Thermodynamics

TOPICS COVERED

- Enthalpy (H)
- Relation between heat capacities

ENTHALPY OF A SYSTEM

Therefore, ***the total heat content of a system at*** **constant pressure is equivalent to the internal energy E plus the PV energy. This is called the Enthalpy** ***of the system and is represented by the symbol H.***

Thus enthalpy is defined by the equation :

$$H = E + PV \text{ --------(1)}$$

UNITS AND SIGN CONVENTIONS OF ENTHALPY

Since $\Delta H = H_2 - H_1$

ΔH *is positive if* $H_2 > H_1$ *and the process or reaction will be endothermic.*

ΔH *is negative if* $H_1 > H_2$ *and the reaction will be exothermic.*

In case of a chemical reaction carried in the laboratory in an open vessel,

$$\Delta H = H_{products} - H_{reactants} = q_p$$

The units of ΔH *are kilocalories (kcal) or kilojoules (kJ).*

CHANGE IN ENTHALPY

If Δ *H be the difference of enthalpy of a system in the final state (H2) and that in the initial state* (*H1*),

$$\Delta H = H2 - H1 \qquad ...(2)$$

Substituting the values of *H2 and H1, as from (1) and (2), we have*

$$\Delta H = (E2 + P2V2) - (E1 + P1V1)$$
$$= (E2 - E1) + (P2V2 - P1V1)$$
$$= \Delta E + \Delta PV$$

If *P is constant while the gas is expanding, we can write*

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

or $$\Delta H = \Delta E + w \; (w = work) \qquad ...(3)$$

According to the First Law,

$$\Delta E = q - w \qquad ...(4)$$

where *q = heat transferred*

From equations (3) and (4)

Δ*H = q when change in state occurs at constant pressure*

This relationship is usually written as $\mathbf{\Delta H = q_p}$

where subscript *p means constant pressure.*

Thus Δ *H can be measured by measuring the heat of a process occurring at constant pressure.*

RELATION BETWEEN ΔH AND ΔE

Calorific values of many gaseous fuels are determined in constant volume calorimeters. These values are, therefore, given by the expression

$$q_v = \Delta E$$

When any fuel is burnt in the open atmosphere, additional energy of expansion, positive or negative, against the atmosphere is also involved. The value of *q thus actually realised,* *i.e.,* $q_p = \Delta H$, may be different from the equation

$$\Delta H = \Delta E + P\Delta V \quad ...(1)$$

If gases are involved in a reaction, they account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison.

Suppose we have n_1 *moles of gases before reaction, and* n_2 *moles of gases after it. Assuming* ideal gas behaviour, we have

$$P V_2 = n_2 RT$$

$$P V_1 = n_1 RT$$

$$\therefore P (V_2 - V_1) = (n_2 - n_1) RT$$

$$\text{or } P\Delta V = \Delta n RT$$

Substituting in equation (1) we have,

$$\Delta H = \Delta E + \Delta n RT$$

For the reaction

$H_2F_2\ (g) \longrightarrow H_2(g) + F_2(g)$
$\Delta E = -14.2$ kcal/mole at 25º C. Calculate ΔH for the reaction.

SOLUTION

$$\Delta H = \Delta E + \Delta n RT$$
$$\Delta n = n_2 - n_1$$
Now $n_2 = 1 + 1 = 2$
$$n_1 = 1$$
$$n_2 - n_1 = 2 - 1 = 1$$

$$\Delta H = \Delta E + 1 \times 1.987 \times 298/1000$$
$$= -14.2 + 0.592$$
$$= \mathbf{-13.6\ kcal/mole}$$

References

Text Books

1. Atkins, P. W. & Paula, J. de ***Atkin's Physical Chemistry***10th Ed., Oxford University Press (2014).

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1. Castellan, G. W. ***Physical Chemistry***4th Ed. Narosa (2004).
2. Engel, T. & Reid, P. ***Physical Chemistry***3rd Ed. Pearson (2013).
3. Levine, I .N. ***Physical Chemistry***6th Ed., Tata Mc Graw Hill (2010)
4. Puri Sharma Pathania Physical Chemistry Book.


THANK YOU