CONCEPT MAP

THERMODYNAMICS

Class XI

In thermodynamics, interaction between large ensembles of objects are studied and categorized. Central to this are the concepts of system and surroundings. A system is composed of particles whose average motions define its properties. Properties can be combined to express internal energy and thermodynamic potentials.

Thermodynamic terms

Properties of system: Physical quantities which are used to define the system.

Intensive: These do not depend upon quantity of matter. e.g., T, P

Extensive: These depend upon quantity of matter. e.g., mass, volume, energy

Thermodynamic processes
- If $dq = 0$, process is adiabatic.
- If $dT = 0$ and $dE = 0$, the process is isothermal.
- If $dV = 0$, process is isochoric.
- If $dP = 0$, process is isobaric.

Heat (q) and heat capacity (C)
- Heat capacity: $C = dq/dT$
- $C_v = \left(\dfrac{\partial U}{\partial T}\right)_V$, $C_p = \left(\dfrac{\partial H}{\partial T}\right)_p$
- When n_1 moles of gas A and n_2 moles of gas B are mixed.
  $(C_v)_{mix} = \dfrac{n_1 C_{v_1} + n_2 C_{v_2}}{n_1 + n_2}$
- $C_p - C_v = nR$

Work (W)
- $W = -P_{ext}\Delta V$ [irreversible isothermal expansion]
- $W = -2.303 nRT \log(P_1 / P_2)$
- $W = -2.303 nRT \log(V_2 / V_1)$ [reversible isothermal expansion]
- $W = nC_v dT = \dfrac{nR}{\gamma - 1}(T_2 - T_1)$ [reversible adiabatic expansion] where $\gamma = C_p/C_v$
- $W = -P_{ext} R \left(\dfrac{T_2 P_1 - T_1 P_2}{P_1 P_2}\right)$ [irreversible adiabatic expansion]

Bond enthalpy
It is the enthalpy change accompanying the breaking of one mole of covalent bonds.
Bond enthalpy =
$\sum$ Bond enthalpies of reactants
$-\sum$ Bond enthalpies of products

Enthalpy (H)
Total heat of the system
- $H = U + PV$
- $\Delta H = \Delta U + P\Delta V = C_p \Delta T = \Delta U + \Delta n_g RT$ (at constant pressure)
- $\Delta H = \sum H_{product} - \sum H_{reactant}$
  = $-ve$ (exothermic)
  = $+ve$ (endothermic)

Gibbs Free Energy (G)
Useful work done by the system
- $G = H - TS$
- $\Delta G = \Delta H - T\Delta S$ (Gibbs–Helmholtz equation)
  $\Delta G = \sum G_{(product)} - \sum G_{(reactant)}$
- $\Delta G^\circ = -2.303\, RT \log K_{eq}$
- If $\Delta G = +ve$ (Non-spontaneous)
- If $\Delta G = -ve$ (Spontaneous)

Enthalpy of combustion, $\Delta_c H$
It is the enthalpy change when 1 mole of a substance burnt completely in air.

Hess's law of constant heat summation
$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Enthalpy change of a reaction
It is the enthalpy change when a given reactant reacts completely.

Enthalpy of formation
It is the enthalpy change occurring during the formation of 1 mole of a substance from its elements.

Enthalpy of solution
$\Delta_{sol} H = \Delta_{lattice} H + \Delta H_{hyd}$
where, $\Delta_{lattice} H = S + I + \frac{1}{2}D - \Delta_f H + E.A.$

Thermodynamic laws

Zeroth law: System in thermal equilibrium with each other have same temperature.

First law: The total energy of the universe remains constant although it may undergo transformation from one form to the other.
$\Delta U = q + w$ (ΔU – internal energy)

Second law: In a spontaneous process total energy of the universe increases.
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$

Entropy (S)
Measure of randomness or disorder
- $\Delta S = \dfrac{q_{rev}}{T}$ (reversible process)
- $\Delta S = 2.303 nC_v \log\left(\dfrac{V_2}{V_1}\right) + 2.303 nR \log\left(\dfrac{V_2}{V_1}\right)$
- $\Delta S = 2.303 nC_v \log\left(\dfrac{T_2}{T_1}\right) + 2.303 nR \log\left(\dfrac{P_1}{P_2}\right)$
- $\Delta S = 2.303 nR \log\left(\dfrac{V_2}{V_1}\right)$ (isotherm)
- $\Delta S = 2.303 nR \log\left(\dfrac{P_1}{P_2}\right)$
- $\Delta S = 2.303 nC_p \log\left(\dfrac{T_2}{T_1}\right)$ (isobaric)

Third law
- Entropy of all pure crystals is zero at the absolute zero temperature.
  $\lim_{T \to 0} S = 0$
- Residual Entropy
  $S_0 = k \ln W$
  (W: thermodynamic probability)

## CONCEPT MAP

THERMODYNAMIC PROCESSES

Class XI

State of a thermodynamic system can be changed by interacting with its surroundings through work and heat. When this change occurs in a system, it is said that the system is undergoing a process. Most processes of interest to pyrometallurgists can be idealised as operating at constant temperature (isothermal) or constant pressure (isobaric).
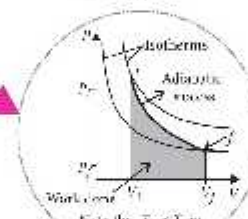
Isothermal Process
A process in which temperature remains constant i.e.
$\Delta T = 0$
$\Delta U = 0$
$q = -w$
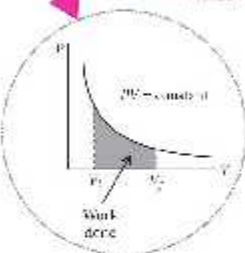
Reversible Process
A process in which the direction may be reversed at any stage by mere by a small change in a variable like temperature, pressure, etc.
For isothermal reversible process:
$q = -w = nRT \ln \dfrac{V_f}{V_i}$ or $q = nRT \ln \dfrac{P_i}{P_f}$
V_f and P_f – Final volume and pressure
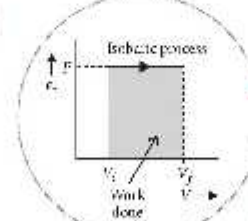V_i and P_i – Initial volume and pressure

Irreversible Process
A process which is not reversible is called an irreversible process.
All the natural processes are irreversible.
For isothermal irreversible process:
$q = -w = -P_{ext}(V_f - V_i)$
Note: (i) If gas expands $V_f > V_i$, w is negative.
(ii) If gas contracts, $V_f < V_i$, w is positive.

Adiabatic Process
A process in which the system does not exchange heat with the surroundings, i.e., $q = 0$; $\Delta U = w_{ad}$
Work done in adiabatic process:
$w = (P_1 V_1 - P_2 V_2)/(\gamma - 1)$
For an adiabatic process, $PV^\gamma = $ constant
where $\gamma = C_p/C_v$

	C_V	C_p
Monoatomic gas	$3/2R$	$5/2R$
Diatomic gas	$5/2R$	$7/2R$
Triatomic gas	$7/2R$	$9/2R$

Isobaric Process
A process in which the pressure of the system remains constant.
$P = $ constant, $\Delta U = q - w$
$w = -P\Delta V = -nR\Delta T, \Delta U = nC_v \Delta T$
$q_p = \Delta U + w = n(C_v \Delta T - nR\Delta T)$
$= n(C_p + R)\Delta T = nC_p \Delta T$
$C_p = C_v + R$ – molar specific heat at constant pressure
C_v – molar specific heat at constant volume

Isochoric Process
A process in which volume of the system is constant.
$V = $ constant, $\Delta V = 0$,
$w = -P\Delta V = 0$
$\Delta U = q_v = nC_v \Delta T$
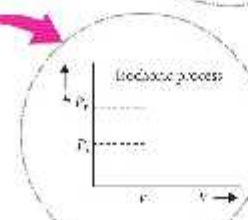
Important Points
- Sign conventions:
  Heat absorbed by the system = $+q$
  Heat evolved by the system = $-q$
  Work done on the system = $+w$
  Work done by the system = $-w$
- Free expansion: Expansion of a gas in vacuum ($P_{ext} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.
  q (at constant volume) = ΔU
  q (at constant pressure) = ΔH
  $\Delta H = \Delta U + P\Delta V$
  or $\Delta H = \Delta U + \Delta n_g RT$