Thermodynamics

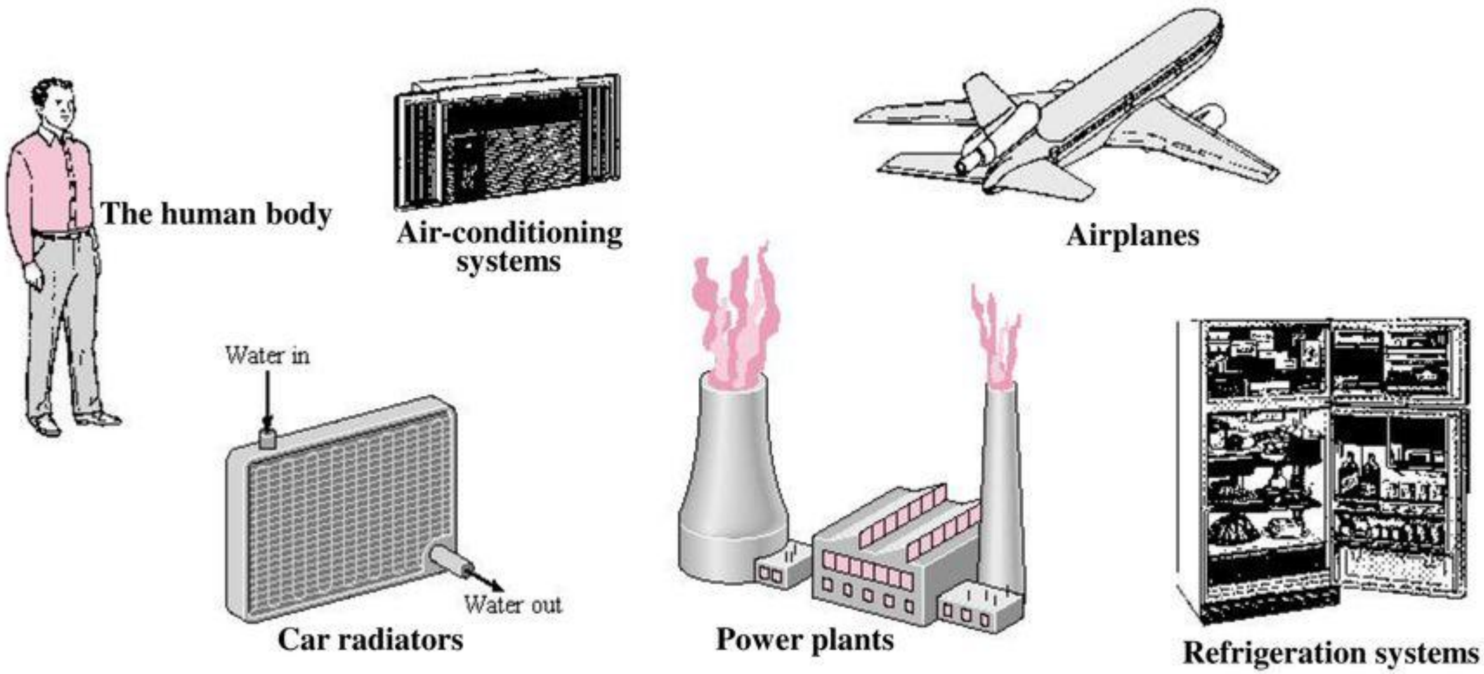
The name *thermodynamics* stems from the Greek words *therme* (heat) and *dynamis* (power), which is most descriptive of the early efforts to convert heat into power.

Today the same name is broadly interpreted to include all aspects of energy and energy transformations, including power generation, refrigeration, and relationships among the properties of matter.

One of the most fundamental laws of nature is the conservation of energy principle.

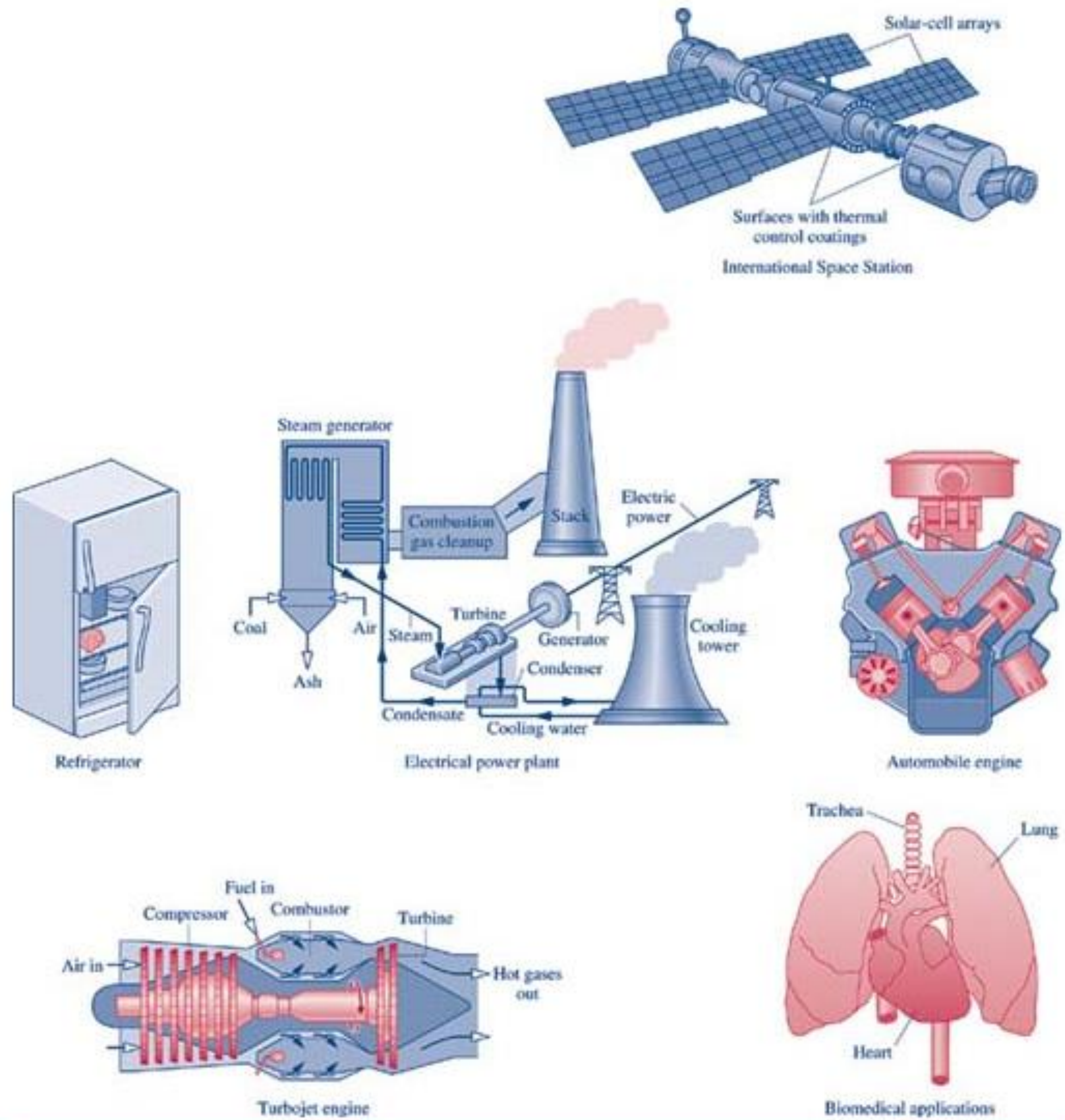
It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant.

Applications of Thermodynamics



Çengel
Boles
Thermodynamics
Third Edition

WCB/McGraw-Hill


Solar-cell arrays
Surfaces with thermal control coatings
International Space Station
Steam generator
Combustion gas cleanup
Stack
Electric power
Coal
Air
Steam
Ash
Turbine
Generator
Condenser
Cooling tower
Condensate
Cooling water
Refrigerator
Electrical power plant
Automobile engine
Trachea
Lung
Heart
Fuel in
Compressor
Combustor
Turbine
Air in
Hot gases out
Turbojet engine
Biomedical applications

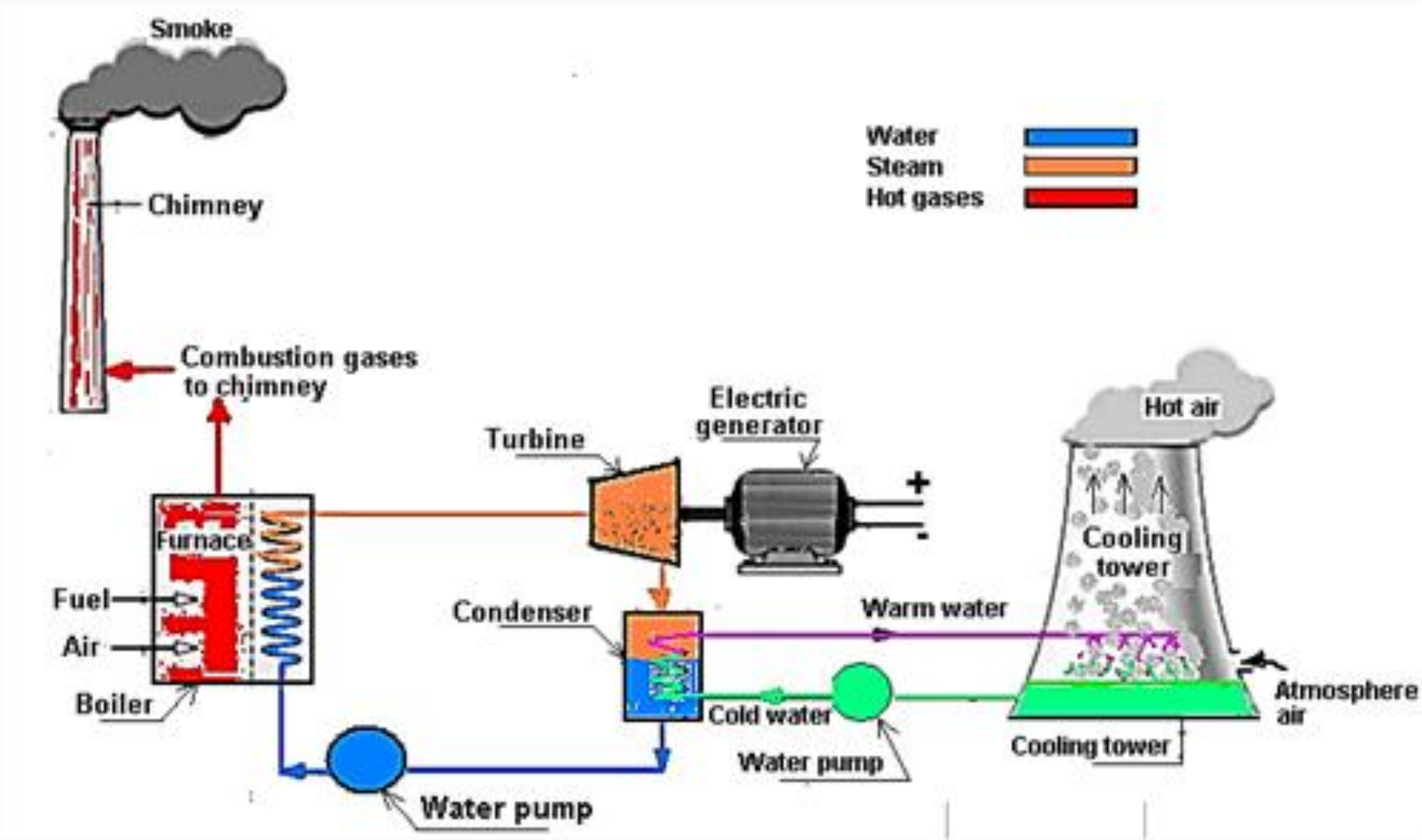


Fig. 11.1. Steam power plant

Crescent Dunes near Las Vegas, the blueprint for the new plant. Credit: Solar Reserve

- The study of thermodynamics is concerned with ways energy is stored within a body and how energy transformations, which involve heat and work, may take place.

- Approaches to studying thermodynamics
  - Macroscopic (Classical thermodynamics)
    - study large number of particles (molecules) that make up the substance in question
    - does not require knowledge of the behavior of individual molecules
  - Microscopic (Statistical thermodynamics)
    - concerned within behavior of individual particles (molecules)
    - study average behavior of large groups of individual particles

Macroscopic v/s Microscopic Approaches

Macroscopic Approach:

- In this approach a certain quantity of matter is considered without taking into account the events occurring at molecular level.
- The analysis of macroscopic system does not require knowledge of behaviour Individual particles.
- Macroscopic properties are effect of action of many particles or average value of large no of particles.
- This approach is followed in classical thermodynamics

Example. Tyre pressure measured at station

Microscopic Approach:

- Microscopic point of view system is made up of a very large number of discrete particles known as molecules and atoms.
- Microscopic approach require knowledge of behaviour Individual particles.
- Microscopic properties are effect of action of individual particle.
- This approach is followed in Statistical thermodynamics

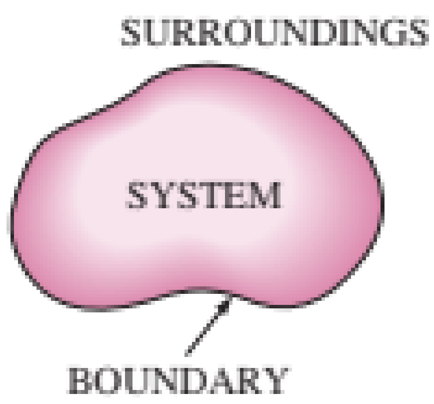
Example Properties of atoms

S. No.	*Macroscopic approach*	*Microscopic approach*
1.	In this approach a certain quantity of matter is considered *without* taking into account the events occurring at molecular level. In other words this approach to thermodynamics is concerned with *gross or overall behaviour*. This is known as *classical thermodynamics*.	The approach considers that the system is made up of a very large number of discrete particles known as *molecules*. These molecules have different velocities and energies. The values of these energies are constantly changing with time. This approach to thermodynamics which is concerned directly with the *structure of the matter* is known as *statistical thermodynamics*.
2.	The analysis of macroscopic system requires simple mathematical formulae.	The behaviour of the system is found by using statistical methods as the number of molecules is very large. So advanced statistical and mathematical methods are needed to explain the changes in the system.
3.	The values of the properties of the system are their average values. For example, consider a sample of a gas in a closed container. The *pressure* of the gas is the average value of the pressure exerted by millions of individual molecules. Similarly the *temperature* of this gas is the average value of translational kinetic energies of millions of individual molecules. These properties like *pressure* and *temperature* can be measured very easily. *The changes in properties can be felt by our senses.*	The properties like *velocity, momentum*, impulse, kinetic energy, force of impact etc. which describe the molecule *cannot be easily measured by instruments. Our senses cannot feel them.*
4.	In order to describe a system only a few properties are needed.	Large number of variables are needed to describe a system. So the approach is complicated.

SYSTEMS AND CONTROL VOLUMES

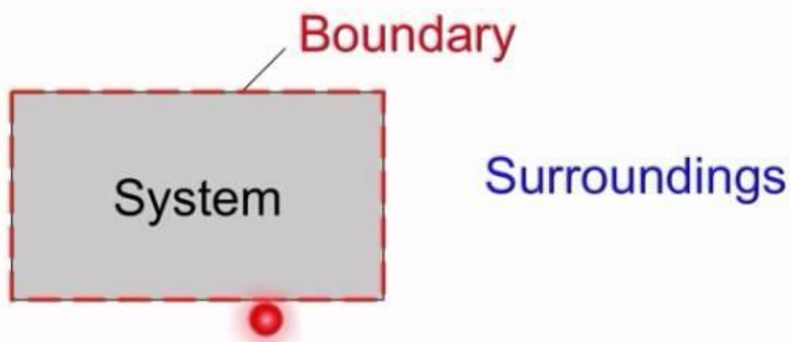
A system is defined as a ***quantity of matter*** *or a region in space chosen for study*. The mass or region outside the system is called the **surroundings.**

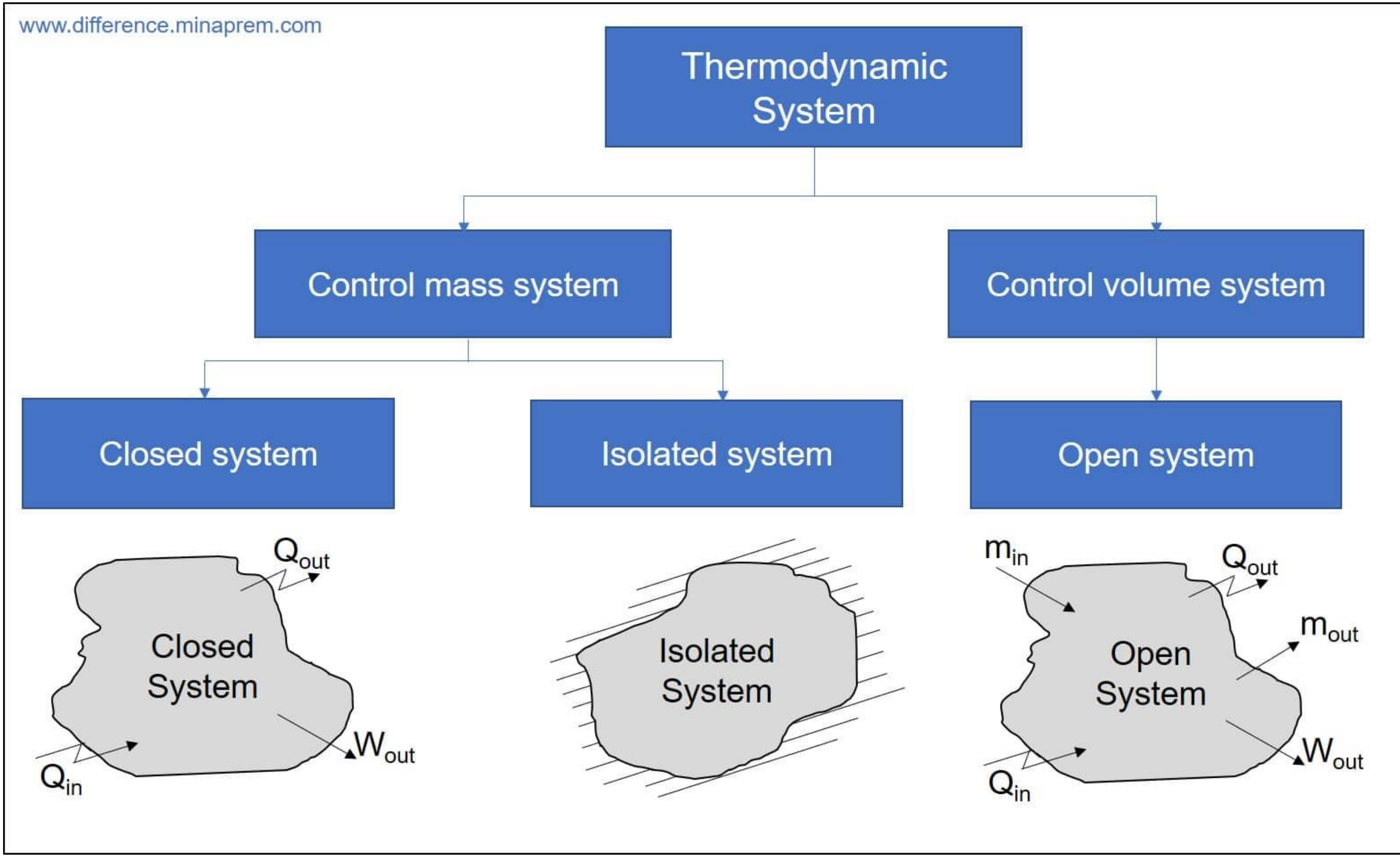
The real or imaginary surface that separates the system from its surroundings is called the **boundary.**



Defining Systems

- System: whatever we want to study.
- Surroundings: everything external to the system.
- Boundary: distinguishes system from its surroundings.





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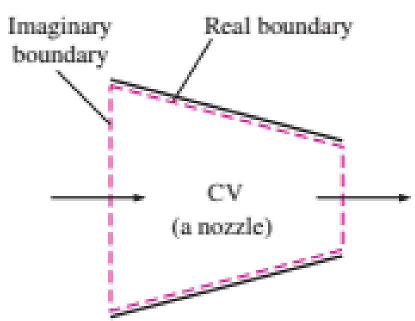
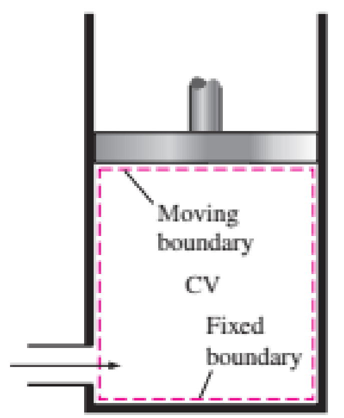
Thermodynamic System
Control mass system
Control volume system
Closed system
Isolated system
Open system
Q_{out}
Closed System
W_{out}
Q_{in}
Isolated System
m_{in}
Q_{out}
m_{out}
Open System
W_{out}
Q_{in}

Thermodynamic systems

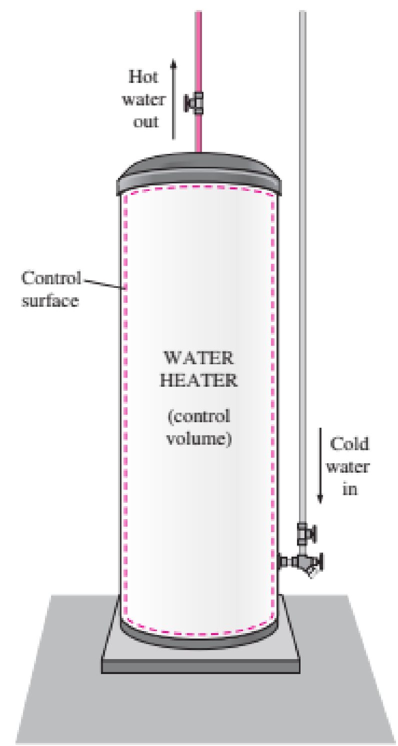
An **open system,** or a **control volume,** as it is often called, is a properly selected region in space. An open system is one in which *matter flows into or out of the system*. Most of the engineering systems are open.

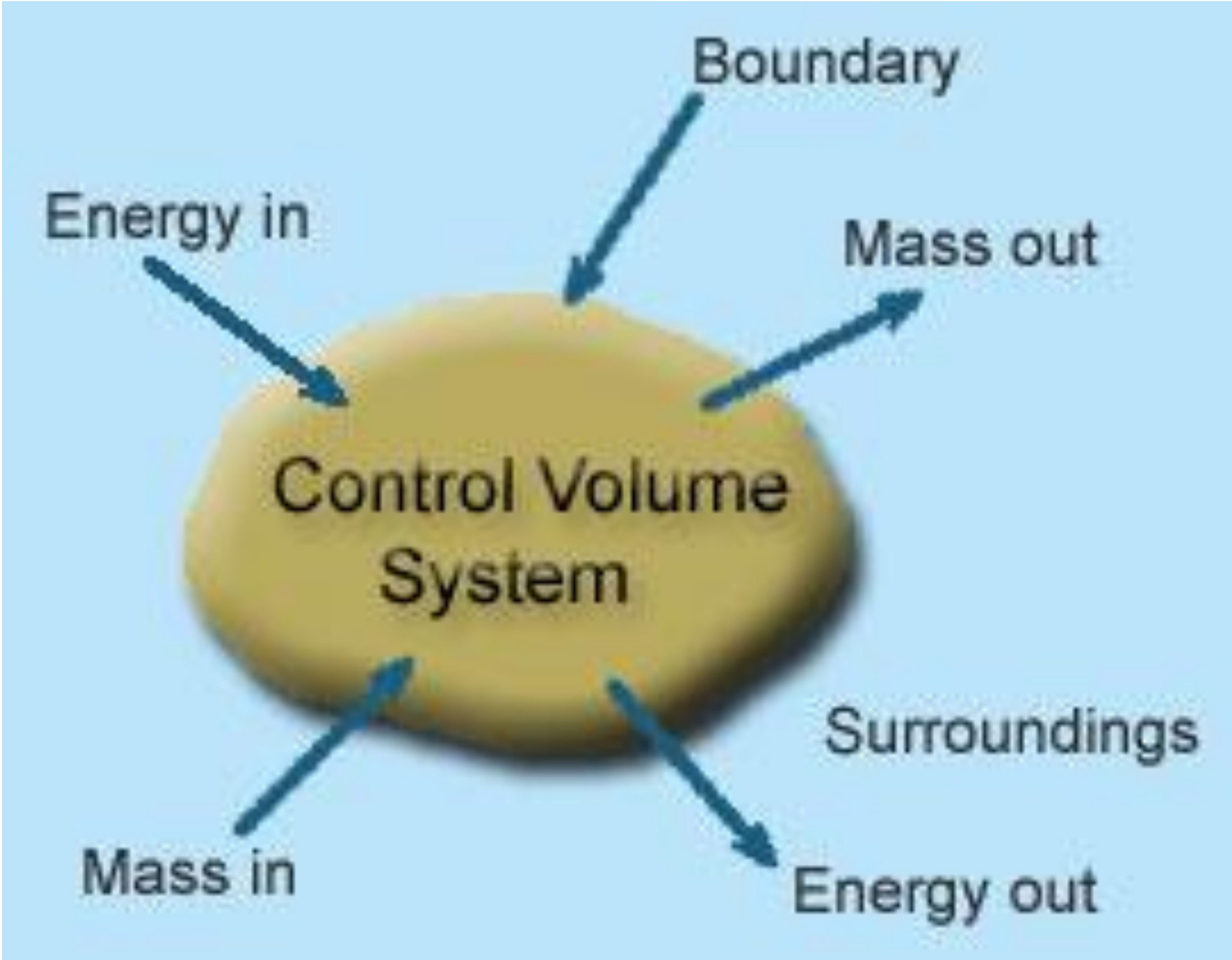


(*a*) A control volume with real and imaginary boundaries



(*b*) A control volume with fixed and moving boundaries

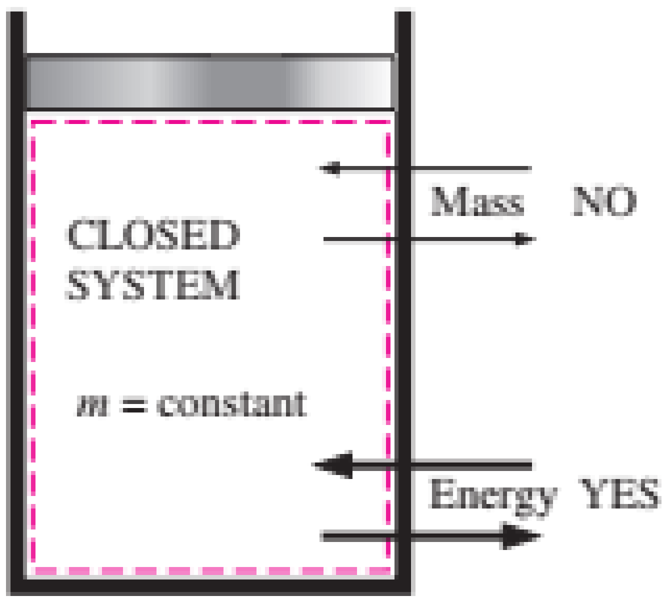



Boundary
Energy in
Mass out
Control Volume
System
Surroundings
Mass in
Energy out

Thermodynamic systems

Systems may be considered to be *closed* or *open*, depending on whether a fixed mass or a fixed volume in space is chosen for study.

A **closed system** (also known as a **control mass**) consists of a fixed amount of mass, and no mass can cross its boundary. That is, no mass can enter or leave a closed system



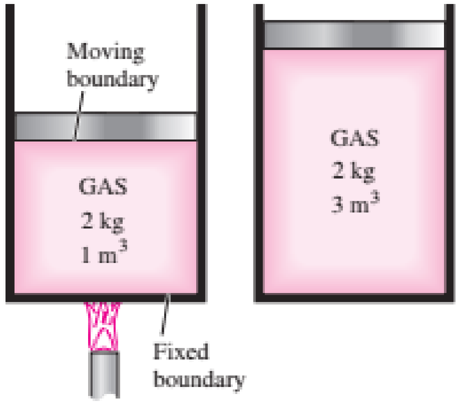
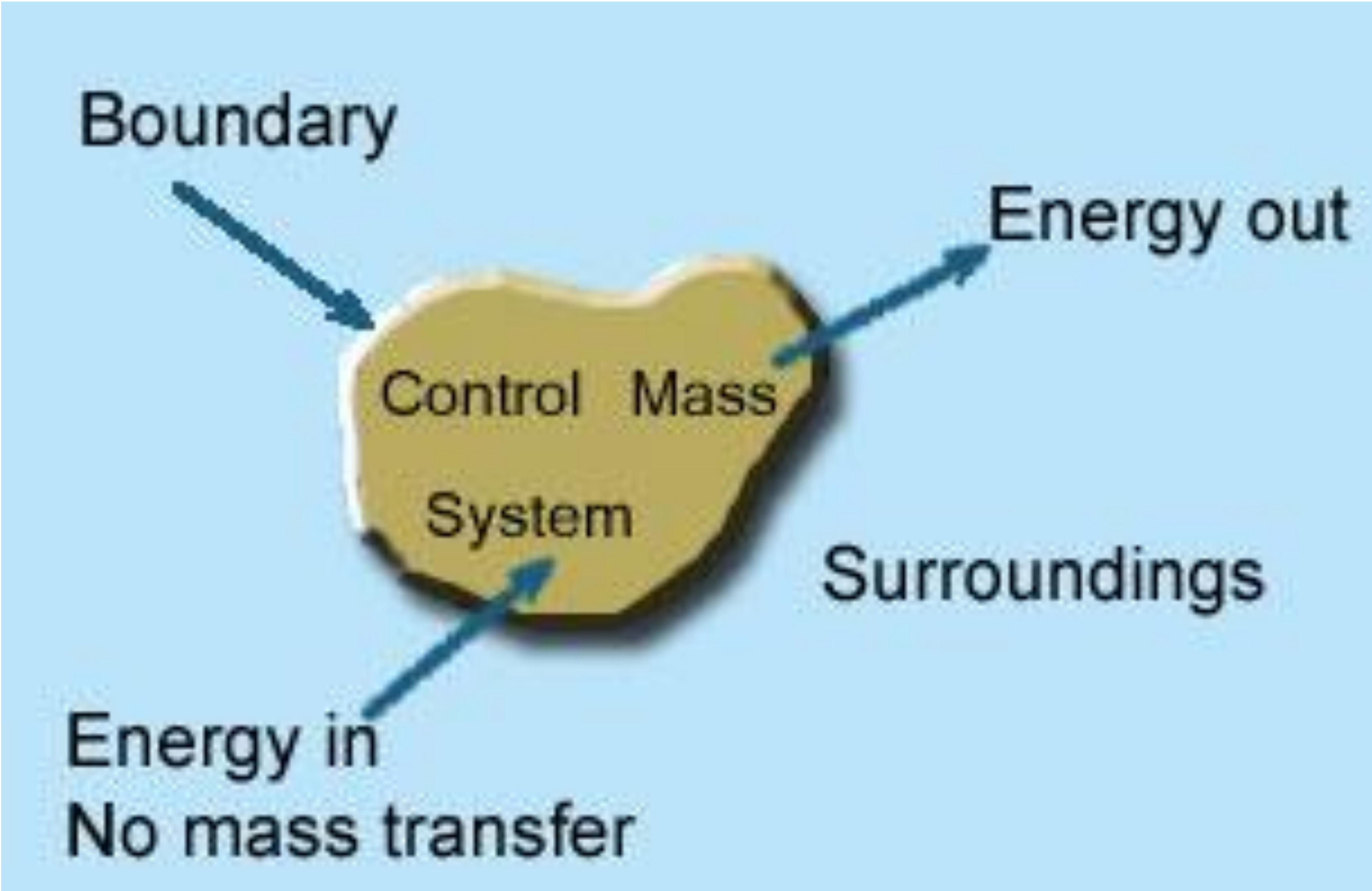
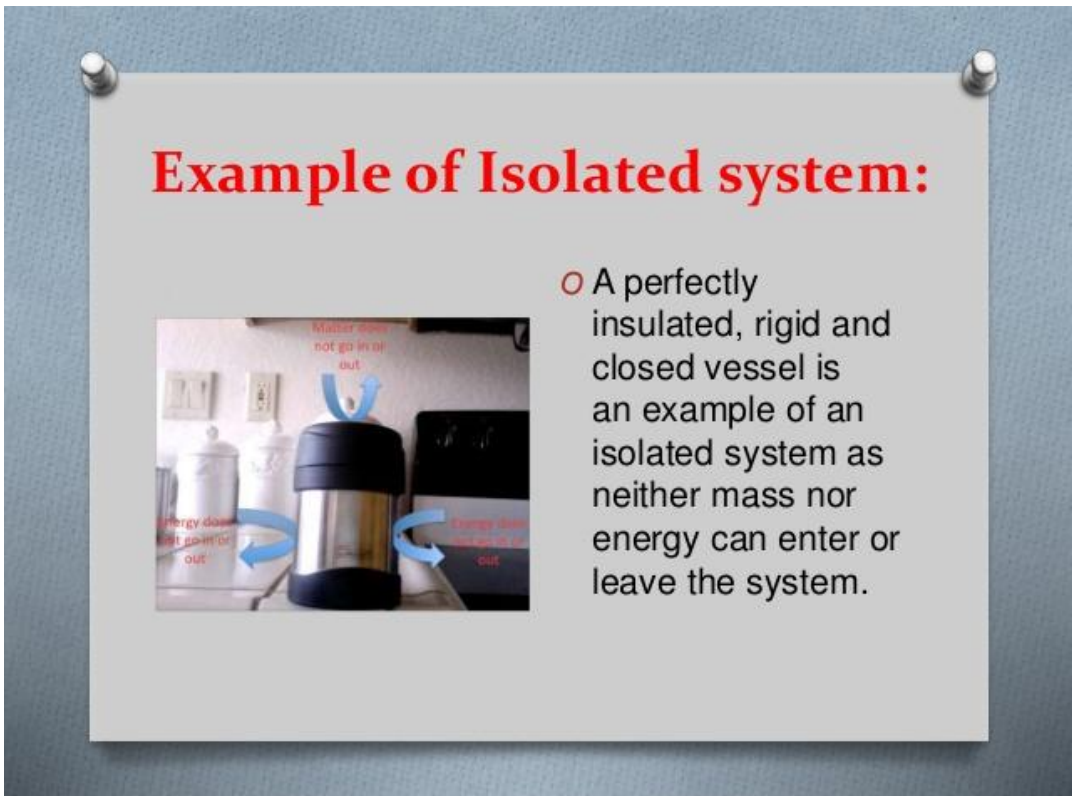


FIGURE 1–17
A closed system with a moving boundary.


Boundary
Energy out
Control Mass
System
Surroundings
Energy in
No mass transfer

Isolated System

An isolated system is that system *which exchanges neither energy nor matter with any other system or with environment*.



What is Thermodynamic System? – Open, Closed & Isolated (With Examples)

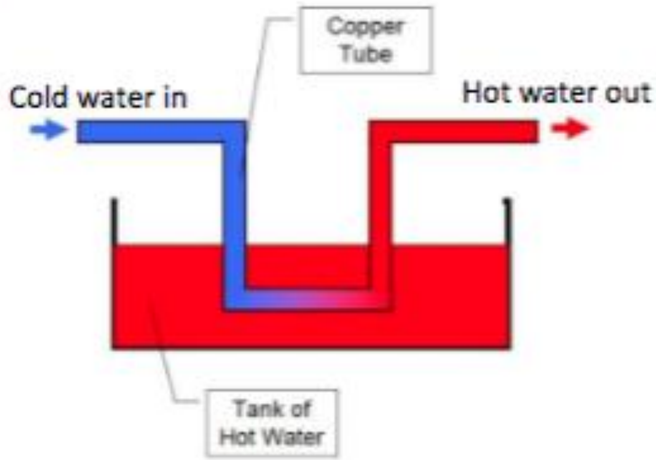
Open system
Mass transfer (yes)
Heat transfer (yes)

Closed system
Mass transfer (yes)
Heat transfer (No)

Isolated system
Mass transfer (No)
Heat transfer (No)

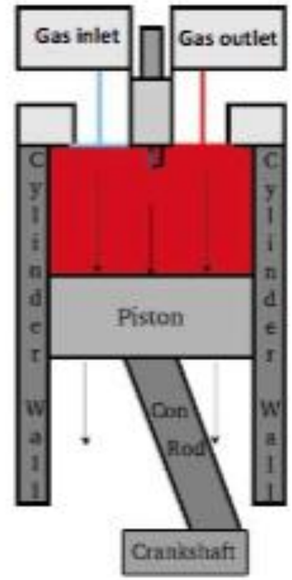
2. Identify whether the following are open (control volume), closed (control mass) or isolated systems. Please provide reasoning for your choice.

(a)



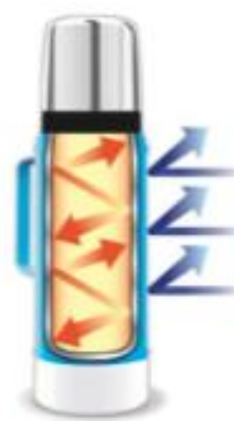
(b)

Both valves are closed



(c)

(d)



Perfectly insulated thermos with hot coffee inside

PROPERTIES OF A SYSTEM

Any characteristic of a system is called a **property.** Some familiar properties are pressure P, temperature T, volume V, and mass m.

The list can be extended to include less familiar ones such as viscosity, thermal conductivity, modulus of elasticity, thermal expansion coefficient, electric resistivity, and even velocity and elevation.

Properties are considered to be either *intensive* or *extensive*

1. **Intensive properties.** These properties *do not depend on the mass of the system*.

Examples : Temperature and pressure

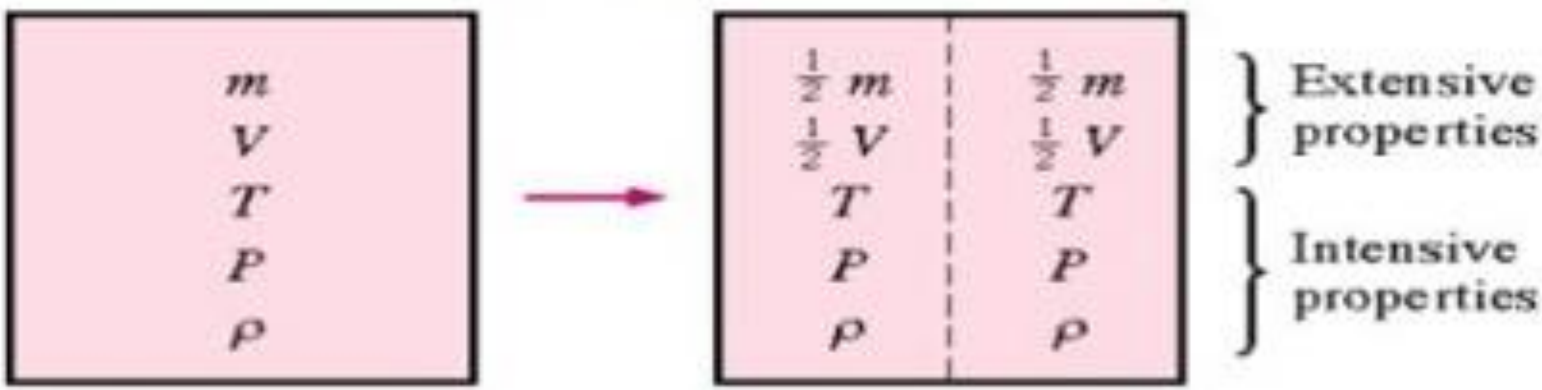
2. **Extensive properties.** These properties *depend on the mass of the system*. *Example* : Volume. Extensive properties are often divided by mass associated with them to obtain the intensive properties. For example, if the volume of a system of mass m is V, then the specific volume of matter within the system is $V/m = v$ which is an intensive property.

Properties of a system

Properties of a system is a measurable characteristic of a system that is in equilibrium.
Properties may be intensive or extensive.

- **Intensive – Are independent of the amount of mass:**
e.g: Temperature, Pressure, and Density,

- **Extensive – varies directly with the mass**
e.g: mass, volume, energy, enthalpy



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Thermodynamic Property

Intensive property

(Independent of mass of the system)

1. Pressure
2. Temperature
3. Density
4. Concentration
5. Melting point
6. Boiling point
7. Surface tension
8. Viscosity, etc.

Extensive property

(depends on the mass of the system)

1. Mass
2. Volume
3. Internal energy
4. Heat capacity
5. Enthalpy
6. Entropy
7. Helmholtz energy
8. Gibbs energy, etc.

INTENSIVE PROPERTIES

- Chemical potential
- Concentration
- Density (or specific gravity)
- Ductility
- Elasticity
- Hardness
- Melting point and boiling point
- Pressure
- Specific energy
- Specific heat capacity
- Specific volume
- Spectral absorption maxima (in solution)
- Temperature
- Viscosity

EXTENSIVE PROPERTY

- Energy
- Entropy
- Gibbs energy
- Length
- Mass
- particle number
- number of moles
- Volume
- electrical charge
- Weight

THERMODYNAMIC EQUILIBRIUM

- A system is in *thermodynamic equilibrium* if the temperature and pressure at all points are same ; there should be no velocity gradient ; the chemical equilibrium is also necessary.
- Systems under temperature and pressure equilibrium but not under chemical equilibrium are sometimes said to be in meta stable equilibrium conditions.

It is only under thermodynamic equilibrium conditions that ***the properties of a system can be fixed.***

Thus for attaining a state of *thermodynamic equilibrium* the following *three* types of **equilibrium states** must be achieved :

Thermodynamic equilibrium

For attaining a state of thermodynamic equilibrium, the following three types of equilibrium states must be achieved.

1. **Thermal Equilibrium:** The temperature of the system does not change with time and has same value at all points of the system.

2. **Mechanical Equilibrium:** There are no unbalanced forces within the system or between the surroundings. The pressure in the system is same at all points and does not change with respect to time.

1. **Chemical Equilibrium:** No chemical reaction takes place in the system and the chemical composition which is same throughout the system does not vary with time.

Thermal equilibrium

- The temperature of the system does not change with time and has same value at all points of the system.

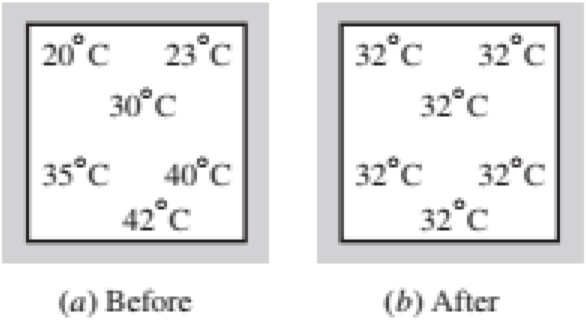


FIGURE 1–24

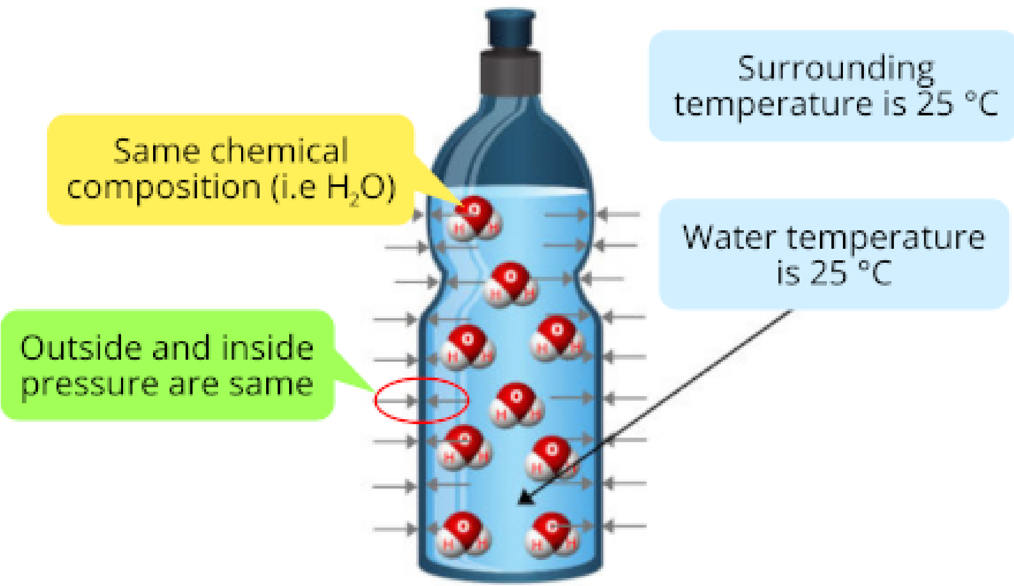
A closed system reaching thermal equilibrium.

Mechanical equilibrium. There are no unbalanced forces within the system or between the surroundings. The pressure in the system is same at all points and does not change with respect to time.

Chemical equilibrium. No chemical reaction takes place in the system and the chemical composition which is same throughout the system does not vary with time.

What is Thermodynamic Equilibrium?

"Two systems are said to be in thermodynamic equilibrium when they are in thermal, mechanical and chemical equilibrium with each other"



Thermal equilibrium, because water temperature and surrounding temperature are same (i.e 25 °C)

Mechanical equilibrium, because outside pressure and inside pressure are same

Chemical equilibrium, because chemical composition of water is same in entire bottle (i.e H_2O)

Explanation:

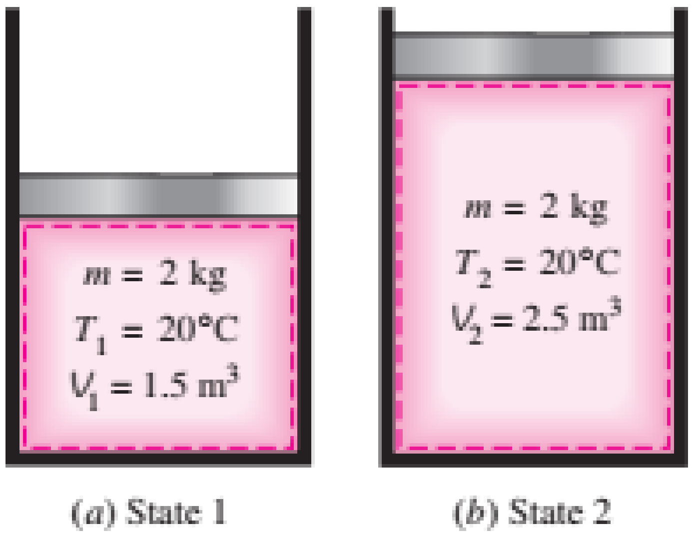
1). The temperature of water is 25 °C and the temperature of surrounding air is also 25 °C. Thus the water is in thermal equilibrium with the surrounding air.

2). All the water molecules exerts equal pressure on each other as well as on the walls of

STATE

Consider a system not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition, or the **state,** of the system.

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



PROCESSES AND CYCLES

Any change that a system undergoes from one equilibrium state to another is called a **process**, and the series of states through which a system passes during a process is called the **path** of the process

To describe a process completely, one should specify the **initial and final states** of the process, as well as the path it follows, and the interactions with the surroundings.

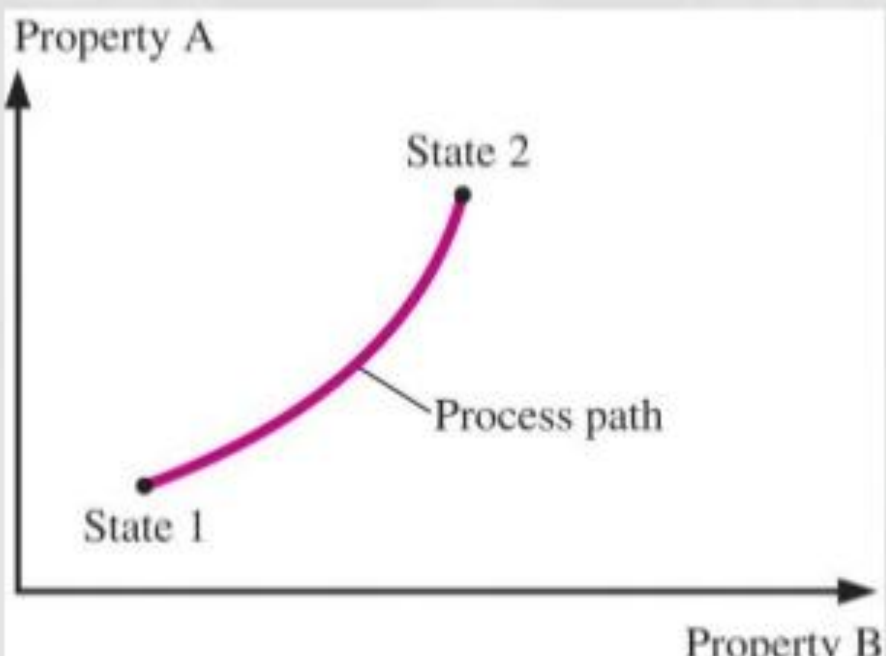
PROCESSES AND CYCLES

Process: Any change that a system undergoes from one equilibrium state to another.

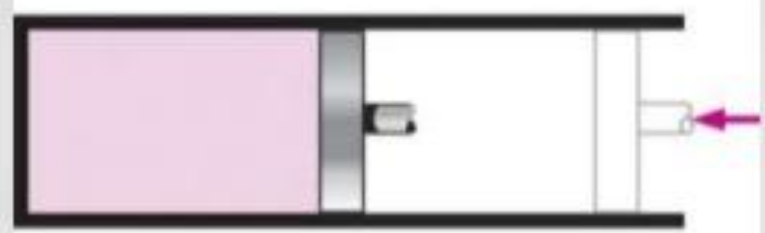
Path: The series of states through which a system passes during a process.

To describe a process completely, one should specify the initial and final states, as well as the path it follows, and the interactions with the surroundings.

Quasistatic or quasi-equilibrium process: When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times.



(*a*) Slow compression (quasi-equilibrium)

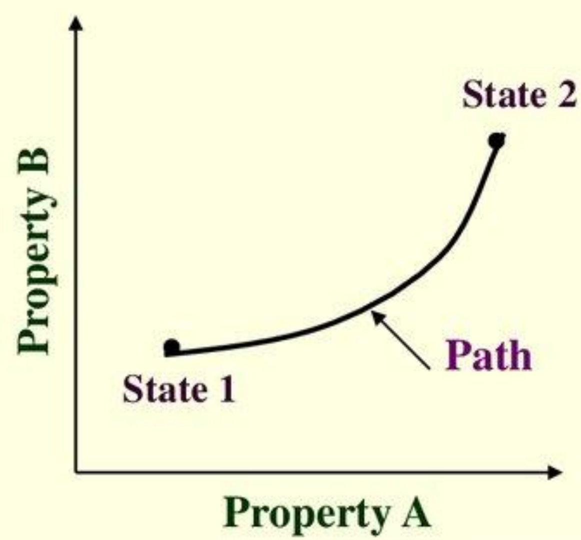


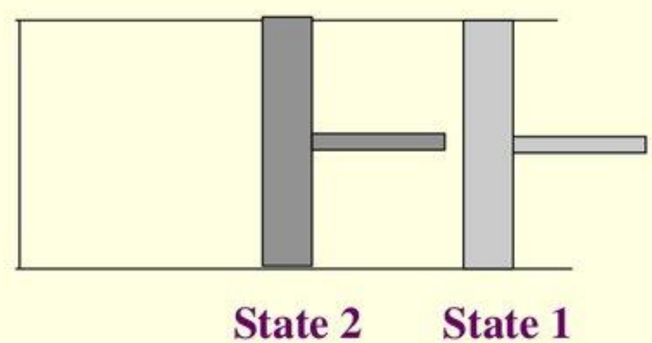
(*b*) Very fast compression (nonquasi-equilibrium)

Path & Process

Any change a system undergoes from one equilibrium state to another is known as PROCESS.

Series of states through which system passes during the process is known as its PATH.





- Process
  - when a system changes from one equilibrium state to another one
  - some special processes:
    - isobaric process - constant pressure process
    - isothermal process - constant temperature process
    - isochoric process - constant volume process
    - isentropic process - constant entropy process
- Path
  - series of states which a system passes through during a process

Thermodynamic Process

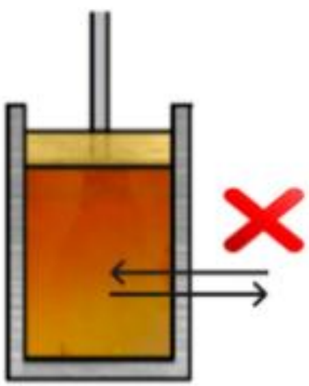
Isobaric process

Thermodynamic process in which the pressure remains constant is known as *isobaric process*.

Isochoric process

Thermodynamic process in which the volume remains constant is called *isochoric process*.

Adiabatic process

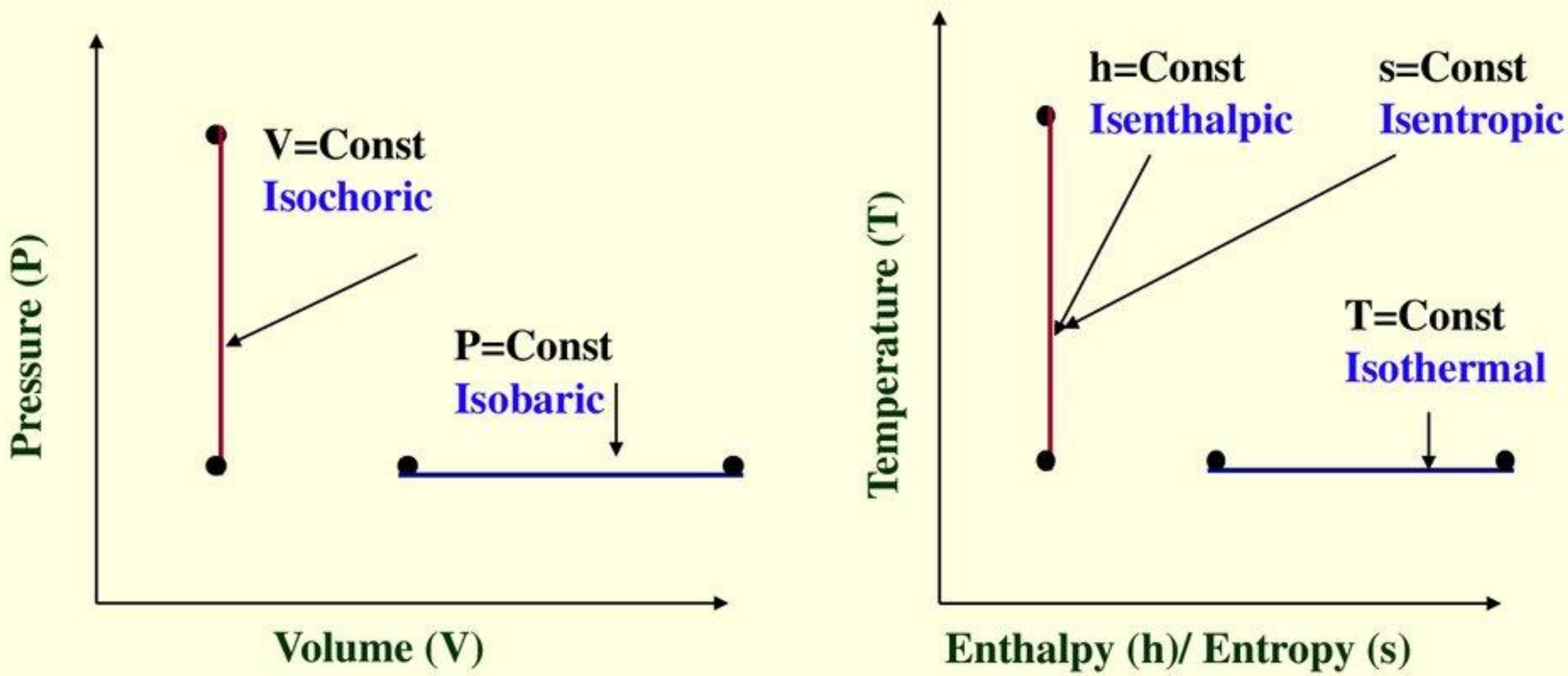


Thermodynamic process in which there is no heat transfer involved is called *adiabatic process*.

Isothermal process

The process in which the temperature remains constant is known as *Isothermal process.*

Path & Process



Any process or series of processes whose end states are identical is termed a **cycle**. The processes through which the system has passed can be shown on a state diagram, but a complete section of the path requires in addition a statement of the **heat and work crossing the boundary** of the system. Fig. 2.6 shows such a cycle in which a system commencing at condition '1' changes in pressure and volume through a path 123 and returns to its initial condition '1'.

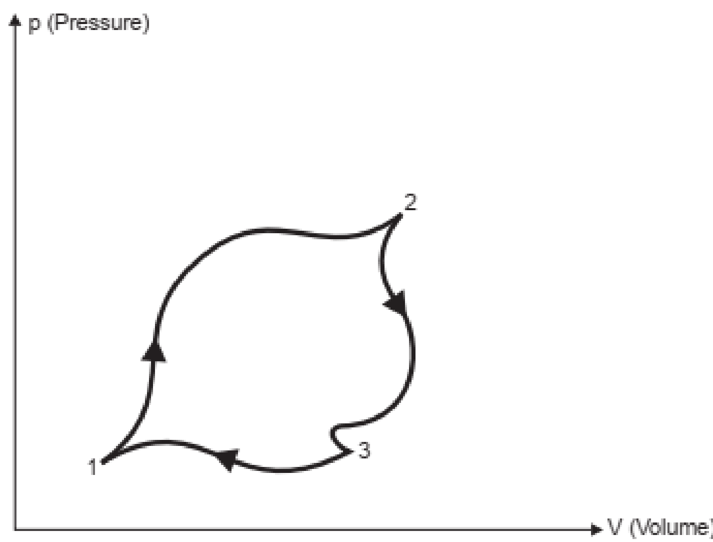


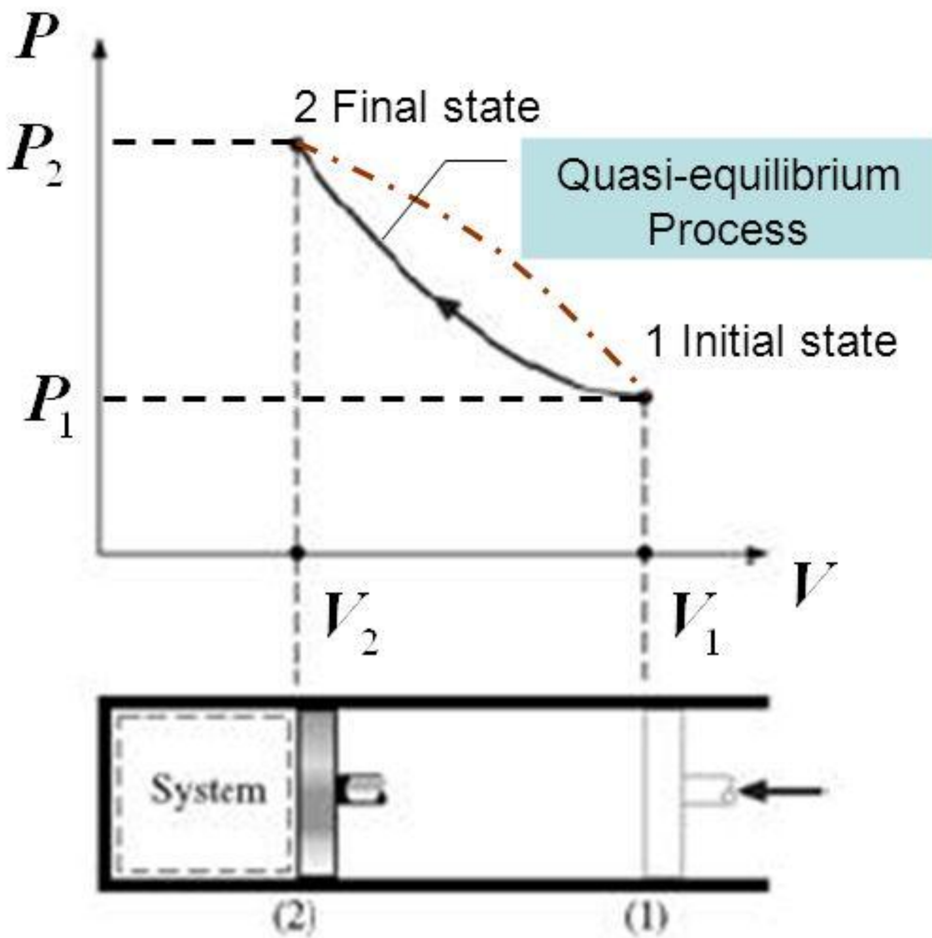
Fig. 2.6. Cycle of operations.

Quasi-equilibrium process

When a process proceeds in such a manner that the **system remains infinitesimally close** to an equilibrium state at all times, it is called a **quasistatic, or quasi-equilibrium, process.**

A quasi-equilibrium process can be viewed as a **sufficiently slow process** that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

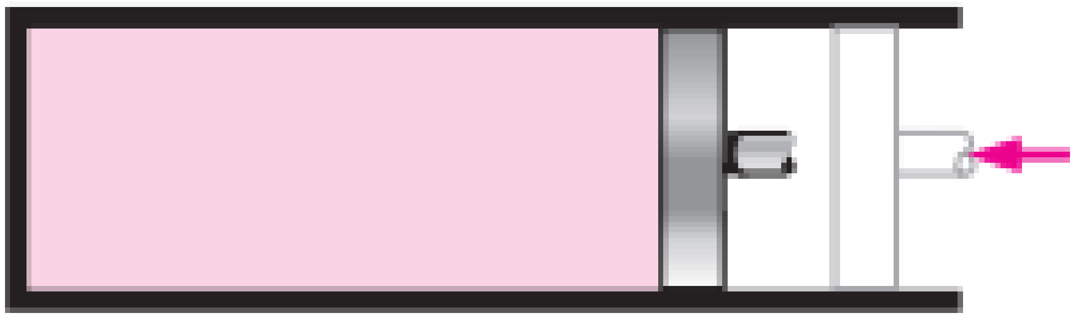
Quasi-Equilibrium Process



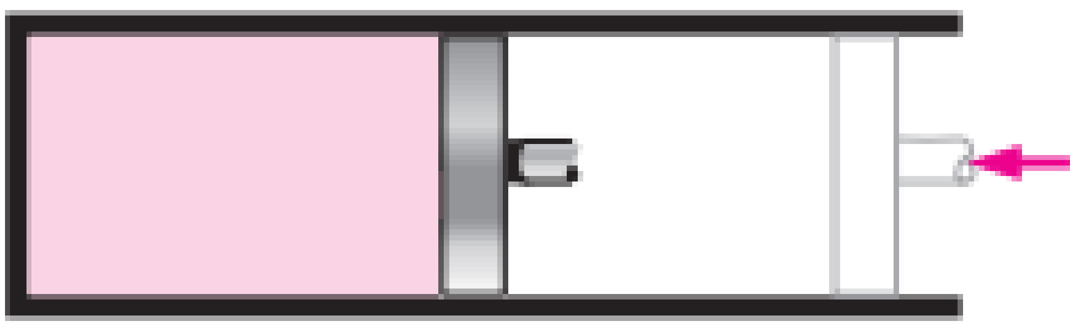
System remains infinitesimally close to an equilibrium state at all times.

Process occurs slow enough to keep the properties identical throughout the system.
The interval of process change takes much longer time than system spontaneously adjusts to a new state after the previous equilibrium state was destroyed.

To connect states with line must be QE process.

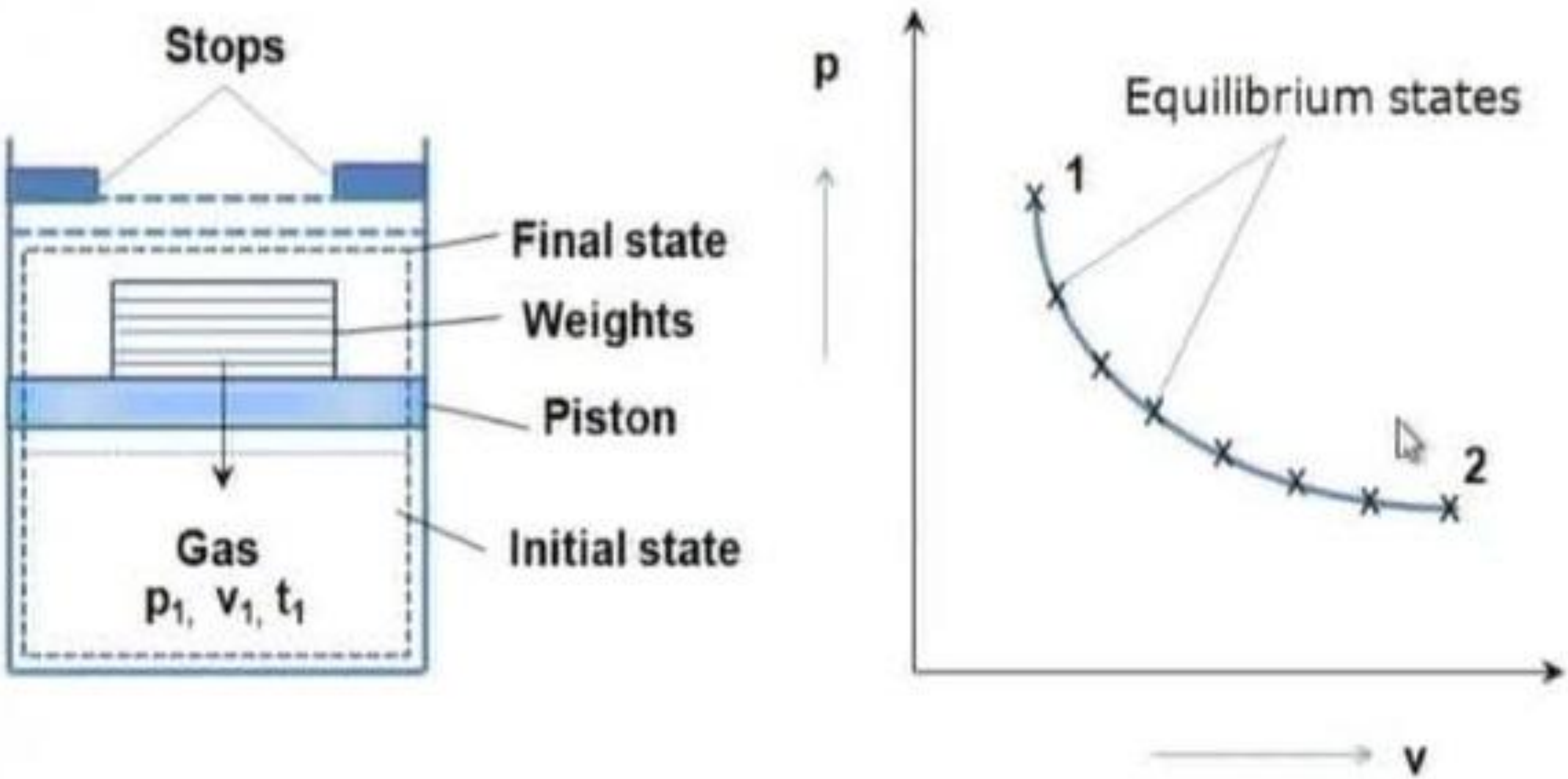


(*a*) Slow compression
(quasi-equilibrium)



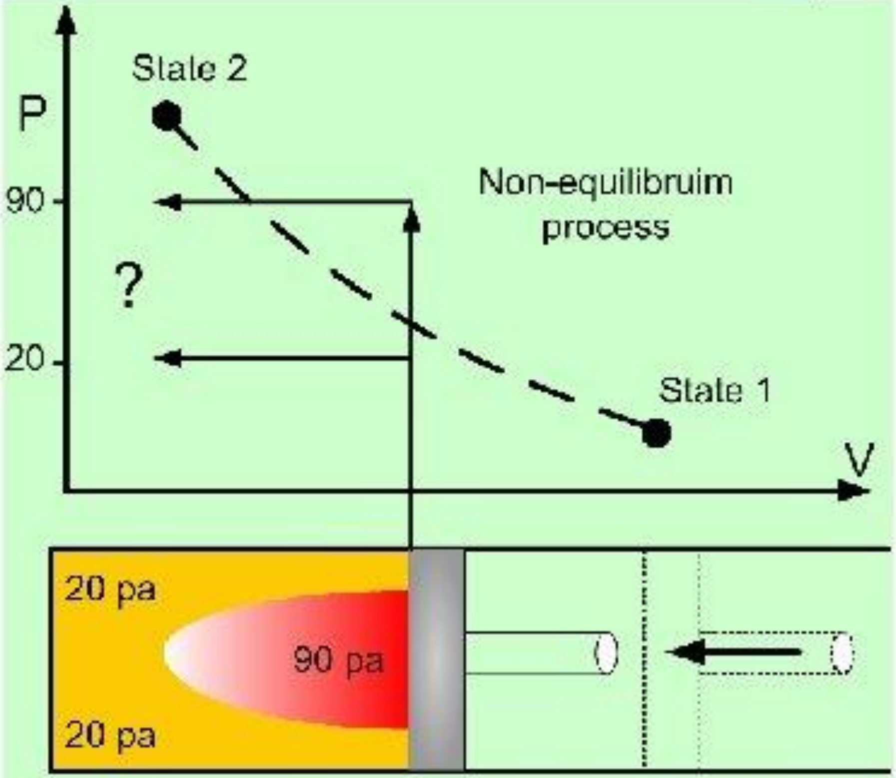
(*b*) Very fast compression
(nonquasi-equilibrium)

Quasi-static processes

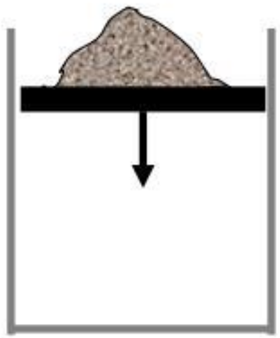


Non-Quasi-Equilibrium process

- Compression process is fast and thus equilibrium can not be attained.
- Intermediate states can not be determined and the process path can not be defined. Instead we represent it as dashed line.



(b) Fast compression (non quasi-equilibrium)



Quasi-Static Processes

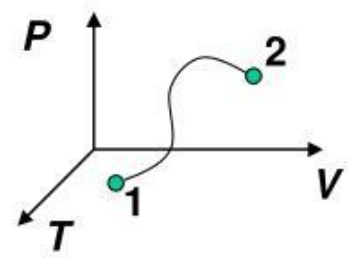
Quasi-static (quasi-equilibrium) processes – sufficiently slow processes, *any* intermediate state can be considered as an equilibrium state (the macroparamers are well-defined for all intermediate states).

Advantage: the state of a system that participates in a quasi-equilibrium process can be described with the ***same (small) number of macro parameters*** as for a system in equilibrium (e.g., for an ideal gas in quasi-equilibrium processes, this could be $\boldsymbol{T}$ and $\boldsymbol{P}$). By contrast, for ***non-equilibrium processes*** (e.g. turbulent flow of gas), we need a ***huge number of macro parameters***.

***Examples of quasi-equilibrium processes*:**

- isochoric: V = const
- isobaric: P = const
- isothermal: T = const
- adiabatic: Q = 0

For quasi-equilibrium processes, ***P***, ***V***, ***T*** are ***well-defined*** – the "path" between two states is a *continuous lines* in the ***P, V, T*** space.



POINT FUNCTION

When two properties locate a point on the graph (co-ordinate axes) then those properties are called as **point function.**

Examples. Pressure, temperature, volume etc.

$$\int_1^2 dV = V_2 - V_1 \ (\text{an } \textit{exact differential}).$$

PATH FUNCTION

There are certain quantities which cannot be located on a graph by a *point* but are given by the *area* or so, on that graph. In that case, the area on the graph, pertaining to the particular process, *is a function of the path of the process.* Such quantities are called **path functions.** *Examples*. Heat, work etc.

Heat and work are *inexact differentials*. Their change cannot be written as difference between their end states.

Thus $\int_1^2 \delta Q \neq Q_2 - Q_1$ and is shown as $_1Q_2$ or Q_{1-2}

Similarly $\int_1^2 \delta W \neq W_2 - W_1$, and is shown as $_1W_2$ or W_{1-2}

Note. The operator δ is used to denote inexact differentials and operator d is used to denote exact differentials.

Point Function	Path Function
Its values are based on the state of the system (i.e. pressure, volume, temperature etc.)	Its values are based on how that particular thermodynamic state is achieved.
No matter by which process the state is obtained, its values will always remain the same.	Different processes to obtain a particular state will give us different values.
Only initial and final states of the process are sufficient	We need to know exact path followed by the process
Its values are independent of the path followed	Its values are dependent on the path followed
It is an exact or perfect differential	It is an inexact or imperfect differential.
Its cyclic integral is always zero	Its cyclic integral may or may not be zero
It is property of the system	It is not the property of the system
Its examples are density, enthalpy, internal energy, entropy etc.	Its examples are Heat, work etc.

REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible process. *A reversible process (also sometimes known as quasi-static process) is one which can be stopped at any stage and reversed so that the system and surroundings are exactly restored to their initial states*.

This process has the following *characteristics* :

1. It must pass through the same states on the reversed path as were initially visited on the forward path.
2. This process when undone will leave no history of events in the surroundings.
3. It must pass through a continuous series of equilibrium states.

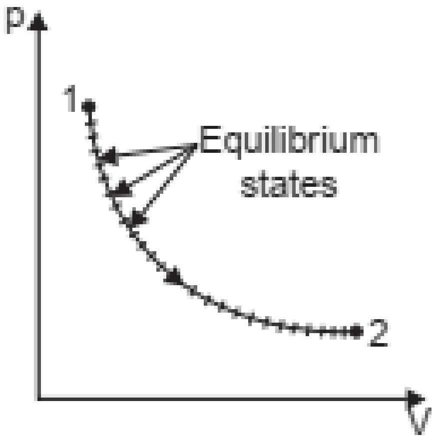


Fig. 2.29. Reversible process.

*REVERSIBLE AND IRREVERSIBLE PROCESSES

- A **reversible process** is defined as a *process that can be reversed without leaving any trace on the surroundings* . That is, both the system *and* the surroundings are returned to their initial states at the end of the reverse process.
- Processes that are not reversible are called **irreversible processes.**
- The factors that cause a process to be irreversible are called **irreversibilities**. They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions. The presence of any of these effects renders a process irreversible.

No real process is truly reversible but some processes may approach reversibility, to close approximation .

Examples. Some examples of nearly reversible processes are :

(*i*) Frictionless relative motion.

(*ii*) Expansion and compression of spring.

(*iii*) Frictionless adiabatic expansion or compression of fluid.

(*iv*) Polytropic expansion or compression of fluid.

(*v*) Isothermal expansion or compression.

(*vi*) Electrolysis.

Irreversible process. An *irreversible process* is one *in which heat is transferred through a finite temperature.*

Examples.

(*i*) Relative motion with friction

(*ii*) Combustion

(*iii*) Diffusion

(*iv*) Free expansion

(*v*) Throttling

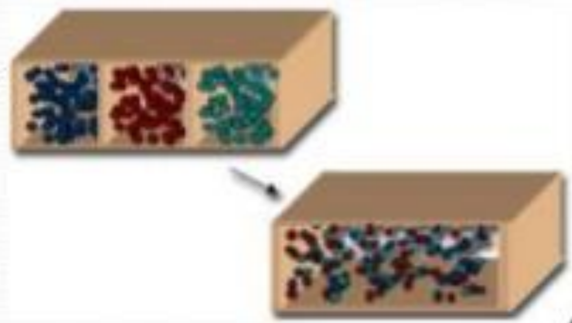
(*vi*) Electricity flow through a resistance

(*vii*) Heat transfer

(*viii*) Plastic deformation.

Irreversible Process

- The factors that cause a process to be Irreversible are :
  i. Friction
  ii. Free Expansion
  iii. Mixing of two gases
  iv. Heat transfer between finite temperature difference
  v. Electric resistance
  vi. Inelastic deformation
  vii. Chemical reactions
- The presence of any of these effects makes a process irreversible.



SPECIFIC VOLUME

The *specific volume* of a system is the volume occupied by the unit mass of the system. The symbol used is *v* and units are ; for example, m^3/kg. The symbol *V* will be used for volume. (Note that specific volume is *reciprocal of density*).

Note: *Specific Volume*

The specific volume of a substance is the ratio of the substance's volume to its mass. It is the reciprocal of density and is an intrinsic property of matter.

$$v - Specific\,Volume\ {}^{m^3}/_{Kg}$$

$$\nu = \frac{V}{m} = \rho^{-1}$$

Substance Name	Density	Specific Volume
	Kg/m³	m³/Kg
Air	1.2	0.83
Ice	916.7	0.00109
Water (liquid)	1000	0.00100
Salt Water	1030	0.00097
Mercury	13546	0.00007

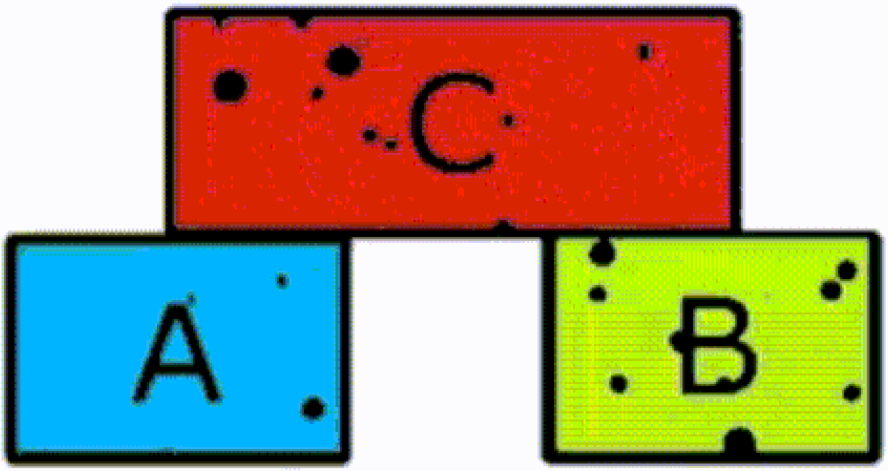
TEMPERATURE AND THE ZEROTH LAW OF THERMODYNAMICS

•*The temperature is a thermal state of a body which distinguishes a hot body from a cold body*.

•The temperature of a body is *proportional to the stored molecular energy i.e.*, the average molecular kinetic energy of the molecules in a system. (A particular molecule does not have a temperature, it has energy. The gas as a system has temperature).

•Instruments for measuring *ordinary temperatures* are known as ***thermometers*** and those for measuring *high temperatures* are known as ***pyrometers*****.**

Zeroth law of Thermodynamics



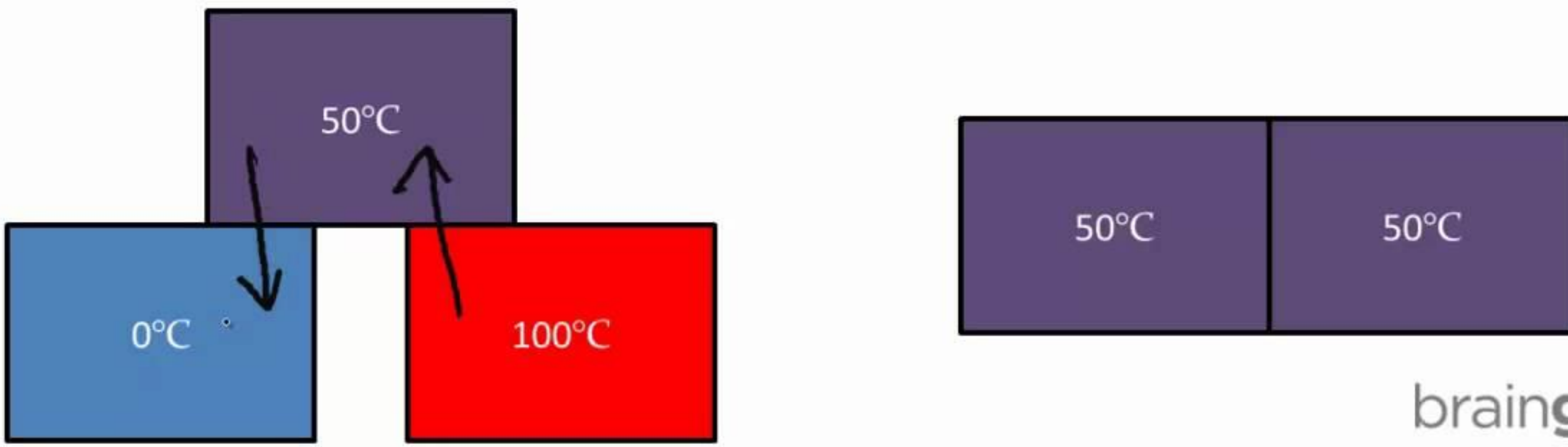
Zeroth law of thermodynamics statement:

"If two bodies A and B are in thermal equilibrium with third body C, then body A and B are also in thermal equilibrium with each other."

For example, in the above animation, you can see that body A and body B are

The Zeroth Law of Thermodynamics (the law of thermal equilibrium)

The Zeroth Law of Thermodynamics states that heat will always flow in a direction from hot objects to colder ones, but never the other way around.



braingenie

It is a common experience that a cup of hot coffee left on the table eventually cools off and a cold drink eventually warms up. That is, when a body is brought into contact with another body that is at a different temperature, heat is transferred from the body at higher temperature to the one at lower temperature until both bodies attain the same temperature (Fig. 1–31).

At that point, the heat transfer stops, and the two bodies are said to have reached **thermal equilibrium.** The equality of temperature is the only requirement for thermal equilibrium.

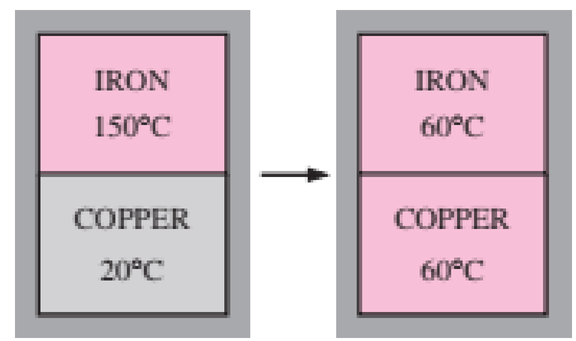


FIGURE 1–31

Two bodies reaching thermal equilibrium after being brought into contact in an isolated enclosure.

It has been found that a gas will not occupy any volume at a certain temperature. This temperature is known as ***absolute zero temperature.***

The temperatures measured with absolute zero as basis are called *absolute temperatures*. Absolute temperature is stated in degrees centigrade.

The point of absolute temperature is found to occur at 273.15°C below the freezing point of water.

Then : **Absolute temperature = Thermometer reading in °C + 273.15**.

This law was enunciated by R.H. Fowler in the year 1931. However, since the first and second laws already existed at that time, it was designated as ***zeroth law*** so that it *precedes* the first and second laws *to form a logical sequence*.

PRESSURE

Pressure is defined as *a normal force exerted by a fluid per unit area*. We speak of pressure only when we deal with a gas or a liquid. The counterpart of pressure in solids is *normal stress*. Since pressure is defined as force per unit area, it has the unit of newtons per square meter (N/m^2), which is called a **pascal** (Pa). That is, 1 Pa 1 N/m^2

1 bar= 10^5 Pa= 0.1 MPa = 100 kPa

1 atm =101,325 Pa= 101.325 kPa= 1.01325 bars

FIGURE 1–37

Some basic pressure gages.

Dresser Instruments, Dresser, Inc. Used by permission.

The actual pressure at a given position is called the **absolute pressure,** and it is measured relative to absolute vacuum (i.e., absolute zero pressure).

Most pressure-measuring devices, however, are calibrated to read zero in the atmosphere (Fig. 1–37), and so they indicate the difference between the absolute pressure and the local atmospheric pressure. This difference is called the **gage pressure.**

Pressures below atmospheric pressure are called **vacuum pressures** and are measured by vacuum gages that indicate the difference between the atmospheric pressure and the absolute pressure. Absolute, gage, and vacuum pressures are all positive.

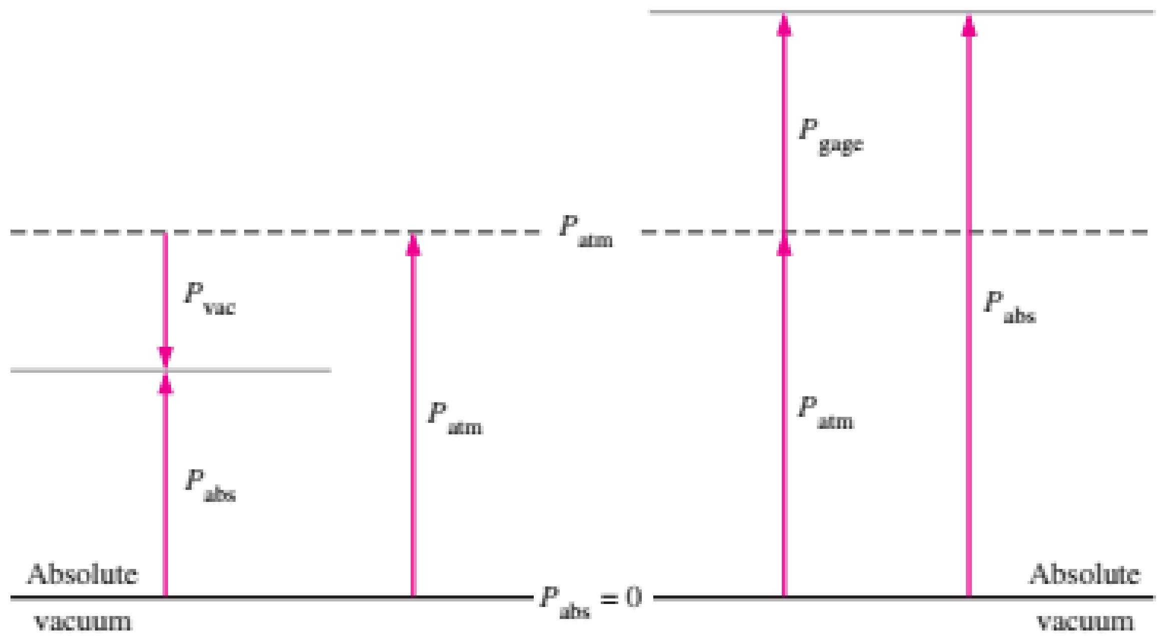
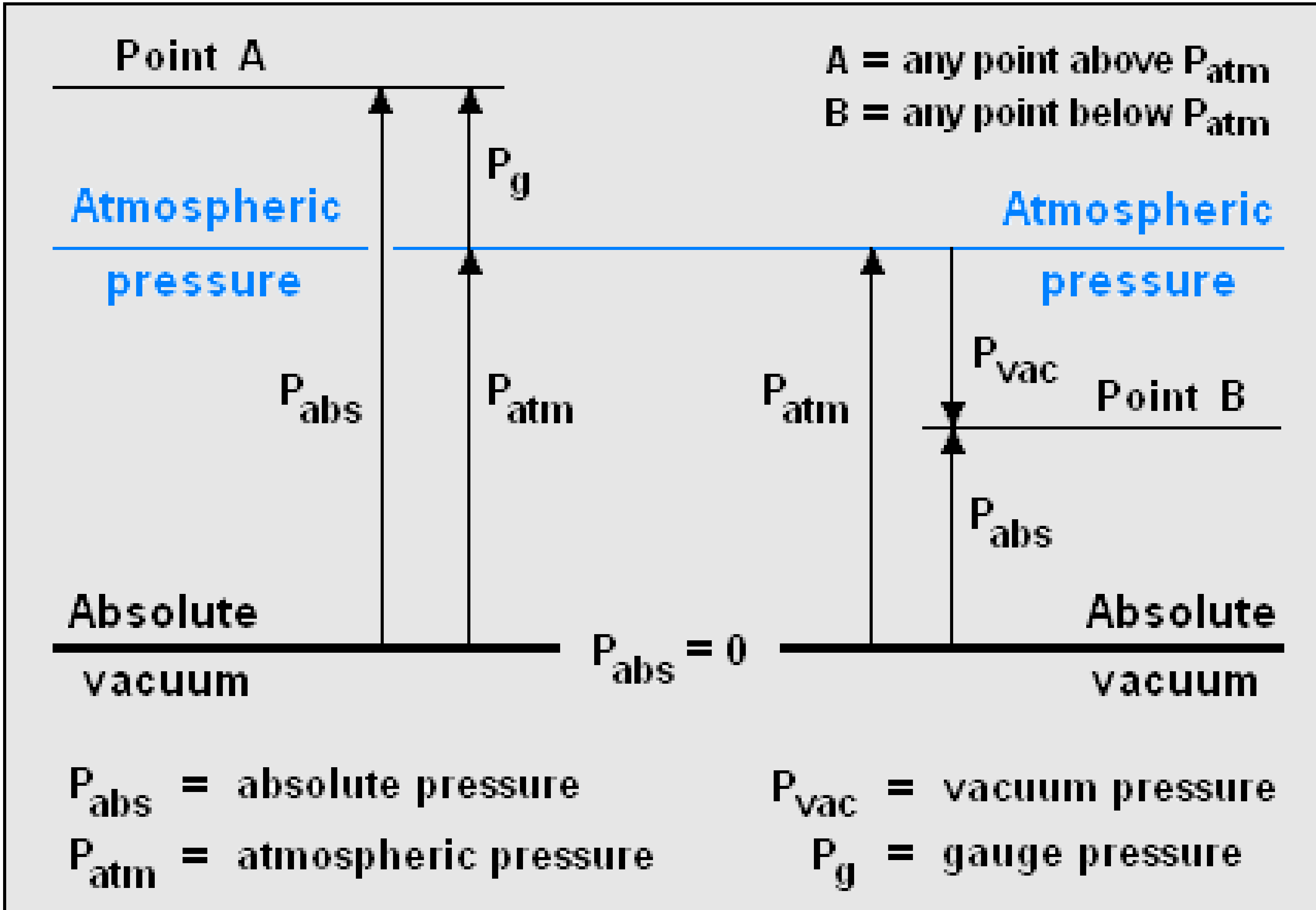


FIGURE 1–38

Absolute, gage, and vacuum pressures.

$$P_{gage} = P_{abs} - P_{atm}$$

$$P_{vac} = P_{atm} - P_{abs}$$



The relationship between absolute, gauge and vacuum pressures.

Like other pressure gages, the gage used to measure the air pressure in an automobile tire reads the gage pressure.

FIGURE 1–37

Some basic pressure gages.

Dresser Instruments, Dresser, Inc. Used by permission.