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INSTITUTE OF SCIENCE AND TECHNOLOGY

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**SCHOOL OF BIO AND CHEMICAL
DEPARTMENT OF CHEMICAL ENGINEERING**

UNIT – I -Chemical Engineering Thermodynamics-I– SCHA1202

Basic Concepts and First Law of Thermodynamics

Thermodynamics is:

- the science of heat and work and related properties
- the basic science that deals with energy
- the study of energy movements

The name was coined in 1849 by Lord Kelvin by combining Greek words for heat (*thermos*) and power (*dynamis*).

1.1 Energy

- Potential Energy (EP) -- depends on position within reference frame
- Kinetic Energy (EK) -- depends on movement within reference frame
- Internal Energy (U) -- includes all chemical energy. It lumps together the microscopic energies, including EP and EK of molecular vibration, rotation, and translation. These can be expressed as functions of the temperature and density of the system and don't really vary much with the position or motion of the system. U thus depends on the thermodynamic state.

$$\begin{aligned}\text{Work} &= \text{Force} * \text{Distance} \\ \text{Work} &= \text{N} * \text{m} = \text{J} \\ &= \text{lbf} * \text{ft}\end{aligned}$$

It isn't really possible to identify a condition that has zero energy, because energy depends so much on our definitions and how we choose to make measurements. Consequently, all energy terms are relative to some reference state.

Physics has often defined work as force (needed to move an object) acting through a distance (moved). This is reflected in energy units:

These are the basic units of energy, heat, and work.

There is another set of units based on heat

- calorie = heat needed to raise 1 gram of water by 1 degree Kelvin
- BTU (British Thermal Unit) = heat needed to raise 1 pound of water by 1 degree Rankine

Power is the rate of change/transport of energy.

$$\text{Power} = \frac{\text{Energy (Work, Heat)}}{\text{Time}}$$

$$\begin{aligned}\text{Power} &= \frac{\text{J}}{\text{s}} = W \\ &= \frac{\text{ft} \cdot \text{lbf}}{\text{s}} \Rightarrow \text{horsepower}\end{aligned}$$

$$\text{kWh} = \text{kW} \cdot \text{hr} = \frac{\text{kJ}}{\text{s}} \cdot \text{hr} = \frac{\text{energy}}{\text{time}} \cdot \text{time}$$

1.2 System and Surroundings

In order to avoid confusion, scientists discuss thermodynamic values in reference to a system and its surroundings. Everything that is not a part of the system constitutes its surroundings. The system and surroundings are separated by a boundary. For example, if the system is one mole of a gas in a container, then the boundary is simply the inner wall of the container itself. Everything outside of the boundary is considered the surroundings, which would include the container itself. The boundary must be clearly defined, so one can clearly say whether a given part of the world is

in the system or in the surroundings. If matter is not able to pass across the boundary, then the system is said to be *closed*; otherwise, it is *open*. A closed system may still exchange energy with the surroundings unless the system is an isolated one, in which case neither matter nor energy can pass across the boundary.

The boundaries are set up in a way most conducive to understanding the energetics of what we're studying.

Defining the system and surroundings is arbitrary, but it becomes important when we consider the exchange of energy between the system and surroundings.

Two types of exchange can occur between system and surroundings: (1) energy exchange (heat, work, friction, radiation, etc.) and (2) matter exchange (movement of molecules across the boundary of the system and surroundings).

Based on the types of exchange which take place or don't take place, we will define three types of systems:

- **isolated systems:** no exchange of matter or energy
- **closed systems:** no exchange of matter but some exchange of energy
- **open systems:** exchange of both matter and energy

1.3 Control Volume

Control volume is defined as a volume which encloses the matter and the device inside a control surface.

- Every thing external to the control volume is the surroundings with the separation given by the control surface.
- The surface may be open or closed to mass flows and it may have flows from energy in terms of heat transfer and work across it.
- The boundaries may be moveable or stationary.
- In the case of a control surface that is closed to the mass flow, so that no mass can enter or escape the control volume, it is called a **control mass** containing same amount of matter at all times.

1.4 Property

- In thermodynamics a property is any characteristic of a system that is associated with the energy and can be quantitatively evaluated.
- The property of a system should have a definite value when the system is in a particular state.
- Thermodynamic property is a point function.
- Properties like volume of a system that depend on the mass of a system are called extensive properties.
- Properties like pressure or temperature which do not depend on the system mass
- The ratio of extensive property to the mass of the system are called specific properties and therefore become intensive properties.
- Substance can be found in three states of physical aggregation namely, solid, liquid and vapor which are called its phases.
- If the system consists of mixture of different phases, the phases are separated from each other by phase boundary.
- The thermodynamic properties change abruptly at the phase boundary, even though the intensive properties like temperature and pressure are identical.

1.5 Equilibrium

- When the property of a system is defined, it is understood that the system is in equilibrium.
- If a system is in thermal equilibrium, the temperature will be same throughout the system.
- If a system is in mechanical equilibrium, there is no tendency for the pressure to change. In a single phase system, if the concentration is uniform and there is no tendency for mass transfer or diffusion, the system is said to be in chemical equilibrium.
- A system which is simultaneously in thermal, mechanical, and chemical equilibrium is said to be in thermal equilibrium.

1.6 Process

A process is path followed by a system in reaching a given final state of equilibrium state starting from a specified initial state.

An actual process occurs only when the equilibrium state does not exist.

An ideal process can be defined in which the deviation from thermodynamic equilibrium is infinitesimal.

All the states the system passes through during a quasi-equilibrium process may be considered equilibrium states.

For non-equilibrium processes, we are limited to a description of the system before the process occurs and after the equilibrium is restored.

Several processes are described by the fact that one property remains constant.

The prefix iso- is used to describe such processes.

A process is said to be reversible if both the system and its surroundings can be restored to their respective initial states by reversing the direction of the process.

- **reversible:** if the process happens slow enough to be reversed.
- **irreversible:** if the process cannot be reversed (like most processes).
- **isobaric:** process done at constant pressure
- **isochoric:** process done at constant volume
- **isothermal:** process done at constant temperature
- **adiabatic:** process where $q=0$
- **cyclic:** process where initial state = final state

1.7 The basic units (SI Units)

Mass-kg.

Mole-The mole is the amount of substance that contains as many atoms (or molecules) as there are atoms in 0.012 kg of carbon-12.

Length-m.

Time: second

SI unit of temperature is Kelvin (abbreviated as K). The Kelvin is defined as the fraction of $1/273.16$ of the thermodynamic temperature of the triple point of water. The relation between Kelvin and Celsius temperature is $K = C + 273.15$ (The triple point of water is at 0.01°C).

Derived units: Force: $1\text{ N} = 1\text{ kg m/s}^2$, pressure $1\text{ Pa} = 1\text{ N/m}^2$, $1\text{ bar} = 10^5\text{ Pa}$, $1\text{ atm.} = 101325\text{ Pa}$. In thermodynamics we are concerned with absolute pressure. Gauge pressure = absolute pressure – atmospheric pressure. Ordinary vacuum gauge pressure = atmospheric pressure – absolute pressure.

1.8 Internal Energy

- The molecule as a whole can move in x, y and z directions with respective components of velocities and hence possesses kinetic energy.
- There can be rotation of molecule about its center of mass and then the kinetic energy associated with rotation is called rotational energy.
- In addition the bond length undergoes change and the energy associated with it is called vibrational energy.
- The electron moves around the nucleus and they possess a certain energy that is called electron energy.
- The microscopic modes of energy are due to the internal structure of the matter and hence the sum of all microscopic modes of energy is called the internal energy.

Bulk kinetic energy (KE) and potential energy (PE) are considered separately and the other energy of control mass as a single property (U).

The total energy possessed by the body is given by:

$$E = KE + PE + U$$

1.9 Work

Whenever a system interacts with its surroundings, it can exchange energy in two ways- work and heat.

In mechanics, work is defined as the product of the force and the displacement in the direction of the force.

Work done when a spring is compressed or extended: According to Hooke's law

$$\text{Spring force} = -k(x - x_0)$$

Where k is the spring constant, x_0 is the equilibrium position, and x is the final position. The negative sign shows that the direction of the spring force is opposite the direction of the displacement from x_0 . The external force is equal in magnitude but opposite in sign to the spring force, so

$$\text{External force (force of your hands)} = k(x - x_0).$$

Now, we want to calculate the work done when we stretch the spring from position 1 to position 2.

$$W = \int F dx = \int k(x - x_0) d(x - x_0) = \frac{1}{2} k [(x_2 - x_0)^2 - (x_1 - x_0)^2]$$

Work done when a volume is increased or decreased

Consider a gas in a container with a movable piston on top. If the gas expands, the piston moves out and work is done by the system on the surroundings.

Alternatively, if the gas inside contracts, the piston moves in and work is done by the surroundings on the system. Why would the gas inside contract or expand?

It would if the external pressure, P_{ex} , and the internal pressure, P_{in} , were different. To calculate the work done in moving the piston, we know that the force = pressure times area and then work equals pressure times area times distance or work equals pressure times the change in volume. So, $W = \int P_{\text{ex}} dV$

The differential work done (dW) associated with a differential displacement (dl) is given by

$$dW = F dl$$

For a piston cylinder assembly,

$$dW = F dl = PA (dl) = P dV$$

If the gas is allowed to expand reversibly from the initial pressure P to final pressure P , then the work done is given by

$$W = \int p dV$$

- The integral represents the area under the curve on a pressure versus volume diagram. Therefore the work depends on the path followed and work is a path function and hence not a property of the system.
- The above expression does not represent work in the case of an irreversible process.
- The thermodynamic definition of work is “ Work is said to be done by a system on the surrounding if the sole effect external to the system could be reduced to the raising of a mass through a distance”.

1.10 Heat

Heat like work, is a form of energy.

The energy transfer between a system and its surroundings is called heat if it occurs by virtue of the temperature difference across the boundary.

The two modes of energy transfer – work and heat- depend on the choice of the system.

Heat energy moves from a hotter body to a colder body upon contact of the two bodies.

If two bodies at different temperatures are allowed to remain in contact, the system of two bodies will eventually reach a thermal equilibrium (they will have the same temperature).

A body never contains heat. Rather heat is a transient phenomenon and can be identified as it crosses the boundary.

1.11 Zeroth law of thermodynamics

The **zeroth law of thermodynamics** states that if two **thermodynamic** systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

1.12 First law of thermodynamics

The first law, also known as Law of Conservation of Energy.

It states that energy cannot be created or destroyed in an isolated system. The first law of thermodynamics, also known as Law of Conservation of Energy, states that energy can neither be created nor destroyed; energy can only be transferred or changed from one form to another. For example, turning on a light would seem to produce energy; however, it is electrical energy that is converted. A way of expressing the first law of thermodynamics is that any change in the internal energy (ΔU) of a system is given by the sum of the heat (q) that flows across its boundaries and the work (w) done on the system by the surroundings:

$$\Delta U = q + w$$

This law says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured and quantified, this is the same as saying that any change in the energy of a system must result in a corresponding change in the energy of the surroundings outside the system. In other words, energy cannot be created or destroyed. If heat flows into a system or the surroundings do work on it, the internal energy increases and the sign of q and w are positive. Conversely, heat flow out of the system or work done by the system (on the surroundings) will be at the expense of the internal energy, and q and w will therefore be negative.

1.13 State Function and Path Function

A **state variable** is a variable that depends only on the final and initial states of a system and not on the path connecting these states. Internal energy and enthalpy are examples of state functions. State variables can be calculated by exact differentials.

A **path variable** is a variable that depends on the sequence of steps that takes the system from the initial state to the final state. This sequence of steps is called the **path**. Heat and work are examples of path variables.

1.14 Types of Properties

Thermodynamic properties are divided into two broad types:

Intensive properties and extensive properties.

An extensive property is any property that depends on the size (or extent) of the system under consideration. Volume is an example. Mass is another. An intensive property is any property that can exist at a point in space. Temperature, pressure and density are good examples.

1.15 Constant flow processes - an open system in steady state

Consider a smooth flowing fluid. Define a system comprising a volume of space in a constant flow process, bounded at its sides by stream lines and two cross sections A1 and A2 perpendicular to the direction of flow at its ends (see figure). The bounding surface along the stream lines could be the walls of a vessel, or any imaginary surface parallel to the steady flow. The properties of the fluid are assumed constant over the cross-sections A1 and A2. This system has constant mass, so we can work with per-unit-mass “intensive” variables. Consider the energy balance. The fluid entering the system does work P_1 per unit volume of fluid crossing the surface; this work is done on the fluid already in the system. Per unit mass of fluid entering, the work is P_1/ρ_1 , where ρ_1 is the density of the fluid at A1. Similarly the system does work $-P_2/\rho_2$ on the surroundings at A2. The total energy entering and leaving the fixed volume is the sum of the kinetic energy, the internal energy and the potential energy of the fluid (all per unit mass), plus the work done by/on the surroundings.

1.16 Reversible and Irreversible processes

A reversible process can be represented by a continuous line and arrow on an indicator diagram.

An irreversible process cannot be represented by a continuous line on an indicator diagram. Such a process may be represented on the graph by a sequence of circles between equilibrium states but only the end points are well-defined. In particular if the process is not quasistatic (for example if a piston moves too quickly temperature and pressure gradients might be set up) the values of the state variables will not be uniform and therefore pressure and density cannot be defined for the whole sample.

1.17 Work done during a reversible change of volume of a fluid

This could be the response to a gradual change in force on a piston or to slow heating (a change in temperature). The area A of the piston multiplied by the pressure P of the fluid balances the force F on the piston $F = P A$. The fluid expands or contracts quasistatically, with the piston moving infinitesimal distances dx much more slowly than the time the system take to reach equilibrium at the new volume. The infinitesimal amount of work done reversibly by the system on its surroundings is $P A dx = P dV$. For a finite quasistatic change in volume from V_1 to V_2 , Is given by

The total work done on the surroundings is: work done on surroundings = $\int_1^2 P dV$



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LAWS OF THERMODYNAMICS

2.1 Thermodynamic Laws

Heat Engines and Second Law Statements: The First Law provides a constraint on the total energy contained in a system and its surroundings. If it disappears in one form from the system during any thermodynamic process of change, it must reappear in another form either within the system or in the surroundings.

2.2 Limitations of First law of thermodynamics:

The first law provides no constraint on the possible direction a process may take place. Nevertheless, in the real world such constraints do exist. For example, heat always flows from a high temperature body to one at a lower temperature. Momentum flow is always prompted in the direction of a pressure gradient, and molecules always migrate from a region of higher to lower chemical potential. These observations clearly are indicative of the existence of a constraint on natural processes, which have never been found to be violated.

Further, it is common observation that work is readily transformed into other forms of energy, including heat. But all efforts to develop a device that may work in a continuous manner and convert heat completely into work or any other form of energy have proved impossible. Experimental observations show that typically no more than 40-50% of the total heat available may be converted to work or other energy forms.

This finding has led to the conclusion that heat is a lower form of energy in that while it may be feasible to “degrade” work to heat, it is impossible to “upgrade” heat completely into work. Heat may be seen as a more primitive form of energy, as it always has to be made available from matter (say by combustion) and subsequently converted to work for carrying out activities useful to humans. In this sense one never derives work directly from the energy locked in matter as enthalpy. This prompts the natural question: what determines the efficiency of such a conversion of heat to work? Evidently one needs a limiting principle that may help answer this question. These considerations provide the basis for formulating the Second Law of Thermodynamics

2.3 Second Law Statements

It need be mentioned that the second law is a product of experiential observations involving heat engines that powered the Industrial Revolution of the 19th century .A heat engine is a machine that produces work from heat through a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically goes through a series of steps in a cyclic manner as follows:

Step 1: Liquid water at ambient temperature is pumped into a boiler operating at high pressure century.

Step 2: Heat released by burning a fossil fuel is transferred in the boiler to the water, converting it to steam at high-temperature and pressure

Step 3: The energy contained in the steam is then transferred as shaft work to a turbine; during this process steam temperature and pressure are reduced.

Step 4: Steam exiting the turbine is converted to water by cooling it and transferring the heat released to the surroundings. The water is then returned to step 1.

Like the steam power plant all heat engines absorb heat at a higher temperature body (source) and release a fraction of it to a low temperature body (sink), the difference between the two quantities constitutes the net work delivered during the cycle. As in the case of the steam cycle, a series of heat and work exchanges takes place, in each case a specific hot source and a cold sink are implicated.

There are indeed a large number other types of practical heat engines and power cycles. Select examples include: Ericsson Cycle, Stirling cycle, Otto cycle (e.g. Gasoline/Petrol engine, high-speed diesel engine), Diesel cycle (e.g. low-speed diesel engine), etc. The Rankine cycle most closely reproduces the functioning of heat engines that use steam as the process fluid function; such heat engines are most commonly found in power generation plants. In such plants typically heat is derived from nuclear fission or the combustion of fossil fuels such as coal, natural gas, and oil. Detailed thermodynamic analysis of the various heat engine cycles may be found in a number of textbooks (for example: J.W. Tester and M. Modell, Thermodynamics and its Applications, 3rd ed., Prentice Hall, 1999)

As evident, the operation of practical heat engines requires two bodies at constant differential temperature levels. These bodies are termed heat reservoirs; they essentially are bodies with – theoretically speaking – infinite thermal mass (i.e., $m_{CP} \rightarrow \infty$) which therefore

do not undergo a change of temperature due to either release or absorption of heat. The above considerations may be converted to a set of statements that are equivalent descriptors of the second law (R. Balzheiser, M. Samuels, and J. Eliassen, Chemical Engineering Thermodynamics, Prentice Hall, 1972):

Kelvin-Planck Statement: It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

Clausius Statement: It is impossible to devise a cyclically operating device, the sole effect of which is to transfer energy in the form of heat from a low temperature body to a high temperature body.

2.4 Carnot Heat Engine Cycle and the 2nd Law

In theory we may say that a heat engine absorbs a quantity of heat Q_H from a high temperature reservoir at T_H and rejects amount of heat Q_C to a colder reservoir at T_C . It follows that the net work W delivered by the engine.

Of the various forms of heat engines ideated, the Carnot engine proposed in 1824 by the French engineer Nicholas Leonard Sadi Carnot (1796-1832), provides a fundamental reference concept in the development of the second law.

- Step 1: A system at the temperature of a cold reservoir T_C undergoes a reversible adiabatic compression which raises its temperature to that of a hot reservoir at T_H
- Step 2: While in contact with the hot reservoir the system absorbs Q_H amount of heat through an isothermal process during which its temperature remains at T_H
- Step 3: The system next undergoes a reversible adiabatic process in a direction reverse of step 1 during which its temperature drops back to T_C
- Step 4: A reversible isothermal process of expansion at T_C , transfers Q_C amount of heat to the cold reservoir and the system state returns to that at the commencement of step 1.

The Carnot engine, therefore, operates between two heat reservoirs in such a way that all heat exchanges with heat reservoirs occur under isothermal conditions for the system and at the temperatures corresponding to those of the reservoirs. This implies that the heat transfer occurs under infinitesimal temperature gradients across the system boundary, and hence these processes are reversible. If in addition the isothermal and adiabatic processes are also carried out under mechanically reversible (quasi-static) conditions the cycle operates in a fully reversible manner. It follows that any other heat engine operating on a different cycle (between two heat reservoirs) must necessarily transfer heat across finite temperature differences and therefore cannot be thermally reversible. Irreversibility also derives from the existence of dissipative forces in nature, which essentially leads to waste of useful energy in the conversion of work to heat. It follows therefore the Carnot cycle (which also comprises mechanically reversible processes) offers the maximum efficiency possible. This conclusion may also be proved more formally (see K. Denbigh, Principles of Chemical Equilibrium, 4th ed., Cambridge University Press, 1981).

Further for the adiabatic paths xy and zw one may easily derive the following equality:

$$|Q_H| = RT_H \ln \frac{V_x}{V_w}$$

$$\text{And } |Q_C| = RT_C \ln \frac{V_y}{V_z}$$

2.5 ENTROPY OF THE SYSTEM

In thermodynamics, entropy (usual symbol S) is a measure of the number of specific realizations or microstates that may realize a thermodynamic system in a defined state specified by macroscopic variables. Most understand entropy as a measure of molecular disorder within a macroscopic system. The second law of thermodynamics states that an isolated system's entropy never decreases. Such a system spontaneously evolves towards thermodynamic equilibrium, the state with maximum entropy. Non-isolated systems may lose entropy, provided they increase their environment's entropy by that increment. Since entropy is a state function, the change in entropy of a system is constant for any process with known initial and final states. This applies whether the process is reversible or irreversible. However, irreversible processes increase the combined entropy of the system and its environment. The change in entropy (ΔS) of a system was originally defined for a thermodynamically reversible process as

$$\Delta S = nR \ln \frac{V}{V_0} = -nR \ln \frac{P}{P_0}.$$

$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T}$$

2.6 ENTROPY CHANGE FOR SIMPLE PROCESS

For certain simple transformations in systems of constant composition, the entropy changes are given by simple formulas.

Isothermal expansion or compression of an ideal gas

For the expansion (or compression) of an ideal gas from an initial volume V_0 and pressure P_0 to a final volume V and pressure P at any constant temperature, the change in entropy is given by:

Here n is the number of moles of gas and R is the ideal gas constant. These equations also apply for expansion into a finite vacuum or a throttling process, where the temperature, internal energy and enthalpy for an ideal gas remain constant.

COOLING AND HEATING

For heating or cooling of any system (gas, liquid or solid) at constant pressure from an initial temperature T_0 to a final temperature T , the entropy change is

$$\Delta S = nC_P \ln \frac{T}{T_0}.$$

provided that the constant-pressure molar heat capacity (or specific heat) C_P is constant and that no phase transition occurs in this temperature interval.

Similarly at constant volume, the entropy change is

$$\Delta S = nC_v \ln \frac{T}{T_0},$$

where the constant-volume heat capacity C_v is constant and there is no phase change.

At low temperatures near absolute zero, heat capacities of solids quickly drop off to near zero, so the assumption of constant heat capacity does not apply.

Since entropy is a state function, the entropy change of any process in which temperature and volume both vary is the same as for a path divided into two steps - heating at constant volume and expansion at constant temperature. For an ideal gas, the total entropy change is

$$\Delta S = nC_v \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0}.$$

Similarly if the temperature and pressure of an ideal gas both vary,

$$\Delta S = nC_P \ln \frac{T}{T_0} - nR \ln \frac{P}{P_0}.$$

PHASE TRANSITIONS

Reversible phase transitions occur at constant temperature and pressure. The reversible heat is the enthalpy change for the transition, and the entropy change is the enthalpy change divided by the thermodynamic temperature. For fusion (melting) of a solid to a liquid at the melting point T_m , the entropy of fusion is

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m}.$$

2.7 ENTROPY CHANGE FOR MIXING

In ideal materials, intermolecular forces are the same between every pair of molecular kinds, so that a molecule "feels" no difference between itself and its molecular neighbours. This is the reference case for examining corresponding mixings of non-ideal materials.

For example, two ideal gases, at the same temperature and pressure, are initially separated by a dividing partition.

Upon removal of the dividing partition, they expand into a final common volume (the sum of the two initial volumes), and the entropy of mixing ΔS_{mix} is given by

$$\Delta S_{\text{mix}} = -nR(x_1 \ln x_1 + x_2 \ln x_2).$$

where R is the gas constant, n the total number of moles and x_i the mole fraction of component i , which initially occupies volume $V_i = x_i V$. After the removal of the partition, $n_i = nx_i$ the moles of component i may explore the combined volume V , which causes an

entropy increase equal to $nx_i R \ln(V/V_i) = -nR x_i \ln x_i$ for each component gas.

In this case, the increase in entropy is due entirely to the irreversible processes of expansion of the two gases, and involves no heat or work flow between the system and its surroundings.

Gibbs free energy of mixing

The Gibbs free energy change $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$ determines whether mixing at constant (absolute) temperature T and pressure P is a spontaneous process. This quantity

combines two physical effects—the enthalpy of mixing, which is a measure of the energy change, and the entropy of mixing considered here.

For an ideal gas mixture or an ideal solution, there is no enthalpy of mixing (ΔH_{mix}), so that the Gibbs free energy of mixing is given by the entropy term only:

$$\Delta G_{mix} = -T\Delta S_{mix}$$

For an ideal solution, the Gibbs free energy of mixing is always negative, meaning that mixing of ideal solutions is always spontaneous. The lowest value is when the mole fraction is 0.5 for a mixture of two components, or $1/n$ for a mixture of n components.

2.8 CLAUSIUS INEQUALITY

Since the concept irreversibility plays a crucial role in the thermodynamics, it is necessary for us to find an approach to determine whether the process is reversible or not. And the most well-known Clausius Inequality provides us this possibility. Imagine that we have a reversible engine which consists of more than two heat reservoirs. We know from the Carnot Principles that between the same reservoirs (one is a constant temperature source and the other a constant temperature sink), the efficiency of a reversible heat engine is always greater than the efficiency of an irreversible one. Hence, for the maximum efficiency, Carnot efficiency, all the heat transfer must take place at highest and lowest reservoir temperatures. In other words, heat is absorbed from temperature source with T_H and released to temperature sink with T_L by heat engine during each sub process. Now we draw an arbitrary reversible cycle process operated by the engine in p-v diagram. We can divide this cycle process into infinite small Carnot process reversible isothermal expansion at T_1 ; Heat q_1 is absorbed. : reversible adiabatic expansion. : reversible isothermal compression at T_2 ; Heat q_2 is released. : reversible adiabatic compression.

2.9 MATHEMATICAL STATEMENT OF 2ND LAW OF THERMODYNAMICS

Consider a mechanically irreversible adiabatic between two equilibrium states X and Y. This path is reproduced as a broken line between points. Next the fluid is returned to the original state by means two sequential processes: (i) a mechanically reversible adiabatic process Y-Z, and then (ii) a reversible isobaric compression Z-X. Assuming that the mechanically irreversible process X-Y leads to an entropy change, heat transfer must occur during process Z-X (since none occurs on Y-Z). This is because for the reversible return path the same entropy change must occur as between X to Y. Since the return path

$$dQ_{rev} = TdS.$$

Thus, integrating this expression for the return path:

$$\Delta S^t = \int_Y^X dS^t = S_X^t - S_Y^t = \int_Y^X \frac{dQ_{rev}}{T}$$

For the entire cycle we must have $\Delta U^t = 0$. Thus, net total work during the cycle may be written as: $W^t = -Q_{rev}$. However, since (as depicted by the P-V diagram) a net work would need to be done on the system over the cycle, it follows that $W^t > 0$; hence $Q_{rev} < 0$. Therefore, using eqn.

$$S_X^t - S_Y^t = \int_Y^X \frac{dQ_{rev}}{T} < 0,$$

that is: $S_X^t < S_Y^t$. This implies that the entropy change for the original irreversible step A to B, we have

we have: $\Delta S^t = S_Y^t - S_X^t > 0$. Therefore, we conclude that the original irreversible step is accompanied by a *positive* change of entropy. It may be additionally shown that if the original process occurred through *irreversible heat transfer* process an increase of entropy would result likewise.

what change in a system is thermodynamically feasible? The second law provides answer to this, i.e., a process can only proceed in a direction that results in a positive change in the *total* entropy of the universe, the limiting value of zero being attained only by a fully reversible process. The corollary to this is: *no process is possible for which the total entropy of the universe decreases*



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UNIT – III -Chemical Engineering Thermodynamics-I– SCHA1202

THERMODYNAMIC EQUATIONS OF STATE

An equation of state is an equation which relates the variables of state (T, P, V, and n). It's particularly useful when you want to know the effect of a change in one of the variables of state

Solids and Liquids: If the pressure on a solid or liquid is increased, the volume does not change much. If the temperature is increased, the volume doesn't change much either. Therefore, an appropriate equation of state describing such systems would be: $V(T,P) = \text{constant}$.

Gases: In contrast, changing the pressure or temperature of a gas will have an easily observable effect on the volume of that gas. For an **ideal gas** (no intermolecular interactions and no molecular volume) an appropriate equation of state would be: $V(T,P,n) = (nRT)/P$.

- There are many equations of state describing **real gases**. These equations take in consideration molecular volume and interactions. The most well-known such equations is probably the Van der Waals equation.

3.1 Ideal and real gases

An ideal gas is one which follows the ideal gas equation of state, namely

$$PV = (m/M) (MR) T = n R_u T$$

The universal gas constant has a value of 8.314 J/mol K or kJ/kmol K and is related to the specific gas constant by the relation $R_u = (R /M)$

The ideal gas equation of state can be derived from the kinetic theory of gases where the following assumptions are made:

1. The molecules are independent of each other. In other words, there are no attractive forces between the molecules.
2. The molecules do not occupy any volume. That is the volume occupied by the molecules is quite negligible compared to the volume available for motion of the molecules.

The internal energy of an ideal gas is a function of temperature only and is independent of pressure and volume. That is,

$$u = u(T)$$

$$(\partial u / \partial P)_T = 0, (\partial u / \partial v)_T = 0$$

3.2 Enthalpy and specific heat

$$h = u + Pv$$

For an ideal gas $u = u(T)$ only and $PV = mRT$ and hence $h = h(T)$ only.

The specific heat at constant volume is defined as the amount of energy transferred as heat at constant volume, per unit mass of a system to raise its temperature by one degree. That is,

$$C_V = (dq/dT)_V$$

The specific heat at constant pressure is defined as the energy transferred as heat at constant pressure, per unit mass of a substance to raise its temperature by one degree. That is

$$C_P = (dq/dT)_P$$

For a constant pressure process $dq = du + dw = du + Pd v = du + Pd v + v dP$ (since $dP=0$ for a constant pressure process)

$$\text{Or } dq = du + d(Pv) = d(u + Pv) = dh$$

$$\text{or } dq = dh$$

$$C_P = (\partial h / \partial T)_P$$

The ratio of specific heat (γ) is given by

$$\gamma = C_P / C_V$$

For mono-atomic ideal gases $\gamma = 1.67$ and for diatomic gases $\gamma = 1.4$.

3.3 Relation between two specific heats:

The two specific heats are related to each other.

$$h = u + Pv \text{ or } dh = du + d(Pv)$$

For an ideal gas, the above equation reduces to

$$dh = du + d(RT) = du + RdT \text{ or}$$

$$dh/dT = du/dT + R \text{ or } C_p = C_v + R$$

or $C_p - C_v = R$ for an ideal gas.

$$\gamma = C_p / C_v \text{ or } C_p = R/(\gamma - 1) \text{ and } C_v = R\gamma/(\gamma - 1)$$

3.4 Real gases:

The ideal gas law is only an approximation to the actual behavior of gases.

At high densities, that is at high pressures and low temperatures, the behavior of actual or real gases deviate from that predicted by the ideal gas law. In general, at sufficiently low pressures or at low densities all gases behave like ideal gases.

3.5 Van der Waals Equation of State

An equation of state taking account the volume occupied by the molecules and the attractive forces between them.

$$(P + a/v^2)(v - b) = RT$$

where a and b are van der Waals constants.

The equation is cubic in volume and in general there will be three values of v for given values of T and P.

However in some range of values of P and T there is only one real value v.

For $T > T_c$ (critical temperature) there will be only one real value of v and for $T < T_c$ there will be three real values.

In Figure, the solid curve represents the value predicted by the van der Waals equation of state and the points represent the experimentally determined values.

It can be observed that at temperatures greater than critical, there is only one real value of volume for a given P and T.

However at temperatures less than the critical, there are three real values of volume for a given value of P and T.

The experimental values differ from those predicted by van der Waals equation of state in region

2345 if $T < T_c$.

One can use the criterion that the critical isotherm (isotherm passing through the critical point) shows a point of inflexion. Stated mathematically

$$(\partial P / \partial v)_{T=T_c} = 0 \text{ and } (\partial^2 P / \partial v^2)_{T=T_c} = 0$$

$$(\partial P / \partial v)_{T=T_c} = -RT_c / (v_c - b)^2 + 2a / v_c^3 = 0$$

or

$$RT_c / (v_c - b)^2 = 2a / v_c^3$$

$$(\partial^2 P / \partial v^2)_{T=T_c} = 2RT_c / (v_c - b)^3 - 6a / v_c^4 = 0$$

or

$$2RT_c / (v_c - b)^3 = 6a / v_c^4$$

Therefore

$$2 / (v_c - b) = 3 / v_c \text{ or } v_c = 3b$$

At the critical point, the van der Waal's equation is given by

$$P_c = RT_c / (v_c - b) - a / v_c^2$$

From these equations,

$$a = 27R^2 T_c^2 / 64 P_c \text{ and } b = RT_c / 8P_c$$

Reference	Equations of state
Redlich-Kwong (1949)	$P = \frac{RT}{V-b} - \frac{a}{V(V+b)T^{0.5}}$
Soave-Redlich-Kwong (1972)	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$
Peng-Robinson (1976)	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$
Stryjek-Vera-Peng-Robinson (1986)	$P = \frac{RT}{V-b} - \frac{a(\theta, T)}{V(V+b)+b(V-b)}$
Patel-Teja (1982)	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$

Reduced pressure, $P_R = P/P_C$,

Reduced temperature, $T_R = T/T_C$

Reduced volume, $v_R = v/v_C$

Where P_C , T_C and v_C denote the critical pressure, temperature and volume respectively.

These equations state that the reduced property for a given state is the value of this property in this state divided by the value of this same property by at the critical point.

The striking fact is that when such Z versus P_R diagrams are prepared for a number of different substances, all of them very nearly coincide, especially when the substances have simple, essentially spherical molecules.

We need to know only critical temperature and critical pressure to use this basic generalized chart.

In general it can be noted that idealized gas behavior for very low pressures as compared to critical) regardless of temperature. Furthermore, at high temperatures (greater than twice T_C), the ideal-gas model can be assumed to good accuracy to pressures as high as 4-5 times P_C .

The term saturation temperature designates the temperature at which vaporization takes place.

For water at 99.6 C the saturation pressure is 0.1 M Pa, and for water at 0.1 Mpa, the saturation temperature is 99.6 C.

If a substance exists as liquid at the saturation temperature and pressure it is called saturated liquid.

If the temperature of the liquid is lower than saturation temperature at the existing pressure it is called sub-cooled liquid or compressed liquid.

1. When a substance exists as part liquid and part vapor at the saturation temperature, its quality is defined as the ratio of the mass of vapor to the total mass.
2. If a substance exists as vapor at the saturation temperature, it is called a saturated vapor.
3. When the vapor is at a temperature greater than the saturation temperature, it is said to exist as superheated vapor.
4. At the critical point, the saturated liquid and saturated vapor state are identical.
5. At supercritical pressures, the substance is simply termed fluid rather than liquid or vapor.
6. If the initial pressure at -20°C is 0.260 kPa, heat transfer results in increase of temperature to -10°C . Ice passes directly from the solid phase to vapor phase.
7. At the triple point (0.6113 kPa) and a temperature of -20°C , let heat transfer increase the temperature until it reaches 0.01°C . At this point, further heat transfer may cause some ice to become vapor and some to become liquid. The three phases may be present simultaneously in equilibrium.

3.6 Tables of Thermodynamic Properties

Tables of thermodynamic properties of many substances are available, and in general, all these have same form.

Steam tables are selected because steam is used extensively in power plants and industrial processes.

The steam tables provide the data of useful thermodynamic properties like T , P , v , u , h and s for saturated liquid, saturated vapor and superheated vapor.

Since the properties like internal energy, enthalpy and entropy of a system cannot be directly measured; they are related to change in the energy of the system.

Hence one can determine Δu , Δh , Δs , but not the absolute values of these properties. Therefore it is necessary to choose a reference state to which these properties are arbitrarily assigned some numerical values.

For water, the triple point ($T = 0.01^{\circ}\text{C}$ and $P = 0.6113\text{ kPa}$) is selected as the reference state, where the internal energy and entropy of saturated liquid are assigned a zero value.

In the saturated steam tables, the properties of saturated liquid that is in equilibrium with saturated vapor are presented.

During phase transition, the pressure and temperature are not independent of each other. If the temperature is specified, the pressure at which both phases coexist in equilibrium is equal to the saturation pressure.

Hence, it is possible to choose either temperature or pressure as the independent variable, to specify the state of two-phase system.

Depending on whether the temperature or pressure is used as the independent variable, the tables are called temperature or pressure tables.

The two phases- liquid and vapor can coexist in a state of equilibrium only up to the critical point.

Therefore the listing of the thermodynamic properties of steam in the saturated steam tables ends at the critical point (374.15°C and 212.2 bar).

If the steam exists in only one phase (superheated steam), it is necessary to specify two independent variables, pressure and temperature, for the complete specification of the state. In the superheated steam tables, the properties- v , u , h , and s - are tabulated from the saturation temperature to some temperature for a given pressure.

The thermodynamic properties of a liquid and vapor mixture can be evaluated in terms of its quality. In particular, the specific volume, specific internal energy, specific enthalpy and specific entropy of a mixture of quality X are given by

$$v = (1-X)v_f + Xv_g, u = (1-X)u_f + Xu_g, h = (1-X)h_f + Xh_g = h_f + Xh_{fg}, s = (1-X)s_f + Xs_g$$

where $h_{fg} = h_g - h_f$ = latent heat of vaporization.

3.7 Temperature-volume diagram

The locus of all the saturated states gives the saturated liquid curve AC and the locus of all the saturated vapor states gives the saturated vapor curve BC.

The point C represents the critical point. The difference between v_g and v_f reduces as the pressure is increased, and at the critical point $v_g = v_f$.

At the critical point, the two phases-liquid and vapor- are indistinguishable.

3.8 Pressure-volume diagram

The pressure-volume (P-V) diagram for a pure substance is shown in Figure. The curves AC and BC represent the saturated liquid curve and saturated vapor curve, respectively, and C is critical point.

The area under the curve represents the two-phase region. Any point M in this region is a mixture of saturated liquid (shown as f) and saturated vapor (g).

3.9 Mollier (h-s) Diagram

The h-s diagram was introduced by Richard Mollier and was named after him.

It consists of a family of constant pressure lines, constant temperature lines and constant volume lines plotted on enthalpy versus entropy coordinates.

In the two-phase region, the constant pressure and constant temperature lines coincide.

3.10 Polytropic Process

$$W = \int p dv = \int p v^n \frac{dv}{v}$$

$$w = (P_1 v_1 - P_2 v_2)/(n-1)$$

$$du = dq - dw$$

$$u_2 - u_1 = q - (P_1 v_1 - P_2 v_2)/(n-1)$$

$$u_2 - u_1 = C_v (T_2 - T_1) = q - w$$

$$q = R(T_2 - T_1)/(\gamma - 1) + (P_1 v_1 - P_2 v_2)/(n-1)$$

$$= R (T_1 - T_2) \{1/(n-1) - 1/(\gamma - 1)\}$$

$$= (P_1 v_1 - P_2 v_2)/(n-1) \{(\gamma - n)/(\gamma - 1)\}$$

$$= w \cdot \{(\gamma - n)/(\gamma - 1)\}$$

Problem: Air (ideal gas with $\gamma = 1.4$) at 1 bar and 300K is compressed till the final volume is one-sixteenth of the original volume, following a polytropic process $Pv^{1.25} = \text{const.}$ Calculate (a) the final pressure and temperature of the air, (b) the work done and (c) the energy transferred as heat per mole of the air.

Solution: (a) $P_1 v_1^{1.25} = P_2 v_2^{1.25}$

$$P_2 = P_1 (v_1/v_2)^{1.25} = 1(16)^{1.25} = \mathbf{32 \text{ bar}}$$

$$T_2 = (T_1 P_2 v_2)/(P_1 v_1) = (300 \times 32 \times 1)/(1 \times 16)$$

$$= \mathbf{600K}$$

(b) $w = (P_1 v_1 - P_2 v_2)/(n-1)$

$$= R_u (T_1 - T_2)/(n-1)$$

$$= 8.314 (300 - 600)/(1.25-1) = \mathbf{-9.977 \text{ kJ/mol}}$$

(c)

$$= -9.977 (1.4 - 1.25)/(1.4-1)$$

$$= -3.742 \text{ kJ/mol}$$

Problem: A rigid and insulated container of 2m^3 capacity is divided into two equal compartments by a membrane. One compartment contains helium at 200kPa and 127°C while the second compartment contains nitrogen at 400kPa and 227°C . The membrane is punctured and the gases are allowed to mix. Determine the temperature and pressure after equilibrium has been established. Consider helium and nitrogen as perfect gases with their C_V as $3R/2$ and $5R/2$ respectively.

Solution: Considering the gases contained in both the compartments as the system, $W=0$ and $Q=0$. Therefore, $\Delta U = 0$ ($U_2 = U_1$)

$$\text{Amount of helium} = N_{\text{He}} = P_A V_A / R_u T_A$$

$$= 200 \times 10^3 \times 1 / (8.314 \times 400)$$

$$= 60.14 \text{ mol.}$$

$$\text{Amount of nitrogen} = N_{\text{N}_2} = P_B V_B / R_u T_B$$

$$= 400 \times 10^3 \times 1 / (8.314 \times 500)$$

$$= 96.22 \text{ mol.}$$

Let T_f be the final temperature after equilibrium has been established. Then,

$$[N C_V (T_f - 400)]_{\text{He}} + [N C_V (T_f - 500)]_{\text{N}_2} = 0$$

$$R_u [60.14 (T_f - 400)^3 + 96.22 (T_f - 500)^5] / 2 = 0$$

$$\text{Or, } T_f = 472.73 \text{ K}$$

The final pressure of the mixture can be obtained by applying the equation of state:

$$P_f V_f = (N_{\text{He}} + N_{\text{N}_2}) R_u T_f$$

$$2 P_f = (60.14 + 96.22) 8.314 (472.73)$$

$$\text{or, } P_f = 307.27 \text{ kPa}$$



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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV -Chemical Engineering Thermodynamics-I– SCHA1202

THERMODYNAMIC FORMULATIONS

4.1 Properties

4.1.1 Reference Properties

Property which enable us to define the state of the system.

Eg., Temperature, Pressure, Volume

4.1.2 Energy Properties

Properties in which the changes in thermodynamic functions such as Internal energy, enthalpy etc.,

Eg., Gibbs free energy, Helmholtz energy

4.1.3 Derived Properties

Properties which are derived mathematically from reference and energy properties.

Eg., Specific heat

4.2 Thermodynamic Property Relations

Apart from internal energy and enthalpy, two other ones that are particularly useful in depiction of thermodynamic equilibrium are Helmholtz free energy (A) and Gibbs free energy (G). We defer expanding upon the concept of these two types of energies to chapter 6; however, we state their definition at this point as they are instrumental in the development of property correlations for real fluids.

- Specific Helmholtz free energy: $A = U - TS$

- Specific Gibbs free energy: $G = H - TS$

$$dU = dQ + dW$$

$$dU = TdS - PdV$$

$H = U + PV$ and taking a total differential of both sides:

4.3 Relation between C_p and C_v

C_p and C_v are related to each other and their difference can be calculated from an equation of state.

$$C_p = C_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p.$$

Let's begin with the definitions of C_p and H .

$$\begin{aligned} C_p &= \left(\frac{\partial H}{\partial T} \right)_p \\ &= \left(\frac{\partial [U + pV]}{\partial T} \right)_p \\ &= \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p. \end{aligned}$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV.$$

Divide the above equation by dT and keeping p constant

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p.$$

$$\begin{aligned} C_p &= \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \\ &= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p. \end{aligned}$$

But

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

$$\begin{aligned} C_p &= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \\ &= \left(\frac{\partial U}{\partial T}\right)_V + \left(T \left(\frac{\partial p}{\partial T}\right)_V - p\right) \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \\ &= C_V + T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \\ &= C_V + T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p, \end{aligned}$$

Which is the desired result. We will let the reader show, using Euler's chain relation and the definitions of α and κ , that this relation can be rewritten as

$$C_p = C_V + TV \frac{\alpha^2}{\kappa}.$$

4.4 Maxwell's Relation

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

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p$$

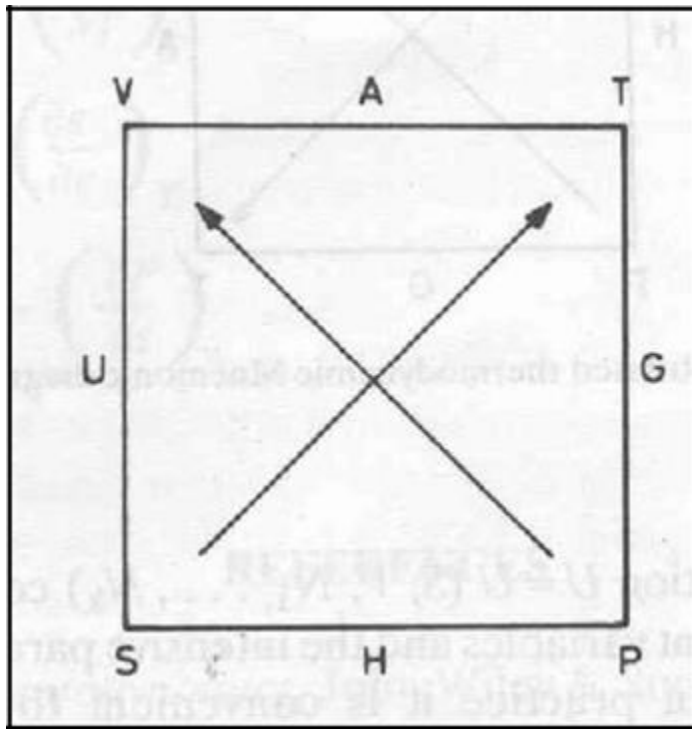
$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T$$

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

4.5 Mnemonic Diagram

The differential expressions for the thermodynamic potentials and Maxwell relations can be remembered conveniently in terms of a thermodynamic Mnemonic diagram.

The diagram consists of a square with two diagonal arrows pointing upwards and the thermodynamic potentials in alphabetical order clockwise on the sides as shown in figure. The natural variables associated with each potential are placed in the corners.



Diagonal arrows indicate the coefficients associated with the natural variables in the differential expression of the potential. The sign of the coefficient depends on whether the arrow is pointing towards (-ve) or away from the natural variable (+ve).

$$du = (\text{sign})(\text{coeff.}) ds + (\text{sign})(\text{coeff.}) dv$$

$$du = (\text{sign})Tds + (\text{sign})Pdv$$

$$du = +Tds - Pdv$$

To write the Maxwell relations we need to concentrate on the direction of the arrows and the natural variables only.

If both the arrows pointing in the same direction, there is no need to change the sign, otherwise the equation should carry a negative sign.

4. 6 Flow through nozzles

A *nozzle* is a duct that increases the velocity of the flowing fluid at the expense of pressure drop. A duct which decreases the velocity of a fluid and causes a corresponding increase in pressure is a *diffuser* . The same duct may be either a nozzle or a diffuser depending upon the end conditions across it. If the cross-section of a duct decreases gradually from inlet to exit, the duct is said to be convergent. Conversely if the cross section increases gradually from the inlet to exit, the duct is said to be divergent. If the cross-section initially decreases and then increases, the duct is called a convergent-divergent nozzle. The minimum cross-section of such ducts is known as throat. A fluid is said to be *compressible* if its density changes with the change in pressure brought about by the flow. If the density does not changes or changes very little, the fluid is said to be incompressible. Usually the gases and vapors are compressible, whereas liquids are *incompressible* .

4.6.1 Stagnation, Sonic Properties And Isentropic Expansion In Nozzle

The stagnation values are useful reference conditions in a compressible flow. Suppose the properties of a flow (such as T, p, ρ etc.) are known at a point. The stagnation properties at a point are defined as those which are to be obtained if the local flow were imagined to cease to zero velocity is entropically. The stagnation values are denoted by a subscript zero. Thus, the stagnation enthalpy is defined as

For a calorically perfect gas, this yields,

$$c_p T_0 = c_p T + \frac{1}{2} V^2$$

$$h_0 = h + \frac{1}{2} V^2$$

which defines the stagnation temperature. It is meaningful to express the ratio of (T_0 / T) in the form
 If we know the local temperature (T) and Mach number (Ma), we can find out the stagnation temperature T_0 . Consequently, isentropic relations can be used to obtain stagnation pressure and stagnation density as.

In general, the stagnation properties can vary throughout the flow field.

However, if the flow is adiabatic, then $h + \frac{V^2}{2}$ is constant throughout the flow. It follows that the

h_0, T_0 and a_0 are constant throughout an adiabatic flow, even in the presence of friction. Here a is the speed of sound and the suffix signifies the stagnation condition. It is understood that all stagnation properties are constant along an isentropic flow. If such a flow starts from a large reservoir where the fluid is practically at rest, then the properties in the reservoir are equal to the stagnation properties everywhere in the flow.

There is another set of conditions of comparable usefulness where the flow is sonic, $Ma=1.0$.

These sonic, or critical properties are denoted by asterisks: p^*, ρ^*, a^* , and T^* . These properties are attained if the local fluid is imagined to expand or compress isentropically until it reaches $Ma=1$.

We have already discussed that the total enthalpy, hence T_0 , is conserved so long the process is adiabatic, irrespective of frictional effects. In contrast, the stagnation pressure p_0 and density ρ_0 decrease if there is friction.

From Equation, we note that

$$V^2 = 2c_p(T_0 - T)$$

$$V = \left[\frac{2\gamma R}{\gamma - 1} (T_0 - T) \right]^{\frac{1}{2}}$$

or,

is the relationship between the fluid velocity and local temperature (T), in an adiabatic flow. The flow can attain a maximum velocity of

$$V_{\max} = \left[\frac{2\gamma RT_0}{\gamma - 1} \right]^{\frac{1}{2}}$$

As it has already been stated, the unity Mach number, $Ma=1$, condition is of special significance in compressible flow, and we can now write from Eq.(18.2), (18.3) and (18.4).

1. At subsonic speeds ($Ma < 1$) a decrease in area increases the speed of flow. A subsonic nozzle should have a convergent profile and a subsonic diffuser should possess a divergent profile. The flow behaviour in the regime of $Ma < 1$ is therefore qualitatively the same as in incompressible flows.
2. In supersonic flows ($Ma > 1$), the effect of area changes are different. According to Eq. (19.4), a supersonic nozzle must be built with an increasing area in the flow direction. A supersonic diffuser must be a converging channel. Divergent nozzles are used to produce supersonic flow in missiles and launch vehicles.
3. Suppose a nozzle is used to obtain a supersonic stream starting from low speeds at the inlet (Fig.19.2). Then the Mach number should increase from $Ma=0$ near the inlet to $Ma > 1$ at the exit. It is clear that the nozzle must converge in the subsonic portion and diverge in the supersonic portion. Such a nozzle is called a *convergent-divergent nozzle*. A convergent-divergent nozzle is also called a *de Laval nozzle*, after Carl G.P. de Laval who first used such a configuration in his steam turbines in late nineteenth century (this has already been mentioned in the introductory note). Mach number must be unity at the throat, where the area is neither increasing nor decreasing. This is consistent with Eq. (19.4) which shows that dV

can be non-zero at the throat only if $Ma=1$. It also follows that the sonic velocity can be achieved only at the throat of a nozzle or a diffuser.

4.7 Compressors

There exist a large number of fluid machines in practice, that use air, steam and gas (the mixture of air and products of burnt fuel) as the working fluids. The density of the fluids change with a change in pressure as well as in temperature as they pass through the machines. These machines are called 'compressible flow machines' and more popularly 'turbomachines'. Apart from the change in density with pressure, other features of compressible flow, depending upon the regimes, are also observed in course of flow of fluids through turbomachines. Therefore, the basic equation of energy transfer (Euler's equation, as discussed before) along with the equation of state relating the pressure, density and temperature of the working fluid and other necessary equations of compressible flow, are needed to describe the performance of a turbomachine. However, a detailed discussion on all types of turbomachines is beyond the scope of this book. We shall present a very brief description of a few compressible flow machines, namely, compressors, fans and blowers in this module. In practice two kinds of compressors: centrifugal and axial are generally in use.

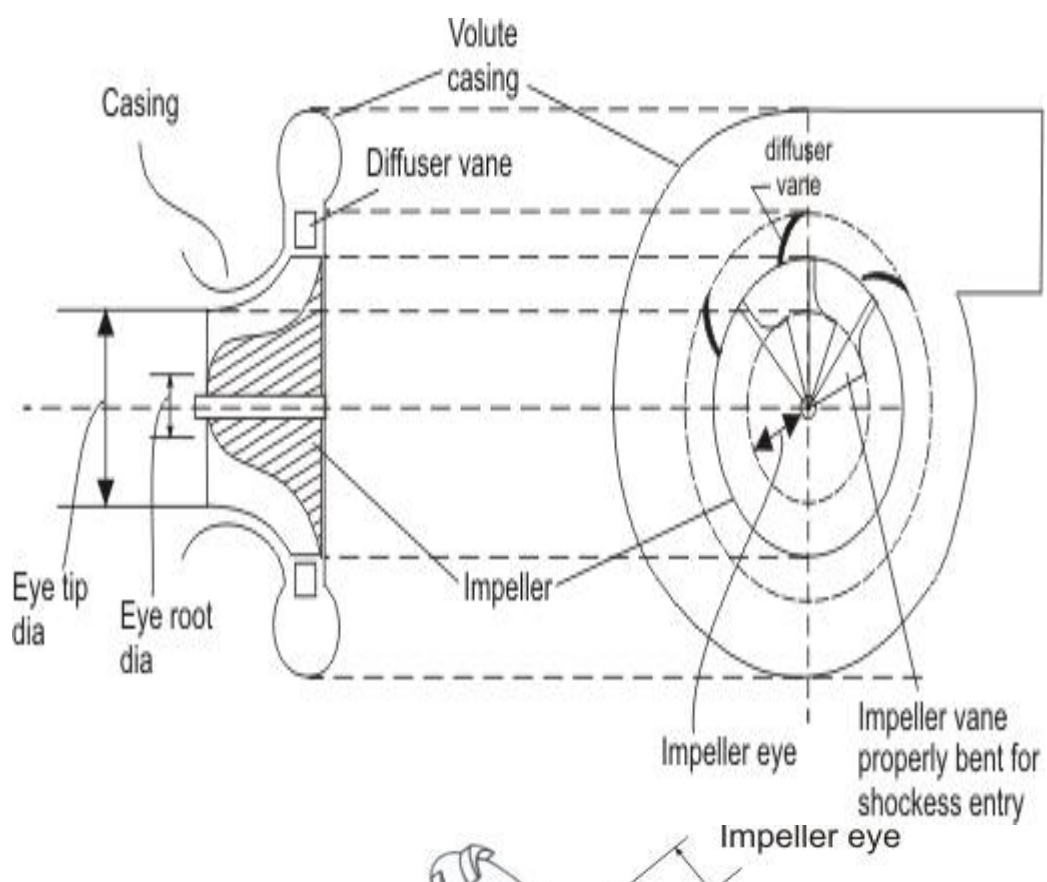
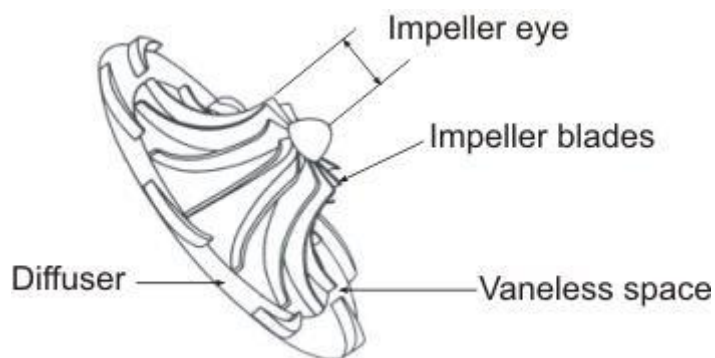
4.7.1 Centrifugal Compressors

A centrifugal compressor is a radial flow rotodynamic fluid machine that uses mostly air as the working fluid and utilizes the mechanical energy imparted to the machine from outside to increase the total internal energy of the fluid mainly in the form of increased static pressure head.

During the second world war most of the gas turbine units used centrifugal compressors. Attention was focused on the simple turbojet units where low power-plant weight was of great importance. Since the war, however, the axial compressors have been developed to the point where it has an appreciably higher isentropic efficiency. Though centrifugal compressors are not that popular today, there is renewed interest in the centrifugal stage, used in conjunction with one or more axial stages, for small turbofan and turboprop aircraft engines.

A centrifugal compressor essentially consists of three components.

1. A **stationary casing**
2. A **rotating impeller** as shown in Fig. 6.1 (a) which imparts a high velocity to the air. The impeller may be single or double sided as show in Fig. 6.1 (b) and (c), but the fundamental theory is same for both.
3. A **diffuser** consisting of a number of fixed diverging passages in which the air is decelerated with a consequent rise in static pressure.



4.7.2 Principle of operation

Air is sucked into the impeller eye and whirled outwards at high speed by the impeller disk. At any point in the flow of air through the impeller the centripetal acceleration is obtained by a pressure head so that the static pressure of the air increases from the eye to the tip of the impeller. The remainder of the static pressure rise is obtained in the diffuser, where the very high velocity of air leaving the impeller tip is reduced to almost the velocity with which the air enters the impeller eye.

Usually, about half of the total pressure rise occurs in the impeller and the other half in the diffuser. Owing to the action of the vanes in carrying the air around with the impeller, there is a slightly higher static pressure on the forward side of the vane than on the trailing face. The air will thus tend to flow around the edge of the vanes in the clearing space between the impeller and the casing. This results in a loss of efficiency and the clearance must be kept as small as possible. Sometimes, a shroud attached to the blades as shown in Figure.6.1(d) may eliminate such a loss, but it is avoided because of increased disc friction loss and of manufacturing difficulties.

The straight and radial blades are usually employed to avoid any undesirable bending stress to be set up in the blades. The choice of radial blades also determines that the total pressure rise is divided equally between impeller and diffuser.

Before further discussions following points are worth mentioning for a centrifugal compressor.

- (i) The pressure rise per stage is high and the volume flow rate tends to be low. The pressure rise per stage is generally limited to 4:1 for smooth operations.
- (ii) Blade geometry is relatively simple and small foreign material does not affect much on operational characteristics.
- (iii) Centrifugal impellers have lower efficiency compared to axial impellers and when used in aircraft engine it increases frontal area and thus drag. Multistaging is also difficult to achieve in case of centrifugal machines.

Compressors are used to move gases and vapors in situations where large pressure differences are necessary.

4.7.3 Types of Compressor

Compressors are classified by the way they work: dynamic (centrifugal and axial) or reciprocating. Dynamic compressors use a set of rotating blades to add velocity and pressure to fluid. They operate at high speeds and are driven by steam or gas turbines or electric motors. They tend to be smaller and lighter for a given service than reciprocating machines, and hence have lower costs.

Reciprocating compressors use pistons to push gas to a higher pressure. They are common in natural gas gathering and transmission systems, but are less common in process applications. Reciprocating compressors may be used when very large pressure differences must be achieved; however, since they produce a pulsating flow, they may need to have a receiver vessel to dampen the pulses.

The *compression ratio*, p_{out}/p_{in} , is a key parameter in understanding compressors and blowers. When the compression ratio is below 4 or so, a blower is usually adequate. Higher ratios require a compressor, or multiple compressor stages, be used.

When the pressure of a gas is increased in an adiabatic system, the temperature of the fluid must rise. Since the temperature change is accompanied by a change in the specific volume, the work necessary to compress a unit of fluid also changes. Consequently, many compressors must be accompanied by cooling to reduce the consequences of the adiabatic temperature rise. The coolant may flow through a jacket which surrounds the housing with liquid coolant. When multiple stage compressors are used, *intercooler* heat exchangers are often used between the stages.

4.7.4 Dynamic Compressors

Gas enters a centrifugal or axial compressor through a suction nozzle and is directed into the first-stage impeller by a set of guide vanes. The blades push the gas forward and into a diffuser section where the gas velocity is slowed and the kinetic energy transferred from the blades is converted to pressure. In a multistage compressor, the gas encounters another set of guide vanes and the compression step is repeated. If necessary, the gas may pass through a cooling loop between stages.

4.8 Entropy

The second law of thermodynamics states that all spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy. It also means that it is impossible for any self-acting machine to transfer energy from a given state to a higher state of availability. To make these statements quantitative there is required some function that always changes in a certain way during a spontaneous process and therefore, will characterise such a change. Internal energy was defined to give quantitative significance to the first law. Internal energy does not change in any characteristic way in a spontaneous process, and it does not help in any way in the development of the second law. The function that is fundamental in the development of the second law is *entropy*, which means transformability (change) in Greek, introduced by Clausius in 1851. Later in this chapter, we will show that the second law of thermodynamics necessitates that all spontaneous processes result in an increase in the entropy and no process is possible that results in a decrease in entropy.

As noted above, the entropy is a measure of the unavailability of the internal energy. Among the various forms, heat is the least available form of energy. Whenever a certain form of energy gets transformed to heat the total energy gets degraded with a corresponding increase in the entropy of the system. Consider 1 kg of water at the top of a mountain of height about 426.8 m. At this position, water possesses a potential energy of nearly 4.187 kJ. When the water falls and strikes the river at the bottom, all its potential energy gets converted to thermal energy with a consequent temperature rise of water by approximately 1 K. This process results in a degradation of total energy. If not, we could have reversed the process and raised the water to its initial position by cooling it by 1 K. This

degradation of energy is measured by a net increase in the entropy. In this case, the increase in entropy was due to the degeneration of mechanical energy into heat. In general, an increase in entropy results from the addition of heat into the system through the degradation of energy in any form or, by the direct supply of heat to the system. In short, *the entropy of the system is increased by the addition of heat through any mechanism or from any source*. The increase in entropy is proportional to the heat exchanged but not equal to it, since, it is necessary to consider the temperature of the system when the heat is transferred.

The amount of heat added to a system is only a partial measure of the magnitude of its entropy increase. It also depends upon the temperature of the system to which heat is added. Consider a system consisting of a weight and two separate reservoirs, one at temperature T_h and the other at a lower temperature T_c . The weight is first allowed to fall to the high-temperature reservoir, transferring to it certain quantity of heat in the process. The heat so transferred is then made to flow into the reservoir at T_c . These two irreversible processes result in a net increase in entropy which would be the same as the increase in entropy that would result if the weight were allowed to fall directly to the reservoir at T_c . This is so, because, the initial and the final conditions are the same in both cases. Entropy, as will be shown later, is a thermodynamic property that depends only on the terminal states and not on the path followed. Therefore, the change in entropy would be the same in both cases. In the first instance, it is the sum of two contributions: one, the entropy change that resulted by the dropping of the weight to the hot reservoir; and the other by the transfer of heat to the cold reservoir. Since, these two together equal the entropy change resulted by the dropping of the weight to the cold reservoir, we can conclude that the change in entropy due to the lowering of weight to a reservoir at a high temperature is less than that resulted when the weight was lowered to the reservoir at a low temperature. It means that the transfer of energy to a low temperature leads to a greater degradation than that resulted by the transfer of the same quantity to a higher temperature. The greater the degradation of the energy, the greater would be the irreversibility of the process. Entropy, being a thermodynamic function, used to measure the degree of degradation or the extent of irreversibility, should therefore, be related not to Q , but to Q/T , where Q is the heat received by the reservoir and T is its temperature.



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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V - Chemical Engineering Thermodynamics-I– SCHA1202

Applications of the Laws of Thermodynamics

5.1.1 Continuity Equation

For a control volume (see Fig. 5.1), the law of conservation of mass may be written as:

$$\begin{array}{ccc} \text{Rate of accumulation of mass} & + & \text{Net rate of mass out} \\ \text{within the control volume} & & \text{by the flowing streams} \end{array} = 0$$

Mathematically, the above relation can be represented as

$$\boxed{\frac{dm}{dt} + \Delta(\rho u A) = 0} \quad (5.1)$$

where ρ is the average fluid density, A is the fluid cross-sectional area and u is the average fluid velocity. Equation (5.1) is known as the continuity equation. For steady-state flow process, there is no accumulation of mass within the control volume, and the equation reduces to

$$\boxed{\Delta(\rho u A) = 0} \quad (5.2)$$

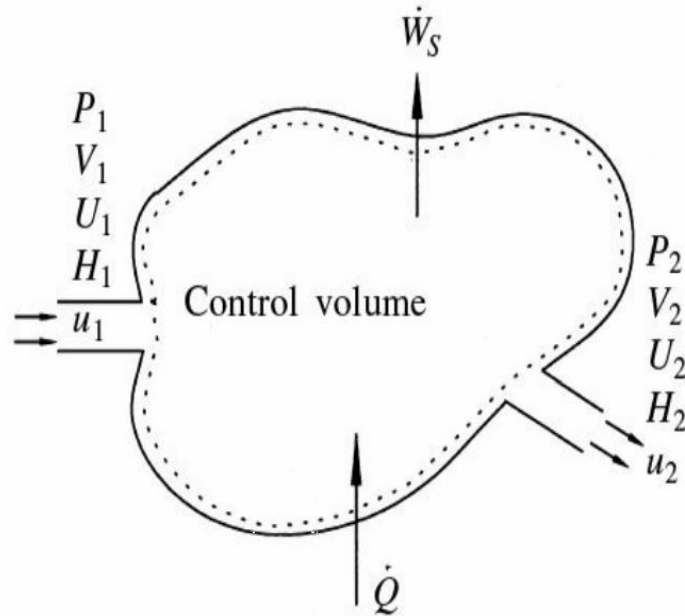


Fig. 5.1 Energy balance for a control volume.

Denoting the conditions at the entrance to the control volume by subscript 1 and the conditions at the exit by subscript 2, Eq. (5.2) may be re-written as

$$\rho_1 u_1 A_1 = \rho_2 u_2 A_2$$

5.1.2 Energy Equation

The law of conservation of energy for a control volume is given by

$$\begin{array}{c} \text{Rate of accumulation of energy} \\ \text{within the control volume} \end{array} + \begin{array}{c} \text{Net rate of energy out} \\ \text{by the flowing streams} \end{array} = \dot{Q} - \dot{W}$$

where $\dot{Q}$ and $\dot{W}$ are the rate at which heat is supplied to the fluid and the rate at which shaft work is done by the fluid respectively.

Rate of accumulation of energy is dU^t/dt , where U^t is the total internal energy within the control volume. The total energy of the fluid stream is the sum of its kinetic energy (KE), potential energy (PE), and internal energy (IE). The law of conservation of energy can now be expressed as

$$\frac{dU^t}{dt} + \Delta(KE) + \Delta(PE) + \Delta(IE) = \dot{Q} - \dot{W} \quad (5.3)$$

In Eq. (5.3), the symbol Δ represents the difference between exit and entrance streams.

$$\Delta(KE) + \Delta(PE) + \Delta(IE) = \Delta \left[\dot{m} \left(\frac{u^2}{2} + gZ + U \right) \right] \quad (5.4)$$

where $\dot{m}$ is the mass flow rate and Z is the height above a reference plane. The work rate $\dot{W}$ is made up of two parts—the shaft work $\dot{W}_s$ and the flow-work, the latter being the product of the pressure and the volume of the fluid. The flow work is equal to $\Delta[\dot{m}(PV)]$ and it is the net work done by the fluid in pushing it into and out of the control volume.

$$\dot{W} = \dot{W}_s + \Delta[\dot{m}(PV)] \quad (5.5)$$

Substituting Eqs. (5.4) and (5.5) in Eq. (5.3) and noting that $H = U + PV$, the energy equation becomes

$$\frac{dU^t}{dt} + \Delta \left[\dot{m} \left(\frac{u^2}{2} + gZ + H \right) \right] = \dot{Q} - \dot{W}_s \quad (5.6)$$

For steady-state flow process, there is no accumulation of energy within the control volume, and Eq. (5.6) reduces to

$$\Delta \left[\dot{m} \left(\frac{u^2}{2} + gZ + H \right) \right] = \dot{Q} - \dot{W}_s \quad (5.7)$$

For flow systems where the kinetic and potential energy changes are negligible, Eq. (5.7) can be further simplified to

$$\Delta \dot{m}H = \dot{Q} - \dot{W}_s \quad (5.8)$$

If the fluid enters and leaves the control volume in a single stream, the mass rate of flow remains the same at the entrance and exit. Then Eq. (5.7) becomes

$$\Delta \left(\frac{u^2}{2} + gZ + H \right) = Q - W_S \quad (5.9)$$

This equation is known as the *total energy balance*. For the case, where changes in kinetic and potential energies are negligible, Eq. (5.9) becomes

$$\Delta H = Q - W_S \quad (5.10)$$

In both Eqs. (5.9) and (5.10), $Q = (\dot{Q}/\dot{m})$ and $W_S = (\dot{W}_S/\dot{m})$.

The 'total energy balance' considers only the input and output from the system. For fluid mechanics calculations, it is customary to express this equation in the form of mechanical energy balance. The mechanical energy balance takes irreversible effects, such as, fluid friction also into account. Equation (5.9) may be put in the following form:

$$\frac{\Delta u^2}{2} + g\Delta Z + \Delta H = Q - W_S \quad (5.11)$$

From the definition of enthalpy of a fluid [see Eq. (2.9)], we get

$$dH = dU + PdV + VdP \quad (5.12)$$

Using the first law of thermodynamics [see Eq. (2.5)],

$$dU = dQ - dW \quad (5.13)$$

For a reversible process, the work done by the fluid is

$$dW = P dV$$

Substituting this into Eq. (5.13) and combining the resulting equation with Eq. (5.12), we get

$$dH = dQ + V dP \quad (5.14)$$

Integrate Eq. (5.14) between the entrance and exit of the control volume. Then,

$$\Delta H = Q + \int_{P_1}^{P_2} V dP \quad (5.15)$$

Using this relation, Eq. (5.11) can be modified to the following form:

$$-W_S = \frac{\Delta u^2}{2} + g\Delta Z + \int_{P_1}^{P_2} V dP \quad (5.16)$$

If the changes in kinetic and potential energies are negligible, the shaft work is given by

$$W_S = - \int_{P_1}^{P_2} V dP \quad (5.17)$$

The above equations are developed assuming reversible processes. On including the work lost due to the irreversibilities, Eq. (5.16) takes the following form:

$$\boxed{\frac{\Delta u^2}{2} + g\Delta Z + \int_{P_1}^{P_2} V dP + W_S + F = 0} \quad (5.18)$$

Here, F represents the lost work due to friction or mechanical energy dissipated to heat due to irreversibilities in the system. Equation (5.18) is known as the *mechanical energy balance*.

Bernoulli's equation. Bernoulli's equation is a special form of the mechanical energy balance applicable only to non-viscous incompressible fluids, which do not exchange shaft work with the surroundings. For non-viscous fluids, $F = 0$. The integral in Eq. (5.18) can be evaluated if the functional relationship between pressure and volume is known. For incompressible fluids, volume is independent of pressure, and hence

$$\int_{P_1}^{P_2} V dP = V\Delta P = \frac{\Delta P}{\rho} \quad (5.19)$$

where ρ is the density of the fluid. Since no shaft work is exchanged, $W_S = 0$. Using these simplifications, Eq. (5.18) can be written as

$$\frac{\Delta u^2}{2} + g\Delta Z + \frac{\Delta P}{\rho} = 0 \quad (5.20)$$

$$\boxed{\frac{u^2}{2} + gZ + \frac{P}{\rho} = \text{constant}} \quad (5.21)$$

Equation (5.21) is known as *Bernoulli's equation*.

5.1.3 Flow in Pipes

Pressure drop. The pressure drop accompanying the steady-state flow of a fluid through a straight pipe is evaluated from the mechanical energy balance [Eq. (5.18)] expressed in differential form:

$$u du + g dZ + V dP + dW_S + dF = 0 \quad (5.22)$$

The friction term is usually expressed in terms of the flow geometry, dynamics of flow and a dimensionless friction factor f , known as the *Fanning friction factor*.

$$dF = \frac{2fu^2}{D} dL \quad (5.23)$$

In Eq. (5.23), D and L are the length and diameter of the pipe respectively.

Maximum velocity. The maximum velocity attainable in pipe flow can be determined using thermodynamic principles. The total energy balance [Eq. (5.11)] may be put in differential form as follows:

$$\frac{du^2}{2} + g dZ + dH = dQ - dW_s$$

Assuming isentropic flow and neglecting potential energy changes, this equation can be simplified as

$$\frac{du^2}{2} + dH = 0$$

or

$$dH = -u du \quad (5.24)$$

For flow through closed conduits of uniform cross-section, the equation of continuity [Eq. (5.2)] may be put in differential form as $d(u\rho) = 0$, or

$$u d\rho + \rho du = 0 \quad \text{and} \quad du = -u \frac{d\rho}{\rho} \quad (5.25)$$

Substitute Eq. (5.25) into Eq. (5.24). The result is

$$dH = u^2 \frac{d\rho}{\rho} \quad (5.26)$$

Noting that $dQ = T dS$ for a reversible process, Eq. (5.14) may be written as

$$dH = T dS + V dP \quad (5.27)$$

Compare Eq. (5.26) with Eq. (5.27).

$$T dS = u^2 \frac{d\rho}{\rho} - V dP = u^2 \frac{d\rho}{\rho} - \frac{dP}{\rho} \quad (5.28)$$

Equation (5.28) may be written in the following form:

$$\rho T dS = u^2 d\rho - dP \quad (5.29)$$

For flow of gas through a pipe of uniform cross-section, since the flow is in the direction of decrease in pressure ($dP < 0$), the specific volume increases or density decreases ($d\rho < 0$) in the flow direction. The first term on the right is negative and the second term is positive. At a particular pressure, these two contributions to the entropy change will be equal in magnitude so that $dS = 0$. The maximum velocity is attained by the gas at this condition and it can be evaluated as:

$$u_{\max}^2 d\rho - dP = 0 \text{ for constant } S$$

$$u_{\max}^2 = \left(\frac{\partial P}{\partial \rho} \right)_S \quad (5.30)$$

The speed of sound in a fluid is evaluated as the square root of the derivative on the right-hand side of Eq. (5.30). Therefore, c is the sonic velocity. Thus, we see that the maximum fluid velocity

attained in a pipe of uniform cross-section is equal to the speed of sound in the fluid.

5.1.4 Flow through Nozzles

A *nozzle* is a device for converting thermal or mechanical energy into kinetic energy. This is achieved by changing the cross-sectional area available for flow. Nozzles find application in turbines, ejectors, diffusers, etc. In the analysis of flow through nozzles presented below, it is assumed that the flow is isentropic.

Relation between A and u . Let us first see the relationship between cross-sectional area and velocity of the fluid through a pipe of varying cross-section. Equation (5.2), the equation of continuity, expressed in differential form is given below:

$$d(urA) = 0$$

This equation may be put into the following form:

$$(\rho A) du + u d(\rho A) = 0$$

or

$$du = - \frac{u}{\rho A} d(\rho A) \quad (5.31)$$

The mechanical energy balance [Eq. (5.18)] may be put in differential form as given below:

$$u du + g dZ + V dP + dW_s + dF = 0$$

For frictionless flow ($dF = 0$) with no work exchange ($dW_s = 0$), and neglecting change in potential energy ($dZ = 0$), the above equation gives

$$u du + V dP = 0$$

Noting that $V = 1/\rho$, the above equation may be written as

$$dP = -\rho u du \quad (5.32)$$

Combining Eqs. (5.31) and (5.32) we get the following results:

$$\begin{aligned} dP &= \frac{u^2}{A} d(\rho A) = \frac{u^2}{A} (\rho dA + A d\rho) \\ \frac{dP}{d\rho} &= \frac{\rho u^2}{A} \left(\frac{dA}{d\rho} \right) + u^2 \end{aligned} \quad (5.33)$$

Because of our assumption of isentropic flow, $(dP/d\rho)$ in the above equation may be replaced by $(\partial P/\partial \rho)_s$ which was shown to be equal to c^2 , where c is the sonic velocity. Also, $d\rho$ can be replaced by dP/c^2 . The resulting equation can be rearranged as

$$\frac{dA}{A} = \frac{dP}{\rho u^2} \left(1 - \frac{u^2}{c^2} \right) \quad (5.34)$$

The ratio of actual velocity to the speed of sound is known as the *Mach number* and is denoted by M . Equation (5.34) may now be written as

$$\frac{dA}{dP} = \frac{A}{\rho u^2} (1 - M^2) \quad (5.35)$$

Using Eq. (5.32), dP may be eliminated from the above equation.

$$\boxed{\frac{dA}{du} = \frac{A}{u} (M^2 - 1)} \quad (5.36)$$

For subsonic velocity of the gas $M < 1$ and $(dA/du) < 0$. For supersonic velocity, $M > 1$ and $(dA/du) > 0$. For sonic velocity, $M = 1$ and $(dA/du) = 0$. Equation (5.36), therefore, means that if the gas is to be accelerated continuously from subsonic to supersonic velocity, the area of cross-section for flow should first decrease ($dA < 0$), then remain constant ($dA = 0$), and finally increase ($dA > 0$). This principle is used for increasing the velocity of gases beyond Mach number unity in the converging-diverging nozzles (Fig. 5.2).

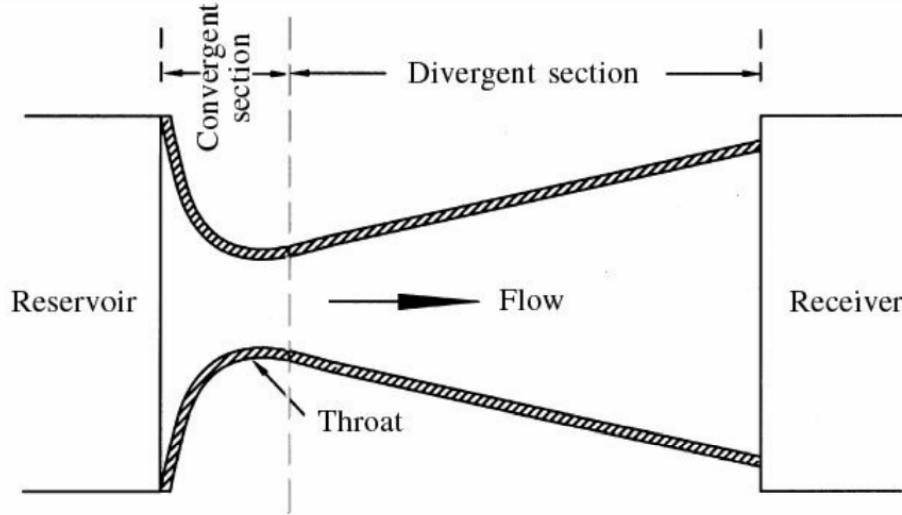


Fig. 5.2 The convergent-divergent nozzle.

Velocity at the throat. It is clear that the maximum velocity attained by the gas in the converging section of the converging-diverging nozzle is the sonic velocity. Therefore, referring to Eq. (5.30), we see that the *velocity at the throat* is given by

$$u_{\text{throat}}^2 = \left(\frac{\partial P}{\partial \rho} \right)_s \quad (5.37)$$

Critical pressure ratio. The relationship between pressure and velocity in a nozzle is given by Eq. (5.32), which may be put in the following form:

$$d \frac{u^2}{2} = - \frac{dP}{\rho} = - V dP \quad (5.38)$$

At the inlet to the nozzle, let $u = 0$ and $P = P_0$, and at any plane normal to the flow within the nozzle, let the velocity and pressure be u and P respectively. Assuming isentropic flow of ideal gases, the pressure and volume are related as $PV^\gamma = \text{constant}$. Substituting this in Eq. (5.38) and integrating, we get

$$u^2 = \frac{2\gamma P_0 V_0}{\gamma - 1} \left[1 - \left(\frac{P}{P_0} \right)^{(\gamma-1)/\gamma} \right] \quad (5.39)$$

The subscript '0' in the above equation denotes the condition at the inlet to the nozzle. Since $PV^\gamma = P/\rho^\gamma = \text{constant}$ for isentropic expansion of ideal gases,

$$\left(\frac{\partial P}{\partial \rho} \right)_s = \gamma \frac{P}{\rho} = \gamma PV \quad (5.40)$$

Comparing this with Eq. (5.37), we obtain

$$u_{\text{throat}}^2 = \gamma PV \quad (5.41)$$

Suppose that the nozzle is connected between a reservoir at pressure P_0 and a receiver at pressure P_r . Flow through the nozzle occurs when P_r is less than P_0 and the velocity of the fluid at the throat is maximum. On further reduction of the receiver pressure, the flow rate and the velocity through the nozzle increases. A limiting value is attained when the velocity at the throat becomes sonic. The pressure at the throat at this condition is P_C , the critical pressure. The critical pressure ratio P_C/P_0 , is the pressure ratio P/P_0 at which the velocity of the fluid at the throat becomes the sonic velocity. Substituting $u = u_{\text{throat}}$ in Eq. (5.39) and using Eq. (5.41), we get:

$$\boxed{\frac{P_C}{P_0} = \left(\frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)}} \quad (5.42)$$

where the ratio P_C/P_0 is the *critical pressure ratio*. This depends only on γ , the ratio of specific heats. Reduction of the receiver pressure below that corresponding to the critical condition, the throat will not affect the flow rate through the nozzle.

The maximum velocity attainable in a converging nozzle is the velocity of sound and it is attained when the pressure ratio reaches the critical value. Therefore, a converging nozzle can discharge a fluid at constant flow rate to a region of variable pressure, independent of the down stream pressure. The pressure ratio, provided it is less than the critical value, will not affect the flow rate through the nozzle. In a converging-diverging nozzle, if the sonic velocity is not attained in the throat because of insufficient pressure drop, the diverging section acts as a diffuser, which increases the pressure and reduces the velocity. Therefore, the purpose of the divergent section is to reduce velocity and regain pressure if the flow is subsonic, and increase velocity and obtain Mach numbers greater than unity if flow is supersonic.

5.1.5 Ejectors

Ejectors or *jet pumps* are devices which employ the momentum and kinetic energy of a high velocity stream to entrain and compress a second gas or vapour stream. Steam-jet ejectors are used for pumping large volumes of vapour and gas at low pressures. See Fig. 5.3.

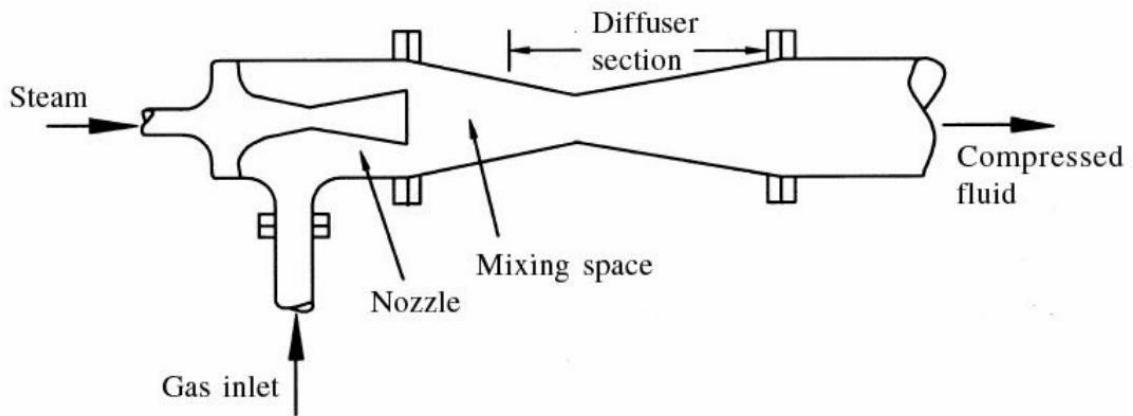


Fig. 5.3 Steam-jet ejector.

An ejector consists of the following parts:

1. A nozzle for accelerating the primary fluid
2. A fluid suction for accelerating the secondary fluid before its entrainment
3. A mixing section, where the secondary fluid is further accelerated and primary fluid is decelerated
4. A diffuser section for decelerating the combined stream of primary and secondary fluids with consequent increase in pressure.

Steam (primary fluid) is first expanded by passing through a nozzle, where it attains supersonic velocity. Due to the high velocity of the steam entering the mixing space, a low-pressure region is created there and as a result the steam transfers some of its momentum to the gas or vapour (secondary fluid) entering through the gas inlet. In the diffuser section, the mixed stream is decelerated and it gets compressed, the work of compression being derived at the expense of its kinetic energy. The compressed gas leaving the ejector is discharged directly to atmosphere or it can be sent to a water-cooled condenser. The latter option is employed in multi-stage ejectors to reduce the quantity of steam handled in the successive stages.

An exhaustive thermodynamic analysis of the ejector performance requires application of the equations of continuity, momentum, and energy to various component parts. The overall efficiency of an ejector is the ratio of work of isentropic compression of the secondary fluid from the suction to the discharge pressure, divided by the work of isentropic expansion of the primary fluid from its initial to the discharge pressure.

5.1.6 Throttling Process (Joule–Thomson Expansion)

Throttling process, also known as *Joule–Thomson expansion*, is a steady-state steady-flow process across a restriction, which results in a reduction in pressure for the fluid. The flow through a partially opened valve or a porous plug is a typical example of throttling process. The throttling process may be treated as an adiabatic operation, because the expansion takes place in a very short time within a very small region, so that the heat exchange between the system and the surroundings is negligible. As no mechanisms are present for extracting work, the process is a highly irreversible one.

Since the kinetic and potential energy changes are negligible, we can use Eq. (5.10) to describe the throttling process. Since $dQ = 0$ and $dW_S = 0$, this equation reduces to $dH = 0$. That is, Joule–Thomson expansion is an isenthalpic process. The temperature of the gas changes as a result of this expansion. The change in temperature resulting from the throttling operation is known as the Joule–Thomson coefficient μ , which is defined as

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H \quad (5.43)$$

During expansion DP is negative. Therefore, a positive value of Joule–Thomson coefficient means that DT is negative and the gas cools on throttling. On the other hand, a negative Joule–Thomson coefficient means that throttling results in an increase in temperature. Joule–Thomson coefficient of a gas can be determined using the pressure-volume-temperature relationship. This is discussed in detail in the next chapter [see Eq. (6.70)]. It is sufficient here to note that, at any given pressure, the Joule–Thomson coefficient is positive only within a temperature range, that is between the upper and lower *inversion temperatures*. Only within these temperatures a gas cools on throttling. For a perfect gas, enthalpy being a function of temperature alone, throttling, which is essentially a constant enthalpy process, produces no temperature change. That is, the Joule–Thomson coefficient of ideal gas is zero. This is true for any gas whose volume varies linearly with temperature at a given pressure (see Exercise 6.30). For real gases, however, above a certain pressure the throttling process always results in cooling. For nitrogen, this pressure is found to be about 375 bar.

5.1.7 Compressors

Compressors may be of reciprocating type or turbo type. The *reciprocating type* compressors are used for developing high pressure-ratios, whereas *turbo type* compressors are preferred for high volumetric rate. The general energy equations are applicable for both types.

Adiabatic compression. For *adiabatic compression* of gases under negligible changes in kinetic and potential energies, Eq. (5.9) reduces to

$$W_S = -DH$$

The minimum shaft work required for compressing a gas adiabatically from a given initial state to a given discharge pressure is the isentropic work which is given as

$$W_S \text{ (isentropic)} = -\Delta H_S \quad (5.44)$$

where ΔH_S is the enthalpy change accompanying the isentropic compression. The ratio of this isentropic work to the actual work required for compression is the compressor efficiency.

$$\eta = \frac{W_s \text{ (isentropic)}}{W_s \text{ (actual)}} \quad (5.45)$$

Equation (5.17) can also be used to evaluate the shaft work required for developing a given pressure ratio in a reversible operation.

$$W_s = - \int_{P_1}^{P_2} V dP \quad (5.17)$$

For an ideal gas undergoing isentropic compression, using the relation $PV^\gamma = \text{constant}$ [see Eq. (3.24)], Eq. (5.17) can be readily integrated.

$$PV^\gamma = \text{constant} = P_1 V_1^\gamma$$

$$V = V_1 \left(\frac{P_1}{P} \right)^{1/\gamma}$$

Using this relation, V in Eq. (5.17) may be replaced and the resulting equation is integrated.

$$W_s = \frac{\gamma}{\gamma - 1} P_1 V_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \right] = \frac{\gamma}{\gamma - 1} RT_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \right] \quad (5.46)$$

The work required for compressing an ideal gas may be written in terms of the initial and final temperatures as well. For an ideal gas, $DH = C_p DT$. Equation (5.44) gives

$$W_s = -DH = C_p(T_1 - T_2) \quad (5.47)$$

The work computed by Eq. (5.46) or by Eq. (5.47) provides the value for the numerator in Eq. (5.45).

Isothermal compression. For reversible isothermal compression of a gas, Eq. (5.10) becomes

$$W_s = Q - DH$$

Since $Q = TDS$ under this condition, we have

$$W_s = TDS - DH \quad (5.48)$$

If the gas is ideal $DH = 0$, because, the enthalpy of ideal gas depends only on temperature. Also,

$$\Delta S = R \ln \frac{P_1}{P_2}$$

For ideal gases, Eq. (5.48) therefore simplifies to

$$W_s = RT \ln \frac{P_1}{P_2} = RT \ln \frac{V_2}{V_1} \quad (5.49)$$

Equation (5.49) gives the shaft work required in isothermal compression of ideal gases. The same result is obtained from Eq. (5.17) also by replacing V by RT/P .

Multi-stage compression. The reversible isothermal and adiabatic paths for the compression of an ideal gas from an initial pressure P_1 to a final pressure P_2 is shown in Fig. 5.4.

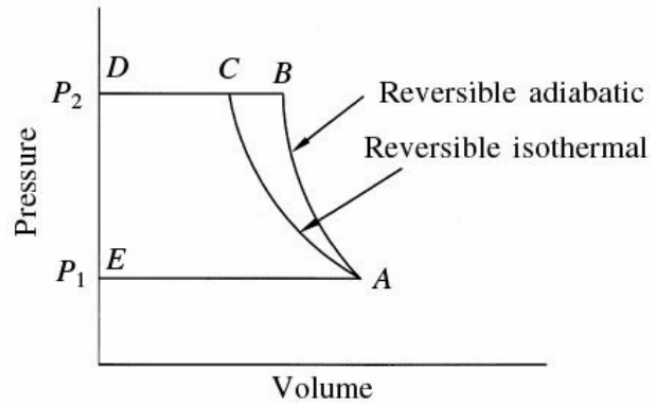


Fig. 5.4 Adiabatic and isothermal compression on a P - V diagram.

The area bounded by the curves, the pressure axis, and the horizontal lines drawn at $P = P_1$ and $P = P_2$ gives the integral $\int_{P_1}^{P_2} V dP$ evaluated between limits P_1 and P_2 , which, by Eq. (5.17), is the shaft work required. From Fig. 5.4, it is evident that compression along the isothermal path requires less work compared to the adiabatic path. The actual compression takes place along a path intermediate to these two limiting paths. However, the isothermal path can be approached in practice by compressing the gas in stages with inter-stage cooling at constant pressure. In Fig. 5.5, it is shown that the compression of gas from pressure P_1 to pressure P_2 achieved in three adiabatic steps.

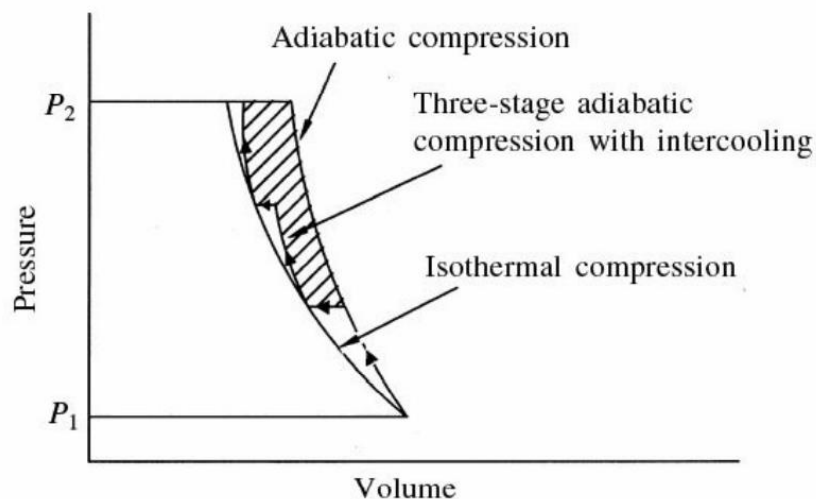


Fig. 5.5 P - V diagram of a three-stage adiabatic compression with interstage cooling.

After the first and second stages the gas is cooled to the original temperature at constant pressure. The actual path traced by the gas is shown with arrows and it is very close to the isothermal path for compressing the gas between the same pressure limits. The shaded area in

Fig. 5.5 is the saving in the work required for compressing the gas from pressure P_1 to pressure P_2 by using a three stage compressor with inter-stage cooling over the work required in a single-stage compressor employing the same compression ratio.

Because of mechanical difficulties, a compression ratio greater than 5 cannot be attained in a single-stage reciprocating compressor. Multi-stage compressors are used to develop high compression ratios. The main advantage of this compression is that it allows inter-stage cooling and thereby an isothermal operation is closely approached. This results in reduction in the work done for compression.

The work requirement in a multi-stage compressor is the sum of the work requirements for the individual stages. For a two-stage compressor in which an ideal gas is compressed from pressure P_1 to P' in the first stage and cooled to the initial temperature T_1 before it is sent to the second stage for the final compression to a pressure P_2 , the total work required according to

Eq. (5.46) is

$$W_s = \frac{\gamma}{\gamma - 1} RT_1 \left[1 - \left(\frac{P'}{P_1} \right)^{(\gamma-1)/\gamma} + 1 - \left(\frac{P_2}{P'} \right)^{(\gamma-1)/\gamma} \right] \quad (5.50)$$

For a multi-stage compressor with n stages, if the compression ratios in all the stages are equal and are denoted by r , then the total work required may be written as

$$W_s = \frac{n\gamma}{\gamma - 1} RT_1 [1 - (r)^{(\gamma-1)/\gamma}] \quad (5.51)$$

In writing Eq. (5.51) it is assumed that after each stage, the temperature of the gas is brought down to the initial value. It can be shown that for the minimum total work in a multi-stage compressor, the pressure ratios in all the stages are equal and are given by

$$r = \left(\frac{P_2}{P_1} \right)^{1/n}$$

where P_2/P_1 is the overall pressure ratio.

5.2 REFRIGERATION

Refrigeration is the process of producing and maintaining a temperature below that of the surrounding atmosphere. Refrigeration processes find wide applications in chemical process industries. The process is used in manufacturing synthetic rubber, textiles, chlorine, plastics, hydrogen fluoride, etc. Refrigeration is used to remove heat of chemical reactions and to liquefy process gases for gas separation by distillation and condensation. Liquefaction processes for the production of pure gases such as oxygen and nitrogen from air and liquefaction and storage of natural gases employ refrigeration principles. Separation of volatile hydrocarbons in petroleum industries, separation of gasoline from natural gas, solvent recovery, crystallisation of salts from solutions, manufacture of ice, treatment, transport and preservation of food and beverages, etc., are some other important applications of refrigeration operation. Apart from its widespread use in the air-conditioning of houses and buildings and in domestic refrigerators, refrigeration is also used in the air-conditioning of plant areas as in the manufacture of rayon, photographic film, gelatine, etc.

Refrigeration implies production of low temperature by continually absorbing heat at a low level and rejecting it at a high level. Since heat cannot flow from a body at low temperature to one at a higher temperature spontaneously, external work is required to achieve refrigeration. Thus, refrigeration is essentially an operation involving the pumping of heat from one temperature to a higher temperature. In mechanical refrigeration, which is the most commonly used method for commercial applications, the low temperature is produced by the evaporation of a liquid whose properties are, such that, at the pressure of evaporation, the saturation temperature is low. The evaporated liquid is then returned to its original state for continuous operation. The complete series of processes that the working fluid—the refrigerant—undergoes, constitute a refrigeration cycle. A typical refrigeration cycle includes evaporation of the liquid refrigerant, compression of the refrigerant vapour, condensation of the vapour into liquid, and finally expansion of the liquid.

5.2.1 Coefficient of Performance (COP)

Refer Fig. 5.7, which represents schematically the refrigeration process. Let Q_2 be the heat that is absorbed at a low temperature T_2 and Q_1 be the heat rejected at high temperature T_1 . By first law of thermodynamics, the external work required to bring about this transfer is

$$W = Q_1 - Q_2$$

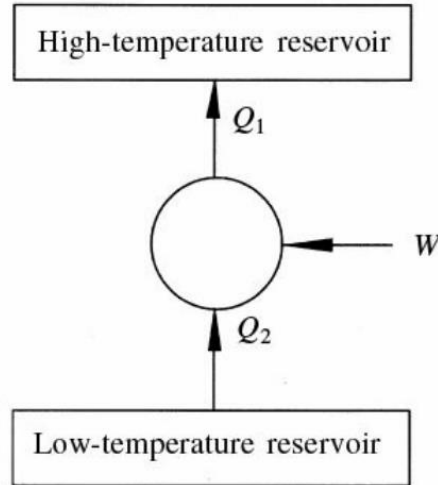


Fig. 5.7 Schematic representation of a refrigeration cycle.

The *efficiency* or *coefficient of performance* (COP) of a refrigerator is defined as the quantity of heat absorbed at the low temperature per unit of work.

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \quad (5.55)$$

5.2.2 Refrigerator Capacity

The *refrigerator capacity* determines the rate of circulation of the refrigerant, which in turn, decides the design and size of the various units such as condenser, compressor, evaporator, and the expansion devices. The capacity is sometimes measured in ton of refrigeration. One ton is defined as the heat absorption at the rate of 12000 BTU per hour (One BTU is the amount of heat required to raise the temperature of one pound, i.e. 0.4536 kg of water by one degree Fahrenheit, or (1/1.8) K. Thus, 1 BTU = 1.055 kJ). This rate corresponds to the rate of heat removal that is required to freeze 1 ton of water in a day originally at 273 K. One ton of refrigeration is equivalent to a refrigeration rate of 12660 kJ/h in SI units.

5.2.3 Carnot Cycle

The *Carnot cycle* can be used as a model of the ideal refrigeration cycle, because, of all the refrigerators operating between the same two thermal reservoirs, the maximum COP is attained by the one based on Carnot cycle. The Carnot refrigeration cycle is depicted in Fig. 5.8(a).

It consists of the following steps: reversible adiabatic compression (*AB*), isothermal heat rejection (*BC*), reversible adiabatic expansion (*CD*) and isothermal heat absorption (*DA*). During the isothermal heat absorption (*DA*), an amount of heat Q_2 is absorbed at low temperature level T_2 . The area *ADXY* on the *T-S* diagram [Fig. 5.8(b)] represents the heat absorbed. It is equal to $T_2 DS$, where DS is the change in entropy of the fluid due to the heat absorption. Heat rejected at higher temperature T_1 is equal to Q_1 and is represented by the area *BCXY*. It is equal to $T_1 DS$. The external work done

for this transfer of heat against a temperature gradient is given by $W = Q_1 - Q_2$, which is the enclosed area $ABCD$ in Fig. 5.8(b).

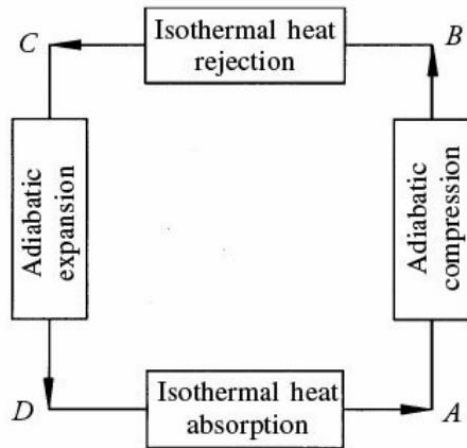


Fig. 5.8(a) Components of a Carnot cycle.

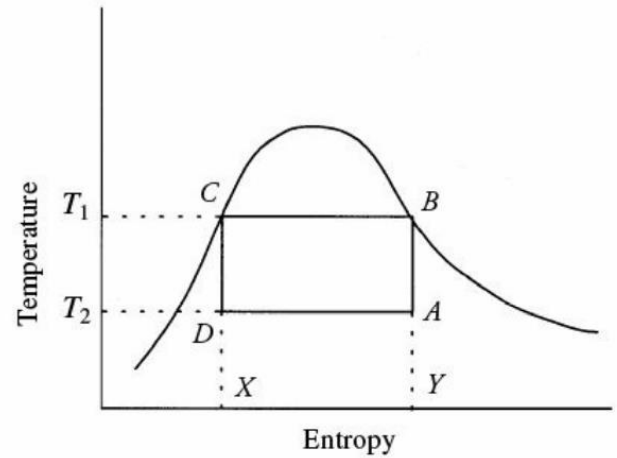


Fig. 5.8(b) T - S diagram of the Carnot cycle.

The coefficient of performance of the Carnot cycle is,

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2 \Delta S}{(T_1 - T_2) \Delta S} = \frac{T_2}{T_1 - T_2} \quad (5.56)$$

We note that the coefficient of performance of the Carnot refrigeration cycle depends only on the temperature levels between which the machine operates and is independent of the working fluid. Equation (5.56) establishes the optimum performance that can be expected of any refrigerating machine operating between given temperature limits. Equation (5.56) on rearrangement gives

$$W = Q_2 \frac{T_1 - T_2}{T_2} \quad (5.57)$$

which is the minimum work required for transferring heat Q_2 from a low temperature T_2 to a higher temperature T_1 . It is impossible to construct a refrigeration machine that will pump heat with less expenditure of work than that given by Eq. (5.57). Because of the inherent irreversibilities in any practical process, the COP of an actual machine will be less than that given by Eq. (5.56) and the work required for transfer of a given quantity of heat will be more than that given by Eq. (5.57). However, these equations can be used as a standard for comparison of the actual processes and suggest possible improvement in such processes. Equation (5.57) indicates that the work input increases with decrease in the temperature of the refrigerator or with increase in the temperature of the heat receiver and is independent of the refrigerant. It may be noted here that even in the actual cycles, the influence of the working fluid on the work input per unit of refrigeration is quite insignificant.

Limitations. A refrigeration machine operating on the Carnot cycle cannot be achieved in practice. Carnot cycle demands reversible operation, and it is difficult to eliminate all irreversibilities in an

actual operation. Isothermal heat interactions at the heat absorption and the heat rejection stages, which proceed at very slow rates necessitate large heat transfer areas. A temperature difference between the refrigerant and the reservoirs in the heat absorption and heat rejection stages is necessary, in order to have a finite rate of heat transfer. If the heat absorption is achieved by the evaporation of a refrigerant then the possibility of the input stream to the compressor containing liquid cannot be overruled. This may lead to severe erosion problems in the compressor. Apart from these, the work output of an expansion engine or a turbine used for reversible expansion is normally very small whereas their costs are prohibitively high.

5.2.4 Vapour-compression Cycle

The actual refrigeration cycles are less efficient than the ideal Carnot cycle, because of the presence of the inevitable irreversible effects, such as friction, imperfect heat insulation, and because of the finite temperature difference that is maintained for a reasonably good rate of heat transfer in the refrigerator and the condenser. In the vapour-compression cycle shown in Fig. 5.9(a), the refrigerant vapour is compressed (AB) to such a pressure that the available cooling water can condense the vapour in a condenser (BC) operated at this pressure which is maintained constant. The vapour, during condensation rejects heat to the cooling medium. By passing through a throttling valve, the pressure of the liquid leaving the condenser is reduced (CD) to the pressure maintained in the evaporator. The liquid then evaporates (DA), absorbing heat at constant temperature T_2 . The vapour thus produced enters the compressor, and the cycle is repeated. The process is represented on the T - S diagram as shown in Fig. 5.9(b). The liquid portion of the refrigerant leaving the throttling valve is vaporised at constant pressure P_2 and constant temperature T_2 in the refrigerator. The vapour leaving the refrigerator is saturated (A). It is possible that the vapour leaving the refrigerator may get slightly superheated or may be slightly unsaturated. On adiabatic compression, the vapour gets super heated (B) and this vapour enters the condenser at pressure P_1 . The reversible adiabatic compression is an isentropic process and is represented by the vertical line AB . In the condenser, the vapour is first cooled and the superheat is removed from the vapour, as shown by the line BE , and then it is condensed at constant temperature T_2 . The saturated liquid (C) leaving the condenser is expanded by throttling. The throttling is a constant enthalpy process and is represented by the curve CD . Throttling results in the partial vaporisation of the liquid, and the point (D) representing the mixture leaving the valve lies in the two-phase region. Figure 5.9(c) shows the vapour-compression cycle on a pressure-enthalpy diagram.

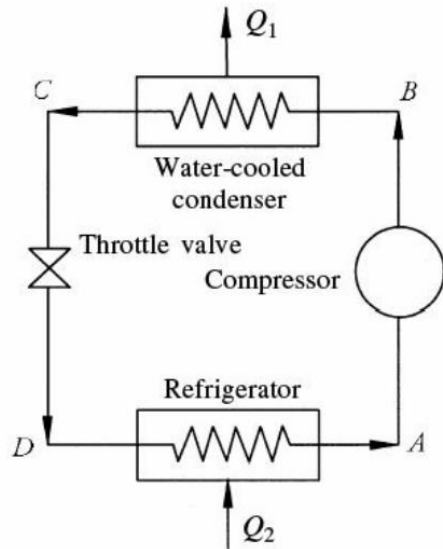


Fig. 5.9(a) Components of an ordinary vapour-compression cycle.

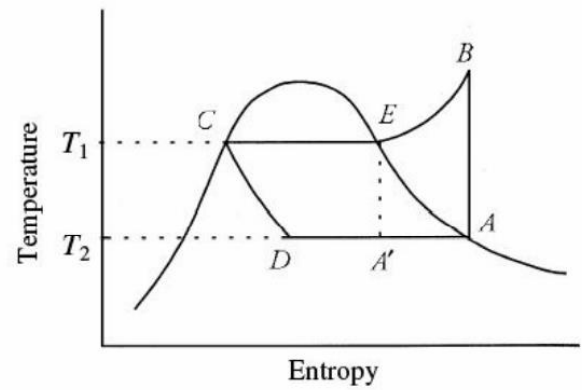


Fig. 5.9(b) T - S diagram of the ordinary vapour-compression cycle.

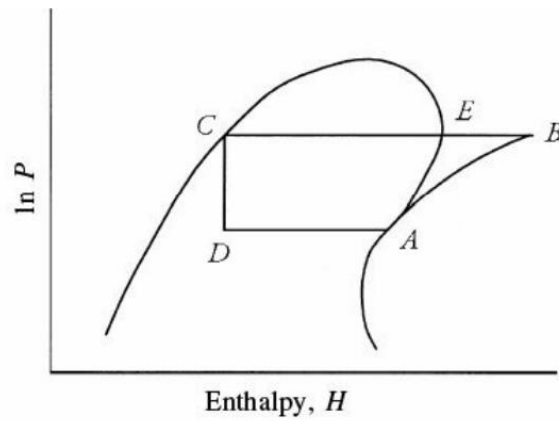


Fig. 5.9(c) P - H diagram of a vapour-compression cycle.

As the heat absorption in the refrigerator occurs at constant pressure, the heat absorbed during vaporisation is equal to the change in the enthalpy of the refrigerant.

$$Q_2 = H_A - H_D \quad (5.58)$$

The heat rejected is

$$Q_1 = H_B - H_C \quad (5.59)$$

Since the work required, $W = Q_1 - Q_2$, and $H_D = H_C$ (the process CD is isenthalpic), we have

$$W = H_B - H_A \quad (5.60)$$

The coefficient of performance is

$$\text{COP} = \frac{Q_2}{W} = \frac{H_A - H_D}{H_B - H_A} \quad (5.61)$$

If the rate of heat absorption is specified, the rate of circulation of the refrigerant ($\dot{m}$) can be easily evaluated.

$$\dot{m}(H_A - H_D) = Q_2 \quad (5.62)$$

For a refrigerator rated at 1 ton ($Q_2 = 12660$ kJ/h), the rate of circulation in kg/h may be evaluated by

$$\dot{m} = \frac{12660}{H_A - H_D} \quad (5.63)$$

where H_A and H_D are in kJ/kg.

The vapour leaving the compressor is superheated at the condenser pressure P_1 . Its temperature is greater than the saturation temperature T_1 . Also, the throttling process is highly irreversible. Because of these two reasons, the ordinary vapour-compression cycle presented above, is less efficient than the Carnot cycle. By allowing the evaporation to proceed up to point A' in Fig. 5.9(b), and

compressing the resultant vapour–liquid mixture adiabatically to saturation at pressure P_1 (process $A \rightarrow E$ in the figure) the first difficulty can be overcome. But the practical gain in such an operation is only very small in comparison with the operational difficulties associated with the compression of a two-phase mixture. If the expansion process (CD) were carried out in an expansion engine instead of throttling, the irreversibilities can be minimised to a great extent. This is what is done in an expansion-engine vapour-compression cycle illustrated in Figs. 5.10(a) and (b). Here, the expansion is isentropic and hence CD is a vertical line on the T - S diagram.

The heat absorbed and heat rejected during this cycle are respectively Q_2 and Q_1 , which are given by $Q_2 = H_A - H_D$ and $Q_1 = H_B - H_C$.

The work input $W = Q_1 - Q_2$. Hence,

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{H_A - H_D}{(H_B - H_C) - (H_A - H_D)} \quad (5.64)$$

As the expansion engine operating on a two-phase mixture is expensive, this cycle is preferred only for large installations. Because of their simplicity and low cost, the throttle valves are preferred over turbines in small installations.

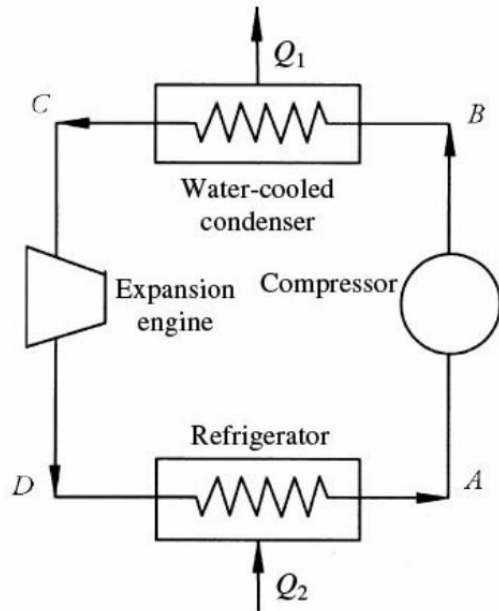


Fig. 5.10(a) Components of an expansion engine vapour-compression cycle.

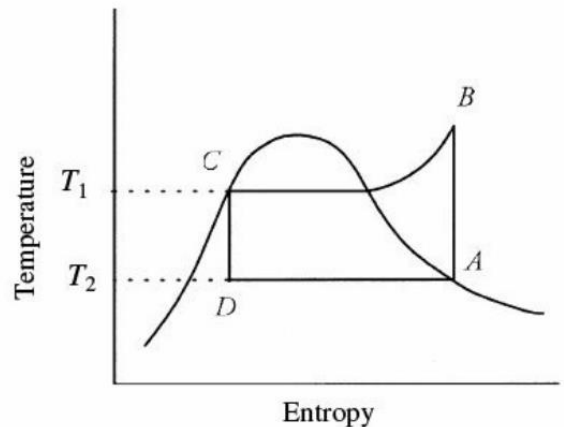


Fig. 5.10(b) T - S diagram of the expansion engine vapour-compression cycle.