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NAAC ACCREDITED ‘A’ GRADE

Topic:	Thermochemistry
Course Title:	General Physical Chemistry
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Thermochemistry:

→ Deals with the transfer of heat between a chemical system and its surroundings when a change of phase or chemical reaction occurs.

→ Since most chemical reactions are carried out under constant pressure (p) conditions, the heat exchanged is equal to the change in enthalpy (H) of the system.

→ Molar enthalpy (H_m) is the enthalpy for 1 mole of a substance.

$$H_m = f(T, P)$$

H°_m = Standard molar enthalpy

Here the pressure dependence is removed by defining standard state of a substance at 1 bar pressure.

e.g. $H^\circ_m(H_2O, l, 273\,K)$ means the molar enthalpy of liquid water at 273 K and 1 bar pressure.

→ If the reactants and products are at the same T and p, the ΔH value gives the enthalpy change for the chemical reaction only.

→ $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

Progress of a reaction is defined as

$$\xi = \frac{\text{Total amount of reactants consumed}}{\text{Stoichiometric no. of reactant}}$$

or,

$$\xi = \frac{\text{Total amount of product formed}}{\text{Stoichiometric no. of product}}$$

→ Let n_0 be the initial amount of N_2O_5.

$\therefore H_{initial} = n_0 H_m(N_2O_5)$ at $\xi = 0$

	$2N_2O_5(g) \longrightarrow$	$4NO_2(g) +$	$O_2(g)$
initial	n_0	–	–
at ξ	$n_0 - 2\xi$	4ξ	ξ

Unit of ξ = mol

$$\therefore H_{final} = (n_0 - 2\xi) H_m(N_2O_5) + 4\xi H_m(NO_2) + \xi H_m(O_2)$$

$$\therefore \Delta H = H_{final} - H_{initial}$$

$$= -2\xi H_m(N_2O_5) + 4\xi H_m(NO_2) + \xi H_m(O_2)$$

$\therefore$ unit of ΔH = (unit of ξ)(unit of H_m)

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

→ Enthalpy of a reaction $= \cancel{\frac{\Delta_r H}{\xi}}$

$$\Delta_r H = \frac{\Delta H}{\xi}$$

$\therefore$ for the above reaction,

$$\Delta_r H = -2H_m(N_2O_5) + 4H_m(NO_2) + H_m(O_2)$$

$\therefore$ Unit of $\Delta_r H$ = kJ mol^{-1}

→ $\Delta_r H$ considers the entire chemical equation for its evaluation.

→ $\Delta_r H$ is the difference of enthalpy between the reactants and products for the entire chemical reaction.

$$\therefore \Delta_r H = \sum_{\text{product}} \nu_B H_m(B) - \sum_{\text{reactants}} \nu_B H_m(B)$$

ν_B → Stoichiometric number in the equation

$H_m(B)$ → molar enthalpy of species B

→ Endothermic reactions have $\Delta_r H$ = positive
→ Exothermic " " $\Delta_r H$ = negative

→ Let us consider a chemical reaction

$$A + B \rightarrow C + D$$

This can be written as

$$0 = C + D - A - B$$

$$\text{i.e. } \boxed{0 = \sum_{B} \nu_B B}$$

ν_B → Stoichiometric no. of species B.

ν_B = negative for reactants
= positive for products

→ For the same previous reaction:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

We can write,

$$0 = 4NO_2(g) + O_2(g) - 2N_2O_5(g)$$

If $(n_B)_0$ be the initial amount of any species B in the reaction, and n_B be the amount after the reaction has progressed by ξ, we can write

$$n_B = (n_B)_0 + \nu_B \xi$$

$$\Rightarrow n_B - (n_B)_0 = \nu_B \xi$$

[Note that for reactants $(n_B)_0 > n_B$
for products $n_B > (n_B)_0$]

$$\therefore \boxed{dn_B = \nu_B \xi}$$

$$\therefore dH = \sum_B H_m(B)\, dn_B$$

$$= \sum_B H_m(B)(\nu_B\, d\xi)$$

$$\therefore \Delta_r H = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} = \sum_B \nu_B H_m(B)$$

i.e. enthalpy of a reaction $(\Delta_r H)$ is the rate of change of enthalpy of a system with the extent of a reaction (ξ) at constant T and p.

→ Enthalpy of a reaction : $\Delta_r H$

→ Standard enthalpy of a reaction : $\Delta_r H^\circ$

$$\Delta_r H^\circ = \left(\frac{\partial H^\circ}{\partial \xi}\right)_{T,p} = \sum_B \nu_B H_m^\circ(B)$$

→ Standard enthalpy of formation :

$$\Delta_f H^\circ$$

→ The standard enthalpy of formation of every element in its stable state of aggregation at 1 bar pressure and at a specified temperature is assigned a value of <u>zero</u>.

e.g. $\Delta_f H^\circ(O_2, g) = 0$

$\Delta_f H^\circ(C, \text{graphite}) = 0$.

→ The standard enthalpy of formation of a compound is the change in the standard enthalpy when 1 mole of the compound is formed from the requisite amount of its reactants in their stable states of aggregation.

e.g. $\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(l) \rightarrow HBr(g)$

$$\Delta_f H^\circ(HBr, g) = \sum_B \nu_B H_m^\circ(B)$$

$$= H_m^\circ(HBr, g) - \frac{1}{2} H_m^\circ(H_2, g)$$

$$- \frac{1}{2} H_m^\circ(Br_2, g)$$

e.g. $S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g)$

$$\Delta_f H^\circ(SO_2, g) = H_m^\circ(SO_2, g) - H_m^\circ(S, \text{rhombic})$$

$$- H_m^\circ(O_2, g)$$

e.g. $ZnO(s) + CO(g) \rightarrow Zn(s) + CO_2(g)$

If $\Delta_f H^\circ(ZnO, s) = -350 \text{ kJ mol}^{-1}$

$\Delta_f H^\circ(CO, g) = -110 \text{ kJ mol}^{-1}$

$\Delta_f H^\circ(CO_2, g) = -390 \text{ kJ mol}^{-1}$

then, $\Delta_r H^\circ = \sum_B \nu_B \Delta_f H^\circ(B)$

$$= \Delta_f H^\circ(Zn, s) + \Delta_f H^\circ(CO_2)$$

$$- \Delta_f H^\circ(ZnO, s) - \Delta_f H^\circ(CO, g)$$

[Note that $\Delta_f H^\circ(Zn, s) = 0$ as defined earlier]

→ Hess' Law of constant heat summation:

The heat involved in a given chemical equation is the same whether the process occurs in a single step or multiple steps.

→ Thus if a given chemical equation is reversed, the numerical value of $\Delta_r H$ remains the same but its sign changes. (Lavoisier & Laplace law)

→ Kirchoff's relation:

It gives the variation of enthalpy of a reaction with temperature (T).

For a general reaction:

$$aA + bB + \cdots = lL + mM + \cdots ,$$

we can write

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

$$= (l H_{m,L} + m H_{m,M} + \cdots)$$

$$- (a H_{m,A} + b H_{m,B} + \cdots)$$

$$\therefore \frac{\partial}{\partial T} \Delta_r H \Big|_p = \left\{ l \left(\frac{\partial H_{m,L}}{\partial T}\right)_p + m \left(\frac{\partial H_{m,M}}{\partial T}\right)_p + \cdots \right\}$$

$$- \left\{ a \left(\frac{\partial H_{m,A}}{\partial T}\right)_p + b \left(\frac{\partial H_{m,B}}{\partial T}\right)_p + \cdots \right\}$$

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

$$\therefore \left(\frac{\partial \Delta_r H}{\partial T}\right)_p = \left[l\, C_{p,m}(L) + m\, C_{p,m}(M) + \cdots\right] - \left[a\, C_{p,m}(A) + b\, C_{p,m}(B) + \cdots\right]$$

. . . . . Equation ①

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

$$\Rightarrow \left(\frac{\partial \Delta_r H}{\partial T}\right)_p = \sum_B \nu_B \left(\frac{\partial H_m(B)}{\partial T}\right)_p$$

$$= \sum_B \nu_B C_{p,m}(B)$$

$$= \Delta_r C_p.$$

$\therefore$ Equation ① reduces to

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

$$\therefore d(\Delta_r H) = \Delta_r C_p \, dT \quad \text{at const. } p.$$

$$\therefore \int d(\Delta_r H) = \int \Delta_r C_p \, dT$$

$$\Rightarrow \boxed{\Delta_r H = \int \Delta_r C_p \, dT + I},$$

where I = const. of integration.

⇒ This is Kirchhoff's relation. It has 2 possibilities.

① C_p does not depend on T.

$$\Rightarrow \Delta_r H = \Delta_r C_p (\Delta T) + I$$

i.e. $\Delta_r H_{T_2} - \Delta_r H_{T_1} = \Delta_r C_p (T_2 - T_1)$

② C_p depends on T.

$C_{p,m} = a' + b'T + c'T^2 + \ldots,$

where $a/b/c$ are constants.

$$\therefore \Delta_r C_p = (\Delta_r a') + (\Delta_r b')T + (\Delta_r c')T^2 + \ldots$$

Now, $\Delta_r H = I + \int \Delta_r C_p \, dT$.

$$\therefore \Delta_r H = I + \int \{ (\Delta_r a') + (\Delta_r b')T + (\Delta_r c')T^2 + \cdots \} dT$$

$$\Rightarrow \Delta_r H = I + \Delta_r a' T + \Delta_r b' \frac{T^2}{2} + \Delta_r c' \frac{T^3}{3} + \cdots$$

$\Rightarrow$ Unit of $\Delta_r H$ = k J mol^{-1}

Unit of $\Delta_r C_p$ = ~~k~~ J mol^{-1} K^{-1}

[Note that the constant I can be easily evaluated if we know the value of $\Delta_r H$ at a particular temperature say 298 K].