600
2100	-5.016	-5.720	-16.898	-1.586	-3.227	-3.434	-2.539	+0.688	3780
2200	-4.502	-5.142	-15.810	-1.484	-2.942	-3.091	-2.226	+0.716	3960
2300	-4.032	-4.614	-14.818	-1.391	-2.682	-2.809	-1.940	+0.742	4140
2400	-3.600	-4.130	-13.908	-1.305	-2.443	-2.520	-1.679	+0.764	4320
2500	-3.202	-3.684	-13.070	-1.227	-2.224	-2.270	-1.440	+0.784	4500
2600	-2.836	-3.272	-12.298	-1.154	-2.021	-2.038	-1.219	+0.802	4680
2700	-2.494	-2.892	-11.580	-1.087	-1.833	-1.823	-1.015	+0.818	4860
2800	-2.178	-2.536	-10.914	-1.025	-1.658	-1.624	-0.825	+0.833	5040
2900	-1.882	-2.206	-10.294	-0.967	-1.495	-1.438	-0.649	+0.846	5220
3000	-1.606	-1.898	-9.716	-0.913	-1.343	-1.265	-0.485	+0.858	5400
3100	-1.348	-1.610	-9.174	-0.863	-1.201	-1.103	-0.332	+0.869	5580
3200	-1.106	-1.340	-8.664	-0.815	-1.067	-0.951	-0.189	+0.878	5760
3300	-0.878	-1.086	-8.186	-0.771	-0.942	-0.809	-0.054	+0.888	5940
3400	-0.664	-0.846	-7.736	-0.729	-0.824	-0.674	+0.071	+0.895	6120
3500	-0.462	-0.620	-7.312	-0.690	-0.712	-0.547	+0.190	+0.902	6300

Source: Based on data from the JANAF Thermochemical Tables, NSRDS-NBS-37, 1971.

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TABLE A-1E**Atomic or Molecular Weights and Critical Properties of Some Selected Elements and Compounds**

Substance	Chemical Formula	<i>M</i> (lb/lbmol)	<i>T_c</i> (°R)	<i>p_c</i> (atm)	$Z_c = \frac{p_c v_c}{R T_c}$
Acetylene	C ₂ H ₂	26.04	556	62	0.274
Air (equivalent)	—	28.97	239	37.2	0.284
Ammonia	NH ₃	17.03	730	111.3	0.242
Argon	Ar	39.94	272	47.97	0.290
Benzene	C ₆ H ₆	78.11	1013	48.7	0.274
Butane	C ₄ H ₁₀	58.12	765	37.5	0.274
Carbon	C	12.01	—	—	—
Carbon dioxide	CO ₂	44.01	548	72.9	0.276
Carbon monoxide	CO	28.01	239	34.5	0.294
Copper	Cu	63.54	—	—	—
Ethane	C ₂ H ₆	30.07	549	48.2	0.285
Ethanol	C ₂ H ₅ OH	46.07	929	63.0	0.249
Ethylene	C ₂ H ₄	28.05	510	50.5	0.270
Helium	He	4.003	9.33	2.26	0.300
Hydrogen	H ₂	2.016	59.8	12.8	0.304
Methane	CH ₄	16.04	344	45.8	0.290
Methanol	CH ₃ OH	32.04	924	78.5	0.220
Nitrogen	N ₂	28.01	227	33.5	0.291
Octane	C ₈ H ₁₈	114.22	1025	24.6	0.258
Oxygen	O ₂	32.00	278	49.8	0.290
Propane	C ₃ H ₈	44.09	666	42.1	0.276
Propylene	C ₃ H ₆	42.08	657	45.6	0.276
Refrigerant 12	CCl ₂ F ₂	120.92	693	40.6	0.278
Refrigerant 22	CHClF ₂	86.48	665	49.1	0.267
Refrigerant 134a	CF ₃ CH ₂ F	102.03	673	40.2	0.260
Sulfur dioxide	SO ₂	64.06	775	77.7	0.268
Water	H ₂ O	18.02	1165	218.0	0.233

Sources: Adapted from *International Critical Tables* and L. C. Nelson and E. F. Obert, Generalized Compressibility Charts, *Chem. Eng.*, 617: 203 (1954).

TABLE A.2E**Properties of Saturated Water (Liquid–Vapor): Temperature Table**

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R		Temp. °F
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
32	0.0886	0.01602	3305	−.01	1021.2	−.01	1075.4	1075.4	−.00003	2.1870
35	0.0999	0.01602	2948	2.99	1022.2	3.00	1073.7	1076.7	0.00607	2.1764
40	0.1217	0.01602	2445	8.02	1023.9	8.02	1070.9	1078.9	0.01617	2.1592
45	0.1475	0.01602	2037	13.04	1025.5	13.04	1068.1	1081.1	0.02618	2.1423
50	0.1780	0.01602	1704	18.06	1027.2	18.06	1065.2	1083.3	0.03607	2.1259
52	0.1917	0.01603	1589	20.06	1027.8	20.07	1064.1	1084.2	0.04000	2.1195
54	0.2064	0.01603	1482	22.07	1028.5	22.07	1063.0	1085.1	0.04391	2.1131
56	0.2219	0.01603	1383	24.08	1029.1	24.08	1061.9	1085.9	0.04781	2.1068
58	0.2386	0.01603	1292	26.08	1029.8	26.08	1060.7	1086.8	0.05159	2.1005
60	0.2563	0.01604	1207	28.08	1030.4	28.08	1059.6	1087.7	0.05555	2.0943
62	0.2751	0.01604	1129	30.09	1031.1	30.09	1058.5	1088.6	0.05940	2.0882
64	0.2952	0.01604	1056	32.09	1031.8	32.09	1057.3	1089.4	0.06323	2.0821
66	0.3165	0.01604	988.4	34.09	1032.4	34.09	1056.2	1090.3	0.06704	2.0761
68	0.3391	0.01605	925.8	36.09	1033.1	36.09	1055.1	1091.2	0.07084	2.0701
70	0.3632	0.01605	867.7	38.09	1033.7	38.09	1054.0	1092.0	0.07463	2.0642
72	0.3887	0.01606	813.7	40.09	1034.4	40.09	1052.8	1092.9	0.07839	2.0584
74	0.4158	0.01606	763.5	42.09	1035.0	42.09	1051.7	1093.8	0.08215	2.0526
76	0.4446	0.01606	716.8	44.09	1035.7	44.09	1050.6	1094.7	0.08589	2.0469
78	0.4750	0.01607	673.3	46.09	1036.3	46.09	1049.4	1095.5	0.08961	2.0412
80	0.5073	0.01607	632.8	48.08	1037.0	48.09	1048.3	1096.4	0.09332	2.0356
82	0.5414	0.01608	595.0	50.08	1037.6	50.08	1047.2	1097.3	0.09701	2.0300
84	0.5776	0.01608	559.8	52.08	1038.3	52.08	1046.0	1098.1	0.1007	2.0245
86	0.6158	0.01609	527.0	54.08	1038.9	54.08	1044.9	1099.0	0.1044	2.0190
88	0.6562	0.01609	496.3	56.07	1039.6	56.07	1043.8	1099.9	0.1080	2.0136
90	0.6988	0.01610	467.7	58.07	1040.2	58.07	1042.7	1100.7	0.1117	2.0083
92	0.7439	0.01611	440.9	60.06	1040.9	60.06	1041.5	1101.6	0.1153	2.0030
94	0.7914	0.01611	415.9	62.06	1041.5	62.06	1040.4	1102.4	0.1189	1.9977
96	0.8416	0.01612	392.4	64.05	1041.2	64.06	1039.2	1103.3	0.1225	1.9925
98	0.8945	0.01612	370.5	66.05	1042.8	66.05	1038.1	1104.2	0.1261	1.9874
100	0.9503	0.01613	350.0	68.04	1043.5	68.05	1037.0	1105.0	0.1296	1.9822
110	1.276	0.01617	265.1	78.02	1046.7	78.02	1031.3	1109.3	0.1473	1.9574
120	1.695	0.01621	203.0	87.99	1049.9	88.00	1025.5	1113.5	0.1647	1.9336
130	2.225	0.01625	157.2	97.97	1053.0	97.98	1019.8	1117.8	0.1817	1.9109
140	2.892	0.01629	122.9	107.95	1056.2	107.96	1014.0	1121.9	0.1985	1.8892
150	3.722	0.01634	97.0	117.95	1059.3	117.96	1008.1	1126.1	0.2150	1.8684
160	4.745	0.01640	77.2	127.94	1062.3	127.96	1002.2	1130.1	0.2313	1.8484
170	5.996	0.01645	62.0	137.95	1065.4	137.97	996.2	1134.2	0.2473	1.8293
180	7.515	0.01651	50.2	147.97	1068.3	147.99	990.2	1138.2	0.2631	1.8109
190	9.343	0.01657	41.0	158.00	1071.3	158.03	984.1	1142.1	0.2787	1.7932
200	11.529	0.01663	33.6	168.04	1074.2	168.07	977.9	1145.9	0.2940	1.7762

H₂O

TABLE A-2E

(Continued)

H₂O

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb			Entropy Btu/lb · °R		Temp. °F
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	Sat. Vapor <i>s_g</i>	
210	14.13	0.01670	27.82	178.1	1077.0	178.1	971.6	1149.7	0.3091	1.7599	210
212	14.70	0.01672	26.80	180.1	1077.6	180.2	970.3	1150.5	0.3121	1.7567	212
220	17.19	0.01677	23.15	188.2	1079.8	188.2	965.3	1153.5	0.3241	1.7441	220
230	20.78	0.01685	19.39	198.3	1082.6	198.3	958.8	1157.1	0.3388	1.7289	230
240	24.97	0.01692	16.33	208.4	1085.3	208.4	952.3	1160.7	0.3534	1.7143	240
250	29.82	0.01700	13.83	218.5	1087.9	218.6	945.6	1164.2	0.3677	1.7001	250
260	35.42	0.01708	11.77	228.6	1090.5	228.8	938.8	1167.6	0.3819	1.6864	260
270	41.85	0.01717	10.07	238.8	1093.0	239.0	932.0	1170.9	0.3960	1.6731	270
280	49.18	0.01726	8.65	249.0	1095.4	249.2	924.9	1174.1	0.4099	1.6602	280
290	57.53	0.01735	7.47	259.3	1097.7	259.4	917.8	1177.2	0.4236	1.6477	290
300	66.98	0.01745	6.472	269.5	1100.0	269.7	910.4	1180.2	0.4372	1.6356	300
310	77.64	0.01755	5.632	279.8	1102.1	280.1	903.0	1183.0	0.4507	1.6238	310
320	89.60	0.01765	4.919	290.1	1104.2	290.4	895.3	1185.8	0.4640	1.6123	320
330	103.00	0.01776	4.312	300.5	1106.2	300.8	887.5	1188.4	0.4772	1.6010	330
340	117.93	0.01787	3.792	310.9	1108.0	311.3	879.5	1190.8	0.4903	1.5901	340
350	134.53	0.01799	3.346	321.4	1109.8	321.8	871.3	1193.1	0.5033	1.5793	350
360	152.92	0.01811	2.961	331.8	1111.4	332.4	862.9	1195.2	0.5162	1.5688	360
370	173.23	0.01823	2.628	342.4	1112.9	343.0	854.2	1197.2	0.5289	1.5585	370
380	195.60	0.01836	2.339	353.0	1114.3	353.6	845.4	1199.0	0.5416	1.5483	380
390	220.2	0.01850	2.087	363.6	1115.6	364.3	836.2	1200.6	0.5542	1.5383	390
400	247.1	0.01864	1.866	374.3	1116.6	375.1	826.8	1202.0	0.5667	1.5284	400
410	276.5	0.01878	1.673	385.0	1117.6	386.0	817.2	1203.1	0.5792	1.5187	410
420	308.5	0.01894	1.502	395.8	1118.3	396.9	807.2	1204.1	0.5915	1.5091	420
430	343.3	0.01909	1.352	406.7	1118.9	407.9	796.9	1204.8	0.6038	1.4995	430
440	381.2	0.01926	1.219	417.6	1119.3	419.0	786.3	1205.3	0.6161	1.4900	440
450	422.1	0.01943	1.1011	428.6	1119.5	430.2	775.4	1205.6	0.6282	1.4806	450
460	466.3	0.01961	0.9961	439.7	1119.6	441.4	764.1	1205.5	0.6404	1.4712	460
470	514.1	0.01980	0.9025	450.9	1119.4	452.8	752.4	1205.2	0.6525	1.4618	470
480	565.5	0.02000	0.8187	462.2	1118.9	464.3	740.3	1204.6	0.6646	1.4524	480
490	620.7	0.02021	0.7436	473.6	1118.3	475.9	727.8	1203.7	0.6767	1.4430	490
500	680.0	0.02043	0.6761	485.1	1117.4	487.7	714.8	1202.5	0.6888	1.4335	500
520	811.4	0.02091	0.5605	508.5	1114.8	511.7	687.3	1198.9	0.7130	1.4145	520
540	961.5	0.02145	0.4658	532.6	1111.0	536.4	657.5	1193.8	0.7374	1.3950	540
560	1131.8	0.02207	0.3877	548.4	1105.8	562.0	625.0	1187.0	0.7620	1.3749	560
580	1324.3	0.02278	0.3225	583.1	1098.9	588.6	589.3	1178.0	0.7872	1.3540	580
600	1541.0	0.02363	0.2677	609.9	1090.0	616.7	549.7	1166.4	0.8130	1.3317	600
620	1784.4	0.02465	0.2209	638.3	1078.5	646.4	505.0	1151.4	0.8398	1.3075	620
640	2057.1	0.02593	0.1805	668.7	1063.2	678.6	453.4	1131.9	0.8681	1.2803	640
660	2362	0.02767	0.1446	702.3	1042.3	714.4	391.1	1105.5	0.8990	1.2483	660
680	2705	0.03032	0.1113	741.7	1011.0	756.9	309.8	1066.7	0.9350	1.2068	680
700	3090	0.03666	0.0744	801.7	947.7	822.7	167.5	990.2	0.9902	1.1346	700
705.4	3204	0.05053	0.05053	872.6	872.6	902.5	0	902.5	1.0580	1.0580	705.4

Source: Tables A-2E through A-6E are extracted from J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York, 1969.

TABLE A.3E**Properties of Saturated Water (Liquid–Vapor): Pressure Table**

Press. lbf/in. ²	Temp. °F	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R			Press. lbf/in. ²	
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	Evap. <i>s_{fg}</i>	Sat. Vapor <i>s_g</i>	
0.4	72.84	0.01606	792.0	40.94	1034.7	40.94	1052.3	1093.3	0.0800	1.9760	2.0559	0.4
0.6	85.19	0.01609	540.0	53.26	1038.7	53.27	1045.4	1098.6	0.1029	1.9184	2.0213	0.6
0.8	94.35	0.01611	411.7	62.41	1041.7	62.41	1040.2	1102.6	0.1195	1.8773	1.9968	0.8
1.0	101.70	0.01614	333.6	69.74	1044.0	69.74	1036.0	1105.8	0.1327	1.8453	1.9779	1.0
1.2	107.88	0.01616	280.9	75.90	1046.0	75.90	1032.5	1108.4	0.1436	1.8190	1.9626	1.2
1.5	115.65	0.01619	227.7	83.65	1048.5	83.65	1028.0	1111.7	0.1571	1.7867	1.9438	1.5
2.0	126.04	0.01623	173.75	94.02	1051.8	94.02	1022.1	1116.1	0.1750	1.7448	1.9198	2.0
3.0	141.43	0.01630	118.72	109.38	1056.6	109.39	1013.1	1122.5	0.2009	1.6852	1.8861	3.0
4.0	152.93	0.01636	90.64	120.88	1060.2	120.89	1006.4	1127.3	0.2198	1.6426	1.8624	4.0
5.0	162.21	0.01641	73.53	130.15	1063.0	130.17	1000.9	1131.0	0.2349	1.6093	1.8441	5.0
6.0	170.03	0.01645	61.98	137.98	1065.4	138.00	996.2	1134.2	0.2474	1.5819	1.8292	6.0
7.0	176.82	0.01649	53.65	144.78	1067.4	144.80	992.1	1136.9	0.2581	1.5585	1.8167	7.0
8.0	182.84	0.01653	47.35	150.81	1069.2	150.84	988.4	1139.3	0.2675	1.5383	1.8058	8.0
9.0	188.26	0.01656	42.41	156.25	1070.8	156.27	985.1	1141.4	0.2760	1.5203	1.7963	9.0
10	193.19	0.01659	38.42	161.20	1072.2	161.23	982.1	1143.3	0.2836	1.5041	1.7877	10
14.696	211.99	0.01672	26.80	180.10	1077.6	180.15	970.4	1150.5	0.3121	1.4446	1.7567	14.696
15	213.03	0.01672	26.29	181.14	1077.9	181.19	969.7	1150.9	0.3137	1.4414	1.7551	15
20	227.96	0.01683	20.09	196.19	1082.0	196.26	960.1	1156.4	0.3358	1.3962	1.7320	20
25	240.08	0.01692	16.31	208.44	1085.3	208.52	952.2	1160.7	0.3535	1.3607	1.7142	25
30	250.34	0.01700	13.75	218.84	1088.0	218.93	945.4	1164.3	0.3682	1.3314	1.6996	30
35	259.30	0.01708	11.90	227.93	1090.3	228.04	939.3	1167.4	0.3809	1.3064	1.6873	35
40	267.26	0.01715	10.50	236.03	1092.3	236.16	933.8	1170.0	0.3921	1.2845	1.6767	40
45	274.46	0.01721	9.40	243.37	1094.0	243.51	928.8	1172.3	0.4022	1.2651	1.6673	45
50	281.03	0.01727	8.52	250.08	1095.6	250.24	924.2	1174.4	0.4113	1.2476	1.6589	50
55	287.10	0.01733	7.79	256.28	1097.0	256.46	919.9	1176.3	0.4196	1.2317	1.6513	55
60	292.73	0.01738	7.177	262.1	1098.3	262.2	915.8	1178.0	0.4273	1.2170	1.6443	60
65	298.00	0.01743	6.647	267.5	1099.5	267.7	911.9	1179.6	0.4345	1.2035	1.6380	65
70	302.96	0.01748	6.209	272.6	1100.6	272.8	908.3	1181.0	0.4412	1.1909	1.6321	70
75	307.63	0.01752	5.818	277.4	1101.6	277.6	904.8	1182.4	0.4475	1.1790	1.6265	75
80	312.07	0.01757	5.474	282.0	1102.6	282.2	901.4	1183.6	0.4534	1.1679	1.6213	80
85	316.29	0.01761	5.170	286.3	1103.5	286.6	898.2	1184.8	0.4591	1.1574	1.6165	85
90	320.31	0.01766	4.898	290.5	1104.3	290.8	895.1	1185.9	0.4644	1.1475	1.6119	90
95	324.16	0.01770	4.654	294.5	1105.0	294.8	892.1	1186.9	0.4695	1.1380	1.6075	95
100	327.86	0.01774	4.434	298.3	1105.8	298.6	889.2	1187.8	0.4744	1.1290	1.6034	100
110	334.82	0.01781	4.051	305.5	1107.1	305.9	883.7	1189.6	0.4836	1.1122	1.5958	110
120	341.30	0.01789	3.730	312.3	1108.3	312.7	878.5	1191.1	0.4920	1.0966	1.5886	120
130	347.37	0.01796	3.457	318.6	1109.4	319.0	873.5	1192.5	0.4999	1.0822	1.5821	130
140	353.08	0.01802	3.221	324.6	1110.3	325.1	868.7	1193.8	0.5073	1.0688	1.5761	140
150	358.48	0.01809	3.016	330.2	1111.2	330.8	864.2	1194.9	0.5142	1.0562	1.5704	150
160	363.60	0.01815	2.836	335.6	1112.0	336.2	859.8	1196.0	0.5208	1.0443	1.5651	160

H₂O

TABLE A-3E

(Continued)

Press. lbf/in. ²	Temp. °F	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb			Entropy Btu/lb · °R			Press. lbf/in. ²
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	Evap. <i>s_{fg}</i>	Sat. Vapor <i>s_g</i>	
170	368.47	0.01821	2.676	340.8	1112.7	341.3	855.6	1196.9	0.5270	1.0330	1.5600	170
180	373.13	0.01827	2.553	345.7	1113.4	346.3	851.5	1197.8	0.5329	1.0223	1.5552	180
190	377.59	0.01833	2.405	350.4	1114.0	351.0	847.5	1198.6	0.5386	1.0122	1.5508	190
200	381.86	0.01839	2.289	354.9	1114.6	355.6	843.7	1199.3	0.5440	1.0025	1.5465	200
250	401.04	0.01865	1.845	375.4	1116.7	376.2	825.8	1202.1	0.5680	0.9594	1.5274	250
300	417.43	0.01890	1.544	393.0	1118.2	394.1	809.8	1203.9	0.5883	0.9232	1.5115	300
350	431.82	0.01912	1.327	408.7	1119.0	409.9	795.0	1204.9	0.6060	0.8917	1.4977	350
400	444.70	0.01934	1.162	422.8	1119.5	424.2	781.2	1205.5	0.6218	0.8638	1.4856	400
450	456.39	0.01955	1.033	435.7	1119.6	437.4	768.2	1205.6	0.6360	0.8385	1.4745	450
500	467.13	0.01975	0.928	447.7	1119.4	449.5	755.8	1205.3	0.6490	0.8154	1.4644	500
550	477.07	0.01994	0.842	458.9	1119.1	460.9	743.9	1204.8	0.6611	0.7941	1.4451	550
600	486.33	0.02013	0.770	469.4	1118.6	471.7	732.4	1204.1	0.6723	0.7742	1.4464	600
700	503.23	0.02051	0.656	488.9	1117.0	491.5	710.5	1202.0	0.6927	0.7378	1.4305	700
800	518.36	0.02087	0.569	506.6	1115.0	509.7	689.6	1199.3	0.7110	0.7050	1.4160	800
900	532.12	0.02123	0.501	523.0	1112.6	526.6	669.5	1196.0	0.7277	0.6750	1.4027	900
1000	544.75	0.02159	0.446	538.4	1109.9	542.4	650.0	1192.4	0.7432	0.6471	1.3903	1000
1100	556.45	0.02195	0.401	552.9	1106.8	557.4	631.0	1188.3	0.7576	0.6209	1.3786	1100
1200	567.37	0.02232	0.362	566.7	1103.5	571.7	612.3	1183.9	0.7712	0.5961	1.3673	1200
1300	577.60	0.02269	0.330	579.9	1099.8	585.4	593.8	1179.2	0.7841	0.5724	1.3565	1300
1400	587.25	0.02307	0.302	592.7	1096.0	598.6	575.5	1174.1	0.7964	0.5497	1.3461	1400
1500	596.39	0.02346	0.277	605.0	1091.8	611.5	557.2	1168.7	0.8082	0.5276	1.3359	1500
1600	605.06	0.02386	0.255	616.9	1087.4	624.0	538.9	1162.9	0.8196	0.5062	1.3258	1600
1700	613.32	0.02428	0.236	628.6	1082.7	636.2	520.6	1156.9	0.8307	0.4852	1.3159	1700
1800	621.21	0.02472	0.218	640.0	1077.7	648.3	502.1	1150.4	0.8414	0.4645	1.3060	1800
1900	628.76	0.02517	0.203	651.3	1072.3	660.1	483.4	1143.5	0.8519	0.4441	1.2961	1900
2000	636.00	0.02565	0.188	662.4	1066.6	671.9	464.4	1136.3	0.8623	0.4238	1.2861	2000
2250	652.90	0.02698	0.157	689.9	1050.6	701.1	414.8	1115.9	0.8876	0.3728	1.2604	2250
2500	668.31	0.02860	0.131	717.7	1031.0	730.9	360.5	1091.4	0.9131	0.3196	1.2327	2500
2750	682.46	0.03077	0.107	747.3	1005.9	763.0	297.4	1060.4	0.9401	0.2604	1.2005	2750
3000	695.52	0.03431	0.084	783.4	968.8	802.5	213.0	1015.5	0.9732	0.1843	1.1575	3000
3203.6	705.44	0.05053	0.0505	872.6	872.6	902.5	0	902.5	1.0580	0	1.0580	3203.6

TABLE A.4E**Properties of Superheated Water Vapor**

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 1 lbf/in. ² (T _{sat} = 101.7°F)								
Sat. 333.6 1044.0 1105.8 1.9779 73.53 1063.0 1131.0 1.8441								
150 362.6 1060.4 1127.5 2.0151					78.15	1076.0	1148.6	1.8715
200 392.5 1077.5 1150.1 2.0508								
250 422.4 1094.7 1172.8 2.0839 84.21 1093.8 1171.7 1.9052								
300 452.3 1112.0 1195.7 2.1150 90.24 1111.3 1194.8 1.9367								
400 511.9 1147.0 1241.8 2.1720 102.24 1146.6 1241.2 1.9941								
500 571.5 1182.8 1288.5 2.2235 114.20 1182.5 1288.2 2.0458								
600 631.1 1219.3 1336.1 2.2706 126.15 1219.1 1335.8 2.0930								
700 690.7 1256.7 1384.5 2.3142 138.08 1256.5 1384.3 2.1367								
800 750.3 1294.4 1433.7 2.3550 150.01 1294.7 1433.5 2.1775								
900 809.9 1333.9 1483.8 2.3932 161.94 1333.8 1483.7 2.2158								
1000 869.5 1373.9 1534.8 2.4294 173.86 1373.9 1534.7 2.2520								
<i>p</i> = 10 lbf/in. ² (T _{sat} = 193.2°F)								
Sat. 38.42 1072.2 1143.3 1.7877 26.80 1077.6 1150.5 1.7567								
200 38.85 1074.7 1146.6 1.7927					28.42	1091.5	1168.8	1.7832
250 41.95 1092.6 1170.2 1.8272								
300 44.99 1110.4 1193.7 1.8592 30.52 1109.6 1192.6 1.8157								
400 51.03 1146.1 1240.5 1.9171 34.67 1145.6 1239.9 1.8741								
500 57.04 1182.2 1287.7 1.9690 38.77 1181.8 1287.3 1.9263								
600 63.03 1218.9 1335.5 2.0164 42.86 1218.6 1335.2 1.9737								
700 69.01 1256.3 1384.0 2.0601 46.93 1256.1 1383.8 2.0175								
800 74.98 1294.6 1433.3 2.1009 51.00 1294.4 1433.1 2.0584								
900 80.95 1333.7 1483.5 2.1393 55.07 1333.6 1483.4 2.0967								
1000 86.91 1373.8 1534.6 2.1755 59.13 1373.7 1534.5 2.1330								
1100 92.88 1414.7 1586.6 2.2099 63.19 1414.6 1586.4 2.1674								
<i>p</i> = 20 lbf/in. ² (T _{sat} = 228.0°F)								
Sat. 20.09 1082.0 1156.4 1.7320 10.50 1093.3 1170.0 1.6767								
250 20.79 1090.3 1167.2 1.7475					11.04	1105.1	1186.8	1.6993
300 22.36 1108.7 1191.5 1.7805								
350 23.90 1126.9 1215.4 1.8110 11.84 1124.2 1211.8 1.7312								
400 25.43 1145.1 1239.2 1.8395 12.62 1143.0 1236.4 1.7606								
500 28.46 1181.5 1286.8 1.8919 14.16 1180.1 1284.9 1.8140								
600 31.47 1218.4 1334.8 1.9395 15.69 1217.3 1333.4 1.8621								
700 34.47 1255.9 1383.5 1.9834 17.20 1255.1 1382.4 1.9063								
800 37.46 1294.3 1432.9 2.0243 18.70 1293.7 1432.1 1.9474								
900 40.45 1333.5 1483.2 2.0627 20.20 1333.0 1482.5 1.9859								
1000 43.44 1373.5 1534.3 2.0989 21.70 1373.1 1533.8 2.0223								
1100 46.42 1414.5 1586.3 2.1334 23.20 1414.2 1585.9 2.0568								

TABLE A-4E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 60 lbf/in. ² (<i>T</i> _{sat} = 292.7°F)								
Sat.	7.17	1098.3	1178.0	1.6444	5.47	1102.6	1183.6	1.6214
300	7.26	1101.3	1181.9	1.6496				
350	7.82	1121.4	1208.2	1.6830	5.80	1118.5	1204.3	1.6476
400	8.35	1140.8	1233.5	1.7134	6.22	1138.5	1230.6	1.6790
500	9.40	1178.6	1283.0	1.7678	7.02	1177.2	1281.1	1.7346
600	10.43	1216.3	1332.1	1.8165	7.79	1215.3	1330.7	1.7838
700	11.44	1254.4	1381.4	1.8609	8.56	1253.6	1380.3	1.8285
800	12.45	1293.0	1431.2	1.9022	9.32	1292.4	1430.4	1.8700
900	13.45	1332.5	1481.8	1.9408	10.08	1332.0	1481.2	1.9087
1000	14.45	1372.7	1533.2	1.9773	10.83	1372.3	1532.6	1.9453
1100	15.45	1413.8	1585.4	2.0119	11.58	1413.5	1584.9	1.9799
1200	16.45	1455.8	1638.5	2.0448	12.33	1455.5	1638.1	2.0130
<i>p</i> = 100 lbf/in. ² (<i>T</i> _{sat} = 327.8°F)								
Sat.	4.434	1105.8	1187.8	1.6034	3.730	1108.3	1191.1	1.5886
350	4.592	1115.4	1200.4	1.6191	3.783	1112.2	1196.2	1.5950
400	4.934	1136.2	1227.5	1.6517	4.079	1133.8	1224.4	1.6288
450	5.265	1156.2	1253.6	1.6812	4.360	1154.3	1251.2	1.6590
500	5.587	1175.7	1279.1	1.7085	4.633	1174.2	1277.1	1.6868
600	6.216	1214.2	1329.3	1.7582	5.164	1213.2	1327.8	1.7371
700	6.834	1252.8	1379.2	1.8033	5.682	1252.0	1378.2	1.7825
800	7.445	1291.8	1429.6	1.8449	6.195	1291.2	1428.7	1.8243
900	8.053	1331.5	1480.5	1.8838	6.703	1330.9	1479.8	1.8633
1000	8.657	1371.9	1532.1	1.9204	7.208	1371.5	1531.5	1.9000
1100	9.260	1413.1	1584.5	1.9551	7.711	1412.8	1584.0	1.9348
1200	9.861	1455.2	1637.7	1.9882	8.213	1454.9	1637.3	1.9679
<i>p</i> = 140 lbf/in. ² (<i>T</i> _{sat} = 353.1°F)								
Sat.	3.221	1110.3	1193.8	1.5761	2.836	1112.0	1196.0	1.5651
400	3.466	1131.4	1221.2	1.6088	3.007	1128.8	1217.8	1.5911
450	3.713	1152.4	1248.6	1.6399	3.228	1150.5	1246.1	1.6230
500	3.952	1172.7	1275.1	1.6682	3.440	1171.2	1273.0	1.6518
550	4.184	1192.5	1300.9	1.6945	3.646	1191.3	1299.2	1.6785
600	4.412	1212.1	1326.4	1.7191	3.848	1211.1	1325.0	1.7034
700	4.860	1251.2	1377.1	1.7648	4.243	1250.4	1376.0	1.7494
800	5.301	1290.5	1427.9	1.8068	4.631	1289.9	1427.0	1.7916
900	5.739	1330.4	1479.1	1.8459	5.015	1329.9	1478.4	1.8308
1000	6.173	1371.0	1531.0	1.8827	5.397	1370.6	1530.4	1.8677
1100	6.605	1412.4	1583.6	1.9176	5.776	1412.1	1583.1	1.9026
1200	7.036	1454.6	1636.9	1.9507	6.154	1454.3	1636.5	1.9358

TABLE A.4E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 180 lbf/in. ² (T _{sat} = 373.1°F)								
<i>p</i> = 200 lbf/in. ² (T _{sat} = 381.8°F)								
Sat.	2.533	1113.4	1197.8	1.5553	2.289	1114.6	1199.3	1.5464
400	2.648	1126.2	1214.4	1.5749	2.361	1123.5	1210.8	1.5600
450	2.850	1148.5	1243.4	1.6078	2.548	1146.4	1240.7	1.5938
500	3.042	1169.6	1270.9	1.6372	2.724	1168.0	1268.8	1.6239
550	3.228	1190.0	1297.5	1.6642	2.893	1188.7	1295.7	1.6512
600	3.409	1210.0	1323.5	1.6893	3.058	1208.9	1322.1	1.6767
700	3.763	1249.6	1374.9	1.7357	3.379	1248.8	1373.8	1.7234
800	4.110	1289.3	1426.2	1.7781	3.693	1288.6	1425.3	1.7660
900	4.453	1329.4	1477.7	1.8174	4.003	1328.9	1477.1	1.8055
1000	4.793	1370.2	1529.8	1.8545	4.310	1369.8	1529.3	1.8425
1100	5.131	1411.7	1582.6	1.8894	4.615	1411.4	1582.2	1.8776
1200	5.467	1454.0	1636.1	1.9227	4.918	1453.7	1635.7	1.9109
<i>p</i> = 250 lbf/in. ² (T _{sat} = 401.0°F)								
<i>p</i> = 300 lbf/in. ² (T _{sat} = 417.4°F)								
Sat.	1.845	1116.7	1202.1	1.5274	1.544	1118.2	1203.9	1.5115
450	2.002	1141.1	1233.7	1.5632	1.636	1135.4	1226.2	1.5365
500	2.150	1163.8	1263.3	1.5948	1.766	1159.5	1257.5	1.5701
550	2.290	1185.3	1291.3	1.6233	1.888	1181.9	1286.7	1.5997
600	2.426	1206.1	1318.3	1.6494	2.004	1203.2	1314.5	1.6266
700	2.688	1246.7	1371.1	1.6970	2.227	1244.0	1368.3	1.6751
800	2.943	1287.0	1423.2	1.7301	2.442	1285.4	1421.0	1.7187
900	3.193	1327.6	1475.3	1.7799	2.653	1326.3	1473.6	1.7589
1000	3.440	1368.7	1527.9	1.8172	2.860	1367.7	1526.5	1.7964
1100	3.685	1410.5	1581.0	1.8524	3.066	1409.6	1579.8	1.8317
1200	3.929	1453.0	1634.8	1.8858	3.270	1452.2	1633.8	1.8653
1300	4.172	1496.3	1689.3	1.9177	3.473	1495.6	1688.4	1.8973
<i>p</i> = 350 lbf/in. ² (T _{sat} = 431.8°F)								
<i>p</i> = 400 lbf/in. ² (T _{sat} = 444.7°F)								
Sat.	1.327	1119.0	1204.9	1.4978	1.162	1119.5	1205.5	1.4856
450	1.373	1129.2	1218.2	1.5125	1.175	1122.6	1209.5	1.4901
500	1.491	1154.9	1251.5	1.5482	1.284	1150.1	1245.2	1.5282
550	1.600	1178.3	1281.9	1.5790	1.383	1174.6	1277.0	1.5605
600	1.703	1200.3	1310.6	1.6068	1.476	1197.3	1306.6	1.5892
700	1.898	1242.5	1365.4	1.6562	1.650	1240.4	1362.5	1.6397
800	2.085	1283.8	1418.8	1.7004	1.816	1282.1	1416.6	1.6844
900	2.267	1325.0	1471.8	1.7409	1.978	1323.7	1470.1	1.7252
1000	2.446	1366.6	1525.0	1.7787	2.136	1365.5	1523.6	1.7632
1100	2.624	1408.7	1578.6	1.8142	2.292	1407.8	1577.4	1.7989
1200	2.799	1451.5	1632.8	1.8478	2.446	1450.7	1621.8	1.8327
1300	2.974	1495.0	1687.6	1.8799	2.599	1494.3	1686.8	1.8648

TABLE A-4E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 450 lbf/in. ² (T _{sat} = 456.4°F)								
<i>p</i> = 500 lbf/in. ² (T _{sat} = 467.1°F)								
Sat.	1.033	1119.6	1205.6	1.4746	0.928	1119.4	1205.3	1.4645
500	1.123	1145.1	1238.5	1.5097	0.992	1139.7	1231.5	1.4923
550	1.215	1170.7	1271.9	1.5436	1.079	1166.7	1266.6	1.5279
600	1.300	1194.3	1302.5	1.5732	1.158	1191.1	1298.3	1.5585
700	1.458	1238.2	1359.6	1.6248	1.304	1236.0	1356.7	1.6112
800	1.608	1280.5	1414.4	1.6701	1.441	1278.8	1412.1	1.6571
900	1.752	1322.4	1468.3	1.7113	1.572	1321.0	1466.5	1.6987
1000	1.894	1364.4	1522.2	1.7495	1.701	1363.3	1520.7	1.7371
1100	2.034	1406.9	1576.3	1.7853	1.827	1406.0	1575.1	1.7731
1200	2.172	1450.0	1630.8	1.8192	1.952	1449.2	1629.8	1.8072
1300	2.308	1493.7	1685.9	1.8515	2.075	1493.1	1685.1	1.8395
1400	2.444	1538.1	1741.7	1.8823	2.198	1537.6	1741.0	1.8704
<i>p</i> = 600 lbf/in. ² (T _{sat} = 486.3°F)								
<i>p</i> = 700 lbf/in. ² (T _{sat} = 503.2°F)								
Sat.	0.770	1118.6	1204.1	1.4464	0.656	1117.0	1202.0	1.4305
500	0.795	1128.0	1216.2	1.4592				
550	0.875	1158.2	1255.4	1.4990	0.728	1149.0	1243.2	1.4723
600	0.946	1184.5	1289.5	1.5320	0.793	1177.5	1280.2	1.5081
700	1.073	1231.5	1350.6	1.5872	0.907	1226.9	1344.4	1.5661
800	1.190	1275.4	1407.6	1.6343	1.011	1272.0	1402.9	1.6145
900	1.302	1318.4	1462.9	1.6766	1.109	1315.6	1459.3	1.6576
1000	1.411	1361.2	1517.8	1.7155	1.204	1358.9	1514.9	1.6970
1100	1.517	1404.2	1572.7	1.7519	1.296	1402.4	1570.2	1.7337
1200	1.622	1447.7	1627.8	1.7861	1.387	1446.2	1625.8	1.7682
1300	1.726	1491.7	1683.4	1.8186	1.476	1490.4	1681.7	1.8009
1400	1.829	1536.5	1739.5	1.8497	1.565	1535.3	1738.1	1.8321
<i>p</i> = 800 lbf/in. ² (T _{sat} = 518.3°F)								
<i>p</i> = 900 lbf/in. ² (T _{sat} = 532.1°F)								
Sat.	0.569	1115.0	1199.3	1.4160	0.501	1112.6	1196.0	1.4027
550	0.615	1138.8	1229.9	1.4469	0.527	1127.5	1215.2	1.4219
600	0.677	1170.1	1270.4	1.4861	0.587	1162.2	1260.0	1.4652
650	0.732	1197.2	1305.6	1.5186	0.639	1191.1	1297.5	1.4999
700	0.783	1222.1	1338.0	1.5471	0.686	1217.1	1331.4	1.5297
800	0.876	1268.5	1398.2	1.5969	0.772	1264.9	1393.4	1.5810
900	0.964	1312.9	1455.6	1.6408	0.851	1310.1	1451.9	1.6257
1000	1.048	1356.7	1511.9	1.6807	0.927	1354.5	1508.9	1.6662
1100	1.130	1400.5	1567.8	1.7178	1.001	1398.7	1565.4	1.7036
1200	1.210	1444.6	1623.8	1.7526	1.073	1443.0	1621.7	1.7386
1300	1.289	1489.1	1680.0	1.7854	1.144	1487.8	1687.3	1.7717
1400	1.367	1534.2	1736.6	1.8167	1.214	1533.0	1735.1	1.8031

TABLE A.4E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 1000 lbf/in. ² (<i>T</i> _{sat} = 544.7°F)								
<i>p</i> = 1200 lbf/in. ² (<i>T</i> _{sat} = 567.4°F)								
Sat.	0.446	1109.0	1192.4	1.3903	0.362	1103.5	1183.9	1.3673
600	0.514	1153.7	1248.8	1.4450	0.402	1134.4	1223.6	1.4054
650	0.564	1184.7	1289.1	1.4822	0.450	1170.9	1270.8	1.4490
700	0.608	1212.0	1324.6	1.5135	0.491	1201.3	1310.2	1.4837
800	0.688	1261.2	1388.5	1.5665	0.562	1253.7	1378.4	1.5402
900	0.761	1307.3	1448.1	1.6120	0.626	1301.5	1440.4	1.5876
1000	0.831	1352.2	1505.9	1.6530	0.685	1347.5	1499.7	1.6297
1100	0.898	1396.8	1562.9	1.6908	0.743	1393.0	1557.9	1.6682
1200	0.963	1441.5	1619.7	1.7261	0.798	1438.3	1615.5	1.7040
1300	1.027	1486.5	1676.5	1.7593	0.853	1483.8	1673.1	1.7377
1400	1.091	1531.9	1733.7	1.7909	0.906	1529.6	1730.7	1.7696
1600	1.215	1624.4	1849.3	1.8499	1.011	1622.6	1847.1	1.8290
<i>p</i> = 1400 lbf/in. ² (<i>T</i> _{sat} = 587.2°F)								
<i>p</i> = 1600 lbf/in. ² (<i>T</i> _{sat} = 605.1°F)								
Sat.	0.302	1096.0	1174.1	1.3461	0.255	1087.4	1162.9	1.3258
600	0.318	1110.9	1193.1	1.3641	0.303	1137.8	1227.4	1.3852
650	0.367	1155.5	1250.5	1.4171				
700	0.406	1189.6	1294.8	1.4562	0.342	1177.0	1278.1	1.4299
800	0.471	1245.8	1367.9	1.5168	0.403	1237.7	1357.0	1.4953
900	0.529	1295.6	1432.5	1.5661	0.466	1289.5	1424.4	1.5468
1000	0.582	1342.8	1493.5	1.6094	0.504	1338.0	1487.1	1.5913
1100	0.632	1389.1	1552.8	1.6487	0.549	1385.2	1547.7	1.6315
1200	0.681	1435.1	1611.4	1.6851	0.592	1431.8	1607.1	1.6684
1300	0.728	1481.1	1669.6	1.7192	0.634	1478.3	1666.1	1.7029
1400	0.774	1527.2	1727.8	1.7513	0.675	1524.9	1724.8	1.7354
1600	0.865	1620.8	1844.8	1.8111	0.755	1619.0	1842.6	1.7955
<i>p</i> = 1800 lbf/in. ² (<i>T</i> _{sat} = 621.2°F)								
<i>p</i> = 2000 lbf/in. ² (<i>T</i> _{sat} = 636.0°F)								
Sat.	0.218	1077.7	1150.4	1.3060	0.188	1066.6	1136.3	1.2861
650	0.251	1117.0	1200.4	1.3517	0.206	1091.1	1167.2	1.3141
700	0.291	1163.1	1259.9	1.4042	0.249	1147.7	1239.8	1.3782
750	0.322	1198.6	1305.9	1.4430	0.280	1187.3	1291.1	1.4216
800	0.350	1229.1	1345.7	1.4753	0.307	1220.1	1333.8	1.4562
900	0.399	1283.2	1416.1	1.5291	0.353	1276.8	1407.6	1.5126
1000	0.443	1333.1	1480.7	1.5749	0.395	1328.1	1474.1	1.5598
1100	0.484	1381.2	1542.5	1.6159	0.433	1377.2	1537.2	1.6017
1200	0.524	1428.5	1602.9	1.6534	0.469	1425.2	1598.6	1.6398
1300	0.561	1475.5	1662.5	1.6883	0.503	1472.7	1659.0	1.6751
1400	0.598	1522.5	1721.8	1.7211	0.537	1520.2	1718.8	1.7082
1600	0.670	1617.2	1840.4	1.7817	0.602	1615.4	1838.2	1.7692

TABLE A-4E

(Continued)

T °F	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R
<i>p = 2500 lbf/in.² (T_{sat} = 668.3°F)</i>								
<i>p = 3000 lbf/in.² (T_{sat} = 695.5°F)</i>								
Sat.	0.1306	1031.0	1091.4	1.2327	0.0840	968.8	1015.5	1.1575
700	0.1684	1098.7	1176.6	1.3073	0.0977	1003.9	1058.1	1.1944
750	0.2030	1155.2	1249.1	1.3686	0.1483	1114.7	1197.1	1.3122
800	0.2291	1195.7	1301.7	1.4112	0.1757	1167.6	1265.2	1.3675
900	0.2712	1259.9	1385.4	1.4752	0.2160	1241.8	1361.7	1.4414
1000	0.3069	1315.2	1457.2	1.5262	0.2485	1301.7	1439.6	1.4967
1100	0.3393	1366.8	1523.8	1.5704	0.2772	1356.2	1510.1	1.5434
1200	0.3696	1416.7	1587.7	1.6101	0.3086	1408.0	1576.6	1.5848
1300	0.3984	1465.7	1650.0	1.6465	0.3285	1458.5	1640.9	1.6224
1400	0.4261	1514.2	1711.3	1.6804	0.3524	1508.1	1703.7	1.6571
1500	0.4531	1562.5	1772.1	1.7123	0.3754	1557.3	1765.7	1.6896
1600	0.4795	1610.8	1832.6	1.7424	0.3978	1606.3	1827.1	1.7201
<i>p = 3500 lbf/in.²</i>								
650	0.0249	663.5	679.7	0.8630	0.0245	657.7	675.8	0.8574
700	0.0306	759.5	779.3	0.9506	0.0287	742.1	763.4	0.9345
750	0.1046	1058.4	1126.1	1.2440	0.0633	960.7	1007.5	1.1395
800	0.1363	1134.7	1223.0	1.3226	0.1052	1095.0	1172.9	1.2740
900	0.1763	1222.4	1336.5	1.4096	0.1462	1201.5	1309.7	1.3789
1000	0.2066	1287.6	1421.4	1.4699	0.1752	1272.9	1402.6	1.4449
1100	0.2328	1345.2	1496.0	1.5193	0.1995	1333.9	1481.6	1.4973
1200	0.2566	1399.2	1565.3	1.5624	0.2213	1390.1	1553.9	1.5423
1300	0.2787	1451.1	1631.7	1.6012	0.2414	1443.7	1622.4	1.5823
1400	0.2997	1501.9	1696.1	1.6368	0.2603	1495.7	1688.4	1.6188
1500	0.3199	1552.0	1759.2	1.6699	0.2784	1546.7	1752.8	1.6526
1600	0.3395	1601.7	1831.6	1.7010	0.2959	1597.1	1816.1	1.6841
<i>p = 4000 lbf/in.²</i>								
650	0.0242	653.6	673.3	0.8535	0.0237	649.8	671.0	0.8499
700	0.0278	732.7	755.3	0.9257	0.0271	725.1	749.1	0.9187
750	0.0415	870.8	904.6	1.0513	0.0352	832.6	863.9	1.0154
800	0.0844	1056.5	1125.3	1.2306	0.0668	1011.2	1070.5	1.1827
900	0.1270	1183.7	1287.1	1.3548	0.1109	1164.8	1263.4	1.3310
1000	0.1552	1260.8	1387.2	1.4260	0.1385	1248.3	1317.4	1.4078
1100	0.1784	1324.7	1469.9	1.4809	0.1608	1315.3	1458.1	1.4653
1200	0.1989	1382.8	1544.7	1.5274	0.1802	1375.4	1535.4	1.5133
1300	0.2176	1437.7	1614.9	1.5685	0.1979	1431.7	1607.4	1.5555
1400	0.2352	1490.7	1682.3	1.6057	0.2143	1485.7	1676.1	1.5934
1500	0.2520	1542.7	1747.6	1.6399	0.2300	1538.2	1742.5	1.6282
1600	0.2681	1593.4	1811.7	1.6718	0.2450	1589.8	1807.4	1.6605

TABLE A-5E**Properties of Compressed Liquid Water**

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 500 lbf/in. ² (T _{sat} = 467.1°F)								
32 0.015994 0.00 1.49 0.00000 0.015967 0.03 2.99 0.00005 50 0.015998 18.02 19.50 0.03599 0.015972 17.99 20.94 0.03592 100 0.016106 67.87 69.36 0.12932 0.016082 67.70 70.68 0.12901								
150 0.016318 117.66 119.17 0.21457 0.016293 117.38 120.40 0.21410 200 0.016608 167.65 169.19 0.29341 0.016580 167.26 170.32 0.29281 300 0.017416 268.92 270.53 0.43641 0.017379 268.24 271.46 0.43552								
400 0.018608 373.68 375.40 0.56604 0.018550 372.55 375.98 0.56472 Sat. 0.019748 447.70 449.53 0.64904 0.021591 538.39 542.38 0.74320								
<i>p</i> = 1000 lbf/in. ² (T _{sat} = 544.7°F)								
32 0.015939 0.05 4.47 0.00007 0.015912 0.06 5.95 0.00008 50 0.015946 17.95 22.38 0.03584 0.015920 17.91 23.81 0.03575 100 0.016058 67.53 71.99 0.12870 0.016034 67.37 73.30 0.12839								
150 0.016268 117.10 121.62 0.21364 0.016244 116.83 122.84 0.21318 200 0.016554 166.87 171.46 0.29221 0.016527 166.49 172.60 0.29162 300 0.017343 267.58 272.39 0.43463 0.017308 266.93 273.33 0.43376								
400 0.018493 371.45 376.59 0.56343 0.018439 370.38 377.21 0.56216 500 0.02024 481.8 487.4 0.6853 0.02014 479.8 487.3 0.6832 Sat. 0.02346 605.0 611.5 0.8082 0.02565 662.4 671.9 0.8623								
<i>p</i> = 1500 lbf/in. ² (T _{sat} = 596.4°F)								
32 0.015939 0.05 4.47 0.00007 0.015912 0.06 5.95 0.00008 50 0.015946 17.95 22.38 0.03584 0.015920 17.91 23.81 0.03575 100 0.016058 67.53 71.99 0.12870 0.016034 67.37 73.30 0.12839								
150 0.016268 117.10 121.62 0.21364 0.016244 116.83 122.84 0.21318 200 0.016554 166.87 171.46 0.29221 0.016527 166.49 172.60 0.29162 300 0.017343 267.58 272.39 0.43463 0.017308 266.93 273.33 0.43376								
400 0.018493 371.45 376.59 0.56343 0.018439 370.38 377.21 0.56216 500 0.02024 481.8 487.4 0.6853 0.02014 479.8 487.3 0.6832 Sat. 0.02346 605.0 611.5 0.8082 0.02565 662.4 671.9 0.8623								
<i>p</i> = 2000 lbf/in. ² (T _{sat} = 636.0°F)								
32 0.015939 0.05 4.47 0.00007 0.015912 0.06 5.95 0.00008 50 0.015946 17.95 22.38 0.03584 0.015920 17.91 23.81 0.03575 100 0.016058 67.53 71.99 0.12870 0.016034 67.37 73.30 0.12839								
150 0.016268 117.10 121.62 0.21364 0.016244 116.83 122.84 0.21318 200 0.016554 166.87 171.46 0.29221 0.016527 166.49 172.60 0.29162 300 0.017343 267.58 272.39 0.43463 0.017308 266.93 273.33 0.43376								
400 0.018493 371.45 376.59 0.56343 0.018439 370.38 377.21 0.56216 500 0.02024 481.8 487.4 0.6853 0.02014 479.8 487.3 0.6832 Sat. 0.02346 605.0 611.5 0.8082 0.02565 662.4 671.9 0.8623								
<i>p</i> = 3000 lbf/in. ² (T _{sat} = 695.5°F)								
32 0.015859 0.09 8.90 0.00009 0.015807 0.10 11.80 0.00005 50 0.015870 17.84 26.65 0.03555 0.015821 17.76 29.47 0.03534 100 0.015987 67.04 75.91 0.12777 0.015942 66.72 78.52 0.12714								
150 0.016196 116.30 125.29 0.21226 0.016150 115.77 127.73 0.21136 200 0.016476 165.74 174.89 0.29046 0.016425 165.02 177.18 0.28931 300 0.017240 265.66 275.23 0.43205 0.017174 264.43 277.15 0.43038								
400 0.018334 368.32 378.50 0.55970 0.018235 366.35 379.85 0.55734 500 0.019944 476.2 487.3 0.6794 0.019766 472.9 487.5 0.6758 Sat. 0.034310 783.5 802.5 0.9732								
<i>p</i> = 4000 lbf/in. ²								

TABLE A-6E**Properties of Saturated Water (Solid–Vapor): Temperature Table**

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb			Enthalpy Btu/lb			Entropy Btu/lb · °R		
		Sat. Solid <i>v_i</i>	Sat. Vapor <i>v_g</i> × 10 ⁻³	Sat. Solid <i>u_i</i>	Subl. <i>u_{ig}</i>	Sat. Vapor <i>u_g</i>	Sat. Solid <i>h_i</i>	Subl. <i>h_{ig}</i>	Sat. Vapor <i>h_g</i>	Sat. Solid <i>s_i</i>	Subl. <i>s_{ig}</i>	Sat. Vapor <i>s_g</i>
32.018	.0887	.01747	3.302	−143.34	1164.6	1021.2	−143.34	1218.7	1075.4	−.292	2.479	2.187
32	.0886	.01747	3.305	−143.35	1164.6	1021.2	−143.35	1218.7	1075.4	−.292	2.479	2.187
30	.0808	.01747	3.607	−144.35	1164.9	1020.5	−144.35	1218.9	1074.5	−.294	2.489	2.195
25	.0641	.01746	4.506	−146.84	1165.7	1018.9	−146.84	1219.1	1072.3	−.299	2.515	2.216
20	.0505	.01745	5.655	−149.31	1166.5	1017.2	−149.31	1219.4	1070.1	−.304	2.542	2.238
15	.0396	.01745	7.13	−151.75	1167.3	1015.5	−151.75	1219.7	1067.9	−.309	2.569	2.260
10	.0309	.01744	9.04	−154.17	1168.1	1013.9	−154.17	1219.9	1065.7	−.314	2.597	2.283
5	.0240	.01743	11.52	−156.56	1168.8	1012.2	−156.56	1220.1	1063.5	−.320	2.626	2.306
0	.0185	.01743	14.77	−158.93	1169.5	1010.6	−158.93	1220.2	1061.2	−.325	2.655	2.330
−5	.0142	.01742	19.03	−161.27	1170.2	1008.9	−161.27	1220.3	1059.0	−.330	2.684	2.354
−10	.0109	.01741	24.66	−163.59	1170.9	1007.3	−163.59	1220.4	1056.8	−.335	2.714	2.379
−15	.0082	.01740	32.2	−165.89	1171.5	1005.6	−165.89	1220.5	1054.6	−.340	2.745	2.405
−20	.0062	.01740	42.2	−168.16	1172.1	1003.9	−168.16	1220.6	1052.4	−.345	2.776	2.431
−25	.0046	.01739	55.7	−170.40	1172.7	1002.3	−170.40	1220.6	1050.2	−.351	2.808	2.457
−30	.0035	.01738	74.1	−172.63	1173.2	1000.6	−172.63	1220.6	1048.0	−.356	2.841	2.485
−35	.0026	.01737	99.2	−174.82	1173.8	998.9	−174.82	1220.6	1045.8	−.361	2.874	2.513
−40	.0019	.01737	133.8	−177.00	1174.3	997.3	−177.00	1220.6	1043.6	−.366	2.908	2.542

TABLE A-7E**Properties of Saturated Refrigerant 22 (Liquid–Vapor): Temperature Table**

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R		Temp. °F
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
-80	4.781	0.01090	9.6984	-10.30	87.24	-10.29	106.11	95.82	-0.0257	0.2538
-60	8.834	0.01113	5.4744	-5.20	89.16	-5.18	103.30	98.12	-0.0126	0.2458
-55	10.187	0.01120	4.7933	-3.91	89.64	-3.89	102.58	98.68	-0.0094	0.2441
-50	11.701	0.01126	4.2123	-2.62	90.12	-2.60	101.84	99.24	-0.0063	0.2424
-45	13.387	0.01132	3.7147	-1.33	90.59	-1.30	101.10	99.80	-0.0031	0.2407
-40	15.261	0.01139	3.2869	-0.03	91.07	0.00	100.35	100.35	0.0000	0.2391
-35	17.335	0.01145	2.9176	1.27	91.54	1.31	99.59	100.90	0.0031	0.2376
-30	19.624	0.01152	2.5976	2.58	92.00	2.62	98.82	101.44	0.0061	0.2361
-25	22.142	0.01159	2.3195	3.89	92.47	3.94	98.04	101.98	0.0092	0.2347
-20	24.906	0.01166	2.0768	5.21	92.93	5.26	97.24	102.50	0.0122	0.2334
-15	27.931	0.01173	1.8644	6.53	93.38	6.59	96.43	103.03	0.0152	0.2321
-10	31.233	0.01181	1.6780	7.86	93.84	7.93	95.61	103.54	0.0182	0.2308
-5	34.829	0.01188	1.5138	9.19	94.28	9.27	94.78	104.05	0.0211	0.2296
0	38.734	0.01196	1.3688	10.53	94.73	10.62	93.93	104.55	0.0240	0.2284
5	42.967	0.01204	1.2404	11.88	95.17	11.97	93.06	105.04	0.0270	0.2272
10	47.545	0.01212	1.1264	13.23	95.60	13.33	92.18	105.52	0.0298	0.2261
15	52.486	0.01220	1.0248	14.58	96.03	14.70	91.29	105.99	0.0327	0.2250
20	57.808	0.01229	0.9342	15.95	96.45	16.08	90.38	106.45	0.0356	0.2240
25	63.529	0.01237	0.8531	17.31	96.87	17.46	89.45	106.90	0.0384	0.2230
30	69.668	0.01246	0.7804	18.69	97.28	18.85	88.50	107.35	0.0412	0.2220
35	76.245	0.01255	0.7150	20.07	97.68	20.25	87.53	107.78	0.0441	0.2210
40	83.278	0.01265	0.6561	21.46	98.08	21.66	86.54	108.20	0.0468	0.2200
45	90.787	0.01275	0.6029	22.86	98.47	23.07	85.53	108.60	0.0496	0.2191
50	98.792	0.01285	0.5548	24.27	98.84	24.50	84.49	108.99	0.0524	0.2182
55	107.31	0.01295	0.5112	25.68	99.22	25.94	83.44	109.37	0.0552	0.2173
60	116.37	0.01306	0.4716	27.10	99.58	27.38	82.36	109.74	0.0579	0.2164
65	125.98	0.01317	0.4355	28.53	99.93	28.84	81.25	110.09	0.0607	0.2155
70	136.18	0.01328	0.4027	29.98	100.27	30.31	80.11	110.42	0.0634	0.2147
75	146.97	0.01340	0.3726	31.43	100.60	31.79	78.95	110.74	0.0661	0.2138
80	158.38	0.01352	0.3452	32.89	100.92	33.29	77.75	111.04	0.0689	0.2130
85	170.44	0.01365	0.3200	34.36	101.22	34.80	76.53	111.32	0.0716	0.2121
90	183.16	0.01378	0.2969	35.85	101.51	36.32	75.26	111.58	0.0743	0.2113
95	196.57	0.01392	0.2756	37.35	101.79	37.86	73.96	111.82	0.0771	0.2104
100	210.69	0.01407	0.2560	38.86	102.05	39.41	72.63	112.04	0.0798	0.2095
105	225.54	0.01422	0.2379	40.39	102.29	40.99	71.24	112.23	0.0825	0.2087
110	241.15	0.01438	0.2212	41.94	102.52	42.58	69.82	112.40	0.0852	0.2078
115	257.55	0.01455	0.2058	43.50	102.72	44.19	68.34	112.53	0.0880	0.2069
120	274.75	0.01472	0.1914	45.08	102.90	45.83	66.81	112.64	0.0907	0.2060
140	352.17	0.01555	0.1433	51.62	103.36	52.64	60.06	112.70	0.1019	0.2021

Source: Tables A-7E through A-9E are calculated based on equations from A. Kamei and S. W. Beyerlein, "A Fundamental Equation for Chlorodifluoromethane (R-22)," *Fluid Phase Equilibria*, Vol. 80, No. 11, 1992, pp. 71–86.

TABLE A-8E**Properties of Saturated Refrigerant 22 (Liquid–Vapor): Pressure Table**

Press. lbf/in. ²	Temp. °F	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb			Entropy Btu/lb · °R		Press. lbf/in. ²
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	Sat. Vapor <i>s_g</i>	
5	-78.62	0.01091	9.3014	-9.95	87.37	-9.93	105.92	95.98	-0.0248	0.2532	5
10	-55.66	0.01119	4.8769	-4.08	89.58	-4.06	102.67	98.61	-0.0098	0.2443	10
15	-40.67	0.01138	3.3402	-0.21	91.00	-0.17	100.45	100.28	-0.0004	0.2393	15
20	-29.22	0.01153	2.5518	2.78	92.07	2.83	98.70	101.52	0.0066	0.2359	20
25	-19.84	0.01166	2.0695	5.25	92.94	5.31	97.22	102.52	0.0123	0.2333	25
30	-11.82	0.01178	1.7430	7.38	93.67	7.44	95.91	103.35	0.0171	0.2313	30
35	-4.77	0.01189	1.5068	9.25	94.30	9.33	94.74	104.07	0.0212	0.2295	35
40	1.54	0.01198	1.3277	10.94	94.86	11.03	93.66	104.70	0.0249	0.2280	40
45	7.27	0.01207	1.1870	12.49	95.37	12.59	92.67	105.26	0.0283	0.2267	45
50	12.53	0.01216	1.0735	13.91	95.82	14.03	91.73	105.76	0.0313	0.2256	50
55	17.41	0.01224	0.9799	15.24	96.23	15.36	90.85	106.21	0.0341	0.2245	55
60	21.96	0.01232	0.9014	16.48	96.62	16.62	90.01	106.63	0.0367	0.2236	60
65	26.23	0.01239	0.8345	17.65	96.97	17.80	89.21	107.01	0.0391	0.2227	65
70	30.26	0.01247	0.7768	18.76	97.30	18.92	88.45	107.37	0.0414	0.2219	70
75	34.08	0.01254	0.7265	19.82	97.61	19.99	87.71	107.70	0.0435	0.2212	75
80	37.71	0.01260	0.6823	20.83	97.90	21.01	86.99	108.00	0.0456	0.2205	80
85	41.18	0.01267	0.6431	21.79	98.17	21.99	86.30	108.29	0.0475	0.2198	85
90	44.49	0.01274	0.6081	22.72	98.43	22.93	85.63	108.56	0.0494	0.2192	90
95	47.67	0.01280	0.5766	23.61	98.67	23.84	84.98	108.81	0.0511	0.2186	95
100	50.73	0.01286	0.5482	24.47	98.90	24.71	84.34	109.05	0.0528	0.2181	100
110	56.52	0.01298	0.4988	26.11	99.33	26.37	83.11	109.49	0.0560	0.2170	110
120	61.92	0.01310	0.4573	27.65	99.71	27.94	81.93	109.88	0.0590	0.2161	120
130	67.00	0.01321	0.4220	29.11	100.07	29.43	80.80	110.22	0.0618	0.2152	130
140	71.80	0.01332	0.3915	30.50	100.39	30.84	79.70	110.54	0.0644	0.2144	140
150	76.36	0.01343	0.3649	31.82	100.69	32.20	78.63	110.82	0.0669	0.2136	150
160	80.69	0.01354	0.3416	33.09	100.96	33.49	77.59	111.08	0.0693	0.2128	160
170	84.82	0.01365	0.3208	34.31	101.21	34.74	76.57	111.31	0.0715	0.2121	170
180	88.78	0.01375	0.3023	35.49	101.44	35.95	75.57	111.52	0.0737	0.2115	180
190	92.58	0.01386	0.2857	36.62	101.66	37.11	74.60	111.71	0.0757	0.2108	190
200	96.24	0.01396	0.2706	37.72	101.86	38.24	73.64	111.88	0.0777	0.2102	200
225	104.82	0.01422	0.2386	40.34	102.28	40.93	71.29	112.22	0.0824	0.2087	225
250	112.73	0.01447	0.2126	42.79	102.63	43.46	69.02	112.47	0.0867	0.2073	250
275	120.07	0.01473	0.1912	45.10	102.91	45.85	66.79	112.64	0.0908	0.2060	275
300	126.94	0.01499	0.1732	47.30	103.11	48.14	64.60	112.73	0.0946	0.2047	300
325	133.39	0.01525	0.1577	49.42	103.26	50.33	62.42	112.75	0.0982	0.2034	325
350	139.49	0.01552	0.1444	51.45	103.35	52.46	60.25	112.71	0.1016	0.2022	350

TABLE A-9E**Properties of Superheated Refrigerant 22 Vapor**

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 5 lbf/in. ² (T _{sat} = -78.62°F)								
<i>p</i> = 10 lbf/in. ² (T _{sat} = -55.66°F)								
Sat.	9.3014	87.37	95.98	0.2532	4.8769	89.58	98.61	0.2443
-70	9.5244	88.31	97.13	0.2562				
-60	9.7823	89.43	98.48	0.2596				
-50	10.0391	90.55	99.84	0.2630	4.9522	90.23	99.40	0.2462
-40	10.2952	91.69	101.22	0.2663	5.0846	91.39	100.81	0.2496
-30	10.5506	92.84	102.61	0.2696	5.2163	92.57	102.23	0.2530
-20	10.8054	94.01	104.01	0.2728	5.3472	93.75	103.65	0.2563
-10	11.0596	95.19	105.43	0.2760	5.4775	94.95	105.09	0.2595
0	11.3133	96.39	106.87	0.2791	5.6073	96.16	106.55	0.2627
10	11.5666	97.60	108.31	0.2822	5.7366	97.39	108.01	0.2658
20	11.8195	98.83	109.77	0.2853	5.8655	98.63	109.49	0.2690
30	12.0720	100.07	111.25	0.2884	5.9941	99.88	110.98	0.2720
40	12.3242	101.33	112.74	0.2914	6.1223	101.15	112.49	0.2751
<i>p</i> = 15 lbf/in. ² (T _{sat} = -40.67°F)								
<i>p</i> = 20 lbf/in. ² (T _{sat} = -29.22°F)								
Sat.	3.3402	91.00	100.28	0.2393	2.5518	92.07	101.52	0.2359
-40	3.3463	91.08	100.38	0.2396				
-30	3.4370	92.28	101.83	0.2430				
-20	3.5268	93.49	103.28	0.2463	2.6158	93.21	102.90	0.2391
-10	3.6160	94.70	104.75	0.2496	2.6846	94.45	104.39	0.2424
0	3.7046	95.93	106.22	0.2529	2.7528	95.69	105.89	0.2457
10	3.7927	97.17	107.71	0.2561	2.8204	96.95	107.39	0.2490
20	3.8804	98.43	109.20	0.2592	2.8875	98.22	108.91	0.2522
30	3.9677	99.69	110.71	0.2623	2.9542	99.49	110.43	0.2553
40	4.0546	100.97	112.23	0.2654	3.0205	100.78	111.97	0.2584
50	4.1412	102.26	113.76	0.2684	3.0865	102.09	113.52	0.2615
60	4.2275	103.57	115.31	0.2714	3.1522	103.40	115.08	0.2645
70	4.3136	104.89	116.87	0.2744	3.2176	104.73	116.65	0.2675
<i>p</i> = 25 lbf/in. ² (T _{sat} = -19.84°F)								
<i>p</i> = 30 lbf/in. ² (T _{sat} = -11.82°F)								
Sat.	2.0695	92.94	102.52	0.2333	1.7430	93.67	103.35	0.2313
-10	2.1252	94.18	104.02	0.2367	1.7518	93.91	103.64	0.2319
0	2.1812	95.45	105.54	0.2400	1.7997	95.19	105.19	0.2353
10	2.2365	96.72	107.07	0.2433	1.8470	96.48	106.74	0.2386
20	2.2914	98.00	108.61	0.2466	1.8937	97.78	108.30	0.2419
30	2.3458	99.29	110.15	0.2498	1.9400	99.09	109.86	0.2451
40	2.3998	100.59	111.70	0.2529	1.9858	100.40	111.43	0.2483
50	2.4535	101.91	113.27	0.2560	2.0313	101.73	113.01	0.2514
60	2.5068	103.23	114.84	0.2590	2.0764	103.06	114.60	0.2545
70	2.5599	104.57	116.42	0.2621	2.1213	104.41	116.19	0.2576
80	2.6127	105.92	118.01	0.2650	2.1659	105.77	117.80	0.2606
90	2.6654	107.28	119.62	0.2680	2.2103	107.13	119.41	0.2635
100	2.7178	108.65	121.24	0.2709	2.2545	108.52	121.04	0.2665

TABLE A-9E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 40 lbf/in. ² (<i>T</i> _{sat} = 1.54°F)								
<i>p</i> = 50 lbf/in. ² (<i>T</i> _{sat} = 12.53°F)								
Sat.	1.3277	94.86	104.70	0.2280	1.0735	95.82	105.76	0.2256
10	1.3593	95.99	106.06	0.2310				
20	1.3960	97.33	107.67	0.2343	1.0965	96.85	107.00	0.2282
30	1.4321	98.66	109.27	0.2376	1.1268	98.22	108.65	0.2316
40	1.4678	100.01	110.88	0.2409	1.1565	99.59	110.30	0.2349
50	1.5032	101.35	112.49	0.2441	1.1858	100.97	111.95	0.2382
60	1.5381	102.71	114.10	0.2472	1.2147	102.35	113.60	0.2414
70	1.5728	104.08	115.73	0.2503	1.2433	103.74	115.25	0.2445
80	1.6071	105.45	117.36	0.2534	1.2716	105.13	116.90	0.2476
90	1.6413	106.84	118.99	0.2564	1.2996	106.53	118.57	0.2507
100	1.6752	108.23	120.64	0.2593	1.3274	107.95	120.24	0.2537
110	1.7089	109.64	122.30	0.2623	1.3549	109.37	121.91	0.2567
120	1.7424	111.06	123.97	0.2652	1.3823	110.80	123.60	0.2596
<i>p</i> = 60 lbf/in. ² (<i>T</i> _{sat} = 21.96°F)								
<i>p</i> = 70 lbf/in. ² (<i>T</i> _{sat} = 30.26°F)								
Sat.	0.9014	96.62	106.63	0.2236	0.7768	97.30	107.37	0.2219
30	0.9226	97.75	108.00	0.2264				
40	0.9485	99.16	109.70	0.2298	0.7994	98.71	109.07	0.2254
50	0.9739	100.57	111.39	0.2332	0.8221	100.15	110.81	0.2288
60	0.9988	101.98	113.07	0.2365	0.8443	101.59	112.53	0.2321
70	1.0234	103.39	114.76	0.2397	0.8660	103.03	114.25	0.2354
80	1.0476	104.80	116.44	0.2428	0.8874	104.46	115.97	0.2386
90	1.0716	106.22	118.13	0.2459	0.9086	105.90	117.68	0.2418
100	1.0953	107.65	119.82	0.2490	0.9294	107.35	119.40	0.2449
110	1.1188	109.09	121.52	0.2520	0.9500	108.80	121.12	0.2479
120	1.1421	110.53	123.22	0.2549	0.9704	110.26	122.84	0.2509
130	1.1653	111.99	124.93	0.2579	0.9907	111.73	124.57	0.2539
140	1.1883	113.45	126.65	0.2608	1.0107	113.21	126.31	0.2568
<i>p</i> = 80 lbf/in. ² (<i>T</i> _{sat} = 37.71°F)								
<i>p</i> = 90 lbf/in. ² (<i>T</i> _{sat} = 44.49°F)								
Sat.	0.6823	97.90	108.00	0.2205	0.6081	98.43	108.56	0.2192
40	0.6871	98.24	108.42	0.2213				
50	0.7079	99.72	110.20	0.2248	0.6186	99.26	109.57	0.2212
60	0.7280	101.19	111.97	0.2283	0.6373	100.77	111.39	0.2247
70	0.7478	102.65	113.73	0.2316	0.6555	102.27	113.19	0.2282
80	0.7671	104.11	115.48	0.2349	0.6733	103.76	114.98	0.2315
90	0.7861	105.58	117.22	0.2381	0.6907	105.24	116.75	0.2348
100	0.8048	107.04	118.97	0.2412	0.7078	106.73	118.52	0.2380
110	0.8233	108.51	120.71	0.2443	0.7246	108.22	120.29	0.2411
120	0.8416	109.99	122.45	0.2474	0.7412	109.71	122.06	0.2442
130	0.8596	111.47	124.20	0.2504	0.7576	111.20	123.83	0.2472
140	0.8775	112.96	125.96	0.2533	0.7739	112.71	125.60	0.2502
150	0.8953	114.46	127.72	0.2562	0.7899	114.22	127.38	0.2531

TABLE A-9E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 100 lbf/in. ² (<i>T</i> _{sat} = 50.73°F)								
<i>p</i> = 120 lbf/in. ² (<i>T</i> _{sat} = 61.92°F)								
Sat.	0.5482	98.90	109.05	0.2181	0.4573	99.71	109.88	0.2161
60	0.5645	100.33	110.79	0.2214				
80	0.5980	103.38	114.46	0.2284	0.4846	102.60	113.37	0.2227
100	0.6300	106.40	118.07	0.2349	0.5130	105.73	117.13	0.2295
120	0.6609	109.42	121.66	0.2412	0.5400	108.83	120.83	0.2360
140	0.6908	112.45	125.24	0.2473	0.5661	111.92	124.50	0.2422
160	0.7201	115.50	128.83	0.2532	0.5914	115.02	128.16	0.2482
180	0.7489	118.58	132.45	0.2589	0.6161	118.15	131.84	0.2541
200	0.7771	121.69	136.08	0.2645	0.6404	121.30	135.53	0.2597
220	0.8051	124.84	139.75	0.2700	0.6642	124.48	139.24	0.2653
240	0.8327	128.04	143.45	0.2754	0.6878	127.69	142.98	0.2707
260	0.8600	131.27	147.19	0.2806	0.7110	130.95	146.75	0.2760
280	0.8871	134.54	150.97	0.2858	0.7340	134.24	150.55	0.2812
300	0.9140	137.85	154.78	0.2909	0.7568	137.57	154.39	0.2863
<i>p</i> = 140 lbf/in. ² (<i>T</i> _{sat} = 71.80°F)								
<i>p</i> = 160 lbf/in. ² (<i>T</i> _{sat} = 80.69°F)								
Sat.	0.3915	100.39	110.54	0.2144	0.3416	100.96	111.08	0.2128
80	0.4028	101.76	112.20	0.2175				
100	0.4289	105.02	116.14	0.2246	0.3653	104.26	115.08	0.2201
120	0.4534	108.21	119.96	0.2313	0.3881	107.56	119.06	0.2271
140	0.4768	111.37	123.73	0.2377	0.4095	110.81	122.94	0.2337
160	0.4993	114.53	127.48	0.2439	0.4301	114.03	126.77	0.2400
180	0.5212	117.70	131.21	0.2498	0.4499	117.25	130.57	0.2460
200	0.5426	120.89	134.96	0.2556	0.4692	120.47	134.37	0.2518
220	0.5636	124.10	138.71	0.2612	0.4880	123.72	138.18	0.2575
240	0.5842	127.35	142.49	0.2666	0.5065	126.99	142.00	0.2631
260	0.6045	130.62	146.30	0.2720	0.5246	130.30	145.84	0.2685
280	0.6246	133.94	150.13	0.2773	0.5425	133.63	149.70	0.2738
300	0.6445	137.29	154.00	0.2824	0.5602	137.00	153.60	0.2790
320	0.6642	140.68	157.89	0.2875	0.5777	140.41	157.62	0.2841
<i>p</i> = 180 lbf/in. ² (<i>T</i> _{sat} = 88.78°F)								
<i>p</i> = 200 lbf/in. ² (<i>T</i> _{sat} = 96.24°F)								
Sat.	0.3023	101.44	111.52	0.2115	0.2706	101.86	111.88	0.2102
100	0.3154	103.44	113.95	0.2159	0.2748	102.56	112.73	0.2117
120	0.3369	106.88	118.11	0.2231	0.2957	106.15	117.10	0.2194
140	0.3570	110.21	122.11	0.2299	0.3148	109.59	121.25	0.2264
160	0.3761	113.50	126.04	0.2364	0.3327	112.96	125.28	0.2330
180	0.3943	116.78	129.92	0.2425	0.3497	116.29	129.25	0.2393
200	0.4120	120.05	133.78	0.2485	0.3661	119.61	133.17	0.2454
220	0.4292	123.33	137.64	0.2542	0.3820	122.94	137.08	0.2512
240	0.4459	126.64	141.50	0.2598	0.3975	126.27	140.99	0.2569
260	0.4624	129.96	145.38	0.2653	0.4126	129.63	144.91	0.2624
280	0.4786	133.32	149.28	0.2706	0.4275	133.01	148.84	0.2678
300	0.4946	136.71	153.20	0.2759	0.4422	136.42	152.79	0.2731
320	0.5104	140.13	157.15	0.2810	0.4566	139.86	156.77	0.2782
340	0.5260	143.59	161.12	0.2860	0.4709	143.33	160.77	0.2833

TABLE A-9E

(Continued)

T °F	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R
<i>p = 225 lbf/in.² (T_{sat} = 104.82°F)</i>								
<i>p = 250 lbf/in.² (T_{sat} = 112.73°F)</i>								
Sat.	0.2386	102.28	112.22	0.2087	0.2126	102.63	112.47	0.2073
120	0.2539	105.17	115.75	0.2149	0.2198	104.10	114.27	0.2104
140	0.2722	108.78	120.12	0.2223	0.2378	107.90	118.91	0.2183
160	0.2891	112.26	124.30	0.2291	0.2540	111.51	123.27	0.2255
180	0.3050	115.67	128.38	0.2356	0.2690	115.02	127.48	0.2321
200	0.3202	119.06	132.40	0.2418	0.2833	118.48	131.59	0.2385
220	0.3348	122.43	136.38	0.2477	0.2969	121.91	135.66	0.2445
240	0.3490	125.81	140.35	0.2535	0.3101	125.33	139.69	0.2504
260	0.3628	129.20	144.32	0.2591	0.3229	128.76	143.71	0.2560
280	0.3764	132.61	148.29	0.2645	0.3354	132.21	147.73	0.2616
300	0.3896	136.05	152.28	0.2699	0.3476	135.67	151.76	0.2669
320	0.4027	139.51	156.29	0.2751	0.3596	139.16	155.81	0.2722
340	0.4156	143.00	160.32	0.2802	0.3715	142.67	159.87	0.2773
360	0.4284	146.33	164.38	0.2852	0.3831	146.22	163.95	0.2824
<i>p = 275 lbf/in.² (T_{sat} = 120.07°F)</i>								
<i>p = 300 lbf/in.² (T_{sat} = 126.94°F)</i>								
Sat.	0.1912	102.91	112.64	0.2060	0.1732	103.11	112.73	0.2047
140	0.2092	106.96	117.61	0.2144	0.1849	105.93	116.20	0.2105
160	0.2250	110.73	122.19	0.2219	0.2006	109.89	121.04	0.2185
180	0.2395	144.35	126.54	0.2288	0.2146	133.64	125.56	0.2257
200	0.2530	117.88	130.77	0.2353	0.2276	117.26	129.91	0.2324
220	0.2659	121.38	134.91	0.2415	0.2399	120.83	134.15	0.2387
240	0.2782	124.85	139.02	0.2475	0.2516	124.35	138.33	0.2447
260	0.2902	128.32	143.10	0.2532	0.2629	127.87	142.47	0.2506
280	0.3018	131.80	147.17	0.2588	0.2739	131.38	146.59	0.2562
300	0.3132	135.29	151.24	0.2642	0.2845	134.90	150.71	0.2617
320	0.3243	138.80	155.32	0.2695	0.2949	138.44	154.83	0.2671
340	0.3353	142.34	159.41	0.2747	0.3051	142.00	158.95	0.2723
360	0.3461	145.90	163.53	0.2798	0.3152	145.58	163.09	0.2774
<i>p = 325 lbf/in.² (T_{sat} = 133.39°F)</i>								
<i>p = 350 lbf/in.² (T_{sat} = 139.49°F)</i>								
Sat.	0.1577	103.26	112.75	0.2034	0.1444	103.35	112.71	0.2022
140	0.1637	104.78	114.63	0.2066	0.1448	103.48	112.86	0.2024
160	0.1796	109.00	119.81	0.2151	0.1605	107.90	118.30	0.2113
180	0.1934	112.89	124.53	0.2226	0.1747	112.06	123.38	0.2194
200	0.2061	116.62	129.02	0.2295	0.1874	115.95	128.10	0.2267
220	0.2179	120.26	133.37	0.2360	0.1987	119.65	132.53	0.2333
240	0.2291	123.84	137.63	0.2422	0.2095	123.31	136.89	0.2396
260	0.2398	127.40	141.83	0.2481	0.2199	126.93	141.18	0.2457
280	0.2501	130.96	146.01	0.2538	0.2297	130.52	145.41	0.2514
300	0.2602	134.51	150.17	0.2593	0.2393	134.12	149.62	0.2571
320	0.2700	138.08	154.33	0.2647	0.2486	137.71	153.82	0.2626
340	0.2796	141.66	158.49	0.2700	0.2577	141.32	158.02	0.2679
360	0.2891	145.26	162.66	0.2752	0.2666	144.95	162.23	0.2730
380	0.2983	148.89	166.85	0.2802	0.2754	148.59	166.43	0.2781

TABLE A-10E**Properties of Saturated Refrigerant 134a (Liquid–Vapor): Temperature Table**

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R		Temp. °F
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Sat. Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
-40	7.490	0.01130	5.7173	-0.02	87.90	0.00	95.82	95.82	0.0000	0.2283
-30	9.920	0.01143	4.3911	2.81	89.26	2.83	94.49	97.32	0.0067	0.2266
-20	12.949	0.01156	3.4173	5.69	90.62	5.71	93.10	98.81	0.0133	0.2250
-15	14.718	0.01163	3.0286	7.14	91.30	7.17	92.38	99.55	0.0166	0.2243
-10	16.674	0.01170	2.6918	8.61	91.98	8.65	91.64	100.29	0.0199	0.2236
-5	18.831	0.01178	2.3992	10.09	92.66	10.13	90.89	101.02	0.0231	0.2230
0	21.203	0.01185	2.1440	11.58	93.33	11.63	90.12	101.75	0.0264	0.2224
5	23.805	0.01193	1.9208	13.09	94.01	13.14	89.33	102.47	0.0296	0.2219
10	26.651	0.01200	1.7251	14.60	94.68	14.66	88.53	103.19	0.0329	0.2214
15	29.756	0.01208	1.5529	16.13	95.35	16.20	87.71	103.90	0.0361	0.2209
20	33.137	0.01216	1.4009	17.67	96.02	17.74	86.87	104.61	0.0393	0.2205
25	36.809	0.01225	1.2666	19.22	96.69	19.30	86.02	105.32	0.0426	0.2200
30	40.788	0.01233	1.1474	20.78	97.35	20.87	85.14	106.01	0.0458	0.2196
40	49.738	0.01251	0.9470	23.94	98.67	24.05	83.34	107.39	0.0522	0.2189
50	60.125	0.01270	0.7871	27.14	99.98	27.28	81.46	108.74	0.0585	0.2183
60	72.092	0.01290	0.6584	30.39	101.27	30.56	79.49	110.05	0.0648	0.2178
70	85.788	0.01311	0.5538	33.68	102.54	33.89	77.44	111.33	0.0711	0.2173
80	101.37	0.01334	0.4682	37.02	103.78	37.27	75.29	112.56	0.0774	0.2169
85	109.92	0.01346	0.4312	38.72	104.39	38.99	74.17	113.16	0.0805	0.2167
90	118.99	0.01358	0.3975	40.42	105.00	40.72	73.03	113.75	0.0836	0.2165
95	128.62	0.01371	0.3668	42.14	105.60	42.47	71.86	114.33	0.0867	0.2163
100	138.83	0.01385	0.3388	43.87	106.18	44.23	70.66	114.89	0.0898	0.2161
105	149.63	0.01399	0.3131	45.62	106.76	46.01	69.42	115.43	0.0930	0.2159
110	161.04	0.01414	0.2896	47.39	107.33	47.81	68.15	115.96	0.0961	0.2157
115	173.10	0.01429	0.2680	49.17	107.88	49.63	66.84	116.47	0.0992	0.2155
120	185.82	0.01445	0.2481	50.97	108.42	51.47	65.48	116.95	0.1023	0.2153
140	243.86	0.01520	0.1827	58.39	110.41	59.08	59.57	118.65	0.1150	0.2143
160	314.63	0.01617	0.1341	66.26	111.97	67.20	52.58	119.78	0.1280	0.2128
180	400.22	0.01758	0.0964	74.83	112.77	76.13	43.78	119.91	0.1417	0.2101
200	503.52	0.02014	0.0647	84.90	111.66	86.77	30.92	117.69	0.1575	0.2044
210	563.51	0.02329	0.0476	91.84	108.48	94.27	19.18	113.45	0.1684	0.1971

Source: Tables A-10E through A-12E are calculated based on equations from D. P. Wilson and R. S. Basu, "Thermodynamic Properties of a New Stratospherically Safe Working Fluid—Refrigerant 134a," *ASHRAE Trans.*, Vol. 94, Pt. 2, 1988, pp. 2095–2118.

TABLE A-11E**Properties of Saturated Refrigerant 134a (Liquid–Vapor): Pressure Table**

Press. lbf/in. ²	Temp. °F	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R		Press. lbf/in. ²
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
5	-53.48	0.01113	8.3508	-3.74	86.07	-3.73	97.53	93.79	-0.0090	0.2311
10	-29.71	0.01143	4.3581	2.89	89.30	2.91	94.45	97.37	0.0068	0.2265
15	-14.25	0.01164	2.9747	7.36	91.40	7.40	92.27	99.66	0.0171	0.2242
20	-2.48	0.01181	2.2661	10.84	93.00	10.89	90.50	101.39	0.0248	0.2227
30	15.38	0.01209	1.5408	16.24	95.40	16.31	87.65	103.96	0.0364	0.2209
40	29.04	0.01232	1.1692	20.48	97.23	20.57	85.31	105.88	0.0452	0.2197
50	40.27	0.01252	0.9422	24.02	98.71	24.14	83.29	107.43	0.0523	0.2189
60	49.89	0.01270	0.7887	27.10	99.96	27.24	81.48	108.72	0.0584	0.2183
70	58.35	0.01286	0.6778	29.85	101.05	30.01	79.82	109.83	0.0638	0.2179
80	65.93	0.01302	0.5938	32.33	102.02	32.53	78.28	110.81	0.0686	0.2175
90	72.83	0.01317	0.5278	34.62	102.89	34.84	76.84	111.68	0.0729	0.2172
100	79.17	0.01332	0.4747	36.75	103.68	36.99	75.47	112.46	0.0768	0.2169
120	90.54	0.01360	0.3941	40.61	105.06	40.91	72.91	113.82	0.0839	0.2165
140	100.56	0.01386	0.3358	44.07	106.25	44.43	70.52	114.95	0.0902	0.2161
160	109.56	0.01412	0.2916	47.23	107.28	47.65	68.26	115.91	0.0958	0.2157
180	117.74	0.01438	0.2569	50.16	108.18	50.64	66.10	116.74	0.1009	0.2154
200	125.28	0.01463	0.2288	52.90	108.98	53.44	64.01	117.44	0.1057	0.2151
220	132.27	0.01489	0.2056	55.48	109.68	56.09	61.96	118.05	0.1101	0.2147
240	138.79	0.01515	0.1861	57.93	110.30	58.61	59.96	118.56	0.1142	0.2144
260	144.92	0.01541	0.1695	60.28	110.84	61.02	57.97	118.99	0.1181	0.2140
280	150.70	0.01568	0.1550	62.53	111.31	63.34	56.00	119.35	0.1219	0.2136
300	156.17	0.01596	0.1424	64.71	111.72	65.59	54.03	119.62	0.1254	0.2132
350	168.72	0.01671	0.1166	69.88	112.45	70.97	49.03	120.00	0.1338	0.2118
400	179.95	0.01758	0.0965	74.81	112.77	76.11	43.80	119.91	0.1417	0.2102
450	190.12	0.01863	0.0800	79.63	112.60	81.18	38.08	119.26	0.1493	0.2079
500	199.38	0.02002	0.0657	84.54	111.76	86.39	31.44	117.83	0.1570	0.2047

TABLE A-12E**Properties of Superheated Refrigerant 134a Vapor**

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p = 10 lbf/in.²</i> (<i>T_{sat}</i> = -29.71°F)								
<i>p = 15 lbf/in.²</i> (<i>T_{sat}</i> = -14.25°F)								
Sat.	4.3581	89.30	97.37	0.2265	2.9747	91.40	99.66	0.2242
-20	4.4718	90.89	99.17	0.2307				
0	4.7026	94.24	102.94	0.2391	3.0893	93.84	102.42	0.2303
20	4.9297	97.67	106.79	0.2472	3.2468	97.33	106.34	0.2386
40	5.1539	101.19	110.72	0.2553	3.4012	100.89	110.33	0.2468
60	5.3758	104.80	114.74	0.2632	3.5533	104.54	114.40	0.2548
80	5.5959	108.50	118.85	0.2709	3.7034	108.28	118.56	0.2626
100	5.8145	112.29	123.05	0.2786	3.8520	112.10	122.79	0.2703
120	6.0318	116.18	127.34	0.2861	3.9993	116.01	127.11	0.2779
140	6.2482	120.16	131.72	0.2935	4.1456	120.00	131.51	0.2854
160	6.4638	124.23	136.19	0.3009	4.2911	124.09	136.00	0.2927
180	6.6786	128.38	140.74	0.3081	4.4359	128.26	140.57	0.3000
200	6.8929	132.63	145.39	0.3152	4.5801	132.52	145.23	0.3072
<i>p = 20 lbf/in.²</i> (<i>T_{sat}</i> = -2.48°F)								
<i>p = 30 lbf/in.²</i> (<i>T_{sat}</i> = 15.38°F)								
Sat.	2.2661	93.00	101.39	0.2227	1.5408	95.40	103.96	0.2209
0	2.2816	93.43	101.88	0.2238				
20	2.4046	96.98	105.88	0.2323	1.5611	96.26	104.92	0.2229
40	2.5244	100.59	109.94	0.2406	1.6465	99.98	109.12	0.2315
60	2.6416	104.28	114.06	0.2487	1.7293	103.75	113.35	0.2398
80	2.7569	108.05	118.25	0.2566	1.8098	107.59	117.63	0.2478
100	2.8705	111.90	122.52	0.2644	1.8887	111.49	121.98	0.2558
120	2.9829	115.83	126.87	0.2720	1.9662	115.47	126.39	0.2635
140	3.0942	119.85	131.30	0.2795	2.0426	119.53	130.87	0.2711
160	3.2047	123.95	135.81	0.2869	2.1181	123.66	135.42	0.2786
180	3.3144	128.13	140.40	0.2922	2.1929	127.88	140.05	0.2859
200	3.4236	132.40	145.07	0.3014	2.2671	132.17	144.76	0.2932
220	3.5323	136.76	149.83	0.3085	2.3407	136.55	149.54	0.3003
<i>p = 40 lbf/in.²</i> (<i>T_{sat}</i> = 29.04°F)								
<i>p = 50 lbf/in.²</i> (<i>T_{sat}</i> = 40.27°F)								
Sat.	1.1692	97.23	105.88	0.2197	0.9422	98.71	107.43	0.2189
40	1.2065	99.33	108.26	0.2245				
60	1.2723	103.20	112.62	0.2331	0.9974	102.62	111.85	0.2276
80	1.3357	107.11	117.00	0.2414	1.0508	106.62	116.34	0.2361
100	1.3973	111.08	121.42	0.2494	1.1022	110.65	120.85	0.2443
120	1.4575	115.11	125.90	0.2573	1.1520	114.74	125.39	0.2523
140	1.5165	119.21	130.43	0.2650	1.2007	118.88	129.99	0.2601
160	1.5746	123.38	135.03	0.2725	1.2484	123.08	134.64	0.2677
180	1.6319	127.62	139.70	0.2799	1.2953	127.36	139.34	0.2752
200	1.6887	131.94	144.44	0.2872	1.3415	131.71	144.12	0.2825
220	1.7449	136.34	149.25	0.2944	1.3873	136.12	148.96	0.2897
240	1.8006	140.81	154.14	0.3015	1.4326	140.61	153.87	0.2969
260	1.8561	145.36	159.10	0.3085	1.4775	145.18	158.85	0.3039
280	1.9112	149.98	164.13	0.3154	1.5221	149.82	163.90	0.3108

TABLE A-12E

(Continued)

T °F	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R
<i>p = 60 lbf/in.² (T_{sat} = 49.89°F)</i>								
<i>p = 70 lbf/in.² (T_{sat} = 58.35°F)</i>								
Sat.	0.7887	99.96	108.72	0.2183	0.6778	101.05	109.83	0.2179
60	0.8135	102.03	111.06	0.2229	0.6814	101.40	110.23	0.2186
80	0.8604	106.11	115.66	0.2316	0.7239	105.58	114.96	0.2276
100	0.9051	110.21	120.26	0.2399	0.7640	109.76	119.66	0.2361
120	0.9482	114.35	124.88	0.2480	0.8023	113.96	124.36	0.2444
140	0.9900	118.54	129.53	0.2559	0.8393	118.20	129.07	0.2524
160	1.0308	122.79	134.23	0.2636	0.8752	122.49	133.82	0.2601
180	1.0707	127.10	138.98	0.2712	0.9103	126.83	138.62	0.2678
200	1.1100	131.47	143.79	0.2786	0.9446	131.23	143.46	0.2752
220	1.1488	135.91	148.66	0.2859	0.9784	135.69	148.36	0.2825
240	1.1871	140.42	153.60	0.2930	1.0118	140.22	153.33	0.2897
260	1.2251	145.00	158.60	0.3001	1.0448	144.82	158.35	0.2968
280	1.2627	149.65	163.67	0.3070	1.0774	149.48	163.44	0.3038
300	1.3001	154.38	168.81	0.3139	1.1098	154.22	168.60	0.3107
<i>p = 80 lbf/in.² (T_{sat} = 65.93°F)</i>								
<i>p = 90 lbf/in.² (T_{sat} = 72.83°F)</i>								
Sat.	0.5938	102.02	110.81	0.2175	0.5278	102.89	111.68	0.2172
80	0.6211	105.03	114.23	0.2239	0.5408	104.46	113.47	0.2205
100	0.6579	109.30	119.04	0.2327	0.5751	108.82	118.39	0.2295
120	0.6927	113.56	123.82	0.2411	0.6073	113.15	123.27	0.2380
140	0.7261	117.85	128.60	0.2492	0.6380	117.50	128.12	0.2463
160	0.7584	122.18	133.41	0.2570	0.6675	121.87	132.98	0.2542
180	0.7898	126.55	138.25	0.2647	0.6961	126.28	137.87	0.2620
200	0.8205	130.98	143.13	0.2722	0.7239	130.73	142.79	0.2696
220	0.8506	135.47	148.06	0.2796	0.7512	135.25	147.76	0.2770
240	0.8803	140.02	153.05	0.2868	0.7779	139.82	152.77	0.2843
260	0.9095	144.63	158.10	0.2940	0.8043	144.45	157.84	0.2914
280	0.9384	149.32	163.21	0.3010	0.8303	149.15	162.97	0.2984
300	0.9671	154.06	168.38	0.3079	0.8561	153.91	168.16	0.3054
320	0.9955	158.88	173.62	0.3147	0.8816	158.73	173.42	0.3122
<i>p = 100 lbf/in.² (T_{sat} = 79.17°F)</i>								
<i>p = 120 lbf/in.² (T_{sat} = 90.54°F)</i>								
Sat.	0.4747	103.68	112.46	0.2169	0.3941	105.06	113.82	0.2165
80	0.4761	103.87	112.68	0.2173				
100	0.5086	108.32	117.73	0.2265	0.4080	107.26	116.32	0.2210
120	0.5388	112.73	122.70	0.2352	0.4355	111.84	121.52	0.2301
140	0.5674	117.13	127.63	0.2436	0.4610	116.37	126.61	0.2387
160	0.5947	121.55	132.55	0.2517	0.4852	120.89	131.66	0.2470
180	0.6210	125.99	137.49	0.2595	0.5082	125.42	136.70	0.2550
200	0.6466	130.48	142.45	0.2671	0.5305	129.97	141.75	0.2628
220	0.6716	135.02	147.45	0.2746	0.5520	134.56	146.82	0.2704
240	0.6960	139.61	152.49	0.2819	0.5731	139.20	151.92	0.2778
260	0.7201	144.26	157.59	0.2891	0.5937	143.89	157.07	0.2850
280	0.7438	148.98	162.74	0.2962	0.6140	148.63	162.26	0.2921
300	0.7672	153.75	167.95	0.3031	0.6339	153.43	167.51	0.2991
320	0.7904	158.59	173.21	0.3099	0.6537	158.29	172.81	0.3060

TABLE A-12E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 140 lbf/in. ² (T _{sat} = 100.56°F)								
Sat. 0.3358 106.25 114.95 0.2161 0.2916 107.28 115.91 0.2157								
120 0.3610 110.90 120.25 0.2254 0.3044 109.88 118.89 0.2209								
140 0.3846 115.58 125.54 0.2344 0.3269 114.73 124.41 0.2303								
160 0.4066 120.21 130.74 0.2429 0.3474 119.49 129.78 0.2391								
180 0.4274 124.82 135.89 0.2511 0.3666 124.20 135.06 0.2475								
200 0.4474 129.44 141.03 0.2590 0.3849 128.90 140.29 0.2555								
220 0.4666 134.09 146.18 0.2667 0.4023 133.61 145.52 0.2633								
240 0.4852 138.77 151.34 0.2742 0.4192 138.34 150.75 0.2709								
260 0.5034 143.50 156.54 0.2815 0.4356 143.11 156.00 0.2783								
280 0.5212 148.28 161.78 0.2887 0.4516 147.92 161.29 0.2856								
300 0.5387 153.11 167.06 0.2957 0.4672 152.78 166.61 0.2927								
320 0.5559 157.99 172.39 0.3026 0.4826 157.69 171.98 0.2996								
340 0.5730 162.93 177.78 0.3094 0.4978 162.65 177.39 0.3065								
360 0.5898 167.93 183.21 0.3162 0.5128 167.67 182.85 0.3132								
<i>p</i> = 180 lbf/in. ² (T _{sat} = 117.74°F)								
Sat. 0.2569 108.18 116.74 0.2154 0.2288 108.98 117.44 0.2151								
120 0.2595 108.77 117.41 0.2166 0.2446 112.87 121.92 0.2226								
140 0.2814 113.83 123.21 0.2264 0.2636 117.94 127.70 0.2321								
160 0.3011 118.74 128.77 0.2355 0.2809 122.88 133.28 0.2410								
180 0.3191 123.56 134.19 0.2441 0.2970 127.76 138.75 0.2494								
200 0.3361 128.34 139.53 0.2524 0.3121 132.60 144.15 0.2575								
220 0.3523 133.11 144.84 0.2603 0.3266 137.44 149.53 0.2653								
240 0.3678 137.90 150.15 0.2680 0.3405 142.30 154.90 0.2728								
260 0.3828 142.71 155.46 0.2755 0.3540 147.18 160.28 0.2802								
280 0.3974 147.55 160.79 0.2828 0.3671 152.10 165.69 0.2874								
300 0.4116 152.44 166.15 0.2899 0.3799 157.07 171.13 0.2945								
320 0.4256 157.38 171.55 0.2969 0.3926 162.07 176.60 0.3014								
340 0.4393 162.36 177.00 0.3038 0.4050 167.13 182.12 0.3082								
<i>p</i> = 200 lbf/in. ² (T _{sat} = 125.28°F)								
Sat. 0.2569 108.18 116.74 0.2154 0.2288 108.98 117.44 0.2151								
120 0.2595 108.77 117.41 0.2166 0.2446 112.87 121.92 0.2226								
140 0.2814 113.83 123.21 0.2264 0.2636 117.94 127.70 0.2321								
160 0.3011 118.74 128.77 0.2355 0.2809 122.88 133.28 0.2410								
180 0.3191 123.56 134.19 0.2441 0.2970 127.76 138.75 0.2494								
200 0.3361 128.34 139.53 0.2524 0.3121 132.60 144.15 0.2575								
220 0.3523 133.11 144.84 0.2603 0.3266 137.44 149.53 0.2653								
240 0.3678 137.90 150.15 0.2680 0.3405 142.30 154.90 0.2728								
260 0.3828 142.71 155.46 0.2755 0.3540 147.18 160.28 0.2802								
280 0.3974 147.55 160.79 0.2828 0.3671 152.10 165.69 0.2874								
300 0.4116 152.44 166.15 0.2899 0.3799 157.07 171.13 0.2945								
320 0.4256 157.38 171.55 0.2969 0.3926 162.07 176.60 0.3014								
340 0.4393 162.36 177.00 0.3038 0.4050 167.13 182.12 0.3082								
<i>p</i> = 300 lbf/in. ² (T _{sat} = 156.17°F)								
Sat. 0.1424 111.72 119.62 0.2132 0.0965 112.77 119.91 0.2102								
160 0.1462 112.95 121.07 0.2155 0.0965 112.79 119.93 0.2102								
180 0.1633 118.93 128.00 0.2265 0.0965 112.79 119.93 0.2102								
200 0.1777 124.47 134.34 0.2363 0.1143 120.14 128.60 0.2235								
220 0.1905 129.79 140.36 0.2453 0.1275 126.35 135.79 0.2343								
240 0.2021 134.99 146.21 0.2537 0.1386 132.12 142.38 0.2438								
260 0.2130 140.12 151.95 0.2618 0.1484 137.65 148.64 0.2527								
280 0.2234 145.23 157.63 0.2696 0.1575 143.06 154.72 0.2610								
300 0.2333 150.33 163.28 0.2772 0.1660 148.39 160.67 0.2689								
320 0.2428 155.44 168.92 0.2845 0.1740 153.69 166.57 0.2766								
340 0.2521 160.57 174.56 0.2916 0.1816 158.97 172.42 0.2840								
360 0.2611 165.74 180.23 0.2986 0.1890 164.26 178.26 0.2912								
380 0.2699 170.94 185.92 0.3055 0.1962 169.57 184.09 0.2983								
400 0.2786 176.18 191.64 0.3122 0.2032 174.90 189.94 0.3051								

TABLE A-13E**Properties of Saturated Ammonia (Liquid–Vapor): Temperature Table**

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb			Entropy Btu/lb · °R		Temp. °F
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	Sat. Vapor <i>s_g</i>	
-60	5.548	0.02278	44.7537	-21.005	543.61	-20.97	610.56	589.58	-0.0512	1.4765	-60
-55	6.536	0.02288	38.3991	-15.765	545.11	-15.73	607.31	591.58	-0.0381	1.4627	-55
-50	7.664	0.02299	33.0880	-10.525	546.59	-10.49	604.04	593.54	-0.0253	1.4492	-50
-45	8.949	0.02310	28.6284	-5.295	548.04	-5.25	600.72	595.48	-0.0126	1.4361	-45
-40	10.405	0.02322	24.8672	-0.045	549.46	0.00	597.37	597.37	0.0000	1.4235	-40
-35	12.049	0.02333	21.6812	5.20	550.86	5.26	593.98	599.24	0.0124	1.4111	-35
-30	13.899	0.02345	18.9715	10.46	552.24	10.52	590.54	601.06	0.0247	1.3992	-30
-25	15.972	0.02357	16.6577	15.73	553.59	15.80	587.05	602.85	0.0369	1.3875	-25
-20	18.290	0.02369	14.6744	21.01	554.91	21.09	583.51	604.61	0.0490	1.3762	-20
-15	20.871	0.02381	12.9682	26.31	556.20	26.40	579.92	606.32	0.0610	1.3652	-15
-10	23.738	0.02393	11.4951	31.63	557.46	31.73	576.26	607.99	0.0729	1.3544	-10
-5	26.912	0.02406	10.2190	36.96	558.70	37.08	572.54	609.62	0.0847	1.3440	-5
0	30.416	0.02419	9.1100	42.32	559.91	42.45	568.76	611.22	0.0964	1.3338	0
5	34.275	0.02432	8.1430	47.69	561.08	47.85	564.92	612.76	0.1080	1.3238	5
10	38.512	0.02446	7.2974	53.09	562.23	53.27	561.00	614.27	0.1196	1.3141	10
15	43.153	0.02460	6.5556	58.52	563.34	58.72	557.01	615.73	0.1311	1.3046	15
20	48.224	0.02474	5.9032	63.97	564.43	64.19	552.95	617.14	0.1425	1.2953	20
25	53.752	0.02488	5.3278	69.43	565.48	69.68	548.82	618.51	0.1539	1.2862	25
30	59.765	0.02503	4.8188	74.93	566.49	75.20	544.62	619.82	0.1651	1.2774	30
35	66.291	0.02517	4.3675	80.44	567.48	80.75	540.34	621.09	0.1764	1.2687	35
40	73.359	0.02533	3.9664	85.98	568.42	86.33	535.97	622.30	0.1875	1.2602	40
45	81.000	0.02548	3.6090	91.55	569.33	91.93	531.54	623.46	0.1986	1.2518	45
50	89.242	0.02564	3.2897	97.13	570.21	97.55	527.02	624.57	0.2096	1.2436	50
55	98.118	0.02581	3.0040	102.73	571.04	103.20	522.42	625.62	0.2205	1.2356	55
60	107.66	0.02597	2.7476	108.35	571.83	108.87	517.74	626.61	0.2314	1.2277	60
65	117.90	0.02614	2.5171	113.99	572.59	114.56	512.97	627.54	0.2422	1.2199	65
70	128.87	0.02632	2.3095	119.65	573.29	120.28	508.12	628.40	0.2530	1.2123	70
75	140.60	0.02650	2.1220	125.33	573.95	126.02	503.18	629.20	0.2636	1.2048	75
80	153.13	0.02668	1.9524	131.02	574.57	131.78	498.15	629.93	0.2742	1.1973	80
85	166.50	0.02687	1.7988	136.73	575.13	137.56	493.03	630.59	0.2848	1.1900	85
90	180.73	0.02707	1.6593	142.46	575.65	143.37	487.81	631.18	0.2953	1.1827	90
95	195.87	0.02727	1.5324	148.21	576.10	149.20	482.49	631.68	0.3057	1.1756	95
100	211.96	0.02747	1.4168	153.98	576.51	155.05	477.06	632.11	0.3161	1.1685	100
105	229.02	0.02768	1.3113	159.76	576.85	160.94	471.52	632.46	0.3264	1.1614	105
110	247.10	0.02790	1.2149	165.58	577.13	166.85	465.86	632.71	0.3366	1.1544	110
115	266.24	0.02813	1.1266	171.41	577.34	172.80	460.08	632.88	0.3469	1.1475	115
120	286.47	0.02836	1.0456	177.28	577.48	178.79	454.16	632.95	0.3570	1.1405	120

Source: Tables A-13E through A-15E are calculated based on equations from L. Haar and J. S. Gallagher, "Thermodynamic Properties of Ammonia," *J. Phys. Chem. Reference Data*, Vol. 7, 1978, pp. 635–792.

TABLE A-14E**Properties of Saturated Ammonia (Liquid–Vapor): Pressure Table**

Press. lbf/in. ²	Temp. °F	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb			Entropy Btu/lb · °R		Press. lbf/in. ²
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	Sat. Vapor <i>s_g</i>	
5	-63.10	0.02271	49.320	-24.24	542.67	-24.22	612.56	588.33	-0.0593	1.4853	5
6	-57.63	0.02283	41.594	-18.51	544.32	-18.49	609.02	590.54	-0.0450	1.4699	6
7	-52.86	0.02293	36.014	-13.52	545.74	-13.49	605.92	592.42	-0.0326	1.4569	7
8	-48.63	0.02302	31.790	-9.09	546.98	-9.06	603.13	594.08	-0.0218	1.4456	8
9	-44.81	0.02311	28.477	-5.09	548.09	-5.05	600.60	595.55	-0.0121	1.4357	9
10	-41.33	0.02319	25.807	-1.44	549.09	-1.40	598.27	596.87	-0.0033	1.4268	10
12	-35.14	0.02333	21.764	5.06	550.82	5.11	594.08	599.18	0.0121	1.4115	12
14	-29.74	0.02345	18.843	10.73	552.31	10.79	590.36	601.16	0.0254	1.3986	14
16	-24.94	0.02357	16.631	15.80	553.60	15.87	587.01	602.88	0.0371	1.3874	16
18	-20.60	0.02367	14.896	20.38	554.75	20.46	583.94	604.40	0.0476	1.3775	18
20	-16.63	0.02377	13.497	24.58	555.78	24.67	581.10	605.76	0.0571	1.3687	20
25	-7.95	0.02399	10.950	33.81	557.97	33.92	574.75	608.67	0.0777	1.3501	25
30	-0.57	0.02418	9.229	41.71	559.77	41.84	569.20	611.04	0.0951	1.3349	30
35	5.89	0.02435	7.984	48.65	561.29	48.81	564.22	613.03	0.1101	1.3221	35
40	11.65	0.02450	7.041	54.89	562.60	55.07	559.69	614.76	0.1234	1.3109	40
45	16.87	0.02465	6.302	60.56	563.75	60.76	555.50	616.26	0.1354	1.3011	45
50	21.65	0.02478	5.705	65.77	564.78	66.00	551.59	617.60	0.1463	1.2923	50
55	26.07	0.02491	5.213	70.61	565.70	70.86	547.93	618.79	0.1563	1.2843	55
60	30.19	0.02503	4.801	75.13	566.53	75.41	544.46	619.87	0.1656	1.2770	60
65	34.04	0.02515	4.450	79.39	567.29	79.69	541.16	620.85	0.1742	1.2703	65
70	37.67	0.02526	4.1473	83.40	567.99	83.73	538.01	621.74	0.1823	1.2641	70
75	41.11	0.02536	3.8837	87.21	568.63	87.57	535.00	622.56	0.1900	1.2583	75
80	44.37	0.02546	3.6520	90.84	569.22	91.22	532.10	623.32	0.1972	1.2529	80
85	47.47	0.02556	3.4466	94.30	569.77	94.71	529.31	624.02	0.2040	1.2478	85
90	50.44	0.02566	3.2632	97.62	570.28	98.05	526.62	624.66	0.2106	1.2429	90
100	56.01	0.02584	2.9497	103.87	571.21	104.35	521.48	625.82	0.2227	1.2340	100
110	61.17	0.02601	2.6913	109.68	572.01	110.20	516.63	626.83	0.2340	1.2259	110
120	65.98	0.02618	2.4745	115.11	572.73	115.69	512.02	627.71	0.2443	1.2184	120
130	70.50	0.02634	2.2899	120.21	573.36	120.85	507.64	628.48	0.2540	1.2115	130
140	74.75	0.02649	2.1309	125.04	573.92	125.73	503.43	629.16	0.2631	1.2051	140
150	78.78	0.02664	1.9923	129.63	574.42	130.37	499.39	629.76	0.2717	1.1991	150
175	88.02	0.02699	1.7128	140.19	575.45	141.07	489.89	630.95	0.2911	1.1856	175
200	96.31	0.02732	1.5010	149.72	576.21	150.73	481.07	631.80	0.3084	1.1737	200
225	103.85	0.02764	1.3348	158.43	576.77	159.58	472.80	632.38	0.3240	1.1630	225
250	110.78	0.02794	1.2007	166.48	577.16	167.77	464.97	632.74	0.3382	1.1533	250
275	117.20	0.02823	1.0901	173.99	577.41	175.43	457.49	632.92	0.3513	1.1444	275
300	123.20	0.02851	0.9974	181.05	577.54	182.63	450.31	632.94	0.3635	1.1361	300

TABLE A-15E

Properties of Superheated Ammonia Vapor

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 6 lbf/in. ² (<i>T</i> _{sat} = -57.63°F)								
<i>p</i> = 8 lbf/in. ² (<i>T</i> _{sat} = -48.63°F)								
Sat.	41.594	544.32	590.54	1.4699	31.790	546.98	594.08	1.4456
-50	42.435	547.22	594.37	1.4793				
-40	43.533	551.03	599.40	1.4915	32.511	550.32	598.49	1.4562
-30	44.627	554.84	604.42	1.5033	33.342	554.19	603.58	1.4682
-20	45.715	558.66	609.45	1.5149	34.169	558.06	608.68	1.4799
-10	46.800	562.47	614.47	1.5261	34.992	561.93	613.76	1.4914
0	47.882	566.29	619.49	1.5372	35.811	565.79	618.84	1.5025
10	48.960	570.12	624.51	1.5480	36.627	569.66	623.91	1.5135
20	50.035	573.95	629.54	1.5586	37.440	573.52	628.99	1.5241
30	51.108	577.78	634.57	1.5690	38.250	577.40	634.06	1.5346
40	52.179	581.63	639.60	1.5791	39.058	581.27	639.13	1.5449
50	53.247	585.49	644.64	1.5891	39.865	585.16	644.21	1.5549
60	54.314	589.35	649.70	1.5990	40.669	589.05	649.29	1.5648
<i>p</i> = 10 lbf/in. ² (<i>T</i> _{sat} = -41.33°F)								
<i>p</i> = 12 lbf/in. ² (<i>T</i> _{sat} = -35.14°F)								
Sat.	25.807	549.09	596.87	1.4268	21.764	550.82	599.18	1.4115
-40	25.897	549.61	597.56	1.4284				
-30	26.571	553.54	602.74	1.4406	22.056	552.87	601.88	1.4178
-20	27.241	557.46	607.90	1.4525	22.621	556.85	607.12	1.4298
-10	27.906	561.37	613.05	1.4641	23.182	560.82	612.33	1.4416
0	28.568	565.29	618.19	1.4754	23.739	564.78	617.53	1.4530
10	29.227	569.19	623.31	1.4864	24.293	568.73	622.71	1.4642
20	29.882	573.10	628.43	1.4972	24.843	572.67	627.88	1.4750
30	30.535	577.01	633.55	1.5078	25.392	576.61	633.03	1.4857
40	31.186	580.91	638.66	1.5181	25.937	580.55	638.19	1.4961
50	31.835	584.82	643.77	1.5282	26.481	584.49	643.33	1.5063
60	32.482	588.74	648.89	1.5382	27.023	588.43	648.48	1.5163
70	33.127	592.66	654.01	1.5479	27.564	592.38	653.63	1.5261
<i>p</i> = 14 lbf/in. ² (<i>T</i> _{sat} = -29.74°F)								
<i>p</i> = 16 lbf/in. ² (<i>T</i> _{sat} = -24.94°F)								
Sat.	18.843	552.31	601.16	1.3986	16.631	553.60	602.88	1.3874
-20	19.321	556.24	606.33	1.4105	16.845	555.62	605.53	1.3935
-10	19.807	560.26	611.61	1.4223	17.275	559.69	610.88	1.4055
0	20.289	564.27	616.86	1.4339	17.701	563.75	616.19	1.4172
10	20.768	568.26	622.10	1.4452	18.124	567.79	621.48	1.4286
20	21.244	572.24	627.31	1.4562	18.544	571.81	626.75	1.4397
30	21.717	576.22	632.52	1.4669	18.961	575.82	632.00	1.4505
40	22.188	580.19	637.71	1.4774	19.376	579.82	637.23	1.4611
50	22.657	584.16	642.89	1.4877	19.789	583.82	642.45	1.4714
60	23.124	588.12	648.07	1.4977	20.200	587.81	647.66	1.4815
70	23.590	592.09	653.25	1.5076	20.609	591.80	652.86	1.4915
80	24.054	596.07	658.42	1.5173	21.017	595.80	658.07	1.5012
90	24.517	600.04	663.60	1.5268	21.424	599.80	663.27	1.5107

TABLE A-15E

(Continued)

T °F	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R
<i>p = 18 lbf/in.² (T_{sat} = -20.60°F)</i>								
<i>p = 20 lbf/in.² (T_{sat} = -16.63°F)</i>								
Sat.	14.896	554.75	604.40	1.3775	13.497	555.78	605.76	1.3687
-20	14.919	555.00	604.72	1.3783				
-10	15.306	559.13	610.14	1.3905	13.730	558.55	609.40	1.3769
0	15.688	563.23	615.52	1.4023	14.078	562.70	614.84	1.3888
10	16.068	567.31	620.87	1.4138	14.422	566.83	620.24	1.4005
20	16.444	571.37	626.18	1.4250	14.764	570.94	625.61	1.4118
30	16.818	575.42	631.47	1.4359	15.103	575.02	630.95	1.4228
40	17.189	579.46	636.75	1.4466	15.439	579.09	636.26	1.4335
50	17.558	583.48	642.00	1.4570	15.773	583.14	641.55	1.4440
60	17.925	587.50	647.25	1.4672	16.105	587.19	646.83	1.4543
70	18.291	591.52	652.48	1.4772	16.436	591.23	652.10	1.4643
80	18.655	595.53	657.71	1.4869	16.765	595.26	657.35	1.4741
90	19.018	599.55	662.94	1.4965	17.094	599.30	662.60	1.4838
<i>p = 30 lbf/in.² (T_{sat} = -0.57°F)</i>								
<i>p = 40 lbf/in.² (T_{sat} = 11.65°F)</i>								
Sat.	9.2286	559.77	611.04	1.3349	7.0414	562.60	614.76	1.3109
0	9.2425	560.02	611.36	1.3356				
10	9.4834	564.38	617.07	1.3479				
20	9.7209	568.70	622.70	1.3598	7.1965	566.39	619.69	1.3213
30	9.9554	572.97	628.28	1.3713	7.3795	570.86	625.52	1.3333
40	10.187	577.21	633.80	1.3824	7.5597	575.28	631.28	1.3450
50	10.417	581.42	639.28	1.3933	7.7376	579.65	636.96	1.3562
60	10.645	585.60	644.73	1.4039	7.9134	583.97	642.58	1.3672
70	10.871	589.76	650.15	1.4142	8.0874	588.26	648.16	1.3778
80	11.096	593.90	655.54	1.4243	8.2598	592.52	653.69	1.3881
90	11.319	598.04	660.91	1.4342	8.4308	596.75	659.20	1.3982
100	11.541	602.16	666.27	1.4438	8.6006	600.97	664.67	1.4081
110	11.762	606.28	671.62	1.4533	8.7694	605.17	670.12	1.4178
<i>p = 50 lbf/in.² (T_{sat} = 21.65°F)</i>								
<i>p = 60 lbf/in.² (T_{sat} = 30.19°F)</i>								
Sat.	5.7049	564.78	617.60	1.2923	4.8009	566.53	619.87	1.2770
40	5.9815	573.30	628.68	1.3149	4.9278	571.25	626.00	1.2894
60	6.2733	582.31	640.39	1.3379	5.1788	580.60	638.14	1.3133
80	6.5574	591.10	651.82	1.3595	5.4218	589.66	649.90	1.3355
100	6.8358	599.75	663.04	1.3799	5.6587	598.52	661.39	1.3564
120	7.1097	608.30	674.13	1.3993	5.8910	607.23	672.68	1.3762
140	7.3802	616.80	685.13	1.4180	6.1198	615.86	683.85	1.3951
160	7.6480	625.28	696.09	1.4360	6.3458	624.44	694.95	1.4133
200	8.1776	642.27	717.99	1.4702	6.7916	641.59	717.05	1.4479
240	8.7016	659.44	740.00	1.5026	7.2318	658.87	739.21	1.4805
280	9.2218	676.88	762.26	1.5336	7.6679	676.38	761.58	1.5116
320	9.7391	694.65	784.82	1.5633	8.1013	694.21	784.22	1.5414
360	10.254	712.79	807.73	1.5919	8.5325	712.40	807.20	1.5702

TABLE A-15E

(Continued)

T °F	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R	v ft ³ /lb	u Btu/lb	h Btu/lb	s Btu/lb · °R
<i>p = 70 lbf/in.² (T_{sat} = 37.67°F)</i>								
<i>p = 80 lbf/in.² (T_{sat} = 44.37°F)</i>								
Sat.	4.1473	567.99	621.74	1.2641	3.6520	569.22	623.32	1.2529
40	4.1739	569.15	623.25	1.2671				
60	4.3962	578.85	635.84	1.2918	3.8084	577.06	633.48	1.2727
80	4.6100	588.19	647.95	1.3147	4.0006	586.69	645.95	1.2963
100	4.8175	597.26	659.70	1.3361	4.1862	595.98	657.99	1.3182
120	5.0202	606.14	671.22	1.3563	4.3668	605.04	669.73	1.3388
140	5.2193	614.91	682.56	1.3756	4.5436	613.94	681.25	1.3583
160	5.4154	623.60	693.79	1.3940	4.7175	622.74	692.63	1.3770
200	5.8015	640.91	716.11	1.4289	5.0589	640.22	715.16	1.4122
240	6.1818	658.29	738.42	1.4617	5.3942	657.71	737.62	1.4453
280	6.5580	675.89	760.89	1.4929	5.7256	675.39	760.20	1.4767
320	6.9314	693.78	783.62	1.5229	6.0540	693.34	783.02	1.5067
360	7.3026	712.02	806.67	1.5517	6.3802	711.63	806.15	1.5357
400	7.6721	730.63	830.08	1.5796	6.7047	730.29	829.61	1.5636
<i>p = 90 lbf/in.² (T_{sat} = 50.44°F)</i>								
<i>p = 100 lbf/in.² (T_{sat} = 56.01°F)</i>								
Sat.	3.2632	570.28	624.66	1.2429	2.9497	571.21	625.82	1.2340
60	3.3504	575.22	631.05	1.2553	2.9832	573.32	628.56	1.2393
80	3.5261	585.15	643.91	1.2796	3.1460	583.58	641.83	1.2644
100	3.6948	594.68	656.26	1.3021	3.3014	593.35	654.49	1.2874
120	3.8584	603.92	668.22	1.3231	3.4513	602.79	666.70	1.3088
140	4.0180	612.97	679.93	1.3430	3.5972	611.98	678.59	1.3290
160	4.1746	621.88	691.45	1.3619	3.7401	621.01	690.27	1.3481
200	4.4812	639.52	714.20	1.3974	4.0189	638.82	713.24	1.3841
240	4.7817	657.13	736.82	1.4307	4.2916	656.54	736.01	1.4176
280	5.0781	674.89	759.52	1.4623	4.5600	674.39	758.82	1.4493
320	5.3715	692.90	782.42	1.4924	4.8255	692.47	781.82	1.4796
360	5.6628	711.24	805.62	1.5214	5.0888	710.86	805.09	1.5087
400	5.9522	729.95	829.14	1.5495	5.3503	729.60	828.68	1.5368
<i>p = 110 lbf/in.² (T_{sat} = 61.17°F)</i>								
<i>p = 120 lbf/in.² (T_{sat} = 65.98°F)</i>								
Sat.	2.6913	572.01	626.83	1.2259	2.4745	572.73	627.71	1.2184
80	2.8344	581.97	639.71	1.2502	2.5744	580.33	637.53	1.2369
100	2.9791	592.00	652.69	1.2738	2.7102	590.63	650.85	1.2611
120	3.1181	601.63	665.14	1.2957	2.8401	600.46	663.57	1.2834
140	3.2528	610.98	677.24	1.3162	2.9657	609.97	675.86	1.3043
160	3.3844	620.13	689.07	1.3356	3.0879	619.24	687.86	1.3240
200	3.6406	638.11	712.27	1.3719	3.3254	637.40	711.29	1.3606
240	3.8905	655.96	735.20	1.4056	3.5563	655.36	734.39	1.3946
280	4.1362	673.88	758.13	1.4375	3.7829	673.37	757.43	1.4266
320	4.3788	692.02	781.22	1.4679	4.0065	691.58	780.61	1.4572
360	4.6192	710.47	804.56	1.4971	4.2278	710.08	804.02	1.4864
400	4.8578	729.26	828.21	1.5252	4.4473	728.92	827.74	1.5147

TABLE A-15E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p = 130 lbf/in.²</i> <i>(T_{sat} = 70.50°F)</i>								
<i>p = 140 lbf/in.²</i> <i>(T_{sat} = 74.75°F)</i>								
Sat.	2.2899	573.36	628.48	1.2115	2.1309	573.92	629.16	1.2051
80	2.3539	578.64	635.30	1.2243	2.1633	576.80	632.89	1.2119
100	2.4824	589.23	648.98	1.2492	2.2868	587.79	647.08	1.2379
120	2.6048	599.27	661.97	1.2720	2.4004	597.85	660.08	1.2604
140	2.7226	608.94	674.48	1.2932	2.5140	607.90	673.07	1.2828
160	2.8370	618.34	686.64	1.3132	2.6204	617.34	685.27	1.3025
180	2.9488	627.57	698.55	1.3321	2.7268	626.77	697.46	1.3222
200	3.0585	636.69	710.31	1.3502	2.8289	635.93	709.27	1.3401
240	3.2734	654.77	733.57	1.3844	3.0304	654.17	732.73	1.3747
280	3.4840	672.87	756.73	1.4166	3.2274	672.38	756.04	1.4071
320	3.6915	691.14	780.00	1.4472	3.4212	690.73	779.42	1.4379
360	3.8966	709.69	803.49	1.4766	3.6126	709.34	802.99	1.4674
400	4.1000	728.57	827.27	1.5049	3.8022	728.27	826.84	1.4958
<i>p = 150 lbf/in.²</i> <i>(T_{sat} = 78.78°F)</i>								
<i>p = 200 lbf/in.²</i> <i>(T_{sat} = 96.31°F)</i>								
Sat.	1.9923	574.42	629.76	1.1991	1.5010	576.21	631.80	1.1737
100	2.1170	586.33	645.13	1.2271	1.5190	578.52	634.77	1.1790
140	2.3332	606.84	671.65	1.2729	1.6984	601.34	664.24	1.2299
180	2.5343	625.95	696.35	1.3128	1.8599	621.77	690.65	1.2726
220	2.7268	644.43	720.17	1.3489	2.0114	641.07	715.57	1.3104
260	2.9137	662.70	743.63	1.3825	2.1569	659.90	739.78	1.3450
300	3.0968	681.02	767.04	1.4141	2.2984	678.62	763.74	1.3774
340	3.2773	699.54	790.57	1.4443	2.4371	697.44	787.70	1.4081
380	3.4558	718.35	814.34	1.4733	2.5736	716.50	811.81	1.4375
420	3.6325	737.50	838.39	1.5013	2.7085	735.86	836.17	1.4659
460	3.8079	757.01	862.78	1.5284	2.8420	755.57	860.82	1.4933
500	3.9821	776.91	887.51	1.5548	2.9742	775.65	885.80	1.5199
540	4.1553	797.19	912.60	1.5804	3.1054	796.10	911.11	1.5457
580	4.3275	817.85	938.05	1.6053	3.2357	816.94	936.77	1.5709
<i>p = 250 lbf/in.²</i> <i>(T_{sat} = 110.78°F)</i>								
<i>p = 300 lbf/in.²</i> <i>(T_{sat} = 123.20°F)</i>								
Sat.	1.2007	577.16	632.74	1.1533	0.9974	577.54	632.94	1.1361
140	1.3150	595.40	656.28	1.1936	1.0568	588.94	647.65	1.1610
180	1.4539	617.38	684.69	1.2395	1.1822	612.75	678.42	1.2107
220	1.5816	637.61	710.82	1.2791	1.2944	634.01	705.91	1.2524
260	1.7025	657.03	735.85	1.3149	1.3992	654.09	731.82	1.2895
300	1.8191	676.17	760.39	1.3481	1.4994	673.69	756.98	1.3235
340	1.9328	695.32	784.79	1.3794	1.5965	693.16	781.85	1.3554
380	2.0443	714.63	809.27	1.4093	1.6913	712.74	806.70	1.3857
420	2.1540	734.22	833.93	1.4380	1.7843	732.55	831.67	1.4148
460	2.2624	754.12	858.85	1.4657	1.8759	752.66	856.87	1.4428
500	2.3695	774.38	884.07	1.4925	1.9663	773.10	882.33	1.4699
540	2.4755	795.01	909.61	1.5186	2.0556	793.90	908.09	1.4962
580	2.5807	816.01	935.47	1.5440	2.1440	815.07	934.17	1.5218

TABLE A-16E**Properties of Saturated Propane (Liquid–Vapor): Temperature Table**

Temp. °F	Press. lbf/in. ²	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R		Temp. °F
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
-140	0.6053	0.02505	128.00	-51.33	139.22	-51.33	204.9	153.6	-0.139	0.501
-120	1.394	0.02551	58.88	-41.44	143.95	-41.43	200.6	159.1	-0.109	0.481
-100	2.888	0.02601	29.93	-31.34	148.80	-31.33	196.1	164.8	-0.080	0.465
-80	5.485	0.02653	16.52	-21.16	153.73	-21.13	191.6	170.5	-0.053	0.452
-60	9.688	0.02708	9.75	-10.73	158.74	-10.68	186.9	176.2	-0.026	0.441
-40	16.1	0.02767	6.08	-0.08	163.80	0.00	181.9	181.9	0.000	0.433
-20	25.4	0.02831	3.98	10.81	168.88	10.94	176.6	187.6	0.025	0.427
0	38.4	0.02901	2.70	21.98	174.01	22.19	171.0	193.2	0.050	0.422
10	46.5	0.02939	2.25	27.69	176.61	27.94	168.0	196.0	0.063	0.420
20	55.8	0.02978	1.89	33.47	179.15	33.78	164.9	198.7	0.074	0.418
30	66.5	0.03020	1.598	39.34	181.71	39.71	161.7	201.4	0.087	0.417
40	78.6	0.03063	1.359	45.30	184.30	45.75	158.3	204.1	0.099	0.415
50	92.3	0.03110	1.161	51.36	186.74	51.89	154.7	206.6	0.111	0.414
60	107.7	0.03160	0.9969	57.53	189.30	58.16	151.0	209.2	0.123	0.413
70	124.9	0.03213	0.8593	63.81	191.71	64.55	147.0	211.6	0.135	0.412
80	144.0	0.03270	0.7433	70.20	194.16	71.07	142.9	214.0	0.147	0.411
90	165.2	0.03332	0.6447	76.72	196.46	77.74	138.4	216.2	0.159	0.410
100	188.6	0.03399	0.5605	83.38	198.71	84.56	133.7	218.3	0.171	0.410
110	214.3	0.03473	0.4881	90.19	200.91	91.56	128.7	220.3	0.183	0.409
120	242.5	0.03555	0.4254	97.16	202.98	98.76	123.3	222.1	0.195	0.408
130	273.3	0.03646	0.3707	104.33	204.92	106.17	117.5	223.7	0.207	0.406
140	306.9	0.03749	0.3228	111.70	206.64	113.83	111.1	225.0	0.220	0.405
150	343.5	0.03867	0.2804	119.33	208.05	121.79	104.1	225.9	0.233	0.403
160	383.3	0.04006	0.2426	127.27	209.16	130.11	96.3	226.4	0.246	0.401
170	426.5	0.04176	0.2085	135.60	209.81	138.90	87.4	226.3	0.259	0.398
180	473.4	0.04392	0.1771	144.50	209.76	148.35	76.9	225.3	0.273	0.394
190	524.3	0.04696	0.1470	154.38	208.51	158.94	63.8	222.8	0.289	0.387
200	579.7	0.05246	0.1148	166.65	204.16	172.28	44.2	216.5	0.309	0.376
206.1	616.1	0.07265	0.07265	186.99	186.99	195.27	0.0	195.27	0.343	0.343
										206.1

TABLE A-17E**Properties of Saturated Propane (Liquid–Vapor): Pressure Table**

Press. lbf/in. ²	Temp. °F	Specific Volume ft ³ /lb		Internal Energy Btu/lb		Enthalpy Btu/lb		Entropy Btu/lb · °R		Press. lbf/in. ²
		Sat. Liquid <i>v_f</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>u_f</i>	Sat. Vapor <i>u_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>	Sat. Liquid <i>s_f</i>	
0.75	-135.1	0.02516	104.8	-48.93	140.36	-48.93	203.8	154.9	-0.132	0.496
1.5	-118.1	0.02556	54.99	-40.44	144.40	-40.43	200.1	159.7	-0.106	0.479
3	-98.9	0.02603	28.9	-30.84	149.06	-30.83	196.0	165.1	-0.079	0.464
5	-83.0	0.02644	18.00	-22.75	152.96	-22.73	192.4	169.6	-0.057	0.454
7.5	-69.3	0.02682	12.36	-15.60	156.40	-15.56	189.1	173.6	-0.038	0.446
10	-58.8	0.02711	9.468	-10.10	159.04	-10.05	186.6	176.6	-0.024	0.441
20	-30.7	0.02796	4.971	4.93	166.18	5.03	179.5	184.6	0.012	0.430
30	-12.1	0.02858	3.402	15.15	170.93	15.31	174.5	189.8	0.035	0.425
40	2.1	0.02909	2.594	23.19	174.60	23.41	170.4	193.8	0.053	0.422
50	13.9	0.02954	2.099	29.96	177.63	30.23	166.8	197.1	0.067	0.419
60	24.1	0.02995	1.764	35.86	180.23	36.19	163.6	199.8	0.079	0.418
70	33.0	0.03033	1.520	41.14	182.50	41.53	160.6	202.2	0.090	0.416
80	41.1	0.03068	1.336	45.95	184.57	46.40	157.9	204.3	0.100	0.415
90	48.4	0.03102	1.190	50.38	186.36	50.90	155.3	206.2	0.109	0.414
100	55.1	0.03135	1.073	54.52	188.07	55.10	152.8	207.9	0.117	0.414
120	67.2	0.03198	0.8945	62.08	191.07	62.79	148.1	210.9	0.131	0.412
140	78.0	0.03258	0.7650	68.91	193.68	69.75	143.7	213.5	0.144	0.412
160	87.6	0.03317	0.6665	75.17	195.97	76.15	139.5	215.7	0.156	0.411
180	96.5	0.03375	0.5890	80.99	197.97	82.12	135.5	217.6	0.166	0.410
200	104.6	0.03432	0.5261	86.46	199.77	87.73	131.4	219.2	0.176	0.409
220	112.1	0.03489	0.4741	91.64	201.37	93.06	127.6	220.7	0.185	0.408
240	119.2	0.03547	0.4303	96.56	202.76	98.14	123.7	221.9	0.194	0.408
260	125.8	0.03606	0.3928	101.29	204.07	103.0	120.0	223.0	0.202	0.407
280	132.1	0.03666	0.3604	105.83	205.27	107.7	116.1	223.9	0.210	0.406
300	138.0	0.03727	0.3319	110.21	206.27	112.3	112.4	224.7	0.217	0.405
320	143.7	0.03790	0.3067	114.47	207.17	116.7	108.6	225.3	0.224	0.404
340	149.1	0.03855	0.2842	118.60	207.96	121.0	104.7	225.8	0.231	0.403
360	154.2	0.03923	0.2639	122.66	208.58	125.3	100.9	226.2	0.238	0.402
380	159.2	0.03994	0.2455	126.61	209.07	129.4	97.0	226.4	0.245	0.401
400	164.0	0.04069	0.2287	130.51	209.47	133.5	93.0	226.5	0.251	0.400
450	175.1	0.04278	0.1921	140.07	209.87	143.6	82.2	225.9	0.266	0.396
500	185.3	0.04538	0.1610	149.61	209.27	153.8	70.4	224.2	0.282	0.391
600	203.4	0.05659	0.1003	172.85	200.27	179.1	32.2	211.4	0.319	0.367
616.1	206.1	0.07265	0.07265	186.99	186.99	195.3	0.0	195.3	0.343	0.343
										616.1

TABLE A-18E**Properties of Superheated Propane Vapor**

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 0.75 lbf/in. ² (<i>T</i> _{sat} = -135.1°F)								
<i>p</i> = 1.5 lbf/in. ² (<i>T</i> _{sat} = -118.1°F)								
Sat.	104.8	140.4	154.9	0.496	54.99	144.4	159.7	0.479
-130	106.5	141.6	156.4	0.501				
-110	113.1	146.6	162.3	0.518	56.33	146.5	162.1	0.486
-90	119.6	151.8	168.4	0.535	59.63	151.7	168.2	0.503
-70	126.1	157.2	174.7	0.551	62.92	157.1	174.5	0.520
-50	132.7	162.7	181.2	0.568	66.20	162.6	181.0	0.536
-30	139.2	168.6	187.9	0.584	69.47	168.4	187.7	0.552
-10	145.7	174.4	194.7	0.599	72.74	174.4	194.6	0.568
10	152.2	180.7	201.9	0.615	76.01	180.7	201.8	0.583
30	158.7	187.1	209.2	0.630	79.27	187.1	209.1	0.599
50	165.2	193.8	216.8	0.645	82.53	193.8	216.7	0.614
70	171.7	200.7	224.6	0.660	85.79	200.7	224.5	0.629
90	178.2	207.8	232.6	0.675	89.04	207.8	232.5	0.644
<i>p</i> = 5.0 lbf/in. ² (<i>T</i> _{sat} = -83.0°F)								
Sat.	18.00	153.0	169.6	0.454	9.468	159.0	176.6	0.441
-80	18.15	153.8	170.6	0.456				
-60	19.17	159.4	177.1	0.473				
-40	20.17	165.1	183.8	0.489	9.957	164.5	183.0	0.456
-20	21.17	171.1	190.7	0.505	10.47	170.5	190.0	0.473
0	22.17	177.2	197.7	0.521	10.98	176.7	197.1	0.489
20	23.16	183.5	205.0	0.536	11.49	183.1	204.5	0.504
40	24.15	190.1	212.5	0.552	11.99	189.7	212.0	0.520
60	25.14	196.9	220.2	0.567	12.49	196.6	219.8	0.535
80	26.13	204.0	228.2	0.582	12.99	203.6	227.8	0.550
100	27.11	211.3	236.4	0.597	13.49	210.9	236.0	0.565
120	28.09	218.8	244.8	0.611	13.99	218.5	244.4	0.580
140	29.07	226.5	253.4	0.626	14.48	226.2	253.1	0.594
<i>p</i> = 20.0 lbf/in. ² (<i>T</i> _{sat} = -30.7°F)								
Sat.	4.971	166.2	184.6	0.430	2.594	174.6	193.8	0.422
-20	5.117	169.5	188.5	0.439				
0	5.385	175.8	195.8	0.455				
20	5.648	182.4	203.3	0.471	2.723	180.6	200.8	0.436
40	5.909	189.1	211.0	0.487	2.864	187.6	208.8	0.453
60	6.167	195.9	218.8	0.502	3.002	194.6	216.9	0.469
80	6.424	203.1	226.9	0.518	3.137	201.8	225.1	0.484
100	6.678	210.5	235.2	0.533	3.271	209.4	233.6	0.500
120	6.932	218.0	243.7	0.548	3.403	217.0	242.2	0.515
140	7.184	225.8	252.4	0.562	3.534	224.9	251.1	0.530
160	7.435	233.9	261.4	0.577	3.664	232.9	260.1	0.545
180	7.685	242.1	270.6	0.592	3.793	241.3	269.4	0.559
200	7.935	250.6	280.0	0.606	3.921	249.8	278.9	0.574

TABLE A-18E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 60.0 lbf/in. ² (<i>T</i> _{sat} = 24.1°F)								
Sat. 1.764 180.2 199.8 0.418 1.336 184.6 204.3 0.415								
30 1.794 182.4 202.3 0.384					1.372	187.9	208.2	0.423
50 1.894 189.5 210.6 0.400								
70 1.992 196.9 219.0 0.417 1.450 195.4 216.9 0.440								
90 2.087 204.4 227.6 0.432 1.526 203.1 225.7 0.456								
110 2.179 212.1 236.3 0.448 1.599 210.9 234.6 0.472								
130 2.271 220.0 245.2 0.463 1.671 218.8 243.6 0.487								
150 2.361 228.0 254.2 0.478 1.741 227.0 252.8 0.503								
170 2.450 236.3 263.5 0.493 1.810 235.4 262.2 0.518								
190 2.539 244.8 273.0 0.508 1.879 244.0 271.8 0.533								
210 2.626 253.5 282.7 0.523 1.946 252.7 281.5 0.548								
230 2.713 262.3 292.5 0.537 2.013 261.7 291.5 0.562								
250 2.800 271.6 302.7 0.552 2.079 270.9 301.7 0.577								
<i>p</i> = 100 lbf/in. ² (<i>T</i> _{sat} = 55.1°F)								
Sat. 1.073 188.1 207.9 0.414 0.8945 191.1 210.9 0.412								
60 1.090 189.9 210.1 0.418								
80 1.156 197.8 219.2 0.435 0.9323 196.2 216.9 0.424								
100 1.219 205.7 228.3 0.452 0.9887 204.3 226.3 0.441								
120 1.280 213.7 237.4 0.468 1.043 212.5 235.7 0.457								
140 1.340 221.9 246.7 0.483 1.094 220.8 245.1 0.473								
160 1.398 230.2 256.1 0.499 1.145 229.2 254.7 0.489								
180 1.454 238.8 265.7 0.514 1.194 237.9 264.4 0.504								
200 1.510 247.5 275.5 0.529 1.242 246.7 274.3 0.520								
220 1.566 256.4 285.4 0.544 1.289 255.6 284.3 0.534								
240 1.620 265.6 295.6 0.559 1.336 264.8 294.5 0.549								
260 1.674 274.9 305.9 0.573 1.382 274.2 304.9 0.564								
280 1.728 284.4 316.4 0.588 1.427 283.8 315.5 0.579								
<i>p</i> = 140 lbf/in. ² (<i>T</i> _{sat} = 78.0°F)								
Sat. 0.7650 193.7 213.5 0.412 0.6665 196.0 215.7 0.411								
80 0.7705 213.3 214.5 0.413								
100 0.8227 222.9 224.2 0.431 0.6968 201.2 221.9 0.422								
120 0.8718 232.4 233.8 0.448 0.7427 209.9 231.9 0.439								
140 0.9185 242.1 243.5 0.464 0.7859 218.4 241.7 0.456								
160 0.9635 251.7 253.2 0.480 0.8272 227.2 251.7 0.472								
180 1.007 261.4 263.0 0.496 0.8669 235.9 261.6 0.488								
200 1.050 271.4 273.0 0.511 0.9054 244.9 271.7 0.504								
220 1.091 281.5 283.2 0.526 0.9430 254.0 282.0 0.519								
240 1.132 291.7 293.5 0.541 0.9797 263.4 292.4 0.534								
260 1.173 302.1 303.9 0.556 1.016 272.8 302.9 0.549								
280 1.213 312.7 314.6 0.571 1.051 282.6 313.7 0.564								
300 1.252 323.6 325.5 0.585 1.087 292.4 324.6 0.578								

TABLE A-18E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 180 lbf/in. ² (<i>T</i> _{sat} = 96.5°F)								
<i>p</i> = 200 lbf/in. ² (<i>T</i> _{sat} = 104.6°F)								
Sat.	0.5890	198.0	217.6	0.410	0.5261	199.8	219.2	0.409
100	0.5972	199.6	219.5	0.413				
120	0.6413	208.4	229.8	0.431	0.5591	206.8	227.5	0.424
140	0.6821	217.1	239.9	0.449	0.5983	215.8	238.0	0.441
160	0.7206	226.1	250.1	0.465	0.6349	224.9	248.4	0.458
180	0.7574	234.9	260.2	0.481	0.6694	233.9	258.7	0.475
200	0.7928	244.0	270.4	0.497	0.7025	243.1	269.1	0.491
220	0.8273	253.2	280.8	0.513	0.7345	252.4	279.6	0.506
240	0.8609	262.6	291.3	0.528	0.7656	261.7	290.1	0.522
260	0.8938	272.1	301.9	0.543	0.7960	271.4	300.9	0.537
280	0.9261	281.8	312.7	0.558	0.8257	281.1	311.7	0.552
300	0.9579	291.8	323.7	0.572	0.8549	291.1	322.8	0.567
320	0.9894	301.9	334.9	0.587	0.8837	301.3	334.0	0.581
<i>p</i> = 220 lbf/in. ² (<i>T</i> _{sat} = 112.1°F)								
Sat.	0.4741	201.4	220.7	0.408	0.4303	202.8	221.9	0.408
120	0.4906	205.1	225.1	0.416	0.4321	203.2	222.4	0.409
140	0.5290	214.4	236.0	0.435	0.4704	212.9	233.8	0.428
160	0.5642	223.6	246.6	0.452	0.5048	222.4	244.8	0.446
180	0.5971	232.9	257.2	0.469	0.5365	231.6	255.5	0.463
200	0.6284	242.1	267.7	0.485	0.5664	241.1	266.3	0.480
220	0.6585	251.5	278.3	0.501	0.5949	250.5	277.0	0.496
240	0.6875	261.0	289.0	0.516	0.6223	260.1	287.8	0.511
260	0.7158	270.6	299.8	0.532	0.6490	269.8	298.7	0.527
280	0.7435	280.5	310.8	0.547	0.6749	279.8	309.8	0.542
300	0.7706	290.5	321.9	0.561	0.7002	289.8	320.9	0.557
320	0.7972	300.6	333.1	0.576	0.7251	300.1	332.3	0.571
340	0.8235	311.0	344.6	0.591	0.7496	310.5	343.8	0.586
<i>p</i> = 240 lbf/in. ² (<i>T</i> _{sat} = 119.2°F)								
Sat.	0.3928	204.1	223.0	0.407	0.3604	205.3	223.9	0.406
130	0.4012	206.3	225.6	0.411				
150	0.4374	216.1	237.2	0.431	0.3932	214.5	234.9	0.424
170	0.4697	225.8	248.4	0.449	0.4253	224.4	246.5	0.443
190	0.4995	235.2	259.3	0.466	0.4544	234.1	257.7	0.461
210	0.5275	244.8	270.2	0.482	0.4815	243.8	268.8	0.477
230	0.5541	254.4	281.1	0.498	0.5072	253.5	279.8	0.494
250	0.5798	264.2	292.1	0.514	0.5317	263.3	290.9	0.510
270	0.6046	274.1	303.2	0.530	0.5553	273.3	302.1	0.525
290	0.6288	284.0	314.3	0.545	0.5783	283.4	313.4	0.540
310	0.6524	294.3	325.7	0.560	0.6007	293.5	324.7	0.555
330	0.6756	304.7	337.2	0.574	0.6226	304.0	336.3	0.570
350	0.6984	315.2	348.8	0.589	0.6441	314.6	348.0	0.585

TABLE A-18E

(Continued)

<i>T</i> °F	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R	<i>v</i> ft ³ /lb	<i>u</i> Btu/lb	<i>h</i> Btu/lb	<i>s</i> Btu/lb · °R
<i>p</i> = 320 lbf/in. ² (T _{sat} = 143.7°F)								
<i>p</i> = 360 lbf/in. ² (T _{sat} = 154.2°F)								
Sat.	0.3067	207.2	225.3	0.404	0.2639	208.6	226.2	0.402
150	0.3187	210.7	229.6	0.412				
170	0.3517	221.4	242.3	0.432	0.2920	217.9	237.4	0.420
190	0.3803	231.7	254.2	0.450	0.3213	228.8	250.2	0.440
210	0.4063	241.6	265.7	0.468	0.3469	239.3	262.4	0.459
230	0.4304	251.6	277.1	0.485	0.3702	249.5	274.2	0.476
250	0.4533	261.6	288.5	0.501	0.3919	259.8	285.9	0.493
270	0.4751	271.7	299.9	0.517	0.4124	270.1	297.6	0.509
290	0.4961	281.9	311.3	0.532	0.4320	280.4	309.2	0.525
310	0.5165	292.3	322.9	0.548	0.4510	290.8	320.9	0.540
330	0.5364	302.7	334.5	0.563	0.4693	301.4	332.7	0.556
350	0.5559	313.4	346.3	0.577	0.4872	312.2	344.7	0.570
370	0.5750	324.2	358.3	0.592	0.5047	323.0	356.7	0.585
<i>p</i> = 400 lbf/in. ² (T _{sat} = 164.0°F)								
<i>p</i> = 450 lbf/in. ² (T _{sat} = 175.1°F)								
Sat.	0.2287	209.5	226.5	0.400	0.1921	209.9	225.9	0.396
170	0.2406	213.6	231.4	0.408				
190	0.2725	225.6	245.8	0.430	0.2205	220.7	239.1	0.416
210	0.2985	236.7	258.8	0.450	0.2486	233.0	253.7	0.439
230	0.3215	247.4	271.2	0.468	0.2719	244.3	267.0	0.458
250	0.3424	257.8	283.2	0.485	0.2925	255.2	279.6	0.476
270	0.3620	268.3	295.1	0.502	0.3113	266.0	292.0	0.493
290	0.3806	278.8	307.0	0.518	0.3290	276.8	304.2	0.510
310	0.3984	289.4	318.9	0.534	0.3457	287.6	316.4	0.526
330	0.4156	300.1	330.9	0.549	0.3617	298.4	328.5	0.542
350	0.4322	311.0	343.0	0.564	0.3772	309.4	340.8	0.557
370	0.4484	321.9	355.1	0.579	0.3922	320.4	353.1	0.572
390	0.4643	333.1	367.5	0.594	0.4068	331.7	365.6	0.587
<i>p</i> = 500 lbf/in. ² (T _{sat} = 185.3°F)								
<i>p</i> = 600 lbf/in. ² (T _{sat} = 203.4°F)								
Sat.	0.1610	209.3	224.2	0.391	0.1003	200.3	211.4	0.367
190	0.1727	213.8	229.8	0.399				
210	0.2066	228.6	247.7	0.426	0.1307	214.3	228.8	0.394
230	0.2312	240.9	262.3	0.448	0.1661	232.2	250.7	0.426
250	0.2519	252.4	275.7	0.467	0.1892	245.8	266.8	0.449
270	0.2704	263.6	288.6	0.485	0.2080	258.1	281.2	0.469
290	0.2874	274.6	301.2	0.502	0.2245	269.8	294.8	0.487
310	0.3034	285.6	313.7	0.519	0.2396	281.4	308.0	0.505
330	0.3186	296.6	326.1	0.534	0.2536	292.8	321.0	0.521
350	0.3331	307.7	338.6	0.550	0.2669	304.2	333.9	0.538
370	0.3471	318.9	351.0	0.565	0.2796	315.7	346.8	0.553
390	0.3607	330.2	363.6	0.580	0.2917	327.3	359.7	0.569
410	0.3740	341.7	376.3	0.595	0.3035	338.9	372.6	0.584

TABLE A-19E**Properties of Selected Solids and Liquids: c_p , ρ , and κ**

Substance	Specific Heat, c_p (Btu/lb · °R)	Density, ρ (lb/ft ³)	Thermal Conductivity, κ (Btu/h · ft · °R)
Selected Solids, 540°R			
Aluminum	0.216	169	137
Coal, anthracite	0.301	84.3	0.15
Copper	0.092	557	232
Granite	0.185	164	1.61
Iron	0.107	491	46.4
Lead	0.031	705	20.4
Sand	0.191	94.9	0.16
Silver	0.056	656	248
Soil	0.439	128	0.30
Steel (AISI 302)	0.115	503	8.7
Tin	0.054	456	38.5
Building Materials, 540°R			
Brick, common	0.199	120	0.42
Concrete (stone mix)	0.210	144	0.81
Glass, plate	0.179	156	0.81
Hardboard, siding	0.279	40	0.054
Limestone	0.193	145	1.24
Plywood	0.291	34	0.069
Softwoods (fir, pine)	0.330	31.8	0.069
Insulating Materials, 540°R			
Blanket (glass fiber)	—	1.0	0.027
Cork	0.43	7.5	0.023
Duct liner (glass fiber, coated)	0.199	2.0	0.022
Polystyrene (extruded)	0.289	3.4	0.016
Vermiculite fill (flakes)	0.199	5.0	0.039
Saturated Liquids			
Ammonia, 540°R	1.151	37.5	0.269
Mercury, 540°R	0.033	845	4.94
Refrigerant 22, 540°R	0.303	74.0	0.049
Refrigerant 134a, 540°R	0.343	75.0	0.047
Unused Engine Oil, 540°R	0.456	55.2	0.084
Water, 495°R	1.006	62.42	0.332
540°R	0.998	62.23	0.354
585°R	0.999	61.61	0.373
630°R	1.002	60.79	0.386
675°R	1.008	59.76	0.394
720°R	1.017	58.55	0.398

Source: Drawn from several sources, these data are only representative. Values can vary depending on temperature, purity, moisture content, and other factors.

TABLE A-20E**Ideal Gas Specific Heats of Some Common Gases (Btu/lb · °R)**

Temp. °F	<i>c_p</i>	<i>c_v</i>	<i>k</i>	<i>c_p</i>	<i>c_v</i>	<i>k</i>	<i>c_p</i>	<i>c_v</i>	<i>k</i>	Temp. °F
	Air			Nitrogen, N ₂			Oxygen, O ₂			
40	0.240	0.171	1.401	0.248	0.177	1.400	0.219	0.156	1.397	40
100	0.240	0.172	1.400	0.248	0.178	1.399	0.220	0.158	1.394	100
200	0.241	0.173	1.397	0.249	0.178	1.398	0.223	0.161	1.387	200
300	0.243	0.174	1.394	0.250	0.179	1.396	0.226	0.164	1.378	300
400	0.245	0.176	1.389	0.251	0.180	1.393	0.230	0.168	1.368	400
500	0.248	0.179	1.383	0.254	0.183	1.388	0.235	0.173	1.360	500
600	0.250	0.182	1.377	0.256	0.185	1.383	0.239	0.177	1.352	600
700	0.254	0.185	1.371	0.260	0.189	1.377	0.242	0.181	1.344	700
800	0.257	0.188	1.365	0.262	0.191	1.371	0.246	0.184	1.337	800
900	0.259	0.191	1.358	0.265	0.194	1.364	0.249	0.187	1.331	900
1000	0.263	0.195	1.353	0.269	0.198	1.359	0.252	0.190	1.326	1000
1500	0.276	0.208	1.330	0.283	0.212	1.334	0.263	0.201	1.309	1500
2000	0.286	0.217	1.312	0.293	0.222	1.319	0.270	0.208	1.298	2000
Temp. °F	Carbon Dioxide, CO ₂			Carbon Monoxide, CO			Hydrogen, H ₂			Temp. °F
40	0.195	0.150	1.300	0.248	0.177	1.400	3.397	2.412	1.409	40
100	0.205	0.160	1.283	0.249	0.178	1.399	3.426	2.441	1.404	100
200	0.217	0.172	1.262	0.249	0.179	1.397	3.451	2.466	1.399	200
300	0.229	0.184	1.246	0.251	0.180	1.394	3.461	2.476	1.398	300
400	0.239	0.193	1.233	0.253	0.182	1.389	3.466	2.480	1.397	400
500	0.247	0.202	1.223	0.256	0.185	1.384	3.469	2.484	1.397	500
600	0.255	0.210	1.215	0.259	0.188	1.377	3.473	2.488	1.396	600
700	0.262	0.217	1.208	0.262	0.191	1.371	3.477	2.492	1.395	700
800	0.269	0.224	1.202	0.266	0.195	1.364	3.494	2.509	1.393	800
900	0.275	0.230	1.197	0.269	0.198	1.357	3.502	2.519	1.392	900
1000	0.280	0.235	1.192	0.273	0.202	1.351	3.513	2.528	1.390	1000
1500	0.298	0.253	1.178	0.287	0.216	1.328	3.618	2.633	1.374	1500
2000	0.312	0.267	1.169	0.297	0.226	1.314	3.758	2.773	1.355	2000

Source: Adapted from K. Wark, *Thermodynamics*, 4th ed., McGraw-Hill, New York, 1983, as based on "Tables of Thermal Properties of Gases," NBS Circular 564, 1955.

TABLE A-21E**Variation of \bar{c}_p with Temperature for Selected Ideal Gases**

Gas	T is in °R, equations valid from 540 to 1800 °R				
	α	$\beta \times 10^3$	$\gamma \times 10^6$	$\delta \times 10^9$	$\varepsilon \times 10^{12}$
CO	3.710	-0.899	1.140	-0.348	0.0228
CO ₂	2.401	4.853	-2.039	0.343	0
H ₂	3.057	1.487	-1.793	0.947	-0.1726
H ₂ O	4.070	-0.616	1.281	-0.508	0.0769
O ₂	3.626	-1.043	2.178	-1.160	0.2053
N ₂	3.675	-0.671	0.717	-0.108	-0.0215
Air	3.653	-0.7428	1.017	-0.328	0.02632
NH ₃	3.591	0.274	2.576	-1.437	0.2601
NO	4.046	-1.899	2.464	-1.048	0.1517
NO ₂	3.459	1.147	2.064	-1.639	0.3448
SO ₂	3.267	2.958	0.211	-0.906	0.2438
SO ₃	2.578	8.087	-2.832	-0.136	0.1878
CH ₄	3.826	-2.211	7.580	-3.898	0.6633
C ₂ H ₂	1.410	10.587	-7.562	2.811	-0.3939
C ₂ H ₄	1.426	6.324	2.466	-2.787	0.6429
Monatomic gases ^a	2.5	0	0	0	0

^aFor monatomic gases, such as He, Ne, and Ar, \bar{c}_p is constant over a wide temperature range and is very nearly equal to $5/2 \bar{R}$.

Source: Adapted from K. Wark, *Thermodynamics*, 4th ed., McGraw-Hill, New York, 1983, as based on NASA SP-273, U.S. Government Printing Office, Washington, DC, 1971.

TABLE A-22E**Ideal Gas Properties of Air**

				T(°R), h and u(Btu/lb), s°(Btu/lb · °R)									
				when $\Delta s = 0^1$						when $\Delta s = 0$			
T	h	u	s°	p _r	v _r	T	h	u	s°	p _r	v _r		
360	85.97	61.29	0.50369	0.3363	396.6	940	226.11	161.68	0.73509	9.834	35.41		
380	90.75	64.70	0.51663	0.4061	346.6	960	231.06	165.26	0.74030	10.61	33.52		
400	95.53	68.11	0.52890	0.4858	305.0	980	236.02	168.83	0.74540	11.43	31.76		
420	100.32	71.52	0.54058	0.5760	270.1	1000	240.98	172.43	0.75042	12.30	30.12		
440	105.11	74.93	0.55172	0.6776	240.6	1040	250.95	179.66	0.76019	14.18	27.17		
460	109.90	78.36	0.56235	0.7913	215.33	1080	260.97	186.93	0.76964	16.28	24.58		
480	114.69	81.77	0.57255	0.9182	193.65	1120	271.03	194.25	0.77880	18.60	22.30		
500	119.48	85.20	0.58233	1.0590	174.90	1160	281.14	201.63	0.78767	21.18	20.29		
520	124.27	88.62	0.59172	1.2147	158.58	1200	291.30	209.05	0.79628	24.01	18.51		
537	128.34	91.53	0.59945	1.3593	146.34	1240	301.52	216.53	0.80466	27.13	16.93		
540	129.06	92.04	0.60078	1.3860	144.32	1280	311.79	224.05	0.81280	30.55	15.52		
560	133.86	95.47	0.60950	1.5742	131.78	1320	322.11	231.63	0.82075	34.31	14.25		
580	138.66	98.90	0.61793	1.7800	120.70	1360	332.48	239.25	0.82848	38.41	13.12		
600	143.47	102.34	0.62607	2.005	110.88	1400	342.90	246.93	0.83604	42.88	12.10		
620	148.28	105.78	0.63395	2.249	102.12	1440	353.37	254.66	0.84341	47.75	11.17		
640	153.09	109.21	0.64159	2.514	94.30	1480	363.89	262.44	0.85062	53.04	10.34		
660	157.92	112.67	0.64902	2.801	87.27	1520	374.47	270.26	0.85767	58.78	9.578		
680	162.73	116.12	0.65621	3.111	80.96	1560	385.08	278.13	0.86456	65.00	8.890		
700	167.56	119.58	0.66321	3.446	75.25	1600	395.74	286.06	0.87130	71.73	8.263		
720	172.39	123.04	0.67002	3.806	70.07	1650	409.13	296.03	0.87954	80.89	7.556		
740	177.23	126.51	0.67665	4.193	65.38	1700	422.59	306.06	0.88758	90.95	6.924		
760	182.08	129.99	0.68312	4.607	61.10	1750	436.12	316.16	0.89542	101.98	6.357		
780	186.94	133.47	0.68942	5.051	57.20	1800	449.71	326.32	0.90308	114.0	5.847		
800	191.81	136.97	0.69558	5.526	53.63	1850	463.37	336.55	0.91056	127.2	5.388		
820	196.69	140.47	0.70160	6.033	50.35	1900	477.09	346.85	0.91788	141.5	4.974		
840	201.56	143.98	0.70747	6.573	47.34	1950	490.88	357.20	0.92504	157.1	4.598		
860	206.46	147.50	0.71323	7.149	44.57	2000	504.71	367.61	0.93205	174.0	4.258		
880	211.35	151.02	0.71886	7.761	42.01	2050	518.61	378.08	0.93891	192.3	3.949		
900	216.26	154.57	0.72438	8.411	39.64	2100	532.55	388.60	0.94564	212.1	3.667		
920	221.18	158.12	0.72979	9.102	37.44	2150	546.54	399.17	0.95222	233.5	3.410		

1. p_r and v_r data for use with Eqs. 6.41 and 6.42, respectively.

TABLE A-22E

(Continued)

				$T(^{\circ}\text{R})$, h and u (Btu/lb), s° (Btu/lb · $^{\circ}\text{R}$)							
				when $\Delta s = 0^1$							
T	h	u	s°	p_r	v_r	T	h	u	s°	p_r	v_r
2200	560.59	409.78	0.95868	256.6	3.176	3700	998.11	744.48	1.10991	2330	0.5882
2250	574.69	420.46	0.96501	281.4	2.961	3750	1013.1	756.04	1.11393	2471	0.5621
2300	588.82	431.16	0.97123	308.1	2.765	3800	1028.1	767.60	1.11791	2618	0.5376
2350	603.00	441.91	0.97732	336.8	2.585	3850	1043.1	779.19	1.12183	2773	0.5143
2400	617.22	452.70	0.98331	367.6	2.419	3900	1058.1	790.80	1.12571	2934	0.4923
2450	631.48	463.54	0.98919	400.5	2.266	3950	1073.2	802.43	1.12955	3103	0.4715
2500	645.78	474.40	0.99497	435.7	2.125	4000	1088.3	814.06	1.13334	3280	0.4518
2550	660.12	485.31	1.00064	473.3	1.996	4050	1103.4	825.72	1.13709	3464	0.4331
2600	674.49	496.26	1.00623	513.5	1.876	4100	1118.5	837.40	1.14079	3656	0.4154
2650	688.90	507.25	1.01172	556.3	1.765	4150	1133.6	849.09	1.14446	3858	0.3985
2700	703.35	518.26	1.01712	601.9	1.662	4200	1148.7	860.81	1.14809	4067	0.3826
2750	717.83	529.31	1.02244	650.4	1.566	4300	1179.0	884.28	1.15522	4513	0.3529
2800	732.33	540.40	1.02767	702.0	1.478	4400	1209.4	907.81	1.16221	4997	0.3262
2850	746.88	551.52	1.03282	756.7	1.395	4500	1239.9	931.39	1.16905	5521	0.3019
2900	761.45	562.66	1.03788	814.8	1.318	4600	1270.4	955.04	1.17575	6089	0.2799
2950	776.05	573.84	1.04288	876.4	1.247	4700	1300.9	978.73	1.18232	6701	0.2598
3000	790.68	585.04	1.04779	941.4	1.180	4800	1331.5	1002.5	1.18876	7362	0.2415
3050	805.34	596.28	1.05264	1011	1.118	4900	1362.2	1026.3	1.19508	8073	0.2248
3100	820.03	607.53	1.05741	1083	1.060	5000	1392.9	1050.1	1.20129	8837	0.2096
3150	834.75	618.82	1.06212	1161	1.006	5100	1423.6	1074.0	1.20738	9658	0.1956
3200	849.48	630.12	1.06676	1242	0.9546	5200	1454.4	1098.0	1.21336	10539	0.1828
3250	864.24	641.46	1.07134	1328	0.9069	5300	1485.3	1122.0	1.21923	11481	0.1710
3300	879.02	652.81	1.07585	1418	0.8621						
3350	893.83	664.20	1.08031	1513	0.8202						
3400	908.66	675.60	1.08470	1613	0.7807						
3450	923.52	687.04	1.08904	1719	0.7436						
3500	938.40	698.48	1.09332	1829	0.7087						
3550	953.30	709.95	1.09755	1946	0.6759						
3600	968.21	721.44	1.10172	2068	0.6449						
3650	983.15	732.95	1.10584	2196	0.6157						

TABLE A-23E

Ideal Gas Properties of Selected Gases

$T(R)$	Enthalpy \bar{h} (T) and internal energy \bar{u} (T) in Btu/lbmol. Absolute entropy at 1 atm $\bar{s}^\circ(T)$, in Btu/lbmol · °R.						Oxygen, O ₂ ($\bar{h}_f = -104,040$ Btu/lbmol)						Nitrogen, N ₂ ($\bar{h}_f = 0$ Btu/lbmol)																	
	Carbon Dioxide, CO ₂ ($\bar{h}_f = -169,300$ Btu/lbmol)			Water Vapor, H ₂ O ($\bar{h}_f = -47,540$ Btu/lbmol)			\bar{h}			\bar{u}			\bar{s}°			\bar{h}			\bar{u}			\bar{s}°								
	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°	\bar{h}	\bar{u}	\bar{s}°						
300	2108.2	1512.4	46.353	2081.9	1486.1	43.223	2367.6	1771.8	40.439	2073.5	1477.8	44.927	2082.0	1486.2	41.695	300	1486.2	104,040	2221.0	1585.5	42.143	320	1585.5	104,040						
320	2256.6	1621.1	46.832	2220.9	1585.4	43.672	2526.8	1891.3	40.952	2212.6	1577.1	45.375	2221.0	1585.5	42.143	320	1585.5	104,040	2360.0	1684.4	42.564	340	1684.4	104,040						
340	2407.3	1732.1	47.289	2359.9	1684.7	44.093	2686.0	2010.8	41.435	2351.7	1676.5	45.797	2360.0	1684.4	42.564	340	1684.4	104,040	2498.9	1784.0	42.962	360	1784.0	104,040						
360	2560.5	1845.6	47.728	2498.8	1783.9	44.490	2845.1	2130.2	41.889	2490.8	1775.9	46.195	2630.0	1875.3	46.571	360	1875.3	104,040	2638.0	1883.4	43.337	380	1883.4	104,040						
380	2716.4	1961.8	48.148	2637.9	1883.3	44.866	3004.4	2249.8	42.320	2630.0	1875.3	46.571	2638.0	1883.4	43.337	380	1883.4	104,040	2638.0	1883.4	43.337	380	1883.4	104,040						
400	2874.7	2080.4	48.555	2776.9	1982.6	45.223	3163.8	2369.4	42.728	2769.1	1974.8	46.927	2777.0	1982.6	43.694	400	1982.6	104,040	2908.3	2074.3	47.267	2916.1	2082.0	44.034	420	2082.0	104,040			
420	3035.7	2201.7	48.947	2916.0	2081.9	45.563	3323.2	2489.1	43.117	2908.3	2074.3	47.267	2916.1	2082.0	44.034	420	2082.0	104,040	2908.3	2074.3	47.267	2916.1	2082.0	44.034	420	2082.0	104,040			
440	3199.4	2325.6	49.329	3055.0	2181.2	45.886	3482.7	2608.9	43.487	3047.5	2173.8	47.591	3055.1	2181.3	44.357	440	2181.3	104,040	3186.9	2273.4	47.900	3194.1	2280.6	44.665	460	2280.6	104,040			
460	3365.7	2452.2	49.698	3194.0	2280.5	46.194	3642.3	2728.8	43.841	3186.9	2273.4	47.900	3326.5	2373.3	48.198	460	2373.3	104,040	3202.0	2848.8	44.182	3333.1	2379.9	44.962	480	2379.9	104,040			
480	3534.7	2581.5	50.058	3333.0	2379.8	46.491	3802.0	3802.0	44.182	3333.0	2373.3	47.900	3274.5	3274.5	49.276	480	3274.5	104,040	3886.6	3333.0	45.415	3889.5	2777.4	46.034	560	3889.5	104,040			
500	3706.2	2713.3	50.408	3472.1	2479.2	46.775	3962.0	2969.1	44.508	3466.2	2473.2	48.483	3472.2	2479.3	45.246	500	2479.3	104,040	3089.4	3089.4	44.821	3606.1	2573.4	48.757	3611.3	2578.6	45.519	520	2578.6	104,040
520	3880.3	2847.7	50.750	3641.2	2578.6	47.048	4122.0	3089.4	44.821	3606.1	2573.4	48.757	3611.3	2578.6	45.519	520	2578.6	104,040	4258.0	3725.1	46.235	3729.5	2663.1	45.743	537	2663.1	104,040			
537	4027.5	2963.8	51.032	3725.1	2663.1	47.272	4258.0	3191.9	45.079	3725.1	2658.7	48.982	3729.5	2663.1	45.743	537	2663.1	104,040	4451.4	3746.2	46.124	3750.3	2678.0	45.781	540	2678.0	104,040			
540	4056.8	2984.4	51.082	3750.3	2677.9	47.310	4282.4	3210.0	45.124	3746.2	2673.8	49.021	3750.3	2678.0	45.781	540	2678.0	104,040	4442.8	3330.7	45.415	3886.6	3282.9	49.276	560	3886.6	104,040			
560	4235.8	3123.7	51.408	3889.5	2777.4	47.563	4442.8	3330.7	45.415	3889.5	2774.5	49.276	3889.5	2777.4	46.034	560	2777.4	104,040	4593.5	3282.9	50.437	4585.8	3275.2	47.178	660	3275.2	104,040			
580	4417.2	3265.4	51.726	4028.7	2876.9	47.807	4603.7	3451.9	45.696	4027.3	2875.5	49.522	4028.7	2876.9	46.278	580	2876.9	104,040	4167.0	3078.4	49.762	4167.9	2976.4	46.514	600	2976.4	104,040			
600	4600.9	3409.4	52.038	4168.0	2976.5	48.044	4764.7	3573.2	45.970	4168.3	2976.8	49.762	4167.9	2976.4	46.514	600	2976.4	104,040	4258.0	3725.1	46.235	3729.5	2663.1	45.743	537	2663.1	104,040			
620	4786.6	3555.6	52.343	4307.4	3076.2	48.272	4926.1	3694.9	46.235	4309.7	3078.4	49.993	4307.1	3075.9	46.742	620	3075.9	104,040	4451.4	3746.2	46.124	3750.3	2678.0	45.781	540	2678.0	104,040			
640	4974.9	3704.0	52.641	4446.9	3177.9	48.494	5087.8	3816.8	46.492	4451.4	3180.4	50.218	4446.4	3177.5	46.964	640	3177.5	104,040	4593.5	3282.9	50.437	4585.8	3275.2	47.178	660	3275.2	104,040			
660	5165.2	3854.6	52.934	4586.6	3275.8	48.709	5250.0	3939.3	46.741	4593.5	3282.9	50.437	4585.8	3275.2	47.178	660	3275.2	104,040	4673.8	3746.2	46.964	3750.3	2678.0	45.781	540	2678.0	104,040			
680	5357.6	4007.2	53.225	4726.2	3375.8	48.917	5412.5	4062.1	46.984	4736.2	3385.8	50.650	4725.3	3374.9	47.386	680	3374.9	104,040	4167.0	3489.2	50.858	4864.9	3474.8	47.588	700	3474.8	104,040			
700	5552.0	4161.9	53.503	4866.0	3475.9	49.120	5575.4	4185.3	47.219	4879.3	3489.2	50.858	4864.9	3474.8	47.588	700	3474.8	104,040	4258.0	3593.1	51.059	5004.5	3574.7	47.785	720	3574.7	104,040			
720	5748.4	4318.6	53.780	5006.1	3576.3	49.317	5738.8	4309.0	47.450	5022.9	3593.1	51.257	5144.3	3697.4	51.257	720	3697.4	104,040	4451.4	3802.2	51.450	5284.1	3774.9	48.164	760	3774.9	104,040			
740	5946.8	4477.3	54.051	5146.4	3676.9	49.509	5902.6	4433.1	47.673	5167.0	3697.4	51.257	5144.3	3674.7	47.977	740	3674.7	104,040	4593.5	3802.2	51.450	5284.1	3774.9	48.164	760	3774.9	104,040			
760	6147.0	4637.9	54.319	5286.8	3777.5	49.697	6066.9	4557.6	47.893	5311.4	3774.9	51.257	5144.3	3674.7	47.977	760	3674.7	104,040	4673.8	3802.2	51.450	5284.1	3774.9	48.164	760	3774.9	104,040			
780	6349.1	4800.1	54.582	5427.4	3878.4	49.880	6231.7	4682.7	48.106	5456.4	3907.5	51.638	5424.2	3875.2	48.345	780	3875.2	104,040	4736.2	50.650	51.821	5564.4	3975.7	48.522	800	3975.7	104,040			
800	6552.9	4964.2	54.839	5568.2	3979.5	50.058	6396.9	4808.2	48.316	5602.0	4913.3	51.821	5564.4	3975.7	48.522	800	3975.7	104,040	4873.8	50.650	51.821	5564.4	3975.7	48.522	800	3975.7	104,040			
820	6758.3	5129.9	55.093	5709.4	4081.0	50.232	6562.6	4934.2	48.520	5748.1	4119.7	52.002	5704.7	4074.7	47.977	820	4074.7	104,040	4946.4	50.650	51.821	5564.4	4074.7	47.977	840	4074.7	104,040			
840	6965.7	5297.6	55.343	5850.7	4182.6	50.402	6728.9	5060.8	48.721	5894.8	4226.6	52.179	5845.3	4177.1	48.865	840	4177.1	104,040	5065.6	51.821	52.179	5845.3	4177.1	48.865	860	4177.1	104,040			
860	7174.7	5466.9	55.589	5992.3	4284.5	50.569	6895.6	5187.8	48.916	6041.9	4334.1	52.352	5985.9	4278.1	49.031	860	4278.1	104,040	5186.6	52.352	53.170	6693.1	4278.1	49.031	860	4278.1	104,040			
880	7385.3	5637.7	55.831	6134.2	4386.6	50.732	7062.9	5315.3	49.109	6189.6	4442.0	52.522	6126.9	4379.4	49.193	880	4379.4	104,040	5258.0	52.522	53.170	6693.1	4379.4	49.193	900	4379.4	104,040			
900	7597.6	5810.3	56.																											

Table A-23E

(Continued)

$T^{\circ}\text{R}$	Carbon Dioxide, CO_2 ($\bar{h}_f^\circ = -169,360 \text{ Btu/lbmol}$)				Carbon Monoxide, CO ($\bar{h}_f^\circ = -47,540 \text{ Btu/lbmol}$)				Water Vapor, H_2O ($\bar{h}_f^\circ = -104,040 \text{ Btu/lbmol}$)				Oxygen, O_2 ($\bar{h}_f^\circ = 0 \text{ Btu/lbmol}$)				Nitrogen, N_2 ($\bar{h}_f^\circ = 0 \text{ Btu/lbmol}$)			
	\bar{h}	\bar{u}	s°	\bar{h}	\bar{u}	s°	\bar{h}	\bar{u}	s°	\bar{h}	\bar{u}	s°	\bar{h}	\bar{u}	s°	\bar{h}	\bar{u}	s°	$T^{\circ}\text{R}$	
1080	9575.8	7431.1	58.072	7571.1	5426.4	52.203	8768.2	6623.5	50.854	7696.8	5552.1	54.064	7551.0	5406.2	50.651	1080				
1100	9802.6	7618.1	58.281	7716.8	5532.3	52.337	8942.0	6757.5	51.013	7850.4	5665.9	54.204	7695.0	5510.5	50.783	1100				
1120	10030.6	7806.4	58.485	7862.9	5638.7	52.468	9116.4	6892.2	51.171	8004.5	5780.3	54.343	7839.3	5615.2	50.912	1120				
1140	10260.1	7996.2	58.689	8009.2	5745.4	52.598	9291.4	7027.5	51.325	8159.1	5895.2	54.480	7984.0	5720.1	51.040	1140				
1160	10490.6	8187.0	58.889	8156.1	5851.5	52.726	9467.1	7163.5	51.478	8314.2	6010.6	54.614	8129.0	5825.4	51.167	1160				
1180	10722.3	8379.0	59.088	8303.3	5960.0	52.852	9643.4	7300.1	51.630	8469.8	6126.5	54.748	8274.4	5931.0	51.291	1180				
1200	10955.3	8572.3	59.283	8450.8	6067.8	52.976	9820.4	7437.4	51.777	8625.8	6242.8	54.879	8420.0	6037.0	51.413	1200				
1220	11189.4	8766.6	59.477	8598.8	6176.0	53.098	998.0	7575.2	51.925	8782.4	6359.6	55.008	8566.1	6143.4	51.534	1220				
1240	11424.6	8962.1	59.668	8747.2	6284.7	53.218	10176.1	7713.6	52.070	8939.4	6476.9	55.136	8712.6	6250.1	51.653	1240				
1260	11661.0	9158.8	59.858	8896.0	6393.8	53.337	10354.9	7852.7	52.212	9096.7	6594.5	55.262	8859.3	6357.2	51.771	1260				
1280	11898.4	9356.5	60.044	9045.0	6503.1	53.455	10534.4	7992.5	52.354	9254.6	6712.7	55.386	9006.4	6464.5	51.887	1280				
1300	12136.9	9555.3	60.229	9194.6	6633.0	53.571	10714.5	8132.9	52.494	9412.9	6831.3	55.508	9153.9	6572.3	51.001	1300				
1320	12376.4	9755.0	60.412	9344.6	6723.2	53.685	10895.3	8274.0	52.631	9571.6	6950.2	55.630	9301.8	6680.4	52.114	1320				
1340	12617.0	9955.9	60.593	9494.8	6833.7	53.799	11076.6	8415.5	52.768	9730.7	7069.6	55.750	9450.0	6788.9	52.225	1340				
1360	12858.5	10157.7	60.772	9645.5	6944.7	53.910	11258.7	8557.9	52.903	9890.2	7189.4	55.867	9598.6	6897.8	52.335	1360				
1380	13101.0	10360.5	60.949	9796.6	7056.1	54.021	11441.4	8700.9	53.037	10050.1	7309.6	55.984	9747.5	7007.0	52.444	1380				
1400	13344.7	10564.5	61.124	9948.1	7167.9	54.129	11624.8	8844.6	53.168	10210.4	7430.1	56.099	9896.9	7116.7	52.551	1400				
1420	13589.1	10769.2	61.298	10100.0	7280.1	54.237	11808.8	8988.9	53.299	10371.0	7551.1	56.213	10046.6	7226.7	52.658	1420				
1440	13834.5	10974.8	61.469	10252.2	7392.6	54.344	11993.4	9133.8	53.428	10532.0	7672.4	56.326	10196.6	7337.0	52.763	1440				
1460	14080.8	11181.4	61.639	10404.8	7505.4	54.448	12178.8	9279.4	53.556	10693.3	7793.9	56.437	10347.0	7447.6	52.867	1460				
1480	14328.0	11388.9	61.800	10557.8	7668.7	54.522	12364.8	9425.7	53.682	10855.1	7916.0	56.547	10497.8	7558.7	52.969	1480				
1500	14576.0	11597.2	61.974	10711.1	7732.3	54.665	12551.4	9572.7	53.808	11017.1	8038.3	56.656	10648.0	7670.1	53.071	1500				
1520	14824.9	11806.4	62.138	10864.9	7846.4	54.757	12738.8	9720.3	53.932	11179.6	8161.1	56.763	10800.4	7781.9	53.171	1520				
1540	15074.7	12016.5	62.302	11019.0	7960.8	54.858	12926.8	9868.6	54.055	11342.4	8284.2	56.869	10952.2	7893.9	53.271	1540				
1560	15325.3	12227.3	62.464	11173.4	8075.4	54.958	13115.6	10017.6	54.117	11505.4	8407.4	56.975	11104.3	8006.4	53.369	1560				
1580	15576.7	12439.0	62.624	11328.2	8190.5	55.056	13305.0	10167.3	54.298	11668.8	8531.1	57.079	11256.9	8119.2	53.465	1580				
1600	15829.0	12651.6	62.783	11483.4	8306.0	55.154	13494.4	10317.6	54.418	11832.5	8655.1	57.182	11409.7	8232.3	53.561	1600				
1620	16081.9	12864.8	62.939	11638.9	8421.8	55.251	13685.7	10468.6	54.535	11996.6	8779.5	57.284	11562.8	8345.7	53.656	1620				
1640	16335.7	13078.9	63.095	11794.7	8537.9	55.347	13877.0	10620.2	54.653	12160.9	8904.1	57.385	11716.4	8459.6	53.751	1640				
1660	16590.2	13293.7	63.250	11950.9	8654.4	55.441	14069.2	10772.7	54.770	12325.5	9029.0	57.484	11870.2	8573.6	53.844	1660				
1680	16845.5	13509.2	63.403	12107.5	8771.2	55.535	14261.9	10925.6	54.886	12490.4	9154.1	57.582	12024.3	8688.1	53.936	1680				
1700	17101.4	13725.4	63.555	12264.3	8888.3	55.628	14455.4	11079.4	54.999	12655.6	9279.6	57.680	12178.9	8802.9	54.028	1700				
1720	17358.1	13942.4	63.704	12421.4	9005.7	55.720	14664.5	11233.8	55.113	12821.1	9405.4	57.777	12333.7	8918.0	54.118	1720				
1740	17615.5	14160.1	63.853	12579.0	9123.6	55.811	14844.3	11388.9	55.226	12986.9	9531.5	57.873	12488.8	9033.4	54.208	1740				
1760	17873.5	14378.4	64.001	12736.7	9241.6	55.900	15039.8	11544.7	55.339	13153.0	9657.9	57.968	12644.3	9149.2	54.297	1760				
1780	18132.2	14597.4	64.147	12894.9	9360.0	55.990	15236.1	11701.2	55.449	13319.2	9784.4	58.062	12800.2	9265.3	54.385	1780				
1800	18391.5	14816.9	64.292	13053.2	9478.6	56.078	15433.0	11858.4	55.559	13485.8	9911.2	58.155	12956.3	9381.7	54.472	1800				
1820	18651.5	15037.2	64.435	13212.0	9597.7	56.166	15630.6	12016.3	55.668	13652.5	10038.2	58.247	13112.7	9498.4	54.559	1820				
1840	18912.2	15258.2	64.578	13371.0	977.0	56.253	15828.7	12174.7	55.777	13819.6	10165.6	58.339	13269.5	9615.5	54.645	1840				
1860	19173.4	15479.7	64.719	13530.2	9836.5	56.339	16027.6	12333.9	55.884	13986.8	10293.1	58.428	13426.5	9732.8	54.729	1860				

TABLE A-23E
(Continued)

<i>T(R)</i>	Carbon Dioxide, CO ₂				Carbon Monoxide, CO ($\bar{h}_f^o = -47,540$ Btu/lbmol)				Water Vapor, H ₂ O ($\bar{h}_f^o = -104,040$ Btu/lbmol)				Oxygen, O ₂ ($\bar{h}_f^o = 0$ Btu/lbmol)				Nitrogen, N ₂ ($\bar{h}_f^o = 0$ Btu/lbmol)			
	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	
1900	19,698	15,925	64,999	13,850	10,077	56,599	16,428	12,654	56,097	14,322	10,549	58,607	13,742	9,968	54,896	1900	19,40	10,205	55,061	
1940	20,224	16,372	65,272	14,170	10,318	56,677	16,830	12,977	56,307	14,658	10,806	58,782	14,058	10,205	55,061	1940	20,753	10,443	55,223	
1980	20,753	16,821	65,543	14,492	10,560	56,841	17,235	13,303	56,514	14,995	11,063	58,954	14,375	10,443	55,223	1980	21,284	10,682	55,383	
2020	21,284	17,273	65,809	14,815	10,803	57,007	17,643	13,632	56,719	15,333	11,321	59,123	14,694	10,682	55,383	2020	21,818	10,923	55,540	
2060	21,818	17,727	66,069	15,139	11,048	57,161	18,054	13,963	56,920	15,672	11,581	59,289	15,013	10,923	55,540	2060				
2100	22,353	18,182	66,327	15,463	11,293	57,317	18,467	14,297	57,119	16,011	11,841	59,451	15,334	11,164	55,694	2100				
2140	22,890	18,640	66,581	15,789	11,539	57,470	18,883	14,633	57,315	16,351	12,101	59,612	15,656	11,406	55,846	2140				
2180	23,429	19,101	66,830	16,116	11,787	57,621	19,301	14,972	57,509	16,692	12,363	59,770	15,978	11,649	55,995	2180				
2220	23,970	19,561	67,076	16,443	12,035	57,770	19,722	15,313	57,701	17,036	12,625	59,926	16,302	11,893	56,141	2220				
2260	24,512	20,024	67,319	16,722	12,284	57,917	20,145	15,657	57,889	17,376	12,888	60,077	16,626	12,138	56,286	2260				
2300	25,056	20,489	67,557	17,101	12,534	58,062	20,571	16,003	58,077	17,719	13,151	60,228	16,951	12,384	56,449	2300				
2340	25,602	20,955	67,792	17,431	12,784	58,204	20,999	16,352	58,261	18,062	13,416	60,376	17,277	12,630	56,570	2340				
2380	26,150	21,423	68,025	17,762	13,035	58,344	21,429	16,703	58,445	18,407	13,680	60,522	17,604	12,878	56,708	2380				
2420	26,699	21,893	68,253	18,093	13,287	58,482	21,862	17,057	58,625	18,572	13,946	60,666	17,932	13,126	56,845	2420				
2460	27,249	22,364	68,479	18,426	13,541	58,619	22,298	17,443	58,803	19,097	14,212	60,808	18,260	13,375	56,980	2460				
2500	27,801	22,837	68,702	18,759	13,794	58,754	22,735	17,771	58,980	19,443	14,479	60,946	18,590	13,625	57,112	2500				
2540	28,355	23,310	68,921	19,993	14,048	58,885	23,175	18,131	59,155	19,790	14,746	61,084	18,919	13,875	57,243	2540				
2580	28,910	23,786	69,138	19,427	14,303	59,016	23,618	18,494	59,328	20,138	15,014	61,220	19,250	14,127	57,372	2580				
2620	29,465	24,262	69,352	19,762	14,559	59,145	24,062	18,859	59,500	20,485	15,282	61,354	19,582	14,379	57,499	2620				
2660	30,023	24,740	69,563	20,098	14,815	59,272	24,508	19,226	59,669	20,834	15,551	61,486	19,914	14,631	57,625	2660				
2700	30,581	25,220	69,771	20,434	15,072	59,398	24,957	19,595	59,837	21,183	15,821	61,616	20,246	14,885	57,750	2700				
2740	31,141	25,701	69,977	20,771	15,330	59,521	25,408	19,967	60,003	21,533	16,091	61,744	20,580	15,139	57,872	2740				
2780	31,702	26,181	70,181	21,108	15,588	59,644	25,861	20,340	60,167	21,883	16,362	61,871	20,914	15,393	57,993	2780				
2820	32,264	26,664	70,382	21,446	15,846	59,765	26,316	20,715	60,330	22,232	16,633	61,996	21,248	15,648	58,113	2820				
2860	32,827	27,148	70,580	21,785	16,105	59,884	26,773	21,093	60,490	22,584	16,905	62,120	21,584	15,905	58,231	2860				
2900	33,392	27,633	70,776	22,124	16,365	60,002	27,231	21,472	60,650	22,936	17,177	62,242	21,920	16,161	58,348	2900				
2940	33,957	28,118	70,970	22,463	16,625	60,118	27,692	21,853	60,809	23,288	17,450	62,363	22,256	16,417	58,463	2940				
2980	34,523	28,605	71,160	22,803	16,885	60,232	28,154	22,237	60,965	23,641	17,723	62,483	22,593	16,675	58,576	2980				
3020	35,090	29,093	71,350	23,144	17,146	60,346	28,619	22,621	61,120	23,994	17,997	62,599	22,930	16,933	58,688	3020				
3060	35,659	29,582	71,537	23,485	17,408	60,458	29,085	23,085	61,274	24,348	18,271	62,716	23,268	17,192	58,800	3060				
3100	36,228	30,072	71,722	23,826	17,670	60,569	29,553	23,397	61,426	24,703	18,546	62,831	23,607	17,451	58,910	3100				
3140	36,798	30,562	71,904	24,168	17,932	60,679	30,023	23,787	61,577	25,057	18,822	62,945	23,946	17,710	59,019	3140				
3180	37,369	31,054	72,085	24,510	18,195	60,787	30,494	24,179	61,727	25,413	19,098	63,057	24,285	17,970	59,126	3180				
3220	37,941	31,546	72,264	24,853	18,458	60,894	30,967	24,572	61,874	25,769	19,374	63,169	24,625	18,231	59,232	3220				
3260	38,513	32,039	72,441	25,196	18,722	61,000	31,442	24,968	62,022	26,175	19,651	63,279	24,965	18,491	59,338	3260				
3300	39,087	32,533	72,616	25,539	18,986	61,105	31,918	25,365	62,167	26,442	19,928	63,386	25,306	18,753	59,442	3300				
3340	39,661	33,028	72,788	25,883	19,250	61,209	32,396	25,763	62,312	26,839	20,206	63,494	25,647	19,014	59,544	3340				
3380	40,236	33,524	72,960	26,227	19,515	61,311	32,876	26,164	62,454	27,197	20,485	63,601	25,989	19,277	59,646	3380				
3420	40,812	34,020	73,129	26,572	19,780	61,412	33,357	26,565	62,597	27,555	20,763	63,706	26,331	19,539	59,747	3420				
3460	41,338	34,517	73,297	26,917	20,045	61,513	33,839	26,968	62,738	27,914	21,043	63,811	26,673	19,802	59,846	3460				

Table A-23E

Table A-23E

(Continued)

<i>T</i> ^o R	Carbon Dioxide, CO ₂ (<i>h</i> ^o = -169,390 Btu/lbmol)				Carbon Monoxide, CO (<i>h</i> ^o = -47,540 Btu/lbmol)				Water Vapor, H ₂ O (<i>h</i> ^o = -104,040 Btu/lbmol)				Oxygen, O ₂ (<i>h</i> ^o = 0 Btu/lbmol)				Nitrogen, N ₂ (<i>h</i> ^o = 0 Btu/lbmol)			
	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>h</i>	<i>ū</i>	<i>s</i> ^o	<i>T</i> ^o R	
3500	41,965	35,015	73,462	27,262	20,311	61,612	34,324	27,373	62,875	28,273	21,323	63,914	27,016	20,065	59,944	3500				
3540	42,543	35,513	73,627	27,608	20,576	61,710	34,809	27,779	63,015	28,633	21,603	64,016	27,359	20,329	60,041	3540				
3580	43,121	36,012	73,789	27,954	20,844	61,807	35,296	28,187	63,153	28,994	21,884	64,114	27,703	20,593	60,138	3580				
3620	43,701	36,512	73,951	28,300	21,111	61,903	35,785	28,596	63,288	29,354	22,165	64,217	28,046	20,858	60,234	3620				
3660	44,280	37,012	74,110	28,647	21,378	61,998	36,274	29,006	63,423	29,716	22,447	64,316	28,391	21,122	60,328	3660				
3700	44,861	37,513	74,267	28,994	21,646	62,093	36,765	29,448	63,557	30,078	22,730	64,415	28,735	21,387	60,422	3700				
3740	45,442	38,014	74,423	29,341	21,914	62,186	37,258	29,831	63,690	30,440	23,013	64,512	29,080	21,653	60,515	3740				
3780	46,023	38,517	74,578	29,688	22,182	62,279	37,752	30,245	63,821	30,803	23,296	64,609	29,425	21,919	60,607	3780				
3820	46,605	39,019	74,732	30,036	22,450	62,370	38,247	30,661	63,952	31,166	23,580	64,704	29,771	22,185	60,698	3820				
3860	47,188	39,522	74,884	30,384	22,719	62,461	38,743	31,077	64,082	31,529	23,864	64,800	30,117	22,451	60,788	3860				
3900	47,771	40,026	75,033	30,733	22,988	61,511	39,240	31,495	64,210	31,894	24,149	64,893	30,463	22,718	60,877	3900				
3940	48,355	40,531	75,182	31,082	23,257	62,640	39,739	31,955	64,338	32,258	24,434	64,986	30,809	22,985	60,966	3940				
3980	48,939	41,035	75,330	31,431	23,527	62,728	40,239	32,335	64,465	32,623	24,720	65,078	31,156	23,252	61,053	3980				
4020	49,524	41,541	75,477	31,780	23,797	62,816	40,740	32,757	64,591	32,989	25,006	65,169	31,503	23,520	61,139	4020				
4060	50,109	42,047	75,622	32,129	24,067	62,902	41,242	33,179	64,715	33,355	25,292	65,260	31,850	23,788	61,225	4060				
4100	50,695	42,553	75,765	32,479	24,337	62,988	41,745	33,603	64,839	33,722	25,580	65,350	32,198	24,056	61,310	4100				
4140	51,282	43,060	75,907	32,829	24,608	63,072	42,250	34,028	64,962	34,089	25,867	65,439	32,546	24,324	61,395	4140				
4180	51,868	43,568	76,048	33,179	24,878	63,156	42,755	34,454	65,084	34,456	26,155	65,527	32,894	24,593	61,479	4180				
4220	52,456	44,075	76,188	33,530	25,149	63,240	43,267	34,881	65,204	34,824	26,444	65,615	33,242	24,862	61,562	4220				
4260	53,044	44,584	76,327	33,880	25,421	63,323	43,769	35,310	65,325	35,192	26,733	65,702	33,591	25,131	61,644	4260				
4300	53,632	45,093	76,464	34,231	25,692	63,405	44,278	35,739	65,444	35,561	27,022	65,788	33,940	25,401	61,726	4300				
4340	54,221	45,602	76,601	34,582	25,934	63,486	44,788	36,169	65,563	35,930	27,312	65,873	34,289	25,670	61,806	4340				
4380	54,810	46,112	76,736	34,934	26,235	63,567	45,298	36,600	65,680	36,300	27,602	65,958	34,638	25,940	61,887	4380				
4420	55,400	46,622	76,870	35,285	26,508	63,647	45,810	37,032	65,797	36,670	27,823	66,042	34,988	26,210	61,966	4420				
4460	55,990	47,133	77,003	35,637	26,780	63,726	46,322	37,465	65,913	37,041	28,184	66,125	35,338	26,481	62,045	4460				
4500	56,581	47,645	77,135	35,989	27,052	63,805	46,836	37,900	66,028	37,412	28,475	66,208	35,688	26,751	62,123	4500				
4540	57,172	48,156	77,266	36,341	27,325	63,883	47,350	38,334	66,142	37,783	28,768	66,290	36,038	27,022	62,201	4540				
4580	57,764	48,668	77,395	36,693	27,598	63,960	47,866	38,770	66,255	38,155	29,060	66,372	36,389	27,293	62,278	4580				
4620	58,356	49,181	77,581	37,046	27,871	64,036	48,382	39,207	66,368	38,528	29,353	66,453	36,739	27,565	62,354	4620				
4660	58,948	49,694	77,652	37,398	28,144	64,113	48,899	39,645	66,480	38,900	29,646	66,533	37,090	27,836	62,429	4660				
4700	59,541	50,208	77,779	37,751	28,417	64,188	49,417	40,083	66,591	39,274	29,940	66,613	37,441	28,108	62,504	4700				
4740	60,134	50,721	77,905	38,104	28,691	64,263	49,936	40,523	66,701	39,647	30,234	66,691	37,792	28,379	62,578	4740				
4780	60,728	51,236	78,029	38,457	28,965	64,337	50,455	40,963	66,811	40,021	30,529	66,770	38,144	28,651	62,652	4780				
4820	61,322	51,750	78,153	38,811	29,239	64,411	50,976	41,404	66,920	40,396	30,824	66,848	38,495	28,924	62,725	4820				
4860	61,916	52,265	78,276	39,164	29,513	64,484	51,497	41,856	67,028	40,771	31,120	66,925	38,847	29,196	62,798	4860				
4900	62,511	52,781	78,398	39,518	29,787	64,556	52,019	42,288	67,135	41,146	31,415	67,003	39,199	29,468	62,870	4900				
5000	64,000	54,071	78,698	40,403	30,473	64,735	53,327	43,398	67,401	42,086	32,157	67,193	40,080	30,151	63,049	5000				
5100	65,491	55,363	78,994	41,289	31,161	64,910	54,640	44,512	67,662	43,021	32,901	67,380	40,962	30,834	63,223	5100				
5200	66,984	56,658	79,284	42,176	31,849	65,082	55,957	45,631	67,918	43,974	33,648	67,562	41,844	31,518	63,395	5200				
5300	68,471	57,954	79,569	43,063	32,538	65,252	57,279	46,754	68,172	44,922	34,397	67,743	42,728	32,203	63,563	5300				

TABLE A-24E**Constants for the van der Waals, Redlich–Kwong, and Benedict–Webb–Rubin Equations of State**1. van der Waals and Redlich–Kwong: Constants for pressure in atm, specific volume in ft³/lbmol, and temperature in °R

Substance	van der Waals		Redlich–Kwong	
	a atm $\left(\frac{\text{ft}^3}{\text{lbmol}}\right)^2$	b $\frac{\text{ft}^3}{\text{lbmol}}$	a atm $\left(\frac{\text{ft}^3}{\text{lbmol}}\right)^2$ $(^\circ\text{R})^{1/2}$	b $\frac{\text{ft}^3}{\text{lbmol}}$
Air	345	0.586	5,409	0.4064
Butane (C ₄ H ₁₀)	3,509	1.862	98,349	1.2903
Carbon dioxide (CO ₂)	926	0.686	21,972	0.4755
Carbon monoxide (CO)	372	0.632	5,832	0.4382
Methane (CH ₄)	581	0.685	10,919	0.4751
Nitrogen (N ₂)	346	0.618	5,280	0.4286
Oxygen (O ₂)	349	0.509	5,896	0.3531
Propane (C ₃ H ₈)	2,369	1.444	61,952	1.0006
Refrigerant 12	2,660	1.558	70,951	1.0796
Sulfur dioxide (SO ₂)	1,738	0.910	49,032	0.6309
Water (H ₂ O)	1,400	0.488	48,418	0.3380

Source: Calculated from critical data.

2. Benedict–Webb–Rubin: Constants for pressure in atm, specific volume in ft³/lbmol, and temperature in °R

Substance	a	A	b	B	c	C	α	γ
C ₄ H ₁₀	7736.7	2587.6	10.26	1.9921	4.214×10^9	8.254×10^8	4.527	8.724
CO ₂	562.3	702.4	1.850	0.7995	1.987×10^8	1.152×10^8	0.348	1.384
CO	150.6	344.1	0.675	0.8737	1.385×10^7	7.118×10^6	0.555	1.540
CH ₄	203.0	476.0	0.867	0.6824	3.389×10^7	1.876×10^7	0.511	1.540
N ₂	103.2	270.4	0.597	0.6526	9.700×10^6	6.700×10^6	0.523	1.360

Source: H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing*, 46 (12): 141 (1967).

TABLE A-25E**Thermochemical Properties of Selected Substances at 537°R and 1 atm**

Substance	Formula	Molar Mass, M (lb/lbmol)	Enthalpy of Formation, \bar{h}_f° (Btu/lbmol)	Gibbs Function of Formation, \bar{g}_f° (Btu/lbmol)	Absolute Entropy, \bar{s}° (Btu/lbmol · °R)	Heating Values	
						Higher, HHV (Btu/lb)	Lower, LHV (Btu/lb)
Carbon	C(s)	12.01	0	0	1.36	14,100	14,100
Hydrogen	H ₂ (g)	2.016	0	0	31.19	61,000	51,610
Nitrogen	N ₂ (g)	28.01	0	0	45.74	—	—
Oxygen	O ₂ (g)	32.00	0	0	48.98	—	—
Carbon monoxide	CO(g)	28.01	-47,540	-59,010	47.27	—	—
Carbon dioxide	CO ₂ (g)	44.01	-169,300	-169,680	51.03	—	—
Water	H ₂ O(g)	18.02	-104,040	-98,350	45.08	—	—
Water	H ₂ O(l)	18.02	-122,970	-102,040	16.71	—	—
Hydrogen peroxide	H ₂ O ₂ (g)	34.02	-58,640	-45,430	55.60	—	—
Ammonia	NH ₃ (g)	17.03	-19,750	-7,140	45.97	—	—
Oxygen	O(g)	16.00	107,210	99,710	38.47	—	—
Hydrogen	H(g)	1.008	93,780	87,460	27.39	—	—
Nitrogen	N(g)	14.01	203,340	195,970	36.61	—	—
Hydroxyl	OH(g)	17.01	16,790	14,750	43.92	—	—
Methane	CH ₄ (g)	16.04	-32,210	-21,860	44.49	23,880	21,520
Acetylene	C ₂ H ₂ (g)	26.04	97,540	87,990	48.00	21,470	20,740
Ethylene	C ₂ H ₄ (g)	28.05	22,490	29,306	52.54	21,640	20,290
Ethane	C ₂ H ₆ (g)	30.07	-36,420	-14,150	54.85	22,320	20,430
Propylene	C ₃ H ₆ (g)	42.08	8,790	26,980	63.80	21,050	19,700
Propane	C ₃ H ₈ (g)	44.09	-44,680	-10,105	64.51	21,660	19,950
Butane	C ₄ H ₁₀ (g)	58.12	-54,270	-6,760	74.11	21,300	19,670
Pentane	C ₅ H ₁₂ (g)	72.15	-62,960	-3,530	83.21	21,090	19,510
Octane	C ₈ H ₁₈ (g)	114.22	-89,680	7,110	111.55	20,760	19,270
Octane	C ₈ H ₁₈ (l)	114.22	-107,530	2,840	86.23	20,610	19,110
Benzene	C ₆ H ₆ (g)	78.11	35,680	55,780	64.34	18,180	17,460
Methanol	CH ₃ OH(g)	32.04	-86,540	-69,700	57.29	10,260	9,080
Methanol	CH ₃ OH(l)	32.04	-102,670	-71,570	30.30	9,760	8,570
Ethanol	C ₂ H ₅ OH(g)	46.07	-101,230	-72,520	67.54	13,160	11,930
Ethanol	C ₂ H ₅ OH(l)	46.07	-119,470	-75,240	38.40	12,760	11,530

Source: Based on JANAF Thermochemical Tables, NSRDS-NBS-37, 1971; *Selected Values of Chemical Thermodynamic Properties*, NBS Tech. Note 270-3, 1968; and API Research Project 44, Carnegie Press, 1953. Heating values calculated.

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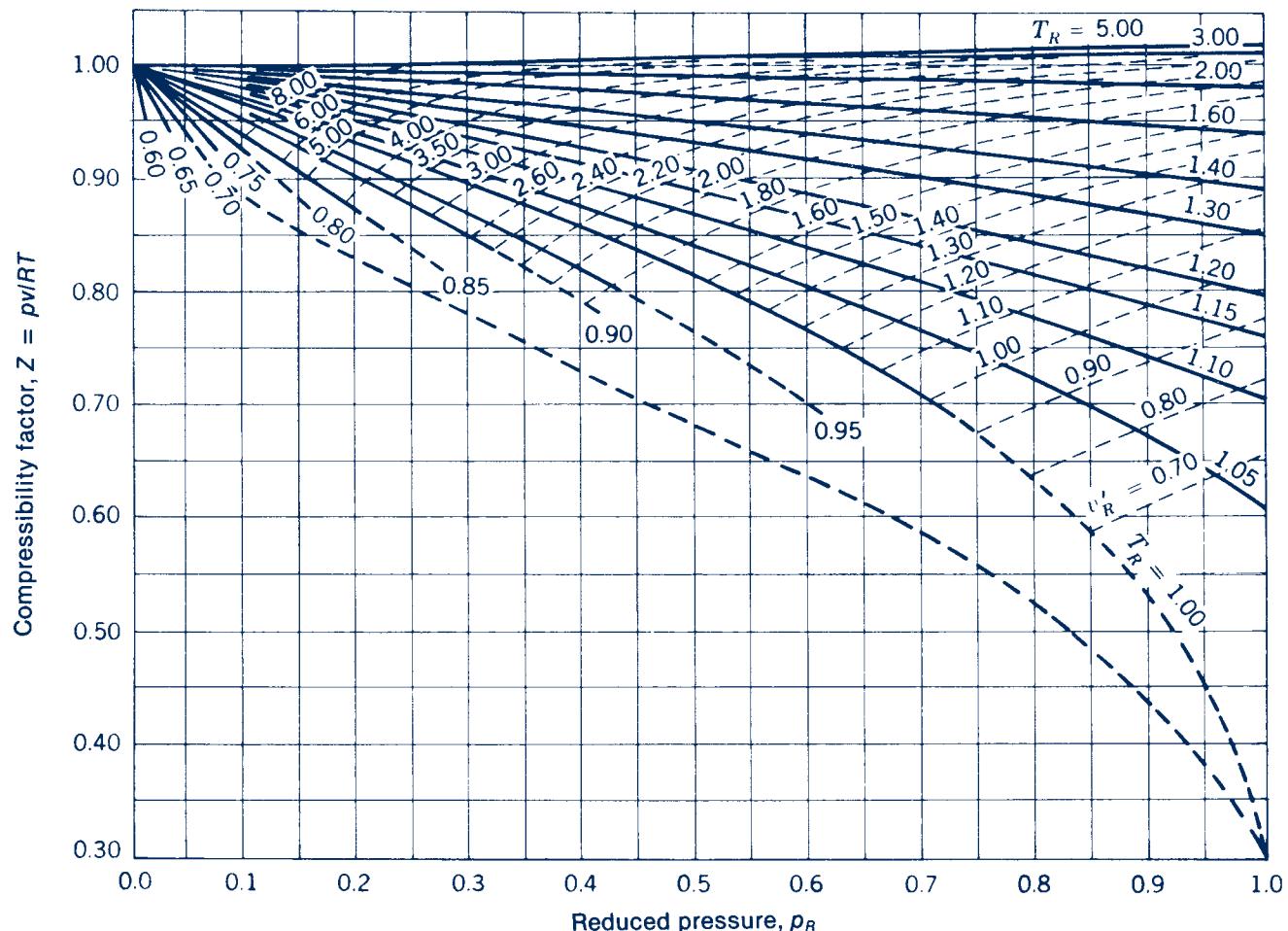


Figure A-1 Generalized compressibility chart, $p_R \leq 1.0$. Source: E. F. Obert, *Concepts of Thermodynamics*, McGraw-Hill, New York, 1960.

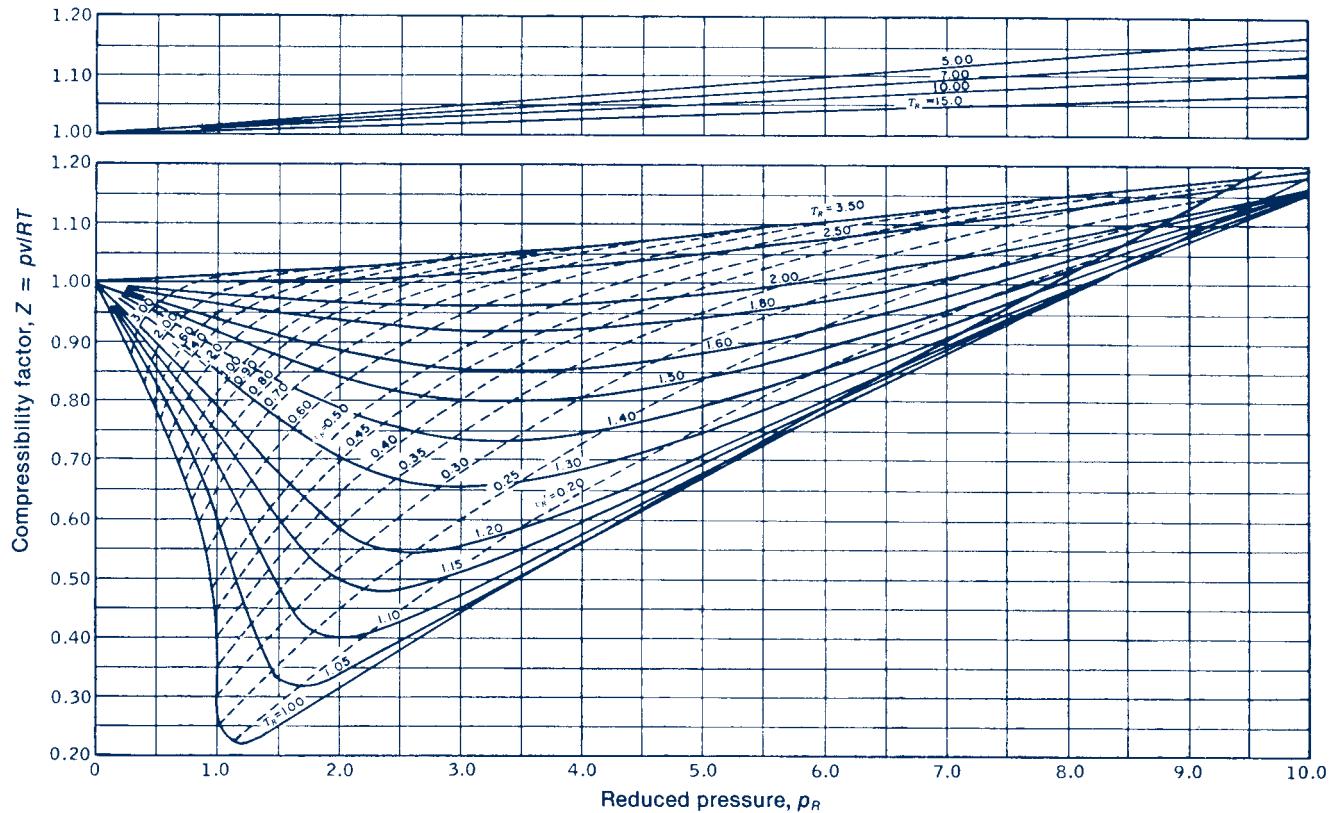


Figure A-2 Generalized compressibility chart, $p_R \leq 10.0$. Source: E. F. Obert, *Concepts of Thermodynamics*, McGraw-Hill, New York, 1960.

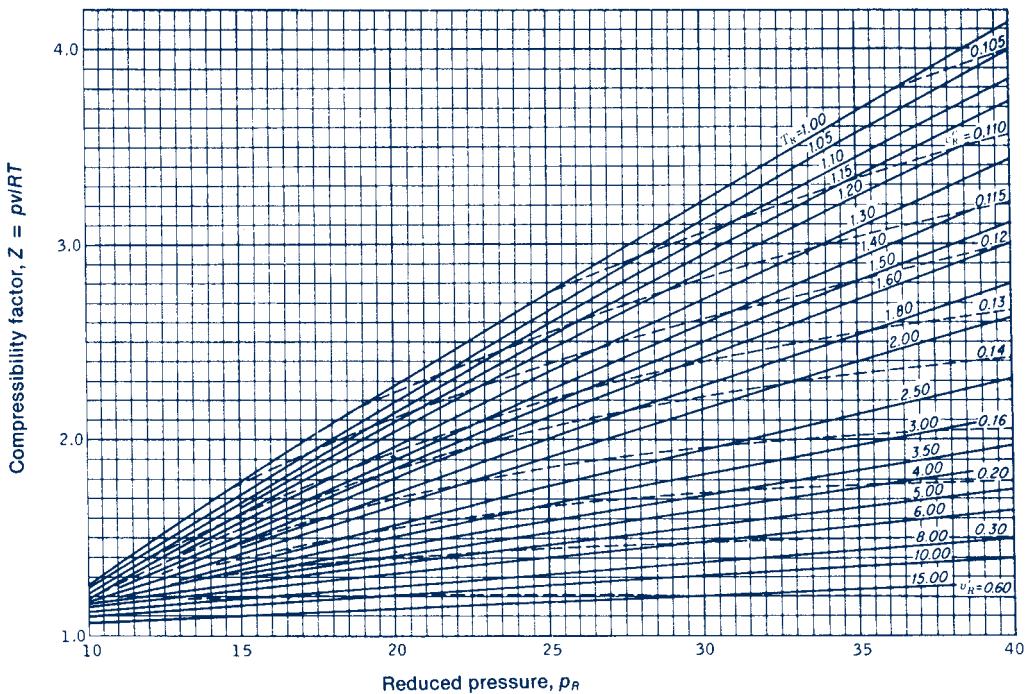


Figure A-3 Generalized compressibility chart, $10 \leq p_R \leq 40$. Source: E. F. Obert. *Concepts of Thermodynamics*, McGraw-Hill, New York, 1960.

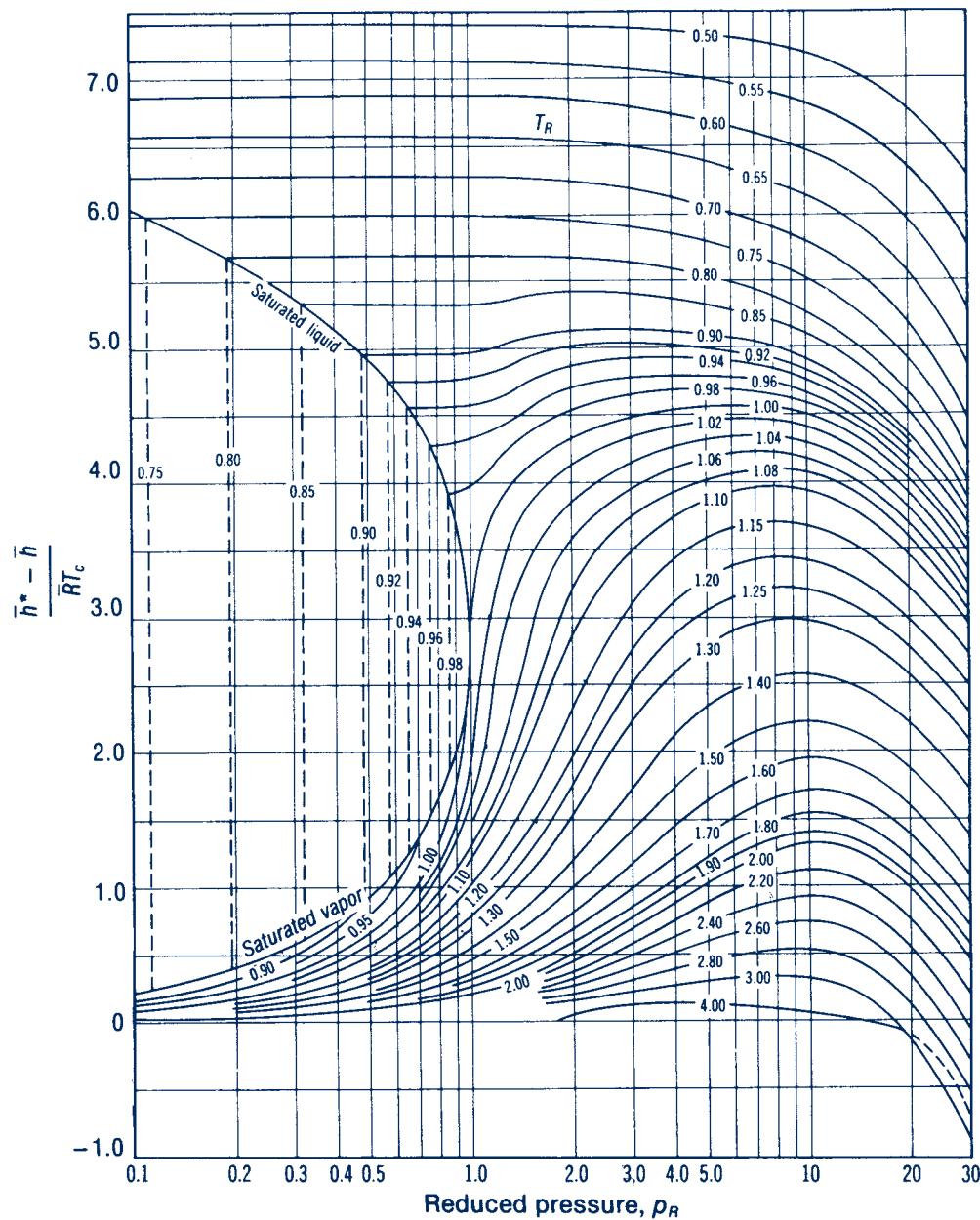


Figure A-4 Generalized enthalpy correction chart. Source: Adapted from G. J. Van Wylen and R. E. Sonntag, *Fundamentals of Classical Thermodynamics*, 3rd. ed., English/SI, Wiley, New York, 1986.

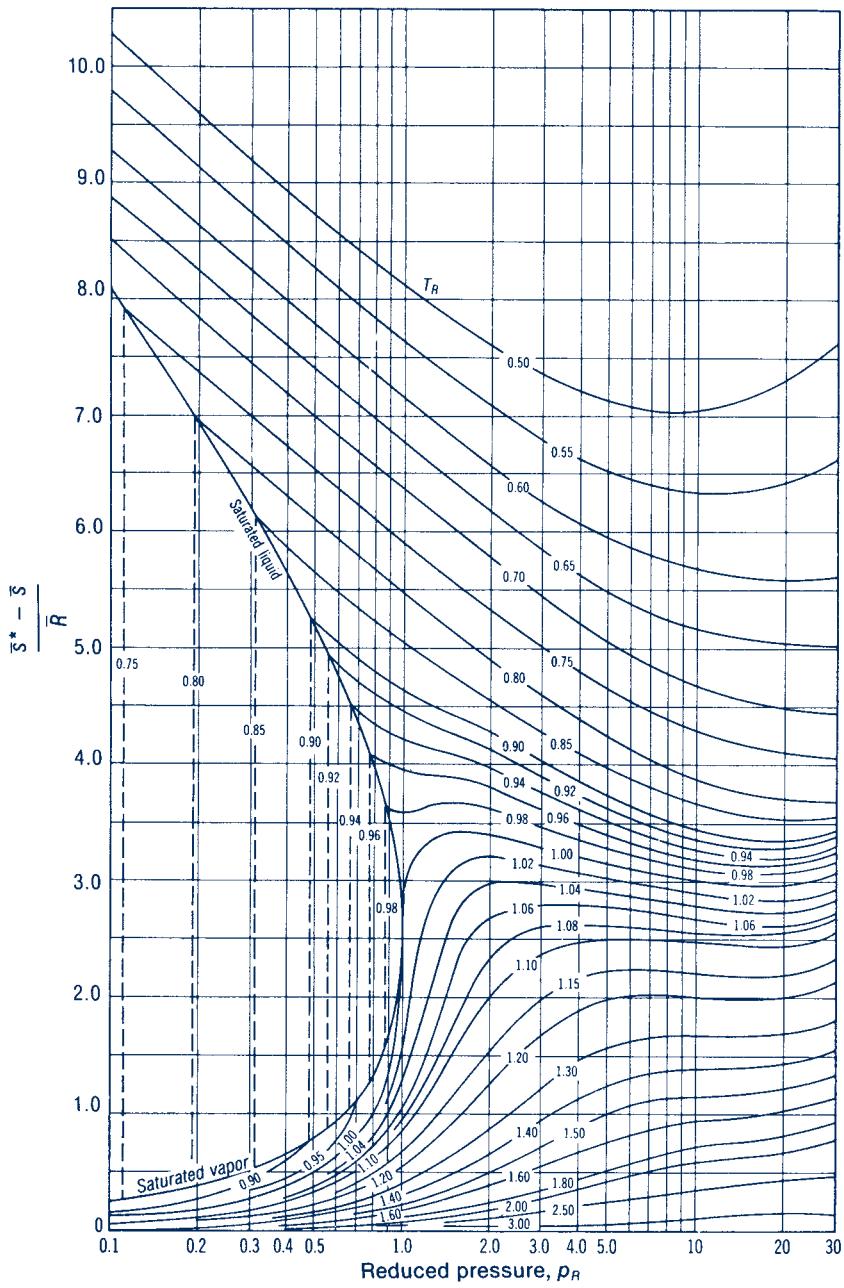


Figure A-5 Generalized entropy correction chart. Source: Adapted from G. J. Van Wylen and R. E. Sonntag, *Fundamentals of Classical Thermodynamics*, 3rd. ed., English/SI, Wiley, New York, 1986.

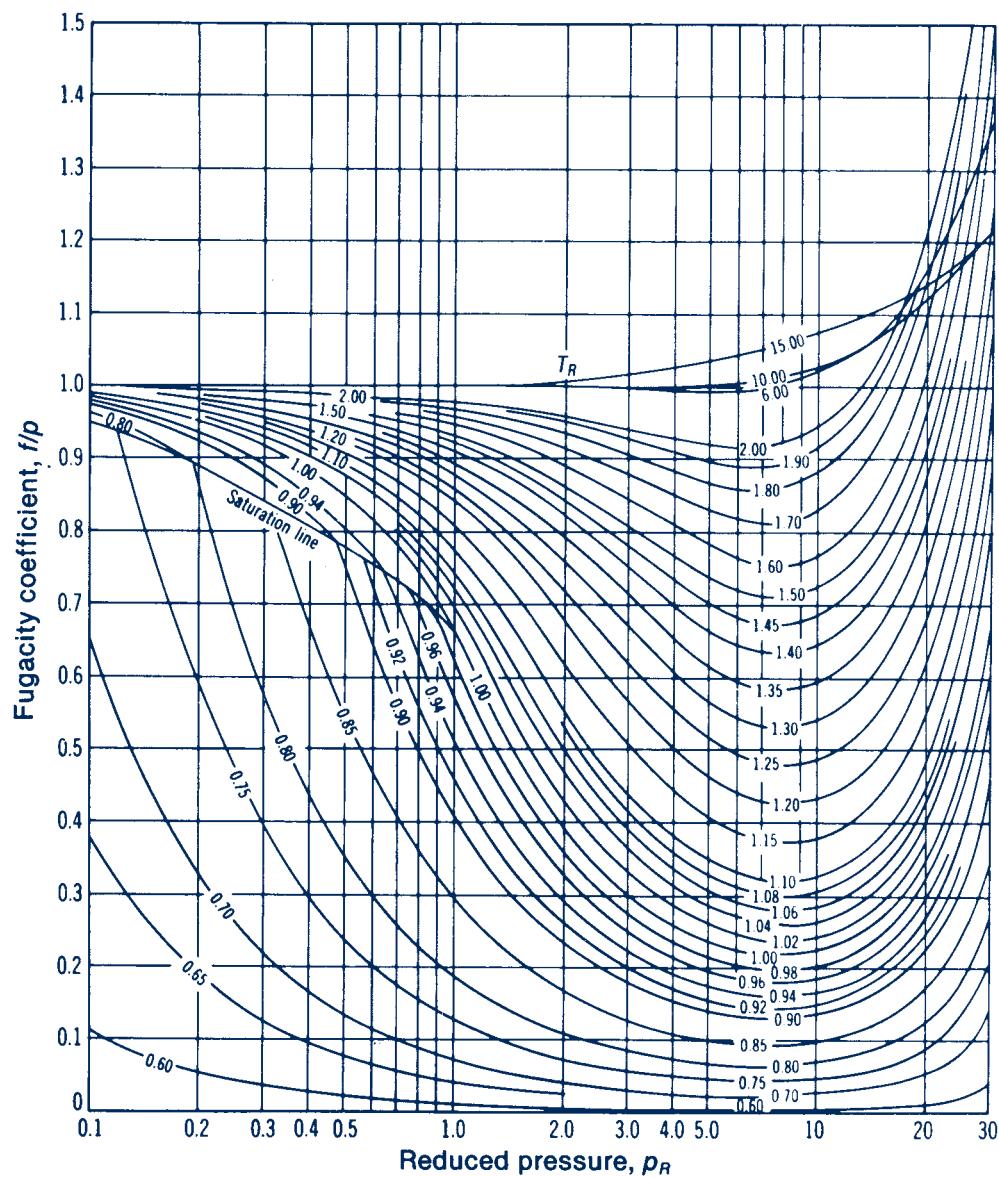


Figure A-6 Generalized fugacity coefficient chart. Source: G. J. Van Wylen and R. E. Sonntag, *Fundamentals of Classical Thermodynamics*, 3rd. ed., English/SI, Wiley, New York, 1986.

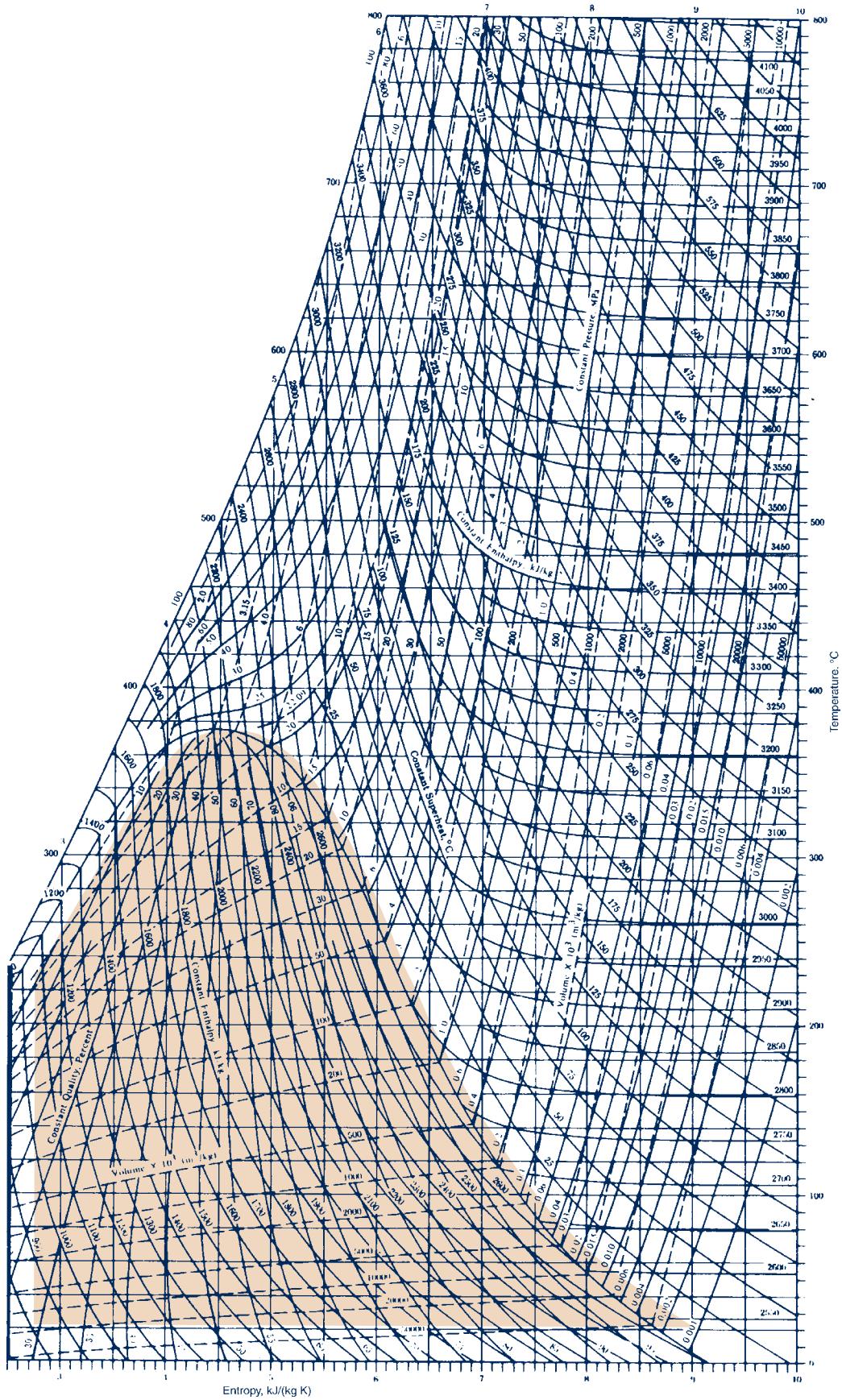


Figure A-7 Temperature-entropy diagram for water (SI units). Source: J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York, 1978.

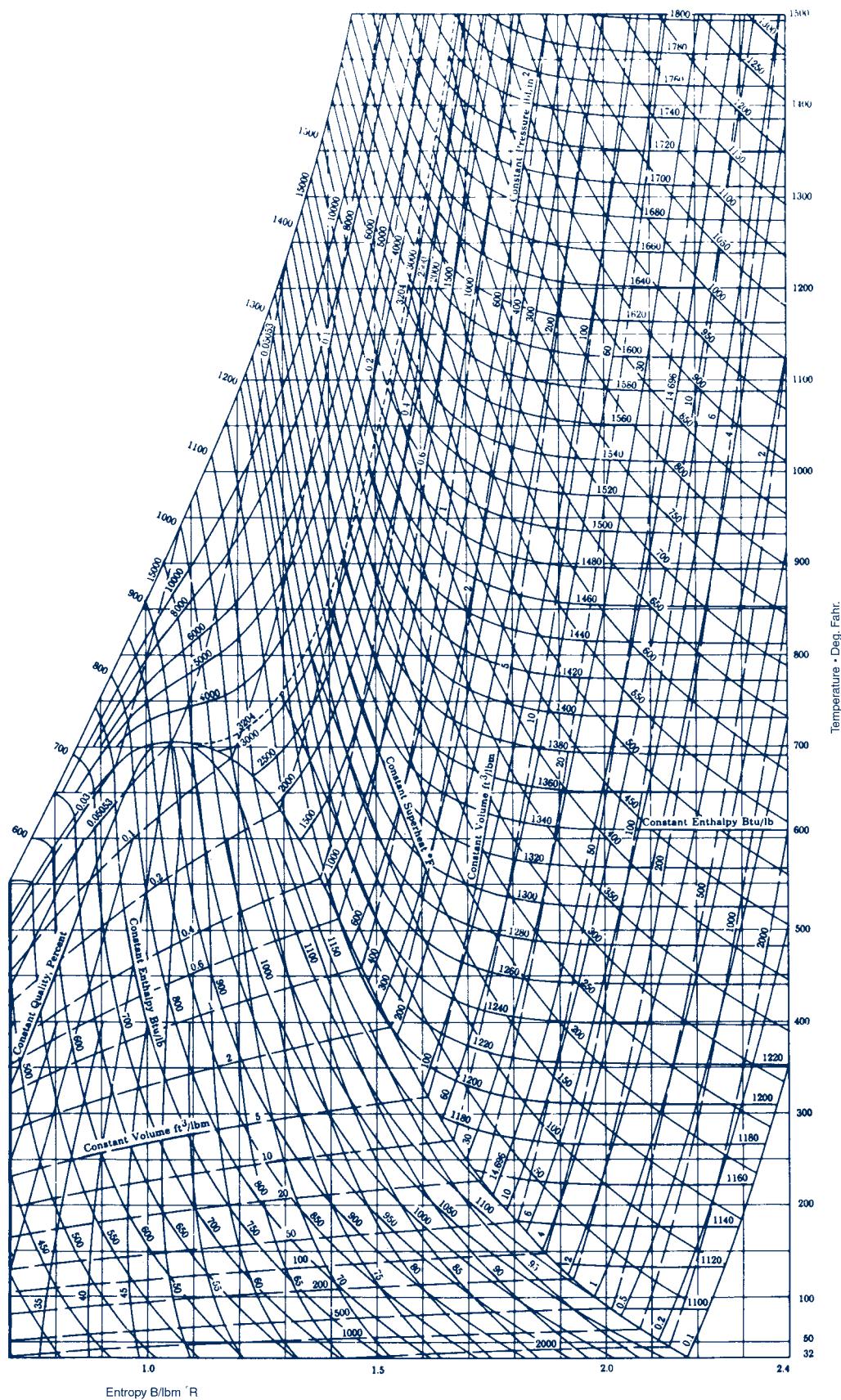


Figure A-7E Temperature-entropy diagram for water (English units). *Source:* J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York, 1969.

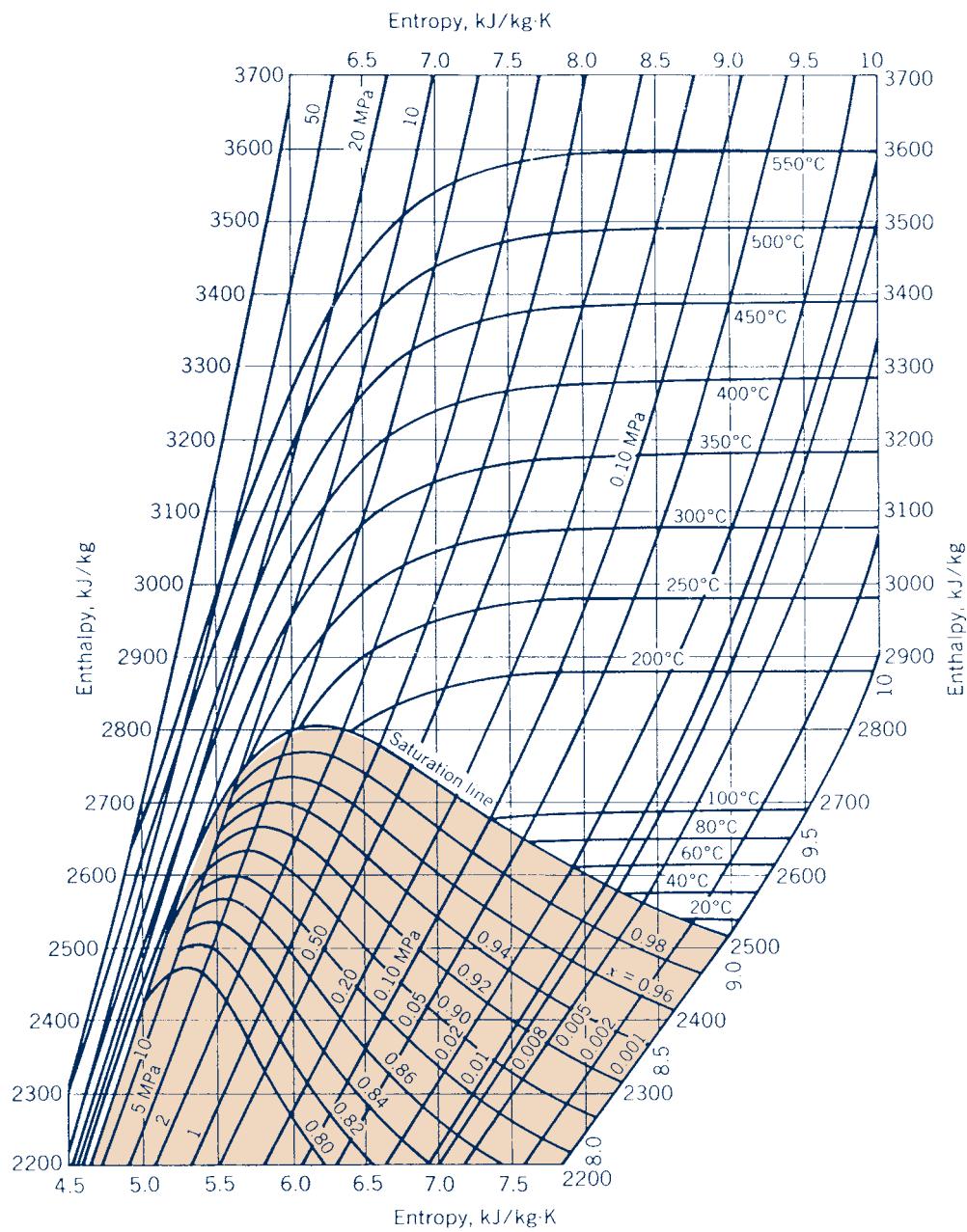


Figure A-8 Enthalpy-entropy diagram for water (SI units). Source: J. B. Jones and G. A. Hawkins, *Engineering Thermodynamics*, 2nd ed., Wiley, New York, 1986.

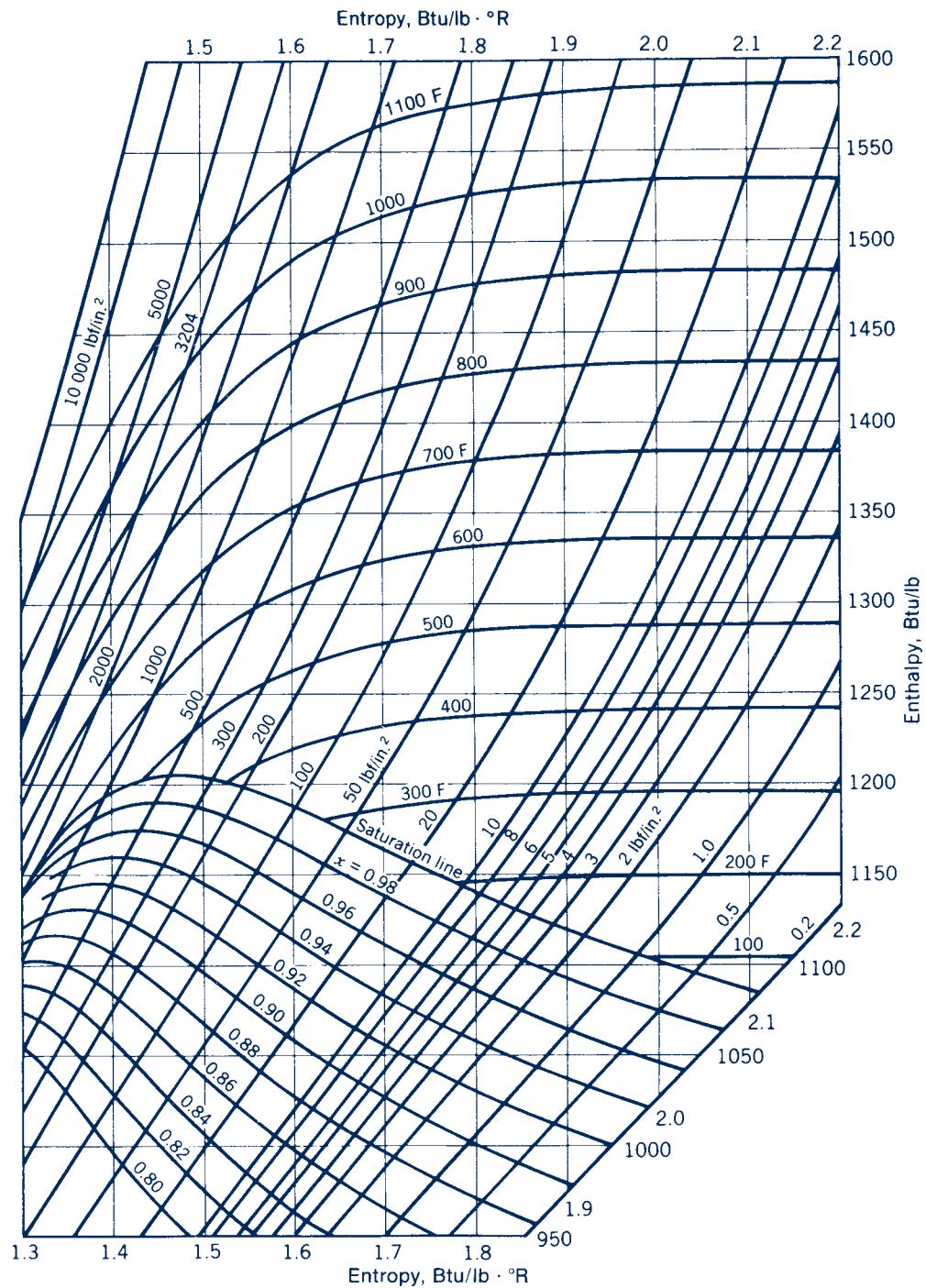


Figure A-8E Enthalpy-entropy diagram for water (English units). Source: J. B. Jones and G. A. Hawkins, *Engineering Thermodynamics*, 2nd ed., Wiley, New York, 1986.

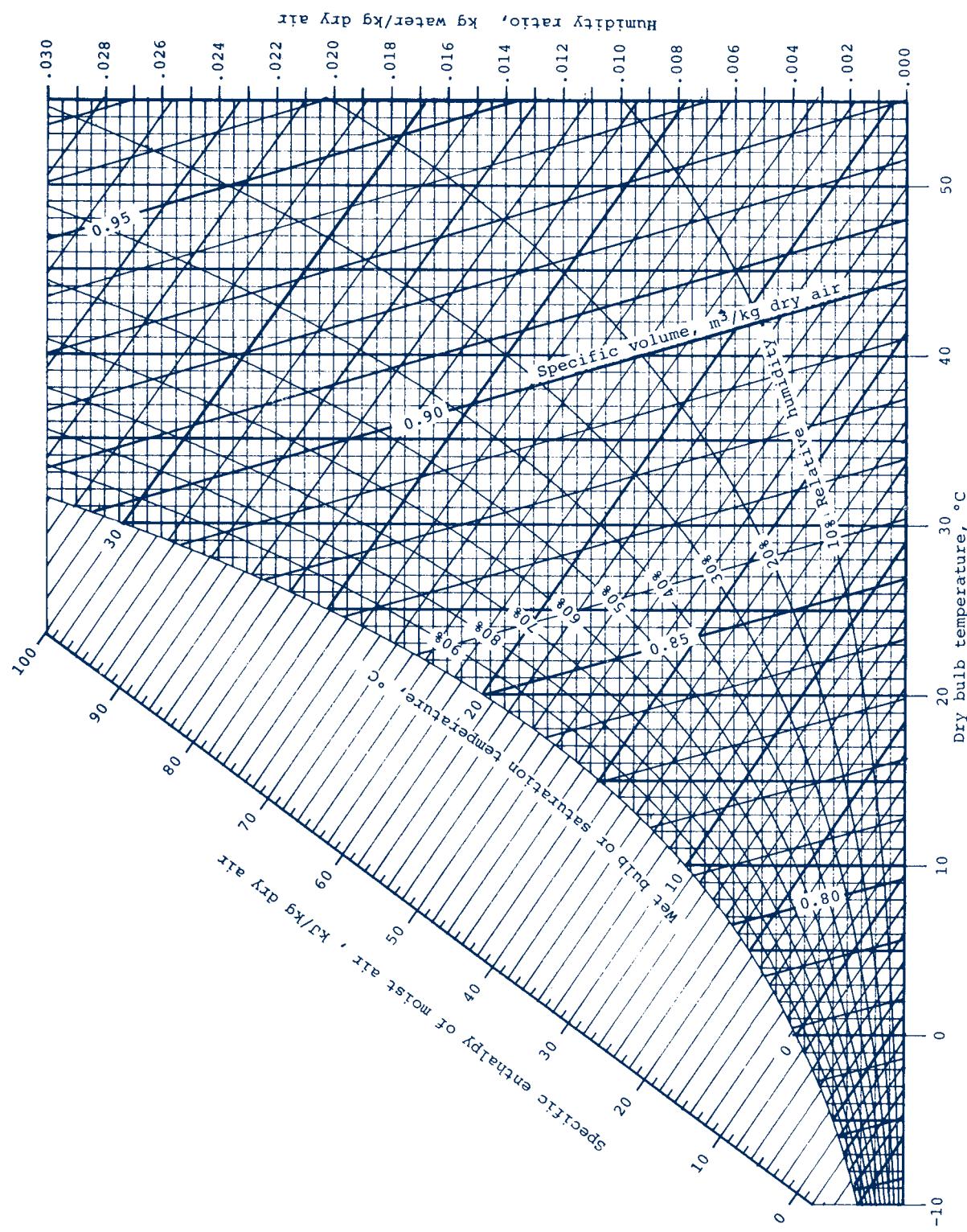


Figure A-9 Psychrometric chart for 1 atm (SI units). *Source:* Z. Zhang and M. B. Pate, "A Methodology for Implementing a Psychrometric Chart in a Computer Graphics System," *ASHRAE Transactions*, Vol. 94, Pt. 1, 1988.

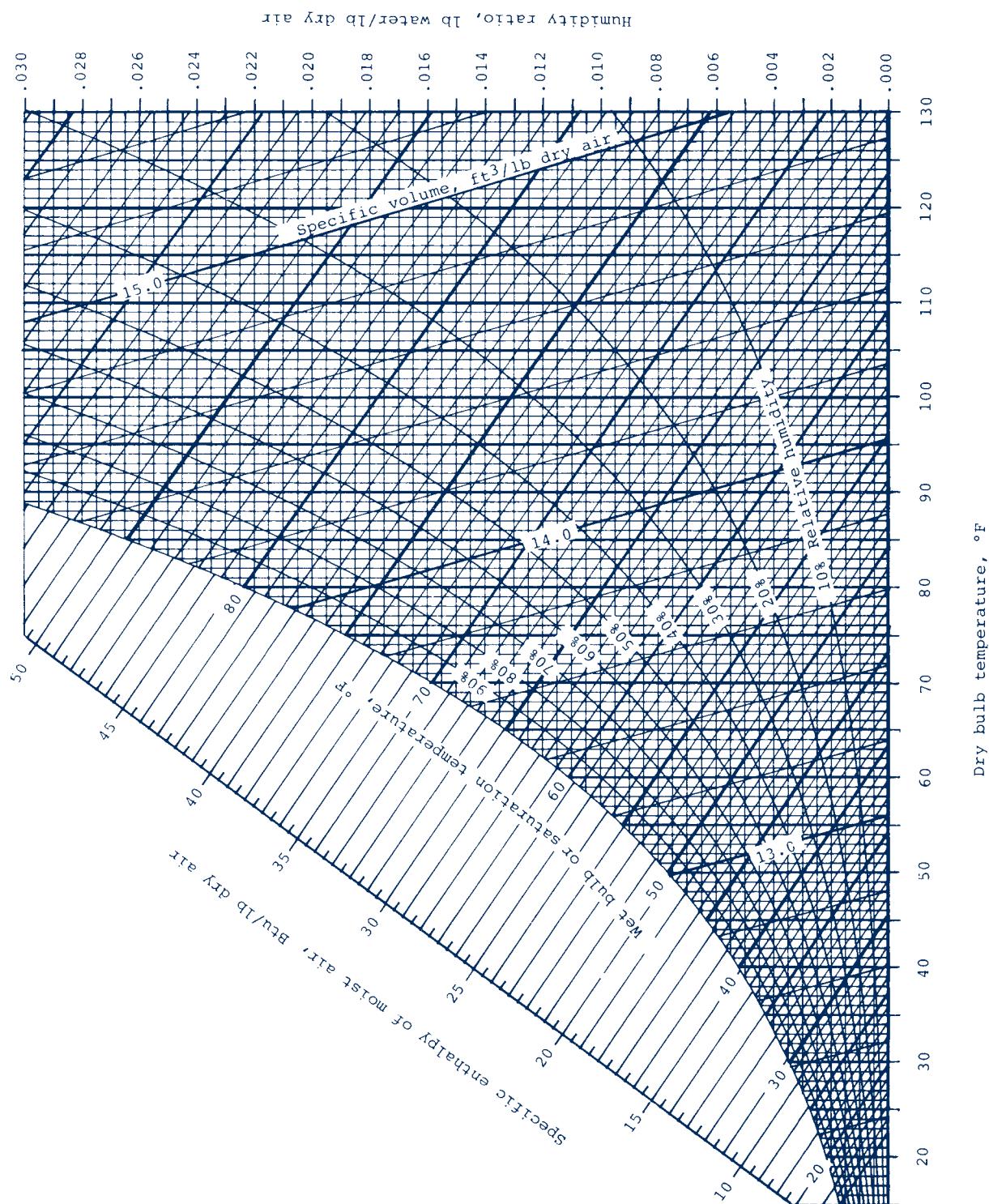


Figure A-9E Psychrometric chart for 1 atm (English units). Source: Z. Zhang and M. B. Pate, "A Methodology for Implementing a Psychrometric Chart in a Computer Graphics System," *ASHRAE Transactions*, Vol. 94, Pt. 1, 1988.

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Symbols

a	acceleration, activity	mep	mean effective pressure
A	area	mf	mass fraction
AF	air-fuel ratio	n	number of moles, polytropic exponent
bwr	back work ratio	N	number of components in the phase rule
c	specific heat of an incompressible substance, velocity of sound	p	pressure
c	unit cost	p_{atm}	atmospheric pressure
\dot{C}	cost rate	p_i	pressure associated with mixture component i , partial pressure of i
C_aH_b	hydrocarbon fuel	p_r	relative pressure as used in Tables A-22
c_p	specific heat at constant pressure, $\partial h/\partial T)_p$	p_R	reduced pressure: p/p_c
c_v	specific heat at constant volume, $\partial u/\partial T)_v$	P	number of phases in the phase rule
c_{p0}	specific heat c_p at zero pressure	\mathbf{P}	electric dipole moment per unit volume
e, E	energy per unit of mass, energy	pe, PE	potential energy per unit of mass, potential energy
e, E	exergy per unit of mass, exergy	\dot{q}	heat flux
e_f, \dot{E}_f	specific flow exergy, flow exergy rate	\dot{Q}	heat transfer
E_d, \dot{E}_d	exergy destruction, exergy destruction rate	$\dot{\dot{Q}}$	heat transfer rate
E_q, \dot{E}_q	exergy transfer accompanying heat transfer, rate of exergy transfer accompanying heat transfer	\dot{Q}_x	conduction rate
E_w	exergy transfer accompanying work	\dot{Q}_c, \dot{Q}_e	convection rate, thermal radiation rate
\mathbf{E}	electric field strength	r	compression ratio
\mathcal{E}	electrical potential, electromotive force (emf)	r_c	cutoff ratio
f	fugacity	R	gas constant: \bar{R}/M , resultant force, electric resistance
\bar{f}_i	fugacity of component i in a mixture	\bar{R}	universal gas constant
F	degrees of freedom in the phase rule	s, S	entropy per unit of mass, entropy
\mathbf{F}, F	force vector, force magnitude	s°	entropy function as used in Tables A-22, absolute entropy at the standard reference pressure as used in Table A-23
FA	fuel-air ratio	t	time
g	acceleration of gravity	T	temperature
g, G	Gibbs function per unit of mass, Gibbs function	T_R	reduced temperature: T/T_c
\bar{g}_f°	Gibbs function of formation per mole at standard state	\mathcal{T}	torque
h, H	enthalpy per unit of mass, enthalpy	u, U	internal energy per unit of mass, internal energy
h	heat transfer coefficient	v, V	specific volume, volume
\mathbf{H}	magnetic field strength	\mathbf{V}, V	velocity vector, velocity magnitude
\bar{h}_f°	enthalpy of formation per mole at standard state	v_r	relative volume as used in Tables A-22
\bar{h}_{RP}	enthalpy of combustion per mole	v'_R	pseudoreduced specific volume: $\bar{v}/(\bar{R}T_c/p_c)$
HHV	higher heating value	V_i	volume associated with mixture component i , partial volume of i
i	electric current	W	work
k	specific heat ratio: c_p/c_v	\dot{W}	rate of work, or power
k	Boltzmann constant	x	quality, position
K	equilibrium constant	X	extensive property
ke, KE	kinetic energy per unit of mass, kinetic energy	y	mole fraction, mass flow rate ratio
l, L	length	z	elevation, position
LHV	lower heating value	Z	compressibility factor, electric charge
m	mass	\dot{Z}	cost rate of owning/operating
\dot{m}	mass flow rate		
M	molecular weight, Mach number		
\mathbf{M}	magnetic dipole moment per unit volume		

Greek Letters

α	isentropic compressibility
β	coefficient of performance for a refrigerator, volume expansivity
γ	coefficient of performance for a heat pump, activity coefficient
Δ	change = final minus initial
ε	exergetic (second law) efficiency, emissivity, extent of reaction
η	efficiency, effectiveness
θ	temperature
κ	thermal conductivity, isothermal compressibility
μ	chemical potential
μ_J	Joule–Thomson coefficient
ν	stoichiometric coefficient
ρ	density
$\sigma, \dot{\sigma}$	entropy production, rate of entropy production
σ	normal stress, Stefan–Boltzmann constant
Σ	summation
τ	surface tension
ϕ	relative humidity
ψ, Ψ	Helmholtz function per unit of mass, Helmholtz function
ω	humidity ratio (specific humidity), angular velocity

Subscripts

a	dry air
ad	adiabatic
as	adiabatic saturation
ave	average
b	boundary
c	property at the critical point, compressor, overall system
cv	control volume
cw	cooling water
C	cold reservoir, low temperature
db	dry bulb
e	state of a substance exiting a control volume
e	exergy reference environment
f	property of saturated liquid, temperature of surroundings, final value
F	fuel
fg	difference in property for saturated vapor and saturated liquid

g	property of saturated vapor
H	hot reservoir, high temperature
i	state of a substance entering a control volume, mixture component
i	initial value, property of saturated solid
I	irreversible
ig, if	difference in property for saturated vapor (saturated liquid) and saturated solid
isol	isolated
int rev	internally reversible
j	portion of the boundary, number of components present in a mixture
n	normal component
p	pump
ref	reference value or state
reg	regenerator
res	reservoir
P	products
R	reversible, reactants
s	isentropic
sat	saturated
surr	surroundings
t	turbine
tp	triple point
0	property at the dead state, property of the surroundings
o	stagnation property
v	vapor
w	water
wb	wet bulb
x	upstream of a normal shock
y	downstream of a normal shock
1,2,3	different states of a system, different locations in space

Superscripts

ch	chemical exergy
e	component of the exergy reference environment
–	bar over symbol denotes property on a molar basis (over X, V, H, S, U, Ψ, G , the bar denotes partial molal property)
.	dot over symbol denotes time rate
°	property at standard state or standard pressure
*	ideal gas, quantity corresponding to sonic velocity

How to Use This Book Effectively

This book is organized by chapters and sections within chapters. For a listing of contents, see pp. ix–xvi. Fundamental concepts and associated equations within each section lay the foundation for applications of engineering thermodynamics provided in solved examples, end-of-chapter problems and exercises, and accompanying discussions. **Boxed material** within sections of the book allows you to explore selected topics in greater depth, as in the boxed discussion of properties and nonproperties on p. 10.

Contemporary issues related to thermodynamics are introduced throughout the text with three unique features: **ENERGY & ENVIRONMENT** discussions explore issues related to energy resource use and the environment, as in the discussion of hybrid vehicles on p. 39. **BIOCONNECTIONS** tie topics to applications in bioengineering and biomedicine, as in the discussion of control volumes of living things and their organs on p. 7.

Horizons  link subject matter to emerging technologies and thought-provoking issues, as in the discussion of nanotechnology on p. 15.

Other core features of this book that facilitates your study and contributes to your understanding include:

Examples

- ▶ Numerous annotated solved examples are provided that feature the **solution methodology** presented in Sec. 1.9 and illustrated in Example 1.1. We encourage you to study these examples, including the accompanying comments.
- ▶ Each solved example concludes with a list of the **Skills Developed** in solving the example and a **Quick Quiz** that allows an immediate check of understanding.
- ▶ Less formal examples are given throughout the text. They open with ▶ **FOR EXAMPLE** and close with ◀◀◀◀◀. These examples also should be studied.

Exercises

- ▶ Each chapter has a set of discussion questions under the heading ▶ **EXERCISES: THINGS ENGINEERS THINK ABOUT** that may be done on an individual or small-group basis. They allow you to gain a deeper understanding of the text material, think critically, and test yourself.
- ▶ A large number of end-of-chapter problems also are provided under the heading ▶ **PROBLEMS: DEVELOPING ENGINEERING SKILLS**. The problems are sequenced to coordinate with the subject matter and are listed in increasing order of difficulty. The problems are also classified under headings to expedite the process of selecting review problems to solve. Answers to selected problems are provided on the **student companion website** that accompanies this book.
- ▶ Because one purpose of this book is to help you prepare to use thermodynamics in engineering practice, design considerations related to thermodynamics are included. Every chapter has a set of problems under the heading ▶ **DESIGN & OPEN ENDED PROBLEMS: EXPLORING ENGINEERING PRACTICE** that provide opportunities for practicing creativity, formulating and solving design and open-ended problems, using the Internet and library resources to find relevant information, making engineering judgments, and developing communications skills. See, for example, problem 1.10 D on p. 35.

Further Study Aids

- ▶ Each chapter opens with an introduction giving the **engineering context**, stating the **chapter objective**, and listing the **learning outcomes**.
- ▶ Each chapter concludes with a ▶ **CHAPTER SUMMARY AND STUDY GUIDE** that provides a point of departure to study for examinations.
- ▶ For easy reference, each chapter also concludes with lists of ▶ **KEY ENGINEERING CONCEPTS** and ▶ **KEY EQUATIONS**.
- ▶ Important terms are listed in the margins and coordinated with the text material at those locations.
- ▶ Important equations are set off by a color screen, as for Eq. 1.8.
- ▶ **TAKE NOTE...** in the margin provides just-in-time information that illuminates the current discussion, as on p. 8, or refines our problem-solving methodology, as on p. 12 and p. 22.
- ▶  in the margin identifies an animation that reinforces the text presentation at that point. Animations can be viewed by going to the **student companion website** for this book. See **TAKE NOTE...** on p. 8 for further detail about accessing animations.
- ▶  in the margin denotes end-of-chapter problems where the use of appropriate computer software is recommended.
- ▶ For quick reference, conversion factors and important constants are provided on the next page.
- ▶ A list of symbols is provided on the inside back cover.

Conversion Factors

Mass and Density

1 kg	= 2.2046 lb
1 g/cm ³	= 10 ³ kg/m ³
1 g/cm ³	= 62.428 lb/ft ³
1 lb	= 0.4536 kg
1 lb/ft ³	= 0.016018 g/cm ³
1 lb/ft ³	= 16.018 kg/m ³

Length

1 cm	= 0.3937 in.
1 m	= 3.2808 ft
1 in.	= 2.54 cm
1 ft	= 0.3048 m

Velocity

1 km/h	= 0.62137 mile/h
1 mile/h	= 1.6093 km/h

Volume

1 cm ³	= 0.061024 in. ³
1 m ³	= 35.315 ft ³
1 L	= 10 ⁻³ m ³
1 L	= 0.0353 ft ³
1 in. ³	= 16.387 cm ³
1 ft ³	= 0.028317 m ³
1 gal	= 0.13368 ft ³
1 gal	= 3.7854 × 10 ⁻³ m ³

Force

1 N	= 1 kg · m/s ²
1 N	= 0.22481 lbf
1 lbf	= 32.174 lb · ft/s ²
1 lbf	= 4.4482 N

Pressure

1 Pa	= 1 N/m ²
	= 1.4504 × 10 ⁻⁴ lbf/in. ²
1 bar	= 10 ⁵ N/m ²
1 atm	= 1.01325 bar
1 lbf/in. ²	= 6894.8 Pa
1 lbf/in. ²	= 144 lbf/ft ²
1 atm	= 14.696 lbf/in. ²

Energy and Specific Energy

1 J	= 1 N · m = 0.73756 ft · lbf
1 kJ	= 737.56 ft · lbf
1 kJ	= 0.9478 Btu
1 kJ/kg	= 0.42992 Btu/lb
1 ft · lbf	= 1.35582 J
1 Btu	= 778.17 ft · lbf
1 Btu	= 1.0551 kJ
1 Btu/lb	= 2.326 kJ/kg
1 kcal	= 4.1868 kJ

Energy Transfer Rate

1 W	= 1 J/s = 3.413 Btu/h
1 kW	= 1.341 hp
1 Btu/h	= 0.293 W
1 hp	= 2545 Btu/h
1 hp	= 550 ft · lbf/s
1 hp	= 0.7457 kW

Specific Heat

1 kJ/kg · K	= 0.238846 Btu/lb · °R
1 kcal/kg · K	= 1 Btu/lb · °R
1 Btu/h · °R	= 4.1868 kJ/kg · K

Others

1 ton of refrigeration = 200 Btu/min = 211 kJ/min
1 volt = 1 watt per ampere

Constants

Universal Gas Constant

$$\bar{R} = \begin{cases} 8.314 \text{ kJ/kmol} \cdot \text{K} \\ 1545 \text{ ft} \cdot \text{lbf/lbmol} \cdot {}^{\circ}\text{R} \\ 1.986 \text{ Btu/lbmol} \cdot {}^{\circ}\text{R} \end{cases}$$

Standard Acceleration of Gravity

$$g = \begin{cases} 9.80665 \text{ m/s}^2 \\ 32.174 \text{ ft/s}^2 \end{cases}$$

Standard Atmospheric Pressure

$$1 \text{ atm} = \begin{cases} 1.01325 \text{ bar} \\ 14.696 \text{ lbf/in.}^2 \\ 760 \text{ mm Hg} = 29.92 \text{ in. Hg} \end{cases}$$

Temperature Relations

$$\begin{aligned} T({}^{\circ}\text{R}) &= 1.8 T(\text{K}) \\ T({}^{\circ}\text{C}) &= T(\text{K}) - 273.15 \\ T({}^{\circ}\text{F}) &= T({}^{\circ}\text{R}) - 459.67 \end{aligned}$$