

MAA OMWATI DEGREE COLLEGE,
HASSANPUR (PALWAL)

NOTES

**SUBJECT : Computer Programming &
Thermodynamics (Physics)**

CLASS : B.SC 3rd Sem

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B.Sc - 2nd year
3rd sem

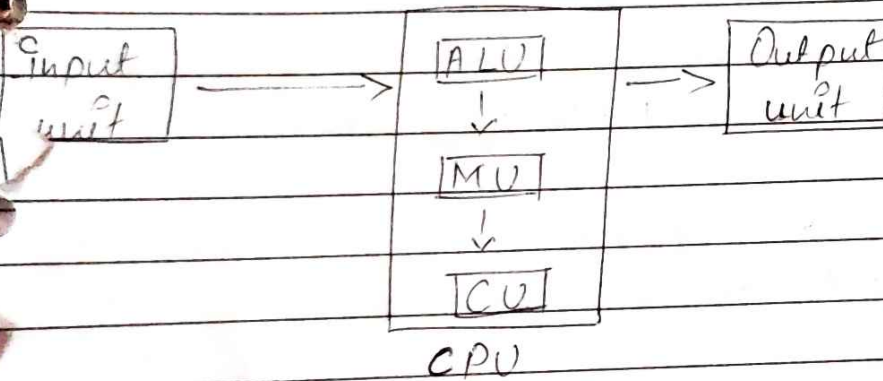
Unit - 1st

COMPUTER PROGRAMMING

CHAPTER - 1st

COMPUTER ORGANISATION

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C - Commonly
O - Operated
M - Machine
P - Primarily
U - Used For
T - Trade
E - Education and
R - Research

* Basic components of COMPUTER :-
A digital computer consists of three basic components :-

1. Input unit.
2. Central Processing unit (CPU).
 - a) Arithmetic logical unit (ALU).
 - b) Control unit (CU).
 - c) Memory unit (MU).
3. Output unit.

1. Input unit :-

Input unit acts as an interface between the user and computer.

There are many types of input devices :-
eg:- keyboard, mouse, (Light pen, Joystick, touch screen.

Functions of input units :-

- It reads the data, programmes, and instructions from users.
- It converts the data and instructions etc. into computer-understandable form.
- It supplies the converted data and instructions etc. to the computer for further processing.

2. Central Processing unit (CPU) :-

There are three parts of CPU :-

- ALU.
- CU.
- MU.

CPU also known as the brain of computer. In computer system, all the major functions like calculations, comparisons, activations and control of operations of all the units of the computer are done inside the CPU.

Functions of CPU parts are :-

a) Arithmetic logical unit (ALU) :-

ALU of a computer is a place where the actual execution of instructions involving mathematical calculations and logical decisions.

It takes place during the processing of operation.

b) Control unit (CU) :-

Control unit is also the brain of CPU. Control unit generates the electrical signals to control and coordinates the functioning of other units. One by one, instructions are fetched from the (main memory, interpreted in this unit and control signals are generated to various signals. Control unit also handles.

Major Functions of CU :-

- about storage allocation of devices.
- about storage deallocation of devices.
- attachment of new hardware.
- proper functions of software.
- user interaction.

c). Memory unit (MU) :-

Memory data instructions entered into the computer have to be stored inside the computer. It is called memory unit or storage components of computer of memory.

Parts of Memory unit :-

(i) Primary unit (ii) Secondary unit (iii) Cache unit.

(i) Primary unit :- Primary unit is also known as main memory or internal memory or essential memory. (It is very fast in nature.

Before execution all the data and instructions are stored first into this memory.

Primary Memory divides into two parts:-

- a) RAM
- b) ROM

a) RAM:- This is also known as Read-Write-Memory, because any information on it can be written, read and deleted. It is a volatile in nature. It means that when power of the computer is switched off, its contents gets lost.

b) ROM:- This memory is used to store the programs that do not need regular alteration. Data stored in non-volatile in nature. i.e. data is not lost when power of computer is switched off.

(ii) Secondary Memory unit:- It also store data programs permanently. It is also Non-volatile in nature. It has much larger capacity than that of primary memory and are not very fast in access. It is lighter, cheaper and easy to travel.

For e.g:- Magnetic tapes, Magnetic discs, Magnetic drums and hard disc etc.

(iii) Cache Memory unit:- It is used to increase the speed of processing by making current programs and data available to CPU at rapid rate. It is used to store frequently accessed data of main memory. It increases the memory speed of the system and is much costly, costlier than other types of memory.

3. Output Unit:-

This unit converts the information from the computer - understandable form to human-understandable form. This transformation is accomplished by the units called output interfaces.

types of output units:-

- (i) Visual display units (VDU)
- (ii) Printers.
- (iii) Graph plotters.
- (iv) Card punch.
- (v) Paper tape punch.
- (vi) Magnetic tapes etc.

BINARY REPRESENTATION* Number systems:-

Every no. stores numbers, letters, and other special characters in a coded form i.e. binary form.

(The No. systems are of two types:-

- (i) Non-positional Number systems.
- (ii) Positional Number systems.

* Decimal Number systems:- Dec. means (10) ten

The number system that we use most of the time in our daily life is Decimal Number system.

Because it has ten unique digits (0, 1, 2, 3, 4, 5, 6, 7, 8, 9) and its base is 10, it is called as decimal No. system.

In general, a decimal no. having 'n' digits in its integer part and m digits in its fractional part can be represented as:-

$$d_n 10^{n-1} + d_{n-1} 10^{n-2} + \dots + d_1 10^0 + d_{-1} 10^{-1} + d_{-2} 10^{-2} + \dots + d_{-m} 10^{-m}$$

for e.g:- 8674.23

$$= 8 \times 10^3 + 6 \times 10^2 + 7 \times 10^1 + 4 \times 10^0 + 2 \times 10^{-1} + 3 \times 10^{-2}$$

$$= 8000 + 600 + 70 + 4 + .2 + .03$$

$$= (8674.23)_{10}$$

* Binary Number Systems:-

is similar to decimal system. The binary no. system's base is 2

and has only two symbols 0 or 1. Each symbol 0 or 1 is referred as BIT which is an abbreviated form of the expression Binary digit.

* Its Representation:-

In computers, binary number system is used due to the following reasons:-

(i) Electronic configuration operates in a binary mode. An electric switch is either ON (1 state) or OFF (0 state), a transistor is either conducting (1 state) or non-conducting (0 state).

(ii) Computer systems circuits have to handle only two binary digits (bits).

(iii) Everything that can be converted into decimal numbers and vice-versa.

$$d_n 2^{n-1} + d_{n-1} 2^{n-2} + \dots + d_1 2^0 + d_{-1} 2^{-1} + \dots + d_{-m} 2^{-m}$$

where d_n is the most significant bit and d_{-m} is the least significant bit.

* Conversion of Integer Decimal Number to Binary Number:-

$$(d)_{10} = (d_n 2^{n-1} + d_{n-1} 2^{n-2} + \dots + d_1 2^1 + d_0 2^0)_2$$

for e.g:- $(121)_{10} = (1111001)_2$

		Remainder	Least significant digit (LSD)
2	121		
2	60	1	
2	30	0	
2	15	0	
2	7	1	
2	3	1	
2	1	1	
	0	1	Most significant digit (MSD)

* Conversion of Fractional decimal number into Binary No.:-

$$(d)_{10} = (d_1 \cdot 2^{-1} + d_2 \cdot 2^{-2} + \dots + d_m \cdot 2^{-m})_2$$

So, if we multiply the fractional decimal no. by 2,

$$2^1(d)_{10} = (d_1 \cdot 2^0 + d_2 \cdot 2^{-1} + \dots + d_m \cdot 2^{-m+1})_2$$

$\downarrow$ $\leftarrow$ fractional part of (d_1)
 M.S.D (to cont.)

The fractional part of the product may be multiplied again by 2 to get the next significant digit d_2 . This procedure is repeated till the fractional part becomes zero.

For e.g.:- 116.5625 convert the decimal no. into binary.

(i) For integer part 116

	2	116	Remainder	L.S.D
	2	58	0	
	2	29	0	
	2	14	0	
	2	7	0	
	2	3	1	
	2	1	1	
		0	1	M.S.D

$$(116)_{10} = (1110100)_2$$

(ii) For fractional part $.5625$

M.S.D	2 th	.5625
		2
	1	.1250
		2
	0	.2500
		2
	0	.5000
		2
L.S.D		1
		.0000

$$(.5625)_{10} = (.1001)_2$$

$$(116.5625)_{10} = (1110100.1001)_2$$

* Conversion of Binary number into Decimal Number:-

- Find the positional values of each digit.
- Multiply the positional values (of above step i) by the digits in corresponding position.
- Sum the products obtained in step (ii). The total is equivalent to decimal no.

For e.g.:- $(1100.001)_2 = (?)_{10}$

$$\begin{aligned}
 (1100.001)_2 &= 1 \times 2^3 + 1 \times 2^2 + 0 \times 2^1 + 0 \times 2^0 + 0 \times 2^{-1} + 0 \times 2^{-2} + 1 \times 2^{-3} \\
 &= 8 + 4 + 0 + 0 + 0 + 0 + \frac{1}{8} \\
 &= 12.125
 \end{aligned}$$

$$(1100.001)_2 = (12.125)_{10}$$

Ques. (1) Convert the following binary numbers into their decimal equivalents:-

(i) 1101

$$\begin{aligned}
 &= 1 \times 2^3 + 1 \times 2^2 + 0 \times 2^1 + 1 \times 2^0 \\
 &= 8 + 4 + 0 + 1 = 13
 \end{aligned}$$

$$(1101)_2 = (13)_{10}$$

(ii) 101101

$$\begin{aligned}
 &= 1 \times 2^5 + 0 \times 2^4 + 1 \times 2^3 + 1 \times 2^2 + 0 \times 2^1 + 1 \times 2^0 \\
 &= 32 + 0 + 8 + 4 + 0 + 1 = 44
 \end{aligned}$$

$$(101101)_2 = (44)_{10}$$

(iii) 1010.111

$$\begin{aligned}
 &= 1 \times 2^3 + 0 \times 2^2 + 1 \times 2^1 + 0 \times 2^0 + 1 \times 2^{-1} + 1 \times 2^{-2} + 1 \times 2^{-3} \\
 &= 8 + 0 + 2 + 0 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} = 10 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8}
 \end{aligned}$$

$$= \frac{87}{8} = 10.875$$

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$$(1010.111)_2 = (91.8)_{10}$$

$$(iv) 100111$$

$$\Rightarrow 1 \times 2^5 + 0 \times 2^4 + 0 \times 2^3 + 1 \times 2^2 + 1 \times 2^1 + 1 \times 2^0$$

$$= 32 + 0 + 0 + 4 + 2 + 1 = 39$$

$$(100111)_2 = (39)_{10}$$

$$(vi) 11011.011$$

$$\Rightarrow 1 \times 2^4 + 1 \times 2^3 + 0 \times 2^2 + 1 \times 2^1 + 1 \times 2^0 + 0 \times 2^{-1} + 1 \times 2^{-2}$$

$$= 16 + 8 + 0 + 2 + 1 + 0 + \frac{1}{4} + \frac{1}{8} + 1 \times 2^{-3}$$

$$= 27 + \frac{1}{4} + \frac{1}{8}$$

$$= \frac{216 + 2 + 1}{8} = \frac{219}{8} = 27.375$$

Que 2 Convert the following decimal numbers into binary equivalents :-

$$(i) 26$$

	2	26	Remainder
	2	13	0
	2	6	1
	2	3	0
	2	1	1
		0	1

L.S.D

M.S.D

$$(26)_{10} = (11010)_2$$

$$(ii) 111$$

	2	111	Remainder
	2	55	1
	2	27	1
	2	13	1
	2	6	1
	2	3	0
	2	1	1
		0	1

L.S.D

M.S.D

$$(111)_{10} = (1101111)_2$$

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$$(iii) 99.26$$

	2	99	Remainder
	2	49	1
	2	24	1
	2	12	0
	2	6	0
	2	3	0
	2	1	1
		0	1

$$2 \quad .26 \quad R$$

$$2 \quad .13 \quad 0$$

$$2 \quad .6 \quad 1$$

$$2 \quad .3 \quad 0$$

$$2 \quad .1 \quad 1$$

$$2 \quad .0 \quad 1$$

$$(99.26)_{10} = (1100011.011010)_2$$

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ALGORITHM DEVELOPMENT

* Definition of Program:-

A sequence of sets of instructions of programmes. It has the following stages:-

Stage 1:- Defining the Problem

This is a most important stage as it acts as a foundation for building up a programme.

The basic concepts of programmes should be clearly known at the end of this phase.

Stage 2:- Algorithm Development

An algorithm is a map or an outline to a problem solution. This outline shows the precise order, in which the programme will execute individual functions to arrive at the solution. It should be emphasised here that an algorithm is language development.

Stage 3:- Program Coding

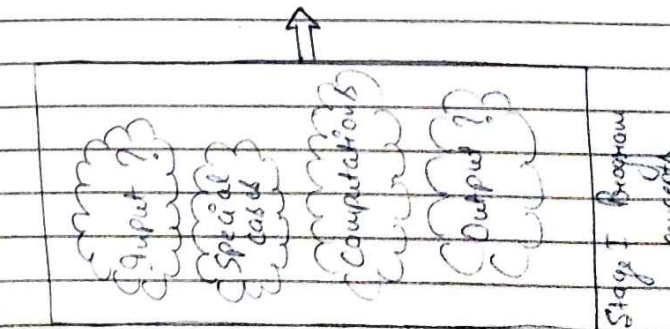
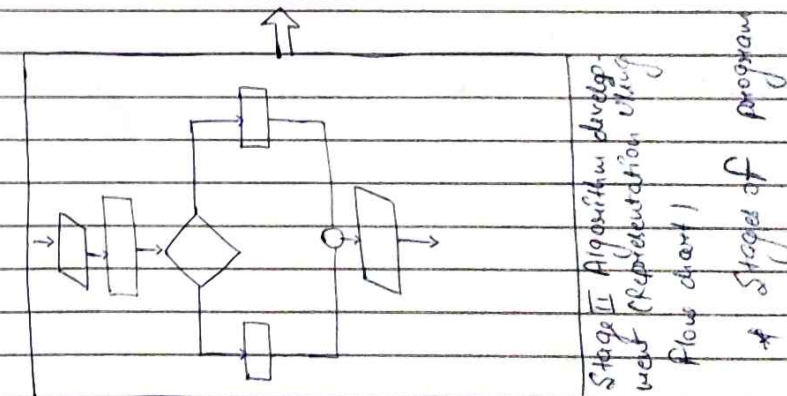
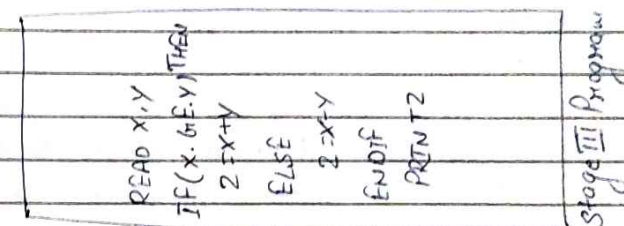
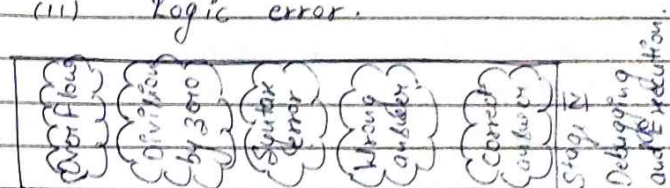
It is a process of converting an algorithm into a more structured device i.e., the source code, by using the defined computer languages. Every programming language has its own set of rigid rules, known as syntax which should be followed carefully, while writing the source code.

Stage 4:- Compilation, Debugging and Execution.

While compiling the programme's code, process of finding out the errors (bug), if any in the programme, is known as

debugging. It is the final step in the programming process. There can be two types of errors in the programme.

- (i) Syntax error.
- (ii) Logic error.



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Ques. 1 Define Algorithms.

An algorithm is defined as a step by step sequence followed for finding solution of a given problem.

Ques 2 State the stages of Program development.

Different stages of program development are:-

- i> Defining the problem.
- ii> Algorithm development.
- iii> Program coding.
- iv> Debugging.

Ques 3 What are the basic building blocks of control structures

The following building blocks of control structures

- i> Sequence.
- ii> Selection or Branching.
- iii> Repetition or Iteration or looping.

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CHAPTER- 4th

Flow Charts

* Definition of flow charts:-

Definition I:-

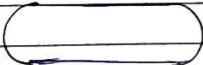
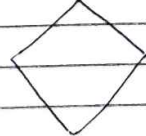
"Flow charts is a pictorial representation of sequence of steps, in which logical conditions are to be tested and calculations are performed for solving a problem."

Definition II:-

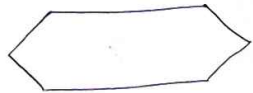
"Flow charts is a pictorial representation that uses predefined symbols to describes either the logic of a computer program (program flow charts) or the data flow and processing steps of a system (system flow charts)

* Flow chart symbols:-

Flow chart symbols and their functions:-

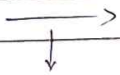
Symbol	Name	Function
	Terminal	It indicates the entry ENTRY or EXIT Point of the flow charts e.g:- START, STOP, END
	Input/output	It denotes any function of an input/output (operation in the program)
	Compute	It represents the arithmetic and data movement instructions.
	Decision	It indicates a point at which decision has to be made and a branch of one or more alternative points is possible.

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Loop

It indicates the flow of control of operation, i.e., exact sequence in which instructions are to be executed.



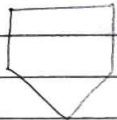
Flow lines

It indicates how many times group of instructions are to be executed.



Line connector

It indicates the flow of entry from or exit to another part of flow chart on same page.



Page connector

It indicates the entry from or exit to another page of a flow chart. It is so placed that its point indicates the direction of flow.

* Advantages of Flow charts:-

There are advantages of using flow charts for program planning. There are as follows:-

- Better understanding.
- Effective analysis.
- Effective synthesis.
- Proper program documentation.
- Efficient coding.
- Systematic Debugging.

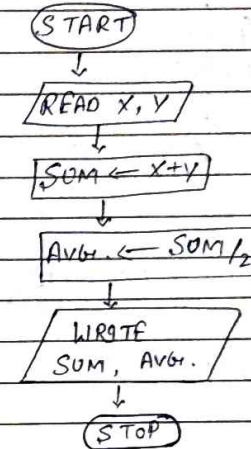
* Limitations of Flow charts:-

There are some limitations also as,

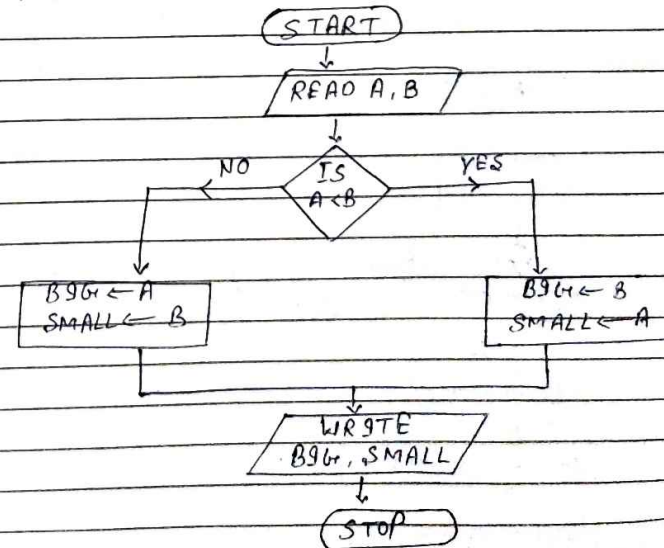
- Take more time to draw.
- Difficult to make changes.
- Non-standardization.

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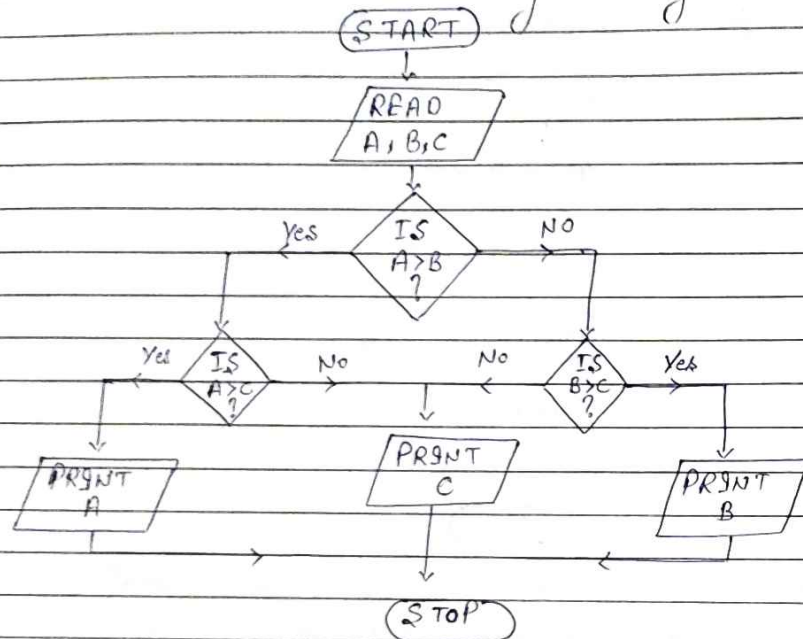
Ques.1 Draw a flow chart for finding the sum S and average A of two given numbers X and Y .



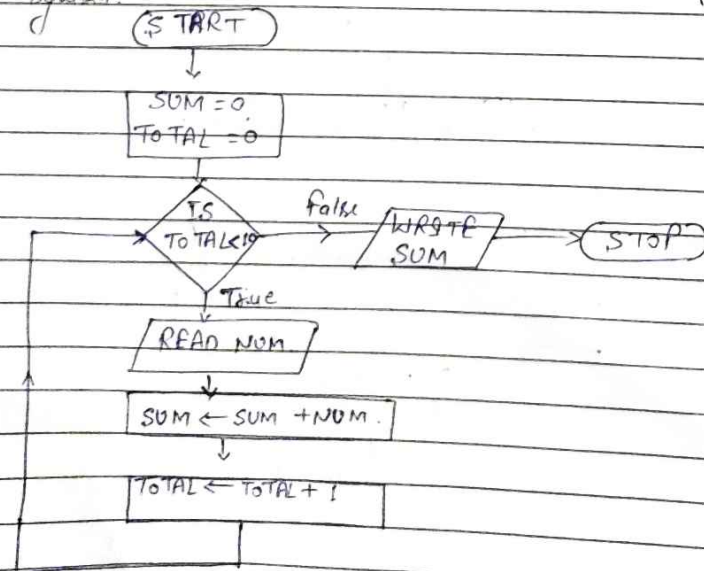
Ques.2 Draw a flow chart which reads two no. A and B , then print them in descending order, after assigning the larger no. to BIG and the smaller no. to $SMALL$.



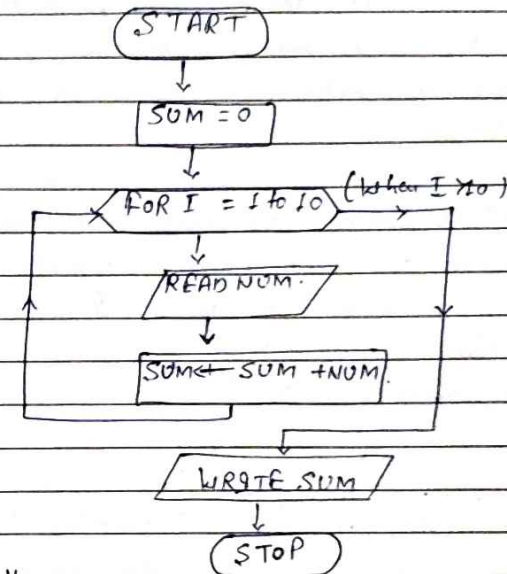
Ques. 3 Draw a Flow chart of Finding the largest of the three no.



Ques. 4 Draw a Flow chart to find sum of ten no. using condition symbol.



Ques. 5 Draw a Flow chart to find sum of the ten no. using 'Loop'



CHAPTER - 5th

FORTAN PROGRAMMING PRELIMINARIES

* Program Preliminaries :- Program preliminaries include all those basic terms, which are required in programming of a problem, in any computer-language. Some of these basic terms are as follows :-

(i) PROGRAM :-

Program is a sequenced set of instructions, written in a programming language, to solve a particular problem.

(ii) SOURCE PROGRAM :-

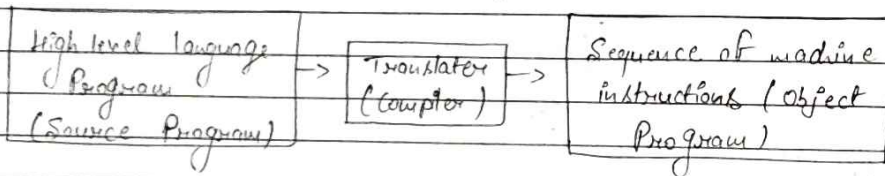
Program written in by user in any programming language, eg Fortan, Pascal, C etc.

(iii) OBJECT PROGRAM:-

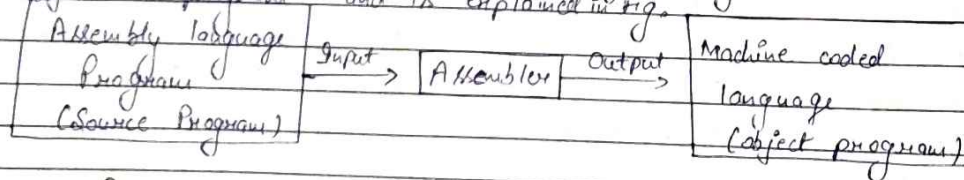
The machine code produced, after translating the source program, into corresponding machine level-language program is known as object program.

(iv) COMPILER:-

It is system software that translates source program written in High Level Language into object program in machine language. It is also called language processor.
These forms are explained below:-



(v) ASSEMBLER:- It is a system software that translates source program written in assembly language into the object program and is explained in fig.



(vi) PROGRAMMING LANGUAGE:- All the programming languages are broadly categorized into two types:-

1. Low level language. (LLL)
2. High level language. (HLL).

* Integer constants:-

Integer constants are whole no. without any fractional part. Their typical range for 32 bit computers is from -2147483648 to 2147483647.

* Real / Floating point constant:-

Real constants are also called as Floating-point constants and have fractional part. They may be written in one of the two forms:-

- Fractional form.
- Exponent form.

* Constants:-

Constants are the values which represent themselves rather they are the numbers which do not change during the execution of the program. e.g:- 1, 2, 3 etc.

* Variables:-

Variables are the data names which represent constants. Their values can be changed during the execution of the program. e.g:- $x = d$, $x = 3.65$

* Classification of FORTRAN constants:-

The FORTRAN constants can be classified broadly in two categories:-

- (i) Numeric constants.
- (ii) Non-numeric constants.

CHAPTER-8th

Executable And Non-Executable Statements

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* Executable Statements:-

- Executable statements are converted into object code by the compiler.
 - During the execution of the program these statements are executed and lead to an action, such as arithmetic assignment, input output, or branching.
- Examples:- READ, WRITE, GO TO, IF, DO, COMPUTED GO TO, ASSIGNED GO TO etc.

* Non-Executable Statements:-

- These statements help the compiler to allocate space to determine type of the variables, INPUT, OUTPUT FORMATS etc.
 - These are not converted into object code.
- Examples:- FORMAT, DIMENSION, IMPLICIT, COMMON, COMMON statements, TYPE statements, ELSE, END, TYPE, ENDTF, COMMON etc.

CHAPTER-9th

Input - Output Statements And Formats specifications:-

FORTAN-77 has provided they us with many input-output statements like:-

- (i) READ statement.
- (ii) WRITE statement.
- (iii) PRINT statement etc.

In general, input-output statements consists of two parts:-

- an executable part.
- a declarative parts.

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• Executable Part:- This part commands contain items, to be read into the memory of the computer or read out of it.

• Declarative Part:- This part gives information on the exact form, in which data will be displayed. therefore, it is also called the FORMAT statements.

* READ Statement:-

To input data, to the program, READ statement is used. It is an executable statements.

Purpose:- It is used to read data from input devices, such as keyboard, input data file.

SYNTAX:-

READ (unit, Format) < list of input variables > SI FORMAT (list of instructions).
--

• UNIT is an integer variables named or an integer const. which refers to a code assigned to the input unit to be accessed.

• Format is the statement no. label of the format declaration for the list.

2) • List is the list of input variables separated by comma. we can write in FORTRAN is as:-

READ (*, 3a) X, Y, Z

READ (*, *) X, Y, Z

This statement is also known as list directed input statement.

* WRITE STATEMENT :-

To output data from computer memory, WRITE statement is used. It is an executable statement.

Purpose :- It is used to display or print the values of variables / constants or to store the values of variables / constants to file.

SYNTAX :-

WRITE (unit, format) < list of output variables >

we can write in FORTRAN 77 :-

WRITE (*, 20) X, Y, Z

WRITE (*, *) X, Y, Z

This statement is also called as list directed output statements.

* PRINT STATEMENTS :-

PRINT statements are used in places of WRITE statements :-

SYNTAX :-

PRINT label, variable 1, variable 2
label FORMAT (list of instructions).

e.g. :-

PRINT 25, A, B
25 FORMAT (IX, A)

* FORMAT STATEMENTS :-

A programmer, by using giving the FORMAT specifications, has greater freedom to input the data to the computer and to get the final results to be printed out.

FORMAT statement is non-executable statements.

The list of instructions that follows the FORMAT statement consists of :-

- (i) carriage control characters.
- (ii) list of edit descriptors.

The general form of the FORMAT statement is :-

1) FORMAT (< field specifications >)

or

1) FORMAT (CCC, specifier 1, specifier 2, --- etc.)

* STOP & END statements :-

• STOP statement :- STOP statement is used to stop the execution of the program. STOP statement may occur anywhere in the given program. E.g., 1) read x, 2) if x is (-ve) then go to step 3) if x is zero then go to step 4) print x is (+ve). 5) stop.

• END statement :- END statement informs the computer about the end of the program. END statement is the last statement in any program.

Main points of difference b/w STOP & END statements are :-

STOP	END
1) STOP statement may occur anywhere in the program.	1) END statements occur only at the end of the program.
2) Any number of STOP statements may occur in the program.	2) Only one END statement must occur in the program.
3) STOP statement is used to instruct the computer to stop the execution of the program.	3) END statement is used to inform the computer that it is the last line of the program.

* Carnot Engine:-

A heat engine is a device, which converts heat energy into mechanical energy.

Constructious:- The essential of a Carnot engine are:-

(i) Cylinder:- A cylinder with non-conducting sides and conducting base. The cylinder contains a perfect gas as the working substance.

(ii) Source:- It is a reservoir of heat, kept at a fixed temperature T_1 .

(iii) Sink:- It is another reservoir of heat, kept at a lower fixed temperature T_2 .

(iv) Insulating Stand:- When the base of the cylinder is kept on this stand, the cylinder becomes perfectly insulated i.e. neither heat can enter the cylinder nor it can leave it.

Working:- The working of Carnot engine can be explained in four operations, it is called a Carnot cycle.

(i) Let the cylinder of the engine contain 1 mole of a perfect gas. The base of the cylinder is placed in contact with the source at temperature T_1 , so that gas attains the temp T_1 of the source. Its pressure and volume at this stage are P_1 and V_1 respectively.

The workdone by the gas during this process is,

$$W_1 = Q_1 = \int_{V_1}^{V_2} P dV = RT_1 \log_e \frac{V_2}{V_1}$$

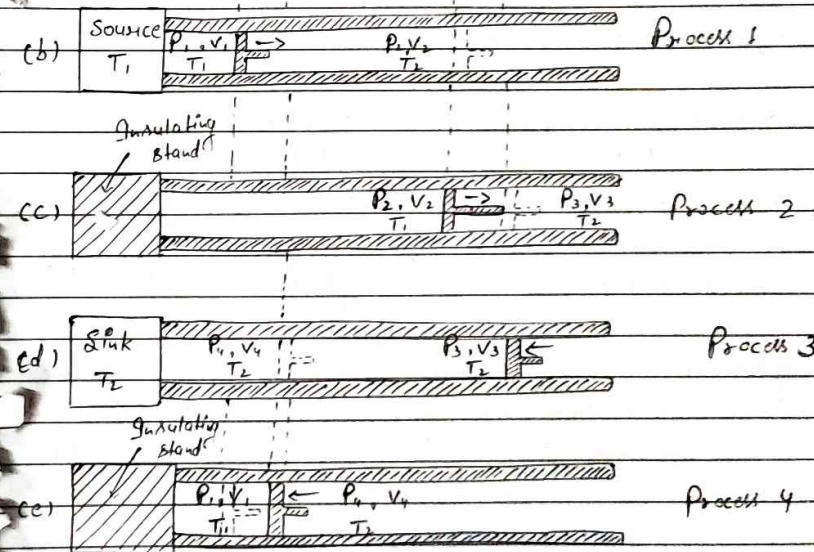
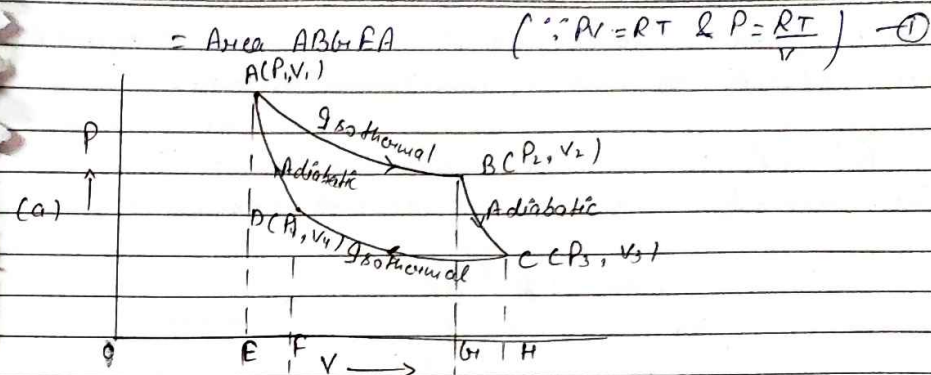


Fig:- Carnot engine And Carnot cycle

(ii) The cylinder is removed from the source and placed on the insulating stand, so that cylinder becomes perfectly non-conducting. The pressure on the working substance is

reduced from P_2 to P_3 and the gas is allowed to expand under adiabatic conditions, from volume V_2 to V_3 .

$$P_2 V_2^r = P_3 (V_3)^r = \text{constant}, k \quad (2)$$

The work done by the gas during adiabatic expansion is,

$$W_2 \Rightarrow \int_{V_2}^{V_3} P \, dV = k \int_{V_2}^{V_3} \frac{dV}{(V)^r} \quad [\text{using eq. (2)}]$$

$$\Rightarrow k \int_{V_2}^{V_3} V^{-r} \, dV = k \left[\frac{V^{1-r}}{1-r} \right]_{V_2}^{V_3}$$

$$= \frac{k}{1-r} [(V_3)^{1-r} - (V_2)^{1-r}]$$

$$\Rightarrow \frac{k (V_3)^{1-r}}{1-r} - \frac{k (V_2)^{1-r}}{1-r} = \frac{P_3 V_3 - P_2 V_2}{1-r}$$

$$\Rightarrow \frac{R (T_2 - T_1)}{1-r} - \frac{R (T_1 - T_2)}{r-1} \quad (3)$$

$$= \text{Area BCHKGB} \quad [\text{using } P_3 V_3 = RT_2, P_2 V_2 = RT_1]$$

(iii) The engine is now placed on the sink, so that base of the cylinder is in contact with the sink. The pressure is increased from P_3 to P_4 , so that volume is decreased from V_3 to V_4 . The work done is,

$$W_3 = \int_{V_3}^{V_4} P \, dV = RT_2 \log_e \frac{V_4}{V_3}$$

$$= -RT_2 \log_e \frac{V_3}{V_4}$$

$$= \text{Area CHFDC} \quad (4)$$

(iv) The cylinder is again placed on the insulating stand and the pressure is increased from P_4 to P_1 . As that volume decreases from V_4 to V_1 under adiabatic conditions. The temperature will increase from T_2 to T_1 . The work done on the gas is,

$$W_4 = \int_{V_4}^{V_1} P \, dV = -\frac{R (T_1 - T_2)}{r-1} \quad (5)$$

$$W_4 = \text{Area DFEAD}$$

From eq. (3), (5), W_2 , W_4 are equal to and opposite and hence they cancel each other.

Thus, net amount of work done during complete cycle is,

$$W = W_1 + W_2 + W_3 + W_4$$

$$= W_1 + W_3$$

$$W = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4} \quad (6)$$

The net amount of heat absorbed is,

$$Q = Q_1 - Q_2$$

Acc. to 1st law of thermodynamics,

$$W = Q = Q_1 - Q_2 \quad (6a)$$

$$W = \text{Area ABGFEA} + \text{Area BCHKGB} - \text{Area CHFDC} - \text{Area DFEAD}$$

$$W = \text{Area ABCOA} \quad (7)$$

The point B and C lie on the same adiabatic curve,

$$T_1 (V_2)^{r-1} = T_2 (V_3)^{r-1} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{V_2}{V_3} \right)^{r-1} \quad (8)$$

Similarly, the point A and D lies on the same curve,

$$T_1 (V_1)^{r-1} = T_2 (V_4)^{r-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4} \right)^{r-1} \quad (9)$$

From eq. (8), (9), so we get,

$$\frac{V_2}{V_3} = \frac{V_1}{V_4}$$

or
$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \text{--- (10)}$$

Substituting in eq. (10) in eq. (6)

$$W = R \log_e \frac{V_2}{V_1} [T_1 - T_2] \quad \text{--- (11)}$$

Efficiency of Carnot engine:-

The efficiency of a heat engine is defined as the ratio of output (mechanical energy) to the input heat energy.

$$\text{Efficiency, } \eta = \frac{W}{Q_1}$$

or
$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

Using relations (1), (6) and (10), so we get,

$$\eta = \frac{R[T_1 - T_2] \log_e \frac{V_2}{V_1}}{RT_1 \log_e \frac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1}$$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$\Rightarrow \eta = 1 - \frac{T_2}{T_1} \quad \text{--- (12)}$$

From eq. (12), we get,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

* Second law of thermodynamics:-

The second law of thermodynamics was formulated to overcome the difficulties not explained by first law. The second law was not derived on any theoretical or mathematical reasoning. It is purely ~~deducted~~ derived on the basis of experiments conducted.

Lord Kelvin stated the second law in the following manner:-

It is impossible to derive continuous supply of energy from a body by cooling it below the coldest of the surroundings.

Clausius stated the law in the following form:-

It is impossible for a self-acting machine, unaided by any external agency to convey heat from a body at lower temperature to another body at higher temperatures.

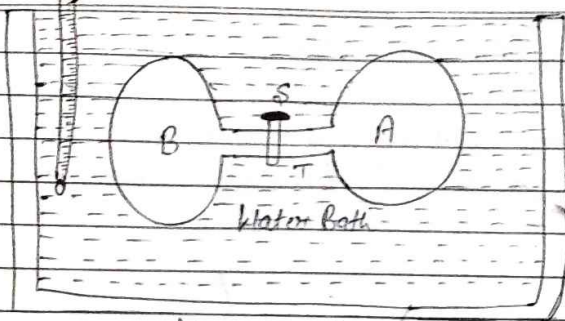
or

Heat by itself cannot pass from a cold body to a hot body.

* Joule's free expansion:-

When a gas is made to expand without doing external work and without allowing the heat to enter or leave it during the expansion, the expansion is known as Joule's free expansion.

If there is no molecular force of attraction as assumed for gases, no internal work is done and thus there will be no change in the temperature of the gas.



Joule's free expansion.

The apparatus designed by him consists of two spherical bulbs A and B connected with each other by a tube T, fitted with a stopcock S. The two flasks were placed in a water bath kept at a constant temperature. The bulb A is filled with a gas at high pressure, while the bulb B was kept evacuated. The temperature was noted. The stop-cock was opened, so that gas could rush from bulb A to B. No change in temperature of the gas was observed.

* Joule's Thomson's effect:-

Acc. to Joule's Thomson effect, when a gas escapes through a porous plug under a large pressure difference, it undergoes a change in temperature.

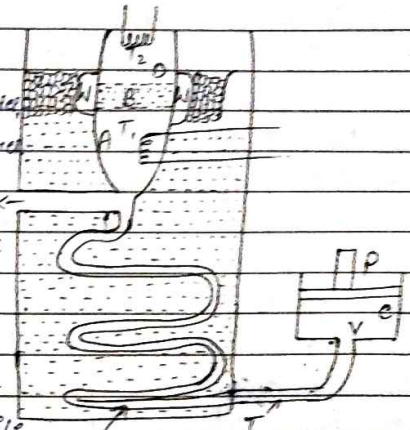
Joule - Thomson Porous plug experiments:-

It consists of a porous plug B surrounded by two perforated brass plates D, D'. The plug is packed with cotton wool or silk fibres. The plug is surrounded by a wooden tube W to have perfect insulation. On one side, the porous plug is connected with tube A, which is connected through a spiral

tube T to a cylinder C in which gas is compressed to a high pressure with a piston P.

The experiment was repeated by Joule and Thomson for different gases for different ranges of temperatures. The results obtained by them can be summarised as under:-

- 1) At sufficiently low ^{Pressure} ^{range} temperatures, all gases show a cooling effect.
- 2) (At ordinary temperature, most gases show a cooling effect, while hydrogen and helium show a heating effect.)



* Pollution Due to internal combustion engine:-

An internal combustion engine is a heat engine in which combustion of the fuel takes place in the cylinder of the engine itself.

e.g:- Petrol (gasoline) engine, diesel engine.

Air pollution can be defined as addition to our atmosphere of any material, which have a deleterious effect on our lives. The main polluting materials contributed by automobiles are Carbon monoxide (CO), unburnt hydrocarbons (UHC), oxides of nitrogen (NO)_x, lead etc.

(A). Pollution From Petrol engines:-

The pollution from a petrol engine can be caused from fuel tank, the carburettor, the crank case and from the exhaust pipe.

The contribution of pollution is as follows:-

- Evaporation loss (both from tank and carburettor)
- Crank case blow by,
- Tail pipe exhaust.

(B). Methods to reduce pollutants in internal combustion engine:-

The emission control programme aims at reducing the concentration of CO, HC and NO_x in the exhaust.

This may be carried by,

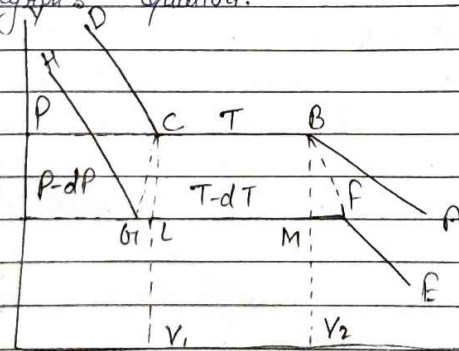
- Engine design modifications.
- Treatment of exhaust gases.
- Fuel Variation (the fuel used CN gas as alternative fuel).

* Clausius - Clapeyron equation by latent heat :-

The equation deals with the effect of melting point or boiling point of a substance due to change of pressure. The equation was first derived by Clapeyron in 1834 and by Clausius in 1850 and hence is known as Clausius Clapeyron's equation.

The pressure P and temperature T remains constant during the change of state. At P , the substance is completely in liquid state and along CD it remains in this state. Similarly, let $EFGH$ be another isothermal

For the unit mass of the substance $v \rightarrow x$ at $(T-dT)$ K. Along FG , the pressure remains const. at $(P-dP)$



Obviously, T is the boiling point of the liquid at pressure P and $(T-dT)$ is the boiling point of the liquid at the pressure of $(P-dP)$

The Carnot engine works in the following steps:-

i) The substance completely changes from liquid to the gaseous state. The amount of heat absorbed for this change of state is L , where L is the latent heat of vaporisation,

ii) During this operation the temperature of the vapour falls to $(T-dT)$ when the pressure is decreased to $(P-dP)$

iii) The vapour is now compressed isothermally at const. temp. $(T-dT)$. The heat rejected to the sink during this process is $(L-dL)$, so that $dL = dW$.

The efficiency of Carnot engine is given by,

$$\eta \rightarrow \frac{dW}{Q} = \frac{dL}{L} = \frac{1 - (T-dT)}{T} = \frac{dT}{T} \quad \text{--- (1)}$$

The workdone is also given by the area CBMFC enclosed by the Carnot cycle = $dP (v_2 - v_1)$
 $dW = dP (v_2 - v_1) \quad \text{--- (2)}$

Substituting in the relations, (1), as we get,

$$\frac{dP (v_2 - v_1)}{L} = \frac{dT}{T}$$

$$\text{or } \frac{dP}{dT} = \frac{L}{T(v_2 - v_1)} \quad \text{--- (3)}$$

This relation is known as Clausius - Clapeyron equation.

* Maxwell's Thermodynamical Relations:-

From Ist laws of thermodynamics, if dQ is the small amount of heat energy absorbed by thermodynamic system,

$$dQ = dU + P.dv$$

where dU is small increase in the internal energy,
 dv is the small increase in volume at pressure P

$$\therefore dU = dQ - P.dv$$

From IInd laws of thermodynamics,

$$dQ = T.dS$$

where dS is the increase in the entropy of the system at const. temperature T .

Combining the two laws,

$$dU = T.dS - P.dv \quad - (1)$$

Let the internal energy U , entropy S and volume v be expressed as the functions of two variables x and y where x and y may be two of the variables S, T, P and v ,

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy \quad - (2)$$

$$dv = \left(\frac{\partial v}{\partial x}\right)_y dx + \left(\frac{\partial v}{\partial y}\right)_x dy \quad - (3)$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \quad - (4)$$

Substituting the values of dU , dv and dS from relations (2), (3), (4) in eq. (1), we get,

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T \left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] - P \left[\left(\frac{\partial v}{\partial x}\right)_y dx + \left(\frac{\partial v}{\partial y}\right)_x dy \right]$$

Comparing the coefficients of dx, dy as,

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial v}{\partial x}\right)_y \quad - (5)$$

$$\text{and, } \left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial v}{\partial y}\right)_x \quad - (6)$$

taking partial derivatives of eq. (5), (6) w.r. to x, y .

$$\frac{\partial^2 U}{\partial y \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y - P \frac{\partial^2 v}{\partial y \partial x} \quad - (7)$$

$$\text{and, } \frac{\partial^2 U}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial v}{\partial y}\right)_x - P \frac{\partial^2 v}{\partial x \partial y} \quad - (8)$$

Then, dU, dv, dS are perfect differentials,

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}, \quad \frac{\partial^2 S}{\partial y \partial x} = \frac{\partial^2 S}{\partial x \partial y}, \quad \frac{\partial^2 v}{\partial y \partial x} = \frac{\partial^2 v}{\partial x \partial y}$$

Substituting in the relation (7), (8) and simplifying,

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial v}{\partial y}\right)_x$$

This is the general thermodynamical relation. - (9)

Now, taking $x=S$, $y=v$ as independent variables,

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial v}{\partial y} = 1, \quad \frac{\partial S}{\partial y} = 0, \quad \frac{\partial v}{\partial x} = 0$$

Substituting in relation (9), we get,

$$\left(\frac{\partial T}{\partial v}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_v \quad - (10)$$

This is the Ist thermodynamical relation.

Let us take $x=T$, $y=v$ as

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial v}{\partial y} = 1, \quad \frac{\partial T}{\partial y} = 0, \quad \frac{\partial v}{\partial x} = 0$$

Substituting in relation (9), we get,

$$0 = \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{or} \quad \left(\frac{\partial S}{\partial T} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (11)$$

This is the Ist Maxwell's relation.

Substituting, $x=S, y=P$,

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial S}{\partial y} = 0, \quad \frac{\partial P}{\partial y} = 1, \quad \frac{\partial P}{\partial x} = 0$$

$$\left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P \quad \text{or} \quad \left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P \quad (12)$$

This is the IInd relation.

Again substituting $x=T, y=P$,

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial y} = 1, \quad \frac{\partial P}{\partial x} = 0$$

$$- \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial S}{\partial P} \right)_T \quad \text{or} \quad \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad (13)$$

This is the IVth thermodynamical relation.

Taking $x=P, y=V$,

$$\frac{\partial S}{\partial x} = 0, \quad \frac{\partial S}{\partial y} = 1, \quad \frac{\partial P}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 1$$

and substituting in relation (1), we get,

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

$$\text{or} \quad \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial S}{\partial V} \right)_P - \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial S}{\partial P} \right)_V = 1 \quad (14)$$

This is the Vth relation.

Taking $x=T, y=S$,

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial T}{\partial y} = 0, \quad \frac{\partial S}{\partial y} = 1, \quad \frac{\partial S}{\partial x} = 0$$

Substituting in eq. (1), we get,

$$\left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial V}{\partial T} \right)_S = 1 - \left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial S} \right)_T$$

$$\text{or} \quad \left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial S} \right)_T - \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial V}{\partial T} \right)_S = 1 \quad (15)$$

* Pollution from Diesel engines:-

The emissions from the Diesel engines are similar to those in a gasoline engine, but the level of the emission in Diesel engines vary considerably, i.e. if we take a sample of exhaust from such an engine, it may be free from smoke, odour, unburnt hydrocarbons (UHC). The total amount of pollutants in the two types of engines may be same. The constituents of exhaust emission are almost same, i.e. unburnt hydrocarbons, aldehydes, RCHO, CO, and oxides of nitrogen.

The engine type and mode of operation are two main factors:-

- Effect of engine type on the diesel exhaust.
- Effect of mode of operation on diesel exhaust.
- Diesel smoke and controls.

* Maxwell's Thermodynamics relations from Thermodynamical Functions:-

The state of a thermodynamical system can be described in terms of thermodynamical variables like pressure P , volume V , temperature T , and entropy S . For the complete study of a thermodynamical system, we have introduced four new functions, depending upon the variables P, V, T, S . These new functions are called thermodynamical functions or thermodynamical potentials.

These are:- internal energy U , Helmholtz function F , Enthalpy H , Gibbs function G .

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1) Internal energy or intrinsic energy :-

The increase in internal energy is given by,

$$dU = Tds - PdV \quad \text{--- (i)}$$

taking partial derivative,

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{--- (ii)}$$

$$\text{and } \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{--- (iii)}$$

The internal energy is a single valued function and hence dU is a perfect differential

$$\therefore \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S \quad \text{--- (iv)}$$

Substituting eq. (ii), (iii), we get,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{--- (v)}$$

This is also called one of the thermodynamical relations of Maxwell's 1st law.

2) Helmholtz Function :- If the temperature of the system remains constant.

$$T dS = d(TS)$$

Substituting in eq. (i), we get,

$$dU = d(TS) - dW, \text{ where } dW = PdV$$

or

$$d(U - TS) = -dW$$

$$dF = -dW$$

$$\text{where, } F = U - TS \quad \text{--- (vi)}$$

It is called the Helmholtz free energy or work function.

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$$dF = d(U - TS) = dU - Tds - SdT$$

$$= Tds - PdV - Tds - SdT$$

[Substituting the value of dU from eq. (i)]

$$dF = -PdV - SdT \quad \text{--- (vii)}$$

taking partial derivatives,

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

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{--- (ix)}$$

Now, dF is a perfect differential

$$\therefore \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T = \frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V$$

Substituting eq. (viii), (ix), we get,

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

$$\text{or } \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \text{--- (x)}$$

This relation is called the Maxwell's 2nd thermodynamical relation.3. Enthalpy or total heat H :-

The enthalpy of a thermodynamical system is given by,

$$H = U + PV \quad \text{--- (xi)}$$

This is also called the total heat, change in enthalpy is,

$$dH = dU + PdV + VdP$$

Substituting the values of dU from eq. (i),

$$dH = Tds - PdV + PdV + VdP$$

$$dH = Tds + VdP \quad \text{--- (xii)}$$

Spiral

Spiral

taking partial derivatives of H w.r. to S, P , we get,

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{--- (xiii)}$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{--- (xiv)}$$

dH is a perfect differential.

$$\therefore \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right)_S = \frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right)_P \quad \text{--- (xv)}$$

substituting (3), (4) in (15), we get,

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{--- (xvi)}$$

This relation is called the third thermodynamical relation.

4) Gibbs' Potential G :-

from the relation (xii),

$$dH = TdS + VdP$$

If the process is isothermal, T is const.

$$\therefore TdS = d(TS)$$

Also if the process is isobaric, $dP=0$

$$dH = d(TS) \quad \text{or} \quad d(H-TS)=0$$

$$H-TS = \text{constant} = G \text{ (key)}$$

$$G = H-TS \quad \text{--- (xvii)}$$

$$G = U + PV - TS$$

Also from eq (vi), [Substituting H from eq (xi)]

$$U-TS = F$$

$$\text{Substituting, } G = F + PV \quad \text{--- (xviii)}$$

Both the relations (xvii), (xviii), we get,

$$\text{Also, } G = U + PV - TS$$

differentiating,

$$\begin{aligned} dG &= dU + P.dV + V.dP - T.dS - S.dT \\ &= T.dS - P.dV + P.dV + V.dP - T.dS - S.dT \\ &= V.dP - S.dT \quad \text{--- (19)} \end{aligned}$$

taking partial derivatives,

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{--- (20)}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{--- (21)}$$

Since dG is a perfect differential.

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{--- (22)}$$

This relation may be called TV^H thermodynamical relation.

We can rewrite again as,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P$$

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

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

* Enthalpy :-

The enthalpy is a thermodynamical function, which remains constant during a throttling process. It is also called the total heat function and for any mass of gas, it is represented by H ,

$$H = U + PV$$

* Helmholtz Free energy:-

The Helmholtz Free Energy (F) is a physical quantity in energy units, which never increases during a process, which is isothermal as well as isochoric.

From the principle of increase of entropy is,

$$ds + ds' \geq 0 \quad (1)$$

if heat given out by the reservoir,

$$ds' = -\frac{dQ}{T}$$

Substituting in eq. (1), we get,

$$ds - \frac{dQ}{T} \geq 0$$

$$Tds - dQ \geq 0$$

$$Tds - (du + pdv) \geq 0$$

$$Tds - du \geq pdv$$

at temp is const.

$$d(TS - U) \geq PdV$$

If the isothermal process is carried out at const. volume,

$$dV = 0$$

$$\therefore d(TS - U) \geq 0$$

$$d(U - TS) \leq 0$$

$$dF \leq 0$$

$$dF = U - TS$$

* Gibbs's Free energy:-

The Gibbs's Free energy or Gibbs's function is a physical quantity in energy units, which never increases

during a process, which is isothermal as well as isobaric.

Acc' to inequality,

$$d(TS - U) \geq PdV$$

when pressure P is const, the above inequality can be written as,

$$d(TS - U) \geq d(PV)$$

$$d(TS - U - PV) \geq 0$$

$$d(U + PV - TS) \leq 0$$

$$dG \leq 0$$

$$\text{where } G = U + PV - TS$$

* Carnot theorem:-

According to this theorem, 'the efficiency of a Carnot reversible engine is maximum and is independent of the nature of the working substance.'

OR

"The efficiency of all reversible heat engines operating b/w the same two temperatures is the same and no irreversible heat engines working between the same two temperatures can have a greater efficiency than Carnot heat engine"

In order to prove Carnot theorem,

let us consider two heat engines

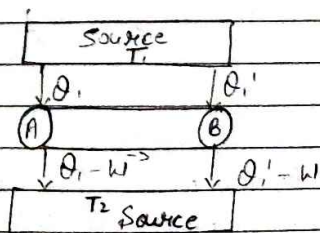
A and B working b/w same

temperatures T_1 and T_2 .

Let engine A be irreversible and

B be reversible. If, let A be more efficient than B

or $\eta_A > \eta_B$, where η_A and η_B are the coefficients of



heat engine A and B respectively.

The engine A absorbs heat Q_1 from the source at temperatures T_1 , does work W and transfers heat $Q_2 = Q_1 - W$ to the sink at lower temperatures T_2 .

The engine B, which works in the reverse direction, absorbs heat $(Q_1' - W)$ from the sink at temperature T_2 . The work W is done by the engine A and heat Q_1' is rejected to the source at temp. T_1 .
The net loss of heat from the sink $= (Q_1' - W) - (Q_1 - W) = Q_1' - Q_1$.

Similarly, the source receives heat Q_1' from B and rejects Q_1 to the engine A.

$\therefore$ Net gain by the source $= Q_1' - Q_1$
Net heat lost by the sink.

If A is more efficient than B,

$$\eta_A > \eta_B \quad \text{--- (1)}$$

$$\eta_A = \frac{W}{Q_1}, \quad \eta_B = \frac{W}{Q_2}$$

From eq. (1), we get,

$$\frac{W}{Q_1} > \frac{W}{Q_2}$$

$$\frac{1}{Q_1} > \frac{1}{Q_2} \quad \text{or} \quad [Q_1' > Q_1]$$

* Second law of thermodynamics in terms of entropy:-

Acc. to classical first law of thermodynamics implies that the total energy of the universe remains constant and the entropy of the universe tends to have maximum values.

Every process in nature taking place tends to increase the entropy of the system.

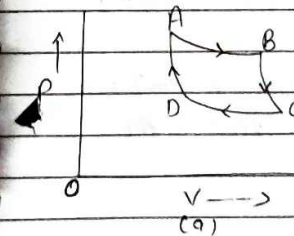
$$dS = \frac{dQ}{T} \quad \text{or} \quad dQ = T dS \quad \text{--- (2)}$$

* Temperature - Entropy (T-S) Diagram:-

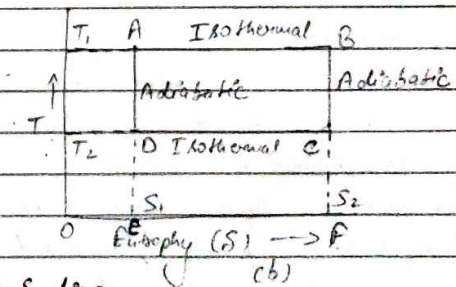
If we plot a graph between temperature and entropy of the thermodynamic state of function, the graph obtained is called the temperature - entropy indicator diagram.

Let us draw a P-V diagram and T-S diagram for a complete Carnot cycle. A Carnot cycle is represented by

isothermal AB, which is an adiabatic BC, isothermal CD and adiabatic DA. On T-S diagram, the isothermal AB will be a line parallel to entropy. At each temp. of the working substance remains const. at T_1 . Along the adiabatic BC, the entropy remains const. so on T-S diagram, BC will be a line parallel to temperature axis at constant values of entropy S_2 . Thus, ABCDA on the T-S diagram is a rectangle.



(a) P-V diagram



(b) T-S diagram

The amount of heat energy absorbed during isothermal expansion AB is Q_1 , and is given by the area below isothermal AB,

$$Q_1 = \text{Area ABFEA} = T_1 (S_2 - S_1)$$

Similarly, the amount of heat energy rejected to the sink during isothermal compression CO is Q_2 and is given by the area below isothermal CO.

$$Q_2 = \text{Area CFEDC} = T_2(S_2 - S_1)$$

$\therefore$ Heat energy converted into work is,

$$= Q_1 - Q_2$$

$$= \text{Area ABCDA}$$

$$= (T_1 - T_2)(S_2 - S_1)$$

The efficiency of Carnot engine is,

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = \frac{(T_1 - T_2)(S_2 - S_1)}{T_1(S_2 - S_1)} = \frac{T_1 - T_2}{T_1}$$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$

* Third law of thermodynamics:-
Third law of thermodynamics is also known as Nernst heat law. Acc. to this law:-

Entropy change associated with any isothermal reversible process of condensed system approaches zero as the temp. is reduced to zero.

Third law of thermodynamics, is also stated as:-

It is impossible by any means to reduce any system to the absolute zero temp. in a finite no. of oscillations.

Mathematical form of 3rd law of thermodynamics:-

Distribution of particles in different compartments is called Macrostate. Hence, the study of microstate is

more important than Macrostate. It is denoted by W .
i.e. that, the change in entropy is given by,

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

As we know that,

$$dS = k d(\log W) \text{ [Boltzmann relation]}$$

$$k = \text{Boltzmann constant } (1.38 \times 10^{-23}) \text{ J K}^{-1}$$

$\log W$ - dimensionless quantity

$$S = k \log (W)$$

Hence, value of W goes on decreasing as T is lowered.

* Maximum value of $W = 1$ i.e. all the particles of thermodynamical system possess same energy.

Further cooling is not possible.

Hence at $T=0$, $W=1$, $S = k(\log 1) = 0$, entropy of the system is zero. Further cooling is not possible.

* Using Maxwell's eq. show that:-

$$C_p - C_v = -T \left(\frac{\partial v}{\partial T} \right)_p^2 \left(\frac{\partial p}{\partial v} \right)_T$$

$$\left. \begin{aligned} C_p &= \left(\frac{\partial Q}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \\ C_v &= \left(\frac{\partial Q}{\partial T} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v \end{aligned} \right\} \quad \text{--- (1)}$$

$$dS = f(T, v)$$

$$[\because \partial Q = T \partial S]$$

dS is a perfect differential.

$$dS = \left(\frac{\partial S}{\partial T} \right)_v dT + \left(\frac{\partial S}{\partial v} \right)_T dv$$

$$\left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial S}{\partial T} \right)_v + \left(\frac{\partial S}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \quad \text{--- (2)}$$

But, from Maxwell's relation,

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \quad - (3)$$

from eq. (2), (3), we get,

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_v + \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P \quad - (4)$$

Multiplying both sides of eq. (4) by T , we get,

$$T \left(\frac{\partial S}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_v + T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P \quad - (5)$$

from eq. (1), (5), we get,

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P$$

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_v \times \left(\frac{\partial v}{\partial T}\right)_P \quad - (6)$$

As, pressure is function of volume v and temperature T and P is perfect differentiable.

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT$$

If pressure is const. i.e. $dP = 0$,

$$\left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT = 0$$

$$\left(\frac{\partial P}{\partial T}\right)_v dT = - \left(\frac{\partial P}{\partial v}\right)_T dv$$

$$\left(\frac{\partial P}{\partial T}\right)_v = - \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \quad - (7)$$

from eq. (6), (7), we get,

$$C_p - C_v = T \left[- \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \right] \times \left(\frac{\partial v}{\partial T}\right)_P$$

$$C_p - C_v = - T \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2$$

$$C_p - C_v = - T \left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T$$

* Expression for cooling produced by van der Waal's eq.:-
Suppose two thermally insulated cylinders A and B are separated from each other, by a porous plug. k.

External work done by on the gas - $P_1 v_1$.

External work done

by the gas - $P_2 v_2$.

Net work done by work done

by the gas - $P_2 v_2 - P_1 v_1$.

the internal work done is,

$$\int_{v_1}^{v_2} P dv = \int_{v_1}^{v_2} \frac{a}{v^2} dv$$

$$= \frac{a}{v_1} - \frac{a}{v_2}$$

$\therefore$ total work done by the gas = Ext. work + Int. Work.

$$W = (P_2 v_2 - P_1 v_1) + \left(\frac{a}{v_1} - \frac{a}{v_2} \right) \quad - (i)$$

But, we know that,

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT \quad [\because \text{van der Waal's eq.}]$$

$$Pv + \frac{a}{v} - Pb - \frac{ab}{v^2} = RT$$

As, $\frac{ab}{v^2}$ is very very small, then neglecting,

from eq. (i), (ii), we get,

$$W = \left(P_2 v_2 + P_2 b - \frac{a}{v_2} \right) - \left(P_1 v_1 + P_1 b - \frac{a}{v_1} \right) + \left(\frac{a}{v_1} - \frac{a}{v_2} \right)$$

$$W = R(T_2 - T_1) + b(P_2 - P_1) + \frac{2a}{v_1} - \frac{2a}{v_2} \quad - (iii)$$

As, a, b are very small, so we get,
 $PV = RT$ or $V = \frac{RT}{P}$

$$\therefore V_1 = \frac{RT_1}{P_1}, V_2 = \frac{RT_2}{P_2} \quad \text{--- (iv)}$$

From eq. (iii), (iv), we get,

$$W = -R(T_1 - T_2) - b(P_1 - P_2) + \frac{2aP_1}{RT_1} - \frac{2aP_2}{RT_2}$$

When T_1 & T_2 are nearly equal.

$$T_2 = T_1 = T \text{ (say)}$$

$$T_1 - T_2 = dT$$

$$W = -RdT - b(P_1 - P_2) + \frac{2a}{RT}(P_1 - P_2)$$

$$= (P_1 - P_2) \left(\frac{2a}{RT} - b \right) - RdT \quad \text{--- (v)}$$

The work W is given by $W = C_v dT$ --- (vi)

From eq. (v), (vi), we get,

$$C_v dT = (P_1 - P_2) \left(\frac{2a}{RT} - b \right) - RdT$$

$$dT(C_v + R) = (P_1 - P_2) \left(\frac{2a}{RT} - b \right)$$

But $C_p - C_v = R$ or $C_v + R = C_p$

$$C_p dT = (P_1 - P_2) \left(\frac{2a}{RT} - b \right)$$

$$\text{Fall in temperature} = \frac{(P_1 - P_2)}{C_p} \left(\frac{2a}{RT} - b \right)$$