

Heat transferred at constant volume increases the internal energy of the system. If the specific heat of a substance is defined in terms of heat transfer, then

$$c_v = \left(\frac{\partial Q}{\partial T} \right)_v$$

Since Q is not a property, this definition does not imply that c_v is a property of a substance. Therefore, this is not the appropriate method of defining the specific heat, although $(dQ)_v = du$.

Since u , T , and v are properties, c_v is a property of the system. The product $mc_v = C_v$ is called the *heat capacity at constant volume* (J/K).

4.6 Enthalpy

The enthalpy of a substance, h , is defined as

$$h = u + pv \quad (4.24)$$

It is an intensive property of a system (kJ/kg).

Internal energy change is equal to the heat transferred in a constant volume process involving no work other than $p dV$ work. From equation (4.22), it is possible to derive an expression for the heat transfer in a constant pressure process involving no work other than $p dV$ work. In such a process in a closed stationary system of unit mass of a pure substance

$$dQ = du + pdv$$

At constant pressure

$$pdv = d(pv)$$

$$\therefore (dQ)_p = du + d(pv)$$

$$\text{or} \quad (dQ)_p = d(u + pv)$$

$$\text{or} \quad (dQ)_p = dh \quad (4.25)$$

where $h = u + pv$ is the *specific enthalpy*, a property of the system.

Heat transferred at constant pressure increases the enthalpy of a system.

For an ideal gas, the enthalpy becomes

$$h = u + RT \quad (4.26)$$

Since the internal energy of an ideal gas depends only on the temperature (Eq. 4.11), the enthalpy of an ideal gas also depends on the temperature only, i.e.

$$h = f(T) \text{ only} \quad (4.27)$$

Total enthalpy $H = mh$

$$\text{Also} \quad H = U + pV$$

$$\text{and} \quad h = H/m \text{ (J/kg)}$$

4.7 Specific Heat at Constant Pressure

The specific heat at constant pressure c_p is defined as the rate of change of enthalpy with respect to temperature when the pressure is held constant

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p \quad (4.28)$$

Since h , T and p are properties, so c_p is a property of the system. Like c_v , c_p should not be defined in terms of heat transfer of constant pressure, although $(dQ)_p = dh$.

For a constant pressure process

$$(\Delta h)_p = \int_{T_1}^{T_2} c_p \cdot dT \quad (4.29)$$

The first law for a closed stationary system of unit mass

$$\begin{aligned} \delta Q &= du + p dv \\ \text{Again } h &= u + pv \\ \therefore dh &= du + p dV + v dp \\ &= dQ + v dp \\ \therefore dQ &= dh - v dp \\ \therefore (\delta Q)_p &= dh \\ \text{or } (Q)_p &= (\Delta h)_p \\ \therefore \text{From equations (4.19) and (4.20)} \end{aligned} \quad (4.30)$$

$$(Q)_p = \int_{T_1}^{T_2} c_p dT$$

c_p is a property of the system, just like c_v . The *heat capacity at constant pressure* C_p is equal to mc_p (J/K).

4.8 Energy of an Isolated System

An isolated system is one in which there is no interaction of the system with the surroundings. For an isolated system, $\delta Q = 0$, $\delta W = 0$.

The first law gives

$$dE = 0$$

$$\text{or } E = \text{constant}$$

The energy of an isolated system is always constant.

4.9 Perpetual Motion Machine of the First Kind—PMM1

The first law states the general principle of the conservation of energy. *Energy is neither created nor destroyed, but only gets transformed from one form to another.* There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously (Fig. 4.8). Such a *fictitious machine* is called a *perpetual motion machine of the first kind*, or in brief, PMM1. *A PMM1 is thus impossible.*

The converse of the above statement is also true, i.e., there can be no machine which would continuously consume work without some other form of energy appearing simultaneously (Fig. 4.9).

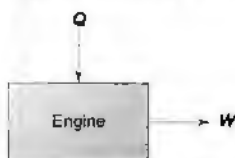


Fig. 4.8 A PMM1

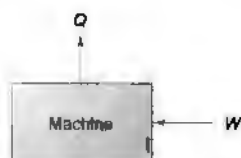


Fig. 4.9 The converse of PMM1

4.10 Limitations of the First Law

The first law deals with the amounts of energy of various forms transferred between the system and its surroundings and with changes in the energy stored in the system. It treats work and heat interactions as equivalent forms of energy in transit and does not indicate the possibility of a spontaneous process proceeding in a certain direction. It is the second law which assigns a quality to different forms of energy, and also indicates the direction of any spontaneous process.

SOLVED EXAMPLES

Example 4.1 A stationary mass of gas is compressed without friction from an initial state of 0.3 m^3 and 0.105 MPa to a final state of 0.15 m^3 and 0.105 MPa , the pressure remaining constant during the process. There is a transfer of 37.6 kJ of heat from the gas during the process. How much does the internal energy of the gas change?

Solution First law for a stationary system in a process gives

$$Q = \Delta U + W$$

$$\text{or} \quad Q_{1-2} = U_2 - U_1 + W_{1-2} \quad (1)$$

Here

$$\begin{aligned} W_{1-2} &= \int_{V_1}^{V_2} p \, dV = p(V_2 - V_1) \\ &= 0.105 (0.15 - 0.30) \text{ MJ} \\ &= -15.75 \text{ kJ} \\ Q_{1-2} &= -37.6 \text{ kJ} \end{aligned}$$

\therefore Substituting in equation (1)

$$-37.6 \text{ kJ} = U_2 - U_1 - 15.75 \text{ kJ}$$

$$\therefore \quad U_2 - U_1 = -21.85 \text{ kJ}$$

Ans.

The internal energy of the gas decreases by 21.85 kJ in the process.

Example 4.2 When a system is taken from state a to state b , in Fig. Ex. 4.2, along path acb , 84 kJ of heat flow into the system, and the system does 32 kJ of work. (a) How much will the heat that flows into the system along path adb be, if the work done is 10.5 kJ? (b) When the system is returned from b to a along the curved path, the work done on the system is 21 kJ. Does the system absorb or liberate heat, and how much of the heat is absorbed or liberated? (c) If $U_a = 0$ and $U_d = 42$ kJ, find the heat absorbed in the processes ad and db .

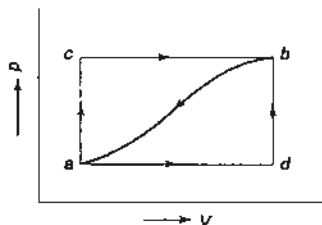


Fig. Ex. 4.2

Solution

$$Q_{acb} = 84 \text{ kJ}$$

$$W_{acb} = 32 \text{ kJ}$$

We have

$$Q_{acb} = U_b - U_a + W_{acb}$$

$$\therefore U_b - U_a = 84 - 32 = 52 \text{ kJ} \quad \text{Ans.}$$

$$\begin{aligned} \text{(a)} \quad Q_{adb} &= U_b - U_a + W_{adb} \\ &= 52 + 10.5 \\ &= 62.5 \text{ kJ} \end{aligned} \quad \text{Ans.}$$

$$\begin{aligned} \text{(b)} \quad Q_{b-a} &= U_a - U_b + W_{b-a} \\ &= -52 - 21 \\ &= -73 \text{ kJ} \end{aligned} \quad \text{Ans.}$$

The system liberates 73 kJ of heat.

$$\text{(c)} \quad W_{adb} = W_{ad} + W_{db} = W_{ad} = 10.5 \text{ kJ}$$

$$\begin{aligned} \therefore Q_{ad} &= U_d - U_a + W_{ad} \\ &= 42 - 0 + 10.5 = 52.5 \text{ kJ} \end{aligned}$$

$$\text{Now} \quad Q_{adb} = 62.5 \text{ kJ} = Q_{ad} + Q_{db}$$

$$\therefore Q_{db} = 62.5 - 52.5 = 10 \text{ kJ} \quad \text{Ans.}$$

Example 4.3 A piston and cylinder machine contains a fluid system which passes through a complete cycle of four processes. During a cycle, the sum of all heat transfers is -170 kJ. The system completes 100 cycles per min. Complete the

following table showing the method for each item, and compute the net rate of work output in kW.

Process	Q (kJ/min)	W (kJ/min)	ΔE (kJ/min)
a-b	0	2,170	—
b-c	21,000	0	—
c-d	-2,100	—	-36,600
d-a	—	—	—

Solution Process a-b:

$$Q = \Delta E + W$$

$$0 = \Delta E + 2170$$

\therefore

$$\Delta E = -2170 \text{ kJ/min}$$

Process b-c:

$$Q = \Delta E + W$$

$$21,000 = \Delta E + 0$$

\therefore

$$\Delta E = 21,000 \text{ kJ/min}$$

Process c-d:

$$Q = \Delta E + W$$

$$-2100 = -36,600 + W$$

\therefore

$$W = 34,500 \text{ kJ/min}$$

Process d-a:

$$\sum_{\text{cycle}} Q = -170 \text{ kJ}$$

The system completes 100 cycles/min.

$$\therefore Q_{ab} + Q_{bc} + Q_{cd} + Q_{da} = -17,000 \text{ kJ/min}$$

$$0 + 21,000 - 2,100 + Q_{da} = -17,000$$

\therefore

$$Q_{da} = -35,900 \text{ kJ/min}$$

Now $\oint dE = 0$, since cyclic integral of any property is zero.

$$\therefore \Delta E_{a-b} + \Delta E_{b-c} + \Delta E_{c-d} + \Delta E_{d-a} = 0$$

$$-2,170 + 21,000 - 36,600 + \Delta E_{d-a} = 0$$

\therefore

$$\Delta E_{d-a} = 17,770 \text{ kJ/min}$$

\therefore

$$\begin{aligned} W_{d-a} &= Q_{d-a} - \Delta E_{d-a} \\ &= -35,900 - 17,770 \\ &= -53,670 \text{ kJ/min} \end{aligned}$$

The table becomes

Process	Q (kJ/min)	W (kJ/min)	ΔE (kJ/min)
a-b	0	2,170	-2,170
b-c	21,000	0	21,000

c-d	- 2,100	34,500	- 36,600
d-a	- 35,900	- 53,670	17,770

Since

Rate of work output

$$\begin{aligned}\sum_{\text{cycle}} Q &= \sum_{\text{cycle}} W \\ &= -17,000 \text{ kJ/min} \\ &= -283.3 \text{ kW}\end{aligned}$$

Ans.

Example 4.4 The internal energy of a certain substance is given by the following equation

$$u = 3.56 pv + 84$$

where u is given in kJ/kg, p is in kPa, and v is in m^3/kg .

A system composed of 3 kg of this substance expands from an initial pressure of 500 kPa and a volume of 0.22 m^3 to a final pressure 100 kPa in a process in which pressure and volume are related by $pv^{1.2} = \text{constant}$.

- If the expansion is quasi-static, find Q , ΔU , and W for the process.
- In another process the same system expands according to the same pressure-volume relationship as in part (a), and from the same initial state to the same final state as in part (a), but the heat transfer in this case is 30 kJ. Find the work transfer for this process.
- Explain the difference in work transfer in parts (a) and (b).

Solution

(a)

$$u = 3.56 pv + 84$$

$$\Delta u = u_2 - u_1 = 3.56 (p_2 v_2 - p_1 v_1)$$

\therefore

$$\Delta U = 3.56 (p_2 V_2 - p_1 V_1)$$

Now

$$p_1 V_1^{1.2} = p_2 V_2^{1.2}$$

\therefore

$$V_2 = V_1 \left(\frac{p_1}{p_2} \right)^{1/1.2} = 0.22 \left(\frac{5}{1} \right)^{1/1.2}$$

$$= 0.22 \times 3.83 = 0.845 \text{ m}^3$$

\therefore

$$\Delta U = 356 (1 \times 0.845 - 5 \times 0.22) \text{ kJ}$$

$$= -356 \times 0.255 = -91 \text{ kJ}$$

Ans. (a)

For a quasi-static process

$$W = \int p dV = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

$$= \frac{(1 \times 0.845 - 5 \times 0.22) 100}{1 - 1.2} = 127.5 \text{ kJ}$$

\therefore

$$Q = \Delta U + W$$

$$= -91 + 127.5 = 36.5 \text{ kJ}$$

Ans. (a)