Thermodynamics

Thermodynamics

- A branch of chemistry which gives information about the flow of heat.

Objectives of Thermodynamics

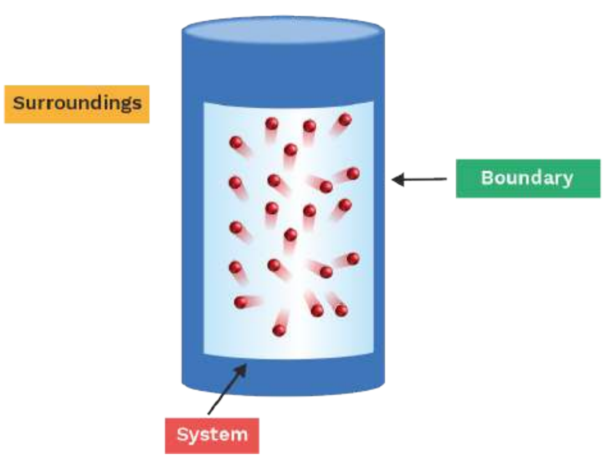
- Various Heat changes such as ΔH, ΔE and ΔG etc.
- Various Thermodynamic Processes
- Various Thermodynamic Laws
- Spontaneous and non spontaneous processes

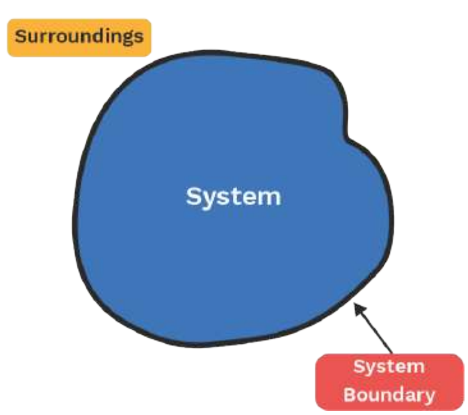
Limitations

- Doesn't give information about the rate of reaction.
- Thermodynamics process are not applicable for micro system such as e^-, p^+, n etc

Objectives of Universe

- **System**: A part of universe covered with real or imaginary boundary where we study about various thermodynamic properties such as P & T
- **Surrounding**: Rest part of universe





- For a system the change in energy is identical in magnitude but opposite in sign to the change in energy of its surrounding.

Rack your Brain

An open container and open system. Are they same ?

Types of system

1. **Open system :**

   The type of system where both mass and heat transfer takes place. with surrounding. Example. Boiled water in an open vessel

2. **Closed system :**

   The type of system where only heat transfer takes place with surrounding but there is no mass transfer. Example. Boiled water in a closed vessel.

3. **Isolated system :**

   The type of system where neither heat transfer nor mass transfer takes place. Example. Boiled water in thermo flask.

Concept Ladder

In lab experiments, the room is considered as surrounding.

$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0$

$\Delta U_{sys} = -\Delta U_{surr}$

Rack your Brain

Can you compare the relative magnitude of the change in energy of system and surrounding?

- The universe is isolated, because it contains everything by definition, and thus there can be no exchange of energy with anything. Reactants undergo reaction to decrease their energy and will proceed until they reach a state of low energy and will remain in this state unless disturbed. This state is called equilibrium.

Concept Ladder

Universe is considered as an isolated system. So, all the laws applicable for universe are applicable for isolated system.

Q.1 Write down system of following:

1. Helium filled balloon
2. Coffee in a thermos flask
3. The earth
4. Satellite in an orbit
5. Human being
6. Refrigeration cycle

A.1

1. Helium filled balloon	Closed
2. Coffee in a thermos flask	Isolated
3. The earth	Open
4. Satellite in an orbit	Closed
5. Human being	Open
6. Refrigeration cycle	Closed

Thermodynamic Properties

Intensive Properties | **Extensive Properties**

Thermodynamic properties

1. Intensive properties :

(i) Those properties which are independent of mass.

(ii) Their values remain uniform throughout system.

(iii) They are non-additive.

2. Extensive properties :

(i) Those properties which depend on mass.

(ii) Ratio of two extensive properties become an intensive property.

(iii) They are additive.

Rack your Brain

Is Pressure an intensive property?

Extensive properties	Intensive Properties
Volume	Molar volume
Number of Moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy	Viscosity
Enthalpy	Free energy per mole
Internal Energy (E & U)	Specific heat
Heat Capacity	Pressure, Temperature, Boiling point, freezing Point. Etc.

State Functions

Those thermodynamic properties which depend on initial and final state.

Eg: Pressure, volume, temperature, Gibb's free energy, internal energy, entropy etc.

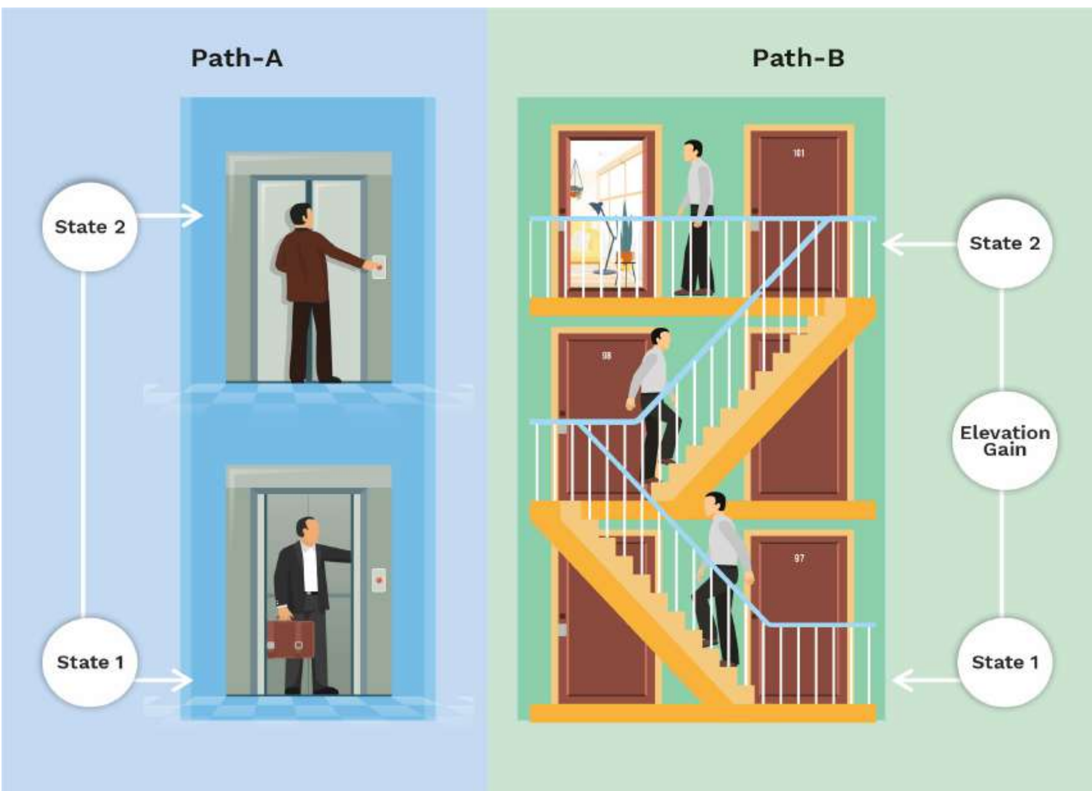
Path function

Those properties which depend on path.

Eg: Heat, Work, Loss of energy due to friction.

Concept Ladder

Both q and w are not state functon sice their values depend upon the path by which the change is carried, but the quality q + w is a state function, this is because q + w = ΔV and ΔU is a state function.

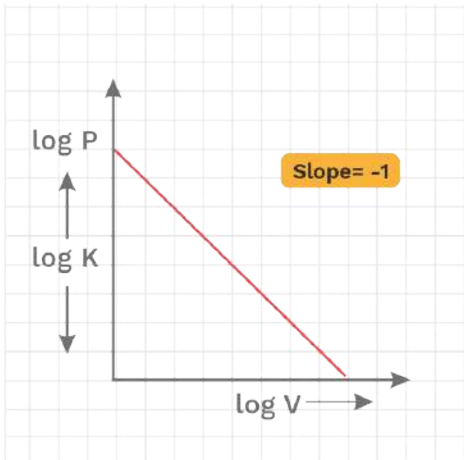


Thermodynamic Process

The change of thermodynamic state from one condition to another condition is called thermodynamic process.

Rack your Brain

What are the condition for the various process can a occur?



Rack your Brain

When a system undergoes a change at constant pressure then the process will be?

Q.2 5 mole of O_2 is expanded from 1L to 10L at 300K then which relation is correct?

(i) $\Delta E = 0$ (ii) $\Delta H = 0$ (iii) $W = 0$ (iv) $\Delta S = 0$

(1) i,ii,iii (2) ii,iii (3) i,ii (4) ii,iii,iv

A.2 (3)

As moles and temperature are constant

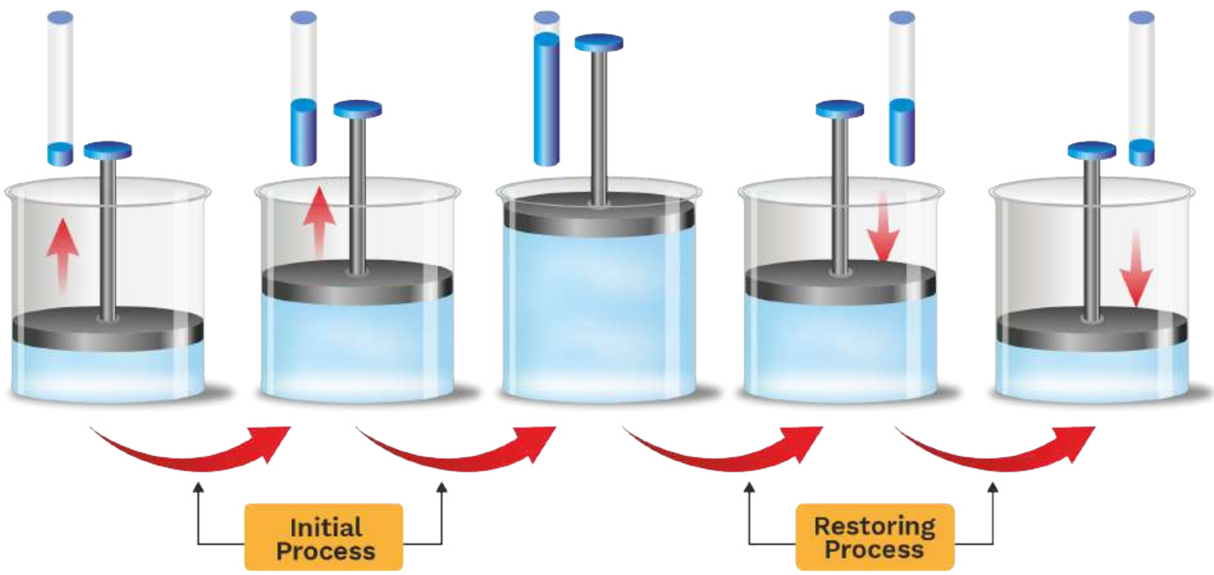
$\Delta H = \Delta E + \Delta n_g RT$

$\Delta H = 0$

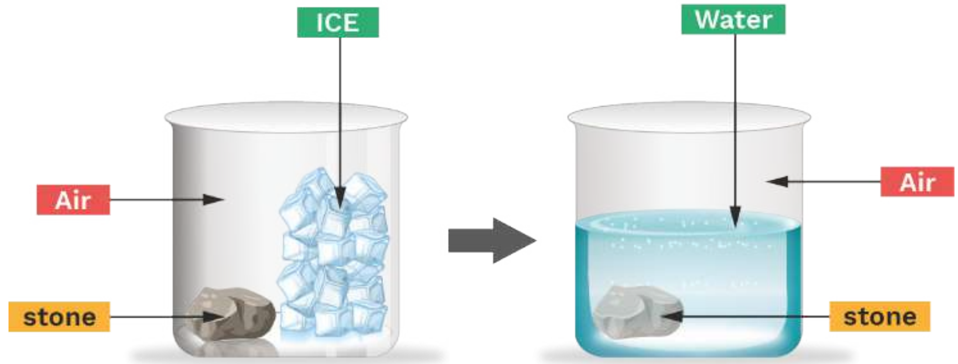
Reversible process	Irreversible process
Driving force is infinitesimally small.	Driving force is large and finite.
PV work is done across pressure difference dP.	PV work is done across pressure difference ΔP.
A reversible heat transfer takes place across temperature difference dT.	Irreversible heat transfer take place across difference ΔT.
It is an ideal process.	It is a real process.
It takes infinite time for completion of process.	It takes finite time for completion of process.
It is an imaginary process and can not be realised in actual practice.	It is a natural process and occurs in particular direction under given set of conditions.

Throughout the process, the system remain infinitesimally closer to state of equilibrium and exact path of process can be drawn.	The system is far away from state of equilibrium and exact path of process can not be defined as different part of the system are under different conditions.

Reversible Process



Irreversible Process



1. State Functions

(i) Those thermodynamic properties which depend on initial and final state

(ii) e.g ΔE or ΔU
ΔH
ΔS
ΔG etc.

2. Path function

(i) Those properties which depend on path

(ii) e.g Work and heat

General Terms :

Those properties which depends on path ;
e.g Work, Heat

1. Work :

(i) Thermodynamic work
$W = \pm P\Delta V$

2. Sign Convention

(i) Compression : (Positive) → Work done on the system

(ii) Expansion : (Negative) → Work done by the system, means expansions

3. Unit of work : atm × litre

1 atm × lit = 24.23 cal

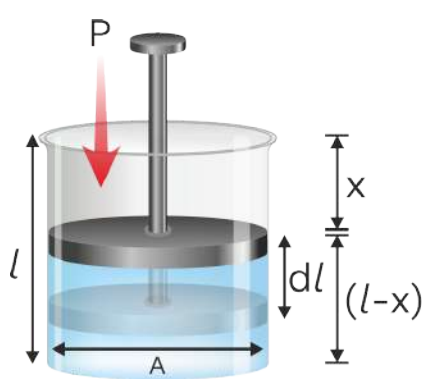
1 atm × lit = 101.3 J

1 cal = 4.18 J

1 J = 107 erg

1 J = 0.24 calorie

$$\boxed{1\,\text{atm} \times \text{litre} > 1\,\text{cal} > 1\,\text{joule} > 1\,\text{erg}}$$



Rack your Brain

Why the energy of system at equilibrium is minimum?

Concept Ladder

The negative work sign represents decrease in energy content of system. During compression, the sign of dV is negative which gives positive value of W representing the increase in energy content of system during compression.

- For a small displacement dx due to force F, work done on the system.
  $dW = F.dx$
  Also
  $F = PA$
  $dW = PA.dx$
  [Here P = pressure, A = Area, V = volume]
  $V = (l-x)A$
  $\Rightarrow dV = -A \, . \, dx$
  $\Rightarrow dW = -P_{ext.} \, dV$
  $\Rightarrow W_{PV} = -\int_{V_1}^{V_2} P_{ext.} dV$

4. Heat (Q)

(i) By difference in temperature the total amount of energy transferred from one body to another is known as Heat.

(ii). Sign convention :
Heat absorb by the system (+)
Heat evolved by the system (–)

Internal Energy (E or U) Or Hidden Energy

1. Sum of various type of energy related with a system is known as internal energy
   E or U = P.E + K.E + T.E + ...
2. Energy due to gravitational pull is not considered in internal energy
3. It is impossible to calculate the absolute value of internal energy because it is not possible to calculate the exact value of all type of energy at a time
4. Internal energy is an extensive property
5. It is a state function
6. Relation between Internal Energy & Pressure for 1 mole of ideal gas and per unit volume
   In ideal gas internal energy = K.E = $\frac{3}{2}RT$
   (1 mole)
   $PV = nRT$
   $P \times 1 = 1 \times RT$

Concept Ladder

If the system is at lower temperature than the surroundings the energy is gained by the system from the surrounding causing a rise in the temperature of the system.

Definitions

It is the amount of heat evolved or absorbed when a chemical reaction is carried out at constant volume and temperature.

Rack your Brain

Why there is no change in internal energy in a cyclic process?

$$P = RT$$

$$U = \frac{3}{2}P$$

$$I.E = K.E = \frac{3}{2}P$$

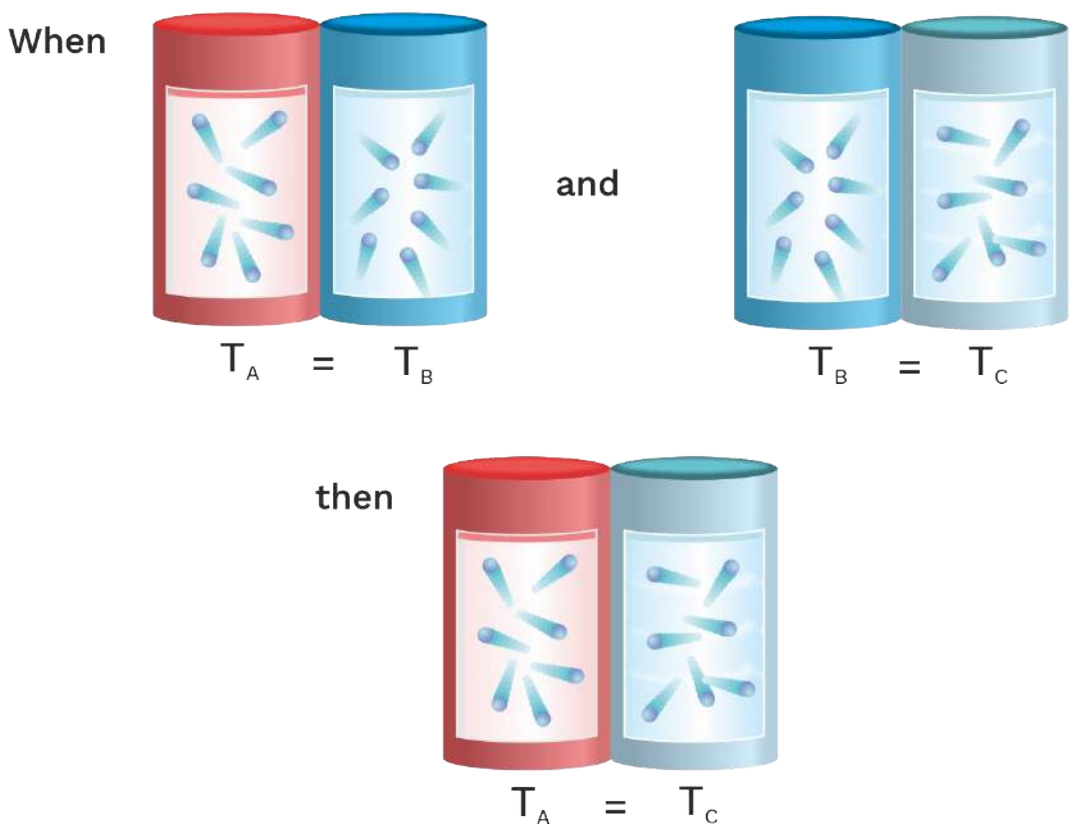
7. The properties which arise out of collective behavior of large number of chemical entities.
   Example. Pressure, volume temperature, composition, colour refractive index etc.

Concept Ladder

The macroscopic energy changes with velocity and elevation of the system are not considered in internal energy change of system.

Zeroth Law of Thermodynamics

When two different system are in thermal equilibrium with 3rd system separately then will also in thermal equilibrium with each other



Types of Thermodyanmic Processes

1. Isobaric process

(i) Pressure $\rightarrow$ constant

$\Delta P = 0$

(ii) Thermodynamic work

$\boxed{W = \pm P\Delta V}$

$W = F \times dl$

$= P \times A \times dl$

$=$ Pressure $\times$ Area $\times$ change in length

$= P \times V = \Delta(PV)$

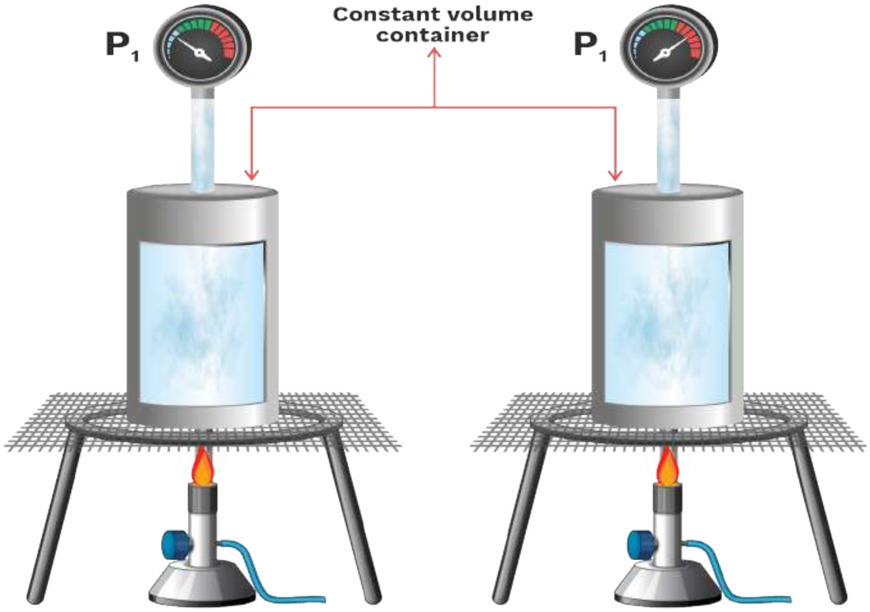
$W = P(\Delta V)$ because P constant

(iii) If in question process is not given then we will consider Isobaric because maximum processes are carried out in open vessel where pressure is constant.

2. Isochoric Process :

(i) Volume $\rightarrow$ Constant $\Delta V = 0$

(ii) Thermodynamics work $W = 0$



Isochoric Process

Rack your Brain

When a system undergoes a change at constant pressure then the process will be?

Note : If not given then we may consider.

3. Isothermal Process

(i) Temperature → constant

$\Delta T = 0$

(ii) Ideal gas equation, PV = nRT

So, PV = Constant

$P_1V_1 = P_2V_2$

(iii) For ideal gas and isothermal process, then Change in internal energy $\Delta U = 0$

Internal Energy = Kinetic Energy = 3/2 RT

Internal Energy $\propto$ Temperature = ΔI.E. $\propto \Delta T = \Delta U = 0$

(iv) Ideal gas Isothermal & moles are constant :

Change in enthalpy $\Delta H = 0$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = 0$

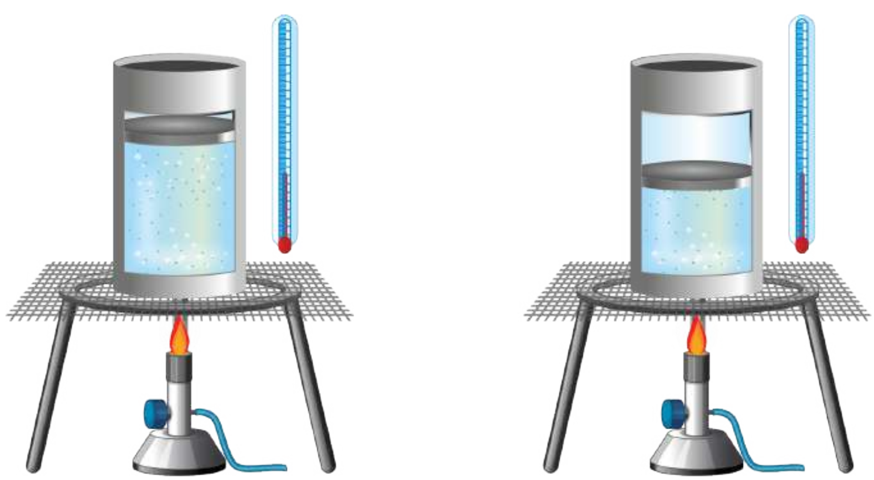
(vi) Graph log P v/s log V

For isotherm = PV = K

log P + log V = log K

log P = –log V + log K

y = mx + c



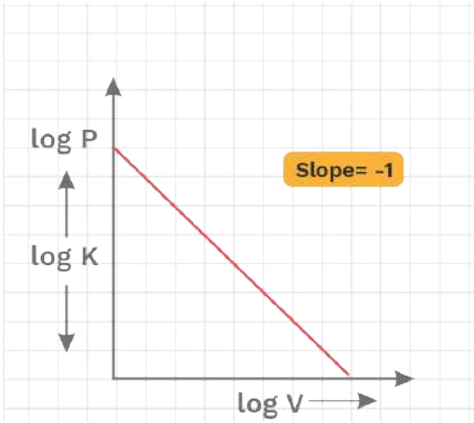
Isothermal Process

Concept Ladder

Generally all non reacting gases such as H_2, O_2, N_2, Ne etc are considered as an ideal gas.

Rack your Brain

Why work done during the isothermal reversible process is greater than adiabatic process?



4. Adiabatic process

(i) No transformation of heat with surrounding means Q =0

(ii) (a) PV^{γ} = constant

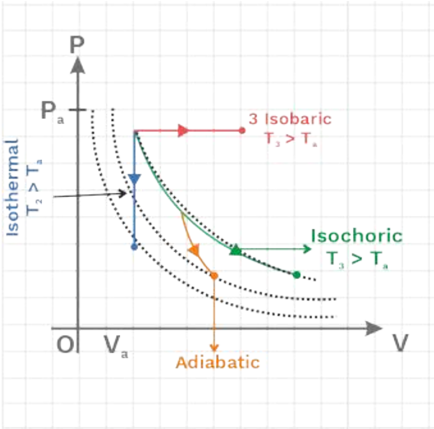
(b) $TV^{\gamma-1}$ = constant

(c) $TP^{(1-\gamma)/\gamma}$ = constant

γ = Poison Ratio

$$\gamma = \frac{C_p}{C_v}$$

$$\boxed{PV^{\gamma} = K}$$



Concept Ladder

log P v/s log V

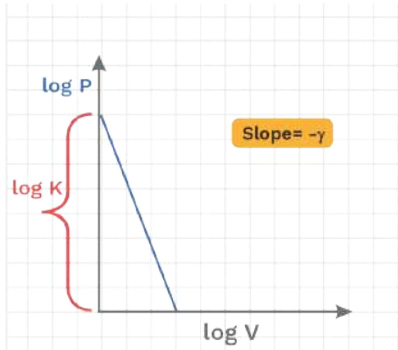
log PV^{γ} = log K

[log P + γ log V] = log K

log P = − γ log V + log K

Rack your Brain

In adiabatic expansion, final volume is less than that of an isothermal expansion. Why?



(iv) Slope of PV graph of adiabatic process is more than isothermal.

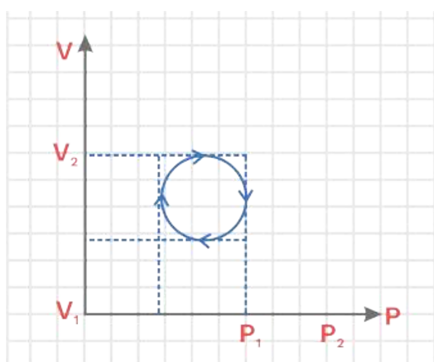
5. Equilibrium :

It is process for no change in thermodynamic property (P,V,T etc) of system with time.

6. **Cyclic process :**

(i) If a system goes through different changes and finally obtains its initial position then this process is known as cyclic process.

(ii) $\Delta U = 0$; $\Delta H = 0$



Work done in Reversible process

1. Isobaric Process

Work done = + $[V_H - V_L]$

2. Isochoric Process ($\Delta V = 0$)

So, Work done = 0

Rack your Brain

Why the energy of system at equilibrium is minimum?

Previous Year's Question

An ideal gas expands isothermally from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 105 N m^{-2}. The work done on the gas is **[NEET]**

(1) +270 kJ

(2) −900 J

(3) + 900 kJ

(4) −900 kJ

Rack your Brain

At which condition in thermodynamics a process is called reversible ?

3. **Isothermal process**

$$W = \pm\ 2.303\ nRT\ \log\left[\frac{T_H}{T_L}\right]$$

R = 8.31 Joule/ K/ mole

R = 2 cal / K/ mole

R = 0.082 atm × litre /K/mole

4. **Adiabatic Process**

$$W = \pm\frac{nR}{\gamma - 1}\left[T_H - T_L\right]$$

- In adiabatic process increment in temperature indicates compression of gas.

Work Done In Irreversible Process :

- Generally these processes are carried out in open vessel in which gas show expansion It is two types.

1. **Free Expansion**

Expansion of gas in vacuum is known as free expansion. In this process,

P = 0

So, W = 0

2. **Intermediate Expansion**

Gas do work against the external pressure to expand i.e known as intermediate work.

$$W = -P_{ext}\left[V_2 - V_1\right]$$

[P_{ext} = External Pressure]

PV = nRT

$P\Delta V = \Delta n_g RT$

$W = -\Delta n_g RT$

Note:

These formulae are applicable for all irreversible processes :

$$\Delta n_g = \begin{bmatrix}\text{Total Moles}\\ \text{of gaseous}\\ \text{Product}\end{bmatrix} - \begin{bmatrix}\text{Total Moles}\\ \text{of gaseous}\\ \text{rectant}\end{bmatrix}$$

First of all reaction will be written according to given quantity after it we will find out Δn_g.

Concept Ladder

For an isothermal isobaric expansion, At constant T and P

q = -W

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

Rack your Brain

Why maximum work is done is case of reversible isothermal expansion process?

Concept Ladder

Relationship between q, (-w) ΔU and ΔH in intermediate expansion

$0 < P_{ex}(V_2 - V_1) < 2.303nRT\log(V_2/V_1)$

Q.3 90 gram water is vaporized

$H_2O(l) \rightarrow H_2O(g)$

then find out Δn_g.

A.3 $5\ H_2O\ (l) \rightarrow 5\ H_2O\ (g)$

$90\ gm \rightarrow n = \frac{90}{18} = 5$ mole

$\Delta n_g = 5$

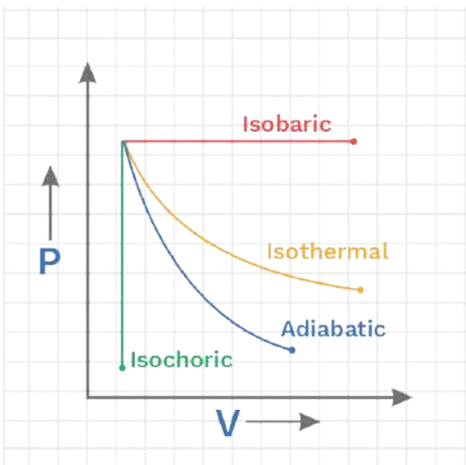
P–V Graph

A–Isobaric

B–Isothermal

C–Adiabatic

D–Isochoric



- Rapid change or sudden change indicate that the process is adiabatic
- In P–V graph

  Area under the curve shows the work done.

Concept Ladder

For an isothermal expansion, $\Delta T = 0$ (R and n are constants)

$\Delta H = \Delta U = 0$

For an isochoric process

$\Delta V = 0 \quad \therefore q = \Delta U$

For an adiabatic prcoss

$q = 0 \quad \therefore \Delta U = W$

for a cyclic process

$\Delta U = 0 \quad \therefore q = -W$

Previous Year's Question

The correct option for free expansion of an ideal gas under adiabatic condition is **[NEET]**

(1) $q = 0$, $\Delta T = 0$ and $w = 0$
(2) $q = 0$, $\Delta T < 0$ and $w > 0$
(3) $q < 0$, $\Delta T = 0$ and $w = 0$
(4) $q > 0$, $\Delta T > 0$ and $w > 0$

Q.4 2 lit of a gas is expanded against an external pressure of 2 atm upto 12 lit. then calculate the work done in joule

(1) −2206 J (2) −2026 J (3) −1996 J (4) −2006 J

A.4 (2)

$W = -P_{ext}(V_2 - V_1)$

$W = -2\ (12-2)$

$= -20$ atm lit

$= -\ 20 \times 101.3$ J

$= -2026$ J

Q.5 2 mole of an ideal gas is expanded in reversible and isothermal process from 2.24 lit. to 22.4 litre. Then find out the amount of work done for expansion in cal. at 300 K.

(1)−2763 cal (2) 3276 cal (3) −3276 cal (4) 2763 cal

A.5 (4)

$W\ = -2303\ nRT \log \frac{V_H}{V_L}$

$= 2.303 \times 2 \times 2 \times 300 \log\left[\frac{22.40}{2.24}\right]$

$= -2.303 \times 1200 \times 1$

$= 2763.600$

$= -2763.6$ cal

$W\ = 2763$ cal

Q.6 260 g Zn reacts with HCl

$Zn\ (s) + 2HCl\ (l) \rightarrow ZnCl_2\ (s) + H_2\ (g)$

Then calculate the work done in cal (Zn = 65)

(1) −3200 cal (2) +3200 cal (3) −3100 cal (4) +3100 cal

A.6 (1)

$4\ [Zn\ (s) + 2HCl\ (l) \rightarrow ZnCl_2\ (s) + H_2\ (g)]$

$4\ Zn + 8\ HCl \rightarrow 4\ ZnCl_2 + 4\ H_2$

$n = \frac{260}{65} = 4$

$\Delta n_g = 4-0 = 4$

$W\ = \Delta n_g RT$

$= -4 \times 2 \times 400$

$= -3200$ cal

Q.7 22 gm CO_2 changes from 500 ml, 300 K to 4l reversible and adiabaticaly then find out (i) final temperature, (ii) work done in cal (γ = 4/3)

(1) 150 K, –450 cal (2) 250 K, –450 cal

(3) 150 K, –250 cal (4) 250 K, –250 cal

A.7 (1)

(i) $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{4000}{500}\right)^{\frac{4}{3}-1}$$

$= [8]^{1/3} = [2^3]^{1/3}$

$$\Rightarrow \frac{300}{T_2} = 2$$

$\Rightarrow T_2 = 150$ K

(ii)
$$W = \frac{-nR}{\gamma-1}[T_H - T_L]$$

$$= \frac{-0.5\times 2}{\frac{4}{3}-1}[300-150]$$

$= -1\times3\ [150]$

$= -450$ cal

Q.8 2 lit. N_2 is at 0° C and 5 atm pressure it is expanded isothermally against an external pressure of 1 atm until the pressure of gas becomes 1 atm. Calculate the amount of work in expansion in Joule.

(1) –810.4 J (2) –635.5 J (3) 635.5 J (4) 810.4 J

A.8 (4)

$P_1V_1 = P_2V_2$

$5 \times 2 = 1 \times V_2$

$V_2 = 10$ lit

$W = -P_{ext}(V_2 - V_1)$

$= -1(10-2)$

$= -8$ atm × 1

$= -8 \times 101.3$

$= -810.4$ J

$\rightarrow$ Amount work = 810.4 J

Q.9 Indicate the sign of work in following process :

1. $PCl_5 \rightarrow PCl_3 + Cl_2$
2. $N_2 + 3H_2 \rightarrow 2NH_3$

A.9
1. $\Delta n_g = 2 - 1 = 1$ (+ve)
2. $\Delta n_g = 2 - 4 = -2$

$W = -n_gRT$

$W = -ve$

First Law of Thermodynamics (FLOT)

Robert Mayer & Helmholtz

1. Total energy of universe always remains constant. Therefore, energy can neither be created nor be destroyed.
2. According to FLOT one form of energy can be completely converted into another form.
3. Mathematically.

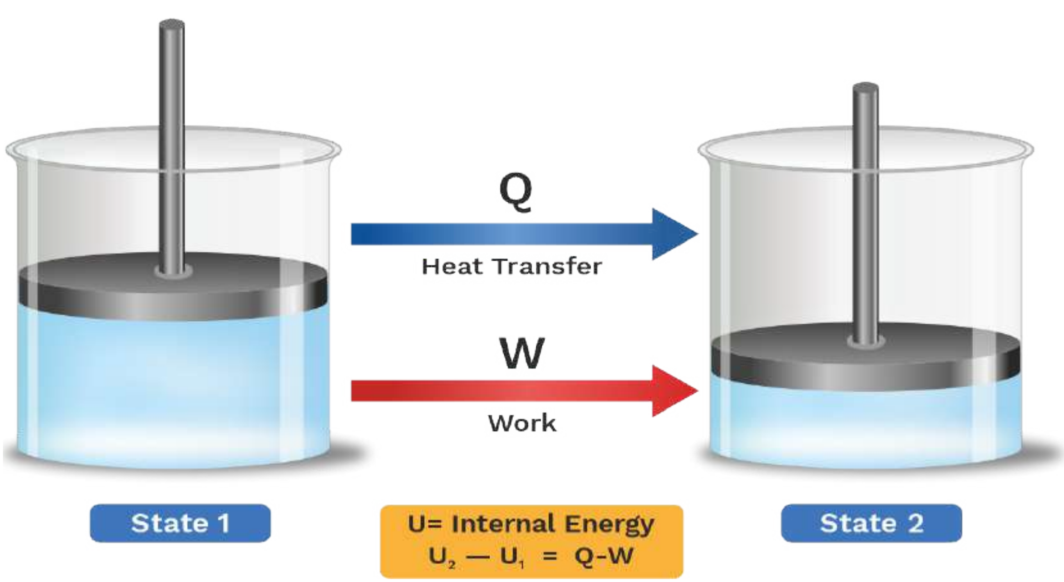
Let work done on the system = W

Heat absorbed by the system = q

Then $\Delta E = q + W$

Concept Ladder

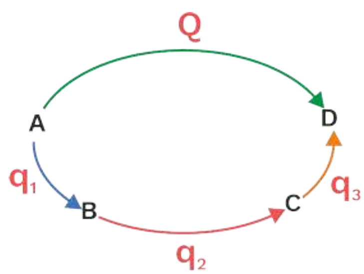
$\Delta E = q + w$ is invalid for open system.



Application of First law of Thermodynamics :

Hess's law of constant heat summation:

According to this law the net amount of heat change in the complete process is the same regardless of the method employed when the chemical change can be made to take place in two or more ways which involves one or more steps.



$$Q = q_1 + q_2 + q_3$$

According to FLOT different thermodynamic processes

1. **Isothermal Process**

$$\Delta U = 0 \quad ; \qquad q = -W \left\{ \begin{array}{ccc} \Delta U & = & q + w \\ 0 & = & q + w \\ q & = & -w \end{array} \right\}$$

According to FLOT in isothermal process heat absorb by the system is equal to work done by the system.

2. **Adiabatic process (q = 0)**

$\Delta U = W$;

$$IE \uparrow \propto T \uparrow \qquad \left\{ I.E = \frac{3}{2} RT \right\} \qquad \{ I.E \propto T \}$$

In adiabatic process work done on the system (compression) indicates the increment in internal energy so temperature of system increases.

3. **Isochoric Process : (W =0)**

$\Delta U = q_v$

Means heat at constant volume is known as

Previous Year's Question

An ideal gas expands isothermally from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 N m^3. The work done on the gas is *[NEET]*

(1) +270 kJ (2) −900 J

(3) + 900 kJ (4) −900 kJ

Concept Ladder

Transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

internal energy change.

4. **Isobaric Process : (P $\rightarrow$ constant)**

Generally these process are carried out in open vessel where gas shows expansion so FLOT.

$\Delta U = q - W \quad [q = \Delta U + P\Delta V]$

$\Delta U = q - P\Delta V \quad q_p = \Delta H$

- Heat at constant pressure is known as

Concept Ladder

Unit of pressure

1 Pascal = 1 kg $m^{-1}s^{-2}$

1 bar 1 × 10^5 Pa

1 atmosphere (atm) = 101,325 Pa

1 torr = 1/760 atm

Note : 1 L-atm = 101.3 J

Q.10 In the compression of air 5KJ work is done and amount of heat evolved is 3 KJ then find out ΔU

(1) 2 KJ (2) 4 KJ (3) 5KJ (4) 6 KJ

A.10 (1)

$\Delta U = q + w$

$w = + 5KJ$

$q = -3$ KJ

$\Delta U = q + w$

$= -3 + 5$

$= 2$ KJ

Q.11 At 300K temperature 1 mole of ideal gas expanded from 1 litre to 10 litre then calculate change in internal energy (ΔU in cal).

(1) 1381 (2) –1381 (3) Zero (4) –690

A.11 (3)

Isothermal

$\Delta U = 0$

Q.12 1 mole of ideal gas is expanded at 400 K temperature from 10 litre to 100 litre reversibly then calculate the heat in cal :

(1) –1842 (2) 1842.4 (3) –2418 (4) 2418

A.12 (2)

1842.4

$W = -2.303\ nRT \log \frac{V_H}{V_L}$

$= -2.303 \times 1\times 2 \times 400 \times 1$

$= -\ 2.303 \times 800 \qquad = -1842.4$ cal

$\Delta U = 0 \qquad q = -w$

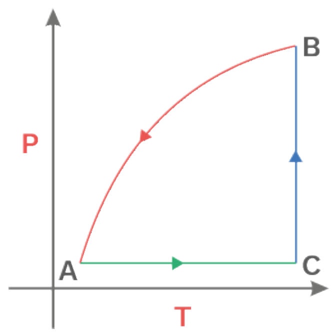
$= -\ (-1842.4)$cal $= 1842.4$ cal.

Q.13 An ideal gas is expanded reversibly and adiabatically then which relation is correct :

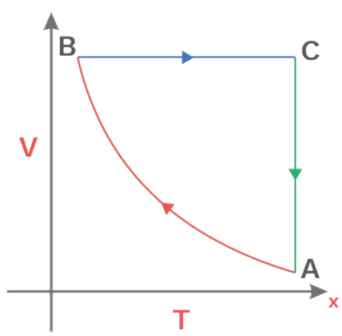
(1) $T_f > T_i$ (2) $T_f = T_i$ (3) $T_f < T_i$ (4) None

A.13 (3) $T_f < T_i$

Q.14 For a cyclic process P–T graph is given. Then which of the given V–T graph is correct ?



(1)



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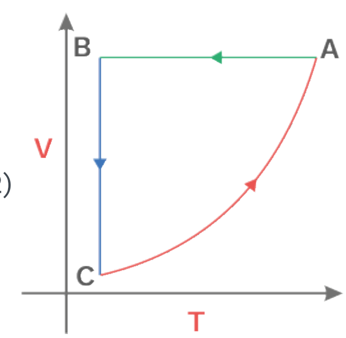

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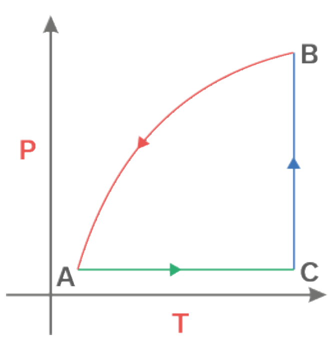

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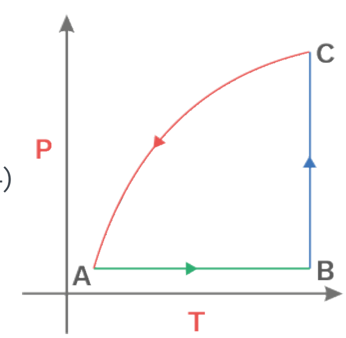


A.14 (4)

Q.15 16 gm O_2 is expanded reversibly at 300K temperature from 5 dm^3 to 25 dm^3 then find out ΔU, ΔH, W and q (in cal)

A.15 (i) $\Delta U = 0$

(ii) $\Delta H = 0$

(iii) $W = -\ 2.303\ nRT \log \frac{V_H}{V_L}$

$= -2.303 \times \frac{1}{2} \times 2 \times 300 \times 0.7$

$= -2.303 \times 210 = -483.63$ cal

(iv) $q = -\ (-483.63) = 483.63$ cal

enthalpy change.

Molar Heat capacity (C) & gm Specific Heat Capacity (c)

1. Molar Heat capacity (C)

(i) $C = \frac{q}{\Delta T}$ (for 1 mole)

(ii) Molar heat capacity at constant pressure (C_p)

$$C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T} \quad \text{(for 1 mole)}$$

$\Delta H = C_p\ \Delta T$ [for 1 mole]

For n mole [$\Delta H = nC_p\ \Delta T$]

$\Delta T = T_f - T_i$

Unit of $C_p = \frac{J}{K - mole}$ or $\frac{Cal}{K - mole}$

(iii) Molar heat capacity at constant volume (C_v)

$$C_v = \frac{q_v}{\Delta T} = \frac{\Delta U}{\Delta T} \quad \text{[for 1 mole]}$$

$q_v = \Delta U = C_v\ \Delta T$ [for 1 mole]

Then for n mol $\Delta E = nC_v\Delta T$

Definitions

Amount of heat required to raise the temperature of one mole substance by 1°C or 1K is known as molar heat capacity.

Rack your Brain

Why work done during the isothermal reversible process is greater than adiabatic process?

Unit of $C_v = \frac{J}{K - mole}$ or $\frac{cal}{K - mole}$

2. Gram specific Heat (c)

(i) Amount of heat require to raise the temperature of 1 gm substance by 1°C or 1K is known as gram specific heat

$C = \frac{q}{\Delta T}$ (for 1 gm)

(ii) gm specific heat at constant pressure (C_p)

$C_p = \frac{q_p}{\Delta T}$ (for 1 gm)

$C_p = \frac{\Delta H}{\Delta T}$ (for 1 gm)

For m gm $\Delta H = mC_p \Delta T$

Unit of $C_p = \frac{Joule}{K - gm}$ or $\frac{cal}{K - gm}$

3. gm specific heat at constant volume (C_v)

$C_V = \frac{q_v}{\Delta T}$ (for 1 gm)

$C_V = \frac{\Delta E}{\Delta T}$ (for 1 gm)

For m gm $\Delta U = mC_v \Delta T$

Unit of $C_v = \frac{joule}{K - gm}$ or $\frac{cal}{K - gm}$

4. Different Relations of C_p and C_v

(i) $C_p - C_v = R$ [Mayer's equation]

(ii) $\frac{C_p}{C_v} = \gamma$

Gases	C_p	C_v	$\gamma = \frac{C_p}{C_v}$

Rack your Brain

Why C_p always greater than C_v?

Definitions

1 calorie
Amount of heat require to raise the temperature by 1°C or 1K of 1 gm H_2O is known as one calorie.

1 . Monoatomic	$\frac{5}{2}R$	$\frac{3}{2}R$	$\frac{5}{3} = 1.66$
2. Diatomic	$\frac{7}{2}R$	$\frac{5}{2}R$	$\frac{7}{5} = 1.4$
3. Triatomic	4R	3R	$\frac{4}{3} = 1.33$

5. Relation between C_p and C_V for 1 mole substance & Temperature difference is of 1°C

$C_P - C_v = P\Delta V$

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

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

$nC_p\Delta T - nC_v\Delta T = P\Delta V$

$n\Delta T(C_p - C_v) = P\Delta V$

$1 \times 1 \times (C_p - C_v) = P\Delta V$

$(C_p - C_v) = P\Delta V$

6. Conditions for molar Heat capacity (C) :

$$C = \frac{q}{\Delta T} \text{ (for 1 mole)}$$

- Isothermal process
  $\Delta T = 0$, so $C = \infty$
- At equilibrium position means at constant pressure & temperature $\Delta T = 0$
  $C = \infty$

Concept Ladder

Dulong and Petit law. The product of specific heat and molar mass of any metallic element is equal to 6.4 cal/mole °C,
i.e., specific heat × Molar mass = 6.4
This law is applicable to solid elements only, exception belong Be, B, C and Si.

Q.16 For 2 mol of an ideal gas which relation is correct :

(1) $C_p - C_v = R$ (2) $C_p - C_v = 2R$

(3) $C_p - C_v = \frac{R}{2}$ (4) $C_p - 2C_v = R$

A.16 (1)

Q.17 At constant volume, to raise the temperature of 5 mole O_2 from 10 K to 20 K. How much heat is required while at constant pressure molar heat capacity is $7\frac{\text{cal}}{\text{K mol}}$

(1) 220 cal (2) 250 cal (3) 270 cal (4) 300 cal

A.17 (2)

$C_p = 7$, $n = 5$

$C_p - C_v = R$

$7 - C_v = 2$

$C_v = 5$

$\Delta U = nC_v\Delta T$

$\Delta U = 5 \times 5 \times (20-10)$

$= 250$ cal

Q.18 To raise the temperature of 1 mole gas from 400 K to 500 K, how much heat is require while $C_p = 3 + 1.2 \times 10^{-3}\,T$ cal/mol

(1) 450 cal (2) 354 cal (3) 545 cal (4) 625 cal

A.18 (2)

$$\Delta H = \int_{400}^{500} nC_p dT = \int_{400}^{500} 1 \times (3 + 1.2 \times 10^{-3}\,T)dT$$

$$= 3\int_{400}^{500} dT + 1.2 \times 10^{-3} \int_{400}^{500} TdT$$

$$= 3\left[T\right]_{400}^{500} + \frac{1.2 \times 10^{-3}}{2}\left[T^2\right]_{400}^{500}$$

$$= 3(100) + 6\times10^{-4}\left[(500)^2 - (400)^2\right]$$

$$= 300 + 6 \times 10^{-4} \times 90000$$

$$= 354 \text{ cal}$$

Q.19 To raise the temperature of 2 mol ideal gas from 100 K to 200 K at constant volume, how much heat is required while $C_v = 2.4 \times 10^{-3}$ T cal/mol

(1) 72 cal (2) 64 cal (3) 68 cal (4) 36 cal

A.19 (1)

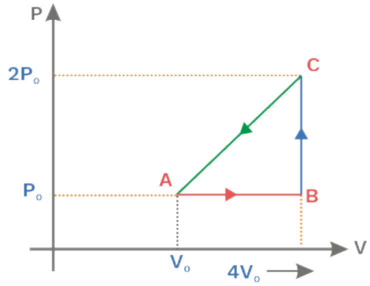
$$\Delta U = nC_v\Delta T = \int_{100}^{200} 2 \times 2.4 \times 10^{-3}\, TdT$$

$$= 2 \times 2.4\times10^{-3} \int_{100}^{200} TdT$$

$$= 4.8 \times 10^{-3} \left[\frac{T^2}{2}\right]_{100}^{200}$$

$$= 2.4 \times 10^{-3} [(200)^2 - (100)^2]$$
$$= 2.4 \times 10^{-3} [40000-10000]$$
$$= 2.4 \times 10^{-3} \times 30000$$
$$= 72 \text{ cal}$$

Q.20 1 mol of monoatomic gas shows the following changes. Find out the ΔU for C to A process



(1) 6 RT_0 (2) 9.5 RT_0 (3) 10.5 RT_0 (4) 11 RT_0

A.20 (3)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{P_0V_0}{T_0} = \frac{2P_0 4V_0}{T_2}$$

$$T_2 = 8T_0$$
$$\Delta U = nC_v\Delta T = 1 \times R\,[8T_0 - T_0] = \frac{21RT_0}{2} = 10.5\ RT_0$$

Q.21 To raise the temperature of 2 mol gas from 100 K to 200 K , how much heat is required while

$$C_P = 20\frac{J}{K\,mol}$$

(1) 3500 J (2) 3000 J (3) 4000 J (4) 4500 J

A.21 (3)

$$\begin{aligned}\Delta H &= nC_p\Delta T \\ &= 2 \times 20 \times 1000 \\ &= 4000\ J\end{aligned}$$

- For adiabatic process
  q = 0, so C = 0

Enthalpy (H)

- Mathematically it is heat contained in the system measured at constant pressure.
- The sum of internal energy and pressure volume (PV) energy is known as enthalpy

$$\boxed{H = U + PV}$$

- It is impossible to determine absolute value of enthalpy so we determine change in enthalpy (ΔH)

$$\boxed{\Delta H = H_{final} - H_{intial}}$$

- Enthalpy is an extensive property because E and V are extensive properties
- It is a state function because E,P and V are state function

$H = U + PV$

$$\boxed{\Delta H = \Delta U + \Delta(PV)} \quad ......i$$

(When P,V and T are variable)

At constant Pressure

$\Delta H = \Delta U + P.\Delta V)$ ii

At constant volume

$\Delta H = \Delta U + V.\Delta P)$ iii

For chemical reactions at constant temperature and pressure

Rack your Brain

C(diamond) $\longrightarrow$ ΔC (Graphite), ΔH = –ve. This shows that?

Concept Ladder

The standard enthalpy of formation of graphite is taken as zero but of diamond it is not zero but is equal to 1.816 kJ mol^{-1}.

$P.\Delta V = \Delta n_g RT$

So from equation (1)

$\boxed{\Delta H = \Delta U + \Delta n_g RT}$ iv

Where $\Delta H = q_p$ at constant P, $\Delta U = q_v$ at constant V

So equation (iv) can be also written as

$q_p = q_v + \Delta n_g RT$ v

Q.22 ΔU of combustion of methane is $-X$ kJ mol^{-1}. The value of ΔH is

(1) $= \Delta U$ (2) $> \Delta U$ (3) $< \Delta U$ (4) 0

A.22 The valanced chemical equation for the combustion reaction is

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$\Delta n_g = 1 - 3 = -2$$

$$\Delta H = \Delta U + \Delta n_g RT = \Delta U - 2RT$$

$\Delta H < \Delta U$ or (iii) is the correct answer

Q.23 Calculate the number of kJ of heat necessary to raise the temperature of 60g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J $mol^{-1}K^{-1}$.

A.23 No. of moles of Al (m) = (60g)/(27 g mol^{-1}) = 2.22 mol
Molar heat capacity (C) = 24 J $mol^{-1}K^{-1}$
Rise in temperature (ΔT) = 55 — 35 = 20°C = 20K
Heat evolved (q) = C × m × T = (24 J mol^{-1} K^{-1}) × (2.22 mol) × (20 K)
= 1065.6 J = 1.067 kJ

MEASUREMENT OF ΔU AND ΔH: CALORIMETRY

(a) ΔU Measurements

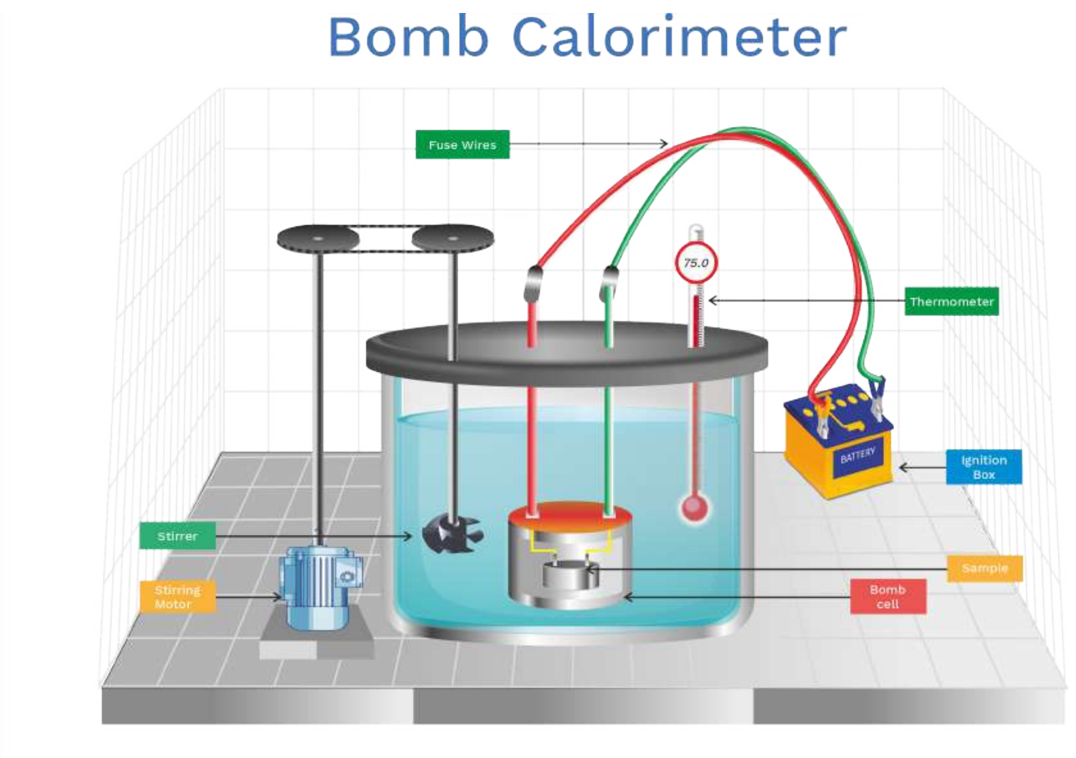
For chemical reactions, in a bomb calorimeter, heat absorbed at constant volume is measured. Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as ΔV = 0. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter.

Concept Ladder

Internal energy change (ΔU) per mole is caluclate by
$\Delta U = (C \times \Delta T \times M_W)/m$
C = Heat Capacity
ΔT = Rise in temperature
M.W. = Molecular weight of Substance
m = Amount of Substance taken

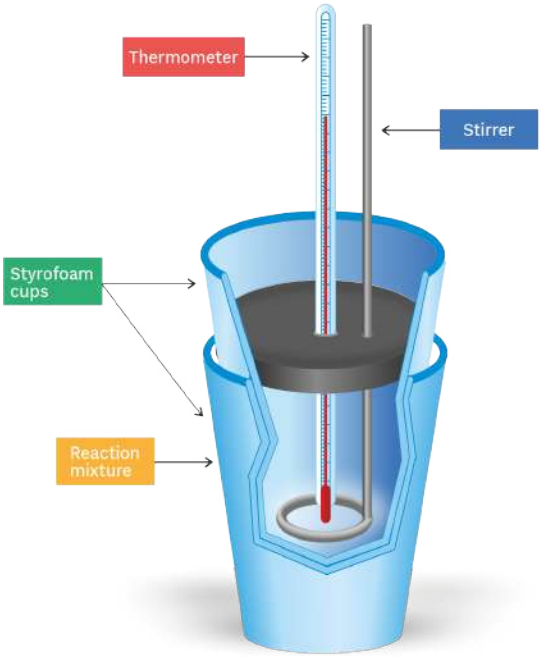
Concept Ladder

In a bomb calorimeter,
$\Delta V = 0$
Hence ΔH should be equal to ΔU. but this is not true. This is becasue the relation, $\Delta H = \Delta U + P\Delta V$ holds good only at constant pressure.
$\Delta H = \Delta U + P\Delta V + V\Delta P$
At constant pressure,
$\Delta P = 0$
At constant volume,
$\Delta V = 0$



(b) ΔH Measurements

Measurement for change in heat at constant pressure (generally under atmospheric pressure) can be done in a calorimeter. We know that $\Delta H = q_p$ (at constant p) and, therefore, heat evolved or absorbed, q_p (at constant P) is also known as the heat of reaction or enthalpy of reaction, $\Delta_r H$. Heat is evolved for an exothermic reaction, and system will lose heat to the surroundings. Therefore, q_p will has negative value and $\Delta_r H$ will also have negative value. Similarly heat is absorbed for an endothermic reaction, q_p is positive and $\Delta_r H$ will be positive.



Entropy (S)

1. Degree of randomness or disorderness is known as entropy
2. Entropy change for a system

$$(\Delta S)_{system} = \frac{q}{T}$$

3. $s < l < g$

$\xrightarrow[\text{Entropy}]{} \uparrow$

4. On increasing temperature, volume, mole or molecule, dissociation/decomposition/vapourisation/ fusion entropy increases.
5. On increasing pressure, crystallization/Bond formation/association entropy decreases
6. On mixing two solid or two liquid or two gases (non reacting) randomness increases
7. Mobility or Randomness

$$\propto \frac{1}{\text{molecular weight}}$$

8. If molecular weight of 2 species is same then more atomicity indicate more randomness
   e.g : $H_2 > N_2 > O_2$
   e.g : $C_2H_4 > N_2$
9. a. Unit of Entropy –

$$\frac{J}{K} \text{ or } \frac{cal}{K}$$

   b. Unit of molar Entropy-

$$\frac{J}{K - mole} \text{ or } \frac{cal}{K - mole}$$

10. a. Entropy is an extensive property
    b. Molar entropy is an intensive property
    c. It is a state function
11. At equilibrium position or a reversible process at constant P,T

$$\Delta S = \frac{\Delta H}{T}$$

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium $\Delta G = 0$, so $0 = \Delta H - T\Delta S$

$$\Delta H = T\Delta S$$

$$\frac{\Delta H}{T} = \Delta S$$

12. Total entropy change for the universe is always (+ve)

Rack your Brain

Solidification of liquid shows ________ in entropy?

Concept Ladder

Like U and H, S is also a state function.

Previous Year's Question

For the reaction $2Cl(g) \longrightarrow Cl_2(g)$
The correct option is

[NEET]

(1) $\Delta_rH > 0$ and $\Delta_rS > 0$
(2) $\Delta_rH > 0$ and $\Delta_rS < 0$
(3) $\Delta_rH < 0$ and $\Delta_rS > 0$
(4) $\Delta_rH < 0$ and $\Delta_rS < 0$

$\Delta S_{Total} > 0$ $(\Delta S)_{sys} + (\Delta S)_{surr} > 0$

13. At equilibrium position total entropy change is 0

$\Delta S_{Total} = 0$ $\left(\Delta S_{sys}\right) + \left(\Delta S_{surr}\right) = 0$

14. An ideal crystal has a perfect order of its constituent particles while a real crystal has less order because of some defects. Therefore a real crystal has more entropy than an ideal crystal.

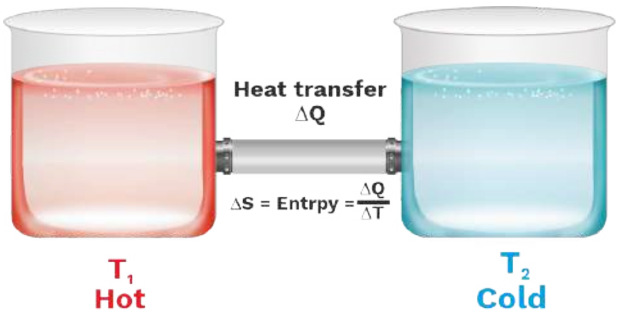
Rack your Brain

A real crystal has higher entropy than the ideal crystal?

Second law of Thermodynamics

1. Total entropy change is always positive for universe.
2. For a spontaneous or irreversible process total entropy change is always positive.

$\left(\Delta S_{system} + \Delta S_{surrounds} > 0\right)$



Q.24 Indicate the sign of Entropy change for following :

1. Fe (300K) $\rightarrow$ Fe (500 K)
2. $N_2 + 3H_2 \rightarrow 2NH_3$
3. Boiling an egg
4. Stretching a rubber
5. Rusting of Iron

A.24

1. Fe (300K) $\rightarrow$ Fe (500 K) $\longrightarrow$ Positive
2. $N_2 + 3H_2 \rightarrow 2NH_3 \longrightarrow$ Negative
3. Boiling an egg $\rightarrow$ Positive
   In the liquid of egg peptide bonding is present between protein molecule. It will dissociate when egg will boil so, randomness increases
4. Stretching a rubber $\rightarrow$ Negative
   On stretching a rubber its molecules indicate an orderly arrangement so randomness decreases
5. Rusting of Iron $\rightarrow$ Positive
   In iron, metallic bond is present between Fe atoms due to rusting there bonds dissociate so ΔS = Positive

Q.25 Latent heat of fusion of ice at 1 atm pressure & 0°C is 6016 J/mol then find out the entropy change:

(i) When solid convert into liq. (ii) Liq. Convert into solid

(1) (i) 22 $\frac{J}{mol.K}$ (ii)—22 $\frac{J}{mol.K}$

(2) (i)–22 $\frac{J}{mol.K}$ (ii)22 $\frac{J}{mol.K}$

(3) (i) & (ii) both are same

(4) (i)11 $\frac{J}{mol.K}$ (ii)—11 $\frac{J}{mol.K}$

A.25 (1)

For solid to liquid

$$\Delta S = \frac{\Delta H}{T} = \frac{6016}{273} = 22\frac{J}{mol.K}$$

For liquid to solid

$$\Delta S = -22 \frac{J}{mol.K}$$

Q.26 Cu block is at 130°C, amount of heat evolved by Cu block to surrounding is 340 J. Temperature of surrounding is 32°C. Then calculate

1. Entropy change for the reaction
2. Entropy change for the surrounding
3. Total entropy change

Assuming that temperature of system and surround remain same

A.26

1. $(\Delta S)_{Sys.} = \frac{q}{T} = \frac{-340}{403} = -0.85 J / cal$

2. $(\Delta S)_{Surr.} = \frac{q}{T} = \frac{340}{305} = 1.1 J / cal$

3. $(\Delta S)_{Total.} = 0.85 + 1.1$

$= 1.95$ J/cal

- **Entropy change for different Thermodynamic process :**
- Maximum process are carried out in open vessel where gas show expansion

  So FLOT

  $\Delta U = q - W$

$$\frac{q}{T} = \frac{\Delta U + W}{T}$$

$$dS = \frac{nC_v dT}{T} + \frac{PdV}{T}$$

$$dS = \frac{nC_v dT}{T} + \frac{nRdV}{T}$$

- Integrate both side from stage (1) $\rightarrow$ (2)

$$\int_1^2 dS = nC_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

- $\Delta S = nC_V \left[\ell nT\right]_{T_1}^{T_2} + nR\left[\ell nV\right]_{V_1}^{V_2}$
- $\Delta S = \left(nC_V \log_e \frac{T_2}{T_1} + nR \log_e \frac{V_2}{V_1}\right)$
- $\Delta S = \left(2.303\ nC_V \log \frac{T_2}{T_1} + 2.303\ nR \log \frac{V_2}{V_1}\right)$

Process	Constants	Value of entropy
Isothermal Process	$T_1 = T_2$	$\Delta S = 2.303\ nR\ \log \frac{V_2}{V_1}$
Isochoric Process	$V_1 = V_2$	$\Delta S = 2.303\ nC_V \log \frac{T_2}{T_1}$
Isobaric Process	$P_1 = P_2$	$\Delta S = 2.303\ nC_P \log \frac{T_2}{T_1}$
Adiabatic	q =0	$\Delta S = 0$

Previous Year's Question

In which case change in entropy is negative

[NEET]

(1) $2H(g) \longrightarrow H_2(g)$
(2) Evaporation of water
(3) Expansion of a gas at constant temperature
(4) Sublimation of solid to gas

Rack your Brain

Heat exchanged in a chemical reaction at constant temperature and pressure is called ?

Q.27 1 Mole of ideal gas expanded reversibly and isothermally from 1 lit to 10 lit. then find out the entropy change in cal/Kelvin.

(1) 2.303 (2) 6.604 (3) 7.606 (4) 4.606

A.27 $\Delta S = 2.303\ nR\log\frac{V_2}{V_1}$

$= 2.303 \times 1 \times 2 \times \log\frac{10}{1}$

$\Delta S = 4.606$ cal/K

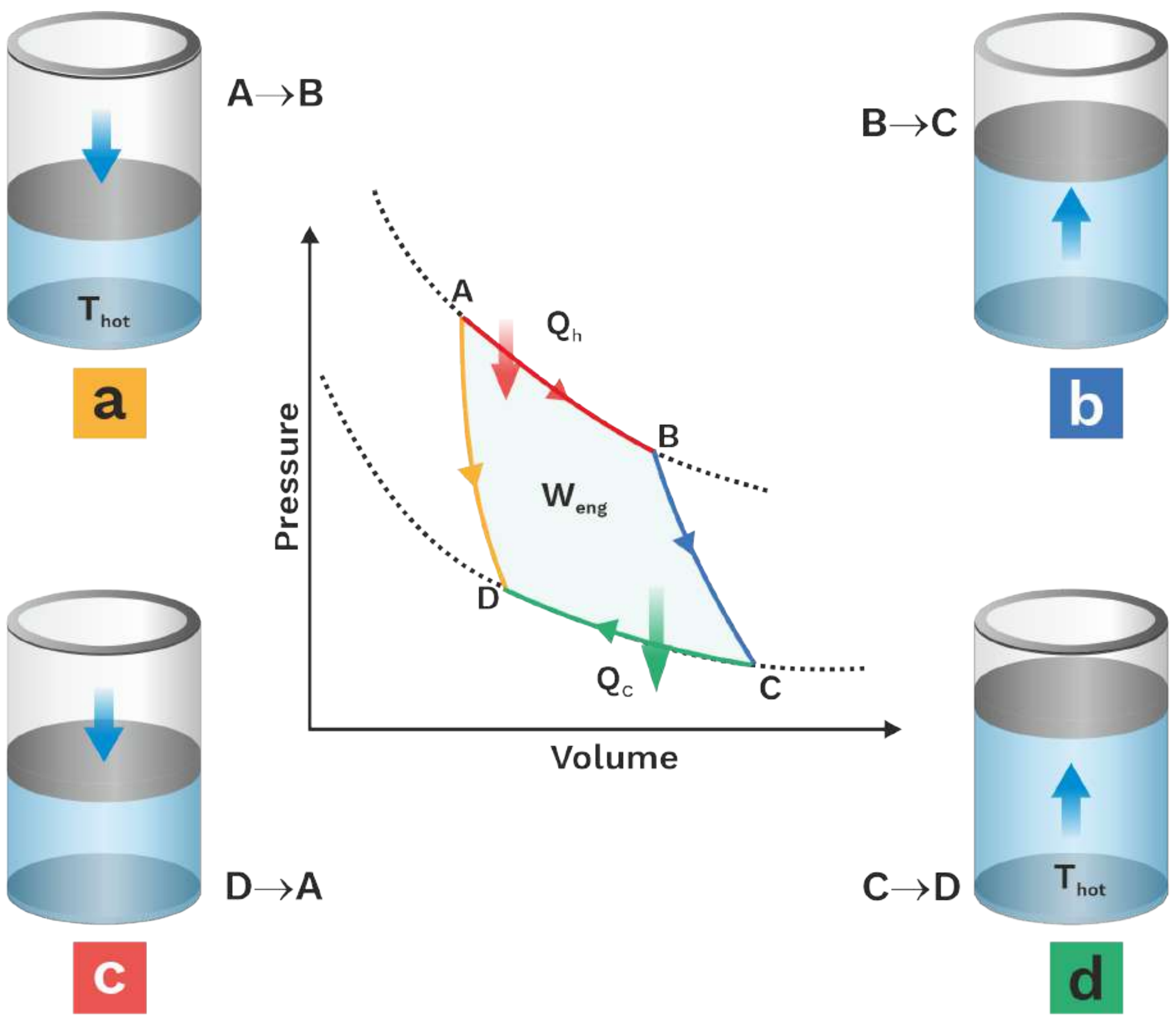
Carnot cycle

The Carnot cycle consists of the following 4 processes:

- This process has a reversible isothermal gas expansion. In it the ideal gas in the system absorbs q_{in} amount of heat from a heat source at a high temperature T_{high}, expands and does work on surroundings.
- This process has a reversible adiabatic gas expansion. In it the system is thermally insulated. The gas continuously expands and do work on surroundings, which causes the system to cool to a lower temperature, T_{low}.
- This process has a reversible isothermal gas compression. In it surroundings do work to the gas at T_{low}, and causes a loss of heat, q_{out}.
- This process has a reversible adiabatic gas compression. In it the system is thermally insulated. Surroundings continuously do work to the gas, which causes the temperature to rise back to T_{high}.

Concept Ladder

Carnot engine is used as standard performans of all the heat engines operating between two body of different temerpatures i.e., high temeprature body and law temperature body.



A→B isothermal expansion ← W-, Q+

B→C adiabatic expansion ← W-, ΔT-

D→A adiabatic compression ← W-, ΔT-

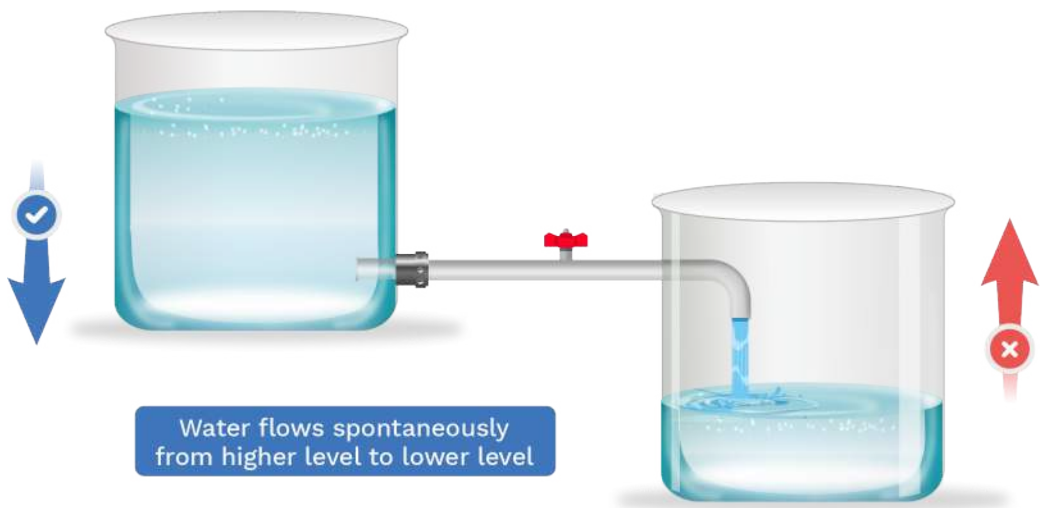
C→D isothermal compression ← W+, Q-

Process	W	q	ΔU	ΔH
1	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	$nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	0	0
2	$nC_v\left(T_{low}-T_{high}\right)$	0	$nC_v\left(T_{low}-T_{high}\right)$	$nC_p\left(T_{low}-T_{high}\right)$
3	$-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0
4	$nC_v\left(T_{high}-T_{low}\right)$	0	$nC_v\left(T_{high}-T_{low}\right)$	$nC_p\left(T_{high}-T_{low}\right)$
Full Cycle	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{high}\ln\left(\frac{V_2}{V_1}\right)+nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0

Spontaneous Process :

i. The process in which physical and chemical change occur due to its own means without any external help.

ii. Spontaneous process are irreversible.



1. Gibbs free energy (G)

(i) Energy obtained from a system which can be put into useful work mean

$\Delta G = (W)_{useful}$

According to FLOT

$\Delta U = q + W$

Here (W) includes 2 types of work

A. Thermodynamic work = $P\Delta V$

B. Useful work = Wuseful

Example of useful work :

- $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$
- $KClO_3(s) \rightarrow KCl(s) + \frac{3}{2}O_2(g)$
- $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

In above reactions 2 types of work are present

(A) Thermodynamic work due to expansion of gases

(B) Useful work to dissociate the compound

2. Galvanic cell reaction is spontaneous. So obtained free energy is converted into useful work

$\Delta G = W_{useful} = W_{elect} = -nFE°$

3. $C_{diamond} \rightarrow C_{graphite}$

$\Delta G = W_{usrful} = P\Delta V$

To convert one allotropic form to another free energy change is equal to useful work

Mathematically, free energy is the difference of enthalpy and the product of temperature and entropy.

$G = H - TS$

$G = (U + PV) - TS$

4. It is impossible to calculate the absolute value of free energy because it is not possible to calculate the absolute value of enthalpy or internal energy.

$\Delta G = \Delta U + \Delta(PV) - \Delta(TS)$

Previous Year's Question

For a sample of perfect gas when its pressure is changed isothermally from P_i to P_f the entropy change is given by

[NEET]

(1) $\Delta S = nR\ ln\left(\frac{P_f}{P_i}\right)$

(2) $\Delta S = nR\ ln\left(\frac{P_i}{P_f}\right)$

(3) $\Delta S = nRT\ ln\left(\frac{P_f}{P_i}\right)$

(4) $\Delta S = RT\ ln\left(\frac{P_i}{P_f}\right)$

At constant P,T

$\Delta G = (\Delta U + P\Delta V) - T\Delta S$

$\Delta G = \Delta H - T\Delta S$ for system

- In standard condition[P = 1 atm]

  [T = 25°C]

  $\Delta G° = \Delta H° - T\Delta S°$

- Free energy is an extensive property
- Free energy is a state function
- Free energy change for a reversible reaction

  $\Delta G = \Delta G_f^0 + 2.303\ RT \log Q$

ΔH	**ΔS**	**ΔG**	**Process**
Negative	Positive	Negative	Spontaneous
Positive	Negative	Positive	Non-spontaneous Spontaneous
Negative	Negative	High temp then ΔG = (+)	Non-spontaneous Spontaneous
Positive	Positive	Low temp then ΔG= (–)	Spontaneous Non-Spontaneous

- If temperature is more than the equilibrium temperature then it is known as high temperature and if temperature is less than equilibrium temperature then it's known as low temperature.

Q.28 At 1 atm pressure heat of vapourisation of H_2O is 44.3 KJ/mol and entropy change is 120 $\frac{J}{mol.K}$ then find out the equilibrium temperature.

(1) 396 K (2) 369 K (3) 693 K (4) 639 K

A.28 $\Delta G = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{44.3 \times 1000}{120} = 369\,K$$

Q.29 2 mole of ideal gas is expanded reversibly and isothermally from 1 lit to 10 lit at 127°C. Then find out the free energy change in cal

(1) −230.3 cal (2) −3386.5 cal

(3) −3366.8 cal (4) −3683.8 cal

A.29 $\Delta G = -T\Delta S$

because $\Delta H = 0$

$$\Delta G = -T\left(2.303\, nR \log \frac{V_2}{V_1}\right)$$

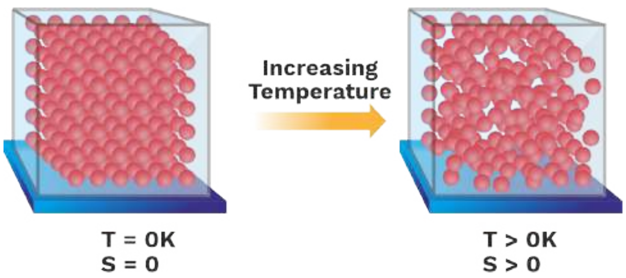
$$\Delta S = -2.303 \times 2 \times 2 \times 400 \log \frac{10}{1}$$

$$\Delta S = -2.303 \times 1600$$
$$= -3683.8 \text{ cal}$$

- **Coupled reaction**
  A reaction whose ΔG is positive is non spontaneous another reaction whose ΔG is negative is spontaneous when both reaction are coupled then non spontaneous reaction may become spontaneous.

Third law of Thermodynamics

- Entropy of pure crystalline substance is zero at absolute zero temperature.
- Information about the entropy is given by SLOT while it is calculated by TLOT.



Limitation

- Mixture of isotopes do not show zero entropy at absolute zero temperature.
- Glassy solid such as CO, CO_2, NO, N_2O, NO_2, H_2O etc doesn't show zero entropy at absolute zero temperature.

Rack your Brain

What is the condition for a process to be spontaneous according to second law of thermodynamics ?

Q30 Find the work done, when one mole of ideal gas in 10 litre container at 1 atm. is allowed to enter evacuated bulb of capacity 100 litre.

Sol. $W = -P\Delta V$

Sol. But since gas enters the vacuum bulb and pressure in vacuum is zero.

$W = 0$

Q31 If 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure than calculate the work done.

Sol. $W = -P\Delta V = -1 (5 - 1) = -4$ litre-atm.

Q32 A system expands from 5 L to 10 L against a constant external pressure of 2 atm. If it absorbs 800 J of energy in the process. Calculate the change in its internal energy.

Sol. $\Delta U = q + w$

$w = -P(V_2 - V_1) = -2 (10 - 5) = -10$ atm -L × 101.3 J = –1013 J U = 800 – 1013 J

$\Delta U = 800 - 1013 = -213$ J

Q33 $FeCO_3(s)$ decomposes at constant pressure as $FeO(s) + CO_2(g)$

$FeCO_3(s) \xrightarrow{\Delta} FeO(s) + CO_2(g)$

at 25°C, the heat absorbed during the reaction is 80 kJ.

Calculate ΔH & ΔU for the reaction

Sol. $FeCO_3(s) \longrightarrow FeO(s) + CO_2(g)$

$\Delta H = q_p = 80$ kJ

$\Delta H = \Delta U = \Delta n_g RT$

$\Rightarrow 80 \text{ kJ} = \dfrac{[1 \times 8.314 \times 298]}{1000} \text{kJ} \qquad \Rightarrow \Delta U = 77.522 \text{ kJ}$

Q34 Gases ΔG°_f (Cal/mole)

CO	−32.80
H_2O	−54.69
CO_2	−94.26
H_2	0

Estimate the standard free energy change in the chemical reaction.

$CO + H_2O \longrightarrow CO_2 + H_2$

Sol. Sol. Using the necessary data from the table.

CO	H_2O	CO_2	H_2	
ΔG°	−32.8	−54.69	−94.26	0 kcal

$\therefore$ ΔG° $-94.26 + 0 - (-32.8) - (-54.69) = -6.8$ kcal/mol

Q35 A liquid of volume of 100 L and at the external pressure of 10 atm−litre the liquid is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find, (i) work (ii) ΔU (iii) ΔH

Sol. Sol. Work done $= - 100 \times -1 = 100$ L. Atm

$\Delta q = 0$ $\Delta w = \Delta U$ $\Rightarrow 100 = \Delta U$ $\Rightarrow \Delta H = \Delta U + (P_1V_2 - P_1V_1)$

$= 100 + (100 \times 99 - 100 \times 10) = 100 + 100 \times 89 = 9000$ lit atm.

$\therefore$ 1 L. Atm = 101.3 Joule

Q36 For the combustion of 1 mole of liquid benzene at 25°C, the heat of reaction at constant pressure is given by ,

$$C_6H_6(\ell) + 7\frac{1}{2}O_2(g) \rightarrow 6\,CO_2(g) + 3H_2O(\ell);\quad \Delta H = -780980 \text{ cal.}$$

What would be the heat of reaction at constant volume ?

Sol. We have, $\Delta H = \Delta U + \Delta n_gRT$

Here, $\Delta n_g = 6 - 7.5 = -1.5.$

Thus, $\Delta U = \Delta H + \Delta n_gRT = -780980 - (-1.5.) \times 2 \times 298 = -780090$ calories.

Q37 At 25°C, a 0.01 mole sample of a gas is compressed in volume from 4.0 L to 1.0 L at constant temperature. What is work done for this process if the external pressure is 4.0 bar ?

Sol. 1.2×10^3 J

$W = -P_{ext}(V_2 - V_1) = -4(1 - 4)$ bar. L $= 1.2 \times 10^3$ J.

Q38 Calculate q, W, ΔU and ΔH when 100 gm of $CaCO_3$ is converted into its aragonite form given density of calcite = 2g/cc and density of aragonite = 2.5 g/cc.

Sol. $CaCO_3 \rightleftharpoons CaCO_3$

CalciteAragonite $\Delta H = 2$kJ/mole

Generally for solid $\longrightarrow$ Solid

solid $\longrightarrow$ Liquid

solid $\longrightarrow$ Liquid

Transitions W << q So, $\Delta U \simeq q = \Delta H$

While for gaseous conversion for example.

Solid $\longrightarrow$ Gas

Liquid $\longrightarrow$ Gas

$q = \Delta H \neq \Delta E$, as W will be significant.

Q39 A thermodynamic system goes from states (i) P_1, V to $2P_1$, V (ii) P, V_1 to P, $2V_1$. Then work done in the two cases is

(A) Zero, Zero

(B) Zero, $-PV_1$

(C) $-PV_1$, Zero

(D) $-PV_1$, $-P_1V_1$

Sol. case (i) V = 0, W = 0

case (ii) P = constant, $W = -P(2V_1 - V_1) = -PV_1$

Q40 Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in (a) an open beaker (b) a closed beaker at 300 K.

Sol. (a) From 1 mole of Zn, the no. of moles of H_2 gas evolved = 1

Hence volume of H_2 gas evolved = 22.4 litre (when P = 1 atm and T = 273 K)

$\therefore \quad W = -P\Delta V = -1 \times 22.4$ litre atm

$$= -22.4 \times \frac{8.314}{0.082} \text{ J} = -2271.14 \text{ J}$$

(b) For a closed system $P_{ext} = 0.$, therefore, W = 0.

Chapter Summary

1. Universe = System + Surrounding

2. Intensive property is defined as the value which is independent of the size (or mass) of the system.
   Extensive property is defined as the value which depends on the size (or mass) of the system.

Extensive properties	Intensive Properties
Volume	Molar volume
Number of Moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy Viscosity	
Enthalpy	Free energy per mole
Internal Energy (E & U)	Specific heat
Heat Capacity	Pressure, Temperature, Boiling point, freezing Point. Etc.

3. **State functions :**
   The thermodynamic quantities which depend only on the initial and final state of the system
   Ex Pressure, volume, temperature, Gibb's free energy, internal energy, entropy etc.

   Path function :
   The properties which depend on path.
   Heat, Work, Loss of energy due to friction etc.

4. Work is also a mode of transfer of energy between system and the surroundings. Work done on surroundings by the system is given by PΔV.

5. Internal energy (U) :
   The energy associated with the system at a particular conditions of temperature and pressure. Internal energy change (ΔU) : It is a measure of heat change occurring during the process at constant temperature and constant volume
   $q_v = \Delta G$

6. **Enthalpy (H) :**
It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content
(H=U+PV)
Enthalpy change (ΔH) :
$\Delta H = \Delta U + P\Delta V$
$\Delta H = \Delta U + \Delta n_g RT$
Where Δn_g = Gaseous moles of product – gaseous moles of reactants

7. Law of conservation of energy :
It states that the energy of the universe always remains constant during chemical and physical changes. Mathematically,
$\Delta U = q + w$
First law of thermodynamics
$\Delta U = q + w$
or $\Delta U = q - P\Delta V$

8. Work of expansion, $W = -P\Delta V$.
Work of expansion in vacuum
$P_{ext} = 0, w = 0$

9. $\Delta S = \frac{q_{rev}}{T}$

10. Gibb's Energy :
Gibb's energy is the energy in a system that can be converted into useful work
$\Delta G = -w_{useful}$
$\Delta G = \Delta H - T\Delta S$
For a spontaneous process $\Delta G < 0$
For a non spontaneous process $\Delta G > 0$
For process at equilibrium $\Delta G = 0$