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Lecture .6

Special cases of the equation $\Delta \mathbf{H} = \Delta \mathbf{E} + \mathbf{P} \Delta \mathbf{V}$

1) Reactions involving gaseous substances

Where $(\mathbf{n}_R \neq \mathbf{n}_P)$ and in which the volume changes are large and cannot be neglected, and by imposing the behavior of gases ideally,

$$PV_{R} = n_{R} RT$$
$$PV_{P} = n_{p} RT$$

Where :

 n_R : Number of gas moles produced.

 $\mathbf{n}_{\mathbf{R}}$: Number of gas moles interacting (At constant pressure and temperature).

T : Temperature in kelvin (K).

 \mathbf{R} : The general Fixed of gases (8.314 J / K. Mole).

From the equation: $\Delta \mathbf{H} = \Delta \mathbf{E} + \mathbf{P} \Delta \mathbf{V}$

We will modify $P\Delta V$ as follows:

 $P\Delta V = P (V_P - V_R)$ $P\Delta V = P V_P - P V_R$ $P \Delta V = n_P RT - n_R RT$ $P \Delta V = RT (n_P - n_R)$ $P \Delta V = \Delta n_{(g)} RT$

Compensate the last equation in equation $\Delta H = \Delta E + P \Delta V$, therefore we get on :

$$\Delta \mathbf{H} = \Delta \mathbf{E} + \Delta \mathbf{n}_{(g)} \mathbf{R} \mathbf{T}$$

2) Reactions in which interacting and resulting gases are involved)

Where $(\mathbf{n}_{\mathbf{P}} = \mathbf{n}_{\mathbf{R}})$ and therefore the value of $\Delta \mathbf{n} = 0$

Then the equation: $\Delta \mathbf{H} = \Delta \mathbf{E} + \mathbf{P} \Delta \mathbf{V}$ From the equation: $\Delta \mathbf{H} = \Delta \mathbf{E} + \Delta \mathbf{n} \ \mathbf{RT}$ Since $\Delta \mathbf{n} = 0$ $\therefore \Delta \mathbf{H} = \Delta \mathbf{E}$

3) Reactions involving solid or liquid substances only (not involving gas substances):

In which the volume changes are small $\Delta V=0$ and therefore can be neglected, then

the equation: $\Delta \mathbf{H} = \Delta \mathbf{E} + \mathbf{P} \Delta \mathbf{V}$

since

$$\Delta \mathbf{n} = 0$$

$$\therefore \Delta \mathbf{H} = \Delta \mathbf{E}$$

Example :

Calculating the change in the internal energy of the reaction:

 $Zn_{(s)} + H_2 SO_{4(L)} ZnSO_{4(aq)} + H_{2(g)}$

If the released heat is 34200 Cal of zinc at (17 $^{\circ}$ C)

Note that (R = 2 Cal / mole .K)

Solution :

 $\Delta n = 1 - 0 = 1$

Applying the relationship $\Delta H = \Delta E + \Delta n RT$

 $\Delta \mathbf{E} = \Delta \mathbf{H} - \mathbf{n} \ \mathbf{R} \mathbf{T}$

 $\Delta E = [(-34200 \text{ Cal}) - (1x \ 2 \ x \ (17 + 273)]$

 $\Delta E = -34780 \text{ Cal}$

Example :

If the change in internal energy is equal to -333kJ for the following interaction:

 $NH_4Cl_{(aq)} + NaNO_2_{(aq)} \rightarrow N_2_{(g)} + 2H_2O_{(L)} + NaCl_{(aq)}$

When one mole of N_2 is produced, if the production of one mole of nitrogen makes the system increase by 22.4 L, at one air pressure. Calculate the change in the Enthalpy interaction?

Solution :

 $\Delta E = -333 \text{ X}10^{3} \text{ J}, \qquad P = 1 \text{ atom }, \Delta V = 22.4 \text{ L}$ $P \Delta V = 1 \text{ atom } \text{X} 22.4 \text{ L} = 22.4 \text{ L}. \text{ atom}$ 22.4 L. atom X 101.325 J / L. atom = 2269.68 JApplying the relationship: $\Delta H = \Delta E + P\Delta V$ $\Delta H = [(-333 \text{ x}10^{3}) + (1 \text{ x}22.4) 101.325]$ $\Delta H = -330730.88 \text{ J}$ $\Delta H = -330.73 \text{ kJ}$

Example :

If the heat associated with combustion of one molten gasoline is equal to(-3264.3) kJ at a fixed volume and temperature (298K), Calculate the change in the enthalpy of the reaction (Δ H), if you know that gasoline burns with oxygen equation: C₆H_{6 (L)} + 7.5 O_{2 (g)} \rightarrow 6CO₂ (g) + 3H₂O (L)

Note that the value of ($R = 8.314 \text{ J} / \text{mole} \cdot \text{K}$).

Solution :

The amount of heat at a fixed volume reflects the internal energy:

$$\begin{split} q_v &= \Delta E \\ \Delta E &= -3264.3 \ x \ 10^3 \ J \\ \Delta n &= n_p - n_R = 6 - 7.5 = -1.5 \\ \Delta H &= \Delta E + \Delta n \ RT \\ \Delta H &= (-3264.3 \ x 10^3 \ J \) + \ (-1.5 \ mole \ x \ 8.314 \ J \ / \ K. \ mole \ x \ 298 \ K) \\ \Delta H &= -3268016.358 \ J \\ \Delta H &= -3268.02 \ k J \end{split}$$