

THERMODYNAMICS

Extensive Property (V, U, C, ΔG, ΔH) depend on size → **Internal energy**

Intensive property (P, T, S, μ, ρ, β, P, η, M, X, m, mass) independent of size

Molar extn is intensive

$W = -P_{ext} \Delta V$ $\Delta V = V_2 - V_1$

Exp. in more no. of stages leads to greater work done

$W = -2.303 nRT \log \frac{V_f}{V_i}$

$W = -2.303 nRT \log \frac{P_i}{P_f}$

1 L-atm = 1 x 101.3 Joule.

Reversible expansⁿ } Max. work done.
Irreversible compressⁿ }

expansⁿ in vacuum
dW=0 q=0 ΔU=0

$\Delta U = q + W$ q, w are not state functⁿ

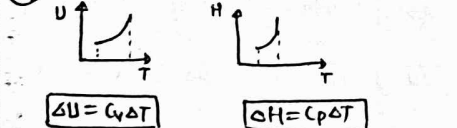


$\Delta H = \Delta U + P \Delta V$
 $\Delta U = q_v$ $\Delta H = q_p$

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

Heat capacity = $\frac{q}{\Delta T}$

$C_p > C_v$ $C_v = \frac{\Delta U}{\Delta T}$ $C_p = \frac{q_p}{\Delta T}$
 $C_v = \frac{\Delta H}{\Delta T}$ $C_p = \frac{\Delta H}{\Delta T} = \frac{\Delta U + P \Delta V}{\Delta T}$



$\Delta U = C_v \Delta T$ $\Delta H = C_p \Delta T$

$C_p - C_v = R$ $C_{p,m} - C_{v,m} = R$

$C_p - C_v = nR$ NO. of moles.
 $C_p - C_v = \frac{R}{m_w}$ Always

$\gamma (C_p/C_v)$

- Monatomic - 1.67 (5/3)
- Diatomic - 1.40 (7/5)
- Polyatomic - 1.33 (4/3)

Entropy, extensive
 $\Delta S = \frac{q_{rev}}{T}$ $\Delta S \propto \text{Atomicity}$

$S = \frac{q}{T} = 2.303 nR \log \frac{V_f}{V_i}$

ΔS for adiabatic reversible process → 0

$\Delta S_{sys} + \Delta S_{sur} = \Delta S_{Total}$

$\Delta S_{Total} = +ve$ spontaneous
 $\Delta S_{Total} = -ve$ non-spontaneous
 $\Delta S_{Total} = 0$ equilibrium

Boiling of egg ΔS = +ve
stretching of rubber ΔS = -ve
precipitatⁿ ΔS = -ve (s → l)
formatⁿ of gas product ΔS = +ve (l/s → g)

$\Delta S_{sys} = -\frac{q}{T_1}$
 $\Delta S_{sys} = +\frac{q}{T_2}$

$\Delta S_{Total} = +ve$
cooling will be sp. Heating will be sp.
 $T_1 > T_2$ $T_2 > T_1$

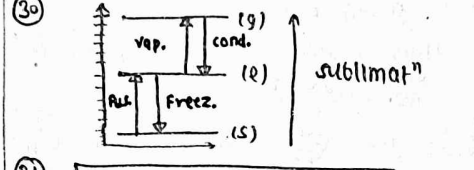
$\Delta G = \Delta H - T \Delta S$

$\Delta G = +ve$ Non spontaneous
 $\Delta G = -ve$ spontaneous
 $\Delta G = 0$ equil.

ΔG=0 phase change

$\Delta_{vap} H = -\Delta_{cond} H$

$\Delta_{fus} H = -\Delta_{freez} H$



$\Delta H_{sub} = \Delta_{fus} H + \Delta_{vap} H$

Enthalpy of formation

- exothermic
- formatⁿ must be from elements in elemental form.

$\Delta_f H = 0$ in ref. state

$\Delta_r H = \sum \Delta_f H_{(p)} - \sum \Delta_f H_{(r)}$

Enthalpy of combustion

- exothermic (ΔH = -ve)
- element oxidise into its best o.s.

$\Delta_r H = \sum \Delta_{comb} H_{(p)} - \sum \Delta_{comb} H_{(r)}$

Enthalpy of Neutralisation

Its for 1 eq. not for 1 mole.

$S.A + S.B \rightarrow \Delta_{neut} H = -13.7 \text{ kcal/mole}$
 $\frac{1}{2} \frac{1}{4} \text{ mole } \left(\frac{-57.4}{4} \right) = -14.35 \text{ kcal}$

for weak acid Δ_{neut} H is less than -13.7 kcal

Δ_{neut} H of HF is more than 13.7 kcal coz. (F) has ↑ value of Δ_{hyd} H coz of small size.

Energy released & No. of eq. Neutralised

Temp rise ∝ $\frac{\text{No. of eq Neut.}}{\text{Vol.}}$

Bond dissociatⁿ enthalpy
 $A \cdot V \ B \cdot O \cdot E = \frac{x+y+\dots+z}{n}$

$\Delta_r H = \sum \Delta_{B-O} H_{(r)} - \sum \Delta_{B-O} H_{(p)}$

calorific value

Best fuel ∝ C.V
∝ $\frac{1}{HOC}$

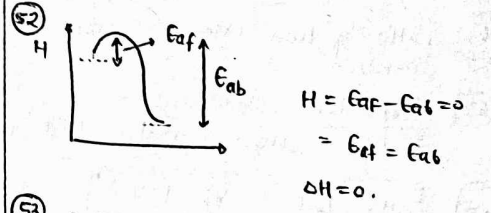
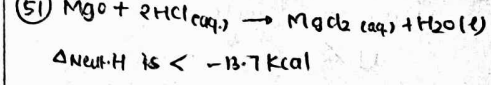
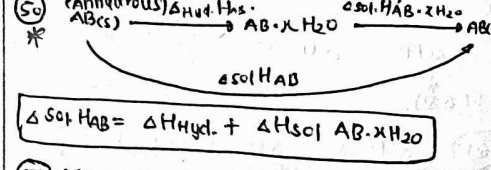
Bomb calorimeter

- energy released in Heat of combustⁿ It is ΔU → In calorimetry.
- ΔV=0. C = m.s
- $q = ms \Delta T$ s → Heat capacity
- $\Delta U = q_v = S \Delta T$ $q_p = \Delta H$

readily form होने के लिए
ΔS = +ve, ΔG = -ve, ΔH = -ve

reversible isothermal expansion
ΔH=0

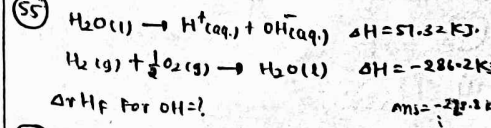
Heat of formatⁿ is given for 1 mol.



Enthalpy of formatⁿ ne

1 mole $H_2SO_4 \rightarrow 2 \text{ eq.}$
= 27.4 kcal
13.2 kcal/eq.

maxi. internal energy
 $O_2 \rightarrow O_3$ तो O_3 की energy ↑



HOH of ethene x1 Benzene x2 R.E = ?
3x1 - x2

HOC of benzene in Bms calorimetry is -870 kcal. then ΔU = ?

ice \rightarrow water $\Delta S = +ve$ (1)

Two ideal mixed.
 $\Delta S_{mix} > 0$ $\Delta H_{mix} = 0$.

60 $N_2 + O_2 \rightleftharpoons NO$ $K_c = 25$
 $K_p = ?$

61 diff. of Heat of Ran at P & V for 2 mole benzene at 25°C in KJ
 $(C_6H_6 + O_2 \rightarrow CO_2 + H_2O)$ $\Delta H = -2085.7$ -743

62 in isothermal expansⁿ
 $\Delta U = 0, \Delta T = 0, W = -q$.

63 For ideal gas expansⁿ in vacuum.
 $\Delta U = 0, q = 0, w = 0$

64 All sudden expansⁿ are adiabatic

65 for isothermal process
 $\Delta S_{surr} = -\Delta S_{system}$

66 $Cl_2(g) \rightarrow 2Cl(g)$ 242.3 KJ/mole
 $I_2(g) \rightarrow 2I(g)$ 151
 $I_2(s) \rightarrow I_2(g)$ 62.76
 $I_2(s) \rightarrow 2I(g)$ 211.3

Hint: $\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \rightarrow ICl(g)$
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

67 $\Delta T = 0$
 $\Delta H = 0, \Delta U = 0$

68 $\Delta T = 0$ ΔU is raised by adding more molecule to it
 $U \propto n f \frac{1}{2} kT$ $n \uparrow U \uparrow$

69 ratio of two extensive prop. is intensive.

70 for ideal Gas $H = f(T)$
 $T \rightarrow \Delta H = 0$

71 $\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$
 $P \neq \text{const}$ $Vol \neq \text{const}$ $Temp \neq \text{const}$ No chem. rxn

72 cyclic process $\Delta S = 0$
 * Constant bench

73 isobaric.
 $\Delta S = \frac{dq_{rev}}{T} = \frac{\Delta H}{T} = \int n C_p \frac{dT}{T}$
 $\Delta S = 2.303 n C_p \log \left[\frac{T_2}{T_1} \right]$

74 $(\Delta S)_{irr} > \frac{dq_{irr}}{T}$

75 $A + B \rightleftharpoons C$
 $\Delta S = (\Delta S_C) - (\Delta S_B + \Delta S_A)$

76 OH_2 (rhombic) = 0

77 $K_a \propto \frac{1}{H_2O} \propto H_2O \cdot n$

78 Acid + Base
 10 ml \rightarrow TK 1
 100 ml \rightarrow TK 1

79 Resonance energy.
 $R.E = \text{energy of bond when not in res.} - \text{energy of bond in res.}$

80 B.S.L of Gas at 25°C rise by 15°C
 $C_p = ?$ at $V = \text{const}$
 $n = \frac{8.5}{22.4}$

81 $S \propto \text{work}$

82 $2 Cl_2(s) \rightarrow Cl_2(g)$
 $\Delta H, \Delta S \rightarrow -ve$

83 ΔH_f Given asked etc.
 $\Delta H_c = (\Delta H_f)_p - (\Delta H_f)_r$
 ΔH_c given asked ΔH_f
 $\Delta H_f = (\Delta H_c)_r - (\Delta H_c)_p$

84 $\Delta T = 0$ expansⁿ.
 $w = \text{heat ab. by system}$

85 3mole H_2SO_4 + 2mole $NaOH$
 $\frac{3 \text{ mole}}{2 \text{ mole}} \rightarrow 57$
 $\frac{3 \text{ mole}}{2 \text{ mole}} \rightarrow 2 \times 57$

86 $\frac{\Delta V}{V_i} = \frac{\Delta T}{T_i}$
 imp: $\frac{\Delta V}{V_i} = \frac{\Delta T}{T_i}$ $\frac{\Delta V}{V_i} = \frac{\Delta T}{T_i}$ respect to T_i

87 P vs V graph showing isotherms $T_1 > T_2 > T_3$

88 $CO_2 + H_2 \rightarrow CO + H_2O$ ΔH
 Heat of Ran

89 $S + 3/2 O_2 \rightarrow SO_3 + 2x \text{ kcal}$
 $SO_2 + 1/2 O_2 \rightarrow SO_3 + y \text{ kcal}$
 HOF of SO_2 $\Delta H = -2x$ $\Delta H = -y$

90 P vs V graph showing work done $w_r > w_{in}$

91 $\Delta S_{tot} > \Delta S_{adiv}$
 $\Delta S_1 > \Delta S_2$

92 for (R) at $\Delta T = 0 \rightarrow \Delta U = 0$
 for IR $(\Delta S_{syst} \Delta S_{surr} \neq 0)$
 ΔS discriminate b/w (R) + (IR) but ΔS does not.