Chapter One - Introduction to Energy Balance

21.1   The Terminology Associated with Energy Balances

Before starting an excursion into the semantics associated with energy balances, let us lay out a map of the ground to be covered. We first review a number of terms discussed in previous chapters, particularly Chapter 7, namely
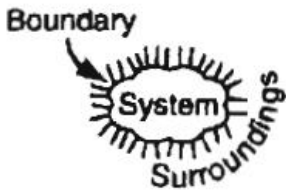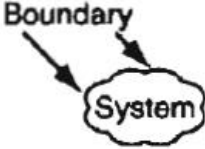
system	state
surroundings	steady state
boundary	unsteady state (transient)
open system (flow system)	equilibrium
closed system (nonflow system)	phase
property	intensive property
	extensive property

Next we introduce some new terms with which you may or may not be familiar

isothermal system	independent property
isobaric system	state function
isochoric system	path function
adiabatic system	

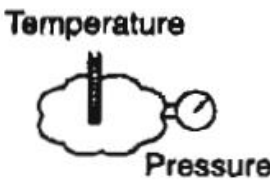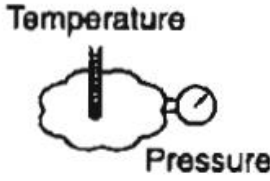The terms adiabatic, isothermal, isobaric, and **isochoric,** listed in Table 21.2, are useful to specify conditions that do not change in a process. Be aware that the concept of a **state (or point) function** or **variable** is an important concept to understand. Temperature, pressure, and all of the other intensive variables are known as state variables because between two states their change in value is the same no matter what the path taken between the two states. If two systems are in the same state, their state variables such as temperature or internal energy must be identical. If the state of a system is changed, say by heating so that energy flows in, the values of its state variables **such as temperature or internal energy must be identical.**

TABLE 21.1 Terminology Pertaining to Energy Balances

Term	Definition or Explanation	
System	The quantity of matter or region of space chosen for study enclosed by a boundary.	
Surroundings	Everything outside the system boundary.	
Boundary	The surface that separates the system from the surroundings. It may be a real or imaginary surface, either ridged or movable.	
Open system (flow system)	A system that is open to interchange of mass with the surroundings. Heat and work can also be exchanged.	
Closed system (nonflow system)	A system that does not interchange mass with the surroundings. But heat and work can be exchanged.	
Property	Observable (or calculable) characteristic of the system such as pressure, temperature, volume, etc.	
State	Conditions of the system (specified by the values of temperature, pressure, composition, etc.)	
Steady state	The accumulation in the system is zero, the flows in and out are constant, and the properties of the system are invariant.	
Unsteady state (transient)	The system is not in the steady state	

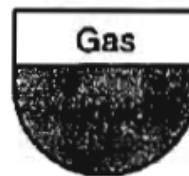|		
Equilibrium (state)	The properties of the system are invariant; implies a state of balance. Types are thermal, mechanical, phase, and chemical equilibrium.	
Phase	A part (or whole) of the system that is physically distinct, and macroscopically homogeneous of fixed or variable composition, such as gas, liquid, or solid.	Gas
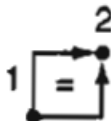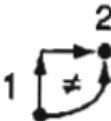
TABLE 21.2   ADDITIONAL TERMINOLOGY PERTAINING TO ENERGY BALANCES

Term	Definition or explanation	
Adiabatic system	A system that does not exchange heat with the surroundings during a process (perfectly insulated).	
Isothermal system	A system in which the temperature is invariant during a process.	
Isobaric system	A system in which the pressure is constant during a process.	
Isochoric system	A system in which the volume is invariant during a process.	
State variable (point function) (state function)	Any variable (function) whose value depends only on the state of the system and not upon its previous history (e.g., internal energy).	
Path variable (function)	Any variable (function) whose value depends on how the process takes place, and can differ for different histories (e.g., heat and work).	

21.2 Types of Energy

Before we begin the discussion of the types of energy we will be including in the energy balance, we need to mention certain notation that will be used. All of the terms in the energy balance will be integrated quantities just as were the terms in the mass balance in Chapter 7. Thus, for example, heat, Q, will be the *net amount of heat transferred to or from the system over a fixed interval no matter how the local transfer occurred at any selected instant of time*. If we have to identify a *rate of transfer*, we will place an overlay dot on the symbol for the variable, thus

$$\dot{Q} \quad \text{heat transfer per unit time.}$$

Because many of the variables with which we will be working are extensive variables, if we want to designate the related intensive variables, we place an overlay caret (^) on the symbol for the variable, thus

$$\hat{Q} \quad \text{heat transfer/unit mass}$$

With these preliminaries out of the way, we next discuss the six types of energy that we will include in our energy balances. The categories have been selected because they help you in problem solving, and allow you to easily tie the results of calculations to the performance of equipment such as turbines, compressors, heat engines, and so on. **Energy** itself is often defined as the capacity to do work or transfer heat, a fuzzy concept. It is easier to understand specific types of energy. Two things energy is *not* is (a) some sort of invisible fluid or (b) something that can be measured directly.

The first two types of energy we discuss, namely work and heat, are **energy transfer** between the system and surroundings without any accompanying mass transfer. These two types of energy *cannot be stored* in a system—they are solely transfers into and out of a system.

21.2-1 Work

Work (W) is a term that has wide usage in everyday life (such as "I am going to work"), but has a specialized meaning in connection with energy balances. Work is a form of energy that represents a **transfer** of energy between the system and surroundings. Work cannot be stored. ***Work is positive when the surroundings perform work on the system. Work is negative when the system performs work on the surroundings.***

- **Mechanical work**—work that occurs because of a mechanical force that **moves the boundary** of a system. You might calculate W on the system or by the system as

$$W = \int_{\text{state 1}}^{\text{state 2}} F \cdot ds \qquad (21.1)$$

where **F** is an external force (a vector) in the direction of **s** (a vector) acting on the system boundary (or a system force acting at the boundary on the surroundings). However, the amount of mechanical work done by or on a system can be difficult to calculate because (a) the displacement **ds** may not be easy to define,

and (b) the integration of $F \cdot ds$ as shown in Equation (21.1) does not necessarily give the amount of work actually being done on the system or by the system. Some of the energy involved may be dissipated as heat. In this text, the symbol W refers to the net work done over a period of time, *not* the rate of work. The latter is the **power,** namely work per unit time.

- **Electrical work**—electrical work occurs when an electrical current passes through an electrical resistance in the circuit. If the system generates an electrical current (e.g., an electrical generator inside the system) and the current passes through an electrical resistance outside the system, the electrical work is negative because the electrical work is done on the surroundings. If the electrical work is done inside the system and the electrical current is generated outside the system, the electrical work is positive.

- **Shaft work**—shaft work occurs by a force acting on a shaft to turn it against a mechanical resistance. When a pump outside the system is used to circulate a fluid in the system, the shaft work is positive. When a fluid in the system is used to turn a shaft that performs work on the surroundings, the shaft work is negative.

- **Flow work**—flow work is performed on the system when fluid is pushed into the system by the surroundings. For example, when a fluid enters a pipe some work is done on the system to force the fluid into the pipe. Similarly, when fluid exits the pipe, the system does some work on the surroundings to push the exiting fluid into the surroundings. Flow work will be described in more detail in Chapter 22.

Note that unless the process (path) under which work is carried out is specified from the initial to the final state of the system, you cannot calculate the value of the work done by integrating Equation (21.1). In other words, work done in going between the initial and final states can have *any* value, depending on the path taken. **Work is therefore called a path function,** and the value of W depends on the initial state, the path, and the final state of the system as illustrated in Example 21.1.

EXAMPLE 21.1   Calculation of Mechanical Work by a Gas on a Piston Showing How the Path Affects the Value of the Work

Suppose that an ideal gas at 300 K and 200 kPa is enclosed in a cylinder by a frictionless piston, and the gas slowly forces the piston so that the volume of gas expands from 0.1 to 0.2m³. Examine Figure E21.1a. Calculate the work done by the gas on the piston (the only part of the system boundary that moves) if two different paths are used to go from the initial state to the final state:

Path A: the expansion occurs at constant pressure (**isobaric**) (p = 200 kPa)
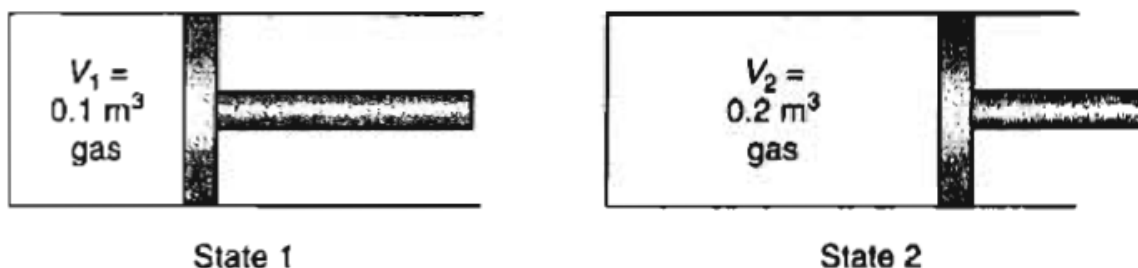Path B: the expansion occurs at constant temperature (**isothermal**) (T = 300 K)

| State 1 | State 2 |

Figure E21.1a

Solution

As explained in more detail in Chapter 27, the piston must be frictionless and the process ideal (occur very slowly) for the following calculations to be valid. Otherwise, some of the calculated work will be changed into a different form of unmeasured energy such as internal energy or heat (which are discussed later). The system is the gas. You are asked to use Equation (21.1) to calculate the work, but because you do not know the force exerted by the gas on the piston, you will have to use the pressure (force/area) as the driving force, which is OK since you do not know the area of the piston anyway, and because p is exerted normally on the piston face. All of the data you need is provided in the problem statement. Let the basis be the amount of gas cited in the problem statement

$$n = \frac{200 \text{ kPa} \left| 0.1 \text{ m}^3 \right|}{\left| 300 \text{ K} \right| 8.314 (\text{kPa})(\text{m}^3)} \frac{(\text{kg mol})(\text{K})}{} = 0.00802 \text{ kg mol}$$

Figure E21.1b illustrates the two processes.

The mechanical work done by the system on the piston (in moving the system boundary) *per unit area* is

$$W = - \int_{\text{state 1}}^{\text{state 2}} \frac{F}{A} \cdot A ds = - \int_{V_1}^{V_2} p \, dV$$

Note that by definition, the work done by the system is *negative*. If in the integral alone dV is positive (such as in expansion), the value of the integral will be positive
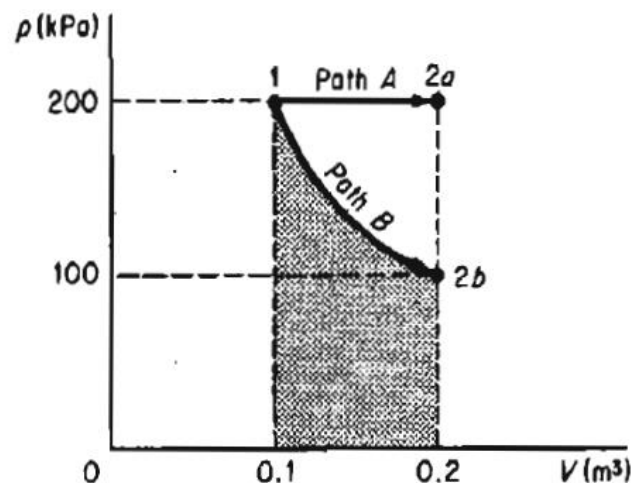

Figure E21.1b

and W negative (work done on the surroundings). If dV is negative, W will be positive (work done on the system).

Path A (the constant pressure process)

$$W = -p \int_{V_1}^{V_2} dV = -p(V_2 - V_1)$$

$$= -\frac{200 \times 10^3 \text{ Pa}}{\left|\frac{1 \text{ N}}{1 \text{ (m}^2\text{)(Pa)}}\right|} \left|\frac{0.1 \text{ m}^3}{}\right| \left|\frac{1 \text{ J}}{1\text{(N)(m)}}\right| = -20 \text{ kJ}$$

Path B (the constant temperature process)

The gas is ideal. Then

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$W = -\frac{0.00802 \text{ kg mol}}{\left|\frac{8.314 \text{ kJ}}{(\text{kg mol})(\text{K})}\right|} \left|\frac{300 \text{ K}}{}\right| \ln 2 = -20 \ln 2 = -13.86 \text{ kJ}$$

In Figure E21.1b the two integrals are areas under the respective curves in the p-V plot.

21.2-2. Heat

In a discussion of *heat* we enter an area in which our everyday use of the term may cause confusion, since we are going to use heat in a very restricted sense when we apply the laws governing energy changes. **Heat** (Q) is commonly defined as that part of the total energy flow across a system boundary that is caused by a temperature difference (potential) between the system and the surroundings (or between two systems). See Figure 21.3. Engineers say "heat" when meaning "heat transfer" or "heat flow." Heat is neither stored nor created. **Heat is positive when transferred to the system.**

A process in which no heat transfer occurs is an **adiabatic** process ($Q = 0$). Examples of an adiabatic process include processes in which the system and its surroundings are at the same temperature and processes in which the system is perfectly insulated.
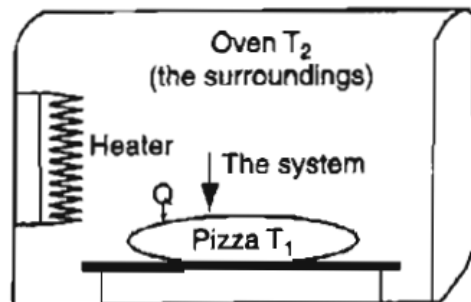
Figure 21.3 Heat transfer is energy crossing the system boundary because of a temperature difference.

Heat transfer is usually classified in three categories: conduction, convection, and radiation. Heat, as is work, is a path function. To evaluate heat transfer *quantitatively,* you must apply the energy balance. One example of such a formula is the rate of heat transfer by convection that can be calculated from

$$\dot{Q} = UA(T_2 - T_1) \tag{21.2}$$

where $\dot{Q}$ is the rate of heat transfer (such as J/s), A is the area for heat transfer (such as m²), $(T_2 - T_1)$ is the temperature difference between the surroundings at T_2 and the system at T_1 (such as °C), and U is the heat transfer coefficient determined from experimental data for the equipment involved [it would have the units of J/(s)(m²)(°C)]. Recall that in this text we use the symbol Q to denote the total amount of heat transferred in a time interval, and not the rate of heat transfer, hence $\dot{Q}$ would have to be summed or integrated to get Q. For example, ignoring conduction and radiation, the convective heat transfer rate from a person (the system) to a room (the surroundings) can be calculated using $U = 7$ W/(m²)(°C) and the data in Figure 21.4.

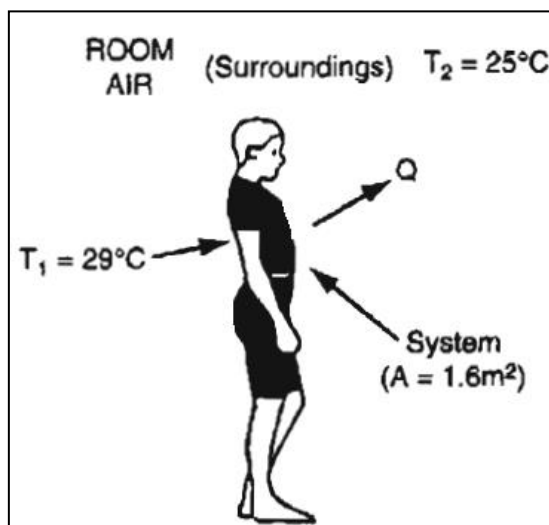**Figure 21.4** Heat transfer from a person.

$$\dot{Q} = \frac{7W}{(m^2)(°C)} \left| \frac{1.6\ m^2}{} \right| \frac{(25-29)°C}{} = -44.8\ W\ or\ -44.8\ J/s$$

21.2-3 Kinetic Energy

Kinetic energy (KE) is the energy a system, or some material, possesses because of its velocity relative to the surroundings, which are usually, *but not always,* at rest. The wind, moving automobiles, waterfalls, flowing fluids, and so on, possess kinetic energy. The kinetic energy of a material refers to what is called the macroscopic kinetic energy, namely the energy that is associated with the gross movement (velocity) of the system or material, and not the kinetic energy of the individual molecules that belong in the category of internal energy that is discussed in Section 21.2-5 below.

Do you recall the equation used to calculate the kinetic energy relative to stationary surroundings? It is

$$KE = \frac{1}{2}mv^2 \tag{21.3a}$$

for the kinetic energy or

$$\widehat{KE} = \frac{1}{2}v^2 \tag{21.3b}$$

for the specific kinetic energy where the superscript caret (^) refers to the energy per unit mass and not the total kinetic energy, as in Equation 21.3a. In Equation (21.3a), m refers to the center of mass of the material and v to a suitably averaged velocity of the material. The value of a *change* in the specific kinetic energy ($\Delta\widehat{KE}$) occurs in a specified time interval, and depends only on the mass and the initial and final values of the velocity of the material.

EXAMPLE 21.2 Calculation of the Specific Kinetic Energy for a Flowing Fluid

Water is pumped from a storage tank through a tube of 3.00 cm inner diameter at the rate of 0.001 m³/s. See Figure E21.2 What is the specific kinetic energy of the water in the tube?
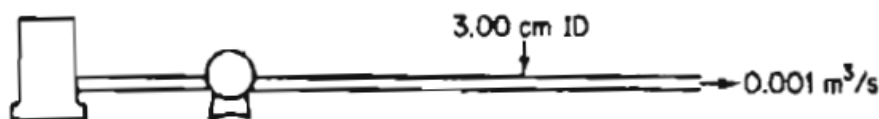

Figure E21.2

Solution

Basis: 0.001 m³/s of water

$$\text{Assume that } \rho = \frac{1000 \text{ kg}}{m^3} \qquad r = \frac{1}{2}(3.00) = 1.50 \text{ cm}$$

$$v = \frac{0.001 \text{ m}^3}{s} \left| \frac{}{\pi(1.50)^2 \text{ cm}^2} \right| \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 = 1.415 \text{ m/s}$$

$$\widehat{KE} = \frac{1}{2} \left(\frac{1.415 \text{ m}}{s} \right)^2 \left| \frac{1(N)(s^2)}{1(kg)(m)} \right| \frac{1 \text{ J}}{1(N)(m)} = 1.00 \text{ J/kg}$$

21.2-4 Potential Energy

Potential energy (PE) is energy the system possesses because of the force exerted on its mass by a gravitational or electromagnetic field with respect to a reference surface. When an electric car or bus goes uphill it gains potential energy (Figure 21.6), energy that can be recovered to some extent by regeneration—charging the batteries if needed when the automobile goes down the hill on the other side. You can calculate the potential energy in a gravitational field from

Figure 21.6 Gain of potential energy by an electric automobile going uphill.

$$PE = mgh \tag{21.4a}$$

or the specific potential energy

$$\widehat{PE} = gh \tag{21.4b}$$

where h is the distance from the reference surface and the symbol ($\widehat{}$) again means potential energy per unit mass. The measurement of h takes place to the center of mass of a system. Thus, if a ball suspended inside a container somehow is permitted to drop from the top of the container to the bottom, and in the process raises the thermal energy of the system slightly, we do not say work is done on the system but instead say that the potential energy of the system is reduced (slightly). The value of a *change* in the specific potential energy, $\Delta\widehat{PE}$, occurs in a specified time interval, and depends only on the initial and final states of the system (state variable), and not on the path followed.

EXAMPLE 21.3   Calculation of Potential Energy Change of Water

Water is pumped from one reservoir to another 300 ft away, as shown in Figure E21.3. The water level in the second reservoir is 40 ft above the water level of the first reservoir. What is the increase in specific potential energy of the water in Btu/lb$_m$?
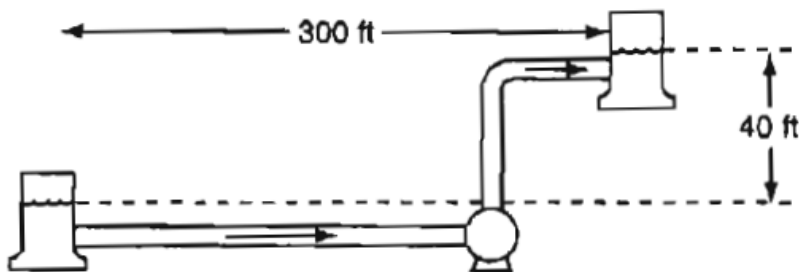

Figure E21.3

Solution

Because you are asked to calculate the potential energy change of one pound of water and not of the whole reservoir, which would require knowledge of the mass of water in the reservoir, you can assume that the 40 ft corresponds to the difference in height of the one pound of water when it is pumped from one level to the other level. Think of a ping-pong ball riding on top of the water.

Let the water level in the first reservoir be the reference plane. Then $h = 40$ ft.

$$\Delta\widehat{PE} = \frac{32.2 \text{ ft}}{s^2}\left|\frac{(40 - 0)\text{ ft}}{}\right|\frac{1 \text{ (lb}_f)(s^2)}{32.2 \text{ (lb}_m)(\text{ft})}\left|\frac{1 \text{ Btu}}{778.2(\text{ft})(\text{lb}_f)}\right. = 0.0514 \text{ Btu/lb}_m$$

21.2-5   Internal Energy

Internal energy (U) is a *macroscopic* concept that takes into account all of the molecular, atomic, and subatomic energies, all of which follow definite microscopic conservation rules for dynamic systems. Internal energy can be stored. Because no instruments exist with which to measure internal energy directly on a macroscopic scale, internal energy must be calculated from certain other variables that can be measured macroscopically, such as pressure, volume, temperature, and composition.

To calculate the internal energy per unit mass ($\hat{U}$) from the variables that can be measured, we make use of a special property of internal energy, namely that it is an exact differential because it is a *point* or *state variable*.

For a pure component, $\hat{U}$ can be expressed in terms of just two intensive variables according to the phase rule for one phase:

$$\mathscr{F} = 2 - \mathscr{P} + C = 2 - 1 + 1 = 2$$

Custom dictates the use of temperature and specific volume as the two variables. For a *single phase* and single component, we say that $\hat{U}$ is a function of T and $\hat{V}$

$$\hat{U} = \hat{U}(T, \hat{V})$$

By taking the total derivative, we find that

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_{T} d\hat{V} \tag{21.5}$$

By definition $(\partial \hat{U}/\partial T)_{\hat{V}}$ is the "**heat capacity**" (specific heat) at constant volume, given the special symbol C_V. C_V can also be defined to be the amount of heat necessary to raise the temperature of one kilogram of substance by one degree in a closed system, and so has the SI units of J/(kg)(K), if the process is carried out at constant volume. We discuss how to get numerical values for heat capacities in Chapter 23. For all practical purposes in this text, the term $(\partial \hat{U}/\partial \hat{V})_T$ is so small that the second term on the righthand side of Equation (21.5) can be neglected. Consequently, *changes in the specified internal energy* over a specified time interval can be computed by integrating Equation (21.5) as follows:

$$\Delta \hat{U} = \hat{U}_2 - \hat{U}_1 = \int_{\hat{U}_1}^{\hat{U}_2} d\hat{U} = \int_{T_1}^{T_2} C_V \, dT \qquad (21.6)$$

Note that you can only calculate differences in internal energy, or calculate the internal energy relative to a reference state, *but not absolute values* of internal energy. Look up the values of p and $\hat{V}$ for water for the reference state that has been assigned a zero value for $\hat{U}$. In the SI tables did you get $p = 0.6113$ kPa, and for liquid water, $\hat{V} = 0.001000$ m³/kg? The reference internal energy cancels out when you calculate an internal energy difference

$$\Delta \hat{U} = (\hat{U}_2 - \hat{U}_{ref}) - (\hat{U}_1 - \hat{U}_{ref}) = \hat{U}_2 - \hat{U}_1 \qquad (21.7)$$

What would be the value for $\Delta \hat{U}$ for a constant volume system if 1 kg of water at 100 kPa was heated from 0°C to 100°C, and then cooled back to 0°C and 100 kPa? Would $\Delta \hat{U} = 0$? Yes, because it is a state variable, and the integral in Equation (21.6) would be zero because $\hat{U}_2 = \hat{U}_1$.

The internal energy of a system containing more than one component is the sum of the internal energies of each component

$$U_{tot} = m_1 \hat{U}_1 + m_2 \hat{U}_2 + \cdots + m_n \hat{U}_n \qquad (21.8)$$

EXAMPLE 21.4   Calculation of an Internal Energy Change Using the Heat Capacity

What is the change in internal energy when 10 kg mol of air is cooled from 60°C to 30°C in a constant volume process?

Solution

Since you don't know the value of C_V, you have to look the value up. It is 2.1×10^4 J/(kg mol)(°C) over the temperature range. Use Equation (21.6) to carry out the calculation:

$$\Delta U = 10 \text{ kg mol} \int_{60°C}^{30°C} \left(2.1 \times 10^4 \frac{J}{(\text{kg mol})(°C)} \right) dT = 2.1 \times 10^5 (30 - 60)$$

$$= -6.3 \times 10^6 \text{ J}$$

21.2-6 Enthalpy

You will find in Chapter 22 and subsequent chapters that the term $U + pV$ (or $\hat{U} + p\hat{V}$ per unit mass or mole) occurs repeatedly in an energy balance. The combined variables are called the **enthalpy** (pronounced en-*thal*-py).

$$H = U + pV \tag{21.9a}$$

where p is the pressure and V is the volume, or per unit mass or mole

$$\hat{H} = \hat{U} + p\hat{V} \tag{21.9b}$$

To calculate the specific enthalpy (enthalpy per unit mass), as with the internal energy, we use the property that the enthalpy is an exact differential. As you saw for internal energy, the state for the enthalpy for a **single phase** and single component can be completely specified by two intensive variables. We will express the enthalpy in terms of the temperature and pressure (a more convenient variable than the specific volume). If we let

$$\hat{H} = \hat{H}(T, p)$$

by taking the total derivative of $\hat{H}$ we can form an expression analogous to Equation (21.5):

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_p dT + \left(\frac{\partial \hat{H}}{\partial p}\right)_T dp \tag{21.10}$$

By definition $(\partial H/\partial T)_p$ is the heat capacity at constant pressure, and is given the special symbol C_p. For most practical purposes $(\partial \hat{H}/\partial p)_T$ is so small at modest pressures that the second term on the righthand side of Equation (21.10) can be neglected. Changes in enthalpy over a specified time interval can then be calculated by integration of Equation (21.10) as follows:

$$\Delta\hat{H} = \hat{H}_2 - \hat{H}_1 = \int_{\hat{H}_1}^{\hat{H}_2} d\hat{H} = \int_{T_1}^{T_2} C_p \, dT \tag{21.11}$$

As with internal energy, **enthalpy has no absolute value; only changes in enthalpy can be calculated.** Often you will use a reference set of conditions (perhaps implicitly) in computing enthalpy changes. For example, the reference conditions used in the steam tables are liquid water at 0°C (32°F) and its vapor pressure. This does not mean that the enthalpy is actually zero under these conditions, but merely that the enthalpy has arbitrarily been assigned a value of zero at these conditions. In computing enthalpy changes, the reference conditions cancel out, as can be seen from the following:

Initial state of system (1)   *Final state of system (2)*

$$\text{enthalpy} = \hat{H}_1 - \hat{H}_{ref} \qquad\qquad \text{enthalpy} = \hat{H}_2 - \hat{H}_{ref}$$

$$\text{net enthalpy change} = (\hat{H}_2 - \hat{H}_{ref}) - (\hat{H}_1 - \hat{H}_{ref}) = \hat{H}_2 - \hat{H}_1$$

EXAMPLE 21.6   Calculation of the Change in Enthalpy by Two Different Paths

Figure E21.6 illustrates the change in the state of a gas from A to D by two paths. Will $\Delta\hat{H}$ be greater by going via route A-B-D or by A-C-D from point A to point D?
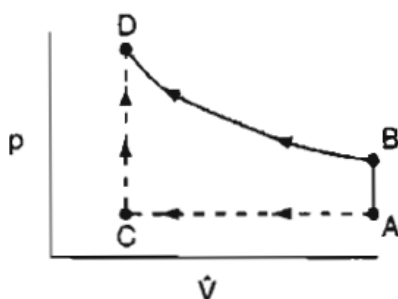

Figure E21.6

Solution

Because $\hat{H}$ is a state (point) variable, only the beginning and ending conditions are involved in calculating $\Delta\hat{H}$. Consequently, the answer is both paths will result in the same value of $\Delta\hat{H}$.

EXAMPLE 21.7   Calculation of an Enthalpy Change

Calculate the enthalpy change for the process in Example 21.4, except assume that the enthalpy change occurs in a constant pressure, steady-state flow process.

Solution

For the example you have to look up the value of C_p. It is 2.9×10^4 J/(kg mol)(°C). Use Equation (21.11) to carry out the calculation:

$$\Delta H = 10 \text{ kg mol} \int_{60°C}^{30°C} (2.9 \times 10^4) \frac{J}{(\text{kg mol})(°C)} dT = 2.9 \times 10^5 (30 - 60)$$

$$= -8.7 \times 10^6 \text{ J}$$

Notice This **Home Work**: *Basic Princeples and Calculation in Chemical Engineering*, 7th edition, **Problems of chapter 21, page 637 – 644**.