

Thermodynamics

Thermodynamics is the branch of science that deals with quantitative relationship between heat and other forms of energy.

Why study thermodynamics —

1. To predict the feasibility of process.
2. To " " spontaneity of a process
or chemical reaction
3. To estimate the yield of products

4. To deduce some important relationship in physical chemistry such as deduction of important and useful results -

1. Raoult's law of lowering of vapour pressure -

2. Freezing point depression.

3. Boiling point elevation.

4. Distribution law, Phase Rule.

Basic Terminology

1. **Open System** - A system which can exchange both energy and matter with the surroundings.
2. **Closed System** - A system which permits passage of energy but not mass, across its boundary.
3. **Isolated system** - A system which can neither exchange energy nor matter

with its surrounding.

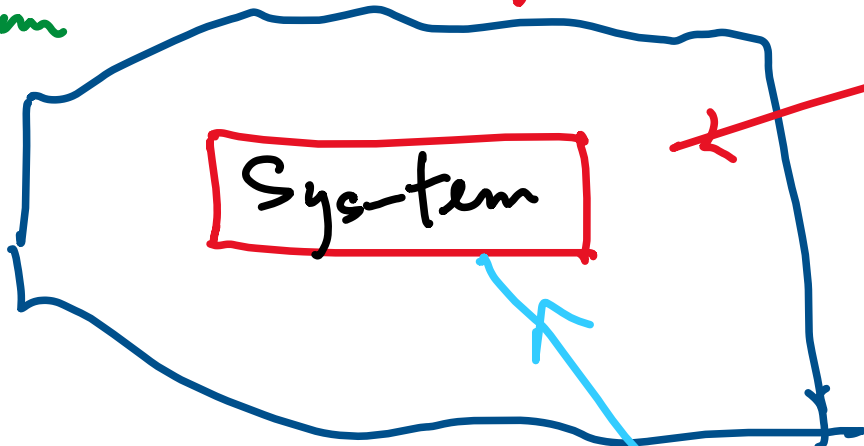
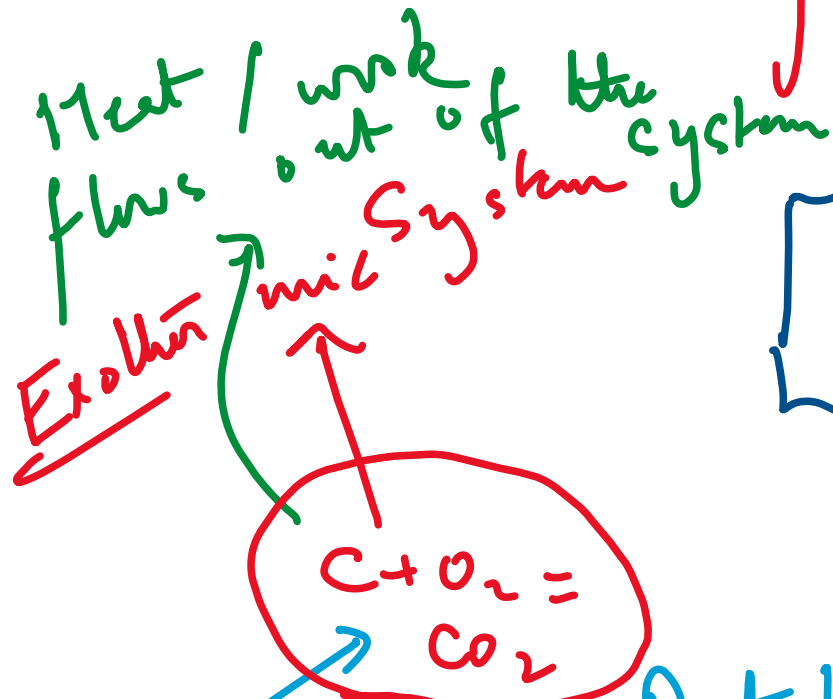
System and Surrounding

System — The part of the universe
chosen for thermodynamic consideration
i.e. to study the effect of
temperature, pressure etc. is called
system.

Surrounding — The remaining part of the

universe is called surrounding -

Boundary - Any thing which separates the system from surroundings.



Out here is the surrounding.

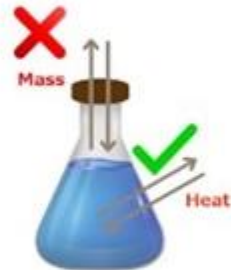
Boundaries of system -

Endothermic

Open and Closed Systems



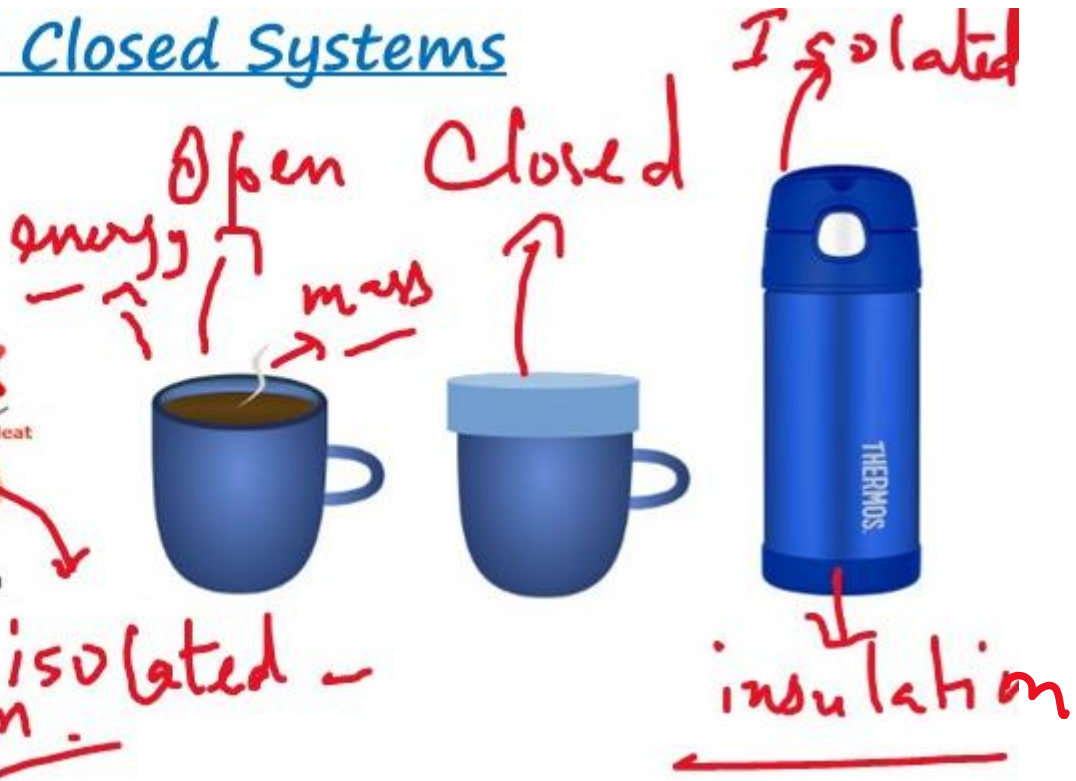
Open system



Closed system



Isolated system



State Variables:

required to define state of volume,

The variables which are defined in order to of any system i.e. pressure, mass, temperature,

Surface area etc.

State Function: Property of a system which depends only on the state of the system and not on the path are called state function.

Eg: Pressure, Volume, Temperature, Internal energy, Enthalpy, Entropy etc.

Intensive and Extensive properties.

Properties of a system that do not depend on mass of the system i.e. Temperature, pressure, density, concentration - are called Intensive property

Extensive properties are those properties of a system which depend on mass
e.g. Volume, energy, enthalpy, entropy etc.

Isothermal, Isobaric, Isochoric and
Adiabatic process.

Isothermal : Process which takes place
at constant temperature -
↓ equal ↓ temperature

Isobaric : Process which takes place at
constant pressure -

Isochoric : Process which takes place at
constant volume.

Adiabatic Process during which transfer of heat cannot take place between system and surrounding.

An adiabatic system has to be isolated in order to prevent energy exchange between system & surroundings.

Cyclic process Process in which system comes back to its original / initial state after undergoing a series of changes.

Reversible process

Process during which the system always departs infinitesimally from the state of equilibrium i.e. its direction can be reversed at any moment.

an indefinitely small quantity i.e. $\rightarrow 0$

infinitesimal

extremely small

a value approaching zero

$\rightarrow 0$

Irreversible Process:

A process which does not meet the requirements of a reversible process is called irreversible process -

Reversible process: Infinitely slowly
Reversal possible

System almost remains in a state of equilibrium at all times.

A $\xrightarrow{\text{driving force}}$ B
 $\xleftarrow{\text{opposing force}}$

A reversible process is almost impossible because it would take infinite time to complete.

Irreversible processes are not infinitesimally slow and carried out rapidly.

Any change in the external condition will disturb the equilibrium.

Internal Energy The energy associated with a substance is called internal energy.

It is usually denoted by 'U'

Internal energy depends on temperature, pressure, volume and composition.

It is not possible to know the absolute value of internal energy possessed by a

system because it involves certain quantities which cannot be measured.

What are these quantities?

Translational, vibrational & Rotational kinetic energy

We measure the changes in internal energy when the system changes from reactant to product or initial state to final state. Measurable quantity = ΔU

$$\Delta U = U_2 - U_1$$

where $U_1 =$ initial energy of the system
 $U_2 =$ final " " " "

For a chemical reaction,

$U_r =$ energy of reactants
 $U_f =$ " " products

$$\Delta U = U_p - U_r$$

Sign convention:

ΔU is taken as positive if the internal energy of the system increases.

$\Delta U = -ve$, if the internal energy of the system decreases.

$\Delta U = +ve$: Endothermic change
 $\Delta U = -ve$: Exothermic "

Heat : When the energy of a system is changed by changing the temperature difference between system and surrounding, we say that the energy has been transferred as heat -

Heat is expressed as q (Q)

Work : Work is said to be done when a force acting on a system

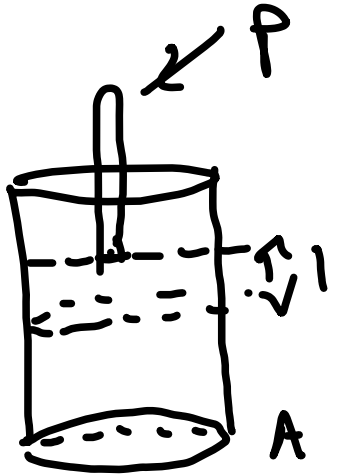
displaces the body in its own direction.

$$dW = F \times dl = P dv$$

$$dW = P dv$$

$$\int dW = P \int_{v_1}^{v_2} dv$$

$$\Rightarrow W = P (v_2 - v_1) \\ = P \Delta v$$



where $v_1 =$
initial vol.
 $v_2 =$ final
vol.

Work of Expansion Against Constant Pressure

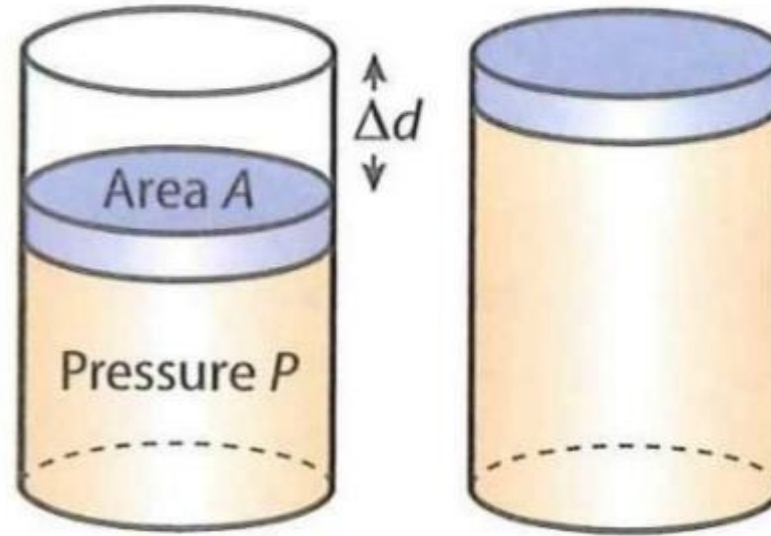
Pistons

Work Done = Force x Change of Distance

$$W_d = F \cdot \Delta d$$

but

$$P = \frac{F}{A}$$



$$W_d = P \cdot A \cdot \Delta d$$

$$W_d = P \cdot \Delta V$$

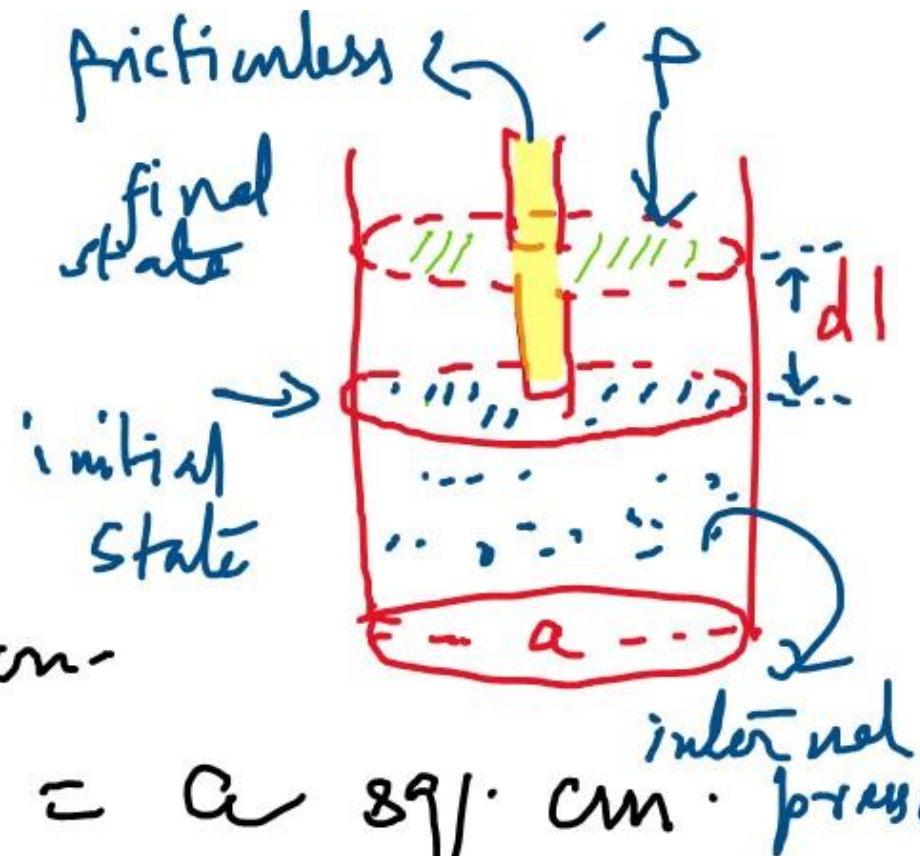
Work of Expansion

Let us consider a gas enclosed in a cylinder fitted with a frictionless piston.

Area of cross-section = a sq. cm. internal pressure

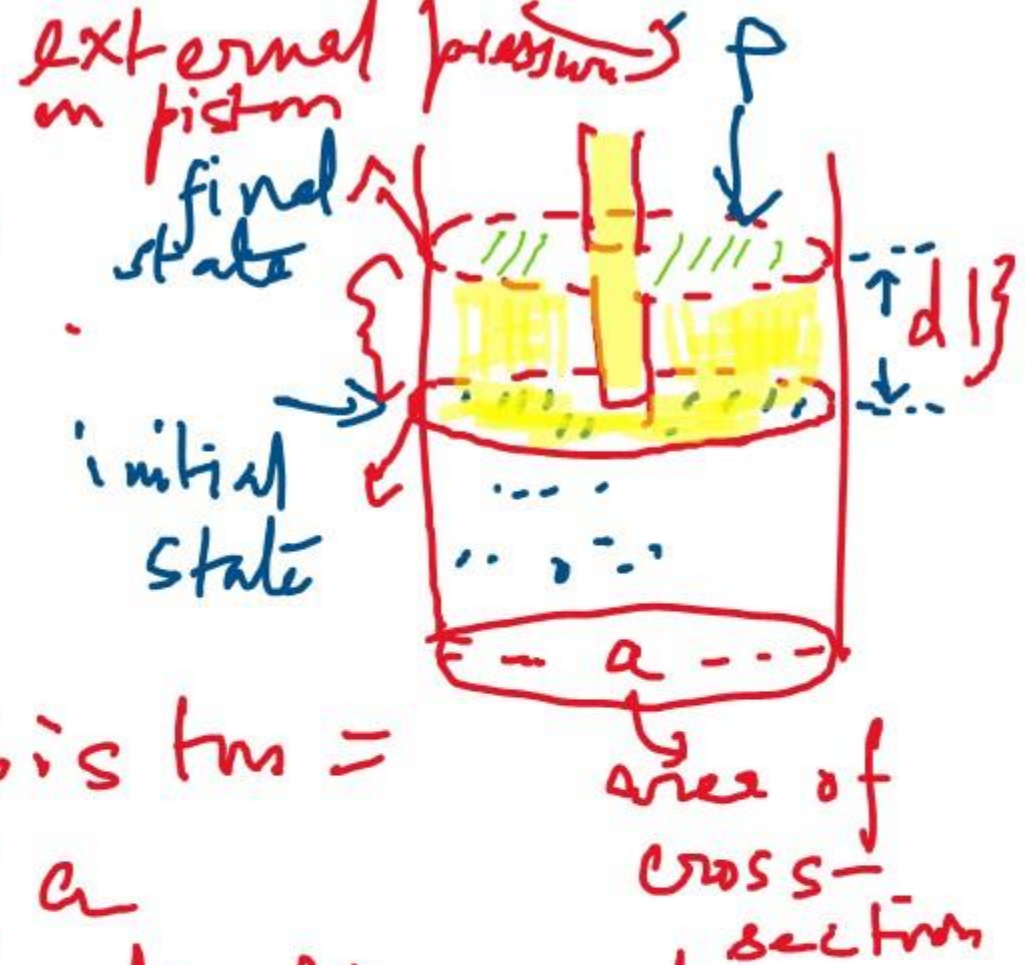
Let the pressure on the piston be P .

Note: The pressure on the piston must be less than the internal pressure of the gas.



Distance through which the gas expands
 = dl

Pressure = $\frac{\text{Force}}{\text{Area}}$



Force acting on the piston =

$f = P \times a$

Work done by the gas (i.e. system) = Force \times displacement
 = $f \times dl$

where $dv = a \times dl$ increase in volume
 = $\int P \times a \times dl = P \times dv$

Work done
by the system

$$\text{Volume} = l \times b \times h \\ = a \times h'$$

d

$$= \int f \times dl = P \times (a \times dl)$$

force = $P \times dv$ small length

Small amount of work done is

$$\delta W = P \times dv$$

Total work done, $W = \int_{v_1}^{v_2} P \times dv$

v_1 → initial volume
 v_2 → final volume

constant

a) If the gas expands, work is said to be done by the system -

In this case, $V_2 > V_1$ \therefore w will be $\rightarrow +ve$ -

b) If the gas is compressed, work is said to be done on the system.

In this case, $V_2 < V_1$, \therefore Work done is negative -

Exothermic and Endothermic process.

Exothermic \equiv A process in which heat is released into the surrounding - $\Delta U = -ve$

Endothermic \equiv A process in which energy is acquired from the surrounding as heat $\Delta U = +ve$

N.B: Internal energy is a state function -

in the sense that its value depends only on the current state of the system and is independent of how the system has been prepared.

Changing any one of the state variables, i.e. temperature / pressure / volume / mass can lead to change in the internal energy of the system.

Internal energy is an extensive property.

Extensive : Mass, Volume, Amount of matter \rightarrow dependent.

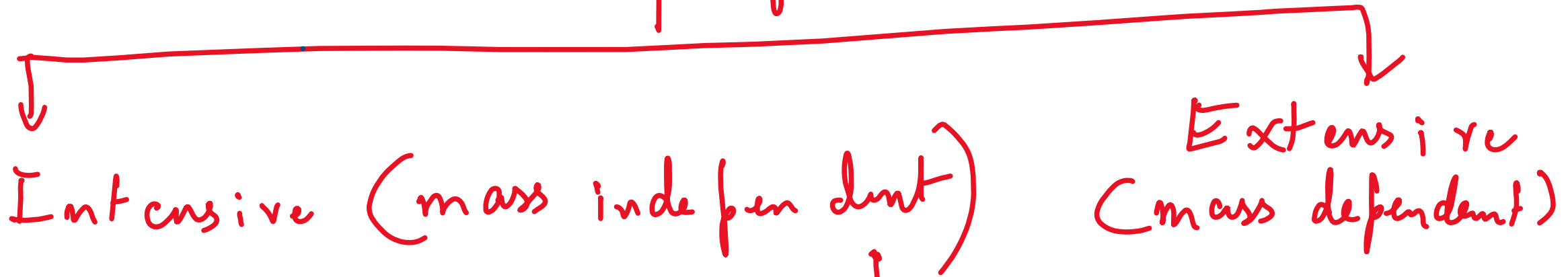
Intensive : Independent on the amount of substance.

Unit of internal energy - Joules (S.I.)
1 calorie \approx 4.2 Joules.

Thermodynamic Property

$$A = U - TS$$

$$G = H - TS$$

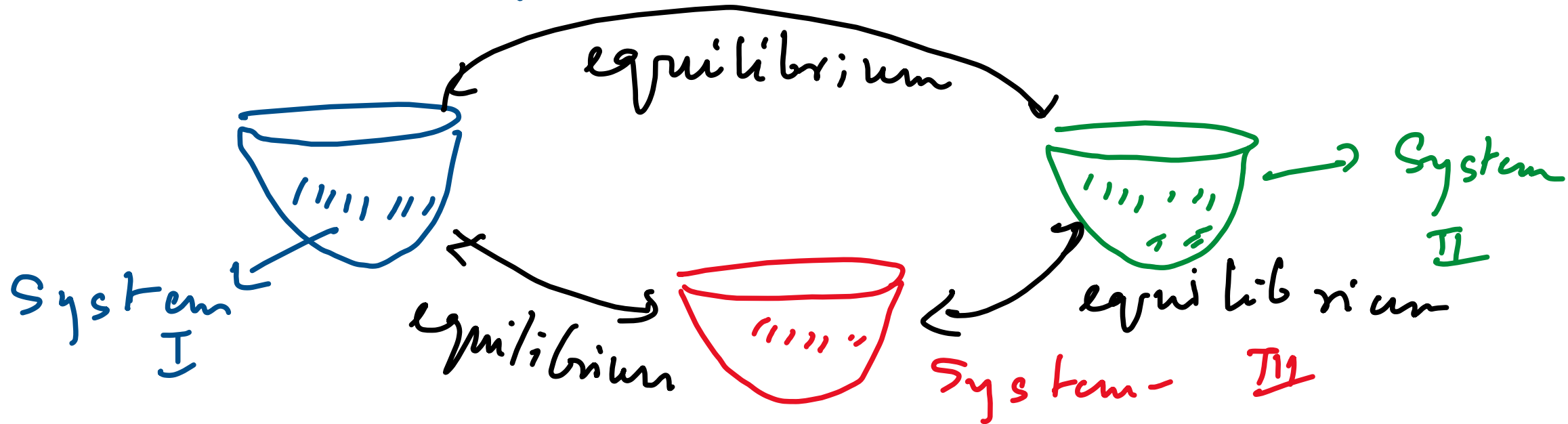


1. Pressure
2. Temperature
3. Density
4. Concentration
5. Melting point
6. Boiling point
7. Surface Tension
8. Viscosity etc

1. Mass
2. Volume
3. Internal energy
4. Heat capacity
5. Enthalpy
6. Entropy
7. Helmholtz energy
8. Gibb's free energy

In thermal energy - Joules / Calorie
Work - Joules / Calorie
Heat - Joules / Calorie

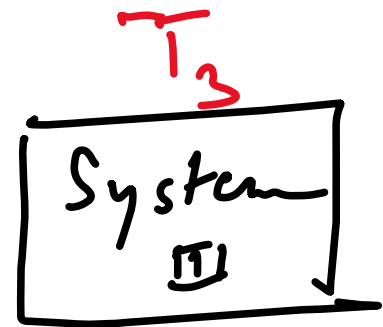
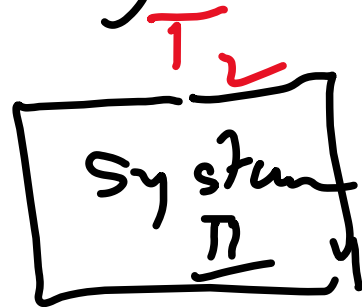
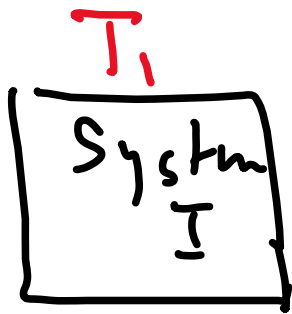
Zeroth law of thermodynamics



If two thermodynamic systems are each in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

If $x = a$ & $y = a$ then, $x = y$

Temp. \rightarrow



If $T_1 = T_3$ & $T_2 = T_3$ then $T_1 = T_2$

When two bodies have equality in temperature with a third body then they in turn have equality of temperature with each other.

Zeroth Law: Defines the concept of temperature scale.

Thermal equilibrium between systems is a transitive relation.

Transitive property

If $x = y$
& $x = z$
then $y = z$

First Law of Thermodynamics

Energy can neither be created nor destroyed, however it can be transformed from one form to another.

$$E = mc^2 \longrightarrow \text{Einstein's}$$

mass velocity of light

Mass & energy are interconvertible.

Different statements of 1st Law:

① Energy can neither be created nor destroyed

② The total energy of an isolated system is constant, though one form of energy can be transferred into another form.

③ Concept of perpetual motion machine:

Perpetual \equiv continuing forever.

It is impossible to construct a perpetual motion machine i.e. a machine that could produce work continuously without consuming energy.

N.B: Internal energy is a state function, work & heat are not. Work and heat both depends on the path followed.
So, work & heat are path functions

If heat q is supplied to a system, it may be used up partly to increase the internal energy of the system and partly to do some mechanical work.

$$q = \Delta U + w$$

$$\Rightarrow \Delta U = q - w$$

$$\delta q = du + \delta w$$

$$\Rightarrow du = \delta q - \delta w = \delta q - P dv$$

$$\delta w = P dv$$

for P - V work.

Concept of Enthalpy from 1st Law:

Mathematical form of 1st Law

$$q = \Delta U + w$$

where q = heat absorbed by the system

ΔU = internal energy

w = work done by the system.

At constant pressure,

$$w = P \Delta V$$

we can put,

$$q_p = \Delta U + P \Delta V$$

constant pressure

When the system absorbs heat i.e. equivalent to q_p calories of heat, its internal energy, say U_1 , increases to U_2

$$\begin{array}{c} P \\ U_1, V_1 \end{array}$$

State I

$$\Delta U = U_2 - U_1$$

$$\Delta V = V_2 - V_1$$

$$\begin{array}{c} P \\ U_2, V_2 \end{array}$$

State II

$$\begin{aligned} q_p &= \Delta U + P \Delta V \\ &= (U_2 - U_1) + P(V_2 - V_1) \\ &= U_2 - U_1 + PV_2 - PV_1 \end{aligned}$$

$$\begin{aligned}
 q_p &= \Delta U + P \Delta v & \Delta U &= u_2 - u_1 \\
 &= (u_2 - u_1) + P(v_2 - v_1) & \Delta v &= v_2 - v_1 \\
 &= u_2 - u_1 + P v_2 - P v_1 \\
 &= (u_2 + P v_2) - (u_1 + P v_1)
 \end{aligned}$$

\therefore u , P , and v are state functions
 then $u + Pv$ must be a state function

The thermodynamic quantity $u + Pv$ is
 called heat content or enthalpy of a system

Enthalpy is represented by 'H'

$$H = U + PV$$

$$H_1 = U_1 + PV_1$$
$$H_2 = U_2 + PV_2$$

substituting the values

$$q_p = (U_2 + PV_2) - (U_1 + PV_1)$$
$$= H_2 - H_1 = \Delta H$$

Heat absorbed $q_p = \Delta H$ by a system under constant pressure \rightarrow change in enthalpy

The enthalpy change of a system is equal to the heat absorbed by the system at constant pressure.

$$\Delta H = \Delta U + P\Delta V$$

Enthalpy change accompanying a process may be defined as the sum of the increase in internal energy of the system and pressure-volume work done i.e. the work of expansion.

$$\Delta H = \Delta U + P \Delta V$$

For an ideal gas, $PV = nRT$

$$P \Delta V = \Delta n RT$$

$$\Rightarrow \Delta H = \Delta U + \Delta n RT$$

Physical Significance of Enthalpy

Every substance or system has some definite energy stored in it, called internal energy. The energy stored within the

Substance or the system is called heat content
or enthalpy of the substance or the
system.

Absolute value of enthalpy cannot be measured
and not required also.

If q is the amount of heat required to raise the temperature of the system from $T_1 \rightarrow T_2$ then heat capacity of the system is given by,

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

\therefore Heat capacity depends on temperature or varies with temp. \therefore the value of C has to be considered over a narrow temp. change.

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$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

\therefore Heat capacity depends on temperature or varies with temp. \therefore the value of C has to be considered over a narrow temp. change.

Since q \neq a state function
and depends upon the path followed,
 $\therefore C$ is also not a state function.

A state function depends only on
the final and initial state of the
system. It does not depend on
how we get from initial to final state.
Heat is the energy transferred
between the system and surroundings.

during some process. The amount that transfers does depend on how the process happens and therefore it is not a state function.

$$C = \frac{\delta Q}{dT}$$

C is not a state function.

In order to find out the value of C, the condition such as constant pressure or constant volume must be specified.

Heat Capacity

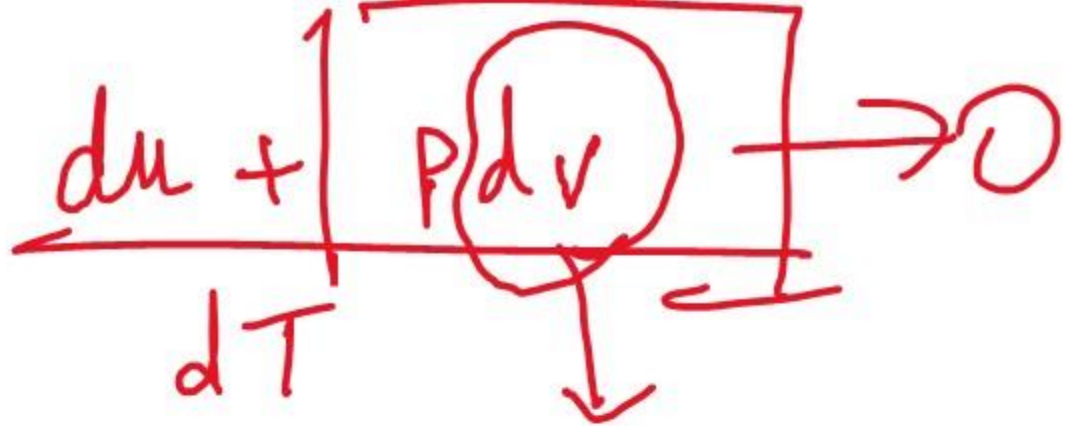
Heat capacity
at constant pressure

Heat capacity
at constant volume

$$C = \frac{\delta Q}{dT} = \frac{du + Pdv}{dT} \rightarrow \text{1st law.}$$

When the volume is kept constant,
 $v_2 - v_1 = 0$ i.e. $dv = 0$

$$C = \frac{\delta q}{dT}$$



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

when volume

= constant

$$dv = 0$$

heat capacity at
constant volume

For an ideal gas,

$$C_v = \frac{du}{dT}$$

$\frac{d}{dT}$ = rate of change w.r.t } T

$$C_v = \frac{dU}{dT}$$

The heat capacity at constant volume may be defined as the rate of change of internal energy at constant volume.

Heat capacity at constant pressure

$$C = \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}$$

$$C = \frac{du + Pdv}{dT}$$

$$C_p = \left(\frac{\partial u}{\partial T} \right)_P + P \left(\frac{\partial v}{\partial T} \right)_P \rightarrow \text{constant pressure}$$

$$H = U + PV$$

Differentiating both sides w.r.t. T at constant P , we have

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial u}{\partial T} \right)_P + P \left(\frac{\partial v}{\partial T} \right)_P + \left(\frac{\partial \pi}{\partial T} \right)_P$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P$$

no work of expansion

only increase in internal energy

$$H = U + PV$$

i) increase in internal energy

ii) do some work

$$C_p > C_v$$

$C_p =$ int energy + work

$C_v =$ " " \rightarrow no work.

Relationship between C_p & C_v .

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

For ideal gas, we can simply write,

$$C_p = \frac{dH}{dT} \rightarrow \textcircled{1} \quad C_v = \frac{dU}{dT} \rightarrow \textcircled{2}$$

$$\therefore C_p - C_v = \frac{dH}{dT} - \frac{dU}{dT} \rightarrow \textcircled{3}$$

$$C_p = \frac{dH}{dT}$$

$$C_v = \frac{dU}{dT}$$

$$H = U + PV$$

For 1 mole of an ideal gas,

$$PV = RT \quad \text{universal gas constant}$$

Differentiating

$$H = U +$$

$$RT$$

both sides w.r.t - T, we have

$$\frac{dH}{dT} = \frac{dU}{dT} + R \times \frac{dT}{dT} \left(\frac{d}{dT}(T) = 1 \right)$$

$$\Rightarrow \frac{dH}{dT} = \frac{dU}{dT} + R$$

$$\Rightarrow C_p = C_v + R$$

$$C_p = C_v + R$$

$$C_p - C_v = R$$

$$H = U + PV$$

$$= U + RT$$

$$\frac{dH}{dT} = \frac{dU}{dT} + R$$

$$\Rightarrow \frac{dH}{dT} - \frac{dU}{dT} = R$$

$$C_p = \frac{dH}{dT} \quad C_v = \frac{dU}{dT}$$

$$C_p - C_v = \frac{dH}{dT} - \frac{dU}{dT} = R$$

Thermodynamics (Problems)

1. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 15 K) \rightarrow (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0$ L atm. The change in enthalpy, ΔH of the process in L atm. is

- a) 40.0 b) 42.3 c) 44.0 d) Not defined because pressure is not constant.

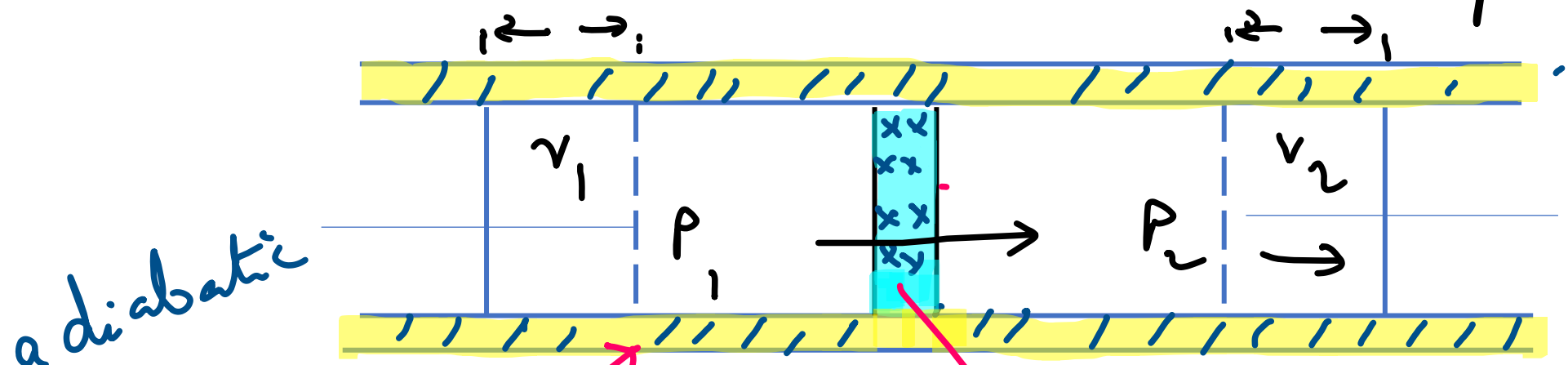
2. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm. from an initial volume of 2.5 L to a final volume of 4.5 L. The change in internal energy ΔU of the gas in joules will be -

- a) 1131.25 J b) - 500 J c) - 505 J
 d) + 505 J. 1 L atm = 101.325 J

Joule Thomson Effect

When a real gas at certain pressure expands adiabatically through a porous plug or a fine hole into a region of low pressure it is accompanied by cooling (except for H and He, which gets heated up). This phenomenon is called Joule Thomson effect.

Joule - Thomson Experiment.



a diabatic process

Insulated Tube

Porous plug

Expansion of a real gas through a porous plug.

Since the process is carried out adiabatically, $q = 0$

According to 1st law of thermodynamics,

$$\Delta U = q - w$$

$$\because q = 0,$$

$$\Delta U = -w$$

$$\Rightarrow w = -\Delta U$$

Under a diabatic condition,
the work done is at the cost of
internal energy. When the work of
expansion is done adiabatically,

the internal energy of the gas decreases
and hence the temperature decreases.
In fact, a part of the internal
energy is used up to overcome
the forces of attraction existing among
the molecules (Van der Waal's forces)

In J.T. effect, which is an example
of a diabatic process, on the L.H.S

of the fluid, the work is done on
the system, whereas on the R.H.S.,
the work is done by the system

Work done on the system on the L.H.S.

" " by the " on the R.H.S. :

\therefore Net work done by the system $= P_2 V_2 - P_1 V_1$

$$\omega = -\Delta U \Rightarrow \Delta U = -\omega$$

$$\therefore \Delta U = -(P_2 V_2 - P_1 V_1)$$

$$= P_1 V_1 - P_2 V_2 \rightarrow \textcircled{1}$$

$$\Delta U = V_2 - V_1 \rightarrow \textcircled{2}$$

\therefore Putting the value of ΔU from
 $\textcircled{2}$ in $\textcircled{1}$, we have,
 $V_2 - V_1 = P_1 V_1 - P_2 V_2$

$$\begin{aligned}
 u_2 - u_1 &= P_1 v_1 - P_2 v_2 \\
 \Rightarrow u_2 + P_2 v_2 &= u_1 + P_1 v_1 \\
 \Rightarrow H_2 &= H_1 \quad (\because H = u + Pv)
 \end{aligned}$$

$$\therefore H_2 - H_1 = 0 \Rightarrow \Delta H = 0$$

When the expansion of a gas takes place adiabatically $\Delta H = 0$.

Joule Thomson Coefficient

The J.T. coefficient (μ) may be defined as the temperature change in degrees produced by a drop of one atmosphere when the gas expands under conditions of constant enthalpy.

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

H = constant (iso-enthalpic)

$$\mu = \left(\frac{\partial T}{\partial P} \right)_{\eta}$$

- i) For cooling, μ will be +ve
(because dT and dP are both negative)
- ii) For heating, μ will be -ve
(because dT is positive & dP is -ve)
- iii) If $\mu = 0$, the gas is neither heated up nor cooled on an adiabatic expansion.

(because $\alpha = 0$ only when $dT = 0$ for any value of dP)

Inversion Temperature
Every gas has a definite temperature at a particular pressure at which $\alpha = 0$. Below this temperature α is +ve, and above this temperature α is negative.

The temperature at which $\mu = 0$ i.e.
at a particular pressure) the gas is neither
cooled down nor heated up on adiabatic
expansion and below which μ is +ve
adiabatic expansion and above which μ
is -ve is called inversion temp.

Why H_2 & He show heating on adiabatic
expansion?

The inversion temp. of most of the gases are very high (much higher than the room temp.). That is why these gases undergo cooling on adiabatic expansion under ordinary conditions of temperature. On the other hand, the inversion temp. of H_2 & He are very low ($\ll 0^\circ C$). Hence these gases undergo heating on adiabatic

expansion under ordinary conditions of
temperature.

Q

$$\alpha = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

Deduce this relationship: --

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P \quad \left(\frac{\partial T}{\partial P} \right)_H = \alpha \downarrow$$

coefficient J. T.

$$H = f(T, P) \quad \text{---} \quad \textcircled{1}$$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad \text{---} \quad \textcircled{2}$$

In J.T. effect, the enthalpy of the system remains constant.

$$\therefore dH = 0$$

$$C_p \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = 0 \quad \text{---} \quad \textcircled{3}$$

heat capacity at constant pressure

$$\left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT = 0 \rightarrow (3)$$

Dividing the entire eqn. by dP , we have,

$$\left(\frac{\partial H}{\partial P}\right)_T + \left(\frac{\partial H}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_H = 0$$

H, T, P

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = - \frac{C_p \times \alpha}{\frac{1}{C_p} \left(\frac{\partial H}{\partial P}\right)_T}$$

Work done in isothermal reversible expansion

Let P be the pressure of the gas within a system undergoing isothermal expansion by a reversible process. Then, in order that the expansion takes place very slowly, the external pressure should be $P - dP$, where dP is very small quantity.

The small amount of work (δw) done by the system when its volume increases by an infinitesimal amount, dv , is given by,

$$\delta w = (P - dP) dv \rightarrow (i)$$

$$= P dv - dP \cdot dv$$

$\therefore dP \cdot dv$ is very small,
 we can neglect this term -
 $\therefore \delta w = P \cdot dv$

Volume increases from $v_1 \rightarrow v_2$

$$w = \int_{v_1}^{v_2} P \, dv \longrightarrow \text{Total work done by the system}$$

n moles of an ideal gas

$$PV = nRT \Rightarrow P = \frac{nRT}{V}$$

$$w = \int_{v_1}^{v_2} \frac{nRT}{V} \, dv = nRT \left[\ln \cdot V \right]_{v_1}^{v_2}$$

constant constant

$$\omega = nRT \left[\ln v_2 - \ln v_1 \right]$$

$$= nRT \ln \frac{v_2}{v_1} = 2.303 nRT \log \frac{v_2}{v_1}$$

$$\omega = 2.303 nRT \log \frac{v_2}{v_1}$$

Now \therefore according to Boyle's law,
 $P_1 V_1 = P_2 v_2$ (for ideal gas)

$$\begin{aligned} \omega &= 2.303 n R T \log \frac{P_1}{P_2} \\ &= 2.303 n R T \log \frac{V_2}{V_1} \end{aligned}$$

Work done in a reversible process is the maximum work obtainable from a system. Hence ω may be replaced by ω_{\max} .

$$W_{max} = 2.303 nRT \log \frac{V_2}{V_1}$$

$$= 2.303 nRT \log \frac{P_1}{P_2}$$

Expression for Q : (Heat absorbed)

According to 1st Law of Thermodynamics,

$$Q = \Delta U + W$$

$$U = f(T)$$

Since the internal energy of an ideal gas is function of temperature only,

$$\Delta U = 0$$

therefore, in an isothermal process, as the temperature remains constant, the internal energy of the system (containing an ideal gas) remains constant.

$$q = \Delta U + w$$

For an isothermal process, $\Delta U = 0$

$$\Delta U = 0 \quad \text{Isothermal} \quad \therefore \quad q = w = 2.303 n R T \log \frac{V_2}{V_1}$$

Expansion

$$= 2.303 n R T \log \frac{P_1}{P_2}$$

Expression for ΔH :

Reversible

$$\begin{aligned}
 H &= U + PV \\
 \Delta H &= \Delta U + \Delta(PV) \quad [\because \text{For ideal gas} \\
 &= \Delta U + \Delta(nRT) \quad [PV = nRT] \\
 &= \Delta U + \Delta n R \Delta T \\
 &= 0 + 0
 \end{aligned}$$

$\Delta H = 0$

Isobaric process: $\Delta U = 0$

for isothermal process, $\Delta T = 0$

$$\begin{aligned}
 w &= q = 2.303 nRT \log \frac{V_2}{V_1} \\
 \Delta H &= 0 = - 2.303 nRT \log \frac{P_1}{P_2}
 \end{aligned}$$

Q Deduce values of q , w , ΔU , ΔH
in case of isothermal irreversible
expansion when -

i) opposed pressure is 0

ii) opposing pressure is constant and less
than P_2 but greater than 0.

~~Solⁿ~~ i)

For free expansion:
 $w = \int P_{\text{opp}} \cdot dV$

intermediate expansion

For free expansion, $P_{\text{opp}} = 0$

$$w = \int P_{\text{opp}} \cdot dV = \int 0 \cdot dV = 0$$

Hence

$$\Delta U = \Delta H = 0$$

(as the gas is ideal and expansion is isothermal)

ii)

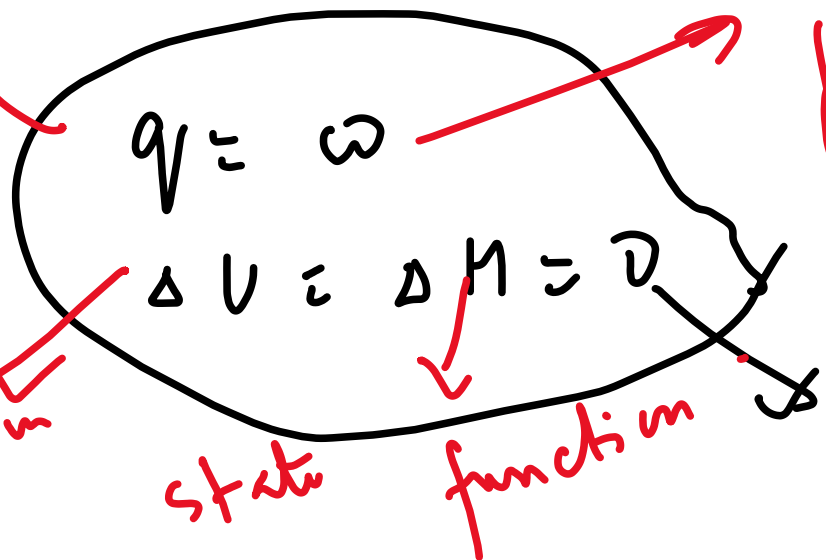
For intermediate expansion: $P_{\text{opp}} = \text{constant}$
and lies in the range $0 < P_{\text{opp}} < P_2$

$$w = \int_{v_1}^{v_2} P_{opp} dv = P_{opp} (v_2 - v_1)$$

$$q = w = P_{opp} (v_2 - v_1)$$

$\Delta U = \Delta H = 0$ (as the gas is ideal & expansion is isothermal)

~~path function~~



state function

state function

~~path function~~

isothermal process:
(whether reversible or irreversible)

Isothermal Process (for ideal gas)

Parameter

Reversible

Irreversible

ΔU

0

0

w

$$2.303 nRT \log \frac{v_2}{v_1}$$

$$= 2.303 nRT \log \frac{P_1}{P_2}$$

$P_{opp} (v_2 - v_1)$
 < for intermediate expansion

$q = w$

.

0 < for free expansion

ΔH

0

0

Adiabatic Expansion

Calculation of w , q , ΔU , and ΔH in
adiabatic expansion of an ideal gas.

An adiabatic process is the one in which no heat enters or leaves the system at any stage.

Thus, for every infinitesimal change of the process, $\delta q = 0$.

According to 1st law, $du = \delta q - \delta w$.

$$du = \delta q - \delta w$$

For adiabatic process,

$$\delta q = 0$$

$$du = -\delta w$$

(i.e. work is done at the expense of internal energy)

$$\Rightarrow du = -P dv$$

where dv is the small increase in volume & P is the pressure of the gas.

(if the work of expansion is the only work involved, is the only relation true)

$$du = -P dv. \quad \longrightarrow \textcircled{1}$$

For an ideal gas, $C_v = \frac{du}{dT}$

$$\Rightarrow du = C_v \cdot dT$$

$$\therefore C_v dT = -P dv \quad \longrightarrow \textcircled{2}$$

$$\begin{aligned} \Delta H &= \Delta(U + PV) \\ &= \Delta U + \Delta(PV) \\ &= \Delta U + \Delta(RT) \\ &= \Delta U + R \Delta T. \end{aligned}$$

$$\begin{aligned} \Rightarrow \Delta H &= C_v \Delta T + R \Delta T \\ &= (C_v + R) \Delta T \\ &= C_p (T_2 - T_1) \end{aligned}$$

To sum up, for any adiabatic process,
(reversible or irreversible)

1. $q = 0$

adiabatic process

2. $w = -\Delta U$

3. $\Delta U = C_v \Delta T = C_v (T_2 - T_1)$

4. $\Delta H = C_p \Delta T = C_p (T_2 - T_1)$

Q

Derive a relationship between temperature & volume in reversible adiabatic expansion.

Soln

$$PV = RT \Rightarrow P = \frac{RT}{V}$$

$$C_v dT = \Delta U = -w$$

$$\Rightarrow C_v dT = -\frac{RT}{V} dv$$

$$\Rightarrow C_v \frac{dT}{T} = -R \frac{dv}{v} \longrightarrow \textcircled{1}$$

If the vol. of the gas changes

from $v_1 \rightarrow v_2$ and $\ln p$ from $T_1 \rightarrow T_2$
 assuming C_v to be independent of T
 $\ln p$ and integrating eqn. (1) between T_1, T_2 & v_1, v_2
 we have,

$$\Rightarrow C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{v_1}^{v_2} \frac{dv}{v}$$

$$\Rightarrow C_v \cdot \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$C_p - C_v = R \quad (\text{for 1 mole of an ideal gas})$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = (C_p - C_v) \ln \frac{V_1}{V_2}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = \left(\frac{C_p}{C_v} - 1 \right) \ln \frac{V_1}{V_2}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2}$$

where $\frac{C_p}{C_v} = \gamma$ (ratio of two heat capacities)

$$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2}$$

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

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

$$\Rightarrow T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} = \text{constant}$$

Temperature - Pressure relationships:

For 1 mole of an ideal gas under consideration,

$$P_1 V_1 = R T_1 \Rightarrow V_1 = \frac{R T_1}{P_1}$$

$$P_2 V_2 = R T_2 \Rightarrow V_2 = \frac{R T_2}{P_2}$$

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

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

$$\frac{T_2}{T_1} \propto \left(\frac{v_1}{v_2} \right)^{\gamma-1}$$

$$P V^\gamma = \text{constant}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{T_1 P_2}{T_2 P_1} \right)^{\gamma-1}$$

$$\Rightarrow \frac{T_2}{T_1} \times \left(\frac{T_2}{T_1} \right)^{\gamma-1} \propto \left(\frac{P_2}{P_1} \right)^{\gamma-1}$$

$$\Rightarrow \left(\frac{T_2}{T_1} \right)^{\gamma} \propto \left(\frac{P_2}{P_1} \right)^{\gamma-1}$$

$T P^{\frac{1-\gamma}{\gamma}} = \text{constant}$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}}$$

Work done in an adiabatic reversible expansion of an ideal gas.

For an adiabatic process, $PV^\gamma = \text{constant}$.

Differentiating this eqn. -

$$P \times (\gamma V^{\gamma-1}) dv + V^\gamma dP = 0$$

$$\Rightarrow \gamma P V^{\gamma-1} dv + V^\gamma dP = 0$$

Dividing throughout by $V^{\gamma-1}$, we have

$$\gamma P dv + V dP = 0$$

$$\gamma P dv + v dP = 0$$

$$\Rightarrow v dP = - \gamma P \cdot dv \rightarrow \textcircled{1}$$

For n moles of an ideal gas,

$$Pv = nRT$$

$$\Rightarrow Pdv + v dP = nRdT \quad \left(\text{complete diff.} \right)$$

Substituting the value of $v dP$ from $\textcircled{1}$ in $\textcircled{2}$, we get,
 $Pdv + (-\gamma P \cdot dv) = nRdT$

$$P dv - \gamma P dv = nR dT$$

$$\Rightarrow (1 - \gamma) P dv = nR dT$$

$$\Rightarrow P dv = \frac{nR}{1 - \gamma} \cdot dT$$

Work done in an adiabatic process is given by the general eqn

$$W = \int_{v_1}^{v_2} P dv = \int_{T_1}^{T_2} \frac{nR}{1 - \gamma} \cdot dT$$

(changing the limits)

$$\omega = \int_{T_1}^{T_2} \frac{nR}{1-\gamma} \cdot dT$$

$$\Rightarrow \omega = \frac{nR}{1-\gamma} [T]_{T_1}^{T_2} = \frac{nR}{1-\gamma} (T_2 - T_1)$$

$$\omega = \frac{nR(T_2 - T_1)}{1-\gamma}$$

Paltiye

$$R = C_p - C_v$$

$$\gamma = C_p / C_v$$

$$\gamma = C_p / C_v$$

$$\gamma = C_p / C_v$$

$$\omega = \frac{n R (T_2 - T_1)}{1 - \gamma}$$

$$= \frac{n (C_p - C_v) (T_2 - T_1)}{1 - \frac{C_p}{C_v}}$$

$$= \frac{n \cancel{(C_p - C_v)} C_v (T_2 - T_1)}{\cancel{(C_p - C_v)}}$$

$$= \frac{n C_v (T_2 - T_1)}{C_v (T_2 - T_1)} \left\{ \begin{array}{l} \text{for } n \text{ moles} \\ \text{for } 1 \text{ mole} \end{array} \right\} \text{ of ideal gas}$$

For n moles of an ideal gas,

$$P_1 V_1 = n R T_1 \quad \text{---} \rightarrow \text{initial state}$$

$$P_2 V_2 = n R T_2 \quad \text{---} \rightarrow \text{final state}$$

$$\omega = \frac{n R (T_2 - T_1)}{1 - \gamma}$$

$$= \frac{n R T_2 - n R T_1}{1 - \gamma}$$

$$= \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$$

$$1. \quad \omega = \frac{nR(T_2 - T_1)}{1 - \gamma}$$

$$2. \quad \omega = -nC_v(T_2 - T_1)$$

$$3. \quad \omega = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$$

adiabatic reversible expansion of an ideal gas.