5.6 THE CONSTANT-VOLUME AND CONSTANT-PRESSURE SPECIFIC HEATS

In this section we will consider a homogeneous phase of a substance of constant composition. This phase may be a solid, a liquid, or a gas, but no change of phase will occur. We will then define a variable termed the *specific heat*, the amount of heat required per unit mass to raise the temperature by one degree. Since it would be of interest to examine the relation between the specific heat and other thermodynamic variables, we note first that the heat transfer is given by Eq. 5.10. Neglecting changes in kinetic and potential energies, and assuming a simple compressible substance and a quasi-equilibrium process, for which the work in Eq. 5.10 is given by Eq. 4.2, we have

$$\delta Q = dU + \delta W = dU + P\, dV$$

We find that this expression can be evaluated for two separate special cases:

1. Constant volume, for which the work term $(P\, dV)$ is zero, so that the specific heat (at constant volume) is

$$C_v = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v \qquad (5.14)$$

2. Constant pressure, for which the work term can be integrated and the resulting PV terms at the initial and final states can be associated with the internal energy terms, as in Section 5.5, thereby leading to the conclusion that the heat transfer can be expressed in terms of the enthalpy change. The corresponding specific heat (at constant pressure) is

$$C_p = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p \qquad (5.15)$$

Note that in each of these special cases, the resulting expression, Eq. 5.14 or 5.15, contains only thermodynamic properties, from which we conclude that the constant-volume and constant-pressure specific heats must themselves be thermodynamic properties. This means that, although we began this discussion by considering the amount of heat transfer required to cause a unit temperature change and then proceeded through a very specific development leading to Eq. 5.14 (or 5.15), the result ultimately expresses a relation among a set of thermodynamic properties and therefore constitutes a definition that is independent of the particular process leading to it (in the same sense that the definition of enthalpy in the previous section is independent of the process used to illustrate one situation in which the property is useful in a thermodynamic analysis). As an example, consider the two identical fluid masses shown in Fig. 5.9. In the first system 100 kJ of heat is transferred to it, and in the second system 100 kJ of work is done on it. Thus, the change of internal energy is the same for each, and therefore the final state and the final temperature are the same in each. In accordance with Eq. 5.14, therefore, exactly the same value for the average constant-volume specific heat would be found for this substance for the two processes, even though the two processes are very different as far as heat transfer is concerned.

FIGURE 5.9 Sketch showing two ways in which a given $\Delta U/m$ may be achieved.
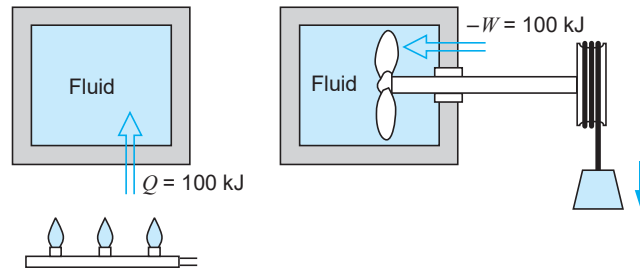
Solids and Liquids

As a special case, consider either a solid or a liquid. Since both of these phases are nearly incompressible,

$$dh = du + d(Pv) \approx du + v\, dP \qquad (5.16)$$

Also, for both of these phases, the specific volume is very small, such that in many cases

$$dh \approx du \approx C\, dT \qquad (5.17)$$

where C is either the constant-volume or the constant-pressure specific heat, as the two would be nearly the same. In many processes involving a solid or a liquid, we might further assume that the specific heat in Eq. 5.17 is constant (unless the process occurs at low temperature or over a wide range of temperatures). Equation 5.17 can then be integrated to

$$h_2 - h_1 \simeq u_2 - u_1 \simeq C(T_2 - T_1) \qquad (5.18)$$

Specific heats for various solids and liquids are listed in Tables A.3, A.4 and F.2, F.3.

In other processes for which it is not possible to assume constant specific heat, there may be a known relation for C as a function of temperature. Equation 5.17 could then also be integrated.

5.7 | THE INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEAT OF IDEAL GASES

In general, for any substance the internal energy u depends on the two independent properties specifying the state. For a low-density gas, however, u depends primarily on T and much less on the second property, P or v. For example, consider several values for superheated vapor steam from Table B.1.3, shown in Table 5.1. From these values, it is evident that u depends strongly on T but not much on P. Also, we note that the dependence of u on P is

TABLE 5.1

Internal Energy for Superheated Vapor Steam

T, °C	P, kPa			
	10	**100**	**500**	**1000**
200	2661.3	2658.1	2642.9	2621.9
700	3479.6	3479.2	3477.5	3475.4
1200	4467.9	4467.7	4466.8	4465.6

less at low pressure and is much less at high temperature; that is, as the density decreases, so does dependence of u on P (or v). It is therefore reasonable to extrapolate this behavior to very low density and to assume that as gas density becomes so low that the ideal-gas model is appropriate, internal energy does not depend on pressure at all but is a function only of temperature. That is, for an ideal gas,

$$Pv = RT \quad \text{and} \quad u = f(T) \text{ only} \tag{5.19}$$

The relation between the internal energy u and the temperature can be established by using the definition of constant-volume specific heat given by Eq. 5.14:

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v$$

Because the internal energy of an ideal gas is not a function of specific volume, for an ideal gas we can write

$$C_{v0} = \frac{du}{dT}$$

$$du = C_{v0} \, dT \tag{5.20}$$

where the subscript 0 denotes the specific heat of an ideal gas. For a given mass m,

$$dU = mC_{v0} \, dT \tag{5.21}$$

From the definition of enthalpy and the equation of state of an ideal gas, it follows that

$$h = u + Pv = u + RT \tag{5.22}$$

Since R is a constant and u is a function of temperature only, it follows that the enthalpy, h, of an ideal gas is also a function of temperature only. That is,

$$h = f(T) \tag{5.23}$$

The relation between enthalpy and temperature is found from the constant-pressure specific heat as defined by Eq. 5.15:

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p$$

Since the enthalpy of an ideal gas is a function of the temperature only and is independent of the pressure, it follows that

$$C_{p0} = \frac{dh}{dT}$$

$$dh = C_{p0} \, dT \tag{5.24}$$

For a given mass m,

$$dH = mC_{p0} \, dT \tag{5.25}$$

The consequences of Eqs. 5.20 and 5.24 are demonstrated in Fig. 5.10, which shows two lines of constant temperature. Since internal energy and enthalpy are functions of temperature only, these lines of constant temperature are also lines of constant internal
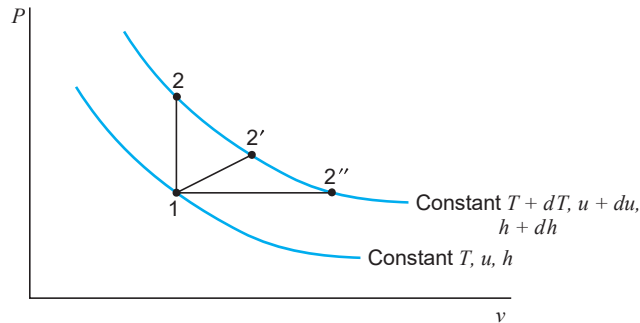
FIGURE 5.10 P–v diagram for an ideal gas.

energy and constant enthalpy. From state 1 the high temperature can be reached by a variety of paths, and in each case the final state is different. However, regardless of the path, the change in internal energy is the same, as is the change in enthalpy, for lines of constant temperature are also lines of constant u and constant h.

Because the internal energy and enthalpy of an ideal gas are functions of temperature only, it also follows that the constant-volume and constant-pressure specific heats are also functions of temperature only. That is,

$$C_{v0} = f(T), \quad C_{p0} = f(T) \tag{5.26}$$

Because all gases approach ideal-gas behavior as the pressure approaches zero, the ideal-gas specific heat for a given substance is often called the *zero-pressure specific heat*, and the zero-pressure, constant-pressure specific heat is given the symbol C_{p0}. The zero-pressure, constant-volume specific heat is given the symbol C_{v0}. Figure 5.11 shows C_{p0} as a function
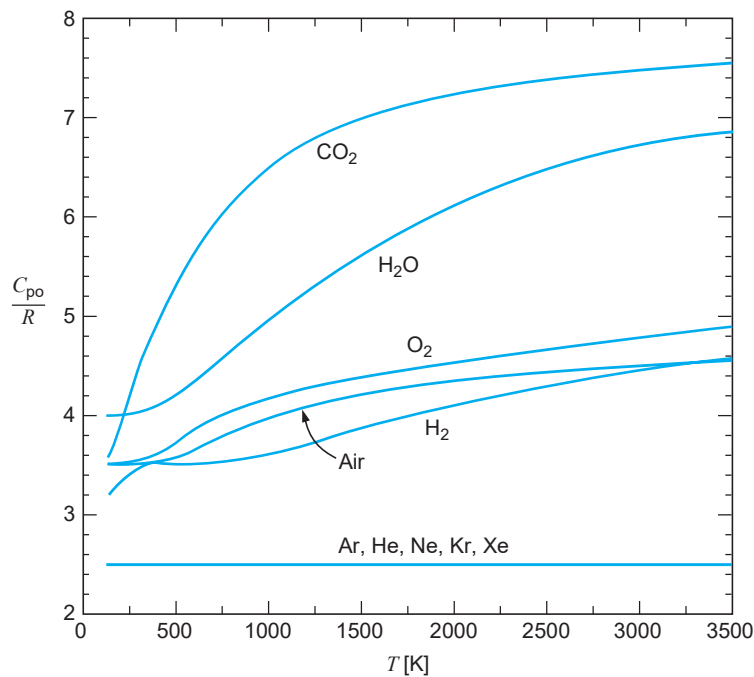
FIGURE 5.11 Heat capacity for some gases as a function of temperature.

of temperature for a number of substances. These values are determined by the techniques of statistical thermodynamics and will not be discussed here. A brief summary presentation of this subject is given in Appendix C. It is noted there that the principal factor causing specific heat to vary with temperature is molecular vibration. More complex molecules have multiple vibrational modes and therefore show greater temperature dependency, as is seen in Fig. 5.11. This is an important consideration when deciding whether or not to account for specific heat variation with temperature in any particular application.

A very important relation between the constant-pressure and constant-volume specific heats of an ideal gas may be developed from the definition of enthalpy:

$$h = u + Pv = u + RT$$

Differentiating and substituting Eqs. 5.20 and 5.24, we have

$$dh = du + R \, dT$$
$$C_{p0} \, dT = C_{v0} \, dT + R \, dT$$

Therefore,

$$C_{p0} - C_{v0} = R \tag{5.27}$$

On a mole basis this equation is written

$$\overline{C}_{p0} - \overline{C}_{v0} = \overline{R} \tag{5.28}$$

This tells us that the difference between the constant-pressure and constant-volume specific heats of an ideal gas is always constant, though both are functions of temperature. Thus, we need examine only the temperature dependency of one, and the other is given by Eq. 5.27.

Let us consider the specific heat C_{p0}. There are three possibilities to examine. The situation is simplest if we assume constant specific heat, that is, no temperature dependence. Then it is possible to integrate Eq. 5.24 directly to

$$h_2 - h_1 = C_{p0}(T_2 - T_1) \tag{5.29}$$

We note from Fig. 5.11 the circumstances under which this will be an accurate model. It should be added, however, that it may be a reasonable approximation under other conditions, especially if an average specific heat in the particular temperature range is used in Eq. 5.29. Values of specific heat at room temperature and gas constants for various gases are given in Table A.5 and F.4.

The second possibility for the specific heat is to use an analytical equation for C_{p0} as a function of temperature. Because the results of specific-heat calculations from statistical thermodynamics do not lend themselves to convenient mathematical forms, these results have been approximated empirically. The equations for C_{p0} as a function of temperature are listed in Table A.6 for a number of gases.

The third possibility is to integrate the results of the calculations of statistical thermodynamics from an arbitrary reference temperature to any other temperature T and to define a function

$$h_T = \int_{T_0}^{T} C_{p0} \, dT$$

This function can then be tabulated in a single-entry (temperature) table. Then, between any two states 1 and 2,

$$h_2 - h_1 = \int_{T_0}^{T_2} C_{p0} \, dT - \int_{T_0}^{T_1} C_{p0} \, dT = h_{T_2} - h_{T_1} \tag{5.30}$$

and it is seen that the reference temperature cancels out. This function h_T (and a similar function $u_T = h_T - RT$) is listed for air in Table A.7 and F.5. These functions are listed for other gases in Table A.8 and F.6.

To summarize the three possibilities, we note that using the ideal-gas tables, Tables A.7 and A.8, gives us the most accurate answer, but that the equations in Table A.6 would give a close empirical approximation. Constant specific heat would be less accurate, except for monatomic gases and gases below room temperature. It should be remembered that all these results are part of the ideal-gas model, which in many of our problems is not a valid assumption for the behavior of the substance.

EXAMPLE 5.8

Calculate the change of enthalpy as 1 kg of oxygen is heated from 300 to 1500 K. Assume ideal-gas behavior.

Solution

For an ideal gas, the enthalpy change is given by Eq. 5.24. However, we also need to make an assumption about the dependence of specific heat on temperature. Let us solve this problem in several ways and compare the answers.

Our most accurate answer for the ideal-gas enthalpy change for oxygen between 300 and 1500 K would be from the ideal-gas tables, Table A.8. This result is, using Eq. 5.30,

$$h_2 - h_1 = 1540.2 - 273.2 = 1267.0 \, \text{kJ/kg}$$

The empirical equation from Table A.6 should give a good approximation to this result. Integrating Eq. 5.24, we have

$$h_2 - h_1 = \int_{T_1}^{T_2} C_{p0} \, dT = \int_{\theta_1}^{\theta_2} C_{p0}(\theta) \times 1000 \, d\theta$$

$$= 1000 \left[0.88\theta - \frac{0.0001}{2}\theta^2 + \frac{0.54}{3}\theta^3 - \frac{0.33}{4}\theta^4 \right]_{\theta_1 = 0.3}^{\theta_2 = 1.5}$$

$$= 1241.5 \, \text{kJ/kg}$$

which is lower than the first result by 2.0%.

If we assume constant specific heat, we must be concerned about what value we are going to use. If we use the value at 300 K from Table A.5, we find, from Eq. 5.29, that

$$h_2 - h_1 = C_{p0}(T_2 - T_1) = 0.922 \times 1200 = 1106.4 \, \text{kJ/kg}$$

which is low by 12.7%. However, suppose we assume that the specific heat is constant at its value at 900 K, the average temperature. Substituting 900 K into the equation for

specific heat from Table A.6, we have

$$C_{p0} = 0.88 - 0.0001(0.9) + 0.54(0.9)^2 - 0.33(0.9)^3$$
$$= 1.0767 \text{ kJ/kg K}$$

Substituting this value into Eq. 5.29 gives the result

$$h_2 - h_1 = 1.0767 \times 1200 = 1292.1 \text{ kJ/kg}$$

which is high by about 2.0%, a much closer result than the one using the room temperature specific heat. It should be kept in mind that part of the model involving ideal gas with constant specific heat also involves a choice of what value is to be used.

EXAMPLE 5.9 A cylinder fitted with a piston has an initial volume of 0.1 m³ and contains nitrogen at 150 kPa, 25°C. The piston is moved, compressing the nitrogen until the pressure is 1 MPa and the temperature is 150°C. During this compression process heat is transferred from the nitrogen, and the work done on the nitrogen is 20 kJ. Determine the amount of this heat transfer.

Control mass:	Nitrogen.
Initial state:	P_1, T_1, V_1; state 1 fixed.
Final state:	P_2, T_2; state 2 fixed.
Process:	Work input known.
Model:	Ideal gas, constant specific heat with value at 300 K, Table A.5.

Analysis

From the first law we have

$$_1 Q_2 = m(u_2 - u_1) + _1 W_2$$

Solution

The mass of nitrogen is found from the equation of state with the value of R from Table A.5:

$$m = \frac{PV}{RT} = \frac{150 \text{ kPa} \times 0.1 \text{ m}^3}{0.2968 \dfrac{\text{kJ}}{\text{kg K}} \times 298.15 \text{ K}} = 0.1695 \text{ kg}$$

Assuming constant specific heat as given in Table A.5, we have

$$_1 Q_2 = mC_{v0}(T_2 - T_1) + _1 W_2$$
$$= 0.1695 \text{ kg} \times 0.745 \frac{\text{kJ}}{\text{kg K}} \times (150 - 25) \text{ K} - 20.0$$
$$= 15.8 - 20.0 = -4.2 \text{ kJ}$$

It would, of course, be somewhat more accurate to use Table A.8 than to assume constant specific heat (room temperature value), but often the slight increase in accuracy does not warrant the added difficulties of manually interpolating the tables.

EXAMPLE 5.9E   A cylinder fitted with a piston has an initial volume of 2 ft^3 and contains nitrogen at 20 lbf/in.^{2}, 80 F. The piston is moved, compressing the nitrogen until the pressure is 160 lbf/in.^{2} and the temperature is 300 F. During this compression process heat is transferred from the nitrogen, and the work done on the nitrogen is 9.15 Btu. Determine the amount of this heat transfer.

Control mass:	Nitrogen.
Initial state:	P_1, T_1, V_1; state 1 fixed.
Final state:	P_2, T_2; state 2 fixed.
Process:	Work input known.
Model:	Ideal gas, constant specific heat with value at 540 R, Table F.4.

Analysis

First law:
$$_1Q_2 = m(u_2 - u_1) + {_1W_2}$$

Solution

The mass of nitrogen is found from the equation of state with the value of R from Table F.4.

$$m = \frac{PV}{RT} = \frac{20\dfrac{\text{lbf}}{\text{in.}^2} \times 144 \times \dfrac{\text{in.}^2}{\text{ft}^2} 2\,\text{ft}^3}{55.15\dfrac{\text{ft lbf}}{\text{lbm } R} \times 540\,R} = 0.1934\,\text{lbm}$$

Assuming constant specific heat as given in Table F.4,

$$
\begin{aligned}
_1Q_2 &= mC_{v0}(T_2 - T_1) + {_1W_2} \\
&= 0.1934\,\text{lbm} \times 0.177\frac{\text{Btu}}{\text{lbm } R} \times (300 - 80)\,R - 9.15 \\
&= 7.53 - 9.15 = -1.62\,\text{Btu}
\end{aligned}
$$

It would, of course, be somewhat more accurate to use Table F.6 than to assume constant specific heat (room temperature value), but often the slight increase in accuracy does not warrant the added difficulties of manually interpolating the tables.

In-Text Concept Questions

g. To determine v or u for some liquid or solid, is it more important that I know P or T?

h. To determine v or u for an ideal gas, is it more important that I know P or T?

i. I heat 1 kg of a substance at constant pressure (200 kPa) 1 degree. How much heat is needed if the substance is water at 10°C, steel at 25°C, air at 325 K, or ice at −10°C.

5.8 THE FIRST LAW AS A RATE EQUATION

We frequently find it desirable to use the first law as a rate equation that expresses either the instantaneous or average rate at which energy crosses the control surface as heat and work and the rate at which the energy of the control mass changes. In so doing we are departing from a strictly classical point of view, because basically classical thermodynamics deals with systems that are in equilibrium, and time is not a relevant parameter for systems that are in equilibrium. However, since these rate equations are developed from the concepts of classical thermodynamics and are used in many applications of thermodynamics, they are included in this book. This rate form of the first law will be used in the development of the first law for the control volume in Section 6.2, and in this form the first law finds extensive applications in thermodynamics, fluid mechanics, and heat transfer.

Consider a time interval δt during which an amount of heat δQ crosses the control surface, an amount of work δW is done by the control mass, the internal energy change is ΔU, the kinetic energy change is ΔKE, and the potential energy change is ΔPE. From the first law we can write

$$\Delta U + \Delta\text{KE} + \Delta\text{PE} = \delta Q - \delta W$$

Dividing by δt, we have the average rate of energy transfer as heat work and increase of the energy of the control mass:

$$\frac{\Delta U}{\delta t} + \frac{\Delta\text{KE}}{\delta t} + \frac{\Delta\text{PE}}{\delta t} = \frac{\delta Q}{\delta t} - \frac{\delta W}{\delta t}$$

Taking the limit for each of these quantities as δt approaches zero, we have

$$\lim_{\delta t \to 0} \frac{\Delta U}{\delta t} = \frac{dU}{dt}, \quad \lim_{\delta t \to 0} \frac{\Delta(\text{KE})}{\delta t} = \frac{d(\text{KE})}{dt}, \quad \lim_{\delta t \to 0} \frac{\Delta(\text{PE})}{\delta t} = \frac{d(\text{PE})}{dt}$$

$$\lim_{\delta t \to 0} \frac{\delta Q}{\delta t} = \dot{Q} \quad \text{(the heat transfer rate)}$$

$$\lim_{\delta t \to 0} \frac{\delta W}{\delta t} = \dot{W} \quad \text{(the power)}$$

Therefore, the rate equation form of the first law is

$$\frac{dU}{dt} + \frac{d(\text{KE})}{dt} + \frac{d(\text{PE})}{dt} = \dot{Q} - \dot{W} \tag{5.31}$$

We could also write this in the form

$$\frac{dE}{dt} = \dot{Q} - \dot{W} \tag{5.32}$$

EXAMPLE 5.10   During the charging of a storage battery, the current i is 20 A and the voltage $\mathcal{E}$ is 12.8 V. The rate of heat transfer from the battery is 10 W. At what rate is the internal energy increasing?

Solution

Since changes in kinetic and potential energy are insignificant, the first law can be written as a rate equation in the form of Eq. 5.31:

$$\frac{dU}{dt} = \dot{Q} - \dot{W}$$

$$\dot{W} = \mathcal{E}i = -12.8 \times 20 = -256 \text{ W} = -256 \text{ J/s}$$

Therefore,

$$\frac{dU}{dt} = \dot{Q} - \dot{W} = -10 - (-256) = 246 \text{ J/s}$$

EXAMPLE 5.11   A 25-kg cast-iron wood-burning stove, shown in Fig. 5.12, contains 5 kg of soft pine wood and 1 kg of air. All the masses are at room temperature, 20°C, and pressure, 101 kPa. The wood now burns and heats all the mass uniformly, releasing 1500 W. Neglect any air flow and changes in mass of wood and heat losses. Find the rate of change of the temperature (dT/dt) and estimate the time it will take to reach a temperature of 75°C.

Solution

C.V.: The iron, wood and air.
This is a control mass.

Energy equation rate form: $\dot{E} = \dot{Q} - \dot{W}$

We have no changes in kinetic or potential energy and no change in mass, so

$$U = m_{\text{air}} u_{\text{air}} + m_{\text{wood}} u_{\text{wood}} + m_{\text{iron}} u_{\text{iron}}$$

$$\dot{E} = \dot{U} = m_{\text{air}} \dot{u}_{\text{air}} + m_{\text{wood}} \dot{u}_{\text{wood}} + m_{\text{iron}} \dot{u}_{\text{iron}}$$

$$= (m_{\text{air}} C_{V\text{air}} + m_{\text{wood}} C_{\text{wood}} + m_{\text{iron}} C_{\text{iron}})\frac{dT}{dt}$$

Now the energy equation has zero work, an energy release of $\dot{Q}$, and becomes

$$(m_{\text{air}} C_{V\text{air}} + m_{\text{wood}} C_{\text{wood}} + m_{\text{iron}} C_{\text{iron}})\frac{dT}{dt} = \dot{Q} - 0$$

$$\frac{dT}{dt} = \frac{\dot{Q}}{(m_{\text{air}} C_{V\text{air}} + m_{\text{wood}} C_{\text{wood}} + m_{\text{iron}} C_{\text{iron}})}$$

$$= \frac{1500}{1 \times 0.717 + 5 \times 1.38 + 25 \times 0.42} \frac{W}{\text{kg (kJ/kg)}} = 0.0828 \text{ K/s}$$
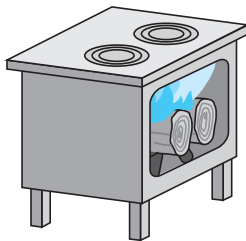
FIGURE 5.12 Sketch for Example 5.11.

Assuming the rate of temperature rise is constant, we can find the elapsed time as

$$\Delta T = \int \frac{dT}{dt} dt = \frac{dT}{dt} \Delta t$$

$$\Rightarrow \Delta t = \frac{\Delta T}{\dfrac{dT}{dt}} = \frac{75 - 20}{0.0828} = 664 \text{ s} = 11 \text{ min}$$

5.9 CONSERVATION OF MASS

In the previous sections we considered the first law of thermodynamics for a control mass undergoing a change of state. A control mass is defined as a fixed quantity of mass. The question now is whether the mass of such a system changes when its energy changes. If it does, our definition of a control mass as a fixed quantity of mass is no longer valid when the energy changes.

We know from relativistic considerations that mass and energy are related by the well-known equation

$$E = mc^2 \tag{5.33}$$

where c = velocity of light and E = energy. We conclude from this equation that the mass of a control mass does change when its energy changes. Let us calculate the magnitude of this change of mass for a typical problem and determine whether this change in mass is significant.

Consider a rigid vessel that contains a 1-kg stoichiometric mixture of a hydrocarbon fuel (such as gasoline) and air. From our knowledge of combustion, we know that after combustion takes place, it will be necessary to transfer about 2900 kJ from the system to restore it to its initial temperature. From the first law

$$_1Q_2 = U_2 - U_1 + _1W_2$$

we conclude that since $_1W_2 = 0$ and $_1Q_2 = -2900$ kJ, the internal energy of this system decreases by 2900 kJ during the heat transfer process. Let us now calculate the decrease in mass during this process using Eq. 5.33.

The velocity of light, c, is 2.9979×10^8 m/s. Therefore,

$$2900 \text{ kJ} = 2\,900\,000 \text{ J} = m \text{ (kg)} \times (2.9979 \times 10^8 \text{ m/s})^2$$

and so

$$m = 3.23 \times 10^{-11} \text{ kg}$$

Thus, when the energy of the control mass decreases by 2900 kJ, the decrease in mass is 3.23×10^{-11} kg.

A change in mass of this magnitude cannot be detected by even our most accurate chemical balance. Certainly, a fractional change in mass of this magnitude is beyond the accuracy required in essentially all engineering calculations. Therefore, if we use the laws of conservation of mass and conservation of energy as separate laws, we will not introduce significant error into most thermodynamic problems and our definition of a control mass as having a fixed mass can be used even though the energy changes.