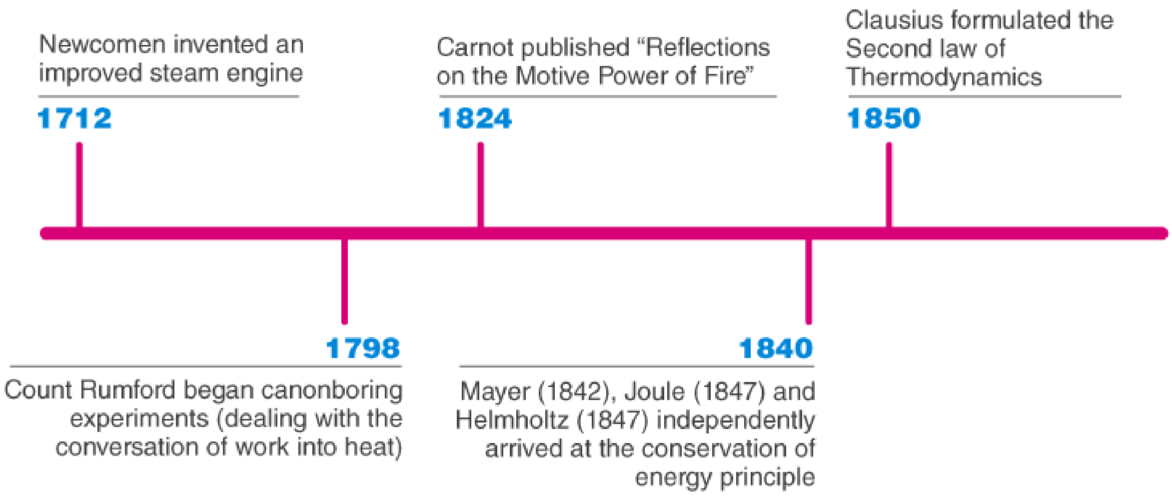
Thermodynamics

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, radiation, and properties of matter. The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics. Thermodynamics applies to a wide variety of topics in science and engineering, but also in other complex fields such as meteorology



Time line

(4)

(2)

Branches of thermodynamics

The study of thermodynamical systems has developed into several related branches, each using a different fundamental model as a theoretical or experimental basis, or applying the principles to varying types of systems.

Classical thermodynamics

Classical thermodynamics is the description of the states of thermodynamic systems at near-equilibrium, that uses macroscopic, measurable properties. It is used to model exchanges of energy, work and heat based on the laws of thermodynamics. The qualifier *classical* reflects the fact that it represents the first level of understanding of the subject as it developed in the 19th century and describes the changes of a system in terms of macroscopic empirical (large scale, and measurable) parameters. A microscopic interpretation of these concepts was later provided by the development of *statistical mechanics*.

Statistical mechanics

Statistical mechanics, also called statistical thermodynamics, emerged with the development of atomic and molecular theories in the late 19th century and early 20th century, and supplemented classical thermodynamics with an interpretation of the microscopic interactions between individual particles or quantum-mechanical states. This field relates the microscopic properties of individual atoms and molecules to the macroscopic, bulk properties of materials that can be observed on the human scale, thereby explaining classical thermodynamics as a natural result of statistics, classical mechanics, and quantum theory at the microscopic level.

Chemical thermodynamics

Chemical thermodynamics is the study of the interrelation of energy with chemical reactions or with a physical change of state within the confines of the laws of thermodynamics.

Laws of thermodynamics

Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each.

Zeroth Law

The zeroth law of thermodynamics frames an idea of temperature as an indicator of thermal equilibrium.

First Law

The first law of thermodynamics is basically law of conservation of energy relating Heat, Work & Internal energy

Second Law

This law is an expression of the universal principle of decay observable in nature. Entropy is a measure of how much this process has progressed. The entropy of an isolated system which is not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium.. There are many versions of the second law, but they all have the same effect, which is to express the phenomenon of irreversibility in nature.

Third Law

The third law of thermodynamics states: *As the temperature of a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.*

Alternate definitions include "the entropy of all systems and of all states of a system is smallest at absolute zero," or equivalently "it is impossible to reach the absolute zero of temperature by any finite number of process

Thermodynamic system

An important concept in thermodynamics is the thermodynamic system, which is a precisely defined region of the universe under study.

Surroundings

Everything in the universe except the system which can influence thermodynamic system is called the *surroundings*.

Boundary

A system is separated from the remainder of the universe by a *boundary* which may be a physical "boundary" or notional, but which by convention defines a finite volume. Segments of the "boundary" are often described as 'walls'; they have respective defined 'permeabilities'. Transfers of energy as work, or as heat, or of matter, between the system and the surroundings, take place through the walls, according to their respective permeabilities..

Boundaries are of four types: fixed, movable, real, and imaginary. For example, in an engine, a fixed boundary means the piston is locked at its position, within which a constant volume process might occur. If the piston is allowed to move that boundary is movable while the cylinder and cylinder head boundaries are fixed. For closed systems, boundaries are real while for open systems boundaries are often imaginary

- **Universe = System + Surrounding**

Generally, thermodynamics distinguishes three classes of systems, defined in terms of what is allowed to cross their boundaries:

Open system: The system across the boundary of which transfer of both mass as well as energy can take place to the surroundings. System is separated from surrounding by imaginary boundary. Example: Boiling water in a pan without a lid .Heat escape into the air.At the same time steam (which is matter) also escapes into the air.

Closed system: The system across the boundary of which no mass transfer can take place but energy transfer may take place to the surrounding. The system separated from surrounding by diathermic (conducting) boundary. Example - pressure cooker.

Isolated system: In this system no mass or energy transfer takes place across the boundary to the surrounding, the system separated from the surroundings by insulating boundary. Example – Thermoflask. .

Type of system	Mass flow	Work	Heat
Open	✓	✓	✓
Closed	✗	✓	✓

Thermally isolated	✗	✓	✗
Mechanically isolated	✗	✗	✓
Isolated	✗	✗	✗

Macroscopic Approach Vs Microscopic Approach In Tabular Form

BASIS OF COMPARISON	MACROSCOPIC APPROCH	MICROSCOPIC APPROACH
Description	In macroscopic Approach a certain quantity of matter is considered without taking into account the events occurring at molecular level. It is more concerned with gross or overall behavior.	Microscopic approach considers that the system is made up of very large number of discrete particles referred to as molecules. These molecules have different velocities and energies. The values of these energies are constantly changing with time.
Also Referred To As	Can also be referred to as classical thermodynamics.	Can also be referred to as statistical thermodynamics.
Analysis	The analysis of macroscopic system requires elementary mathematics formulas.	The behavior of the system is found by involving statistical methods because the number of molecules is large. Consequently, both complex mathematics and statistical methods are required to analyze the changes in the system.
Description Of System	When describing a system Using macroscopic approach, only a few properties are required. This makes the approach simple.	When describing a system using microscopic approach, large numbers of variables are needed and this makes the approach complex.
Values	It is an average value of activities happening at molecular level.	These are real values and hence difficult to measure.
Assumptions	No assumptions are to be made regarding structure of matter.	Molecular theory of matter is assumed.

Thermodynamic Variable/Function/Coordinate

Thermodynamic state of a system is at any instant is represented by its condition at that instant, the condition being completely specified by a set of adequate and minimum number of measurable quantities, called **Thermodynamic variable/Function/Coordinate** . Example : For Chemical System P,V,T are thermodynamic variable (**see table 2)**

Once such a set of values of thermodynamic variables has been specified for a system, the values of all thermodynamic properties of the system are uniquely determined. Usually, by default, a thermodynamic state is taken to be in thermodynamic equilibrium.

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Intensive and extensive variable

Thermodynamic variables are of two different kinds 1) Intensive , 2) Extensive

- **Intensive variable** is one whose magnitude is independent of the size of the system. Example : Pressure, surface tension, electrical Potential
- **Extensive variable** is one that depends on the size (or extent) of the system under consideration. Example Volume, area, entropy
- extensive quantity is one whose magnitude is additive for subsystems. See table (2)

Thermodynamic equation of state

Thermodynamic equation of state is an equation relating Thermodynamic variables which describe the **state** of matter under a given set of physical conditions. See table (2)

State Functions

state function or **function of state** or **point function** is a function defined for a system properties relating several state variable that depends only on the current equilibrium state.

- State functions do not depend on the path by which the system arrived at its present state.
- A state function describes the equilibrium state of a system and thus also describes the properties of system.
- integrals illustrate how state functions depend only on the final and initial value and not on the object's history or the path taken to get from the initial to the final value.

Here is an example of the integral of enthalpy, H, where t0 represents the initial state and t1 represents the final state.

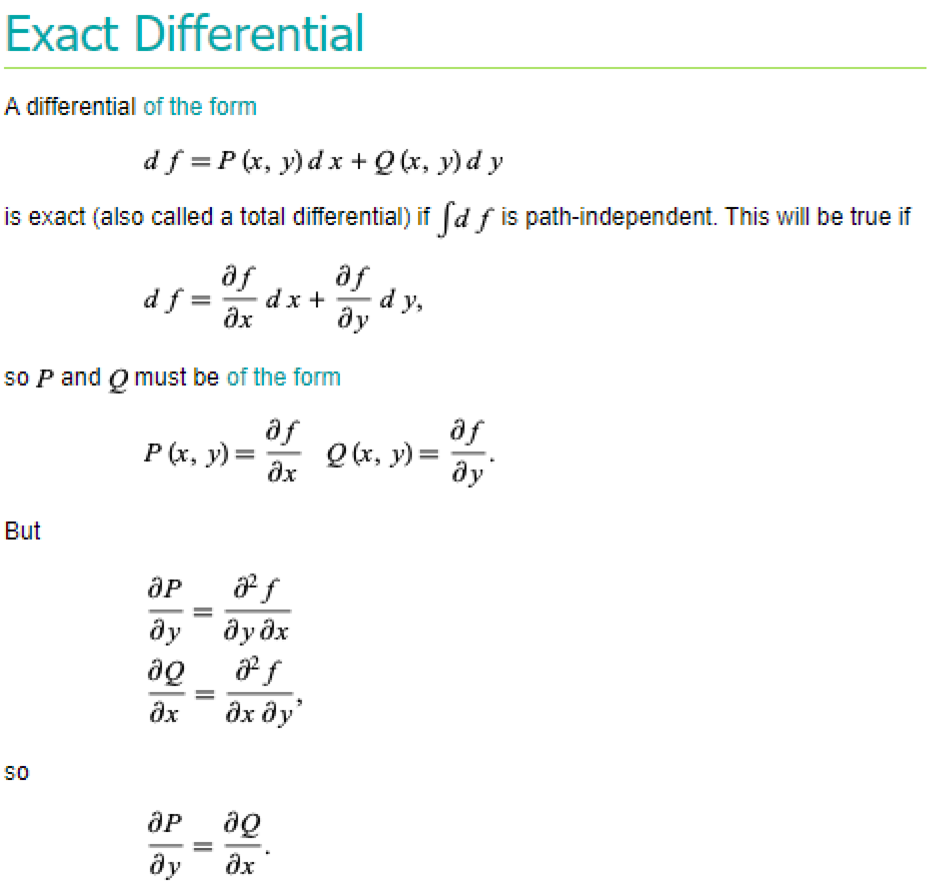
$\int_{t0}^{t1} H(t)dt$ =H(t1)−H(to)

- Closed integral of state function is zero.$\oint H(t)dt = 0$
- Differential form of state function is exact differential. So they follow properties of exact differential, So 2nd order derivative of state function is independent of order.
- Examples of state functions include Temperature, pressure ,volume internal energy, enthalpy, entropy.

Path Function

Functions whose value depends on the **path** taken to get between two states are called **path functions**.

- Different routes give different quantities.
- Examples of path functions include work, heat
- Path function require multiple integral and limit of integration to integrate properly
- Their differential form are inexact differential
- Examples of path functions : work, heat



Exact Differential

A differential of the form

$$d f = P(x, y) d x + Q(x, y) d y$$

is exact (also called a total differential) if $\int d f$ is path-independent. This will be true if

$$d f = \frac{\partial f}{\partial x} d x + \frac{\partial f}{\partial y} d y,$$

so P and Q must be of the form

$$P(x, y) = \frac{\partial f}{\partial x} \quad Q(x, y) = \frac{\partial f}{\partial y}.$$

But

$$\frac{\partial P}{\partial y} = \frac{\partial^2 f}{\partial y \, \partial x}$$
$$\frac{\partial Q}{\partial x} = \frac{\partial^2 f}{\partial x \, \partial y},$$

so

$$\frac{\partial P}{\partial y} = \frac{\partial Q}{\partial x}.$$

Table 2

	System	Thermodynamic Variable	Intensive Variable	Extensive Variable	Work	Equation of State
1	Chemical or Hydrostatic System	P(pressure),V(volume),T(temperature)	P,T	V	PdV	f(P,V,T)=0
2	Stretched Wire(elastic System)	L (length),F (tension),T (temperature)	F ,T	L	-FdL	f(L,F,T)=0
3	Magnetic System	M(total magnetisation),B/H(magnetic field intensity),T	B/H,T	M	-HdM	f(M,H,T)=0
4	Electric Cell	Z (charge),E (potential difference),T	E,T	Z	-EdZ	f(E,Z,T)=0
5	Surface Film	S(surface tension), A(area),T	S,T	A	-SdA	f(S,A,T)=0

Thermodynamic equilibrium

condition or state of a thermodynamic system, the properties of which do not change with time and that can be changed to another condition only at the expense of effects on other systems

Mechanical Equilibrium: The absence of unbalanced force in the interior of a system or between the system & surroundings, implies Mechanical equilibrium

Chemical Equilibrium: The absence of any spontaneous change of internal structure (by way of diffusion or chemical reaction or by both) in a system or between system and surroun in mechanical equilibrium implies chemical equilibrium.

Thermal Equilibrium: For a system in mechanical & chemical equilibrium *thermal equilibrium* is said to be attained when there is no spontaneous change in the coordinates of the system when separated from the surroundings by a diathermic wall. In thermal equilibrium the temperature is same all throughout the system and is identical with the surroundings.

When all three equilibrium mentioned above are attained by a system, the system is said to be in.

The state of thermodynamic equilibrium is specified in terms of macroscopic coordinates (not involving time) which may be designate as *thermodynamic variables*

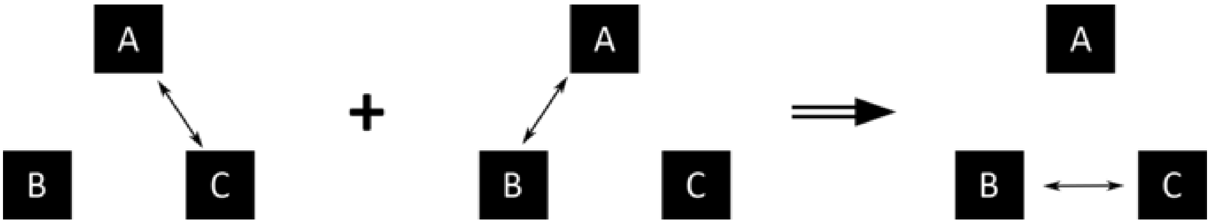
Zeroth Law

Zeroth law of thermodynamics is one of the four laws of thermodynamics. The credit for formulating the law goes to Ralph H. Fowler. Interestingly, the zeroth law of thermodynamics was actually developed much later than the original three laws. However, there were few confusions regarding the nomenclature whether it should be named the fourth law or some other name. The complication arose because the new law gave a much clearer definition of the temperature and basically replaced what the other three laws had to state. Fowler finally came up with the name to end this conflict.

The zeroth law of thermodynamics frames an idea of temperature as an indicator of thermal equilibrium.

What is Zeroth Law of Thermodynamics?

When a body 'A' is in thermal equilibrium with another body 'b', and also separately in thermal equilibrium with a body 'C', then body 'B' and 'C' will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics. The law is based on temperature measurement.



Zeroth Law of Thermodynamics: The double arrow represents thermal equilibrium between systems. If systems A and C are in equilibrium, and systems A and B are in equilibrium, then systems B and C are in equilibrium. The systems A, B, and C are at the same temperature.

Concept of Temperature

Let the state variable of system A be (x_A, y_A) & those of system B and C be (x_B, y_B) and (x_c, y_c) respectively. The approach to thermal equilibrium between A and B would be indicated by changes in the four variable (x_A, y_A, x_B, y_B) and when finally the state of thermal equilibrium would be attained. A general relation of the type below would exist among the variables,

$$F_1(x_A, y_A, x_B, y_B) = 0 \qquad (1)$$

Similarly when the system B & C are in thermal equilibrium

$$F_2(x_B, y_B, x_C, y_C) = 0 \qquad (2)$$

Where F_2 may be different from function F_1, but both are assumed to be well behaved.

According to Zeroth law, when (1) & (2)hold , the system A & C will also be in thermal equilibrium

$F_3(x_A, y_A, x_C, y_C) = 0$ (3)

$x_B = \alpha_1 (x_A, y_A, y_B)$ From (1)

$x_B = \alpha_2 (x_C, y_C, y_B)$ From (2)

$\alpha_1 (x_A, y_A, y_B) = \alpha_2 (x_C, y_C, y_B)$ (4)

Relation (3) & (4) must also be equal . Thus (4) must hold independent of y_B & must be equivalent to an equation

$f_1 (x_A, y_A) = f_3(x_C, y_C)$ (5)

This implies : $\alpha_1 (x_A, y_A, y_B) = f_1 (x_A, y_A) \beta (y_B) + \zeta (y_B)$

And $\alpha_2 (x_C, y_C, y_B) = f_3(x_C, y_C)\beta (y_B) + \zeta (y_B)$

$\therefore$ Eq (3) & (5) must be equal.

By similar arguments, we have from equilibrium of system A and B and C

$f_1 (x_A, y_A) = f_2(x_B, y_B)$

$f_2(x_B, y_B) = f_3(x_C, y_C)$

Finally we have the three systems are in thermal equilibrium, we have

It follows therefore, that there exists for each set of variables a function and these functions are all equal when the systems are in thermal equilibrium with one another. If θ be the common value of these function

$\Theta = f_1 (x_A, y_A) = f_2(x_B, y_B) = f_3(x_C, y_C)$ (6)

This θ is the Emperic Temperature common to all system.

Definition : The temperature is the property that determines whether or not a system is in thermal equilibrium with other system.

- The relation $\Theta = f_1 (x_A, y_A)$ is simply the equation of an isotherm of the system A. for different numerical value of θ different isotherm will be obtained.
- Temperature is scaler character.
- Temperature is not a additive.

Temperature is determined by mean kinetic energy of molecules.

Heat

Heat is a transfer of thermal energy caused by a difference in temperature. This temperature difference is also called a temperature gradient. Since heat is a movement of energy, it is measured in the same units as energy: joules (J). It should also be noted that work and heat are closely related (see heat vs work for more information)

The second law of thermodynamics proves that heat will always flow spontaneously from higher temperatures to lower temperatures. This energy flow can be harnessed by a heat engine to do useful work. Heat pumps can also force thermal energy to flow backwards (from cold to hot), but these require energy input.

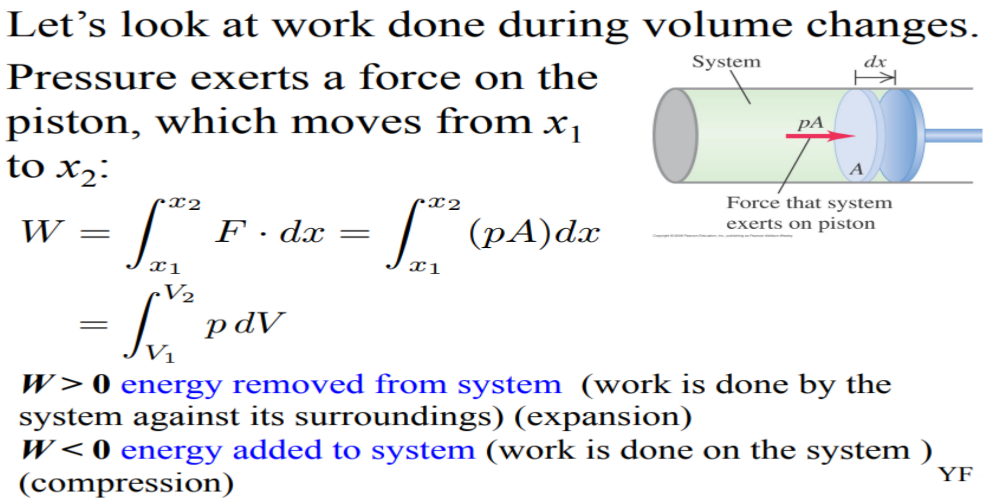
There are three heat transfer mechanisms

- **Conduction ,Convection, .Radiation**

Work in Thermodynamics
In general, work is defined for mechanical systems as the action of a force on an object through a
W = F . d
where: W = work (J), F = force (N). d = displacement (m)

If thermodynamic system as a whole, exert a force on the surroundings and a displacement occours, work is said to be done either by the system or on the system eg. Expansion of gas in a cylinder with piston at constant pressure. This work is external work. It is distinguished from intrernal work, when one part of the system exerts a force on other part causing a displacement**. Internal work has no role in thermodynamics & the term work means external work.**

Work for a hydrostatic/Chemical System



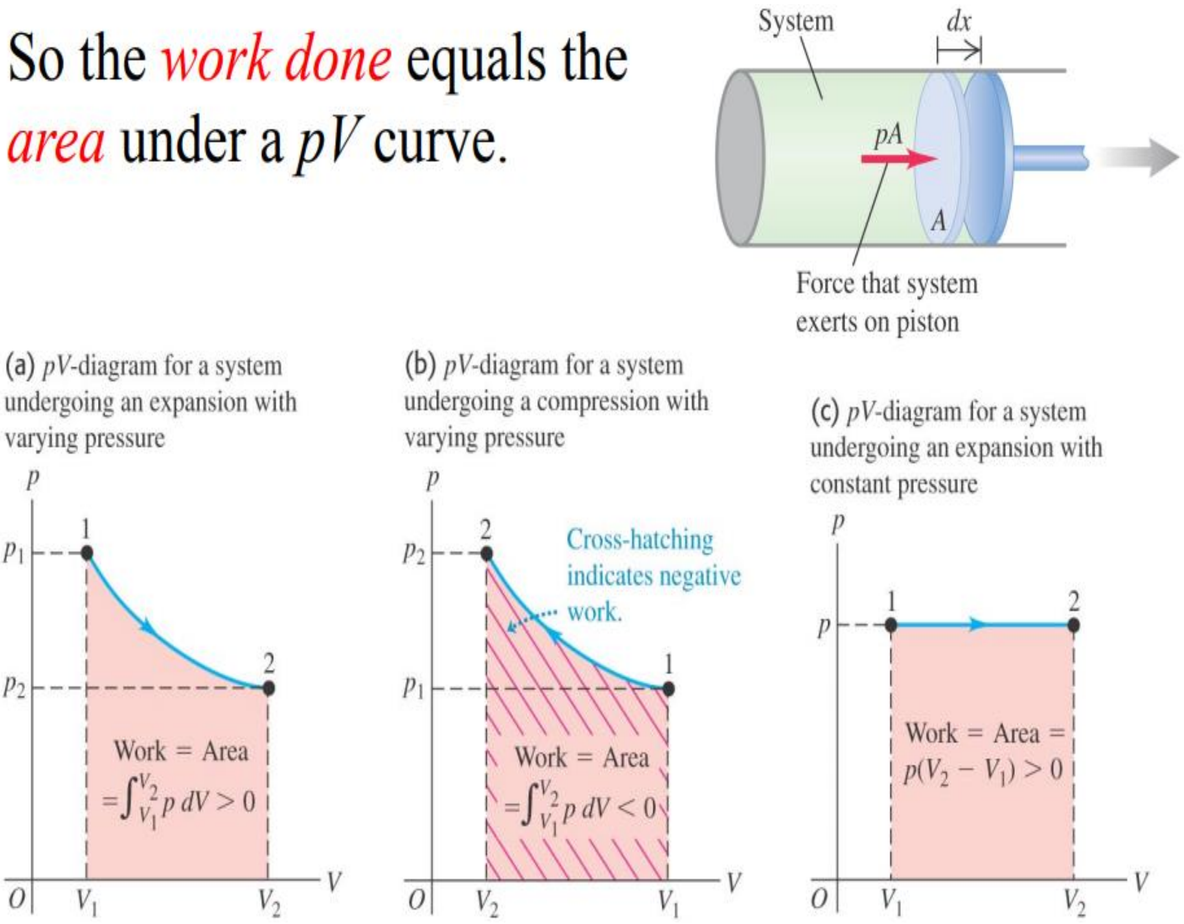
Let's look at work done during volume changes.

Pressure exerts a force on the piston, which moves from x_1 to x_2:

$$W = \int_{x_1}^{x_2} F \cdot dx = \int_{x_1}^{x_2} (pA)dx$$
$$= \int_{V_1}^{V_2} p\,dV$$

$W > 0$ energy removed from system (work is done by the system against its surroundings) (expansion)
$W < 0$ energy added to system (work is done on the system) (compression)

YF



So the *work done* equals the *area* under a pV curve.

(a) pV-diagram for a system undergoing an expansion with varying pressure

(b) pV-diagram for a system undergoing a compression with varying pressure

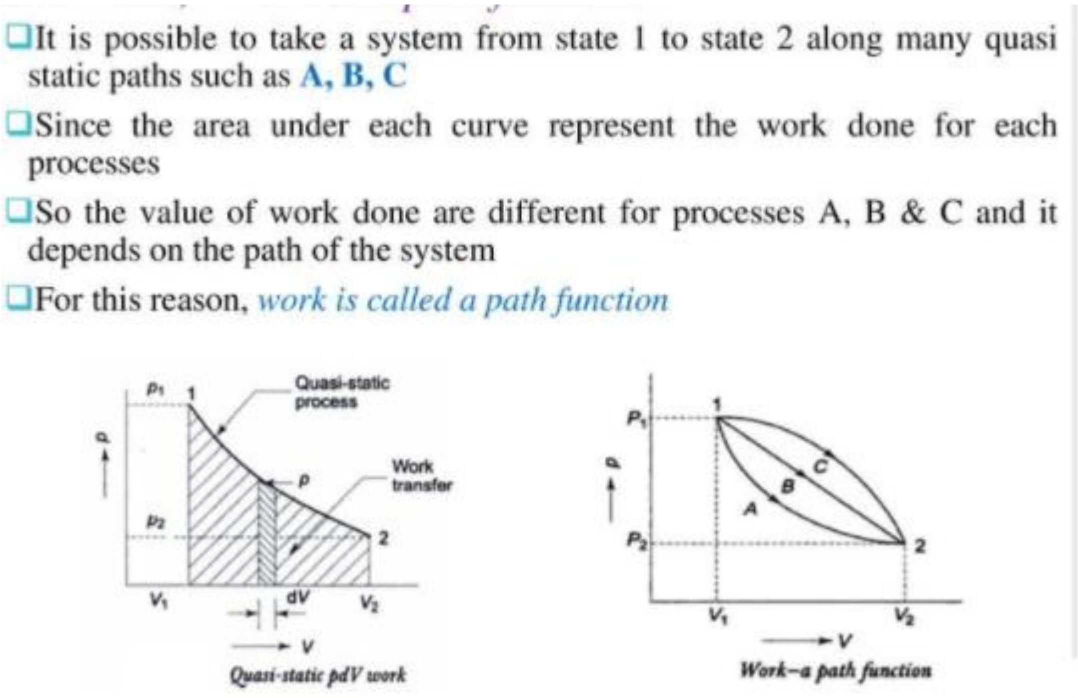
(c) pV-diagram for a system undergoing an expansion with constant pressure

Show That Work is a Path Function/inexact Differential

A Path function is a function whose value depends on the path followed by the thermodynamic process irrespective of the initial and final states of the process.

An example of path function is work done in a thermodynamic process.
Work done in a thermodynamic process is dependent on the path followed by the process.
A path function is an inexact or imperfect differential.

Approach 1

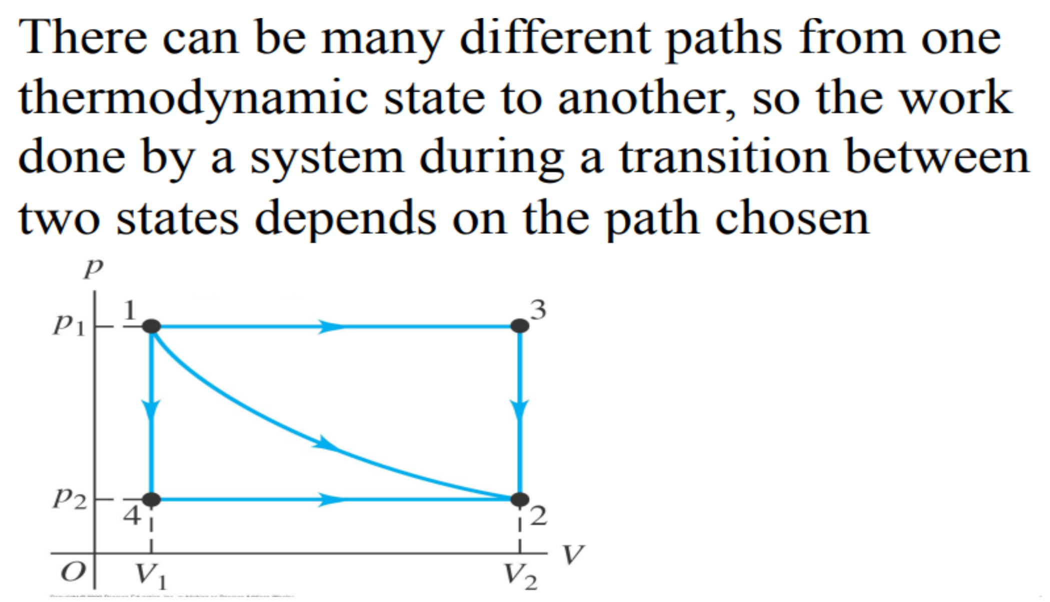


- ❑It is possible to take a system from state 1 to state 2 along many quasi static paths such as **A, B, C**
- ❑Since the area under each curve represent the work done for each processes
- ❑So the value of work done are different for processes A, B & C and it depends on the path of the system
- ❑For this reason, *work is called a path function*

Quasi-static pdV work

Work–a path function

Approach 2



There can be many different paths from one thermodynamic state to another, so the work done by a system during a transition between two states depends on the path chosen

Calculation of work

Let initial Position of a thermodynamic system is 1 & final position is 2.   Thermodynamic system can move from Initial to final position by performing work along various path.

- Work done along path 1-4-2 is
  Along 1-4 no work as no change in volume,
  along 4-2 work done = $P_2 (V_2-V_1)$

$\therefore W_{142} = P_2 (V_2 - V_1)$

- Work done along 1-3-2
  Along 1-3 work done = $P_1(V_2 - V_1)$
  Along 3-2 no work as no change in volume
  $W_{132} = P_1(V_2 - V_1)$
- Work along 1-2 by isothermal process
  $W_{12} = RT \ln(V_2/V_1)$

This shows that work done is different along different path chosen. So work is a path function

Heat vs work

Heat and work are two different ways of transferring energy from one system to another. The the distinction between **Heat and Work** is important in the field of thermodynamics. Heat is the transfer of thermal energy between systems, while work is the transfer of mechanical energy between two systems. Heat can be transformed into work and vice verse , but they aren't the same thing. The first law of thermodynamics states that heat and work both contribute to the total internal energy of a system, but the second law of thermodynamics limits the amount of heat that can be turned into work.

Main Differences

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	Work (W)	Heat (Q)
Interaction	Mechanical	Thermal
Requires	Force and Displacement	Temperature difference
Process	Macroscopic pushes and pulls	Microscopic collisions

Positive value	W > 0 when a gas is compressed. Energy is transferred into system.	Q > 0 when the environment is at a higher temperature than the system. Energy is transferred into system.
Negative value	W < 0 when a gas expands. Energy is transferred out of system.	Q < 0 when the system is at a higher temperature than the environment. Energy is transferred out of system.
Equilibrium	A system is in mechanical equilibrium when there is no net force or torque on it.	A system is in thermal equilibrium when it is at the same temperature as the environment.

Thermodynamic process

Defined by change in the system, a thermodynamic process is a passage of a thermodynamic system from an initial to a final state of thermodynamic equilibrium. The initial and final states are the defining elements of the process.

A cyclic process

If a system undergoes two or more processes and returns to its original state, after conclusion 0f processes, the system is said to have undergone a cycle. Therefore, ā thermodynamic path in a cycle forms a closed loop. In a cyclic process, the system starts and returns to the same thermodynamic state.

The net work involved is the enclosed area on the P-V diagram. If the cycle goes clockwise, the system does work. A cyclic process is the underlying principle for an engine.

If the cycle goes counter clockwise, work is done on the system every cycle. An example of such a system is a refrigerator or air conditioner.

Reversible Process

A thermodynamic process is reversible if the process can return back in such a that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. It means both system and surroundings are returned to their initial states at the end of the reverse process.

A process can be reversible only when its satisfying two conditions

- Dissipative force must be absent.
- The process should occur in infinite small time i.e **in quasistatic process**

Irreversible Process

- An irreversible process is one in which the system and its environment cannot return together to exactly the states that they were in.
- All Natural Process are irreversible -second law of thermodynamics.

Quasistatic Process

A quasi-static process refers to an idealized or imagined process where the change in state is made infinitesimally slowly so that at each instant, the system can be assumed to be at a thermodynamic equilibrium with itself and with the environment. Physically an infinitely slow τ×ŦŦor quasitatic variation of any parameter A with time t (dA/dT) is considerably smaller than its mean rate of variation in relaxation. If relaxation time is Ŧ and the corresponding variation of the parameter is ΔA, then for a quasistatic process to occur,

(dA/dT) $\ll \Delta A/Ŧ$

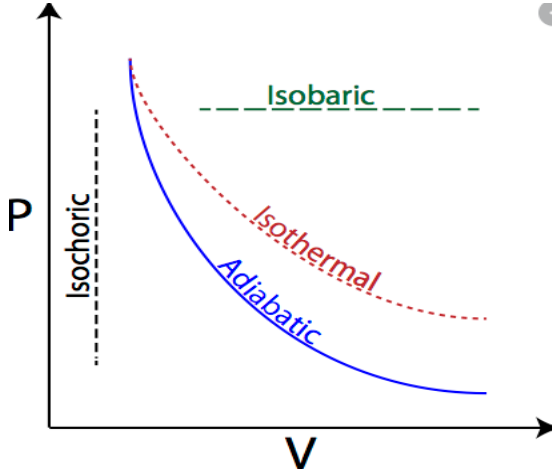
This means that at any stage of the process, there will be enough time for the parameters to equalise over the entire system and such a process will represent a continuous succession of equilibrium states infinitely close to each other. They are practically quasi equilibrium or quasistatic.

- It is a **thermodynamic process** which occurs **infinitesimal slowly.**
- Every state passed by the quasi static process **tends to equilibrium .**
- Quasi means **almost** and static means the thermodynamic properties static with time. Quasi static process is also a reversible process.

Four Main **Thermodynamic** Processes

- An **adiabatic process** is a process during which no heat enters or leaves the system. In this process entropy remain constant
- An **isobaric process** is a process that occurs at constant pressure. An **isovolumetric or isochoric process** takes place at constant volume.

- An **isothermal process** occurs at constant temperature.



First Law of Thermodynamics

1st law of thermodynamics A thermodynamic system is a collection of objects we can regard as a unit, that can exchange energy with its surroundings. We can now think about energy transfers into and out of these systems; through –

- **heat transfer Q**
- **work W**

Sign convention We need to be careful about signs:

- Qin is positive
- Qout is negative
- W done by the system is positive
- W done on the system is negative

Heat and work So both heat and work are only recognized as they cross the boundary of a system.

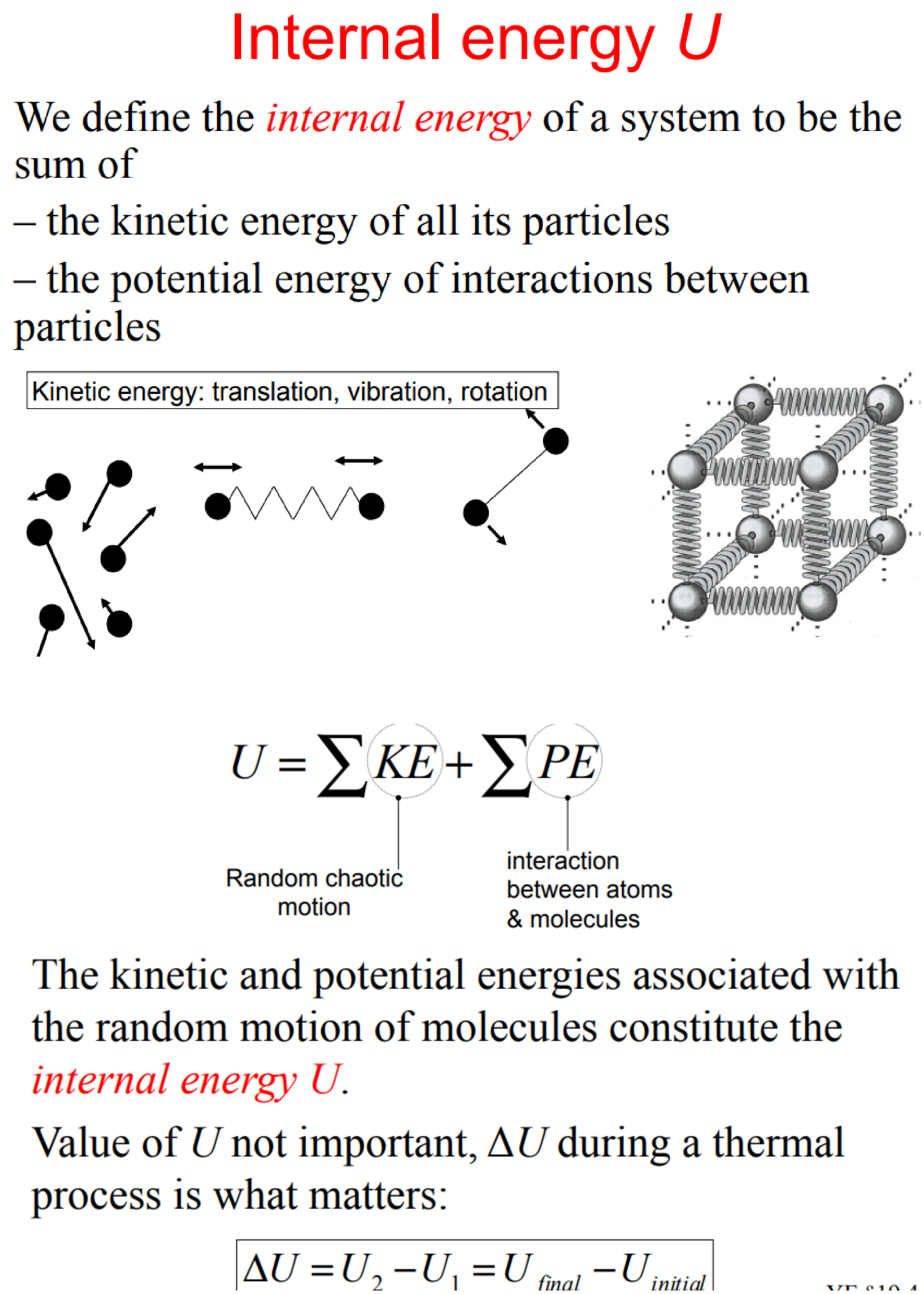
- They are associated with a process, not a state.

- They are both path-dependent functions.

- A system in general does not possess heat or work.

Three term **Heat, Work, Internal Energy** are related in 1st law of Thermodynamics. We have already discussed about Heat & Work

Now we discussed about Internal Energy.



Internal energy *U*

We define the *internal energy* of a system to be the sum of

– the kinetic energy of all its particles

– the potential energy of interactions between particles

Kinetic energy: translation, vibration, rotation

$$U = \sum KE + \sum PE$$

Random chaotic motion

interaction between atoms & molecules

The kinetic and potential energies associated with the random motion of molecules constitute the *internal energy U*.

Value of U not important, ΔU during a thermal process is what matters:

$$\boxed{\Delta U = U_2 - U_1 = U_{final} - U_{initial}}$$

Internal energy U represents the total of all the microscopic modes of energy associated with the random motion and the internal structure of molecules. By microscopic modes of energy, we mean, for example, the energy associated with the translational, rotational and vibrational motion of individual molecules and the energy associated with the intermolecular forces. The energy associated with the position, motion and spin of the electrons, with the nucleus-electrons interactions in an atom, and with the nucleus-nucleus interactions also contribute towards the microscopic modes of energy.

These different microscopic modes of energies are strongly related to macroscopic properties such as the temperature(T) , pressure (P), volume (V),electrical charge, magnetic dipole-moment, surface tension, etc. Internal energy U , which represents the total of all the microscopic modes of energy in a system, can therefore be taken as a function of all the macroscopic properties, and can be expressed as

U = U (P, T, V, electrical charge, magnetic dipole-moment, etc.)

The change in internal energy of a system during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other. i.e**. U is an intrinsic property of the system. U is a State function.**

Internal energy of a system is a single valued state function and it is the sum of the energy of all the internal degrees of freedom that the system possesses.

Internal energy of an ideal gas

U = Nf (KT/2) where f is the degrees of freedom

So internal energy of ideal gas is function of temp only.

Mathematical formulation of First law of thermodynamics

The 1st law of thermodynamics is a mathematical formulation of the quantitative aspect of the law of conservation and transformation of energy.

Imagine two distinct experiments performed on a definite system.

In one we measure the adiabatic work necessary to change the system from i – f.

The adiabatic work = $U_f - U_i$

In the second case also, the system undergoes the same change of state (i – f) but non adiabatically. $W_{non\text{-}adiabatic} \neq U_f - U_i$ The principle of conservation of energy leads us to conclude that energy has been transferred by means other than performance of work. This energy whose transfer can be attributed to difference of temperature between the system and the surrounding is nothing other than **Heat**

Thermodynamically Heat is defined as: If a system whose temperature is different from surroundings and on which work may be performed, undergoes transformation ,energy transferred by means other than performance of work (non mechanical) is equal to the

difference between the adiabatic work ($U_f - U_i$) and non adiabatic work (-W) and is called Heat.

$Q = (U_f - U_i) - (-W) = U_f - U_i + W \qquad (1)$

The eq (1) may be written for an infinitesimal process as

$d\bar{Q} = dU + d\bar{W}$

This is the mathematical formulation of 1st law of thermodynamics.

Where dQ is +ve when heat is absorbed & -ve when heat is rejected by the system. It is a path function & inexact differential.

dU is the change in internal energy. It is a state function.so dU is an perfect differential.

dW is the work done. It is +ve when work is done by the system & -ve when work is done upon the system.

It is a path function so dW is an inexact differential.

So Mathematical statement of 1st law can be written as During a thermodynamic process there lies an single valued state function called internal energy, whose change is equal to heat absorbed And work done upon the system.

Conclusion

- The **first law of thermodynamics** is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat and as thermodynamic work, and relating them to a function of a body's state, called Internal energy.
- Internal Energy is a state function ,its differential is exact differential and it is expressible as the algebraic sum of two inexact differential.
- No useful work can be obtained without spending an equivalent amount of some other energy, **thus prepetual motion of 1st kind is impossible.**
- Heat as an energy during transit by virtue of temperature difference. Heat spontaneously flows from the system at the higher temperature to the system at the lower temperature

Limitations of First Law of Thermodynamics

- The limitation of the first law of thermodynamics is that it does not say anything about the direction of flow of heat.
- It does not say anything whether the process is a spontaneous process or not.

- The reverse process is not possible. In actual practice, the heat doesn't convert completely into work. If it would have been possible to convert the whole heat into work, then we could drive ships across the ocean by extracting heat from the water of the ocean.

Application of The First Law of Thermodynamics in different thermodynamic process

(a)**Cyclic Process** Energies operate in cycles, in which the system --- for example, a gas --- periodically returns to its initial state. Since the system returns to its initial state, the change in the internal energy in one complete cycle is zero; that is, $\Delta U=0$. From the first law we see that

Cyclic Process $dQ = dW$

(b) **In isothermal process (Constant Temp)** $dU = C_v dT=0$, $dQ=dW$

(c) **In a Isochoric system (constant-volume)** process, the volume of the system stays constant. Consequently, $W=PdV= 0$. From the first law we see that Constant-Volume Process $dU =d Q$

(d) **In isobaric process** $dU=dQ-dW$

(e) **In an adiabatic process**, the system does not change heat with its surrounding; that is, $Q=0$. From the first law we see that In an adiabatic expansion the internal energy decreases. That is usually manifested as a drop in temperature. Conversely, when a gas is compressed adiabatically, its internal energy increases and the temperature rises.

Adiabatic Process $dU = -dW$

Heat capacity and internal energy

The goal in defining heat capacity is to relate changes in the internal energy to measured changes in the variables that characterize the states of the system. For a system consisting of a single pure substance, the only kind of work it can do is atmospheric work, and so the first law reduces to

$dU = d'Q - P\,dV$ (1)

Suppose now that U is regarded as being a <u>function</u> $U(T, V)$ of the independent pair of va

The differential quantity dU can always be expanded in terms of its partial <u>derivatives</u> according to

dU = $(\frac{\partial U}{\partial T})_V\, dT + (\frac{\partial U}{\partial V})_T\, dV$ (2)

where the subscripts denote the quantity being held constant when calculating derivatives. Substituting (2) in (1)equation yields the general expression

$$dQ = (\frac{\partial U}{\partial T})_V \;dT \;+ [P + (\frac{\partial U}{\partial V})_T\;]dV \qquad (3)$$

$$\frac{dQ}{dT} = (\frac{\partial U}{\partial T})_V \;dT \;+ [P + \left(\frac{\partial U}{\partial V}\right)_T\;]dV \qquad (4)$$

Valid for any change in T or V

For a temperature change at constant volume, $dV = 0$ and, by definition of heat capacity at constant volume& using eq (4) we get

$C_V = (\frac{dQ}{dT})_V = (\frac{\partial U}{\partial T})_V$ (5) [For 1 Mole C_V is molar heat capacity]

For a temperature change at constant pressure, $dP = 0$, and, by definition of heat capacity at constant pressure & using (4) we get

$C_p = (\frac{dQ}{dT})_P = (\frac{\partial U}{\partial T})_V \;+ [P + \left(\frac{\partial U}{\partial V}\right)_T\;](\frac{dV}{dT})_P$ (6)

$C_p = C_V \;+ [P + \left(\frac{\partial U}{\partial V}\right)_T\;](\frac{dV}{dT})_P$ (7) [using (5)]

$$\mathbf{C_P - C_V = [P + \left(\frac{\partial U}{\partial V}\right)_T\;](\frac{dV}{dT})_P} \qquad \mathbf{(8)}$$

(C_p – C_v) for Ideal gas

$\left(\frac{\partial U}{\partial V}\right)_T$ represents the internal work that must be done to pull the system apart against the forces of attraction between the molecules of the substance (internal stickiness). Because there is no internal stickiness for an ideal gas, this term is zero, and, from the ideal gas law, the remaining partial derivative is

$$P\left(\frac{\partial V}{\partial T}\right)_P = nR. \qquad \textbf{(7)}$$

With these substitutions the equation for C_P becomes simply

$$C_P - C_V = nR \qquad \textbf{(8)}$$

This is known as Mayer's relation

(C_p – C_v) For real Gas

For real gas internal energy varies with volume, forwork has to be done against the intermolecular forces. For vander Waals model of real gas,

$(p + a/V^2)(V-b)=RT$ for 1 mole (9)

$\left(\frac{\partial U}{\partial V}\right)_T = a / V^2$ (10)

so from eq (6) , using (9) & (10) we get

$C_P - C_V = \frac{RT}{V-b}\left(\frac{\partial V}{\partial T}\right)_P$ (11)

Differentiating eq (9) with respect to T, keeping P constant,

$\{p + a/V^2 - (V-b)\frac{2a}{V3}\} \left(\frac{\partial V}{\partial T}\right)_P = R$

$\left(\frac{\partial V}{\partial T}\right)_P = R/ \{p + a/V^2 - (V-b)\frac{2a}{V3}\} = R(V-b)/\{RT - \frac{2a}{V3}(V-b)^2\}$

$= R(V-b)/[RT\{1 - \frac{2a}{RTV3}(\mathrm{V} - \mathrm{b})2\}] = \frac{(V-b)}{T}\{1 - \frac{2a}{RTV3}(\mathrm{V} - \mathrm{b})^2\}^{-1}$

$= \frac{(V-b)}{T}\{1 + \frac{2a}{RTV3}(\mathrm{V} - \mathrm{b})^2\}$ (12)

Substituting (11) in (12) we obtain

$\boldsymbol{C_P - C_V = R\{1 + \frac{2a}{RTV3}(\mathrm{V} - \mathrm{b})^2\}}$ **(13)**

As b very small

$$C_p - C_V = R\left(1 + \frac{2a}{VRT}\right). \quad \textbf{(14)}$$

Comparing (8) & (14) it is observed that the difference is more for a real gas. For large molecular separation , the second term in the braket of (13) is ignorable and the result is same as (8) with n=1 mole.

Two forms of 1st law of thermodynamics for hydrostatic /chemical system

$d\bar{Q} = dU + PdV$

$= C_v dT + PdV$ [as $C_v = \left(\frac{dU}{dT}\right)_v \rightarrow dU = C_v dT$]

$d\bar{Q} = C_v dT + PdV$ (1)

$= (C_p - R)dT + PdV$ [as $(C_p - C_v) = R$ for 1 mole]

$= C_p dT - PdV - VdP + PdV$ (as $PV = RT$ & differentating we get

$PdV + VdP = RdT$)

$d\bar{Q} = C_p dT - VdP$ (2)

Eq (1) is used for solving problem where there is variation in V & T. Eq (2) is used for problem where there is variation in P & T.

Adiabatic Relation for an ideal gas derived from 1st Law of Thermodynamics

In an adiabatic process, the system and the surroundings are not in thermal contact. That is, no heat exchange takes place and dQ = 0. hence the first law of thermodynamics tells us that

$C_v dT + PdV = 0 \rightarrow C_v dT = -PdV$ (1)

$C_p dT - VdP = 0 \rightarrow C_p dT = VdP$ (2)

From (1) & (2)

We get

$$\frac{dP}{p} = -\left(\frac{Cp}{Cv}\right)\frac{dV}{V} = -\gamma\frac{dV}{V}$$

Integrating we obtain $\ln P = -\gamma \ln V + \ln(\text{const})$

$PV^{\gamma} = Const$ (3)

$(RT/V)V^{\gamma} = RT\, V^{\gamma-1} = Const$

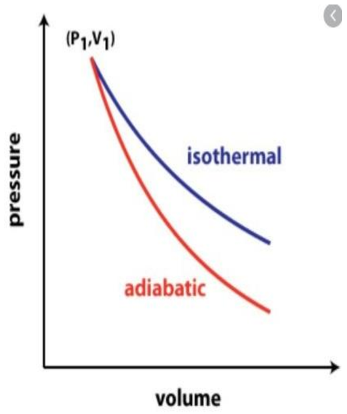
$T V^{\gamma-1} = Const$ (4)

$PV^{\gamma} = P(RT/P)^{\gamma} = Const$

$T^{\gamma}/P^{\gamma-1} = Const$ (5)

Eq 3, 4,5 are (P-V) , (T-V) , (T-P) relation of adiabatic process respectively.

Show that adiabatic curve is more steeper than isothermal curve



We know in adiabatic process of ideal gas is

PV^{γ} = Constant **(1)**

On differentiation, you would obtain

$$\gamma p V^{\gamma - 1} dV + V^{\gamma} dp = 0$$

which gives

$$\left(\frac{\partial p}{\partial V}\right)_s = -\frac{\gamma p}{V} \qquad \textbf{(2)}$$

So slope of adiabatic curve $(\partial P/\partial V)_S = -\gamma P/V$

For Isothermal process ideal gas

$$PV = \text{Constant} \qquad (3)$$

Differentiating both side of (3) we get

$PdV + VdP = 0$

$$(\partial p/\partial V)_T = -(P/V) \qquad (4)$$

So slope of isothermal curve is $(\partial P/\partial V)_T = -P/V$

Combining (2) & (4) we conclude that slope of adiabatic curve is γ times slope of isothermal curve & both are negative . ($\gamma > 1$)

So we conclude that adiabatic curve is more steeper than isothermal one

as($\gamma > 1$)

Ratio of adiabatic & Isothermal Compressibility

We know that compressibility and hence elasticity of a gas depend upon the conditions under which a change occurs. 'There are two possibilities : Either temperature remains constant or heat energy is conserved. Accordingly, we define isothermal and adiabatic compressibility. We will now show that their ratio is equal to the ratio of two heat capacity

Isothermal gas **compressibility**, is also called the **coefficient** of **isothermal compressibility** of gas. It is defined as the relative change in the volume of the gas with respect to the change in pressure at constant temperature. It is expressed in units of reciprocal pressure (usually psi^{-1}).

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

Adiabatic gas **compressibility** is defined as the relative change in the volume of the gas with respect to the change in pressure at constant Entropy. It is expressed in units of reciprocal pressure (usually psi^{-1})

$K_S = -1/V \left(\left(\frac{\partial V}{\partial P}\right)_S\right.$

Since the entropy is defined by **dS = dqrev/T**

it follows that any adiabatic pathway (dq=0) is also **isentropic** (dS=0), or proceeds at constant entropy.

The negative sign is important in order to keep the value of compressibility positive, since an increase in pressure will lead to a decrease in volume. Compressibility is inverse of bulk modulus of elasticity.

For Isothermal process ideal gas

PV = Constant (1)

Differentiating both side of (1) we get

$PdV + VdP = 0 \rightarrow (\partial V/\partial P)_T = -$ (V/P) (2)

For Adiabatic process of ideal gas

$PV^{\gamma} = \text{Constant}$ (3)

Differentiating both side of (3) we get

$\gamma PV^{\gamma-1}dV + V^{\gamma}dP = 0 \rightarrow (\partial V/\partial P)_S = -1/\gamma(V/P)$ (4)

Combining (2) & (4) we get ratio of isothermal to adiabatic compressibility

$K_T/K_S = \gamma = C_p/C_V$ (ratio of specific heat)

Isothermal Bulk Modulus of Elasticity (E_T) =1/K_T

Adiabatic Bulk modulus of elasticity (E_S) = 1/K_S

$E_S/E_T = \gamma$

The Adiabatic Lapse Rate:

Convective Equilibrium The heat from the sun, on being absorbed by the ground, heats up the air in immediate contact. The heated air rises upward and a vertical density gradient is established. This gives rise to convection currents which transport cooler air downwards and hot air upwards. As hot air rises, it expands. Will it exchange heat with its environment? It may not do so because air is a poor conductor of heat. This means that in intermixing of air we have an adiabatic expansion. To calculate the drop in temperature with height, we assume that air behaves as a perfect gas. That is, we ignore the presence of water vapour in atmosphere. This means that we can use Eq. (4.13a). For one mole of the gas, Eq. (4.13a) in

$$\gamma \ \ln T - (\gamma - 1) \ln p = \ln K_1$$

On differentiation, we get

$$\frac{dT}{T} - \frac{\gamma - 1}{\gamma} \frac{dp}{p} = 0$$

which can be rearranged as

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T}$$

We wish to calculate variation of temperature with height, i.e. dT/dh. To do so, we must relate pressure with height. For this, we recall that as we go up, pressure decreases. Mathematically **this can be expressed as**

$$dp = -pg\, dh$$

where ρ is average density of air and g is acceleration due to gravity. The negative sign signifies that pressure decreases as we move up.

Since we have assumed that air behaves as perfect gas, we can use the equation of state $p = RTIV$ in the above expression. This gives

$$\frac{dp}{p} = -\frac{Mg}{RT} dh$$

where M = pV is the average molecular weight (=28.9u) of air. On combining Eqs. (4.14) and' (4.15), we get

$$\frac{dT}{dh} = -\frac{\gamma - 1}{\gamma} \frac{Mg}{R}$$

This is the required expression for adiabatic lapse rate. The negative sign on the RHS indicates that temperature decreases as we move upwards.

(1) (2)

Enthalpy

Let us express U as a function of T and p:

$$U = U(T, p)$$

Then we can write

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

Substituting this in First law of Thermodynamics

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp + p\, dV$$

Hence, heat capacity at constant pressure is given by

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

which can be rewritten as

$$C_p = \frac{\partial}{\partial T}(U + pV)$$

The sum $(U + pV)$ is represented by a new function, called enthalpy. It by the symbol H. Thus

$$H = U + pV$$

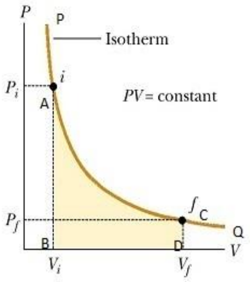
so that

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

enthalpy will also be a function of state of the system. Moreover, it is an extensive property of the system.

Work in quasistatic Isothermal process

Consider that one gram molecule of a perfect gas is taken in a cylinder having perfectly conducting walls and bottom, provided with a piston. Let the cylinder be placed on a source of heat at temperature T°A. If the piston is now moved slowly outwards, the gas expands, does some work and tends to cool but it absorbs required amount of heat from the source to keep it at the same temperature. The expansion is thus isothermal.



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(a) Graphical Method

The isotherm PQ for the process is shown in below figure.

The net work done to expand the gas from a volume V_1 to volume V_2 will be,

W = Area ABDC

Thus, area occupied below the curve in between AB and CD gives the required value of work done.

(b) Analytical Method

Analytically, we can be calculated by integrating dW between the limits V_1 to V_2.

$$W = \int_0^W dW = \int_{v_1}^{v_2} PdV$$

For a perfect gas, PV = RT or P = RT/V

Substituting P = RT/V in the above equation, we get,

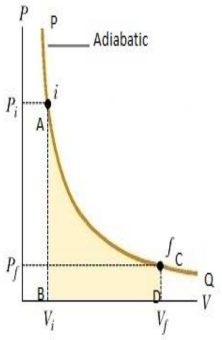
$$W = \int_{V_1}^{V_2} \frac{RT}{V} dV$$

As temperature is constant during isothermal expansion and R is a gas constant,

$$W = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT[log_e V]_{V_1}^{V_2}$$

$= RT\ (\log eV_2 - \log eV_1)$

Work done in adiabatic compression



(a) Graphical Method

This case is different from the case of isothermal change in two respects.

(i) The container is made up an insulating material.

(ii) The curve is much sharper.

The adiabatic curve PQ for the process is shown in below figure.

The net work done to expand the gas from a volume V1 to volume V2 will be,

W = Area ABDC

Thus, area occupied below the curve in between AB and CD gives the required value of work done.

(b) Analytical Method

Analytically, net work W can be calculated by integrating dW between the limits V_1 and V_2.

$$W = \int_0^W dW = \int_{V_1}^{V_2} PdV - - - - (1)$$

For an adiabatic change,

PV^{γ} = constant = K (say)

Or, $P = K / V^{\gamma}$

Equation (1) gives,

$$W = \int_{V_1}^{V_2} \frac{K}{V\gamma} dV = K \int_{V_1}^{V_2} V^{-\gamma} dV$$

$$So, \mathrm{W} = \mathrm{K} \left| \frac{V^{1-\gamma}}{1-\gamma} \right|$$

$$= \frac{K}{1-\gamma} \left[V_2^{1-\gamma} - V_1^{1-\gamma} \right]$$

Now $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$

So, $W = [1/1-\gamma] [P_2 V_2^{\gamma} V_{2\text{-}\gamma}^{1} - P_1 V_1^{\gamma} V_1^{1-\gamma}]$

Or, $W = [1/1-\gamma] [P_2V_2 - P_1V_1]$ ------- (2)

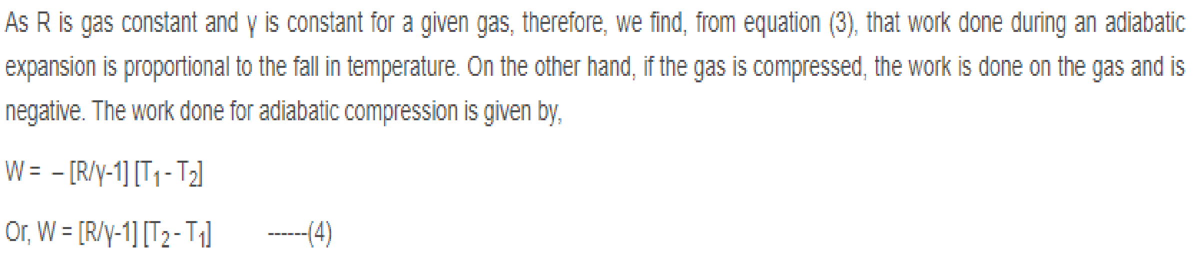
If T_1 and T_2 are the initial and final temperatures of the gas,

$P_1V_1 = RT_1$ and $P_2V_2 = RT_2$

Substituting in equation (2) we get,

$W = [R/1-\gamma] [T_2 - T_1]$

Or, $W = [R/\gamma-1] [T_1 - T_2]$ --------(3)



As R is gas constant and γ is constant for a given gas, therefore, we find, from equation (3), that work done during an adiabatic expansion is proportional to the fall in temperature. On the other hand, if the gas is compressed, the work is done on the gas and is negative. The work done for adiabatic compression is given by,

$W = -[R/\gamma\text{-}1]\,[T_1 - T_2]$

Or, $W = [R/\gamma\text{-}1]\,[T_2 - T_1]$ ------(4)

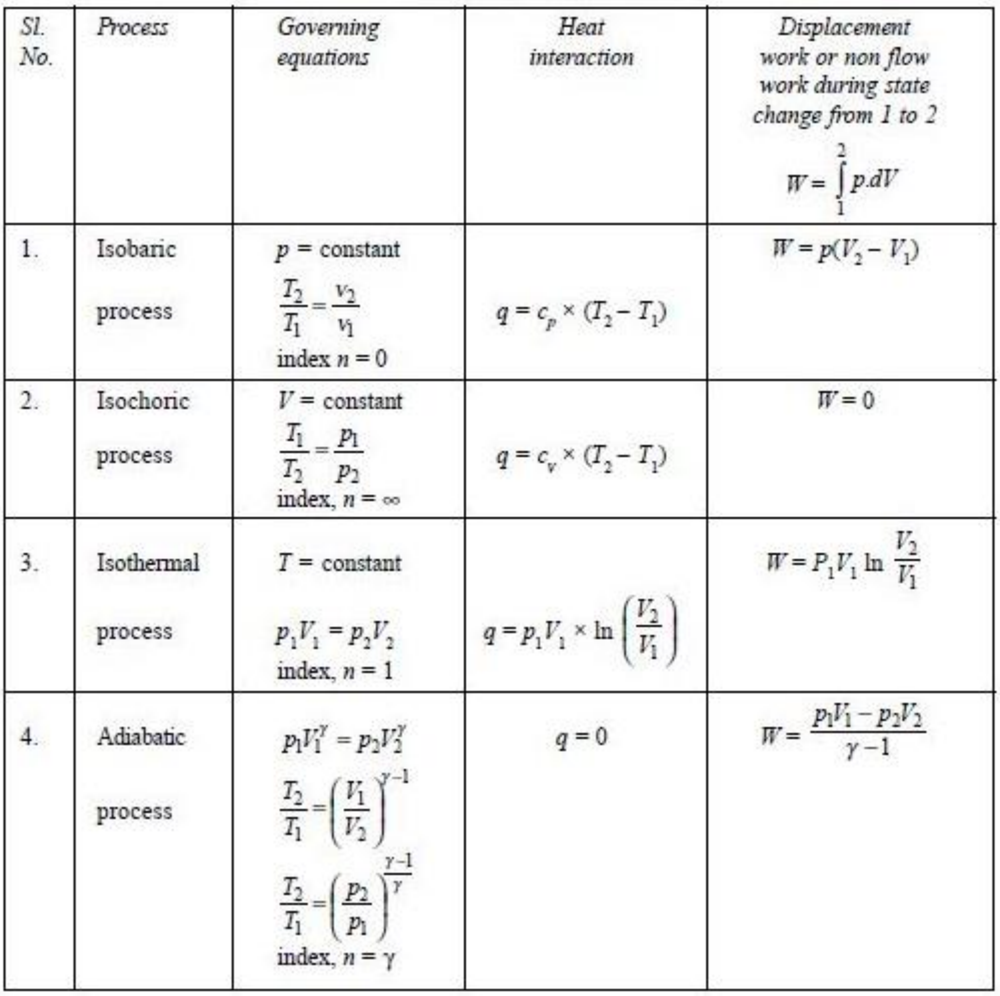
Constant Volume (Isochoric)

A constant volume process is the vertical path $dV = 0$ in the P-V plane---up if heat is added and down if heat is removed. Because dV = 0, the work done is $dW = P\,dV = 0$

Constant Pressure (Isobaric)

A constant pressure process is a horizontal path in the P-V diagram---right for expansion and left for compression. *Example:* a gas in a container sealed with a freely-sliding massive piston.

The work done during gas expansion is: $dW = P\,dV = Nk\,dT$



Sl. No.	Process	Governing equations	Heat interaction	Displacement work or non flow work during state change from 1 to 2 $W = \int_1^2 p.dV$
1.	Isobaric process	p = constant $\frac{T_2}{T_1} = \frac{v_2}{v_1}$ index $n = 0$	$q = c_p \times (T_2 - T_1)$	$W = p(V_2 - V_1)$
2.	Isochoric process	V = constant $\frac{T_1}{T_2} = \frac{p_1}{p_2}$ index, $n = \infty$	$q = c_v \times (T_2 - T_1)$	$W = 0$
3.	Isothermal process	T = constant $p_1V_1 = p_2V_2$ index, $n = 1$	$q = p_1V_1 \times \ln\left(\frac{V_2}{V_1}\right)$	$W = P_1V_1 \ln \frac{V_2}{V_1}$
4.	Adiabatic process	$p_1V_1^{\gamma} = p_2V_2^{\gamma}$ $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$ index, $n = \gamma$	$q = 0$	$W = \frac{p_1V_1 - p_2V_2}{\gamma - 1}$

Isobaric Thermal Expansivity (α)

Another very important property of a substance is how its volume will respond to changes in temperature. Again, gases respond profoundly to changes in temperature whereas solids and liquid will have more modest (but not negligible) responses to changes in temperature.

The definition of the **isobaric thermal expansivity** (or sometimes called the expansion coefficient) is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

In the case of expansion, volume tends to increase with increasing temperature, so $(\partial V/\partial T)_p$ is positive (exception : water below 4^0C, Indian rubber)

Linear expansion Coefficient It is the fractional change in length per degree of temperature change. Assuming negligible effect of pressure, we may write:

$$\alpha_L = \frac{1}{L}\frac{dL}{dT}$$

Area expansion Coefficient It is the fractional change in area per degree of temperature change. Ignoring pressure, we may write:

$$\alpha_A = \frac{1}{A}\frac{dA}{dT}$$

Volume Coefficient of thermal expansion the volumetric coefficient of thermal expansion is given by Fractional change in volume per degree of temperature change keeping pressure constant. The fact that the pressure is held constant is important, because the volume of a gas will vary appreciably with pressure as well as temperature.

$$\alpha = \alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Partial derivative & cyclic Rule

Suppose a function *f(x,y,z)=0*, where *x,y* and *z* are functions of each other. Write the total differentials of the variables

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

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

Substitute *dy* into *dx*

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

Now dx & dz are independent of each other ,so equating coefficient of dx on both side we get

$(\partial x/dy)_z(\partial y/\partial x)_z = 1$

$(\partial x/dy)_z = 1/(\partial y/\partial x)_z$ (1) -Reciprocal theorem

Equating coefficient of dz on both side we get

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

Subtracting the second term and using reciprocal theorem (1) we get

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \qquad (2)$$

Equation (1) & (2) together constitute Cyclic Rule very useful for thermodynamic variable.

- **The Cyclic Rule:**

If z is a function two variable, then we can write: z = z (x, y),

then, $\left(\frac{dy}{dz}\right)_x\left(\frac{dz}{dx}\right)_y\left(\frac{dx}{dy}\right)_z = -1$

Example:

If V = f (p, T); p = f (V, T); T= f (p, V), then we can write

$$\left(\frac{dp}{dT}\right)_V\left(\frac{dT}{dV}\right)_p\left(\frac{dV}{dp}\right)_T = -1$$

Example 1:

Use the Equation of state for Ideal gas to verify the cyclic rule

p = nRT/V; V= nRT/p; T= pV/nR

$$\left(\frac{dp}{dT}\right)_V = \frac{nR}{V};\left(\frac{dT}{dV}\right)_p = \frac{p}{nR};\left(\frac{dV}{dp}\right)_T = -\frac{nRT}{p^2}$$

$$\therefore\left(\frac{dp}{dT}\right)_V\left(\frac{dT}{dV}\right)_p\left(\frac{dV}{dp}\right)_T = \left(\frac{nR}{V}\right)\left(\frac{p}{nR}\right)\left(-\frac{nRT}{p^2}\right)$$

$$= -\left(\frac{nRT}{pV}\right) = -1$$

Some important formula frequently used in problem

Three eq for adiabatic process

i) PV^{γ} = Const ; ii) $TV^{\gamma-1}$ = Const ; iii) $T^{\gamma}/P^{\gamma-1}$ = Const

eq for Isothermal process

PV= Const

Infinitesimal work for hydrostatic/chemical process

PdV - (Area under P-V curve)

Work for Isothermal expansion at temp T

RT ln V_2/V_1

Work for adiabatic expansion

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} = \frac{R(T_1 - T_2)}{\gamma - 1}$$

Ist law of thermodynamics

dQ = dU + p dv

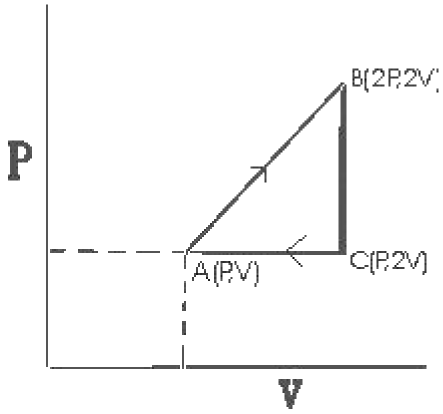
d Q=C_v dT + p d V

d Q = C_p dT – V d p

Enthalpy H = U + PV

Sample Problem (MCQ) on this chapter

1)An ideal gas taken round the cycle ABCA as shown in PV diagram



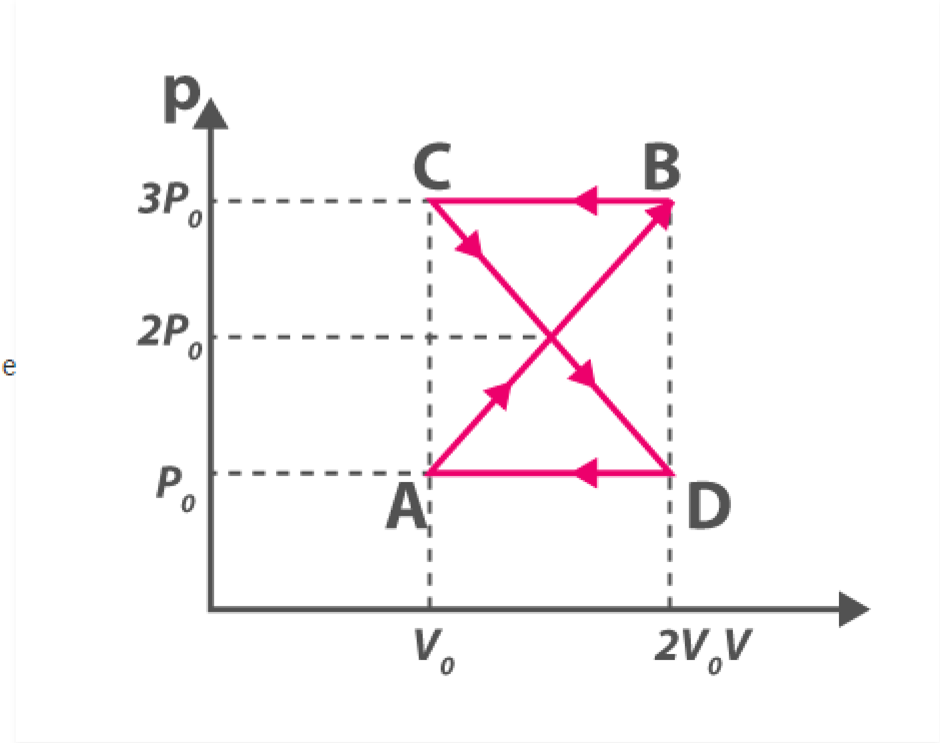
Calculate the work done during the cycle,

a. PV
b. $\mathrm{PV}/2$
c. $2\mathrm{PV}$
d. $\mathrm{PV}/3$

Solution

Work done is area of the closed loop
= 1 / 2 x V x P = PV / 2
So b is correct

ABCDA is a cyclic process explaining the thermodynamic process. What is the work done by the system in the cycle



(a) Zero

(b) $\frac{\rho_0 V_0}{2}$

(c) $\rho_0 V_0$

(d) $2\rho_0 V_0$

Ans Zero

3) Consider the following statements

(Assertion) The internal energy of an ideal gas does not change during an Isothermal process
(Reason) The decrease in the volume of the gas is compensated by a corresponding increase in pressure when its temperature is constant in accordance with Boyle law

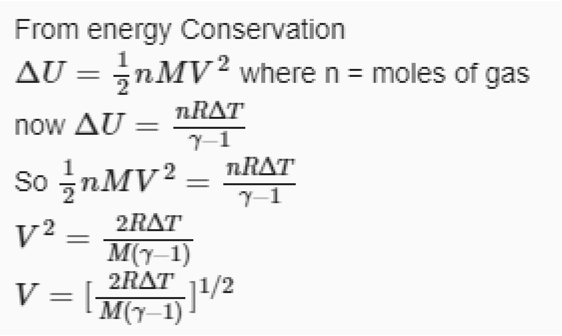
a. Both A & R are true and R is correct Explanation of A
b. Both A & R are true and R is not correct Explanation of A
c. A is true R is false
d. A is false but R is true

3) A thermally insulated vessel containing an gas when molar mass is M and Ratio of specific heat C_p / C_v = γ move with a velocity V. The gas temperature increase by ΔT due to sudden stoppage of vessel. Find the value of V in terms of ΔT, M, γ

a. $V = [\frac{2R\Delta T}{M(\gamma - 1)}]^{1/2}$
b. $V = [\frac{2R\Delta T}{M(\gamma + 1)}]^{1/2}$
c. $V = [\frac{2R\Delta T}{M\sqrt{(\gamma - 1)}}]^{1/2}$
d. $V = [\frac{2R\Delta T}{M\sqrt{(\gamma + 1)}}]^{1/2}$

Solution

Thermally insulated – adiabatic process



From energy Conservation

$\Delta U = \frac{1}{2} nMV^2$ where n = moles of gas

now $\Delta U = \frac{nR\Delta T}{\gamma - 1}$

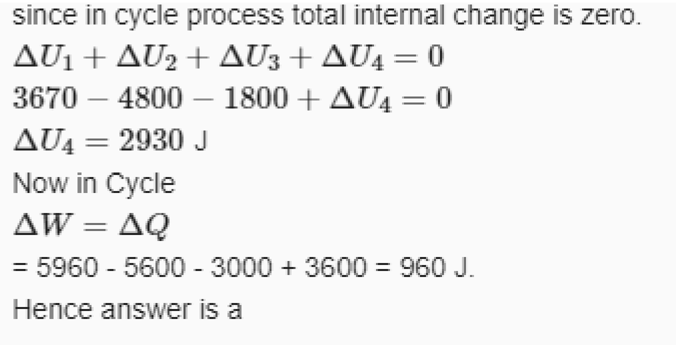
So $\frac{1}{2} nMV^2 = \frac{nR\Delta T}{\gamma - 1}$

$V^2 = \frac{2R\Delta T}{M(\gamma - 1)}$

$V = [\frac{2R\Delta T}{M(\gamma - 1)}]^{1/2}$

4. An ideal gas is taken through a cyclic thermodynamics process through four steps.
The amount of heat involved in the steps are Q_1 = 5960 J,Q_2 = - 5600 J,Q_3= -3000 J,Q_4 = - 3600 J
respectively. The corresponding quantities of Internal energy changes are ΔU_1 = 3.760 J ,ΔU_2 = - 4800 J,ΔU_3 = -1800 J,ΔU_4 = ?
find the value ΔU_4 & net work done
a. 2930 J, 960 J
b. 2830 J, 900 J
C. 2930 J, -960 J
d. -2930 J, 960 J

Solution



since in cycle process total internal change is zero.

$\Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 = 0$

$3670 - 4800 - 1800 + \Delta U_4 = 0$

$\Delta U_4 = 2930$ J

Now in Cycle

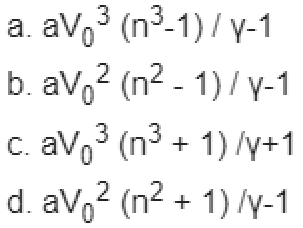
$\Delta W = \Delta Q$

= 5960 - 5600 - 3000 + 3600 = 960 J.

Hence answer is a

5) An ideal gas who ratio of specific heat $C_p / C_v = \gamma$ is Expanded according to the law

$P = av^2$ when a is constant. The ratio of final volume to Initial value is n .find the ΔU.Initial volume is V_0



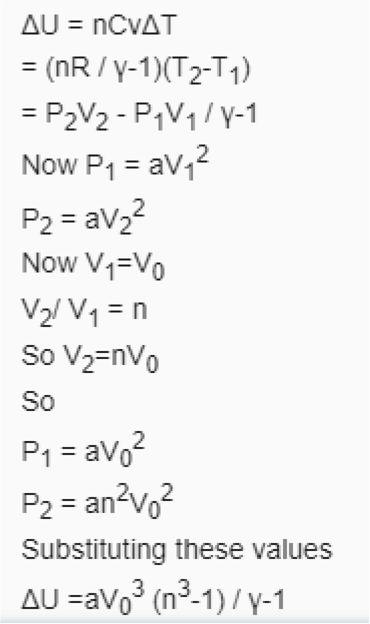
a. $aV_0^3 (n^3-1) / \gamma-1$

b. $aV_0^2 (n^2 - 1) / \gamma-1$

c. $aV_0^3 (n^3 + 1) /\gamma+1$

d. $aV_0^2 (n^2 + 1) /\gamma-1$

Solution



$\Delta U = nCv\Delta T$

$= (nR / \gamma-1)(T_2-T_1)$

$= P_2V_2 - P_1V_1 / \gamma-1$

Now $P_1 = aV_1^2$

$P_2 = aV_2^2$

Now $V_1=V_0$

$V_2/ V_1 = n$

So $V_2=nV_0$

So

$P_1 = aV_0^2$

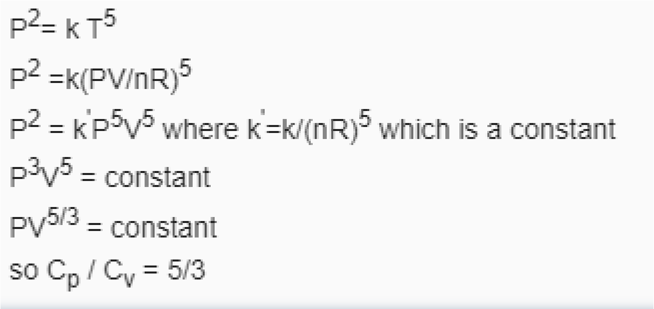
$P_2 = an^2V_0^2$

Substituting these values

$\Delta U =aV_0^3 (n^3-1) / \gamma-1$

5) During an adiabatic process the square of the pressure of a gas is proportional to the fifth power of its absolute temperature. The ratio of specific heat C_p / C_v for that gas is
a. 3/5
b. 4/3
c. 5/3
d. 3/2

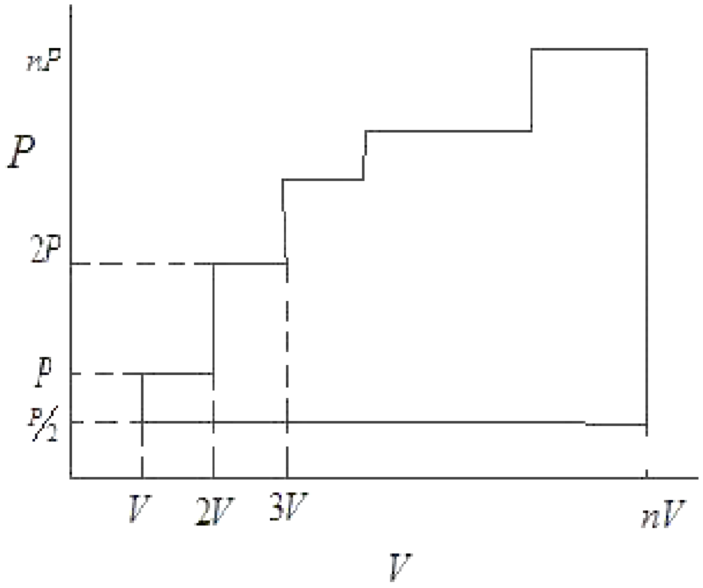
Solution



$P^2 = k\,T^5$
$P^2 = k(PV/nR)^5$
$P^2 = k'P^5V^5$ where $k' = k/(nR)^5$ which is a constant
P^3V^5 = constant
$PV^{5/3}$ = constant
so C_p / C_v = 5/3

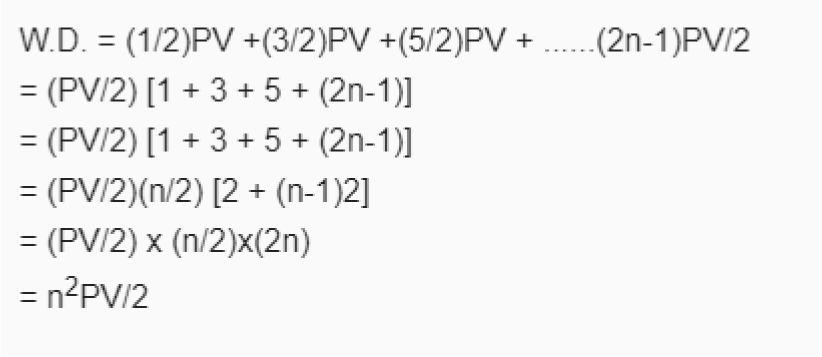
6)

Find the wok done in the cyclic process as shown in figure



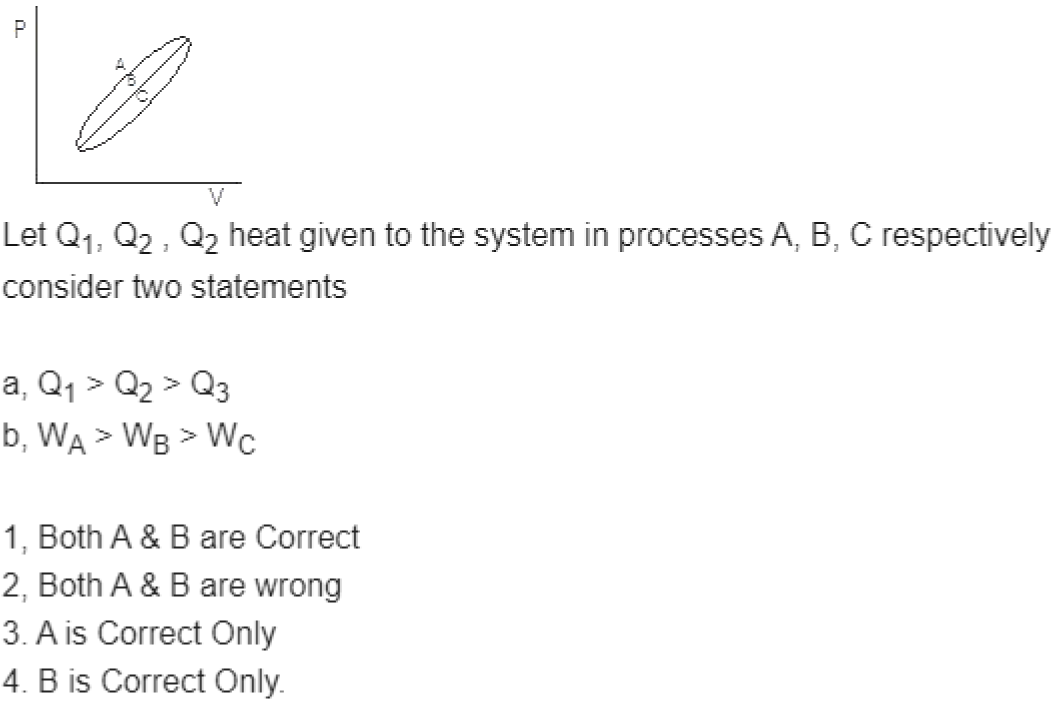
a. $\frac{n^2PV}{2}$
b. $\frac{n^2PV}{8}$
c. $\frac{n^2PV}{16}$
d. none of these

Solution



W.D. = (1/2)PV +(3/2)PV +(5/2)PV + ...(2n-1)PV/2
= (PV/2) [1 + 3 + 5 + (2n-1)]
= (PV/2) [1 + 3 + 5 + (2n-1)]
= (PV/2)(n/2) [2 + (n-1)2]
= (PV/2) x (n/2)x(2n)
= n^2PV/2

8)



Let Q_1, Q_2 , Q_2 heat given to the system in processes A, B, C respectively consider two statements

a, $Q_1 > Q_2 > Q_3$

b, $W_A > W_B > W_C$

1, Both A & B are Correct

2, Both A & B are wrong

3. A is Correct Only

4. B is Correct Only.

Solution

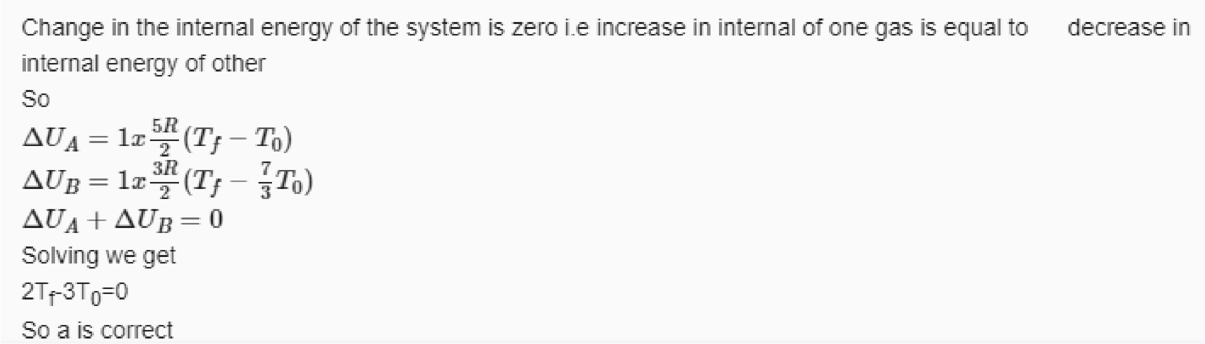
Now we know that
$\Delta U = Q - W$
for three process
$\Delta U = Q_1 - W_A$ $Q_1 = \Delta U + W_A$
$\Delta U = Q_2 - W_B$ $Q_2 = \Delta U + W_B$
$\Delta U = Q_3 - W_C$ $Q_3 = \Delta U + W_C$
Now Work done is given by Area under curve so $W_A > W_B > W_C$

So
$Q_1 > Q_2 > Q_3$
So A & B both are correct

10) Find the ratio of adiabatic bulk modulus and isothermal bulk modulus of a gas

11)Two boxes A and B containing different ideal gases are placed on table
Box A contain one mole of gas m where ($C_v=5R/2$) at Temperature T_0
Box B contains one mole of gas n where ($C_v=3R/2$) at temperature (7/3) T_0
The boxes are then put into thermal contact with each other and heat flows between until the gases reach a common final temperature T_f
Which of the following relation is correct?
a. $2T_f-3T_0=0$
b. $2T_f-7T_0=0$
c. $2T_f-5T_0=0$
d. $T_f-3T_0=0$

Solution


Change in the internal energy of the system is zero i.e increase in internal of one gas is equal to decrease in internal energy of other

So

$\Delta U_A = 1x\frac{5R}{2}(T_f - T_0)$

$\Delta U_B = 1x\frac{3R}{2}(T_f - \frac{7}{3}T_0)$

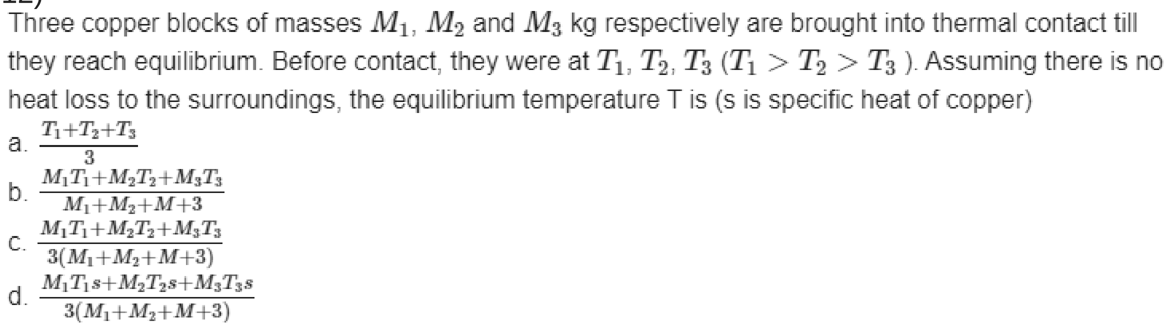
$\Delta U_A + \Delta U_B = 0$

Solving we get

$2T_f - 3T_0 = 0$

So a is correct

12)


Three copper blocks of masses M_1, M_2 and M_3 kg respectively are brought into thermal contact till they reach equilibrium. Before contact, they were at T_1, T_2, T_3 ($T_1 > T_2 > T_3$). Assuming there is no heat loss to the surroundings, the equilibrium temperature T is (s is specific heat of copper)

a. $\frac{T_1+T_2+T_3}{3}$

b. $\frac{M_1T_1+M_2T_2+M_3T_3}{M_1+M_2+M+3}$

c. $\frac{M_1T_1+M_2T_2+M_3T_3}{3(M_1+M_2+M+3)}$

d. $\frac{M_1T_1s+M_2T_2s+M_3T_3s}{3(M_1+M_2+M+3)}$

Solution

Let the equilibrium temperature of the system = T

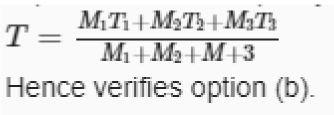
Let $T_1, T_2 < T < T_3$T1,T2<T<T3

As there is no loss to the surroundings.

heat lost by M_3 = Heat gain by M_1 + Heat gain by M_2

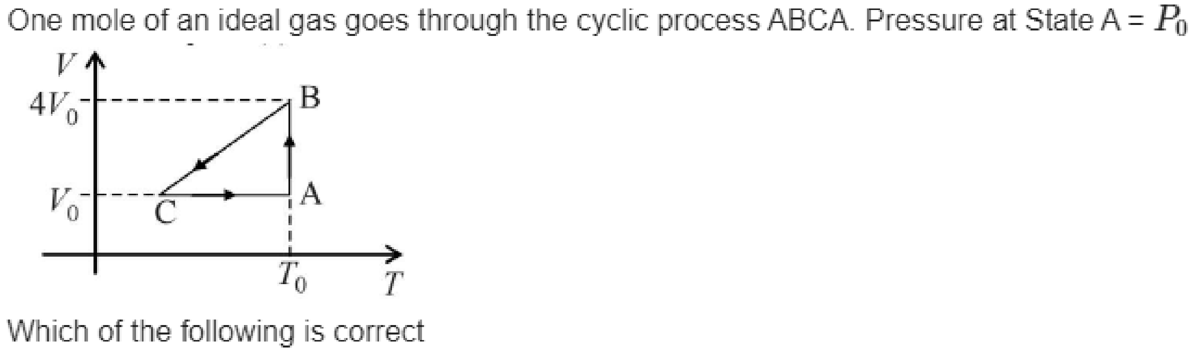
$M_3S(T_3 - T) = M_1S(T - T_1) + M_2S(T - T_2)$

Solving eq


$T = \frac{M_1T_1+M_2T_2+M_3T_3}{M_1+M_2+M+3}$

Hence verifies option (b).

13)


One mole of an ideal gas goes through the cyclic process ABCA. Pressure at State A = P_0

Which of the following is correct

a. Pressure at C is $P_0/4$

b. temperature at C is $T_0/4$

c. $W_{AB} = P_0V_0\ln4$

d. $U_A = U_B$

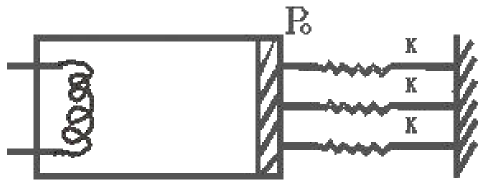
Solution

For Process AB, as temperature remains same, this is isothermal process
So, $U_A=U_B$
Also
$P_0V_0=P_B\times4V_0$
$P_B= P_0/4$
Also $W_{AB}=nRT_0\ln4V_0/V_0=P_0V_0\ln4$
The process BC is not clear as it is not mentioned line BC passes through origin, so nothing can be said about state C
So (c) and (d) are correct

14)We have a Polytropic process defined as PV^n= Constant
and we have an adiabatic process defined by PV^γ= Constant
and so thermal process defined as PV=Constant
find the Ratio of Bulk modules of Poly-tropic, adiabatic, isothermal process
a. $n:\gamma:1$
b. $1:n:\gamma$
c. $n_2:\gamma_2:1$
d. $1:n_2:\gamma_2$

Ans a)

15)

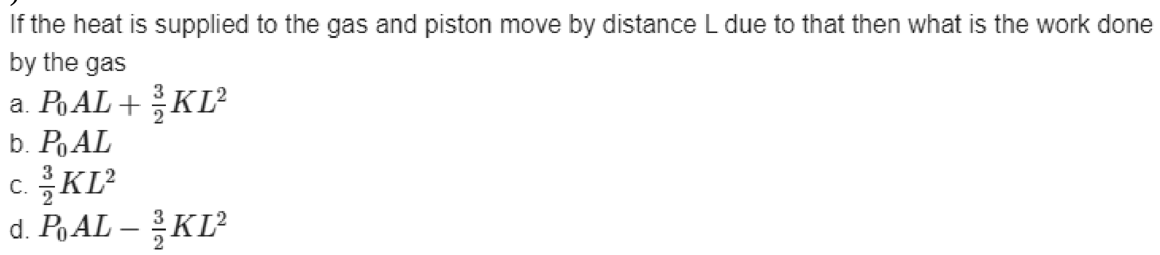


1 mole of a diatomic idea gas is enclosed in a adiabatic cylinder filled with a smooth light adiabatic Piston. The Piston is connected to three spring of spring constant K as shown in figure. The area of cross-section of Cylinder is A Initially spring is in its natural length and atmosphere pressure is P_0

i)find the pressure of the gas
a. P_0
b. $2P_0$
c. $P_0/2$
d. $4P_0$

Ans

(a) as Gas pressure is equal to atmosphere pressure ii)



If the heat is supplied to the gas and piston move by distance L due to that then what is the work done by the gas

a. $P_0AL + \frac{3}{2}KL^2$

b. P_0AL

c. $\frac{3}{2}KL^2$

d. $P_0AL - \frac{3}{2}KL^2$

Solution

at any distance Force on the piston is
$F=P_0A+3Kx$
so Work done $=\int Fdx=\int (P_0A+3Kx)dx$
Integrating from 0 to L
$=P_0AL+ (3/2)KL^2$