

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

HEAT (q)

Energy exchange due to temperature difference:

$$q = C\Delta T,$$

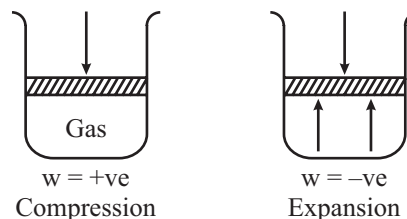
$$q = nC_m\Delta T,$$

$$q = ms\Delta T$$

WORK (W)

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

SIGN CONVENTION



- ❖ 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.

$$U = U_{\text{Kinetic}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

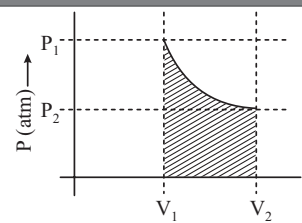
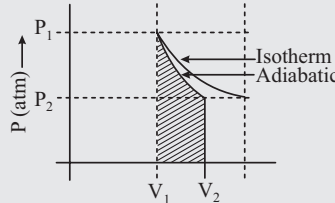
FIRST LAW OF THERMODYNAMICS

Law of conservation of energy

$$\Delta U = q + W$$

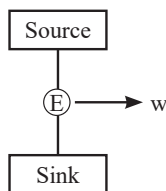
ENTHALPY

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

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	$w = nC_V(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	

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.

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

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

$$\text{of an ideal gas } \Delta S = nR \ln \frac{V_2}{V_1}$$

THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline 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

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_P)_r (T_2 - T_1) \quad \{\text{Kirchoff's equation}\}$$

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_V)_r (T_2 - T_1)$$

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) $\Delta G_r = (\Delta G_f)_{\text{product}} - (\Delta G_f)_{\text{reactant}}$

$$\Delta H_r = (\Delta H_f)_{\text{product}} - (\Delta H_f)_{\text{reactant}}$$

$$\Delta S_r = (\Delta S_f)_{\text{product}} - (\Delta S_f)_{\text{reactant}}$$

(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.

$$\Delta_r H = (\text{Sum of bond enthalpy of gaseous reactant}) - (\text{Sum of bond enthalpy of gaseous product})$$

Resonance Energy

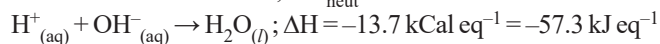
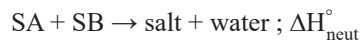
$$\begin{aligned}\Delta H_{\text{resonance}}^{\circ} &= \Delta_f H^{\circ} (\text{experimental}) - \Delta_f H^{\circ} (\text{calculated}) \\ &= \Delta_c H^{\circ} (\text{calculated}) - \Delta_c H^{\circ} (\text{experimental})\end{aligned}$$

Enthalpy Change

$$\Delta H^{\circ} = \sum H^{\circ} (\text{products}) - \sum H^{\circ} (\text{reactants})$$

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.



In case of weak acid/ base or both $|\Delta H_{\text{N}}^{\circ}| < 13.7 \text{ Kcal/eq}^{-1}$ and the difference is enthalpy of ionisation of weak species except in case of HF when $|\Delta H_{\text{N}}^{\circ}| > 13.7 \text{ Kcal/eq}^{-1}$ 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

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

- (b) For heat of formation

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

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.