chapter- Thermodynamics

It is the branch of science which deals with different forms of energy and their relationships

Some Basic Terms

(1) System :- The part of universe chosen for investigation.

(2) Surrounding :- Remaining portion of universe.

System + Surrounding = Universe

(3) Open system :- A system is said to be open if both Matter & Energy are exchanged with surrounding.

(4) Closed System :- A system only exchange energy not matter with surrounding.

(5) Isolated system :- Neither matter nor energy gets exchanged.

OPEN CLOSED ISOLATED

A perfectly isolated system does not exist.

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(6) State :- It is represented by some measurable properties like Temperature, Pressure.

(7) State function :- All those thermodynamics quantities which depends on initial and final state not on path followed.
Eg:- Pressure (P), Vol^m, T

(8) Macroscopic System :- A system contains large no. of chemical species, i.e., atoms, ions/molecules.

a) Extensive Property :- All those properties which depends upon amount of substance.
Eg- Internal Energy, Enthalpy, Entropy

b) Intensive Property :- All those properties which do not depends upon amount of substance.
Eg :- Temp., P, density

(9) Thermodynamic equilibrium :- A system is said to be in Thermodynamic equilibrium if its properties do not change with time.

(10) Process :- It is done when system's state is changed.

Δ = change

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a) Isothermal process :- If during a process, temperature remains constant

(same Temp.)

$\Delta T = 0$

b) Adiabatic process :- If during a process, no heat exchange between system and surrounding

Heat = q ; $\Delta q = 0$

c) Isobaric process :- Pressure remains constant during the process

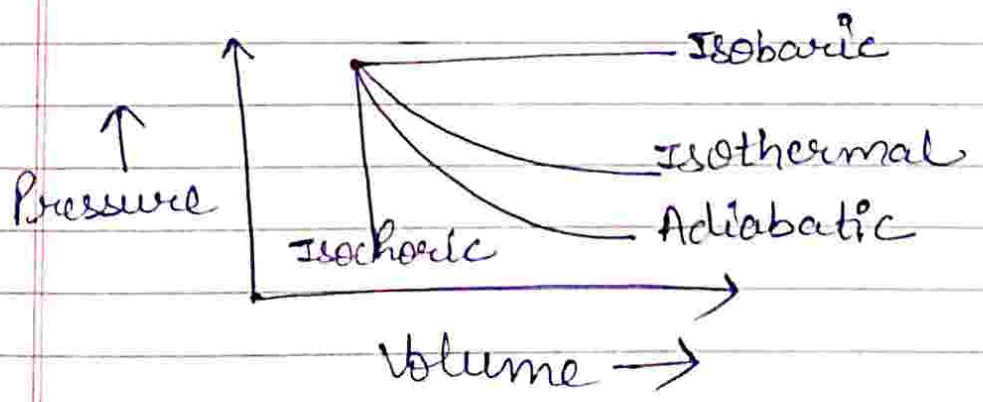
(same Pressure)

$\Delta P = 0$

d) Isochoric process :- Volume remains constant during the process

(same Volume)

$\Delta V = 0$



(11) Reversible process :- Process in which is carried out infinitesimally small steps System & surroundings remain in equilibrium

(12) Irreversible process :- Process which is not carried out infinite steps but is carried out rapidly.

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(13) Internal Energy (U):- The total energy associated with a system is known as internal energy.

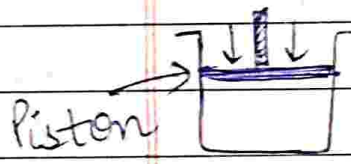
$U = K.E. + P.E. + R.E. + V.E. + T.E. + \ldots$

It is the sum of many energies, thus it is difficult to calculate exact value of U.

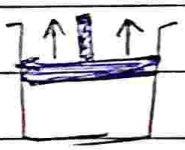
→ Internal energy of a system changes when
i) heat passes in or out of system
ii) work is done on or by the system
iii) matter enters or leaves the system

→ It is a state function, doesn't depend on path.

(14) Work



Contraction → Work done on the system
(W will be negative)



Expansion – Work done by the system
(W will be positive)

Consider a gas enclosed in a cylinder fitted with frictionless piston.
Let the pressure on piston = P
Area of cross-section = a
Thus, we get $P = \frac{\text{force}}{\text{Area}}$

(Work done) W = Pressure (P) × Area (a) × displacement

$$\boxed{dW = P\,dV}$$

dV = small change in volume
final Vol^m – initial Vol^m

If gas expands from Vol^m $V_1 \rightarrow V_2$, then total work can be obtained by integrating

$$\int dW = \int P_{ext}.dV$$

$$\int dW = P_{ext} \int_{V_1}^{V_2} dV$$

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

$$\boxed{W = P_{ext}.\Delta V}$$

* If external Pressure is slightly more than internal pressure (Pressure of gas) then gas will contract [Work done on the system]

$(V_2 < V_1)$

$\boxed{W = -PdV}$ [Contraction]

* If $P_{ext} < P_{int}$ so $V_2 > V_1$ [Work done by the system]

ΔV = +ve $\quad \boxed{W = +PdV}$ (Expansion)

Unit of Work = Joules

$\boxed{1 \text{ Joules} = 1 Kg m^2 s^{-2}}$

Work done in Isothermal Reversible Expansion of ~~an gas~~ ideal gas

$$dW = -P_{ext}.dV$$

$$dW = -(P_{in} - dP)dV \quad [P_{ext} = P_{in} - dP]$$

$$= -P_{in}dV + \underbrace{dP.dV}_{\text{Negligible}}$$

$$dW = -P_{in}dV \quad [P_{in} = \text{internal Pressure}]$$

ln (Natural log) $\xrightarrow{2.303}$ $\log_{10}$ (Base)

$$dW = -\frac{nRT}{V}dV$$

Integrating, $\int dW = \int_{V_1}^{V_2} -\frac{nRT}{V}dV$

$$W = -nRT\left[\ln V\right]_{V_1}^{V_2}$$

$$W = -nRT\left[\ln V_2 - \ln V_1\right]$$

$$= -nRT \ln \frac{V_2}{V_1}$$

$$W = -2.303nRT \log \frac{V_2}{V_1}$$

$$W = -2.303nRT \log \frac{P_2}{P_1}$$

Ideal Gas Eqn

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$\because \log_e = \ln$

$\int \frac{1}{x}dx = \ln x$

$\ln \frac{a}{b} = \ln a - \ln b$

$[\because \ln = \log \times 2.303]$

$\left[\because \frac{V_2}{V_1} = \frac{P_2}{P_1}\right]$

★ Free Expansion of an Ideal Gas

i.e. expansion against vacuum (irreversible)

$P_{ext} = 0$

$W_{irr.} = W_{rev.} = -P_{ext}\Delta V$

$$W_{irr.} = W_{rev.} = 0$$

(15) **Heat (q)**:- Mode of Energy exchange between system & surrounding as result of difference of temperature between them. Both work & heat appear only at boundary of the system.

q = -ve (released by system)

q = +ve (absorbed by system)

Unit = Joules

1 Calorie = 4.184 Joules

1 Joule = 0.239 Calories.

* R = Gas constant = 8.314 J mol^{-1} K^{-1}
= 1.987 cal mol^{-1} K^{-1}
= 0.08205 L atm mol^{-1} K^{-1}
= 0.08314 L bar mol^{-1} K^{-1}

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Q Two moles of an Ideal gas initially 27°C, 1 atm pressure are compressed Isothermally & Reversibly till final pressure of gas is 10 atm. Calculate q, w and ΔV.

Ans Given:- $n = 2$,
$T = 27°C = 273 + 27 = 300K$
$P_1 = 1$ atm, $P_2 = 10$ atm
$q = ?, w = ?, \Delta V = ?$
Isothermal, reversible, compression [$\Delta U = 0$]

$$W = -2.303\, nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 2 \times 8.314 \times 300 \log \frac{1}{10}$$

$$= -1.148 \times 10^4 [\log 1 - \log 10]$$

$$\boxed{W = +1.148 \times 10^4 J} \text{ or } W = +11.4882 KJ$$

$\left[\log \frac{a}{b} = \log a - \log b;\ \log 1 = 0, \log 10 = 1\right]$

From I Law of Thermodynamics, $\Delta U = q + W$
$q = -W = -11.4882 KJ$

— X —

first Law of Thermodynamics

It states that energy cannot be created or destroyed, however it can be changed from one form to another form.

Mathematical Expression

$$\Delta U = U_2 - U_1 = q + W = q - P\Delta V$$

$$\boxed{q = \Delta U + P\Delta V}$$

(1) System $\xrightarrow{+q}$ $\boxed{U_1 + q}$ $\xrightarrow{+W}$ $\boxed{U_1 + q + W = U_2}$

Enthalpy (H)

* Internal energy change is the heat absorbed or evolved at constant volume.

$$\boxed{q_v = \Delta U}$$

* Enthalpy change of a system is equal to the heat absorbed or evolved by the system at constant pressure

$$\boxed{q_p = \Delta H}$$

A/c to I law,

$\Delta U = q - P\Delta V$ [at const. Volm $= \Delta V = 0$]

$\boxed{\Delta U = q_v}$

q_v = Heat absorbed / lost at const. volm,

At constant Pressure,

(A/c to I law) $H = U + PV$

$H_1 = U_1 + PV_1$; $H_2 = U_2 + PV_2$

$q_p = \Delta H = H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1)$

$= (U_2 - U_1) + P(V_2 - V_1)$

The Energy stored within the substance or the system that is available for conversion into heat is called the heat content / Enthalpy of the substance or the system.

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Relationship between q_p and q_v

$q_p = \Delta H$; $q_v = \Delta U$ —(1)

Alc to I Law,

$$\Delta H = \Delta U + P\Delta V$$
$$= \Delta U + P(V_2 - V_1)$$
$$= \Delta U + (PV_2 - PV_1)$$

For Ideal Gas, $PV = nRT$

$PV_1 = n_1RT$; $PV_2 = n_2RT$

$$\Delta H = \Delta U + (n_2RT - n_1RT)$$
$$= \Delta U + RT(n_2 - n_1)$$

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

$$\boxed{q_p = q_v + \Delta n_g RT} \quad \text{(from (1))}$$

where, Δn_g = Difference in no. of moles of Gaseous product ~~of Product~~ and reactant respectively.

Heat capacity (C)

Amount of heat required to raise the temp. of the system through $1^\circ C$.

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

$$C = \frac{\delta q}{\Delta T}$$

[δq = small amount of heat absorbed by system]

Types of Heat Capacity

There are two types

a) Heat capacity at const. Volume (C_v)

b) Heat capacity at const. Pressure (C_p)

a) Heat supplied to a system to raise its temperature through 1°C keeping the volume of system constant called Heat capacity at constant volume.

$$\delta q = dU + PdV \quad \text{(from I Law)}$$

$$C = \frac{\delta q}{dT} = \frac{dU + PdV}{dT} \quad \text{--- (I)}$$

At const. Volm, $dV = 0$

$$\boxed{C_v = \frac{dU}{dT}}$$

It is also defined as rate of change of internal energy with temperature at const. Volm.

b) At const. Pressure

$$C_p = \frac{dU + PdV}{dT} \quad \text{[from (I)]}$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \quad \text{--- (II)}$$

From I law; $H = U + PV$

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \quad \text{--- (III)}$$

From (II) & (III),

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Heat capacity at constant pressure defined as rate of change of enthalpy with temperature at constant pressure.

Relation between C_p and C_v

$$C_p = \left(\frac{dH}{dT}\right)_p \quad ; \quad C_v = \left(\frac{dU}{dT}\right)_v$$

$H = U + PV$ (I Law)

$PV = nRT$ (Ideal Gas Equation)

$H = U + nRT$

differentiate wrt Temp.

$$\frac{dH}{dT} = \frac{dU}{dT} + nR\left(\frac{dT}{dT}\right)$$

$C_p = C_v + nR$

$\boxed{C_p - C_v = nR}$ for n moles

For 1 Mole $\boxed{C_p - C_v = R}$

★ Reaction in which heat is evolved are called Exothermic Reaction (ΔH = -ve)
Reaction in which heat is absorbed are called Endothermic Reaction (ΔH = +ve)

(THERMO-CHEMISTRY)

Thermochemical Equations

When a balanced chemical equation not only indicates the quantities of different reactants and products but also indicates amount of heat evolved or absorbed is called a thermochemical equation.

Eg $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
$\Delta H = 285.8\ KJ/mol$

Note: $A \longrightarrow B \quad \Delta H = +ve$
$B \longrightarrow A \quad \Delta H = -ve$

Heat of Reaction (Enthalpy of Reaction)

Amount of heat evolved/absorbed when no. of moles of reactant as represented in chemical eqn have completed Reaction.

Enthalpy of Reaction = Sum of Enthalpies of Product − Sum of Enthalpies of Reactant

$$\Delta H = \sum_{\text{Product}} H_i - \sum_{\text{Reactant}} H_i \qquad [\Sigma = \text{Sum}]$$

Types of Enthalpies

(1) Enthalpy of Combustion ($\Delta_c H^\circ$)
It is defined as heat change (heat evolved) when 1 mole of substance is

completely burnt / oxidized in oxygen

Eg $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
$\Delta_c H = -890.4 KJ mol^{-1}$

② Enthalpy of formation ($\Delta_f H^\circ$)

It is defined as heat change when 1 mole of a substance is formed from its element under given condition of T & P.

Eg $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta_f H^\circ = -393.5 KJ mol^{-1}$.

③ Enthalpy of Neutralization ($\Delta_{neut} H^\circ$)

It is defined as heat change when 1 mole of acid is neutralized by a base, reaction is carried out in dilute aqueous solution.

Eg $NaOH + HCl \rightarrow NaCl + H_2O$ $\Delta_{neut} H = -57.1 KJ mol^{-1}$.

④ Enthalpy of Atomisation ($\Delta_a H^\circ$)
When one mole of a given substance dissociates into gaseous atoms, enthalpy change is $\Delta_a H^\circ$.

Eg $H_2(g) \rightarrow 2H(g)$ $\Delta_a H^\circ = 435 KJ mol^{-1}$.

⑤ Enthalpy of Ionisation ($\Delta_{ion} H^\circ$)
When one mole of a covalent compound on dissolution in water splits to produce ions in solution.

Eg $HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$ $\Delta_{ion} H^\circ = -75.2 KJ mol^{-1}$.

Calculation of Lattice Enthalpy (Born Haber Cycle)

Lattice enthalpy is the amount of energy required to convert one mole of crystalline solid into its constituent ions in gaseous state

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$ $[\Delta_f H]$

$Na(s) \longrightarrow Na(g)$ $(\Delta_a H)$

$Na(g) \longrightarrow Na^+(g)$ $(\Delta_{ionisation} H)$

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ $\frac{1}{2}(\Delta_a H)$

$Cl(g) \longrightarrow Cl^-(g)$ $(\Delta_{eg} H)$ [e^- gain enthalpy]

$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ $(\Delta_{lattice} H)$

Thus, $\boxed{\Delta_f H = \Delta_a H + \Delta_{IE} H + \frac{1}{2}\Delta_a H + \Delta_{eg} H + \Delta_{lattice} H}$

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Note:- Enthalpy change during phase Transformation
→ Solid → Liquid (Enthalpy of fusion)
→ Gas → Liquid (Enthalpy of condensation)
→ Liquid → Solid (Enthalpy of Freezing)
→ Solid → Gas (Enthalpy of sublimation)
→ Liquid → Gas (Enthalpy of Vaporisation)

Hess's Law of Constant Heat Summation

Amount of heat evolved / Absorbed in a reaction is the same whether the reaction takes place in 1 step or in multiple steps.

Applications

(I) Calculation of Enthalpy of formation
(II) Predicting Enthalpy change for any Reaction.

Q Calculate ΔH of formation of Methane from following data

1 → $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta_f H^\circ = -393.5\ KJ\ mol^{-1}$
2 → $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta_f H = -285.8\ KJ\ mol^{-1}$
3 → $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta_f H^\circ = -890.3\ KJ\ mol^{-1}$

To find / Proove: $C(s) + 2H_2(g) \rightarrow CH_4(g)$

(1) + [(2) × 2] − (3)

$C(s) + O_2(g) + 2H_2(g) + O_2(g) \rightarrow CO_2 + 2H_2O - CO_2 - 2H_2O$

$C(s) + 2H_2(g) \rightarrow CH_4(g)$

$-CH_4 - 2O_2$

→ $(\Delta_c H^\circ)_1 + 2(\Delta_c H^\circ)_2 - (\Delta_c H^\circ)_3$

→ $-393.5 + 2(-285.8) - (-890.3)$

→ $-74.8\ KJ\ mol^{-1}$

∴ Enthalpy of formation of methane is:
$\Delta_f H^\circ = -74.8\ KJ\ mol^{-1}$.

Bond Enthalpy / Bond Energy ($\Delta_b H$)

It is the amount of energy released when one mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in gaseous molecules.

Q Calculate Enthalpy change for the reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given that bond enthalpies of H-H, Br-Br, H-Br are 435, 192, 364 KJ mol^{-1} respectively.

Sol^n $\Delta_r H = \Sigma$ B.E. (Reactants) $- \Sigma$ B.E. (Products)

$= [B.E.(H_2) + B.E.(Br_2)] - 2\ B.E.(HBr)$

$= 435 + 192 - 2 \times 364 = -101\ KJ$

Limitation of I Law of Thermo.

1) It does not provide no information concerning spontaneity / feasibility of process, i.e. whether process is possible / not
2) does not explain direction of heat flow cold to hot end or hot to cold end.

Spontaneous and Non-spontaneous processes

* All those processes which occurs at their own or by initiation independence of rate is called a spontaneous process.

Eg → Dissolution of salt in water, evaporation of water, burning of coal etc.

* All those processes which does not occur by their own but requires some external energy is called Non-spontaneous process.

Eg → Dissolution of sand in water, flow of water up a hill.

* The force which is responsible for the spontaneity of a process is called the driving force.

Driving force for a spontaneous process

(1) → Tendency to have minimum energy

→ Reactant (large Energy) → Product + Heat
(Exothermic Process) (less Energy)

Limitation:- There are many processes which are endothermic but are spontaneous too. for Eg - Evaporation of water.

(2) → Tendency to have maximum randomness:
All those processes in which disorderness increases are called spontaneous process.

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for Example → during evaporation of water, randomness of water molecules increases and thus it is a spontaneous process.

→ Dissolution of Ammonium chloride is an endothermic process but it is spontaneous in nature. Why? During dissolution of NH_4Cl, their randomness increases, thus it is a spontaneous process.

Entropy (S)

It is a thermodynamic quantity which tells us the degree of randomness / disorderness of a system.

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

where, q_{rev} = heat absorbed / released in Reversible process

ΔT = change in temperature.

Factors on which Entropy depends :-

1. Volume : With increase in vol^m, Entropy ↑.
2. Temperature :- T↑; S↑
3. On adding substances, randomness increases.

Entropy change is state function, path independent.

$\Delta S_{Total} = \Delta S_{System} + \Delta S_{surrounding}$

ΔS = +ve Spontaneous

ΔS = -ve Non-Spontaneous

$\Delta S = 0$ Equilibrium.

Second Law of Thermo.
Entropy of all spontaneous process is always positive & entropy of Universe is always increases.

Third law of Thermo.
Entropy of a perfect crystalline solid is zero, there is no Randomness in perfect order.

Gibbs free Energy (G)
It helps to predict spontaneity of reaction.

$G = H - TS$

where, H = Enthalpy ; T = Temp. , S = Entropy

$\boxed{\Delta G = \Delta H - T\Delta S}$

Decrease in G $\Leftrightarrow$ useful work done by system

ΔG = -ve Spontaneous
ΔG = +ve Non-spontaneous
$\Delta G = 0$ Equilibrium

A/c to I law,

$q = \Delta U + W$

$T\Delta S = \Delta U + W_{expansion} + W_{non-expansion}$

$T\Delta S = \Delta U + P\Delta V + W_{non-expansion}$

$[\because \Delta S = \frac{q}{T}]$ $T\Delta S - \Delta H = W_{Non-Expansion}$

$[\Delta G = -W_{non-expansion}]$ $[\because \Delta G = \Delta H - T\Delta S]$

Condition for Spontaneity of a process

ΔH	ΔS	ΔG	
-ve	+ve	-ve (At All Temp.)	Spontaneous
-ve	-ve	-ve Temp. low	Spontaneous
		+ve Temp. high	Non-spontaneous
+ve	+ve	+ve Temp. low	Non-Spontaneous
		-ve Temp. high	Spontaneous
+ve	-ve	+ve (At All Temp.)	Non-Spontaneous

[Using the formula : $\Delta G = \Delta H - T\Delta S$]

NCERT (Back Exercise)

Q17 soln $\Delta S = 0.2$, $\Delta H = 400\ KJ\ mol^{-1}$

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

$$T = \frac{\Delta H}{\Delta S} = 2,000\ K$$

Thus, above 2000K temperature, system gets spontaneous process.

Q19 soln $\Delta U = -10.5\ KJ$, $\Delta S = -44.1\ JK^{-1}$

$2A(g) + B(g) \longrightarrow 2D(g)$

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

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

$= -10.5 \times 10^3 + (-1)(8.314)(298)$

$= -12977.5\ KJ\ mol^{-1}$

$\Delta G = -12977.5 - 298(-44.1) = 164.3\ KJ\ mol^{-1}$.

Value is +ve

Non-Spontaneous Reaction.

[Δn_g = No. of moles of Product − No. of moles of Reactant = 2 − 3 = −1]