LECTURE NOTES

ON

THERMODYNAMICS

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INTRODUCTION

Thermodynamics is the science that deals with heat and work and those properties of substance that bear a relation to heat and work.

Thermodynamics is the study of the patterns of energy change. Most of this course will be concerned with understanding the patterns of energy change.

More specifically, thermodynamics deals with (a) energy conversion and (b) the direction of change.

Basis of thermodynamics is experimental observation. In that sense it is an empirical science. The principles of thermodynamics are summarized in the form of four laws known as zeroth, first, second, and the third laws of thermodynamics.

The zeroth law of thermodynamics deals with thermal equilibrium and provides a means of measuring temperature.

The first law of thermodynamics deals with the conservation of energy and introduces the concept of internal energy.

The second law of thermodynamics dictates the limits on the conversion of heat into work and provides the yard stick to measure the performance of various processes. It also tells whether a particular process is feasible or not and specifies the direction in which a process will proceed. As a consequence it also introduces the concept of entropy.

The third law defines the absolute zero of entropy.

Macroscopic and Microscopic Approaches:

Microscopic approach uses the statistical considerations and probability theory, where we deal with “average” for all particles under consideration. This is the approach used in the disciplines known as kinetic theory and statistical mechanics.

In the macroscopic point of view, of classical thermodynamics, one is concerned with the time-averaged influence of many molecules that can be perceived by the senses and measured by the instruments.

The pressure exerted by a gas is an example of this. It results from the change in momentum of the molecules, as they collide with the wall. Here we are not concerned with the actions of individual molecules but with the time-averaged force on a given area that can be measured by a pressure gage.

From the macroscopic point of view, we are always concerned with volumes that are very large compared to molecular dimensions, and therefore a system (to be defined next) contains many molecules, and this is called continuum. The concept of continuum loses validity when the mean free path of molecules approaches the order of typical system dimensions.
System:

We introduce boundaries in our study called the system and surroundings. 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

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.

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 are called intensive properties.
• 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.

**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.

**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

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**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 N = 1 kg m/s, pressure 1 Pa = 1 N/m\(^2\), 1 bar = 10 Pa, 1 atm. = 101325 Pa. In thermodynamics we are concerned with absolute pressure. Gauge pressure = absolute pressure – atmospheric pressure. Ordinary vacuum gauge pressure = atmospheric pressure – absolute pressure.

**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 than 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 move 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 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:

\[
E = KE + PE + U
\]
**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.

\[
W = F \, dx = k (x - x_0) \, d(x-x_0) = 1/2 k \left[ (x_2-x_0)^2 - (x_1-x_0)^2 \right]
\]

**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, \(P_{\text{ex}}\), and the internal pressure, \(P_{\text{in}}\), were different. To calculate the work done in moving the piston, we know that the force \(= \text{pressure times area}\) and then work equals pressure times area times distance or work equals pressure times the change in volume. So, \(W = \text{the integral of} \ (P_{\text{ex}}) \, dV\)

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”.

**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.

**The State Postulate**

The state of the system is described by its properties.

Once a sufficient number of properties are specified, the rest of the properties assume some values automatically.

The number of properties required to fix a state of a system is given by the **state postulate**:

The state of a simple compressible system is completely specified by two independent, intensive properties. The system is called a **simple compressible system** in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.
The state postulate requires that the two properties specified be independent to fix the state. Two properties are independent if one property can be varied while the other one is held constant. Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system. Thus, temperature and pressure are not sufficient to fix the state of a two-phase system.

Otherwise an additional property needs to be specified for each effect that is significant. An additional property needs to be specified for each other effect that is significant.

Zeroth Law of Thermodynamics:
We cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading. Several properties of material changes with temperature in a repeatable and predictable way, and this forms the basis of accurate temperature measurement. The commonly used mercury-in-glass thermometer for example, is based on the expansion of mercury with temperature. Temperature is also measured by using several other temperature dependant properties. Two bodies (eg. Two copper blocks) in contact attain thermal equilibrium when the heat transfer between them stops. The equality of temperature is the only requirement for thermal equilibrium.

The Zeroth Law of Thermodynamics

If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.

This obvious fact cannot be concluded from the other laws of thermodynamics, and it serves as a basis of temperature measurement.

By replacing the third body with a thermometer, the zeroth law can be restated two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact

The zeroth law was first formulated and labeled by R.H. Fowler in 1931.
Temperature Scales:

All temperature scales are based on some easily reproducible states such as the freezing and boiling point of water, which are also called the ice-point and the steam-point respectively.

A mixture of ice and water that is in equilibrium with air saturated with water vapour at 1atm pressure is said to be at the ice-point, and a mixture of liquid water and water vapour (with no air) in equilibrium at 1atm is said to be at the steam-point.

Celsius and Fahrenheit scales are based on these two points (although the value assigned to these two values is different) and are referred as two-point scales.

In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of the substance or substances.

Such a temperature scale is called a thermodynamic temperature scale.(Kelvin in SI)

Ideal gas temperature scale:

The temperatures on this scale are measured using a constant volume thermometer.
Based on the principle that at low pressure, the temperature of the gas is proportional to its pressure at constant volume.

The relationship between the temperature and pressure of the gas in the vessel can be expressed as \( T = a + bP \)

Where the values of the constants \( a \) and \( b \) for a gas thermometer are determined experimentally.

Once \( a \) and \( b \) are known, the temperature of a medium can be calculated from the relation above by immersing the rigid vessel of the gas thermometer into the medium and measuring the gas pressure.

Ideal gas temperature scale can be developed by measuring the pressures of the gas in the vessel at two reproducible points (such as the ice and steam points) and assigning suitable values to temperatures those two points.

Considering that only one straight line passes through two fixed points on a plane, these two measurements are sufficient to determine the constants \( a \) and \( b \) in the above equation.

If the ice and the steam points are assigned the values 0 and 100 respectively, then the gas temperature scale will be identical to the Celsius scale.

In this case, the value of the constant \( a \) (that corresponds to an absolute pressure of zero) is determined to be \(-273.15^0\text{C}\) when extrapolated.

The equation reduces to \( T = bP \), and thus we need to specify the temperature at only one point to define an absolute gas temperature scale.
Absolute gas temperature is identical to thermodynamic temperature in the temperature range in which the gas thermometer can be used. We can view that thermodynamic temperature scale at this point as an absolute gas temperature scale that utilizes an ideal gas that always acts as a low-pressure gas regardless of the temperature.

At the Tenth international conference on weights and measures in 1954, the Celsius scale has been redefined in terms of a single fixed point and the absolute temperature scale.

The triple point occurs at a fixed temperature and pressure for a specified substance.

The selected single point is the **triple point** of water (the state in which all three phases of water coexist in equilibrium), which is assigned the value 0.01 C. As before the boiling point of water at 1 atm. Pressure is 100.0 C. Thus the new Celsius scale is essentially the same as the old one.

On the Kelvin scale, the size of Kelvin unit is defined as “the fraction of 1/273.16 of the thermodynamic temperature of the triple point of water, which is assigned a value of 273.16K”. The ice point on Celsius and Kelvin are respectively 0 and 273.15 K.

**Example 1.** Consider as a system, the gas in the cylinder shown in the figure. The cylinder is fitted with a piston on which number of small weights is placed. The initial pressure is 200 kPa, and the initial volume of the gas is 0.04 m$^2$.

1. Let the gas in the cylinder be heated, and let the volume of the gas increase to 0.1 m$^3$ while the pressure remains constant. Calculate the work done by the system during this process.

\[
W = \int_{1}^{2} P \, dV
\]

Since the pressure is constant, we conclude from the above equation that

\[
W = P \int_{1}^{2} dV = P(V_2 - V_1)
\]

\[
W = 200 \text{kPa} \times (0.1 - 0.04) \text{m}^3 = 12.0 \text{kJ}
\]
2. Consider the same system and initial condition, but at the same time the cylinder is being heated and the piston is rising, let the weights be removed from the piston at such a rate that, during the process the temperature of the gas remains constant.

If we assume that the ideal-gas model is valid. We note that this is a polytropic process \((PV^n = \text{const.})\) with exponent \(n = 1\). For such a process,

\[
W = \int_1^2 P \, dV = P_1 V_1 \int_1^2 \frac{dV}{V} = P_1 V_1 \ln \frac{V_2}{V_1}
\]

\[
= 200 \text{kPa} \times 0.04 \text{m}^3 \times \ln \frac{0.10}{0.04} = 7.33 \text{kJ}
\]

3. For the same system, let the weights be removed at such a rate that the expression \(PV^{1.3} = \text{const.}\). Again the final volume is 0.1 m\(^3\). Calculate the work.

\[
P = \frac{\text{cons tan }\, t}{V^n} = \frac{P_1 V_1^n}{V^n} = \frac{P_2 V_2^n}{V^n}
\]

\[
\int_1^2 P \, dV = \text{cons tan }\, t \int_1^2 \frac{dV}{V^n} = \text{cons tan }\, t \left( \frac{V^{-n+1}}{-n+1} \right)_1^2
\]

\[
= \text{cons tan }\, t \left( V_2^{1-n} - V_1^{1-n} \right) = \frac{P_2 V_2^n V_2^{1-n} - P_1 V_1^n V_1^{1-n}}{1-n}
\]

\[
P_2 = 200 \left( \frac{0.04}{0.1} \right)^{1.3} = 60.77 \text{kPa}
\]

\[
W = \frac{P_2 V_2 - P_1 V_1}{1-1.3} = \frac{60.77 \times 0.1 - 200 \times 0.04}{1-1.3}
\]

\[
= 6.41 \text{kJ}
\]
4. Consider the system and initial state as before, but let the piston be held by a pin so that the volume remains constant. In addition, let heat transfer take place from the cylinder so that the pressure drops to 100kPa. Calculate the work.

Since $dV = 0$, the work is zero because there is no change in volume.
Example 2. Consider a piston cylinder arrangement as shown. The piston is loaded with a mass, \(m_p\), the outside atmospheric pressure \(P_0\), a linear spring and a single point force \(F_1\). The piston is restricted in its motion by lower and upper stops trapping the gas with a pressure \(P\).

For zero acceleration in a quasi-equilibrium process,

\[
\sum F_{\uparrow} = \sum F_{\downarrow}
\]

The forces when the piston is between the stops are

\[
\sum F_{\uparrow} = PA \quad \sum F_{\downarrow} = m_p g + P_0 A + k(x - x_0) + F_1
\]

with the linear spring constants \(k\).

The piston position for a relaxed spring is \(x_0\), which depends on how the spring is installed.

The force balance then gives the gas pressure by division with the area, \(A\), as

\[
P = P_0 + \left[ m_p g + k(x - x_0) + F_1 \right] / A
\]

To illustrate the process in a P-V diagram, the distance \(x\) is converted to volume by division and multiplication with \(A\):

\[
P = P_0 + \frac{m_p g}{A} + \frac{F_1}{A} + \frac{k}{A^2} (V - V_0) = C_1 + C_2 V
\]
This relation gives the pressure as a linear function of the volume with slope of \( C_2 = k/A^2 \)

The work in a quasi-equilibrium process, is

\[
W = \int_{V_1}^{V_2} P \, dV = \text{Area under the curve}
\]

\[
= \frac{1}{2} (P_1 + P_2) (V_2 - V_1)
\]

With \( P_1 = P_1 \) and \( P_2 = P_2 \) subject to the constraint that

\[
P_{\min} \leq P_1, \quad P_2 \leq P_{\max}
\]

An part of the process with a pressure smaller that \( P_{\min} \) or larger than \( P_{\max} \) does not involve work.
Example 3. **Balloon initially collapsed and flat. Slowly filled with helium from a cylinder**

Dia = 5 m.

Ambient pressure = 100 kPa

Temperature const. = 300 K

System: Helium contained in cylinder and balloon.

Filling process quasi-static process

Work done by Helium, $W$

$$W = \int_{V_1}^{V_2} P \, dV = P(V_2 - V_1)$$

$$= PV_2$$

$$= 100 \times 10^3 \times \frac{4\pi}{3} \left(\frac{5}{2}\right)^3 = 6544.98 \text{kJ}$$
### Ideal and Real Gases

**Pure Substance:**

A pure substance is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase but chemical composition is the same in all phases.

Some times the mixture of gases, such as air is considered a pure substance as long as there is no change of phase. Further our emphasis will be on simple compressible substances.

Early experiments on the **variables of state** (such as T, P, V, and n) showed that only two of these variables of state need to be known to know the state of a sample of matter.

- **Extensive variables**: depend on the amount of substance present. Examples include the volume, energy, enthalpy, and heat capacity.

- **Intensive variables**: do not depend on the amount of substance present. Examples include the temperature and pressure.

### 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: \( V(T,P,n) = \frac{(nRT)}{P} \).
  - 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.
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,

\[ u = u(T) \]

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

Enthalpy and specific heat:

\[ h = u + P v \]

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 \( dq = du + dw = du + Pdv = du + Pdv +vdP \) (since \( dP = 0 \) for a constant pressure process)

\[
\text{Or } dq = du + d(Pv) = d(U + Pv) = dh
\]

or \( dq = dh \)

\[
C_P = \left( \frac{\partial h}{\partial T} \right)_P
\]

The ratio of specific heat (\( \gamma \)) is given by

\[
\gamma = \frac{C_P}{C_v}
\]

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

**Relation between two specific heats:**

The two specific heats are related to each other.

\[
h = u + P v \quad \text{or} \quad dh = du + d(Pv)
\]

For an ideal gas, the above equation reduces to

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

\[
dh/dT = du/dT + R \quad \text{or} \quad C_P = C_v + R
\]

or \( C_P - C_v = R \) for an ideal gas.

\[
\gamma = \frac{C_P}{C_v} \quad \text{or} \quad C_P = \frac{R}{(\gamma - 1)} \quad \text{and} \quad C_v = \frac{R \gamma}{(\gamma - 1)}
\]

**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.
**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

\[\left(\partial P/\partial v\right)_{T=T_c} = 0 \text{ and } \left(\partial^2 P/\partial v^2\right)_{T=T_c} = 0\]

\[\left(\partial P/\partial v\right)_{T=T_c} = -RT/(v_c - b)^2 + 2a/v_c^3 = 0\]

or

\[RT/(v_c - b)^2 = 2a/v_c^3\]

\[\left(\partial^2 P/\partial v^2\right)_{T=T_c} = 2RT/(v_c - b)^3 - 6a/v_c^4 = 0\]
or

\[ \frac{2RT_c}{(v_c - b)^3} = \frac{6a}{v_c^4} \]

Therefore

\[ \frac{2}{(v_c - b)} = \frac{3}{v_c} \text{ or } v_c = 3b \]

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

\[ P_c = \frac{RT_c(v_c - b) - a}{v_c^2} \]

From these equations,

\[ a = \frac{27R^2T_c^2}{64 P_c} \text{ and } b = \frac{RT_c}{8P_c} \]

**Compressibility Factor:**

The deviation from ideal behavior of a gas is expressed in terms of the compressibility factor \( Z \), which is defined as the ratio of the actual volume to the volume predicted by the ideal gas law.

\[ Z = \frac{\text{Actual volume}}{\text{volume predicted by ideal gas law}} = \frac{v}{RT/P} = \frac{Pv}{RT} \]

For an ideal gas \( Pv = RT \) and hence \( Z = 1 \) at all temperatures and pressures.

The experimental \( P-v-T \) data is used to prepare the compressibility chart.

Reduced pressure, \( P_R = \frac{P}{P_c} \),
Reduced temperature, \( T_R = \frac{T}{T_c} \),
Reduced volume, \( v_R = \frac{v}{v_c} \)

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\textsubscript{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\textsubscript{c}), the ideal-gas model can be assumed to good accuracy to pressures as high as 4-5 times P\textsubscript{c}.

**GRAPHICAL REPRESENTATION OF DATA**

1. **Pressure** versus **temperature** (P-T)

2. **Pressure** vs. **volume** (P-v)

3. **Temperature** vs. **volume** (T-v)

4. **Temperature** vs. **entropy** (T-s)

5. **Enthalpy** vs. **entropy** (h-s)

6. **Pressure** vs. **enthalpy** (P-h)

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 is 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 –200°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 –200°C, let heat transfer increase the temperature until it reaches 0.010°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.

### 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 \( \Delta u \), \( \Delta h \), \( \Delta s \), 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°C and P = 0.6113 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

\[
v = (1-X)v_f + Xv_g, \quad u = (1-X)u_f + Xu_g, \quad h = (1-X)h_f + Xh_g = h_f + Xh_g, \quad s = (1-X)s_f + Xs_g
\]

where \( h_{fg} = h_g - h_f \) = latent heat of vaporization.

**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.

**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).

**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.
TD First Law Analysis to Non-flow Processes

**Constant Volume process:**

1. Heating of gas enclosed in a rigid vessel:
   \[ dU = dQ \text{ or } U_2 - U_1 = m C_v (T_2 - T_1) \]

2. Shaft work done on a system at constant volume
   \[ dU = dQ - dW = dQ - (dW_{pdv} + dW_s) \]
   or \[ dU = -dW_s \text{ or } -W_s = U_2 - U_1 \]

3. Constant volume process involving electrical work:
   \[ -W_s = U_2 - U_1 \]

For an adiabatic process the work is done is independent of path.

**Constant Pressure Process:**

1. Reversible heating of a gas

2. Phase Change at constant pressure (Rev.)

3. Shaft work at constant pressure

4. Electrical work at constant pressure
   \[ W = P (V_2 - V_1) \]

   \[ dU = dQ - dW = dQ - PdV = dQ - d(PV) \]

   or, \[ dQ = dU + d(PV) = d(U + PV) = dH \]

   \[ Q = \Delta H \text{ the heat interaction is equal to increase in enthalpy} \]
**Constant Temperature Process:**

\[ dU = dQ - dW = dQ - PdV \]

for an ideal gas \( u = u(T) \) then \( dU = 0 \)

\[ dQ = PdV = RT \frac{dv}{v} \]

\[ Q = W = RT \ln \left( \frac{v_2}{v_1} \right) \]

**Reversible Adiabatic Process:**

\[ dU = -dW \text{ or } W = -\Delta U \]

This equation is true for reversible as well as irreversible process.

\[ C_v \, dT = -Pdv = -RT/v \, dv \]

\[ \frac{dT}{T} = -\frac{R}{C_v} \frac{dv}{v} \]

\[ \frac{R}{C_v} = \gamma - 1 \quad , \frac{dT}{T} = -(\gamma - 1) \frac{dv}{v} \]

\[ \frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{(\gamma - 1)} \quad T v^{(\gamma - 1)} \text{ = constant} \]

Also \( P v^{\gamma} = \text{Constant using perfect gas relation} \)

**FIRST LAW OF THERMODYNAMICS:**

The first law of thermodynamics is the thermodynamic expression of **the conservation of energy**.

This law most simply stated by saying that “energy can not be created or destroyed” or that “the energy of the universe is constant”.

This law can be stated for a system (control mass) undergoing a cycle or for a change of state of a system.

Stated for a system undergoing a cycle, the cyclic integral of the work is proportional to the cyclic integral of the heat.

Mathematically stated, for a control mass undergoing a cyclic process such as in Joule’s experiment and for consistent set of units

\[ \int dQ_{\text{from system}} = \int dW_{\text{on system}} \]

or \[ \int dQ_{\text{from system}} - \int dW_{\text{on system}} = 0 \]

The important thing to remember is that the first law states that the energy is conserved always.
**Sign convention:**

The work done by a system on the surroundings is treated as a positive quantity.

Similarly, energy transfer as heat to the system from the surroundings is assigned a positive sign. With the sign convention one can write,

\[ \int dQ = \int dW \]

**Consequences of the first law:**

Suppose a system is taken from state 1 to state 2 by the path 1-a-2 and is restored to the initial state by the path 2-b-1, then the system has undergone a cyclic process 1-a-2-b-1. If the system is restored to the initial state by path 2-c-1, then the system has undergone the cyclic change 1-a-2-c-1. Let us apply the first law of thermodynamics to the cyclic processes 1-a-2-b-1 and 1-a-2-c-1 to obtain

\[ \int_{1\rightarrow a \rightarrow 2} dQ \quad + \quad \int_{2\rightarrow b \rightarrow 1} dQ \quad - \quad \int_{1\rightarrow a \rightarrow 2} dW \quad - \quad \int_{2\rightarrow b \rightarrow 1} dW = 0 \]

\[ \int_{1\rightarrow a \rightarrow 2} dQ \quad + \quad \int_{2\rightarrow c \rightarrow 1} dQ \quad - \quad \int_{1\rightarrow a \rightarrow 2} dW \quad - \quad \int_{2\rightarrow c \rightarrow 1} dW = 0 \]

Subtracting, we get

\[ \int_{2\rightarrow b \rightarrow 1} dQ - \int_{2\rightarrow c \rightarrow 1} dQ - (\int_{2\rightarrow b \rightarrow 1} dW - \int_{2\rightarrow c \rightarrow 1} dW) = 0 \]

We know that the work is a path function and hence the term in the bracket is non-zero. Hence we find

\[ \int_{2\rightarrow b} dQ = \int_{2\rightarrow c} dQ \]

That is heat is also a path function.
**Energy is a property of the system:**

By rearranging we can have

\[ \int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW) \]

It shows that the integral is the same for the paths 2-b-1 and 2-c-1, connecting the states 2 and 1. That is, the quantity \( \int (dQ - dW) \) does not depend on the path followed by a system, but depends only on the initial and the final states of the system. That is \( \int (dQ - dW) \) is an exact differential of a property. This property is called energy (E). It is given by

\[ dE = dQ - dW \]

\[ E = KE + PE + U \]

where U is the internal energy. Therefore,

\[ dE = d(KE) + d(PE) + dU = dQ - dW \]

Quite often in many situations the KE or PE changes are negligible.

\[ dU = dQ - dW \]

An isolated system does not exchange energy with the surroundings in the form of work as well as heat. Hence \( dQ = 0 \) and \( dW = 0 \). Then the first law of thermodynamics reduces to \( dE = 0 \) or \( E_2 = E_1 \) that is energy of an isolated system remains constant.

**Perpetual Motion Machine of the first kind**: PMM.I

An imaginary device which delivers work continuously without absorbing energy from the surroundings is called a Perpetual Motion machine of the first kind. Since the device has to deliver work continuously, it has to operate on a cycle. If such a device does not absorb energy from its surroundings \( \int dQ = 0 \). From the first law, it can be observed that \( \int dW = 0 \), if \( \int dQ = 0 \). Therefore such a device is impossible from first law of thermodynamics.

**First law analysis of non-flow processes:**

The first law of thermodynamics can be applied to a system to evaluate the changes in its energy when it undergoes a change of state while interacting with its surroundings. The processes that are usually encountered in thermodynamic analysis of systems can be identified as any one or a combination of the following elementary processes:

- Constant volume (isochoric) process
- Constant pressure (isobaric) process
- Constant temperature (isothermal) process.
- Adiabatic process.
**Constant volume (isochoric) process:**

Constant volume process: Suppose a gas enclosed in a rigid vessel is interacting with the surroundings and absorbs energy $Q$ as heat. Since the vessel is rigid, the work done $W$ due to expansion or compression is zero. Applying the first law, we get

$$dU = dQ$$

That is, heat interaction is equal to the change in internal energy of the gas. If the system contains a mass $m$ equal of an ideal gas, then

$$Q = mC_v (T_2 - T_1)$$

The path followed by the gas is shown on a $P$-$V$ diagram. Now consider the fluid contained in a rigid vessel as shown. The vessel is rigid and insulated. Shaft work is done on the system by a paddle wheel as shown in Fig. a. In Fig. b electric work is done on the system. Since the vessel is rigid, the $PdV$ work is zero. Moreover, the vessel is insulated and hence $dQ = 0$. Application of the first law of thermodynamics gives

$$dU = dQ - dW = dQ - (dW_{pdv} + dW_s)$$

Where $dW_{pdv}$ is the compression/expansion work and $dW_s$ is the shaft work. That is increase in internal energy of a system at a constant volume, which is enclosed by an adiabatic wall, is equal to the shaft work done on the system.

**Constant pressure process:**

Several industrial processes are carried out at constant pressure. A few examples of constant pressure processes are: (a) reversible heating/cooling of a gas (b) phase change (c) paddle wheel work (d) electrical work. For a constant pressure process, the work done $W$ is given by

$$W = \int PdV = P (V_2 - V_1)$$

Application of the first law of thermodynamics gives

$$dU = dQ - dW = dQ - PdV = dQ - d(PV)$$

or $dQ = dU + d(PV) = d(U + PV) = dH$

That is in a constant pressure process, the heat interaction is equal to the increase in the enthalpy of the system. Now consider the constant pressure processes in which the system is enclosed by an adiabatic boundary. Application of the first law gives:

$$dU = dQ - dW = dQ - (PdV + dW_s)$$

Here, the net work done ($dW$) consists of two parts – the $PdV$ work associated with the motion of the boundary and ($-dW_s$), the shaft work (or electrical work) done by the
surroundings. Since the system is enclosed by an adiabatic boundary, \( dQ = 0 \) the equation can be written as

\[-dW_s = dU + d(PV) = dH\]

That is, the increase in the enthalpy of the system is equal to the shaft work done on the system.

**Constant temperature process:**

Suppose a gas enclosed in the piston cylinder assembly is allowed to expand from \( P_1 \) to \( P_2 \) while the temperature is held constant. Then application of the first law gives:

\[dU = dQ - dW = dQ - PdV\]

It is not possible to calculate work and heat interactions unless the relationships between the thermodynamic properties of the gas are known. Suppose the gas under consideration is an ideal gas (which follows the relation \( P \)\( V \) = \( RT \) and \( u = u(T) \) only) then for an isothermal process,

\[dU = 0\]

\[dQ = PdV = RTdv/v \text{ or } Q = W = RT\ln(v_2/v_1)\]

**Constant Pressure Process-1**

A gas in the piston-cylinder assembly is considered as the system of interest (figure 7.1)

- The pressure is maintained at a constant value by loading the system with a mass.
- The cylinder is brought into contact with a heat source.
Energy transfer as heat takes place reversibly. The work is done by system when it changes from the initial state (1) to the final state (2).

\[ W = \int_1^2 P \, dV = P(V_2 - V_1) \]  \hspace{1cm} (7.1)

Applying the first law, we get

\[ dU = dQ - dW = dQ - P \, dV = dQ - d(PV) \]  \hspace{1cm} (7.2)

or

\[ dQ = dU + d(PV) = d(U + PV) \]  \hspace{1cm} (7.3)

or

\[ dQ = dH \quad \text{or} \quad Q = H_2 - H_1 \]  \hspace{1cm} (7.4)

The quantity \((U + PV)\) is known as enthalpy, \(H\) (a property) of the system. The specific enthalpy \(h\) is defined as

\[ h = H / m = u + PV \]  \hspace{1cm} (7.5)

The molar enthalpy is \(h = H / N\), where \(N\) is the mole number of the substance.

**Constant Pressure Process-2**

Let us assume paddle wheel work is done on the system figure 7.2. Also, consider adiabatic walls, so that

\[ dQ = 0 \]
Now the application of first law enables us to write

\[ dU = dQ - dW = dQ - (PdV + W_{sh}) \quad (7.6) \]

or

\[ -dW_{sh} = dU + PdV = d(U + PV) = dH \quad (7.7) \]

or

\[ -W_{sh} = H_2 - H_1 \quad (7.8) \]

Therefore, the increase in the enthalpy of the system is equal to the amount of shaft work done on the system.

**Specific Heat at Constant Pressure**

Let us focus on Figure 7.3

![Figure 7.3](image)

- System changes its state from 1 to 2 following a constant pressure process.
- There will be an accompanying change in temperature.

Specific heat at constant pressure is defined as the quantity of energy required to change the temperature of a unit mass of the substance by one degree during a constant pressure process.

\[ c_p = \left( \frac{dQ}{dT} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (7.9) \]

The total heat interaction for a change in temperature from \( T_1 \) to \( T_2 \) can be calculated from

\[ Q = m \int_{T_1}^{T_2} c_p dT = H_2 - H_1 \quad (7.10) \]

The molar specific heat at constant pressure can be defined as

\[ c_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (7.11) \]
**Constant Temperature process**

Let us refer to figure 7.4

![Figure 7.4](image.png)

The system is allowed to undergo an expansion process while in contact with constant temperature bath. During the expansion process, the opposing force is continuously reduced. System is in equilibrium at all times. Applying the first law, one can write

\[
dU = dQ - dW = dQ - W dv
\]  

(7.12)

For an ideal gas, the desired property relations are

\[
Pv = RT \quad \text{and} \quad u = u(T)
\]  

(7.13)

Since the temperature is held constant, \(du=0\) and \(Q=W\). We can also write

\[
q - w = \int_{V_1}^{V_2} \bar{F} dv = \int_{V_1}^{V_2} \frac{RT}{v} dv = RT \ln \frac{v_2}{v_1}
\]
Adiabatic Process:

1. Irreversible Adiabatic Process

A process in which there is no energy transfer as heat across the boundaries of the system, is called an adiabatic process. For an adiabatic process, \( Q = 0 \). Paddle wheel work is performed on the system (Figure 7.5).

![Figure 7.5](image)

Application of first law gives

\[
dU = dQ - dW = 0 - dW
\]

or

\[
\Delta U = -W
\]

2. Reversible Adiabatic (ISENTROPIC) Process

Consider a gas contained in the cylinder piston assembly as the system. The cylinder wall and the piston act as adiabatic walls. Suppose the gas is allowed to expand from the initial pressure \( P_1 \) to the final pressure \( P_2 \) and the opposing pressure is so adjusted that it is equal to inside gas pressure. For such a process, \( dW = PdV \)

The first-law of thermodynamics will give

\[
dU = dQ - dW = -PdV
\]

Let us consider the system as an ideal gas which satisfies the relation \( PV = RT \) and \( u = u(T) \). Also, we know that \( du = c_v dT \).

or
\[ du = -Pdv \]  \hspace{1cm} (7.17)

or,

\[ c_v(T_2 - T_1) = -\int Pdv \]  \hspace{1cm} (7.18)

or

\[ c_v(T_1 - T_2) = \int Pdv = w \]  \hspace{1cm} (7.19)

or

For an ideal gas, \( h = u + P_v = u + RT \)

Therefore,

\[ c_p = \left( \frac{\partial h}{\partial T} \right)_p = c_v + R \]  \hspace{1cm} (7.20)

The ratio of specific heats is given by

\[ \gamma = \frac{c_p}{c_v} = 1 + \frac{R}{c_v} \]  \hspace{1cm} (7.21)

or,

\[ c_v = \frac{R}{(\gamma - 1)} \]  \hspace{1cm} (7.22)

Thus,

\[ w = c_v(T_2 - T_1) = \frac{R(T_1 - T_2)}{\gamma - 1} = \frac{Rv_1 - Rv_2}{\gamma - 1} \]  \hspace{1cm} (7.23)

Therefore when an ideal gas expands reversibly and adiabatically from the initial state \( (P_1, v_1, T_1) \) to final state \( (P_2, v_2, T_2) \), the work done per mole of the gas is given by the above expression.
Characterisation of Reversible Adiabatic Process

Let us find out the path followed by the system in reaching the final state starting from the initial state. We have already seen that for an ideal gas

\[ c_v dT = -P d\nu = -\frac{RT}{\nu} d\nu \]  

(8.1)

or,

\[ \frac{dT}{T} = -\frac{R}{c_v} \frac{d\nu}{\nu} = -(\gamma - 1) \frac{d\nu}{\nu} \]  

(8.2)

or,

\[ \ln \frac{T_2}{T_1} = -(\gamma - 1) \ln \frac{\nu_2}{\nu_1} \]  

(8.3)

or,

\[ \frac{T_2}{T_1} = \left( \frac{\nu_1}{\nu_2} \right)^{\gamma-1} \]  

(8.4)

or

\[ \frac{T_2}{T_1} \nu_2^{\gamma-1} = 1 \quad \text{or} \quad T_0 \nu_0^{\gamma-1} = \text{constant} \]  

(8.5)

Since, \( P \nu = RT \)

\[ \frac{T_2}{T_1} = \frac{P_2 \nu_2}{P_1 \nu_1} \]  

(8.6)

From (8.4) and (8.6) we get

\[ \frac{P_2 \nu_2}{P_1 \nu_1} = \left( \frac{\nu_1}{\nu_2} \right)^{\gamma-1} \]  

(8.7)

or

\[ \frac{P_2 \nu_2^\gamma}{P_1 \nu_1^\gamma} = 1 \]  

(8.8)

or,

\[ \frac{P \nu^\gamma}{\text{constant}} \]  

(8.9)
Polytropic Process:

Ideal gas undergoes a reversible-adiabatic process; the path followed by the system is given by

\[ P\nu^T = \text{constant} \]  \hspace{1cm} (8.10)

and the work done per kg of gas

\[ w = \frac{R \nu_1 - P_2 \nu_2}{\gamma - 1} \]  \hspace{1cm} (8.11)

To generalise,

\[ P\nu^n = \text{constant} \Rightarrow w = \frac{R \nu_1 - P_2 \nu_2}{n - 1} \]  \hspace{1cm} (8.12)

\( n \) is polytropic index (\( \gamma \) is the property of the system, also it indicates reversible-adiabatic process)

- \( n = 0 \), constant pressure process
  \[ w = P(\nu_2 - \nu_1) \]

- \( n = 1 \), constant temperature process
  \[ w = q = RT \ln \frac{\nu_2}{\nu_1} \]

- \( n = \gamma \), reversible adiabatic process
  \[ w = \frac{R \nu_1 - P_2 \nu_2}{\gamma - 1} \]

- \( n = \infty \), constant volume process
  \[ w = 0 \]
**Polytropic Process**

\[
W = \int \frac{cdv}{v^n}
\]

\[
w = \frac{(P_1v_1 - P_2v_2)}{(n-1)}
\]

\[
du = dq - dw
\]

\[
u_2 - u_1 = q - \frac{(P_1v_1 - P_2v_2)}{(n-1)}
\]

\[
u_2 - u_1 = C_v \ (T_2 - T_1) = q - w
\]

\[
q = R(T_2 - T_1)/((\gamma-1) + \frac{(P_1v_1 - P_2v_2)}{(n-1)}
\]

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

\[
=\frac{(P_1v_1 - P_2v_2)}{(n-1)} \{\frac{\gamma-n}{(\gamma-1)}
\]

\[
=w.\{\frac{\gamma-n}{(\gamma-1)}
\]

**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) \(P_1v_1^{1.25} = P_2v_2^{1.25}\)

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

\[
T_2 = \frac{P_1P_2v_2}{P_1v_1} = \frac{(300 \times 32 \times 1)}{(1 \times 16)}
\]

\[
= 600\text{K}
\]

(b) \(w = \frac{(P_1v_1 - P_2v_2)}{(n-1)}\)

\[
= R_u(T_1 - T_2)/(n-1)
\]

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

(c) \(q = w.\{\frac{\gamma-n}{(\gamma-1)}\}\)

\[
= -9.977 \ (1.4 - 1.25)/(1.4-1)
\]

\[
= -3.742 \text{kJ/mol}
\]
**Unresisted or Free expansion**

In an irreversible process, \( w \neq \int P \, dv \)

Vessel A: Filled with fluid at pressure

Vessel B: Evacuated/low pressure fluid

Valve is opened: Fluid in A expands and fills both vessels A and B. This is known as unresisted expansion or free expansion.

No work is done on or by the fluid.

No heat flows (Joule’s experiment) from the boundaries as they are insulated.

\[ U_2 = U_1 \quad (U = U_A + U_B) \]
**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, $\Delta U = 0$ ($U_2 = U_1$)

Amount of helium = $N_{He} = PAVA/R_uTA$

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

\[= 60.14 \text{ mol.}
\]

Amount of nitrogen = $N_{N2} = PBVB/R_uTB$

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

\[= 96.22 \text{ mol.}
\]

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

\[
[N_Cv(T_f-400)]_{He} + [N_Cv(T_f-500)]_{N2} = 0
\]

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

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

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

$P_fV_f = (N_{He} + N_{N2})R_u T_f$

\[
2P_f = (60.14 + 96.22) 8.314 \times (472.73)
\]

Or, $P_f = \textbf{307.27 kPa}$
Control-Volume Analysis:

Control volume is a volume in space of special interest for particular analysis. The surface of the control volume is referred as a control surface and is a closed surface. The surface is defined with relative to a coordinate system that may be fixed, moving or rotating.

Mass, heat and work can cross the control surface and mass and properties can change with time within the control volume.

Examples: turbines, compressors, nozzle, diffuser, pumps, heat exchanger, reactors, a thrust-producing device, and combinations of these.

First law of thermodynamics for a continuous system

Let the continuous system be in state 1 at time t and after a differential time dt, let it be in the state 2. The change in the energy of the continuous system is,

\[
dE = \frac{d[\int \rho edV]}{dt} dt
\]

Now,

\[
dE = dQ – dW
\]

or,

\[
\frac{dE}{dt} = \dot{Q} – \dot{W}
\]

\[
\frac{d}{dt} \int \rho edV = \dot{Q} – \dot{W}
\]

First law of thermodynamics to a control volume

\[
\frac{dm}{dt} = \dot{m}_i – \dot{m}_e
\]

Or

[Rate of accumulation of mass inside the control volume] = [Rate of mass entering the control volume at inlet] – [Rate of mass leaving the control volume at exit]

The above is commonly known as **continuity equation.**
We should identify a definite quantity of matter which remains constant as the matter flows. For this purpose, let the boundary of the system include all matter inside the control volume and that which is about to enter the control volume during the differential time interval $dt$.

At time $t$, the system is defined as the mass contained in the control volume and the mass in region $A$ which is about to enter the control volume in a differential time $dt$.

At time $t+dt$, the system is defined as the mass contained in the control volume and the mass in region $B$.

Therefore, during the differential time $dt$, the system configuration undergoes a change.

Mass contained in region $A = m_i\ dt$

Mass contained in region $B = m_e\ dt$

From mass balance,

$$m(t) + m_i\ dt = m(t+dt) + m_e\ dt$$

The work done as the mass enters the control volume = $-P_i v_i m_i\ dt$

The work done by mass exiting the control volume = $P_e v_e m_e\ dt$

Energy of the system at time $t = E(t) + m_i\ e_i dt$

Energy of the system at time $(t+dt) = E(t+dt) + m_e\ e_e\ dt$

Energy transferred as heat to the system = $Q\ dt$

Shaft work done by the system = $W_{sh}\ dt$

From the first law,

$$[E(t+dt) + e_e m_e\ dt] - [E(t) + m_i\ e_i dt] = Q\ dt - W_{sh}\ dt - (P_e v_e m_e - P_i v_i m_i)\ dt$$
\[ m_e (e_e + P_e v_e) - m_i (e_i + P_i v_i) = \dot{Q} - \frac{E(t + dt) - E(t)}{dt} W_{sh} \]

or,

\[ \dot{m}_e (h_e + \frac{V_e^2}{2} + gZ_e) - \dot{m}_i (h_i + \frac{V_i^2}{2} + gZ_i) = \dot{Q} - \dot{W}_{sh} - \frac{dE}{dt} \]

where, \( h_e = u_e + P_e v_e \), \( h_i = u_i + P_i v_i \)

Or, Rate of energy accumulation = rate of energy inflow – rate of energy outflow

**Steady state flow process**

Assumptions:

\[ \dot{m}_i = \dot{m}_e = \dot{m} \]

The state of matter at the inlet, exit and at any given point inside the control volume does not change with respect to time.

\[ \frac{dE}{dt} = 0 \]

The rate of energy transfers across the control surface is constant.

\[ m (h_e + \frac{V_e^2}{2} + gZ_e) - (h_i + \frac{V_i^2}{2} + gZ_i) = \dot{Q} - \dot{W}_{sh} \]
Steady state steady flow process

\[ q - w = \Delta h + \Delta Ke + \Delta Pe = h_e - h_i + \frac{V_e^2 - V_i^2}{2} + g(Z_e - Z_i) \]

where \( q = \frac{Q}{m} \) and \( w = \frac{W_{sh}}{m} \)

For negligible change in kinetic and potential energies through the control volume,

\[ q - w = \Delta h \quad (kJ / kg) \]

If the control volume is well insulated (i.e. adiabatic), then, \( q = 0 \).

For steady flow devices, such as turbines, compressors and pumps, \( W_{sh} \) is power transmitted through a shaft.

\[ \Delta Ke = \frac{(V_e^2 - V_i^2)}{2} \]
The unit of \( ke \) is \( m^2/s^2 \) which is equivalent to Joule/kg. The enthalpy is usually given in kJ/kg. So kinetic energy should be expressed in kJ/kg. This is accomplished by dividing it by 1000.

Kinetic energy term at low velocities is negligible, but should be accounted for at high velocities.

By similar argument, the elevation difference between inlet and exit of most industrial devices such as compressors and turbines is small and potential energy term is negligible (particularly for gases). The only time the potential energy term is significant is when a process involves pumping a fluid to high elevations.

**Turbine**

A turbine is a rotary steady state steady flow machine whose purpose is the production of shaft power at the expense of the pressure of the working fluid.

Two general classes of turbines are steam and gas turbines depending on the working substance used.

Usually, changes in potential energy are negligible, as is the inlet kinetic energy. Often the exit kinetic energy is neglected (if in a problem, the flow velocities are specified, the kinetic energy term should be included).

Normally, the process in the turbine is adiabatic and the work output reduces to decrease in enthalpy from the inlet to exit states.

\[
W_{sh} = \dot{m}(h_i - h_e)
\]

**Compressor / pump**

The purpose of a compressor (gas) or pump (liquid) is the same, to increase the pressure of a fluid by putting in shaft work (power). There are two fundamentally different types of compressors:

1. The rotary type (either axial or centrifugal flow)
2. A piston/cylinder type compressor.

The first type is analyzed using control volume approach (steady state steady flow process). The working fluid enters the compressor at low pressure and exits at high pressure.

Usually, changes in potential energy are negligible as is the inlet kinetic energy. Often, exit kinetic energy is neglected as well (wherever, in a problem, velocities are specified, \( ke \) term should not be neglected).
The compression process is usually adiabatic.

\[
\dot{W}_{sh} = \dot{m} \left[ (h_i - h_e) + \frac{(V_i^2 - V_e^2)}{2} \right]
\]

**Nozzle**

A nozzle is a steady state steady flow device to create a high velocity fluid stream at the expense of its pressure. It is contoured in an appropriate manner to expand the fluid to a lower pressure.

Since the objective of the device is to increase the flow velocity, hence kinetic energy, the kinetic energy term cannot be ignored. Usually, the process through the nozzle is treated as adiabatic.

Since there are no moving parts, shaft work is zero. The potential energy term (for gases) is negligible and hence omitted.

\[
(h_i - h_e) = \frac{(V_e^2 - V_i^2)}{2}
\]

**A systematic approach to problem solving**

**Step 1.** Identify the system and draw a sketch of it. The system that is about to be analyzed should be identified on the sketch by drawing its boundaries using the dashed lines.

**Step 2.** List the given information on the sketch. Heat and work interactions if any should also be indicated on the sketch with proper directions.

**Step 3.** State any assumptions:

The simplifying assumptions that are made to solve a problem should be stated and fully justified.

Commonly made assumptions:

(a) Assuming process to be quasi-equilibrium
(b) Neglecting \(PE\) and \(KE\)
(c) Treating gas as ideal
(d) Neglecting heat transfer from insulated systems.
Step 5. Apply the conservation equations.

Step 6. Draw a process diagram.

Determine the required properties and unknowns.

Problem # 1 A 0.1 m$^3$ rigid tank contains steam initially at 500 kPa and 200°C. The steam is now allowed to cool until the temperature drops to 50°C. Determine the amount of heat transfer during this process and the final pressure in the tank.

State 1: $P_1 = 500$ kPa, $T_1 = 200$°C

$v_1 = 0.4249$ m$^3$/kg, $u_1 = 2642.9$ kJ/kg

State 2: $v_2 = v_1 = 0.4269$ m$^3$/kg

$T_2 = 50$°C $\rightarrow$ $v_f = 0.001$ m$^3$/kg

$v_g = 12.03$ m$^3$/kg

$u_f = 209.32$ kJ/kg

$u_g = 2443.5$ kJ/kg

$P_2 = P_{sat}@50°C = \textbf{12.349 kPa}$

$v_2 = v_f + x_2v_g$

$0.4249 = 0.001 + x_2(12.03 = 0.001)$

$x_2 = 0.0352$

$u_2 = u_f + x_2u_g$

$= 209.32 + (0.0352)(2443.5 - 209.32)$

$= 288.0$ kJ/kg

$m = V/u = (0.1$ m$^3$/kg)/(0.4249 m$^3$/kg)
\[ Q_{out} = \Delta U = m(u_2 - u_1) \]
\[ Q_{out} = m(u_1 - u_2) \]
\[ = (0.235)(2642.9 - 288) \]
\[ = 553.4 \text{ kg} \]

Problem #2 A piston/cylinder contains 50 kg of water at 200 kPa with a volume of 0.1 m³. Stop in the cylinder is placed to restrict the enclosed volume to 0.5 m³. The water is now heated until the piston reaches the stops. Find the necessary heat transfer.

At 200 kPa,
\[ v_f = 0.001061 \text{ m}^3/\text{kg} \]
\[ v_{fg} = 0.88467 \text{ m}^3/\text{kg} \]
\[ h_f = 504.68 \text{ kJ/kg} \]
\[ h_{fg} = 2201.96 \text{ kJ/kg} \]

This is a constant pressure process. Hence, \[ Q = \Delta H \]

The specific volume initially,
\[ v_i = 0.1 /50 = 0.002 \text{ m}^3/\text{kg} \]
\[ v = v_f + x v_{fg} \]
\[ = 0.001061 + x (0.88467) \]
Therefore, \[ x = (0.002 - 0.001061) / 0.88467 \]
\[ = 0.001061 \]
\[ h = h_f + x h_{fg} \]
\[ = 504.68 + 0.001061(2201.96) \]
\[ = 507.017 \text{ kJ/kg} \]

\[ v_{final} = 0.5 /50 = 0.01 \text{ m}^3/\text{kg} \]
\[ v = v_f + x v_{fg} \]
Therefore, \( x = (0.01 - 0.001061) / 0.88 \) = 0.01

\[
h_{final} = 504.68 + 0.01(2201.96)
\]

= 526.69 kJ/kg

\[
Q = \Delta H = 50 (526.69 - 507.017)
\]

= 983.65 kJ/kg

**Problem # 3**  A rigid insulated tank is separated into two rooms by a stiff plate. Room A of 0.5 m\(^3\) contains air at 250 kPa, 300 K and room B of 1 m\(^3\) has air at 150 kPa, 1000 K. The plate is removed and the air comes to a uniform state without any heat transfer. Find the final pressure and temperature.

The system comprises of room A and B together. This is a constant internal energy process as there is no heat and work exchange with the surroundings.

\[
m_A = \frac{P_AV_A}{RT_A} = \frac{(250 \times 1000 \times 0.5)}{(287 \times 300)} = 1.452 \text{ kg}
\]

\[
m_B = \frac{P_BV_B}{RT_B} = \frac{(150 \times 1000 \times 1.0)}{(287 \times 1000)} = 0.523 \text{ kg}
\]

\[
\Delta U_A + \Delta U_B = 0
\]

Let \( T_f \) be the final temperature at equilibrium

\[
m_A (T_f - 300) + m_B (T_f - 1000) = 0
\]

1.452 \( (T_f - 300) + 0.523 \( (T_f - 1000) = 0

\[
T_f = 485.37 \text{ K}
\]

\[
P_f = \frac{(1.452 + 0.523) \times 287 \times 485.37}{1.5}
\]

= 183.41 kPa
SYSTEM: Steam

System boundaries

Step 1: Draw a sketch of the system and system boundaries.

Step 2: List the given information on the sketch.

\[ V = 0.1 \text{ m}^3 \]
\[ P_1 = 500 \text{ kPa} \]
\[ T_1 = 200 \, ^\circ\text{C} \]
\[ T_2 = 50 \, ^\circ\text{C} \]

Heat

Step 3: Look for simplifications.

\[ v_1 = v_2 \]
\[ \dot{V} = 0 \]

Step 4: Make realistic assumptions, if necessary.

Assume:

(1) \( \Delta PE = 0 \) (since there is no mention of elevation change).

(2) \( \Delta KE = 0 \) (since there is no mention of velocity change).
**Problem # 4** A piston / cylinder assembly contains 0.1m³ of superheated steam at 10 bar and 400°C. If the steam is allowed to expand reversibly and adiabatically to a pressure of 3 bar, calculate the work done by the steam.

At 10 bar and 400°C,

\[ v = 0.3065 \text{ m}^3/\text{kg} \]
\[ h = 3264.4 \text{ kJ/kg} \]
\[ s = 7.4665 \text{ kJ/kg K} \]

At 3 bar,

\[ s_g = 6.9909 \text{ kJ/kg K} \]

This is an isentropic process as initial entropy value is greater than \( s_g \) at 3 bar, the steam is superheated at the end of the process.

At 3 bar and 200°C,

\[ s = 7.3119 \text{ kJ/kg K} \text{ and} \]
\[ \text{at 300°C, } s = 7.7034 \text{ kJ/kg K} \]

therefore, the final state is having a temperature between 200°C and 300°C.

Equating \( s_i = s_{\text{final}} \).

Find the enthalpy and specific volume by interpolation. Then calculate \( u_i \) and \( u_{\text{final}} \).

The work done = \( \Delta U = m(u_i - u_{\text{final}}) \)
Enthalpy of a compressed liquid

Determine the enthalpy of water at 100°C and 15 MPa (a) by using compressed liquid tables, (b) by approximating it as a saturated liquid, and (c) by using the correction factor.

At 100°C, the saturation pressure of water is 101.35 kPa, and since P>P_{sat}, the water exists as a compressed liquid at the specified state.

(a) from the compressed liquid tables,
\[ P = 15 \text{ Mpa, } T = 100°C, \ h = 430.28 \text{ kJ/kg} \]
This is the exact value.

(b) Approximating the compressed liquid as a saturated liquid at 100°C, as is commonly done, we obtain
\[ h = h_{f100°C} = 419.04 \text{ kJ/kg} \]
This value is in error by about 2.6 percent.

(c) From equation
\[ h_{P,T} = h_{fT} + v_{fT}(P - P_{sat}) \]
\[ = 419.04 + 0.001(15000 - 101.35) \text{ kJ/kg} \]
\[ = 434.60 \text{ kJ/kg} \]

**Problem # 1 (Nozzle)**

Nitrogen gas flows into a convergent nozzle at 200 kPa, 400 K and very low velocity. It flows out of the nozzle at 100 kPa, 330 K. If the nozzle is insulated, find the exit velocity.

\[ V_i = 0 \]
Adiabatic nozzle

The SSSF equation:
\[ V_e^2/2 = (h_i - h_o) = C_p(T_i - T_o) \]
\[ = \{\gamma R_u/M(\gamma - 1)\}(T_i - T_o) \]
\[ = \{1.4 * 8314/(28*0.4)\}(400-330) \]
\[ = 72747.5 \text{ m}^2/\text{s}^2 \]
We get, \[ V_e = 381.44 \text{ m/s} \]
Compressing air by a compressor

Air at 100 kPa and 280 K is compressed steadily to 600 kPa and 400 K. The mass flow rate of air is 0.02 kg/s and a heat loss of 16 kJ/kg occurs during the process. Assuming the changes in KE and PE are negligible, determine the necessary power input to the compressor.

We take the compressor as the system. This is a control volume since the mass crosses the system boundary during the process. Heat is lost from the system and work is supplied to the system.

With similar assumptions as in the diffuser problem,

\[ w = q + (h_2 - h_1) \]

The input power = \( m (q + (h_2 - h_1)) \)

= 0.02 (16 + (1.004*(400 - 280)))

= 2.73 kW
Power generation by a steam turbine

The power output of an adiabatic steam turbine is 5 MW, and the inlet and exit conditions of the steam are as indicated in the figure.

(a) Compare the magnitude of $\Delta h$, $\Delta KE$, and $\Delta PE$
(b) Determine the work done per unit mass of the steam flowing through the turbine
(c) Calculate the mass flow rate of the steam.

We take the turbine as a system. The control volume is shown in the figure. The system, the inlet and exit velocities do work and elevations are given and thus the kinetic and potential energies are to be considered.

At the inlet, the steam is in superheated vapor state.

$$ h_1 = 3247.6 \text{ kJ/kg} $$

At the turbine exit, we have a saturated liquid-vapor mixture at 15 kPa pressure. The enthalpy at this state is

$$ h_2 = h_f + x_2h_g $$

$$ = 225.94 + 0.9 \times 2373.1 $$

$$ = 2361.73 \text{ kJ/kg} $$

$$ \Delta h = h_2 - h_1 $$
\[
\Delta e = (V_2^2 - V_1^2) / 2 = (180^2 - 50^2) / 2 * 1000 \\
= 14.95 \text{ kJ/kg}
\]

\[
\Delta Pe = g(Z_2 - Z_1) = 9.807 * (6 - 10) / 1000 \\
= -0.04 \text{ kJ/kg}
\]

\[
\omega_{out} = -(h_2 - h_1) + (V_2^2 - V_1^2) / 2 + g(Z_2 - Z_1)
\]

\[
= -(-885.87 + 14.95 - 0.04)
\]

\[
= 870.96 \text{ kJ/kg}
\]

(d) The required mass flow rate for a 5MW power output is \( \frac{5000}{870.96} = 5.74 \text{ kg/s} \)

**Limitations of First Law:**
First law is a statement of conservation of energy principle. Satisfaction of first law alone does not ensure that the process will actually take place.

Examples:

1. A cup of hot coffee left in a cooler room eventually cools off. The reverse of this process- coffee getting hotter as a result of heat transfer from a cooler room does not take place.
2. Consider heating of a room by passage of electric current through an electric resistor. Transferring of heat from room will not cause electrical energy to be generated through the wire.
3. Consider a paddle-wheel mechanism operated by fall of mass. Potential energy of mass decreases and internal energy of the fluid increases. Reverse process does not happen, although this would not violate first law.
4. Water flows down hill where by potential energy is converted into K.E. Reverse of this process does not occur in nature.

**Conclusion:**
Processes proceed in a certain direction and not in the reverse direction. The first law places no restriction on direction. A process will not occur unless it satisfies both the first and second.
UNIT.III

Second Law of Thermodynamics

**Kelvin-Planck Statement:** - It is impossible to devise a cyclically operating device, which produces no other effect than the extraction of heat from a single thermal reservoir and delivers an equivalent amount of work.

Heat engine with single thermal reservoir is not possible.

For a 1-T engine the thermal efficiency $\eta=W/Q=1$. No heat engine can have efficiency equal to unity.

Second law not only identifies the direction of process, it also asserts that energy has quality as well as quantity.

**Thermal Reservoir**

A thermal reservoir is a large system (very high mass x specific heat value) from which a quantity of energy can be absorbed or added as heat without changing its temperature. The atmosphere and sea are examples of thermal reservoirs.

Any physical body whose thermal energy capacity is large relative to the amount of energy it supplies or absorbs can be modeled as a thermal reservoir.

A reservoir that supplies energy in the form of heat is called a source and one that absorbs energy in the form of heat is called a sink.

**Heat Engine**

It is a cyclically operating device which absorbs energy as heat from a high temperature reservoir, converts part of the energy into work and rejects the rest of the energy as heat to a thermal reservoir at low temperature.

The working fluid is a substance, which absorbs energy as heat from a source, and rejects energy as heat to a sink.
Q_2 – Heat rejected to cooling water in condenser

W_P – Work done on the pump

W_{net} = W_T - W_P

W = Q_1 - Q_2
Thermal Efficiency,

\[ \eta = \frac{W_{net}}{Q_1} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \]

Schematic representation of Heat Engine:
**Schematic representation of Refrigerator and Heat pump.**

QL – Heat absorbed from low temperature thermal reservoir

QH – Heat rejected to a high temperature thermal reservoir when work (W) is done on it.
\[(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}\]

\[(COP)_{HP} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}\]

In a reversible, isothermal expansion of an ideal gas, all the energy absorbed as heat by the system is converted completely into work. However this cannot produce work continuously (not a cycle).

Single reservoir heat engine (1 T engine) is not possible.

**Clausius Statement**: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body.

**Equivalence of the two statements**

To prove that violation of the Kelvin-Planck Statement leads to a violation of the Clausius...
Statement, let us assume that Kelvin-Planck statement is incorrect.

Consider a cyclically working device 1, which absorbs energy $Q_1$ as heat from a thermal reservoir at $T_H$. Equivalent amount of work $W (W=Q_1)$ is performed.

Consider another device 2 operating as a cycle, which absorbs energy $Q_L$ as heat from a low temperature thermal reservoir at $T_L$ and rejects energy $Q_H$ ($Q_H=Q_L+W$). Such a device does not violate Clausius statement.

If the two devices are now combined, the combined device (enclosed by the dotted boundary) transfers heat $Q_L$ from the low temperature reservoir at $T_L$ to a high temperature reservoir at $T_H$ without receiving any aid from an external agent, which is the violation of the Clausius statement.

Likewise let us assume that the Clausius statement is incorrect. So we have a device 1, cyclically working transferring heat $Q$ from a low temperature reservoir at $T_L$ to a high temperature thermal reservoir at $T_H$. Consider another device 2, which absorbs heat $Q_1$ from a high temperature reservoir at $T_H$ does work $W$ and rejects energy $Q$ as heat to the low temperature reservoir at $T_L$ as shown in figure.

If the two devices are combined (shown in figure by a dotted enclosure), then the combined device receives energy $(Q_1-Q)$ as heat from a thermal reservoir and delivers equivalent work $(W=Q_1-Q)$ in violation of the Kelvin-Planck statement.

Therefore violation of Clausius statement leads to the violation of the Kelvin-Planck statement. Hence, these two statements are equivalent.

**Perpetual Motion Machines**

A device that violates the First law of thermodynamics (by creating energy) is called a Perpetual Motion Machine of the first kind.

A device that violates the Second law of thermodynamics is called a Perpetual Motion Machine of the Second kind.
The first device supplies continuously energy without receiving it. So this is a system creating energy and therefore violating the first law.

The second device exchanges heat with a single reservoir and thus a net amount of work. This need not violate the first law, but violates the second law and therefore will not work.

**Reversible and Irreversible Processes**

A process is said to be reversible if both the system and the surroundings can be restored to their respective initial states, by reversing the direction of the process. A reversible process is a process that can be reversed without leaving a trace on the surroundings. Processes that are not reversible are called Irreversible processes.

**Irreversibilities**

The factors that cause a process to be irreversible are called irreversibilities. Examples:

1. Friction
2. Unrestrained expansion
3. Mixing of two gases
4. Heat transfer across a finite temperature difference
5. Spontaneous chemical reactions
6. Expansion or Compression with finite pressure difference
7. Mixing of matter at different states

**Carnot cycle:**

![Diagram of the Carnot cycle](image)

The Carnot cycle uses only two thermal reservoirs – one at high temperature $T_1$ and the other at two temperature $T_2$.

If the process undergone by the working fluid during the cycle is to be reversible, the heat transfer must take place with no temperature difference, i.e. it should be isothermal.

The Carnot cycle consists of a reversible isothermal expansion from state 1 to 2, reversible adiabatic expansion from state 2 to 3, a reversible isothermal compression from state 3 to 4 followed by a reversible adiabatic compression to state 1.

The thermal efficiency, $\eta$ is given by

$$\eta = \frac{\text{Net work done}}{\text{Energy absorbed as heat}}$$

During processes 2-3 and 4-1, there is no heat interaction as they are adiabatic.
\[
Q_{1-2} = \int_1^2 P \, dv = \int_1^2 RT_1 \, \frac{dv}{v} = RT_1 \ln \left( \frac{v_2}{v_1} \right)
\]

Similarly for the process 3-4,
\[
Q_{3-4} = \int_3^4 P \, dv = \int_3^4 RT_2 \, \frac{dv}{v} = RT_2 \ln \left( \frac{v_4}{v_3} \right)
\]

Net heat interaction = Net work done
\[
= RT_1 \ln \left( \frac{v_2}{v_1} \right) + RT_2 \ln \left( \frac{v_4}{v_3} \right)
\]

The processes 2-3 and 4-1 are reversible, adiabatic and hence
\[
T_1 v_2^{\gamma-1} = T_2 v_3^{\gamma-1}
\]
Or,
\[
v_2/v_3 = \left( \frac{T_2}{T_1} \right)^{1/(\gamma-1)}
\]

\[
T_2 v_4^{\gamma-1} = T_1 v_1^{\gamma-1}
\]
Or,
\[
v_1/v_4 = \left( \frac{T_2}{T_1} \right)^{1/(\gamma-1)}
\]

\[
v_2/v_3 = v_1/v_4 \quad \text{or} \quad v_2/v_1 = v_3/v_4
\]
\[
\eta = \frac{RT_1 \ln \left( \frac{v_2}{v_1} \right) - RT_2 \ln \left( \frac{v_3}{v_4} \right)}{RT_1 \ln (v_2/v_1)}
\]
\[
\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}
\]

The Carnot Principles

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between same two thermal reservoirs.
2. The efficiencies of all reversible heat engines operating between the same two thermal reservoirs are the same.
Let us assume it is possible for an engine I to have an efficiency greater than the efficiency of a reversible heat engine R.

\[ \eta_I > \eta_R \]

Let both the engines absorb same quantity of energy \( Q_1 \). Let \( Q \) and \( Q_2 \) represent the energy rejected as heat by the engines R, and I respectively.

\[ W_I = Q_1 - Q \]
\[ W_R = Q_1 - Q_2 \]
\[ \eta_I = W_I / Q_1 = (Q_1 - Q)/Q_1 = 1 - Q/Q_1 \]
\[ \eta_R = W_R/Q_1 = (Q_1 - Q_2)/Q_1 = 1 - Q_2/Q_1 \]

Since \( \eta_I > \eta_R \),

\[ 1 - Q/Q_1 > 1 - Q_2/Q_1 \]

or, \( Q < Q_2 \)
Therefore, \( W_I = Q_1 - Q > W_R = Q_1 - Q_2 \)

Since the engine R is reversible, it can be made to execute in the reverse order. Then, it will absorb energy \( Q_2 \) from the reservoir at \( T_2 \) and reject energy \( Q_1 \) to the reservoir at \( T_1 \) when work \( W_R \) is done on it.

If now engines I and R are combined, the net work delivered by the combined device is given by

\[
W_I - W_R = Q_1 - Q - (Q_1 - Q_2) = Q_2 - Q
\]

The combined device absorbs energy \( Q_2 - Q \) as heat from a single thermal reservoir and delivers an equivalent amount of work, which violates the second law of thermodynamics.

Hence, \( \eta_R \geq \eta_I \)

---

Carnot principle 2

---
Consider two reversible heat engines $R_1$ and $R_2$, operating between the two given thermal reservoirs at temperatures $T_1$ and $T_2$.

Let $\eta_{R1} > \eta_{R2}$

$Q_1 =$ energy absorbed as heat from the reservoir at $T_1$ by the engines $R_1$ and $R_2$, separately.

$Q =$ energy rejected by reversible engine $R_1$ to the reservoir at $T_2$

$Q_2 =$ energy rejected by reversible engine $R_2$ to the reservoir at $T_2$.

$W_{R1} = Q_1 - Q =$ work done by a reversible engine $R_1$.

$W_{R2} = Q_1 - Q_2 =$ work done by a reversible engine $R_2$

According to assumption,

$\eta_{R1} > \eta_{R2}$

Or, $1 - Q/Q_1 > 1 - Q_2/Q_1$

$Q_1 - Q > Q_1 - Q_2$ or $W_{R1} > W_{R2}$

$W_{R1} - W_{R2} = (Q_1 - Q) - (Q_1 - Q_2) = Q_2 - Q$

Since the engine $R_2$ is reversible, it can be made to execute the cycle in the reverse by supplying $W_{R2}$.

Since $W_{R1} > W_{R2}$ the reversible engine $R_2$ can be run as a heat pump by utilizing part of the work delivered by $R_1$.

For the combined device,
\[ W_{R1} - W_{R2} = Q_2 - Q, \] by absorbing energy \( Q_2 - Q \) from a single thermal reservoir which violates the second law of thermodynamics.

Hence \( \eta_{R1} > \eta_{R2} \) is incorrect.

By similar arguments, if we assume that \( \eta_{R2} > \eta_{R1} \) then,

\[ \eta_{R1} \geq \eta_{R2} \]

Therefore, based on these two equations,

\[ \eta_{R1} = \eta_{R2} \]

The efficiency of a reversible heat engine is also independent of the working fluid and depends only on the temperatures of the reservoirs between which it operates.

**Thermodynamic Temperature Scale**

To define a temperature scale that does not depend on the thermometric property of a substance, Carnot principle can be used since the Carnot engine efficiency does not depend on the working fluid. It depends on the temperatures of the reservoirs between which it operates.

Consider the operation of three reversible engines 1, 2 and 3. The engine 1 absorbs energy \( Q_1 \) as heat from the reservoir at \( T_1 \), does work \( W_1 \) and rejects energy \( Q_2 \) as heat to the reservoir at \( T_2 \).
Let the engine 2 absorb energy $Q_2$ as heat from the reservoir at $T_2$ and does work $W_2$ and rejects energy $Q_3$ as heat to the reservoir at $T_3$.

The third reversible engine 3, absorbs energy $Q_1$ as heat from the reservoir at $T_1$, does work $W_3$ and rejects energy $Q_3$ as heat to the reservoir at $T_3$.

$$\eta_1 = \frac{W_1}{Q_1} = 1 - \frac{Q_2}{Q_1} = f(T_1, T_2)$$

or, $Q_1/Q_2 = F(T_1, T_2)$

$$\eta_2 = 1 - \frac{Q_3}{Q_2} = f(T_2, T_3)$$

or, $T_2/T_3 = F(T_2, T_3)$

$$\eta_3 = 1 - \frac{Q_3}{Q_1} = f(T_1, T_3)$$

$T_1/T_3 = F(T_1, T_3)$

Then, $Q_1/Q_2 = (Q_1/Q_3)/(Q_2/Q_3)$

Or, $F(T_1, T_2) = F(T_1, T_3)/F(T_2, T_3)$

Since $T_3$ does not appear on the left side, on the RHS also $T_3$ should cancel out. This is possible if the function $F$ can be written as

$$F(T_1, T_2) = \phi(T_1) \psi(T_2)$$

$$\phi(T_1) \psi(T_2) = \{\phi(T_1) \psi(T_3)\} / \{\phi(T_2) \psi(T_3)\}$$

$$= \phi(T_1) \psi(T_2)$$

Therefore, $\psi(T_2) = 1 / \phi(T_2)$

Hence, $Q_1/Q_2 = F(T_1, T_2) = \phi(T_1)/\phi(T_2)$

Now, there are several functional relations that will satisfy this equation. For the thermodynamic scale of temperature, Kelvin selected the relation

$$Q_1/Q_2 = T_1/T_2$$

That is, the ratio of energy absorbed to the energy rejected as heat by a reversible engine is equal to the ratio of the temperatures of the source and the sink.

The equation can be used to determine the temperature of any reservoir by operating a reversible engine between that reservoir and another easily reproducible reservoir and by measuring efficiency (heat interactions). The temperature of easily reproducible thermal reservoir can be arbitrarily assigned a numerical value (the reproducible reservoir can be at triple point of water and the temperature value assigned 273.16 K).

The efficiency of a Carnot engine operating between two thermal reservoirs the temperatures of which are measured on the thermodynamic temperature scale, is given by

$$\eta_1 = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

The efficiency of a Carnot engine, using an ideal gas as the working medium and the temperature measured on the ideal gas temperature scale is also given by a similar expression.

$$(\text{COP})_R = Q_L/(Q_H - Q_L) = T_L / (T_H - T_L)$$
\[(\text{COP})_{\text{HP}}= \frac{Q_H}{(Q_H - Q_L)} = \frac{T_H}{(T_H - T_L)}\]

**Clausius Inequality**

For a Carnot cycle

\[\frac{Q_1}{Q_2} = \frac{T_1}{T_2}\]

Or \[\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0\] for a reversible engine.

With the usual sign convention, that is, heat flow into a system taken as positive and heat outflow of the system taken as negative

\[\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0\] or \[\Sigma \frac{Q_i}{T_i} = 0\]

For an irreversible engine absorbing \(Q_1\) amount of heat from a reservoir at \(T_1\) and rejecting \(Q_2\) to a reservoir at \(T_2\), then

\[1 - \frac{1}{Q_1} < 1 - \frac{1}{Q_2} < 1 - \frac{1}{Q_1}\]

or \[1 - \frac{1}{Q_2} < 1 - \frac{1}{T_2/T_1}\]

or \[\frac{1}{Q_2} > \frac{T_2}{T_1}\]

or \[\frac{1}{Q_2} > \frac{T_2}{Q_1/T_1}\]

making use of the sign convention, we get

\[\frac{1}{Q_2} + \frac{Q_1}{T_1} < 0\]

Or \[\Sigma Q/T < 0\] for an irreversible engine

**Replacement of a Reversible process by an equivalent process**

Let us consider cyclic changes in a system other than heat engines. If the cycle can be split up into a large number of heat engine cycles then the above observation can be made use of in relating the heat interactions with the absolute temperatures.

Any reversible process can be approximated by a series of reversible, isothermal and reversible, adiabatic processes.
Consider a reversible process 1-2. The same change of a state can be achieved by process 1-a (reversible adiabatic process), isothermal process a-b-c and a reversible adiabatic process c-2. The areas 1-a-b and b-c-2 are equal. From the first law

\[ U_2 - U_1 = Q_{1-a-b-c-2} - W_{1-a-b-c-2} \]

Consider the cycle 1-a-b-c-2-b-1. The net work of the cycle is zero. Then

\[ \int dW = W_{1-a-b-c-2} + W_{2-b-1} = 0 \]

or

\[ W_{1-a-b-c-2} = - W_{2-b-1} = W_{1-b-2} \]

the heat interaction along the path 1-a-b-c-2 is

\[ Q_{1-a-b-c-2} = Q_{1-a} + Q_{a-b-c} + Q_{c-2} = Q_{a-b-c} \]

Since 1-a and c-2 are reversible adiabatic paths. Hence

\[ U_2 - U_1 = Q_{a-b-c} - W_{1-b-2} \]

Application of the first law of the thermodynamics to the process 1-b-2 gives

\[ U_2 - U_1 = Q_{1-b-2} - W_{1-b-2} \]

Comparing the two equations

\[ Q_{a-b-c} = Q_{1-b-2} \]

The heat interaction along the reversible path 1-b-2 is equal to that along the isothermal path a-b-c. Therefore a reversible process can be replaced by a series of reversible adiabatic and reversible isothermal processes.

**Clausius Inequality:**

A given cycle may be subdivided by drawing a family of reversible, adiabatic lines. Every two adjacent adiabatic lines may be joined by two reversible isotherms.
The heat interaction along the reversible path is equal to the heat interaction along the reversible isothermal path.

The work interaction along the reversible path is equal to the work interaction along the reversible adiabatic and the reversible isothermal path.

That is,

$$Q_{a-b} = Q_{a_1-b_1}$$

$$Q_{c-d} = Q_{c_1-d_1}$$

a1-b1-d1-c1 is a Carnot cycle.

The original reversible cycle thus is a split into a family of Carnot cycles. For every Carnot cycle

$$\int \frac{dQ}{T} = 0$$

Therefore for the given reversible cycle,

$$\int \frac{dQ}{T} = 0$$

If the original cycle is irreversible

$$\int \frac{dQ}{T} < 0$$

so the generalized observation is

$$\int \frac{dQ}{T} \leq 0$$

Whenever a system undergoes a cyclic change, however complex the cycle may be (as long as it involves heat and work interactions), the algebraic sum of all the heat interactions divided by the absolute temperature at which heat interactions are taking place considered over the entire cycle is less than or equal to zero (for a reversible cycle).
Entropy

\[ \int \frac{dQ}{T} \] has the same value irrespective of path as long as path is reversible

\[ \left( \frac{dQ}{T} \right)_R \] is an exact differential of some function which is identical as entropy

\[ S_2 - S_1 = \Delta S = \int_{1}^{2} dS = \int_{1}^{2} \left( \frac{dQ}{T} \right)_R \]

\[ dS = \left( \frac{dQ}{T} \right)_R \] for reversible process only

Calculation of Entropy change

1. Entropy is a state function. The entropy change is determined by its initial and final states only

2. In analyzing irreversible process, it is not necessary to make a direct analysis of actual reversible process.

Substitute actual process by an imaginary reversible process. The entropy change for imaginary reversible process is same as that of an irreversible process between given final and initial states.
(a) **Absorption of energy by a constant temperature reservoir**

Energy can be added reversibly or irreversibly as heat or by performing work.

\[ \Delta S = \int \left( \frac{dQ}{T} \right)_R \]

**Example:-**

The contents of a large constant-temperature reservoir maintained at 500 K are continuously stirred by a paddle wheel driven by an electric motor. Estimate the entropy change of the reservoir if the paddle wheel is operated for two hours by a 250W motor.

Paddle wheel work converted into internal energy- an irreversible process. Imagine a reversible process with identical energy addition.

\[ \Delta S = \int \left( \frac{dQ}{T} \right)_R = \frac{Q}{T} = \frac{0.25 \times 2(3600)}{500} = 0.6kJ \]

(b) **Heating or cooling of matter**
\[ Q = \Delta U \] for constant volume heating
\[ Q = \Delta H \] for constant pressure heating

\[ \Delta S = \int \frac{dQ}{T} = m \int_{T_1}^{T_2} C_p \frac{dT}{T} = mC_p \ln \left( \frac{T_2}{T_1} \right) \]

, for constant pressure

\[ \Delta S = \int \frac{dQ}{T} = m \int_{T_1}^{T_2} C_v \frac{dT}{T} = mC_v \ln \left( \frac{T_2}{T_1} \right) \]

, for constant volume process

Example: -

Calculate entropy change if 1kg of water at 30\(^0\)C is heated to 80\(^0\)C at 1 bar pressure. The specific heat of water is 4.2kJ/kg-K

\[ \Delta S = C_p \ln \left( \frac{T_2}{T_1} \right) = 4.2 \times 10^3 \times \ln \left( \frac{273 + 80}{273 + 30} \right) \]

\[ = 0.6415 \frac{kJ}{kg.K} \]
(c) **Phase change at constant temperature and pressure**

\[
S_{sf} = \int \frac{dQ}{T} = \frac{h_{sf}}{T_{sf}}
\]

\[
S_{fg} = \int \frac{dQ}{T} = \frac{h_{fg}}{T}
\]

**Example:**

Ice melts at \(0^\circ\)C with latent heat of fusion= 339.92 kJ/kg. Water boils at atmospheric pressure at \(100^\circ\)C with \(h_{fg}= 2257\) kJ/kg.

\[
S_{sf} = \frac{334.92}{273.15} = 1.2261 \frac{kJ}{kg.K}
\]

\[
S_{fg} = \frac{2257}{373.15} = 6.0485 \frac{kJ}{kg.K}
\]
(d) **Adiabatic mixing**

Example:-

A lump of steel of mass 30kg at 427$^0$C is dropped in 100kg oil at 27$^0$C. The specific heats of steel and oil is 0.5kJ/kg-K and 3.0 kJ/kg-K respectively. Calculate entropy change of steel, oil and universe.

T= final equilibrium temperature.

\[
\left( mC_p \Delta T \right)_{steel} = \left( mC_p \Delta T \right)_{oil}
\]

\[
300 \times 0.5 \times (700 - T) = 100 \times 3 \times (T - 300)
\]

or T=319K

\[
\Delta S_{steel} = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{mC_p dT}{T} = \left( mC_p \ln \frac{T2}{T1} \right)_{steel}
\]

\[
= 30 \times 0.5 \times \ln \left( \frac{319}{700} \right) = -11.7883 \text{kJ/K}
\]

\[
\Delta S_{oil} = \left( mC_p \ln \frac{T2}{T1} \right)_{oil}
\]

\[
= 100 \times 3 \times \ln \left( \frac{319}{300} \right) = 18.4226 \text{kJ/K}
\]
\[(\Delta S)_{universe} = -11.7883 + 18.4226 = 6.6343 kJ / K\]

**Tds relations:**

From the definition of entropy,

\[dQ = Tds\]

From the first law of thermodynamics,

\[dW = PdV\]

Therefore,

\[TdS = dU + PdV\]

Or, \[Tds = du + Pdv\]

This is known as the first Tds or, *Gibbs equation*. The second Tds equation is obtained by eliminating \(du\) from the above equation using the definition of enthalpy.

\[h = u + Pv \rightarrow dh = du + vdp\]

Therefore, \[Tds = dh – vdp\]

The two equations can be rearranged as

\[ds = (du/T) + (Pdv/T)\]

\[ds = (dh/T) – (vdP/T)\]
Change of state for an ideal gas

If an ideal gas undergoes a change from $P_1$, $v_1$, $T_1$ to $P_2$, $v_2$, $T_2$ the change in entropy can be calculated by devising a reversible path connecting the two given states.

Let us consider two paths by which a gas can be taken from the initial state, 1 to the final state, 2.

The gas in state 1 is heated at constant pressure till the temperature $T_2$ is attained and then it is brought reversibly and isothermally to the final pressure $P_2$.

Path 1-a: reversible, constant-pressure process.
Path a-2: reversible, isothermal path

Path 1-b-2: The gas initially in state 1 is heated at constant volume to the final temperature $T_2$ and then it is reversibly and isothermally changed to the final pressure $P_2$. 

\[
\Delta s_{1-a} = \int \frac{dq}{T} = \int \frac{C_p}{T}dT = C_p \ln \left( \frac{T_2}{T_1} \right)
\]

\[
\Delta s_{a-2} = \int \frac{dq}{T} = \int \left( \frac{du + P dv}{T} \right) = \int \frac{P dv}{T} = R \ln \left( \frac{v_2}{v_a} \right)
\]

(Since $du = 0$ for an isothermal process)

Since $P_2 v_2 = P_a v_a = P_1 v_a$

Or, $v_2 / v_a = P_1 / P_2$

Or, $\Delta s_{a-2} = R \ln \left( \frac{P_2}{P_1} \right)$

Therefore, $\Delta s = \Delta s_{1-a} + \Delta s_{a-2}$

\[
= C_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right)
\]
1-b: reversible, constant volume process

\[ \Delta s_{1-b} = C_v \ln(T_2/T_1) \]

\[ \Delta s_{b-2} = R \ln(v_2/v_1) \]

or, \[ \Delta s = C_v \ln(T_2/T_1) + R \ln(v_2/v_1) \]

The above equation for \( \Delta s \) can also be deduced in the following manner:

\[ ds = (dq/T)_R = (du + Pdv)/T = (dh - vdp)/T \]

or,

\[ \Delta s = \int_1^2 \frac{du + pdv}{T} = \int_1^2 \frac{C_v dT}{T} + \frac{Rdv}{v} \]

\[ = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \]

Similarly,

\[ \Delta s = \int_1^2 \frac{(dh - vdp)}{T} = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \]

Principle of increase of entropy

Let a system change from state 1 to state 2 by a reversible process A and return to state 1 by another reversible process B. Then 1A2B1 is a reversible cycle. Therefore, the Clausius inequality gives:
If the system is restored to the initial state from 1 to state 2 by an irreversible process C, then 1A2C1 is an irreversible cycle. Then the Clausius inequality gives:

\[ \int \frac{dQ}{T} = \int \frac{dQ}{T} + \int \frac{dQ}{T} = o \]

Subtracting the above equation from the first one,

\[ \int \frac{dQ}{T} > \int \frac{dQ}{T} \]

Since the process 2B1 is reversible,

\[ \int \frac{dQ}{T} = \int \frac{dQ}{T} \]

or, \[ \int dS > \int \frac{dQ}{T} \]

In general,

\[ dS \geq \frac{dQ}{T} \]

Where the equality sign holds good for a reversible process and the inequality sign holds good for an irreversible process.

Now let us apply the above result to evaluate the entropy change of the universe when a system interacts with its surroundings and exchanges energy as heat with the surroundings.
Let $T_{\text{sur}}$ and $T_{\text{sys}}$ be the temperatures of the surroundings and the system such that $T_{\text{sur}}>T_{\text{sys}}$. Let $dQ$ represent the energy transfer as heat from the surroundings to the system during the given irreversible process.

$$dS_{\text{sys}} = \frac{dQ}{T_{\text{sys}}}$$
$$dS_{\text{sur}} = -\frac{dQ}{T_{\text{sur}}}$$
$$dS_{\text{uni}} = dS_{\text{sys}} + dS_{\text{sur}} = (\frac{dQ}{T})_{\text{sys}} - (\frac{dQ}{T})_{\text{sur}} > 0$$

$\Delta S_{\text{uni}} > 0$ (since $T_{\text{sur}}>T_{\text{sys}}$)

If the system is isolated, there is no change in the entropy of the surroundings and $\Delta S \geq 0$, for an isolated system

Therefore the entropy of an isolated system either increases or, in the limit, remains constant.

The equality sign holds good when the process undergone by the system is reversible, the inequality sign holds good if there is any irreversibility present in the process. This statement is usually called the **principle of entropy increase**.

Irreversible or spontaneous processes can occur only in that direction for which the entropy of the universe or that of an isolated system, increases. These processes cannot occur in the direction of decreasing entropy.

For an isolated system,

$\Delta S > 0$, for irreversible processes

$\Delta S = 0$, for reversible processes

$\Delta S < 0$, the process is impossible
Example:

One kg of superheated steam at 0.2MPa and 200°C contained in a piston cylinder assembly is kept at ambient conditions of 300K till the steam is condensed to saturated liquid at constant pressure. Calculate the change in the entropy of the universe with this process.

Solution:

Initial state of the steam: superheated at 0.2 MPa and 200°C
\[ h_1 = 2870.4 \text{ kJ/kg}; \text{ and } s_1 = 7.5033 \text{ kJ/kgK} \]

Final state: saturated liquid at 0.2 MPa.
\[ h_2 = 504.52 \text{ kJ/kg and } s_2 = 1.5295 \text{ kJ/kgK} \]

Hence \( \Delta S_{\text{steam}} = s_2 - s_1 = 1.5295 - 7.5033 = -5.9738 \text{ kJ/kgK} \)

For a constant pressure process: \( q = \Delta h \)

Therefore, \( q = h_2 - h_1 = 504.52 - 2870.4 \) =
\[ -2365.68 \text{ kJ} \]

Entropy change of the surroundings = \( \Delta S_{\text{sur}} = Q/T_{\text{sur}} = \frac{2365.88}{300} = 7.886 \text{ kJ/K} \)

Hence, \( \Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = -5.9738 + 7.886 = 1.9122 \text{ kJ/K} \)

\( \Delta S_{\text{uni}} > 0 \) and hence the process is irreversible and feasible.
**Temperature-Entropy diagram**

Entropy change of a system is given by $dS = (dQ/T)_R$. during energy transfer as heat to the system from the surroundings is given by

$$dQ = TdS.$$ Hence if $T$ and $S$ are chosen as independent variables, then the integral $\int TdS$ is the area under the curve.

![Temperature-Entropy diagram](image)

*Fig. 7.27 T-s diagram for a Carnot cycle.*

The first law of thermodynamics gives

$$dU = dQ - dW$$

also for a reversible process,
\[ dQ = TdS \text{ and } dW = PdV \]

Therefore, \[ dU = TdS - PdV \]

For a cyclic process, the above equation reduces to \[ \oint TdS - \oint PdV \]

For a cyclic process, \[ \oint TdS \] represents the net heat interaction which is equal to the net work done by the system. Hence the area enclosed by a cycle on a T-S diagram represents the net work done by a system.

**Second law analysis of a control volume**

\[ dS \geq \frac{dQ}{T} \]

where the equality sign holds good for reversible processes and the inequality sign holds good for all irreversible processes. This can be expressed as

\[ \Delta S = \frac{dQ}{T} + S_G \]

where \( S_G \) represents the entropy generation in the system and it cannot take a negative value. \( S_G = 0 \) for a reversible process
$S_G > 0$ for an irreversible process

Consider a control volume through which material flows continuously in and out. At time $t$, the system constitutes both the mass inside the control volume and the mass about to enter the control volume during a small time interval $dt$.

The entropy of the system

$$= m(t)s(t) + m_i s_i dt$$

$$= S(t) + m_i s_i dt$$

At time $(t+dt)$ the entropy of the system

$$= m(t + dt)s(t + dt) + m_e s_e dt = S(t + dt) + m_e s_e dt$$

where,

$m(t) = \text{mass inside the control volume at time } t$

$s(t) = \text{specific entropy of matter inside the control volume at time } t$

$m(t+dt) = \text{mass inside the control volume at time } (t+dt)$

$s(t+dt) = \text{specific entropy of the mass inside the control volume at time } (t+dt)$
$S(t+dt) = \text{entropy of control volume at time } (t+dt)$

Then,

$$\left[ S(t+dt) + m_e s_e dt \right] - \left[ S(t) + m_i s_i dt \right] = \frac{Q}{T} dt + \dot{S}_G dt$$

$$\frac{S(t+dt) - s(t)}{dt} + m_e s_e - m_i s_i = \frac{Q}{T} + \dot{S}_G$$

or, $dS/dt + m_e s_e - m_i s_i = \frac{Q}{T} + \dot{S}_G$

This can be rearranged as:

$$dS/dt = (m_i s_i + \frac{Q}{T}) - (m_e s_e) + \dot{S}_G$$

or stated in words:

[The rate of accumulation of entropy] = [Rate of inflow of entropy] − [Rate of outflow of entropy] + [Rate of generation of entropy]

Example:
An inventor claims to have designed a device which takes in 2kmol/s of air at 250 kPa and 350 K and delivers equal amounts of hot stream of air at 100kPa and 400 K as also a cold stream of air at 100 kPa and 250 K. He further claims that
his device does not require any additional energy as heat or work to operate. Judge whether such a device is feasible or not. Consider air to be an ideal gas with \( C_p = 7R/2 \)

Solution:

The first law of thermodynamics for a control volume gives:

\[
\dot{m}_i h_i = \dot{m}_{e1} h_{e1} + \dot{m}_{e2} h_{e2}
\]

or

\[
2h_i = h_{e1} + h_{e2}
\]

or

\[
(h_i - h_{e1}) + (h_i - h_{e2}) = 0
\]

\[
C_p(T_i - T_{e1}) + C_p(T_i - T_{e2}) = 0
\]

\[
(350-450) + (350-250) = 0
\]

The first law is thus satisfied.

The second law of thermodynamics gives:

\[
\dot{m}_{e1} s_{e1} + \dot{m}_{e2} s_{e2} \geq \dot{m}_i s_i
\]
his device does not require any additional energy as heat or work to operate. Judge whether such a device is feasible or not. Consider air to be an ideal gas with $C_p = 7R/2$

Solution:

The first law of thermodynamics for a control volume gives:

$$m_i h_i = m_{e1} h_{e1} + m_{e2} h_{e2}$$

or

$$2h_i = h_{e1} + h_{e2}$$

or

$$(h_i - h_{e1}) + (h_i - h_{e2}) = 0$$

$$C_p(T_i - T_{e1}) + C_p(T_i - T_{e2}) = 0$$

$$(350 - 450) + (350 - 250) = 0$$

The first law is thus satisfied.

The second law of thermodynamics gives:

$$m_{e1} s_{e1} + m_{e2}s_{e2} \geq m_i s_i$$
The material balance gives
\[ m_{c1} + m_{c2} = m_i \]

Therefore \( (m_{c1}s_{c1} + m_{c2}s_{c2}) \geq (m_{c1} + m_{c2})s_i \)

Or, \( m_{c1}(s_{c1} - s_i) + m_{c2}(s_{c2} - s_i) \geq 0 \)

The change in entropy is given by
\[ \Delta s = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) \]

hence,
\[ m_{c1}(s_{c1} - s_i) = C_p \ln\left(\frac{450}{350}\right) - R \ln\left(\frac{100}{250}\right) \]

and,
\[ m_{c2}(s_{c2} - s_i) = C_p \ln\left(\frac{250}{350}\right) - R \ln\left(\frac{100}{250}\right) \]

then,
\[ m_{c1}(s_{c1} - s_i) + m_{c2}(s_{c2} - s_i) = 12.7581 \text{ kJ/K} > 0 \]

Hence it satisfies the second law of thermodynamics also Therefore the device is feasible.
**Thermodynamic relations**

**Gibbs Function and Helmholtz Function**

Gibbs equation is

\[ du = Tds - Pdv \]

The enthalpy \( h \) can be differentiated,

\[ dh = du + pdv + vdP \]

Combining the two results in

\[ dh = Tds + vdP \]

The coefficients \( T \) and \( v \) are partial derivative of \( h(s,P) \),

\[
\left( \frac{\partial h}{\partial s} \right)_P = T
\]

\[
\left( \frac{\partial h}{\partial P} \right)_s = v
\]

Since \( v > 0 \), an isentropic increase in pressure will result in an increase in enthalpy.

We introduce Helmholtz function
\[ a = u - Ts \]

Combine Gibbs equation with the differential of \( a \),

\[ da = -P dv - s dT \]

The coefficient \(-P\) and \(-s\) are the partial derivatives of \( f(v, T) \), so

\[
\left( \frac{\partial a}{\partial v} \right)_T = -P \\
\left( \frac{\partial a}{\partial T} \right)_v = -s
\]

Similarly, using the Gibbs function

\[ g = h - Ts \]

\[ dg = vdP - sdT \]

Consequently,

\[
\left( \frac{\partial g}{\partial P} \right)_T = v \\
\left( \frac{\partial g}{\partial T} \right)_P = -s
\]
Note:

1. The decrease in Helmholtz function of a system sets an upper limit to the work done in any process between two equilibrium states at the same temperature during which the system exchanges heat only with a single reservoir at this temperature. Since the decrease in the Helmholtz potential represents the potential to do work by the system, it is also a thermodynamic potential.

2. The decrease in Gibbs function of a system sets an upper limit to the work, exclusive of “pdv” work in any process between two states at the same temperature and pressure, provided the system exchanges heat only with a single reservoir at this temperature and that the surroundings are at a constant pressure equal to that in the end states of the pressure.

The maximum work is done when the process is isothermal isobaric. Gibbs function is also called Chemical Potential.

**Some important property relations**

\[ dz(x,y) = Mdx + Ndy \]

where, \( M = \left( \frac{\partial z}{\partial x} \right)_y \) \( N = \left( \frac{\partial Z}{\partial y} \right)_x \)

Mathematically, we would say that \( dz \) is an exact differential, which simply means that \( z \) is a continuous function of the two independent variables \( x \) and \( y \). Since the order in which a second partial derivative is taken is unimportant, it follows that,

\[ \left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial P}{\partial x} \right)_y \]
Maxwell’s relations:

\[
\left( \frac{\partial T}{\partial v} \right)_s = -\left( \frac{\partial P}{\partial s} \right)_v \quad \text{[From equation } du = Tds - Pdv \]

\[
\left( \frac{\partial T}{\partial P} \right)_s = \left( \frac{\partial v}{\partial s} \right)_P \quad \text{[From equation } dh = Tds + vdp \]

\[
\left( \frac{\partial P}{\partial T} \right)_v = \left( \frac{\partial s}{\partial v} \right)_T \quad \text{[From equation } da = -Pdv - sdt \]

\[
\left( \frac{\partial v}{\partial T} \right)_P = -\left( \frac{\partial s}{\partial P} \right)_T \quad \text{[From equation } dg = vdp - sdt \]

**Available and Unavailable Energy**

The second law of thermodynamics tells us that it is not possible to convert all the heat absorbed by a system into work.

Suppose a certain quantity of energy Q as heat can be received from a body at temperature T.

The maximum work can be obtained by operating a Carnot engine (reversible engine) using the body at T as the source and the ambient atmosphere at T_0 as the sink.

\[
W = Q\eta = Q\left(1 - \frac{T_0}{T}\right) = Q - T_0 |\Delta s|
\]

Where \(\Delta s\) is the entropy of the body supplying the energy as heat.

The Carnot cycle and the available energy is shown in figure.

The area 1-2-3-4 represents the available energy.
The shaded area 4-3-B-A represents the energy, which is discarded to the ambient atmosphere, and this quantity of energy cannot be converted into work and is called *Unavailable energy*.

Suppose a finite body is used as a source. Let a large number of differential Carnot engines be used with the given body as the source.

\[
dW = dQ \eta = dQ \left(1 - \frac{T_0}{T}\right)
\]

If the initial and final temperatures of the source are \(T_1\) and \(T_2\) respectively, the total work done or the available energy is given by

\[
W = \int_{T_1}^{T_2} dQ \eta = \int_{T_1}^{T_2} dQ \left(1 - \frac{T_0}{T}\right) = Q - T_0 \int_{T_1}^{T_2} \frac{dQ}{T}
\]

*or* \(W = Q - T_0 |\Delta s|\)
**Loss in Available Energy**

Suppose a certain quantity of energy $Q$ is transferred from a body at constant temperature $T_1$ to another body at constant temperature $T_2$ ($T_2 < T_1$).

Initial available energy, with the body at $T_1$,

$$= Q \left( 1 - \frac{T_0}{T} \right)$$

Final available energy, with the body at $T_2$,

$$= Q \left( 1 - \frac{T_0}{T_2} \right)$$

Loss in available energy

$$= Q \left( 1 - \frac{T_0}{T_1} \right) - Q \left( 1 - \frac{T_0}{T_2} \right) = T_0 \left( \frac{Q}{T_2} - \frac{Q}{T_1} \right) = T_0 \Delta s_{uni}$$

where $\Delta s_{uni}$ is the change in the entropy of the universe.

**Availability Function**

The availability of a given system is defined as *the maximum useful work that can be obtained in a process in which the system comes to equilibrium with the surroundings or attains the dead state.*
(a) Availability Function for Non-Flow process:-

Let $P_0$ be the ambient pressure, $V_1$ and $V_0$ be the initial and final volumes of the system respectively.

If in a process, the system comes into equilibrium with the surroundings, the work done in pushing back the ambient atmosphere is $P_0(V_0-V_1)$.

$$\text{Availability} = W_{\text{useful}} = W_{\text{max}} - P_0(V_0-V_1)$$

Consider a system which interacts with the ambient at $T_0$. Then,

$$W_{\text{max}} = (U_1-U_0) - T_0(S_1-S_0)$$

$$\text{Availability} = W_{\text{useful}} = W_{\text{max}} - P_0(V_0-V_1)$$

$$= (U_1-T_0 S_1)-(U_0-T_0 S_0) - P_0(V_0-V_1)$$

$$= (U_1+P_0V_1-T_0 S_1)-(U_0+P_0V_0-T_0 S_0)$$

$$= \phi_1 - \phi_0$$

where $\phi = U + P_0V - T_0S$ is called the availability function for the non-flow process. Thus, the availability: $\phi_1 - \phi_0$

If a system undergoes a change of state from the initial state 1 (where the availability is $(\phi_1-\phi_0)$ to the final state 2 (where the availability is $(\phi_2-\phi_0)$), the change in the availability or the change in maximum useful work associated with the process, is $\phi_1 - \phi_2$.

(b) Availability Function for Flow process:-

The maximum power that can be obtained in a steady flow process while the control volume exchanges energy as heat with the ambient at $T_0$, is given by:
\[ W_{sh(\text{max})} = (H_1 - H_0) - T_0 (S_1 - S_0) \]
\[ W_{sh(\text{max})} = (H_1 - T_0 S_1) - (H_1 - T_0 S_0) \]

Sometimes the availability for a flow process is written as:

\[ W_{\text{useful}} = B_1 - B_0 \]
\[ \text{where, } B = H - T_0 S \]

which is called the **Darrieus Function**.
UNIT.IV

Ideal Rankine Cycle

(a) Schematic representation of an ideal Rankine cycle (b) T-s diagram of an ideal Rankine cycle

Application of the First law of thermodynamics to the control volume (pump, steam generator, turbine and condenser), gives

Work done on pump, per kg of water, \( W_p = h_2 - h_1 \)

Energy added in steam generator, \( q_1 = h_3 - h_2 \)

**Work delivered by turbine, \( W_T = h_3 - h_4 \)**

Energy rejected in the condenser, \( q_2 = h_4 - h_1 \)

The thermal efficiency of the Rankine cycle is given by,

\[
\eta = \frac{q_1 - q_2}{q_1} = \frac{(h_3 - h_2) - (h_4 - h_1)}{h_3 - h_2} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}
\]
\[ \eta = \frac{\text{Net work done}}{\text{Energy absorbed}} \]

**Practical Rankine cycle**

Pump and Turbine do not operate isentropically in practice.

The practical Rankine cycle is shown as 1-2'-3'-4'-1.

In the actual turbine, the work delivered is less than the isentropic turbine. Similarly, the work consumed by an actual pump is greater than the work consumed by an isentropic pump.

That is,
\[ h_3-h_4' < h_3-h_4 \]

\[ h_2'-h_1 > h_2-h_1 \]

Thermal efficiency of a practical Rankine cycle,

\[ \eta = \frac{(h_3-h_4')-(h_2'-h_1)}{h_3-h_2'} \]

The performance of an actual turbine or pump is usually expressed in terms of isentropic efficiency.

Isentropic efficiency of turbine (\( \eta_T \)) is defined as the ratio of ‘Work delivered by actual turbine’ to ‘Work delivered by an isentropic turbine’.

\[ \eta_T = \frac{h_3-h_4'}{h_3-h_4} \]

Isentropic efficiency of pump (\( \eta_P \)) is defined as the ratio of ‘Work required by isentropic pump’ to ‘Work required by actual pump’.

\[ \eta_P = \frac{h_2-h_1}{h_2-h_1} \]

Methods to increase the efficiency of the Rankine cycle
Basic idea: Increase the average temperature at which heat is transferred to the working fluid in the boiler, or decrease the average temperature at which heat is rejected from the working fluid in the condenser.

1. Lowering the condenser Pressure:-

![Diagram showing the effect of lowering condenser pressure on cycle efficiency]

Lowering the operating pressure of the condenser lowers the temperature at which heat is rejected. The overall effect of lowering the condenser pressure is an increase in the thermal efficiency of the cycle.

2. Superheating the steam to high temperatures:-
The average temperature at which heat is added to the steam can be increased without increasing the boiler pressure by superheating the steam to high temperatures.

Superheating the steam to higher temperatures has another very desirable effect: It decreases the moisture content of the steam at the turbine exit.

3. Increasing the Boiler pressure:-
Increasing the operating pressure of the boiler, automatically raises the temperature at which boiling takes place.

This raises the average temperature at which heat is added to the steam and thus raises the thermal efficiency of the cycle..

**Reheat Rankine Cycle**

(a) schematic representation of a reheat Rankine cycle (b) T-s diagram of a reheat Rankine cycle

The energy added (per unit mass of steam) in the steam generator is given by,

\[ q_1 = (h_3 - h_2) + (h_5 - h_4) \]

The energy rejected in the condenser,

\[ q_2 = h_6 - h_1 \]

The thermal efficiency,

\[ \eta = \frac{(h_3 - h_2) + (h_5 - h_4) - (h_6 - h_1)}{(h_3 - h_2) + (h_5 - h_4)} \]
Regenerative Cycle

(a) schematic diagram (b) T-s diagram

Consider the feed water heater as the control volume and apply the first law of thermodynamics to obtain,

\[ \dot{m}_2 + \dot{m}_8 = \dot{m}_3 \]

and

\[ \dot{m}_2 h_2 + \dot{m}_8 h_8 = \dot{m}_3 h_3 \]
or \[ \dot{m}_3 h_3 = (\dot{m}_3 - \dot{m}_8) h_2 + \dot{m}_8 h_8 \]

or \[ h_3 = \left( \frac{\dot{m}_8}{\dot{m}_3} \right) h_8 + \left( 1 - \frac{\dot{m}_8}{\dot{m}_3} \right) h_2 \]

Let, \[ \frac{\dot{m}_8}{\dot{m}_3} = Y' = \text{the fraction of steam extracted from the turbine for preheating} \]

\[ h_3 = Y' h_8 + (1 - Y') h_2 \]

Energy added in the boiler per unit mass of the working fluid,

\[ q_1 = h_7 - h_4 \]

Energy rejected in the condenser,

\[ q_2 = (1 - Y')(h_9 - h_1) \]

Thermal efficiency,

\[ \eta = \frac{(h_7 - h_4) - (1 - Y')(h_9 - h_1)}{(h_7 - h_4)} \]
The work output of the turbines =

$$(h_7 - h_8) - (1 - Y')(h_8 - h_9)$$

Work spent on the pumps =

$$(h_4 - h_3) - (1 - Y')(h_2 - h_1)$$
UNIT.V

Air standard Otto Cycle

Air standard Otto cycle on (a) P-v diagram (b) T-s diagram

Processes: -

0-1: a fresh mixture of fuel-air is drawn into the cylinder at constant pressure
1-2: isentropic compression
2-3: energy addition at constant volume
3-4: isentropic expansion
4-1: combustion products leave the cylinder
1-0: the piston pushes out the remaining combustion products at constant pressure

Since the net work done in processes 0-1 and 1-0 is zero, for thermodynamic analysis, we consider the 1-2-3-4 only.
The thermal efficiency of the cycle is given by

\[ \eta = \frac{W_{net}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \]

where \( Q_1 \) and \( Q_2 \) denote the energy absorbed and rejected as heat respectively.

For a constant volume process \( Q = \Delta U \). If ‘\( m \)’ is the mass of the air which is undergoing the cyclic process,

\[ \Delta U = mC_v \Delta T \]

Energy is absorbed during the process 2-3

Energy is rejected during the process 4-1

Hence,

\[ Q_1 = U_3 - U_2 = mC_v (T_3 - T_2) \]
\[ Q_2 = U_4 - U_1 = mC_v (T_4 - T_1) \]

\[ \therefore \eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} \]

For an ideal gas undergoing an isentropic process (process 1-2 and 3-4),

\[ T_v \gamma^{-1} = \text{constant} \]

Hence,

\[ \frac{T_1}{T_2} = \left( \frac{v_2}{v_1} \right)^{\gamma^{-1}} \]
and 
\[
\frac{T_4}{T_3} = \left( \frac{v_3}{v_4} \right)^{\gamma-1}
\]

But \(v_1=v_4\) and \(v_2=v_3\). Hence we get,
\[
\frac{T_1}{T_2} = \frac{T_4}{T_3} \quad \text{or} \quad \frac{T_1}{T_4} = \frac{T_2}{T_3}
\]

\[
1 - \frac{T_1}{T_4} = 1 - \frac{T_2}{T_3} \quad \text{or} \quad \frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3} = \frac{T_1}{T_2}
\]

\[
\eta = 1 - \frac{T_1}{T_2} = 1 - \left( \frac{v_2}{v_1} \right)^{\gamma-1} = 1 - \left( \frac{1}{r_0} \right)^{\gamma-1}
\]

Hence,
\[
\eta = 1 - \frac{T_1}{T_2} = 1 - \left( \frac{v_2}{v_1} \right)^{\gamma-1} = 1 - \left( \frac{1}{r_0} \right)^{\gamma-1}
\]

Where the compression ratio \(r_0\) is defined as
\[
r_0 = \frac{v_1}{v_2}
\]
Sometimes it is convenient to express the performance of an engine in terms of *Mean effective Pressure*, $P_m$, defined as the ratio of “Net work done” to “Displacement volume”

$$
P_m = \frac{W}{v_1 - v_2}
$$

$$
W = P_m (v_1 - v_2)
$$

Thermal efficiency of the ideal Otto cycle as a function of compression ratio ($\gamma=1.4$)
The thermal efficiency of the Otto cycle increases with the specific heat ratio, $\gamma$ of the working fluid.

**Air standard Diesel cycle:**

Diesel cycle on (a) P-v diagram (b) T-s diagram
**Processes: -**

0-1: fresh air is drawn into the cylinder
1-2: isentropic compression
2-3: constant pressure energy addition
3-4: isentropic expansion
4-1: combustion products leave the cylinder
1-0: remaining combustion products are exhausted at constant pressure

**Defining cutoff ratio, \( r_c \) as,**

\[
r_c = \frac{V_3}{V_2}
\]

For a constant pressure process (2-3),

\[Q = \Delta H.\]

Hence, the energy addition during process 2-3,

\[Q_1 = H_3 - H_2 = m(h_3 - h_2) = mC_p(T_3 - T_2)\]

where ‘\( m \)’ is the mass of gas undergoing the cyclic change.

The energy rejection during the process 4-1,

\[Q_2 = U_4 - U_1 = m(u_4 - u_1) = mC_v(T_4 - T_1)\]

The thermal efficiency, \( \eta \) is given by
\[ \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{mC_p (T_3 - T_2) - mC_v (T_4 - T_1)}{mC_p (T_3 - T_2)} \]

\[ \eta = 1 - \frac{T_4 - T_1}{\gamma(T_3 - T_2)} = 1 - \frac{T_1 \left( \frac{T_4}{T_1} - 1 \right)}{T_2 \gamma \left( \frac{T_3}{T_2} - 1 \right)} \]

Since the process 1-2 is isentropic,

\[ \frac{T_1}{T_2} = \left( \frac{v_2}{v_1} \right)^{\gamma-1} = \left( \frac{1}{r_0} \right)^{\gamma-1} \]

Since the process 4-1 is a constant volume process,

\[ \frac{T_4}{T_1} = \frac{P_4}{P_1} = \frac{P_4}{P_3} \left( \frac{P_3}{P_1} \right) = \frac{P_4}{P_3} \left( \frac{P_2}{P_1} \right) \]

since \( P_2 = P_3 \)

The processes 1-2 and 3-4 are isentropic. Hence,

\[ \frac{P_4}{P_3} = \left( \frac{v_3}{v_4} \right)^{\gamma} \] and \[ \frac{P_2}{P_1} = \left( \frac{v_1}{v_2} \right)^{\gamma} \]
Hence we get,

\[
\frac{T_4}{T_1} = \left(\frac{v_3}{v_4}\right)^\gamma \left(\frac{v_1}{v_2}\right)^\gamma = \left(\frac{v_3}{v_2}\right)^\gamma = r_c^\gamma
\]

For the constant pressure process,

\[
\frac{T_3}{T_2} = \frac{v_3}{v_2} = r_c
\]

Hence the efficiency becomes,

\[
\eta = 1 - \frac{1}{\gamma - 1} \left[ \frac{r_c^\gamma - 1}{r_c - 1} \right]
\]

The mean effective pressure of an air standard diesel cycle is given by,

\[
P_m = P_1 \frac{\gamma r_0^\gamma (r_c - 1) - r_0 (r_c^\gamma - 1)}{(\gamma - 1)(r_0 - 1)}
\]

Thermal efficiency of the ideal diesel cycle as a function of compression and cutoff ratios

\((\gamma = 1.4)\)
**Air standard Dual cycle:**

Dual cycle on (a) P-v diagram (b) T-s diagram

Energy addition is in two stages: Part of energy is added at constant volume and part of the energy is added at constant pressure

Energy added, $q_1$

$$q_1 = C_v (T_3 - T_2) + C_p (T_4 - T_3)$$

Energy rejected, $q_2$

$$q_2 = C_v (T_5 - T_1)$$

Thermal efficiency, $\eta$
\[ \eta = 1 - \frac{q_2}{q_1} \]
\[ \eta = 1 - \frac{C_v(T_5 - T_1)}{C_v(T_3 - T_2) + C_p(T_4 - T_3)} \]
\[ \eta = 1 - \frac{(T_5 - T_1)}{(T_3 - T_2) + \gamma(T_4 - T_3)} \]

The efficiency can be expressed also in terms of, Compression ratio, \( r_0 = \frac{V_1}{V_2} \)
Cut-off ratio, \( r_c = \frac{V_4}{V_3} \)  
Constant volume pressure ratio, \( r_v p = \frac{P_3}{P_2} \)

**Air standard Brayton cycle:**

Schematic representation of an air standard Brayton cycle
Processes: -

1-2: isentropic compression

2-3: constant pressure energy addition

3-4: isentropic expansion

4-1: constant pressure energy rejection

Energy added, $Q_1 = mC_p (T_3 - T_2)$

Energy rejected, $Q_2 = mC_p (T_4 - T_1)$

Thermal efficiency,
\[ \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \]

\[ \eta = 1 - \frac{T_1 \left[ \frac{T_4}{T_1} - 1 \right]}{T_2 \left[ \frac{T_3}{T_2} - 1 \right]} \]

The pressure ratio of the Brayton cycle, \( r_p \), is defined as,

\[ r_p = \frac{P_2}{P_1} \]

\[ \frac{P_3}{P_2} = \frac{P_4}{P_1} \]

The processes 1-2 and 3-4 are isentropic. Hence,
\[
\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right) \frac{(\gamma-1)}{\gamma}
\]

\[
\frac{T_3}{T_4} = \left( \frac{P_3}{P_4} \right) \frac{(\gamma-1)}{\gamma}
\]

We get,

\[
\frac{T_2}{T_1} = \frac{T_3}{T_4} \quad \text{or} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2}
\]

\[
\eta = 1 - \frac{T_1}{T_2} = 1 - \left( \frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}}
\]

\[
\eta = 1 - \left( \frac{1}{r_p} \right)^{\frac{\gamma-1}{\gamma}}
\]

Work delivered by the cycle is given by \( W = \eta Q_1 \)
Increasing $Q_1$ can increase work done by the cycle

Since the Turbine blade material cannot withstand very high temperature, $T_3$ and hence $Q_1$ is limited

The optimum pressure ratio for fixed values of $T_1$ and $T_3$, for which work is maximum, is obtained by,

\[ W_{net} = Q_1 - Q_2 = mC_p(T_3 - T_2) - mC_p(T_4 - T_1) \]
\[ W_{net} = mC_p[(T_3 - T_4) - (T_2 - T_1)] \]
\[ W_{net} = mC_p \left[ T_3 \left(1 - \frac{T_4}{T_3}\right) - T_1 \left(\frac{T_2}{T_1} - 1\right)\right] \]
\[ W_{net} = mC_p \left[ T_3 \left(1 - \left(\frac{1}{r_p}\right)^\gamma\right) - T_1 \left((r_p)^\frac{\gamma-1}{\gamma} - 1\right)\right] \]

For optimum pressure ratio,
\[
\frac{dW_{net}}{dr_p} = mC_p T_3 \left( \frac{\gamma - 1}{\gamma} \right) \left( r_p \right)^{\frac{1-2\gamma}{\gamma}} - mC_p T_1 \left( \frac{\gamma - 1}{\gamma} \right) \left( r_p \right)^{-\frac{1}{\gamma}} = 0
\]

\[
T_3 \left( r_p \right)^{\frac{1-2\gamma}{\gamma}} = T_1 \left( r_p \right)^{-\frac{1}{\gamma}}
\]

or

\[
\frac{T_3}{T_1} = \left( r_p \right)^{\frac{2(\gamma-1)}{\gamma}}
\]

or

\[
r_p = \left( \frac{T_3}{T_1} \right)^{\frac{\gamma}{2(\gamma-1)}}
\]
Carnot Vapour compression Refrigeration cycle:

(a) Schematic representation (b) T-s diagram

Processes: -

1-2: Isentropic compression from state 1 (wet vapour) to state 2 (saturated vapour)

2-3: Heat rejection \( (Q_H) \) in the condenser

3-4: Isentropic expansion from state 3 (saturated liquid)

4-1: Heat absorption \( (Q_L) \) in the evaporator

The COP of the refrigerator,

\[
(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L}
\]
Practical Vapour compression refrigeration cycle

(a) schematic diagram (b) T-s diagram

Application of the first law of thermodynamics to the control volume compressor, condenser, throttle and evaporator gives

$$ (W_s)_{compressor} = h_2 - h_1 $$

$$ Q_H = h_2 - h_3 $$

$$ h_3 = h_4 $$

and

$$ Q_L = h_1 - h_4 $$
The COP of the refrigerator is given by,

\[(COP)_R = \frac{Q_L}{W} = \frac{h_1 - h_4}{h_2 - h_1}\]

In the ideal refrigeration cycle, the refrigerant leaves the evaporator as wet vapour.

In some cases the refrigerant leaves the evaporator as either saturated vapour or superheated vapour.

T-s diagram for a vapour compression refrigeration cycle when the refrigerant leaves the evaporator as (a) saturated vapour (b) superheated vapour
Gas refrigeration cycle:

(a) Schematic diagram (b) T-s diagram

The simplest gas refrigeration cycle is the reversed Brayton cycle

Processes: - 

1-2: isentropic compression for state 1 (atmospheric air) to state 2

2-3: energy exchange with the surrounding, air is cooled

3-4: isentropic expansion to state 4
Work obtained during the expansion process can be used to run the compressor

Work done on the compressor,

\[ W_c = h_2 - h_1 = C_p (T_2 - T_1) \]

Work delivered by the expander,

\[ W_e = h_3 - h_4 = C_p (T_3 - T_4) \]

The net work required = \( C_p(T_2 - T_1 - T_3 + T_4) \)

The COP of this refrigeration system is given by,

\[ COP = \frac{Q_L}{W} = \frac{T_1 - T_4}{T_2 - T_1 - T_3 + T_4} \]