

1. Heat Capacity:

Heat capacity is defined as the change in temperature of a system with a change of heat transferred to the system:

$$C \equiv \frac{dQ}{dT}$$

C= heat capacity

Q= heat

T= Temperature

Heat Capacity at Constant Volume

The constant-volume heat capacity is defined as:

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V \quad (2.16)$$

This definition accommodates both the molar heat capacity and the specific heat capacity (usually called specific heat), depending on whether U is the molar or specific internal energy.

Specific heat capacity: the amount of heat needed to raise the temperature of a unit mass of material by one degree.

Eq. (2.16) may be written for a constant-volume process in a closed system as

$$dU = C_V dT \quad (\text{const } V) \quad (2.17)$$

Integration yields:

$$\Delta U = \int_{T_1}^{T_2} C_V dT \quad (\text{const } V) \quad (2.18)$$

The combination of this result with Eq. (2.10) for a mechanically reversible, constant-volume process gives:

$$Q = n \Delta U = n \int_{T_1}^{T_2} C_V dT \quad (\text{const } V) \quad (2.19)$$

If the volume varies during the process but returns at the end of the process to its initial value, the process cannot rightly be called one of constant volume, even though $V_2 = V_1$ and $\Delta V = 0$

Heat Capacity at Constant Pressure

The constant-pressure heat capacity is defined as:

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P \quad (2.20)$$

Eq. (2.20) is equally well written for a constant-pressure, closed-system process as:

$$dH = C_P dT \quad (\text{const } P) \quad (2.21)$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (\text{const } P) \quad (2.22)$$

For a mechanically reversible, constant-pressure process, this result may be combined with Eq. (2.13) to give

$$Q = n \Delta H = n \int_{T_1}^{T_2} C_P dT \quad (\text{const } P) \quad (2.23)$$

Example 2.9

Air at 1 bar and 298.15 K (25°C) is compressed to 5 bar and 298.15 K by two different mechanically reversible processes:

- (a) Cooling at constant pressure followed by heating at constant volume.
- (b) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

$$C_V = 20.78 \quad \text{and} \quad C_P = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume also for air that PV/T is a constant, regardless of the changes it undergoes. At 298.15 K and 1 bar the molar volume of air is $0.02479 \text{ m}^3 \text{ mol}^{-1}$.

Solution 2.9

In each case take the system as 1 mol of air contained in an imaginary piston/cylinder arrangement. Because the processes considered are mechanically reversible, the piston is imagined to move in the cylinder without friction. The final volume is:

$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479 \left(\frac{1}{5} \right) = 0.004958 \text{ m}^3$$

(a) During the first step the air is cooled at the constant pressure of 1 bar until the final volume of 0.004958 m^3 is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15 \left(\frac{0.004958}{0.02479} \right) = 59.63 \text{ K}$$

Whence,

$$\begin{aligned} Q &= \Delta H = C_p \Delta T = (29.10)(59.63 - 298.15) = -6,941 \text{ J} \\ \Delta U &= \Delta H - \Delta(PV) = \Delta H - P \Delta V \\ &= -6,941 - (1 \times 10^5)(0.004958 - 0.02479) = -4,958 \text{ J} \end{aligned}$$

During the second step the volume is held constant at V_2 while the air is heated to its final state. By Eq. (2.19),

$$\Delta U = Q = C_v \Delta T = (20.78)(298.15 - 59.63) = 4,958 \text{ J}$$

The complete process represents the sum of its steps. Hence,

$$Q = -6,941 + 4,958 = -1,983 \text{ J}$$

and
$$\Delta U = -4,958 + 4,958 = 0$$

Because the first law applies to the entire process, $\Delta U = Q + W$, and therefore,

$$0 = -1,983 + W \quad \text{whence} \quad W = 1,983 \text{ J}$$

Equation (2.15), $\Delta H = \Delta U + \Delta(PV)$, also applies to the entire process. But $T_1 = T_2$, and therefore, $P_1 V_1 = P_2 V_2$. Hence $\Delta(PV) = 0$, and

$$\Delta H = \Delta U = 0$$

(b) Two different steps are used in this case to reach the same final state of the air. In the first step the air is heated at a constant volume equal to its initial value until the final pressure of 5 bar is reached. The air temperature at the end of this step is:

$$T' = T_1 \frac{P_2}{P_1} = 298.15 \left(\frac{5}{1} \right) = 1,490.75 \text{ K}$$

For this step the volume is constant, and

$$Q = \Delta U = C_V \Delta T = (20.78)(1,490.75 - 298.15) = 24,788 \text{ J}$$

In the second step the air is cooled at $P = 5 \text{ bar}$ to its final state:

$$Q = \Delta H = C_P \Delta T = (29.10)(298.15 - 1,490.75) = -34,703 \text{ J}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P \Delta V$$

$$= -34,703 - (5 \times 10^5)(0.004958 - 0.02479) = -24,788 \text{ J}$$

For the two steps combined,

$$Q = 24,788 - 34,703 = -9,915 \text{ J}$$

$$\Delta U = 24,788 - 24,788 = 0$$

$$W = \Delta U - Q = 0 - (-9,915) = 9,915 \text{ J}$$

and as before

$$\Delta H = \Delta U = 0$$

The property changes ΔU and ΔH calculated for the given change in state are the same for both paths. On the other hand the answers to parts (a) and (b) show that Q and W depend on the path.

Example 2.10

Calculate the internal-energy and enthalpy changes that occur when air is changed from an initial state of $40(^{\circ}\text{F})$ and $10(\text{atm})$, where its molar volume is $36.49(\text{ft}^3)(\text{lb mole})^{-1}$, to a final state of $140(^{\circ}\text{F})$ and $1(\text{atm})$. Assume for air that PV/T is constant and that $C_V = 5$ and $C_P = 7(\text{Btu})(\text{lb mole})^{-1}(^{\circ}\text{F})^{-1}$.

Solution 2.10

Because property changes are independent of the process that brings them about, calculations may be based on a two-step, mechanically reversible process in which $1(\text{lb mole})$ of air is (a) cooled at constant volume to the final pressure, and (b) heated at constant pressure to the final temperature. The absolute temperatures here are on the Rankine scale:

$$T_1 = 40 + 459.67 = 499.67(\text{R}) \qquad T_2 = 140 + 459.67 = 599.67(\text{R})$$

Because $PV = kT$, the ratio T/P is constant for step (a). The intermediate temperature between the two steps is therefore:

$$T' = (499.67)(1/10) = 49.97(\text{R})$$

and the temperature changes for the two steps are:

$$\Delta T_a = 49.97 - 499.67 = -449.70(\text{R})$$

$$\Delta T_b = 599.67 - 49.97 = 549.70(\text{R})$$

For step (a), by Eqs. (2.18) and (2.15),

$$\Delta U_a = C_V \Delta T_a = (5)(-449.70) = -2,248.5(\text{Btu})$$

$$\begin{aligned}\Delta H_a &= \Delta U_a + V \Delta P_a \\ &= -2,248.5 + (36.49)(1 - 10)(2.7195) = -3,141.6(\text{Btu})\end{aligned}$$

The factor 2.7195 converts the PV product from $(\text{atm})(\text{ft})^3$, which is an energy unit, into (Btu).

For step (b), the final volume of the air is:

$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1} = 36.49 \left(\frac{10}{1} \right) \left(\frac{599.67}{499.67} \right) = 437.93(\text{ft})^3$$

By Eqs. (2.22) and (2.15),

$$\Delta H_b = C_P \Delta T_b = (7)(549.70) = 3,847.9(\text{Btu})$$

$$\begin{aligned}\Delta U_b &= \Delta H_b - P \Delta V_b \\ &= 3,847.9 - (1)(437.93 - 36.49)(2.7195) = 2,756.2(\text{Btu})\end{aligned}$$

For the two steps together,

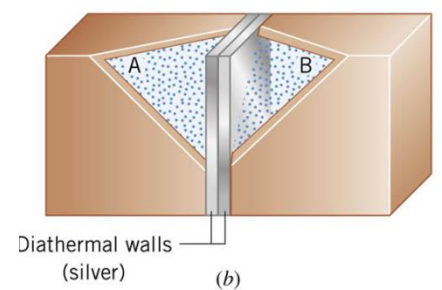
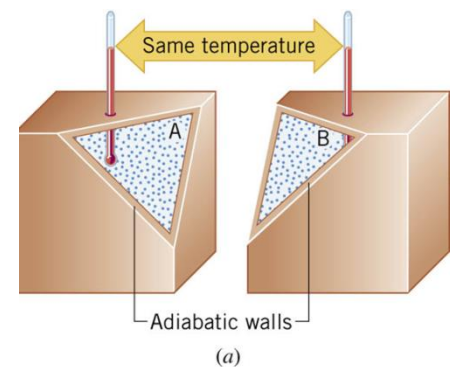
$$\Delta U = -2,248.5 + 2,756.2 = 507.7(\text{Btu})$$

$$\Delta H = -3,141.6 + 3,847.9 = 706.3(\text{Btu})$$

Zeroth Law of Thermodynamics:

- The forgotten Law of Science
- Two systems are said to be in thermal equilibrium if there is no heat flow between them when they are brought into contact.
- Temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature.

Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other.



2. MASS AND ENERGY BALANCES FOR OPEN SYSTEMS

Measures of Flow

Open systems are characterized by flowing streams, for which there are four common measures of flow:

Mass flowrate, m , Molar flowrate, n Volumetric flowrate, q Velocity, u

The measures of flow are interrelated:

$$m = Mn \quad \text{and} \quad q = uA$$

where M is molar mass. Importantly, mass and molar flowrates relate to velocity:

$$\dot{m} = uA\rho \quad (2.24a)$$

$$\dot{n} = uA\rho \quad (2.24b)$$

The area for flow A is the cross-sectional area of a conduit, and ρ is specific or molar density. Although velocity is a vector quantity, its scalar magnitude u is used here as the average speed of a stream in the direction normal to A . Flowrates m , n , and q represent measures of quantity per unit of time. Velocity u is quite different in nature, as it does not suggest the magnitude of flow. Nevertheless, it is an important design parameter.

Mass Balance for Open Systems

The region of space identified for analysis of open systems is called a **control volume**; it is separated from its surroundings by a **control surface**. The fluid within the control volume is the thermodynamic system for which mass and energy balances are written. The control volume shown schematically in Fig. 2.5 is separated from its surroundings by an extensible control surface.

Two streams with flow rates m_1 and m_2 are shown directed into the control volume, and one stream with flow rate m_3 is directed out. Since mass is conserved, the rate of change of mass within the control volume, dm_{cv}/dt , equals the net rate of flow of mass into the control volume. The convention is that flow is positive when directed into the control volume and negative when directed out. The mass balance is expressed mathematically by:

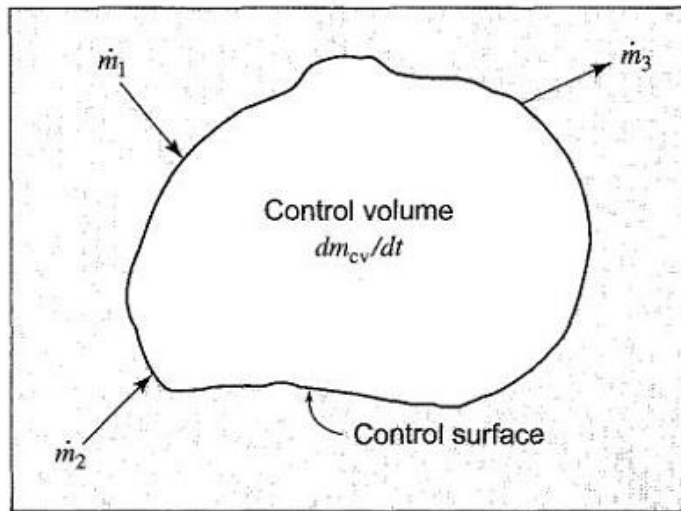


Figure 2.5 Schematic representation of a control volume

$$\boxed{\frac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0} \quad (2.25)$$

where the second term for the control volume shown in Fig. 2.5 is:

$$\Delta(\dot{m})_{fs} = \dot{m}_3 - \dot{m}_1 - \dot{m}_2$$

The difference operator " Δ " here signifies the difference between exit and entrance flows and the subscript "fs" indicates that the term applies to all flowing streams.

When the mass flowrate m is given by Eq. (2.24a), Eq. (2.25) becomes:

$$\frac{dm_{cv}}{dt} + \Delta(\rho u A)_{fs} = 0 \quad (2.26)$$

In this form the mass-balance equation is often called the *continuity equation*.

The flow process characterized as steady state is an important special case for which conditions within the control volume do not change with time. The control

volume then contains a constant mass of fluid, and the first or accumulation term of Eq. (2.25) is zero, reducing Eq. (2.26) to:

$$\Delta(\rho u A)_{fs} = 0$$

When there is but a single entrance and a single exit stream, the mass flowrate \dot{m} is the same for both streams; then,

$$\rho_2 u_2 A_2 - \rho_1 u_1 A_1 = 0$$

or
$$m = \text{const} = \rho_2 u_2 A_2 = \rho_1 u_1 A_1$$

Since specific volume is the reciprocal of density,

$$\boxed{\dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{u A}{V}} \quad (2.27)$$

This form of the continuity equation finds frequent use.

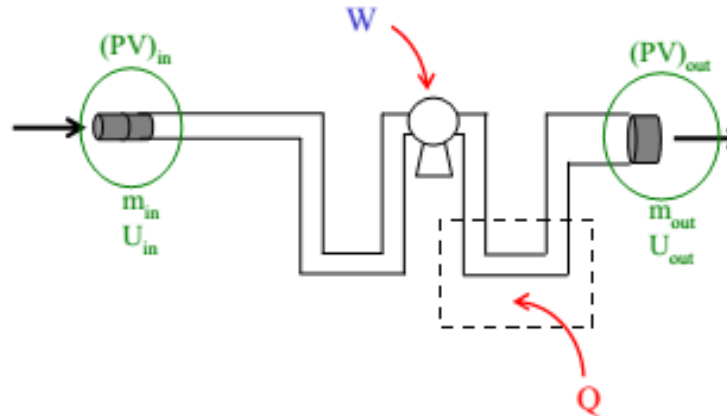
General Energy Balance

Since energy, like mass, is conserved, the rate of change of energy within the control volume equals the net rate of energy transfer into the control volume. Streams flowing into and out of the control volume have associated with them energy in its internal, potential, and kinetic forms, and all contribute to the energy change of the system.

$$\boxed{\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}} \quad (2.28)$$

$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W} \quad (2.29)$$

Steady state flow process



Flow processes for which the accumulation term of Eq. (2.28), $d(mU)_{cv}/dt$, is zero are said to occur at steady state. As discussed with respect to the mass balance, this means that the mass of the system within the control volume is constant; it also means that no changes occur with time in the properties of the fluid within the control volume nor at its entrances and exits. No expansion of the control volume is possible under these circumstances. The only work of the process is shaft work, and the general energy balance, Eq. (2.28), becomes:

Shaft Work: The work associated with the transmission of energy through a **rotating shaft** is commonly encountered in many engineering problems.

$$\Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s \quad (2.30)$$

The same mass flow rate \dot{m} then applies to both streams, and Eq. (2.30) then reduces to:

$$\Delta \left(H + \frac{1}{2}u^2 + zg \right) \dot{m} = \dot{Q} + \dot{W}_s \quad (2.31)$$

where subscript "fs" has been omitted in this simple case and "A" denotes the change from entrance to exit. Division by \dot{m} gives:

$$\Delta H + \frac{\Delta u^2}{2} + g \Delta z = Q + W_s \quad (2.32a)$$

In many applications, kinetic- and potential-energy terms are omitted, because they are negligible compared with other terms. For such cases, Eqs. (2.32a) and (2.32b) reduce to:

$$\Delta H = Q + W_s \quad (2.33)$$

This equation is the mathematical expression of the first law for a steady-state, steady-flow process between one entrance and one exit. All terms represent energy per unit mass of fluid

What does steady state process mean?

- The conditions at all points in apparatus are constant with time
- Mass flow rate to the system equal to mass transfer out of the system.
- Rate of work or heat transfer must be constant.

Examples 2.11-.2.16

Example 2.14

An insulated, electrically heated tank for hot water contains 190 kg of liquid water at 60°C when a power outage occurs. If water is withdrawn from the tank at a steady rate of $\dot{m} = 0.2 \text{ kg s}^{-1}$, how long will it take for the temperature of the water in the tank to drop from 60 to 35°C? Assume cold water enters the tank at 10°C, and negligible heat losses from the tank. For liquid water let $C_V = C_P = C$, independent of T and P .

Solution 2.14

Here, $\dot{Q} = \dot{W} = 0$. Additionally, assume perfect mixing of the contents of the tank; this implies that the properties of the water leaving the tank are those of the water in the tank. With the mass flowrate into the tank equal to the mass flowrate out, \dot{m}_{cv} is constant; moreover, the differences between inlet and outlet kinetic and potential energies can be neglected. Equation (2.29) is therefore written:

$$\dot{m} \frac{dU}{dt} + \dot{m}(H - H_1) = 0$$

where unsubscripted quantities refer to the contents of the tank and H_1 is the specific enthalpy of the water entering the tank. With $C_V = C_P = C$,

$$\frac{dU}{dt} = C \frac{dT}{dt} \quad \text{and} \quad H - H_1 = C(T - T_1)$$

The energy balance then becomes, on rearrangement,

$$dt = - \frac{\dot{m}}{\dot{m}} \frac{dT}{T - T_1}$$

Integration from $t = 0$ (where $T = T_0$) to arbitrary time t yields:

$$t = - \frac{\dot{m}}{\dot{m}} \ln \left(\frac{T - T_1}{T_0 - T_1} \right)$$

Substitution of numerical values into this equation gives, for the conditions of this problem,

$$t = - \frac{190}{0.2} \ln \left(\frac{35 - 10}{60 - 10} \right) = 658.5 \text{ s}$$

Thus, it takes about 11 minutes for the water temperature in the tank to drop from 60 to 35°C.

Example 2.16

Air at 1 bar and 25°C enters a compressor at low velocity, discharges at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m s⁻¹ at the initial conditions of pressure and temperature. If the work of compression is 240 kJ per kilogram of air, how much heat must be removed during compression?

Solution 2.16

Because the air returns to its initial conditions of T and P , the overall process produces no change in enthalpy of the air. Moreover, the potential-energy change of the air is presumed negligible. Neglecting also the initial kinetic energy of the air, we write Eq. (2.32a) as:

$$Q = \frac{u_2^2}{2} - W_s$$

The kinetic-energy term is evaluated as follows:

$$\begin{aligned} \frac{1}{2}u_2^2 &= \frac{1}{2} \left(600 \frac{\text{m}}{\text{s}} \right)^2 = 180,000 \frac{\text{m}^2}{\text{s}^2} \\ &= 180,000 \frac{\text{m}^2}{\text{s}^2} \cdot \frac{\text{kg}}{\text{kg}} = 180,000 \text{ N m kg}^{-1} = 180 \text{ kJ kg}^{-1} \end{aligned}$$

Then
$$Q = 180 - 240 = -60 \text{ kJ kg}^{-1}$$

Heat in the amount of 60 kJ must be removed per kilogram of air compressed.