

THERMODYNAMICS

(AME003)

B.TECH - SEMESTER-III

**PREPARED
BY**

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INTRODUCTION

Basic Concepts: System, Control Volume, Surrounding, Boundaries, Universe, Types of Systems, Macroscopic and Microscopic viewpoints, Concept of Continuum, Thermodynamic Equilibrium, State, Property, Process, Cycle, Reversibility, Quasi static Process, Irreversible Process, Causes of Irreversibility, Various flow and non-flow processes, Energy in State and in Transition, Types-Work and Heat, Point and Path function., Zeroth Law of Thermodynamics, Concept of quality of Temperature, Principles of Thermometry, Reference Points, Constant Volume gas Thermometer, Ideal Gas Scale, PMMI - Joule's Experiments, First law of Thermodynamics, Corollaries First law applied to a Process, Applied to a flow system, Steady Flow Energy Equation.

BASIC DEFINITIONS

- **Definition of Thermodynamics**

Thermodynamics is a branch of science ,phenomena of energy and related properties of matter, especially of laws of transformation of heat into other forms of energy and vice versa.

- **Macroscopic Approach**

- **Microscopic Approach**

- This approach considers that the system is made up of a very large numbers of the discrete particles known as molecules.

- These molecules have different velocities and energies.

- The behaour of system is found by using statistical method as the number of molecules is very large.

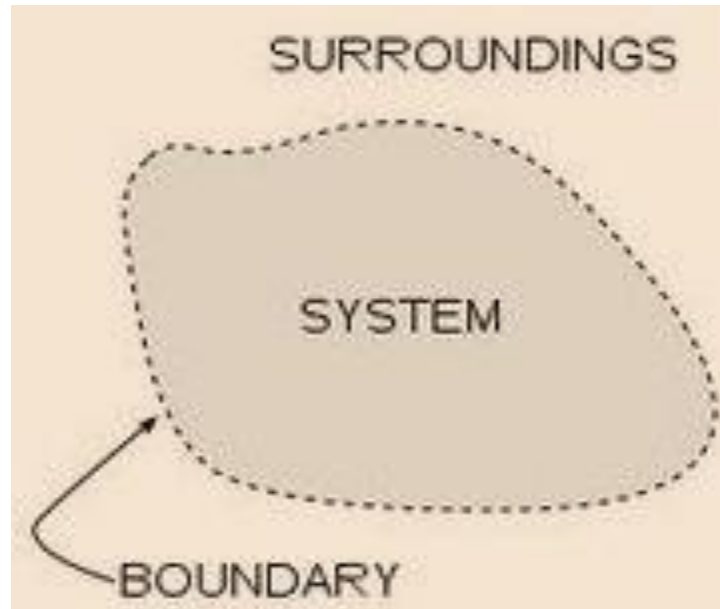
- The properties like velocity, momentum, impulse, kinetic energy etc, which describes the molecule cannot be easily measured by instruments.

- Large number of variables is needed to describe such a system. So approach is complicated.

Macroscopic Approach:

- In this approach, we do not follow the behavior of individual molecules but study the properties of particular mass of the substances.
- The analysis of macroscopic system requires simple mathematical formulae.
- The values of the properties of system are their average values.
- Only few properties are needed to describe such a system.

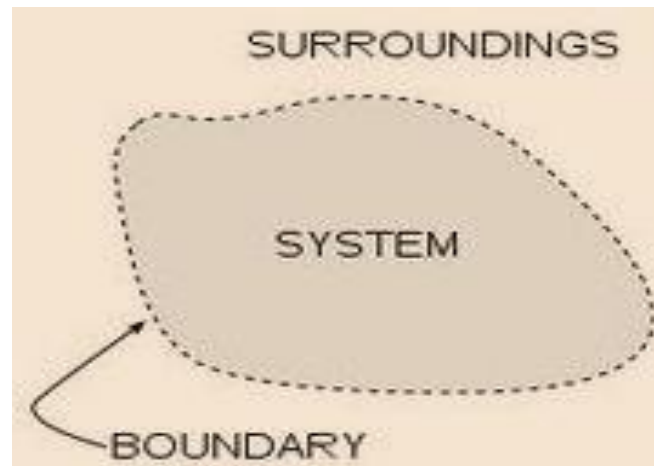
Thermodynamic systems are defined by using a real or imaginary boundary. Anything beyond real or imaginary boundary is known as surroundings



Definitions of thermodynamics terminology

Thermodynamic systems: A thermodynamic system may be defined as the quantity of matter or definite region in space upon which some thermodynamic process is taking place.

Thermodynamic system are defined by using a real or imaginary boundary anything beyond real or imaginary boundary is known as surroundings.



Surrounding: The space outside the thermodynamic system is known as surrounding

Boundary: The line separating the system and surrounding is known as boundary.

Universe: The combination of system, surrounding and boundary is known as universe.

State of System:

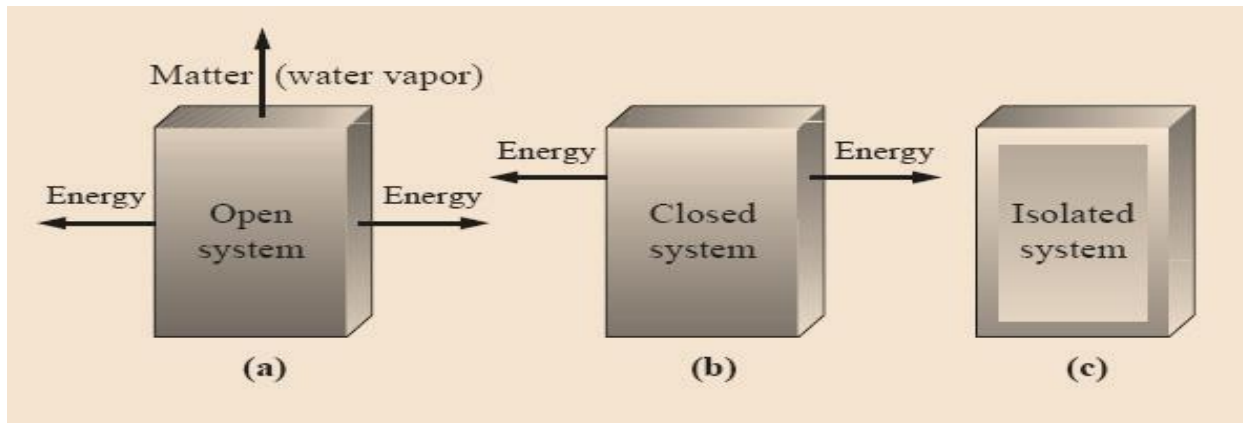
A state is a macroscopic condition of a thermodynamic system as described by its particular thermodynamic parameters.

Some thermodynamic parameters are pressure, temperature, density, composition etc.

Classification of thermodynamic system

Thermodynamic systems may be broadly classified in three categories:

1. Open system
2. Closed system
3. Isolated system



THERMODYNAMIC EQUILIBRIUM

Chemical Equilibrium

Mechanical Equilibrium

Thermal Equilibrium

Equilibrium:

Equilibrium indicates the state of balance. In an equilibrium state there are no unbalanced potentials within the system. Equilibrium may be classified as

- (i) **Chemical Equilibrium:** If there is no chemical reaction or diffusion of matter from one part of the system to another, the system is said to be in chemical equilibrium.
- (ii) **Mechanical Equilibrium:** If there are no unbalanced forces in the system, the system is said to be in mechanical equilibrium.
- (iii) **Thermal Equilibrium:** When a system is prevailing in chemical and mechanical equilibrium is separated from its surroundings by a diathermic wall and if no spontaneous change in any property of the system, the system is said to be in state of thermal equilibrium.

Thermodynamic Properties of a system

Properties are those characteristics of the system which can be used for defining the system. Such as volume, pressure, temperature, viscosity etc.

Classification of properties of a thermodynamic system

The thermodynamic properties may be classified into two categories:

- 1.Intensive property
- 2.Extensive property

1.Intensive property:

Intensive properties are those properties which have same value for any part of the system or these are those properties that are independent of the mass of the system. Such as temperature, pressure and density.

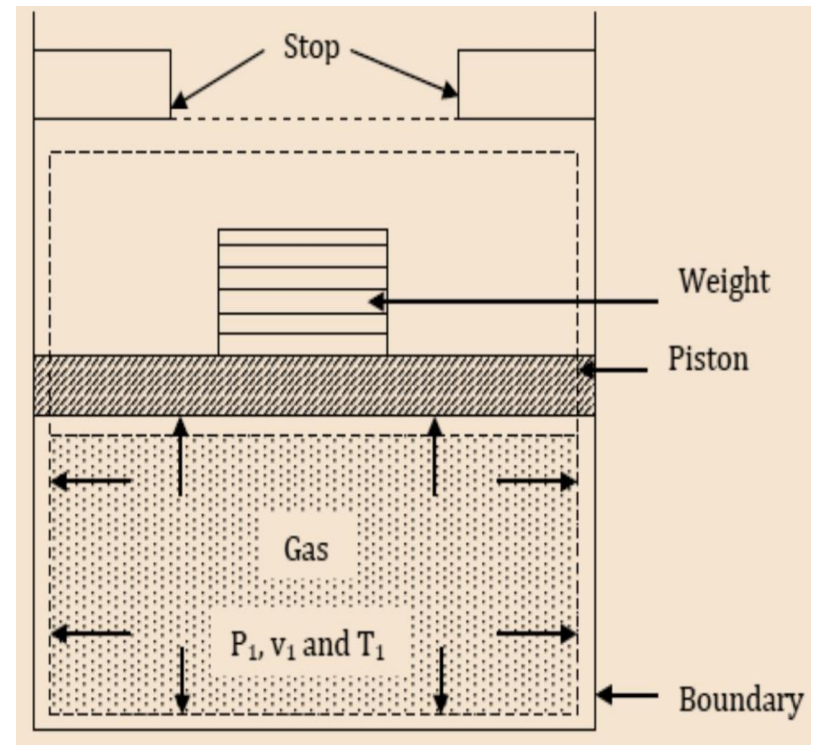
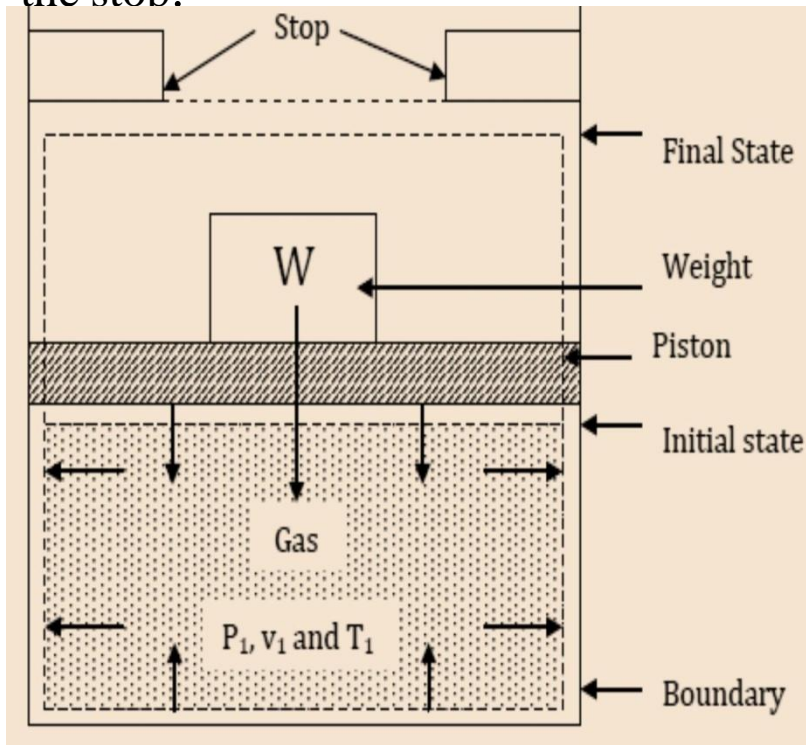
2.Extensive property:

Extensive properties are those properties which depend upon the mass of the system and do not maintain the same value for any path of the system. Such as mass, enthalpy, volume and energy etc.

- **Path:** If all the changes of states of the system are plotted, then line joining the change of states of the system is known as path.
- **Process:** A process is a complete description of change of state of a thermodynamic system through a specified path.
- **cycle:** A thermodynamic cycle is defined as the series of state of changes such that the initial state is identical with the final state.

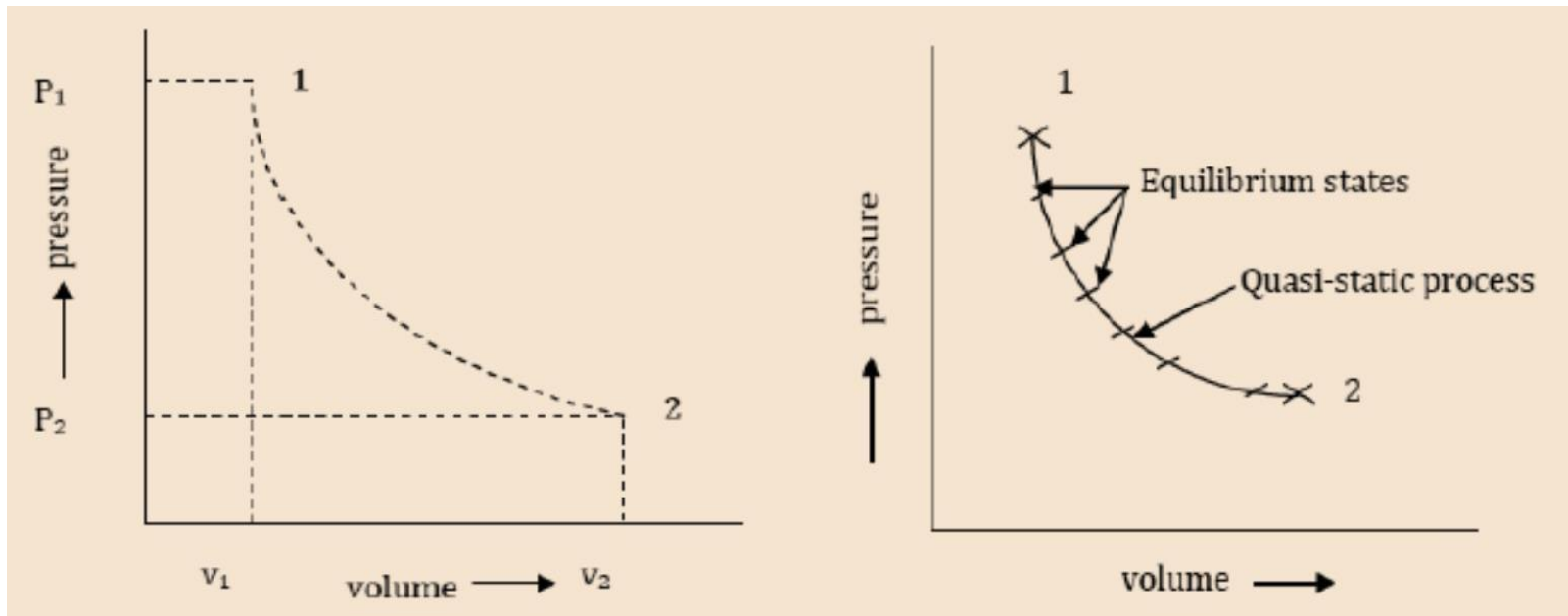
Quasi-Static Process

Consider a system which contained gas in a cylinder in fig. Initially it is in an equilibrium state, represents the properties P_1, v_1, T_1 . The weight on the piston just balance the force exerted by the gas. When weight is removed from the piston the system become unbalanced. The unbalanced force is between the system and the surrounding, and gas pressure will moves the piston in upward direction till it hits the stop.



The system again comes to an equilibrium states, being described by the properties P_2 , v_2 , T_2 . But the immediate states passed through by the system are non-equilibrium states which cannot be described by thermodynamic coordinates. Figure shows the points 1 and 2 as the initial and final equilibrium states joined by dotted line.

Now if the single weight on the piston is made up of many very small pieces of weights and these weights are removed one by one very slowly, at any instant of the upward travel of the piston, if the gas is isolated, the departure of the state of the system from thermodynamic equilibrium state will be infinitesimally small. So every state passed through by the system will be an equilibrium state.



FORMS OF ENERGY

1. Work

2. Heat

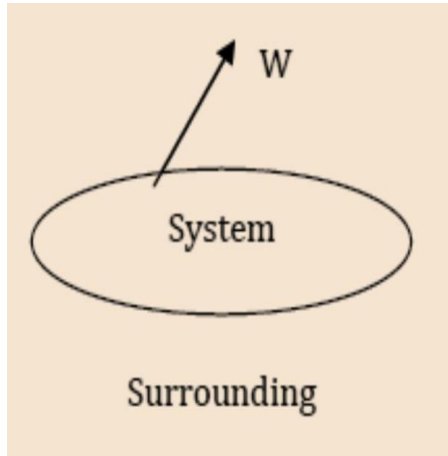
Work

Work is one of the basic modes of energy transfer.

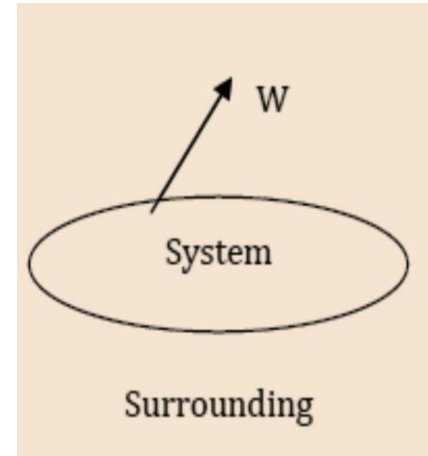
In mechanics the action of a force on a moving body is identified as work. The work is done by a force as it acts upon a body moving in the direction of force.

In thermodynamics, work transfer is considered as occurring between the system and the surroundings. Work is said to be done by a system if the sole effect on the things external to the system can be reduced to the raising of a weight.

The work is done by a system, it is taken to be positive, and when work is done on a system, it is taken to be negative.



(a) Work is Positive (+ve)



(b) Work is negative (-ve)

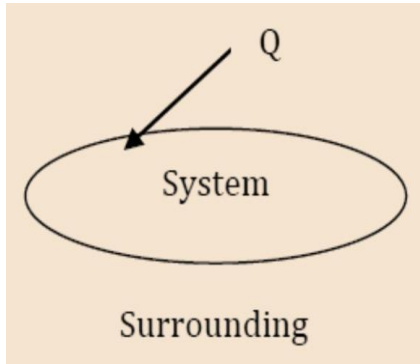
Power: The rate of energy transfer is known as power or the rate of work transfer is known as power. The unit of power is J/s or Watt.

Heat

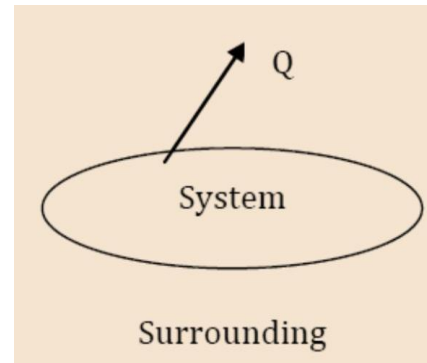
Heat is defined as the form of energy that is transferred across a boundary by virtue of a temperature difference. The temperature difference is the potential or force and heat transfer is the flux.

Heat flow into a system is taken to be positive, and heat flow out of a system is taken as negative.

A process in which no transfer of heat through boundary is known as adiabatic process.



(a) Heat transfer is Positive (+ve)



(b) Heat transfer is negative (-ve)

The symbol used for heat transfer is Q . The unit of heat transfer in SI (System international) system is Nm or Joule (J). The rate of heat transfer is given by W or kW.

Types of Heat

1. Specific Heat: Specific heat is defined as the amount of heat required to raise the temperature of a unit mass (1kg) of the substance by unit degree (1°C or 1K) change in temperature.

The quantity of heat absorbed or rejected by a system during heating or cooling is measured by the formula as given below:

$$Q = m \times c \times (T_2 - T_1)$$

Where, Q = heat gain or loss by the system in kJ,

m = mass of the substance in kilograms (kg),

c = specific heat in kJ/kgK

$(T_2 - T_1)$ = Temperature rise or drop in degree Celsius or Kelvin

Types of specific heat: Basically there are two types of specific heats as given below:

(i) Specific heat at constant pressure (c_p)

(ii) Specific heat at constant volume (c_v)

It is defined as the amount of heat required to raise the temperature of a unit mass (1kg) of the substance by unit degree (1°C or 1K) change in temperature when the pressure is constant. It is represented by c_p . Its unit is kJ/kgK.

(ii) Specific heat at constant volume (c_v): It is defined as the amount of heat required to raise the temperature of a unit mass (1kg) of the substance by unit degree (1°C or 1K) change in temperature when the volume is constant. It is represented by c_v . Its unit is kJ/kgK.

Specific heat of water: $c = 4.186$ kJ/kgK

Specific heats of air: $c_p = 1.005$ kJ/kgK $c_v = 0.718$ kJ/kgK

2. Latent heat of vaporization: defined as the amount of heat required to evaporate one kilogram of water at its saturation temperature (boiling point) without change of temperature. It is represented by h_{fg} . Its unit is kJ/kg. The latent heat of vaporization of water or latent heat of steam is 2257 kJ/kg.

FIRST LAW OF THERMODYNAMICS

FIRST LAW OF THERMODYNAMICS

First law of thermodynamics also states that, “the energy can neither be created nor be destroyed it can only be transformed from one form to another.” According to this law, when a system undergoes a thermodynamic process, both heat and work transfer takes place. The net energy is stored within the system and is termed as stored energy or total energy of the system. Mathematically it is written as:

$$\delta Q - \delta W = dE$$

First law of thermodynamics for a cyclic process

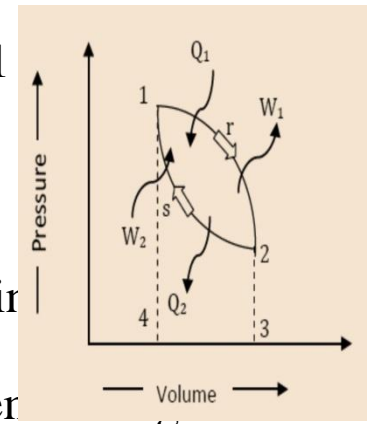
A process is cyclic if the initial and final states of the system are identical. A system represented by state 1 undergoes a process 1-r-2 and returns to the initial state following the path 2-s-1. All the properties of the system are restored, when the initial and final state is reached.

During the completion of these processes:

(a) Area 2-3-4-1-s-2 denotes the work done W_1 by the system during process 2-s-1.

(b) Area 4-3-1-s-4 denotes the work done W_2 supplied to the system during compression process 4-s-1.

(c) Area 1-r-2-s-1 denotes the net work done ($W_1 - W_2$) delivered by the system.



Note:

The total energy is the sum of potential energy, kinetic energy and internal energy of the system. It is mathematically written as:

$$E = P.E. + K.E. + U$$

Where, P.E. = Potential energy,
K.E. = Kinetic energy, U = Internal Energy.

Internal Energy: Internal energy of steam is defined as the energy stored in the steam, above 0°C (freezing point) of water. It may be obtained by subtracting the work done during evaporation to the enthalpy of steam. It is represented by U. Mathematically it is written as,

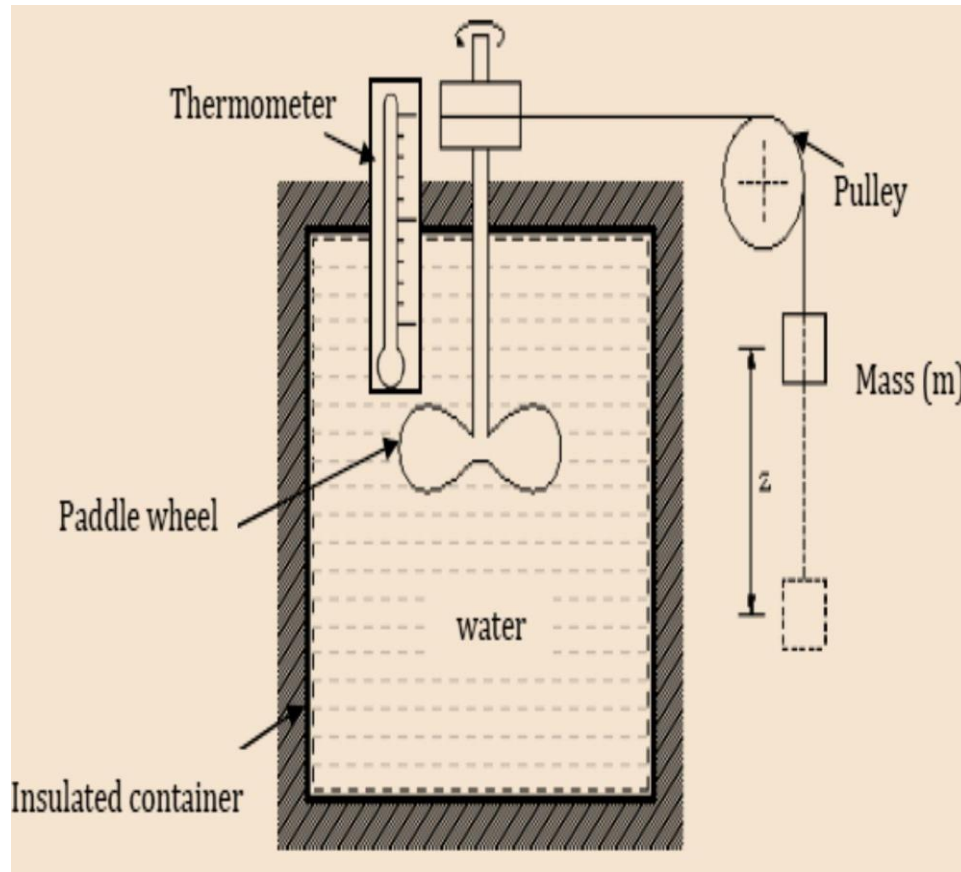
Internal energy of steam = Enthalpy of steam - Work done during evaporation

Enthalpy: It is defined as the amount of heat absorbed by water from 0°C (freezing point) to saturation point (sensible heat) plus heat absorbed during evaporation (latent heat). It is represented by h_g .

So that,

Enthalpy = sensible heat + latent heat

Joule's Experiment



TYPES OF 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

ISOBARIC PROCESS

An **isobaric process** is a [thermodynamic process](#) in which the pressure stays constant.

- An example would be to have a movable piston in a cylinder, so that the pressure inside the cylinder is always at atmospheric pressure, although it is isolated from the atmosphere.
- In other words, the system is **dynamically connected**, by a movable boundary.

ISOCHORIC PROCESS

- Also called a **constant-volume process**, an **isovolumetric process**, or an **isometric process**
- It is a process during which the volume of the closed system undergoing such a process remains constant.

Volume=constant

- An isochoric process is exemplified by the heating or the cooling of the contents of a sealed, inelastic container:

STEADY FLOW ENERGY EQUATION

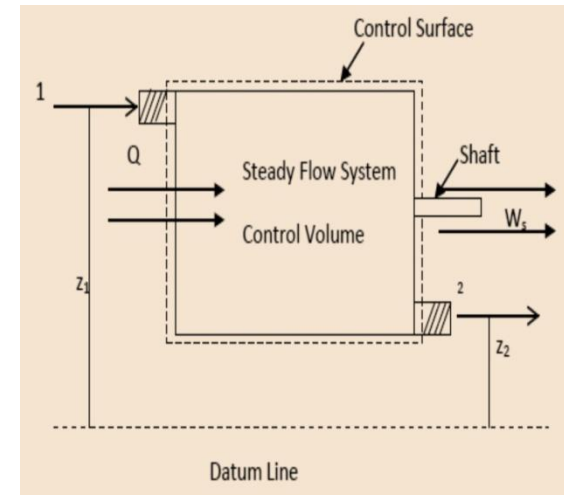
CONTROL VOLUME ANALYSIS

STEADY FLOW ENERGY EQUATION (S.F.E.E.)

- Assume the flow through a system as shown in figure.
- During a small time interval dt there occurs a flow of mass and energy into a fixed control volume; entry is at point 1 and exit at point 2.
- The fluid enters the control volume at point 1 with a average velocity V_1 , pressure P_1 , specific volume v_1 and internal energy U_1 . The fluid exit the control volume at point 2 and the corresponding values are V_2 , P_2 , v_2 , U_2 . During the fluid flow from the two sections, heat Q and mechanical work W may also cross the control surface.

The following points are taken into consideration for energy balance equation:

- (i) Internal energy
- (ii) Kinetic and potential energies.
- (iii) Flow work
- (iv) Heat and mechanical work which cross the control volume.



From the law of conservation of energy, energy neither be created nor be destroyed we can write,

Total energy flow rate into the control volume = Total energy flow rate out of control volume

$m(\text{energy carried into the system}) + m(\text{flow work}) + \text{rate of heat flow} = m(\text{energy carried out of the system}) + m(\text{flow work}) + \text{rate of work transfer}$

$$m(\text{I.E.} + \text{P.E.} + \text{K.E.})_1 + m(\text{flow work})_1 + Q = m(\text{I.E.} + \text{P.E.} + \text{K.E.})_2 + m(\text{flow work})_2 + W$$

Where, $Q = \frac{dQ}{dt}$ and $W = \frac{dW}{dt}$

$$m \left(U_1 + gz_1 + \frac{V_1^2}{2} \right) + m(P_1 v_1) + Q = m \left(U_2 + gz_2 + \frac{V_2^2}{2} \right) + m(P_2 v_2) + W$$

Arranging the equation,

$$m \left(U_1 + P_1 v_1 + g z_1 + \frac{V_1^2}{2} \right) + Q = m \left(U_2 + P_2 v_2 + g z_2 + \frac{V_2^2}{2} \right) + W$$
$$m \left((U_1 + P_1 v_1) + g z_1 + \frac{V_1^2}{2} \right) + Q = m \left((U_2 + P_2 v_2) + g z_2 + \frac{V_2^2}{2} \right) + W$$

Since $h = (U + Pv)$, so that $h_1 = (U_1 + P_1 v_1)$ and $h_2 = (U_2 + P_2 v_2)$

$$m \left(h_1 + g z_1 + \frac{V_1^2}{2} \right) + Q = m \left(h_2 + g z_2 + \frac{V_2^2}{2} \right) + W$$

This equation is known as steady flow energy equation (SFEE).

If the mass of fluid is taken as unity then steady flow energy equation is reduces to,

$$\left(h_1 + g z_1 + \frac{V_1^2}{2} \right) + q_{1-2} = \left(h_2 + g z_2 + \frac{V_2^2}{2} \right) + w$$

All the terms represent energy flow per unit mass of fluid (J/kg).

Applications of Steady flow energy equation

Steady flow energy equation is commonly used in flow processes in many engineering plants. Some commonly used engineering systems which works on steady flow energy equation (SFEE) are as follows:

- (i) Compressor
- (ii) Condenser
- (iii) Boiler
- (iv) Turbine
- (v) Nozzle and
- (vi) Pump

(i) Compressor: Compressor is a device which is used to compress the fluid (may be air) and deliver it at a high pressure and large flow rate. There are two types of compressors as follows:

(a) Rotary compressor

(b) Reciprocating compressor

(a) Rotary compressor: Rotary compressors are the devices which are used to develop high pressure and have a rotor as their primary element. The characteristic features of flow through a rotary compressor are:

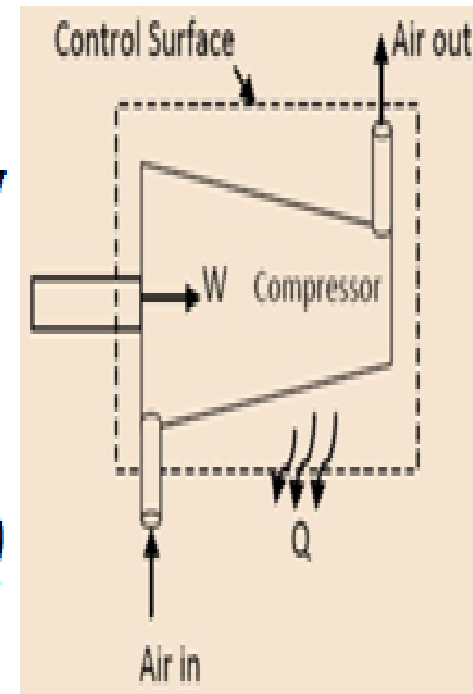
- Work is done on the system so that W is negative.
- Negligible change in Potential energy.
- Heat is lost from the system so that Q is negative

Steady flow energy equation may be written as follows:

$$m \left(h_1 + \frac{V_1^2}{2} \right) - Q = m \left(h_2 + \frac{V_2^2}{2} \right) - W$$

Or

$$W = m \left(h_2 + \frac{V_2^2}{2} \right) - m \left(h_1 + \frac{V_1^2}{2} \right) + Q$$



If the change in velocity is negligible and the flow process is assumed as adiabatic (i.e. $Q=0$) due to very high flow rates, then

$$W = m(h_2 - h_1)$$

Steady flow energy equation may be written as follows:

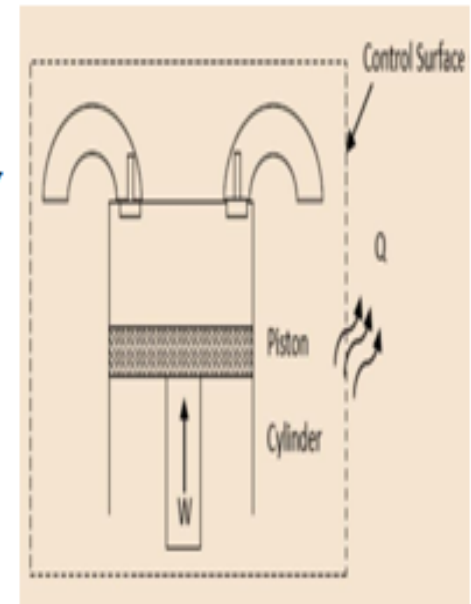
$$m \left(h_1 + \frac{V_1^2}{2} \right) - Q = m \left(h_2 + \frac{V_2^2}{2} \right) - W$$

Or

$$W = m \left(h_2 + \frac{V_2^2}{2} \right) - m \left(h_1 + \frac{V_1^2}{2} \right) + Q$$

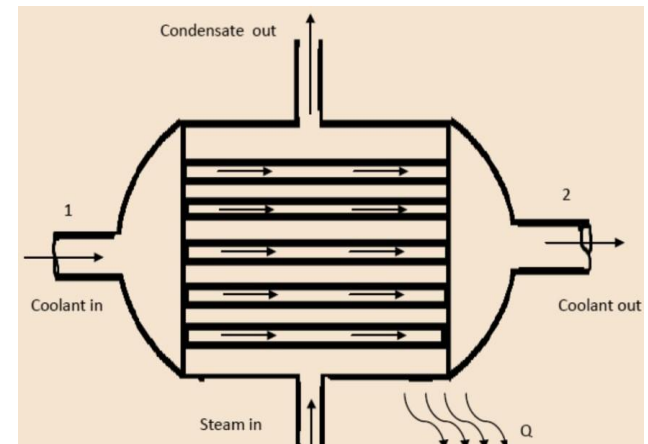
If the change in velocity is negligible, then

$$W = m(h_2 - h_1) + Q$$



Condenser: Condenser is a type of heat exchanger. It is used to transfer heat from one fluid to another. The characteristic features of a condenser are as follows

- No mechanical work (i.e., $W=0$).
- No change in kinetic and potential energies.
- No external heat interaction (Since it is perfectly insulated).
- Heat is absorbed by the one fluid (Steam) to the another fluid (coolant), so that heat is taken negative.
- Thus steady flow energy equation reduces to

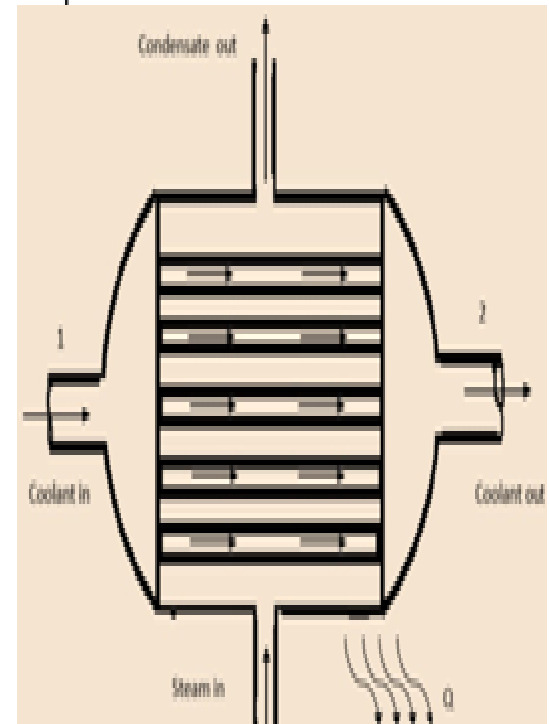


Thus steady flow energy equation reduces to;

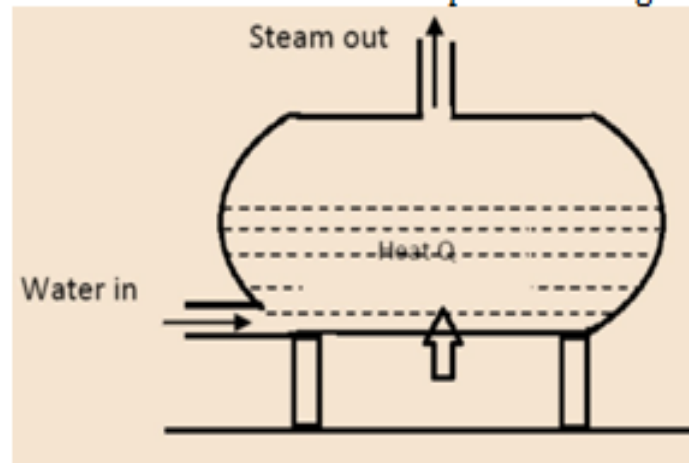
$$m \left(h_1 + gz_1 + \frac{V_1^2}{2} \right) + Q = m \left(h_2 + gz_2 + \frac{V_2^2}{2} \right) + W$$

$$h_1 - Q = h_2$$

$$Q = h_1 - h_2$$



(iii) **Boiler:** Boiler is an equipment used for generation of steam. Thermal energy released by combustion of fuel is transferred to water which vaporizes and gets converted into steam.



The characteristic features of a boiler are as follows:

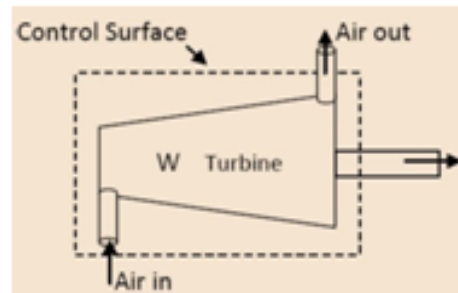
- No mechanical work (i.e., $W=0$).
- No change in kinetic and potential energies
- Height change between inlet and exit point is negligible.

Thus steady flow energy equation reduces to;

$$m \left(h_1 + gz_1 + \frac{V_1^2}{2} \right) + Q = m \left(h_2 + gz_2 + \frac{V_2^2}{2} \right) + W$$
$$h_1 + Q = h_2$$
$$Q = h_2 - h_1$$

(iv) Turbine: Turbine is a device which converts thermal energy into useful work. In turbine fluids expand from high pressure to a low pressure. The work output from the turbine may be used to drive a generator to produce electricity. The characteristic features of a turbine are as follows:

- ❑ Negligible change in velocity so that negligible change in kinetic energy.
- ❑ Negligible change in potential energy.
- ❑ Isentropic expansion takes place since the walls of turbine are thermally insulated.



Thus steady flow energy equation reduces to;

$$m \left(h_1 + gz_1 + \frac{V_1^2}{2} \right) + Q = m \left(h_2 + gz_2 + \frac{V_2^2}{2} \right) + W$$
$$W = m(h_2 - h_1)$$

(v) Nozzle: Nozzle is a device of varying cross-section used for increasing the velocity of a flowing stream at the expense of its pressure drop. In nozzle pressure energy of the fluid is converted into kinetic energy. It is used in turbines, fuel pumps and jet engines etc.

The characteristic features of a nozzle are as follows:

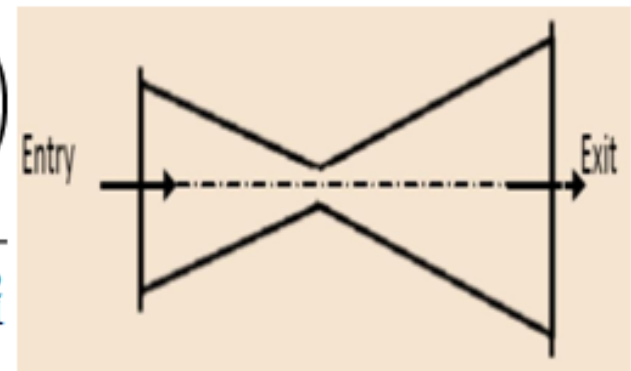
- ❑ No mechanical work (i.e. $W=0$)
- ❑ Flow is isentropic (i.e. $Q=0$)
- ❑ Change in height between entry and exit is negligible. (i.e. $z_1=z_2$)

Thus steady flow energy equation reduces to;

$$\left(h_1 + \frac{V_1^2}{2} \right) = \left(h_2 + \frac{V_2^2}{2} \right)$$

Let V_1 is known then,

$$V_2 = \sqrt{2(h_1 - h_2) + V_1^2}$$



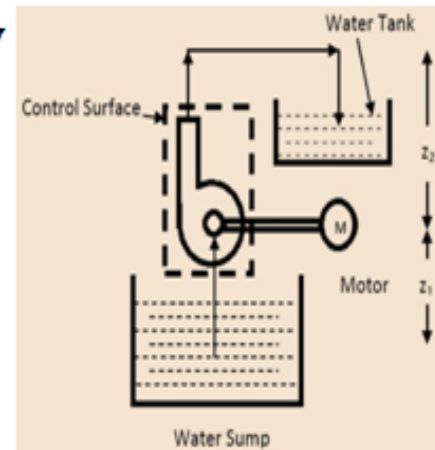
(vi) **Pump:** A pump is a device which takes the fluid from a low level and delivers it to a high level. The characteristic features of a pump are as follows:

- ❑ No change in internal energy.
- ❑ Work is done on the system, so that work is taken negative.

Thus steady flow energy equation reduces to;

- ❑ Flow is assumed to be adiabatic (i.e. $Q=0$)

$$m \left(h_1 + gz_1 + \frac{V_1^2}{2} \right) + Q = m \left(h_2 + gz_2 + \frac{V_2^2}{2} \right) + W$$
$$m \left(gz_1 + \frac{V_1^2}{2} \right) = m \left(gz_2 + \frac{V_2^2}{2} \right) - W$$



LIMITATIONS OF FIRST LAW

Thermal Reservoir, Heat Engine, Heat pump, Parameters of performance, Second Law of Thermodynamics, Kelvin Planck and Clausius Statements and their Equivalence / Corollaries, PMM of Second kind, Carnot's principle, Carnot cycle and its specialties, Thermodynamic scale of Temperature, Clausius Inequality, Entropy, Principle of Entropy Increase, Availability and Irreversibility, Thermodynamic Potentials, Gibbs and Helmholtz Functions, Maxwell Relations, Elementary Treatment of the Third Law of Thermodynamics

PROBLEMS FROM 1ST LAW

- The first law of thermodynamics is simple, general, but does not constitute a complete theory because certain processes it permits do not occur in nature!

The problems arise from:

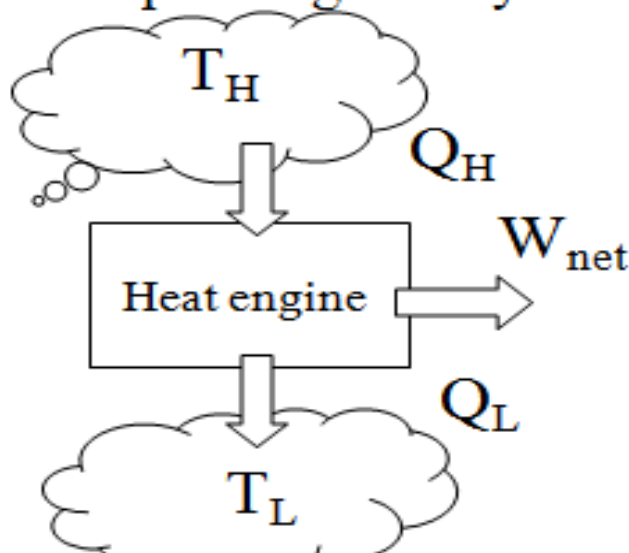
1. Classical thermodynamics is connected with states of equilibrium and various processes connecting them.
2. The exact process by which a system reaches the final state from its initial state is immaterial. i.e. the transition is independent of the particular path taken
3. The theory emphasizes reversible processes! Yet, real processes are irreversible!

Examples of processes which are not prohibited by the first law, but cannot happen in a real world.

- Perfect machine Transfer heat from cold to hot subject
- Gas expansion

- Identifies the direction of a process. (e.g.: Heat can only *spontaneously* transfer from a hot object to a cold object, *not vice versa*)
- Used to determine the “Quality” of energy. (e.g.: A high-temperature energy source has a higher quality since it is easier to extract energy from it to deliver useable work.)
- Used to exclude the possibility of constructing 100% efficient heat engine and perpetual-motion machines. (violates the *Kevin-Planck* and the *Clausius statements* of the second law)
- Used to introduce concepts of *reversible processes* and *irreversibilities*.
- Determines the *theoretical performance limits* of engineering systems. (e.g.: A Carnot engine is theoretically the most efficient heat engine; its performance can be used as a standard for other practical engines)

- A process can not happen unless it satisfies both the first and second laws of thermodynamics. The first law characterizes the balance of energy which defines the “quantity” of energy. The second law defines the direction which the process can take place and its “quality”.
- Define a “**Heat Engine**”: A device that converts heat into work while operating in a cycle.



$$\Delta Q - W_{net} = \Delta U \quad (\text{since } \Delta U = 0 \text{ for a cycle})$$

$$\Rightarrow W_{net} = Q_H - Q_L$$

Thermal efficiency, η_{th} is defined as

$$\eta_{th} = W_{net} / Q_H = (Q_H - Q_L) / Q_H$$

$$= 1 - (Q_L / Q_H)$$

Question: Can we produce an 100% heat engine, i.e. a heat engine where $Q_L = 0$?

Steam Power Plant

- A **steam power plant** is a good example of a heat engine where the working fluid, water, undergoes a thermodynamic cycle

$$W_{\text{net}} = W_{\text{out}} - W_{\text{in}} = Q_{\text{in}} - Q_{\text{out}}$$

Q_{in} is the heat transferred from the high temp. reservoir, and is generally referred to as Q_{H}

Q_{out} is the heat transferred to the low temp. reservoir, and is generally referred to as Q_{L}

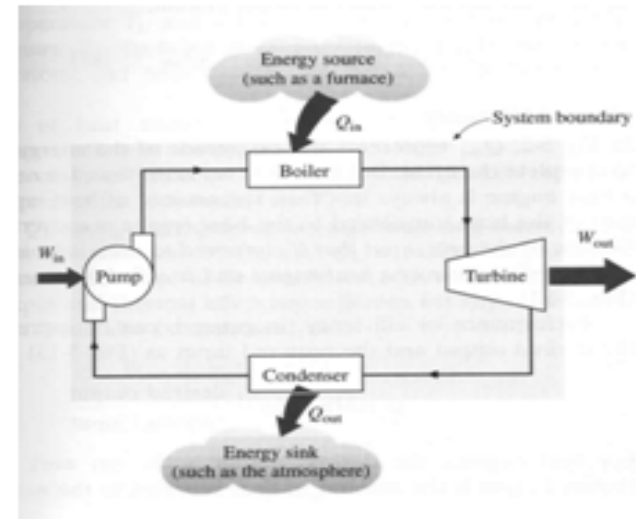
Thermal efficiency

$$\eta_{\text{th}} = W_{\text{net}}/Q_{\text{H}} = (Q_{\text{H}} - Q_{\text{L}})/Q_{\text{H}} = 1 - (Q_{\text{L}}/Q_{\text{H}})$$

Typical Efficiency of a large commercial steam power plant $\approx 40\%$

Thermal Reservoir

A hypothetical body with a very large thermal capacity (relative to the system being examined) to/from which heat can be transferred without changing its temperature. E.g. the ocean, atmosphere, large lakes.



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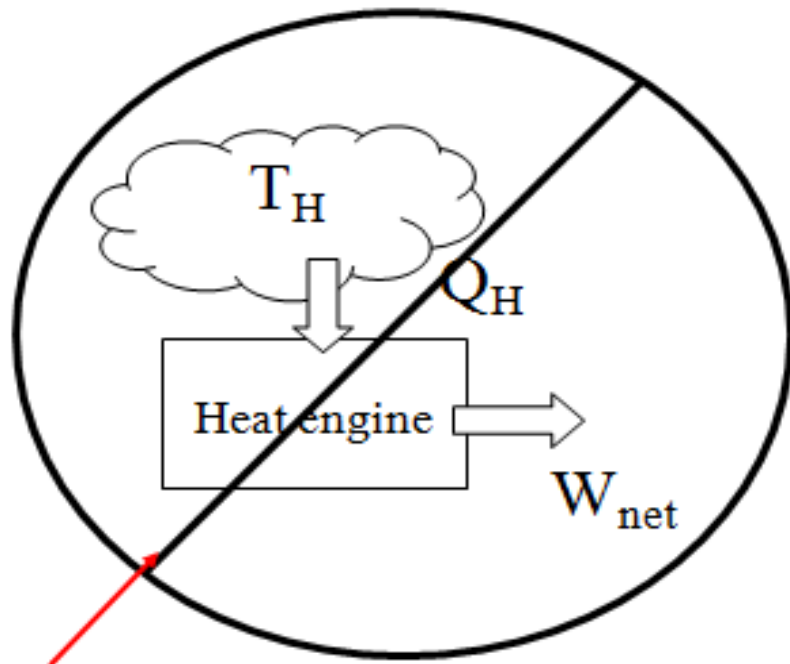
Rank

Kevin-Planck Statement

- The Kelvin-Planck Statement is another expression of the second law of thermodynamics. It states that:

It is **impossible** for any device that operates on a *cycle* to receive heat from a *single reservoir* and *produce net work*.

- This statement is without proof, however it has not been violated yet.
- Consequently, it is **impossible to built a heat engine that is 100%**.



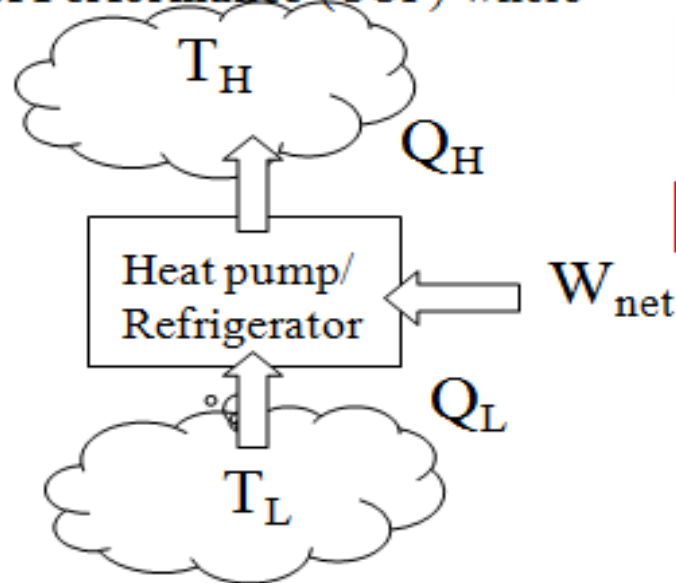
- A heat engine *has to* reject some energy into a lower temperature sink in order to complete the cycle.

- $T_H > T_L$ in order to operate the engine. Therefore, the higher the temperature, T_H , the higher the *quality* of the energy source and more work is produced.

Impossible because it violates the Kelvin-Planck Statement/Second Law

Heat Pumps and Refrigerators

- A “heat pump” is defined as a device that transfers heat from a low-temperature source to a high-temperature one. E.g. a heat pump is used to extract energy from outside cold outdoor air into the warm indoors.
- A refrigerator performs the same function; the difference between the two is in the type of heat transfer that needs to be optimized.
- The efficiencies of heat pumps and refrigerators are denoted by the **Coefficient of Performance (COP)** where



For a Heat Pump:

$$COP_{HP} = Q_H / W_{net} = Q_H / (Q_H - Q_L) = 1 / (1 - Q_L / Q_H)$$

For a Refrigerator:

$$COP_R = Q_L / W_{net} = Q_L / (Q_H - Q_L) = 1 / (Q_H / Q_L - 1)$$

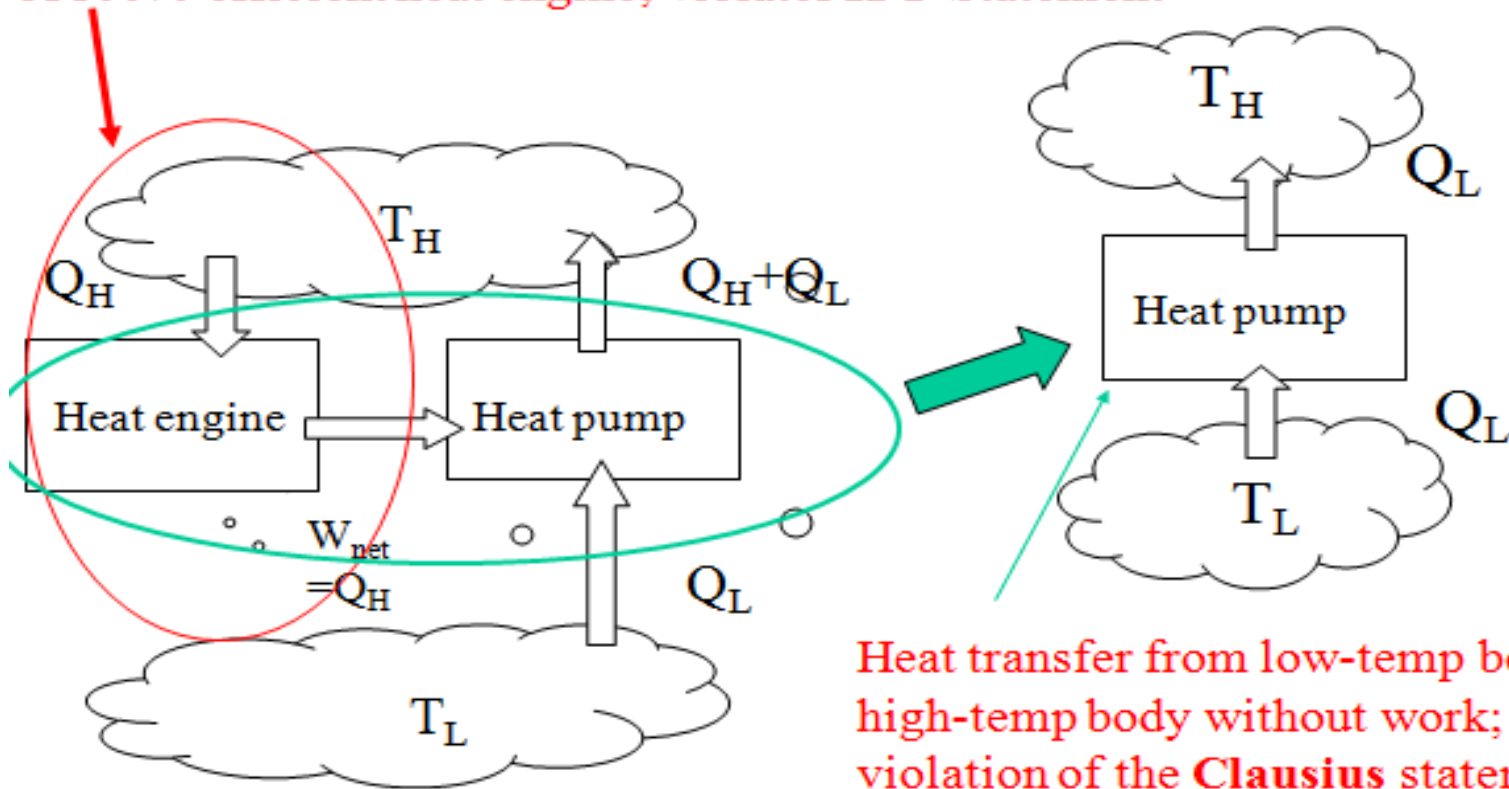
Note: $COP_{HP} = COP_R + 1$

- $COP_{HP} > 1$, ex: a typical heat pump has a COP in the order of 3
- **Question:** Can one build a heat pump operating $COP = \infty$, that is $W_{net} = 0$ and $Q_H = Q_L$?

Equivalence of the Two Statements

It can be shown that the violation of one statement leads to a violation of the other statement, i.e. they are equivalent.

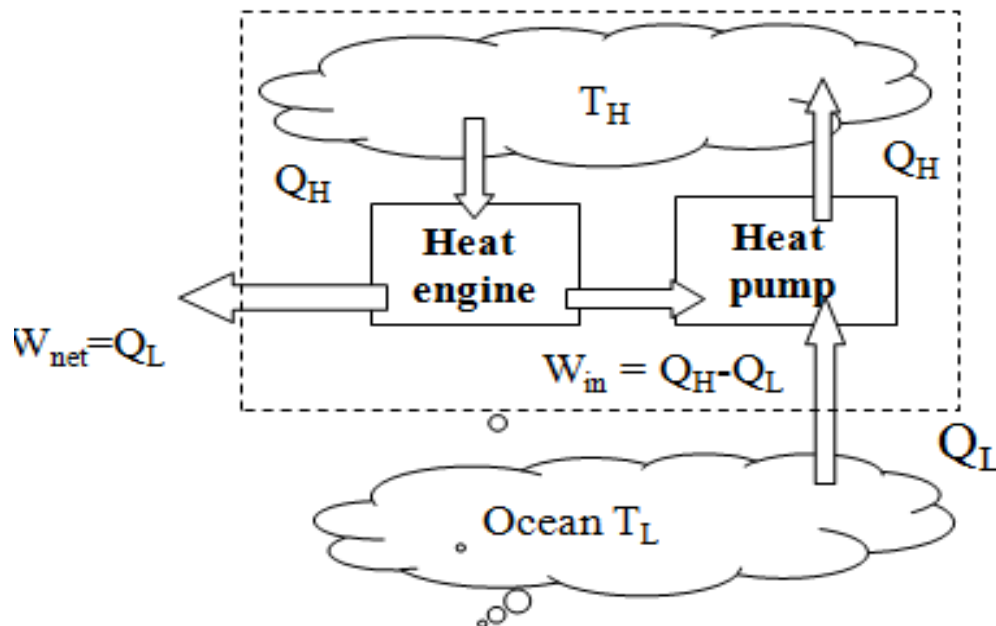
A 100% efficient heat engine; violates **K-P** Statement



Heat transfer from low-temp body to high-temp body without work; A violation of the **Clausius** statement

Perpetual-Motion Machines (YAC: 5-5)

Imagine that we can extract energy from unlimited low-temperature energy sources such as the ocean or the atmosphere (both can be thought of as thermal reservoirs).



It is against the Kelvin-Planck statement: it is impossible to build a 100% heat engine.

Perpetual Motion Machines, PMM, are classified into two types:

PMM1- Perpetual Motion Machines of the First Kind: They violate the First Law of Thermodynamics

PMM2 - Perpetual Motion Machines of the Second Kind : Violate the Second Law of Thermodynamics

Reversible Processes and Irreversibilities

- A reversible process is one that can be executed in the reverse direction with no net change in the system or the surroundings.
- At the end of a forwards and backwards reversible process, *both system and the surroundings are returned to their initial states.*
- *No real processes are reversible.*
- However, *reversible processes are* theoretically *the most efficient* processes.
- All real processes are irreversible due to *irreversibilities*. Hence, real processes are less efficient than reversible processes.

Common Sources of Irreversibility:

- Friction
- Sudden Expansion and compression
- Heat Transfer between bodies with a *finite temperature difference.*
- A **quasi-equilibrium process**, e.g. very slow, frictionless expansion or compression is a reversible process.

Reversible Processes and Irreversibilities (cont'd)

- A *work-producing* device which employs quasi-equilibrium or reversible processes *produces the maximum amount of work* theoretically possible.
- A *work-consuming* device which employs quasi-equilibrium or reversible processes *requires the minimum amount of work* theoretically possible.
- One of the most common idealized cycles that employs all reversible processes is called the *Carnot Cycle* proposed in 1824 by Sadi Carnot.

The Carnot Cycle

French military engineer Nicolas Sadi Carnot (1769-1832) was among the first to study the principles of the second law of thermodynamics. Carnot was the first to introduce the concept of cyclic operation and devised a reversible cycle that is composed of four reversible processes, two isothermal and two adiabatic.

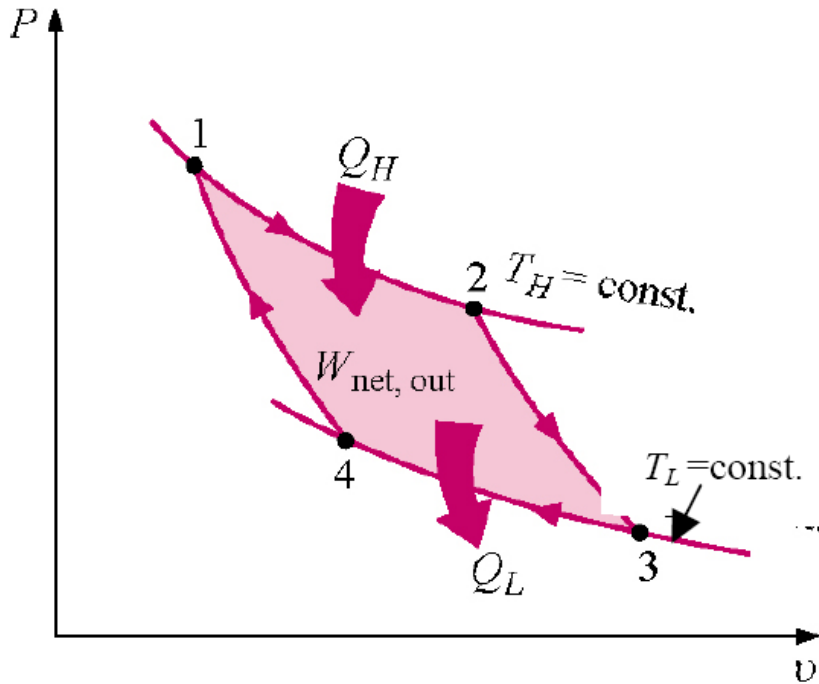
The Carnot Cycle

Process 1-2: Reversible isothermal heat addition at high temperature, $T_H > T_L$, to the working fluid in a piston-cylinder device that does some boundary work.

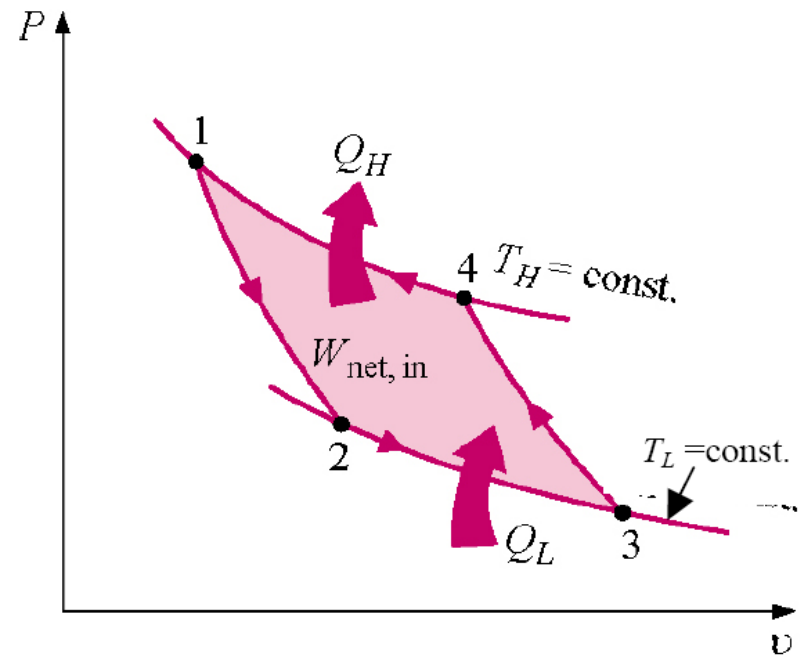
Process 2-3: Reversible adiabatic expansion during which the system does work as the working fluid temperature decreases from T_H to T_L .

Process 3-4: The system is brought in contact with a heat reservoir at $T_L < T_H$ and a reversible isothermal heat exchange takes place while work of compression is done on the system.

Process 4-1: A reversible adiabatic compression process increases the working fluid temperature from T_L to T_H .



P-v diagram for Carnot heat engine



P-v diagram for Carnot refrigerator

You may have observed that power cycles operate in the clockwise direction when plotted on a process diagram. The Carnot cycle may be reversed, in which it operates as a refrigerator. The refrigeration cycle operates in the counterclockwise direction.

Carnot Principles

The second law of thermodynamics puts limits on the operation of cyclic devices as expressed by the Kelvin-Planck and Clausius statements. A heat engine cannot operate by exchanging heat with a single heat reservoir, and a refrigerator cannot operate without net work input from an external source.

Consider heat engines operating between two fixed temperature reservoirs at $T_H > T_L$. We draw two conclusions about the thermal efficiency of reversible and irreversible heat engines, known as the Carnot principles.

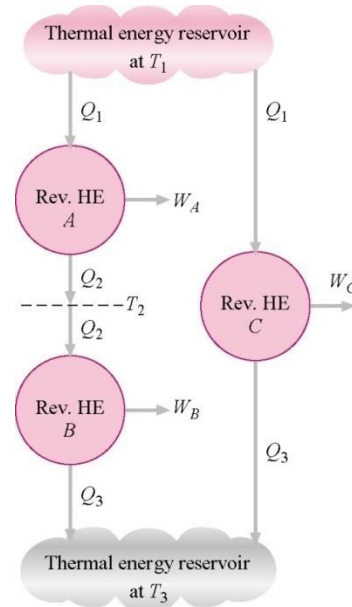
(a) The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.

$$\eta_{th} < \eta_{th, Carnot}$$

(b) The efficiencies of all reversible heat engines operating between the same two constant-temperature heat reservoirs have the same efficiency.

As the result of the above, Lord Kelvin in 1848 used energy as a thermodynamic property to define temperature and devised a temperature scale that is independent of the thermodynamic substance.

The following is Lord Kelvin's Carnot heat engine arrangement.



Since the thermal efficiency in general is

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

For the Carnot engine, this can be written as

$$\eta_{th} = g(T_L, T_H) = 1 - f(T_L, T_H)$$

Considering engines A, B, and C

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \frac{Q_2}{Q_3}$$

This looks like

$$f(T_1, T_3) = f(T_1, T_2) f(T_2, T_3)$$

One way to define the f function is

$$f(T_1, T_3) = \frac{\theta(T_2)}{\theta(T_1)} \frac{\theta(T_3)}{\theta(T_2)} = \frac{\theta(T_3)}{\theta(T_1)}$$

The simplest form of θ is the absolute temperature itself.

$$f(T_1, T_3) = \frac{T_3}{T_1}$$

The Carnot thermal efficiency becomes

$$\eta_{th, rev} = 1 - \frac{T_L}{T_H}$$

This is the maximum possible efficiency of a heat engine operating between two heat reservoirs at temperatures T_H and T_L . Note that the temperatures are absolute temperatures.

These statements form the basis for establishing an absolute temperature scale, also called the Kelvin scale, related to the heat transfers between a reversible device and the high- and low-temperature heat reservoirs by

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

Then the Q_H/Q_L ratio can be replaced by T_H/T_L for reversible devices, where T_H and T_L are the absolute temperatures of the high- and low-temperature heat reservoirs, respectively. This result is only valid for heat exchange across a heat engine operating between two constant temperature heat reservoirs. These results do not apply when the heat exchange is occurring with heat sources and sinks that do not have constant temperature.

The thermal efficiencies of actual and reversible heat engines operating between the same temperature limits compare as follows:

$$\eta_{th} \begin{cases} < \eta_{th, rev} & \text{irreversible heat engine} \\ = \eta_{th, rev} & \text{reversible heat engine} \\ > \eta_{th, rev} & \text{impossible heat engine} \end{cases}$$

Reversed Carnot Device Coefficient of Performance

If the Carnot device is caused to operate in the reversed cycle, the reversible heat pump is created. The COP of reversible refrigerators and heat pumps are given in a similar manner to that of the Carnot heat engine as

$$\begin{aligned} COP_R &= \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} \\ &= \frac{T_L}{T_H - T_L} = \frac{1}{\frac{T_H}{T_L} - 1} \end{aligned}$$

$$\begin{aligned} COP_{HP} &= \frac{Q_H}{Q_H - Q_L} = \frac{\frac{Q_H}{Q_L}}{\frac{Q_H}{Q_L} - 1} \\ &= \frac{T_H}{T_H - T_L} = \frac{\frac{T_H}{T_L}}{\frac{T_H}{T_L} - 1} \end{aligned}$$

Again, these are the maximum possible COPs for a refrigerator or a heat pump operating between the temperature limits of T_H and T_L .

The coefficients of performance of actual and reversible (such as Carnot) refrigerators operating between the same temperature limits compare as follows:

$$COP_R \begin{cases} < COP_{R, rev} & \text{irreversible refrigerator} \\ = COP_{R, rev} & \text{reversible refrigerator} \\ > COP_{R, rev} & \text{impossible refrigerator} \end{cases}$$

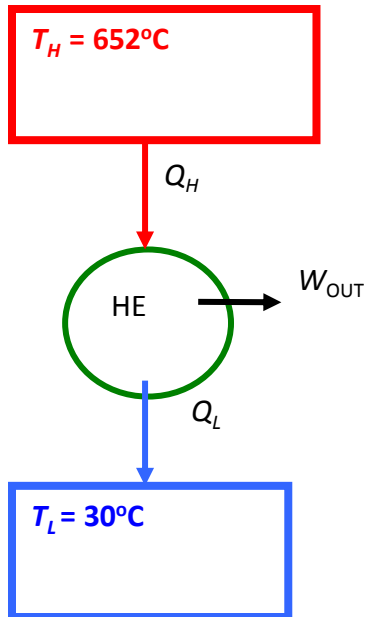
A similar relation can be obtained for heat pumps by replacing all values of COP_R by COP_{HP} in the above relation.

Example

A Carnot heat engine receives 500 kJ of heat per cycle from a high-temperature heat reservoir at 652°C and rejects heat to a low-temperature heat reservoir at 30°C. Determine

- The thermal efficiency of this Carnot engine.
- The amount of heat rejected to the low-temperature heat reservoir.

a.



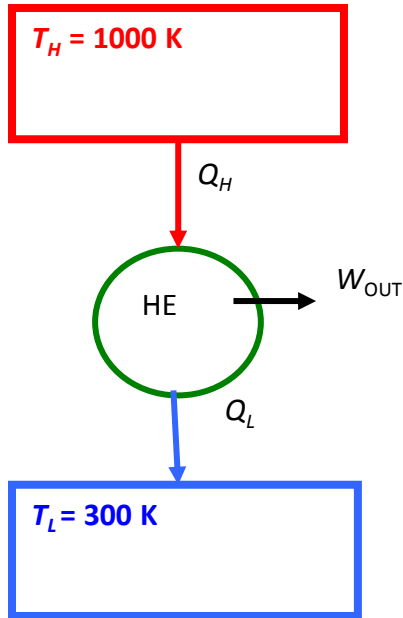
$$\begin{aligned}\eta_{th, rev} &= 1 - \frac{T_L}{T_H} \\ &= 1 - \frac{(30 + 273) K}{(652 + 273) K} \\ &= 0.672 \quad \text{or} \quad 67.2\%\end{aligned}$$

b.

$$\begin{aligned}\frac{Q_L}{Q_H} &= \frac{T_L}{T_H} \\ &= \frac{(30 + 273) K}{(652 + 273) K} = 0.328 \\ Q_L &= 500 \text{ kJ} (0.328) \\ &= 164 \text{ kJ}\end{aligned}$$

Example

An inventor claims to have invented a heat engine that develops a thermal efficiency of 80 percent when operating between two heat reservoirs at 1000 K and 300 K. Evaluate his claim.

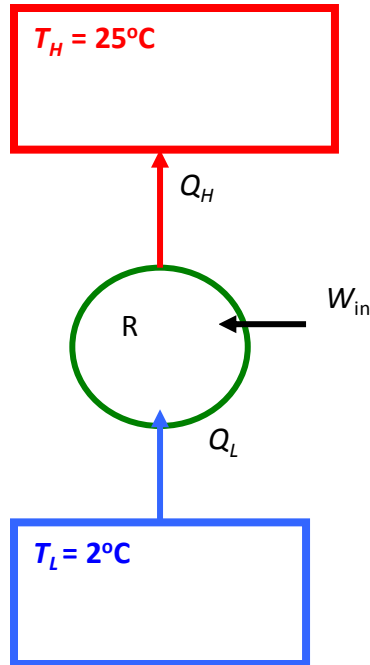


$$\begin{aligned}\eta_{th, rev} &= 1 - \frac{T_L}{T_H} \\ &= 1 - \frac{300 \text{ K}}{1000 \text{ K}} \\ &= 0.70 \quad \text{or} \quad 70\%\end{aligned}$$

The claim is false since no heat engine may be more efficient than a Carnot engine operating between the heat reservoirs.

Example

An inventor claims to have developed a refrigerator that maintains the refrigerated space at 2°C while operating in a room where the temperature is 25°C and has a COP of 13.5. Is there any truth to his claim?

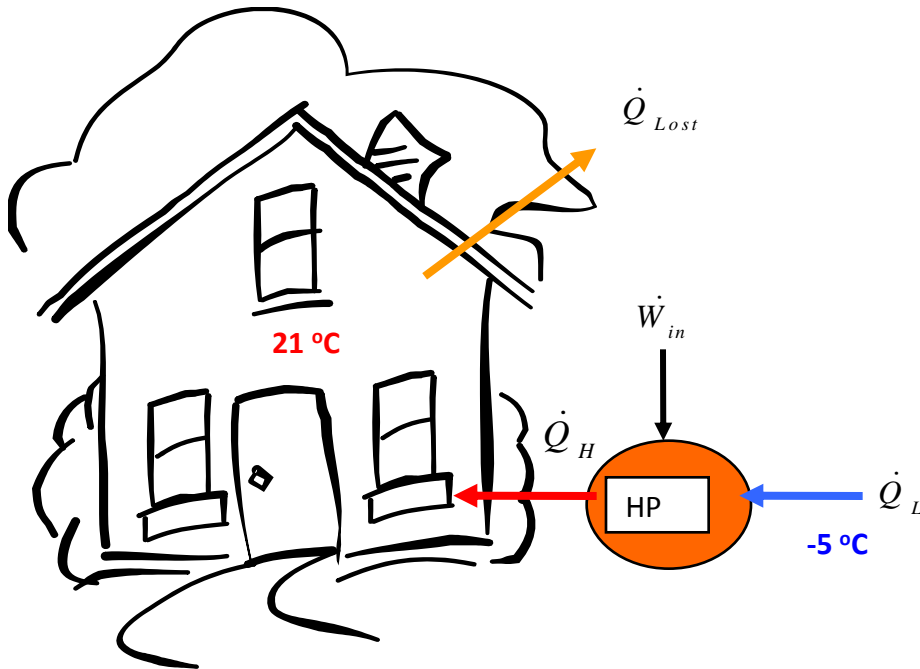


$$\begin{aligned} COP_R &= \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L} \\ &= \frac{(2 + 273) K}{(25 - 2) K} \\ &= 11.96 \end{aligned}$$

The claim is false since no refrigerator may have a COP larger than the COP for the reversed Carnot device.

Example

A heat pump is to be used to heat a building during the winter. The building is to be maintained at 21°C at all times. The building is estimated to be losing heat at a rate of $135,000 \text{ kJ/h}$ when the outside temperature drops to -5°C . Determine the minimum power required to drive the heat pump unit for this outside temperature.



The heat lost by the building has to be supplied by the heat pump.

$$\dot{Q}_H = \dot{Q}_{Lost} = 135000 \frac{kJ}{h}$$

$$\begin{aligned} COP_{HP} &= \frac{\dot{Q}_H}{\dot{Q}_H - \dot{Q}_L} = \frac{T_H}{T_H - T_L} \\ &= \frac{(21 + 273) K}{(21 - (-5)) K} \\ &= 11.31 \end{aligned}$$

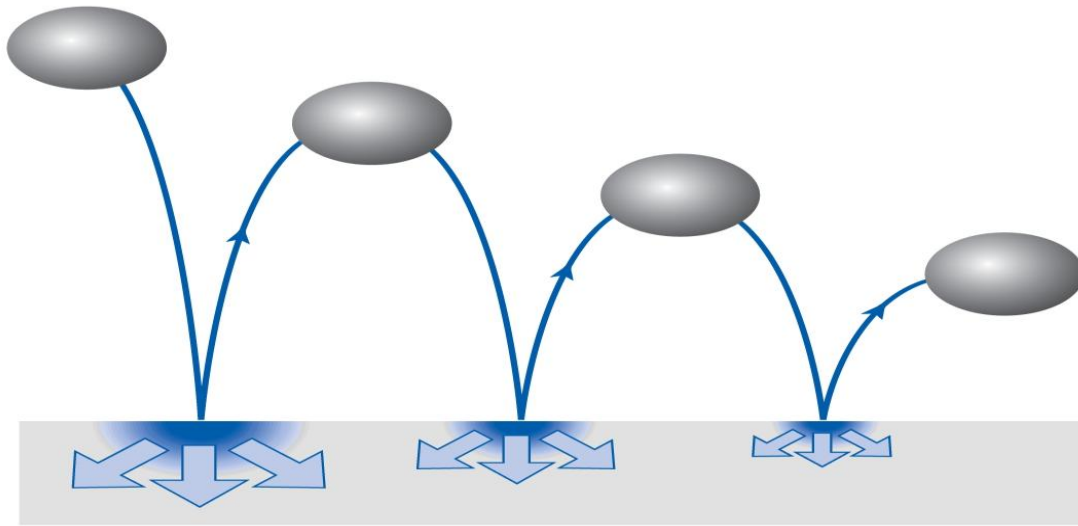
Using the basic definition of the COP

$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{net, in}}$$

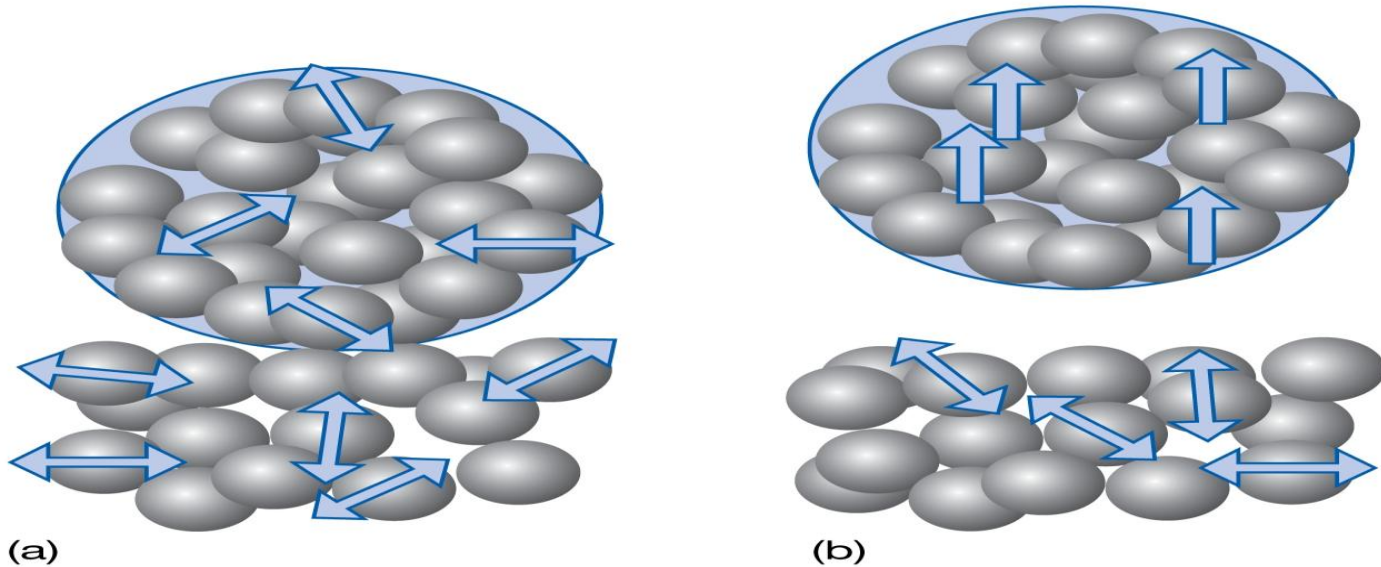
$$\dot{W}_{net, in} = \frac{\dot{Q}_H}{COP_{HP}}$$

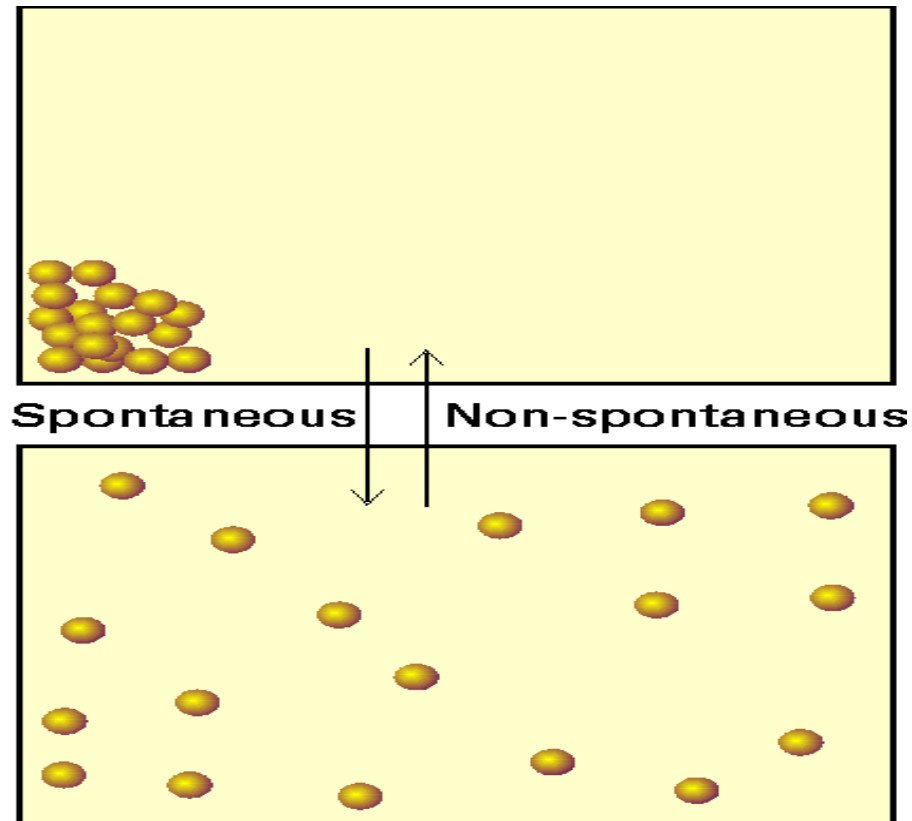
$$\begin{aligned} &= \frac{135,000 \text{ kJ} / h}{11.31} \frac{1 h}{3600 s} \frac{1 \text{ kW}}{kJ / s} \\ &= 3.316 \text{ kW} \end{aligned}$$

A ball bouncing on the floor



A ball resting on the warm surface.





Entropy is measure of randomness/ chaosness.

Total entropy of the system and its surroundings increases in the course of a spontaneous change.

Irreversible Processes and Entropy:

Examples to show the arrow of time...

Changes in energy within a closed system do not set the direction of irreversible processes.

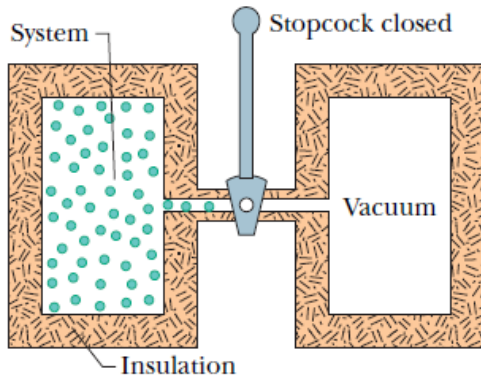
Calling for another state variable to account for the arrow of time...

Entropy Postulate:

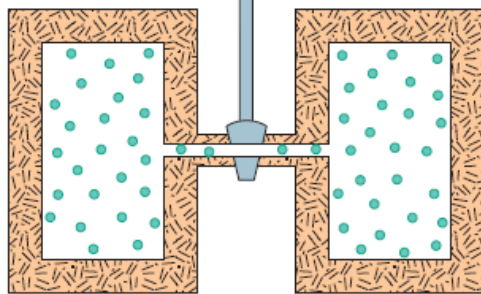
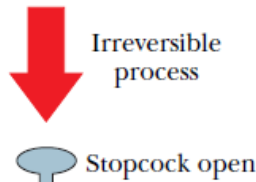
If an irreversible process occurs in a closed system, the entropy S of the system always increases; it never decreases.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad (\text{change in entropy defined}).$$

Here Q is the energy transferred as heat to or from the system during the (reversible) process, and T is the temperature of the system in kelvins.



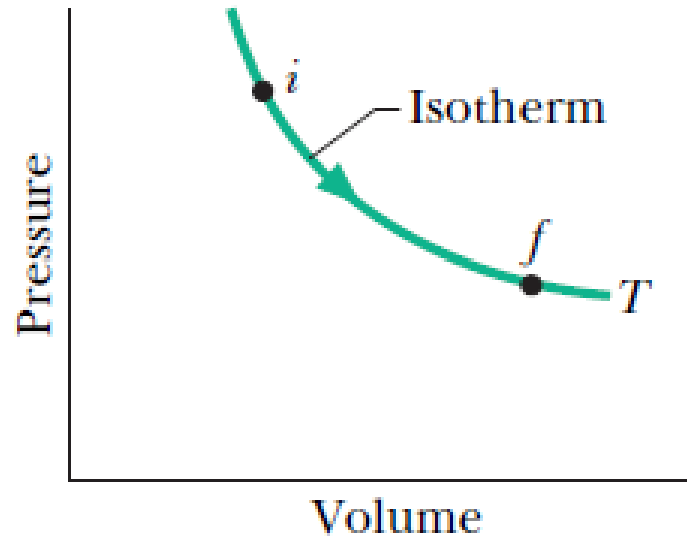
(a) Initial state i



(b) Final state f

free expansion

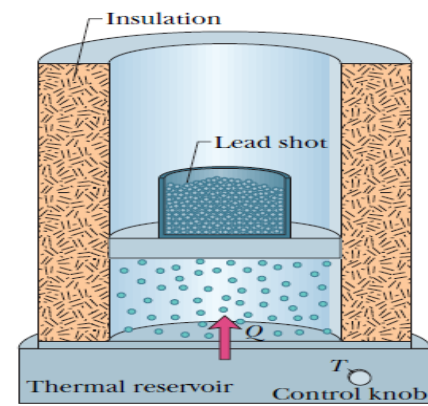
Entropy change of an irreversible process can be found with a reversible one connecting the initial and final states.



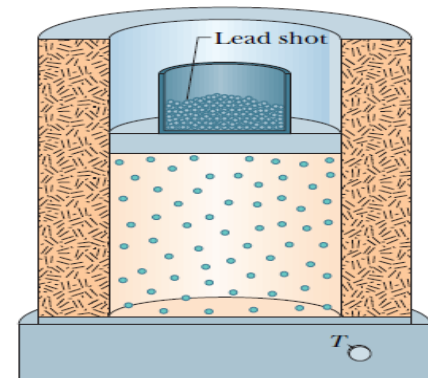
$$\Delta S = S_f - S_i = \frac{1}{T} \int_i^f dQ.$$

$$\int dQ = Q,$$

$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process}).$$



(a) Initial state i



(b) Final state f

an isothermal process

Change in Entropy: Entropy is a State Function

Suppose that an ideal gas is taken through a reversible process, with the gas in an equilibrium state at the end of each step.

For each small step, the energy transferred as heat to or from the gas is dQ , the work done by the gas is dW , and the change in internal energy is dE_{int} .

$$dE_{int} = dQ - dW.$$

We have:

Since the process is reversible

$$dQ = p dV + nC_V dT.$$

$$dW = p dV \text{ and } dE_{int} = nC_V dT.$$

Therefore,

$$\frac{dQ}{T} = nR \frac{dV}{V} + nC_V \frac{dT}{T}.$$

Using ideal gas law, we obtain:

$$\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_V \frac{dT}{T}.$$

Integrating,

$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}.$$

Finally,

The change in entropy ΔS between the initial and final states of an ideal gas depends only on properties of the initial and final states; ΔS does not depend on how the gas changes between the two states.

Clausius inequality theorem

$$dS_{sys} + dS_{surr} \geq 0$$

$$dS_{sys} \geq -dS_{surr}$$

$$dS_{sys} \geq \frac{dq}{T}$$

If the system is isolated,

$$dq = 0$$

$$\Rightarrow dS_{sys} \geq 0$$

The entropy of an isolated system increases in the course of a spontaneous change.

Entropy change for a reversible process

$$dq_{sys} = -dq_{surr}$$

$$dS_{sys} = -dS_{surr}$$

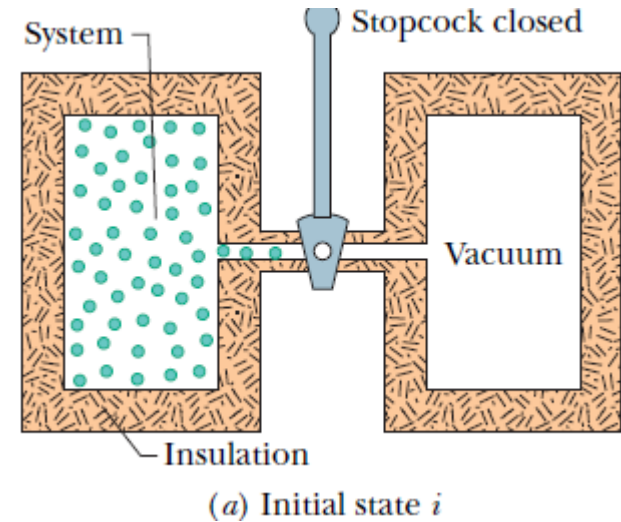
$$\Rightarrow dS_{sys} + dS_{surr} = 0$$

Example, Change of Entropy, Free Expansion of Gas:

Suppose 1.0 mol of nitrogen gas is confined to the left side of the container of Fig. 20-1a. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process? Treat the gas as ideal.

Calculations: the energy Q added as heat to the gas as it expands isothermally at temperature T from an initial volume V_i to a final volume V_f is

$$Q = nRT \ln \frac{V_f}{V_i},$$



Here n is the number of moles of gas present. The entropy change for this reversible process in which the temperature is held constant is

$$\begin{aligned} \Delta S_{\text{rev}} &= \frac{Q}{T} = \frac{nRT \ln(V_f/V_i)}{T} = nR \ln \frac{V_f}{V_i} &= nR \ln \frac{V_f}{V_i} &= (1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(\ln 2) \\ & & &= +5.76 \text{ J/K}. \end{aligned}$$



$$\Delta S_{\text{irrev}} = \Delta S_{\text{rev}} = +5.76 \text{ J/K}.$$

The Second Law of Thermodynamics

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

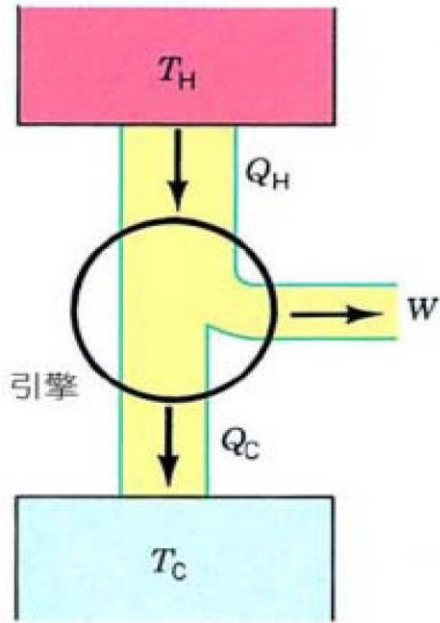
$$\Delta S \geq 0 \quad (\text{second law of thermodynamics})$$

Here the greater-than sign applies to irreversible processes and the equals sign to reversible processes. This relation applies only to closed systems.

The reversible processes as dictated in a P - V diagram, however, can have any signs of entropy change since they describe only part of a closed system, which includes the environment.

Entropy in the Real World: Engine Efficiency

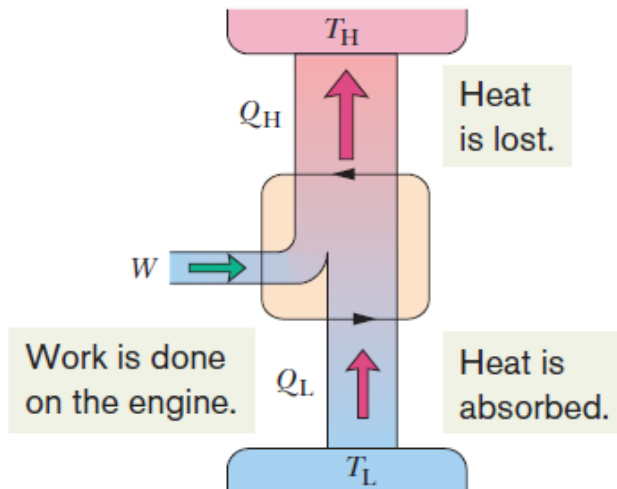
An engine (or a refrigerator) is a system of some substance to undergo a cycle between two thermal reservoirs of high and low temperatures.



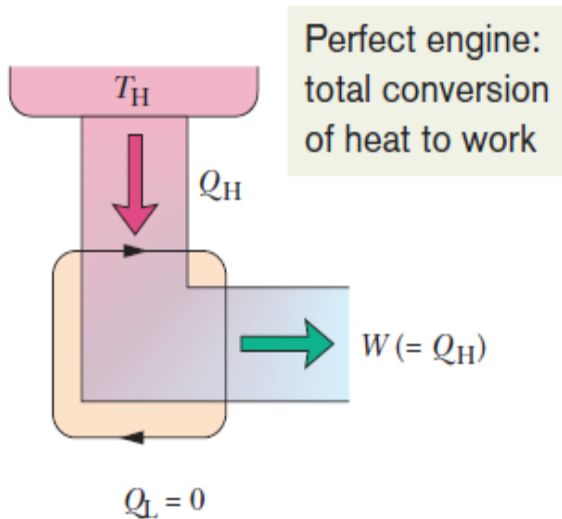
$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|} \quad (\text{efficiency, any engine})$$

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|} \quad (\text{coefficient of performance, any refrigerator}),$$

Schematic of a refrigerator



Entropy in the Real World: Perfect Engines



To have a ‘perfect’ engine, i.e., all the absorbed heat transferred to work, we require $Q_L=0$. With the engine entropy change being zero, and the environment entropy change being

$$DS_{env} = -\frac{|Q_H|}{T_H} < 0$$

the total entropy change for such an engine to work will be negative, violating the 2nd law.

The 2nd law of thermodynamics can be stated as:

No perfect engine!

(The Kelvin-Planck statement)

Isothermal process for an ideal gas

Reversible process :

$$dS_{sys} = \frac{C_v dT}{T} + \left(\frac{\partial p}{\partial T} \right)_v dV$$

At constant Temperature,

$$dS_{sys} = \left(\frac{\partial p}{\partial T} \right)_v dV$$

$$dS_{sys} = \frac{nR}{V} dV$$

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{surr} = -nR \ln \frac{V_2}{V_1}$$

For an irreversible process,

$$dS_{sys} = \frac{dq_{rev}}{T} = nR \ln \frac{V_2}{V_1} = \frac{-w_{rev}}{T}$$

$$dS_{surr} = \frac{dq_{surr}}{T} = \frac{-dq_{sys}}{T} = \frac{w}{T} = \frac{P_{ext}(V_2 - V_1)}{T}$$

Adiabatic Processes for an ideal gas

$$dS_{surr} = \frac{-dq_{sys}}{T}$$

Since, in an adiabatic process,

$$dq_{sys} = 0$$

$$\Delta S_{surr} = 0$$

(a) Reversible process :

$$dS_{sys} = \frac{dq_{sys,rev}}{T} = \frac{dq_{sys}}{T} = 0$$

(b) Irreversible process :

$$dS_{sys} = \frac{dq_{sys,rev}}{T} \neq \frac{dq_{sys}}{T}$$

For an ideal gas,

$$\Delta S_{sys} = R \ln \frac{V_f}{V_i} + C_{v,m} \ln \frac{T_{f,irrev}}{T_i}$$

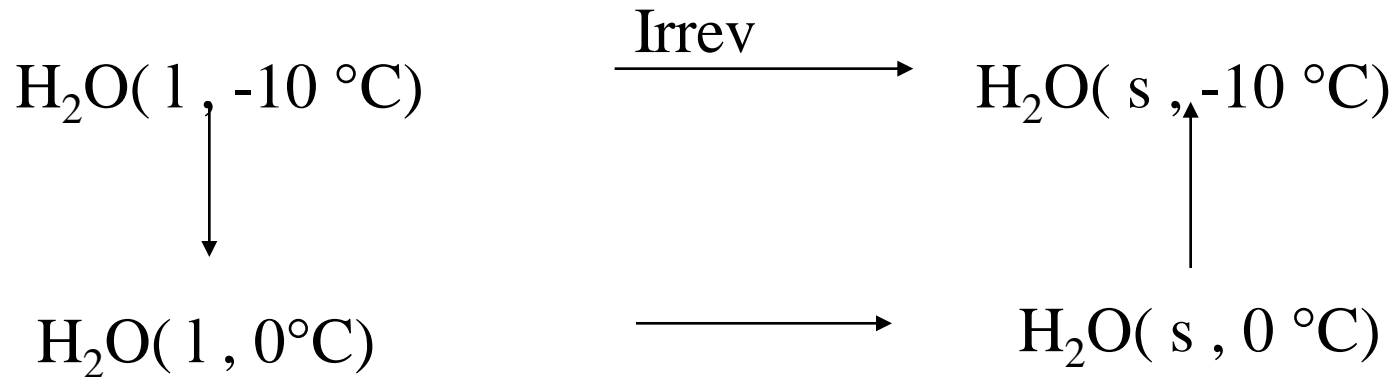
$$\Delta S_{sys} = -C_{v,m} \ln \frac{T_{f,rev}}{T_i} + C_{v,m} \ln \frac{T_{f,irrev}}{T_i}$$

$$\Delta S_{sys} = C_{v,m} \ln \frac{T_{f,irrev}}{T_{f,rev}}$$

Entropy changes in irreversible Processes

To obtain the change in entropy in an irreversible process we have to calculate ΔS along a reversible path between the initial state and the final state.

Freezing of water below its freezing point



$$\Delta S = C_{liq} \ln \frac{273}{263} + \frac{\Delta H_{crys}}{T} + C_{ice} \frac{263}{273}$$

Absolute entropy of a substance

$$\begin{aligned} S(T) = S(0) &+ \int_0^{T_f} \frac{C_p(s) dT}{T} + \frac{\Delta_f H}{T_f} \\ &+ \int_{T_f}^{T_b} \frac{C_p(l) dT}{T} + \frac{\Delta_v H}{T_b} \\ &+ \int_{T_b}^T \frac{C_p(g) dT}{T} \end{aligned}$$

Third law of thermodynamics:

The entropy of each pure element or substance in a perfectly crystalline form is zero at absolute zero.

Spontaneous process

$$dS_{sys} + dS_{surr} \geq 0$$

$$dS_{sys} \geq -dS_{surr}$$

$$dS_{sys} \geq \frac{dq}{T}$$

$$dq - TdS \leq 0$$

At constant volume, no additional work

$$dq_v - TdS \leq 0$$

$$dU - TdS \leq 0$$

$$dS_{U,v} \geq 0 \text{ or}$$

$$dU_{S,v} \leq 0$$

At constant V and T

$$dU - TdS = dU - d(TS)$$

$$= d(U - TS)_{v,T} \leq 0$$

$$= d(A)_{v,T} \leq 0$$

A is called helmholtz free energy.

$$dS_{sys} + dS_{surr} \geq 0$$

$$dS_{sys} \geq -dS_{surr}$$

$$dS_{sys} \geq \frac{dq}{T}$$

$$dq - TdS \leq 0$$

At constant pressure, no additional work

$$dq_p - TdS \leq 0$$

$$dH - TdS \leq 0$$

$$dS_{H,p} \geq 0 \text{ or}$$

$$dH_{S,p} \leq 0$$

At constant P and T

$$dH - TdS = dH - d(TS)$$

$$= d(H - TS)_{P,T} \leq 0$$

$$= d(G)_{V,T} \leq 0$$

G is called Gibb' s free energy.

Some thermodynamic properties can be measured directly, but many others cannot. Therefore, it is necessary to develop some relations between these two groups so that the properties that cannot be measured directly can be evaluated. The derivations are based on the fact that properties are point functions, and the state of a simple, compressible system is completely specified by any two independent, intensive properties.

Some Mathematical Preliminaries

Thermodynamic properties are continuous point functions and have exact differentials. A property of a single component system may be written as general mathematical function $z = z(x,y)$. For instance, this function may be the pressure $P = P(T,v)$. The total differential of z is written as

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

$$dz = M dx + N dy$$

where

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y} \right)_x$$

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

$$\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

Since properties are continuous point functions and have exact differentials, the following is true

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

The equations that relate the partial derivatives of properties P , v , T , and s of a simple compressible substance to each other are called the *Maxwell relations*. They are obtained from *the four Gibbs equations*. The first two of the Gibbs equations are those resulting from the internal energy u and the enthalpy h .

$$du = T ds - P dv$$

$$dh = T ds + v dP$$

The second two Gibbs equations result from the definitions of the Helmholtz function a and the Gibbs function g defined as

$$\begin{aligned}a &= u - T s \\d a &= d u - T d s - s d T \\d a &= - s d T - P d v\end{aligned}$$

$$\begin{aligned}g &= h - T s \\d g &= d h - T d s - s d T \\d g &= - s d T + v d P\end{aligned}$$

Setting the second mixed partial derivatives equal for these four functions yields the *Maxwell relations*

$$\begin{aligned}\left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial P}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_P \\ \left(\frac{\partial s}{\partial v}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_v \\ \left(\frac{\partial s}{\partial P}\right)_T &= -\left(\frac{\partial v}{\partial T}\right)_P\end{aligned}$$

Now we develop two more important relations for partial derivatives—the reciprocity and the cyclic relations. Consider the function $z = z(x,y)$ expressed as $x = x(y,z)$. The total differential of x is

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

Now combine the expressions for dx and dz .

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

Rearranging,

$$\left[\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial z}{\partial y} \right)_x \right] dy = \left[1 - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y \right] dz$$

Since y and z are independent of each other, the terms in each bracket must be zero. Thus, we obtain the reciprocity relation that shows that the inverse of a partial derivative is equal to its reciprocal.

$$1 - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y = 0$$

or

$$\left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{\left(\frac{\partial z}{\partial x} \right)_y}$$

The second relation is called the cyclic relation.

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

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

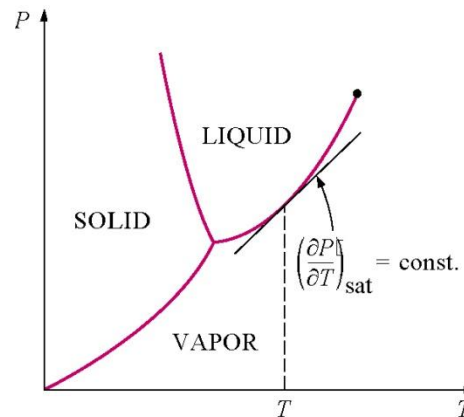
$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

Another way to write this last result is

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

The Clapeyron Equation

The *Clapeyron equation* enables us to determine the enthalpy change associated with a phase change, h_{fg} , from knowledge of P , v , and T data alone.



Consider the third Maxwell relation

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

During phase change, the pressure is the saturation pressure, which depends on the temperature only and is independent of the specific volume. That is $P_{\text{sat}} = f(T_{\text{sat}})$. Therefore, the partial derivative $\left(\frac{\partial P}{\partial T}\right)_v$ can be expressed as a total derivative $(dP/dT)_{\text{sat}}$, which is the slope of the saturation curve on a P - T diagram at a specified state. This slope is independent of the specific volume, and thus it can be treated as a constant during the integration of the third Maxwell relation between two saturation states at the same temperature. For an isothermal liquid-vapor phase-change process, the integration yields

$$\int_f^g ds = \int_f^g \left(\frac{\partial P}{\partial T}\right)_v dv$$
$$s_g - s_f = \left(\frac{dP}{dT}\right)_{\text{sat}} (v_g - v_f)$$

During the phase-change process, the pressure also remains constant. Therefore, from the enthalpy relation

$$dh = T ds + v dP$$
$$\int_f^g dh = \int_f^g T ds = T \int_f^g ds$$
$$h_g - h_f = h_{fg} = T s_{fg}$$

Now we obtain the Clapeyron equation expressed as

$$\frac{h_{fg}}{T} = \left(\frac{dP}{dT} \right)_{sat} v_{fg}$$
$$\left(\frac{dP}{dT} \right)_{sat} = \frac{h_{fg}}{T v_{fg}}$$

Example 12-1

Using only P - v - T data, estimate the enthalpy of vaporization of water at 45°C .

The enthalpy of vaporization is given by the Clapeyron equation as

$$h_{fg} = T v_{fg} \left(\frac{dP}{dT} \right)_{sat}$$

Using *the* P - v - T data for water from Tables

$$\begin{aligned} v_{fg} &= (v_g - v_f)_{@ 45^\circ\text{C}} = (15.251 - 0.001010) \frac{\text{m}^3}{\text{kg}} \\ &= 15.250 \frac{\text{m}^3}{\text{kg}} \end{aligned}$$

$$\begin{aligned} \left(\frac{dP}{dT} \right)_{sat} &\cong \left(\frac{\Delta P}{\Delta T} \right)_{sat, 45^\circ\text{C}} = \frac{P_{sat @ 50^\circ\text{C}} - P_{sat @ 40^\circ\text{C}}}{50^\circ\text{C} - 40^\circ\text{C}} \\ &= \frac{(12.35 - 7.385) \text{kPa}}{10^\circ\text{K}} = 0.4965 \frac{\text{kPa}}{\text{K}} \end{aligned}$$

$$\begin{aligned}
 h_{fg} &= T v_{fg} \left(\frac{dP}{dT} \right)_{sat} \\
 &= (40 + 273.15)K \left(15.250 \frac{m^3}{kg} \right) \left(0.4965 \frac{kPa}{K} \right) \frac{kJ}{m^3 kPa} \\
 &= 2371.1 \frac{kJ}{kg}
 \end{aligned}$$

The actual value of h_{fg} is 2394.0 kJ/kg. The Clapeyron equation approximation is low by about 1 percent due to the approximation of the slope of the saturation curve at 45°C.

Clapeyron-Clausius Equation

For liquid-vapor and solid-vapor phase-change processes at low pressures, an approximation to the Clapeyron equation can be obtained by treating the vapor phase as an ideal gas and neglecting the specific volume of the saturated liquid or solid phase compared to that of the vapor phase. At low pressures

$$v_g \gg v_f$$

$$v_{fg} \cong v_g$$

$$v_g = \frac{RT}{P}$$

$$\begin{aligned}\left(\frac{dP}{dT}\right)_{sat} &= \frac{h_{fg}}{Tv_{fg}} \\ &= \frac{h_{fg}}{T \frac{RT}{P}} = \frac{Ph_{fg}}{RT^2}\end{aligned}$$

$$\left(\frac{dP}{P}\right)_{sat} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{sat}$$

For small temperature intervals, h_{fg} can be treated as a constant at some average value. Then integrating this equation between two saturation states yields

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)_{sat}$$

General Relations for du , dh , ds , C_v , and C_p

The changes in internal energy, enthalpy, and entropy of a simple, compress-ible substance can be expressed in terms of pressure, specific volume, tem-perature, and specific heats alone.

Consider internal energy expressed as a function of T and v .

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

Recall the definition of the specific heat at constant volume

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v$$

Then du becomes

$$du = C_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

Now let's see if we can evaluate $(\partial u / \partial v)_T$ terms of P - v - T data only. Consider the entropy as a function of T and v ; that is,

$$s = s(T, v)$$
$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

Now substitute ds into the $T ds$ relation for u .

$$du = T \left[\left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv \right] - P dv$$
$$= T \left(\frac{\partial s}{\partial T} \right)_v dT + \left[T \left(\frac{\partial s}{\partial v} \right)_T - P \right] dv$$

Comparing these two results for du , we see

$$C_V = T \left(\frac{\partial s}{\partial T} \right)_v \quad \text{or} \quad \left(\frac{\partial s}{\partial T} \right)_v = \frac{C_V}{T}$$
$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial s}{\partial v} \right)_T - P$$

Using the third Maxwell's relation

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

Notice that the derivative $(\partial u / \partial v)_T$ is a function of P - v - T only. Thus the total differential for $u = u(T, v)$ is written as

$$du = C_v dT + \left[T \left(\frac{\partial P}{\partial T}\right)_v - P \right] dv$$

Example 12-2

Do you remember that we agreed that the internal energy of an ideal gas depended only on temperature? Let's evaluate the following partial derivative for an ideal gas.

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

For ideal gases

$$P = \frac{RT}{v}$$
$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$
$$\left(\frac{\partial u}{\partial v}\right)_T = T \frac{R}{v} - P = P - P = 0$$

This result helps to show that the internal energy of an ideal gas does not depend upon specific volume. To completely show that internal energy of an ideal gas is independent of specific volume, we need to show that the specific heats of ideal gases are functions of temperature only. We will do this later.

We could also find the following relations for dh and ds where $h = h(T,P)$ and $s = s(T,v)$ or $s = s(T,P)$

$$dh = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv$$

$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_P dP$$

Example 12-3

Determine an expression for the entropy change of an ideal gas when temperature and pressure data are known and the specific heats are constant.

$$s = s(T, P)$$
$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_P dP$$
$$\Delta s = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T} \right)_P dP$$

For an ideal gas

$$v = \frac{P}{RT}$$
$$\left(\frac{\partial v}{\partial T} \right)_P = \frac{P}{R}$$

For constant specific heat this becomes

$$\Delta s = C_p \int_{T_1}^{T_2} \frac{dT}{T} - \int_{P_1}^{P_2} \frac{R}{P} dP$$
$$= C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

Available and unavailable energy

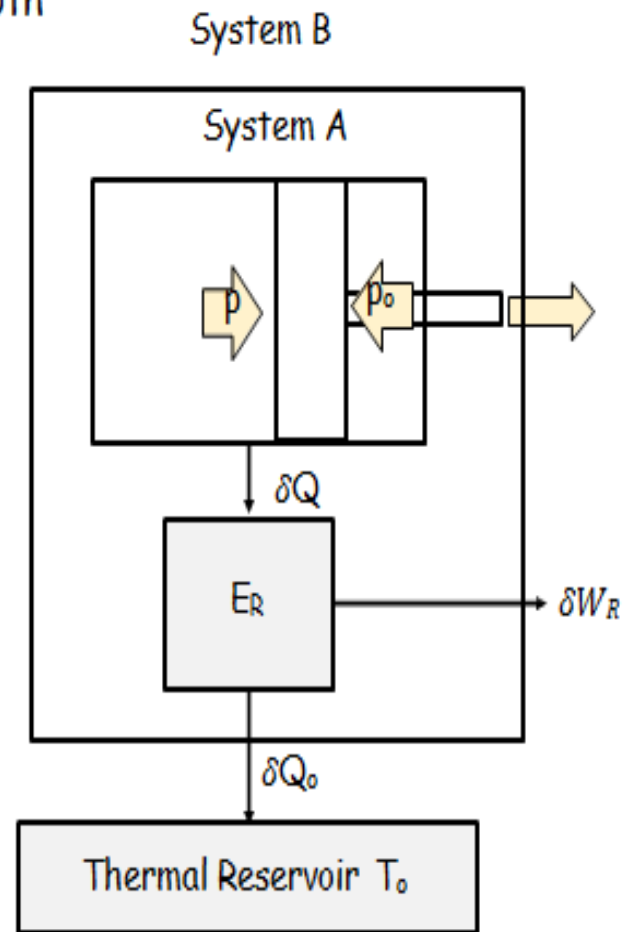
- There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts :
 - *Available part*
 - *Unavailable part*
- ‘**Available energy**’ or ‘**Exergy**’: is the *maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state* (a state in equilibrium with the earth and its atmosphere).
 - There can be only one value for maximum work which the system alone could do while descending to its dead state, therefore '*Available energy*' is a property
- ‘**Unavailable energy**’ or ‘**Anergy**’: is the portion of energy which could not be converted into useful work and is rejected to the surroundings

- A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is *unavailable*
- Summarily available energy denote, the latent capability of energy to do work, and in this sense it can be applied to energy in the system or in the surroundings.
- *The theoretical maximum amount of work which can be obtained from a system at any state p_1 and T_1 when operating with a reservoir at the constant pressure and temperature p_0 and T_0 is called ‘availability’.*

- **F**or stability of any system it is necessary and sufficient that, in all possible variations of the state of the system which do not alter its energy, the variation of entropy shall be negative
- This can be stated mathematically as $\Delta S < 0$
- It can be seen that the statements of equilibrium based on energy and entropy, namely $\Delta E > 0$ and $\Delta S < 0$

System A, which is a general system of constant composition in which the work output, δW , can be either shaft or displacement work, or a combination of both

Figure b, the workoutput is displacement work, $p \delta V$



For a specified change of state these quantities, which are changes in properties, would be independent of the process or work done. Applying the First Law of Thermodynamics to System **A**

$$\delta W = -dE + Q$$

If the heat engine (E_R) and System **A** are considered to constitute another system, System **B**, then, applying the First Law of Thermodynamics to System **B** gives

$$\delta W_{\text{net}} = \delta W + \delta W_R$$

—
|

- The change in Helmholtz energy is the maximum work that can be obtained from a closed system undergoing a reversible process whilst remaining in temperature equilibrium with its surroundings
 - A decrease in Helmholtz energy corresponds to an increase in entropy, hence the minimum value of the function signifies the equilibrium condition
 - A decrease in entropy corresponds to an increase in F ; hence the criterion $dF > 0$ is that for stability
- This criterion corresponds to work being done on the system
- For a constant volume system in which $W = 0$, $dF = 0$
- For reversible processes, $F_1 = F_2$; for all other processes there is a decrease in Helmholtz energy
 - The minimum value of Helmholtz energy corresponds to the equilibrium condition

Gibbs energy (Gibbs Function)

System **A** could change its volume by δV , and while it is doing this it must perform work on the atmosphere equivalent to $p_o \delta V$, where p_o is the pressure of the atmosphere. This work detracts from the work previously calculated and gives the maximum useful work, as $W_u = \delta W_{net} - P_o dV$

if the system is in pressure equilibrium with surroundings.

$$\delta W_u = -d(E - T_o S) - p_o dV$$

$$= -d(E + p_o V - T_o S) \quad \text{because } p_o = \text{constant} \quad \text{Hence } \delta W_u = -d(H - T_o S)$$

•The quantity $H - TS$ is called the *Gibbs energy*, *Gibbs potential*, or the *Gibbs function*, G

Hence $G = H - TS$

- Gibbs energy is a property which has the units of energy
- Indicates the maximum useful work that can be obtained from a system
- It can be seen that this is less than the enthalpy

Hence the work done by the system is not all converted into useful work, but some of it is used to do displacement work against the surroundings, i.e.

$$\delta W_{sym} = \delta W_{use} + \delta W_{surr}$$

which can be rearranged to give

$$\delta W_{use} = \delta W_{sys} - \delta W_{surr}$$

All the displacement work done by a system is available to do useful work

This concept will now be generalized to consider all the possible work outputs from a system that is not in thermodynamic and mechanical equilibrium with its surroundings (i.e. not at the ambient, or dead state, conditions)

The maximum work that can be obtained from a *constant volume, closed system*

$$\delta W_S + \delta W_R = -(dU - T_0 dS)$$

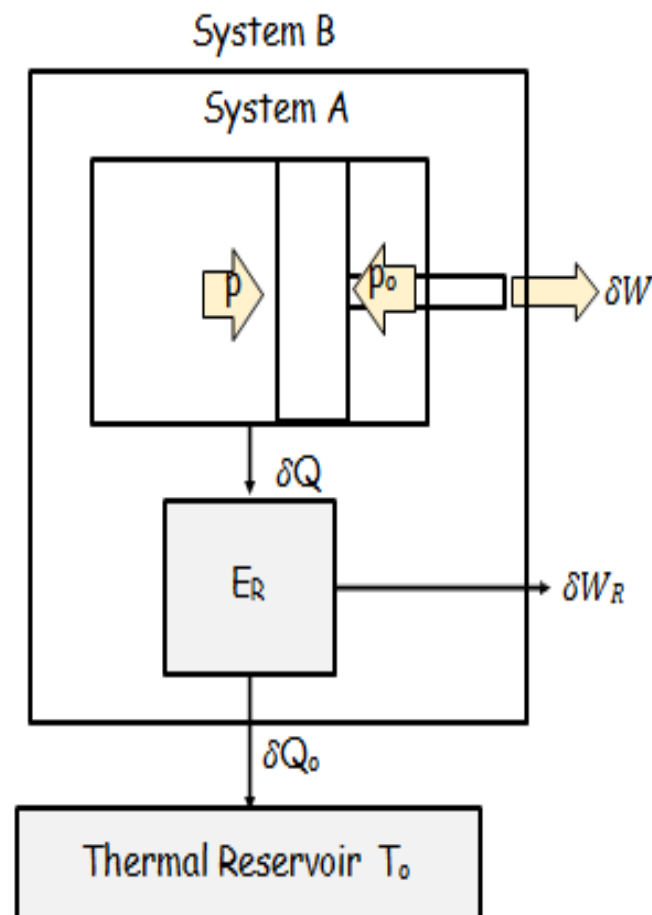
Hence, the *maximum useful work* which can be achieved from a closed system is $\delta W_S + \delta W_R = -(dU + P_0 dV - T_0 dS)$

This work is given the symbol dA

Since the surroundings are at fixed pressure and temperature (i.e. p_0 and T_0 are constant) dA can be integrated to give

$$A = U + p_0 V - T_0 S$$

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- ***A is called the non-flow availability function***

- It is a combination of properties

- A is not itself a property because it is defined in relation to the arbitrary datum values of p_o and T_o

- It is not possible to tabulate values of A without defining both these datum levels

- The datum levels are what differentiates A from Gibbs energy G

- The maximum useful work achievable from a system changing state from 1 to 2 is given by

$$W_{\max} = \Delta A = -(A_2 - A_1) = A_1 - A_2$$

- The specific availability, a , i.e. the availability per unit mass is $a = u + p_o v - T_o s$

- If the value of a were based on unit amount of substance (i.e. kmol) it would be referred to as the molar availability

- The change of specific (or molar) availability is

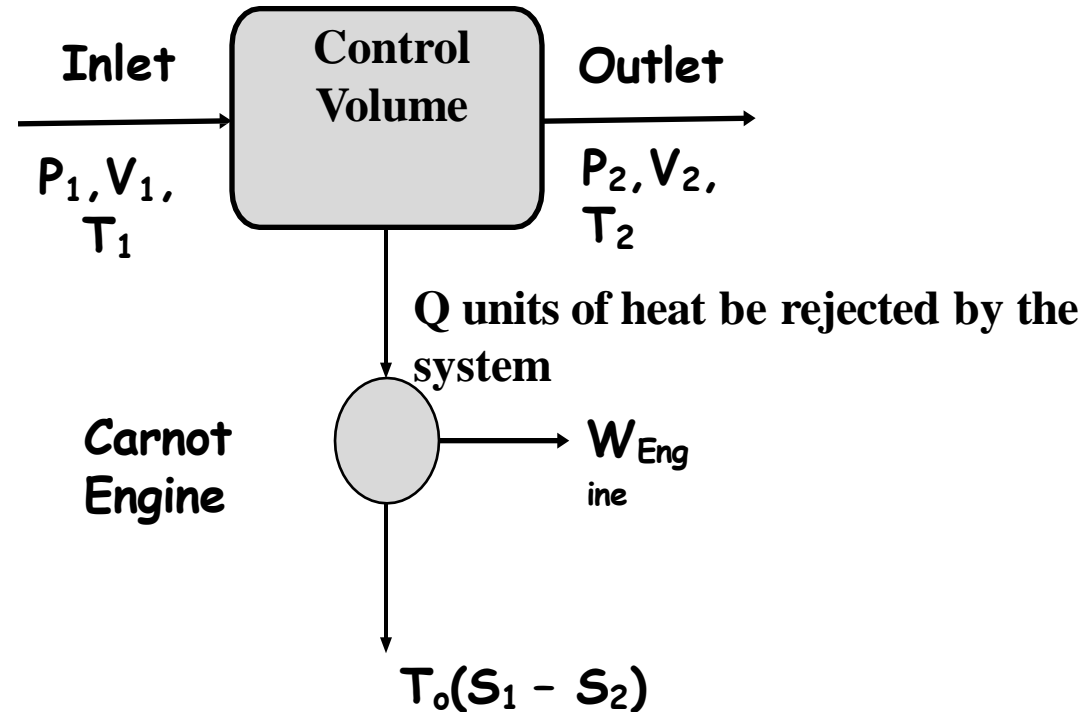
$$\Delta a = a_2 - a_1 = (u_2 + p_o v_2 - T_o s_2) - (u_1 + p_o v_1 - T_o s_1)$$

$$= (h_2 + v_2(P_o - P_2) - (h_1 + v_1(P_o - P_1))) - T_o(S_2 - S_1)$$

Availability of a Steady Flow System

- Consider a steady flow system and let it be assumed that the flowing fluid has the following properties and characteristics; Internal energy u , specific volume v , specific enthalpy h , pressure p , velocity c and location z

System delivers a work output W units



Normally, P_2 & T_2 ambient or state dead condition

$$U_1 + p_1 v_1 + \frac{V_1^2}{2} + gz_1 - Q = U_2 + p_2 v_2 + \frac{V_2^2}{2} + gz_2 + W_s$$

Neglecting the kinetic and potential energy changes

$$U_1 + p_1 v_1 - Q = U_2 + p_2 v_2 + W_s$$

$$H_1 - Q = H_2 + W_s$$

$$\text{Shaft work } W_s = (H_1 - H_2) - Q$$

Heat Q rejected by the system may be made to run a reversible heat engine, the output from engine equals

$$\begin{aligned} W_{\text{engine}} &= Q \left(1 - \frac{T_0}{T_1}\right) \\ &= Q - T_0 (S_1 - S_2) \end{aligned}$$

Maximum available useful work or net work $W_{\text{net}} = W_s + W_{\text{engine}}$

$$= (H_1 - H_2) - Q + Q - T_0 (S_1 - S_2)$$

$$= (H_1 - H_2) - Q + Q - T_0 (S_1 - S_2)$$

$$= (H_1 - T_0 S_1) - (H_2 - T_0 S_2)$$

$$= B_1 - B_2 \quad \text{Steady flow availability function } H - T_0 S \text{ or Darrius function} \\ \text{and the Keenan function}$$

$$dB = (B_1 - B_0) - (B_2 - B_0) = B_1 - B_2$$

Clearly, the availability B is a state function in the strictest mathematical sense so the maximum (or minimum) work associated with any steady state process is also independent of the path

Availability: Yields the maximum work producing potential or the minimum work requirement of a process

- Allows evaluation and quantitative comparison of options in a sustainability context

EXERGY

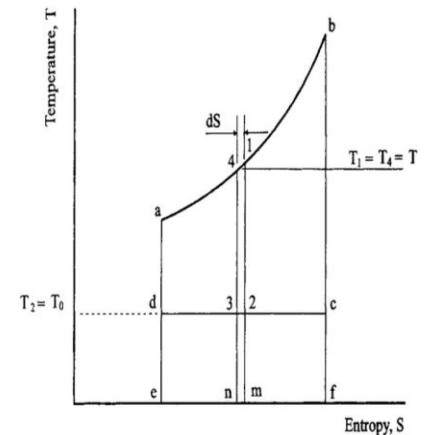
- If a certain portion of energy is available then obviously another part is unavailable
 - the unavailable part is that which must be thrown away
 - Diagram indicates an internally reversible process from a to b
 - This can be considered to be made up of an infinite number of strips 1-m-n-4-1 where the temperature of energy transfer is essentially constant

δQ = heat transferred to system and

δQ_0 = heat rejected from system,

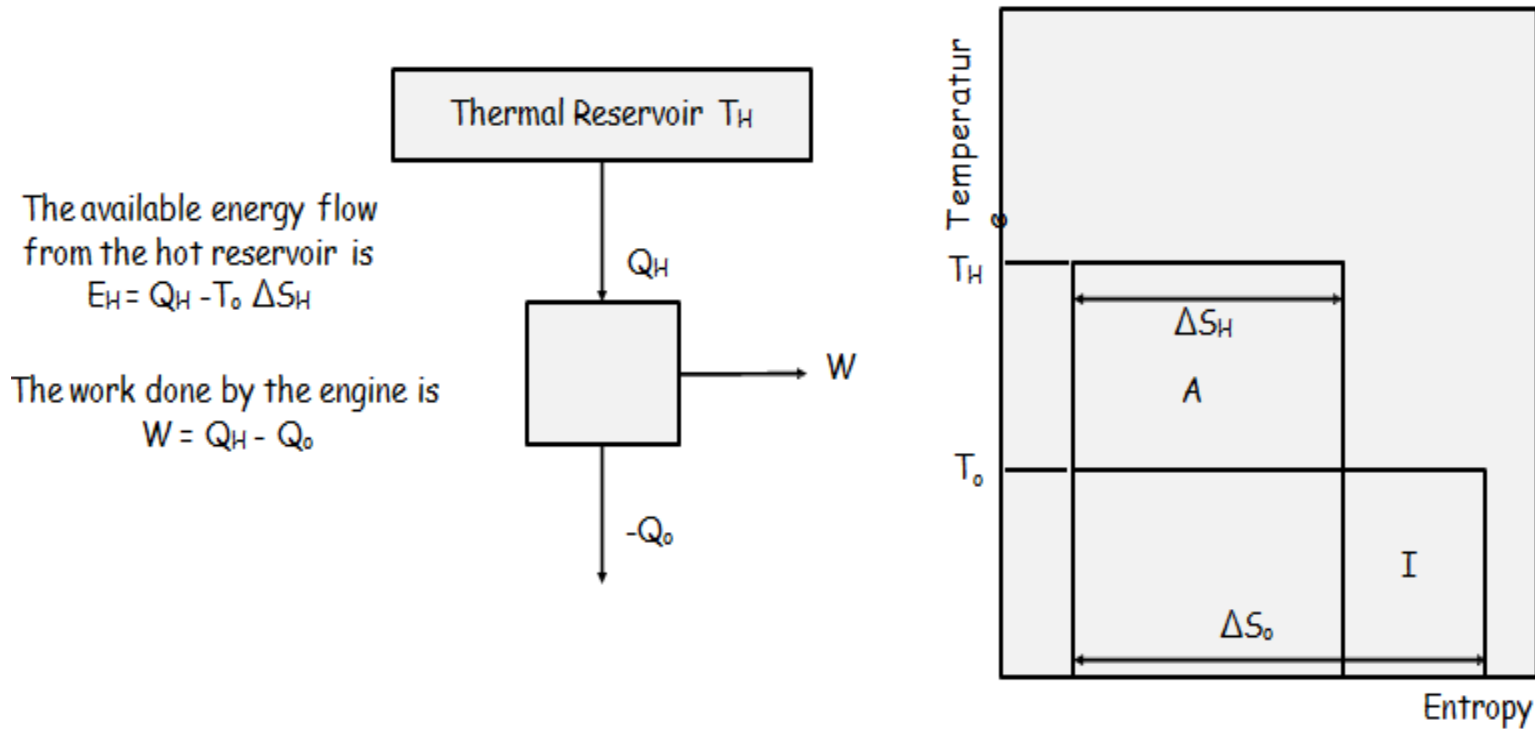
As in an engine (E_R) undergoing an infinitesimal Carnot cycle

- In reality δQ_0 is the minimum amount of heat that can be rejected because processes 1 to 2 and 3 to 4 are both isentropic, i.e. adiabatic and *reversible*



Graphical Representation of Available Energy, and Irreversibility

Consider the energy transfer from a high temperature reservoir at T_H through a heat engine (not necessarily reversible)



IRREVERSIBILITY

- The entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).
- The second law states: $\Delta S_{\text{system}} + \Delta S_{\text{surr.}} = 0$

where, $\Delta = \text{final} - \text{initial} > 0$ irreversible (real world)

= 0 reversible (frictionless, ideal)

- In an ideal case if Q is the heat supplied from a source at T, its availability or the maximum work it can deliver is $Q(1-T_0/T_1)$ where T_0 is the temperature of the surroundings.
 - Invariably it will be less than this value.
 - The difference is termed as irreversibility.
 - Availability = Maximum possible work - Irreversibility $w_{\text{useful}} = w_{\text{rev}} - I$

- Irreversible Processes increase the entropy of the universe
- Reversible Processes do not effect the entropy of the universe
- Impossible Processes decrease the entropy of the universe

$$\Delta S_{\text{universe}} = 0$$

- Entropy Generation in the universe is a measure of lost work

$$\Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$

- The losses will keep increasing
- The sin keeps accumulating and damage to environment keeps increasing
- When the entropy of the universe goes so high, then some one has to come and set it right

- Irreversibility can also be construed as the amount of work to be done to restore the system to the original state.
 - Eg: If air at 10 bar is throttled to 1 bar, the irreversibility will be $p.v \ln (10)$ which is the work required to get 10 bar back.
 - Here p is 1 bar and v is the specific volume at this condition.
 - Note that the system has been restored to the original state but not the surroundings
 - Therefore increase in entropy will be $R \ln 10$.
- Combining first & second laws $TdS \geq \Delta u + \delta W$
 - It implies that the amount of heat energy to be supplied in a real process is larger than the thermodynamic limit

Heat Transfer from a Finite Source

- Consider certain quantity of heat Q is transferred from a system at constant temperature T_1 to another system at constant temperature T_2 ($T_1 > T_2$)

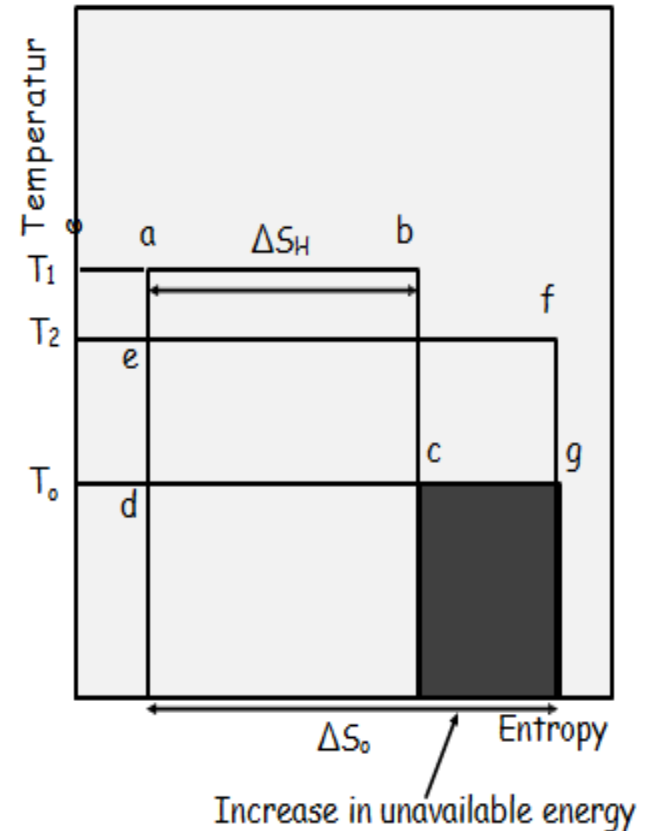
- Initial available energy

- Final available energy $E_{av2} = Q \left(1 - \frac{T_0}{T_2}\right)$

- Change in the available energy = $E_{av1} - E_{av2}$
 $= Q \left(1 - \frac{T_0}{T_1}\right) - Q \left(1 - \frac{T_0}{T_2}\right)$
 $= T_0 \left(\frac{Q}{T_1} - \frac{Q}{T_2}\right)$
 $= T_0 (dS_1 + dS_2)$
 $= T_0 (dS)_{net}$

This total change is called entropy of universe or entropy production

Dr. Rohit Singh Lather



PROPERTIES OF PURE SUBSTANCES

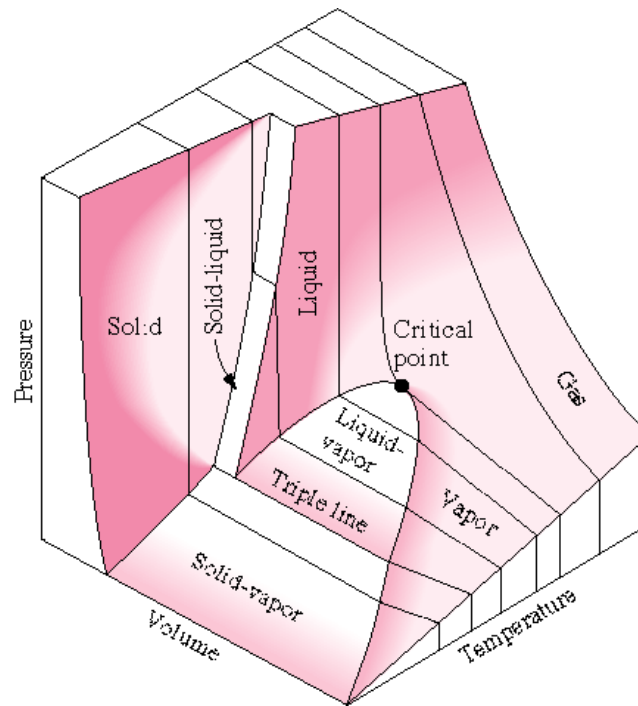
Phase Transformations, T-S and h-s diagrams, P-V-T- surfaces, Triple point at critical state properties during change of phase, Dryness Fraction, Mollier charts, Various Thermodynamic processes and energy Transfer, Steam Calorimeter

State Postulate

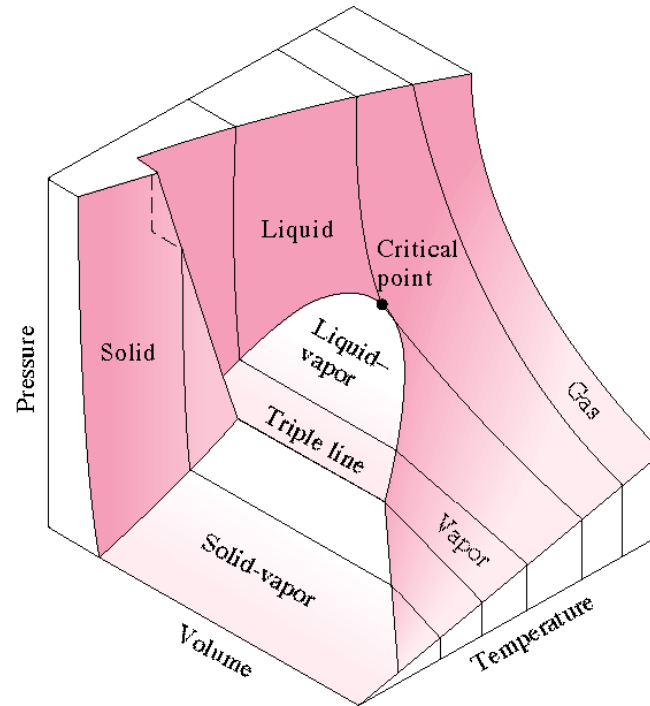
Again, the state postulate for a simple, pure substance states that the equilibrium state can be determined by specifying any two independent intensive properties.

The P - V - T Surface for a Real Substance

◆ P - V - T Surface for a Substance that contracts upon freezing



◆ *P-V-T* Surface for a Substance that expands upon freezing



Real substances that readily change phase from solid to liquid to gas such as water, refrigerant-134a, and ammonia cannot be treated as ideal gases in general. The pressure, volume, temperature relation, or equation of state for these substances is generally very complicated, and the thermodynamic properties are given in table form. The properties of these substances may be illustrated by the functional relation $F(P,v,T)=0$, called an equation of state. The above two figures illustrate the function for a substance that contracts on freezing and a substance that expands on freezing. Constant pressure curves on a temperature-volume diagram are shown .

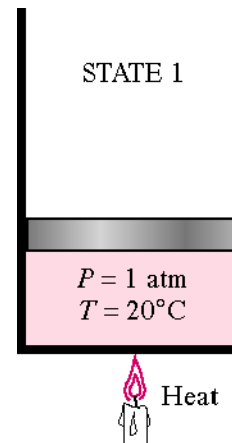
These figures show three regions where a substance like water may exist as a solid, liquid or gas (or vapor). Also these figures show that a substance may exist as a mixture of two phases during phase change, solid-vapor, solid-liquid, and liquid-vapor.

Water may exist in the compressed liquid region, a region where saturated liquid water and saturated water vapor are in equilibrium (called the saturation region), and the superheated vapor region (the solid or ice region is not shown).

Let's consider the results of heating liquid water from 20°C, 1 atm while keeping the pressure constant. We will follow the constant pressure process shown in Figure 3-11. First place liquid water in a piston-cylinder device where a fixed weight is placed on the piston to keep the pressure of the water constant at all times. As liquid water is heated while the pressure is held constant, the following events occur.

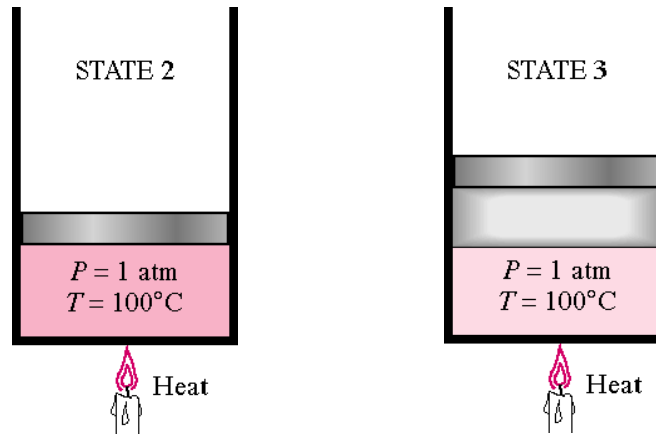
Process 1-2:

The temperature and specific volume will increase from the compressed liquid, or subcooled liquid, state 1, to the saturated liquid state 2. In the compressed liquid region, the properties of the liquid are approximately equal to the properties of the saturated liquid state at the temperature.



Process 2-3:

At state 2 the liquid has reached the temperature at which it begins to boil, called the saturation temperature, and is said to exist as a saturated liquid. Properties at the saturated liquid state are noted by the subscript **f** and $v_2 = v_f$. During the phase change both the temperature and pressure remain constant (according to the International Temperature Scale of 1990, ITS-90, water boils at $99.975^\circ\text{C} \cong 100^\circ\text{C}$ when the pressure is 1 atm or 101.325 kPa). At state 3 the liquid and vapor phase are in equilibrium and any point on the line between states 2 and 3 has the same temperature and pressure.



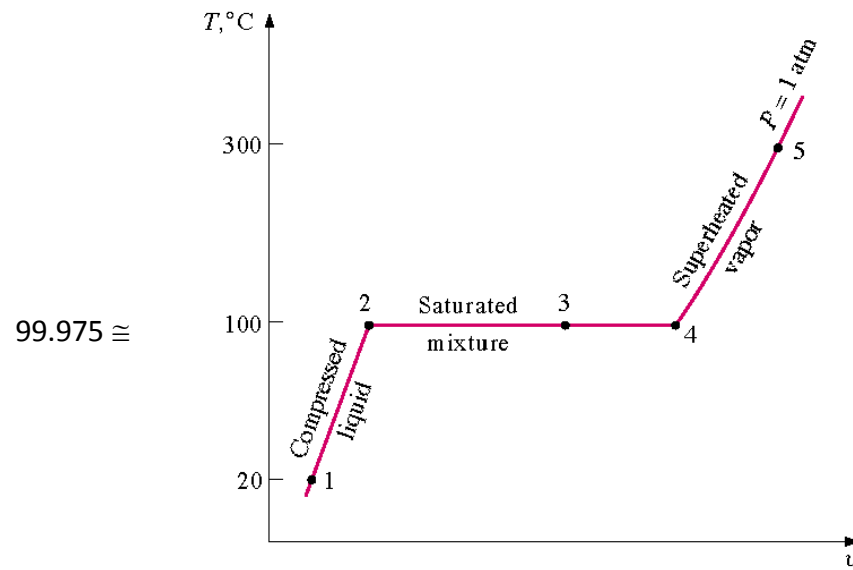
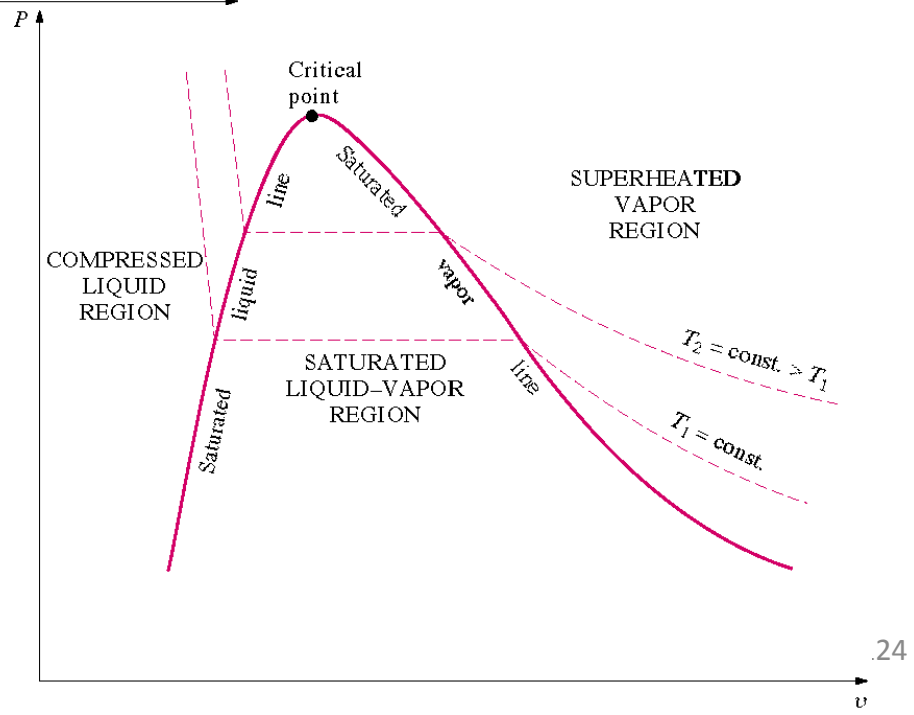
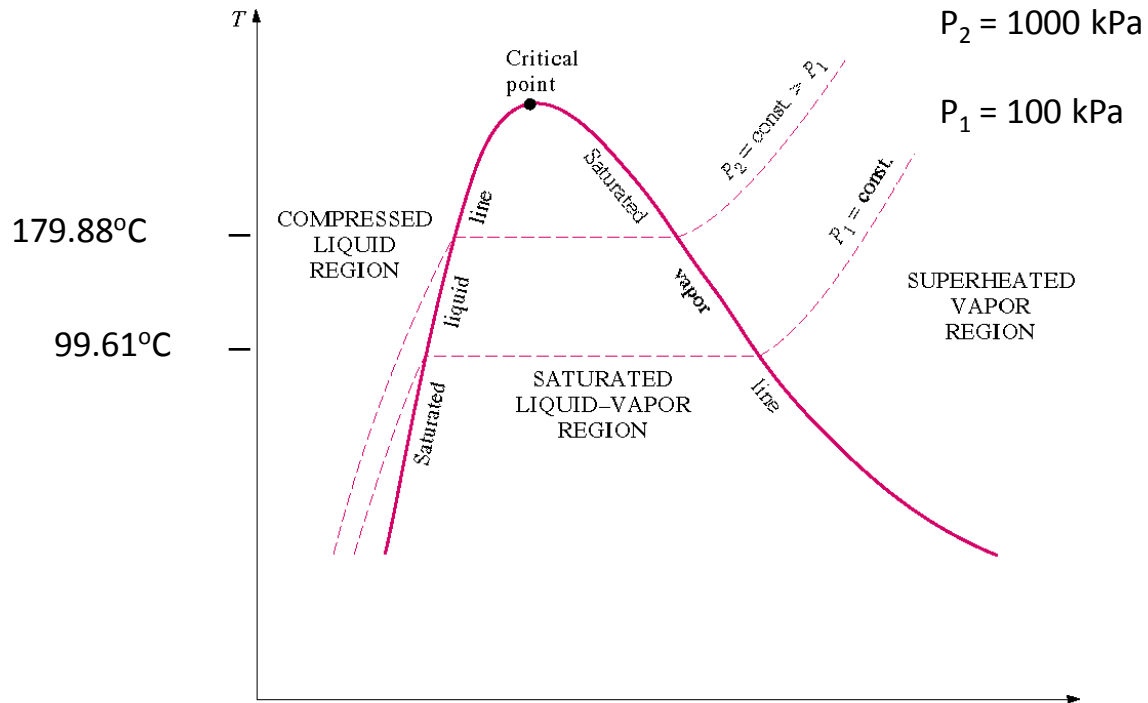


Figure 3-11

Consider repeating this process for other constant pressure lines as shown below.



The region to the left of the saturated liquid line and below the critical temperature is called the compressed liquid region. The region to the right of the saturated vapor line and above the critical temperature is called the superheated region. See Table A-1 for the critical point data for selected substances.

Review the P - v diagrams for substances that contract on freezing and those that expand on freezing given in Figure 3-21 and Figure 3-22.

At temperatures and pressures above the critical point, the phase transition from liquid to vapor is no longer discrete.

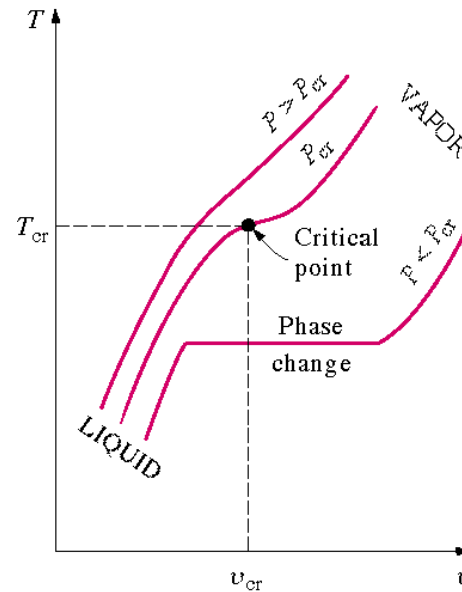
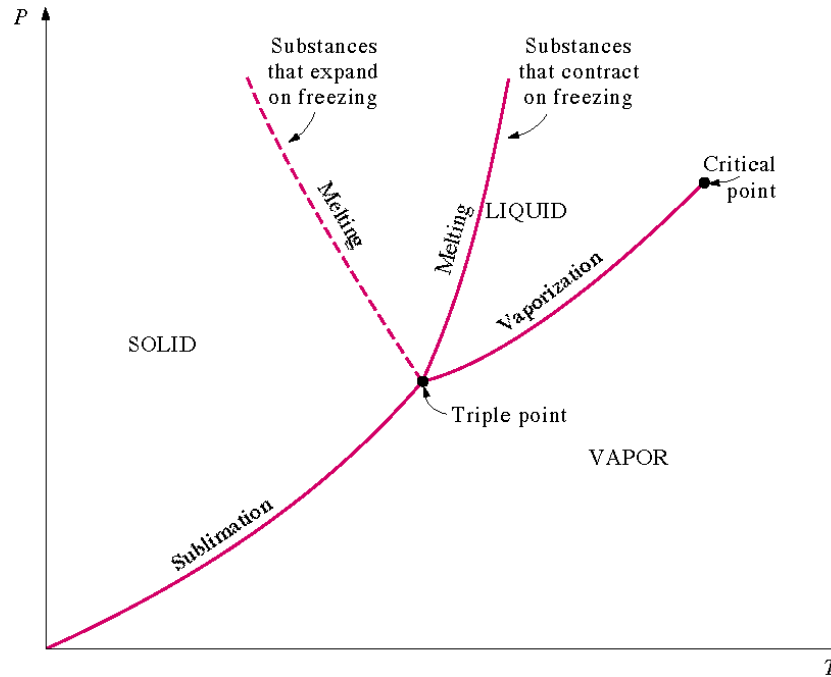


Figure shows the P - T diagram, often called the phase diagram, for pure substances that contract and expand upon freezing.

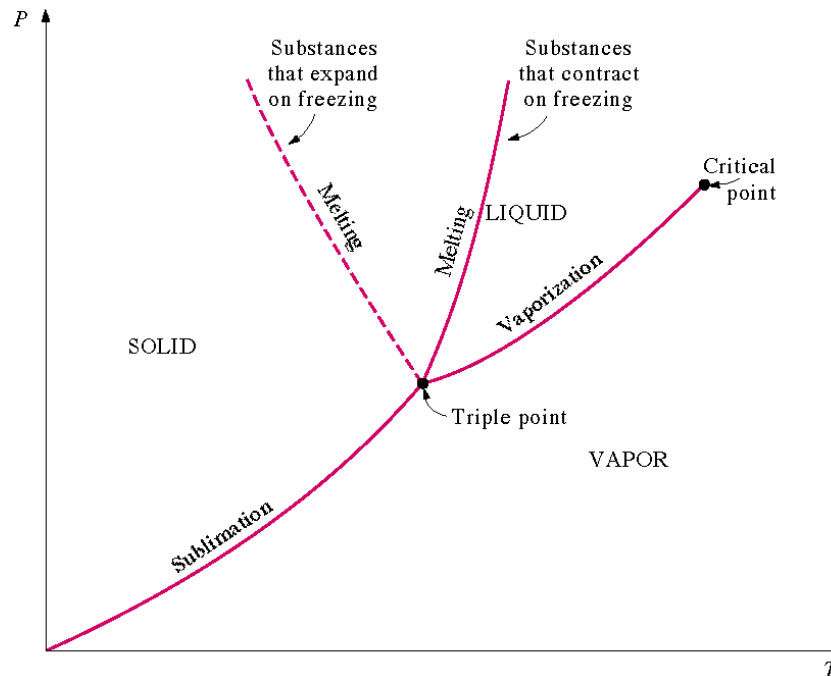


The triple point of water is 0.01°C , 0.6117 kPa

The critical point of water is 373.95°C , 22.064 MPa

Plot the following processes on the P - T diagram for water (expands on freezing) and give examples of these processes from your personal experiences.

1. process a-b: liquid to vapor transition
2. process c-d: solid to liquid transition
3. process e-f: solid to vapor transition



Property Tables

In addition to the temperature, pressure, and volume data, Tables A-4 through A-8 contain the data for the specific internal energy u the specific enthalpy h and the specific entropy s . The enthalpy is a convenient grouping of the internal energy, pressure, and volume and is given by

$$H = U + PV$$

The enthalpy per unit mass is

$$h = u + Pv$$

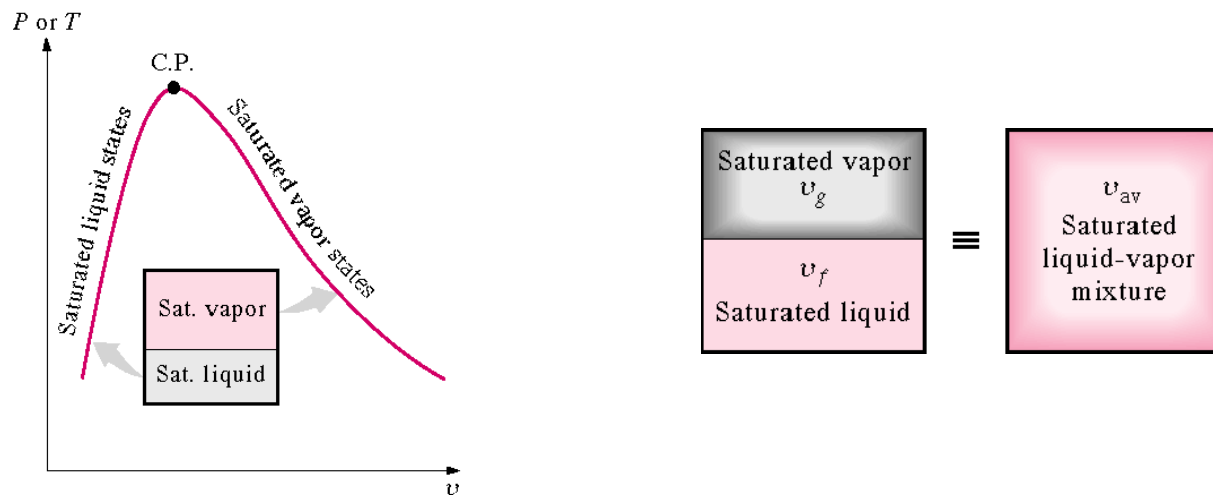
We will find that the enthalpy h is quite useful in calculating the energy of mass streams flowing into and out of control volumes. The enthalpy is also useful in the energy balance during a constant pressure process for a substance contained in a closed piston-cylinder device. The enthalpy has units of energy per unit mass, kJ/kg. The entropy s is a property defined by the second law of thermodynamics and is related to the heat transfer to a system divided by the system temperature; thus, the entropy has units of energy divided by temperature.

Quality and Saturated Liquid-Vapor Mixture

Now, let's review the constant pressure heat addition process for water shown in Figure 3-11. Since state 3 is a mixture of saturated liquid and saturated vapor, how do we locate it on the T-v diagram? To establish the location of state 3 a new parameter called the quality x is defined as

$$x = \frac{mass_{saturated\ vapor}}{mass_{total}} = \frac{m_g}{m_f + m_g}$$

The quality is zero for the saturated liquid and one for the saturated vapor ($0 \leq x \leq 1$). The average specific volume at any state 3 is given in terms of the quality as follows. Consider a mixture of saturated liquid and saturated vapor. The liquid has a mass m_f and occupies a volume V_f . The vapor has a mass m_g and occupies a volume V_g .



We note

$$V = V_f + V_g$$

$$m = m_f + m_g$$

$$V = m v, \quad V_f = m_f v_f, \quad V_g = m_g v_g$$

$$m v = m_f v_f + m_g v_g$$

$$v = \frac{m_f v_f}{m} + \frac{m_g v_g}{m}$$

Recall the definition of quality x

$$x = \frac{m_g}{m} = \frac{m_g}{m_f + m_g}$$

Then

$$\frac{m_f}{m} = \frac{m - m_g}{m} = 1 - x$$

Note, quantity $1 - x$ is often given the name moisture. The specific volume of the saturated mixture becomes

$$v = (1 - x)v_f + xv_g$$

The form that we use most often is

$$v = v_f + x(v_g - v_f)$$

It is noted that the value of any extensive property per unit mass in the saturation region is calculated from an equation having a form similar to that of the above equation. Let Y be any extensive property and let y be the corresponding intensive property, Y/m , then

$$\begin{aligned}y &= \frac{Y}{m} = y_f + x(y_g - y_f) \\ &= y_f + x y_{fg}\end{aligned}$$

$$\text{where } y_{fg} = y_g - y_f$$

The term y_{fg} is the difference between the saturated vapor and the saturated liquid values of the property y ; y may be replaced by any of the variables v , u , h , or s .

We often use the above equation to determine the quality x of a saturated liquid-vapor state.

The following application is called the Lever Rule:

Equations of State

The relationship among the state variables, temperature, pressure, and specific volume is called the equation of state. We now consider the equation of state for the vapor or gaseous phase of simple compressible substances.

$$F(P, T, \nu) \equiv 0$$

Ideal Gas

Based on our experience in chemistry and physics we recall that the combination of Boyle's and Charles' laws for gases at low pressure result in the equation of state for the ideal gas as

$$P = R \left(\frac{T}{\nu} \right)$$

where R is the constant of proportionality and is called the **gas constant** and takes on a different value for each gas. If a gas obeys this relation, it is called an ideal gas. We often write this equation as

$$P\nu = RT$$

The gas constant for ideal gases is related to the universal gas constant valid for all substances through the molar mass (or molecular weight). Let R_u be the universal gas constant. Then,

$$R = \frac{R_u}{M}$$

The mass, m , is related to the moles, N , of substance through the molecular weight or molar mass, M , see Table A-1. The molar mass is the ratio of mass to moles and has the same value regardless of the system of units.

$$M_{air} = 28.97 \frac{g}{gmol} = 28.97 \frac{kg}{kmol} = 28.97 \frac{lbm}{lbmol}$$

Since $1 \text{ kmol} = 1000 \text{ gmol}$ or 1000 gram-mole and $1 \text{ kg} = 1000 \text{ g}$, 1 kmol of air has a mass of 28.97 kg or $28,970 \text{ grams}$.

$$m = N M$$

The ideal gas equation of state may be written several ways.

$$P v = R T$$

$$P \frac{V}{m} = R T$$

$$P V = m R T$$

$$PV = \frac{m}{M} (MR)T$$

$$PV = NR_u T$$

$$P \frac{V}{N} = R_u T$$

$$P\bar{v} = R_u T$$

Here

P = **absolute pressure** in MPa, or kPa

\bar{v} = molar specific volume in m^3/kmol

T = **absolute temperature** in K

R_u = 8.314 kJ/(kmol·K)

Some values of the universal gas constant are

Universal Gas Constant, R_u

8.314 kJ/(kmol·K)

8.314 kPa·m³/(kmol·K)

1.986 Btu/(lbmol·R)

1545 ft·lbf/(lbmol·R)

10.73 psia·ft³/(lbmol·R)

The ideal gas equation of state can be derived from basic principles if one assumes

1. Intermolecular forces are small.
2. Volume occupied by the particles is small.

Example 2-5

Determine the particular gas constant for air and hydrogen.

$$R = \frac{R_u}{M}$$

$$R_{air} = \frac{8.314 \frac{kJ}{kmol \cdot K}}{28.97 \frac{kg}{kmol}} = 0.287 \frac{kJ}{kg \cdot K}$$

$$R_{hydrogen} = \frac{8.314 \frac{kJ}{kmol \cdot K}}{2.016 \frac{kg}{kmol}} = 4.124 \frac{kJ}{kg \cdot K}$$

The ideal gas equation of state is used when (1) the pressure is small compared to the critical pressure or (2) when the temperature is twice the critical temperature and the pressure is less than 10 times the critical pressure. The critical point is that state where there is an instantaneous change from the liquid phase to the vapor phase for a substance. Critical point data are given in Table A-1.

Compressibility Factor

To understand the above criteria and to determine how much the ideal gas equation of state deviates from the actual gas behavior, we introduce the compressibility factor Z as follows.

$$P \bar{v} = Z R_u T$$

or

$$Z = \frac{P \bar{v}}{R_u T}$$

Useful Ideal Gas Relation: The Combined Gas Law

By writing the ideal gas equation twice for a fixed mass and simplifying, the properties of an ideal gas at two different states are related by

$$m_1 = m_2$$

or

$$\frac{P_1 V_1}{R T_1} = \frac{P_2 V_2}{R T_2}$$

But, the gas constant is _____ (fill in the blank), so

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Example 2-7

An ideal gas having an initial temperature of 25°C under goes the two processes described below. Determine the final temperature of the gas.

Process 1-2: The volume is held constant while the pressure doubles.

Process 2-3: The pressure is held constant while the volume is reduced to one-third of the original volume.

Other Equations of State

Many attempts have been made to keep the simplicity of the ideal gas equation of state but yet account for the intermolecular forces and volume occupied by the particles. Three of these are

van der Waals:

$$\left(P + \frac{a}{v^2}\right)(v - b) = R T$$

where

$$a = \frac{27 R^2 T_{cr}^2}{64 P_{cr}} \quad \text{and} \quad b = \frac{R T_{cr}}{8 P_{cr}}$$

Extra Assignment

When plotted on the P - v diagram, the critical isotherm has a point of inflection at the critical point. Use this information to verify the equations for van der Waals' constants a and b .

Beattie-Bridgeman:

$$P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3} \right) (\bar{v} + B) - \frac{A}{\bar{v}^2}$$

where

$$A = A_o \left(1 - \frac{a}{\bar{v}} \right) \quad \text{and} \quad B = B_o \left(1 - \frac{b}{\bar{v}} \right)$$

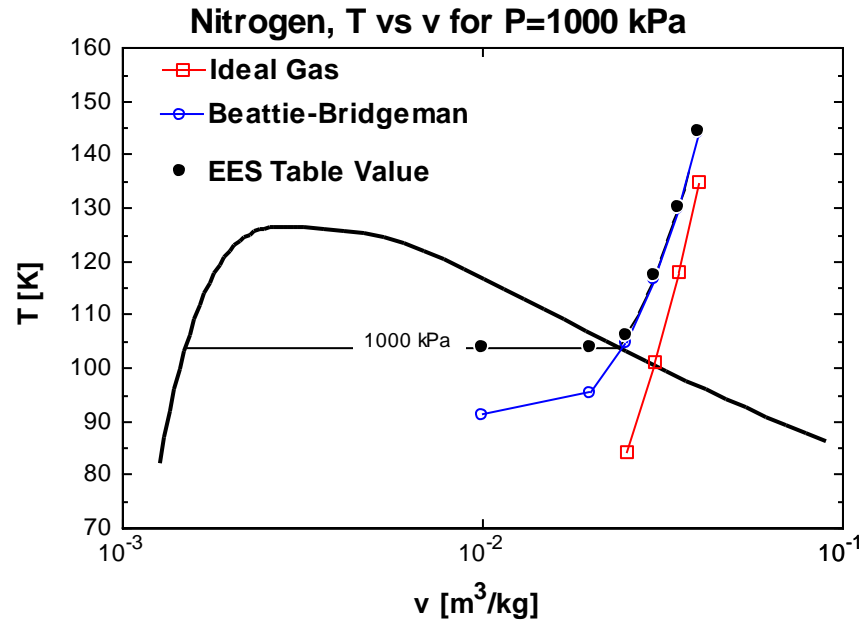
The constants a, b, c, A_o, B_o for various substances are found in.

Benedict-Webb-Rubin:

$$P = \frac{R_u T}{\bar{v}} + \left(B_o R_u T - A_o - \frac{C_o}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a \alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2}$$

The constants for various substances appearing in the Benedict-Webb--Rubin equation are given in Table .

Compare the results from the ideal gas equation, the Beattie-Bridgeman equation, and the EES software for nitrogen at 1000 kPa. The following is an EES solution to that problem.



Notice that the results from the Beattie-Bridgeman equation compare well with the actual nitrogen data provided by EES in the gaseous or superheated region. However, neither the Beattie-Bridgeman equation nor the ideal gas equation provides adequate results in the two-phase region, where the gas (ideal or otherwise) assumption fails.

GAS LAWS

Equation of State, Specific and Universal Gas constants, Throttling and Free Expansion Processes, Deviations from perfect Gas Model, Vander Waals Equation of State.

Boyle's Law: For a fixed amount of gas and constant temperature, $PV =$
constant.

Charles's Law: at constant pressure the volume is linearly proportional to temperature. $V/T = \text{constant}$

Gay-Lussac's Law

Old man Lussac studied the direct relationship between temperature and pressure of a gas.

As the temperature increases the pressure a gas exerts on its container increases. During his experiments volume of the system and amount of gas were held constant.

Dalton's Law = the sum of the partial pressures of the gases in a mixture = the total pressure or $P = P_A + P_B + P_C + \dots$ where P_i = the partial pressure of component i.

Avagadro's law for a fixed pressure and temperature, the volume of a gas is directly proportional to the number of moles of that gas. $V/n = k = \text{constant}$.

Avogadro's Law - EQUAL VOLUMES OF DIFFERENT GASES CONTAIN EQUAL NUMBERS OF MOLECULES WHEN MEASURED AT THE SAME TEMPERATURE AND PRESSURE.

Ideal gas law the functional relationship between the pressure, volume, temperature and moles of a gas. $PV = nRT$; all gases are ideal at low pressure. $V = nRT/P$. Each of the individual laws is contained in this equation.

GAS MIXTURES

Mole Fraction, Mass fraction, Gravimetric and volumetric Analysis, Volume fraction, Dalton's Law of partial pressure, Avogadro's Laws of additive volumes, and partial pressure, Equivalent Gas constant, Internal Energy, Enthalpy, sp. Heats and Entropy of Mixture of perfect Gases

COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

To determine the properties of a mixture, we need to know the *composition* of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture:

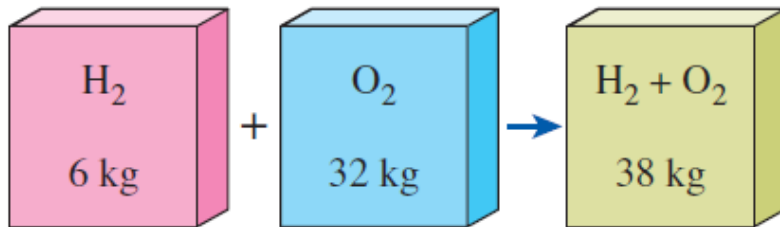


FIGURE 13–1

The mass of a mixture is equal to the sum of the masses of its components.

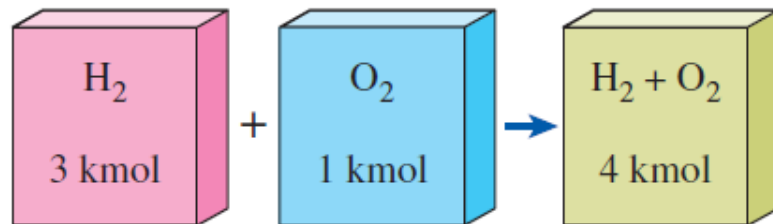


FIGURE 13–2

The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components.

Molar analysis: specifying the number of moles of each component

Gravimetric analysis: specifying the mass of each component

$$m_m = \sum_{i=1}^k m_i \quad N_m = \sum_{i=1}^k N_i$$

$$mf_i = \frac{m_i}{m_m} \quad \text{Mass fraction}$$

$$y_i = \frac{N_i}{N_m} \quad \text{Mole fraction}$$

COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

To determine the properties of a mixture, we need to know the *composition* of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture:

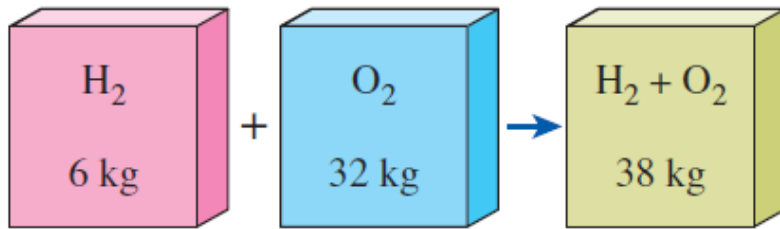


FIGURE 13–1

The mass of a mixture is equal to the sum of the masses of its components.

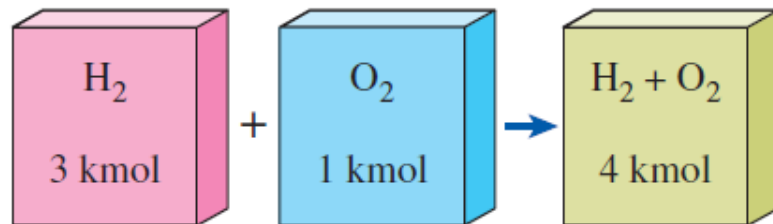


FIGURE 13–2

The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components.

Molar analysis: specifying the number of moles of each component

Gravimetric analysis: specifying the mass of each component

$$m_m = \sum_{i=1}^k m_i \quad N_m = \sum_{i=1}^k N_i$$

$$mf_i = \frac{m_i}{m_m} \quad \text{Mass fraction}$$

$$y_i = \frac{N_i}{N_m} \quad \text{Mole fraction}$$

Apparent (or average) molar mass

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i$$

$$m = NM$$

Gas constant

$$R_m = \frac{R_u}{M_m}$$

The molar mass of a mixture

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}}$$

Mass and mole fractions of a mixture are related by

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

The sum of the mass and mole fractions of a mixture is equal to 1.

$$\sum_{i=1}^k mf_i = 1 \quad \text{and} \quad \sum_{i=1}^k y_i = 1$$

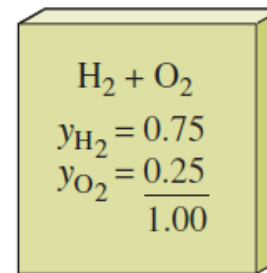


FIGURE 13–3

The sum of the mole fractions of a mixture is equal to 1.

P - v - T BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

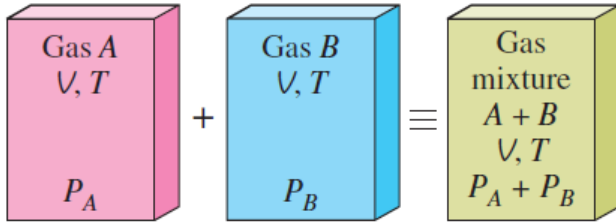


FIGURE 13–5

Dalton's law of additive pressures for a mixture of two ideal gases.

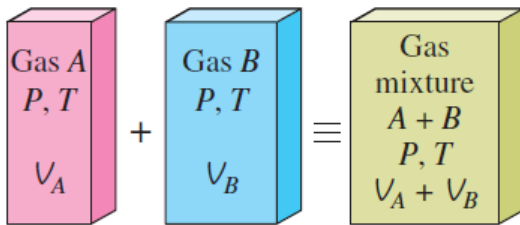


FIGURE 13–6

Amagat's law of additive volumes for a mixture of two ideal gases.

The prediction of the P - v - T behavior of gas mixtures is usually based on two models:

Dalton's law of additive pressures: The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume.

Amagat's law of additive volumes: The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.

Dalton's law:

$$P_m = \sum_{i=1}^k P_i(T_m, V_m)$$

Amagat's law:

$$V_m = \sum_{i=1}^k V_i(T_m, P_m)$$

exact for ideal gases,
approximate
for real gases

P_i component pressure

V_i component volume

P_i/P_m pressure fraction

V_i/V_m volume fraction

For ideal gases, Dalton's and Amagat's laws are identical and give identical results.

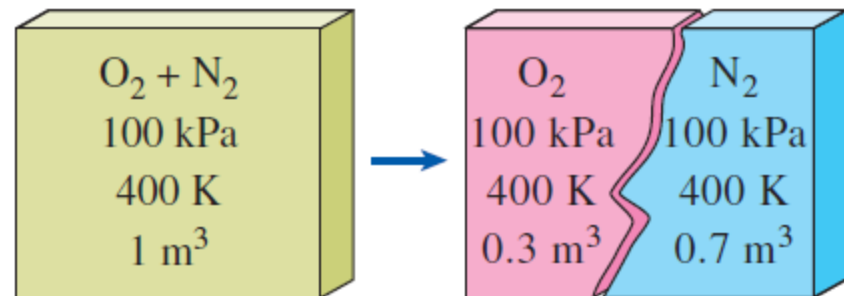



FIGURE 13–7

The volume a component would occupy if it existed alone at the mixture T and P is called the *component volume* (for ideal gases, it is equal to the partial volume $y_i V_m$).

Ideal-Gas Mixtures

$$\frac{P_i(T_m, V_m)}{P_m} = \frac{N_i R_u T_m / V_m}{N_m R_u T_m / V_m} = \frac{N_i}{N_m} = y_i$$

$$\frac{V_i(T_m, P_m)}{V_m} = \frac{N_i R_u T_m / P_m}{N_m R_u T_m / P_m} = \frac{N_i}{N_m} = y_i$$


$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

This equation is only valid for ideal-gas mixtures as it is derived by assuming ideal-gas behavior for the gas mixture and each of its components.

The quantity $y_i P_m$ is called the **partial pressure** (identical to the *component pressure* for ideal gases), and the quantity $y_i V_m$ is called the **partial volume** (identical to the *component volume* for ideal gases).

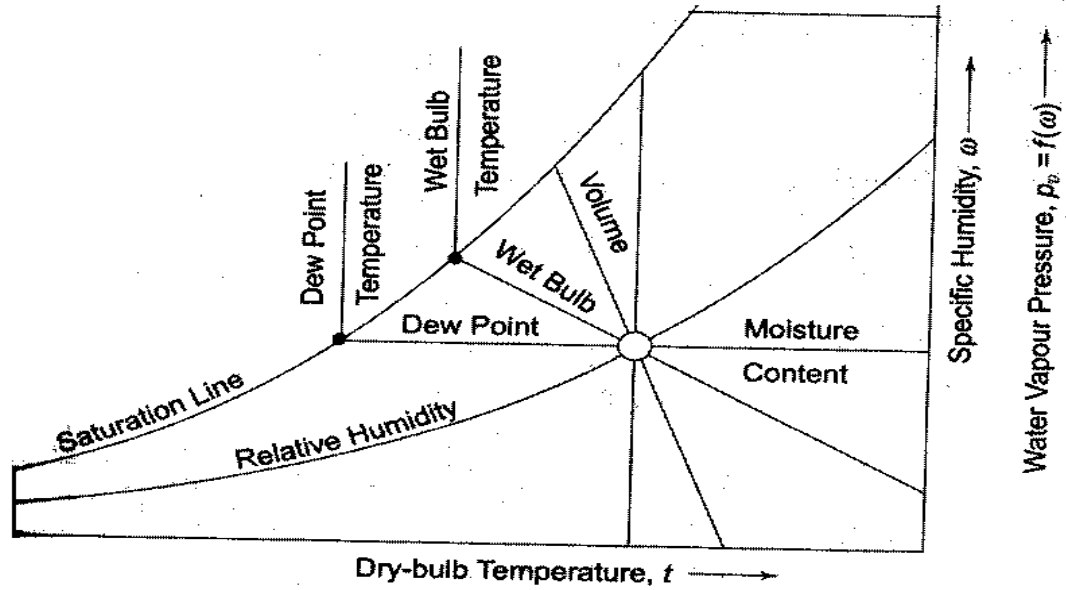
Note that for an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.

The composition of an ideal-gas mixture (such as the exhaust gases leaving a combustion chamber) is frequently determined by a volumetric analysis (Orsat Analysis).

PSYCHROMETRY

Psychrometric properties-Dry bulb temperature, wet bulb temperature, specific humidity, Relative humidity, saturated air, Degree of saturation-adiabatic saturation, carrier equation, psychrometric chart.

Psychrometric chart



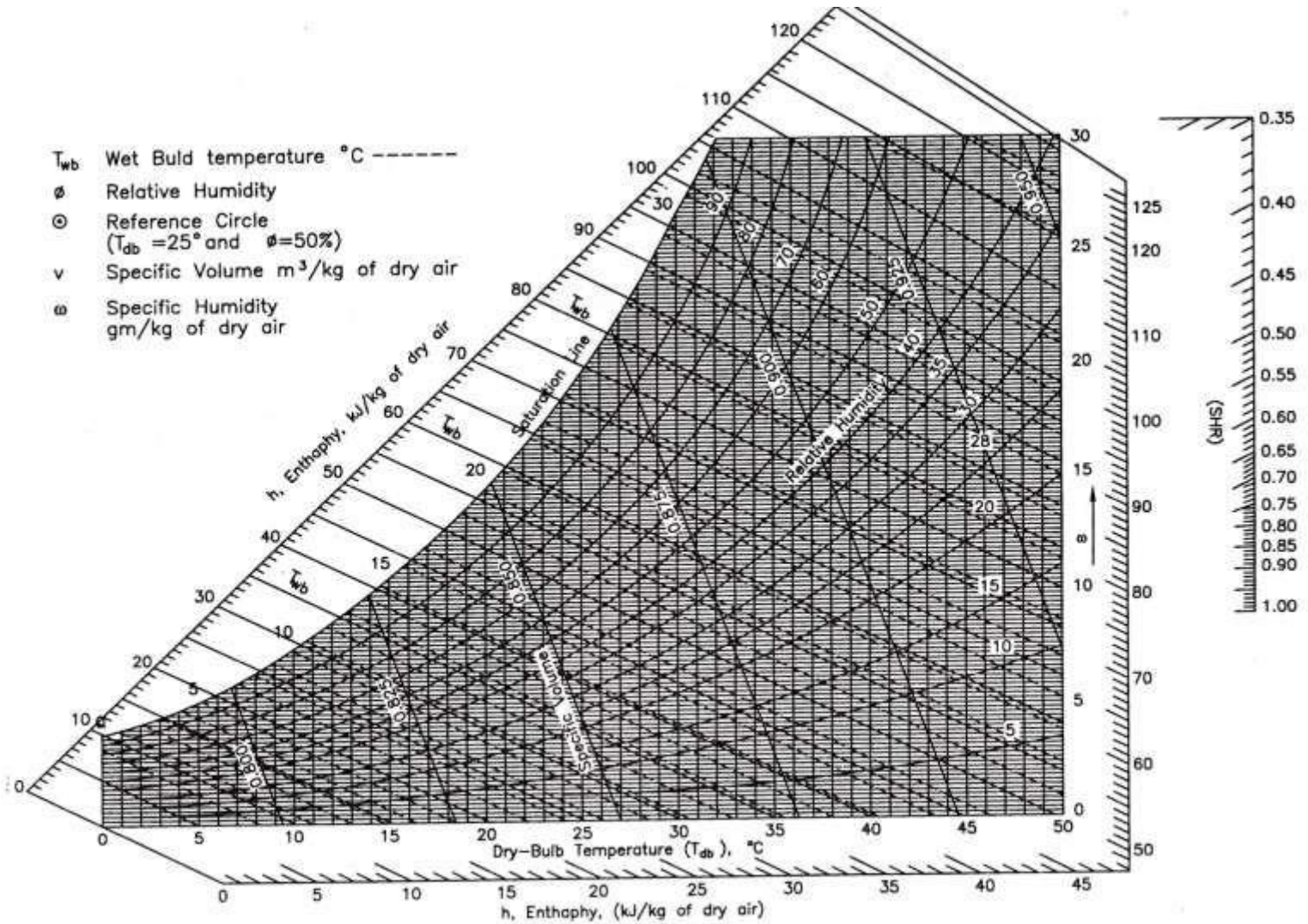
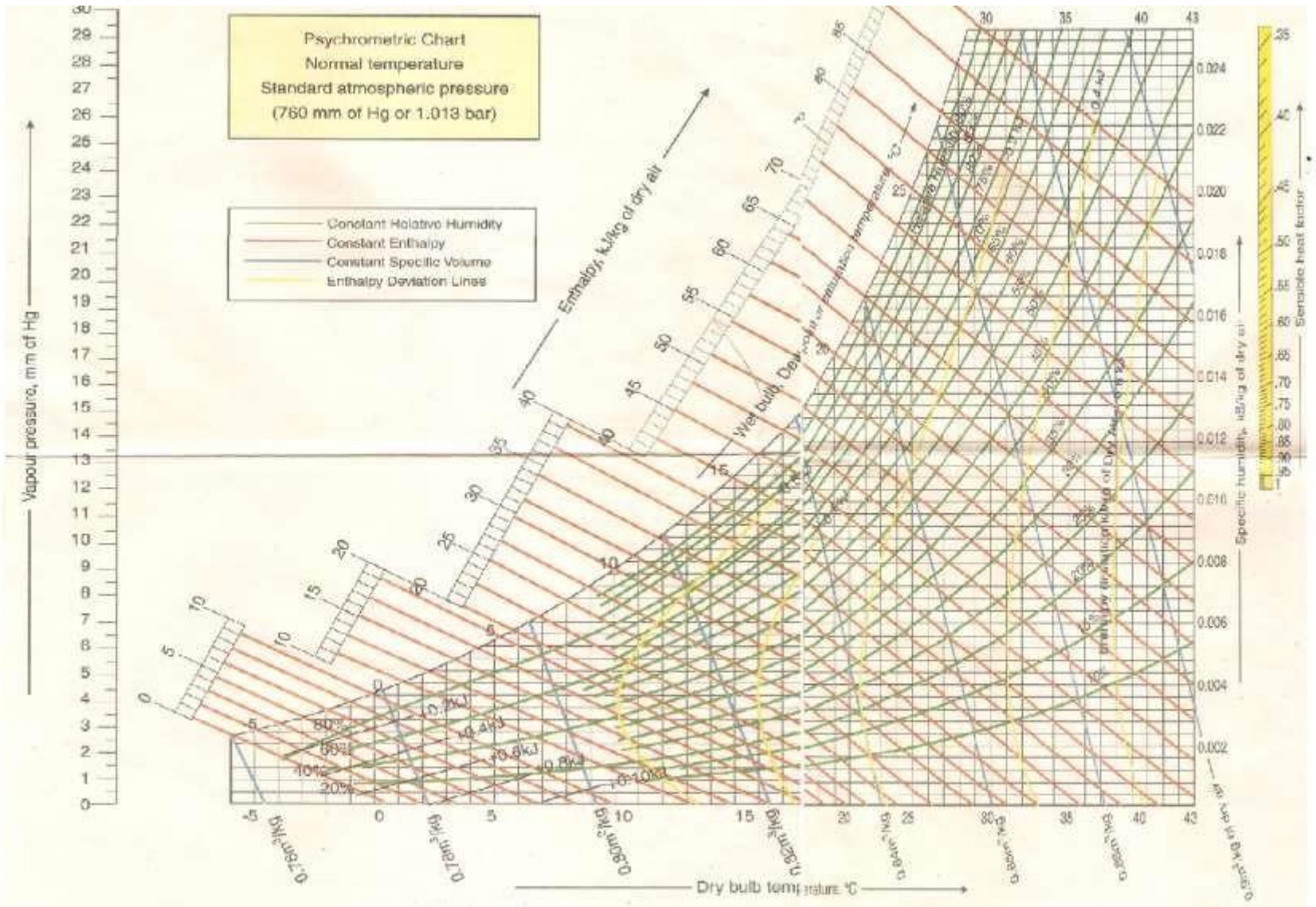


Fig. 4.1. Psychrometric chart on $T_{db} - \omega$ plane.
 at 1.01325 bar
 or 760 mm of Hg.

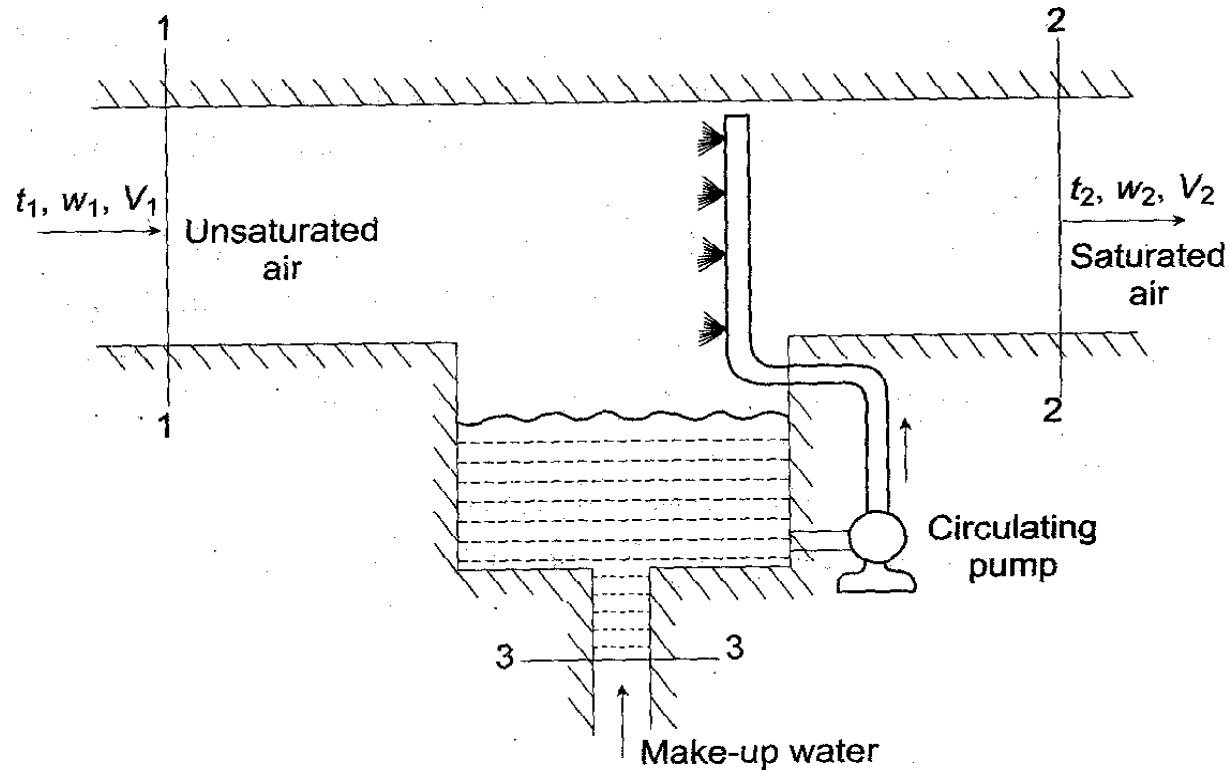
- Psychrometric chart is prepared to represent graphically all the necessary moist air properties

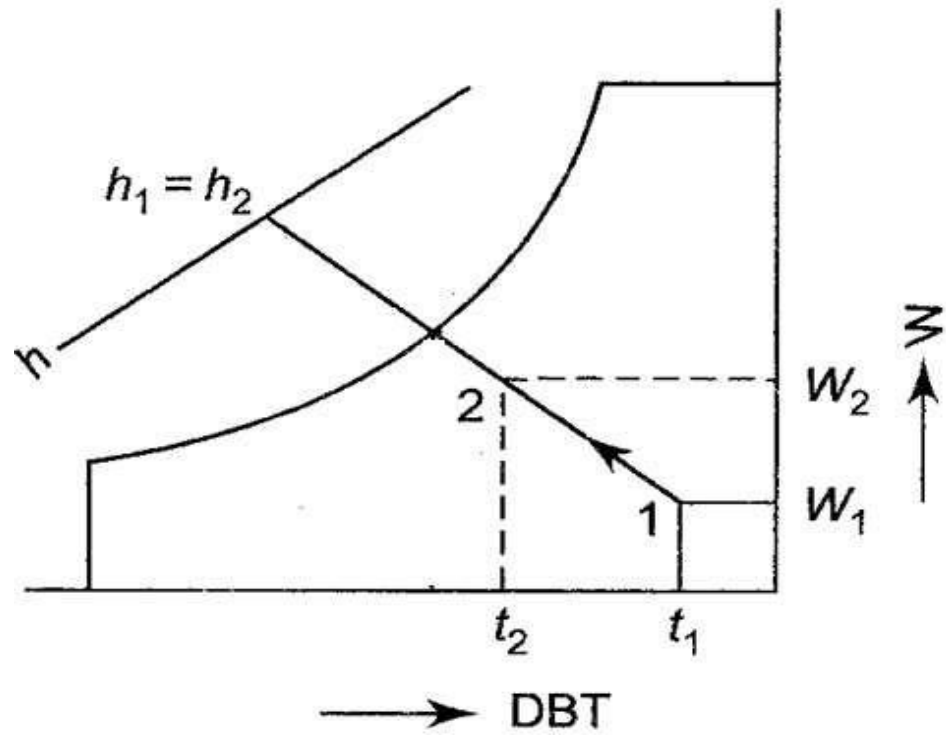
It gives

- Specific humidity.
- RH
- Specific volume of the air-vapour mixture.
- Enthalpy of air-vapour mixture (with datum 0 degree C)



Adiabatic saturation process.





Partial pressure of water vapour

$$P_v = (P_{vs})_{wb} - \frac{\{P_t - (P_{vs})_{wb}\} (T_{db} - T_{wb})}{1547 - 1.44 T_{wb}}$$
$$P_v = 0.0378 - \frac{\{1.03 - 0.0378\} (40 - 28)}{1547 - 1.44 * 28}$$
$$P_v = 0.0299 = 0.03 \text{ Bar}$$

- ω

$$\text{Specific humidity} = 0.622 \left(\frac{P_v}{P_t - P_v} \right)$$

$$\text{Specific humidity} = 0.622 \left(\frac{0.03}{1.03 - 0.03} \right)$$

$$= 0.01866 \text{ kg/kg of dry air}$$

$$\text{Relative humidity } \phi = \frac{P_v}{P_{\text{vs at } 40^\circ\text{C}}}$$

$$\text{Relative humidity } \phi = \frac{0.03}{0.0738} = 40 \%$$

- Dew point temperature is the saturation temperature of the water vapour at the existing pressure of water vapour.
- From the steam table, the saturation temperature at 0.03038 bar is 25 degree C
- DPT= 25 degree C (table 2.1 page 2.1)

$$h = 1.005 (T_{db} - 0) + w \{ 4.18 T_{dp} + (h_{fg})_{dp} + 1.88 (T_{db} - T_{dp}) \}$$

$$h = 1.005 (40) + 0.01866 \{ 4.18 * 25 + (2442) + 1.88 (40 - 25) \}$$

$$h = 88.24 \text{ kJ/kg of dry air}$$

to find specific volume/ Kg of dry air

$$p_a V = m_a R_a T_{DBT}$$

$$\frac{V}{m_a} = \frac{R_a T_{DBT}}{p_a}$$

$$\frac{V}{m_a} = \frac{R_a T_{DBT}}{(p_t - p_a)}$$

$$\frac{V}{m_a} = \frac{287 * (40 + 273)}{(1.03 - 0.03) * 10^5} = 0.898 \text{ m}^3/\text{kg of dry air}$$

The Carnot cycle was introduced as the most efficient heat engine that operate between two fixed temperatures T_H and T_L . The thermal efficiency of Carnot cycle is given by

$$\eta_{th, Carnot} = 1 - \frac{T_L}{T_H}$$

Upon derivation the performance of the real cycle is often measured in terms of its thermal efficiency

$$\eta_{th} = \frac{W_{net}}{Q_{in}}$$

The Δu and Δh of ideal gases can be expressed as

$$\Delta u = u_2 - u_1 = C_v (T_2 - T_1)$$

$$\Delta h = h_2 - h_1 = C_p (T_2 - T_1)$$

Δu - constant volume process

Δh - constant pressure process

According to a law of $PV^n = \text{constant}$

<i>Process</i>	<i>Description</i>	<i>Result of IGL</i>
<i>isochoric</i>	constant volume ($V_1 = V_2$)	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
<i>isobaric</i>	constant pressure ($P_1 = P_2$)	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
<i>isothermal</i>	constant temperature ($T_1 = T_2$)	$P_1V_1 = P_2V_2$
<i>polytropic</i>	-none-	$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^n = \left(\frac{T_1}{T_2}\right)^{\frac{n}{n-1}}$
<i>isentropic</i>	constant entropy ($S_1 = S_2$)	$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\frac{n}{n-1}} = \left(\frac{T_1}{T_2}\right)^{\frac{n}{n-1}}$

REVIEW

Properties of Air

$$R = 0.2871 \text{ kJ/kg.K}$$

$$C_p = 1.005 \text{ kJ/kg.K}$$

$$C_v = 0.718 \text{ kJ/kg.K} \quad k = 1.4$$

where

R = ideal gas constant

C_p = specific heat at constant pressure

C_v = specific heat at constant volume

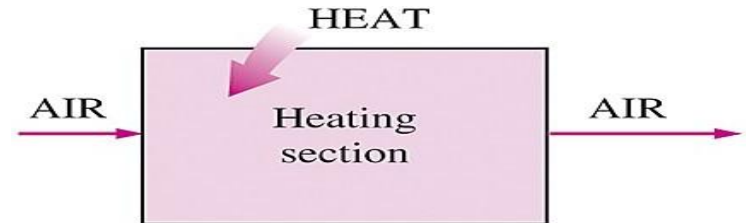
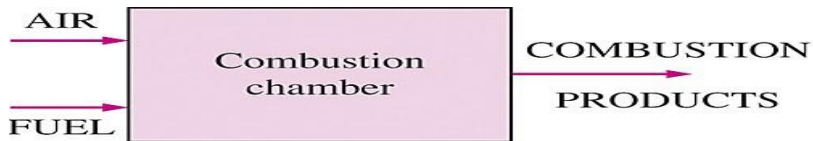
k = specific heat ratio

UNIT -V

POWER CYCLES: Otto, Diesel, Dual Combustion cycles, Description and representation on P-V and T-S diagram, Thermal Efficiency, Mean Effective Pressures on Air standard basis, comparison of Cycles, Introduction to Brayton cycle and Bell Coleman cycle

AIRSTANDARD ASSUMPTIONS

- Air continuously circulates in a closed loop.
- Always behaves as an ideal gas.
- All the processes that make up the cycle are internally reversible.
- The combustion process is replaced by a heat-addition process from an external source.



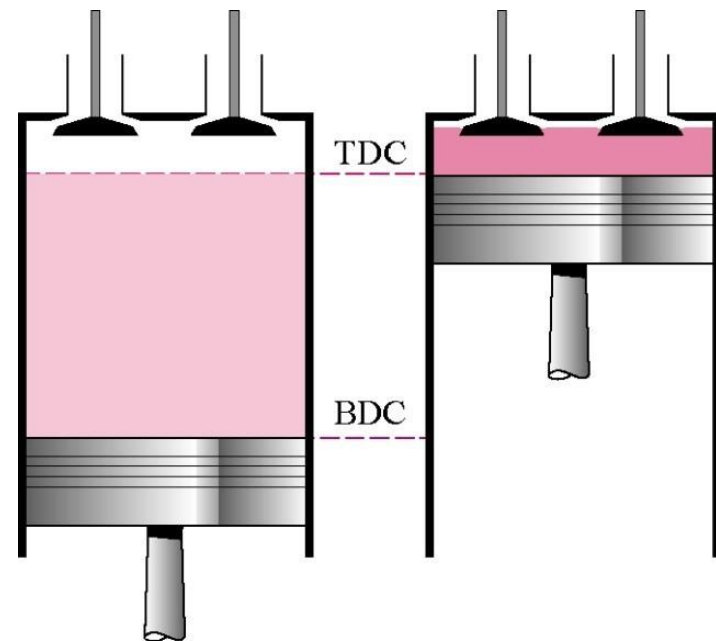
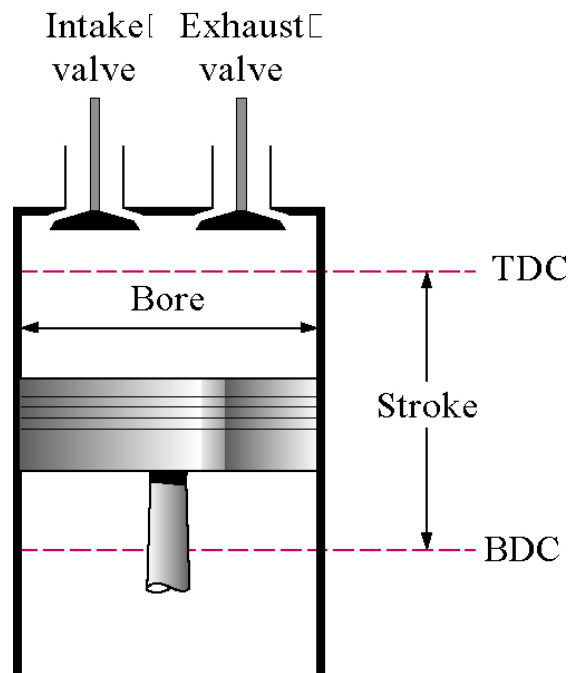
Air-Standard Assumptions

A heat rejection process that restores the working fluid to its initial state replaces the exhaust process.

The cold-air-standard assumptions apply when the working fluid is air and has constant specific heat evaluated at room temperature (25°C or 77°F). No chemical reaction takes place in the engine.

TERMINOLOGY

TDC, BDC, Stroke, bore, intake valve, exhaust valve, clearance volume, displacement volume, compression ratio, and mean effective pressure



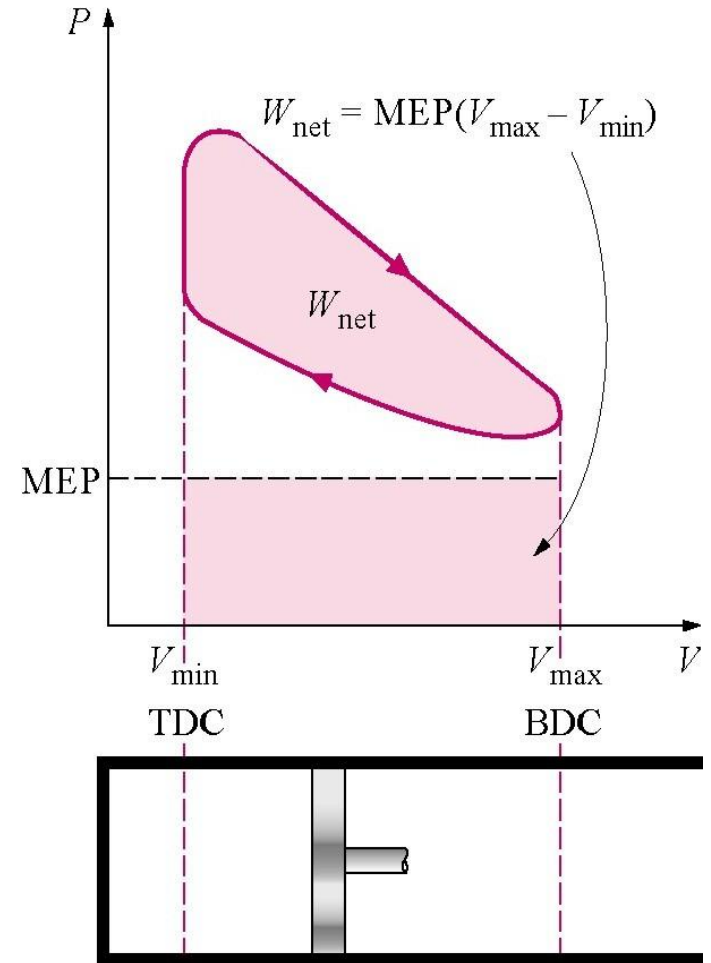
(a) Displacement volume

(b) Clearance volume

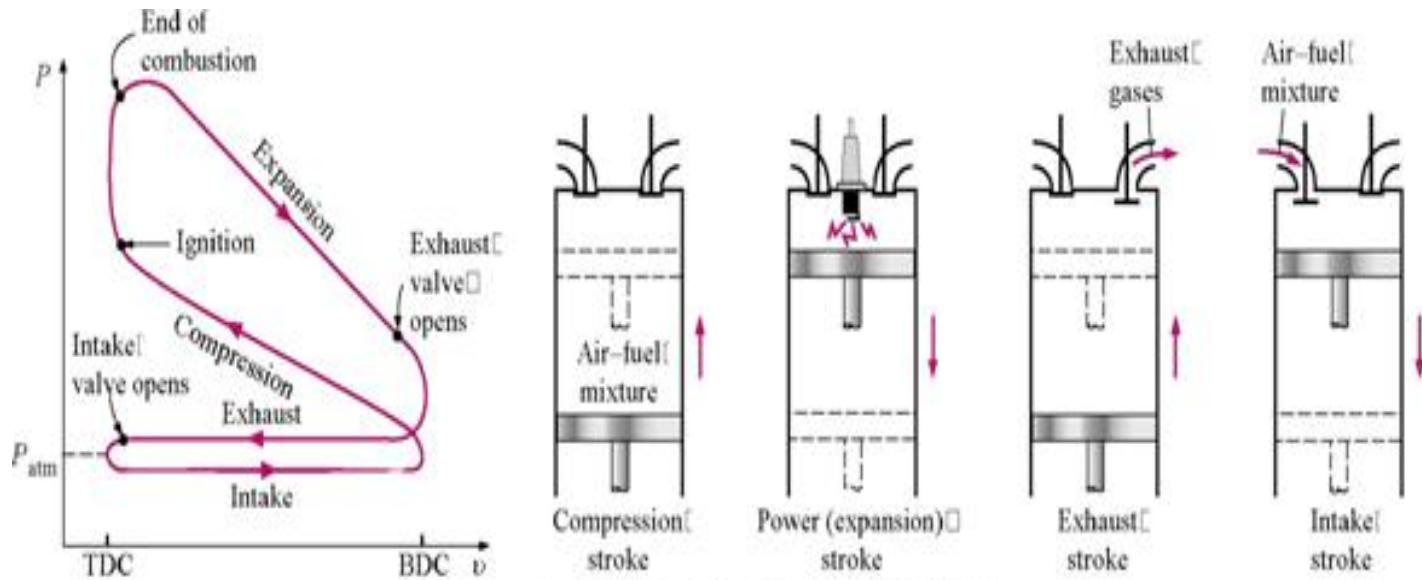
The compression ratio r of an engine is defined as

$$r = \frac{V_{\max}}{V_{\min}} = \frac{V_{BDC}}{V_{TDC}}$$

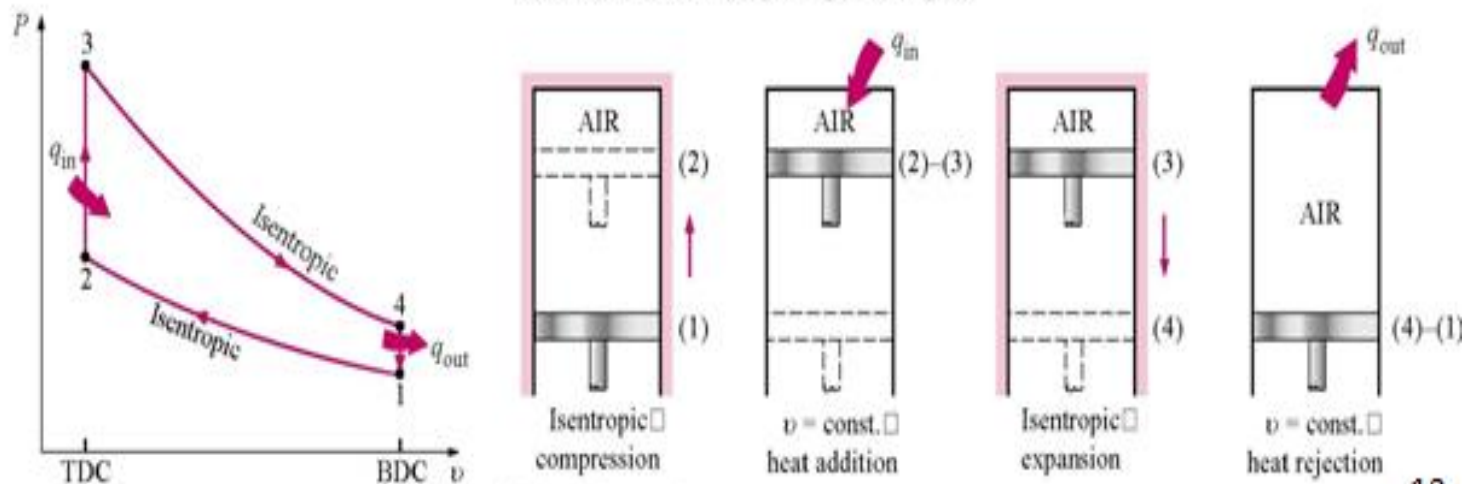
The mean effective pressure (**MEP**) is a fictitious pressure that, if it operated on the piston during the entire power stroke,



$$MEP = \frac{W_{net}}{V_{\max} - V_{\min}} = \frac{W_{net}}{v_{\max} - v_{\min}}$$



(a) Actual four-stroke spark-ignition engine



(b) Ideal Otto cycle

PROCESSES

<i>Process</i>	<i>Description</i>	<i>Related formula</i>
1-2	Isentropic compression	$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^n = \left(\frac{T_1}{T_2} \right)^{\frac{n}{n-1}}$
2-3	Constant volume heat addition	$Q_{in} = mC_v(T_3 - T_2)$
3-4	Isentropic expansion	$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^n = \left(\frac{T_1}{T_2} \right)^{\frac{n}{n-1}}$
4-1	Constant volume heat rejection	$Q_{out} = mC_v(T_4 - T_1)$

$$\eta_{th} = \frac{W_{net}}{Q_{in}} = \frac{Q_{net}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \boxed{1 - \frac{Q_{out}}{Q_{in}}}$$

Apply first law closed system to process 2-3, $V = \text{constant}$.

$$Q_{net,23} - W_{net,23} = \Delta U_{23}$$

$$W_{net,23} = W_{other,23} + W_{b,23} = 0 + \int_2^3 P dV = 0$$

Thus, for constant specific heats

$$Q_{net,23} = \Delta U_{23}$$

$$\boxed{Q_{net,23} = Q_{in} = mC_v(T_3 - T_2)}$$

Apply first law closed system to process 4-1, $V = \text{constant}$.

$$Q_{net,41} - W_{net,41} = \Delta U_{41}$$

$$W_{net,41} = W_{other,41} + W_{b,41} = 0 + \int PdV = 0$$

Thus, for constant specific heats,

$$Q_{net,41} = \Delta U_{41}$$

$$Q_{net,41} = -Q_{out} = mC_v(T_1 - T_4)$$

$$Q_{out} = -mC_v(T_1 - T_4) = mC_v(T_4 - T_1)$$

The thermal efficiency becomes

$$\begin{aligned}\eta_{th, Otto} &= 1 - \frac{Q_{out}}{Q_{in}} \\ &= 1 - \frac{mC_v(T_4 - T_1)}{mC_v(T_3 - T_2)}\end{aligned}$$

$$\begin{aligned}\eta_{th, Otto} &= 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} \\ &= 1 - \frac{T_1(T_4 / T_1 - 1)}{T_2(T_3 / T_2 - 1)}\end{aligned}$$

Recall processes 1-2 and 3-4 are isentropic, so

$$\boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{k-1} \quad \text{and} \quad \frac{T_3}{T_4} = \left(\frac{V_4}{V_3} \right)^{k-1}}$$

Since $V_3 = V_2$ and $V_4 = V_1$,

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} \quad \text{or} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2}$$

The Otto cycle efficiency becomes

$$\eta_{th, Otto} = 1 - \frac{T_1}{T_2}$$

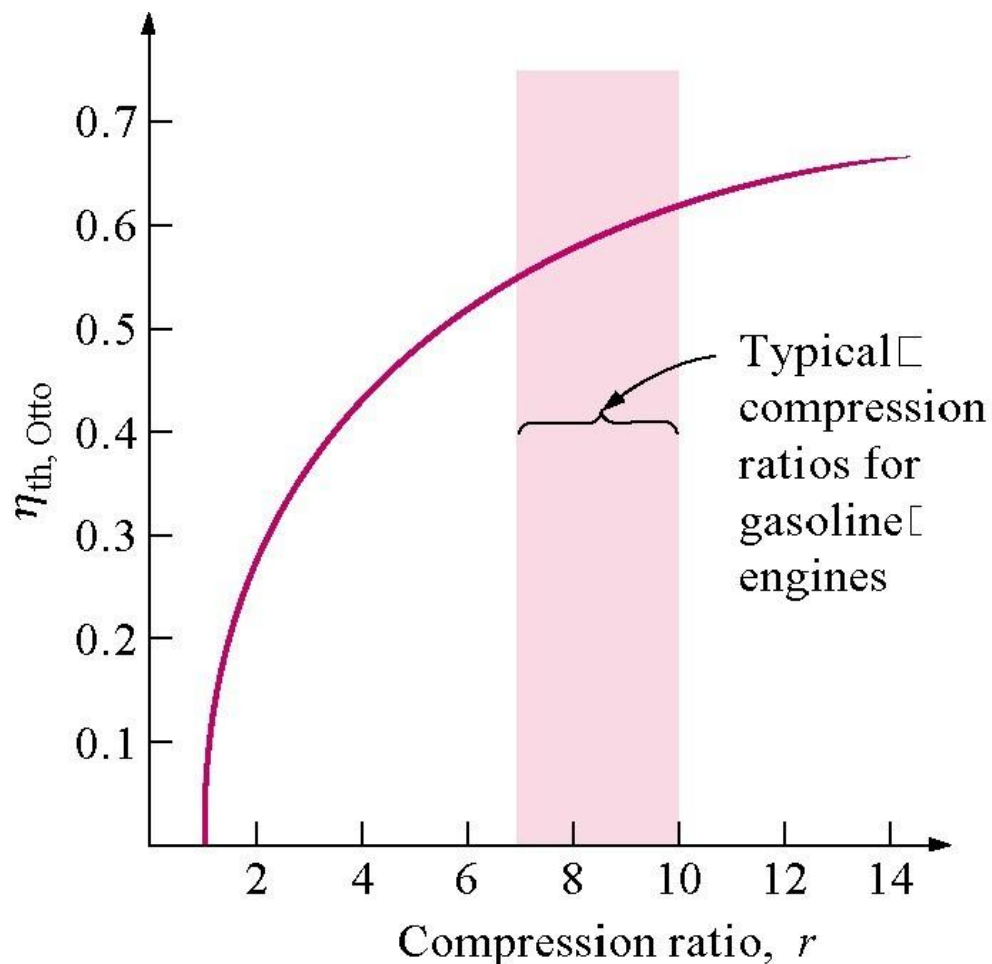
Since process 1-2 is isentropic,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{k-1}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{k-1} = \left(\frac{1}{r} \right)^{k-1}$$

where the compression ratio is $r = V_1/V_2$ and

$$\eta_{th, Otto} = 1 - \frac{1}{r^k}$$



An Otto cycle having a compression ratio of 9:1 uses air as the working fluid. Initially $P_1 = 95 \text{ kPa}$, $T_1 = 17^\circ\text{C}$, and $V_1 = 3.8 \text{ liters}$. During the heat addition process, 7.5 kJ of heat are added. Determine all T 's, P 's, η_{th} , the back work ratio and the mean effective pressure.

Solution:

Data given:

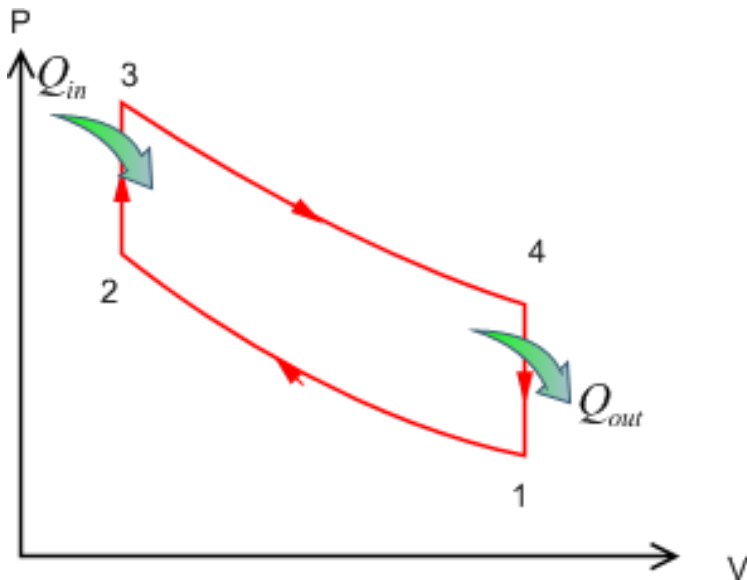
$$T_1 = 290\text{K}$$

$$\frac{V_1}{V_2} = 9$$

$$Q_{23} = 7.5\text{kJ}$$

$$P_1 = 95\text{kPa}$$

$$V_1 = 3.8\text{Litres}$$



Process 1–2 (isentropic compression)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{k-1} \Rightarrow T_2 = 290 (9)^{0.4} = 698.4K$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{k-1} \Rightarrow P_2 = 95 (9)^{1.4} = 2059kPa$$

Process 2–3 (Const. volume heat addition)

$$1^{st} \text{ law: } Q_{net} - W_{net} = \Delta U$$

$$Q_{23} = mC_v (T_3 - T_2)$$

$$IGL: P_1 v_1 = RT_1 \Rightarrow v_1 = \frac{0.2871(290)}{95} = 0.875 \frac{m^3}{kg}$$

$$q_{23} = \frac{Q_{23}}{m} = Q_{23} \frac{v_1}{V_1} = 1727 \frac{kJ}{kg}$$

Back to IGL:

$$q_{23} = C_v (T_3 - T_2)$$

$$= 0.718 (T_3 - 698.4)$$

$$T_3 = 3103.7 K$$

Process 3–4 (isentropic expansion)

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4} \right)^{k-1} \Rightarrow T_4 = T_3 (1/9)^{0.4} = 1288.8 K$$

$$\frac{P_4}{P_3} = \left(\frac{V_3}{V_4} \right)^k \Rightarrow P_4 = P_3 (1/9)^{1.4} = 422 kPa$$

But $V_3 =$

$$\frac{V_2 P_3}{P_2 T_2} =$$

$$P_3 = 9.15 MPa$$

Process 4-1 (Const. volume heat rejection) $Q_{41} =$

$$mC_v (T_4 - T_1)$$

$$q_{41} = C_v (T_4 - T_1)$$

$$= 0.718(1288.8 - 290)$$

$$= 717.1 \frac{\text{kJ}}{\text{kg}}$$

Then:

$$W_{net} = q_{in} - q_{ou}$$

$$= q_{23} - q_{41}$$

$$= 1009.6 \frac{\text{kJ}}{\text{kg}}$$

$$\eta_{th, Otto} = \frac{W_{net}}{q_{in}} = \underline{\underline{0.585(58.5%)}}$$

Example 5.1

What else?

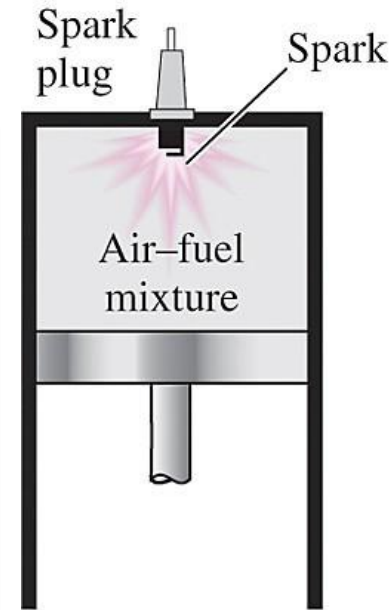
$$\begin{aligned} MEP &= \frac{W_{net}}{V_{max} - V_{min}} = \frac{w_{net}}{v_{max} - v_{min}} \\ &= \frac{w_{net}}{v_1 - v_2} = \frac{w_{net}}{v_1(1 - v_2/v_1)} \\ &= \frac{w_{net}}{v_1(1 - \frac{1}{r})} = \frac{1009.6}{0.875(1 - 1/9)} = \underline{\underline{1298 \text{ kPa}}} \end{aligned}$$

$$\begin{aligned} r_{bw} &= \frac{w_{compr}}{w_{expans}} = \frac{\Delta u_{12}}{-\Delta u_{34}} = \frac{\cancel{C_v}(T_2 - T_1)}{\cancel{C_v}(T_3 - T_4)} \\ &= \underline{\underline{0.225(22.5\%)}} \end{aligned}$$

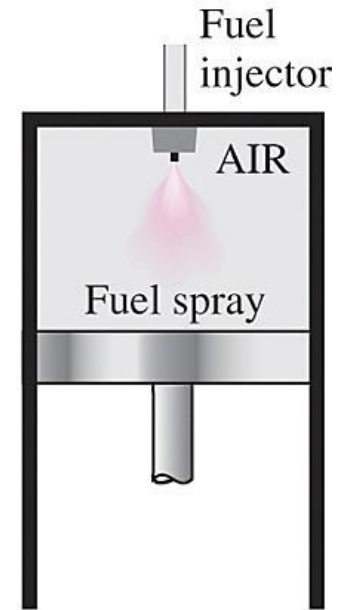
Diesel Cycle

The processes in the Diesel cycle are as per following:

<i>Process</i>	<i>Description</i>
1-2	Isentropic compression
2-3	Constant pressure heat addition
3-4	Isentropic expansion
4-1	Constant volume heat rejection

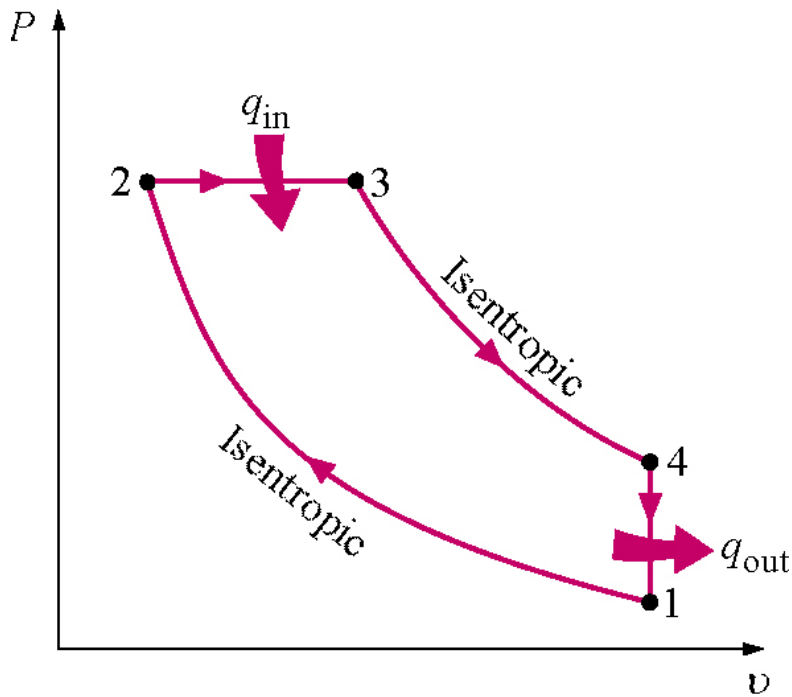


Gasoline engine

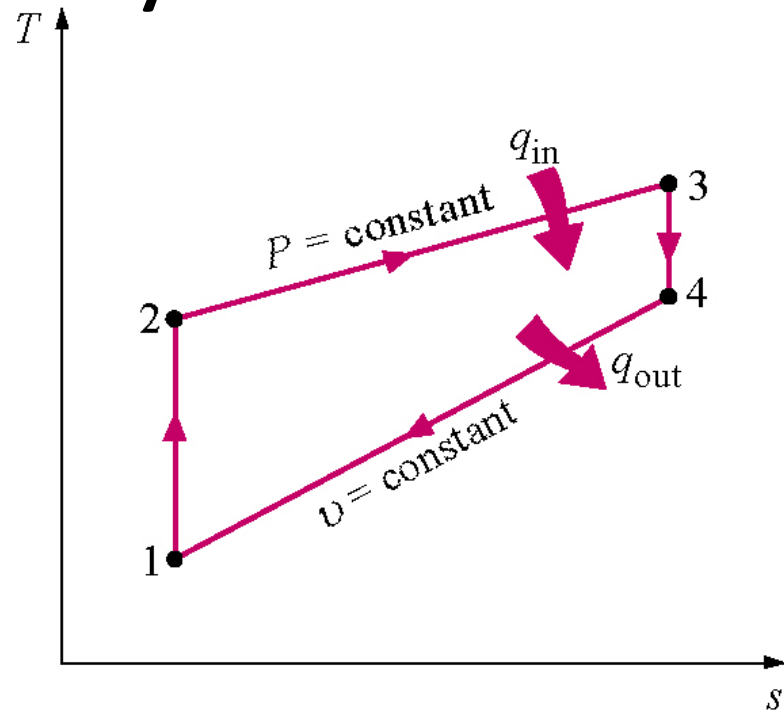


Diesel engine

Diesel Cycle



(a) P - v diagram



(b) T - s diagram

$$\frac{v_1}{v_2} = \text{Compression ratio}, r_v \quad \text{and} \quad \frac{v_3}{v_2} = \text{Cut-off ratio}, r_c$$

Related formula based on basic thermodynamics:

<i>Process</i>	<i>Description</i>	<i>Related formula</i>
1-2	Isentropic compression	$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^n = \left(\frac{T_1}{T_2} \right)^{\frac{n}{n-1}}$
2-3	Constant pressure heat addition	$Q_{in} = mC_p (T_3 - T_2)$
3-4	Isentropic expansion	$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^n = \left(\frac{T_1}{T_2} \right)^{\frac{n}{n-1}}$
4-1	Constant volume heat rejection	$Q_{out} = mC_v (T_4 - T_1)$

θ Thermal efficiency of the Diesel cycle

$$\eta_{th, Diesel} = \frac{W_{net}}{Q_{in}} = \boxed{1 - \frac{Q_{out}}{Q_{in}}}$$

θ Apply the first law closed system to process 2-3, $P = \text{constant}$.

$$Q_{net, 23} - W_{net, 23} = \Delta U_{23}$$

$$\begin{aligned} W_{net, 23} &= W_{other, 23} + W_{b, 23} = 0 + \int_2^3 P dV = 0 \\ &= P_2 (V_3 - V_2) \end{aligned}$$

θ Thus, for constant specific heats

$$Q_{net, 23} = \Delta U_{23} + P_2 (V_3 - V_2)$$

$$Q_{net, 23} = Q_{in} = mC_v (T_3 - T_2) + mR(T_3 - T_2)$$

$$\boxed{Q_{in} = mC_p (T_3 - T_2)}$$

θ Apply the first law closed system to process 4-1, $V = \text{constant}$

$$Q_{net,41} - W_{net,41} = \Delta U_{41}$$

$$W_{net,41} = W_{other,41} + W_{b,41} = 0 + \int_4^1 P dV = 0$$

θ Thus, for constant specific heats

$$Q_{net,41} = \Delta U_{41}$$

$$Q_{net,41} = -Q_{out} = mC_v(T_1 - T_4)$$

$$\boxed{Q_{out} = -mC_v(T_1 - T_4) = mC_v(T_4 - T_1)}$$

θ The thermal efficiency becomes

$$\begin{aligned} \eta_{th, Diesel} &= 1 - \frac{Q_{out}}{Q_{in}} \\ &= 1 - \frac{mC_v(T_4 - T_1)}{mC_p(T_3 - T_2)} \end{aligned}$$

$$\frac{P_4 V_4}{T_4} = \frac{P_1 V_1}{T_1} \quad \text{where } V_4 = V_1$$

$$\frac{T_4}{T_1} = \frac{P_4}{P_1}$$

θ Recall processes 1-2 and 3-4 are isentropic, so

$$\boxed{P_1 V_1^k = P_2 V_2^k \quad \text{and} \quad P_2 V_2^k = P_4 V_4^k} \quad 3 \ 3$$

θ Since $V_4 = V_1$ and $P_3 = P_2$, we divide the second equation by the first equation and obtain

$$\frac{P_4}{T_4} = \left(\frac{V_3}{V_2} \right)^k = r_c^k$$

θ Therefore,

$$\boxed{\eta_{th,Diesel} = 1 - \frac{1}{r^{k-1}} \frac{r_c^k - 1}{k(r_c - 1)}}$$

An air-standard Diesel cycle has a compression ratio of 18 and a cut-off ratio of 2.5. The state at the beginning of compression is fixed by $P = 0.9$ bar and $T = 300\text{K}$. Calculate:

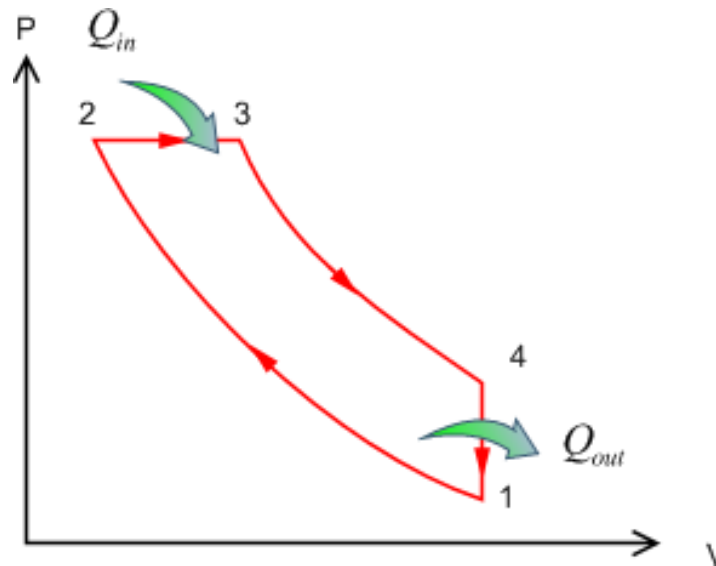
- i. the thermal efficiency of the cycle,
- ii. the maximum pressure, P_{\max} , and
- iii. The mean effective pressure.

Solution:

Data given:

$$\frac{V_1}{V_2} = 18$$

$$\frac{V_3}{V_2} = 2.5$$



Process 1–2 (isentropic compression)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{k-1} \Rightarrow T_2 = 300(18)^{0.4} = 953.3K$$

Process 2–3 (Const. pressure heat addition)

$$P_2 = P_3 \Rightarrow \frac{V_2}{T_2} = \frac{V_3}{T_3} \Rightarrow T_3 = T_2 \left(\frac{V_3}{V_2} \right) = 2383.3 K$$

Process 3–4 (isentropic expansion)

$$\frac{V_4}{V_3} = \frac{V_1}{V_2} \cdot \frac{V_2}{V_3} = 18(1/2.5) = 7.2$$

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4} \right)^{k-1} \Rightarrow T_4 = 2383.3(1/7.2)^{0.4} = 1082 K$$

$$Q_{in} = Q_{23} = mC_p (T_3 - T_2) \Rightarrow q_{in} = C_p (T_3 - T_2) = 1437.15 \frac{\text{kJ}}{\text{kg}}$$

$$Q = Q_{41} = mC_p (T_4 - T_1) \Rightarrow q_{out} = C_p (T_4 - T_1) = 561.48 \frac{\text{kJ}}{\text{kg}}$$

$$w_{out} = q_{in} - q_{out} = 875.67 \frac{\text{kJ}}{\text{kg}}$$

What we need?

$$(i) \eta_{th,diesel} = \frac{W_{net}}{q_{in}} = \underline{\underline{0.6093 (60.93\%)}}$$

$$(ii) P_{max} = P_2 = P_3$$

$$\left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}} = \left(\frac{T_2}{T_1} \right)^{\frac{\gamma-1}{\gamma}} \Rightarrow P_2 = \underline{\underline{5148 \text{ kPa} (P_{max})}}$$

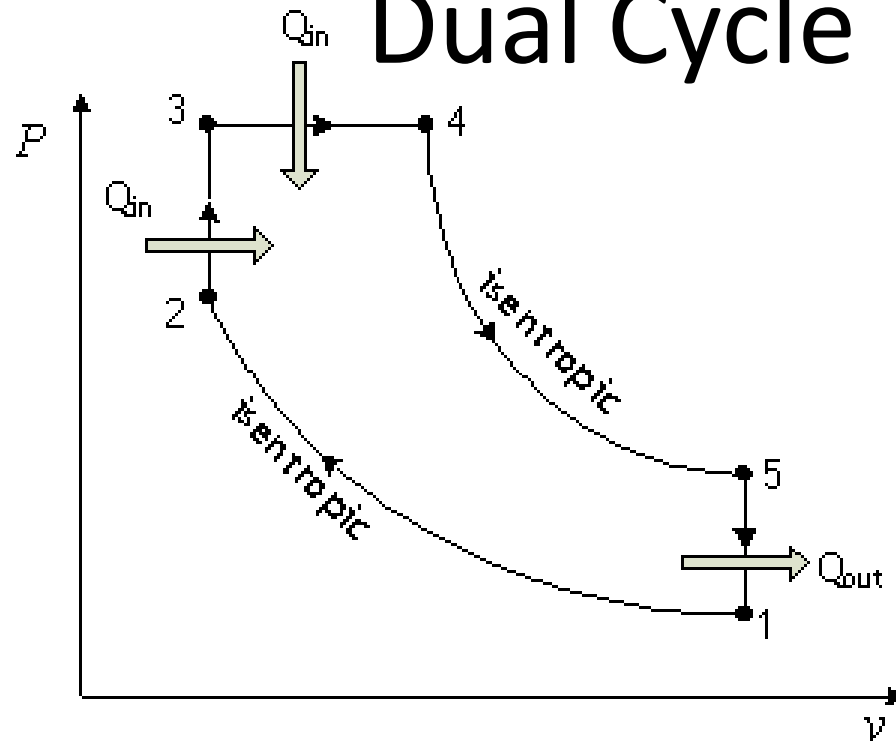
$$(iii) MEP = \frac{W_{net}}{V_1(1-1/r)} = \frac{875.67}{0.9566(1-1/18)} = \underline{\underline{969.1 \text{ kPa}}}$$

1. An ideal diesel engine has a compression ratio of 20 and uses air as the working fluid. The state of air at the beginning of the compression process is 95 kPa and 20°C. If the maximum temperature in the cycle is not to exceed 2200 K, determine (a) the thermal efficiency and (b) the mean effective pressure. Assume constant specific heats for air at room temperature.

[(a) 63.5 percent, (b) 933 kPa]

2. An ideal diesel cycle has a compression ratio of 16 to 1. The maximum cycle temperature is 1700°C and the minimum cycle temperature is 15°C. Calculate:
 - i. the specific heat transfer to the cycle
 - ii. the specific work of the cycle
 - iii. the thermal efficiency of the cycle

Dual Cycle



- θ Dual cycle gives a better approximation to a real engine. The heat addition process is partly done at a constant volume and partly at constant pressure. From the P-v diagram, it looks like the heat addition process is a combination of both Otto and Diesel cycles.

Dual Cycle

<i>Process</i>	<i>Description</i>
1-2	Isentropic compression
2-3	Constant volume heat addition
3-4	Constant pressure heat addition
4-5	Isentropic expansion
5-1	Constant volume heat rejection

θ The same procedure as to Otto and Diesel cycles can be applied to Dual cycle. Upon substitutions, the thermal efficiency of Dual cycle becomes

$$\eta_{th} = 1 - \frac{r_p r_c^k - 1}{\left[(r_p - 1) + k c_p (r_c - 1) \right] r_v^{k-1}}$$

Example 5.3

At the beginning of the compression process of an air-standard dual cycle with a compression ratio of 18, the temperature is 300 K and the pressure is 1 bar. The pressure ratio for the constant volume part of the heating process is 1.5 to 1. The volume ratio for the constant pressure part of the heating process is 1.2 to 1. Determine (a) the thermal efficiency and (b) the mean effective pressure. (**WRONG SOLUTION!!**)

Solution:

Data given:

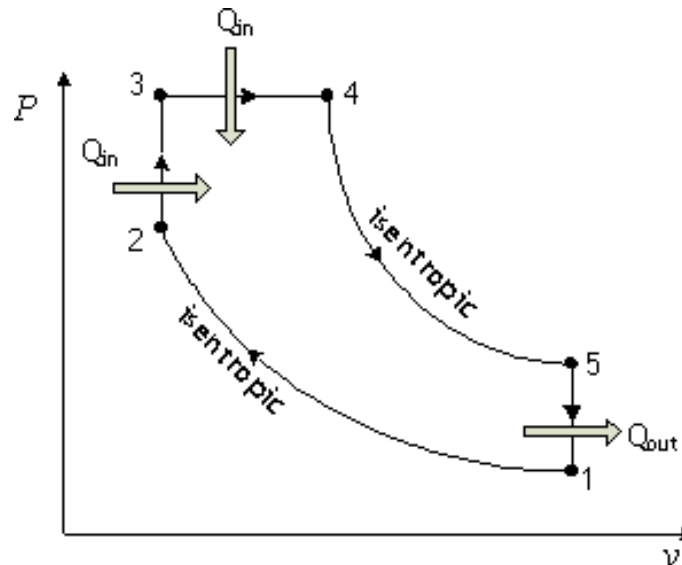
$$\frac{V_1}{V_2} = 18$$

$$\frac{P_3}{P_2} = 1.5$$

$$T_1 = 300K$$

$$\frac{V_4}{V_3} = 1.2$$

$$P_1 = 1 \text{ bar}$$



Process 1–2 (isentropic compression)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{k-1} \Rightarrow T_2 = 300(18)^{0.4} = 953.3K$$

Process 2–3 (Const. pressure heat addition)

$$P_2 = P_3 \Rightarrow \frac{V_2}{T_2} = \frac{V_3}{T_3} \Rightarrow T_3 = T_2 \left(\frac{V_3}{V_2} \right) = 2383.3 K$$

Process 3–4 (isentropic expansion)

$$\frac{V_4}{V_3} = \frac{V_1}{V_2} \cdot \frac{V_2}{V_3} = 18(1/2.5) = 7.2$$

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4} \right)^{k-1} \Rightarrow T_4 = 2383.3(1/7.2)^{0.4} = 1082 K$$

Process 4 – 5 (isentropic expansion)

$$\begin{aligned}
 \frac{T_5}{T_4} &= \left(\frac{V_4}{V_5} \right)^{k-1} \Rightarrow T_5 = T_4 \left(\frac{V_4}{V_5} \right)^{k-1} = T_4 \left[\left(\frac{V_4}{V_3} \right) \left(\frac{V_3}{V_5} \right) \right]^{k-1} \\
 &= 1715.94 \left[(1.2) \left(\frac{1}{18} \right) \right]^{0.4} \\
 &= 584.85 K
 \end{aligned}$$

Information needed?

$$\begin{aligned}
 Q_{out} &= Q_{51} = m C_v (T_5 - T_1) = 204.52 \frac{kJ}{kg} \\
 Q_{in} &= Q_{23} + Q_{34} = m C_v (T_3 - T_2) + m C_p (T_4 - T_3) \\
 &= 629.65 \frac{kJ}{kg}
 \end{aligned}$$

Answer the questions ?

$$(a) \eta_{th} = \frac{W_{net}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{204.52}{629.65} = \underline{\underline{0.675(67.5%)}}$$

$$(b) MEP = \frac{W_{net}}{v_1 \left(1 - \frac{1}{r}\right)}$$
$$= \frac{425.13}{0.8613 \left(1 - \frac{1}{18}\right)}$$
$$= \underline{\underline{522.63 kPa}}$$

Real Case



$$IP = \frac{p_i LANn}{2}$$

$$bp = 2\pi N\tau$$

Engine

Engine type:	Liquid-cooled, 4-stroke, single cylinder, 4-valve, SOHC
Displacement:	124.66 cc
Bore x stroke:	52.0 x 58.6 mm
Compression ratio:	11.2 : 1
Maximum power:	11.0 kW (15 PS) @ 9,000 rpm
Maximum torque:	12.24 Nm (1.25 kg-m) @ 8,000 rpm

AIR STANDARD EFFICIENCY

- The efficiency of engine using air as the working medium is known as Air Standard Efficiency
- The actual gas power cycles are rather complex. To reduce the analysis to a manageable level, we utilize the following approximations, commonly known as the **air-standard assumptions**

AIR STANDARD ASSUMPTIONS

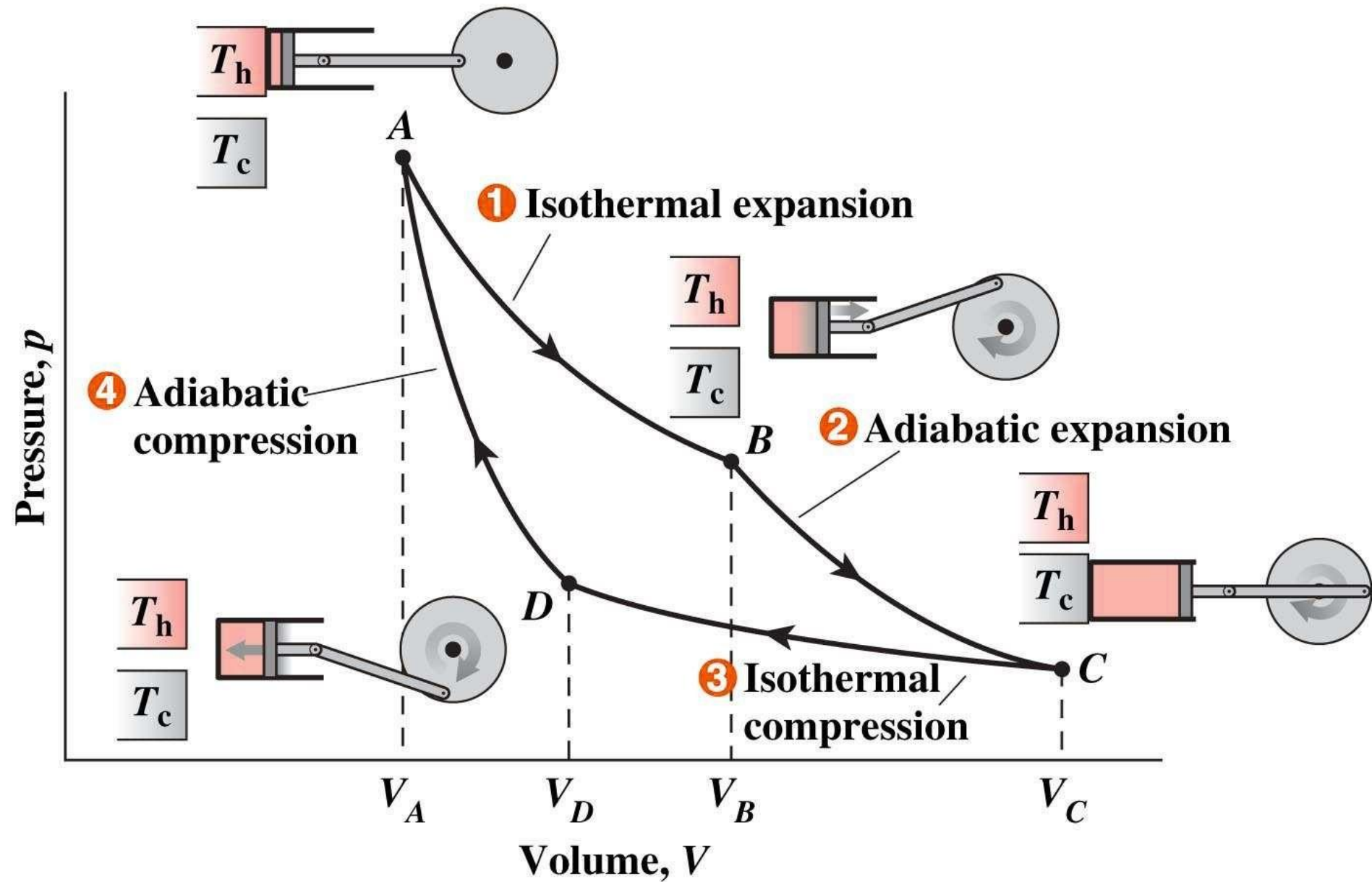
- The working fluid is air
- In the cycle, all the processes are reversible
- Mass of working fluid remains constant through entire cycle
- The working fluid is homogenous throughout the cycle and no chemical reaction takes place
- The air behaves as an ideal gas and its specific heat is constant at all temperatures
- The cycle is considered closed with the same 'air' always remaining in the cylinder to repeat the cycle

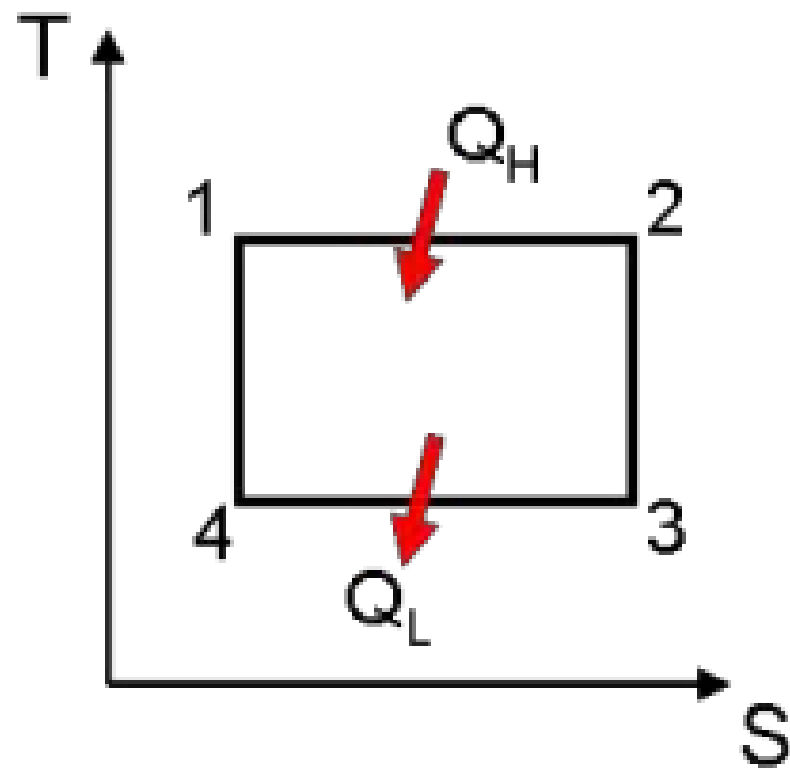
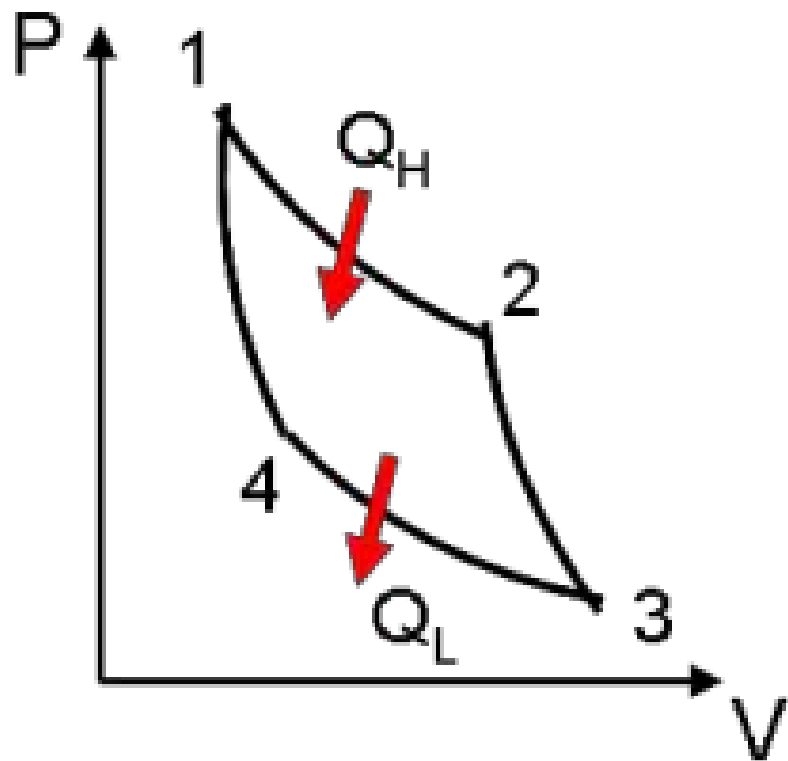
CARNOT CYCLE

- This cycle is a hypothetical cycle having highest possible efficiency
- Consists of four simple operations namely:
 1. Isothermal expansion
 2. Adiabatic expansion
 3. Isothermal compression
 4. Adiabatic compression

ASSUMPTIONS MADE IN CARNOT CYCLE

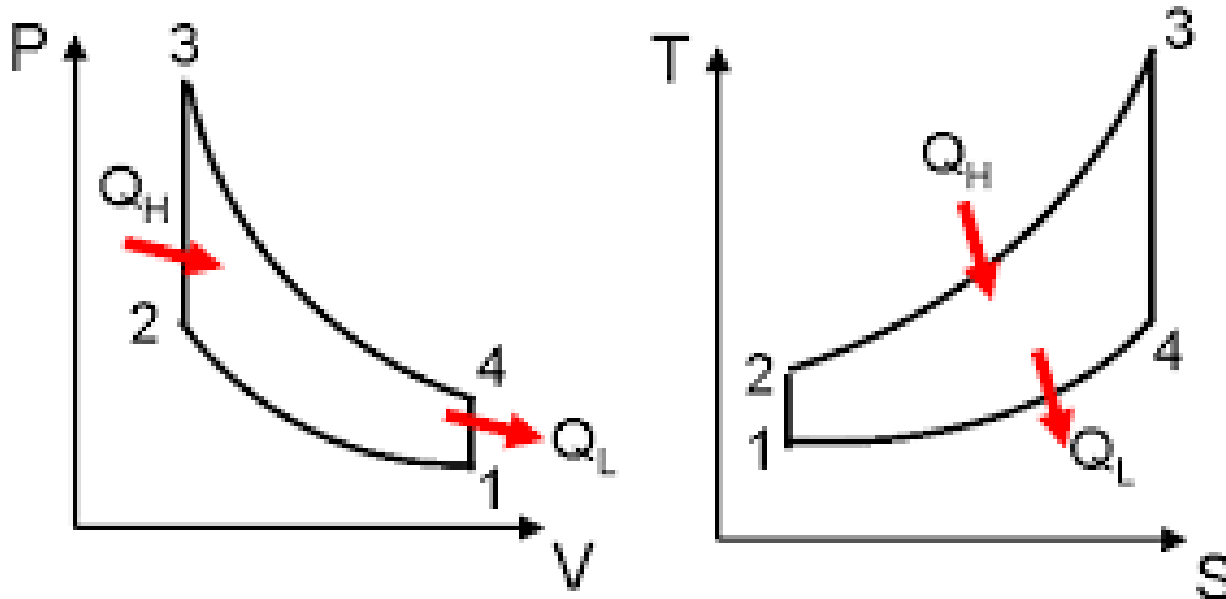
- The piston moving in the cylinder does not produce any friction during motion
- The cylinder head is arranged such a way that it can be perfect heat conductor or insulator
- The walls of cylinder and piston are considered as perfect insulators of heat
- Heat transfer does not affect the temperature of source or sink
- Compression and expansion processes are reversible
- Working medium is a perfect gas and has constant specific heat





$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

OTTO CYCLE(CONSTANT VOLUME CYCLE)



Process 1-2: Reversible adiabatic compression

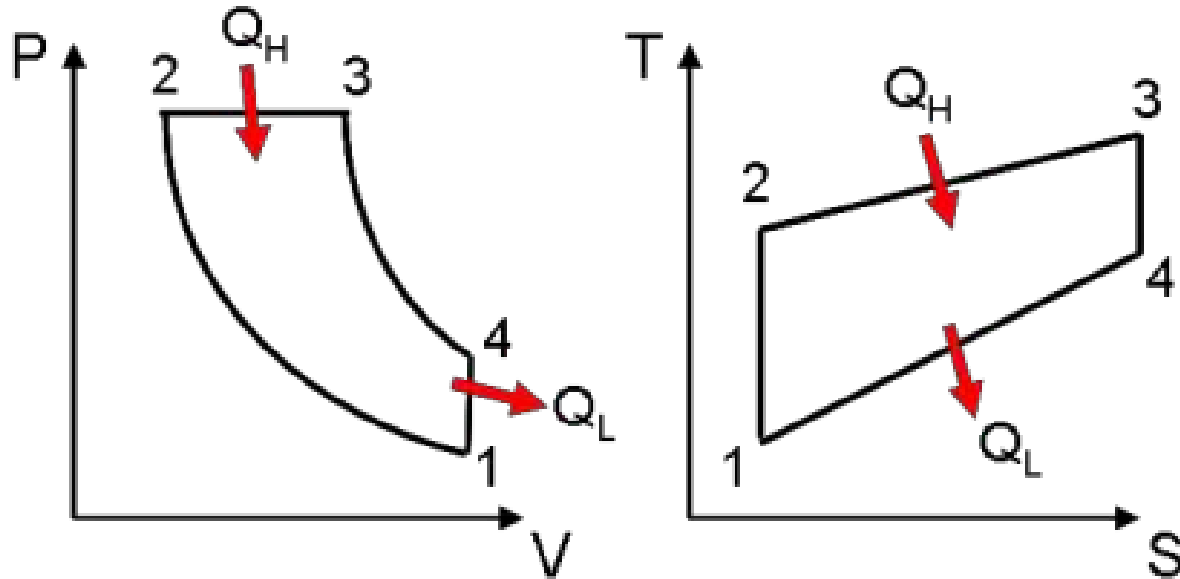
Process 2-3: Addition of heat at constant volume

Process 3-4: Reversible adiabatic expansion

Process 4-1: Rejection of heat at constant volume

$$\eta = 1 - \left(\frac{1}{r^{(\gamma-1)}} \right)$$

DIESEL CYCLE(CONSTANT PRESSURE CYCLE)

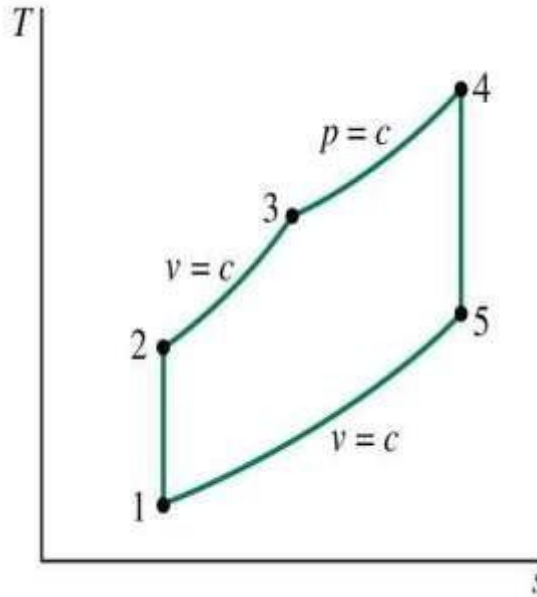
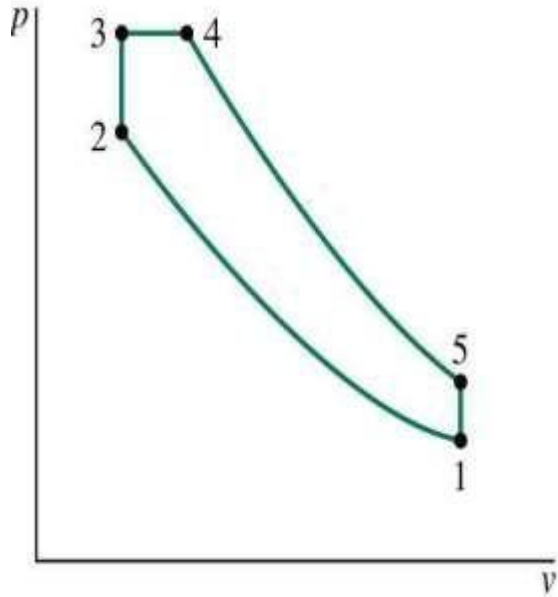


- Process 1-2:** Reversible adiabatic compression
- Process 2-3:** Addition of heat at constant pressure
- Process 3-4:** Reversible adiabatic expansion
- Process 4-1:** Rejection of heat at constant volume

Point 3: Cut-off point

$$\eta_{th} = 1 - \frac{1}{r^{\gamma-1}} \left(\frac{\alpha^{\gamma} - 1}{\gamma(\alpha - 1)} \right)$$

DUAL CYCLE



- Process 1-2:** Reversible adiabatic compression
- Process 2-3:** Addition of heat at constant volume
- Process 3-4:** Addition of heat at constant pressure
- Process 4-5:** Reversible adiabatic expansion
- Process 5-1:** Rejection of heat at constant volume

$$\eta_{Dual, \text{const } c_v} = 1 - \frac{1}{r^{k-1}} \left[\frac{\alpha r_c^k - 1}{(\alpha - 1) + \alpha k (r_c - 1)} \right]$$

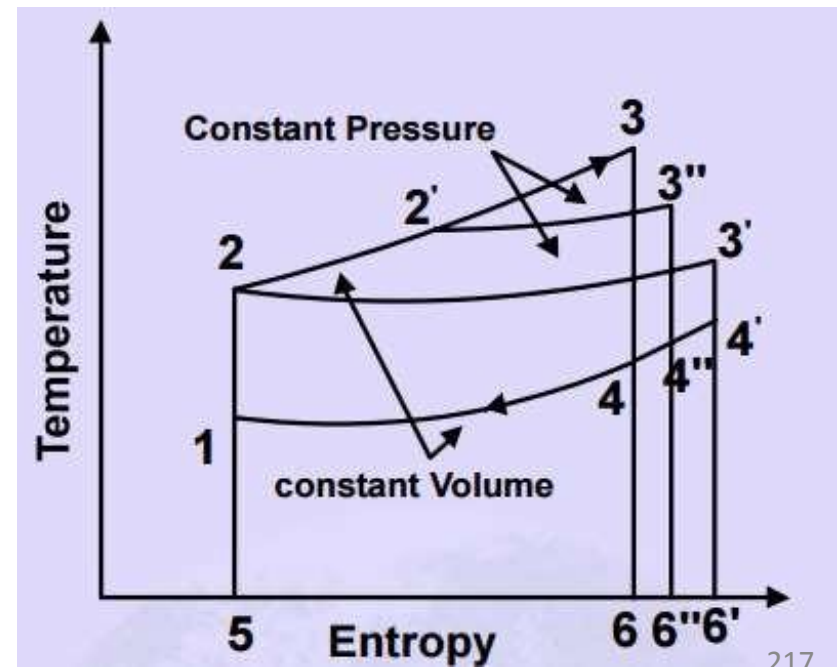
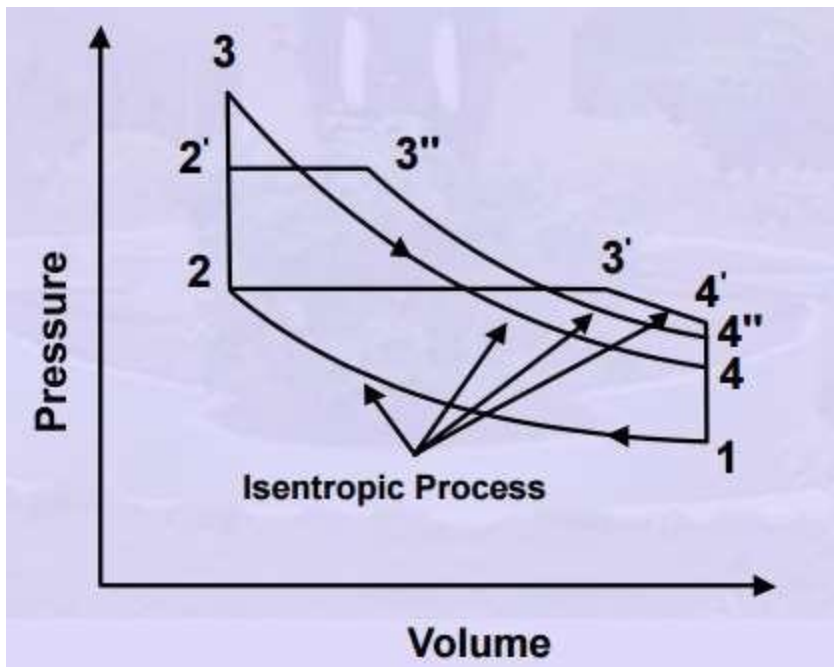
COMPARISON OF OTTO, DIESEL AND DUAL CYCLES

- Following are the important variable factors which are used for comparison of these cycles:
 1. Compression ratio
 2. Maximum pressure
 3. Heat supplied
 4. Heat rejected
 5. Net work

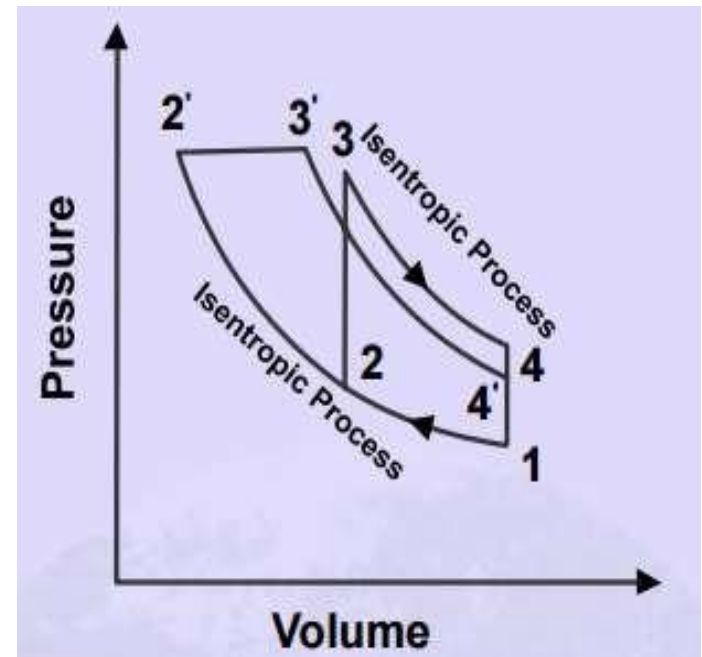
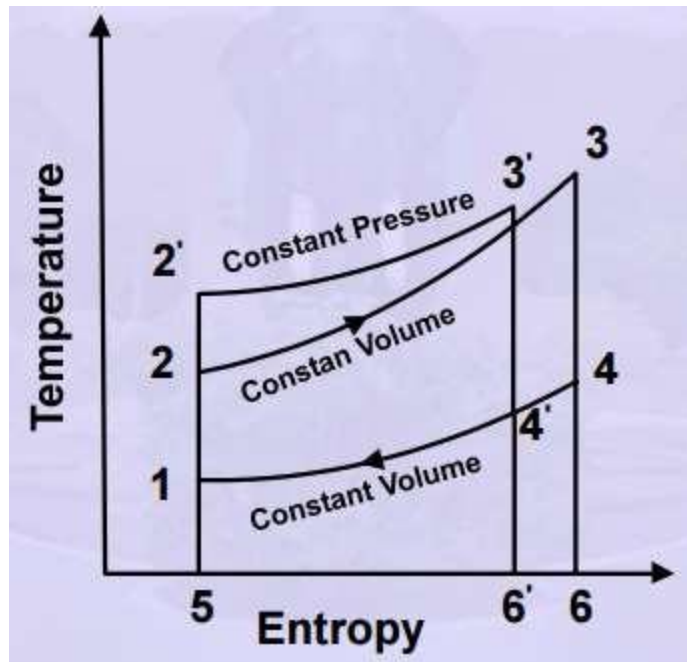
Efficiency versus compression ratio

• For a given compression ratio, Otto cycle is the most efficient while the diesel cycle is the least efficient

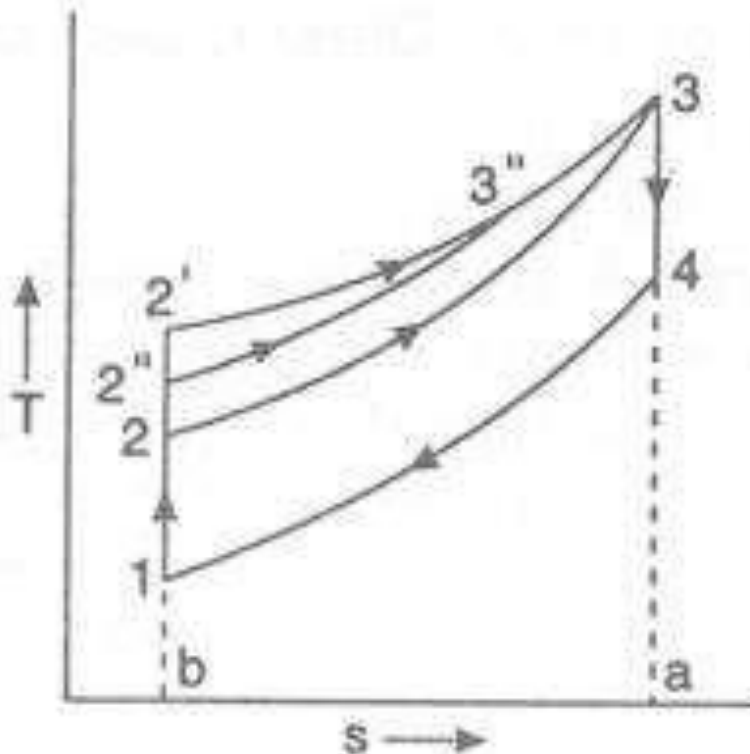
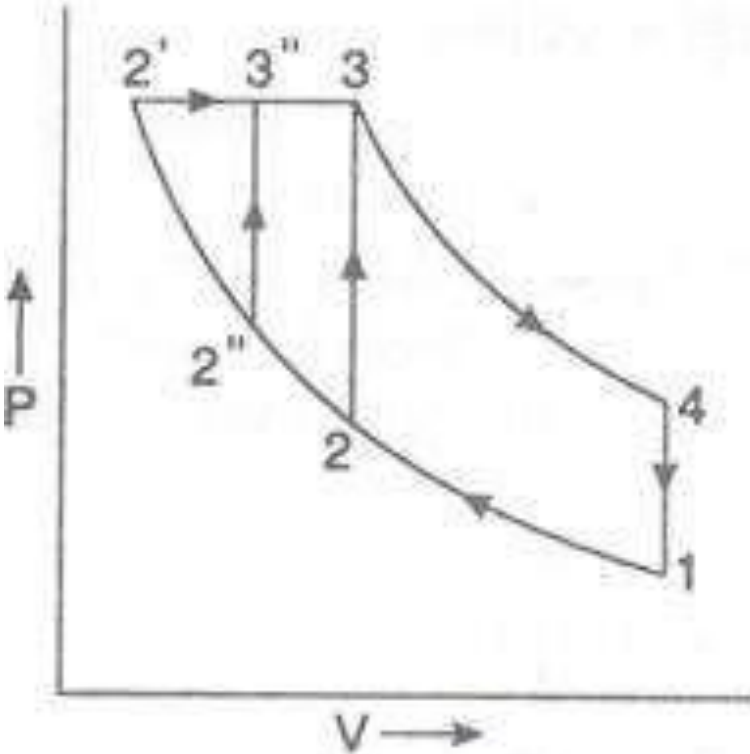
2. For the same compression ratio and the same heat input



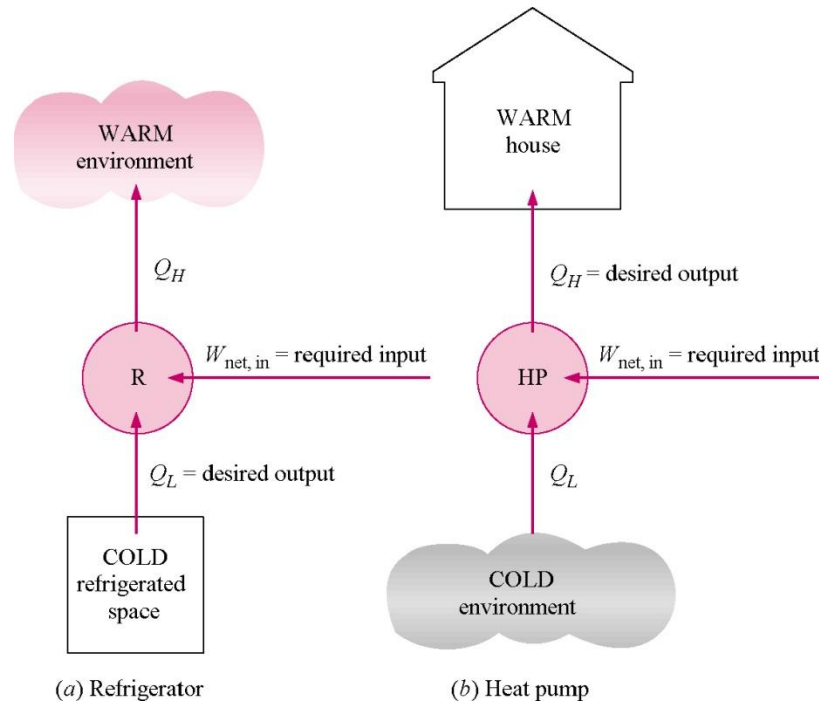
For constant maximum pressure and heat supplied



For the same maximum pressure and maximum temperature



The vapor compression refrigeration cycle is a common method for transferring heat from a low temperature to a high temperature.

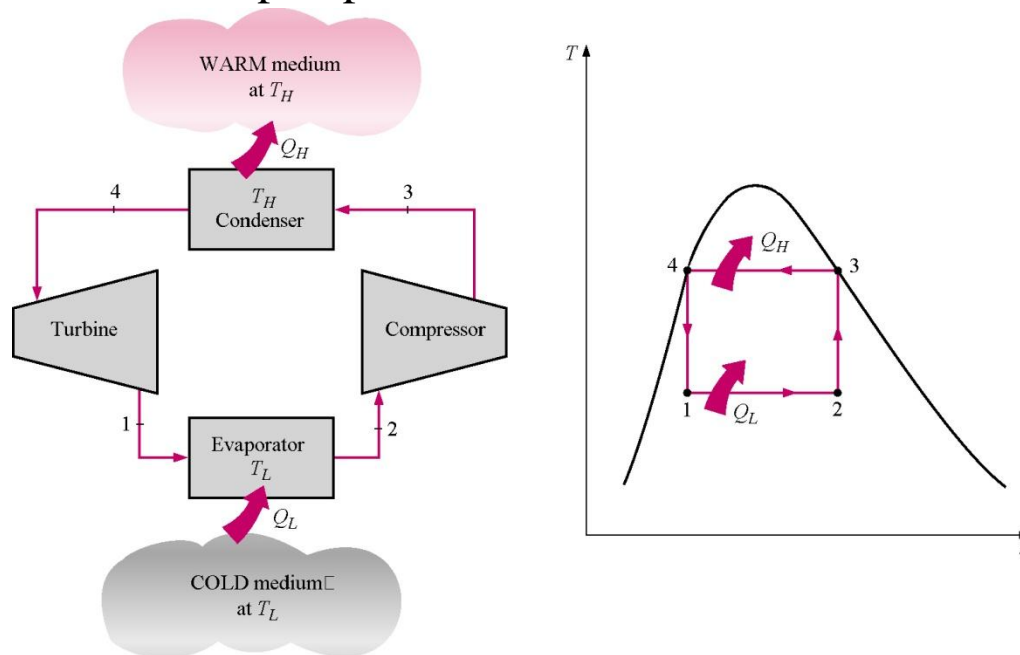


The above figure shows the objectives of refrigerators and heat pumps. The purpose of a refrigerator is the removal of heat, called the cooling load, from a low-temperature medium. The purpose of a heat pump is the transfer of heat to a high-temperature medium, called the heating load. When we are interested in the heat energy removed from a low-temperature space, the device is called a refrigerator. When we are interested in the heat energy supplied to the high-temperature space, the device is called a heat pump.

Refrigeration systems are also rated in terms of tons of refrigeration. One ton of refrigeration is equivalent to 12,000 Btu/hr or 211 kJ/min. How did the term “ton of cooling” originate?

Reversed Carnot Refrigerator and Heat Pump

Shown below are the cyclic refrigeration device operating between two constant temperature reservoirs and the T - s diagram for the working fluid when the reversed Carnot cycle is used. Recall that in the Carnot cycle heat transfers take place at constant temperature. If our interest is the cooling load, the cycle is called the Carnot refrigerator. If our interest is the heat load, the cycle is called the Carnot heat pump.



The standard of comparison for refrigeration cycles is the *reversed Carnot cycle*. A refrigerator or heat pump that operates on the reversed Carnot cycle is called a *Carnot refrigerator* or a *Carnot heat pump*, and their COPs are

$$COP_{R,Carnot} = \frac{1}{T_H / T_L - 1} = \frac{T_L}{T_H - T_L}$$

$$COP_{HP,Carnot} = \frac{1}{1 - T_L / T_H} = \frac{T_H}{T_H - T_L}$$

Notice that a turbine is used for the expansion process between the high and low-temperatures. While the work interactions for the cycle are not indicated on the figure, the work produced by the turbine helps supply some of the work required by the compressor from external sources.

Why not use the reversed Carnot refrigeration cycle?

- Easier to compress vapor only and not liquid-vapor mixture.
- Cheaper to have irreversible expansion through an expansion valve.

What problems result from using the turbine instead of the expansion valve?

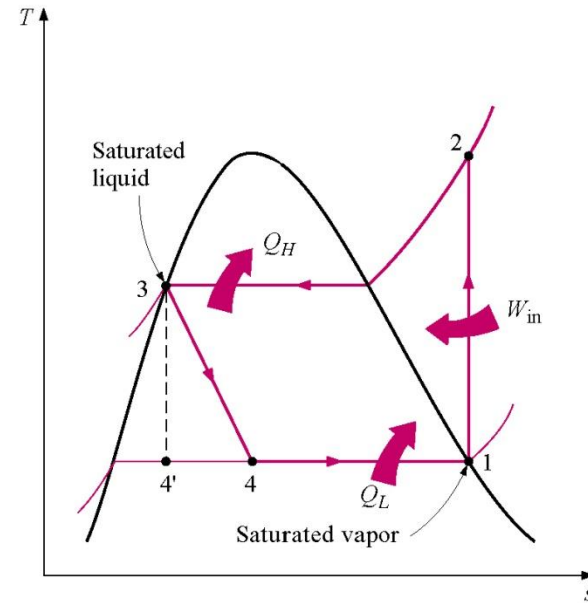
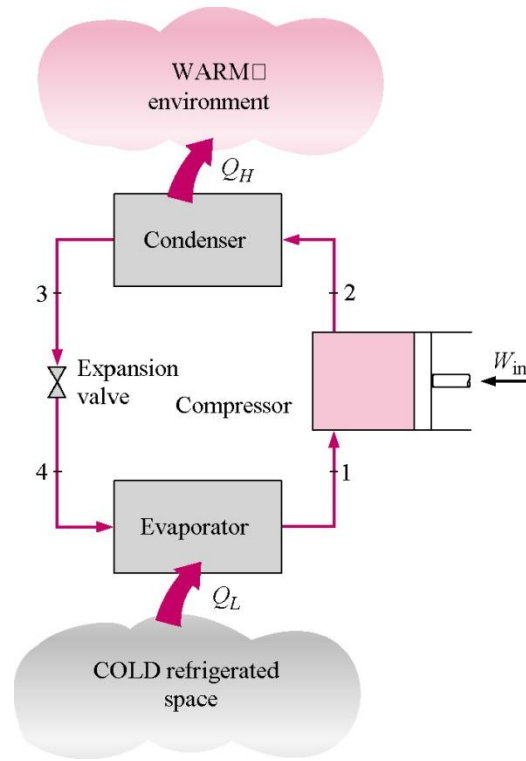
The Vapor-Compression Refrigeration Cycle

The vapor-compression refrigeration cycle has four components: evaporator, compressor, condenser, and expansion (or throttle) valve. The most widely used refrigeration cycle is the *vapor-compression refrigeration cycle*. In an ideal vapor-compression refrigeration cycle, the refrigerant enters the compressor as a saturated vapor and is cooled to the saturated liquid state in the condenser. It is then throttled to the evaporator pressure and vaporizes as it absorbs heat from the refrigerated space.

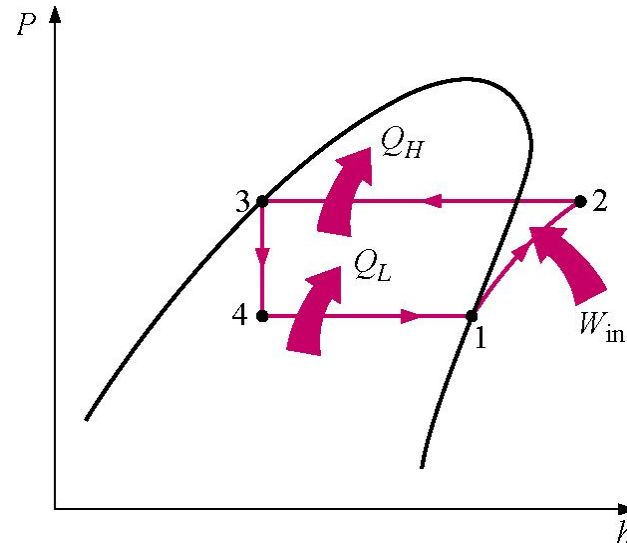
The ideal vapor-compression cycle consists of four processes.

Ideal Vapor-Compression Refrigeration Cycle

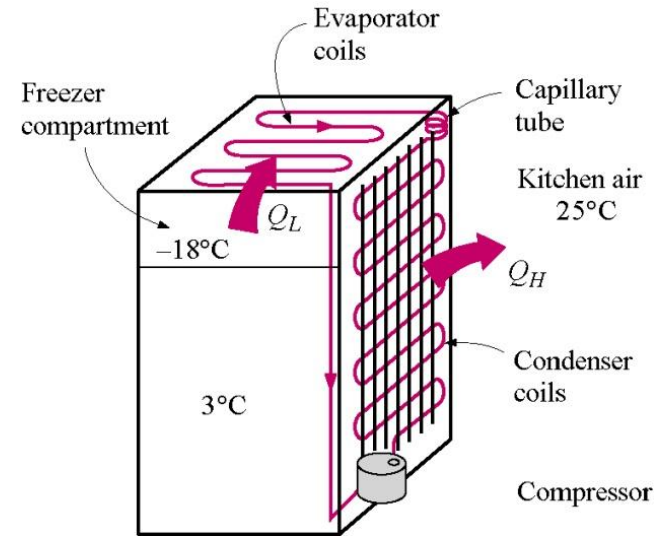
Process	Description
1-2	Isentropic compression
2-3	Constant pressure heat rejection in the condenser
3-4	Throttling in an expansion valve
4-1	Constant pressure heat addition in the evaporator



The P - h diagram is another convenient diagram often used to illustrate the refrigeration cycle.



The ordinary household refrigerator is a good example of the application of this cycle.



Results of First and Second Law Analysis for Steady-Flow

Component	Process	First Law Result
Compressor	$s = \text{const.}$	$\dot{W}_{in} = \dot{m}(h_2 - h_1)$
Condenser	$P = \text{const.}$	$\dot{Q}_H = \dot{m}(h_2 - h_3)$
Throttle Valve	$\Delta s > 0$	$h_4 = h_3$
Evaporator	$P = \text{const.}$	$\dot{Q}_L = \dot{m}(h_1 - h_4)$

$$COP_R = \frac{\dot{Q}_L}{\dot{W}_{net,in}} = \frac{h_1 - h_4}{h_2 - h_1}$$

$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{net,in}} = \frac{h_2 - h_3}{h_2 - h_1}$$

Example 11-1

Refrigerant-134a is the working fluid in an ideal compression refrigeration cycle. The refrigerant leaves the evaporator at -20°C and has a condenser pressure of 0.9 MPa . The mass flow rate is 3 kg/min . Find COP_R and $\text{COP}_{R, \text{Carnot}}$ for the same T_{max} and T_{min} , and the tons of refrigeration.

Using the Refrigerant-134a Tables, we have

$$\left. \begin{array}{l} \text{State 1} \\ \text{Compressor inlet} \\ T_1 = -20^{\circ}\text{C} \\ x_1 = 1.0 \end{array} \right\} \left\{ \begin{array}{l} h_1 = 238.41 \frac{\text{kJ}}{\text{kg}} \\ s_1 = 0.9456 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right.$$

$$\left. \begin{array}{l} \text{State 2} \\ \text{Compressor exit} \\ P_{2s} = P_2 = 900\text{ kPa} \\ s_{2s} = s_1 = 0.9456 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right\} \left\{ \begin{array}{l} h_{2s} = 278.23 \frac{\text{kJ}}{\text{kg}} \\ T_{2s} = 43.79^{\circ}\text{C} \end{array} \right.$$

$$\left. \begin{array}{l} \text{State 3} \\ \text{Condenser exit} \\ P_3 = 900\text{ kPa} \\ x_3 = 0.0 \end{array} \right\} \left\{ \begin{array}{l} h_3 = 101.61 \frac{\text{kJ}}{\text{kg}} \\ s_3 = 0.3738 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right.$$

$$\left. \begin{array}{l} \text{State 4} \\ \text{Throttle exit} \\ T_4 = T_1 = -20^{\circ}\text{C} \\ h_4 = h_3 \end{array} \right\} \left\{ \begin{array}{l} x_4 = 0.358 \\ s_4 = 0.4053 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right.$$

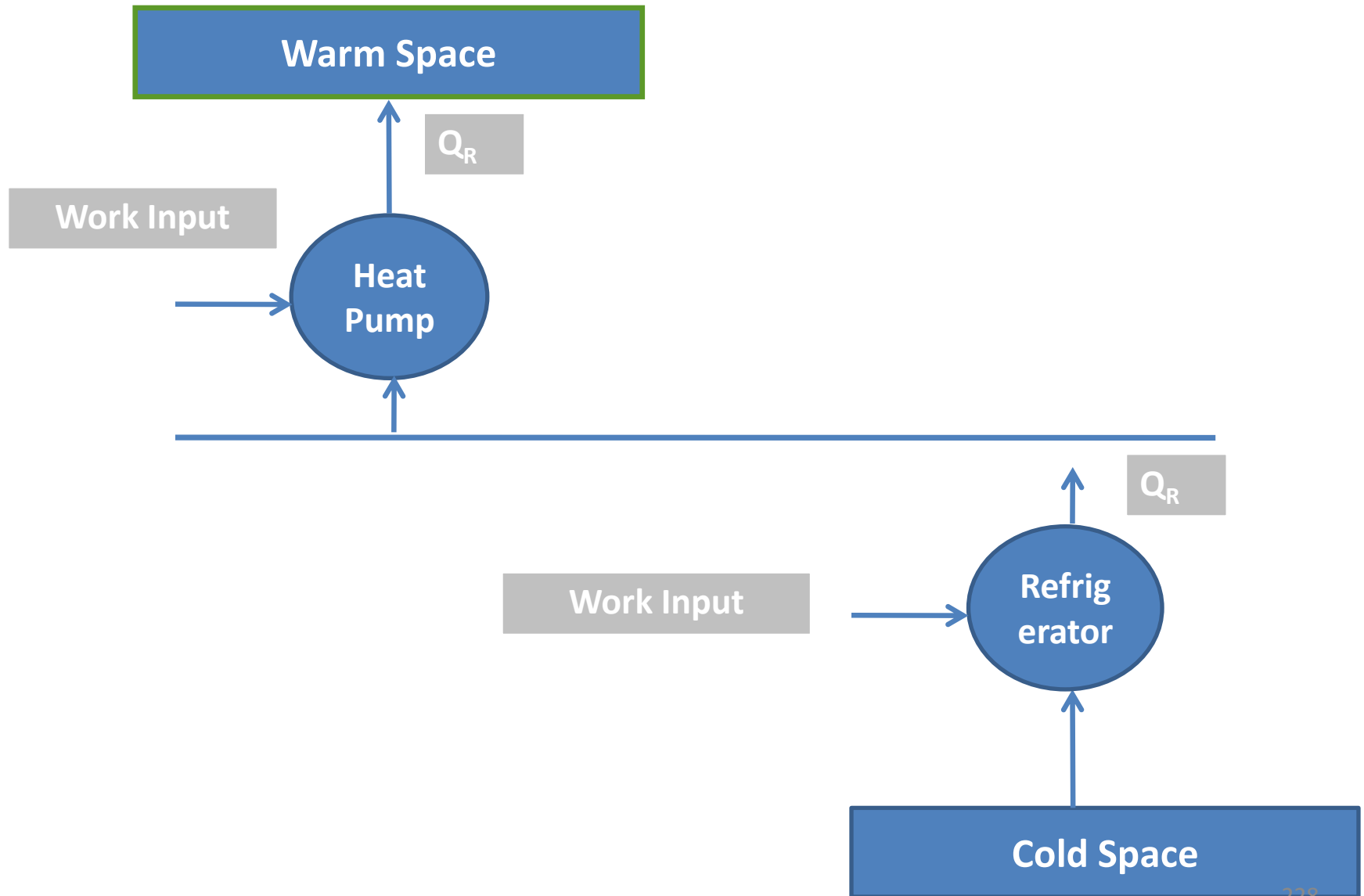
$$\begin{aligned}
 COP_R &= \frac{\dot{Q}_L}{\dot{W}_{net,in}} = \frac{\dot{m}(h_1 - h_4)}{\dot{m}(h_2 - h_1)} = \frac{h_1 - h_4}{h_2 - h_1} \\
 &= \frac{(238.41 - 101.61) \frac{kJ}{kg}}{(278.23 - 238.41) \frac{kJ}{kg}} \\
 &= 3.44
 \end{aligned}$$

The tons of refrigeration, often called the cooling load or refrigeration effect, are

$$\begin{aligned}
 \dot{Q}_L &= \dot{m}(h_1 - h_4) \\
 &= 3 \frac{kg}{min} (238.41 - 101.61) \frac{kJ}{kg} \frac{1Ton}{211 \frac{kJ}{min}} \\
 &= 1.94 Ton
 \end{aligned}$$

$$\begin{aligned}
 COP_{R,Carnot} &= \frac{T_L}{T_H - T_L} \\
 &= \frac{(-20 + 273) K}{(43.79 - (-20)) K} \\
 &= 3.97
 \end{aligned}$$

Refrigerator and Heat pump



Terminologies of Refrigeration

Refrigerating Effect (N): It is defined as the quantity of heat extracted from a cold body or space to be cooled in a given time.

$$N = \frac{\text{Heat extracted from the cold space}}{\text{Time taken}}$$

Specific Heat of water and ice : It is the quantity of heat required to raise or lower the temperature of one kg of water (or ice), through one kelvin or (1°C) in one second.

Specific heat of water, $C_{pw} = 4.19 \text{ kJ/kg K}$

Specific heat of ice, $C_{pice} = 2.1 \text{ kJ/kg K}$.

Terminologies of Refrigeration

Capacity of a Refrigeration Unit :

- Capacity of a refrigerating machines are expressed by their cooling capacity.
- The standard unit used for expressing the capacity of refrigerating machine is ton of refrigeration.
- One ton of refrigeration is defined as, “the quantity of heat abstracted (refrigerating effect) to freeze one ton of water into one ton of ice in a duration of 24 hours at 0° c”.

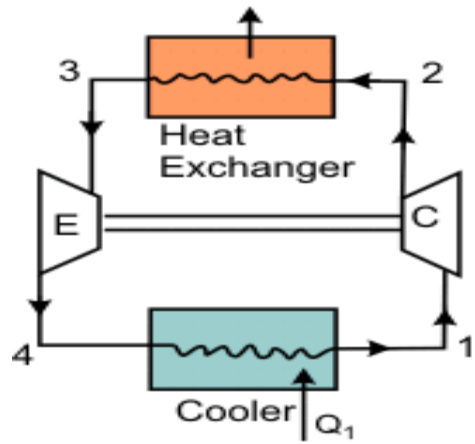
Heat extracted from at 0° c = latent heat of ice

Latent heat of ice = 336 kJ/kg

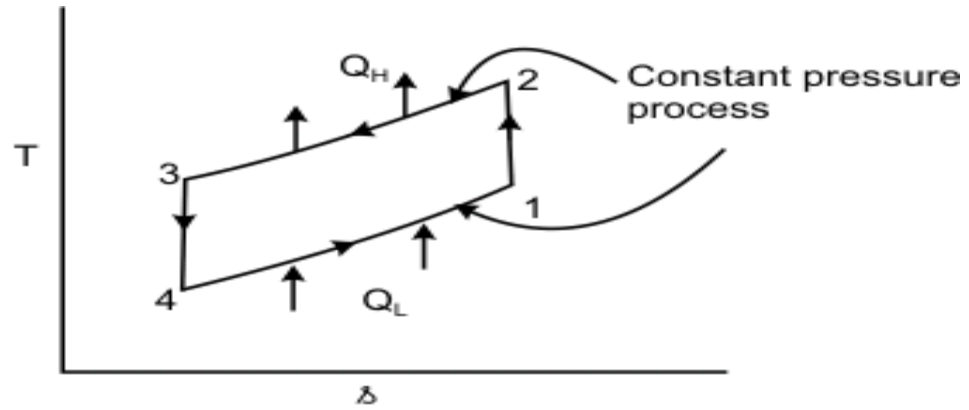
i.e., 336 kJ of heat should be extracted from one kg of water at 0° C to convert it into ice.

Terminologies of Refrigeration

$$\begin{aligned}\text{One ton of refrigeration} &= 336 \times 1000 \text{ kJ}/24 \text{ hrs.} \\ &= \frac{336 \times 1000 \text{ kJ}}{24 \times 60} \\ \text{One ton of refrigeration} &= 233.333 \text{ kJ}/\text{min} \\ &= 3.8889 \text{ kJ}/\text{sec}\end{aligned}$$



(a)



(b)