$\Delta H_f^\circ = \Sigma H_f^\circ$ Products $- \Sigma H_f^\circ$ Reactants
$= H^\circ_{(HBr,g)} - [\frac{1}{2} H^\circ(H_2,g) + \frac{1}{2} H^\circ(Br_2,l)]$

Engineering Chem — $\Delta_f H^\circ$ +ve (formation of …)
Thermochemistry — $\Delta_{comb} H^\circ = -ve$ (for all …)
$\Delta_{neut} H^\circ$ = -ve (1 gm …)

* Heat of reaction ($\Delta_r H$)
  - $A \rightarrow B$, $\Delta H = -ve$ — Exothermic (release energy)
  - $A \rightarrow B$, $\Delta H = +ve$ — Endothermic (Amount of heat involve in the chemical rxn)

Type of Heat of Rxn

1) Heat of formation ($\Delta_f H^\circ$) [Product = 1 mol]
Amount of heat involve in the formation of 1 mol of a compound by its constituent atoms or molecules
Eg $\frac{1}{2} H_2 + \frac{1}{2} F_2 \rightarrow 1HF$ $\Delta_f H^\circ$

Formation of CO_2
$C_{(graphite)} + O_2(g) \rightarrow CO_2(g)$ $\Delta_f H^\circ$
$C_{diamond} + O_2(g) \rightarrow CO_2(g)$ No $\Delta_f H$, ΔH°
Solid state wale $= 0$

→ Standard state ($\Delta_f H^\circ = 0$) molecules used for $\Delta_f H^\circ$
$H_2(g)$, $F_2(g)$, $Cl_2(g)$, $Br_2(l)$, $I_2(s)$, $O_2(g)$, $N_2(g)$.
P_4 (white), S_8 (rhombic), $C_{graphite}$

eg:- Formation of H_2O
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta_f H^\circ = 0$

Q The species which by definition has zero standard molar enthalpy of formation at 298 K is.
(a) $Br_2(g)$ (b) $Cl_2(g)$ (c) $H_2O(g)$ (d) $CH_4(g)$

2) Heat of combustion (ΔH°_{comb}) :- Heat released when 1 mol of a substance is combined with O_2 to form products.
[Reactant = 1 mol]

For WA & Strong Base
$\Delta H^\circ_{neut} = 2.09$ kJ/mol

Page No.
Date:

Eg:- $1\,CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\quad \Delta H^\circ_{comb} = -ve$

3) Heat of transition (ΔH°_{trans})
The heat absorbed or released during conversion of one allotropic form to another.

4) Heat of neutralization (ΔH°_{neut}) $\quad \Delta H^\circ_{neut} = -ve$.
:- Heat released when 1 gm equivalent of acid is neutralized by 1 gm equivalent of base

$H^+ + \bar{O}H \rightarrow H_2O$
Strong acid, Strong base

ΔH°_{neut} for SB & SA $= -13.7$ cal/mol $= -57.1$ kJ/mol

Learn ΔH°_{neut} :- (SA+SB) > (WA+SB) > (WA+WB)
WB = NH_4OH, SA → HCl, SB → NaOH, WA → CH_3COOH,

Q) 200 mL of 0.1 M H_2SO_4 is mixed with 150 mL of 0.2M KOH.
Find value of heat involved (in kJ)
nf = No. of H^+ ions

Ans H_2SO_4 (SA), KOH (SB)
gm equi of H_2SO_4 = Molarity × nf × Vol.
= 0.1 × 2 × 0.2L
= 0.04L
gm equi of KOH = Molarity × nf × Vol.
= 0.2 × 1 × 0.15
= 0.03L

1 gm equi releases -57.1 kJ/mol
30×10^{-3} gm eq → $-57.1 \times 30 \times 10^{-3}$

5) Heat of ionisation (or dissociation) [ΔH°_{diss} or $\Delta H^\circ_{ion} = +ve$]
Heat required for the diss of 1 mol of acid (or base)
$HA \rightarrow H^+ + A^-$ $\quad \Delta H^\circ_{diss}$
$\Delta H^\circ_{diss} \uparrow$, Weaker is acid

6) Enthalpy of Hydration (ΔH_{hyd}) :- (ΔH°_{hyd} = -ve)
Amount of heat released when a given anhydrous or partially hydrated salt combines with requisite amount of water to form a new hydrated salt.

- Case [1] for salt

(1) Anhydrous salt

$$CuSO_4(s) + 3H_2O_{(l)} \rightarrow CuSO_4 \cdot 3H_2O_{(s)}$$

(2) Partially Hydrated

$$CuSO_4 \cdot 3H_2O(s) + 2H_2O(l) \rightleftharpoons CuSO_4 \cdot 5H_2O(s)$$

- Case [2] for ion

$$Cl_{(g)} + aq \rightarrow Cl^-_{(aq)}$$

Note :- ΔH°_f of $H^+(aq) = 0$

So, $H^+(g) + aq \rightarrow H^+(aq)$

Eg - $CuSO_4 + 800H_2O \rightarrow CuSO_4 - ① \quad \Delta H = -68.74\ kJ/mol$

$CuSO_4 \cdot 5H_2O + 795H_2O \rightarrow CuSO_4 - ② \quad \Delta H = +10.125\ kJ/mol$

Subtracting ① from ②

$$CuSO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O(s)$$

$\Delta H_{hyd} = 10.125 - (-68.74)$ kJ/mol.

$= -78.87$ kJ/mol

7) Heat of solution (ΔH°_{sol})

Heat absorbed or released when one mole of substance is dissolved in water.

$$KCl(s) + aq \rightarrow KCl(aq)$$

→ A solute is transferred from a solute phase (solid, liquid or gas) to a solvent or solution phase

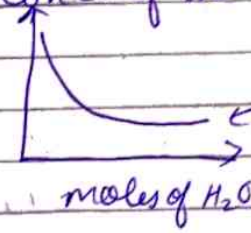
(ΔH°_{dil})

8) Heat of dilution :- Amount of heat released or absorbed when a solution containing 1 mol of a solution dilutes from one conc to other.

- solvent is transferred from pure solvent phase to soln phase.
- Amount of heat absorbed/released depends on nature of solute, solvent and concentration of soln

Eg :- Heat of soln
$KCl(s) + 50H_2O \rightarrow KCl(50H_2O)$ $\Delta H = +17.5$ kJ
$KCl(s) + 200H_2O \rightarrow KCl(200H_2O)$ $\Delta H = +18.5$ kJ

- Infinite dilution :- a soln contains so much solvent that if one adds more solvent to it, there will be no change in conc. of solution. (Heat change becomes constant)



Eg (Heat of dilution) :- $HCl(40H_2O) + aq \rightarrow HCl(aq)$ $\Delta H = ?$
$HCl(g) + aq \rightarrow HCl(aq)$ $\Delta H_1 = -75.145$ kJ/mol
$HCl(g) + 40H_2O \rightarrow HCl \cdot 40H_2O$ $\Delta H_2 = -73.023$ kJ/mol

On subtraction.
$HCl \cdot 40H_2O + aq \rightarrow HCl(aq)$ $\Delta H = -75.145 + 73.023$
$= -2.122$ kJ/mol

★ Calculation of $\Delta_r H^\circ$ when $\Delta_f H^\circ$ given.

$\alpha A + \beta B \rightarrow \gamma C + \delta D$ $\Delta_r H^\circ$

$\Delta_r H^\circ = [\gamma \Delta_f H^\circ(C) + \delta \Delta_f H^\circ(D)] - [\alpha \Delta_f H^\circ(A) + \beta \Delta_f H^\circ(B)]$

Q Find $\Delta_r H^\circ$ for Rxn.
$ZnO + CO \rightarrow Zn + CO_2$

$\Delta_f H^\circ$
$ZnO = -250$
$CO_2 = -390$
$CO = -110$

Ans $\Delta_r H^\circ = 1 \times 0 + 1 \times (-390) - [1 \times -250 + (1 \times -110)]$
$= -30$ kJ/mol

Page No.
Date

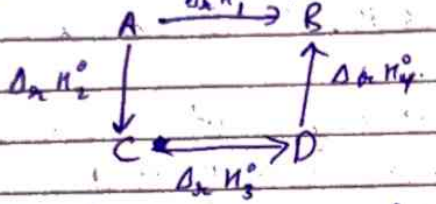
Q ΔH_f° $CO_2 = -393.5$, $H_2O = -241.8$ kJ/mol.
$CO = -110.5$

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$

Ans. ΔH_f° of $H_2(g) = 0$.

$\Delta_r H^\circ = 1 \times (-110.5) + 1 \times (-241.8) - [0 + 1 \times -393.5$

* Hess Law :- The total heat content of a Rxn is same whether Rxn is carried out by direct or indirect path.



$[\Delta_r H_1^\circ = \Delta_r H_2^\circ + \Delta_r H_3^\circ + \Delta_r H_4^\circ]$

$\Delta H^\circ = \sum \Delta H_n^\circ$ [ΔH° = heat absorbed/released
$\sum \Delta H_n$ = sum of heat absorbed/released in individual steps]

① $A \rightarrow B$ $\Delta_r H_1^\circ$
$B \rightarrow A$ $\Delta_r H_2^\circ = -\Delta_r H_1^\circ$

② $A \rightarrow B$ $\Delta_r H_1^\circ$
$aA \rightarrow aB$ $\Delta_r H_2^\circ = a \times \Delta_r H_1^\circ$

③ $A \rightarrow B$ $\Delta_r H_1^\circ$
$C \rightarrow D$ $\Delta_r H_2^\circ$
$A + C \rightarrow B + D$, $\Delta_r H_3^\circ = \Delta_r H_1^\circ + \Delta_r H_2^\circ$
$A + D \rightarrow B + C$, $\Delta_r H_4^\circ = \Delta_r H_1^\circ + (-\Delta_r H_2^\circ)$

Q $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ - ① $\Delta_r H_1^\circ = -27$ kJ
$FeO + CO \rightarrow Fe + CO_2$ - ② $\Delta_r H_2^\circ = -16.5$ kJ
Find ΔH_f or $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

Ans $\Delta_r H_3^\circ = \Delta_r H_1^\circ + (-2\ \Delta_r H_2^\circ)$ FeO ko palatkr 2 se multiply kiya hai
$= -27$ kJ $+ 2 \times 16.5$
$= 8.5$ kJ.

BrF_3.

Page No.
Date:

Q	Rxn	$\Delta_r H$ (kJ/mol
①	$\frac{1}{2}A \rightarrow B$	+150.
②	$3B \rightarrow 2C + D$.	−125
③	$A + E \rightarrow 2D$.	+350

Find ΔH for $B + D \rightarrow E + 2C$ - ④

Ans $-\frac{1}{2}$ ① + ② + ③

$\Delta_r H^\circ_4 = 150 \times 2 - 125 - 350$

$= -175$.

Q ① $C_{graphite} + O_2 \rightarrow CO_2$ $\Delta_r H^\circ = x$ kJ/mol.

② $C_{graphite} + \frac{1}{2} O_2 \rightarrow CO_2(g)$ $\Delta_r H^\circ = y$ kJ/mol

③ $CO + \frac{1}{2} O_2 \rightarrow CO_2$ $\Delta_r H^\circ = z$ kJ/mol.

Ans From ① & ② find ③

$x - y = z$

Q $C_{graphite} + O_2 \rightarrow CO_2$ $\Delta_r H = -393.5$ kJ/mol

$H_2 + \frac{1}{2} H_2 \rightarrow H_2O$ $\Delta_r H = -285.8$ kJ/mol.

$CO_2 + 2H_2O \longrightarrow CH_4 + 2O_2$ $\Delta_r H = +890.3$ kJ/mol.

Value of $\Delta_r H^\circ$ at 298 K.

$C_{graphite} + 2H_2 \longrightarrow CH_4(g)$

Ans $\Delta_r H^\circ = -393.5 + 2(-285.8) + 890.3$

+ Kirchoff's law :- It describes the enthalpy of a rxn's variation with temp changes. Enthalpy of a substance increases with temp, which means both products & reactants enthalpy increase

Page No
Date

At constant Pressure:

$(\Delta H)_{T_2} - (\Delta H)_{T_1} = \Delta C_p (T_2 - T_1)$

At constant Volume:

$(\Delta U)_{T_2} - (\Delta U)_{T_1} = \Delta C_v (T_2 - T_1)$

$\gamma = \frac{C_p}{C_v}$, $\Delta C_p = (C_p)_{Product} - (C_p)_{Reactant}$

Q Find ΔH at 400 K for

$\frac{1}{2}N_2 + O_2 \rightarrow NO_2$ $\quad \Delta H_{300K} = -35$ kJ/mol

	C_p (J/K mol)
NO_2	35
N_2	30
O_2	30

Thus $(\Delta H)_{400} - (\Delta H)_{300} = \Delta C_p (T_2 - T_1)$

$(\Delta H)_{400} + 35$ kJ/mol $= \left[35 - \frac{1}{2} \times 30 - 30\right](400 - 300)$

$(\Delta H)_{400} = -4000 + 3000 - 3500$

$(\Delta H)_{400} = -36000$

* Determination of lattice energy (Born-Haber cycle)

Lattice energy is defined as energy released when no. of +ve & -ve ions combine to form one mole of ionic compound.

↑ Lattice energy, ↑ Stable Ionic compounds ↑

* Adiabatic flame temp:-

The max. temp attained by the flame zone due to the heat liberated during combustion of fuel under adiabatic condition at constant pressure is called maximum flame temp. (Isobaric)

$\Delta H = \Delta C_p (T_f - T_i)$ $\quad \Delta C_p = C_p$ (products)

$T_f - T_i = \frac{|\Delta H|}{\Delta C_p}$

$T_f = T_i + \frac{|\Delta H|}{\Delta C_p}$ $\quad T_f$ = Max temp

For constant volume

$$|\Delta U| = \Delta C_v (T_f - T_i) \qquad T_f = \text{Max explosion temp.}$$

$$T_f = T_i + \frac{|\Delta U|}{\Delta C_v}$$

→ If compound is burnt in air & each mole of oxygen is associated with 4 moles of nitrogen and hence these will be raised to final temp.

~~ΔC_p = sum of C_ps of products + $C_p N_2$~~

ΔC_p = sum of C_p of products + C_p of 4 moles of unreacted N_2 per mole of O_2

$$\Delta C_p = \Sigma C_{p\,\text{products}} + 4 C_p N_2$$