(Classical)

Thermodynamics

Thermo +Dynamics

Heat + Power

It is the branch of science dealing with inter-relationship and inter-conversions between different forms of energy, more particularly work and heat without even considering the existence of the atoms or molecules.

.

Four Laws

Thermodynamics is an empirical science which assumes the two laws- first law and the second law as axioms, though they were arrived at empirically. Classical thermodynamics makes no attempt to prove them.

- . **First law** establishes the conservation of energy for any process to happen. **Second law** eliminates some of those processes, feasible according to **first law,** by putting restriction on the path of flow of energy.

- **Zeroth law** lays the foundation defining temperature.

- On the other hand, neither the first law nor the second law provide information concerning evaluating magnitude of any **property**. **Third law** enable us to do the calculation.

Historical Development

1st law was formulated by Hermann Helmholtz and William Thomson using experimental data gathered by James Prescott Joule in 1848. It establishes conservation of energy of an isolated system.

The 2nd law of thermodynamics was postulated earlier than 1st law in 1824 by French engineer Sadi Carnot during his study of steam engine. It puts some restriction on the direction of heat flow while still being conserved.

In combination with first law 2nd law predicts natural course of a process with help of some mathematical functions like U, S, G ,H

1stlaw and 2nd law allow us to calculate only the changes in properties of a **system** while moving over from **one state** to **other state**

System and Surrounding

- A **system** is a restricted region of space having a closed surface separating it from the rest of the universe . It may be some water contained in a beaker, a certain amount of gas enclosed in a cylinder, a spring or the whole universe.

- Anything outside the system that affects the system or is affected by it, is the surrounding.

A system can be i. open ii. closed iii. Isolated

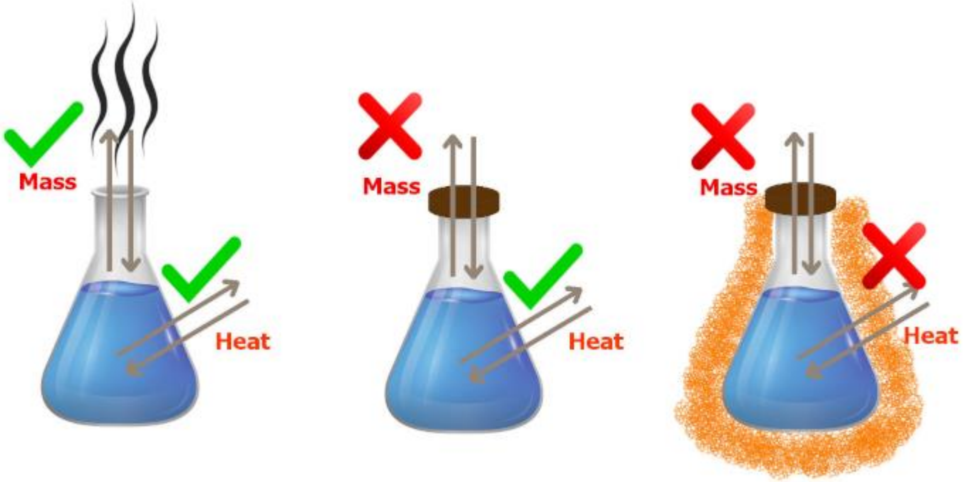
Isolated System: An isolated system is that system which does not allows either energy, in any form, or matter to pass through it.

Closed System : A closed system is that system which allows energy, in any form(work, heat) to pass through it but not any matter. A gas enclosed in a cylinder covered by a movable piston is example of a closed system. It may be covered with diathermal wall or adiabatic wall.

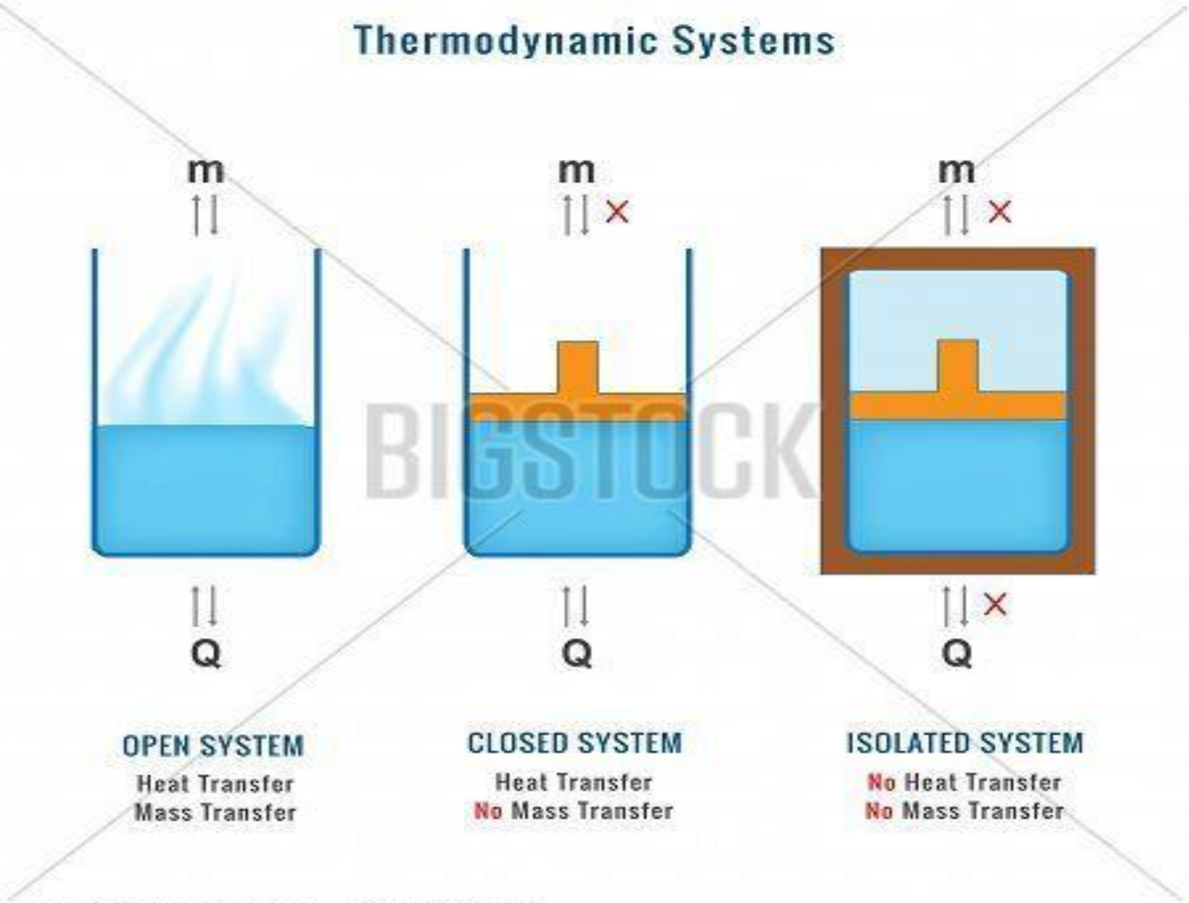
- When closed system has diathermal enclosure it allows energy to pass through it both in the form of work and heat. However, when it has adiabatic enclosure , it exchanges energy with the surrounding only in the form of work.
-

<u>Open System</u>: An open system is that system which can exchange both matter and energy with the surrounding . A very simple open system is a gas enclosed in a cylinder with diathermal wall covered by a piston with an outlet that allows matter to enter or escape **.**

Thermodynamic System



Open system	**Closed system**	**Isolated system**
Mass transfer (yes)	Mass transfer (~~yes~~ No)	Mass transfer (No)
Heat transfer (yes)	Heat transfer (~~No~~ Yes)	Heat transfer (No)


Thermodynamic Systems
m
Q
OPEN SYSTEM
Heat Transfer
Mass Transfer
m
Q
CLOSED SYSTEM
Heat Transfer
No Mass Transfer
m
Q
ISOLATED SYSTEM
No Heat Transfer
No Mass Transfer

Thermodynamic Coordinates or Properties of a System

Thermodynamic properties or thermodynamic coordinates of a system are its physical attributes by which it may be described. They are measurable. They are macroscopic in nature.

Intensive Property: It depend only on the nature of the system but do not depend on its mass and remains constant throughout the system. Pressure, Temperature(T), viscosity(η), dipole moment (μ), refractive index (i) etc. are examples of the intensive properties.

Extensive Property: It depends on the mass of the system as well as intrinsic property of the system. If the system is divided into several parts, an extensive property of the system is sum of corresponding extensive property of each of the parts. Volume, Energy, mass, enthalpy, entropy, free energy etc are the other examples of extensive property.

- When an extensive property is divided by another extensive property, it becomes intensive. For example, both mass(m) and volume(V) are extensive. However, density (ρ) which is m/V is intensive. Similarly, molar volume which is volume divided by number of moles (V/n), molar heat capacity($C_{p,m}$ or $C_{v,m}$) etc are intensive.

It deals with macroscopic properties of a system and do so with inclusion of macroscopic coordinate(property) of temperature.

State of a System and its change

A **state** of a system is defined by specifying some of its properties. When the system is in thermodynamic **equilibrium** then only the system can be described by thermodynamic coordinates or properties

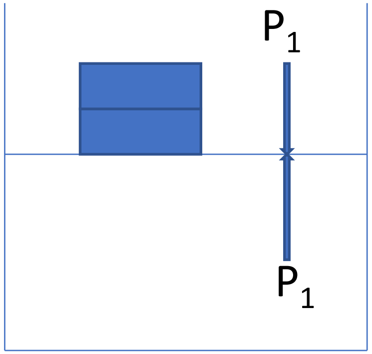
Equilibrium State

When the properties of the system do not change with time, the system is considered to be at equilibrium.

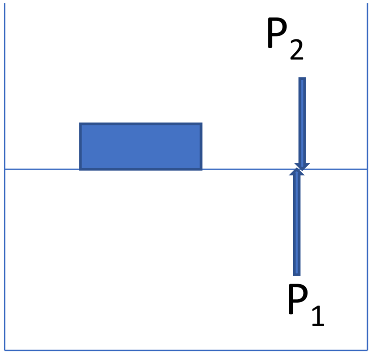
Let us consider the simple system of a gas confined in a cylinder fitted with a movable piston. When the piston moves, properties of the gas cannot be specified, since they are changing with time till the piston comes to rest. A system is said to be in **thermodynamic equilibrium** when all three types of equilibrium , namely **mechanical, thermal and chemical** equilibrium, are satisfied.

- **Mechanical Equilibrium:** If there is no unbalanced force acting between different parts of a system and between system and surrounding, the system is in mechanical equilibrium. At mechanical equilibrium, there will be no observable movement of the system. It does not mean that the pressure or force is same everywhere. It only means that there is no imbalance, e,g., a column of water.
- **Thermal Equilibrium:** If the temperature is same throughout the system and there is no difference of temperature between system and the surrounding, then the system is at thermal equilibrium. If thermal equilibrium is not present, heat will move from high temperature to low temperature and this may lead to mechanical movement.
- **Chemical Equilibrium:** Mechanical equilibrium and thermal equilibrium are sufficient for a system of non-reacting substances to remain at equilibrium. However, if there is chemical reaction, the system cannot remain at equilibrium even if there is no imbalance of pressure and temperature. Thus if the chemical composition remains same throughout the system, the system is at chemical equilibrium.

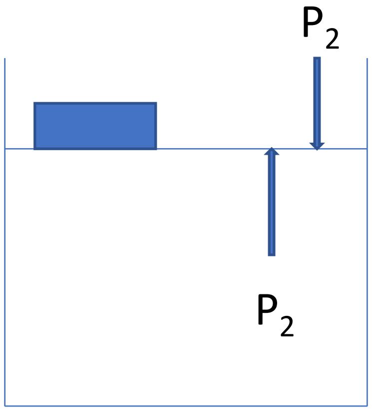
Equilibrium State



Non- Equilibrium State



Equilibrium State



Initial State: A

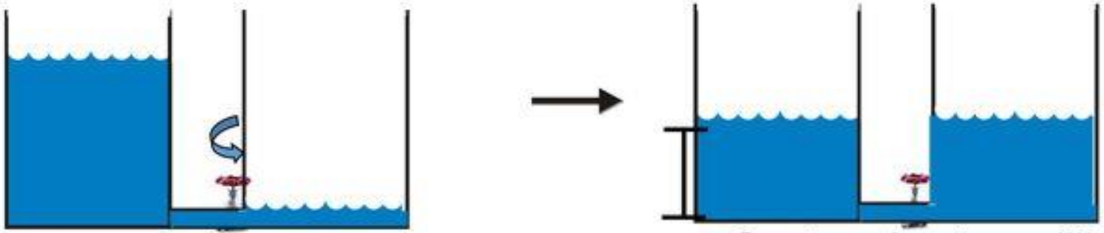
Final State: B

If the system is such that the properties do not change with time, but when the system is withdrawn from the contact of surrounding they change, then such a system is in a **steady state or stationary state**. For example, a metal rod in contact at one end with a large body at 180° and in contact with a large body at 160° at the other end. A uniform temperature gradient is set up in the rod, which does not change with time. However, as soon as the rod is removed from the contact with the large bodies, temperature changes and becomes uniform throughout the system.

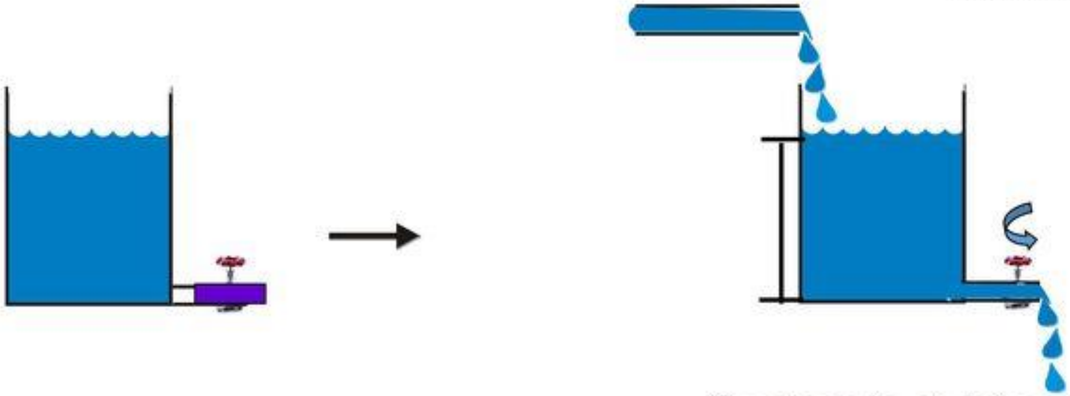
-

Steady state is not the same as equilibrium

This slide for
afternoon class



System is at equilibrium
Constant level
No net flow Molecules are flowing,
but back and forth



System is at "steady state"
Constant level but, *plenty* of net flow

- A state of a system in thermodynamic equilibrium is described by specifying its properties. If the system moves from one equilibrium state to another, its properties change and it is, now, described by different set of values of the properties.
- A homogeneous system is one which has the intensive properties(T, P etc) uniform throughout the system, e.g., a column of water. If some of the intensive properties, e.g., composition of the system, are not uniform, the system is heterogeneous

The state of a one component homogeneous system can be described by specifying two intensive variables. Its changes can be studied if one extensive property is mentioned. We normally specify pressure (P), volume(V) and temperature(T). They are the thermodynamic parameters or variables for the mechanical change in a hydrostatic system.

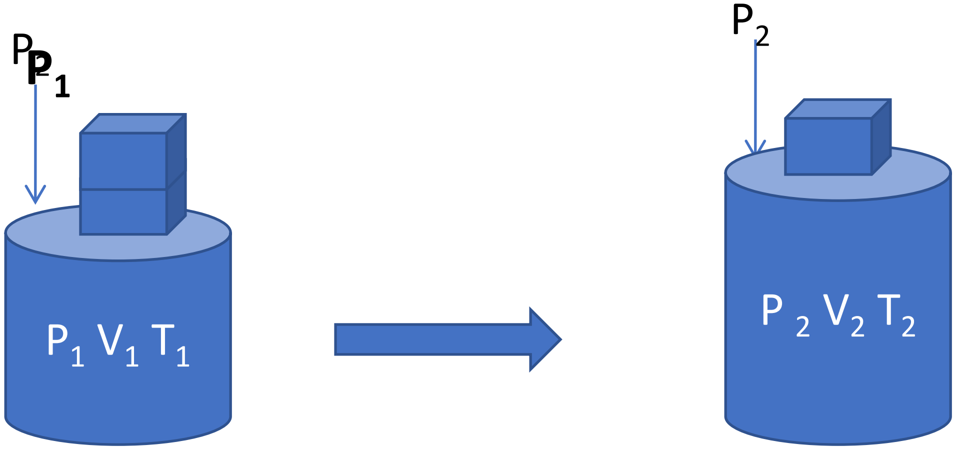
Mathematical relation, known as **equation of state**, exists between the properties of a system *e.g.*, pressure(P), temperature(T), volume(V) and number of moles(n) etc. For example, for ideal gas, $PV=nRT$ i.e., $P = f(T,V,n)$, $V=f(P,T,n)$, $T=f(P,V,n)$, $n=f(P,V,T)$.

For closed or isolated system, specification of three properties is sufficient.

Change of State- Reversible, Irreversible, Cyclic Processes

Changes are always taking place in bewildering nature e.g., downhill flow of water, falling of a body, passing heat from a body at high temperature to a body at low temperature etc.

If there is an imbalance in some of the intensive properties *e.g.,* P or T change, then a change take place..



The change may be

(i) isothermal (T_1=T_2)

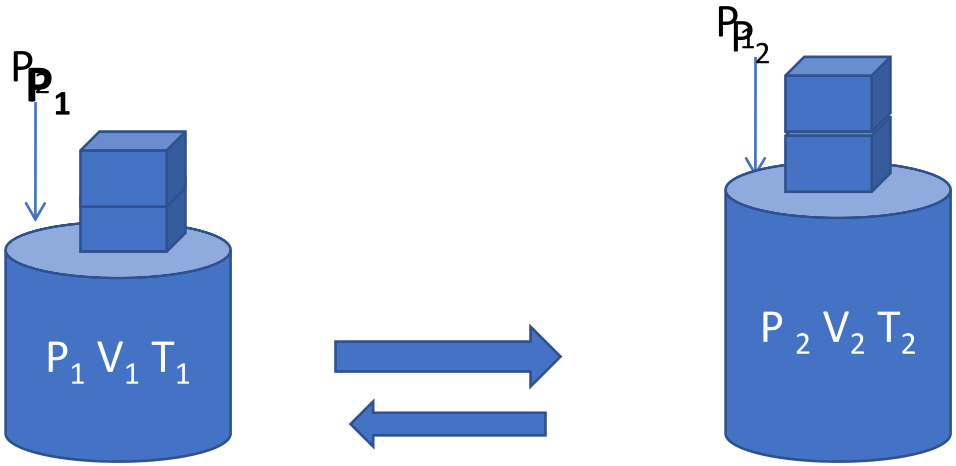
(ii) isobaric (constant pressure) *i.e.*, P_1 =P_2,

(iii) isochoric (constant volume) *i.e.*, V_1= V_2.

.

- Cyclic Process

A change may be cyclic. In cyclic process the system is restored to its initial state



- A change or a process may be **reversible or irreversible**. If both the system and surroundings are restored to their initial condition in a cyclic process, the change is reversible.

The criteria are:

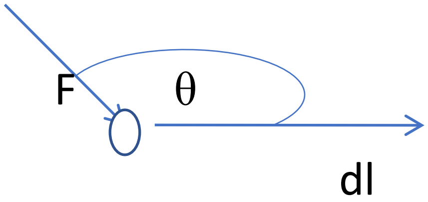
- i. infinitesimal rate
- ii. continuous sequence of equilibrium states through which the process is carried out *i.e.*, exact description of thermodynamic coordinates along the path
- iii. absence of dissipative force (e.g., friction) and
- iv. infinitesimal difference between the external force creating the motion and the internal forces preventing it (e.g., infinitesimally small difference between external and internal force).

Work

- When a body moves against an external force, the body performs work. If the force, F, acting on the body at an angle θ to its direction of motion causes the body to move through dl , work done by the system

  $dW = F\cos\theta . \, dl$

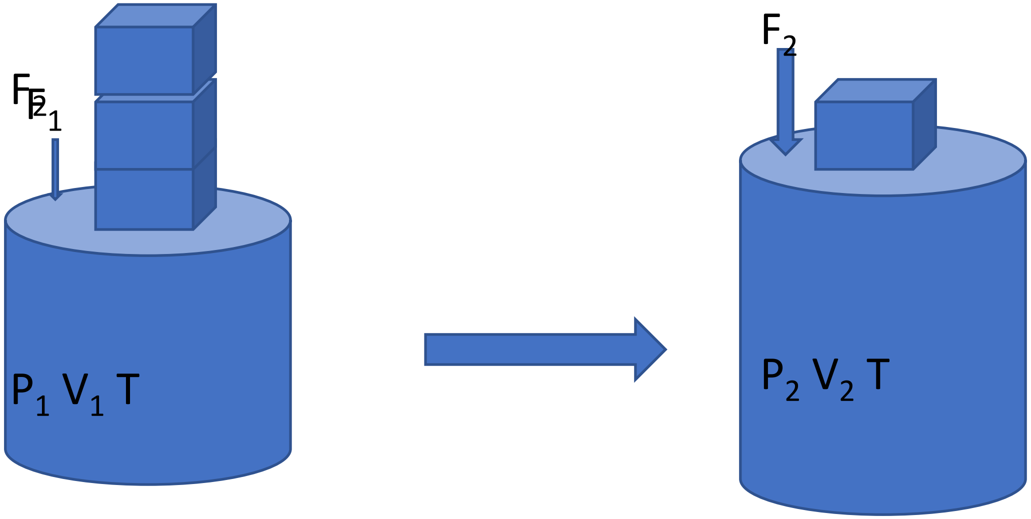
- work done by a gas is zero when it expands into vacuum (free expansion), since external force is zero.



Work in Thermodynamics

- Thermodynamic work can always be interpreted in terms of raising weight against gravity. So work done by freely falling body is zero.
- Work is energy in transit, appears across the boundary.
- Work appears only during the change of state
- Work is manifested by an effect in surrounding

Mechanical Work done by Hydrostatic System: Expansion Work



Work (isothermal) done by the gas=$dW= F_{ext}dl\cos\theta =-F_2dl$, $\theta=180^{o}$

$F_2= P_2A$, A= area of the piston

Thus, $dW= - P_2A\ dl = -P_2\ dV$`

$$W=-\int_{V_1}^{V_2} P_2\,dV \quad =-P_2(V_2 - V_1)$$ since P_2 remains constant during the process

Heat

- Heat is the quantity that flows across the boundary by virtue of temperature difference between the system and the surrounding.
- Heat is energy in transit, appears across the boundary.
- Heat appears only during the change of state
- Heat is manifested by an effect in surrounding

The Sign Convention

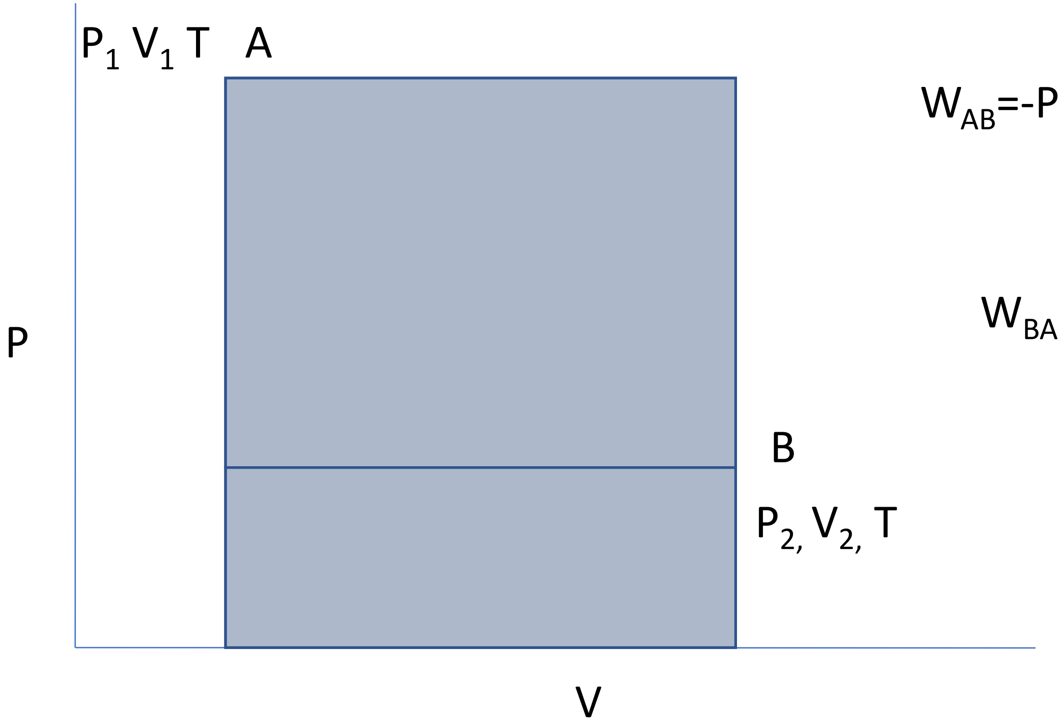
The work done upon a system is positive and the work done by a system is negative. Expansion Work is negative and compression work is positive

Heat absorbed by a system is positive and heat rejected by the system is negative.

Previously Work done by a gas expressed as PdV. But to keep conformity with definition of work given in mechanics , it is now defined as -PdV

System	Intensive Coordinate	Extensive Coordinate	Work
Hydrostatic System	P	V	$-PdV$
Electrochemical cell	E	Q	EdQ
Surface Film	γ	A	γdA

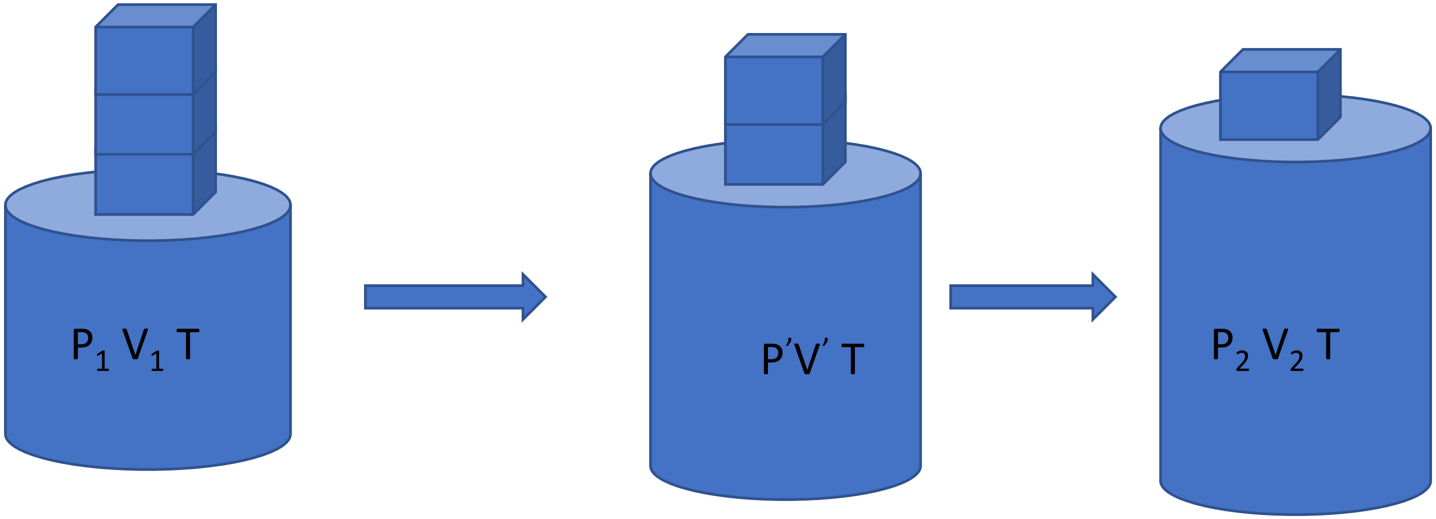
Indicator Diagram

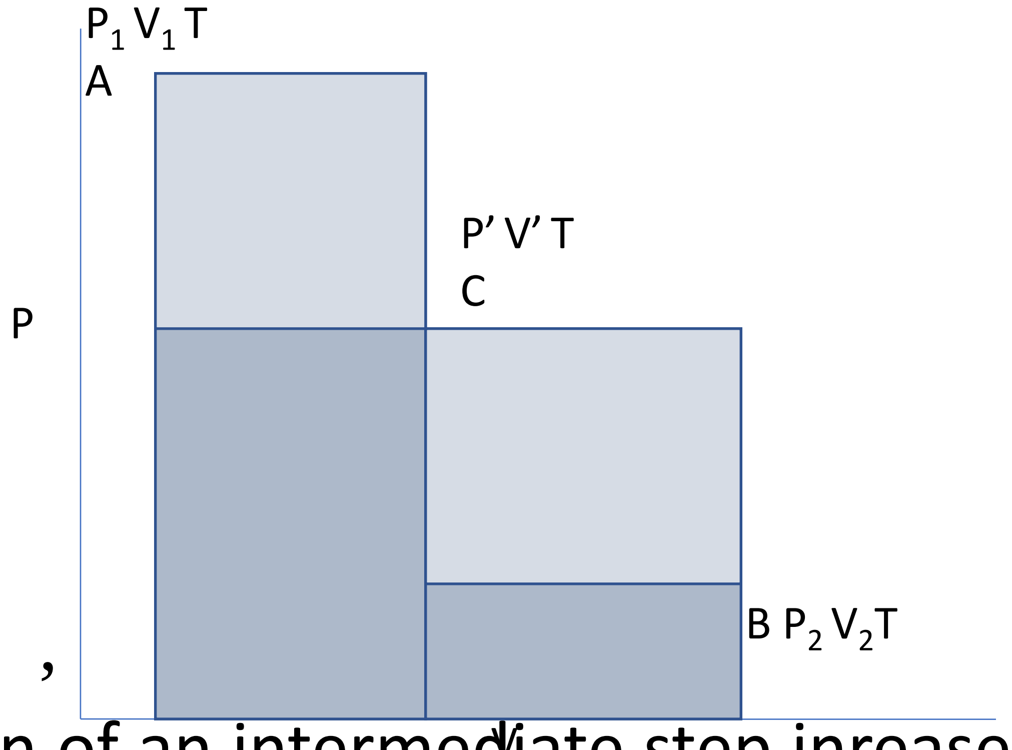


$W_{AB}=-P_2(V_2-V_1)$

$W_{BA}=-P_1(V_1-V_2)$

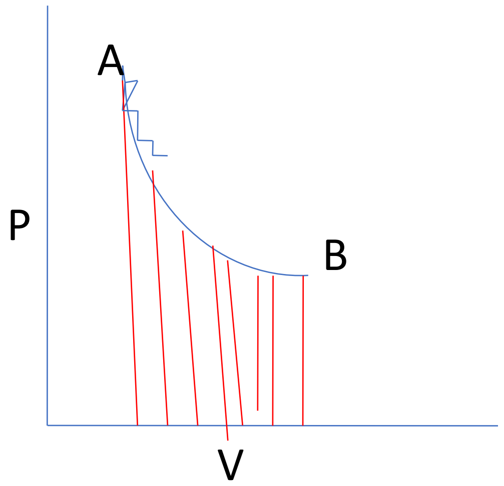
$W_{cy} = W_{AB} + W_{BA} = (P_2 - P_1) (V_1 - V_2) \neq 0$
This is an irreversible process


P_1 V_1 T
$P'V'$ T
P_2 V_2 T



- $W_{CY} \neq 0$,
- Inclusion of an intermediate step inreases W_{exp} for the same initial state and final state and deceases W_{com}

Reversible Work



- $P_{ext1} = P_1 - dP$
- $P_{ext2} = (P_1 - dP) - dp$ So on and same path is retraced back to the initial sate during compression.
- So $W_{cy} = 0$

Calculation of Work

Reversible isothermal work done by ideal gas

$$W = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRTln\frac{V_2}{V_1} = nRTln\frac{P_2}{P_1}$$

Reversible isothermal work done by van der Waals gas

$$W = nRTln\frac{V_1 - nb}{V_2 - nb} + n^2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

For solid or liquid effect of effect of pressure on volume is insignificant.

V= f(P, T), $dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$

Coefficient of thermal expansion= $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal Compressibility coefficient= $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$dV = \alpha VdT - \beta VdP$

$W_{iso.rev} = \int \beta VdP = \frac{\beta V}{2}(P_2^2 - P_1^2)$

$W_{iso,rev} > W_{iso,irr}$ between same two states

- $W_{irr} = -P_2(V_2 - V_1)$
- if the gas is ideal and is doing isothermal work

$$W_{irr,iso} = nP_2\left(\frac{RT}{P_1} - \frac{RT}{P_2}\right) = nRT\left(\frac{P_2 - P_1}{P_1}\right)$$

$$W_{rev,iso} = nRT ln\frac{P_2}{P_1} \quad = -nRT ln\frac{P_1}{P_2}$$

$$= ln\left(1 + \frac{P_1 - P_2}{P_2}\right)$$

ln(1+x)=x when x is small

$$= -nRT\frac{P_1 - P_2}{P_2}$$

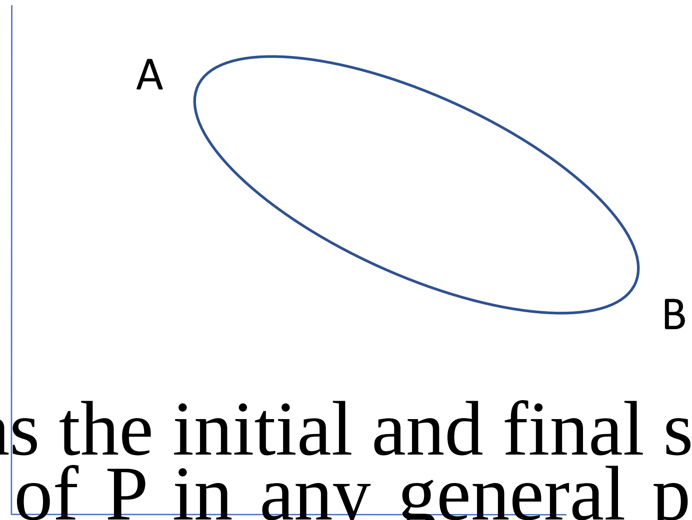
$$W_{rev,iso} - W_{irr,iso} = -nRT\frac{P_1 - P_2}{P_2} - nRT\left(\frac{P_2 - P_1}{P_1}\right) \quad = -\frac{nRT}{P_1P_2}(P_1 - P_2)^2$$

State Functions and Exact Differentials

- Properties are the state functions as they are the functions of the variables or parameters chosen to specify a state of a system completely and differential form of any state function is an **exact differential**.
- Any property, P, thus, can then be written as P = f(x, y)
- If the system passes from state A (specified by x_A and y_A) to state B (specified by x_B and y_B) via path I, change in P, irrespective of the path (reversible or irreversible)
- $$\Delta P_I = P_B - P_A$$
- The system is now brought back to initial state A via another path II. Thus,
- $$\Delta P_{II} = P_A - P_B$$
- Thus, for the net change in P in the **cyclic process,** we may write

$$\oint dP = \int_A^B dP + \int_B^A dP = \Delta P_I + \Delta P_{II} = 0$$

- **State Function Vs Path Functions**



- As long as the initial and final states are identical, the variation of P in any general process is independent of the way used to realize the change.
- P is, thus, called **state function**(or variable) and differential form(dP) of any state function is **exact differential**. A
- All the properties are **state functions**.
- Infinitesimal change of **path functions** are not exact differential

Mathematical Criterion For A State Function-Euler Reciprocity Relation

- Infinitesimal change dx in x and dy in y move the system from one equilibrium state to another. If the changes bring about the infinitesimal change dP in P,

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

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

dP = Mdx + Ndy

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{\partial P}{\partial x}\right)_y\right]_x = \frac{\partial^2 P}{\partial x \partial y}$$

and $\left(\frac{\partial N}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(\frac{\partial P}{\partial y}\right)_x\right]_y = \frac{\partial^2 P}{\partial x \partial y}$, Thus $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Double derivative does not depend on order of differentiation

Example

- P=f(V,T)
- x=V,   y=T
- Using ideal gas equation
- $\left(\frac{\partial P}{\partial x}\right)_y$=-nRT/V^2=M $\left(\frac{\partial P}{\partial y}\right)_x$=nR/V= N
- $\left(\frac{\partial M}{\partial y}\right)_x$ = -nR/V^2 $\left(\frac{\partial N}{\partial x}\right)_y$ = -nR/V^2

Two simple theorems in partial differential calculus

- If x, y and z are thermodynamic coordinates of a system,
- f(x, y, z) =0 *i.e.,*

$x = f_1(y, z)$

$y = f_2(x, z)$ and

$Z = f_3(x, y)$

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

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

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

or

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

Of the three coordinates, only two are independent. Choosing x and z as the independent coordinates, the above equation must be true for all sets of values of dx and dz. Thus, if $dz = 0$ and $dx \neq 0$, it follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1,$$

or

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z}.}$$

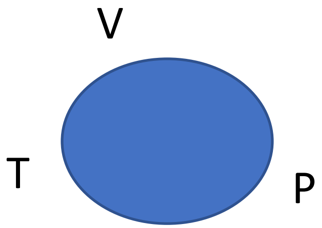
If $dx = 0$ and $dz \neq 0$, it follows that

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

and

$$\boxed{\begin{aligned} \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x &= -\left(\frac{\partial x}{\partial z}\right)_y \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1. \end{aligned}}$$

Application



$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

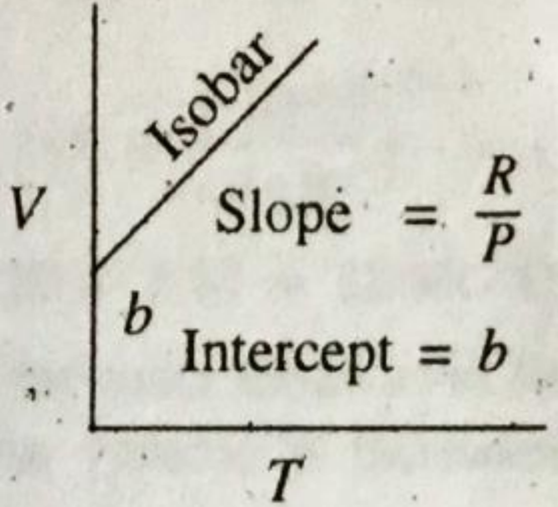
$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T}$$

$$= -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{\alpha V}{\beta V} = \frac{\alpha}{\beta}$$

(b) plot P vs. V at constant T.

(c) plot P vs. T at constant V.

. : (a) Plot of V vs. T at constant P

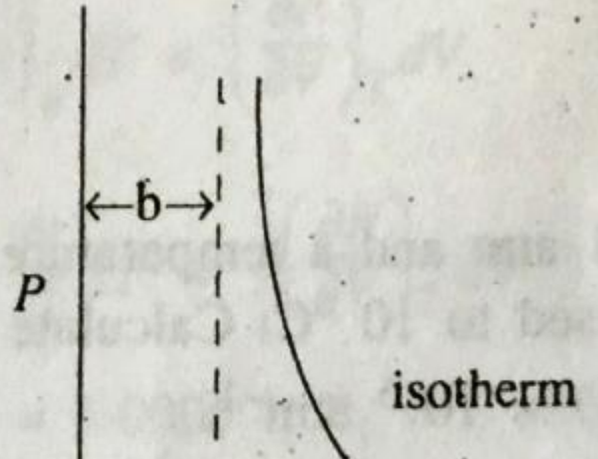


The equation is

$$(V - b) = \frac{RT}{P}.$$

$$V = \frac{R}{P}.T + b.$$

Plot of P vs. V (at constant T) :



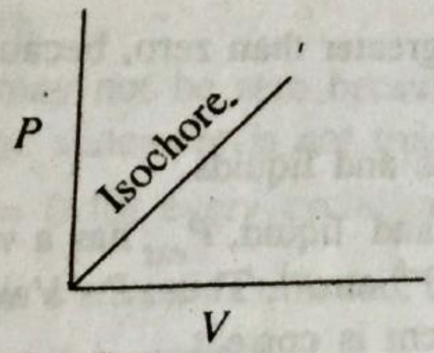
The equation is

$$P = \frac{\text{const.}}{V - b}$$

$$\therefore \quad P \propto \frac{1}{V - b}$$

$$V \to \infty \text{ as } P \to 0$$

(c) Plot of P vs. T at constant V



Slope = $\frac{R}{V-b}$. The equation is $P = \frac{RT}{\text{const.}}$

Intercept = 0.

- $V=f(P,T)$
- $dV=MdP+NdT \quad x=P,\ y=T$

$V=nRT/P+n(b-a/RT)$

$M=-nRT/P^2$

$N=nR/P+a/RT^2$

$= -nR/P^2 \qquad\qquad = -nR/P^2$

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