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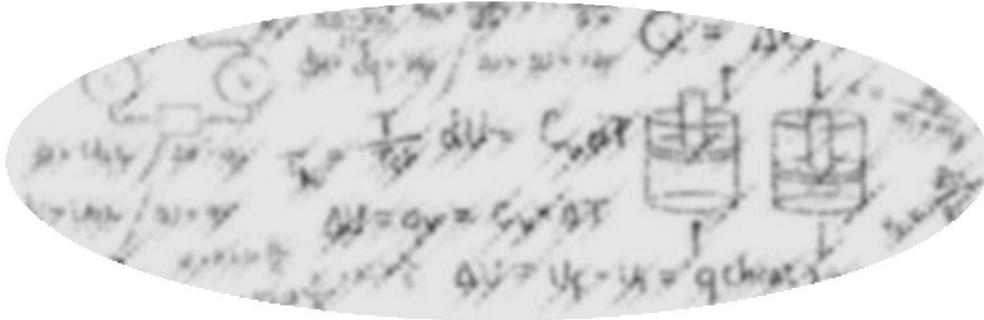
Course of

Basic Thermodynamics

Mechanical & Thermal Equilibrium

(Undergraduate Students)

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Preface

Dear student,

After studying the thermodynamics from the view of chemical equilibrium in your first year of undergraduate degree, we present to you in this course the second part that include mechanical and thermal equilibrium, where we deal with the basic principles that govern those two equilibriums, starting with an introduction of the fundamental concepts, then the first law analysis of control mass and control volume systems, after that the second law and its corollaries and finally the properties of pure substances .

At the end of this course, the student will be able to predict the different behavior of a substance when subjected to various conditions. In addition, this course is a prerequisite for many follow-on courses such as heat transfer and applied thermodynamics.

Content of the Course

I Introduction and Fundamental Concepts

- Introduction	5
- Definitions of System and State	5
- Thermodynamic Properties	7
- Zeroth law and Basic Concepts	8
- Thermodynamic Process and Cycle	9
- Thermodynamic Concept of Energy	10
- Equations of State	13

II The First Law of Thermodynamic

- The First Law for Cyclic Process	18
- Conservation of Energy for Close System	19
- First Law Applied to Thermodynamic Process	20
- First Law Applied to an Open System	26
- Steady Flow Engineering Devices	28

III The Second Law of Thermodynamic and its Corollaries

- Concept of Reversibility	33
- Reversible Cycles	33
- Carnot's Theorem	35
- Entropy	41
- Availability (Exergy) Balance for Closed and Open System	44
- Thermodynamic Property Relations	46

IV Property of Pure Substances

- Definition of Pure Substance	49
- Phase of Pure Substances	49
- Property Diagrams for Phase-Change Processes	54

References

Arabic Course Summary

Nomenclature

Capital Letters:

<i>A</i>	Availability/Exergy	[J]
	Area	[m ²]
<i>C</i>	Number of component in a system	[-]
	Velocity	[m/s]
	Heat capacity	[J/kg K]
<i>E</i>	Total energy	[J]
<i>F</i>	Force	[N]
<i>H</i>	Total enthalpy	[J]
<i>I</i>	Irreversibility	[J]
<i>L</i>	length	[m]
<i>M</i>	Molar masse of gas	[kg/mol]
	Variable	[-]
<i>N</i>	Variable	[-]
<i>P</i>	Pressure	[Pa]
<i>Q</i>	Heat amount	[J]
<i>R</i>	Universal gas constant	[J /mol K]
<i>S</i>	Total entropy	[J/K]
<i>T</i>	Temperature	[K]
<i>U</i>	Total internal energy	[J]
<i>V</i>	Volume	[m ³]
<i>W</i>	Work	[J]
<i>Z</i>	Elevation	[m]
	Compressibility Factor	[-]
	Variable	[-]

Small Letters:

<i>a</i>	Van der Waals constant	[bar(m ³ /kmol) ²]
	Redlich–Kwong constant	[bar(m ³ /kmol) ² K ^{0.5}]
<i>b</i>	Van der Waals constant	[m ³ /kmol]
	Redlich–Kwong constant	[m ³ /kmol]
<i>e</i>	Specific total energy	[J/kg]
<i>f</i>	Number of independent intensive proprieties	[-]
	Specific Helmholtz fonction	[J/kg]
<i>g</i>	Gravity acceleration	[m/s ²]
	Specific Gibbs fonction	[J/kg]
<i>h</i>	Specific enthalpy	[J/kg]
<i>k</i>	Polytropic index	[-]
<i>m</i>	mass	[kg]
<i>n</i>	Number of moles	[mol]
<i>q</i>	Heat amount per unit mass	[J/kg]
<i>r</i>	Constant for the particular gas	[J/kg K]
<i>s</i>	Specific entropy	[J/kg K]
<i>t</i>	Time	[s]
<i>u</i>	Specific internal Energy	[J/kg K]
<i>v</i>	Specific volume	[m ³ /kg]
<i>w</i>	Specific work	[J/kg]
<i>x</i>	quality	[-]
	Distance	[m]
<i>m</i>	Mass flow	[kg/s]

Greek Symbols:

<i>η</i>	Efficiency	[-]
<i>ρ</i>	Density	[kg/m ³]
<i>γ</i>	Adiabatic index	[-]
<i>ϕ</i>	Number of phases in a system	[-]
<i>ψ</i>	Specific availability	[J/kg]
<i>σ</i>	Entropy generated	[J/kg]

Acronyms :

<i>KE</i>	Kinetic energy	[J]
<i>KP</i>	Potential energy	[J]
<i>COP</i>	Coefficient of performance	[-]

Subscripts :

<i>th</i>	Thermal
<i>is</i>	Isentropic
<i>v</i>	Vapor
<i>g</i>	Gas
<i>f</i>	Fluid
<i>res</i>	Reservoir
<i>o</i>	Environment
<i>sys</i>	System
<i>surr</i>	surrounding
<i>i</i>	Irreversibility
<i>add</i>	Add to a system
<i>net</i>	Net quantity
<i>rev</i>	Reversible
<i>H</i>	Quantity add/rejected from source
<i>L</i>	Quantity add/rejected from sink
<i>P</i>	Isobaric process
<i>V</i>	Constant volume process
<i>T</i>	Isothermal process
	Total
<i>S</i>	Isentropic process
<i>cr</i>	critical
<i>R</i>	refrigeration
<i>HP</i>	Heat pump
<i>cv</i>	Control volume
<i>Q</i>	Associated to a heat amount
<i>W</i>	Associated to a work

I. Introduction and Fundamental Concepts

I. Introduction

Thermodynamics can be defined in short as the science of energy or thermal devices. It is a fundamental science that describes the basic laws in relation to different processes which involve transfer or transformation of heat and other form of energy and the relationships among the different physical properties of substances which are affected by such processes. There are two views in the study of thermodynamics, macroscopic or classical view which is considered in this course, and microscopic or statistical view which is beyond the scope of this course.

In the study of classical thermodynamics or the macroscopic view, attention is made on a certain quantity of matter called system without consideration of the event acquiring at the molecular level. The analysis of such a system requires simple mathematical formulae and a few properties are needed in order to describe its state.

In the study of statistical thermodynamics known also as microscopic view, the properties of matter are considered at the molecular level using statistical method. As the number of molecules is very large, advanced statistical and mathematical methods are essential and these complicate its approaches.

I.1 Definitions of System and State

I.1.1 Thermodynamic System

A system is defined as a quantity of matter or a region in space chosen for study. Everything external or outside the system as separated by the system boundary is known as surroundings see figure I.1. The boundary of a system can be fixed or movable, real or imaginary surface. There are in general three types of systems:

- 1- Control mass system called also closed system
- 2- Control volume system or open system
- 3- Isolated system

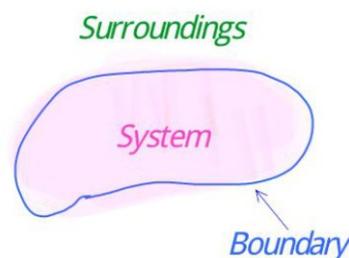


Figure I.1 System, surrounding and its boundary

1.1.1.1 Closed System

A closed system of fixed mass is known as control mass system where there is only energy transfer but no mass transfer across the system boundary. Figure I.2 shows a closed system that is a quantity of gas in a piston-cylinder assembly. The gas can be compressed or expand in the piston-cylinder arrangement in this case the mass of the gas remains constant and it can also get heated or cooled.

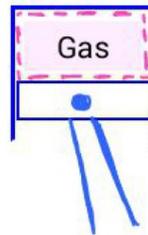


Figure I.2 Closed system a gas in a piston-cylinder assembly

1.1.1.2 Open System

An open system which the transfer of mass as well as energy can take place across the system boundary which remains fixed without any change in the volume of the system is called as control volume as shown in figure I.3. In this example we provide fuel to engine and it produces power which is given out, thus there is exchange of mass as well as energy. The engine also emits heat which is exchanged with the surroundings.

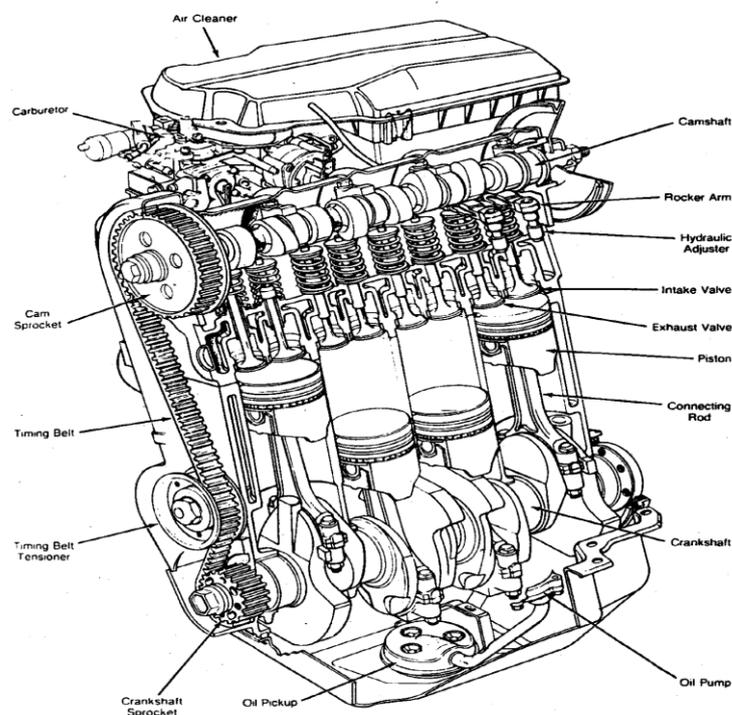


Figure I.3 Open system (Internal combustion engine) [1]

I.1.1.3 Isolated System

An isolated system is one in which there is neither mass nor energy interaction between the system and the surrounding, in classical thermodynamic this reflect the concept of universe.

I.1.2 Thermodynamic State

At a given state, all the properties of a system have fixed values. If the value of even one property changes, the state will change to a different one. So the state of a system is described by its properties.

I.2 Thermodynamic Properties

Any characteristic of a system is called a property. Properties are the coordinates to describe the stats of the system and therefore they are termed as state variables.

The important conditions to be fulfilled to specify the state of a system:

- 1- The properties must be uniform throughout the system.
- 2- The values of all properties should be invariant with time.

Properties are considered to be either intensive or extensive:

- 1- Extensive properties: the properties which depend on the extent of the system are hence directly proportional to the mass of the system are known as extensive properties.
- 2- Intensive properties: the properties that do not depend upon the mass of the system and assume finite values even if the mass of the system approaches zero are known as intensive properties.

The number of independent intensive properties f to specify the state of system is given by:

$$\boxed{f = C - \phi + 2} \quad (\text{I.1})$$

where: C is number of components in the system.

ϕ is number of phases in the system.

Example I.1

What is the number of intensive properties to specify the state of liquid water and boiling water?

Solution:

From equation I.1

- for liquid water

number of components $C=1$

number of phases $\phi=1$

number of intensive properties

$$f = 1 - 1 + 2 \\ = 2 \text{ (intensive properties)}$$

For a system with single phase, the substance needs two intensives properties to specify its state.

- for boiling water

number of components $C=1$

number of phases $\phi=2$

number of intensive properties

$$f = 1 - 2 + 2 \\ = 1 \text{ (intensive property)}$$

For a system with two phases, the substance needs only one intensive property to specify its state.

I.3 Zeroth Law and Basic Concepts

I.3.1 Thermal Equilibrium

The equilibrium state achieved by two (or more) systems in thermal contact with each other, when they cease to have a net exchange of energy (heat energy) between each other.

I.3.1.1 Zeroth Law

Two systems which are equal in temperature to a third system are equal in temperature to each other [2]. In another way, if the temperature of the system 1 (T_1), see figure I.4, is equal to the temperature of the system 3 (T_3), and the temperature of the system 2 (T_2) is equal to the temperature of the system 3 (T_3), this mean that the temperature of all systems is equal to each other.

$$(T_1 = T_3) \wedge (T_2 = T_3) \Rightarrow T_1 = T_2 = T_3$$

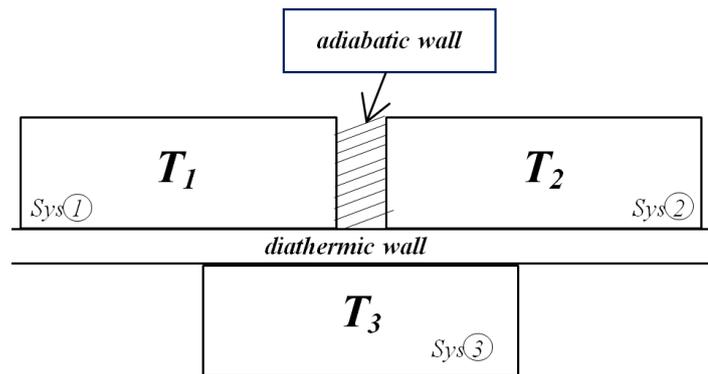


Figure I.4 Thermal equilibrium of three systems

I.3.1.2 Temperature

It is a thermodynamic property that determines whether or not a system is in thermal equilibrium with other systems in the classical view of thermodynamics and it is the average kinetic energy of molecules in static view of thermodynamics. The Celsius temperature scale, or the centigrade scale, uses the degree Celsius ($^{\circ}\text{C}$), which has the same magnitude as the Kelvin. Thus, temperature differences are identical on both scales. However, the zero point on the Celsius scale is shifted to 273.15 K, as shown by the following relationship:

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15 \quad (\text{I.2})$$

I.4 Thermodynamic Process and Cycle

Two states are identical if, and only if, the properties of the two states are identical. When any of the properties of a system change, the state changes and the system is said to have undergone a thermodynamic process. The change that a system undergoes from one equilibrium state to another is called a process and the series of states through which a system passes during a process is called the path of the process. When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a quasi-static, or quasi-equilibrium, process as shown in figures I.5.

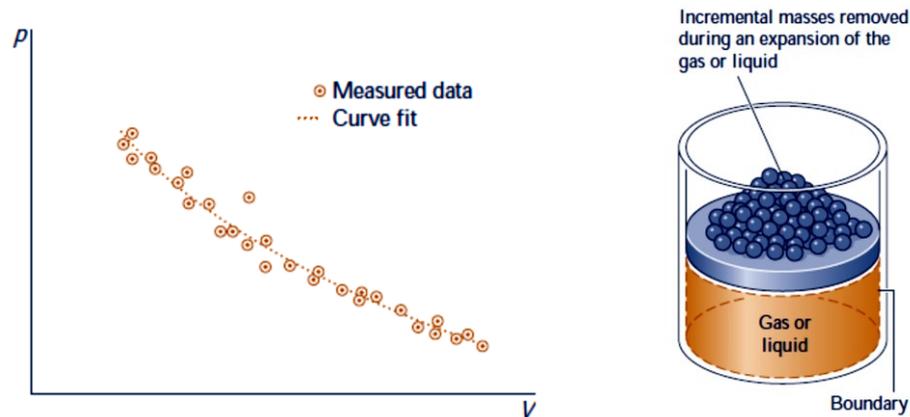


Figure I.5 Quasi-equilibrium expansion or compression [3]

When a system in a given initial state goes through a sequence of processes and finally returns to its initial state, it is said to have undergone a thermodynamic cycle.

I.5 Thermodynamic Concept of Energy

Two major types of energy are considered from the thermodynamic view, energy in storage and energy in transit.

1. Energy in storage (referred to internal energy) is a point function or state variable.
2. Energy in transit or in transfer which is a path function as work transfer and heat transfer.

The work transfer in thermodynamic can be occur in different types and forms, such as displacement and paddle wheel work for closed system, as well as flow and shaft work for the open system.

I.5.1 Displacement or Pdv Work

This work is defined as force acting through a distance as illustrated in figure I.6. The expression of this work may be written as

$$W = F \cdot L \quad [\text{J}] \quad (\text{I.3})$$

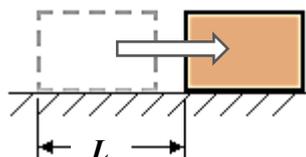


Figure I.6 Work done by acting force (F) on a system which traveled a distance (l)

During compression of a gas in piston-cylinder dispositive, figure I.7, the force acting on the piston is expressed as

$$F = P \cdot A$$

where P is the pressure of the gas and A is the area cross section. The displacement work is done because of the displacement of the system bounded by a distance dx and subsequently

$$A \cdot dx = dV$$

where V is the volume of the gas. Since the friction is not taken on consideration, we call this work as reversible work and its expression from state 1 to state 2 is given by:

$$W_{12} = \int_1^2 P A dx$$

$$\boxed{W_{12} = \int_1^2 P dV} \quad (I.4)$$

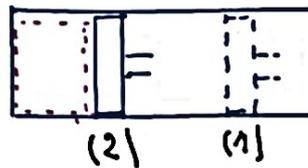


Figure I.7 Displacement of piston from equilibrium state (1) to (2)

If the process is at constant pressure then

$$\boxed{W_{12} = P(V_2 - V_1)} \quad (I.5)$$

I.5.2 Paddle Wheel Work

It is a kind of work transfer to a fluid only by dissipative effect. This work is then purely irreversible and it occurs only in closed system due to stir of some liquid or fluid in a container, see figure I.8. The exchange of energy between the fluid and the rotary part is done by the mechanical friction.

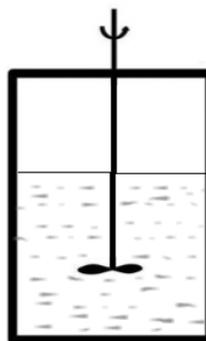


Figure I.8 Paddle wheel work

I.5.3 Flow Work

It is the work that is required to push certain amount of fluid across a section in a flow process or in a control volume as shown in figure I.9. The force acting on an element of mass dm is

$$F = P \cdot A$$

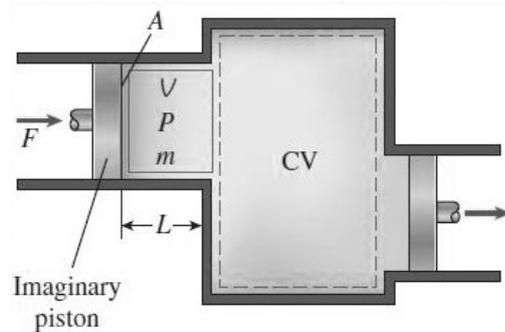


Figure I.9 Flow work

the work transfer by this element moving a distance dx may be written as

$$W = P \cdot A \cdot dx$$

by division with dm then

$$w_{flow} = \frac{W}{m} = \frac{P \cdot A \cdot dx}{\rho \cdot A \cdot dx}$$

the flow work which is expressed per unit mass may be written as

$$\boxed{w_{flow} = P \cdot v} \quad [\text{J/kg}] \quad (\text{I.6})$$

I.5.4 Shaft Work

It is energy transmission with a rotating shaft as shown in figure I.10. There is a shaft rotating turbine that develops power or work to the surrounding through the rotation of a shaft. Similar case for a compressor or a pump, when the work is being given to the control volume, this is, giving through the rotation of a shaft.

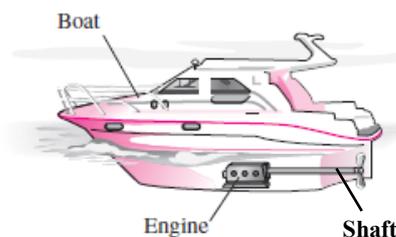


Figure I.10 Shaft work in a boat [4]

I.6 Equations of State

I.6.1 Ideal Gas

An ideal gas is a hypothetical substance. The mathematic definition of an ideal gas is that the ratio Pv/T is constant and equal to r at all pressures and temperatures. The state equation of an ideal gas may be written on those forms as:

$$\left\{ \begin{array}{l} PV = nRT \\ \Rightarrow PV = \left(\frac{m}{M}\right) RT \\ \Rightarrow P \left(\frac{V}{m}\right) = \left(\frac{R}{M}\right) T \\ \Rightarrow P = r \left(\frac{T}{v}\right) \end{array} \right. \quad (I.7)$$

where r is the gas constant of a specified gas and is equal to $r = R/M$ and $v = V/m$ is the specific volume. R is the universal gas constant which is equal to $8.31447 \text{ J/(mol K)}$ and M is the molar mass (molecular weight) of the gas.

I.6.2 Compressibility Factor

The dimensionless ratio Pv/rT is called the compressibility factor and is denoted by Z . That is

$$Z = \frac{Pv}{rT} \quad (I.8)$$

$Z = 1$ for ideal gases. For real gases Z can be greater than, equal or less than unity. The Z factor for all gases is approximately the same at the same reduced pressure and temperature, figure II.11. The reduced pressure and the reduced temperature are $P_R = \frac{P}{P_{cr}}$ and $T_R = \frac{T}{T_{cr}}$ respectively. This is called the principle of corresponding states.

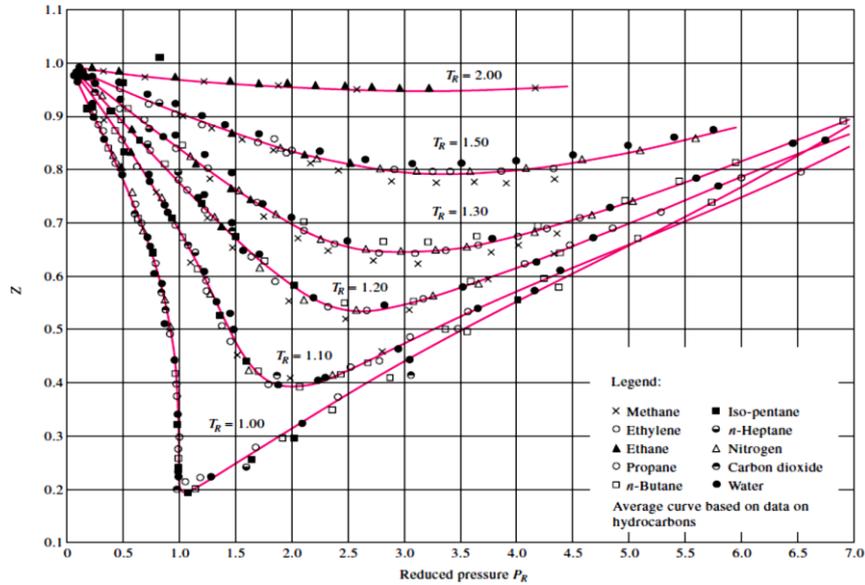


Figure III.11 Comparison of Z factors for various gases [4]

At very low reduced pressures ($P_R \ll 1$), gases behave as an ideal gas regardless of temperature and at high reduced temperatures ($T_R > 2$), ideal-gas behavior can be assumed with good accuracy regardless of pressure (except when $P_R \gg 1$). The deviation of a gas from ideal-gas behavior is greatest in the vicinity of the critical point that will be discussed in the third chapter.

1.6.3 Real Gas

Several state equations exist and each one of them has its application conditions depending on gas state. Most popular equations are cited below.

1.6.3.1 Van der Waals Equation of State

An improvement over the ideal gas equation of state based on elementary molecular arguments was suggested in 1873 by van der Waals. It has two constants that are determined from the behavior of a substance at the critical point.

$$\left(P + \frac{a}{v^2}\right)(v - b) = rT \quad (I.9)$$

where the constant

$$a = \frac{27r^2T_{cr}^2}{64P_{cr}}$$

and

$$b = \frac{rT_{cr}}{8P_{cr}}$$

I.6.3.2 Redlich–Kwong Equation of State

This equation, proposed in 1949, is mainly empirical in nature, and is considered to be the best of the two-constant equations of state

$$P = \frac{rT}{v - b} - \frac{a}{v(v + b)T^{0.5}} \quad (\text{I. 10})$$

where

$$a = 0.42748 \frac{r^2 T_{cr}^{5/2}}{P_{cr}}$$

and

$$b = 0.08664 \frac{r T_{cr}}{P_{cr}}$$

Example I.2

One mole of carbone dioxide (CO_2) stored in a rigid container of volume of $1.5 \times 10^{-3} \text{ m}^3$ at a temperature of 300 K . Determine the pressure of the gas with both, ideal gas and Van der Waals state equation. Constants for the van der Waals equation of state are:

$$a = 3.647 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2$$

$$b = 0.0428 \frac{\text{m}^3}{\text{kmol}}$$

$$R = 8.31447 \text{ J}/(\text{mol K})$$

Solution:

Using ideal gas state equation I.7:

$$\begin{aligned} P &= \frac{n R T}{V} \\ &= \frac{1 * 8.314 * 300}{1.5 \times 10^{-3}} \\ P &= 16.63 \text{ bar} \end{aligned}$$

Using Van der Waals state equation I.9:

$$P = \frac{nRT}{V - nb} - a \left(\frac{n^2}{V^2} \right)$$
$$= \frac{8.314 * 300}{(1.5 \times 10^{-3} - 0.0428 \times 10^{-3})} - 3.647 \times 10^5 \times 10^{-6} \left(\frac{1^2}{(1.5 \times 10^{-3})^2} \right)$$
$$P = 15.5 \text{ bar}$$

The difference between ideal and Van der Waals state equations is *1.13 bar*, which represent about 7.3%.

II. The First Law of Thermodynamic

II.1 First Law for Cyclic Process

Joule carried out an experiment where he placed a known amount of fluid in an insulated container and agitated it with a rotating stirrer. He found that the work done on the fluid by the stirrer conduct to a rise in the temperature of the fluid in such a way that every fixed amount of work done per unit mass on the fluid correspond to certain degree of temperature rise. In his experiment he concluded that there is a relationship between heat and work, or in other word, heat and work are forms of energy which have the same effect on a system.

II.1.1 Sign Convention

In this thermodynamic course we will follow the most popular sign convention which said that unlike heat, the work done by the system is positive and the work done on the system is negative.

That means:

$W > 0$: work done by the system

$W < 0$: work done on the system

For a cyclic process the algebraic sum of net heat and work interactions between a system and its surrounding in a thermodynamic cycle is zero.

$$\boxed{\sum_{Cycle} Q = \sum_{Cycle} W} \quad (II.1)$$

The mathematical expression may be written as

$$\oint Q = \oint W$$

For infinite small process

$$\oint(\delta Q - \delta W) = 0 \quad (II.2)$$

This means that the quantity $(\delta Q - \delta W)$ is a point function since the cyclic integral for any point function is equal to zero, then we write

$$\boxed{\delta Q - \delta W = dE} \quad (II.3)$$

Where E is the total internal energy of the system.

II.1.2 Total Internal Energy

The total internal energy is a property of a system whose change during a process executed by the system equals to the difference between heat and work interaction by the system and its surroundings. The internal energy comprises the intermolecular energy U , kinetic energy KE and potential energy PE and any other form of energy.

$$E = U + KE + PE + \text{any other form of energy} \quad (II.4)$$

II.2 Conservation of Energy for Close System

For a closed system in equilibrium state (system in rest), the internal energy of the system depends only on intermolecular energy since the change in kinetic energy and potential energy is very small. The energy balance may be written as

$$\left\{ \begin{array}{ll} \boxed{\delta q - \delta w = du} & \text{Infinitesimal process per unit mass} \\ \boxed{\delta Q - \delta W = dU} & \text{Infinitesimal process} \\ \boxed{Q - W = \Delta U} & \text{Finite process} \\ \boxed{Q_{12} - W_{12} = U_2 - U_1} & \text{From state 1 state 2} \end{array} \right. \quad (II.5)$$

II.2.1 Intermolecular Energy

Intermolecular energy is defined as the sum of all the microscopic forms of energy of a system in rest. It is related to the molecular structure and the degree of molecular activity and can be viewed as the sum of the kinetic and potential energies of the molecules.

For ideal gas, the assumption is that the intermolecular energy is related directly with the temperature of the substance $U=f(T)$.

II.3 First Law Applied to Thermodynamic Process

The possible thermodynamic process that may be occurs for any transformation of a closed system are shown on a P - V diagram, figure II.1.

Assuming a closed system with displacement work and ideal gas conditions, the first law may be written with respect to the different thermodynamic process shown in figure II.1 as:

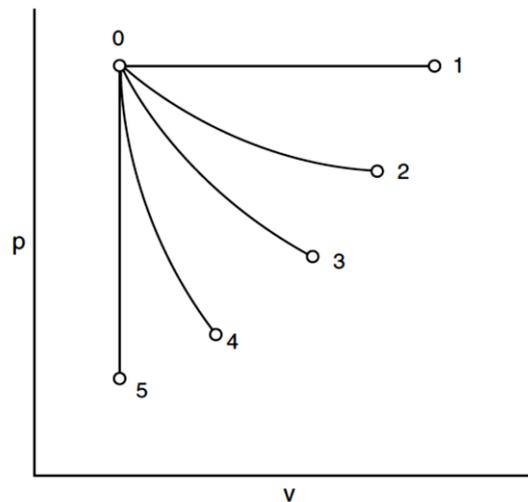


Figure II.1 Different thermodynamic process

II.3.1 Constant Pressure Process (0-1)

The pressure between the two equilibrium states is constant or $P = const \Rightarrow dP = 0$

The first law is:

$$\begin{aligned} \delta Q - \delta W &= dU \\ \Rightarrow \delta Q &= dU + PdV \\ \Rightarrow \delta Q &= d(U + PV) \\ \Rightarrow \boxed{\delta Q = dH} & \end{aligned} \quad (II.6)$$

where H is the total enthalpy,

$$\boxed{H = U + PV} \quad (II.7)$$

II.3.1.1 Enthalpy

The enthalpy is the sum of intermolecular energy and the produce of the pressure and volume of a system. It can be also defined as the heat transferred to or out of a closed system executing a constant pressure process with displacement work. The specific enthalpy is written as: $h = u + Pv$

From state 0 to state 1:

$$Q_{01} = H_1 - H_0$$

the work done:

$$\boxed{W_{01} = P(V_1 - V_0)} \quad (I.8)$$

II.3.1.2 Specific Heat at Constant Pressure c_p

A simple way to define the specific heat at constant pressure is the amount of heat exchanged to increase or decrease the temperature of one kg of the substance by one Kelvin at constant pressure process. The expression of c_p is

$$c_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p \quad (II.9a)$$

if we consider ideal gas, equation (II.6) may be written as

$$\boxed{Q_{01} = mc_p(T_1 - T_0)} \quad (II.9b)$$

II.3.2 Isothermal Process (0-2)

The temperature between the two equilibrium states is constant or $T = const \Rightarrow P.V = const$

Since intermolecular energy is a function of temperature, at a constant temperature process the intermolecular energy is constant, which means that $dU = 0$, and the first law may be written as:

$$\boxed{Q_{02} = W_{02}} \quad (II.10)$$

the work done is

$$\int_0^2 P dV = \int_0^2 P \cdot V \left(\frac{dV}{V} \right)$$

$$\boxed{W_{02} = P \cdot V \ln \left(\frac{V_2}{V_0} \right)} \quad (\text{II. 11})$$

II.3.3 Polytropic Process (0-3)

During a polytropic process the relationship between pressure and volume is given by:

$$\boxed{P \cdot V^k = \text{const}} \quad (\text{II. 12})$$

where k is the polytropic coefficient (index) of the process

The first law may be written as:

$$\boxed{Q_{03} - W_{03} = U_3 - U_0} \quad (\text{II. 13})$$

the work transfer is:

$$\begin{aligned} W_{03} &= \int_0^3 P \cdot dV \\ &= P_0 \cdot V_0^k \int_0^3 \frac{dV}{V^k} = \frac{P_0 \cdot V_0^k}{1-k} (V_3^{1-k} - V_0^{1-k}) \end{aligned}$$

$$\boxed{W_{03} = \frac{P_3 V_3 - P_0 V_0}{1-k}} \quad (\text{II. 14})$$

II.3.4 Adiabatic Process (0-4)

Adiabatic process is a process where there is no heat transfer between the system and its surroundings, the energy balance is written as:

$$\delta Q = 0$$

hence

$$dU + PdV = 0$$

During an adiabatic process the relationship between pressure and volume is given by:

$$\boxed{P \cdot V^\gamma = \text{const}} \quad (\text{II.15})$$

where $\gamma = \left(\frac{c_p}{c_v}\right)$ is the adiabatic index of the process

the work done is

$$\boxed{W_{04} = U_0 - U_4 = \frac{P_0 V_0 - P_4 V_4}{1 - \gamma}} \quad (\text{II.16})$$

II.3.5 Constant Volume Process (0-5)

The volume during this process remained the same or $V = \text{const} \Rightarrow dV = 0$

The first law may be written as:

$$\boxed{Q_{05} = U_5 - U_0} \quad (\text{II.17})$$

and the work is:

$$\boxed{W_{05} = 0} \quad (\text{II.18})$$

II.2.5.1 Specific Heat at Constant Volume c_v

The specific heat at constant volume is the amount of heat exchanged to increase or decrease the temperature of one kg of the substance by one Kelvin at constant volume process. The expression of specific heat at constant volume is

$$c_v = \left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v \quad (\text{II.19a})$$

consider ideal gas, equation (II.17) may be written as

$$\boxed{Q_{05} = mc_v(T_5 - T_0)} \quad (\text{II.19b})$$

Example II.1

Air of mass 1 Kg at 2 bar and 350 K undergoes a quasi-static expansion to 1 bar and 296.2 K. The expansion follows the relationship:

$$Pv^k = \text{constant}$$

Then, air receives a heat amount at constant pressure which brings it to its original temperature.

$$r_{air} = 287 \text{ J/KgK} ; \gamma = 1.4$$

1. Calculate the polytropic coefficient k
2. Determine the amounts of heat and work transfer
3. Check that for cycle $\sum_{cycle} Q - \sum_{cycle} W = 0$

Solution:

1- Polytrophic coefficient

$$\begin{aligned} P_1 v_1^k = P_2 v_2^k &\Rightarrow k = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{v_2}{v_1}\right)} \\ &= \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{P_1 T_2}{P_2 T_1}\right)} \\ &= \frac{\ln\left(\frac{2}{1}\right)}{\ln\left(\frac{2 * 296.2}{1 * 350}\right)} \\ &\Rightarrow k = 1.3 \end{aligned}$$

2- Heat and work transfer

- for polytropic expansion (process 1-2):

$$\begin{aligned} W_{12} &= \frac{P_2 v_2 - P_1 v_1}{1 - k} \\ &= \frac{m \cdot r_{air} (T_2 - T_1)}{1 - k} \\ &= \frac{1 * 287 * (296.2 - 350)}{1 - 1.3} \\ &= 51.47 \text{ KJ} \end{aligned}$$

$$\begin{aligned}
 Q_{12} &= \Delta U_{12} + W_{12} \\
 &= m \cdot c_v \Delta T_{12} + W_{12} \\
 &= m \cdot c_v (T_2 - T_1) + W_{12} \\
 &= m \frac{r_{air}}{(\gamma - 1)} (T_2 - T_1) + W_{12} \\
 &= 1 \frac{287}{(1.4 - 1)} (296.2 - 350) + 51.47 \times 10^3 \\
 &= 12.87 \text{KJ}
 \end{aligned}$$

- for constant pressure heating (process 2-3):

$$\begin{aligned}
 W_{23} &= P(v_3 - v_2) \\
 &= m \cdot r_{air} (T_3 - T_2) \\
 &= 1 * 287(350 - 296.2) \\
 &= 15.44 \text{KJ} \\
 Q_{23} &= \Delta U_{23} + W_{23} \\
 &= m \cdot c_v (T_3 - T_2) + m \cdot r_{air} (T_3 - T_2) \\
 &= m \cdot \frac{r_{air}}{(\gamma - 1)} (T_3 - T_2) + m \cdot r_{air} (T_3 - T_2) \\
 &= m \left(\frac{r_{air}}{(\gamma - 1)} + r_{air} \right) (T_3 - T_2) \\
 &= 1 \left(\frac{287}{(1.4 - 1)} - 287 \right) (350 - 296.2) \\
 &= 54.04 \text{KJ}
 \end{aligned}$$

- for isothermal process 3-1:

$$\begin{aligned}
 Q_{31} &= W_{31} = P_3 v_3 \ln \left(\frac{v_1}{v_3} \right) \\
 &= m \cdot r_{air} \cdot T_3 \ln \left(\frac{P_3}{P_1} \right)
 \end{aligned}$$

$$= 1 * 287 * 350 * \ln\left(\frac{1}{2}\right)$$

$$= -69.62KJ$$

3- for cycle

$$\sum_{cycle} Q = 12.87 + 54.04 - 69.62 = -2.71KJ$$

$$\sum_{cycle} W = 51.47 + 15.44 - 69.62 = -2.71KJ$$

Then

$$\sum_{cycle} Q - \sum_{cycle} W = 0$$

II.3 First Law Applied to an Open System

Energy can enter and exit a control volume by work and heat transfer as represented in figure II.2

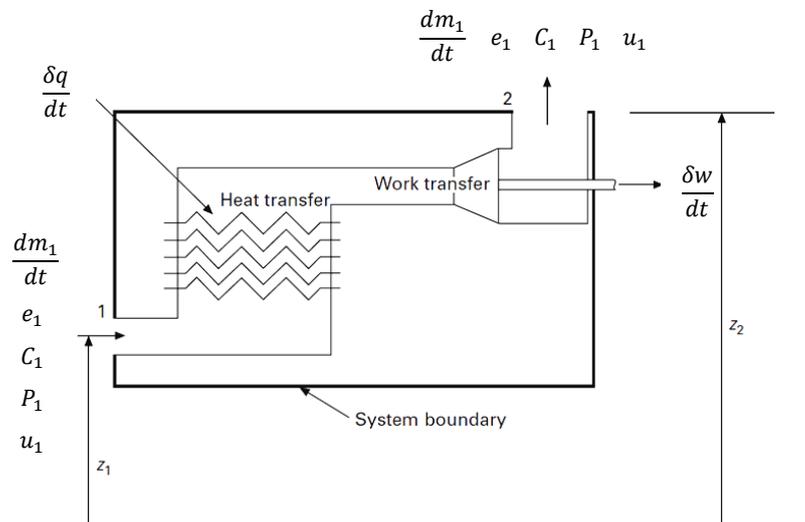


Figure II.2 Schematic representation of a steady flow single steam system exchanging work and heat with the surroundings

Energy also enters and exits with flowing streams of matter.

II.3.1 Conservation of Mass

The mass passing through the control volume is conserved, the continuity equation is written as

$$\frac{dm_1}{dt} - \frac{dm_2}{dt} = \frac{dm_{cv}}{dt} \quad (\text{II. 20})$$

II.3.2 Conservation of Energy

The energy stored in a steam of fluid per unit mass is

$$e = u + Pv + \frac{C^2}{2} + gz \quad (\text{II. 21})$$

where C is the velocity of the steam of fluid

The energy balance is

$$\sum_{in} \frac{dm}{dt} \cdot e + \frac{\delta q}{dt} - \sum_{out} \frac{dm}{dt} \cdot e - \frac{\delta w}{dt} = \frac{dE_{cv}}{dt} \quad (\text{II. 22})$$

at steady state (invariant with time)

$$\begin{cases} \frac{dm_{cv}}{dt} = 0, & \frac{dE_{cv}}{dt} = 0 \\ \frac{dm_1}{dt} = constant \end{cases}$$

The steady flow energy equation for a control volume may be written as:

$$\dot{Q} - \dot{W} = \sum_{out} \dot{m} \left(h + \frac{C^2}{2} + gz \right) - \sum_{in} \dot{m} \left(h + \frac{C^2}{2} + gz \right) \quad (\text{II. 23})$$

Accordingly, for a control volume at a single inlet and outlet called single flow device is:

$$\dot{Q}_{12} - \dot{W}_{12} = \dot{m} \left[h_2 - h_1 + \frac{C_2^2 - C_1^2}{2} + g(z_2 - z_1) \right] \quad (\text{II. 24})$$

The energy equation written in term of the heat transfer and work done per unit mass of the working fluid is:

$$q_{12} - w_{12} = h_2 - h_1 + \frac{C_2^2 - C_1^2}{2} + g(z_2 - z_1) \quad (\text{II. 25})$$

II.4 Steady Flow Engineering Devices

II.4.1 Work Interacting Devices (Turbines, Compressors, Pumps...)

Turbines, compressors, pumps, and fans are work interacting devices. An example is illustrated in figure II.3 that shows a gas turbine which includes compressors, turbines and combustor.

Turbines produce power output whereas compressors, pumps, and fans require power input. Heat transfer from turbines is usually negligible since the area of heat exchange is very small and they are typically well insulated. Heat transfer is also negligible for compressors unless there is intercooling process that leads to a reduction in the work input.

Because the elevation of the inlet and outlet of those devices are more or less the same from a reference potential energy changes are negligible for all of those devices.

With the exception of fans, the velocities change between inlet and outlet in these devices are usually too low to cause any significant change in the kinetic energy between inlet and outlet of the devices. Those devices are designed to convert kinetic energy in to pressure energy or vice versa.

Then, for these devices (turbines, compressors and pumps) the energy equation is written as:

$$w_{12} = h_1 - h_2 \quad (\text{II.26.a})$$

For fan where velocity change between inlet and outlet is considered the energy equation is written as:

$$w_{12} = h_1 - h_2 + \frac{C_1^2 - C_2^2}{2} \quad (\text{II.26.b})$$

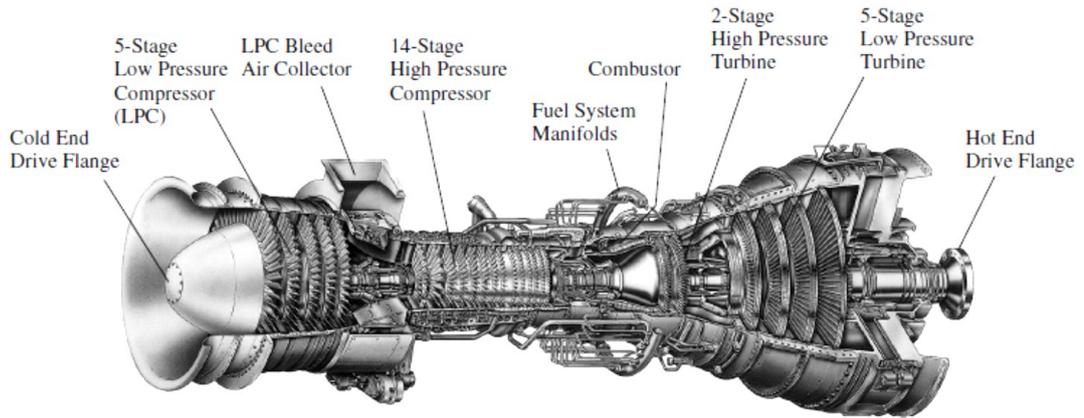


Figure II.3 A gas turbine used for electric power production [4]

II.4.2 Heat Interacting Devices (Heat Exchangers)

Heat exchangers, see figure II.4, typically involve no work interactions and negligible kinetic and potential energy changes for each fluid stream. The energy equation for these devices is written as:

$$q_{12} = h_2 - h_1 \quad (II.27)$$

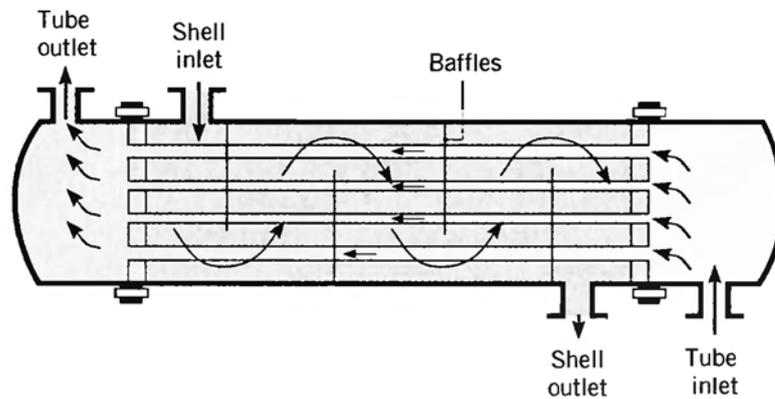


Figure II.4 A heat exchanger [11]

II.4.3 Nozzles and Diffusers

Nozzles and diffusers are commonly utilized in turbojet engines, figure II.5, rockets and all devices that need an increase of the kinetic energy of the fluid at outlet. A nozzle is a device that increases the velocity

of the fluid by transforming its pressure energy into kinetic energy. A diffuser is a device that increases the pressure of a fluid by slowing down its velocity.

The rate of heat transfer between the fluid flowing through a nozzle or a diffuser and the surroundings is usually very small (neglected). Nozzles and diffusers typically involve no shaft work and the change in potential energy is negligible. The energy equation in this case is written as:

$$\boxed{h_1 - h_2 = \frac{C_2^2 - C_1^2}{2}} \quad (\text{II. 28})$$

In this equation the total energy of the fluid is conserved, as it is shown, and the value of $(h + 1/2 C^2)$ is constant.

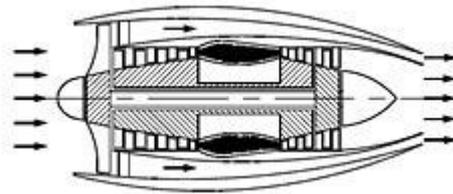


Figure II.5 A turbojet engine [12]

Example II.2

A quasi-static expansion of helium executed through an adiabatic nozzle, the inlet pressure, temperature and velocity are 15 bar, 1300 K and 10 m/s, respectively. The outlet pressure is 1.45 bar. $M_{He}=4.003$ g/mol, $c_p = \frac{5}{2}r_{He}$, $c_v = \frac{3}{2}r_{He}$, $R=8.314$ J/(mol K) et $\gamma = 1.667$.

Calculate the velocity at the outlet

Solution:

- Velocity at the outlet:

Quasi-static expansion + adiabatic nozzle \Rightarrow isentropic expansion

From equation II.14

$$\begin{aligned} C_2 &= \sqrt{2(h_1 - h_2) + C_1^2} \\ &= \sqrt{2c_p(T_1 - T_{2s}) + V_1^2} \end{aligned}$$

$$= \sqrt{\left(2 \left(\frac{5}{2} r_{He}\right) (T_1 - T_{2s}) + C_1^2\right)}$$

$$T_{2s} = T_1 \left(\frac{P_2}{P_1}\right)^{\left(\frac{\gamma-1}{\gamma}\right)}$$

$$= 1300 \left(\frac{1.45}{15}\right)^{\left(\frac{1.667-1}{1.667}\right)}$$

$$T_{2s} = 510.4 \text{ K}$$

then

$$C_2 = \sqrt{\left(2 \left(\frac{5}{2} * \frac{8.314}{4.003 * 10^{-3}}\right) (1300 - 510.4) + 10^2\right)}$$

$$C_2 = 2863.5 [m/s]$$

III. The Second Law of Thermodynamic and its Corollaries

III.1 Concept of Reversibility

The second law is an axiom of directional constraint on naturel process. All naturel processes have a unidirectional characteristic which is visualized in different forms for different types of processes.

A process is said to be a reversible one, if it is performed in such a way that at the end of the process both the system and the surroundings may be restored to their initial states without any change in the rest of the universe. All naturel processes fail to fulfill the above requirement and hence they are irreversible process.

A reversible process is a theoretical concept. An extremely slow process associated with an infinitesimal departure from thermodynamic equilibrium and being almost free from any dissipative effect approximated to a reversible process in reality. The process is known as quasi-static or quasi-equilibrium process.

III.1.1 Causes of Irreversibility

There are a lot of causes of irreversibility but the principle cause is the lack of thermodynamic equilibrium in any naturel process and the dissipative effect that affect the processes such as mechanical friction, fluid viscosity, inelasticity, electrical resistance...

III.2 Reversible Cycles

III.2.1 Thermal Reservoirs

A thermal reservoir is any object or system which can serve as a heat source or sink for another system. Thermal reservoirs usually have accumulated energy capacities which are very large compared with the amounts of heat energy they exchange. Therefore the thermal reservoirs are considered to operate at constant temperatures [7].

III.2.2 Heat Engine and Heat Pump

Heat engines are devices or systems which operate on a thermodynamic cycle so that there is a net heat transfer to the system and a net work transfer from the system, see figure III.1. Heat engines receive heat from a high-temperature source, reject the remaining waste heat to a low-temperature sink and convert part of this heat to work.

The thermal efficiency of a heat engine is defined as:

$$\eta_{th} = \frac{W_{net}}{Q_{in}} \quad (III. 1)$$

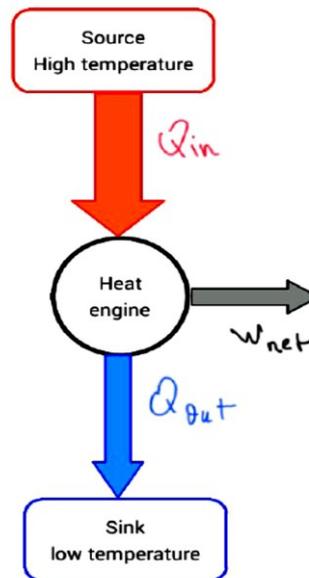


Figure III.1 Heat engine

Heat pumps or refrigerators are systems which operate on a thermodynamic cycle so that there is a net work transfer to the system and a net heat transfer from the system. They transfer heat from a low-temperature medium to a high-temperature one using external net work, see figure III.2. The efficiency of a refrigerator is expressed in terms of the coefficient of performance COP_R where:

$$COP_R = \frac{Q_c}{W_{net,in}} \quad (III. 2)$$

The efficiency of a heat pump is expressed in terms of the coefficient of performance COP_{HP} where:

$$COP_{HP} = \frac{Q_H}{W_{net,in}} \quad (III. 3)$$

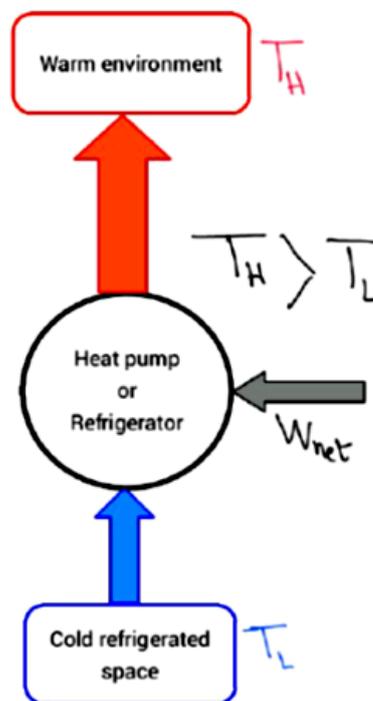


Figure III.2 Heat pump or Refrigerator

III.2.3 The Kelvin-Planck Statement of the Second Law

It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with a body at a single fixed temperature.

III.2.4 Clausius Statement of the Second Law

Heat cannot pass by itself from a cold to a hot body. It can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time [8].

III.3 Carnot's Theorem

No heat engine can be more efficient than a reversible heat engine working between the same temperature limits of heat addition and heat rejection, and all reversible heat engine operating between the same temperature limits have the same efficiency [9].

III.3.1 Absolute Thermodynamic Scale of Temperature

Carnot corollary suggests that the thermal efficiency of a reversible power cycle operating between two thermal reservoirs depends only on the temperatures of the reservoirs and not on the nature of the

substance making up the system executing the cycle or the series of processes. Thermodynamic scale of temperature is defined as:

$$\left(\frac{Q_H}{Q_L}\right)_{rev} = \frac{T_H}{T_C} \quad (\text{III. 4})$$

This expression applies only to systems undergoing reversible cycles while operating between two reservoirs as the reversible heat engine or refrigerator, where Q_H and Q_C are exchanged from the source and the sink respectively. T_H and T_C are temperatures of heat addition and heat rejection respectively.

III.3.2 Carnot's Engine

The four processes of Carnot's engine cycle is illustrated in P - v diagram in figure III.3.

- Process 1–2: Reversible adiabatic process of compression.
- Process 2–3: Reversible isothermal process of heat addition.
- Process 3–4: Reversible adiabatic process of expansion.
- Process 4–1: Reversible isothermal process of heat rejection.

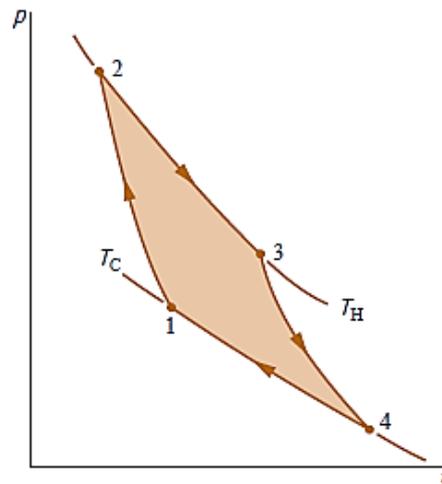


Figure III.3 Carnot engine cycle

The thermal efficiency of Carnot's engine may be written as

$$\eta_{th} = 1 - \frac{T_C}{T_H} \quad (\text{III. 5})$$

The different processes are shown in figure III.4 where:

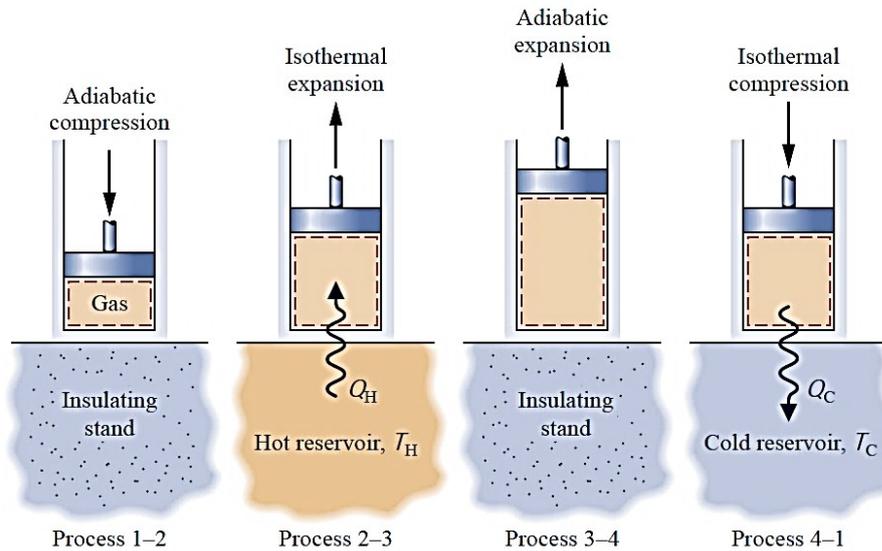


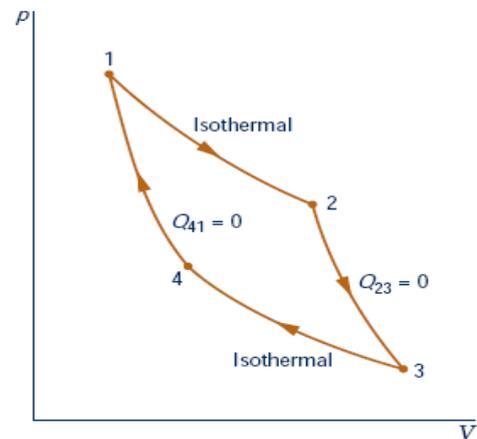
Figure III.4 Carnot engine processes by a gas in a piston-cylinder assembly [3]

Example III.1

An ideal gas undergoes a Carnot power cycle in a piston-cylinder assembly as shown in the diagram.

1- Prove that

- a. $\frac{T_2}{T_3} = \left(\frac{P_2}{P_3}\right)^{\frac{\gamma-1}{\gamma}}$ and $\frac{T_2}{T_3} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$
- b. $V_1V_3 = V_2V_4$
- c. $\eta_{Th} = 1 - \frac{T_3}{T_1}$



- 2- Determine the minimum temperature and the amounts of heat transferred if the thermal efficiency is equal to 70% and the maximum temperature is 600 K. $V_3 = 2 V_4$

Solution:

Piston-cylinder assembly \Rightarrow closed system

1) Prove of a, b and c

a)

$$\frac{T_2}{T_3} = \left(\frac{P_2}{P_3} \right)^{\frac{\gamma-1}{\gamma}}$$

$$P_2 V_2^\gamma = P_3 V_3^\gamma \Rightarrow P_2 \left(\frac{nRT_2}{P_2} \right)^\gamma = P_3 \left(\frac{nRT_3}{P_3} \right)^\gamma$$

$$\Rightarrow \frac{T_2^\gamma}{P_2^{\gamma-1}} = \frac{T_3^\gamma}{P_3^{\gamma-1}}$$

$$\Rightarrow \left(\frac{P_2}{P_3} \right)^{\gamma-1} = \left(\frac{T_2}{T_3} \right)^\gamma$$

$$\Rightarrow \left(\frac{P_2}{P_3} \right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{T_2}{T_3} \right)$$

$$\frac{T_2}{T_3} = \left(\frac{V_3}{V_2} \right)^{\gamma-1}$$

$$P_2 V_2^\gamma = P_3 V_3^\gamma \Rightarrow V_2^\gamma \left(\frac{nRT_2}{V_2} \right) = V_3^\gamma \left(\frac{nRT_3}{V_3} \right)$$

$$\Rightarrow V_2^{\gamma-1} T_2 = V_3^{\gamma-1} T_3$$

$$\Rightarrow \left(\frac{V_3}{V_2} \right)^{\gamma-1} = \left(\frac{T_2}{T_3} \right)$$

b) $V_1 V_3 = V_2 V_4$:

$$\begin{cases} P_4 V_4^\gamma = P_1 V_1^\gamma \\ P_3 V_3^\gamma = P_2 V_2^\gamma \end{cases}$$

$$\Rightarrow \frac{P_4 V_4^\gamma}{P_3 V_3^\gamma} = \frac{P_1 V_1^\gamma}{P_2 V_2^\gamma}$$

$$\Rightarrow \frac{(P_4 V_4) V_4^{\gamma-1}}{(P_3 V_3) V_3^{\gamma-1}} = \frac{(P_1 V_1) V_1^{\gamma-1}}{(P_2 V_2) V_2^{\gamma-1}}$$

$$(P_4 V_4) = (P_3 V_3) \quad \& \quad (P_1 V_1) = (P_2 V_2) \quad (\text{isothermal process})$$

$$\Rightarrow \frac{V_4^{\gamma-1}}{V_3^{\gamma-1}} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}}$$

$$\Rightarrow V_1 V_3 = V_2 V_4$$

$$\text{c) } \eta_{Th} = 1 - \frac{T_{min}}{T_{max}}$$

$$\eta_{TH} = \frac{W_{net}}{Q_{add}}$$

$$\Rightarrow \eta_{TH} = \frac{Q_{12} + Q_{34}}{Q_{12}}$$

$$\Rightarrow \eta_{TH} = 1 + \frac{Q_{34}}{Q_{12}}$$

The processes (1-2 ; 3-4) are isothermal, then $Q = W$ (from the first law) :

$$Q - W = \Delta U = 0$$

$$\Rightarrow \eta_{TH} = 1 + \frac{P_3 V_3 \ln\left(\frac{V_4}{V_3}\right)}{P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)}$$

$$\Rightarrow \eta_{TH} = 1 + \frac{-P_3 V_3 \ln\left(\frac{V_3}{V_4}\right)}{P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)}$$

$$\Rightarrow \eta_{TH} = 1 + \frac{-mrT_3 \ln\left(\frac{V_3}{V_4}\right)}{mrT_1 \ln\left(\frac{V_2}{V_1}\right)}$$

$$\Rightarrow \eta_{TH} = 1 + \frac{-T_3}{T_1}$$

$$\Rightarrow \eta_{TH} = 1 - \frac{T_{min}}{T_{max}}$$

2) The minimum temperature T_{min} and the amount of heat transferred:

$$\eta_{TH} = 1 - \frac{T_{min}}{T_{max}}$$

$$\Rightarrow T_{min} = T_{max}(1 - \eta_{TH})$$

$$\Rightarrow T_{min} = 600(1 - 0,7)$$

$$\Rightarrow T_{min} = 180 K$$

$$r_{air} = \frac{R}{M_{air}}$$

$$= \frac{8.314 \left[\frac{J}{mol K} \right]}{29 * 10^{-3} \left[\frac{kg}{mol} \right]}$$

$$r_{air} = 286.7 \left[\frac{J}{kg K} \right]$$

$$Q_{12} = W_{12} = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$= mr_{air} T_1 \ln\left(\frac{V_3}{V_4}\right)$$

$$= 1 * 286.7 * 600 * \ln(2)$$

$$Q_{12} = 119,24 kJ$$

$$\begin{aligned}
 Q_{34} &= W_{34} = P_3 V_3 \ln\left(\frac{V_4}{V_3}\right) \\
 &= m r_{air} T_3 \ln\left(\frac{V_4}{V_3}\right) \\
 &= 1 * 286.7 * 180 * \ln\left(\frac{1}{2}\right) \\
 Q_{34} &= -35,77 \text{ kJ}
 \end{aligned}$$

III.3.3 The Clausius Inequality

When a system is carried through a complete cycle, the integral of $(\delta Q/T)$ around the cycle is less than or equal to zero [7].

$$\oint \frac{\delta Q}{T} \leq 0 \quad \text{(III. 6)}$$

The Clausius inequality can be expressed equivalently as

$$\oint \frac{\delta Q}{T} = -\sigma_{cycle} \quad \text{(III. 7)}$$

The nature of the cycle executed by the system is indicated by the value of σ_{cycle} as follows:

$$\begin{cases}
 \sigma_{cycle} = 0 & \text{reversible processes} \\
 \sigma_{cycle} > 0 & \text{irreversibilities present within the system} \\
 \sigma_{cycle} < 0 & \text{impossible}
 \end{cases} \quad \text{(III.8)}$$

III.4 Entropy

For a reversible process the quantity $\frac{\delta Q}{T}$ is called entropy and we write

$$\frac{\delta Q}{T} = dS \quad \text{(III. 9)}$$

where S is the entropy [J/K]

The entropy change of a system during a process can be determined by integrating equation (III.9) between the initial and the final states:

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \quad (\text{III.10})$$

III.4.1 Entropy Balance

The entropy balance equation for a process can be written in any of the following forms:

$$(\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}} = (\Delta S)_{\text{univers}} \quad (\text{III.11})$$

$$(\Delta S)_{\text{system}} - \int \frac{\delta Q}{T} = \Delta S_i$$

where ΔS_i is the entropy change due to internal irreversibility or the entropy generation that is always a positive quantity or zero. The reversible adiabatic process ($dS = 0$), is called isentropic process.

III.4.2 Principle of Increase in Entropy

The entropy change of an isolated system is the sum of the entropy changes of its components (each subsystems from 1 to N represent a system and its surroundings as shown in figure III.5). As there is no heat rejection from an isolated system the value of the entropy change can never be less than zero. It may be equal to zero when the subsystems interacting processes are reversible, or greater than zero in the revers case.

$$\boxed{\Delta S_i = (\Delta S_{\text{sys}} + \Delta S_{\text{surr}}) \geq 0} \quad (\text{III.12})$$

Since all natural processes are irreversible, there is an increase in the entropy of the universe. This is what is called principle of increase in entropy.

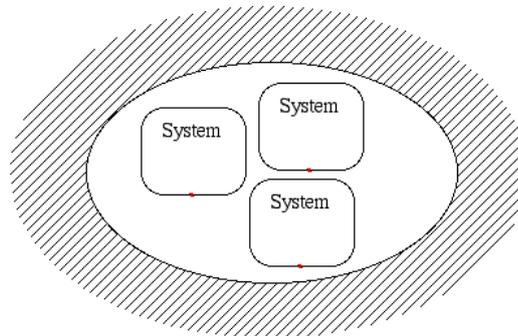


Figure III.5 Isolated system and its subsystem

Example III.2

A 3 kg of gas undergoes in a piston–cylinder assembly a reversible polytropic expansion for which the relationship between pressure and volume is given by: $Pv^{1.2} = \text{constant}$. The initial pressure is 15 bar and the final pressure is 3bar.

- 1- Determine the change in entropy of the system.
- 2- Determine the change in entropy of the system if the process is adiabatic.

Solution:

1) change in entropy of the system

$$\begin{aligned}
 ds &= \frac{\delta q}{T} \\
 &= \frac{du + pdv}{T} \\
 &= \frac{c_v dT}{T} + \frac{rdv}{v} \\
 \Rightarrow \Delta s_{12} &= c_v \ln\left(\frac{T_2}{T_1}\right) + r \ln\left(\frac{v_2}{v_1}\right) \\
 \Rightarrow \Delta s_{12} &= c_v \ln\left(\frac{p_2}{p_1}\right)^{\left(\frac{K-1}{K}\right)} + r \ln\left(\frac{p_1}{p_2}\right)^{\frac{1}{K}} \\
 \Rightarrow \Delta s_{12} &= c_v \ln\left(\frac{p_1}{p_2}\right)^{\left(\frac{1-K}{K}\right)} + r \ln\left(\frac{p_1}{p_2}\right)^{\frac{1}{K}} \\
 \Rightarrow \Delta s_{12} &= \left(\frac{r}{\gamma-1}\right)\left(\frac{1-K}{K}\right) \ln\left(\frac{p_1}{p_2}\right) + r\left(\frac{1}{K}\right) \ln\left(\frac{p_1}{p_2}\right) \\
 \Rightarrow \Delta s_{12} &= \frac{r}{K} \left(\frac{1-K}{\gamma-1} + 1\right) \ln\left(\frac{p_1}{p_2}\right)
 \end{aligned}$$

then

$$\begin{aligned}
 \Delta S_{12} &= m \times \Delta s_{12} \\
 &= 3 \times \frac{286.68}{1.2} \left(\frac{1-1.2}{1.4-1} + 1\right) \ln\left(\frac{15}{3}\right) \\
 &= 576.71 \left[\frac{J}{K}\right]
 \end{aligned}$$

2) change in entropy of the system if the process is adiabatic

$$\text{for adiabatic process } K=\gamma \Rightarrow (\text{isentropic process}) \Delta S_{12} = 0 \left[\frac{J}{K} \right]$$

III.5 Availability (Exergy) Balance for Closed and Open System

III.5.1 Availability (Exergy) Balance for a Closed System

Availability transfer for a closed system is associated with heat and work transfer and is defined with respect to a specified environment temperature and pressure. When the system comes to thermodynamic equilibrium with environment the state of the system is referred as dead state.

Availability of closed system at a state different from the dead state is defined as maximum useful work obtained in a process by which the system comes to its dead state.

The availability function of a closed system is

$$\phi = U + P_0V - T_0S \quad (\text{III.13})$$

where P_0 and T_0 are the pressure and temperature of environment.

The availability balance for a closed system in a process

$$\left(\begin{array}{c} \text{decrease in the} \\ \text{system availability} \end{array} \right) = \left(\begin{array}{c} \text{net availability transferd} \\ \text{out of the system} \end{array} \right) + (\text{irreversibility})$$

$$\boxed{A_1 - A_2 = (W - P_0(V_2 - V_1)) - Q \left(1 - \frac{T_0}{T_H} \right) + I} \quad (\text{III.14})$$

Irreversibility in a process is defined as

$$\boxed{I = T_0 S_i} \quad (\text{III.15})$$

In any naturel process the availability of a system is destructed due to irreversibility and this is the law of degradation of energy.

III.5.2 Availability (Exergy) Balance for an Open System

An open system or control volume is associated with the concept of flow availability where the specific flow availability of a fluid crossing the surface of a control volume is defined by a function ψ as

$$\psi = h - T_0 S + \frac{C^2}{2} + gZ \quad (\text{III. 16})$$

with T_0 the temperature of environment

The availability balance of an open system or control volume

$$\psi_1 - \psi_2 = \frac{\delta W}{\delta m} - \frac{\delta Q}{\delta m} \left(1 - \frac{T_0}{T_H}\right) - \frac{dI}{dm} \quad (\text{III. 17})$$

III.5.3 Second Law Efficiency

The second law efficiency of all natural processes is less than 100%, while it is 100% for a reversible process.

The second-law efficiency of an adiabatic turbine can be determined as

$$\eta_{II,tur} = \frac{w}{w_{rev}} = \frac{h_1 - h_2}{\psi_1 - \psi_2} \quad (\text{III. 18})$$

The second-law efficiency of an adiabatic compressor can be determined as

$$\eta_{II,comp} = \frac{w_{rev}}{w} = \frac{\psi_1 - \psi_2}{h_1 - h_2} \quad (\text{III. 19})$$

III.6 Thermodynamic Property Relations

III.6.1 Review of Mathematical Relations

The exact differential of a function z where $z = f(x, y)$ is

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad (\text{III. 20})$$

This can be expressed alternatively as

$$dz = Mdx + Ndy \quad (\text{III.21})$$

Taking the partial derivative of M with respect to y and of N with respect to x yields

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad (\text{III. 22})$$

III.6.2 The T - ds Relations

The first T - ds equation derived from the energy balance of a closed system with PdV work under the condition of reversible process may be written as follows

$$\boxed{TdS = dU + PdV} \quad (\text{III.23})$$

The second T - ds equation is obtained by eliminating dU from Eq. III.23 by using the definition of enthalpy ($H = U + PV$)

$$\boxed{TdS = dH - VdP} \quad (\text{III.24})$$

III.6.3 Helmholtz and Gibbs Function

This two other equations are very important when chemical reaction takes place and they are written as

$$\text{Helmholtz function or free energy } f = u - T.s \quad (\text{III.25})$$

$$\text{Gibbs function or free enthalpy } g = h - T.s \quad (\text{III.26})$$

The Helmholtz and Gibbs functions are properties because each is defined in terms of properties.

III.6.4 Maxwell Relations

The equations that relate the partial derivatives of properties P , v , T , and s of a simple compressible substance to each other are called the Maxwell relations. They are obtained from this equations expressed as

$$du = T ds - P dv \quad (\text{III.27})$$

$$dh = du + P dv + v dP = T ds + v dP \quad (\text{III.28})$$

$$df = du - T ds - s dT = -P dv - s dT \quad (\text{III.29})$$

$$dg = dh - T ds - s dT = v dp - s dT \quad (\text{III.30})$$

The Maxwell relations are

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad (\text{III.31})$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \quad (\text{III.32})$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (\text{III.33})$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \quad (\text{III.34})$$

IV. Properties of Pure Substances

IV.1 Definition of Pure Substance

A pure substance is a substance that is uniform and invariable in chemical composition. It can exist in more than one phase, but its chemical composition must be the same in each phase. Water is considered as a pure substance since it is uniform and its chemical composition remained the same in all phase.

Air is a mixture of several gases. It consists of two major components (molecules of oxygen and nitrogen) that are chemically distinct. It is common knowledge that nitrogen contributes to 78.08 percentage by volume and oxygen 20.95 percent and the rest is between carbon dioxide and some inert gases. But it has uniform composition which does not change in the operating area of thermodynamic cycles such as Brayton cycle, internal combustion engine cycle... the reason that leads to consider the air in it single gas phase as a pure substance.

IV.2 Phase of Pure Substances

Substances exist in different phases under different conditions each with a different molecular structure as shown in figure IV.1. A region within which all properties are uniform consists of a distinct phase. There are three principal phases which are solid, liquid, and gas. For example, solid ice, liquid water, and gaseous water vapor are separate phases.

The fourth phase of substance is the plasma state which is beyond the scope of this course.

IV.2.1 Solid Phase

In the solid phase particles do not move and the attractive forces of molecules on each other are large to keep them at fixed positions, figure IV.1 (a).

IV.2.2 Liquid Phase

In the liquid phase the fluid takes the shape of the container, the molecules are no longer at fixed positions relative to each other and they can rotate and translate freely. In liquid, the intermolecular forces are weaker compared to solids, but still relatively strong compared with gases, figure IV.1 (b).

IV.2.3 Gas Phase

In the gas phase, the molecules are far apart from each other, and moving randomly in all direction and a molecular order is nonexistent. Gas molecules have large tracts, and move about continually colliding with each other, figure IV.1 (c).

A phase is a distinctive form of a substance, and matter can change among the phases. It may take extreme temperature, pressure or energy, but all matter can be changed. Every phase change has a name: changing a solid to a liquid is called melting, changing a liquid to a gas is called boiling (or evaporating), changing a gas to a liquid is called condensing, and changing a liquid to a solid is called freezing. There are six distinct changes of phase which happens to different substances at different temperatures [10].

The six changes are illustrated in figure IV.1 and the definition of each change may be given as:

- **Freezing:**
When a liquid changes phase and becomes a solid, like when the water you put in the ice cube tray turns solid in the freezer. Freezing involves the loss of energy in the form of heat. At freezing, not only is there a loss of energy, but there is also an increase in the order of the particles in the substance.
- **Melting:**
It is the opposite of freezing, when a solid changes its phase and becomes a liquid. Melting is when the ice in your drink turns to liquid. As a substance melts, it absorbs energy in the form of heat and it becomes less ordered.
- **Condensation:**
It occurs when a substance in the gas phase moves to the liquid phase. This is what happens with air water vapor when it is in contact with the glass surface of cold bottle in a hot day. Condensation involves the loss of energy in the form of heat.
- **Vaporization:**
It is the process of a substance in liquid phase going to a gas phase. During vaporization, liquid absorbs energy in the form of heat, its molecules escape from the surface tension at the surface of a liquid and enter a gas phase.
- **Deposition:**
At certain temperature and pressure conditions, some substances cannot exist as liquids. In these conditions, a substance in solid phase will move directly to a gas without going through the liquid phase. An example of deposition is when dry ice turns directly into gas.
- **Sublimation:**
The opposite of deposition happens here, the change of state from a gas to a solid without going through the liquid phase. An example of sublimation is frost on a window.

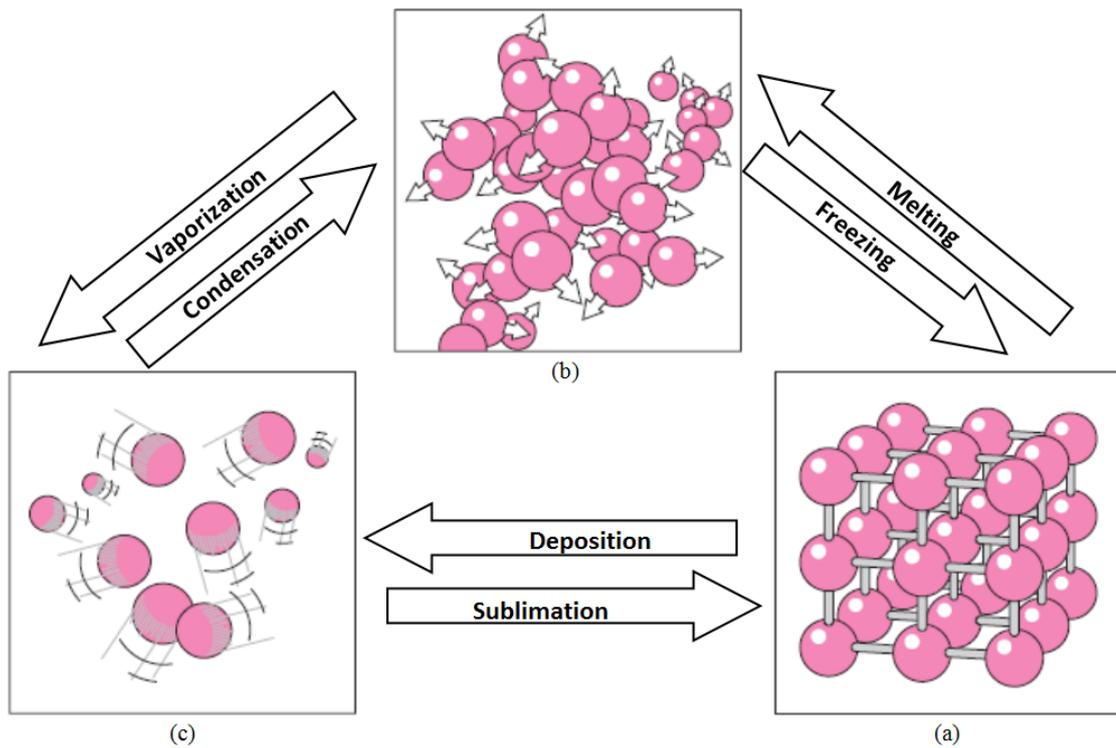


Figure IV.1 The arrangement of atoms in different phases: (a) solid, (b) liquid and (c) gas

IV.2.1 Phase Change Process

Let us consider a pure component, for example water. There are three neutral phases of this substance which are solid, liquid and gases. The phase-change processes of water at constant atmospheric pressure are plotted in figure IV.2.

As we go on heating water from the solid state at constant atmospheric pressure, it first absorbs sensible heat, its temperature rise until it reaches $0\text{ }^{\circ}\text{C}$ where it comes to a saturated state. The solid water is about to melt. We keep heating the substance, and then the melting starts simultaneously with the phase change process from solid to liquid by absorbing latent heat of 334 kJ/kg at constant temperature.

Now we have the liquid water called also a subcooled liquid, since it is not about to vaporize. As its temperature rises again at constant pressure, liquid water expands slightly. It absorbs sensible heat and so its specific volume increases. When the liquid is about to vaporize at $100\text{ }^{\circ}\text{C}$ it is called a saturated liquid. The sensible heat required to heat liquid water at $0\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ at constant atmospheric pressure is 418.6 kJ/kg .

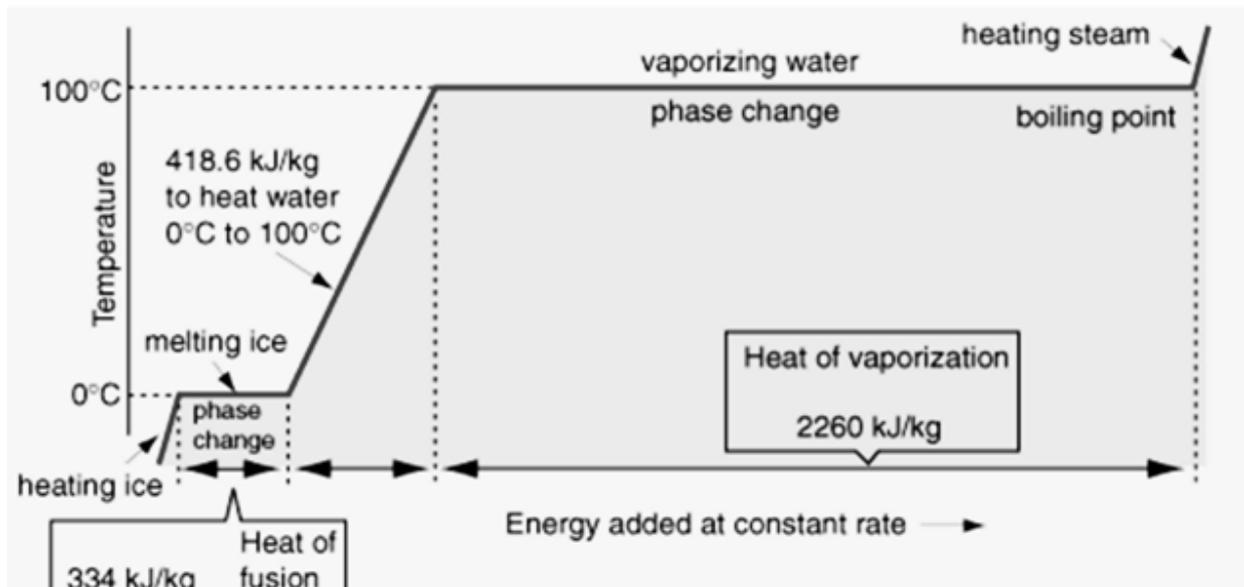


Figure IV.2 Phase-change processes of water at constant atmospheric pressure

Water absorbs latent heat and the boiling starts simultaneously with the phase change process from liquid to vapor state at constant temperature. As heat is continuously transferred, the vaporization process is kept until the last drop of liquid is vaporized and the latent heat of vaporization is equal to 2260 kJ/kg. The vapor now is called a saturated vapor.

As we keep heating the vapor it absorbs sensible heat and its temperature and the specific volume increase. Above the saturated vapor point the vapor is called as a superheated vapor.

And if we go on heating superheated vapor, its temperature will go on increasing. So, there will be no other change or phase in its neutral position until the gas are ionized and goes to the plasma state.

The phase change process is characterized by multiphase or two-phase process and latent heat is exchanged at constant temperature, unlike the single phase region where there is an exchange of the sensible heat.

Now we change the pressure above and below the atmospheric pressure. We will get the same shape of the plot in figure IV.2 characterized by absorption of sensible heat in single phase process and latent heat at two-phase process. All those processes are plotted on a $T-v$ diagram in figure IV.3.

In those plots the saturated liquid points and saturated vapor points converge to each other by increasing the pressure. At the pressure of 22.06 MPa and 373.95 °C saturated liquid points and saturated vapor points are matched and both phases becoming ever more similar. We call this as the critical point or critical state of water. At the critical point, only one phase exists. The heat of vaporization is zero. At this point the water liquid becomes vapor spontaneously.

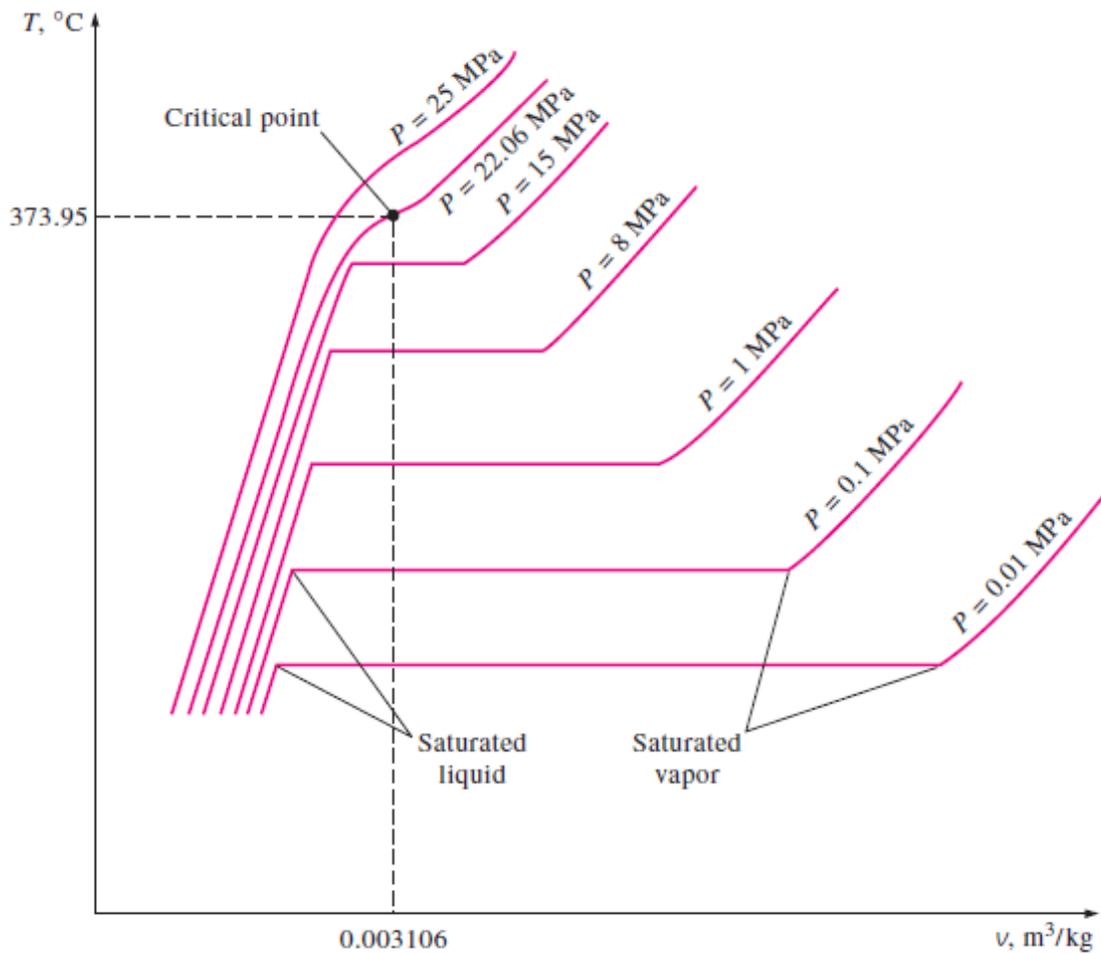


Figure IV.3 T-v diagram of constant-pressure phase-change processes of water at various pressures [4]

IV.2.2 Saturation Temperature and Pressure

At a given pressure, the temperature at which a pure substance changes phase is called the saturation temperature T_{sat} . Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the saturation pressure P_{sat} .

At the stable equilibrium of 273.16 K (0.01 °C) and a partial vapor pressure of 611.657 Pa , all three phases of water (gas, liquid, and solid) can coexist as shown in figure IV.4. This point called triple point is used to define the Kelvin, the base unit of thermodynamic temperature in the International System of Units (SI) (273.16 K , 0.01 °C).

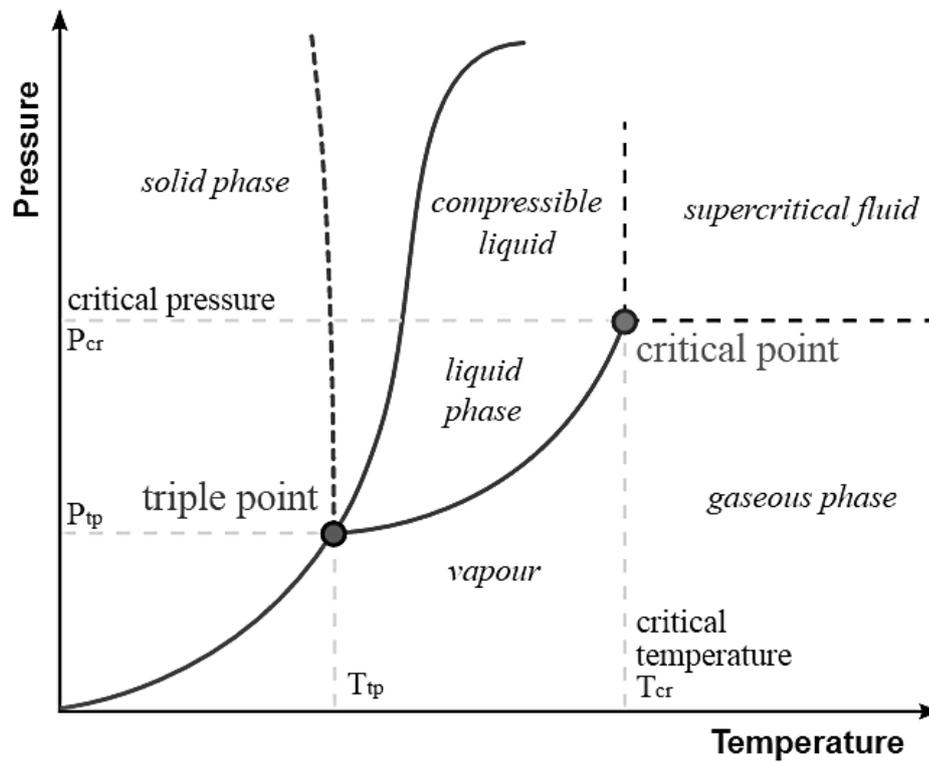


Figure IV.4 Liquid vapor saturation curve of water in a P - T diagram

IV.3 Property Diagrams for Phase-Change Processes

T - v and P - v diagrams are plotted in figure IV.5, and IV.6. The diagrams contain constant pressure lines, the saturated liquid line that separate compressed liquid region from saturated liquid-vapor region. Saturated vapor line separate saturated liquid-vapor region from superheated vapor region.

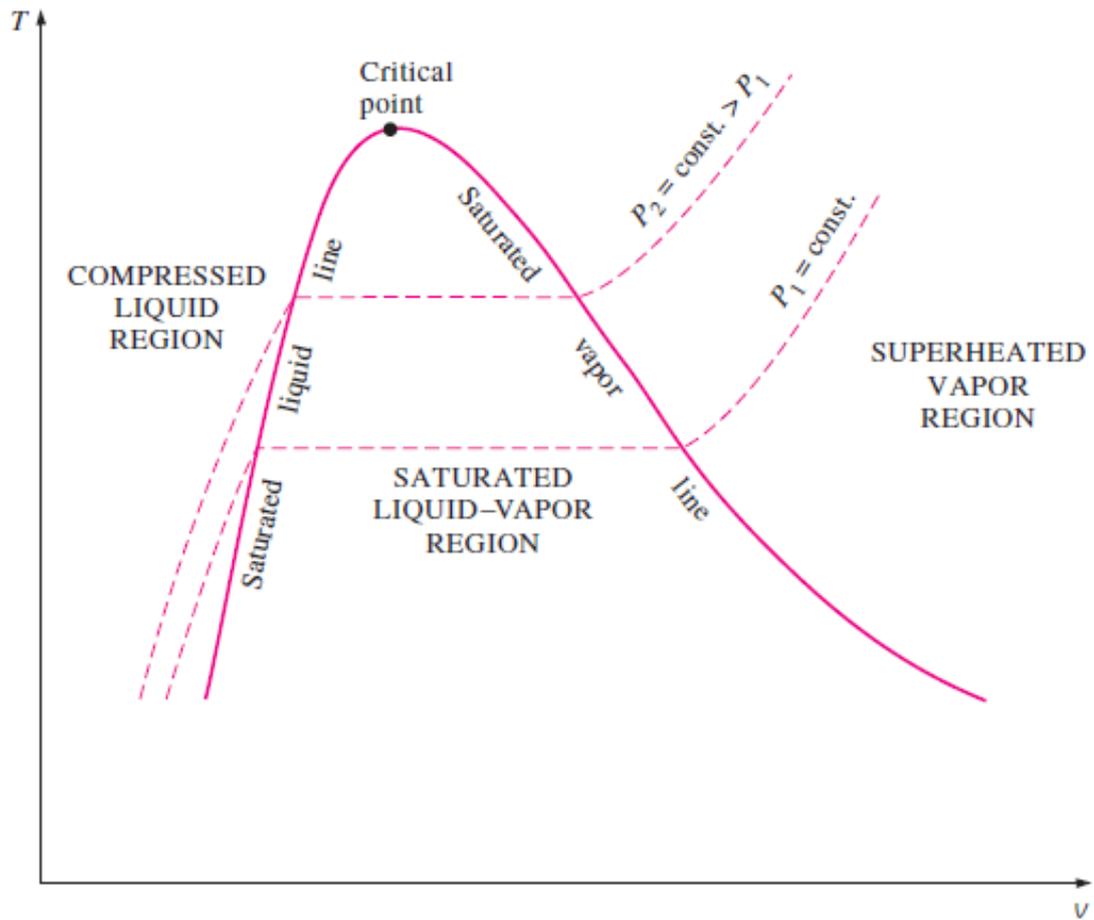


Figure IV.5 T - v diagram of a pure substance [4]

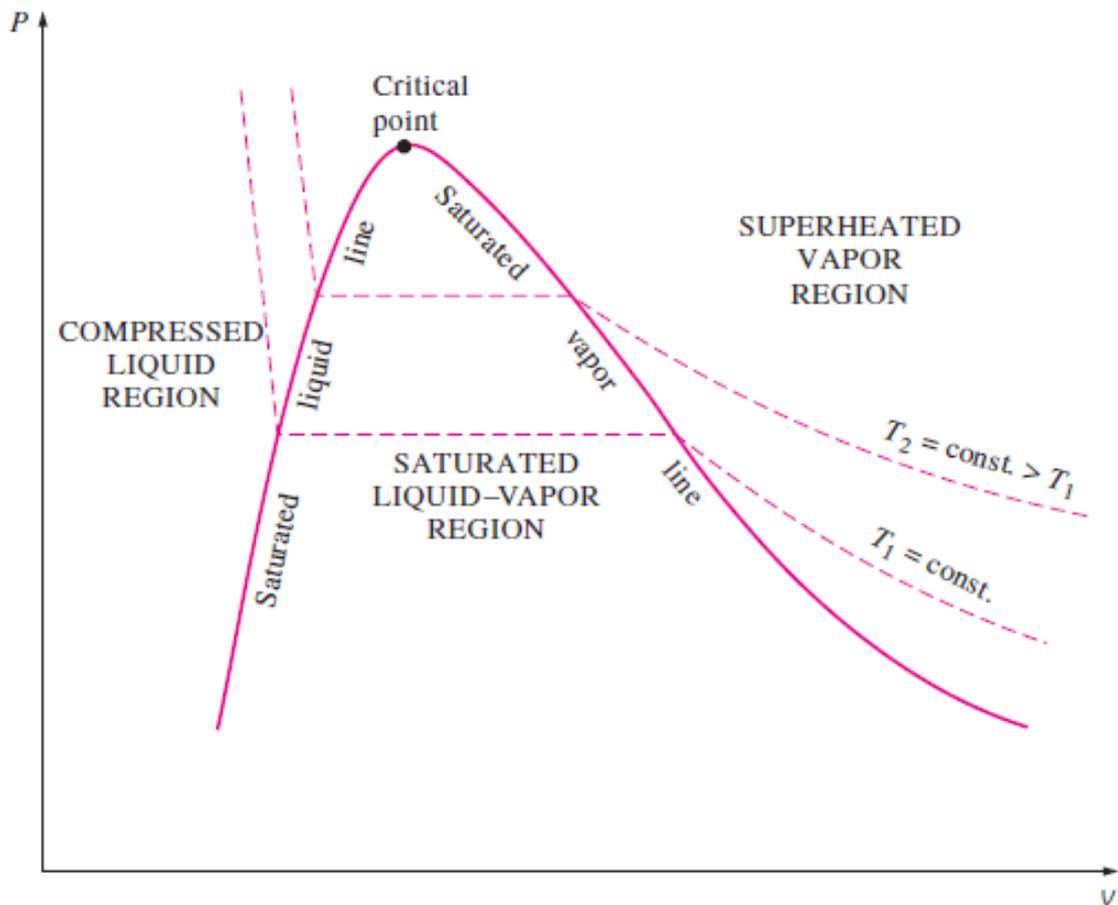


Figure IV.6 P - v diagram of a pure substance [4]

In liquid–vapor region we may have both water and steam that represent a mixture of two phases. In order to specify any property for this region we will have to specify the mixture composition by dryness fraction or the quality of mixture which is defined as

$$x = \frac{\text{mass of dry vapor}}{\text{total mass of the mixture}} \quad (\text{IV.1})$$

$$= \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}}$$

this quantity x is in between $0 < x < 1$

When a mixture of liquid and vapor coexists in equilibrium, the liquid phase is a saturated liquid and the vapor phase is a saturated vapor.

The total volume of any such mixture is

$$V = V_f + V_g$$

where f symbolize fluid or saturated liquid side and g indicate gas or saturated vapor side.

or, alternatively,

$$\frac{V}{m} = \frac{V_f}{m} + \frac{V_g}{m}$$

where the total mass m is

$$m = m_f + m_g$$

Dividing by the total mass of the mixture m and letting the mass fraction of the vapor in the mixture, m_g/m , which is nothing but x , the apparent specific volume v of the mixture is

$$v = (1 - x)v_f + xv_g \quad (\text{IV.2})$$

Now the quality is expressed in terms of specific volume as

$$x = \frac{v_x - v_f}{v_g - v_f} \quad (\text{IV.3})$$

The same thing is done for internal energy, enthalpy and entropy, and then the quality is expressed by the following equations:

$$x = \frac{u_x - u_f}{u_g - u_f} \quad (\text{IV.4})$$

$$x = \frac{h_x - h_f}{h_g - h_f} \quad (\text{IV.5})$$

$$x = \frac{s_x - s_f}{s_g - s_f} \quad (\text{IV.6})$$

During any such phase change the temperature and pressure remain constant and thus are not independent properties. The Clapeyron equation allows the change in enthalpy during a phase change at fixed temperature. For vaporization, the Clapeyron equation reads

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)} \quad (IV.7)$$

where $(dp/dT)_{sat}$ is the slope of the saturation pressure-temperature curve at the point determined by the temperature held constant during the phase change.

Example IV.1

Two kilograms of liquid-vapor mixture water at $300\text{ }^\circ\text{C}$ is heated to saturated vapor state at constant volume process by contact with a thermal reservoir at 900 K . The quality of vapor at initial state is 0.5 , the environment pressure and temperature are 300 K and 1 bar respectively.

Determine:

- 1- the change in exergy,
- 2- the net amount of exergy transfer by heat
- 3- the amount of exergy destruction (irreversibility)

Extract from saturated steam properties tables (Temperature table):

Temp. (°C)	Press. (bar)	Specific Volume m ³ /kg		Internal Energy kJ/kg		Enthalpy kJ/kg		Entropy kJ/(kg k)	
		(v _f × 10 ³)	v _g	u _f	u _g	h _f	h _g	s _f	s _g
300.0	85.81	1.4036	0.02167	1332.0	2563.0	1344.77	2749.57	3.2534	5.7045
336.6	140.0	1.6097	0.01149	1548.6	2474.2	1570.88	2638.09	3.6230	5.3673

Solution:

constant volume process ⇒ closed system

1. change in exergy

$$\begin{aligned} v_1 &= v_{f1} + x_1(v_{g1} - v_{f1}) \\ &= 1.4036 * 10^{-3} + 0.5(0.02167 - 1.4036 * 10^{-3}) \\ &= 0.01154 \left[\frac{m^3}{kg} \right] \end{aligned}$$

$$\begin{aligned} u_1 &= u_{f1} + x_1(u_{g1} - u_{f1}) \\ &= 1332 + 0.5(2563 - 1332) \\ &= 1947.5 \left[\frac{kJ}{kg} \right] \end{aligned}$$

$$\begin{aligned} s_1 &= s_{f1} + x_1(s_{g1} - s_{f1}) \\ &= 3.2534 + 0.5(5.7045 - 3.2534) \\ &= 4.479 \left[\frac{kJ}{kg K} \right] \end{aligned}$$

$$v_1 = v_2 \Rightarrow T_2 = 336.8 \text{ C}^\circ$$

$$u_2 = 2474.2 \left[\frac{kJ}{kg} \right]$$

$$s_2 = 5.3673 \left[\frac{kJ}{kg K} \right]$$

$$\begin{aligned} A_2 - A_1 &= m((u_2 - u_1) + P_0(v_2 - v_1) - T_0(s_2 - s_1)) \\ &= 2((2474.2 - 1947.5) - 300(5.3673 - 4.479)) = 520.4 \text{ kJ} \end{aligned}$$

2. net amount of exergy transfer by heat

$$\begin{aligned} A_Q &= Q \left(1 - \frac{T_0}{T_{res}} \right) \\ &= m * \Delta u \left(1 - \frac{T_0}{T_{res}} \right) \end{aligned}$$

$$\begin{aligned} &= 2(2474.2 - 1947.5) \left(1 - \frac{300}{900} \right) \\ &= 702.3 \text{ kJ} \end{aligned}$$

3. exergy destruction (irreversibility)

$$\begin{aligned} (A_2 - A_1) &= A_Q - A_W - I \Rightarrow I = (A_1 - A_2) + A_Q - A_W \\ &= -520.4 + 702.3 = 181.9 \text{ kJ} \end{aligned}$$

References

- [1] John B. Heywood, *Internal Combustion Engine Fundamentals*. McGraw-Hill Education; 1st edition, 1988
- [2] T. Al-Shemmeri. *Engineering Thermodynamics*. Ventus Publishing ApS, 2011
- [3] Moran, Shapiro, Boettner and Bailey, *Fundamentals of Engineering Thermodynamics*, 7th Edition, 2010
- [4] Yunus A. Cengel, & Michael A. Boles. *Thermodynamics: An engineering approach*. McGraw-Hill, 5nd Edition, 2006
- [5] Wei-Yin Chen, Toshio Suzuki and Maximilian Lackner, *Handbook of Climate Change Mitigation and Adaptation*, Springer Science+Business Media New York, 2015
- [6] A.M.Y Razak. *Industrial Gas Turbines*. Taylor & Francis Group, 2007
- [7] CHIH WU. *Thermodynamics and Heat Powered Cycles: A Cognitive Engineering Approach*. Nova Science Publishers, Inc. New York, 2007
- [8] Ingo Müller, Wolf Weiss, *Entropy and Energy a universal competition*. Springer-Verlag Berlin Heidelberg, 2005
- [9] Rogers and Mayhew, *Engineering Thermodynamics: Work and Heat Transfer*, 4th Edition, 1992
- [10] <http://study.com/>
- [11] F. P. Incropera, D. P. DeWitt, T. L. Bergman, A. S. Lavine, *Fundamentals of heat and mass transfer*. John Wiley, 6th Edition, 2006
- [12] M. Schobeiri, *Turbomachinery Flow Physics and Dynamic Performance*, Springer-Verlag Berlin Heidelberg 2005

ملخص الدرس باللغة العربية

تمهيد

عزيزي الطالب

بعدها درست الديناميك الحرارية في شقها المتعلق بالتوازن الكيميائي في السنة الاولى ليسانس،
نقدم اليك في هذا الدرس الشطر الثاني المتمثل في التوازن الحراري و الميكانيكي، حيث نتطرق
من خلاله الى المبادئ الاساسية التي تحكم هذان التوازنان بداية من التعريف بالمفاهيم
الاساسية ثم تقديم المبدأ الاول و اساسياته و بعده المبدأ الثاني و مسلماته و اخيرا خصائص
المواد النقية مع مختلف الاطوار التي تكون عليها.

في نهاية الدرس يكون الطالب قادرا على التنبؤ بمختلف التصرفات التي تسلكها المواد عند
خضوعها لمختلف التغيرات المؤثرة عليها، و يعتبر هذا الدرس تمهيدا أساسيا للكثير من الدروس
القادمة التي نذكر منها الدرس انتقال الحرارة و الدرس الديناميك الحرارية التطبيقية على سبيل
المثال لا الحصر.

محتويات الدرس

المقدمة

تعريف النظام و محيطه

تعريفات اساسية

المسار في الديناميك الحرارية

طرق تبادل الطاقة

الغازات المثالية

المبدأ الأول للديناميك الحرارية

الطاقة الداخلية لنظام

حفظ الطاقة لنظام مغلق

الإنتالبية و السعة الحرارية

حفظ الطاقة لنظام مفتوح

القانون الثاني للديناميك الحرارية

اتجاه المسارات الطبيعية و العمليات العكوسية

مبدأ كارنو

درجة الحرارة المطلقة للديناميك الحرارية

لا مساوات كلوزيس

إنتروبيا

الطاقة المتاحة

خصائص المواد النقية

حالات المادة

منحنى تغير الاطوار

الدرس باللغة الأجنبية

المقدمة

الديناميك الحرارية هي علم أساسي يصف القوانين الاساسية التي تتعلق بمختلف المسارات الفيزيائية التي تخص تبادل أو تحول الطاقة بالإضافة إلى علاقات الخصائص الفيزيائية للمواد المتأثرة بتلك المسارات.

يوجد منظوران للديناميك الحرارية:

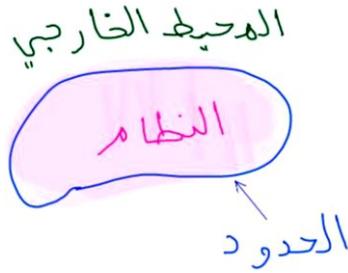
1- المنظور الماكرو سكوبي أو النظرة الكلاسيكية.

2- المنظور الميكروسكوبي أو النظرة الاحصائية (الحديثة).

تهتم النظرة الكلاسيكية بكميات المادة دون التدقيق في مستواها الذري، بعكس النظرة الاحصائية التي تهتم بالمستوى الذري.

تعريف النظام و محيطه

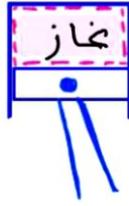
النظام (system) الموضح في الشكل 1 هو كمية من المادة التي نعتمد عليها في حل مشكل ما يخص الديناميك الحرارية. يفصل النظام بحدود (boundary) عن محيطه الخارجي (surroundings).



الشكل 1: النظام، الحدود و المحيط الخارجي

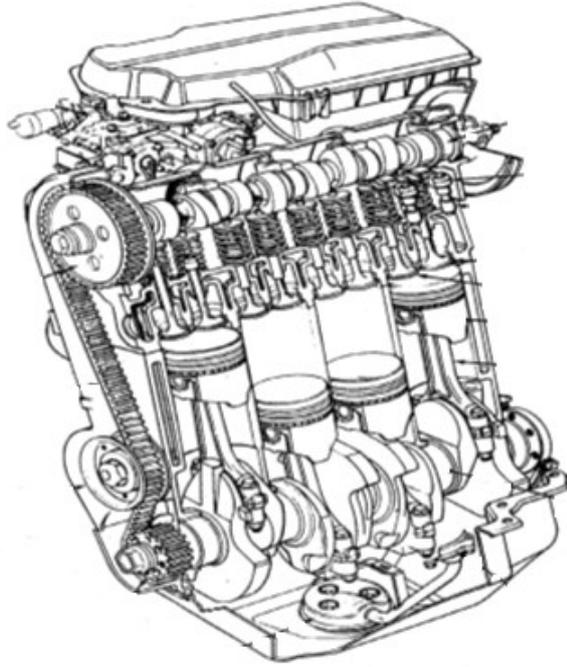
في العموم يوجد ثلاث أنواع من الانظمة:

1- النظام المغلق أين تكون كمية المادة في النظام ثابتة مع امكانية تبادل للطاقة مع المحيط الخارجي مثل عمل المكبس والاسطوانة الشكل 2.



الشكل 2 : نظام مغلق

2- النظام المفتوح اين يكون حجم النظام ثابت مع امكانية تبادل في الطاقة و المادة مثل محرك الاحتراق الداخلي الرباعي الاطوار الشكل 3.



الشكل 3 : نظام مفتوح محرك الاحتراق الداخلي

3- النظام المعزول هو النظام الذي لا يحدث فيه تبادل للمادة او الطاقة مع المحيط الخارجي.

الخصائص في الديناميك الحرارية

النظام يعرف بخصائصه التي تصف حالته و التي يجب ان تكون متجانسة و لا تتغير بمرور الزمن، يوجد نوعان من الخصائص و هي:

1- المرتبطة باتساع النظام مثل الكتلة و الحجم.

2- غير مرتبطة باتساع النظام مثل درجة الحرارة و الضغط.

تعريفات اساسية

التوازن في الديناميك الحرارية

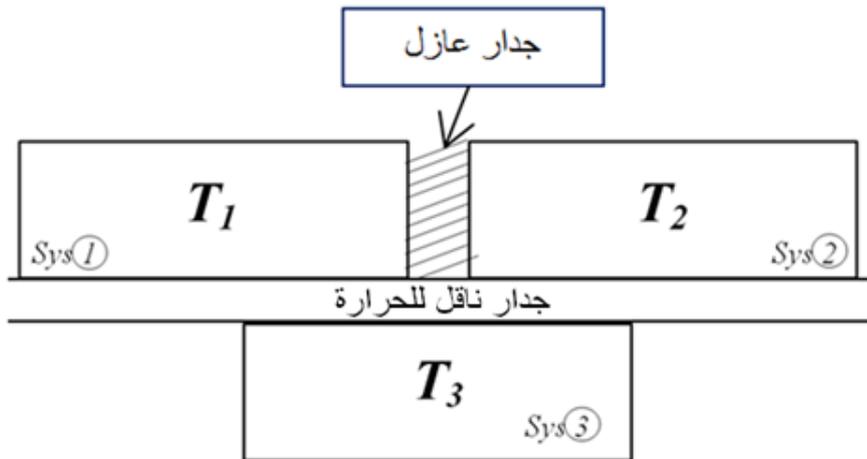
ينقسم إلى التوازن الحراري، الميكانيكي و الكيميائي.

التوازن الحراري:

يتحقق بنظامين أو أكثر حيث تتغير خصائصها عندما تتصل هذه الانظمة بحاجز ناقل للحرارة.

القانون رقم صفر:

عندما يتوازن جسمان أو نظامان حراريا مع نظام ثالث ذلك يعني أنهم في حالة توازن حراري مع بعضهم البعض. في الشكل 4 اذا توازن النظامان 1 و 3 و النظامان الآخرا 2 و 3 حراريا فان النظامان 1 و 2 متوازنان حراريا.



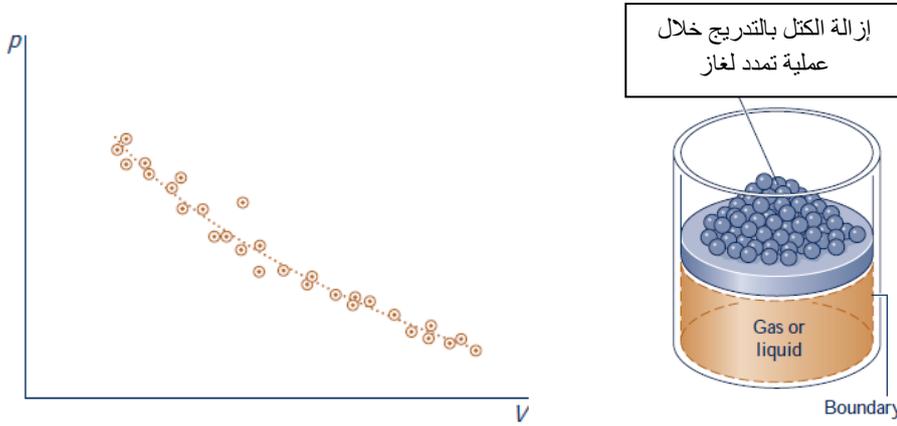
الشكل 4 : التوازن الحراري

درجة الحرارة:

هي خاصية من خصائص الديناميك الحرارية التي من خلالها نستطيع ان نعرف ما اذا كان النظام في توازن حراري مع نظام آخر أو لا من منظور الديناميك الحرارية الكلاسيكية (أو الطاقة الحركية المتوسطة لجزيئات المادة من منظور الديناميك الحرارية الاحصائية).

المسار في الديناميك الحرارية

نستطيع تعيين المسار في الديناميك الحرارية اذا كان يمر من نقطة التوازن 1 إلى نقطة التوازن 2 عبر عدة نقاط توازن و يسمى مسار شبه ثابت أو مسار شبه متوازن، انظر الشكل 5.



الشكل 5: مسار شبه ثابت للضغط أو التمدد

طرق تبادل الطاقة

مفهوم الطاقة

الطاقة المخزنة تكون في شكل طاقة داخلية و يعبر عنها بدالة نقطية (تتعلق بحالة التوازن).

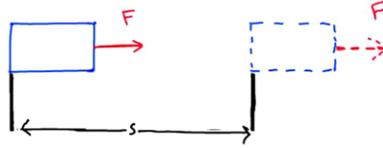
يتم التعبير عن الطاقة المتبادلة بدالة المسار (تبادل الحرارة و العمل).

يكون العمل المنتج من النظام موجبا على غرار الحرارة المضافة للنظام.

أنواع التبادلات في العمل

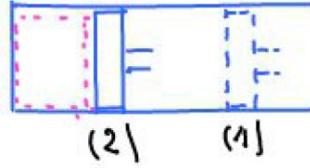
1- عمل التحرك (الانتقال)

هو العمل اللازم لتحريك جسم ما مسافة (s) تحت تأثير قوة (F) انظر الشكل 6



الشكل 6 : عمل التحرك (الانتقال)

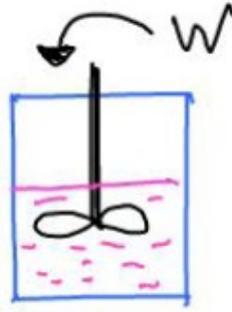
بالنسبة للمكبس يعتبر هذا العمل عملا عكوسا بسبب اهمال الاحتكاك بين المكبس و الاسطوانة ولا يكون هذا العمل الا في الانظمة المغلقة انظر الشكل 7.



الشكل 7 : عمل التحرك المكبس من حالة التوازن (1) الى حالة التوازن (2)

2- عمل جسم دوراني

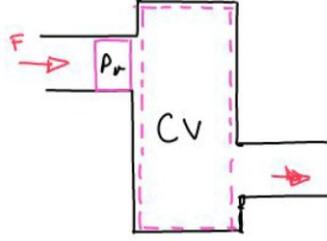
هو عمل دوران جسم صلب في وسط مائع و يعتبر عملا غير عكوسا لأنه يعتمد أساسا على الاحتكاك بين الجسم الصلب و الوسط المائع و لا يكون هذا العمل إلا في الانظمة المغلقة انظر الشكل 8.



الشكل 8 : عمل جسم دوراني

3- عمل التدفق

يعبر عن عمل كمية من المائع في مجرى ما و لا يكون هذا العمل الا في الأنظمة المفتوحة انظر الشكل 9.



الشكل 9 : عمل التدفق

4- عمل المحور

هو دوران محور متصل بنظام بسبب / يسبب عزم دوران و لا يكون الا في الأنظمة المفتوحة. انظر الشكل 10.



الشكل 10 : عمل المحور

الغازات المثالية

هي الغازات التي تخضع لقانون التالي: الضغط \times الحجم = الكتلة \times ثابت الغاز \times درجة الحرارة

في الضغط المنخفض القريب من الضغط الجوي و في درجة الحرارة العالية جدا (ضعف حرارة الحرجة) تتصرف الغازات و كأنها مثالية، أما عندما يرتفع الضغط تبعد الغازات عن التصرف المثالي و تخضع لقوانين تقريبية تسمى قوانين الغازات الحقيقية و نذكر على سبيل المثال قانون فان در فالس الذي يقترح ثابتان من أجل مقارنة جيدة في الضغط العالي.

المبدأ الاو للديناميك الحرارية (قانون حفظ الطاقة)

المجموع الجبري للحرارة و العمل المتبادل بين نظام و محيطه الخارجي خلال دورة يكون معدوما.

الطاقة الداخلية

هي من خصائص النظام التي تتحدد بالفرق بين الحرارة و العمل المتبادل مع المحيط خلال مسار معين و هي تحوي على طاقة التصادم بين الجزيئات، الطاقة الحركية والطاقة الكامنة للنظام.

الاتالية

هي مجموع الطاقة الداخلية و حاصل ضرب الضغط في الحجم لنظام مغلق أو بالأحرى هي كمية الحرارة المتبادلة في نظام مغلق تحت ضغط ثابت.

السعة الحرارية

تعتبر على كمية الحرارة اللازمة لرفع درجة حرارة كيلوغرام من مادة بواحد كلفن تحت ضغط ثابت أو حجم ثابت.

المبدأ الثاني و بديهياته

المبدأ الثاني يحدد اتجاه كل المسارات الطبيعية بحيث أن كل المسارات الطبيعية لها اتجاه واحد أي انها غير عكوسة أو لا يعكس اتجاهها.

نقول عن مسار ما أنه عكوس اذا عاد النظام و محيطه الخارجي الى الحالة الابتدائية بدون أي تغير في الكون. بما ان كل المسارات الطبيعية لا تحقق هذا الشرط فهي اذن غير عكوسة و عليه فان المسار العكوس يعتبر مفهوما نظريا.

المسارات جد البطيئة والمرتبطة بتوازنات حرارية و ميكانيكية متناهية الصغر و التي يكون فيها الضياع في الطاقة شبه منعدم يمكن اعتبارها مسارات عكوسة الى حد ما و نقول عنها انها مسارات شبه ثابتة أو شبه متوازنة.

أسباب لاعكوسية المسارات

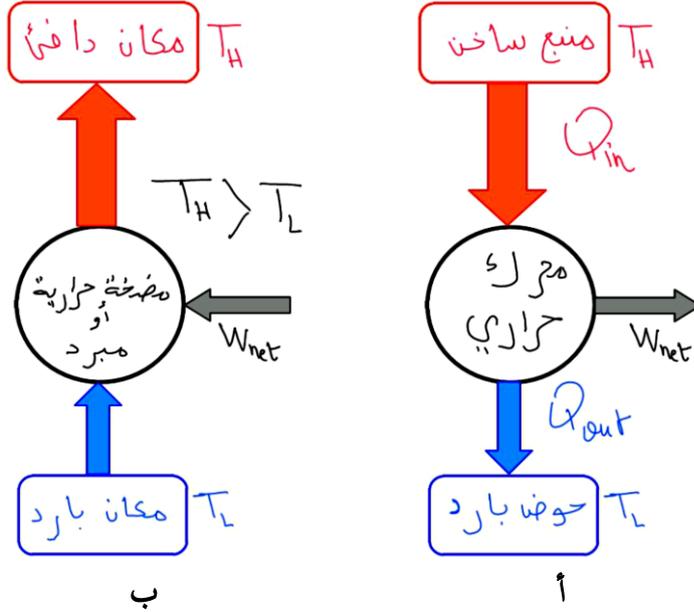
- الاخفاق في توازن الديناميك الحراري.
- العوامل المبددة للطاقة مثل الاحتكاك الميكانيكي، لزوجة الموائع، المقاومة الكهربائية... الخ.

المحرك الحراري

هو نظام يعمل في دورة الديناميك الحرارية بحيث يتبادل الحرارة و ينتج العمل. نعرف فعالية المحرك الحراري بالعمل المنتج الصافي قسمة كمية الحرارة المستهلكة. انظر الشكل 10.

المضخة الحرارية و المبرد

هي نظام يعمل في دورة الديناميك الحرارية حيث يحدث انتقال العمل و انتاج أو استهلاك للحرارة. نعرف معامل المردودية للمضخة الحرارية أو المبرد بكمية الحرارة المنتجة تقسيم عمل الضاغط المستهلك. انظر الشكل 11.



الشكل 11 : المحرك الحراري (أ) و المضخة الحرارية (ب)

بدئية كلفن- بلانك للقانون الثاني

يستحيل على أي محرك حراري يعمل في دورة كاملة يتبادل الحرارة مع أجسام لها نفس درجة الحرارة الثابتة أن ينتج عمل ميكانيكي.

الدورات الالاعكوسه

نظرية كارنو

المحرك العكوس هو الأكثر فعالية من بين كل المحركات حين تعمل هذه المحركات ما بين نفس حدود درجة حرارة المنبع و الحوض البارد.

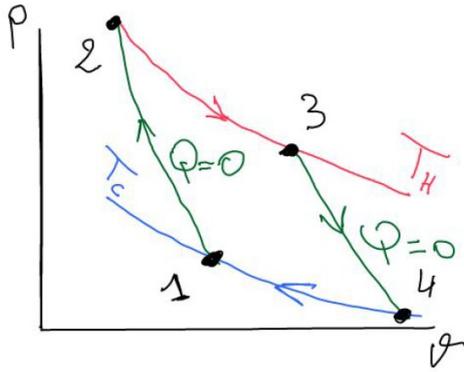
كل المحركات العكوسة التي تعمل ما بين نفس حدود درجة الحرارة لها نفس الفعالية.

درجة الحرارة المطلقة للديناميك الحرارية

انطلاقاً من نظرية كارنو نستنتج أن حاصل قسمة كمية الحرارة المستهلكة و المستنزفة من المحرك العكوس تساوي حاصل قسمة درجة حرارة المنبع الساخن و الحوض البارد.

محرك كارنو

يتميز باربعة أشواط تصف حالات الغاز انظر الشكل 12 و هي:



1- مسار عكوس للتسخين بدرجة حرارة ثابتة.

2- مسار عكوس كتومي للتمدد.

3- مسار عكوس للتبريد بدرجة حرارة ثابتة.

4- مسار عكوس كتومي للضغط.

الشكل 12 : دورة محرك كارنو

الانتروبية

انطلاقاً من درجة الحرارة المطلقة للديناميك الحرارية نستنتج أنه بالنسبة لمحرك عكوس التكامل الدائري للتغير في كمية الحرارة بالنسبة لدرجة الحرارة خلال دورة الديناميك الحرارية يكون معدوماً

لا مساوات كلوزيوس

التكامل الدائري للتغير في كمية الحرارة بالنسبة لدرجة الحرارة خلال دورة الديناميك الحرارية لمحرك غير عكوس يكون أصغر تماماً من نفس التكامل بالنسبة لمحرك عكوس.

معادلة الأنتروبية في مسار ما تكتب على الشكل التالي:

$$\text{انتروبية النظام} + \text{انتروبية المحيط} = \text{انتروبية الكون}$$

حيث أن انتروبية الكون تتعلق بالتغير المرتبط باللاعكوسية الداخلية للنظام و انتروبية المحيط تتعلق بتبريد و تسخين النظام.

الطاقة المتاحة

الطاقة المتاحة لنظام مغلق هي العمل المستغل الأقصى الذي نستطيع استخلاصه من نظام ما عندما يصل الى حالة التوازن بحيث يعتبر في حالته الميتة أين لا يتبادل الطاقة مع محيطه الخارجي بأخذ درجة حرارة و ضغط المحيط كمرجع.

التناقص في الطاقة المتاحة لنظام ما تساوي الطاقة المتاحة الخارجة من النظام زائد عكوسية النظام.

في كل المسارات الطبيعية، الطاقة المتاحة لنظام ما تهدم بسبب اللاعكوسية، يسمى هذا قانون "قانون تبديد الطاقة".

النظام المفتوح متعلق بتدفق الطاقة المتاحة من خلال سريان البخار الذي يتخطى حدود النظام.

المبدأ الثاني للفعالية يمثل قيمة تبديد الطاقة لنظام ما مع العلم أن لكل المسارات الطبيعية للأنظمة تكون فعاليتها أصغر من الواحد و تساويه إذا كان النظام عكوس.

خصائص المواد النقية

المادة النقية هي مادة متجانسة و تركيبها الكيميائية غير متغيرة و تستطيع أن تكون على أكثر من حالة مادية بشرط أن تحافظ على تركيبها الكيميائية. فعلى سبيل المثال الماء له نفس التركيب الكيميائي سواء كان بخار أو سائل أو جليد.

حالات (اطوار) المادة

الحالة الصلبة :

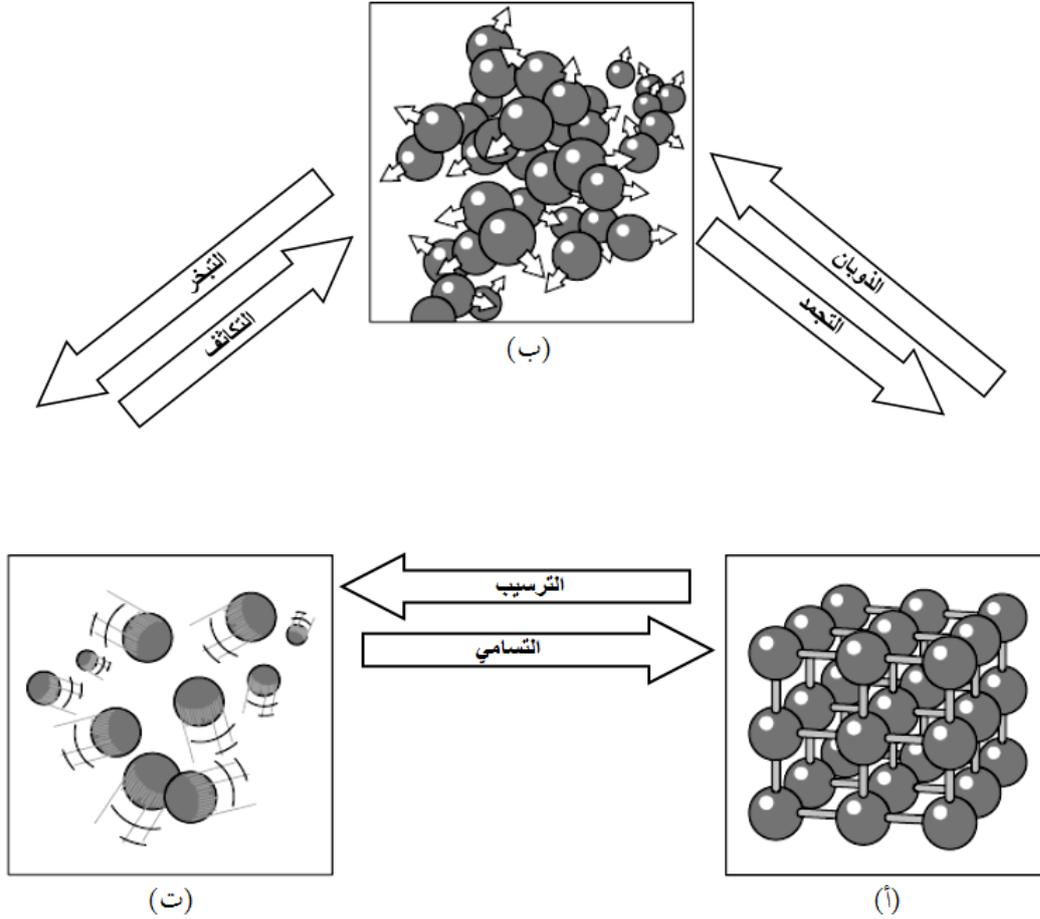
المواد الصلبة لها شكل ثابت حيث أن الجزيئات لا تتحرك من مكانها؛ تكون قوة التجاذب بين الجزيئات كبيرة لتجعلها في الحالة الجامدة. انظر الشكل 13 (أ).

الحالة السائلة:

تأخذ السوائل شكل الوعاء الذي توضع فيه، والجزيئات في السوائل ليست ثابتة حيث انها تستطيع الانزلاق و الدوران على بعضها البعض بكل حرية. في السوائل قوة التجاذب بين الجزيئات تكون ضعيفة مقارنة بالمواد الصلبة لكنها تبقى عالية إلى حد ما بالنسبة للغازات. انظر الشكل 13 (ب).

الحالة الغازية:

في هذه الحالة تكون لجزيئات الغاز مساحات كبيرة فيما بينها و تتحرك بعشوائية في كل الاتجاهات حيث لا يتواجد لها ترتيب معين فتتصادم دوما فيما بينها. انظر الشكل 13 (ت).



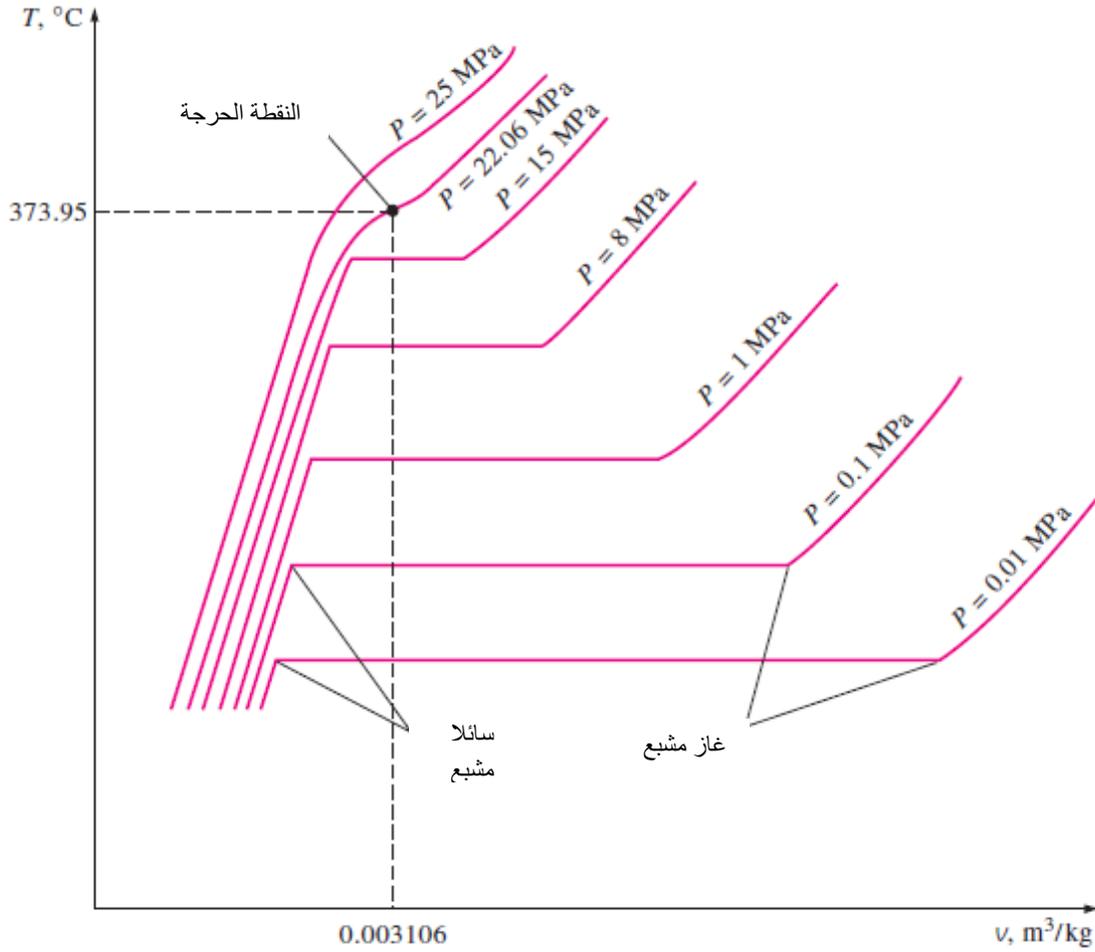
الشكل 13 حالات (أطوار) المادة : الحالة الصلبة (أ) السائلة (ب) و الغازية (ت)

منحنى تغير الاطوار

فعلى سبيل المثال الماء السائل و الذي يسمى أيضا سائلا مضغوطا (compressed liquid) لأنه بعيد عن درجة الغليان. وعند رفع درجة حرارته تحت ضغط ثابت يكاد يتمدد.

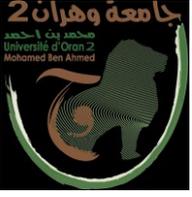
عندما يقترب من الغليان يسمى سائلا مشبعا (saturated liquid) ويبدء التغير في الطور بالتزامن مع عملية التبخر في درجة الحرارة ثابتة. عندما نستمر في تسخينه تستمر عملية التبخر حتى تتبخر آخر قطرة من الماء و يسمى الآن بخار مشبع (saturated vapor). بتسخين البخار المشبع ترتفع درجة حرارته مرة اخرى و يتمدد لنحصل على غاز فائق التسخين (superheated vapor). هذه التغيرات موضحة في الشكل 14.

ملاحظة: عند الاستمرار في تسخين الغاز فائق التسخين يتاين و ينقل الى طور البلازما و هو طور خارج نطاق الدرس



الشكل 14 : منحنى تغير الاطوار درجة الحرارة بدلالة الحجم النوعي (الحجم الكنتلي)

تعتمد درجة حرارة غليان الماء على الضغط فهي تزيد بزيادته كما هو موضح في الشكل 14. معامل الجفاف للبخر يساوي كتلة البخر على كتلة المزيج الكلي.



الجمهورية الجزائرية الديمقراطية الشعبية



وزارة التعليم العالي والبحث العلمي

جامعة وهران 2 محمد بن أحمد

معهد الصيانة والأمن الصناعي

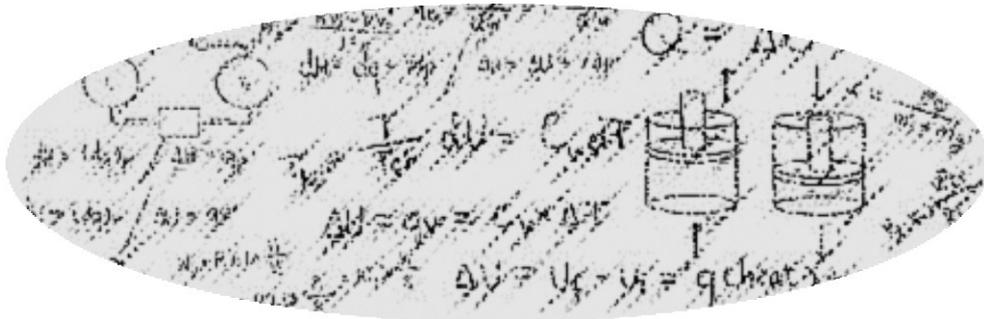
مقياس

الديناميك الحرارية

(التوازن الحراري و الميكانيكي)

(لطلبة ما قبل التدرج)

المؤلف: د. محمد زهير داررمضان



الطبعة الاولى 2016/2017