CHAPTER

6 Chemical Thermodynamics and Energetics

DEFINITION

Deals with interaction of one body with another in terms of energy.
System: Part of universe under investigation.
Surrounding: Rest part of universe except system.
Boundary: Divide system & surrounding.

SYSTEM

1. **Open system:** Can exchange matter and energy with surrounding.
2. **Closed system:** Can exchange energy & not matter with surroundings.
3. **Isolated system:** Can neither exchange energy nor matter with surrounding.

STATE FUNCTION

Properties which depends only on initial & final state of system & not on process or path. e.g. U, H, S, G, etc.

PATH FUNCTION

Depends on path or process. e.g. work, heat.

THERMODYNAMIC PROPERTIES

1. **Intensive:** Independent of amount of substance, e.g. T,P viscosity, specific heat capacity, density, Boiling point, freezing point, etc.
2. **Extensive:** Depend upon amount of substances, e.g. mass, volume, energy, entropy, enthalpy, internal energy, etc.

PROCESSES

1. **Isothermal:** Temperature constant.
2. **Isobaric:** Pressure constant.
3. **Isochoric:** volume constant.
4. **Adiabatic:** Heat change constant.
5. **Cyclic:** Initial & final state of system are same.

Reversible process	Irreversible process
❖ Slow process ❖ At any time system and surrounding are in equilibrium. ❖ $P_{sys} = P_{surr} \pm dP$	❖ Fast process ❖ No equilibrium between system and surrounding ❖ $P_{sys} = P_{surr} \pm \Delta P$

HEAT (q)

Energy exchange due to temperature difference:

$q = C\Delta T$,

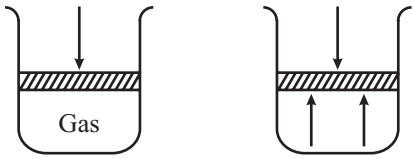
$q = nC_m\Delta T$,

$q = ms\Delta T$

WORK (W)

Reversible	Irreversible
$W_{rev} = -\int_{V_1}^{V_2} P_{ext}.dV$	$W_{irr} = -P_{ext}(V_2 - V_1)$

SIGN CONVENTION



w = +ve
Compression

w = –ve
Expansion

- ❖ Heat absorbed by the system = q (+ve)
- ❖ Heat evolved by the system = q (–ve)
- ❖ Work done on the system = w (+ve)
- ❖ Work done by the system = w (–ve)

INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy called internal energy.

$$U = U_{Kinetic} + U_{Potential} + U_{Electronic} + U_{nuclear} + ...$$

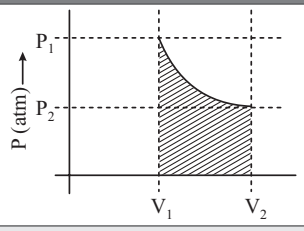
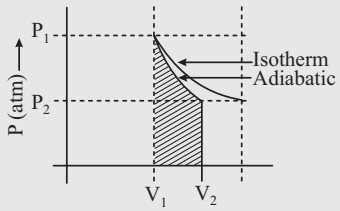
FIRST LAW OF THERMODYNAMICS

Law of conservation of energy

$$\boxed{\Delta U = q + W}$$

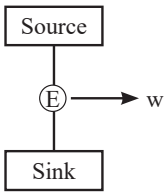
ENTHALPY

$H = U + PV$, $\Delta H = \Delta U + (\Delta n_g)\, RT$

Process	Expression for w	Expression for q	Work on PV-graph
Reversible isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln\left(\frac{V_2}{V_1}\right)$ $q = nRT \ln\left(\frac{P_1}{P_2}\right)$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $PV^{\gamma} = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	

STATEMENTS OF SECOND LAW OF THERMODYNAMICS

(*i*) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.



(*ii*) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

$\Delta S_{syst.} + \Delta S_{surr} = 0$ for rev. process
$\Delta S_{syst.} + \Delta S_{surr} > 0$ for irrev. process
$\Delta S_{syst.} + \Delta S_{surr} \geq 0$ (In general)

CALCULATION OF ENTROPY CHANGE FOR AN IDEAL GAS

General Expression

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Reversible & irreversible isothermal expansion or contraction of an ideal gas $\Delta S = nR \ln \frac{V_2}{V_1}$

THIRD LAW OF THERMODYNAMICS

"At absolute zero, the entropy of a perfectly crytalline substance is zero". which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

VARIATION OF ΔS_r WITH TEMPERATURE & PRESSURE

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_P)_r \ln \frac{T_2}{T_1}$$

$$(\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = \Delta n_g R \ln \frac{P_1}{P_2}$$

Similarly

$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_P)_r (T_2 - T_1)$ **{Kirchoff's equation}**
$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_V)_r (T_2 - T_1)$

GIBBS FREE ENERGY (G) AND SPONTANEITY

A new thermodynamic state function G, the Gibbs free energy is defined as:

$G = H - TS$

at constant temperature and pressure

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

If $(\Delta G)_{T,P} < 0$ Process is irreversible (spontaneous)
$(\Delta G)_{T,P} = 0$ Process is reversible
$(\Delta G)_{T,P} > 0$ Process is impossible (non spontaneous)

SOME FACTS TO BE REMEMBERED

(a) Standard condition

- For gases/solid/liquid
  P = 1 bar
- For ion/substance in solution
  Concentration = 1M

(b) $\Delta G_r = (\Delta G_f)_{product} - (\Delta G_f)_{reactant}$
$\Delta H_r = (\Delta H_f)_{product} - (\Delta H_f)_{reactant}$
$\Delta S_r = (\Delta S_f)_{product} - (\Delta S_f)_{reactant}$
(All above equation will be derived in thermochemistry)

THERMOCHEMISTRY

Bond Enthalpy

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$\Delta_r H$ = (Sum of bond enthalpy of gaseous reactant) – (Sum of bond enthalpy of gaseous product)

Resonance Energy

$\Delta H^\circ_{resonance} = \Delta_f H^\circ$ (experimental) – $\Delta_f H^\circ$ (calculated)

$= \Delta_C H^\circ$ (calculated) – $\Delta_C H^\circ$ (experimental)

Enthalpy Change

$\Delta H^\circ = \sum H^\circ$ (products) – $\sum H^\circ$ (reactants)

1. **Enthalpy of reaction:** The enthalpy change accompanying a chemical reaction when the number of moles of reactants reacts to give the products as given by the balanced chemical equation.
2. **Enthalpy of Combustion ($\Delta_c H^\circ$):** The amount of heat change when 1 mole of substance is completely burnt in excess of oxygen or air. $\Delta_c H^\circ$ is always negative.
3. **Enthalpy of solution:** The enthalpy change when one mole of a substance is dissolved in large excess of solvent so that further dilution does not give any further enthalpy change.
4. **Enthalpy of hydration:** The enthalpy change during the hydration of 1 mole of anhydrous salt to a specific hydrate.
5. **Enthalpy of neutralization (ΔH_{neut}) Always exothermic:** Change in enthalpy when one gram equivalent of an acid is completely neutralized by one g-equivalent of a base in dilute solution.

   $SA + SB \rightarrow$ salt + water ; ΔH°_{neut}

   $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$; $\Delta H = -13.7$ kCal $eq^{-1} = -57.3$ kJ eq^{-1}

   In case of weak acid/ base or both $|\Delta H^\circ_N| < 13.7$ Kcal/eq^{-1} and the difference is enthalpy of ionisation of weak species except in case of HF when $|\Delta H_N| > 13.7$ Kcal/eq^{-1} due to hydration of F^-.

❖ If in a reaction heat of reactant & products are given then heat of that reaction can be measured as follows:

(a) For heat of combustion & for bond enthalpy

$$\Delta_r H = \sum(\Delta H_C)_{reactant} - \sum (\Delta H_C)_{product}$$

(b) For heat of formation

$$\Delta_r H = \sum(\Delta H_f)_{product} - \sum (\Delta H_f)_{reactant}$$

Hess's Law: The enthalpy change in a particular reaction is the same whether the reaction take place in one step or in a number of steps.