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Deg II Chem. Hons, Paper - III

Topic :- Thermodynamics

Kirchoff's equation :-

The heat change of any Process, whether Physical or chemical varies with the temperature. The exact influence of temperature can be worked out by applying the first law of Thermodynamics

Consider the following hypothetical reaction

$$A \longrightarrow B$$

where A represents one or more reactants and B one or more Products taking Place at Constant Pressure.

Let the reaction proceed at temperature T_1 when the heat change is ΔH_1. If the products represented by B are now brought to the temperature T_2 an amount of heat equal to $Cp'(T_2 - T_1)$ will be absorbed, Cp' being the mean molar heat Capacity of the products

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at Constant Pressure. The net heat change in the entire Process will be $\Delta H_1 + C_p'(T_2 - T_1)$ ✓

Let in another experiment the temperature of the reactants A be raised from T_1 to T_2. The heat absorbed now will be $C_p(T_2 - T_1)$ where C_p is the mean molar heat capacity of the reactants A, between T_1 and T_2 at Constant Pressure.

Let the reaction takes Place at the temperature T_2 when the heat of reaction is say ΔH_2. The net heat change during the entire process will now be

$\Delta H_2 + C_p(T_2 - T_1)$ ✓

In either Case, the reactants A at a temperature T_1 have Changed into Products B at a temperature T_2. Therefore, according to the first law of Thermodynamics the two energy changes should be equal

$$\Delta H_1 + C_p'(T_2 - T_1) = \Delta H_2 + C_p(T_2 - T_1)$$

or $$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = Cp' - Cp = \Delta Cp \quad (1)$$

when ΔCp is the differ-ences in the heat Capacity of the Products and the reactant's at Constant Pressure.

The change in the heat of a reaction at constant Pressure per degree change of temperature is given by the difference in the heat capacities of the products and the reactants at Constant Pressure.

This relationship was first worked out by Kirchoff and is Known as Kirchoff's equation.

If the reaction takes place at constant volume then

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = Cv' - Cv = \Delta Cv \quad (2)$$

where ΔCv is the differce in the heat Capacities of the products and reactants at Constant volume.