14. THERMODYNAMICS

14.1 Thermodynamic Systems and Thermal Equilibrium

The study of the relationship between heat and other forms of energy is known as *thermodynamics*. This often involves the production of heat from work or of work from heat. The former occurs, for instance, when we rub our palms together (mechanical work) to generate heat and the latter when fuel is burnt (heat) in an automobile engine to generate motion of the wheels (mechanical work).

In thermodynamics we are often concerned with the work-heat exchanges of matter (solid, liquid or gas) within a specified region of interest. The term *thermodynamic system* refers to the matter under study. Its immediate environment, which is affected by changes within the system, is called the *surroundings*. When the quantity of matter within the region under investigation is constant, we have a *closed system*. An *open system* is one which is free to exchange matter with its surroundings. Both closed and open systems are free to exchange heat with the surroundings. An *isolated system* is one which exchanges neither matter nor heat with its surroundings.

Macroscopic parameters, such as temperature, pressure and chemical composition, with which the internal state of a system are defined are called *thermodynamic properties*. A system is said to undergo a *thermodynamic process* when there is a change in any of its thermodynamic properties, i.e. a change in state. Quite often, a system is subjected to a process in which one of its thermodynamic properties remains constant. The terms *isothermal, isobaric* and *isochoric* processes refer to processes in which the temperature, the pressure and the volume, in that order, are held constant. An *adiabatic* process is one in which the system does not exchange heat with the surroundings.

Classical thermodynamics deals mainly with equilibrium states, i.e. with systems which are in *thermodynamic equilibrium*. To be in thermodynamic equilibrium, a system must be in mechanical, chemical and thermal equilibrium. This means that mechanical properties (e.g. pressure), ~ chemical properties (e.g. composition) and thermal properties (e.g. temperature) must all be at steady-state, i.e. they must not change with time.

If two systems A and B which are initially at different thermal states are brought into thermal contact, energy exchange will occur between the two systems until eventually, both attain the same thermal state. At this point the thermal properties of A and B no longer vary with time and they are in thermal equilibrium. *Two systems, each of which is in thermal equilibrium with a third system are also in thermal equilibrium with each other.* The foregoing statement is commonly referred to as the *zeroth law of thermodynamics*.

The thermodynamic property which determines the thermal state of a system is the temperature T. Thus if T_A, T_B and T_C are the temperatures of systems A, B and C respectively, the zeroth law states that if $T_A = T_B$ and $T_A = T_C$, then $T_B = T_C$.

14.2 First Law of Thermodynamics

The first law is essentially that o conservation of energy: *If a closed system*

absorbs a net amount of *(heat) energy* *(Q) from its surroundings and does an amount of work (W), the balance (Q - W) is used in raising the internal energy (U) of the system.* In mathematical notation
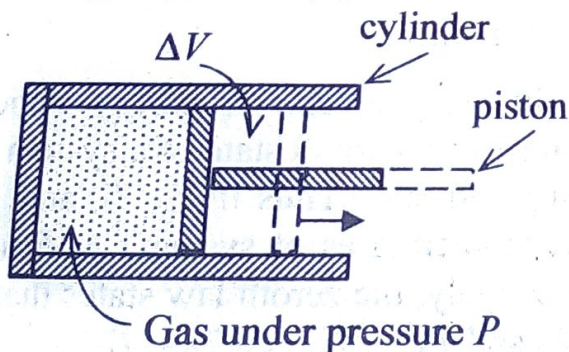
$$Q - W = \Delta U \qquad (14.1)$$

where ΔU is the change in internal energy of the system. If the system is taken from state 1 to state 2, then $Q - W = U_2 - U_1$, where U_1 and U_2 are the values of the internal energy at states 1 and 2 respectively. Conventionally, heat added to a system is positive while heat released by the system is negative.

Work is said to be done when any boundary of a system undergoes a displacement under the action of a force. Consider for instance, a system consisting of a gas under pressure P encased in a cylinder and piston unit (Fig. 14.1). The cylinder walls and the piston constitute the boundary of the system. The work done by the gas (dW) when the piston moves to the right under pressure P such that the volume of the gas increases by dV is

$$dW = PdV \qquad (14.2)$$

Fig. 14.1

cylinder

ΔV

piston

Gas under pressure P

If the piston is moved through a finite distance so that the volume of the gas changes from V_i to V_f, the total work done is found by integrating eq. (14.2), i.e.

$$W = \int_{V_1}^{V_2} PdV \qquad (14.3)$$

By convention, work done by the system is positive while work done on the system is negative.

14.3   Heat Engines

A *heat engine* is a device which produces work from a supply of heat. In such an engine, the working substance is usually taken through a cyclic process in which the initial and final states are identical. A common heat engine is the petrol (or *gasoline*) engine, the type in which the work done is used in propelling an automobile.
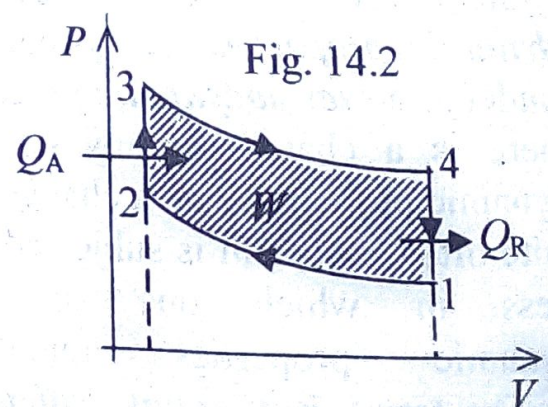
The working cycle for the petrol engine closely approximates the otto cycle, which consists of four main processes (Fig. 14.2):

1-2:   Adiabatic compression of air-petrol mixture (the working substance) from atmospheric pressure to state 2 (Compression stroke)

2-3:   Heating at constant volume to state 3 (Combustion)

3-4:   Adiabatic expansion to state 4 (Working stroke)

4-1:   Cooling at constant volume to state 1 (Exhaust)

Fig. 14.2

In this engine, heat Q_A is added to the system during the combustion process while heat Q_R is rejected to the surroundings during the exhaust. The net work output of the engine (W) is given by eq. (14.3), or the (shaded) area enclosed by the cycle on the P-V diagram.

For any system taken through a complete cycle, the internal energy at the initial and final states is the same. Applying the first law to the cycle gives

$$Q - W = dU = 0, \text{ or } Q = W,$$

i.e. the net work produced by the engine is equal to the net heat absorbed in a cyclic process. Since the net heat absorbed is equal to the heat added (Q_A) minus the heat rejected (Q_R), the first law becomes, for a cyclic process

$$Q_A - Q_R = W \qquad (14.4)$$

The **thermal efficiency** (η) of a heat engine is the ratio of the work done by the engine to the heat added, i.e.

$$\eta = \frac{W}{Q_A} = \frac{Q_A - Q_R}{Q_A}$$

or

$$\eta = 1 - \frac{Q_R}{Q_A} \qquad (14.5)$$

The most efficient engine is thus one for which the ratio Q_R/Q_A is made as small as possible.

14.4 Second Law of Thermodynamics

The first law of thermodynamics merely relates the amount of work derivable from an engine to the net heat absorbed by the engine without imposing restrictions on
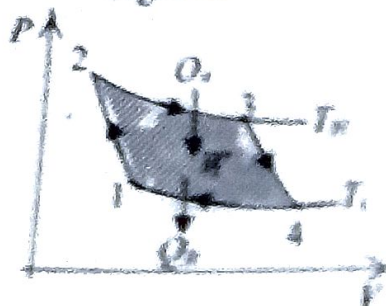
what fraction of the total heat added can be usefully converted into work. An ideal heat engine would be one in which all the heat added is converted into work, i.e. one in which $Q_R = 0$. Unfortunately, according to the second law of thermodynamics, such an engine cannot be built. This law can be stated as: "*It is impossible to construct an engine which absorbs heat from a reservoir at a single temperature and converts all of the heat to work.*" The term reservoir is used to denote any part of a system which can absorb or release a large quantity of heat without showing an appreciable change in temperature. In the petrol engine, for instance, the continuous combustion of the air/fuel mixture provides the hot reservoir while the surrounding atmosphere, into which the exhaust gases are discharged, is the cold reservoir. While the first law states in effect that it is impossible to get more work from an engine than the (heat) energy supplied to it, the second law states further that it is not even possible to convert all of the heat energy supplied into work. In other words, some heat must be rejected ($Q_R > 0$), in which case $W < Q_A$ (eq.14.4). It follows from eq. (14.5) that it is impossible to construct an engine which is 100% efficient.

There are several possible cycles through which the working fluid in a heat engine operating between two heat reservoirs can be taken. Although, according to the second law, none of these cycles can have an efficiency of 100%, it is of interest to know the maximum possible efficiency which can be attained. The **Carnot engine** is an idealized engine with such efficiency which will operate in an idealized cycle (**Carnot cycle**) which consists of four **reversible processes**. A reversible process is one which can be made to reverse itself without external aid. This is an idealized

conception since in reality, not known process is reversible. The reversible process is analogous to the frictionless process in mechanics. The Carnot cycle consists of (Fig. 14.3):

1-2: Reversible adiabatic compression of the working fluid from temperature T_C to temperature T_H

2-3: Reversible isothermal expansion during which heat Q_A is absorbed from the hot reservoir at T_H

3-4: Reversible adiabatic expansion from T_H to T_C

4-1: Reversible isothermal compression during which heat Q_R is rejected to the cold reservoir at T_C.

Fig. 14.3

The work-heat exchange in a heat engine is often depicted schematically as shown in Fig. 14.4. The Carnot engine is the most efficient engine which can operate between two specified temperatures (T_C and T_H). For a Carnot engine, the ratio of the temperatures of the two reservoirs is equal to Q_R/Q_A, i.e.
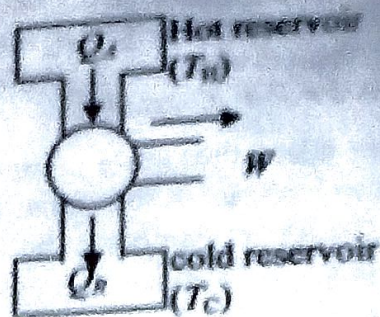
$$\frac{T_C}{T_H} = \frac{Q_R}{Q_A} \qquad (14.6)$$

The efficiency of a Carnot engine is thus given by

$$\eta_C = 1 - \frac{T_C}{T_H} \qquad (14.7)$$

in view of eqs. (14.5) and (14.6).

Fig. 14.4

14.5   Entropy

Suppose a process is carried out from state 1 to state 2 through a series of small intervals along a reversible path such that a small amount of heat ΔQ is added during each interval at which the system is at (absolute) temperature T. The ratio $(\Delta Q/T)_{rev}$ when summed for the whole reversible path gives

$$\int_1^2 \frac{dQ}{T}$$

The value of this integral for any reversible path depends only on the initial and final states of the process. A thermodynamic function is defined such that the differences between its values at states 1 and 2 is the same as the value of the integral. This function is the **entropy** (S) of the system. By definition,

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} \qquad (14.8)$$

for a reversible path linking state 1 to state 2. For an infinitesimal change in the state of the system, eq. (14.8) can be written in differential form as

$$dS = \frac{dQ}{T} \tag{14.9}$$

The change in entropy between any two equilibrium states is found by evaluating the ratio dQ/T and performing the integral in eq. (14.8). The same computation is performed even if the process linking states 1 and 2 is irreversible (as in all real processes) although it must be understood that the entropy change thus computed is based on the premise that the two equilibrium states can be linked in principle by a reversible process.

Problem Solving Tips

1. In applying the first law (eq. 14.1), it should be noted that heat added to a system is positive ($Q > 0$) while heat removed from a system is negative ($Q < 0$). $W > 0$ if work is done by the system, and $W < 0$ if work is done on the system.

2. For an isobaric (constant pressure) process, eq. (14.3) simply gives $W = P(V_f - V_i)$.

3. For an adiabatic process $Q = 0$ and eq. (14.1) gives $-W = \Delta U$.

4. If no work is done on or by the system, $W = 0$ and eq. (14.1) gives $Q = \Delta U$.

5. The maximum efficiency of an engine operating between two reservoirs is the Carnot efficiency.

6. An alternative statement of the second law is that the overall entropy change of all isolated system must be equal to or greater than zero, but the entropy change of a part of the system could be negative (see problems 14.10 and 14.12).

7. For an isothermal (constant temperature) process, eq. (14.8) yields $S_2 - S_1 = Q/T$, where Q is the heat added (or removed) from the system.

SOLVED PROBLEMS

14-1 A 50 kg mass is placed on a frictionless piston fitted to a gas cylinder. If 149 J of heat energy is supplied to the gas cylinder, increasing its internal energy by 100 J, determine the height to which the mass on the piston is raised.
(OAU)

Solution
$$Q = 149\ J,\ \Delta U = 100\ J$$
$$Q - W = \Delta U$$
$$\Rightarrow W = Q - \Delta U = 149-100 = 49\ J$$
But $W = mgh$
$$\Rightarrow h = W/mg = 49/(50 \times 9.8) = 0.10\ m$$

14-2 Three moles of a gas expand isothermally. If the initial temperature of the gas is 300 K and its final volume is twice the initial volume, calculate the work done by the gas.
(OAU)

Solution
$$PV = nRT,\ and$$
$$W = \int_{V_i}^{V_f} P\,dV$$
$$= \int_{V_i}^{V_f} \frac{nRT}{V}\,dV$$

For an isothermal process, $T =$ constant
$$\Rightarrow W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right)$$

Since $V_f = 2V_i$, $V_f/V_i = 2$ hence
$$W = (3)(8.314)(300)\ \ln 2 = 5186.5$$

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14-3 50 g of ice is melted at the same temperature. Calculate the change in internal energy if the latent heat of fusion of ice is 3.35×10^5 J/kg.

Solution

First law: $Q - W = \Delta U.$

Here the work done is zero i.e. $W = 0$ and

$$\Delta U = Q = mL_F$$

Hence $\Delta U = (0.05)(3.35 \times 10^5$

$= 1.68 \times 10^4$ J.

14-4 Compute the change in internal energy when 50 g of water is turned into 8.4×10^4 cm^3 of steam at 100°C under normal atmospheric pressure. The latent heat of vaporization of water is 2.26×10^6 J/kg.

Solution

First law: $Q - W = \Delta U. = \Delta U$

Since the vaporization occurs at constant pressure, eq. (14.3) is integrated to give

$W = P(V_f - V_i)$

$P = 1.013 \times 10^5$ N/m^2, V_f

$= 8.4 \times 10^{-2}$ m^3

$V_i = $ initial volume of 50 g of water ($\rho = 1,000$ kg/m^3)

$= 0.05/1000 = 5 \times 10^{-5}$ m^3

$\Rightarrow W = (1.013 \times 10^5)(8.4 \times 10^{-2} - 5 \times 10^{-5})$

$= 8.50$ kJ

$Q = mL_V$

$= (0.05)(2.26 \times 10^6) = 113.0$ kJ

$\Delta U = Q - W = 113.0 - 8.50$

$= 104.5$ kJ

14-5 A gas stored in an insulated cylinder with a movable piston is compressed adiabatically and 100 J of work is done in the process. The gas is then allowed to expand adiabatically while doing 10 J of work. What is the net change in the internal energy of the gas?

Solution

During adiabatic compression, work is done on the gas i.e. W is negative. Hence $W = -100$ J and $Q = 0$ (adiabatic)

$\Rightarrow \Delta U_C = Q - W = 0 - (-100) = 100$ J

During adiabatic expansion, $W = 10$ J and $Q = 0$

$\Rightarrow \Delta U_E = Q - W = 0 - 10 = -10$ J

Net change in internal energy

$\Delta U = \Delta U_C + \Delta U_E$ or

$\Delta U = 100 - 10 = 90$ J

14-6 A Carnot engine is operated between two heat reservoirs at temperatures 400 K and 300 K. If the engine receives 200 cal from the 400 K reservoir, (a) how many calories does it reject to the lower temperature reservoir? (b) What is the thermal efficiency of the engine? (OAU)

Solution

(a) For a Carnot engine, $T_C/T_H = Q_R/Q_A$

$\Rightarrow Q_R = Q_A \times T_C/T_H = (2000)(300/400)$

$= 1500$ cal.

(b) $\eta_C = 1 - T_C/T_H = 1 - 300/400$

$= 0.25$ (or 25%).

14-7 What is the maximum efficiency of an engine which operates between two reservoirs at temperatures of (a) 25°C and 40°C, and (b) 25°C and 100°C?

Solution

The maximum efficiency is the Carnot efficiency.

(a) $\eta_C = 1 - T_C/T_H$, where

$T_C = 25 + 273 = 298$ K and

$T_H = 40 + 273 = 313$ K

$\Rightarrow \eta_C = 1 - 298/313 = 4.79\%$

(b) $\eta_C = 1 - 298/373 = 20.11\%$

14-8 A Carnot engine operating between two reservoirs at temperatures 0°C and 100°C receives 10 kJ of heat from the high-

temperature reservoir. Calculate (a) the heat rejected to the low temperature reservoir, (b) the work done by the engine, and (c) the thermal efficiency.

Solution

(a) $Q_R/Q_A = T_C/T_H$

$\Rightarrow Q_R = Q_A \times T_C/T_H$

$= (10,000)(273/373) = 7319\ J$

(b) $W = Q_A - Q_R = 10000 - 7319,$

$= 2681\ J$

(c) $\eta_C = 1 - T_C/T_H$

$= 1 - 273/373 = 26.81\%$

14-9 Calculate the change in entropy when 100 g of ice at 0°C is converted to steam at 100°C. The latent heats of fusion of ice and of vaporization of water are 3.35×10^5 J/kg and 2.26×10^6 J/kg respectively and the specific heat of water is 4186 J/kg.C°.

Solution

Three stages must be considered separately. These are:
(1) the melting of ice at 0°C ,
(2) the heating of water from 0°C to 100°C, and (3) the vaporization of water at 100°C.

Stage (1):

$$\Delta S = \int \frac{dQ}{T} = \frac{Q_1}{T} \quad \text{(const. temp.)}$$

$Q = mL_F = (0.1)(3.35 \times 10^5)$

$= 3.35 \times 10^4\ J,$

$T = 273\ K$

$\Rightarrow \Delta S_1 = 3.35 \times 10^4/273 = 122.7\ J/K.$

Stage (2):

$dQ = mc\ dT,$ hence

$$\Delta S_2 = \int_{273}^{373} mc \frac{dT}{T} = mc \ln\left(\frac{373}{273}\right)$$

$$= (0.1)(4186) \ln\left(\frac{373}{273}\right)$$

$$= 130.6\ J/K$$

Stage (3):

$\Delta S_3 = Q_3/T = mL_V/T$

$\Rightarrow \Delta S_3 = (0.1)(2.26 \times 10^6)/373$

$= 605.9\ J/K$

Overall change in entropy,

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 859.2\ J/K.$

14-10 50 g of water at 25°C is frozen into ice at 0°C in a refrigerator. (a) What is the change in entropy of the water? (b) What is the minimum change in entropy of the refrigerator? (For ice, $L_F = 3.35 \times 10^5$ J/kg and for water, $c = 4186$ J/kg. C°).

Solution

(a) To cool water at 25°C to ice at 0°C,

$\Delta S = mc \ln(273/298)$

$= (0.05)(4186) \ln (273/298)$

$= -18.34\ J/kg.$

To freeze water at 0°C,

$\Delta S = -mL_F/T$

$= -(0.05)(3.35 \times 10^5)/273$

$= -61.36\ J/K.$

(negative sign because heat is removed from the water)

Total change in entropy of water $= -79.7$ J/K

(b) Since the overall entropy change of the system (i.e. water + refrigerator) must be positive (second law), the minimum change in the entropy of the refrigerator $+ 79.7$ J/K.

14-11 What is the change in entro[py] when 1 kg of water at 20°C is mix[ed] with 1 kg of water at 100°C? (F[or] water $c = 4186$ J/kg.C°).

Solution

Mixing 1 kg of water at 20°C (293 K) with 1 kg of water at 100°C (373 K) gives 2 kg of water at 60°C (333 K). Let the entropy of water be zero at 0°C (arbitrary reference state).

Entropy of 1 kg of water at 20°C = change in entropy upon heating 1 kg of water from 0°C to 20°C = mc ln (293/273)

$= (1)(4186)$ ln$(293/273) = 296.0$ J/K.

Similarly, entropy of 1 kg of water at 100°C

$= (1)(4186)$ln$(373/273) = 1306.5$ J/K

Total entropy before mixing

$= 296.0 + 1306.5 = 1602.5$ J/K.

After mixing, entropy of 2 kg of water at 60°C

$= (2)(4186)$ ln $(333/273) = 1663.3$ J/K

$\Rightarrow$ Change in entropy $= 1663.3 - 1602.5$

$= 60.8$ J/K.

14-12 *A 0.5 kg piece of metal ($c = 600$ J/kg.C°) at 300°C is dumped into a large pool of water at 20°C. Assuming the change in temperature of the water to be negligible, calculate the overall entropy change for the system.*

Solution

Change in entropy of the metal

$= mc$ ln (293/573)

$= (0.5)(600)$ ln (293/573)

$= -201.2$ J/K.

Heat absorbed by water $= Q =$ heat lost by metal.

Hence $Q = (0.5)(600)(300 - 20) = 84\,000$

Change in entropy of the water $= Q/T$

$= 84000/293 = 286.7$ J/K.

Overall change in entropy

$= 286.7 - 201.2 = 85.5$ J/K.

14-13 A certain mass of a gas is enclosed in a cylinder. When 100 J of heat is supplied to the gas, the volume increased from 1.5 L to 2.2 L at constant pressure 1.013×10^5 Pa. Calculate the increase in the internal energy of the gas. [Answer = 29.1 J]

14-14 Calculate the work done by 0.5 mole of an ideal gas when its volume decreases from 10 L to 4 L, with temperature kept constant at 20°C. [Answer = -1.1 J]

14-15 The volume of a gas decreased from 15 L to 12 L, keeping the pressure constant at 2×10^5 Pa. At the same time 150 J of heat is withdrawn from the gas. Calculate the change in its internal energy. [Answer = 450 J]

14-16 Calculate how much heat is needed to be supplied to a gas initially at a pressure of 1.25×10^5 Pa, such that the pressure increases by 25% at constant volume, and the internal energy increases by 120 J. [Answer = 120 J]

14-17 What is the change in internal energy of 0.5 kg of ice, when it has changed at atmospheric pressure to water at 10°C. Densities of ice and water are 917 kg/m^3 and 1000 kg/m^3. The latent heat of fusion of water is 3.33×10^5 J/kg and specific heat of water is 4.20×10^3 J/kg.K. [Answer = 1.88×10^5 J]

14-18 Calculate the change in internal energy of 2 kg of water at 90°C when it is changed to 3.30 m^3 of steam at 100°C. The whole process occurs at atmospheric pressure. The latent heat

of evaporation of water is 2.26×10^6 J/kg. [Answer = 4.27×10^6 J]

14-19 A Carnot engine operates between a hot reservoir at 120°C and a cold reservoir at 10°C. Calculate (a) its efficiency, and (b) the heat it rejects into the cold reservoir when it absorbs 2.6×10^5 J of heat from the hot reservoir. [Answer = 28%, 1.87×10^5 J]

14-20 A Carnot engine whose efficiency is 25% is to be designed to operate between a hot reservoir and a cold reservoir. The latter's temperature is 30°C. Calculate (a) the temperature of the hot reservoir, and (b) the work done by the engine when it rejects 1.5 $\times 10^4$ J into the cold reservoir. [Answer = 131°C, 5000 J]

14-21 An engine operates under the condition that it absorbs heat from a hot reservoir at 250°C to do some work, and then rejects heat into a cold reservoir at 28°C. Calculate the maximum efficiency that the engine can have. [Answer = 42.4%]

14-22 Calculate the change in entropy of 2.0 kg of water at 100° C when converted to steam at the same temperature. The latent heat of vaporization of water is 2.26×10^6 J/kg. [Answer = 1.21×10^4 J/K]