COURSE TITLE: THERMODYNAMICS

محاضرات

فى الديناميكا الحرارية

إعداد

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Introduction

Thermodynamics is a one-semester course. It is a three - credit hour degree course available to all students to take towards their B.Sc. Physics, B.Sc. Education and other related programmes in the faculty of science.

Thermodynamics owes its origin to the attempt to convert heat energy into mechanical work and to develop the theory of operation of devices for this purpose. Two basic concepts in thermodynamics are work and heat. The zeroth law establishes the existence of thermal equilibrium and allows temperature to be measured using a thermometer. The first law places work and heat as the only way the internal energy of a system or a body can be increased. The second law talks about the entropy of a system. The first and second laws are used in explaining the operations of the Carnot engine, real heat engines and the refrigerators. Refrigerators are devices used to cool a system of a body and the process of doing this is called refrigeration cycle. The third law gives the condition for which a body or a system can be cooled to absolute zero i.e. an infinite number of refrigeration cycle. These four laws of thermodynamics i.e. zeroth, first, second and third laws are based on the observations made in the field of thermodynamics.

What you will Learn in this Course

The course consists of units and a course guide. This course guide tells you briefly what the course is about, what course materials you will be using and how you can work with these materials. In addition, it advocates some general guidelines for the amount of time you are likely to spend on each unit of the course in order to complete it successfully.

It gives you guidance in respect of your Tutor-Marked Assignment which will be available in the assignment file. There will be regular tutorial classes that are related to the course. It is advisable for you to attend these tutorial sessions. The course will introduce you to the four laws of thermodynamics and their implications; and also to prepare you for other specialised courses in physics like atmospheric thermodynamics, geophysics, statistical physics and thermal physics among others.

Course Aims

The aim of this course is to give a comprehensive teaching on the principles and applications of thermodynamics; it is also to prepare students towards scientific advancement in atmospheric physics, geophysics, and thermal Physics among others.

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MODULE 1

UNIT 1 BASIC CONCEPTS OF THERMODYNAMICS

CONTENTS

1.0 INTRODUCTION

Thermodynamics is a branch of physics that deals with heat and flow of energy. The basic idea is that objects are made up of atoms and molecules, which are in ceaseless motion. The faster the motion the hotter the object. However, thermodynamics deals only with the large-scale response of a system, i.e. response that can be observed and measured, to heat flow. This unit examines the basic concepts of thermodynamics as a way of introducing the course.

2.0 OBJECTIVES

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

- explain what thermodynamics is
- mention all thermodynamics coordinates and explain change of state
- describe all thermodynamics processes
- write equation of state and its usefulness
- differentiate between a system and its surrounding.

3.0 MAIN CONTENT

3.1 Definition of Thermodynamics

Thermodynamics is the study of the effects of work, heat, and energy on a system. It deals only with the large-scale response of a system, which can be observed and measured in an experiment, of heat and work. Small-scale gas interactions are described by the kinetic theory of gases.

3.2 Idea of a System and its Surrounding

System is a restricted region of space or a finite portion of matter one has chosen to study. Or the part of the universe, with well-defined boundaries, one has chosen to study.

Surrounding is the rest of the universe outside the region of interest (i.e. the rest of space outside the system).

Boundary or Wall is the surface that divides the system from the surroundings.
This wall or boundary may or may not allow interaction between the system and the surroundings.

3.3 Thermodynamic Properties/Coordinates

These are macroscopic coordinates or properties used to describe or characterise a system. Because they are macroscopic properties or coordinates, they can be observed and measured. Some examples are Temperature **(T),** Pressure **(P),** Volume **(V),** density (ρ), mass **(m),** specific heat capacity at constant volume (C_V), specific heat capacity at constant pressure **(C_P)**, thermal conductivity **(k),** thermal diffusivity (α), and chemical potential (μ).

3.4 Thermodynamic System

This is a system that could be described in terms of thermodynamic coordinates or properties. Thermodynamic Systems can be categorised into the followings depending on the type of boundary:

Open System: This is a system that its boundary allows transfer of mass and energy into or out of the system. In other words, the boundary allows exchange of mass and energy between the system and the surrounding.

Closed System: This is a system that its boundary allows exchange of energy alone (inform of heat) between the system and its surrounding (i.e. the boundary allows exchange of energy alone). This type of boundary that allows exchange of heat is called diathermal boundary.

Isolated System: This is a system that its boundary allows neither mass nor energy between it and the surrounding. In other words, the boundary does not allow exchange of mass nor energy.

3.5 Thermodynamic Processes

A system undergoes a thermodynamic process when there is some sort of energetic change within the system, generally associated with changes in pressure, volume, internal energy, temperature, or any sort of heat transfer.

There are several specific types of thermodynamic processes that happen frequently enough (and in practical situations) that they are commonly treated in the study of thermodynamics. Each has a unique trait that identifies it, and which is useful in analyzing the energy and work change related to the process.

Adiabatic process: This is a thermodynamic process in which there is no heat transfer into or out of the system. For this process, change in quantity of heat is zero (i.e. $\Delta Q = 0$ during this process)

Isochoric process: This is a thermodynamic process that occurs at constant volume (i.e. $\Delta V = 0$ during this process). This implies that during this process no work is done on or by the system.

Isobaric process: This is a thermodynamic process that occurs at constant pressure (i.e. $\Delta p = 0$ during this process).

Isothermal process: This is a thermodynamic process that takes place at constant temperature (i.e. $\Delta T = 0$ during this process)

It is possible to have multiple processes within a single process. A good example would be a case where volume and pressure change during a process, resulting in no change in temperature and no heat transfer. This kind of a process would be both adiabatic and isothermal.

Cyclic Processes: These are series of processes in which after certain interchanges of heat and work, the system is restored to its initial state.

For a cyclic process $\Delta \boldsymbol{U} = \boldsymbol{0}$, and if this is put into the first law (unit 5)

$$\boldsymbol{Q} = \boldsymbol{W}$$

This implies that the net work done during this process must be exactly equal to the net amount of energy transferred as heat; the store of internal energy of the system remains unchanged.

Reversible Process: A reversible process can be defined as one which direction can be reversed by an infinitesimal change in some properties of the system.

Irreversible Process: An irreversible process can be defined as one which direction cannot be reversed by an infinitesimal change in some properties of the system

Quasi-static Process: This is a process that is carried out in such a way that at every instant, the system departs only infinitesimal from an equilibrium state (i.e. almost static). Thus a quasi-static process closely approximates a succession of equilibrium states.

Non-quasi-static Process: This is a process that is carried out in such a way that at every instant, there is finite departure of the system from an equilibrium state.

SELF ASSESSMENT EXERCISE 1

Explain the following:

i. open system
ii. isolated system
iii. isochoric process
iv. isobaric process
v. quasi-static process

3.6 Thermodynamic Equilibrium

Generally, a system is said to be in equilibrium when its properties do not change appreciably with time over the interval of interest (i.e. observation time).

A system is said to be in thermodynamic equilibrium with its surrounding or with another system if and only if the system is in thermal equilibrium, in chemical equilibrium and in mechanical equilibrium with the surrounding or with another system. If any one of the above conditions is not fulfilled, the system is not in thermodynamic equilibrium.

3.6.1 Mechanical Equilibrium

A system attains mechanical equilibrium with its surrounding or with another system when there is no unbalance or net force in the interior of the system and also none between the system and its surroundings or another system. Suppose two systems are separated by a movable boundary that does not allow exchange of mass or heat as shown in figure 1.1. If P_1 is greater than P_2, the partition will continue to move toward system 2 until P_1 is equal to P_2. When this occurs, the two systems are said to be in mechanical equilibrium.

3.6.2 Chemical Equilibrium

A system attains chemical equilibrium when there are no chemical reactions going on within the system or there is no transfer of matter from one part of the system to other due to diffusion. Two systems are said to be in chemical equilibrium with each other when their chemical potentials are same.

3.6.3 Thermal Equilibrium

This occurs when two systems in thermal contact or a system that is in thermal contact with the surrounding attains the same temperature. For example if system 1 with temperature T_1 and system 2 with temperature T_2 are in thermal contact, there will be exchange of heat between the two systems if there is a temperature gradient (i.e. when $T_1 \neq T_2$). This process of heat exchange will continue until thermal equilibrium is attained (i.e. $T_1 = T_2$).

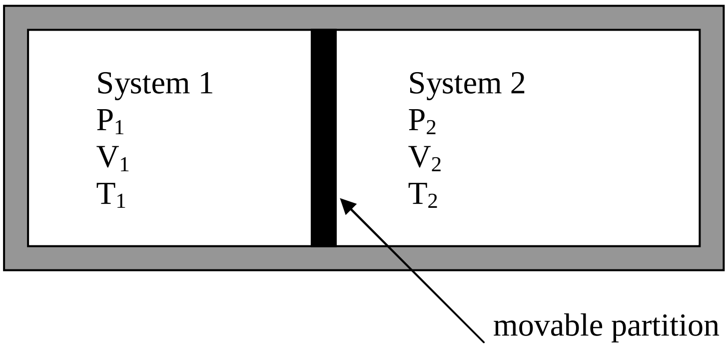

Fig. 1.1: Two Systems Separated by a Movable Partition

SELF ASSESSMENT EXERCISE 2

Explain what is meant by thermodynamic equilibrium.

3.7 State of a System

This is a specific situation in which macroscopic properties (thermodynamic properties) of a system have certain values (e.g. P=10 Pa, V=100 cm^3, and T=300 K would be a state of a gas). It is important to note that the state of a pure substance or a system can be defined or specified by any two of its properties.

Change of state occurs when there is change in one, two or all the properties of the system. Using figure 1.1 above as example, suppose P_1 is greater than P_2 the partition will continue to move towards system 2 until P_1 is equal to P_2. When this happens, the system 1 and 2 have a new set of coordinates in which Temperature remain constant for the two systems but pressure and volume changed. Then we say that the state of system 1 and system 2 has changed.

Note: Change of state is not exactly the same thing as change of phase (Phase change). Change of phase or phase transition is a special case of change of state and it will be treated fully in module 4, unit 1.

3.8 Equation of State

This is the known relationship between the thermodynamic variables or properties. It is an equation which provides a mathematical relationship between two or more state functions associated with matter such as its temperature, pressure, volume, or internal energy.

From the above descriptions, Boyle’s law, Charles’ law, Dalton’s law of partial pressures are examples of equation of state. Some other examples of equation of state are:

3.8.1 The Ideal Gas

The equation of state for ideal gas is

$$PV = nRT$$

where **P** is the pressure, **V** is the volume, **R** is the molar gas constant (**R**=8.314 $JK^{-1}mol^{-1}$), **T** is temperature in Kelvin, and **n** is the number of mole of gas.

3.8.2 Van der Waals Equation of State

The equation of state for real gas also known as Van der Waals Equation is

$$(P+\frac{a}{V_m})(V_m-b)=RT$$

where quantities a and b are constants for a particular gas but differ for different gases.

There are many more equations of state besides these two given above.

3.9 Extensive and Intensive Properties

Thermodynamic properties of a system can be categorised into two namely:

Extensive properties: These are properties of system that depend on the mass of the system (e.g. n, V and total energy U)

Intensive properties: These are properties of system that are independent of the mass of the system (e.g. T, P and ρ).

Block 1

As an illustration of these two categories of thermodynamic properties, assuming you cut into two equal parts a hot bar of metal of uniform temperature T. Each half will still have almost the same temperature T. This clearly shows that temperature is independent of mass of the 'system' (i.e. metal bar). But what about the volume of each part, are they going to be the same as the original volume? This indicates that volume of a system is dependent of mass (volume is extensive property).

Specific Value of an extensive property (for example Volume, V) is defined as the ratio of the volume of the property to the mass of the system, or as volume per unit mass.

Specific volume V_s is

$$V_s=\frac{V}{m}$$

Note that the specific volume is evidently the reciprocal of the density ρ, defined as the mass per unit volume:

$$\rho=\frac{m}{V}=\frac{1}{V_s}$$

Molar Value of an extensive property (for example Volume, V) is defined as the ratio of the volume of the property to the number of moles of the system, or as volume per unit mole.
Molar volume V_m is

$$V_m = \frac{V}{n}$$

SELF ASSESSMENT EXERCISE 3

Differentiate between extensive and in-extensive properties of a system.

4.0 CONCLUSION

You have learnt in this unit, as way of introducing the course, the basic concepts of thermodynamics. This of course will help you in understanding the succeeding topics.

5.0 SUMMARY

In this unit, you have leant that:

- thermodynamics is a branch of physics that deals with heat and flow of energy
- thermodynamics coordinates are used to characterise the state of a system and that a change in any or all of these coordinates brings about a change of state
- base on the type of constraint imposed on a system, the system can undergo thermodynamics processes like adiabatic, isochoric and isothermal processes
- equations of state are the known relation between the thermodynamic coordinate of a system
- a system is a restricted region of space one has chosen to study while the rest of the universe is its surroundings. And that the system and its surrounding constitute the universe.

6.0 TUTOR-MARKED ASSIGNMENT

1. Explain the followings:

a. thermodynamic coordinate
b. thermodynamic system
c. cyclic process
d. isobaric process
e. extensive and inextensive properties of a system

2. The equation for ideal gas is $PV = nRT$, suppose an ideal gas is in equilibrium at initial state with temperature T = 187 ºC, pressure P = 0.75 x 10^7 Nm^{-2}, and volume V = 0.75 m^3. If there is a change of state in which the gas undergoes an isothermal process to a final state of equilibrium during which its volume doubled, calculate the temperature and pressure of the gas at this final state.

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UNIT 2 DIFFERENTIAL CALCULUS

CONTENTS

1.0 INTRODUCTION

One of the useful mathematical topics in thermodynamics is partial derivative. This unit gives a brief summary of some of the most useful formulas involving partial derivatives that we are likely to use in subsequent units and modules of this course.

2.0 OBJECTIVES

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

- explain what partial derivatives are
- explain what exact differentials are
- derive partial derivative of a given function
- solve some problems on partial derivatives
- state some rules of partial derivatives.

3.0 MAIN CONTENT

3.1 Partial Derivatives

A partial derivative of a function of several variables is its derivative with respect to one of those variable with the others held constant.

$$x = x(z, y) \qquad 2.1$$

From equation 2.1, x a dependent variable is a function of two independent variables z and y. Partial derivative of x with respect to y with z held constant is $(\frac{\partial x}{\partial y})_z$.

For example, if

$$x = zy^2 \tag{2.2}$$

then, the partial derivative of x with respect to y with z held constant is

$$(\frac{\partial x}{\partial y})_z = 2zy \tag{2.3}$$

Similarly, the partial derivative of x with respect to z with y held constant is

$$(\frac{\partial x}{\partial z})_y = y^2 \tag{2.4}$$

3.2 Exact Differential

Suppose that there exists a relation among the three coordinates x, y, and z in such a way that x is a function of y and z (i.e. $x(z, y)$); thus

$$f(x, y, z) = 0 \tag{2.5}$$

The exact differential of x (dx) is

$$dx = (\frac{\partial x}{\partial y})_z dy + (\frac{\partial x}{\partial z})_y dz \tag{2.6}$$

Generally for any three variables x, y, and z we have relation of the form

$$dx = M(y,z)dy + N(y,z)dz \tag{2.7}$$

If the differential dx is exact, then

$$(\frac{\partial M}{\partial z})_y = (\frac{\partial N}{\partial y})_z \tag{2.8}$$

3.3 Implicit Differential

Consider an equation of the form

$$xy = x^2 y^2 \tag{2.9}$$

One can differentiate the two sides of the equation 2.9 using equation 2.6 (i.e differentiating both the left and right hands side with respect to x while y is held constant and with respect to y while x is held constant).

$$(\frac{\partial(xy)}{\partial x})_y dx + (\frac{\partial(xy)}{\partial y})_x dy = (\frac{\partial(x^2y^2)}{\partial x})_y dx + (\frac{\partial(x^2y^2)}{\partial y})_x dy \qquad 2.10$$

Equation 2.10 gives

$$ydx + xdy = 2xy^2dx + 2x^2ydy \qquad 2.11$$

Collecting like term and then factorize to have

$$\frac{dy}{dx} = \frac{2xy^2 - y}{x - 2x^2y} \qquad 2.12$$

Another way to obtain expression for $\frac{dy}{dx}$ is to consider equation 2.9 as $f = xy - x^2y^2$ (i.e. moving the expression in the right side of equation 2.9 to the left side and then equate the result to f). Then

$$\frac{dy}{dx} = -\frac{\partial f}{\partial x}\Big/\frac{\partial f}{\partial y} \qquad 2.13$$

3.4 Product of Three Partial Derivatives

Suppose that there exists a relation among the three coordinates x, y, and z; thus

$$f(x,y,z)=0 \qquad 2.14$$

Then x can be imagined as a function of y and z

$$dx=(\frac{\partial x}{\partial y})_z dy+(\frac{\partial x}{\partial z})_y dz \qquad 2.15$$

Also, y can be imagined as a function of x and z, and

$$dy=(\frac{\partial y}{\partial x})_z dx+(\frac{\partial y}{\partial z})_x dz \qquad 2.16$$

Insert equation 2.16 in 2.15

$$dx=(\frac{\partial x}{\partial y})_z[(\frac{\partial y}{\partial x})_z dx + (\frac{\partial y}{\partial z})_x dz]+(\frac{\partial x}{\partial z})_y dz$$

Rearrange to get

$$dx=(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial x})_z dx + [(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x + (\frac{\partial x}{\partial z})_y]dz \qquad 2.17$$

If $dz = 0$ and $dx \neq 0$, it follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y / \partial x)_z} \qquad 2.18$$

Take note of the z in the expression on both sides of the equation 2.18, indicating that the derivatives in equation 2.18 are at constant z.

Block 1

Suppose that there exists a relation among the three coordinates x, y, and z; thus $f(x,y,z)=0$. Going by equation 2.18, then the following hold

$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y / \partial x)_z}$, $\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{(\partial x / \partial z)_y}$, and $\left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{(\partial z / \partial y)_x}$

Also from equation 2.17, if $dx = 0$ and $dz \neq 0$, it follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0$$

Move $\left(\frac{\partial x}{\partial z}\right)_y$ to the other side of equation to get

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y \qquad 2.19$$

Then divide both sides of the equation 2.19 by $\left(\frac{\partial z}{\partial x}\right)_y$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad 2.20$$

This is called minus-one product rule.

3.5 Chain Rule of Partial Derivatives

Another useful relation is called chain rule of partial derivatives. Suppose **T** is a function of **V** and **P**, and that each of **V** and **P** is a function of **Z**, then

$$(\frac{\partial T}{\partial V})_P = (\frac{\partial T}{\partial Z})_P (\frac{\partial Z}{\partial V})_P \qquad 2.21$$

Equation 2.21 is the chain rule of partial derivative. Going by 1.2.21, the following can as well be written:

$$(\frac{\partial S}{\partial P})_T = (\frac{\partial S}{\partial V})_T (\frac{\partial V}{\partial P})_T \qquad 2.22a$$

$$(\frac{\partial U}{\partial V})_P = (\frac{\partial U}{\partial T})_P (\frac{\partial T}{\partial V})_P \qquad 2.22b$$

Equations 2.21 and 2.22 are called chain rule of partial derivatives.

3.6 Second Derivatives or Second Order Derivatives

Let $f(x,y)$ be a function with continuous order derivatives, then we can calculate first derivatives to be $(\frac{\partial f}{\partial x})_z$ and $(\frac{\partial f}{\partial z})_x$. One can further calculate the second derivatives $\frac{\partial^2 f}{\partial x^2}$, $\frac{\partial^2 f}{\partial z^2}$ $\frac{\partial^2 f}{\partial x \partial y}$, and $\frac{\partial^2 f}{\partial y \partial x}$. Take note of these two second order derivates i.e. $\frac{\partial^2 f}{\partial x \partial y}$ and $\frac{\partial^2 f}{\partial y \partial x}$, they are called mixed second derivatives. It can be shown that the mixed second derivatives are equal, i.e. it does not matter the order will perform the differentiation.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \qquad 2.23$$

SELF ASSESSMENT EXERCISE

1. For $xy = x^2y^2$, by using equation 1.2.13 show $\frac{dy}{dx} = \frac{2xy^2 - y}{x - 2x^2y}$.
2. Given that $u = x^2 \ln y$ show that $\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x} = \frac{2x}{y}$.

3.7 Functions of More than Two Variables

Suppose that $f(x,y,z)$, the derivative of f with respect to one of the variables with the other two constant (e.g. derivative of f x with y and z constant) can be written as

$$(\frac{\partial f}{\partial x})_{yz}\ ,\ (\frac{\partial f}{\partial y})_{xz}\ , \text{and } (\frac{\partial f}{\partial z})_{xy}$$

4.0 CONCLUSION

You have learnt in this unit some rules in partial derivatives that you are likely to apply in this course.

5.0 SUMMARY

In this unit you have learnt that:

- the partial derivates for three variables xyz, if $x = zy^2$, the partial derivative of x with respect to y with z held constant is $(\frac{\partial x}{\partial y})_z = 2zy$
- for $x(z, y)$); thus $f(x, y, z) = 0$, the exact differential of x (i.e. dx) is $dx = (\frac{\partial x}{\partial y})_z dy + (\frac{\partial x}{\partial z})_y dy$
- for any three variables xyz, $(\frac{\partial x}{\partial y})_z (\frac{\partial y}{\partial z})_x (\frac{\partial z}{\partial x})_y = -1$.
  this is called minus-one product rule
- for **T** a function of **V** and **P**, and that each of **V** and **P** is a function of **Z**, then $(\frac{\partial T}{\partial V})_P = (\frac{\partial T}{\partial Z})_P (\frac{\partial Z}{\partial V})_P$
- for any $f(x, y)$, $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$.

$$\frac{dy}{dx} = \frac{2xy^2 - y}{x - 2x^2 y}$$

6.0 TUTOR-MARKED ASSIGNMENT

1. If $z = 4x^3 y^2$, show that $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$
2. If $u = x^2 + y^2$ and $v = 4xy$, determine
   $\frac{\partial x}{\partial u}, \frac{\partial x}{\partial v}, \frac{\partial y}{\partial u}, \frac{\partial y}{\partial v}$

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MODULE 2

UNIT 1 FIRST LAW OF THERMODYNAMICS

CONTENTS

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 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.

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 **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 **A**, that the pressure exerted on the system at the piston face is **P**, and that the force is **PA**. The system also exerts an opposing force on the piston. The work done dW on the system in the process described above is

$$dW = PAdx \qquad 5.1$$

but $$Adx = dV$$

Therefore

$$dW = -PdV \qquad 5.2$$

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

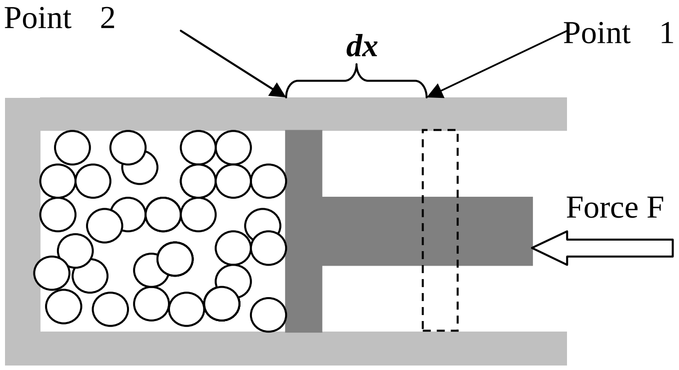

Fig.5.1: The Work Done on a System Compressed by External Force

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

$$W = -\int_{V_i}^{V_f} PdV \qquad 5.3$$

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)	FΔL
Film	Surface Tension (S)	Area (A)	SΔA
Fluid	Pressure (P)	Volume (V)	PΔV
Magnet	Magnetic Field (H)	Magnetization (M)	HΔM
Dielectric	Electric Field (E)	Polarization (P)	EΔP
Chemical reaction	Chemical Potential (μ)	Particle number (N)	μΔN

3.1.2 Work in Quasi-Static Process

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

$$W = -\int_{V_i}^{V_f} PdV \qquad 5.4$$

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

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

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.

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

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

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

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

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

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.

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

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

$$\Delta U = U_f - U_i = Q - W\ , \tag{5.10}$$

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

$$dU = dQ - PdV \tag{5.11}$$

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

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

Heat capacity at constant pressure

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

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

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

and the susceptibility of a magnet

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

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

$$\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P \qquad 5.16$$

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

$$dU = dW = PdV \qquad 5.17$$

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

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

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

$$Q = W \qquad 5.19$$

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

$$dU = 0 \qquad 5.19$$

SELF ASSESSMENT EXERCISE

1. Write the equation for work for the following system

a. Film
b. Wire
c. Magnet

2. State first law of thermodynamics.
3. If there are 2 mole of gas kept at a constant temperature of 20 ºC and if this gas is compressed from a volume of 4 m^3 to 2 m^3, calculate the work done on the gas. (R=8.31J/mol.K)
4. 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 leant 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. Derive the corresponding equation of the first law of thermodynamics under the following processes:

(a) adiabatic process, (b) isochoric process, and (c) cyclic process

2. The equation of state of a gas is $PV = nRT(1 - \frac{B}{V})$, 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

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

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UNIT 2 CONSEQUENCES OF THE FIRST LAW OF THERMODYNAMICS

CONTENTS

1.0 INTRODUCTION

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

2.0 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
- write the expressions for Joule coefficient η and Joule-Thomson coefficient μ.

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 which 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 engine dU between two equilibrium states in which temperature and volume differ by dT and dV is

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

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

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

put 6.2 in 6.1

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

Rearranging

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

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

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

So,

$$(\frac{\partial U}{\partial T})_V = C_V \qquad 6.5$$

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

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

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

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

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

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

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. $H(T, P)$,

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

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

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

Differential of H, dH is

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

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

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

insert 6.8 in 6.11, to obtain

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

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

$$(\frac{\partial H}{\partial T})_P = C_P \qquad 6.13$$

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

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

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

$$C_p - C_V = -[(\frac{\partial H}{\partial P})_T - V](\frac{\partial P}{\partial T})_V \qquad 6.15$$

If the temperature is constant, equation 6.14 becomes

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

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

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

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

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

Consider also U(T,V)

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

and T(P,V) gives

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

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

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

By comparing equation 6.20 with 6.18, it implies that

$$(\frac{\partial U}{\partial P})_V = (\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial P})_V \qquad 6.21$$

and

$$(\frac{\partial U}{\partial V})_p = (\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial V})_P + (\frac{\partial U}{\partial V})_T \qquad 6.22$$

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

$$(\frac{\partial w}{\partial x})_y = (\frac{\partial w}{\partial z})_y (\frac{\partial z}{\partial x})_y \qquad 6.23$$

and

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

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

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

$$(\frac{\partial H}{\partial V})_p = (\frac{\partial H}{\partial T})_P (\frac{\partial T}{\partial V})_P \qquad 6.25$$

and

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

From equation 6.21, using 6.5 we obtain

$$(\frac{\partial U}{\partial P})_V = C_V (\frac{\partial T}{\partial P})_V \qquad 6.27$$

Also from equation 6.25, using equation 6.13 we have

$$(\frac{\partial H}{\partial V})_P = C_P(\frac{\partial T}{\partial V})_P \qquad 6.28$$

We can as well show that

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

and

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

3.5 Gay-Lussac-Joule Experiment

The partial derivative $(\frac{\partial U}{\partial V})_T$ describe the way in which the internal energy of a given system varies with volume at constant temperature. Similarly, $(\frac{\partial H}{\partial P})_T$ 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 **U** in module 4, unit 2).

Using

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

then

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

Also,

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

then

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

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. $(\frac{\partial U}{\partial V})_T$).

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. $(\frac{\partial H}{\partial P})_T$).

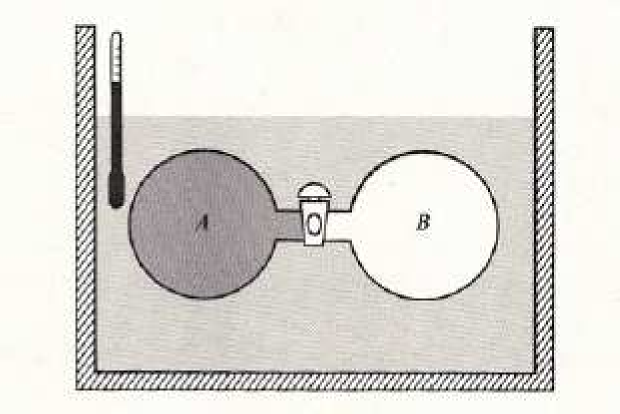

Fig. 6.1: Gay-Lussac-Joule Experiment (After Sear and Salinger 1975)

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 measure 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

$$\Delta U = 0 \qquad 6.33$$

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

$$\left(\frac{\partial T}{\partial V}\right)_U = 0 \qquad \text{(idealgas)} \qquad 6.34$$

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

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

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

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

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

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

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

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

Equation 6.38 is the energy equation of an ideal gas.

3.6 Joule-Thompson 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 $\mathbf{T_1}$, $\mathbf{P_1}$, and $\mathbf{V_1}$) 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. $Q = 0$).

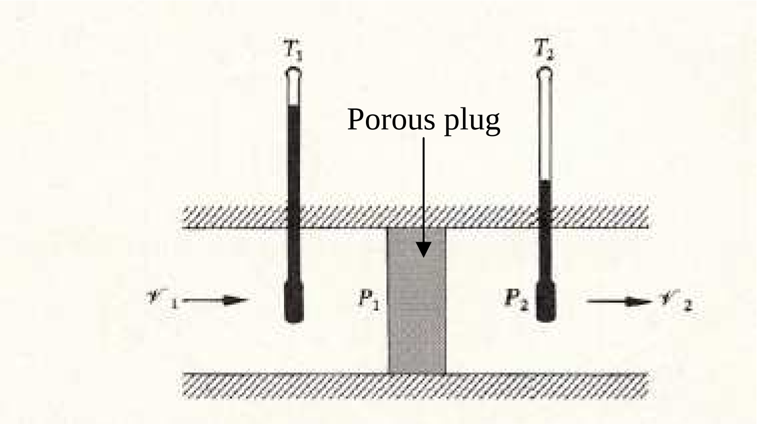

Fig. 6.2: **Joule-Thomson Experiment (After Sear and Salinger 1975)**

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,

T1 and **T2**, are measured directly with sensitive thermocouple thermometers. The total work done during the expansion can be written as

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

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

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

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

rearranging gives

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

But

$$H = U + PV\ ,$$

then, equation 6.41 becomes

$$H_1 = H_2 \qquad 6.42$$

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,

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

For an ideal gas,

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

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

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

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

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

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

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

Then equations 6.7 and 6.17 become

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

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

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

Hence for ideal gas,

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

3.7 Reversible Adiabatic Process

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

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

For an ideal gas,

$$(\frac{\partial P}{\partial V})_T = -\frac{P}{V} \qquad 6.50$$

Check block 1 for how equation 6.50 could be derived

If we representing the ratio C_P / C_V by γ,

That is,

$$\gamma \equiv \frac{C_p}{C_V} \qquad 6.51$$

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

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

Integrating equation 6.52

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

or

$$PV^{\gamma} = K \qquad 6.53$$

where K in equation 6.53 is a constant of integration.

From equation 6.53, eliminating V gives

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

and eliminating P gives

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

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. What is energy equation?
2. Obtain equation 6.54 and 6.55 from 6.53.
3. The internal energy of a van der Waals gas is given by

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

shows that for a van der Waals gas

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

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.

7.0 SUMMARY

In this unit, you have learnt that:

- energy equations are the equations which expresses 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 $C_V = (\frac{\partial U}{\partial T})_V$
- the difference between the specific heat capacities $C_P - C_V = [(\frac{\partial U}{\partial V})_T + P](\frac{\partial V}{\partial T})_P$
- for adiabatic reversible process, $PV^{\gamma} = K$.

8.0 TUTOR-MARKED ASSIGNMENT

1. Show that $(\frac{\partial U}{\partial T})_P = C_P - P\beta V$
2. For an ideal gas show that (a) $(\frac{\partial U}{\partial P})_T = 0$.

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UNIT 3 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

CONTENTS

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 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
- calculate the efficiency of Carnot engine.

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

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

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

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

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

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

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

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

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.

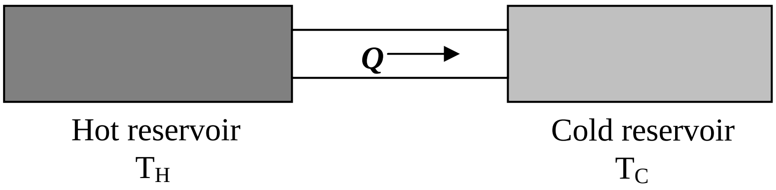

Fig. 7.1: Heat Q Flows from Hot Reservoir to Cold Reservoir

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

$$dS = 0 \qquad 7.5$$

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.

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

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,

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

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

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

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

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

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

$$\Delta S \geq 0 \qquad 7.10$$

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 reservior at constant temperature T_H and ejects 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 transfered at temperature T_C from the working to cold reservior. 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 transfreed as the working substance compresses from volume V_g to V_d. Temperatures increases during the process from T_C and T_H.

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

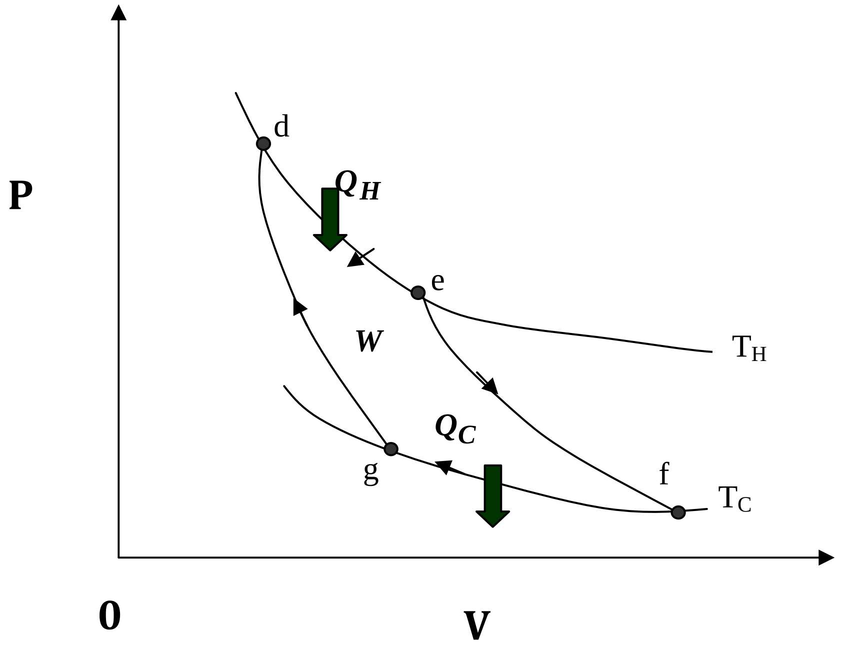

Fig. 7.2: PV Plot for the Carnot Cycle

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

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

3.5.1 Efficiency of a Carnot Engine

The efficiency of a heat engine is

$$\mathrm{E} = \frac{W}{Q_H} = \frac{\textbf{work output}}{\textbf{heat in}} \text{ (in one cycle)} \qquad 7.12$$

Using equation 7.11, equation 7.12 becomes

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

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

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

where temperature T_C and T_H are temperatures in Kelvin.
Rearranging 7.14 gives

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

Insert equation 7.14 in equation 7.13 to obtain

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

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 that 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

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

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

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

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

SELF ASSESSMENT EXERCISE

1. Define entropy.
2. How much heat is required for a reversible isothermal expansion of an ideal gas at 132 ºC if the entropy of the gas increases by 46.0 J/K?
3. A Carnot engine does 20,900 J of work and rejects 7330 J of heat into the hot reservoir at 25 ºC. What is the Kelvin temperature of the hot reservoir?
4. 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.

7.0 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 $E = 1 - \frac{T_C}{T_H}$.

8.0 TUTOR-MARKED ASSIGNMENT

1. 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?
2. A lump of steel weighing 30 kg at a temperature of 427 ºC is dropped in 150 kg of oil at 27 ºC. 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.
3. 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

CONTENTS

8.0 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.

9.0 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
- derive expression for efficiency for each of these heat engines.

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.

3.1.1 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.

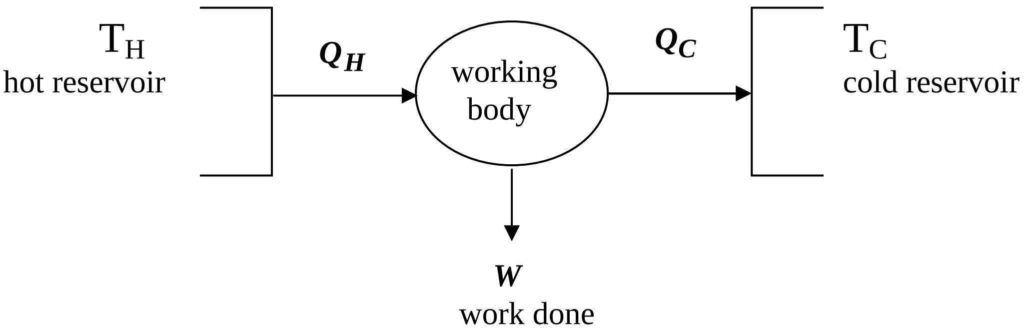

Fig. 8.1: Heat Engine

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 do mechanical work, and then ejected 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

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

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,

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

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.

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

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

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

$\oint_{cycle} dQ = Q_H - Q_C = Q$ the total heat transfer to the working body in a cycle. So equation 8.3 becomes

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

Rearrange to have

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

Insert equation 8.5 in equation 8.1

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

Therefore,

$$E = 1 - \frac{Q_C}{Q_H} = 1 - \frac{heat\,released}{heat\,absorbed} \qquad 8.7$$

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.

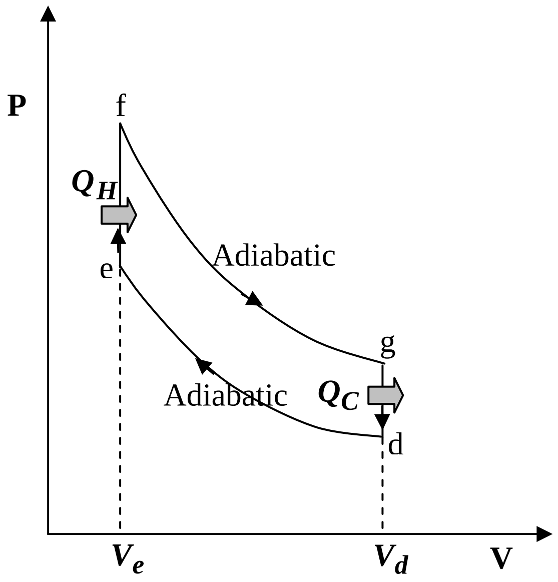

Fig.8.2: PV Diagram for Otto Cycle

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

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

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

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

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

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

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

Two adiabatic processes where involved in the cycle and these give

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

and

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

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

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

And insert equation 8.13 in equation 8.11 to have

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

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

Therefore the efficiency of Otto cycle is

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

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.

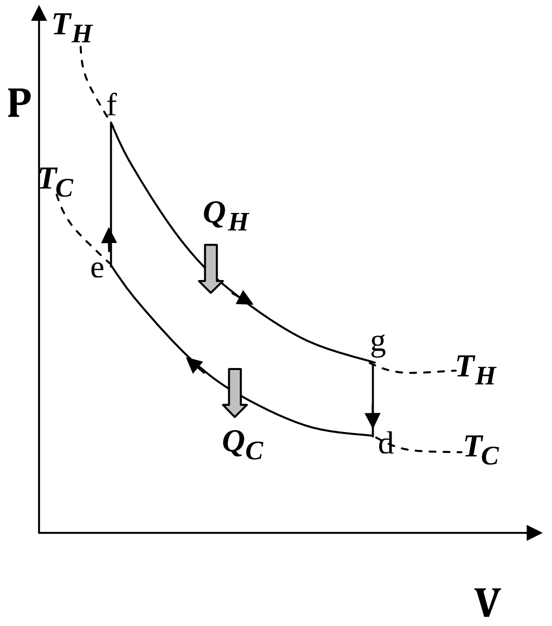

Fig. 8.3: **PV Diagram for Stirling Engine**

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 decreae 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

$$E = \frac{W}{Q_H} = \frac{work\,output}{heat\,in} \qquad 8.15$$

The total work done in Stirling-cycle engine is

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

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

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

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

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

Substitute equation 8.18 into 8.17

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

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

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

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:

$$Q = \int TdS \qquad 8.21$$

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

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

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

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

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

$$TdS = dU + PdV$$

Therefore 8.22 now is

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

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

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

But $V_f = V_e$ so we have

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

Similarly we can show that

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

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

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

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. Draw the PV diagram for Otto engine and describe all the processes in the cycle.
2. 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 $\boldsymbol{E = \frac{W}{Q_H} = \frac{work\ output}{heat\ in}}$
- the efficiency of Otto engine is $\boldsymbol{E = 1 - \left(\frac{V_e}{V_d}\right)^{\frac{C_P - C_V}{C_V}}}$
- the work done by an ideal Stirling engine $\boldsymbol{W = -nR \ln \frac{V_g}{V_e}(T_H - T_C)}$, and its efficiency is $\boldsymbol{E = \frac{T_H - T_C}{T_H}}$.

6.0 TUTOR-MARKED ASSIGNMENT

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 = 2mol and R = 8.3 $JK^{-1}Mol^{-1}$).

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UNIT 5 REFRIGERATORS

CONTENTS

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 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
- derive expression for coefficient of performance for each of the refrigeration cycle.

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 is 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.

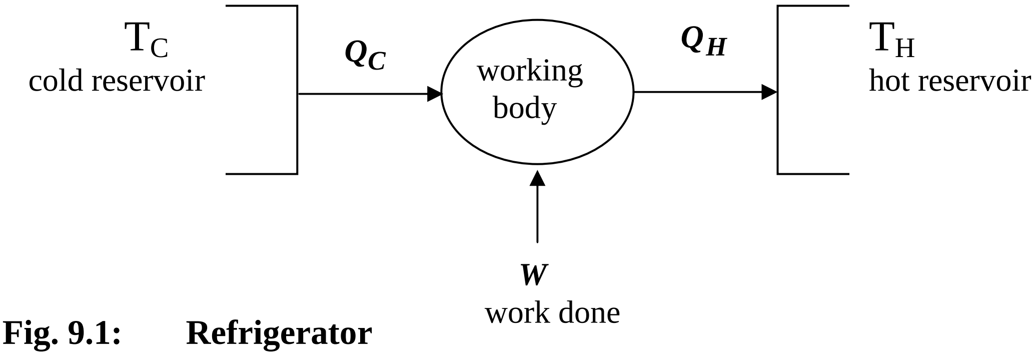

Fig. 9.1: Refrigerator

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 outdoor 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

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

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

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

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.

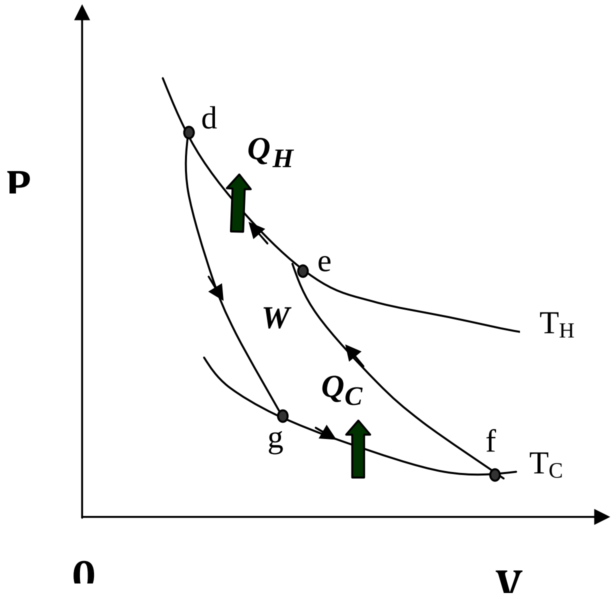

Fig. 9.2: PV Diagram for Carnot-Cycle Refrigerator

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 transfered as the working substance expands from volume V_d to V_g. Temperatures 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 be established that

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

Then

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

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.

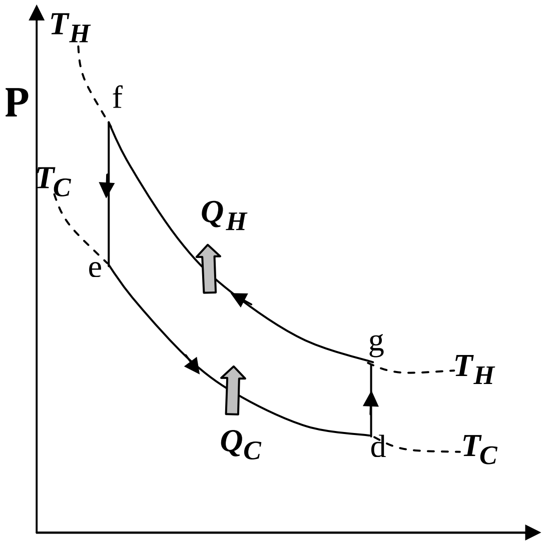

Fig. 9.3: PV Diagram of an Ideal Stirling-Cycle Refrigerator

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

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

Therefore

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

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

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MODULE 3

UNIT 1 COMBINED FIRST AND SECOND LAWS

CONTENTS

1.0 INTRODUCTION

The first and second laws of thermodynamics can be combined to obtain very important thermodynamics relations.

2.0 OBJECTIVES

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

- write the equation for combined first and second laws of thermodynamics
- derive some useful thermodynamics relations from the combine first and second laws.

3.0 MAIN CONTENT

3.1 Combined First and Second Laws of Thermodynamics

The first law of Thermodynamics is

$$dQ = dU + dW \qquad 10.1$$

And the second law of thermodynamics is

$$dQ = TdS \qquad 10.2$$

but differential work

$$dW = PdV \qquad 10.3$$

The combination of these three equations in any infinitesimal reversible process, for a PVT system gives

$$TdS = dU + PdV \qquad 10.4$$

Equation 10.4 is the combined form of the first and second laws of thermodynamics for a PVT system. Some useful thermodynamics relations can be derived from equation 10.4 by selecting T and V, T and P, P and V as independent variables. It is important to note that the state of a pure substance (Module 1 Unit 1) can be defined or specified by any two of its properties.

3.2 T and V Independent

From equation 10.4

$$dS = \frac{1}{T}(dU + PdV) \qquad 10.5$$

Consider the internal energy **U** as a function of **T** and **V**, i.e. **U**(**T,V**), then the derivative of U is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad 10.6$$

Put equation 10.6 in 10.5

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV \qquad 10\ .7$$

Also consider entropy S as function of two independent variables **T** and **V**, i.e. **S**(**T**,**V**), then the derivative of S is

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad 10.8$$

By comparing equation 10.7 with 10.8 (or equate 10.7 and 10.8), we obtain

$$\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \qquad 10.9$$

and

$$\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] = \left(\frac{\partial S}{\partial V}\right)_T \qquad 10.10$$

If we differentiate equation 10.9 partially with respect to V at constant T and differentiate 10.10 partially with respect to T and constant V, equating the mixed second-order partial derivatives of S gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad 10.11$$

It can be shown that (check SEA1 in module 3, unit 4) $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{k}$,

therefore, equation 10.11 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\beta}{k} - P \qquad 10.12$$

Equations 10.11 and 10.12 show the dependence of the internal energy of a system on volume, at constant temperature and this can be calculated from the equation of state (i.e. using equation 10.11), or from the values of **β**, **κ**, **T** and **P** (i.e. using equation 10.12).

Recall from module 2, unit 2 under consequences of the first law of thermodynamics that

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

By making use of equation 10.11, we have

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = \frac{\beta^2 TV}{k} \qquad 10.13$$

Thus the difference ($C_P - C_V$) can be calculated for any substance, from equation of state or from values of **T**, **V**, **β** and **κ**.

SELF ASSESSMENT EXERCISE

1. Derive equation 10.11 from equation 10.9 and 10.10
2. Find $C_P - C_V$ for a certain gas whose equation of state $(P + b)V = nRT$.

3. We know that $(\frac{\partial U}{\partial T})_V = C_V$, put this and equation 10.11 in 10.6 to obtain

$$dU = C_V dT + [T(\frac{\partial P}{\partial T})_V - P]dV \qquad 10.13$$

3.3 T and P Independent

In terms of enthalpy $H = U + PV$, equation 10.4 can be rewritten as

$$dS = \frac{1}{T}(dH - VdP) \qquad 10.14$$

Check block 1 for how we arrived at 10.14

Consider the enthalpy **H** as a function of **T** and **P**, i.e. **H**(**T**,**P**), then the derivative of **H** is

$$dH = (\frac{\partial H}{\partial T})_P dT + (\frac{\partial H}{\partial P})_T dT \qquad 10.15$$

Put equation 10.15 in 10.14, then

$$dS = \frac{1}{T}(\frac{\partial H}{\partial T})_P dT + \frac{1}{T}[(\frac{\partial H}{\partial P})_T - V]dP \qquad 10.16$$

Also consider entropy **S** as function of two independent variables **T** and **P**, i.e. **S**(**T**,**P**), then the derivative of **S** is

$$dS = (\frac{\partial S}{\partial T})_P dT + (\frac{\partial S}{\partial P})_T dP \qquad 10.17$$

By comparing equation 10.16 with 10.17, we obtain

$$(\frac{\partial S}{\partial T})_P = \frac{1}{T}(\frac{\partial H}{\partial T})_p, \qquad 10.18$$

and

$$(\frac{\partial S}{\partial P})_T = \frac{1}{T}[(\frac{\partial H}{\partial P})_T - V]. \qquad 10.19$$

If we differential equation 10.18 partially with respect to **P** at constant **T** and differentiate 10.19 partially with respect to **T** and constant **P**, equating the mixed second-order partial derivatives of **S** gives

$$(\frac{\partial H}{\partial P})_T = -T(\frac{\partial V}{\partial T})_P + V \qquad 10.20$$

From using equation 5.13, $(\frac{\partial V}{\partial T})_P = \beta V$, then

$$(\frac{\partial H}{\partial P})_T = -\beta VT + V \qquad 10.21$$

Equation 10.21 is similar to equation 10.12. It shows the dependence of enthalpy on pressure, at constant temperature and this can be calculated from the equation of state (i.e. from equation 10.20), or from the values of **β**, **T** and **V** (i.e. from equation 10.21).

Also since we know that $(\frac{\partial H}{\partial T})_P = C_P$, put this and equation 10.20 in equation 10.15 to have

$$dH = C_P dT - [T(\frac{\partial V}{\partial T})_P - V]dP \qquad 10.22$$

Block 1

Enthalpy $H = U + PV$

Derivative of H gives

$$dH = dU + PdV + VdP$$

make dU subject of the expression

$$dU = dH - PdV - VdP \qquad *$$

but $dS = \frac{1}{T}(dU + PdV) \qquad **$

put equation (*) in (**) gives

$$dS = \frac{1}{T}(dH - \cancel{PdV} - VdP + \cancel{PdV})$$

Then,

$$dS = \frac{1}{T}(dH - VdP)$$

3.4 P and V Independent

Consider entropy **S** as a function of **P** and **V**, i.e. **S**(**P**,**V**), derivative of **S** is

$$dS = (\frac{\partial S}{\partial P})_V dP + (\frac{\partial S}{\partial V})_P dV \qquad 10.23$$

Also consider internal energy **U** as a function of **P** and **V**, i.e. **U**(**P**,**V**), the derivative of **U** is

$$dU = (\frac{\partial U}{\partial P})_V dP + (\frac{\partial U}{\partial V})_P dV \qquad 10.24$$

Put equation 10.23 in 10.5

$$dS = \frac{1}{T}((\frac{\partial U}{\partial P})_V dP + (\frac{\partial U}{\partial V})_P dV + PdV)$$

Rearrange to get

$$dS = \frac{1}{T}(\frac{\partial U}{\partial P})_V dP + [\frac{1}{T}(\frac{\partial U}{\partial V})_P + \frac{P}{T}]dV \qquad 10.25$$

By comparing equation 10.23 with 10.25, we obtain

$$(\frac{\partial S}{\partial P})_V = \frac{1}{T}(\frac{\partial U}{\partial P})_V \qquad 10.26$$

and

$$(\frac{\partial S}{\partial V})_P = \frac{1}{T}(\frac{\partial U}{\partial V})_P + \frac{P}{T} \qquad 10.27$$

$(\frac{\partial U}{\partial P})_V$ can be written as $(\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial P})_V$ (i.e. chain rule of partial derivatives) then equation 10.26 becomes

$$(\frac{\partial S}{\partial P})_V = \frac{1}{T}(\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial P})_V \qquad 10.28$$

But

$$(\frac{\partial U}{\partial T})_V = C_V \text{, and } (\frac{\partial T}{\partial P})_V = \frac{\kappa}{\beta} \qquad 10.29$$

Put equation 10.29 in 10.28 to give

$$(\frac{\partial S}{\partial P})_V = \frac{C_V}{T}\frac{\kappa}{\beta} \qquad 10.30$$

Equation 10.30 gives the change in entropy with respect to pressure at constant volume $(\frac{\partial S}{\partial P})_V$ in terms of measurable quantities C_V, k, β, and **T**.

4.0 CONCLUSION

We have derived in this unit, some useful relations from the combined first and second laws of thermodynamics.

5.0 SUMMARY

In this unit, you have learnt that:

- the combined first and second laws of thermodynamics is $TdS = dU + PdV$
- the variation in enthalpy with respect to pressure at constant temperature is $(\frac{\partial H}{\partial P})_T = -\beta VT + V$
- the difference between the specific heat capacities from combine first and second law is $C_P - C_V = T(\frac{\partial P}{\partial T})_V (\frac{\partial V}{\partial T})_P = \frac{\beta^2 TV}{k}$
- the variation in entropy with pressure at constant volume is $(\frac{\partial S}{\partial P})_V = \frac{C_V}{T}\frac{\kappa}{\beta}$.

6.0 TUTOR-MARKED ASSIGNMENT

Derive equation 10.20 from equations 10.18 and 10.19.

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UNIT 2 THERMODYNAMIC POTENTIALS

CONTENTS

1.0 INTRODUCTION

Energy functions of thermodynamic systems, also known as thermodynamic potentials, are discussed in this unit. They are useful in explaining many of the physical processes in thermodynamics

2.0 OBJECTIVES

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

- name all the thermodynamics potentials
- define each of the thermodynamic potentials
- derive differential forms of the thermodynamic potentials
- mention the process that each of these thermodynamic potentials can be used to describe.

3.0 MAIN CONTENT

3.1 Thermodynamic Potentials

The four (4) thermodynamic potentials are;

- internal energy **U**
- enthalpy **H**
- Helmholtz free energy **A**
- Gibbs free energy **G**.

Depending on the thermodynamic constraints on a system, it is always convenient to use a particular thermodynamic potential to describe a system. For example, Helmholtz free energy **A** can be used to describe a system in which temperature and volume are held constant. The equilibrium condition for this system is $dA = 0$. Gibbs free energy **G** can be used to describe equilibrium between phases (since the two phases share the same pressure and temperature).

3.2 Internal Energy U

The internal energy **U** of a system is a state function i.e. it depends on the state of a system. The first law of thermodynamics (Module 2, unit 1) gives an insight into the internal energy of a system. Change in internal energy **U** of a system Δ**U**, according to the first law of thermodynamics is

$$\Delta U = Q - W$$

And the differential form is

$$dU = dQ - dW \qquad 11.1$$

The work done on a system may comprise of an irreversible component dW_I (such as stirring with a paddle, or forcing an electric current through a resistor) and some reversible components dW_R. The irreversible component of work is dissipated as heat and is identical to adding heat to the system. So we can write $dS = \frac{dQ + dW_I}{T}$ and this gives $dQ = TdS - dW_I$. The reversible component of the work may consist of work done in compressing the system (PdV), but there may also be other kinds of work, such as the ones listed in section 3.1.1 in module 2, unit 1. In general the expression for each of these forms of reversible work is of the form XdY, where X is an intensive state variable and Y is an extensive state variable. All of these forms of non-dissipative work can collectively be called configuration work.
Therefore, the total work done on the system is of the form

$$dW = dW_I - PdV + \sum XdY \qquad 11.2$$

so, the first law of thermodynamics takes the form

$$dU = dQ + dW_I - PdV + \sum XdY \qquad 11.3$$

Equation 11.3 is a sort of ‘complete form’ of the first law taking into consideration all possible forms of work. Using equation 11.3, if a particular system is held at constant volume, then no PdV work of expansion or compression is done. And if no other sort of work is done (either non-PdV reversible work or irreversible work dW_I), then the increase in internal energy of this system is just equal to the heat added to the system.

Therefore, internal energy **U** can be used to describe a system in which heat is transferred (either in or out) and / or work is done on or by the system.

3.2 Internal Energy U

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And the differential form is

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Therefore, the total work done on the system is of the form

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Equation 11.3 is a sort of 'complete form' of the first law taking into consideration all possible forms of work. Using equation 11.3, if a particular system is held at constant volume, then no PdV work of expansion or compression is done. And if no other sort of work is done (either non-PdV reversible work or irreversible work dW_I), then the increase in internal energy of this system is just equal to the heat added to the system.

Therefore, internal energy **U** can be used to describe a system in which heat is transferred (either in or out) and / or work is done on or by the system.

3.4 Helmholtz Free Energy A

The Helmholtz free energy **A** is defined as

$$A = U - TS \qquad 11.7$$

Its differential form is

$$dA = dU - TdS - SdT \qquad 11.8$$

But $dU = dQ + dW_I - PdV + \sum XdY$, so equation 11.8 becomes

$$dA = -SdT - PdV + \sum XdY \qquad 11.9$$

Equation 11.9 tells us that in an isothermal process (i.e. when $dT = 0$), the increase in the

Helmholtz function of a system is equal to all the reversible work ($-PdV + \sum XdY$)

done on the system. On the other hand, if a machine does any reversible work at constant temperature, the Helmholtz function decreases, and the decrease in the Helmholtz function is equal (if temperature is constant) to the reversible work (of all types) done by the system.

3.5 Gibbs Free Energy G

The Gibbs function is define as

$$G = U - TS + PV \qquad 11.10$$

It can also be defined as

$$G = H - TS \qquad 11.11$$

and as

$$G = A + PV \qquad 11.12$$

Its differential from equation 11.11 is

$$dG = dH - TdS - SdT\ , \qquad 11.13$$

and from 11.12 is

$$dG = dA + PdV + VdP \qquad 11.14$$

But from equation 11.6 ($dH = TdS + VdP + \sum XdY$) or from equation 11.9 ($dA = -SdT - PdV + \sum XdY$) equation 11.13 or 11.14 becomes

$$dG = -SdT + VdP + \sum XdY \qquad 11.15$$

Equation 11.15 can be used to describe a system that undergoes constant temperature and constant pressure processes. Example of a process of this kind is the phase change of a pure substance that usually takes place at constant temperature and pressure. Hence, the Gibbs free function is very useful in describing a process that involves change of phase.

3.6 Differential Form of Thermodynamic Potential

The differential forms of the thermodynamic potentials are:

$$dU = dQ + dW_I - PdV + \sum XdY \qquad 11.16$$

$$dH = TdS + VdP + \sum XdY \qquad 11.17$$

$$dA = -SdT - PdV + \sum XdY \qquad 11.18$$

$$dG = -SdT + VdP + \sum XdY \qquad 11.19$$

The more familiar forms of thermodynamic potentials are:

$$dU = TdS - PdV \qquad 11.20$$

$$dH = TdS + VdP \qquad 11.21$$

$$dA = -SdT - PdV \qquad 11.22$$

$$dG = -SdT + VdP \qquad 11.23$$

Equations 11.20 to 11.23 are for condition under which only reversible work done on or by a system is PdV work of expansion or of compression.

SELF ASSESSMENT EXERCISE

1. Define each of the four thermodynamic potentials.
2. Derive the differential forms of the four thermodynamic potentials.

4.0 CONCLUSION

Thermodynamics potentials are treated in the unit. Emphasis was on their definition, their differential forms, and their usefulness. Besides using these thermodynamic potentials in describing thermodynamic processes, useful relations can also be derived from each of these thermodynamic potentials. This will be the focus of the next unit.

9.0 SUMMARY

In this unit, you have learnt that:

- there are four (4) thermodynamic potentials are namely; entropy **U**, enthalpy **H**, Helmholtz free energy **A** and Gibbs free energy **G**
- their differential forms can be obtained from their definitions
- depending on the constraints imposed on a system, it is always convenient to use a particular thermodynamic potential to describe a system.

7.0 REFERENCES/FURTHER READING

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UNIT 3 THE MAXWELL RELATIONS OF THERMODYNAMICS

CONTENTS

1.0 INTRODUCTION

Useful relations can be derived from each of the four thermodynamic potentials discussed in the last unit. These relations are called Maxwell's relations of thermodynamics. This unit therefore focuses on derivation of Maxwell's relations.

2.0 OBJECTIVES

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

- derive each of the four Maxwell's relations from the differential of the thermodynamics potentials
- state the importance of these relations.

3.0 MAIN CONTENT

3.1 Definition

The differential forms of the thermodynamic potentials are:

$$dU = TdS - PdV \qquad 12.1$$

$$dH = TdS + VdP \qquad 12.2$$

$$dA = -SdT - PdV \qquad 12.3$$

$$dG = -SdT + VdP \qquad 12.4$$

The four Maxwell relations are derived from each of these four thermodynamic potentials.

3.2 1st Relation

The differential form of internal energy **U** is

$$dU = TdS - PdV$$

Differentiating this with respect to **S** while **V** is kept constant gives

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad 12.5a$$

and with respect to **V** while **S** is kept constant gives

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \qquad 12.5b$$

Also differentiating 12.5a with respect to **V** at constant **S** and 12.5b with respect to **S** at constant **V** will give

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S \qquad 12.6a$$

and

$$\frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V \qquad 12.6b$$

The mixed second order derivatives of **U**, which implies that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad 12.7$$

Equation 12.7 is one of the four Maxwell relations.

3.3 2nd Relation

From differential form of Enthalpy **H** (i.e. $dH = TdS + VdP$)

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad 12.8a$$

and

$$\left(\frac{\partial H}{\partial P}\right)_S = P \qquad 12.8b$$

Second derivative gives

$$\frac{\partial^2 H}{\partial P \partial S} = (\frac{\partial T}{\partial P})_S \qquad 12.9a$$

and

$$\frac{\partial^2 H}{\partial S \partial P} = (\frac{\partial P}{\partial S})_p \qquad 12.9b$$

The mixed second order derivatives of **H** are equal, so

$$(\frac{\partial T}{\partial P})_S = (\frac{\partial P}{\partial S})_P \qquad 12.10$$

Equation 12.10 is one of the four Maxwell's relations.

3.4 3rd Relation

From the differential of Helmholtz free energy **A** (i.e. $dA = -SdT - PdV$)

$$(\frac{\partial A}{\partial T})_V = -S \qquad 12.11a$$

and

$$(\frac{\partial A}{\partial V})_T = -p \qquad 12.11b$$

Second derivative gives

$$\frac{\partial^2 A}{\partial V \partial T} = -(\frac{\partial S}{\partial V})_T \qquad 12.12a$$

and

$$\frac{\partial^2 A}{\partial T \partial V} = -(\frac{\partial P}{\partial T})_V \qquad 12.12b$$

The mixed second derivatives of **A** in equation 12.12 are equal, therefore

$$-(\frac{\partial S}{\partial V})_T = -(\frac{\partial P}{\partial T})_V$$

i.e.

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V \qquad 12.13$$

$(\frac{\partial P}{\partial T})_V$ in equation 12.13 can be obtained from equation of state. This implies that the variation of entropy **S** with respect to volume **V** at constant temperature **T** for a system can be obtained from equation of state for the system.

3.5 4th Relation

From differential of Gibb's free energy **G** (i.e. $dG = -SdT + VdP$), partial derivative gives

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad 12.14a$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad 12.14b$$

Differentiating 12.14a with respect to **P** at constant **T**, and 12.14b with respect to **T** at constant **P** give

$$\frac{\partial^2 G}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_T, \qquad 12.15a$$

and

$$\frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial V}{\partial T}\right)_p, \qquad 12.15b$$

respectively.

The mixed second derivatives of **G** in equation 12.15 are equal, therefore

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad 12.16$$

$\left(\frac{\partial V}{\partial T}\right)_P$ in equation 12.16 can be obtained from equation of state.

3.6 Maxwell Relations

The four (4) Maxwell Relations of thermodynamics are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad 12.17$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial P}{\partial S}\right)_P \qquad 12.18$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad 12.19$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad 12.20$$

3.7 Usefulness

These relations (i.e. Maxwell relations) are useful in thermodynamics calculations. For example, one can replace a derivative of entropy with a derivative of a simple thermodynamic variation such as temperature.

Equation 13 and 16 give the derivative of entropy in terms of temperature **T**, volume **V** and pressure **P**.

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V \text{ and } (\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$$

For an ideal gas, $PV = nRT$

$$(\frac{\partial P}{\partial T})_V = \frac{nR}{V} = \frac{P}{T} \qquad 12.21$$

and

$$(\frac{\partial V}{\partial T})_P = \frac{nR}{P} = \frac{V}{T} \qquad 12.22$$

For an ideal gas, using equations 12.21 and 12.22, equations 12.13 and 12.20 respectively become

$$(\frac{\partial S}{\partial V})_T = \frac{P}{T} \qquad 12.23$$

$$(\frac{\partial S}{\partial P})_T = -\frac{V}{T} \qquad 12.24$$

SELF ASSESSMENT EXERCISE

1. Derive the four Maxwell equations.
2. For an ideal gas, show that $(\frac{\partial S}{\partial V})_T = \frac{P}{T}$ and $(\frac{\partial S}{\partial P})_T = -\frac{V}{T}$.

4.0 CONCLUSION

We have derived, in this unit, the four (4) Maxwell relations and we also mentioned the usefulness of these relations. In the next unit, we will be using these relations in deriving the TdS equations.

9.0 SUMMARY

In this unit, you have learnt that:

- each of the four Maxwell's relations is derived from each of the four thermodynamics potentials

- Maxwell relations are useful in thermodynamics calculations e.g. a derivative of entropy can be replace with a simple thermodynamic variation such as temperature.

10.0 TUTOR-MARKED ASSIGNMENT

1. For the differential of x given as:

$$dx = M(y,z)dy + N(y,z)dz \qquad \text{(Equation 2.7)}$$

dx is exact when

$$\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z \qquad \text{(Equation 2.8)}$$

2. It is known that the differentials of the thermodynamic potentials are exact; hence derive the four Maxwell's relations using equations 2.7 and 2.8.

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Francis, W. Sears & Gerhard, L. Salinger (1975). *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics* (Third Edition). Philippines: Addison-Wesley Publishing Company, Inc.

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UNIT 4 TDS EQUATIONS

CONTENTS

10.0 INTRODUCTION

Another useful set of equations in thermodynamics is the TdS equations. They, among other things, enable us to calculate the change in entropy during various reversible processes in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus.

11.0 OBJECTIVES

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

- derive the three TdS equations
- write change in entropy for different reversible processes in term of directly measurable quantities.

3.0 MAIN CONTENT

3.1 First TdS Equation

Entropy (**S**) can be express in terms of any two of **P**, **V**, and **T**. Let us express entropy **S** as a function of **V** and **T**, i.e. **S**(**V**,**T**). The derivative of entropy **S** is

$$dS = (\frac{\partial S}{\partial V})_T\, dV + (\frac{\partial S}{\partial T})_V\, dT \qquad 13.1$$

Multiply equation 13.1 by **T** to obtain

$$TdS = T(\frac{\partial S}{\partial V})_T dV + T(\frac{\partial S}{\partial T})_V dT \qquad 13.2$$

From Maxwell's relation (i.e. 12.19), $(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$ and also at constant volume $T(\frac{\partial S}{\partial T})_V = (\frac{\partial U}{\partial T})_V = C_V$, therefore 13.2 becomes

$$TdS = T(\frac{\partial P}{\partial T})_V dV + C_V dT \qquad 13.3$$

Equation 13.3 is the first **T**d**S** equation.

3.2 Second TdS

Let us express entropy **S** in terms **P** and **T** i.e. **S**(**P**,**T**), its derivative is

$$dS = (\frac{\partial S}{\partial P})_T dP + (\frac{\partial S}{\partial T})_P dT \qquad 13.4$$

Multiplying 13.4 by **T** gives

$$TdS = T(\frac{\partial S}{\partial P})_T dP + T(\frac{\partial S}{\partial T})_P dT \qquad 13.5$$

From Maxwell's relation (equation 12.20), $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$, and also at constant pressure $T(\frac{\partial S}{\partial T})_P = (\frac{\partial H}{\partial T})_P = C_P$. Thus 13.5 becomes

$$TdS = -T(\frac{\partial V}{\partial T})_P dP + C_P dT \qquad 13.6$$

Equation 13.6 is the second **T**d**S** equation

3.3 Third TdS

Then the last option is to express entropy **S** as a function of **P** and **V**, i.e. **S**(**P**,**V**), we have

$$dS = (\frac{\partial S}{\partial P})_V dP + (\frac{\partial S}{\partial V})_P dV \qquad 13.7$$

Multiplying 13.7 by **T** to obtain

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV \qquad 13.8$$

In a constant volume process, it can be proved that $T\left(\frac{\partial S}{\partial P}\right)_V = C_V\left(\frac{\partial T}{\partial P}\right)_V$.

And also in a constant pressure process, it can be proved that $T\left(\frac{\partial S}{\partial V}\right)_P = C_P\left(\frac{\partial T}{\partial V}\right)_P$.

Therefore 13.8 becomes

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV \qquad 13.9$$

Equation 13.9 is the third of the **TdS** equations.

Therefore the three Tds equations are

$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT \qquad 13.10$$

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT \qquad 13.11$$

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV \qquad 13.12$$

These equations enable one to calculate heat flow (TdS) in a reversible process. Also, change in entropy between two states of a system can be calculated from these equations provided that the equations of state are known. This is because all the partial derivatives in these equations can be obtained from equation of state

3.4 Expansion, Compression and TdS Equations

3.4.1 Compression

The way the volume of a material decreases with pressure at constant temperature is described by isothermal compressibility k

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad 13.13$$

Isothermal compressibility is different from another parameter called adiabatic compressibility k_{ad} .

$$k_{ad} = -\frac{1}{V}(\frac{\partial V}{\partial P})_s \qquad 13.14$$

The reciprocal of k (i.e. $\frac{1}{k}$) is called isothermal bulk modulus or isothermal incompressibility.

3.4.2 Expansion

The way the volume of a material increases with temperature at constant pressure is described by coefficient of volume expansion or expansivity β

$$\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P \qquad 13.15$$

The unit of expansivity is K^{-1}

Using equations 13.13 and 13.15, one can show that

$$(\frac{\partial P}{\partial T})_V = \frac{\beta}{k} \quad \text{and} \quad (\frac{\partial V}{\partial T})_P = \beta V \qquad 13.16$$

and the reciprocal of 13.16 gives

$$(\frac{\partial T}{\partial P})_V = \frac{k}{\beta} \quad \text{and} \quad (\frac{\partial T}{\partial V})_P = \frac{1}{\beta V} \quad \text{respectively} \qquad 13.17$$

SELF ASSESSMENT EXERCISE

1. Using equation 13.13 and 13.15, show that $(\frac{\partial P}{\partial T})_V = \frac{\beta}{k}$
2. Determine the heat transferred during a reversible isothermal change in pressure.
3. Calculate the temperature change of a substance which undergoes a reversible adiabatic change of pressure.

3.5 The TdS equations in terms of k and β

Replacing the partial derivatives with these, the three TdS equations become

$$dS = \frac{\beta}{k}dV + \frac{C_V}{T}dT \qquad 13.18$$

$$dS = -\beta V dP + \frac{C_P}{T}dT \qquad 13.19$$

$$dS = \frac{C_V k}{T\beta}dP + \frac{C_P}{T\beta V}dV \qquad 13.20$$

Equations 13.18 to 13.20 give the change in entropy between two states in terms of **P**, **V**, **T**, k, β and heat capacities as a function of temperature and pressure of specific volume. The implication of these equations is that one do not even need equation of state to calculate the change in entropy.

8.0 CONCLUSION

The three TdS equations are useful set of equation in thermodynamics. They are used to calculate heat flow in any reversible process.

9.0 SUMMARY

In this unit, you have learnt:

- how to derive the three **T**d**S** equations
- that these equations can be used to calculate heat flow (TdS) in a reversible process.

10.0 TUTOR-MARKED ASSIGNMENT

Using the TdS equations 13.18 and 13.19 show that $C_P - C_V = \frac{TV\beta^2}{\kappa}$.

11.0 REFERENCES/FURTHER READING

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MODULE 4

UNIT 1 PHASE TRANSITIONS

CONTENTS

1.0 INTRODUCTION

In module 1 unit 1, we discussed change of state and it was mentioned that change of phase or phase transition is a special case of change of state. Phase transition is the transformation of a thermodynamic system from one phase of matter to another. This unit is devoted to phase transition. An important thing to note during phase change is that addition or withdrawer of heat to or from a substance does not result in change of temperature. When matter changes from one phase to another, energy is involved.

2.0 OBJECTIVES

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

- define phase transition
- give conditions under which phase transition occurs
- differentiate between phase transition and change of state
- derive Clapeyron’s equation
- explain the three types of phase transitions.

3.0 MAIN CONTENT

3.1 Phases of Matter

Matter or substance can exist in three (3) familiar phases namely; solid phase, liquid phase, gaseous phase. Matter of some substances can also exist in two (2) less familiar phases namely; super fluid phase, and plasma phase.

Solid Phase: Molecules are arranged in a closely packed form called crystal. These molecules can only vibrate about their lattice point.

Liquid Phase: Molecules are close together and they take the shape of the container. Molecules of liquid, within its volume, can move from place to place, rotate and vibrate.

Gaseous Phase: Molecules are widely separated and free to move around freely.

Super fluid: A supercritical (or critical) fluid is a liquid/gas under extreme pressure.

Plasma: Plasma is a gas that is composed of free-floating ions and free electrons.

3.1.1 Phase Diagram

Figure 14.1 shows the phase diagram for water. The three regions for the three phases are shown in the diagram. The solid curves or lines represent boundary between two phases e.g. fusion curve is the boundary between solid phase and liquid phase. These lines are called equilibrium lines. The implication of this is that under specific conditions of temperature and pressure, a substance can exist in equilibrium in more than one phase at the same time.

Triple Point: This is the point where the three equilibrium lines meet as indicated in the phase diagram 14.1 below. At the triple point, solid, liquid, and vapour phases of a pure substance coexist in equilibrium. The triple point values for common materials are given in table 14.1.

NOTE: All substances have triple point except Helium.

Triple Point Temperature: this is the temperature at which solid, liquid, and vapour phases coexist in equilibrium.

Triple Point Pressure: This is the pressure at which solid, liquid, and vapour phases coexist in equilibrium.

Critical Point: This specifies the conditions of temperature and pressure <u>beyond</u> which it is no longer possible to distinguish a liquid from a gas. The point is indicated in the phase diagram in figure 14.1 and the region beyond the critical point is known as <u>fluid region</u>.

The values of triple point and critical point temperature and pressure for some materials are given in table 14.1

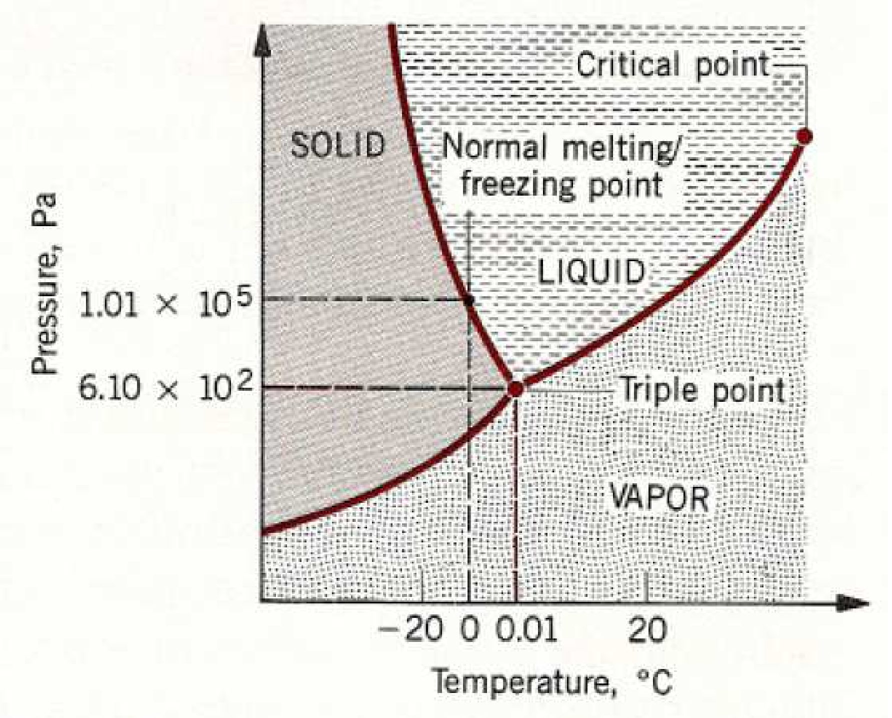

Fig. 14.1: Phase Diagram for Water (After Cutnell and Johnson)

Table 14.1: Triple Point and Critical Point Conditions for some Common Materials

	Triple Point		Critical Point	
Substance	Temperature (ºC)	Pressure (Pa)	Temperature (ºC)	Pressure (Pa)
Ammonia	-77.8	6.05×10^3	132.4	11.30×10^6
Carbon dioxide	-56.6	5.18×10^5	31.1	7.38×10^6
Hydrogen	-259.3	7.04×10^3	-239.9	1.30×10^6
Nitrogen	-210.0	1.25×10^4	-146.9	3.40×10^6
Oxygen	-218.8	1.52×10^2	118.4	5.08×10^6
Sulfur dioxide	75.5	1.67×10^3	157.6	7.88×10^6
Water	0.01	6.10×10^2	374.3	22.10×10^6

Source: Physics by John D. Cutnell and Kenneth W. Johnson

3.1.2 Co-exist Phases

This is when more than one phase of a substance (e.g. liquid-solid) exist side-by-side in equilibrium at the same time. For example, solid water and liquid water can coexist at 0 ºC along the process of fusion or melting. The Gibbs energy (**G**) for two coexisting phases $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ of a pure substance are equal.

$$\boldsymbol{G^{\alpha} = G^{\beta}} \qquad 14.1$$

Using the phase diagram 14.1 for water as example, coexistence of phases occurs only along the equilibrium lines.

3.2 Phase Transitions

Phase transition occurs when matter changes from one of the phases of matter to another. The process always involves withdrawal or addition of heat energy from or to the matter. Using figure 14.1 as an illustration, phase transition occurs whenever any one of the curves in the phase diagram is crossed.

Phase transition for a pure substance occurs at constant temperature and pressure. The implication of this statement is that, for a pure substance $\boldsymbol{dT = dP = 0}$ during a phase change. However, the extensive thermodynamic coordinates or properties (e.g. Volume) change abruptly as a result of a phase transition. Internal energy (U), enthalpy (H), and entropy (S) may also change during a phase transition.

Figure 14.2 shows the three most common phases of matter and the name given to each of the phase transitions.

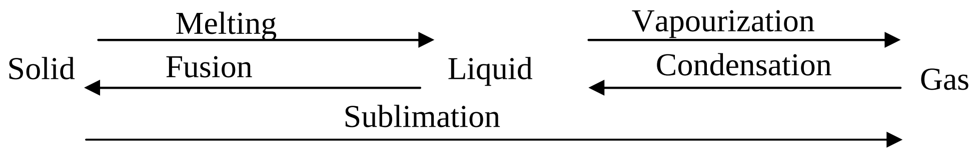

Fig. 14.2: Phase Transitions

3.2.1 Latent Heat, L, during Phase Transition

Latent heat **L** is the amount of heat energy per mole that must be added or removed when a substance changes from one phase to another. If the phase transition takes place reversibly, the heat transfer (i.e. latent heat) per mole for transition from initial phase **α** to a final phase **β** is given by

$$L = T(S^{\beta} - S^{\alpha}) \qquad 14.2$$

3.3 Types of Phase Transition

The three types of phase transitions are: first order, second order and lambda phase transitions.

3.3.1 First Order Phase Transition

The phase transitions that we are familiar with i.e. sublimation, vaporization and fusion are called first order phase transition. They are called first order because the first order derivatives of the Gibbs function are finite.

Therefore, for a first order phase transition:

- there are changes in entropy and volume, and
- the first-order derivatives of the Gibbs function change discontinuously.

The characteristics of the first order phase transition are shown in figure 14.3. The specific heat capacity at constant pressure is infinite, this is because temperature is constant during phase change ($C_P = T \left.\frac{\partial S}{\partial T}\right|_P$).

3.3.2 Second Order Phase Transition

This is a phase transition in which the second derivates of Gibbs are finite.

For order phase transition,

- T, P, G, S, and V (also H, U, and F) remain unchanged
- C_P, β, and κ (i.e. from second derivatives of G) are finite

The only example of second order phase transition is the transition for the superconductor from superconducting to the normal state in zero magnetic fields.

3.3.3 Lambda phase transition

For the lambda phase transition:

- T, P, and G remain constant,
- S and V (also U, H, and F) remain constant, and
- C_P, β, and κ are infinite

The most interesting example of lambda transition is the transition from ordinary liquid helium to super fluid helium at a temperature and corresponding pressure known as a lambda point.

Figure 14.4 shows the variation of C_P with temperature for each of the three phase transitions.

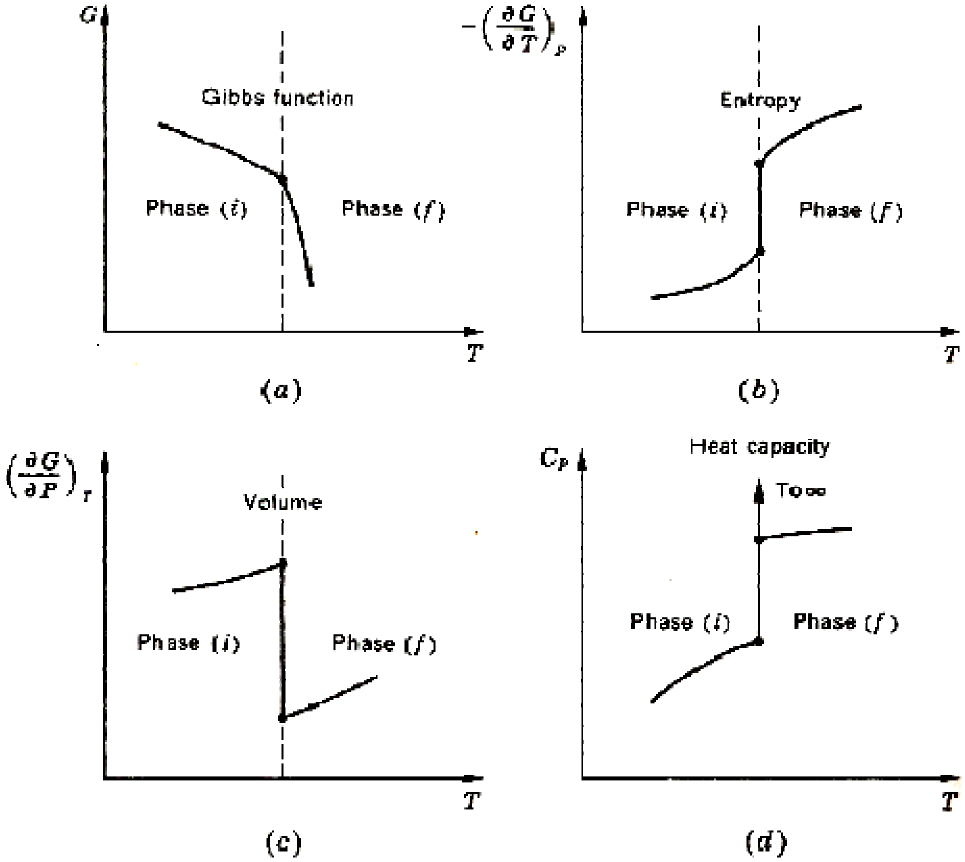

Fig. 14.3: **Characteristics of First Order Phase Transition (After Zemansky and Dittman)**

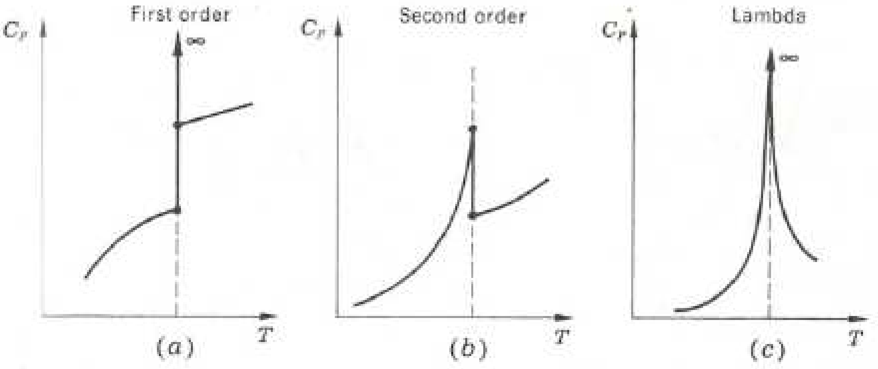

Fig. 14.4: **The Three Types of Phase Transitions (After Zemansky and Dittman)**

3.4 Gibbs Function during Phase Transition

The Gibbs function **G** does not change during phase transition.
For coexisting phases,

$$dG|_{T,P} = 0 \qquad 14.3$$

i.e. change in Gibbs at constant temperature and pressure is zero.

As mention earlier, two phases (e.g. liquid-gas) can coexist in equilibrium. For coexisting phases **α** and **β** of a pure substance

$$G^{\alpha} = G^{\beta} \qquad \Rightarrow \quad dG^{\alpha} = dG^{\beta} \qquad 14.4$$

The Gibbs function **G** is given by equation 14.5 below. For your reference check block 1

$$dG = -SdT + VdP \qquad 14.5$$

Block 1

$G = U - ST + PV$
Differentiating G gives
$dG = dU - SdT - TdS + PdV + VdP$
but $dU = TdS - PdV$, then

If equation 14.5 is put in equation 14.4, we obtain

$$-S^{\alpha}dT + V^{\alpha}dP = -S^{\beta}dT + V^{\beta}dP \qquad 14.6$$

Rearranging (14.6) to obtain

$$\frac{dP}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} \qquad 14.7$$

From equation 14.2

$$S^{\beta} - S^{\alpha} = \frac{L}{T} \qquad 14.8$$

Then, put equation 14.8 in equation 14.7 to obtain

$$\frac{dp}{dT} = \frac{L}{T(V^{\beta} - V^{\alpha})} \tag{14.9}$$

Equation 14.9 is known as the Clapeyron's equation.

If solid phase is labeled 1, liquid 2, and gas or vapour phase 3, equation 14.9 can be written as follows:
For solid – vapour phase transition, we have

$$\left(\frac{dP}{dT}\right)_{13} = \frac{L_{13}}{T(V^{3} - V^{1})}, \tag{14.10}$$

where L_{13} is the latent heat of sublimation.

And for solid - liquid phase transition, we have

$$\left(\frac{dP}{dT}\right)_{12} = \frac{L_{12}}{T(V^{2} - V^{1})}, \tag{14.11}$$

where L_{12} is the latent heat of fusion,

SELF ASSESSMENT EXERCISE

1. Explain the following:

(a) Phase transition (b) Triple point (c) Triple point temperature
(d) Critical point.

2. Derive Clapeyron's equation.
3. The vapour pressure of a particular solid and a liquid of the same material are given by $\ln P = 0.04 - \frac{6}{T}$ and $\ln P = 0.03 - \frac{4}{T}$ respectively, where P is given in atmospheres. Find the temperature and pressure of the triple point of this material.

3.5 Usefulness of Clapeyron's Equation

Equation 14.9 can be integrated to obtain an expression for pressure as a function of temperature. If the following assumptions holds i.e. if the variation in latent heat can be negligible, and if one of the phases is a vapour, and if the vapour is assumed to be an ideal gas, and if the specific volume of the liquid or solid is neglected in comparison with that of the vapour, the integration can be readily carried out.

$$\left(\frac{dP}{dT}\right)_{23}=\frac{L_{23}}{T(RT/P)} \qquad 14.12$$

$$\int\frac{dP}{P}=\frac{L_{23}}{R}\int\frac{dT}{T^2} \qquad 14.13$$

Then,

$$\ln P=-\frac{L_{23}}{RT}+\ln constant \qquad 14.14$$

4.0 CONCLUSION

Matter can exist in three well-known phases i.e. solid, liquid and gaseous phases. Phase transition occurs when changes from one phase to another. During the phase change, the heat added does not bring about a change in temperature. This type of heat is called latent heat of transformation (**L**). Gibbs free energy is a useful thermodynamic potential in describing phase transition.

5.0 SUMMARY

In this unit you have leant that:

- matter can exist in three main phases namely; solid, liquid and gas phases
- two phases of matter can coexist in equilibrium
- phase transition occurs when matter changes from one of the phases of matter to another
- phase transition for a pure substance occurs at constant temperature and pressure
- there are three types of phase transition namely; first order, second order and lambda phase transitions
- the heat transfer (i.e. latent heat) per mole for transition from initial phase **α** to a final phase **β** is $L=T(S^{\beta}-S^{\alpha})$
- the Clapeyron's equation for the first order transition is $\frac{dp}{dT}=\frac{L}{T(V^{\beta}-V^{\alpha})}$.

6.0 TUTOR-MARKED ASSIGNMENT

1. Name and describe the three types of phase transition.
2. Differentiate between a change of state and phase transition.

7.0 REFERENCES/FURTHER READING

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UNIT 2 THROTTLING PROCESS AND FREE EXPANSION OF A GAS

CONTENTS

1.0 INTRODUCTION

You were told in module 3, unit 2 that thermodynamic potentials are used to describe physical processes. In this unit, we are going to use the enthalpy **H** to describe throttling process and the internal energy **U** to describes free expansion of a gas

2.0 OBJECTIVES

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

- explain throttling process
- show that the initial and final enthalpies during a throttling process are equal
- explain free expansion of a gas
- show that for free expansion of ideal gas at constant temperature, $(\frac{\partial U}{\partial P})_T = 0$.

3.0 MAIN CONTENT

3.1 Throttling Process

Throttling Process is an irreversible steady flow expansion process in which a perfect gas is expanded through an orifice of minute dimensions such as a narrow throat of a slightly opened valve. During the process, the fluid passes through a narrow opening (a needle valve) from a region of constant high pressure to a region of constantly lower pressure adiabatically. Throttling is also known as Joule-Kelvin expansion.

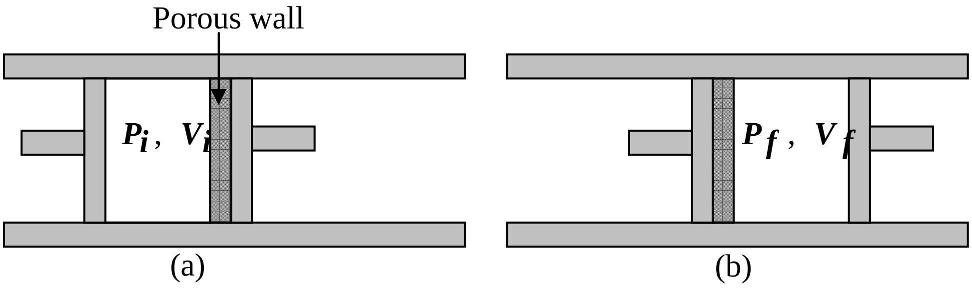

Fig. 15.1: A Throttling Process

Consider a cylinder that is thermally insulated and equipped with two non-conducting pistols on the opposite sides of a porous wall as shown in figure 15.1. As indicated in figure 15.1 (a), the left hand side of the porous plug is filled with gas at P_i and V_i while the right hand side is empty. Suppose the two pistons are moved simultaneously to the right in such a way that a constant pressure P_i is maintained on the right hand side of the wall while a constant lower pressure P_f is maintained on the right hand side. After all the gas has seeped through the porous wall, the final equilibrium state of the system is shown in figure 15.1 (b). This kind of process is known as throttling process.

A throttling process is an irreversible process. This is because the gas passes through non-equilibrium states on its way from initial equilibrium state to its final equilibrium state. As you know, non-equilibriums states cannot be described by thermodynamic coordinates i.e. the non-equilibrium states between the initial and final equilibrium states during a throttling process cannot be described using thermodynamic coordinates. But we can make an interesting conclusion from the initial and final equilibrium states.

3.1.1 Enthalpy during throttling process

One of the most interesting properties of the enthalpy function (H) is in connection with a throttling process.

The equation of the first law of thermodynamics is

$$dQ = dU - W \qquad 15.1$$

but throttling process occurs adiabatically,

$$dQ = 0 \qquad \text{(adiabatic process)} \qquad 15.2$$

Then, the first law of thermodynamics becomes

$$dU = W \qquad 15.3$$

and work

$$W = -\int_{0}^{V_f} P_f \, dV - \int_{V_i}^{0} P_i \, dV \qquad 15.4$$

Since both pressures (P_i and P_f) remain constant, equation 15.3 becomes

$$W = -(P_f V_f - P_i V_i) \qquad 15.5$$

Now, put equation 15.5 in 15.3 to obtain

$$U_f - U_i = P_f V_f - P_i V_i$$

Rearranging gives

$$U_i - P_i V_i = U_f - P_f V_f \qquad 15.6$$

But enthalpy $H = U - PV$, so 15.6 becomes

$$H_i = H_f \qquad 15.7$$

In a throttling process, therefore, the initial and final enthalpies are equal.

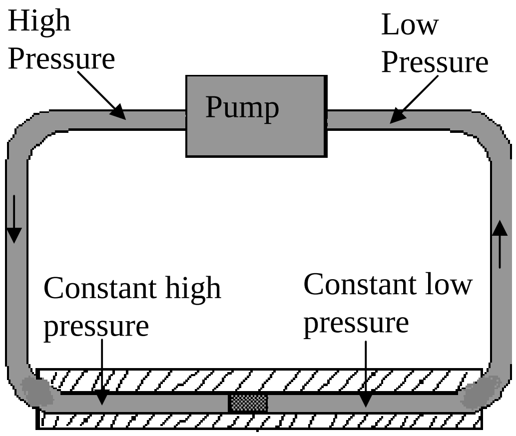

Fig. 15.2: Apparatus for Performing a Continuous Throttling Process

Throttling process is very useful in refrigeration. A continuous throttling process can be achieved using the apparatus shown in figure 15.2.

SELF ASSESSMENT EXERCISE 1

1. What is a throttling process.
2. For a throttling process, show that initial enthalpy H_i is equal to final enthalpy H_f .

3.2 Free Expansion of a Gas

The concept of work done by or on a system has been treated in module 2, unit 1 under the first law of thermodynamics. The work done by or on a gas in a cylinder with a moveable piston was derived to be

$$dW = -PdV \qquad 15.8$$

Equation 15.8 above is as a result of expansion or compression of a gas in a cylinder. That is, in the case of expansion, the molecules move faster and push the piston (exerted a force on the piston) and move the piston through a distance.

Now consider, for example, a composite system consisting of a hydrostatic fluid in the compartments 1 and 2 with (**P_1, V_2**) and (**P_2, V_2**) respectively as shown in figure 15.3 below.

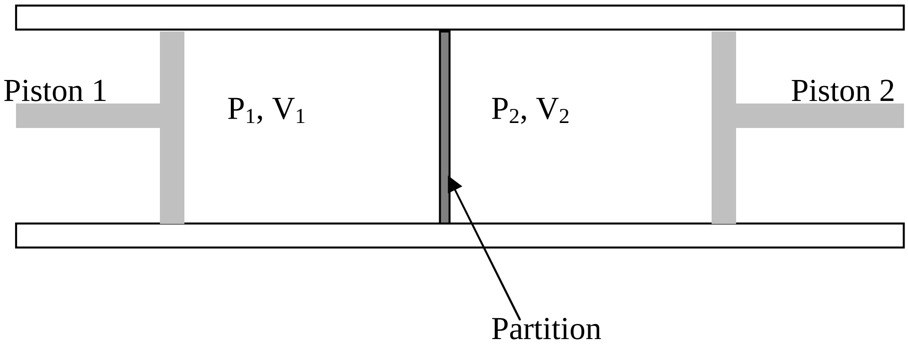

Fig. 15.3: A Composite System

Each compartment or both compartments can undergo an adiabatic work by interacting with the surroundings. This may be done by moving one or both of the pistons in or out, either slowly (a quasi-static process) so that the work done $W = -\int PdV$, with pressure **P** being equal to the equilibrium value (i.e. for a quasi-static process the system is in equilibrium at every instant). Also the piston can be moved very rapidly (a non-quasi-static process) so that the pressure at the face is less that the equilibrium value. For these two examples, work is done on the piston due to expansion of the fluid.

However, if either or both of the pistons is or are pulled out at a faster rate than the velocity of the molecules of the fluid, the fluid will do no work on the piston at all. This type of process is called a free expansion of a gas. Another good example of this process is described below.

Suppose the system in figure 15.3 is thermally insulated and that compartment 1 contains a gas while the other compartment is empty. If the partition is removed, the gas will undergo what is known as a free expansion in which no work is done and no heat is transferred. From the first law of thermodynamics, since both Q and W are zero, it follows that the internal energy remains unchanged during a free expansion.

For free expansion of gas, work is zero ($W = 0$) and no heat is transfer ($Q = 0$). The equation of the first law of thermodynamic reduces to

$$dU = 0 \qquad 15.9$$

3.2.1 Temperature Change during Free Expansion

The value of temperature change $(\frac{\partial T}{\partial V})_U$ during free expansion process has engaged the attention of physicists for over 100 years. Joule in 1843, and many others attempted to measure either the quantity $(\frac{\partial T}{\partial V})_U$, which may be called the Joule Coefficient, or related quantities that are all a measure of the effect of a free expansion-often called the Joule effect. The results of their experiments showed that $(\frac{\partial T}{\partial V})_U = 0$ for ideal gas, but not for real gas (already discussed in module 2, unit 2).

3.2.2 Internal Energy U during Free Expansion

The internal energy **U** of a gas, like any state function, is a function of any two of the coordinates **P**, **V**, and **T**.

Now consider **U** as a function of **T** and **V** i.e. **U**(**T**,**V**), then the derivative of **U** is

$$dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV \qquad 15.10$$

If the temperature change is equal to zero (i.e. $dT = 0$), and for free expansion ($dU = 0$), then equation 15.10 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad 15.11$$

Equation (15.11) implies that **U** does not depend on **V**.

Also consider **U** as a function of T and P i.e. **U**(**T**,**P**)), the derivative of U is

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \qquad 15.12$$

If the temperature change is equal to zero (i.e. $dT = 0$) and for free expansion ($dU = 0$), then equation 15.12 becomes

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \qquad 15.13$$

Equation 15.13 implies that **U** does not depend on **P**.

These (i.e. equation 15.11 and 15.13) follows that if no temperature change takes place in a free expansion process, **U** is independent of **V** and **P**, and therefore **U** is a function of **T** only. This result, of course, has been obtained in Module 2, unit 2, under Gay-Lussac-Joule experiment.

SELF ASSESSMENT EXERCISE 2

1. Explain free expansion of gas.
2. One mole of an ideal gas undergoes a throttling process from pressure of 4.052×10^5 Nm^{-2} to 1.013×10^5 Nm^{-2}. The initial temperature of the gas is 50 ˚C. (a) How much work could have been done by the ideal gas has it undergone a reversible process to the same final state at constant temperature? (b) How much does the entropy of the universe increase as a result of the throttling process? (R=8.3 JK^{-1}mol^{-1})

4.0 CONCLUSION

Throttling process can be described using the enthalpy **H** of the system. During a throttling process, the enthalpy **H** is constant. This process is useful in refrigeration. Free expansion of a gas can be described using the internal energy of the system.

5.0 SUMMARY

In this unit, you have learnt that:

- during the process, the fluid passes through a narrow opening (a needle valve) from a region of constant high pressure to a region of constantly lower pressure adiabatically
- the enthalpy H can be used to describe a throttling process
- for a throttling process, the initial enthalpy is equal to the final enthalpy (i.e. $H_i = H_f$)
- throttling process is very useful in refrigeration
- free expansion of a gas that occurs adiabatically, work is zero ($W = 0$) and no heat is transfer ($Q = 0$), hence from the first law $dU = 0$
- for free expansion process for an ideal gas, the internal energy U is a function of temperature alone i.e. $(\frac{\partial U}{\partial P})_T = 0$.

6.0 TUTOR-MARKED ASSIGNMENT

1. Explain what is meant by free expansion of a gas.
2. 1 mol of an ideal gas for which $C_V = 25.12$ and $C_P = 33.44$ J/mol K expands adiabatically from an initial state at 340 K and 500 Pa to a final state where it volume has doubled. Find the final temperature of the gas, the work done, and the entropy change of the gas, for (a) a reversible expansion and (b) a free expansion of the gas into an evaporated space (Joule expansion). (1 Pa = $1.013\text{x}10^5$ Nm^{-2}).

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UNIT 3 PRODUCTION OF LOW TEMPERATURE

CONTENTS

1.0 INTRODUCTION

We discussed in module 2, unit 5, the device used in lowering the temperature of a body or system i.e. refrigerator. We will discuss in this unit, the cooling method that is being used to obtain extremely low temperature i.e. cooling by adiabatic demagnetisation.

2.0 OBJECTIVES

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

- discuss the process of cooling
- mention different methods being used to achieve low temperature
- discuss the process of cooling by adiabatic demagnetisation
- derive the expression for change in temperature with respect to field **B** at constant entropy i.e. $(\frac{\partial T}{\partial B})_S$.

3.0 MAIN CONTENT

3.1 Cooling Process

Generally, two processes are involved in cooling a gas namely; isothermal process followed by adiabatic process. For example, to cool a gas by adiabatic decompression, the gas is first compressed isothermally i.e. at constant temperature. This is done by compressing the gas in a vessel that is not insulated and wait long enough for the gas to lose any heat that is generated due to compression. In this way, a constant temperature is maintained. The heat that is generated can be explained in terms of the law $\frac{PV}{T} = constant$. Then, the vessel containing the gas is insulated and the gas is allowed to expand adiabatically (i.e. no heat transfer is allowed between the vessel and the surrounding). This kind of expansion brings about reduction in temperature. The expression for change in temperature with respect to pressure at constant entropy $(\frac{\partial T}{\partial P})_S$ can be derived. The process can be repeated until the desired temperature is reached. This method is called cooling by adiabatic decompression.

3.1.1 Methods of Cooling

Some of the methods being used for low temperature cooling are:

- laser cooling
- evaporative cooling (e.g. evaporation of ^{3}He)
- cooling by liquefaction
- cooling by adiabatic demagnetisation

The process of cooling by adiabatic demagnetisation has been used to obtain extremely low temperature. Cooling by adiabatic demagnetisation is therefore discussed below.

3.2 Cooling by Adiabatic Demagnetisation

Different methods have been employed to obtain very low temperature. The method of adiabatic demagnetisation has been used to obtain extremely low temperature. Figure16.1 shows the S-T diagram for adiabatic demagnetisation. Magnetic field B is zero along the curve labeled $B = 0$ while magnetic field is B along the curve labeled B. In process **ab**, a sample of paramagnetic salt (e.g. cerium magnesium nitrate) already cooled to low temperature by other means (e.g. by contact with a bath of liquid helium), is magnetized isothermally. The sample is often suspended in an atmosphere of helium, which can conduct away any heat that is produced, and hence keeps the process isothermal. Hence, process **ab** is isothermal magnetization. Then, in process **bc** (i.e. adiabatic demagnetisation), the paramagnetic salt is insulated (by pumping out the helium) and then demagnetized adiabatically. This process of isothermal magnetization followed by an adiabatic demagnetisation can be repeated over and over again until the desired temperature is reached. Temperature close to 0 K have been reached in this manner.

Note that one could actually reach a temperature of absolute zero if one did this an infinite number of time- but not for any fewer (statement of third law of thermodynamics).

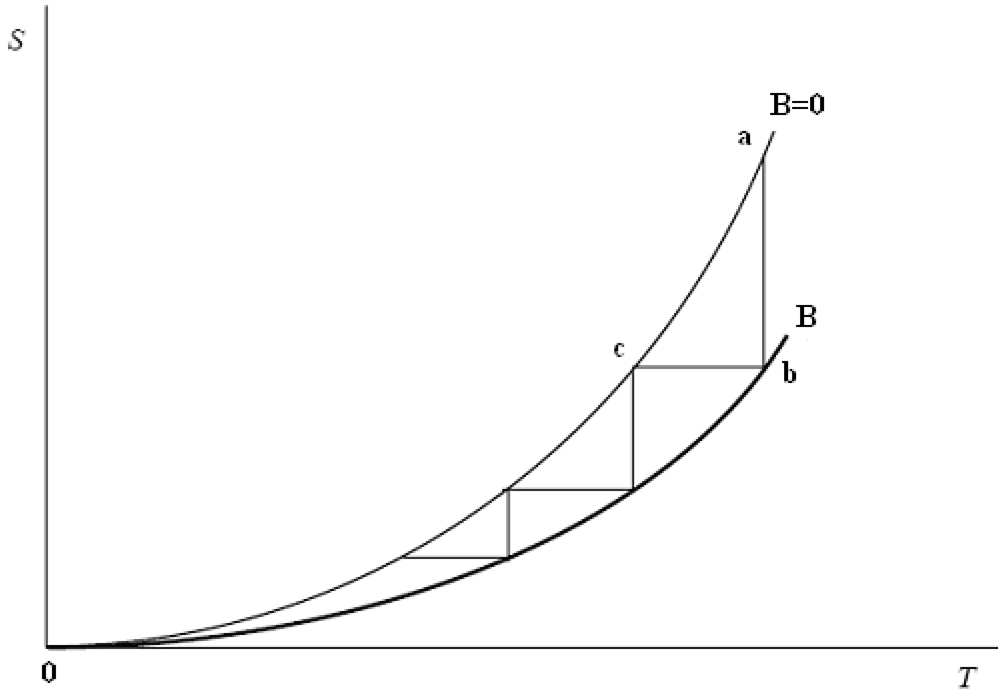

Fig. 16.1: **The Temperature Dependence of the Entropy of a Magnetic System**

3.3 Theory of Adiabatic Demagnetisation

Magnetic dipole moment **P** of a sample is the maximum torque it experiences in unit field **B**. Torque is given by $\boldsymbol{\tau} = \boldsymbol{P} \times \boldsymbol{B}$. The magnetization **M** of a specimen is defined by $\boldsymbol{B} = \mu \boldsymbol{H} = \mu_o(\boldsymbol{H} + \boldsymbol{M})$. The magnetization is also equal to the magnetic moment per unit volume. The differential form of work for a magnetic system is $\boldsymbol{BdM}$ (Module 1, unit 5, section 3.1.1).

$$dW = BdM \qquad 16.1$$

$\boldsymbol{BdM}$ is the work done per unit volume on an isotropic sample in increasing its magnetization from $\boldsymbol{M}$ to $\boldsymbol{M} + \boldsymbol{dM}$.

If we add heat to a magnetisable sample, and do work per unit volume on it by putting it in a magnetic field B and thereby increase its magnetization by d**M**, then, provided there is no change in volume, the increase in its internal energy per unit volume is given by

$$dU = TdS + BdM \qquad 16.2$$

In this magnetic context, we can define state functions H, A, and G per unit volume by

$$H = U - BM \qquad 16.3$$

$$A = U - TS \qquad 16.4$$

$$G = H - TS = A - BM \qquad 16.5$$

And the differential forms as,

$$dH = TdS - MdB \qquad 16.6$$

$$dA = -SdT + BdM \qquad 16.7$$

$$dG = -SdT - MdB \qquad 16.8$$

M is the dipole moment per unit volume, in NmT^{-1}m^{-3}, which is the same as the magnetization in Am-1

We can derive an expression for the lowering of the temperature in an adiabatic decompression $(\frac{\partial T}{\partial P})_S$. Also using the same argument, step-by-step, for the lowering of the temperature in an adiabatic demagnetisation $(\frac{\partial T}{\partial B})_S$.

3.3.1 Adiabatic Decompression $(\frac{\partial T}{\partial P})_S$

Considering entropy as a function of temperature and pressure (i.e. S(T,P)),

$$(\frac{\partial S}{\partial T})_P (\frac{\partial T}{\partial P})_S (\frac{\partial P}{\partial S})_T = -1 \qquad 16.9$$

In a reversible process $dS = \frac{dQ}{T}$, and in an isobaric process,

$$dQ = C_P dT$$

i.e. $$TdS = C_P dT \qquad 16.10$$

From equation 16.10, partial derivative of S with respect to T at constant pressure gives

$$(\frac{\partial S}{\partial T})_P = \frac{C_P}{T} \qquad 16.11$$

Also from a Maxwell relation,

$$(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P \qquad 16.12$$

From equation 16.9

$$(\frac{\partial T}{\partial P})_S = -(\frac{\partial T}{\partial S})_P (\frac{\partial S}{\partial P})_T \qquad 16.13$$

Put equations 16.11 and 16.12 in 16.13 to obtain

$$(\frac{\partial T}{\partial P})_S = \frac{T}{C_P}(\frac{\partial V}{\partial T})_P \qquad 16.14$$

If the gas is an ideal gas, the equation of state is $PV = nRT$, so that

$$(\frac{\partial V}{\partial T})_P = \frac{nR}{P} = \frac{V}{T} \qquad 16.15$$

Put equation 16.15 in 16.14

$$(\frac{\partial T}{\partial P})_S = \frac{V}{C_P} \qquad 16.15$$

3.3.2 Adiabatic Demagnetisation $(\frac{\partial T}{\partial B})_S$

The same argument as above can be used for adiabatic demagnetisation $(\frac{\partial T}{\partial B})_S$.

We can consider the entropy as a function of temperature and magnetic field i.e. $S(T,B)$, we have

$$(\frac{\partial S}{\partial T})_B (\frac{\partial T}{\partial B})_S (\frac{\partial B}{\partial S})_T = -1 \qquad 16.16$$

Then

$$(\frac{\partial T}{\partial B})_S = -(\frac{\partial T}{\partial S})_B (\frac{\partial S}{\partial B})_T \qquad 16.17$$

In a reversible process $dS = \frac{dQ}{T}$, and in a constant magnetic field, $dQ = C_B dT$, C_B is the heat capacity per unit volume (i.e. the heat required to raise the temperature of a unit volume by one degree)

In a constant magnetic field

$$(\frac{\partial S}{\partial T})_B = \frac{C_B}{T} \qquad 16.18$$

Also from a Maxwell relation corresponding to $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$, that is

$$(\frac{\partial S}{\partial B})_T = -(\frac{\partial M}{\partial T})_B \qquad 16.19$$

Now for a paramagnetic material, the magnetization, for a given filed is proportional to B and it falls off inversely as the temperature (that's the equation of state).

That is $M = \frac{aB}{T}$

Therefore,

$$(\frac{\partial M}{\partial T})_B = -\frac{aB}{T^2} = -\frac{M}{T} \qquad 16.20$$

Put 16.20 in 16.19

$$(\frac{\partial S}{\partial B})_T = \frac{M}{T} \qquad 16.21$$

Now put equations 16.18 and 16.21 in 16.17, to obtain

$$(\frac{\partial T}{\partial B})_S = \frac{M}{C_B} \qquad 16.22$$

Equation 16.22 gives the cooling effect, i.e. the variation of temperature with magnetic field at constant entropy, in terms of magnetization **M** and heat capacity C_B.

The cooling effect is particularly effective at low temperature when C_B is small.

3.4 Entropy and Temperature

Cooling by adiabatic demagnetisation involves successive isothermal magnetizations followed by adiabatic demagnetisations, and this suggests that some insight into the process might be obtained by following it on an entropy-temperature (ST) diagram. Using figure 16.1 above, the cooling effect $(\frac{\partial T}{\partial B})_S$ is shown in the process **bc** as well as other subsequent processes indicated by the horizontal lines linking the two curves.

A complete cooling is indicated in processes **ab** and **bc**, which can be repeated until the desired temperature is achieved.

SELF ASSESSMENT EXERCISE

1. Give four methods of achieving low temperature and the minimum temperature attainable with each method.
2. Describe the process of cooling by adiabatic decompression.

4.0 CONCLUSION

We have discussed in this unit a method of cooling being used to achieving extremely low temperature i.e. cooling by adiabatic demagnetisation. The refrigerator that does this is called adiabatic demagnetisation refrigerator. In the next unit, we are going to be looking at the phenomena at extremely low temperature, and then round up the course by stating the third law of thermodynamics i.e. the un-attainability of absolute zero.

5.0 SUMMARY

In this unit, you have learnt:

- about the process of cooling
- about methods being used for low temperature cooling
- about processes and relevant equations involve in cooling by adiabatic demagnetisation
- that the expression for change in temperature with respect to field **B** at constant entropy i.e. $(\frac{\partial T}{\partial B})_S$.

6.0 TUTOR-MARKED ASSIGNMENT

1. Write the differential form of thermodynamic potential for a magnetic system.
2. Using an entropy-temperature (ST) diagram, describe the process of cooling by adiabatic demagnetisation.

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UNIT 4 PHENOMENA AT LOW TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

CONTENTS

1.0 INTRODUCTION

Why do we need to cool material to extremely low temperature? The reason is that the properties of metals, semiconductors, and alloys change dramatically at low temperature. In the last unit, we discussed method of achieving low or extremely low temperature. The focus of this unit will be on the behaviours of materials at low temperature and then we round up our discussion by stating the third law of thermodynamics.

2.0 OBJECTIVES

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

- explain the meaning of low temperature physics
- explain some phenomenon at low temperature
- mention useful applications of low temperature phenomenon
- state Nernst heat theorem
- state third law of thermodynamics.

3.0 MAIN CONTENT

3.1 Low Temperature Physics

Low temperature physics is a specialised area of physics that deals with the behaviour of materials at low or extremely low temperature. Now, the big question is this. How low is low? Low temperature, in this context, is the temperature low enough to observe the phenomena such as superconductivity and super-fluidity. Here, we are going to concentrate only on the meanings of these phenomena and their applications. The theory and the detail description of these two phenomena are beyond the scope of this unit.

3.1.1 Liquefaction of Gases

Liquefaction of gases is the process by which substances in their gaseous state are converted to the liquid state.

Liquefaction of gases can be achieved:

- by compressing the gas at temperatures less than its critical temperature;
- by making the gas do some kind of work against an external force, thereby causing the gas to lose energy and change to the liquid state; and
- by making the gas do work against its own internal forces, this also causing it to lose energy and liquefy.

When gases are liquefied, they can then be stored and transported in much more compact form than in the gaseous state. One kind of liquefied gas that we are familiar with is Liquefied Natural Gas (LNG). In principle, any gas can be liquefied, so their compactness and ease of transportation has made them popular for a number of other applications.

Applications of Liquefaction

Liquefied gases are used in the following application:

- Fuel for rocket engines e.g. liquefied oxygen and hydrogen;
- For welding operation e.g. liquid oxygen and acetylene;
- Aqualung devices e.g. combination of liquid oxygen and liquid nitrogen;
- For research application (cryogenics) e.g. liquid helium is widely used for the study of behaviour of matter at temperatures close to absolute zero.
- Liquid nitrogen for low temperature refrigeration.

3.1.2 Maintenance of Low Temperature

The method on maintaining low temperature is by using liquefied gases as heat sink. For example, some gases liquefy at quite low temperatures (e.g. nitrogen liquefied at 77 K, hydrogen at 20 K, helium at 4.2 K). If such gases are liquefied, the liquid can be used as bath to maintain experiment at these temperatures.

3.1.3 Measurement of Low Temperature

Conventional thermometers may be used at quite low temperatures. Table 17.1 gives the lowest temperature for some convectional thermometers.

Table 17.1: Lowest Temperature for some Conventional Thermometers

Conventional Thermometer	Lowest Temperature
Platinum resistance thermometer	about 20 K
Indium resistance thermometer	about 4 K
Helium gas thermometer	about 3 K
Carbon resistors as thermometer	From 4 K to 0.1 K

3.2 Phenomena at Low Temperature

Two known phenomena at low temperature are superconductivity and superfluidity.

3.2.1 Superconductivity in Metals

At a temperature low enough, most metals as well as many alloys and compounds enters a state at which their resistant to flow of current disappears (i.e. they become a superconductor). This state is called superconductivity in metals. Most metals in the periodic table, many alloys and compounds show this behaviour. The implication of superconductivity is that if a superconductor is a wire loop and a current is generated in that loop, then it flows for years with no significant decay.

3.2.2 Superfluidity

At a temperature low enough, materials enter a state whereby they become fluid that flows with no viscosity. Superfluidity can only be observed at much lower temperatures than the temperature at which superconductivity is observed. For example, helium-4 does not display superfluid-behaviour until it reaches a temperature below 2 K. Note that materials that become solid at low temperatures cannot become superfluids.

When a material becomes a superfluid, the following will be observed:

- Because superfluids have no internal viscosity, a vortex formed within a superfluid persists forever.
- A superfluid has zero thermodynamic entropy and infinite thermal conductivity, meaning that no temperature differential can exist between two superfluids or two parts of the same superfluid.
- A superfluid can also climb up and out of a container in a one-atom-thick layer if the container is not sealed.
- A conventional molecule embedded within a superfluid can move with full rotational freedom, behaving like a gas.

3.3 Application of Low Temperature Phenomena

Applications of low temperature phenomena are listed below:

3.3.1 Applications of Superconductivity

Superconductivity promises a whole lot of applications but the limitation to this is how to maintain this temperature because the whole of these applications are at room temperature in everyday world.

Most significant real application of low temperature physics is the super-conducting magnet. This is being used for magnetic resonance imaging (MRI) and particle accelerators. Other applications are in;

- Supersensor,
- Quantum computing,
- Loss less power transmission line. We know that energy loss on a transmission line is $\boldsymbol{I^2R}$. Imagining using super conduction as transmission cable, meaning that R = 0 i.e. $\boldsymbol{I^2R} = 0$.

3.3.2 Applications of Superfluidity

Superfluidity does not have a wide range of application as superconductivity. The two areas of applications are in dilution refrigerators and spectroscopy.

3.4 Nernst Heat Theorem

Third law of thermodynamics explains the behaviour of systems, which are in internal equilibrium, as the temperature approaches absolute zero (i.e. 0 K).

Consider a chemical reaction taking place in a container at constant pressure, and that the container makes a contact with a heat reservoir at a temperature **T**. If the temperature of the system increases as a result of the reaction (i.e. if the reaction is exothermic) there will be a heat flow to the reservoir until the temperature of the system reduced to its original value **T**. Don't forget that a heat bath or reservoir is so large that its temperature does not change appreciably when heat flow in or out of it.

For a process at constant pressure the heat gain or lost is an increase or decrease in enthalpy. Then

$$\Delta H = H_f - H_i = -Q \qquad 17.1$$

Minus sign in the right hand side of equation 17.1 indicates that heat flows out of the system. The heat of reaction is usually given as ΔH. ΔH is positive for an endothermic reaction and negative for exothermic reaction.

Change in the Gibbs function and change in enthalpy are related as

$$G_f - G_i = H_f - H_i + T\left(\frac{\partial(G_f - G_i)}{\partial T}\right)_P \qquad 17.2$$

written as

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \qquad 17.3$$

This implies that change in enthalpy and change in Gibbs function are equal only when $T\left(\frac{\partial \Delta G}{\partial T}\right)_P$ approaches zero. Nernst proposed that, in the limit, as the temperature approaches zero, the changes in enthalpy and Gibbs function are equal. Since

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad 17.4$$

So that

$$\lim_{T \to o} (S_1 - S_2) = 0 \qquad 17.5$$

This implies that chemical reactions at a temperature of absolute zero take place with no change in entropy.

Planck later extended this to suppose that, not only does $\Delta G \rightarrow \Delta H$, but that, as $T \rightarrow 0$, the enthalpy and the Gibbs function of the system approach each other asymptotically in such a manner that, in the limit, as $T \rightarrow 0$, $G \rightarrow H$ and $(\frac{\partial G}{\partial T})_P \rightarrow 0$.

i.e.

$$\lim_{T \rightarrow 0} S = 0 \qquad 17.6$$

3.5 Third Law of Thermodynamics

Nernst's heat theorem and Planck's extension of it, though derived from observing the behaviour of chemical reactions in solids and liquids, is now believed to apply quite generally to any process. Equation 17.6 is known as the third law of thermodynamics.

3.5.1 The Statement of the Third Law of Thermodynamics

The third of thermodynamics states that it is impossible to reduce the temperature of a material body to the absolute zero of temperature in a finite number of operations.

This is the third law of thermodynamics, and it is an inevitable consequence of Planck's extension of Nernst's heat theorem. The third law is sometimes called the unattainability statement of the third law.

SELF ASSESSMENT EXERCISE

1. What is low temperature physics?
2. Name the two phenomena at low temperature and explain each of them.
3. Derive equation 17.3 from the definitions of Enthalpy and Gibb's free energy.
4. State Nernst's heat theorem.

4.0 CONCLUSION

The quest by scientists to cool a body or a system to extremely low temperature (about 0 K) brought about discoveries, along the way, of two important phenomena of materials at extremely low temperature (i.e. superconductivity and superfluidity). These phenomena have a wide range of applications but the limitation is that these applications are relevant to our every day activity at room temperature. The process of cooling a body by gradual withdrawal of heat becomes more and more difficult as the absolute temperature is approach. This is the statement of the third law of thermodynamic i.e. it is impossible to reduce the temperature of a material body to the absolute zero of temperature in a finite number of operations.

5.0 SUMMARY

In this unit, you have learnt that:

- the properties of materials change dramatically at low temperature
- the phenomena at low temperature are superconductivity and superfluidity
- these phenomena have a wide range of applications but there is limitation i.e. the usage temperature of these applications
- the statement of the third law of thermodynamics is that bodies or systems can be cooled to absolute temperature by infinite number of operations.

6.0 TUTOR-MARKED ASSIGNMENT

1. Explain the limitation of the range of applications of superconductivity.
2. Give five applications of low temperature phenomena.

7.0 REFERENCES/FURTHER READING

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