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NAAC ACCREDITED ‘A’ GRADE

Topic:	Thermochemistry
Course Title:	General Physical Chemistry
Paper:	BCMA CC3
Unit:	Biophysical Properties
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Name of the Department:	Biochemistry

⇒ Relation between H and U of a reaction:

$$\Delta_r H = \sum_B \nu_B H_m(B)$$

And we know, $H_m = U_m + pV_m$

$$\therefore \Delta_r H = \sum_B \nu_B [U_m(B) + (pV_m)_B]$$

$$= \sum_B \nu_B U_m(B) + \sum_B \nu_B (pV_m)_B$$

→ For a solid or liquid, $pV_m \approx 0$ for 1 mole

→ For 1 mole of an ideal gas,

$$pV_m = RT$$

$$\therefore \Delta_r H = \sum_B \nu_B U_m(B) + \sum_B \nu_B (RT)$$

$$\Rightarrow \boxed{\Delta_r H = \Delta_r U + (\Delta \nu_g) RT},$$

Where $\Delta \nu_g$ → change in stoichiometric no. of the gaseous species,

→ $\Delta \nu_g = 0$ for solids / liquids.

e.g. $\Delta_r H = -52 \text{ kJ mol}^{-1}$ at 373 K for the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightarrow HBr(g)$

$\Delta_r U$ at 373 K ??

$$\Delta_r H = \Delta_r U + (\Delta \nu_g) RT$$

$$\Rightarrow \Delta_r U = \Delta_r H - (\Delta \nu_g) RT = -52 - (1 - \tfrac{1}{2} - \tfrac{1}{2}) RT$$

$$= -52 \text{ kJ mol}^{-1}$$

⇒ Born-Haber cycle:

Used for the calculation of Lattice Energy. Lattice energy can be defined as the energy required to disintegrate 1 mole of a crystalline substance into its gaseous ions.

e.g. let us consider the formation of Na^+Cl^- crystal from its constituent elements Na & Cl.

→ The steps involved are:

	Energy
① Vaporization of Na(s) : $Na(s) \rightarrow Na(g)$	$\Delta_r H_1$
② Ionization of Na(g) : $Na(g) \rightarrow Na^+(g) + e$	$\Delta_r H_2$
③ Dissociation of $Cl_2(g)$: $\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ (since we need only 1 Cl atom)	$\Delta_r H_3$
④ Formation of $Cl^-(g)$: $Cl(g) + e \rightarrow Cl^-(g)$	$\Delta_r H_4$
⑤ ~~Formation~~ Condensation of $Na^+(g)$ and $Cl^-(g)$ $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	$\Delta_r H_5$

Net reaction: $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$ $\Delta_r H_6$
(adding 1+2+3+4+5)

According to Hess' law:

$$\Delta_r H_6 = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4 + \Delta_r H_5$$

∴ lattice energy

$$\Delta_r H_5 = \Delta_r H_6 - [\Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4]$$

$\Delta_r H_6$ = Enthalpy of formation i.e. $\Delta_f H^\circ$
$\Delta_r H_1$ = Enthalpy of sublimation i.e. $\Delta_{sub} H^\circ$
$\Delta_r H_2$ = Ionization enthalpy i.e. I.E / I.P.
$\Delta_r H_3$ = Dissociation enthalpy i.e. $\Delta_{diss} H^\circ$

$\Delta_r H_4$ = Electron affinity i.e. E.A.

[Note that the signs must be maintained for evaluating the correct value of $\Delta_r H_5$.
e.g, Electron affinity of Cl is generally negative and ionization potential of Na is positive]

⇒ Example problem:
Evaluate the lattice energy of NaCl from the given data:

$\Delta_f H^\circ (NaCl) = -410 \, kJ \, mol^{-1}$
I.E. of Na(g) = $495 \, kJ \, mol^{-1}$
E.A. of Cl(g) = $365 \, kJ \, mol^{-1}$
$\Delta_{sub} H^\circ (Na) = 317 \, kJ \, mol^{-1}$
$\Delta_{diss} H(Cl) = 241 \, kJ \, mol^{-1}$

$$\Delta_r H_5 = \Delta_r H_6 - [\Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4]$$

Now, $\Delta_r H_6 = -410 \text{ kJ mol}^{-1}$

$\Delta_r H_1 =$ ~~495 kJ mol^{-1}~~ 317 kJ mol^{-1}

$\Delta_r H_2 = 495 \text{ kJ mol}^{-1}$

$\Delta_r H_3 = \left(\frac{241}{2}\right) \text{ kJ mol}^{-1}$ [since we need 1 Cl atom to make 1 NaCl]

$\Delta_r H_4 = -365 \text{ kJ mol}^{-1}$ [since E.A. of Cl is negative]

$$\therefore \Delta_r H_5 = \left(-410 - 317 - 495 - \frac{241}{2} + 365\right) \text{ kJ mol}^{-1}$$

= answer.