THERMAL PHYSICS II

B. Sc. Part II (Hons.) Paper: IV A

University of Calcutta

A course guided by

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ermodynamics is a funny subject. The first time you go through it, you d

erstand it at all. The second time you go through it, you think you understand

ept for one or two points. The third time you go through it, you know you do

erstand it, but by that time you are so used to the subject, it doesn't bot

anymore" – **Arnold Sommerfeld**

theory is the more impressive the greater the simplicity of its premises,

e different kinds of things it relates, and the more extended its area

licability. Therefore the deep impression that classical thermodynamics m

n me. It is the only physical theory of universal content which I am convir

 never be overthrown, within the framework of applicability of its b

cepts" – **Albert Einstein**

Syllabus

asic Concepts

roscopic and macroscopic points of view: thermodynamic variables of a system, St

ction, exact and inexact differentials

irst Law of Thermodynamics

rmal equilibrium, Zeroth law and the concept of temperature. Thermodynam

librium, internal energy, external work, quasistatic process, first law of thermodynam

applications including magnetic systems, specific heats and their ratio, isothermal a

batic changes in perfect and real gases

Syllabus

Second Law of Thermodynamics

...versible and irreversible processes, indicator diagram. Carnot's cycles-efficiency, Carn...

...rem. Kelvin's scale of temperature, relation to perfect gas scale, second law...

...rmodynamics – different formulations and their equivalence, Clausius inequality, entro...

...nge of entropy in simple reversible and irreversible processes, entropy and disord...

...ilibrium and entropy principle, principle of degradation of energy

Syllabus

Thermodynamic Functions

halpy, Helmholtz and Gibbs' free energies; Legendre transformations, Maxwell's relatio

simple deductions using these relations; thermodynamic equilibrium and free energies

Change of States

librium between phases, triple point: Gibbs' phase rule (statement only) and sim

lications. First and higher order phase transitions, Ehrenfest criterion. Clausi

peyron's equation. Joule- Thomson effect

References

Basic Thermodynamics – Evelyn Guha (Narosa)

Heat and Thermodynamics – Dittman & Zeemansky (Tata McGraw Hill)

Thermodynamics – Enrico Fermi (Dover)

Thermal Physics (*Heat & Thermodynamics*) – A. B. Gupta & H. P. Roy (Books & Allied

Basic Concepts

A branch of physics which deals with the transformation of heat into mechanical work

vice-versa. It <u>describes bulk properties of a system containing large number of atom</u>

<u>molecules, in terms of some macroscopic variables</u> defining the system

Classical thermodynamics is studied with four fundamental laws which are derived fr

xperimental evidences. It does not enter into the microscopic description like the kin

mechanism of the constituents of the system

Basic Concepts

at is 'Thermodynamics'?

Statistical thermodynamics considers microscopic interactions between individual partic

nd their collective motions in terms of classical or of quantum mechanics, to extr

verage properties of the system. It provides explanation of the laws of thermodynamics

Basic Concepts

at is 'Thermodynamics'?

Zeroth law of thermodynamics introduces the concept of temperature, (probably) the

mportant parameter in thermodynamics

First law of thermodynamics restates the conservation of energy principle

Second law of thermodynamics is based on an observation that heat can not

pontaneously from a colder body to a hotter body and thus restricts the complete conver

f heat into work

Third law of thermodynamics is a statistical law of nature regarding entropy and

mpossibility of reaching absolute zero temperature

Basic Concepts

y will we learn from thermodynamics?

e you ever thought the following questions?

Why is the air released from a tyre cool?

Why does the pumping cylinder get hot during pumping?

Why does a car's engine get hot when it is running?

Why is the maximum concentration we can get of alcohol is around 95%?

Thermodynamics answers them all

Basic Concepts

hermodynamics is the theory of macroscopic phenomena which is developed empirical

escribes the idea of some very important physical parameters of the nature like tempera

ntropy, enthalpy *etc*.

We will learn phenomenologically the consequences of heat transfer between a system

ts surroundings, the direction of heat flow, the efficiency or the performance of heat eng

& refrigerators

Basic Concepts

ctives of Thermodynamics

hermodynamics sets limits on physical and biological processes and gives relation

etween various properties. As we will see, both of these give us an insight into how nat

ystems work and give us some powerful tools in calculating various quantities

hermodynamics is also unique in the world of physics. Mechanics deals with mechan

ystems, fluid dynamics deals with fluids, and electromagnetism deals with electrical

nagnetic systems. Thermodynamics applies to any macroscopic system: mechar

ystems, fluids, electrical and magnetic systems etc.

Basic Concepts

is the only physical theory of universal content concerning which
convinced that, within the framework of the applicability of
ic concepts, it will never be overthrown" – **Einstein**

Basic Concepts

ualism: Macroscopic point of view

n classical mechanics, the state of a particle is specified by its instantaneous position

nomentum which is a set of six coordinates (x, y, z, p_x, p_y, p_z)

n quantum mechanics the state is specified by a set of quantum numbers

A macroscopic system contains very large number of particles (typically more than 10^{23})

nence it requires a large number of variables to describe the system

n classical thermodynamics, we study macroscopic properties of a system in terms of

ew variables defining the system in equilibrium

Basic Concepts

The microscopic description or the microstate of a system is the complete description of

onstituent in this system. For example, a system containing N number of particles requ

$6N$ coordinates to classically describe the microscopic properties of the system

The structure of the system should be well known, or in some cases assumptions are requ

or microscopic description of the system

A large number of quantities are required for the description

Parameters describing the microstates of system are generally beyond our sensory percep

The parameters can not be measured directly but these are calculated

Basic Concepts

The macroscopic description or the macrostate of a system, in contrast, refers to macroscopic properties. For example, the same system can be macroscopically descr with the help of few parameters like the number of particles in the system (N), pressure volume (V) and the temperature (T) of the system

t does not involve the internal structure of the system and hence macroscopic descrip

loes not require an insight at the atomic or molecular level

Only few parameters are required for macroscopic description

Macroscopic parameters are within our sensory perception

Most important to mention, we can measure these parameters directly

Basic Concepts

oscopic *versus* macroscopic descriptions

e parameters describing the microstates of a system in equilibri

ange with time. However, the macroscopic parameters for a syst

equilibrium do not change with time.

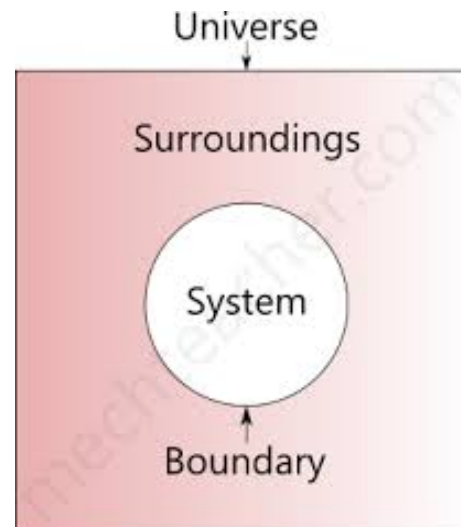n classical thermodynamics we will study a system in equilibrium

Basic Concepts

nition of terminologies

System: A thermodynamic system is the content of a macroscopic volume in s

onsidered for the study

Surroundings: It is separated by its walls from the rest part of the universe, called

urroundings. Practically, 'surroundings' is the immediate neighbourhood of the system
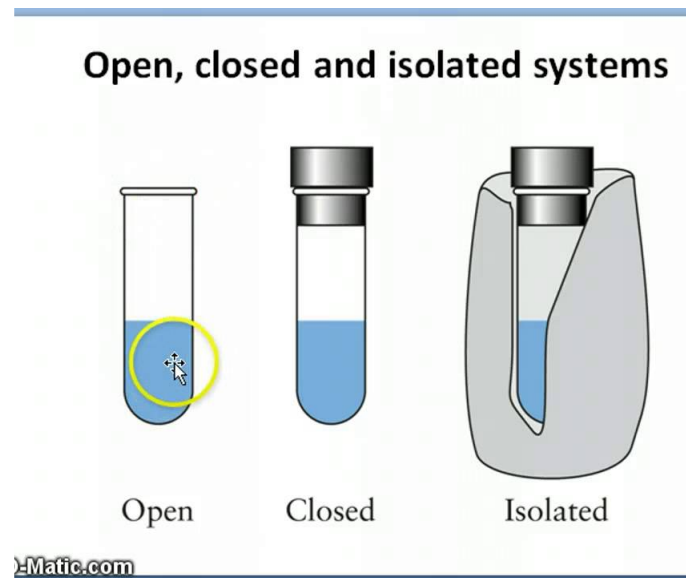
Universe: System + Surroundings

Basic Concepts

Open System: Exchange of matter & energy between the system and the surroundings

Closed System: No exchange of matter but exchange of energy

Isolated System: No exchange of matter & energy between the system and the surround...

Open, closed and isolated systems

Open   Closed   Isolated

Basic Concepts

State of a system: The state of a system in thermodynamics is specified by a se macroscopic parameters, called the thermodynamic coordinates which depend on the syst For a system composed of a chemically defined homogeneous fluid, temperature pressure (P) & volume (V) can be chosen as suitable thermodynamic coordinates and h set of these three coordinates (P, V, T) defines the thermodynamic state of the system

Basic Concepts

For a stretched wire, tension in the wire (F), length of the wire (L) & temperature (T) can

chosen as thermodynamic coordinates and hence its state can be specified by the set (F, L, T)

For a surface film of liquid, surface tension of the liquid (S), surface area (A) & temperature (

are the thermodynamic coordinates and state of the film is described by (S, A, T)

Basic Concepts

Equation of state: In equilibrium, there exists a relation between the thermodyna oordinates of a system and it is called the equation of state for the system

Equation of state of a system composed of a chemically defined homogeneous fluid is g by $f(P, V, T) = 0$ [$PV = RT$: equation of state for an ideal gas]

For the stretched wire the equation of state is given by $f(F, L, T) = 0$

For the surface film, the equation of state is given by $f(S, A, T) = 0$

Basic Concepts

uation of state makes one of the thermodynamic coordinates o

tem dependent on others, i.e. one coordinate can be extracted

ng the equation of state if other coordinates are known

Basic Concepts

modynamic Equilibrium

classical thermodynamics we study a system in equilibrium

Thermodynamic equilibrium is an axiomatic concept – involves internal state of a si

hermodynamic system or a relation between several systems connected by permeable wa

thermodynamic equilibrium, there are no net macroscopic flow of matter or energy, e

within a system or between systems. Thus no macroscopic change occurs within the sys

nd the state of the system does not change

Basic Concepts

modynamic Equilibrium

An unbalanced potential anywhere within the system, or between the systems lead

hange of state of the system under study

Systems in mutual thermodynamic equilibrium are simultaneously in mutual ther

mechanical, and chemical equilibria

Basic Concepts

Mechanical Equilibrium:

An unbalanced force within a system, or between a system and its surroundings exists du
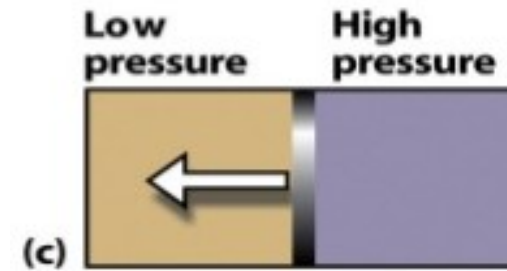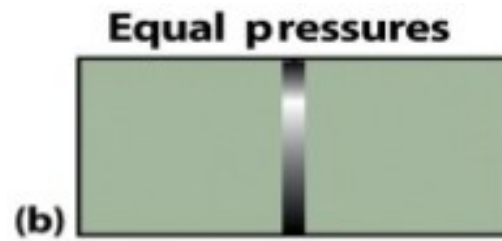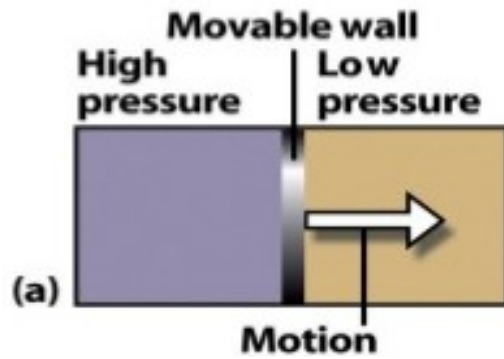
variation of pressure or elastic stress

t results expansion or contraction, turbulence, eddies within the system under study

When such flow of mechanical energy ceases, the system is in mechanical equilibrium

Basic Concepts

Mechanical Equilibrium:

Basic Concepts

modynamic Equilibrium

Thermal Equilibrium:

f a temperature difference exists within a system, or between a system and its surroun

eparated by a diathermic wall, there will be exchange of heat between them and the sta

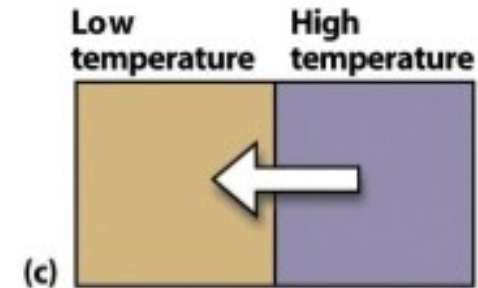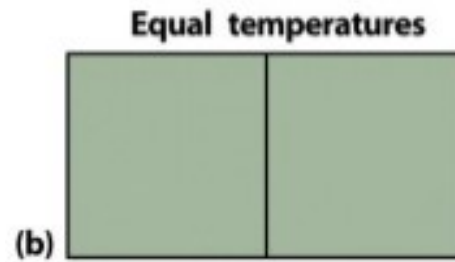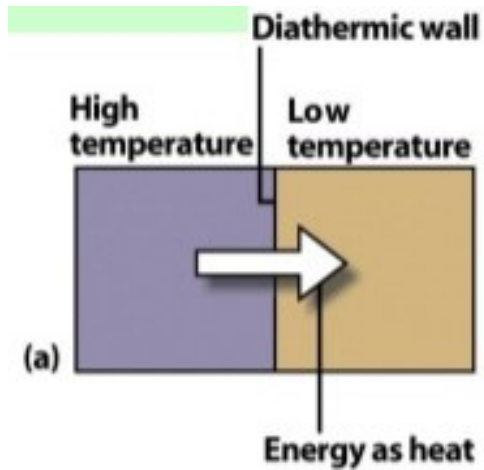he system will change – heat exchange continues until the temperature gradient vanishes

Condition for thermal equilibrium of a system is that the temperature is uniform throug

he system (or between the system and its surroundings)

Basic Concepts

modynamic Equilibrium

Thermal Equilibrium:

Basic Concepts

Chemical Equilibrium:

The chemical composition of a system may change due to variation of the chemical pote

within the system or between the system and its surroundings

For a system in chemical equilibrium, the chemical potential must be uniform

Consider two systems separated by a perforated wall. The systems contain same elemen

of different concentrations – diffusion through the wall from the system having hi

concentration to the system with smaller concentration. The diffusion continues until

the systems achieve same concentration
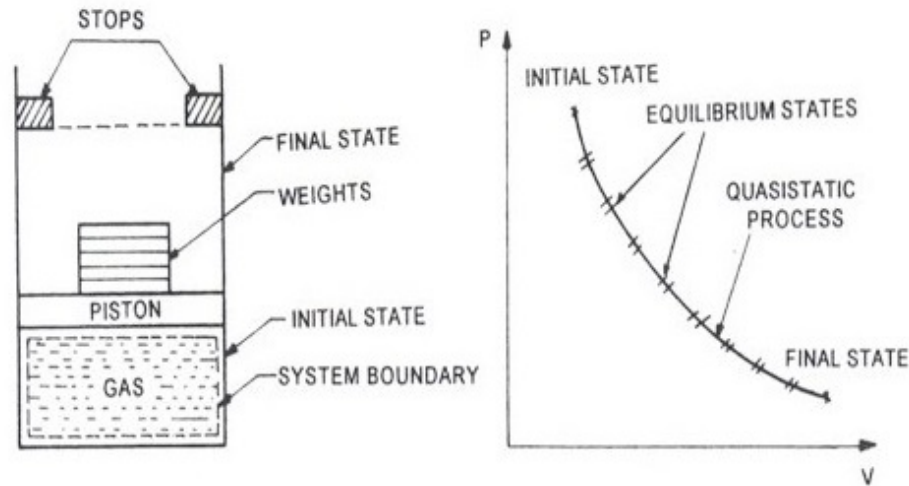
Thermodynamic Processes

Quasi-static process:

Happens 'infinitely slowly' such that the system remains 'infinitesimally close' to equilibrium state at all times

No real process is quasi-static, such process approximated by performing them very slowly

The process proceeds slow enough to allow the system to adjust itself internally so macroscopic properties in one part of the system do not change any faster than its rest parts

Thermodynamic Processes

Reversible process:

Infinitesimal change in the conditions of the surroundings leads to a 'reversal' of the proc

System is very close to equilibrium and infinitesimal changes can restore the system

surroundings to the original state

Any reversible process is necessarily a quasi-static one

During a reversible process, the system is in thermodynamic equilibrium with

surroundings throughout the entire process

Since it would take an infinite amount of time for the reversible process to finish, perfe

reversible processes are impossible

Thermodynamic Processes

...ersible process is quasi-static but the reverse not necessarily true

...si-static process are those processes in which a system is taken from one state to other...

...nitesimal number of steps (slowly) such that there is always an equilibrium maintained betw...

...em and surrounding. For a process which is not quasi-static, it would give system an infi...

...ber of pathways to return to its initial state and thus make the process irreversible. Henc...

...ersible process must be quasi-static.

Thermodynamic Processes

...wever, if a process is quasi-static, it doesn't mean that the process is reversible. ...mple, during the compression of a gas present in cylinder using a piston such that ther... ...tion between the cylinder and piston, in this case there will be generation of dissipa... ...ropy which will make the process irreversible even though it is performed quasi-statical...

Thermodynamic Processes

Irreversible process:

A thermodynamic process which is not reversible, is called an irreversible process

A change in the thermodynamic state of a system and all of its surroundings canno precisely restored to its initial state by infinitesimal changes in some properties of the sy A system that undergoes an irreversible process may still be capable of returning to its i state; however, the impossibility occurs in restoring the environment to its own i conditions

All natural processes are irreversible
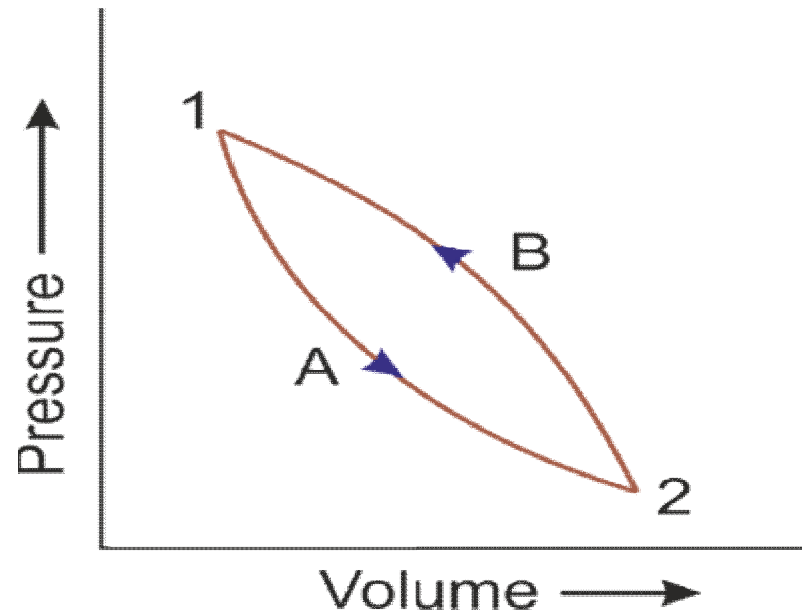
Thermodynamic Processes

Cyclic process:

If the final state of a system in a thermodynamic process is same as its initial state, process is called cyclic

The observable which are state functions, do not change in the cyclic process

However, the observable which are path functions, undergo a net change in cyclic process

Thermodynamic Processes

Isothermal process:

A thermodynamic process which takes place at constant temperature

Melting of ice or freezing of water, evaporation of water etc. are isothermal processes

An isothermal process for an ideal gas is governed by Boyle's law and described by

equation of state PV =constant. P − V relation is called an isotherm – rectangular hyper

or an ideal gas. Internal energy of an ideal gas remains constant in isothermal process
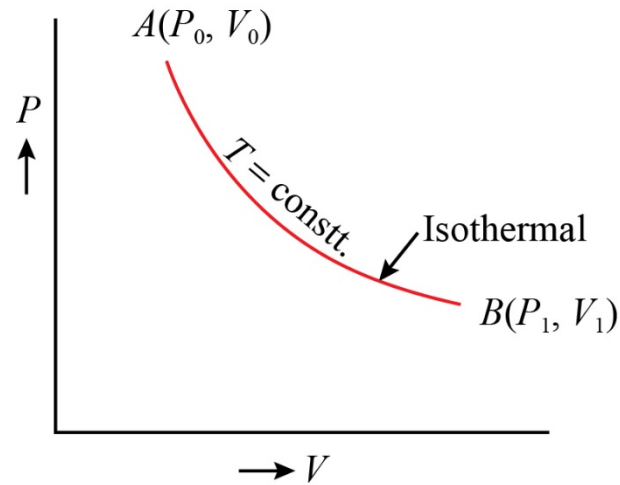
(P–V Diagram)

Thermodynamic Processes

Isobaric process:
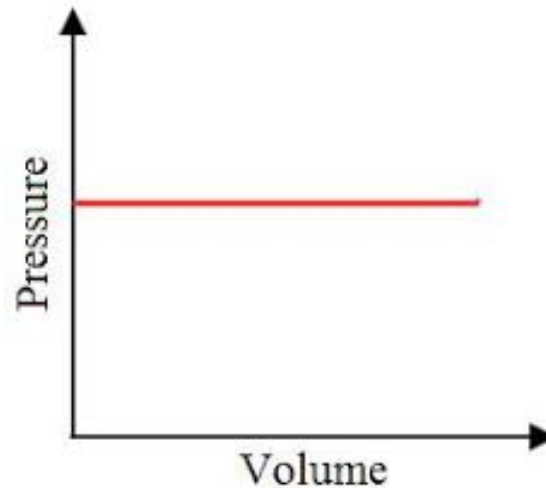
A thermodynamic process which takes place at constant pressure

Heating of water in open air occurs under the atmospheric pressure and hence it ca[n]

[r]egarded as an isobaric process

[A]n ideal gas under the isobaric process follows Charles's law & corresponding equatio[n]

[s]tate is V/T = constant. The P −V relation in this process is called an isobar – straight lin[e]

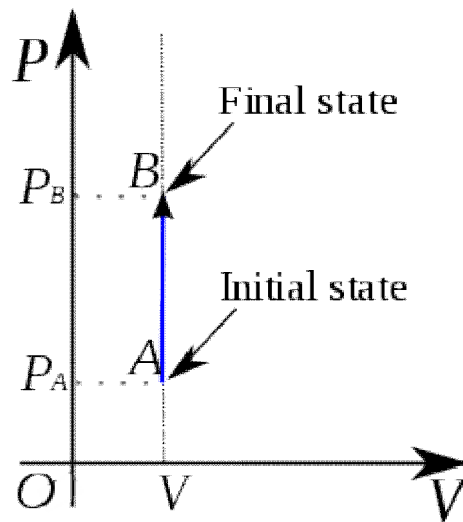[a]n ideal gas

Thermodynamic Processes

Isochoric process:

A thermodynamic process which takes place at constant volume

Heating of gas in sealed metal container–pressure, temperature increases at constant volume

An ideal gas under the isochoric process follows the equation of state: P/T = constant. P

relation in this process is called an isochor which is a straight line for an ideal gas
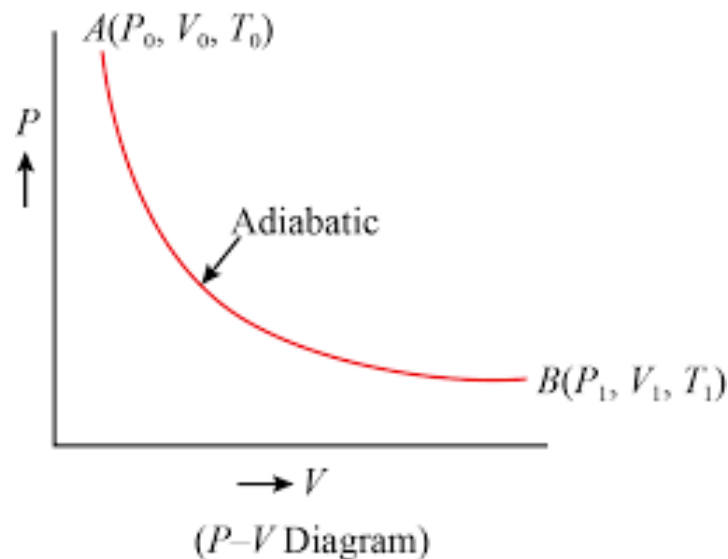
Thermodynamic Processes

Adiabatic process:

No exchange of heat between the system and the surroundings in this process

The equation of state of an ideal gas under an adiabatic process is described by PV^γ

constant, where γ is the ratio of the specific heat at constant pressure & the specific he

constant volume $(\gamma = C_p/C_v)$

(P–V Diagram)

Thermodynamic Functions

Macroscopic observables like heat, work done, internal energy, entropy etc. are the funct

of thermodynamic coordinates

Observables change as the state of a system changes

For some of these observable the change depends on the final and initial states only, w

or other observable the change not only depends on the initial and final states but als

the process through which the state of the system has changed

The observable have been classified accordingly into two categories:

1) State functions

2) Path functions

Thermodynamic Functions

State functions:

Thermodynamic functions, the change of which depends only on the final and initial s

of the system and not on the path or the process, are called state functions

Examples: Internal energy, Entropy, Enthalpy etc.

n a cyclic thermodynamic process, there is no change in these observables

Thermodynamic Functions

Path functions:

Thermodynamic functions, the change of which depends not only on the final and i

states of the system but also on thermodynamic process through which the system is t

from the initial to the final state, are called path functions

Examples: Heat exchange, Work done etc.

In a cyclic thermodynamic process, there is net change in these observables

Intensive & Extensive Properties

Intensive Property:

A bulk property which means it is a physical property of a system that does not depen

he system size or the amount of material in the system

Examples: temperature, pressure, concentration, density, specific heat, refractive in

urface tension, viscosity, elasticity, chemical potential, electrical resistivity or conducti

hermal conductivity, magnetic field, polarization, magnetization etc.

Intensive & Extensive Properties

Extensive Property:

An extensive property is additive for independent, non-interacting subsystems. The prop

s dependent on the amount of material in the system

Examples: mass, length, area, volume, energy, entropy, particle number, number of m

magnetic moment, electric charge etc.

Intensive & Extensive Properties

The ratio of two extensive properties of the same object or system is scale-invariant, an

herefore an intensive property

For example, the ratio of the extensive properties mass and volume, the density, is

ntensive property

Intensive & Extensive Properties

Thermodynamic Systems	Intensive Coordinates	Extensive Coordinates

Heat and Thermodynamics, Dittman & Zeem

Mathematical Preliminaries

ider three variables x, y, z such that $\quad f(x, y, z) = 0$

$$x = f(y, z) \Rightarrow dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \ \ldots\ldots\ldots (1)$$

$$y = f(x, z) \Rightarrow dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \ \ldots\ldots\ldots (2)$$

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

m eq. (1) & (2)

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

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \ \ldots\ldots\ldots (3)$$

Mathematical Preliminaries

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \quad \ldots\ldots\ldots (3)$$

nce $f(x, y, z) = 0$, only two variables are independent – let's take x & z as independent

noose $dz = 0 \Rightarrow dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$

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

⬅ Reciprocal Relation

Mathematical Preliminaries

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \quad \ldots\ldots\ldots (3)$$

choose $dx = 0$

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

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

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \Longleftarrow \quad \text{Cyclic Relation}$$

Mathematical Preliminaries

act and inexact differentials:

$$dz = M\,dx + N\,dy$$

dz is said to be exact if $\dfrac{\partial M}{\partial y} = \dfrac{\partial N}{\partial x}$

Example: $dz = 2xy\,dx + x^2\,dy$

$$M = 2xy \qquad N = x^2$$
$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} = 2x$$

dz is said to be inexact if $\dfrac{\partial M}{\partial y} \neq \dfrac{\partial N}{\partial x}$

Example: $dz = 2x^2y^3\,dx + 3x^3y^2\,dy$

$$M = 2x^2y^3 \qquad N = 3x^3y^2$$
$$\frac{\partial M}{\partial y} \neq \frac{\partial N}{\partial x}$$

Mathematical Preliminaries

act and inexact differentials:

dz is an exact differential $\displaystyle \int_{z_1}^{z_2} dz = z_2 - z_1 \Rightarrow \oint dz = 0$

n thermodynamics, the state functions like the internal energy does not change in a cyclic proce

he change of these functions can be expressed as exact differential and usually denoted with

symbol dz (e.g. dU, dS, dH etc.)

Path functions like work done or heat-exchange are inexact differential and usually denoted with

symbol $đz$ (e.g. $đQ$, $đW$ etc.)

Mathematical Preliminaries

The equation of state for a system of chemically defined homogeneous fluid: $f(P, V, T) = 0$

$\Rightarrow$ Reciprocal and cyclic relations are satisfied by P, V, T

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}$$

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

$(P, V, T) = 0 \Rightarrow P = f(V, T)$

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

$V = f(P, T)$

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

$T = f(P, V)$

$$\Rightarrow dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV$$

Mathematical Preliminaries

ome definitions:

. Thermal coefficient of volume expansion at constant pressure: $\quad \beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

. Pressure coefficient of volume expansion at constant temperature: $\quad K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

. Isothermal compressibility or Isothermal Bulk modulus: $\quad \beta_T = 1/K_T = -V\left(\frac{\partial P}{\partial V}\right)_T$

Mathematical Preliminaries

oblem:

id system −

$$f(p, V, T) = 0 \Rightarrow V = f(P, T)$$

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

$$\Rightarrow \frac{dV}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T dP + \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P dT$$

$$\Rightarrow d(\ln V) = -K_T dP + \beta_P dT$$

$$\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$$

Mathematical Preliminaries

$$d(\ln V) = -K_T dP + \beta_P dT$$

$\ln V)$ is exact differential $\Rightarrow -\left(\dfrac{\partial K_T}{\partial T}\right)_P = \left(\dfrac{\partial \beta_P}{\partial P}\right)_T$
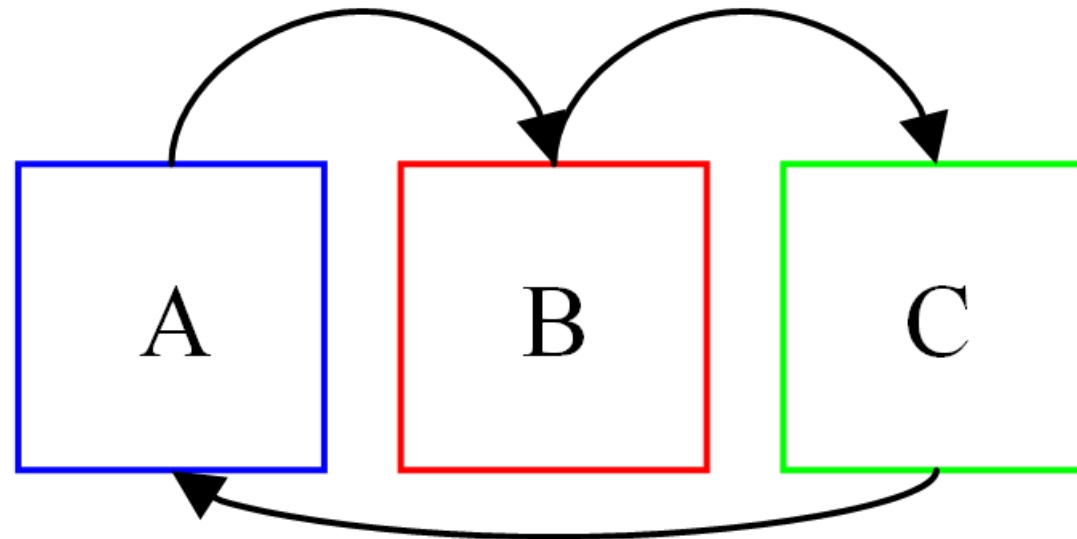
$$\frac{\beta_P}{K_T} = -\frac{\left(\dfrac{\partial V}{\partial T}\right)_P}{\left(\dfrac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$$

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

Zeroth Law of Thermodynamics

o systems are in thermal equilibrium individually with a third system, they will remain in therm
librium with each other

Zeroth Law of Thermodynamics

stem A is in thermal equilibrium with B

$$\Rightarrow \phi_1(P_A, V_A, P_B, V_B) = 0$$

$$P_B = f_1(P_A, V_A, V_B) \ldots (1)$$

stem B is in thermal equilibrium with C

$$\Rightarrow \phi_2(P_B, V_B, P_C, V_C) = 0$$

$$P_B = f_2(P_C, V_C, V_B) \ldots (2)$$

Compare (1) & (2)

$$f_1(P_A, V_A, V_B) = f_2(P_C, V_C, V_B) \ldots \ldots (3)$$

oth law implies System A is in thermal equilibrium with C

$$\Rightarrow \phi_3(P_A, V_A, P_C, V_C) = 0$$

$$f_1{'}(P_A, V_A) = f_2{'}(P_C, V_C) \ldots (4)$$

Zeroth Law of Thermodynamics

ompare (3) & (4)

$$f(P_A, V_A) = f(P_C, V_C)$$

stem A and system B are individually in thermal equilibrium with system C, zeroth law im
em A and system B are in mutual thermal equilibrium

$$f(P_A, V_A) = f(P_B, V_B)$$

$$\Rightarrow f(P_A, V_A) = f(P_B, V_B) = f(P_C, V_C)$$

Zeroth Law of Thermodynamics

Thus for every system there exists a function of its state variables such that the numerical value

function is the same for all systems in thermal equilibrium with each other.

The common value θ of these functions is called the empirical temperature.

Temperature may be defined as a function of state of a system such that it takes the same value
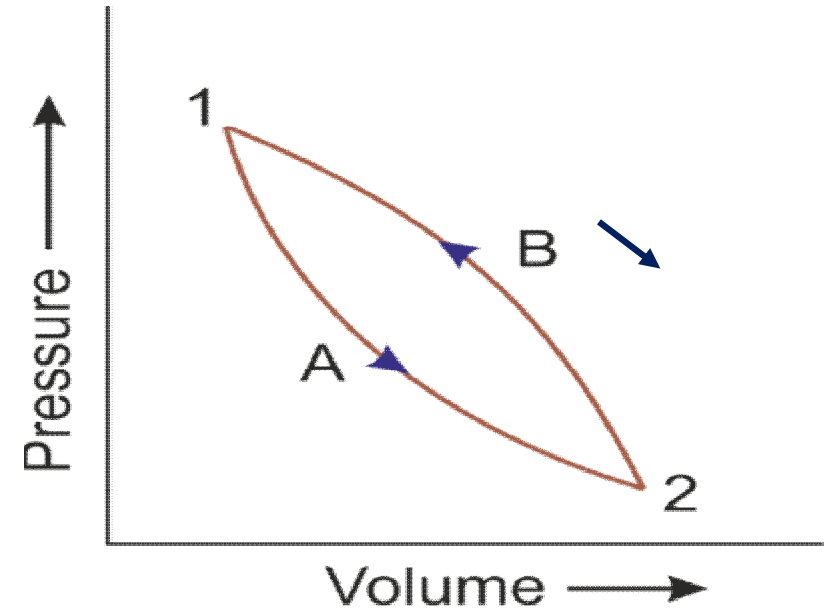
systems in thermal equilibrium with one another.

Work

Work done is path dependent – an inexact differential:

$$\int_1^2 \delta W \neq \int_1^2 \delta W$$

Path A   Path B

$$\boxed{\oint \delta W \neq 0}$$

Adiabatic Work done is same for all paths

Work

Work done δW is positive when the work is done by the system: expansion of gas, contracti wire, contraction of area of surface film etc.

Work done δW is negative when the work is done on the system: compression of gas, stretchi wire, extension of area of surface film etc.
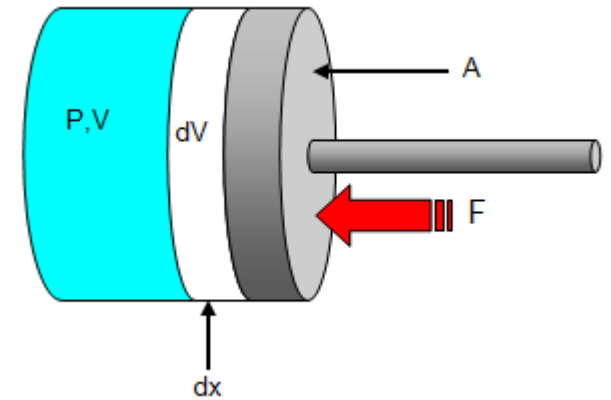
Work

ork done for a simple compressible system:

Force exerted on the piston: $F = p\alpha$

Work done by the system: $\delta W = F.dx = p\,\alpha\,dx = p\,dV$
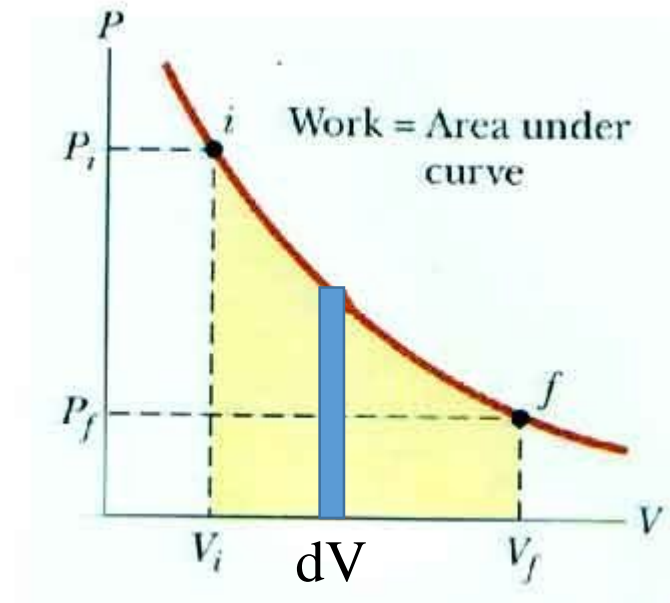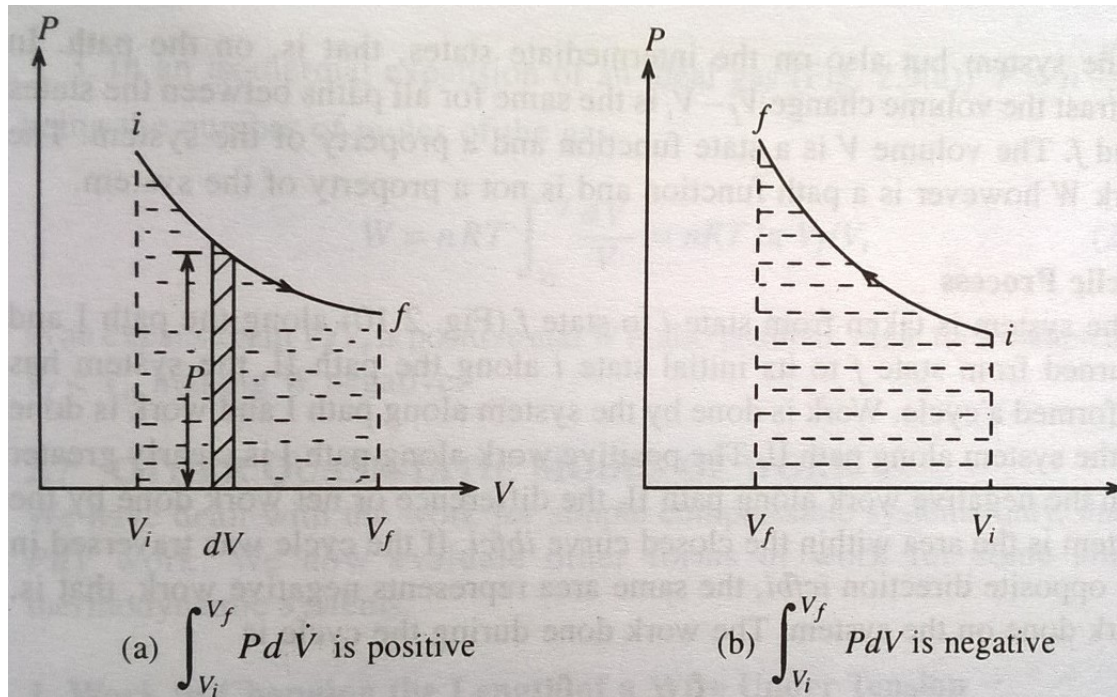
$$\Delta W = \int_i^f \delta W = \int_i^f p\,dV$$

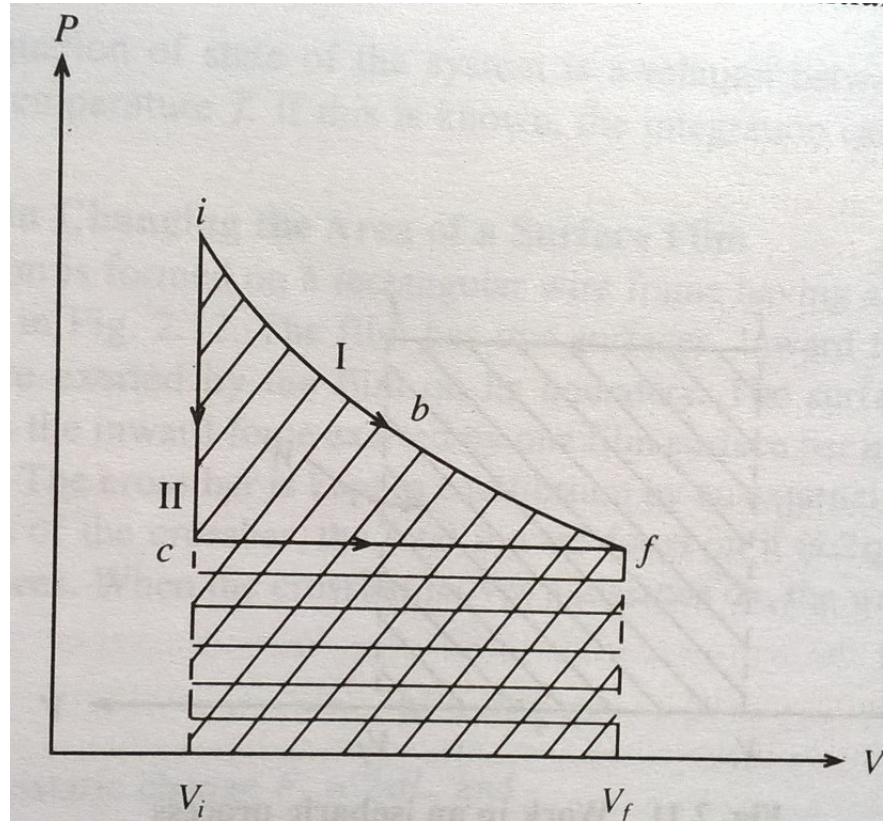ΔW is +ve for $V_f > V_i$ and −ve for $V_f > V_i$

Work

ork done and P-V diagram:

$$\Delta W = \int_{i}^{f} p\,dV = \text{area under the curve in p-V diagram}$$

Work = Area under curve

(a) $\int_{V_i}^{V_f} Pd\dot{V}$ is positive

(b) $\int_{V_i}^{V_f} PdV$ is negative

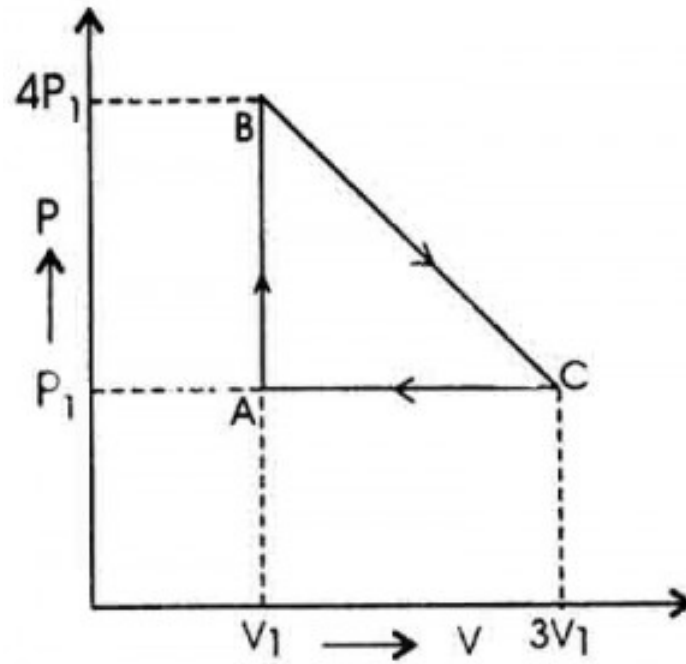# Work

Work done is path dependent:

Work

Work

ork done in isothermal expansion of ideal gas:

$$\Delta W = \int_{V_i}^{V_f} p\, dV = \int_{V_i}^{V_f} \frac{RT}{V}\, dV$$

$$= RT \int_{V_i}^{V_f} \frac{1}{V}\, dV$$

$$= RT \ln\left(\frac{V_f}{V_i}\right)$$

Work

Work done in isobaric process of ideal gas:

$$\Delta W = \int_{V_i}^{V_f} p\,dV = p \int_{V_i}^{V_f} dV \quad = p(V_f - V_i)$$

Work done in isochoric process of ideal gas: $dW = p\,dV = 0$

Work

Work done in adiabatic process of ideal gas:

$$\Delta W = \int_{V_i}^{V_f} p\,dV = c\int_{V_i}^{V_f} V^{-\gamma}\,dV \qquad \boxed{pV^{\gamma} = c \text{ (constant)}}$$

$$= \frac{c}{1-\gamma}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right)$$

$$= \frac{1}{1-\gamma}\left(cV_f^{-\gamma}V_f - cV_i^{-\gamma}V_i\right)$$

$$= \frac{1}{1-\gamma}\left(cV_f^{-\gamma}V_f - cV_i^{-\gamma}V_i\right) \quad = -\frac{R}{\gamma-1}\left(p_fV_f - p_iV_i\right) \ = \frac{R}{\gamma-1}\left(T_i - T\right.$$

Work

ork done in isothermal increase of pressure in solid:

$$\Delta W = \int_{V_i}^{V_f} p\, dV$$

$$= -\int_{p_i}^{p_f} p K_T V\, dp$$

$$\approx -K_T V \int_{p_i}^{p_f} p\, dp \;\boxed{= \frac{1}{2} K_T V \left(p_i^2 - p_f^2 \right)}$$

$$V = V(p, T)$$

$$\Rightarrow\; dV = \left(\frac{\partial V}{\partial p} \right)_T dp + \left(\frac{\partial V}{\partial T} \right)_p dT$$

$$= \left(\frac{\partial V}{\partial p} \right)_T dp$$

$$= -K_T V\, dp \qquad \because K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p} \right.$$

Work

Work done in isothermal increase of tension in wire:

$$\Delta W = - \int_{L_i}^{L_f} F \, dL$$

$$= - \int_{F_i}^{F_f} F \frac{L}{YA} \, dF$$

$$\approx - \frac{L}{YA} \int_{F_i}^{F_f} F \, dF \boxed{= \frac{L}{2YA}\left(F_i^2 - F_f^2\right)}$$

$$L = L(F,T)$$

$$\Rightarrow dL = \left(\frac{\partial L}{\partial F}\right)_T dF + \left(\frac{\partial L}{\partial T}\right)_F dT$$

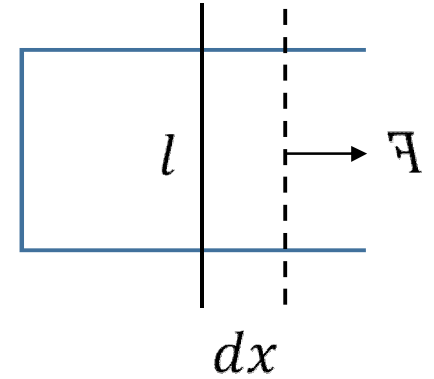$$= \left(\frac{\partial L}{\partial F}\right)_T dF$$

$$= \frac{L}{YA} dF \qquad \because Y = \frac{L}{A}\left(\frac{\partial F}{\partial L}\right)_T$$

Work

Work done in changing the area of a surface film:

$$\delta W = -F dx$$
$$= -\gamma l dx = -\gamma dA$$

$$\Delta W = -\int_{A_i}^{A_f} \gamma dA$$

l

dx

Work done in charging an electric cell:

$$\delta W = -\mathcal{E} dq$$
$$= -\mathcal{E} i dt$$

Work

Work done to magnetize a material:

$$\delta W = -B dM$$
$$= -\mu H dM$$

Work done polarizing a dielectric material:

$$\delta W = -E d P$$

Work

System	Intensive Coordinate ('Force')	Extensive Coordinate ('Displacement')	Work done (δW)
Hydrostatic system (p, V, T)	p	dV	pdV
Stretched wire (F, L, T)	F	dL	$-FdL$
Surface film (γ, A, T)	γ	dA	$-\gamma dA$
Electrochemical cell $(\mathcal{E}, q, T)$	$\mathcal{E}$	dq	$-\mathcal{E}dq$
Magnetic system (H, M, T)	H	dM	$-\mu H dM$
Dielectric system (E, P, T)	E	dP	$-EdP$