

MODULE 2

Unit 1	First Law of Thermodynamics
Unit 2	Consequences of the First Law of Thermodynamics
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1.0 INTRODUCTION

This unit focuses on heat and work as the only means by which the internal energy U of a system can change.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- write expression for work for different systems;
- explain heat transfer Q into or out of a system;
- state first law of thermodynamics;
- write modified equation of the first law under different known processes; and
- Solve problems based on the first law of thermodynamics.

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Work

Imagine a hydrostatic system contained in a cylinder with a movable piston like the one shown in figure 5.1 below. From the diagram, suppose an external force \mathbf{F} acted in the direction showed moving the piston from initial point 1 to final point 2 through a distance dx . Suppose that the cylinder has a cross section area \mathbf{A} , that the pressure exerted on the system at the piston face is \mathbf{P} , and that the force is \mathbf{PA} . The system also exerts an opposing force on the piston. The work done dW on the system in the process described above is

$$dW = PAdx \quad 5.1$$

but $A dx = dV$

Therefore

$$dW = -PdV \quad 5.2$$

The negative sign in the last equation indicate negative change in volume (i.e. a decrease in volume).

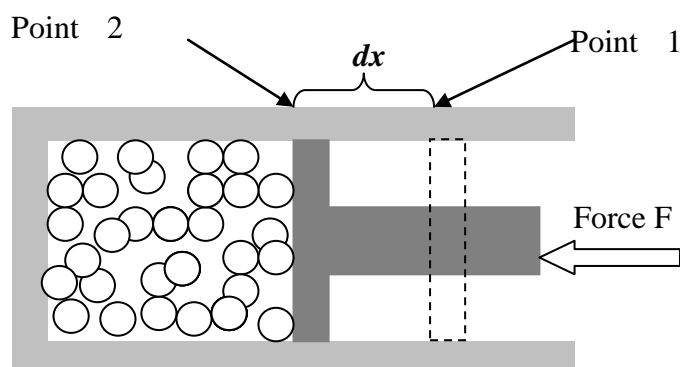


Fig.5.1: The Work Done on a System Compressed by External Force

In a finite quasi-static process in which the volume changes from V_i to V_f , the work done is

$$W = - \int_{V_i}^{V_f} P dV \quad 5.3$$

Note the sign convention, work done on a system is positive work, and work done by system is negative work.

3.1.1 Different Forms of Work

System	Force	Displacement	Work
Wire	Tension (F)	Length (L)	$F\Delta L$
Film	Surface Tension (S)	Area (A)	$S\Delta A$
Fluid	Pressure (P)	Volume (V)	$P\Delta V$
Magnet	Magnetic Field (H)	Magnetization (M)	$H\Delta M$
Dielectric	Electric Field (E)	Polarization (P)	$E\Delta P$
Chemical reaction	Chemical Potential (μ)	Particle number (N)	$\mu\Delta N$

3.1.2 Work in Quasi-Static Process

For a quasi-static isothermal expansion or compression of an ideal gas

$$W = - \int_{V_i}^{V_f} P dV \quad 5.4$$

But an ideal gas is the one which equation of state is $PV = nRT$, where n and R are constant. Replace P with $\frac{nRT}{V}$ in equation 5.4

$$W = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

and since T is constant for isothermal process,

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

Integration gives

$$W = -nRT \ln \frac{V_f}{V_i} \quad 5.5$$

3.1.3 Work and Internal Energy

When an adiabatic work (dW_{ad}) is done on or by the system, the internal energy of the system changes. The change in internal energy (ΔU) is equal to the adiabatic work done.

$$dU = dW_{ad} \quad 5.6$$

If a system changes from state 1 to state 2 by doing adiabatic work, and if the states are differed by a finite amount, then

$$\int_{U_1}^{U_2} dU = U_2 - U_1 = \int_1^2 dW_{ad} = -W_{ad} \quad 5.7$$

Suppose the work done is mechanical work (i.e. mechanical adiabatic work), then

$$U_2 - U_1 = -\int_1^2 PdV \quad 5.8$$

3.2 Heat

Heat (Q) is a form of energy that is transferred from one part of a system to another or to another system by virtue of a difference in temperature. As earlier discussed in unit 3, temperature gradient determines the direction of heat flow. When heat flows in or out of a system from its surroundings, the temperature of the system increases or decreases. And the internal energy of the system changes from initial state (U_i) to final state (U_f). This change in internal energy ΔU must be equal to the heat flow i.e.

$$\Delta U = U_f - U_i = Q \quad 5.9$$

Sign of Q

Q is positive when there is a flow of heat into the system

Q is negative when there is a flow of heat from the system

Heat bath or heat reservoir: This is a body that is so large that its temperature does not change appreciably when heat flows in or out of it.

Heat sink: Just like heat bath, this is a body that is so large that its temperature does not change appreciably when heat flows in or out of it. The temperature of heat sink is lower compare to that of the heat bath.

3.3 First Law of Thermodynamics

From the previous discussions in this unit, we have learnt that the internal energy of a system can change only if:

- a. there is flow of heat into the system or out of the system
- b. work is done on the system or by the system.

Hence, the change in internal ΔU of a system is

$$\Delta U = U_f - U_i = Q - W, \quad 5.10$$

where Q is the heat and W is work. Equation 5.10 is the first law of thermodynamic. The differential for of first law of thermodynamics is

$$dU = dQ - PdV \quad 5.11$$

The Statement of First Law of Thermodynamics

The internal energy of a system tends to increase if energy is added as heat Q and tends to decrease if energy is lost as work W done by the system.

3.4 Response Functions

When heat is added or withdrawn from a system, there is change in one, two or all its properties. This change in the measurable property/properties (macroscopic behaviour) is/are the basis of thermometer as we have discussed in unit 3. We can characterise the macroscopic behaviour of a system response's functions. These functions can be measured experimentally from changes in the thermodynamic coordinates by the use of external probes. Examples of response functions are Heat Capacities, force constant (e.g. isothermal compressibility), and thermal response (e.g. expansivity of a gas).

3.4.1 Heat Capacities

When heat is added to a system, its temperature will change. Heat capacities are obtained from change in temperature of a system upon addition of heat to the system.

From the equation of the first law, $dQ = dU + PdV$

Heat capacity at constant volume

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \quad 5.12$$

Heat capacity at constant pressure

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \quad 5.13$$

Heat capacities can be measured experimentally.

3.4.2 Force Constant

Force constants measure the (infinitesimal) ratio of displacement to force and are generalisation of the spring constant. Examples include isothermal compressibility of a gas

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T, \quad 5.14$$

and the susceptibility of a magnet

$$\chi_T = \frac{1}{V} \left(\frac{\partial M}{\partial B}\right)_T. \quad 5.15$$

It can be shown using equation of state for an ideal gas ($PV \propto T$) that $k_T = \frac{1}{P}$.

3.4.3 Thermal Response

This probes the change in thermodynamic coordinate with temperature. Example, the coefficient of volume expansion (expansivity of a gas) is given by

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad 5.16$$

And this is equal to $\frac{1}{T}$ for ideal gas.

3.5 Special Cases of First Law of Thermodynamics

Here we consider four different thermodynamic processes in which certain restriction is imposed on the system and the corresponding implication when apply to the first law.

Adiabatic process, $dQ = 0$, and equation of first law reduces to

$$dU = dW = PdV \quad 5.17$$

Isochoric process, $dV = 0$, and the equation of the first law becomes

$$dU = dQ = C_V dT \quad 5.18$$

Cyclic Process, $dU = 0$, and the equation of the first law becomes

$$Q = W \quad 5.19$$

Free expansion, $Q = W = 0$, and the equation of the first law becomes

$$dU = 0 \quad 5.19$$

SELF ASSESSMENT EXERCISE 1

- i. Write the equation for work for the following system
 - a. Film
 - b. Wire
 - c. Magnet
- ii. State first law of thermodynamics and write out modified equation of the first law.
- iii. If there are 2 mole of gas kept at a constant temperature of 20 °C and if this gas is compressed from a volume of 4 m³ to 2 m³, calculate the work done on the gas. (R=8.31J/mol.K)
- iv. Consider that 200 J of work is done on a system and 293.3 J is extracted from the system as heat. In the sense of the first law of thermodynamics, what is the value of ΔU ?

4.0 CONCLUSION

The first law of thermodynamics gives an insight to the internal energy of a system i.e. work and heat as the only means by which the internal energy of a system can change. The expression for work done a mechanical system is PdV and similar expression can be derived for work done under different systems. The differential form of first law is $dU = dQ - PdV$. In the next unit, we are going to be looking at some consequences of the first law of thermodynamics.

5.0 SUMMARY

In this unit you have learnt that:

- the expression for mechanical work done on or by a system is PdV
- heat and work are the only way by which the internal energy of a system can change
- the differential for the first law of thermodynamics is $dU = dQ - PdV$
- the modified form of the first law can be obtained for each of the known thermodynamic processes.

6.0 TUTOR-MARKED ASSIGNMENT

1. write out equations for work in different systems you have studied.
2. Derive the corresponding equation of the first law of thermodynamics under the following processes
(a) adiabatic process, (b) isochoric process, and (c) cyclic process.
3. The equation of state of a gas is $PV = nRT\left(1 - \frac{B}{V}\right)$, where R is a constant and B is a function of temperature alone. Show that the work done by 1 mole of this gas during a quasi-static, isothermal expansion from initial volume V_i to a final volume V_f is

$$-RT \left[\ln \frac{V_f}{V_i} + \left(\frac{B}{V_f} - \frac{B}{V_i} \right) \right]$$

7.0 REFERENCES/FURTHER READING

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UNIT 2 CONSEQUENCES OF THE FIRST LAW OF THERMODYNAMICS

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1.0 INTRODUCTION

The focus of the unit will be to derive important relations from the first law of thermodynamics.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- explain what is meant by energy equations;
- derive expression for C_V in terms of derivative of U;
- derive expression for C_P in terms of derivative of H;
- explain Gay-Lussac-Joule and Joule-Thomson experiment; and
- write the expressions for Joule coefficient η and Joule-Thomson coefficient μ .

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
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confirming what you have done.

4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Energy Equation

Energy equations are the equations which express the internal energy of a system as a function of the variables defining the state of the system. The energy equations, like equation of state, are different for different systems or substances. Equation of state and the energy equation together completely determine all the properties of a substance or system. Energy equations are derived independently, but not from equation of state.

We are going to consider systems whose state can be described by the properties P , V , and T .

3.2 T and V Independent

Consider internal energy U as a function of T and V , $U(T,V)$, then the change in internal energy dU between two equilibrium states in which temperature and volume differ by dT and dV is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad 6.1$$

$\left(\frac{\partial U}{\partial T}\right)_V$ is the slope of isochoric line and $\left(\frac{\partial U}{\partial V}\right)_T$ is the slope of isothermal line in which U is plotted as a function of T and V . $\left(\frac{\partial U}{\partial T}\right)_V$ can be measured experimentally and it has physical significance.

The first law

$$dQ = dU + PdV, \quad 6.2$$

put 6.2 in 6.1

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \quad 6.3$$

Rearranging

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV \quad 6.4$$

For a process at constant volume, $dV = 0$ and $dQ = C_V dT$, then 6.4 becomes

$$C_V dT = \left(\frac{\partial U}{\partial T}\right)_V dT$$

So,

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad 6.5$$

The specific heat capacity at constant volume C_V is the slope of isochoric line on U-T-V surface and its experimental measurement determines this slope at any point.

Equation 6.4 can be written for any reversible process as

$$dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV \quad 6.6$$

For a process at constant pressure, $dQ = C_P dT$, so 6.6 becomes

$$C_P dT = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$$

Dividing through by dT and replacing $\frac{dV}{dT}$ by $\left(\frac{\partial V}{\partial T}\right)_P$, we obtain

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \quad 6.7$$

Equation 6.7 holds for a system in any one equilibrium state, but does not refer to a process between two equilibrium states.

3.3 T and P Independent

The enthalpy H of a system, like the internal energy U , is a property of the system that depends on the state only and can be expressed as a function of any two variables P , V , and T . Each of these relations defines an enthalpy surface in a rectangular coordinate system in which H is plotted along one axis while the other two axes are P and V , P and T , or T and V .

Consider enthalpy as function of T and P i.e. $H(T, P)$,

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad 6.8$$

From the definition of enthalpy (to be discussed in module 3 unit 2) for a PVT system:

$$H = U + PV \quad 6.9$$

Differential of H, dH is

$$dH = dU + PdV + VdP \quad 6.10$$

Combining 6.10 with the first law (i.e. replace dU in 6.10 with $dQ - PdV$ and make dQ the subject) gives

$$dQ = dH - VdP \quad 6.11$$

insert 6.8 in 6.11, to obtain

$$dQ = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP \quad 6.12$$

For an isobaric process ($dP = 0$), $dQ = C_P dT$. Hence

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \quad 6.13$$

Equation 6.13 means that the specific heat capacity at constant pressure C_P is equal to the slope of an isobaric line on the $H - T - P$ surface.

Equation 6.12 can be written for any reversible process as

$$dQ = C_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP \quad 6.14$$

In a process at constant volume, $dQ = C_V dT$ and

$$C_P - C_V = -\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial P}{\partial T}\right)_V \quad 6.15$$

If the temperature is constant, equation 6.14 becomes

$$dQ = \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP \quad 6.16$$

In an adiabatic process, $dQ = 0$, then equation 6.14 becomes

$$C_P \left(\frac{\partial T}{\partial P}\right) = -\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \quad 6.17$$

3.4 P and V Independent

Consider U as a function of P and V, $U(P,V)$, then the change in internal energy dU between two equilibrium states is

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \quad 6.18$$

Consider also $U(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad 6.19a$$

and $T(P, V)$ gives

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV \quad 6.19b$$

Eliminating dT in equation 6.19a (i.e. put 6.19b in 6.19a) we have

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V\right] dP + \left[\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad 6.20$$

By comparing equation 6.20 with 6.18, it implies that

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \quad 6.21$$

and

$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \quad 6.22$$

Generally, for any property w , and any three variables x, y, z the form of equations 6.21 and 6.22 are

$$\left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial w}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \quad 6.23$$

and

$$\left(\frac{\partial w}{\partial y}\right)_x = \left(\frac{\partial w}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x + \left(\frac{\partial w}{\partial y}\right)_z \quad 6.24$$

Note that equation 6.23 is the chain rule of partial derivatives.

Therefore for $H(P, V, T)$ we have

$$\left(\frac{\partial H}{\partial V}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P \quad 6.25$$

and

$$\left(\frac{\partial H}{\partial P}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V + \left(\frac{\partial H}{\partial P}\right)_T \quad 6.26$$

From equation 6.21, using 6.5 we obtain

$$\left(\frac{\partial U}{\partial P}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right)_V \quad 6.27$$

Also from equation 6.25, using equation 6.13 we have

$$\left(\frac{\partial H}{\partial V}\right)_P = C_P \left(\frac{\partial T}{\partial V}\right)_P \quad 6.28$$

We can as well show that

$$dQ = C_P \left(\frac{\partial T}{\partial V}\right)_P dV + C_V \left(\frac{\partial T}{\partial P}\right)_V dP \quad 6.29$$

and

$$C_V \left(\frac{\partial P}{\partial V}\right)_S = C_P \left(\frac{\partial P}{\partial V}\right)_T \quad 6.30$$

3.5 Gay-Lussac-Joule Experiment

The partial derivative $\left(\frac{\partial U}{\partial V}\right)_T$ describe the way in which the internal energy of a given system varies with volume at constant temperature. Similarly, $\left(\frac{\partial H}{\partial P}\right)_T$ describe the way in which enthalpy of a given system varies with pressure at constant temperature. These two derivatives can be calculated from equation of state of the system (see free expansion of gas for the partial derivative of \mathbf{U} in module 4, unit 2).

Using

$$\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V = -1$$

then

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_U \quad 6.31$$

Also,

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

then

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P \left(\frac{\partial T}{\partial P}\right)_H \quad 6.32$$

From equation 6.31, measurement of the rate of change of temperature with volume in a process at constant internal energy gives the desired derivatives (i.e. $\left(\frac{\partial U}{\partial V}\right)_T$).

Similarly, from equation 6.32, measurement of the rate of change of temperature with pressure in a process at constant enthalpy gives the desired derivatives (i.e. $\left(\frac{\partial H}{\partial P}\right)_T$).

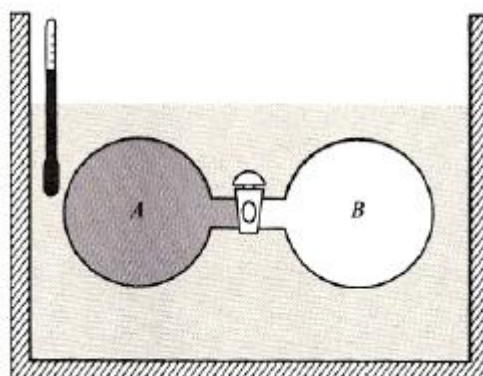


Fig. 6.1: Gay-Lussac-Joule Experiment (After Sear and Salinger 1975)

Gay-Lussac and Joule made an attempt to measure the dependence of the internal energy U of a gas on its volume. The experimental set-up used by Gay-Lussac and Joule is shown in figure 6.1. Vessel A contains a sample of the gas for the investigation and is connected to an evacuated vessel B by a tube in which there is a stopcock that is initially closed. The whole arrangement is immersed in a water tank of known mass which temperature can be measured by a thermometer.

The whole set-up is allowed to attain thermal equilibrium and the temperature is measured and recorded. Then the stopcock is opened and the gas is allowed to undergo a free expansion into the evacuated vessel. The work done W during free expansion process is zero (see free expansion in module 4, unit 2). The system will eventually come to a new equilibrium state if pressure is the same in both vessels. If temperature of the gas changes during this process (i.e. free expansion), there will be heat flow between the gas and the water bath and the final temperature will be different from the initial one already measured and recorded.

Gay-Lussac and Joule found that the temperature change of the water bath, if it changes at all, was too small to be detected. The reason is that the heat capacity of the bath is so large that a small heat flow in or out of it produces only a very small change in temperature. Similar experiments have been performed, using other technique, and the results showed that the temperature change of the gas during free expansion is not large.

Hence the postulate as an additional property of an ideal gas is that temperature change during a free expansion is zero. The first law of thermodynamics (i.e. $\Delta U = U_f - U_i = Q - W$), since both Q and W are zero, becomes

$$\Delta U = 0 \quad 6.33$$

Therefore the internal energy is constant, and for an ideal gas,

$$\left(\frac{\partial T}{\partial V}\right)_U = 0 \quad (\text{ideal gas}) \quad 6.34$$

The partial derivative in equation 6.34 is called the Joule coefficient and is represented by η

$$\eta \equiv \left(\frac{\partial T}{\partial V}\right)_U \quad 6.35$$

Note that η is equal to zero for ideal gas but it is not zero for real gas.

From equation 6.31, since C_V is finite, then for ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad 6.36$$

The implication of equation 6.36 is that the internal energy U , for an ideal gas, is a function of temperature only. That is for an ideal gas, the partial derivative $\left(\frac{\partial U}{\partial T}\right)_V$ is a total derivative and

$$C_V = \frac{dU}{dT}, dU = C_V dT \quad 6.37$$

Integrating equation 6.37 from reference level (U_o, T_o) to (U, T) , and if C_V is constant that is

$$\int_{U_o}^U dU = U - U_o = C_V \int_{T_o}^T dT$$

which gives

$$U = U_o + C_V(T - T_o) \quad 6.38$$

Equation 6.38 is the energy equation of an ideal gas.

3.6 Joule-Thomson Experiment

Joule and Thomson made an attempt to measure the dependence of the enthalpy of a gas on its pressure (i.e. equation 6.30). The experimental set-up used by Joule and Thomson is shown in figure 6.2. The gas in compartment 1 (with T_1 , P_1 , and V_1) was allowed to expand freely through a porous plug. The gas expands from pressure P_1 to P_2 by the throttling action of the porous plug. The entire system is insulated so that the expansion occurs adiabatically (i.e. $Q = 0$).

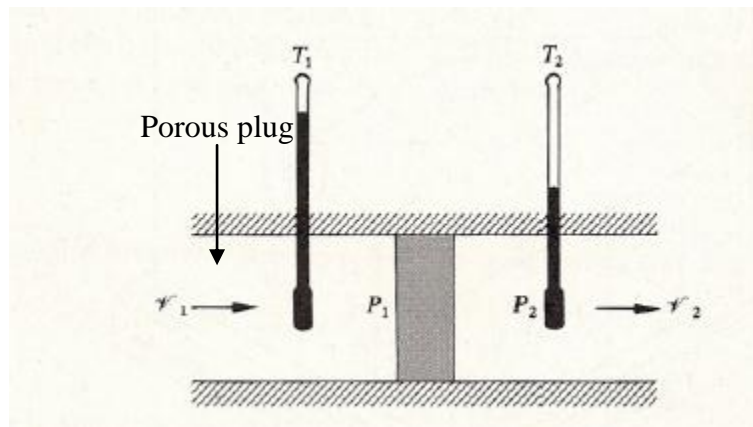


Fig. 6.2 : Joule-Thomson Experiment (After Sear and Salinger 1975)

The Gas is allowed to flow continuously through the porous plug, and when steady state condition have been reached the temperatures of the gas before and after expansion,

T_1 and T_2 , are measured directly with sensitive thermocouple thermometers. The total work done during the expansion can be written as

$$W = W_1 + W_2 = P_1V_1 - P_2V_2 \quad 6.39$$

The overall change in internal energy of the gas during the adiabatic expansion is then

$$\Delta U = Q + W = 0 + W = +W \quad 6.40$$

$$\Delta U = P_1V_1 - P_2V_2 = U_2 - U_1$$

rearranging gives

$$U_2 + P_2V_2 = U_1 + P_1V_1 \quad 6.41$$

But

$$H = U + PV ,$$

then, equation 6.41 becomes

$$H_1 = H_2 \quad 6.42$$

This is therefore an **ISOENTHALPIC** expansion and the experiment measures directly the change in temperature of a gas with pressure at constant enthalpy. The Joule-Thomson coefficient μ is,

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H \quad 6.43$$

For an ideal gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \quad (\text{ideal gas}) \quad 6.44$$

The implication of equation 6.44 is that the enthalpy H , for an ideal gas, is a function of temperature only. That is for an ideal gas, the partial derivative $\left(\frac{\partial H}{\partial P}\right)_T$ is a total derivative and

$$C_P = \frac{dH}{dT}, dH = C_P dT \quad 6.45$$

Integrating equation 6.45 from reference level (H_o, T_o) to (H, T) , and if C_P is constant that is

$$\int_{H_o}^H dH = H - H_o = C_P \int_{T_o}^T dT$$

gives

$$H = H_o + C_P(T - T_o) \quad 6.46$$

Equation 6.46 is the enthalpy equation for an ideal gas and is analogue of equation 6.38.

Therefore for ideal gas, from 6.36 and 6.44

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T = 0 \quad 6.47$$

Then equations 6.7 and 6.17 become

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = V\left(\frac{\partial P}{\partial T}\right)_V = nR$$

And from equation of state of ideal gas, $PV = nRT$

$$P\left(\frac{\partial V}{\partial T}\right)_P = V\left(\frac{\partial P}{\partial T}\right)_V = nR$$

Hence for ideal gas,

$$C_P - C_V = nR \quad 6.48$$

3.7 Reversible Adiabatic Process

From equation 6.30, for any substance in a reversible adiabatic process,

$$\left(\frac{\partial P}{\partial V}\right)_S = \frac{C_P}{C_V} \left(\frac{\partial P}{\partial V}\right)_T \quad 6.49$$

For an ideal gas,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V} \quad 6.50$$

Check block 1 for how equation 6.50 could be derived

If we representing the ratio C_P/C_V by γ ,

That is,

$$\gamma \equiv \frac{C_P}{C_V} \quad 6.51$$

and inserting 6.50 and 6.51 in 6.49, and omitting subscript S for simplicity then,

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0 \quad 6.52$$

Integrating equation 6.52

$$\ln P + \gamma \ln V = \ln K$$

or

$$PV^\gamma = K \quad 6.53$$

where K in equation 6.53 is a constant of integration.

From equation 6.53, eliminating V gives

$$TP^{(1-\gamma)/\gamma} = \text{constant}, \quad 6.54$$

and eliminating P gives

$$TV^{\gamma-1} = \text{constant}. \quad 6.55$$

Equation 6.54 and 6.55 are based on the fact that the gas obeys its equation of state in any reversible process.

Block 1

Ideal gas equation is

$$PV = nRT$$

$$PdV + VdP = nRdT$$

at constant T (i.e. dT=0)

$$VdP = -PdV$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}$$

SELF ASSESSMENT EXERCISE 1

- i. What is energy equation?
- ii. Obtain equation 6.54 and 6.55 from 6.53.
- iii. The internal energy of a van der Waals gas is given by

$$U = C_V T - \frac{a}{V} + \text{constant}$$

show that for a van der Waals gas

$$C_P - C_V = nR \frac{1}{1 - \frac{2a(V-b)^2}{nRTV^3}}$$

4.0 CONCLUSION

Some of the consequences of the first law of thermodynamics were discussed in this unit. From the first law, with partial derivatives as tools, we have derived the expressions for specific heat capacities. Also discussed were the experiments by Gay-Lussac-Joule and Joule-Thomson which established that, for an ideal gas, the internal energy (U) and the enthalpy (H) are functions of temperature only.

5.0 SUMMARY

In this unit, you have learnt that:

- energy equations are the equations which express the internal energy of a system as a function of the variables defining the state of the system
- the specific heat capacity at constant volume is $C_V = \left(\frac{\partial U}{\partial T}\right)_V$
- the difference between the specific heat capacities $C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$
- for adiabatic reversible process, $PV^\gamma = K$.

6.0 TUTOR-MARKED ASSIGNMENT

1. What is an energy equation
2. Derive expression for C_v in terms of derivative of U
3. Derive expression for C_p in terms of derivative of H
4. Explain Gay Lussac Joule and Joule Thompson experiment
5. Write out expression for Joule coefficient and Joule Thompson Co-efficient
6. i. Show that $\left(\frac{\partial U}{\partial T}\right)_P = C_p - P\beta V$
- ii. For an ideal gas show that (a) $\left(\frac{\partial U}{\partial P}\right)_T = 0$.

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UNIT 3 **ENTROPY AND THE SECOND LAW OF THERMODYNAMICS**

CONTENTS

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1.0 INTRODUCTION

One of the statements of the second law of thermodynamics is that the change in entropy of a system cannot be negative (i.e. it is either zero or positive). This unit focuses on entropy, its value during reversible and irreversible processes, and the second law of thermodynamics.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- define entropy;
- write the equation for change in entropy during reversible and irreversible processes;
- state the second law of thermodynamics;
- describe the Carnot cycle / engine; and
- calculate the efficiency of Carnot engine.

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Entropy of a System

In unit 1 we defined a system as a restricted region of space one has chosen to study. Also, we mentioned that the properties or coordinates used to describe thermodynamic system are the thermodynamic properties or coordinates. One of such properties is entropy. Entropy, S , is the degree of disorderliness of a system. Unlike energy, entropy of a system does not always obey a conservation law.

3.2 Change in Entropy

The change in entropy ΔS of a system during a process that takes the system from initial state i to a final state f is defined as

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad 7.1$$

Equation 7.1 implies that change in entropy depends on both the energy transfer as heat during the process and the temperature of the system. The S.I unit of entropy and change in entropy is Joule per Kelvin (JK^{-1}).

3.2.1 Reversible Process

For a reversible process that occurs in a closed system, the entropy always remains constant. That is, the change in entropy for a reversible process is zero ($\Delta S = 0$). This statement can be explained using a Carnot cycle (See section 3.5.3 of this unit).

3.2.2 Irreversible Process

An irreversible process can be defined as one which direction cannot be reversed by an infinitesimal change in some property of the system. A good example of irreversible process is illustrated in figure 7.1. Figure 7.1 shows a hot reservoir at

temperature T_H in thermal contact through a conductor with a cold reservoir at temperature T_C . Suppose the arrangement is isolated from the surrounding (i.e. no heat flows in or out of the arrangement), heat flows from hot reservoir to cold reservoir and not in reversed direction. This process is an irreversible process. Suppose heat Q flows from the hot reservoir to the cold reservoir, we can then write the equation for the total entropy change ΔS during the process.

The change in entropy for the cold reservoir ΔS_C , using equation 7.1 is

$$\Delta S_C = \frac{Q}{T_C} \quad 7.2$$

ΔS_C is positive because heat Q flows into the cold reservoir and is positive Q . Similarly the change in entropy of the hot reservoir ΔS_H , using equation 7.1 is

$$\Delta S_H = -\frac{Q}{T_H} \quad 7.3$$

ΔS_H is negative because heat Q flows out of the hot reservoir (i.e. $-Q$). The total entropy is

$$\Delta S = \Delta S_H + \Delta S_C$$

which gives

$$\Delta S = -\frac{Q}{T_H} + \frac{Q}{T_C} > 0 \quad 7.4$$

The total entropy ΔS is greater than zero because T_H is greater than T_C .

We can then say that $\Delta S > 0$ for irreversible process.

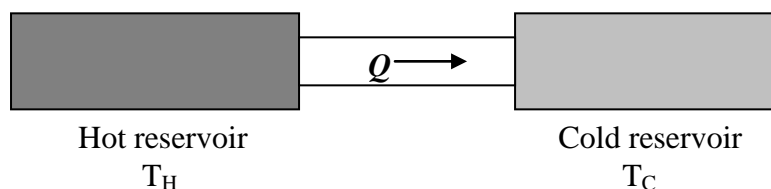


Fig. 7.1 : Heat Q Flows from Hot Reservoir to Cold Reservoir

3.2.3 Change in Entropy during Adiabatic and Isothermal Processes

Change in entropy is given by equation 7.1 and it is a function of Q and T .

Reversible adiabatic process: during adiabatic process, $dQ = 0$, and this implies that during reversible adiabatic process $dQ_r = 0$. Then, going by equation 7.1

$$dS = 0 \quad 7.5$$

Reversible isothermal process: An example of reversible isothermal process is phase change and this occurs at constant pressure during which the temperature also remains constant.

$$S_f - S_i = \int_i^f \frac{dQ_r}{T} = \frac{1}{T} \int_i^f dQ_r = \frac{Q}{T} \quad 7.6$$

where Q is the latent heat or latent heat of transformation.

3.3 Entropy as a State Function

Entropy, like pressure, energy, and temperature, is a property of the state of a system and is independent of how that state is reached.

The above statement can be justify from the equation of the first law of thermodynamics

$$dU = dQ - dW$$

For a reversible isobaric process,

$$dQ = PdV + nC_P dT \quad 7.7$$

Using the equation for the ideal gas, P in equation 7.7 can be replaced with $\frac{nRT}{V}$.

Then dividing through by T , gives

$$\frac{dQ}{T} = nR \frac{dV}{V} + nC_P \frac{dT}{T} \quad 7.8$$

Suppose each term of equation 7.8 is integrated between an arbitrary initial state i and an arbitrary final state f we get

$$\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_P \frac{dT}{T}$$

But change in entropy ΔS is already given to be $\frac{dQ}{T}$ in equation 7.1, so

$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_P \ln \frac{T_f}{T_i} \quad 7.9$$

Equation 7.9 thus implies that the change in entropy ΔS between the initial state and final state of an ideal gas depends only on properties of the initial and properties of final state (i.e. ΔS does not depend on how the gas changes between the two states).

3.4 The Second Law of Thermodynamics

The change in entropy ΔS , as discussed in section 3.2, for a process occurring in a closed system is zero for reversible process and greater than zero for irreversible process. This is one of the statements of the second law of thermodynamics.

The second law of thermodynamics gives the direction in which the natural process will take place.

Statement of the Second law of thermodynamics

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. Entropy of a system never decreases.

Mathematical statement of the Second law of thermodynamics

$$\Delta S \geq 0$$

7.10

3.5 Carnot Engine

Carnot engine is the most efficient kind of heat engine and because of this it is sometime referred to as an ideal heat engine. Ideal in the sense that all processes in the cycle are reversible and no wasteful energy transfer occur due to friction and turbulence. This engine is after a French scientist and engineer N.L. Sadi Carnot. The P-V diagram of the Carnot cycle is shown in figure 7.2 and the arrow on the plot indicate the direction of the cycle (i.e. clockwise). During each cycle, the engine (i.e. the working substance) absorbs energy Q_H as heat from a thermal reservoir at constant temperature T_H and eject energy Q_C as heat to a second reservoir at a constant lower temperature T_C .

Description of the Processes

- Process **de** is an isothermal process during which heat Q_H is transferred at temperature T_H to the working from the hot reservoir. This causes the gas to undergo isothermal expansion from volume V_d to V_e .
- Process **ef** is an adiabatic expansion i.e no heat is added as the working substance expands from volume V_e to V_f . Temperature decreases during the process from T_H to T_C

- Process **fg** is an isothermal process during which heat Q_C is transferred at temperature T_C from the working to cold reservoir. This causes the gas to undergo isothermal compression from volume V_f to V_g .
- Processes **gd** is an adiabatic compression i.e. no heat is transferred as the working substance compresses from volume V_g to V_d . Temperature increases during the process from T_C to T_H .

Heat engine is discussed in more detail in the next unit (i.e. Module 2, unit 4)

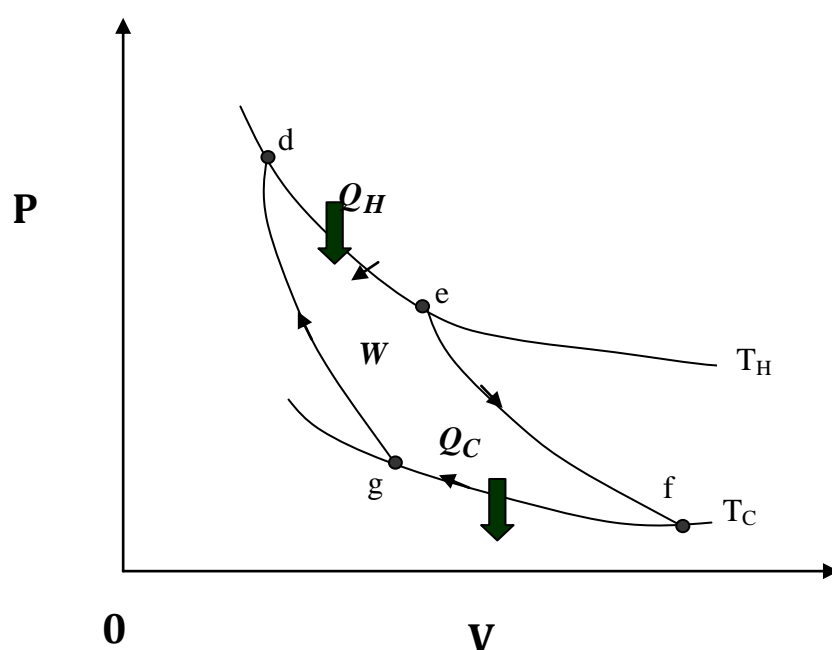


Fig. 7.2: PV Plot for the Carnot Cycle

Work:

From the first law of thermodynamics ($\Delta U = Q - W$), the total work done during a cycle or cyclic process can be calculated. For a cyclic process $\Delta U = 0$, the total heat transfer per cycle $Q = Q_H - Q_C$, and the total work done is W . Then, the first law of thermodynamic for the Carnot cycle is

$$W = Q_H - Q_C \quad 7.11$$

3.5.1 Efficiency of a Carnot Engine

The efficiency of a heat engine is

$$E = \frac{W}{Q_H} = \frac{\text{work output}}{\text{heat in}} \quad (\text{In one cycle}) \quad 7.12$$

Using equation 7.11, equation 7.12 becomes

$$E = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad 7.13$$

But the ratio of the rejected heat Q_C to the input heat Q_H for a reversible process can be written as

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \quad 7.14$$

where temperature T_C and T_H are temperatures in Kelvin.

Rearranging 7.14 gives

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \quad 7.15$$

Insert equation 7.14 in equation 7.13 to obtain

$$E = 1 - \frac{T_C}{T_H} \quad 7.16$$

Equation 7.16 is the efficiency of a Carnot engine operating between two heat reservoirs in which heat is taking in at temperature T_H and heat is ejecting at temperature T_C . Temperatures T_H and T_C must be in Kelvin. The relation in equation 7.16 gives the maximum possible efficiency for a heat engine operating between two Kelvin temperatures T_H and T_C .

3.5.2 Another Statement of Second Law of Thermodynamics

The efficiency of an ideal heat engine is given by equation 7.16. The implication of this is that no heat engine can have efficiency greater than that of a Carnot engine. It is clear from equations 7.13 and 7.16 that the efficiency of a Carnot engine is less than 100%. This of course is another statement of the second law of thermodynamics. That is, the efficiency of heat engine is always less than 100%. This statement is called Kelvin's statement

Kelvin's Statement: No process is possible whose sole result is the complete conversion of heat into work.

3.5.3 Entropy Change of a Reversible Process

A good example of a reversible thermodynamic process is Carnot cycle.

In a Carnot engine, there are only two reversible energy transfers as heat (i.e. entropy change at T_H and at T_C). The net entropy change per cycle is

$$\Delta S = \Delta S_H + \Delta S_C = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} \quad 7.17$$

where ΔS_H is the positive entropy because energy Q_H is added to the working substance (i.e. increase in entropy) and ΔS_C is negative entropy because energy Q_C is removed from the working substance as heat (i.e. decrease in entropy). Using equation 7.15, then equation 7.17 becomes

$$\Delta S = \Delta S_H + \Delta S_C = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0 \quad 7.18$$

Therefore the entropy for a reversible process ΔS is zero (i.e. $\Delta S = 0$).

SELF ASSESSMENT EXERCISE 1

- i. Define entropy.
- ii. How much heat is required for a reversible isothermal expansion of an ideal gas at 132 °C if the entropy of the gas increases by 46.0 J/K?
- iii. A Carnot engine does 20,900 J of work and rejects 7330 J of heat into the hot reservoir at 25 °C. What is the Kelvin temperature of the hot reservoir?
- iv. State the second law of thermodynamics in relation to entropy

4.0 CONCLUSION

Entropy of a system is the degree of disorderliness of a system. The change in entropy of a reversible process is zero while that of an irreversible process is greater than zero. This is the statement of the second law of thermodynamics and mathematically it is $\Delta S \geq 0$. Carnot engine is the most efficient heat engine and no real engine operating between two temperatures as that of Carnot engine has efficiency as high as that of Carnot engine.

5.0 SUMMARY

In this unit you have learnt that:

- entropy of a reversible process is constant and that of an irreversible process increases
- the second law of thermodynamics is $\Delta S \geq 0$
- Carnot engine is the most efficient heat engine

- the efficiency of Carnot engine operating between two temperatures T_H and T_C is $E = 1 - \frac{T_C}{T_H}$.

6.0 TUTOR-MARKED ASSIGNMENT

1. Define entropy.
2. Write equation for change in entropy during reversible and irreversible process.
3. State the second law of thermodynamics.
4. Describe the Carnot engine.
5. A 2.50 mole sample of ideal gas expands reversibly and isothermally at 360 K until its volume is doubled. What is the increase in entropy of the gas?
6. A lump of steel weighing 30 kg at a temperature of 427 °C is dropped in 150 kg of oil at 27 °C. The specific heats of the steel and oil are 0.47 KJ/kgK and 2.5 KJ/kgK respectively. Estimate the entropy change of the steel, the oil and the system consisting of oil and the lump of steel.
7. A Carnot engine operates between reservoirs which temperatures are 700 K and 400 K. To improve the efficiency of the engine, it is decided to either raise the temperature of the hot reservoir by 30 K or to lower the temperature of the cold reservoir by 30 K. Which of these options gives the greater improvement? Justify your answer by calculating the efficiency in each case.

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UNIT 4 HEAT ENGINES

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- 7.0 References/Further Reading

1.0 INTRODUCTION

As discussed in the last unit, Carnot engine is an ideal heat engine and no real heat engine has efficiency as high as that of a Carnot engine. This unit discusses some of the available real engines.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- name some of the available heat engines and draw the P-V diagram for each of them;
- explain the processes involve in the cycle of a particular heat engine; and
- derive expression for efficiency for each of these heat engines.

2.0B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.

3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Heat Energy

A heat engine is a device used to convert thermal energy (i.e. heat) into mechanical work and then exhausts the heat which cannot be used to do work.

1.1.1 Basic Operation of Heat Engine

The working body absorbed heat from the hot reservoir at relatively high temperature. Part of the absorbed heat is used by the working body to do mechanical work. The unused energy is then ejected as heat at lower temperature. The process of converting thermal energy to mechanical work by heat engine is shown in figure 8.1.

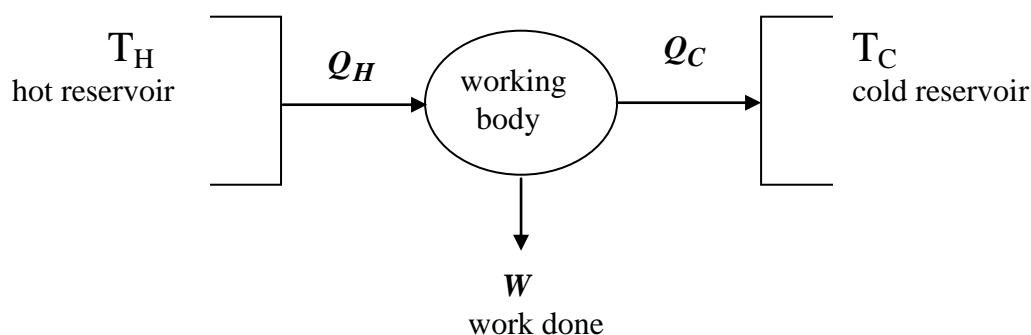


Fig. 8.1: Heat Engine

Heat engine as shown in the figure 8.1 above comprises of two heat reservoirs, one hot at T_H and the other cold at T_C . The interaction between these two reservoirs and the working body leads to the conversion of heat energy to mechanical work. Another explanation is that the working body absorbs heat Q_H at temperature T_H , uses part of it to do mechanical work, and then ejects the unused heat energy (Q_C) at temperature T_C through the cold reservoir.

3.2 Thermodynamic Efficiency ε of Real Engines

The efficiency of a heat engine is

$$E = \frac{W}{Q_H} = \frac{\text{work output}}{\text{heat in}} \quad (\text{in one cycle}) \quad 8.1$$

The efficiency E measures the fraction of heat pumped into the working body that is converted to mechanical work by the working body. The efficiency of real heat engines is always less than unity.

The Changes in energy of the working body are related to the changes in the thermodynamic properties. Using the combined first and second laws of thermodynamics,

$$dU = TdS - PdV = dQ - dW \quad 8.2$$

where dQ is the heat into the working body and dW is the mechanical work (i.e. work output). But the working body operates in a cycle (i.e. cyclic process), returning the system back to its initial state. We can integrate 8.2 over a complete cycle.

$$0 = \oint_{\text{cycle}} dU = \oint_{\text{cycle}} TdS - \oint_{\text{cycle}} PdV \quad 8.3$$

where $\oint_{\text{cycle}} dU = U_{\text{final}} - U_{\text{initial}} = 0$ since the system returns to its initial state.

$\int_{\text{cycle}} PdV = W$ is the work done in a cycle

$\oint_{\text{cycle}} dQ = Q_H - Q_C = Q$ the total heat transfer to the working body in a cycle. So

equation 8.3 becomes

$$0 = Q_H - Q_C - W \quad 8.4$$

Rearrange to have

$$W = Q_H - Q_C \quad 8.5$$

Insert equation 8.5 in equation 8.1

$$E = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad 8.6$$

Therefore,

$$E = 1 - \frac{Q_C}{Q_H} = 1 - \frac{\text{heat released}}{\text{heat absorbed}} \quad 8.7$$

Equation 8.7 is the generalized form of efficiency for heat engine.

Some examples of real engines are Otto engine, Stirling engine, and steam engine. We are going to treat here only Otto engine and Stirling engine.

3.3 Otto Cycle / Engine

Otto cycle consists of two adiabatic processes and two constant volume (isochoric) processes or strokes. The PV diagram of Otto cycle is shown in figure 8.2 and as indicated in the PV diagram, heat is absorbed during one of the isochoric processes and heat is rejected during the other isochoric process.

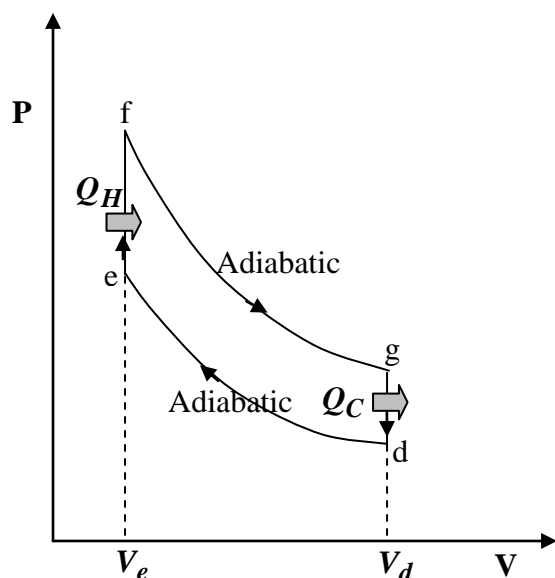


Fig.8.2: PV Diagram for Otto Cycle

3.3.1 Description of the Processes

- Process **de** is an adiabatic compression i.e no heat is added as the volume of the working substance decreases from volume V_d to V_e . The temperature rises from T_d to T_e according to equation $T_d V_d^{\gamma-1} = T_e V_e^{\gamma-1}$
- Process **ef** is an isochoric process during which heat Q_H is added as the temperature of the working substance changes from T_e to T_f and pressure also increases from P_e to P_f .
- Process **fg** is adiabatic expansion i.e. no heat is added as the volume of the working substance increases from volume V_e to V_d . The temperature decreases from T_f to T_g according to equation $T_f V_e^{\gamma-1} = T_g V_d^{\gamma-1}$
- Processes **gd** is an isochoric process during which heat Q_C is ejected as temperature changes from T_g to T_d .

3.3.2 Efficiency of Otto Engine

Generally, the efficiency of heat engine is given in equation 8.6 as

$$E = 1 - \frac{Q_C}{Q_H}$$

Heat is added during isochoric process **ef** and the temperature increases from T_e to T_f and pressure increase also from P_e to P_f . Heat added Q_H is

$$Q_H = \int_{T_e}^{T_f} C_V dT = C_V (T_f - T_e) \quad 8.8$$

Heat is ejected during isochoric process **gd** and the temperature decreases from T_g to T_d and pressure increase also from P_g to P_d . Heat added Q_C is

$$Q_C = \int_{T_d}^{T_g} C_V dT = C_V (T_d - T_g) \quad 8.9$$

Equation 8.9 is because heat ejected is negative Q , otherwise $(T_d - T_g)$ would be $(T_g - T_d)$.

Put equations 8.9 and 8.8 in equation 8.6 to have

$$E = 1 - \frac{Q_C}{Q_H} = 1 - \frac{C_V (T_d - T_g)}{C_V (T_f - T_e)} \quad 8.10$$

$$E = 1 - \frac{(T_d - T_g)}{(T_f - T_e)} \quad 8.11$$

Two adiabatic processes where involved in the cycle and these give

$$T_g V_d^{\gamma-1} = T_f V_e^{\gamma-1} \quad 8.12a$$

and

$$T_d V_d^{\gamma-1} = T_e V_e^{\gamma-1} \quad 8.12b$$

Subtracting equation 8.12b from equation 8.12a gives

$$(T_g - T_d) V_d^{\gamma-1} = (T_f - T_e) V_e^{\gamma-1}$$

Rearrange to have

$$\frac{T_g - T_d}{T_f - T_e} = \left(\frac{V_e}{V_d}\right)^{\gamma-1}, \quad 8.13$$

And insert equation 8.13 in equation 8.11 to have

$$E = 1 - \left(\frac{V_e}{V_d}\right)^{\gamma-1}$$

But $\gamma = \frac{C_P}{C_V}$,

Therefore the efficiency of Otto cycle is

$$E = 1 - \left(\frac{V_e}{V_d}\right)^{\frac{C_P - C_V}{C_V}} \quad 8.14$$

where C_V and C_P are the specific heat at constant volume and pressure respectively

3.4 Stirling Engine

The PV diagram for an ideal Stirling heat engine is shown in figure 8.4 below. The cycle consists of two isochoric processes and two isothermal processes. Three important components of Stirling engine are:

Heat Exchangers: As the name implies, these transfer heat between the working gas and the outside of the system.

Displacer Mechanism: The purpose of this is to move the working gas between the hot and cold ends of the machine through the regenerator.

Regenerator: This is a device normally placed between hot and cold portions of the machine that is in contact with the hot and cold reservoirs respectively. It consists of packing of steel wool or a series of metal baffles of low thermal conductivity. The purpose of this device is to act as thermal barrier and also as thermal store for the cycle.

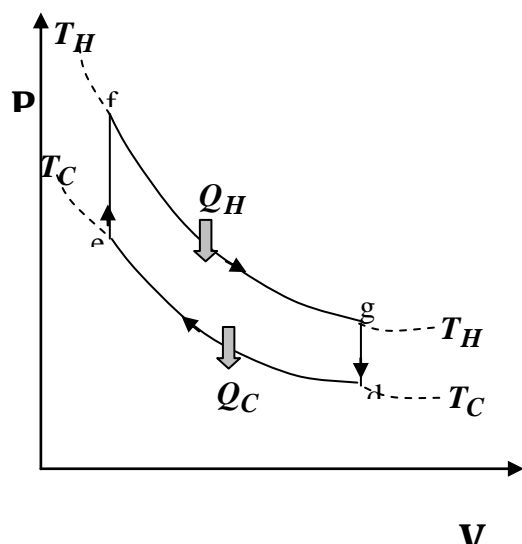


Fig. 8.3: PV Diagram for Stirling Engine

3.4.1 Description of the Processes

- Process **fg** is an isothermal (constant temperature) expansion during which heat Q_H is absorbed at temperature T_H . Due to expansion, work is done during the process (i.e. high pressure the working gas absorbs heat from the heat absorbing heat-exchanger and expands isothermally, thus work is done).
- Process **gd** is an isochoric (constant volume) process. The displacer transfers all the working gas isochorically through the regenerator to the cold end of the machine. Heat is absorbed from the gas as it passes through the regenerator, thus the temperature decreases from T_H to T_C and pressure also decrease from P_g to P_d
- Process **de** is an isothermal compression. During this process, work is done on the gas and this compresses the gas isothermally at temperature T_C , then heat Q_C is ejected to the cold reservoir through the heat rejecting heat exchanger.
- Process **ef** is an isochoric process. During this process, the displacer transfers all the working gas isochorically through the regenerator to the hot end of the machine. Heat is added to the gas as it passes through the regenerator, thus raising the temperature of the gas from T_C to T_H and pressure also increases from P_e to P_f .

3.4.2 Efficiency of Stirling Engine

Generally, the efficiency E is

$$E = \frac{W}{Q_H} = \frac{\text{work output}}{\text{heat in}} \quad 8.15$$

The total work done in Stirling-cycle engine is

$$W = -\oint PdV \quad 8.16$$

The integral in the equation 8.16 is over a closed loop. From the PV diagram, two isochoric processes occurs during the cycle at T_H and T_C (i.e. work is done only during isothermal expansion and compression processes). No work is done during isochoric processes in the cycle.

Therefore total work done W is

$$W = -\left[\int_f^g PdV + \int_d^e PdV \right] \quad 8.17$$

Suppose the equation of state is $PV = nRT$, and since T is constant for the isothermal process, then work done during isothermal process is

$$\int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} nRT \frac{dV}{V} = nRT [\ln V]_{V_1}^{V_2} = nRT \ln \frac{V_2}{V_1} \quad 8.18$$

Substitute equation 8.18 into 8.17

$$W = - \left[nRT_H \ln \frac{V_g}{V_f} + nRT_C \ln \frac{V_e}{V_d} \right] \quad 8.19$$

We can further simplify equation 8.19 since we know that $V_f = V_e$ and $V_g = V_d$ and also know that $\ln \frac{V_e}{V_g} = -\ln \frac{V_g}{V_e}$, so that we have

$$W = -nR \ln \frac{V_g}{V_e} (T_H - T_C) \quad 8.20$$

The work done represents energy out of the system, and so has a negative value according to the sign convention we have been using.

Heat Flow into an Ideal Stirling Engine

The heat flowing into and out of a Stirling-cycle engine can be evaluated by considering the integral of temperature with respect to entropy:

$$Q = \int TdS \quad 8.21$$

For this cycle, heat is transfer into and out of the system only during the two isothermal processes. During closed cycle isothermal expansion process **fg** we have

$$Q_H = \int_{S_f}^{S_g} T_H dS \quad 8.22$$

This integral can be most easily evaluated by considering the first law of thermodynamics

$$dQ = dU - dW \quad 8.23$$

But we know that $dQ = TdS$ and $dW = -PdV$, so 8.23 becomes

$$TdS = dU + PdV$$

Therefore 8.22 now is

$$Q_H = \int_{U_f}^{U_g} dU + \int_{V_f}^{V_g} PdV \quad 8.24$$

Suppose the equation of state is $PV = nRT$, so that $P = \frac{nRT}{V}$ and since

T is constant for the isothermal process, then 8.24 becomes

$$Q_H = \int_{U_f}^{U_g} dU + \int_{V_f}^{V_g} nRT_H \frac{dV}{V} = 0 + nRT_H [\ln V]_{V_f}^{V_g}$$

But $V_f = V_e$ so we have

$$Q_H = nRT_H \ln \frac{V_g}{V_e} \quad 8.25$$

Similarly we can show that

$$Q_C = -nRT_C \ln \frac{V_g}{V_e} \quad 8.26$$

The ratio $\frac{V_g}{V_e} = \frac{V_d}{V_f}$ is called the expansion ratio of the working gas. The inverse of this is called the compression ratio.

The efficiency of an ideal Stirling engine is therefore

$$E = \frac{nR \ln \frac{V_g}{V_e} (T_H - T_C)}{nRT_H \ln \frac{V_g}{V_e}}$$

And it gives

$$E = \frac{T_H - T_C}{T_H} \quad 8.27$$

Recall that the efficiency of the Carnot engine is $E = \frac{T_H - T_C}{T_H}$. This implies that the efficiency of the Carnot engine is equal to that of an **ideal** Stirling engine. Hence the Stirling-cycle engine has the maximum efficiency possible under the Second Law of Thermodynamics. However, the efficiency of a **real** Stirling engine is less than that of Carnot engine.

Note that no real engine can have an efficiency greater than that of a Carnot engine when both engines work between the same two temperatures.

SELF ASSESSMENT EXERCISE 1

- i. Draw the PV diagram for Otto engine and describe all the processes in the cycle.
- ii. Show that the work done W by the ideal Stirling heat engine is

$W = -nR \ln \frac{V_2}{V_1} (T_H - T_C)$ where V_1 and V_2 are the two volumes at which the isochoric processes occur on the PV diagram and that $V_2 > V_1$

4.0 CONCLUSION

Heat engines are devices used to convert heat energy to mechanical work. Real heat engines always have efficiency less than that of Carnot engine when they operate between the same two temperatures. Examples of real engines are Otto engine and Stirling engine. In the next unit, you will learn about a reverse cycle of heat engine i.e. refrigeration cycle.

5.0 SUMMARY

In this unit you have learnt that:

- heat engines are devices used to convert heat to mechanical work
- the efficiency of heat engine is $E = \frac{W}{Q_H} = \frac{\text{work output}}{\text{heat in}}$
- the efficiency of Otto engine is $E = 1 - \left(\frac{V_e}{V_d}\right)^{\frac{C_P - C_V}{C_V}}$
- the work done by an ideal Stirling engine $W = -nR \ln \frac{V_g}{V_e} (T_H - T_C)$, and its efficiency is $E = \frac{T_H - T_C}{T_H}$.

6.0 TUTOR-MARKED ASSIGNMENT

1. List 2 available heat engines which you have studied and draw diagram for each of them
2. Explain the process involved in the cycle of a particular heat engine.
3. Derive expression for efficiency for each of the heat engine.
4. An ideal Stirling engine operates between 325 K and 460 K. If the expansion ratio of the working gas is 2.5, calculate the amount of heat ejected by the engine at cold reservoir and the efficiency of the engine ($n = 2\text{mol}$ and $R = 8.3 \text{ JK}^{-1}\text{Mol}^{-1}$).

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UNIT 5 REFRIGERATORS

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1.0 INTRODUCTION

Refrigerator is necessary household equipment used for preservation of foods and drinks and also for laboratory uses. This unit focuses on the principles of operation of refrigerators

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- describe refrigeration cycles;
- distinguish between refrigerator and heat pump;
- explain what is meant by coefficient of performance of refrigerator; and
- derive expression for coefficient of performance for each of the refrigeration cycle.

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.

2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Refrigerator

This is a device that uses work to transfer energy from a low temperature reservoir to a high temperature reservoir as it continuously repeats a set series of thermodynamic processes. Refrigerator operates in a direction opposite to that of the heat engine. The system that undergoes this reverse cycle of heat engine is called refrigerant. Air conditioners, heat pumps are also example of refrigerators.

Carnot engine is capable of being reversed and when it is reversed it is called a Carnot refrigerator. Just like Carnot engine, Carnot refrigerator is an ideal refrigerator. The Stirling cycle is also capable of being reversed and is the most useful type of refrigerator. This reversed cycle is called Stirling refrigeration cycle.

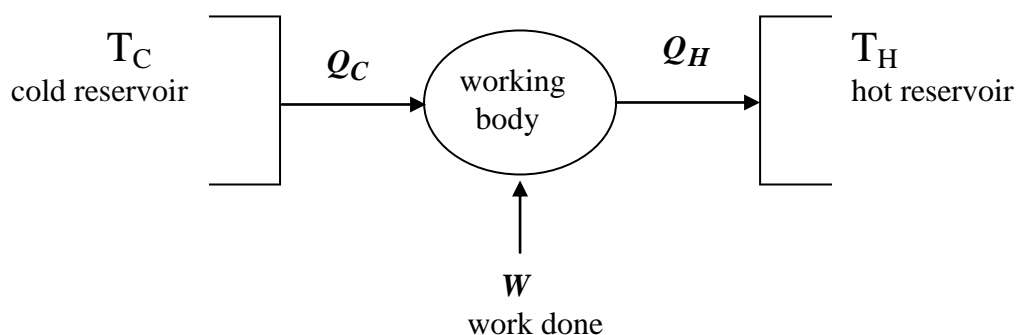


Fig. 9.1: Refrigerator

Figure 9.1 shows the refrigeration process. Comparing this with figure 8.1 in the last unit (module 2, unit 4) and observe the directions of heat and work in the two diagrams. For refrigeration process (figure 9.1) work is done on the working body (i.e. on the refrigerant) and this work is supplied by an electric motor or by other means. The work supplied is used to remove heat Q_C from the cold reservoir and deposit heat Q_H into the hot reservoir. These processes are reversed of the one in heat engine.

The interior of a refrigerator (i.e. the space inside where we put things like food, fruits and drinks) is the cold reservoir, while the exterior is the hot reservoir. You should have noticed that the outside surfaces (usually the sides and back) of most

refrigerators are warm to touch while they are operating. The reason for this is because they are the hot reservoir.

Energy conservation holds also for refrigeration process (i.e. $Q_H = W + Q_C$).

Equation $\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$ also holds for ideal refrigerators.

Heat Pumps: Heat pumps work on the same principle as refrigerator. The only difference is that for the heat pumps, the cold reservoir is the out door while the hot reservoir is the inside of the house. Another name for the heat pump is electric heating system. The electric heating system is normally used to warm the house during winter or cold weather.

Air conditioners: For the air conditioners, the cold reservoir is the inside of the house while the hot reservoir is the outside of the house.

Refrigerators, air conditioners, and heat pumps are similar devices and their principles of operation are similar.

3.1.1 Coefficient of Performance of Refrigerators

A term similar to the efficiency of the heat engine used to measure the performance of a refrigerator is the coefficient of performance ω . The Coefficient of performance is defined as the ratio of heat extracted from the cold reservoir Q_C to the work done W on refrigerant

$$\omega = \frac{\text{Heat extracted from cold reservoir}}{\text{work done on refrigerant}}$$

Therefore

$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} \quad 9.1$$

3.1.2 Coefficient of Performance of Heat Pumps

Coefficient of performance of heat pumps ω is defined as the ratio of heat delivered to the house Q_H to the work done W required to deliver it.

$$\omega = \frac{\text{Heat delivered}}{\text{work done on required}}$$

Therefore

$$\omega = \frac{Q_H}{W} \quad 9.2$$

Two examples of the refrigeration cycles (i.e. Carnot-cycle refrigeration and Stirling-cycle refrigeration) are discussed here.

3.2 Carnot Refrigerator

Carnot refrigeration is a reversed of Carnot cycle. Carnot-cycle refrigerator is identical to Carnot-cycle engine except that the heat-absorbing end of the machine now becomes the cold region, while the heat rejecting end of the machine becomes the hot region. The PV diagram of the Carnot-cycle refrigerator is shown if figure 9.2.

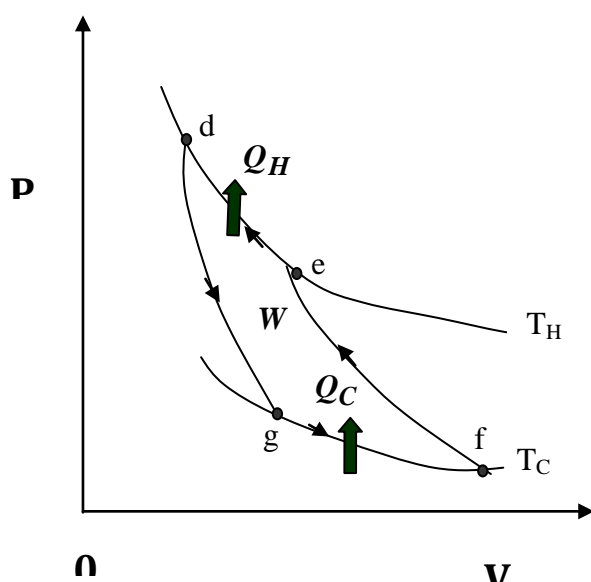


Fig. 9.2: PV Diagram for Carnot-Cycle Refrigerator

3.2.1 Description of the Processes in the Carnot-Cycle Refrigerator

The processes in Carnot-cycle refrigerator as shown in figure 9.2 are described below.

- Process **gf** is an isothermal expansion. During this process, heat Q_C is absorbed from the cold reservoir at temperature T_C and the working substance undergoes isothermal expansion from volume V_g to V_f .
- Process **fe** is an adiabatic compression i.e no heat is added as the working substance compresses from volume V_f to V_e . Temperature increases during the process from T_C to T_H .
- Process **ed** is an isothermal compression. During this process, heat Q_H is ejected to the hot reservoir at temperature T_H .

- Process **dg** is an adiabatic expansion i.e. no heat is transferred as the working substance expands from volume V_d to V_g . Temperature decreases during the process from T_H to T_C .

3.2.2 Coefficient of Performance of Carnot-Cycle Refrigerator

The purpose of any refrigerator is to extract as much heat as possible from a cold reservoir with the expenditure of as little work as possible. The output is the heat extracted from the cold reservoir and the input is work.

Using equation 9.1, coefficient of performance ω is

$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$

For a Carnot cycle, it has been established that

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

Then

$$\omega = \frac{T_C}{T_H - T_C} \quad 9.3$$

ω may be considerably larger than unity.

3.3 Ideal Stirling-Cycle Refrigerator

An ideal Stirling-cycle refrigerator is a reverse of an ideal Stirling-cycle engine. The cycle consists of two isochoric processes and two isothermal processes. The PV diagram of an ideal Stirling-cycle refrigerator is shown in figure 9.3 below.

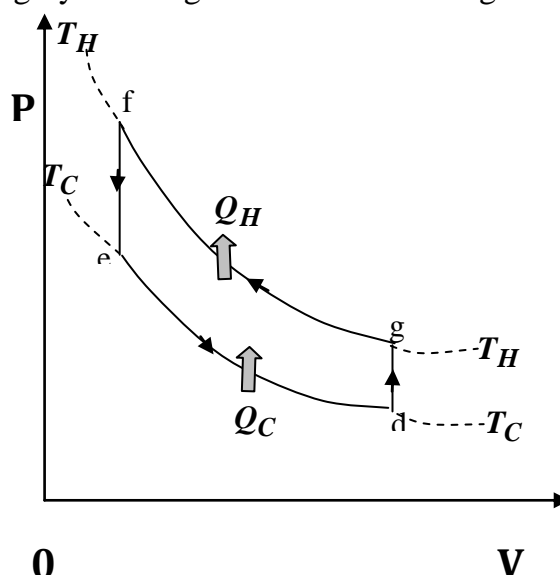


Fig. 9.3: PV Diagram of an Ideal Stirling-Cycle Refrigerator

3.3.1 Description of the Processes in the Ideal Stirling-Cycle Refrigerator

The processes in the ideal Stirling-cycle refrigerator as shown in figure 9.3 are described below.

Process **ed** is an isothermal expansion during which heat Q_C is absorbed from the cold reservoir at temperature T_C .

Process **dg** is an isochoric process. The temperature of the working substance increases from T_H to T_C and pressure also increases from P_d to P_g .

Process **gf** is an isothermal compression during which heat Q_H is ejected to the hot reservoir at temperature T_H .

Process **fe** is an isochoric process. The temperature of the working substance decreases from T_C to T_H and pressure also decreases from P_f to P_e .

3.3.2 Coefficient of Performance an Ideal Stirling-Cycle Engine

Coefficient of performance of refrigerator ω is

$$\omega = \frac{Q_C}{W}$$

From Stirling engine, the expression for work W has been obtained to be

$$W = nR \ln \frac{V_g}{V_e} (T_H - T_C) \quad (\text{i.e. from equation 8.20})$$

And heat Q_C as

$$Q_C = nRT_C \ln \frac{V_g}{V_e} \quad (\text{i.e. from equation 8.26})$$

Therefore

$$\omega = \frac{nRT_C \ln \frac{V_g}{V_e}}{nR \ln \frac{V_g}{V_e} (T_H - T_C)} = \frac{T_C}{T_H - T_C} \quad 9.4$$

Equation 9.4 is the coefficient of performance for ideal Stirling-cycle refrigerator and is equal to that of Carnot-cycle refrigerator. But the efficiency of the real Stirling-cycle refrigerator (i.e. the practical Stirling-cycle refrigerator) is always less than that of Carnot-cycle refrigerator operating between the same temperatures T_C and T_H .

3.4 Clausius Statement of the Second Law

No process is possible whose sole results is the transfer of heat from a cooler body to a hotter body.

SELF ASSESSMENT EXERCISE 1

- i. A Carnot heat pump is used to heat a house to a temperature of 294 K. How much work must be done by the pump to deliver 3350 J of heat into the house when the outdoor temperature is 260 K.
- ii. Draw the PV diagram of the Stirling-cycle refrigerator and describe all the processes.

4.0 CONCLUSION

Refrigeration cycle is a reverse of heat engine cycle. Refrigeration is the process of withdrawing heat from a cold system and ejecting it into a hot reservoir while the mechanical work is done on the system. The Clausius statement of the Second Law of thermodynamics states that no process is possible whose sole results is the transfer of heat from a cooler body to a hotter body.

5.0 SUMMARY

In this unit you have learnt that:

- refrigeration cycles is a reverse of heat engine cycle
- heat pumps, air conditioner and refrigerators similar devices and their principles of operation are similar
- the coefficient of performance of the Carnot cycle refrigeration is $\omega = \frac{T_C}{T_H - T_C}$
- the coefficient of performance of the ideal Stirling cycle refrigeration is $\omega = \frac{T_C}{T_H - T_C}$
- the coefficient of performance of real Stirling cycle refrigeration is always less than that of Carnot cycle refrigeration when both operate between the same temperatures.

6.0 TUTOR-MARKED ASSIGNMENT

1. Describe the refrigeration cycle.
2. Distinguish between the refrigerator and heat pump.
3. Explain the concept of coefficient of performance.
4. Derive expression for coefficient of performance for each of refrigeration cycle.

5. A Carnot air conditioner uses 25, 500 J of electrical energy, and the temperatures indoors and outdoors are 27 °C and 39 °C respectively. Calculate the amount of heat deposited outdoors.
6. Draw the PV diagram of a Carnot-cycle refrigerator and describe all the processes involved.

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