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FOUNDATIONS

NEET

PHYSICS NOTES

Thermodynamics

THERMODYNAMICS

Thermodynamics is used in broader sense involving all kinds of energy changes accompanying the physics (or) chemical transformations.

The objectives:

(i) To predict the feasibility of given transformation.

(ii) To derive the various energy changes taking place during a given change and interrelate them.

(iii) To derive the various laws. Eg: Law of mass action, phase rule … etc. thermodynamically.

(iv) To present the experimental data in systematic order.

(v) To derive, at what condition, the equilibrium is attained during a change.

The limitations:

(i) The law of thermodynamics apply only to matter in bulk and not to individual atoms (or) molecules.

(ii) It suggest for the feasibility of reaction but fails to suggest rate of reaction.

(iii) It fails to explain about the systems away from equilibrium.

Terminology of Thermodynamics:

1. Universe: In thermodynamics universe consists of a system and it’s surroundings.

2. System: A specified part of the universe with real (or) imaginary boundaries, on which studies of P, T, … etc. are to be made.

3. Surroundings: The rest part of universe, adjacent to real (or) imaginary boundaries of system.

4. Boundary: Anything which separate system and surroundings is called boundary.

A boundary may be real (or) imaginary, rigid (or) non-rigid, conductor of heat (Diathermic) (or) non-conductor of heat (Adiabatic).

Types of system:

(i) Homogenous system: A system having uniform nature, throughout made up of one phase only. (i.e. $p = 1$)

(ii) Heterogenous system: A system not uniform throughout, consists of more than one phase. (i.e. $p > 1$)

Systems may also be classified as

a) Open system: Those in which exchange of mass and energy is possible with surroundings.

Eg: Boiling of water in beaker

All living organism (Eg. Human body, earth, glass of water)

b) Closed system: Those in which only exchange of energy (and not of mass) takes place with surroundings.

Eg: Heating of liquid in a sealed tube

Balloon filled with gas

c) Isolated system: Those in which neither exchange of mass nor exchange of energy takes place with surroundings.

Eg: Liquid in a sealed thermos flask.

Note:

1. None of the system is perfectly isolated, these are nearly isolated.
2. An isolated system has no contact with it's surroundings.
3. An isolated system is sealed, inside rigid with thermally insulated walls.
4. The internal energy of an isolated system is constant.

Properties of a system:

Thermodynamic properties of a system are classified as

Intensive properties: The properties of a system which are independent of quantity of matter present in the system. i.e. mass independent.

Eg: Temperature, pressure, density, viscosity, concentration, surface tension, boiling point, melting point, refractive index, molar volume, gas constant, vapour pressure, specific heat, dielectric constant, molar heat capacity, molar conductance and $E°$ of cell.

Extensive properties: The properties of system, which depend on the quantity of matter present in the system, i.e. mass, length, volume, energy, enthalpy, entropy, free energy & heat capacity.

These properties are additive in nature.

Note:

An extensive property becomes intensive by specifying it in unit amount of matter.

Eg: Mass and volume are extensive but density $= \frac{m}{v}$ is intensive property.

State functions:

The fundamental properties – pressure, volume, temperature, energy (*v*), enthalpy (*H*), entropy (*S*), Gibb's energy (*G*) which define the state of system are known as State variables (or) State functions.

The state functions depend only on the state of system and are independent of path.

Thus work and heat are not a state function, however q-w is state function.

Thermodynamic equilibrium:

A system in which the macroscopic properties do not undergo any change with time is said to be in thermodynamic equilibrium.

Thermodynamic state of system:

A system is said to be in given state when it's state functions P, V & T which completely define the system are known.

A system in which variables attain constant values and do not change with time is said to be in thermodynamic equilibrium.

Change in state:

Let the system be present in state '*A*' following some operations it occupies state '*B*'. All the measurable properties such as change in volume, change in pressure, change in internal energy, change in internal energy, change in heat enthalpy, change in temperature, change in entropy etc. are given as change in measurable property $(P) = P_B - P_A$

Let, volume as property then $\Delta v = v_B - v_A$

$$\Delta v = v_{\text{final}} - v_{\text{initial}}$$

Thermodynamic process:

A series of operations made on thermodynamic system, in order to change it from one state to other is known as Thermodynamic process.

The various types of thermodynamic process are

1. Isothermal process:

(i) A process in which temperature of system does not change throughout the studies.

(ii) For an isothermal process, $\Delta T = 0$ & thus $\Delta U = 0$

(iii) An isothermal process is achieved by using thermostatic control.

2. Adiabatic process:

(i) A process in which exchange of heat between system & surroundings does not take place.

(ii) For an adiabatic process, $q = 0$

(iii) It can be achieved by insulating the system boundaries.

3. Cyclic process:

(i) A process in which initial state of system regained after a series of operation.

(ii) For a cyclic process, $\Delta U = 0$ & $\Delta H = 0$

4. Isochoric process:

(i) A process in which volume of system remains constant throughout the studies made in.

(ii) For an isochoric process, $\Delta v = 0$

(iii) Absorption of heat shows an increase in internal energy.

5. Isobaric process:

(i) A process in which pressure of system remain constant throughout the studies made in.

(ii) For an isobaric process, $\Delta p = 0$

(iii) Absorption of heat shows an increase in it's heat enthalpy.

6. Reversible process:

A reversible process (or) quasistatic process is one in which all changes occurring at any part of the process in the system and boundaries are exactly reversed when change is carried out in opposite direction.

A reversible process has following characteristics

(i) It involves a slow change during operations and surroundings are always in equilibrium with system.

(ii) The process may take place in either direction.

(iii) Driving force and the opposing forces differ with each other by an infinitesimal value.

(iv) It gives to maximum work during studies.

(v) The net work involved in two process (if cyclic) = 0.

Note:

(i) A reversible process is a process that can be reversed by an infinitesimal change in a variable.

(ii) Reversible process are quasistatic.

(iii) Reversible process proceeds infinitely slowly.

7. Irreversible process:

An irreversible process in one in which direction of the change cannot be reversed by small change in variables.

An irreversible process is a real one and all processes which naturally occur are irreversible.

An irreversible process has the following characteristics.

(i) It involves fast changes during operations and equilibrium exists at the initial & final stages only.

(ii) These are unidirectional process and can be reversed if energy is provided by any other irreversible process to this.

(iii) Driving force and the opposing force differ by a large amount.

(iv) It give rise to network i.e. somewhat less work than the reversible work (or) $w_{\text{rev}} > w_{\text{irr}}$

(v) The network involved in two (cyclic) process $\neq 0$.

(vi) All natural (or) spontaneous process are irreversible.

Eg: Evaporation of water at room temperature.

Thermodynamic cycle:

It involves a process in which initial state is regained.

Thermodynamic equilibrium:

The essential criteria of a state function are given below.

(a) The change in the value of a state function depends only on the initial and final state and not on the path by which initial & final state.

(b) The state functions are exact differential and cyclic rule to be obeyed.

(c) All thermodynamic properties satisfy requirements of state function.

Change in thermodynamic energy: $\Delta U = q + w$

Change in thermodynamic enthalpy: $H = U + PV$

Change in thermodynamic entropy: $S = \dfrac{q_{\text{rev}}}{T}$

The thermodynamic equilibrium involves these equilibria in one i.e.

1. Mechanical equilibrium: i.e. position (or) velocity of system does not change with time (or) when no work is done on the system (or) done by the system.

2. Thermal equilibrium: i.e. temperature remain constant throughout the system including the surroundings (or) temperature of system does not change with time.

3. Chemical equilibrium: i.e. Composition of system remain constant and definite and does not change with time.

A system is said to be in thermodynamic equilibrium, if it satisfies all the above three equilibria.

Work:

Work is expressed as the product of two factors i.e. $w = \text{intensity factor} \times \text{capacity factor}$

Where, Intensity factor is a measure of force responsible for work.

Capacity factor is a measure of extent for which work is done.

i.e. Mechanical work = Force × Displacement $= F \times d$

Electrical work = Potential difference × Change in charge $= v \times \Delta Q = E \cdot nF$

Expansion work = Pressure × Change in volume $= -P \times \Delta v$

Gravitational work = Gravitational force × Change in height $= mg \times \Delta h$

Extension work = Tension × Change in length $= T \times \Delta l$

Surface expansion work = Surface tension × Change in area $= \gamma \times \Delta A$

Units of work:

In C.G.S = Dyne-cm (or) erg.

In M.K.S = Newton-m (or) Joule.

Work is also expressed in calorie.

Note:

1. A system can do two kinds of work. The first type is expansion work, the work of expansion or compression against an external force showing change in volume.
2. The second type of work is non-expansion work, work that does not involve a change in volume.

Eg: A chemical reaction causing an electrical current to flow in.

According to IUPAC convention

(a) Work done by the system (expansion) is -ve.

(b) Work done on the system (compression) is +ve.

Note:

Work involved in a change $= w$

Work done by the system $= -w$

Work done on the system $= +w$

→ The positive value of "w" signify that the work has been done on the system by the surroundings and it was contributed to an increase in internal energy of the system.

Expression for all types of "P-V" work (or) "PV-work":

Expansion work can be written as $w = -P \cdot \Delta v$

For expansion $\Delta v = V_f - V_i = +\text{ve} \ \left(\because V_f > V_0\right)$

$w = -P_{\text{ext}} \cdot \Delta v = -\text{ve}$

For compression $\Delta v = V_f - V_i = -\text{ve} \ \left(\because V_f < V_i\right)$

$w = -P_{\text{ext}} \cdot \Delta v = -(-) = +\text{ve}$

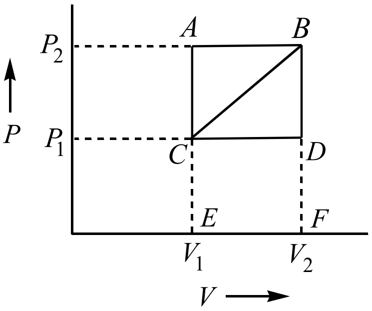
→ Work is not a state function because amount of work performed depends on the path followed. However, when work is done adiabatically at constant pressure it become state function.

$$q_P = \Delta U + (-P\Delta v) = \Delta U + (-w)$$

if, $q_P = 0 \Rightarrow \Delta U = w$

→ In P-V diagram (called indicator diagram, the area under P-V curve represents work done if expansion $w = -\text{ve}$ & if compression $w = +\text{ve}$).

P-V diagram:



w_{AC} = No area covered by straight line $AC(\text{if } \Delta v = 0) = 0$

w_{BA} = Area covered by square $ABFE = P_2 \times (V_2 - V_1)$

w_{CB} = Area covered by $BCEF$

= Area of square $CDEF$ + Area of triangle BCD

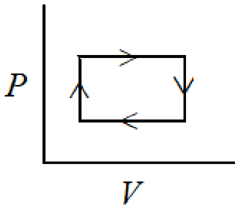
= Area of $CDEF$ + $\frac{1}{2}\times$ Area of square $ABDC$

$$= P_1(V_2 - V_1) + \frac{1}{2}(P_2 - P_1) \times (V_2 - V_1)$$

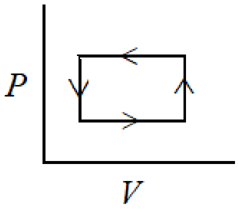
$$= \frac{1}{2}(P_2 + P_1) \times (V_2 - V_1)$$

→ In a cyclic process work done is equal to the area under the cycle is negative work done if the cycle is clockwise and positive if the cycle is anti-clockwise.

→ Work of complete cycle is equal to area occupied by cycle in P-V diagram.



$\boxed{w = -\text{ve}}$



$\boxed{w = +\text{ve}}$

Energy:

Energy is the capacity of ding work. There are many kinds (or) forms of energy such as kinetic energy, potential energy, electrical energy….

Unit: Joule (in SI units)

Heat:

The transfer of energy from a hot body to a cold body is a non-mechanical process. The energy that is transferred from one body to the other, without any mechanical work involved, is called heat.

Heat is a measure of quantity of energy transferred from one body to other as a result of temperature difference between them.

Temperature:

It is a measure of intensity of heat energy i.e. how much energetic each individual particle is?

Note:

1. Both work and heat appear only at the boundary of system.
2. Both work and heat appear only during a change in state.
3. Both work and heat are manifested by an effect in the surroundings.
4. According to IUPAC convention

    Heat absorbed by the system is positive

    Heat given out by the system is negative

To be more clear

Heat involved in a change $=q$

Heat absorbed in that change $=+q$

Heat involved in that change $=-q$

Units: Calorie, Joule, erg.

$10^7\ \text{erg} = 1\ \text{Joule} = 1\ \text{N}-\text{m}$

1 J = 0.2390 calorie

1 calorie = 4.184 J

1 litre-atm = 101.3 J = 24.206 cal.

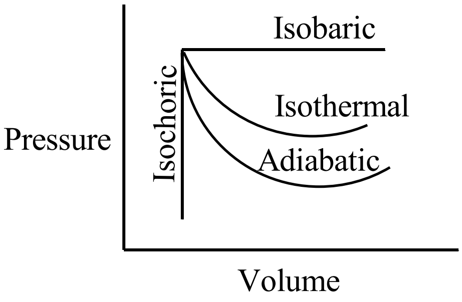
For solids & liquids $q = m \times L\ \ (L = \text{latent heat})$

$q = m \times s \times \Delta T\ \ (\Delta T = \text{change in temperature})$

$q = m \times C_V \times \Delta T\ \ (\text{for gases at constant volume})$

$q = m \times C_p \times \Delta T\ \ (\text{for gases at constant pressure})$

Graphical Representation of various thermodynamic process:



Internal Energy:

1. The energy of a thermodynamic system is generally expressed as internal energy.
2. Internal energy is the energy stored in a system, and if needed a part of this energy may be used to carryout equivalent amount of work (or) to convert equivalent amount of heat.
3. It is comprised of many energy terms such as translational, vibrational, rotational, potential, coulombic, interaction energy.
4. It is represented as "U", the change in internal energy is ΔU, the value which can be derived only by 1st law of thermodynamics.

Note:

1. Internal energy of a system is an extensive-property and depends upon amount & physical state of substance.
2. Change in internal energy $\Delta U \left(U_{\text{Final}} - U_{\text{Initial}}\right)$ during a cyclic process is zero.
3. Internal energy is a state function i.e. path-independent.
4. The change in internal energy does not depend upon the path by which changes are brought in.
5. Like internal energy 'U' some other state functions are also used in thermodynamics. These are Enthalpy (*H*), Entropy (*S*) & Gibb's energy (*G*).

Internal energy change (ΔU) per mole is calculated by using the formula (from Bomb calorimeter)

$$\boxed{\Delta U = \frac{C \times \Delta T \times \text{M.W}}{m}}$$

Where $C =$ Heat capacity of the calorimeter system (including water)

$\Delta T =$ Rise in temperature

M. W = Molecular weight of substance

$m =$ Amount of substance taken

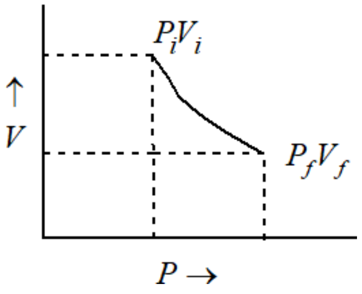
Work done in Irreversible Process:

1. If the volume of system changes by a finite quantity from volume V_i to V_f, then total work done "w" can be obtained by integrating $-P \cdot dv$ (when 'P' is constant) over the volume change from "V_i to V_f."

Thus, $w = -\int_{V_i}^{V_f} P_{ext} \cdot dv$

$= -P_{ext}\left(V_f - V_i\right)$

$= -P_{ext} \cdot \Delta v \quad \left(\because \ \Delta v = V_f - V_i\right)$



2. If the external measure (P_{ext}) is slightly more than the pressure of gas, the gas will contract i.e. the work will be done by the surroundings on system. In that case, V_f will be less than V_i & Δv is negative.

$\therefore \ w = P \cdot \Delta v$

Thus,

a. If the gas expands, $V_f > V_i$ and work done by the system and 'w' is negative.

b. If the gas contracts, $V_f < V_i$ and work done on the system and 'w' is positive.

→ **Work done in Isothermal Reversible Expansion (or) Compression of an ideal gas:**

The expression for the work involved in a reversible-isothermal expansion (or) compression of an ideal gas from volume V_1 to V_2 can be derived as $dq = dU - dW$ at constant temperature.

$$dU = 0$$

$$dW = -P_{ext} \cdot dv \quad (\because dq = -dW)$$

$$P_{ext} = P_{\text{int}} \pm dP$$

i.e. opposing pressure differs from the pressure of gas by an infinitesimal amount; the +ve and –ve sign indicate for compression & expansion respectively.

$$w = -\int_{V_1}^{V_2} P_{ext} \cdot dv = -\int_{V_1}^{V_2} \left(P_{\text{int}} \pm dP\right) \cdot dv$$

$$= -\int_{V_1}^{V_2} P_{\text{int}} \cdot dv \pm -\int_{V_1}^{V_2} dP \cdot dv$$

$$w = -\int_{V_1}^{V_2} P_{\text{int}} \cdot dv$$

(Neglecting $\int_{V_1}^{V_2} dP \cdot dv$ as it is product of two infinitesimal small differentials)

$$w = -\int_{V_1}^{V_2} \frac{nRT}{v} \cdot dv \quad \left(\because P = \frac{nRT}{v}\right)$$

$$w = -nRT \int_{V_1}^{V_2} \frac{dv}{v}$$

(or) $w_{rev} = -nRT \log_e\left(\frac{V_2}{V_1}\right) = -2.303\ nRT \log_{10}\left(\frac{V_2}{V_1}\right) \rightarrow (1)$

Also, $w_{rev} = -2.303\ nRT \log_{10}\left(\frac{P_1}{P_2}\right) \rightarrow (2) \left(\because v \propto \frac{1}{P}\right)$

The work done by the system represented by eqn. (1) & (2) is said to be maximum work (or) work done under reversible isothermal conditions.

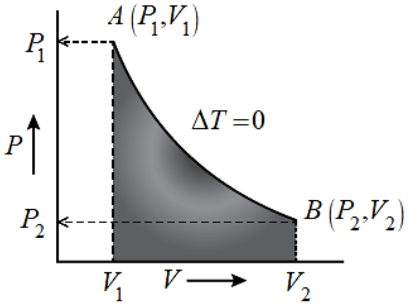
If $V_2 > V_1$ then from eqn. (1)

$w_{rev} = -\text{ve}$ (or) work is done by the system i.e. expansion work.

If $V_2 < V_1$ from eqn. (1)

$w_{rev} = +\text{ve}$ (or) work is done on the system i.e. compression work.

Isothermal reversible expansion work graph:



Shaded area represents work done by the system in isothermal reversible process.

Force expansion:

Expansion of a gas in vacuum $\left(P_{ext}=0\right)$ is called free expansion. No work is done during free expansion, whether the process is reversible (or) irreversible.

Work done in Reversible Adiabatic Process:

During adiabatic expansion (or) compression, heat is neither absorbed nor evolved by the system i.e. $q=0$

Thus, from first law of thermodynamics

$q=\Delta U+(-w)$ (or) $\Delta U=+w$

(Or) Work is done by the system under adiabatic process on the cost of it's internal energy.

Case-I:

If final temperature is known

$U=f(V,T)$

The differential of U is

$$dU=\left(\frac{\partial U}{\partial T}\right)V\cdot dT+\left(\frac{\partial U}{\partial V}\right)T\cdot dV$$

For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)T=0$

Therefore, $dU=\left(\frac{\partial U}{\partial T}\right)V\cdot dT$ (or) $dU=nC_V\cdot dT$

For a finite change, $\Delta U=U_2-U_1=nC_V\left(T_2-T_1\right)$

Thus, $w_{rev}=\Delta U=nC_V\left(T_2-T_1\right)\rightarrow(3)$

$C_P-C_V=R$

$$\frac{C_P}{C_V}-\frac{C_V}{C_V}=\frac{R}{C_V} \text{ (or) } C_V=\frac{R}{\gamma-1}$$

From eqn. (3)

$$w_{rev}=\frac{nR}{\gamma-1}\left(T_2-T_1\right)\rightarrow(4)$$

Where γ is Poisson's ratio, numerically equal to $\frac{C_P}{C_V}$ and greater than unity.

Farther more, if $T_2 > T_1$ then $w_{rev} = +\text{ve}$ i.e. work done on the system.

If $T_2 < T_1$ and then $w_{rev} = -\text{ve}$ i.e. work done by the system.

Also, the change in enthalpy

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + nR\Delta T$$

$$\Delta H = nC_V \times \Delta T + nR\Delta T$$

$$= n(C_V + R) \times \Delta T$$

$$= nC_P \cdot \Delta T = nC_P (T_2 - T_1) \rightarrow (5)$$

Note:

1. The equations (3) & (4) are applicable to any type of adiabatic process (reversible, irreversible or free). However, final temperature will be different in each case and therefore w, ΔU & ΔH will be different.

2. If final temperature is known, the value of q, w, ΔU and ΔH for any type of adiabatic process can be calculated by eqns. (3) or (4).

Case-II:

If final temperature is known, we have

$$w = \int dw = -\int P_{ext} \cdot dV = -\int P_{\text{int}} \cdot dV$$

$\because P_{\text{int}}$ is a function of both V & T and both variable change during adiabatic expansion (or) compression process.

If final temperature is not known then for adiabatic process we have

$$dU = dW \text{ (or) } nC_V \cdot dT = -P_{ext} \cdot dV = -P_{\text{int}} \cdot dV$$

For an ideal gas, $PV = nRT$ then

$$\int nC_V \cdot dT = -\int \frac{nRT}{v} \cdot dV$$

$$\text{(or) } C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

(Assuming C_V independent of temperature) (or)

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\text{(or) } \left[\frac{T_2}{T_1}\right]^{C_V} = \left[\frac{V_2}{V_1}\right]^{-R}$$

$$\text{(or) } C_V \ln \frac{T_2}{T_1} = -\left[C_P - C_V\right] \ln \frac{V_2}{V_1} \quad (R = C_P - C_V)$$

$$\text{(or) } \ln \frac{T_2}{T_1} = -\left[\frac{C_P}{C_V} - 1\right] \ln \frac{V_2}{V_1}$$

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

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

$(\text{or})\ T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1} = \text{constant}$

$TV^{\gamma-1} = \text{constant} \rightarrow (6)$

Using $PV \propto T$ & eqn. (6) we can have

$\boxed{PV^{\gamma} = \text{constant}} \rightarrow (7)$

$T^{\gamma}P^{1-\gamma} = \text{constant} \rightarrow (8)$

We have from eqn. (3)

$$w_{rev} = \frac{nR}{\gamma-1}[T_2 - T_1]$$

$$= \frac{nR}{\gamma-1}\left[\frac{P_2V_2}{nR} - \frac{P_1V_1}{nR}\right]$$

$$w_{rev} = \frac{P_2V_2 - P_1V_1}{\gamma-1} \rightarrow (9)$$

Also, $w_{rev} = \frac{nR}{\gamma-1}[T_2 - T_1] \rightarrow (10)$

$$w_{rev} = \frac{nR}{\gamma-1}[T_1 - T_2] \rightarrow (11)$$

$\because T_1^{\gamma} \cdot P_1^{1-\gamma} = T_2^{\gamma}P_2^{1-\gamma}$

$$T_2^{\gamma} = \frac{T_1^{\gamma} \cdot P_1^{1-\gamma}}{P_2^{1-\gamma}}$$

$$T_2^{\gamma} = T_1^{\gamma} \cdot \left[\frac{P_1}{P_2}\right]^{1-\gamma}$$

$$T_2 = T_1 \cdot \left[\frac{P_1}{P_2}\right]^{\frac{1-\gamma}{\gamma}} = T_1\left[\frac{P_1}{P_2}\right]^{\frac{1-C_P/C_V}{C_P/C_V}}$$

$T_2 = T_1\left[\frac{P_1}{P_2}\right]^{\frac{R}{C_P}}$ from eqn. (8) & (11)

$$w_{rev} = \frac{nR}{1-\gamma}\left[T_1 - T_1\left[\frac{P_1}{P_2}\right]^{-R/C_P}\right]$$

$$= \frac{nRT_1}{1-\gamma}\left[1 - \left[\frac{P_2}{P_1}\right]^{R/C_P}\right] \rightarrow (12)$$

$$w = -nC_V \cdot T_1 \left[1 - \left[\frac{P_2}{P_1} \right]^{R/C_P} \right] \rightarrow (13)$$

Similarly as relation T_1, V_1 & V_2 can be derived.

Work done in Adiabatic Irreversible Expansion (or) Compression:

This type also includes two types of work done.

a. Expansion against a zero pressure (or) Free expansion

On expansion of an ideal gas in vacuum i.e.

$$P_{ext} = 0$$

$$dW = -P_{ext} \cdot dV = 0 \rightarrow (14)$$

Also, $dU = 0$ & $dH = 0$

$\therefore$ For a finite change, we have

$$W = 0,\ \Delta U = 0,\ \Delta T = 0\ \&\ \Delta H = 0$$

Thus, it may be concluded that free expansion of ideal gas under reversible isothermal and adiabatic conditions are identical and equal to zero.

b. Expansion (or) Compression against a constant pressure

On expansion (or) compression of ideal gas against a constant external pressure say P_{ext}

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

$$(\text{or})\ w = \Delta V = -P_{ext}(V_2 - V_1) \quad [\because q = 0] \rightarrow (14)$$

For ideal gas $\Delta U = nC_V \times \Delta T = nC_V(T_2 - T_1) \rightarrow (15)$

Also, $\Delta H = nC_P \times \Delta T = nC_P(T_2 - T_1) \rightarrow (16)$

From eqns. (15) & (16), eliminating ΔT

$$\frac{\Delta H}{\Delta U} = \frac{C_P}{C_V} = \gamma$$

$$\boxed{\Delta H = \gamma \cdot \Delta U} \rightarrow (17)$$

Eqn. (14) can be used to calculate w, if V_1, V_2 and P_{ext} are known. Using this value of $w\ (\text{or})\ \Delta U$, ΔH can be calculated by eqn. (17).

Also, by eqns. (14) & (15)

$$n \times C_V \times \Delta T = -P_{ext}(V_2 - V_1)$$

$$n \times C_V \times \Delta T = P_{ext}(V_1 - V_2)$$

If $P_{ext} = P_2$ i.e. the pressure of the gas after expansion

$$n \times C_V \times (T_2 - T_1) = P_2 \left[\frac{nRT_1}{P_1} - \frac{nRT_2}{P_2} \right]$$

$$(\text{or})\ C_V\times(T_2-T_1)=P_2\left[\frac{RT_1}{P_1}-\frac{RT_2}{P_2}\right]\rightarrow(18)$$

$$C_V\times(T_2-T_1)=P_1\left[\frac{RT_1}{P_1}-\frac{RT_2}{P_2}\right]\rightarrow(19)$$

$$T_2=T_1\left[\frac{C_V+R\,P_2/P_1}{C_P}\right]\rightarrow(20)$$

$$\because\ dU=n\times C_V\times dT\quad\text{and}\quad dw=dU$$

$$\therefore\ w=n\times C_V\times\Delta T=n\times P_{ext}\left[\frac{RT_1}{P_1}-\frac{RT_2}{P_2}\right]\rightarrow(21)$$

$$(\text{or})\ \ w=-n\times P_{ext}\left[\frac{RT_2}{P_2}-\frac{RT_1}{P_1}\right]\rightarrow(22)$$

$$w=-n\times P_{ext}\times R\left[\frac{P_1T_2-P_2T_1}{P_1\cdot P_2}\right]\rightarrow(23)$$

This is known as Pressure-Volume work (or) Expansion work.

Heat capacity of system:

(i) Heat capacity (c) of a system is defined as the amount of heat required to raise the temperature of system by 1°C.

(ii) If the system consists of a single substance (or) a solution and mass 'm' gm (or) 1 mol, the heat capacity of a system is referred as molar heat capacity of system.

(iii) If the system consists of a single substance (or) a solution mass 1 gm the heat capacity of system is referred as specific heat of system.

(iv) Let, a small quantity of heat 'q' be given to system to increase it's temperature by dT, then heat capacity, $c=\frac{q}{dT}$

(v) In case of gases, heat given to system depends upon the condition of constant pressure (P) or constant volume (V). The heat capacity values are given as

Molar heat capacity, at constant volume (C_V)

$$C_V=\frac{q_V}{dT}=\frac{dU}{dT}=\left(\frac{\partial U}{\partial T}\right)_V\rightarrow(1)$$

Molar heat capacity at constant pressure (C_P)

$$C_P=\frac{q_P}{dT}=\frac{dH}{dT}=\left(\frac{\partial H}{\partial T}\right)_P\rightarrow(2)$$

Also, it is evident that $C_P=C_P\times M\rightarrow(3)$

$$C_V=C_V\times M\rightarrow(4)$$

Where C_P & C_V are specific heats at constant pressure and volume respectively and 'M' is molar mass of gas.

Farther more $C_P - C_V = R \rightarrow (5)$

where, 'R' is molar gas constant

$$\therefore\ C_P - C_V = \frac{R}{M} \rightarrow (6)$$

The molar heat capacity at constant volume

$$C_V = \left(\frac{3}{2}\right)R \rightarrow (7)$$

Molar heat capacity at constant pressure

$$C_P = \left(\frac{3}{2}\right)R + R = \left(\frac{5}{2}\right)R \rightarrow (8)$$

Also, Poisson's ratio

$$\gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1.66 \rightarrow (9)$$

Note:

'γ' value depend on atomicity of gaseous molecules due to degree of freedom for molecules to have vibrational & rotational energy in addition to translational energy in case of diatomic molecules and polyatomic molecules.

$\therefore\ \gamma = 1.66;$ the gas is mono atomic

Eg: He, Ne, Ar, Kr, Xe, Rn

$\gamma = 1.40;$ the gas is diatomic

Eg: $O_2, N_2, Cl_2, H_2....$

$\gamma = 1.33;$ the gas is polyatomic

Eg: $CO_2, SO_2, H_2O_2, O_3...$

Zeroth Law of Thermodynamics:

If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.

The zeroth law allows us to introduce the concept of temperature to measure hotness (or) coldness of a body.

First Law of Thermodynamics:

"Helmholtz" proposed the first law of thermodynamics, which is same as the law of conservation of energy.

1. Energy can neither be created nor destroyed.
2. The total energy of universe is constant.
3. The mass & energy of an isolated system remain constant.
4. The total energy of a system and surroundings must remain constant, although it may be changed from one form to other.

Consider a system in a state ‘ A ’, having internal energy U_A. Amount ‘ q ’ of heat is supplied to system so that the system attains the state ‘ B ’, having internal energy U_B.

Let ‘ $-w$ ’ be the work done by the system to attain this change, then from first law of thermodynamics

If $\Delta U = U_B - U_A$ then

$q = \Delta U + (-w) \rightarrow (1)$

$q = \Delta U - w \rightarrow (2)$

$\Delta U = q + w$

Limitations of first law of thermodynamics:

The law does not provide any information:

1. About the direction of heat flow (i.e. flow of heat from a warmer body to colder body)
2. About the expansion of gases in vacuum, where $\Delta U = 0$, $\Delta H = 0$ and $w = 0$
3. About chemical reactions which does not proceed to completion.

Enthalpy (*H*):

1. It is a state function and is an extensive property.
2. It is also called heat content of system.
3. It’s value depends upon amount of the substance, chemical nature of substance & conditions of temperature & pressure.
4. Change in enthalpy (ΔH) taking place during the process can be experimentally determined.
5. Change in enthalpy is equal to the difference between the enthalpies of products (H_P) and reactants (H_R)

$\therefore$ Change in Enthalpy $\Delta H = H_P - H_R$

Enthalpy Change: (ΔH)

Let us consider the chemical reaction $A \rightarrow B$. Under a set of given conditions, the change in enthalpy may be expressed as

$\Delta H = H_B - H_A$

Change in enthalpy may be expressed as

$\Delta H = \Delta U + \Delta(PV)$

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

If the process is carried out at constant pressure i.e. $\Delta P = 0$, then

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

Now, $\Delta U = q + w \rightarrow (1)$

If work done during the change is only expansion work, $w = -P \cdot \Delta V$ so that

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

Substituting in eqn. (1) the value of ΔU, we get

$\Delta H = q - P\Delta V + P\Delta V = q$

$\Delta H = q_P$ (At constant pressure)

Thus, enthalpy change is a measure of heat change (evolved or absorbed) taking place during a process at constant pressure. It is a state function and an extensive property.

Relation between ΔH & ΔU:

$\Delta H = \Delta U + P\Delta V \rightarrow (1)$

Consider, a chemical reaction taking place at a constant temperature (T) and pressure (P). Let V_r is the total volume of gaseous reactants & V_p is the total volume of gaseous products, n_r is the number of moles of gaseous reactants & n_p is the number of moles of gaseous products.

According to ideal gas equation

$PV = nRT$

For reactants $PV_r = n_r RT$ (At constant T & P) $\rightarrow (2)$

For products $PV_p = n_p RT$ (At constant T & P) $\rightarrow (3)$

Subtracting eqn. (2) from eqn. (3), we get

$$P(V_p - V_r) = n_p RT - n_r RT$$

$$= (n_p - n_r) RT$$

(or) $P\Delta V = \Delta n_{(g)} RT \rightarrow (4)$

$n_{(g)}$ is the change in the no. of gaseous moles of product and gaseous moles of reactants.

This, eqn. (1) becomes

$$\boxed{\Delta H = \Delta U + \Delta n_{(g)} RT}$$

Note:

(i) It is important to note that ΔH will be equal to ΔU under the following conditions.

(a) Reactant that do not involve any gaseous components

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

(b) Reactions carried out in closed vessel of fixed volume i.e. $\Delta v = 0$

(c) Reactions that involve gaseous reactants and products but there is no change in number of moles of gaseous components.

Eg: $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

In all such reactions, the volume change is zero i.e. $n_{(g)} = 0$

$\therefore \Delta H = \Delta U + \Delta n_{(g)} RT$

$$= \Delta U + 0 \times RT$$
$$= \Delta U$$

(ii) Reactions in which there is an increase in number of moles of gaseous components

In such cases, $\Delta n_{(g)}$ is positive and consequently, the enthalpy change (ΔH) is greater than the internal energy change (ΔU) i.e. $\Delta H > \Delta U$

Eg: $C_{(s)} + \frac{1}{2}O_{2\,(g)} \rightarrow CO_{(g)} \quad \left[\Delta n_{(g)} = \left(1 - \frac{1}{2}\right) = +\frac{1}{2}\right]$

$PCl_{5\,(g)} \rightarrow PCl_{3\,(g)} + Cl_{2\,(g)} \quad \left[\Delta n_{(g)} = 2 - 1 = +1\right]$

(iii) Reactions in which there is a decrease in number of moles of gaseous components

In such case, $\Delta n_{(g)}$ is negative and consequently, the enthalpy change (ΔH) is less than internal energy change (ΔU) i.e. $\Delta H < \Delta U$

Eg: $CO_{(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow CO_{2\,(g)} \quad \left[\Delta n_{(g)} = \left(1 - 1\frac{1}{2}\right) = -\frac{1}{2}\right]$

$N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)} \quad \left[\Delta n_{(g)} = 2 - 4 = -2\right]$

Thus, for gaseous reactions, the difference between ΔH and ΔU depend upon $\Delta n_{(g)}$

$\therefore\ \Delta n_{(g)} = 0;\ \Delta H = \Delta U$

$\Delta n_{(g)} = -\text{ve};\ \Delta H < \Delta U$

$\Delta n_{(g)} = +\text{ve};\ \Delta H > \Delta U$

Spontaneous process:

A process said to be spontaneous if it occur on it’s own without the intervention of any external agency of any kind.

Eg: Flow of water from high level to level.

Spontaneous (or) Natural processes are thermodynamically irreversible.

Driving force for spontaneous process:

1. Tendency of a system to achieve a state of minimum energy.
2. Tendency of a system to achieve a state of maximum randomness.

The above two tendencies are independent of each other.

Entropy (S):

1. Entropy is a measure of randomness (or) disorderness of particles of a system.
2. Entropy is a state function and an extensive property.

$$\Delta S = \Delta S_{\text{Final}} - \Delta S_{\text{Initial}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}}$$

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

3. Entropy of one mole of a substance in pure state at one bar and $25°C$ is termed as Standard Entropy $\left(S°\right)$

For a reaction in standard state $A \rightarrow B$

$\Delta S° = S_B^\circ - S_A^\circ$

For a spontaneous process in an isolated system $\Delta S > 0$ i.e. positive.

When a system is non isolated the entropy changes of the surroundings also must be considered.

Then $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$

Note:

1. When $\Delta S = 0,$ the process is in equilibrium (or) reversible.

2. In a reversible adiabatic process $q = 0$

$\Delta S_{\text{sys}} = \Delta S_{\text{surr}} = \Delta S_{\text{tot}} = 0$

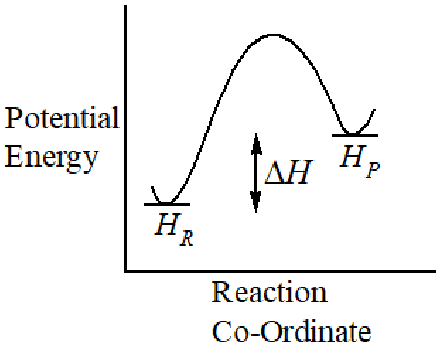
→ The entropy of a system increases when it absorbs heat.

→ ΔS is more positive when the system absorbs heat lower temperature rather that at higher temperature.

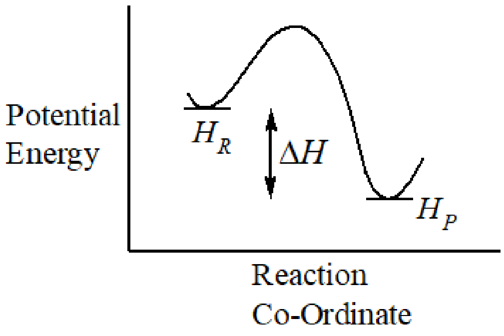
→ At a given temperature $S_{\text{liq}} > S_{\text{solid}}$ & $S_{\text{gas}} > S_{\text{solid}}$

Standard Entropy: $\Delta S° = \Delta S^\circ_{\text{products}} - \Delta S^\circ_{\text{reactants}}$

Entropy changes in Exothermic and Endothermic reactions:



$H_R > H_P \Rightarrow \Delta H = -\text{ve}$



$H_R < H_P \Rightarrow \Delta H = +\text{ve}$

1. In exothermic reactions heat released by the reaction increases the disorderness of the surroundings and overall entropy change is positive. $\left(\Delta S = +\text{ve}\right)$

2. In endothermic reactions, heat flow from the surroundings into the system. The entropy of the surroundings decreases & the system increases.

Entropy change during phase transformation:

a. Entropy of Fusion: It is the entropy change when one mole of a solid changes to a liquid at it's melting point.

$$\Delta S_{\text{fusion}} = \frac{q_{rev}}{T}$$

$$\Delta S = \frac{\Delta H_{\text{fusion}}}{\text{Melting point}\left(K\right)}$$

b. Entropy of Vapourisation: It is the change entropy when one mole of a liquid changes to vapour at it's boiling point.

$$\Delta S_{\text{vapourisation}} = \frac{\Delta H_{\text{vapourisation}}}{\text{Boiling point}\left(K\right)}$$

c. Entropy of Sublimation: It is the change of entropy when one mole of solid changes into vapour at a particular temperature.

$$\Delta S_{\text{sub}} = S_{\text{vap}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

Entropy change in Reversible process:

$$\Delta S = 2.303\ nC_P\ \log\frac{T_2}{T_1} + 2.303\ nR\ \log\frac{P_1}{P_2}$$

$$\Delta S = 2.303\ nC_V\ \log\frac{T_2}{T_1} + 2.303\ nR\ \log\frac{V_2}{V_1}$$

For Isothermal Process:

$$\Delta S = 2.303\ nR\ \log_{10}\frac{P_1}{P_2}$$

$$\Delta S = 2.303\ nR\ \log_{10}\frac{V_2}{V_1}$$

For Isobaric Process:

$$\Delta S = 2.303\ nC_P\ \log\frac{T_2}{T_1}$$

For Isochoric Process:

$$\Delta S = 2.303\ nC_V\ \log\left(\frac{T_2}{T_1}\right)$$

Second Law of Thermodynamics:

1. Heat cannot flow from a colder body to a hotter body on it's own.
2. Heat cannot be converted into work completely without causing some permanent changes in the system (or) in the surroundings.
3. All spontaneous process are thermodynamically irreversible and entropy of system increases.

→ It is impossible to construct a machine working in cycles and transfers heat from a lower temperature region to a higher region temperature without intervention of an external agency.

Gibb's Energy (or) Gibb's Function (G):

Gibbs introduced a thermodynamic function which involved both Enthalpy (H) and Entropy (S) function. This is known as Free Energy Function (G) (or) Gibb's Energy (or) Gibb's Function.

$$\boxed{G = H - TS}$$

→ Gibb's function is an extensive property & a state function.

→ The change in Gibb's energy for the system, ΔG_{sys} can be written as

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} - S_{\text{sys}}\,\Delta T$$

At constant temperature $\Delta T = 0$

$$\therefore\ \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

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

The above equation is referred as Gibb's Equation.

Criteria of Spontaneity:

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

If the system is in thermal equilibrium with the surroundings, then the temperature of the surroundings is same as that of system. Also increase in enthalpy of surroundings is equal to decrease in the enthalpy of system.

$$\therefore\ \text{Entropy change of surroundings} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \left(-\frac{\Delta H_{\text{sys}}}{T}\right)$$

Nature of Reaction	ΔG	ΔH	ΔS
Spontaneous at all temperatures	$-$	$-$	$+$
Non-Spontaneous at all temperatures	$+$	$+$	$-$
Spontaneous at low 'T'	$-$	$-$	$-$
Non-Spontaneous at high 'T'	$+$	$-$	$-$
Non-Spontaneous at low 'T'	$+$	$+$	$+$
Spontaneous at high 'T'	$-$	$+$	$+$

Gibb's energy change and Equilibrium:

ΔG_r° is related to equilibrium constant of the reaction as follows.

$$\Delta G_r^\circ = -RT\ln K$$

$$\Delta G^\circ = -2.303\ RT\log K_{\text{eq}}$$

$K_{\text{eq}} = \text{Equilibrium constant}$

$$K_{\text{eq}} = e^{-\Delta G^\circ/RT} \ (\text{or}) \ K = 10^{-\frac{\Delta G^\circ}{2.303\,RT}}$$

Third Law of Thermodynamics:

The entropy of a pure and perfectly crystalline substance is zero at the absolute zero temperature $(-273°C)$

$S_{\lim T\to 0} = 0$

→ Absolute entropy of a substance at a temperature T, $S_T = \int_0^T \frac{C_P}{T}\,dT$

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