

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,

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

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

CHANGE IN ENTHALPY

If ΔH be the difference of enthalpy of a system in the final state (H_2) and that in the initial state (H_1),

$$\Delta H = H_2 - H_1 \quad \dots(2)$$

Substituting the values of H_2 and H_1 , as from (1) and (2), we have

$$\begin{aligned}\Delta H &= (E_2 + P_2V_2) - (E_1 + P_1V_1) \\ &= (E_2 - E_1) + (P_2V_2 - P_1V_1) \\ &= \Delta E + \Delta PV\end{aligned}$$

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

$$\Delta H = \Delta E + P\Delta V$$

or
$$\Delta H = \Delta E + w \quad (w = \text{work}) \quad \dots(3)$$

According to the First Law,

$$\Delta E = q - w \quad \dots(4)$$

where $q = \text{heat transferred}$

From equations (3) and (4)

$\Delta H = q$ when change in state occurs at constant pressure

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

where subscript p means constant pressure.

Thus ΔH 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

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

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

$$P V_2 = n_2 RT$$

$$P V_1 = n_1 RT$$

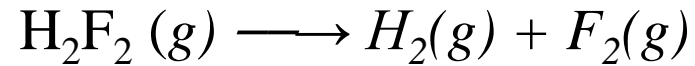
$$\therefore P (V_2 - V_1) = (n_2 - n_1) RT$$

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

Substituting in equation (1) we have,

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

For the reaction



$\Delta E = -14.2 \text{ kcal/mole}$ at 25°C . Calculate ΔH for the reaction.

SOLUTION

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

$$\Delta n = n_2 - n_1$$

Now $n_2 = 1 + 1 = 2$

$$n_1 = 1$$

$$n_2 - n_1 = 2 - 1 = 1$$

$$\Delta H = \Delta E + 1 \times 1.987 \times 298/1000$$

$$= -14.2 + 0.592$$

$$= -13.6 \text{ kcal/mole}$$

References

Text Books

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

Reference Books

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

