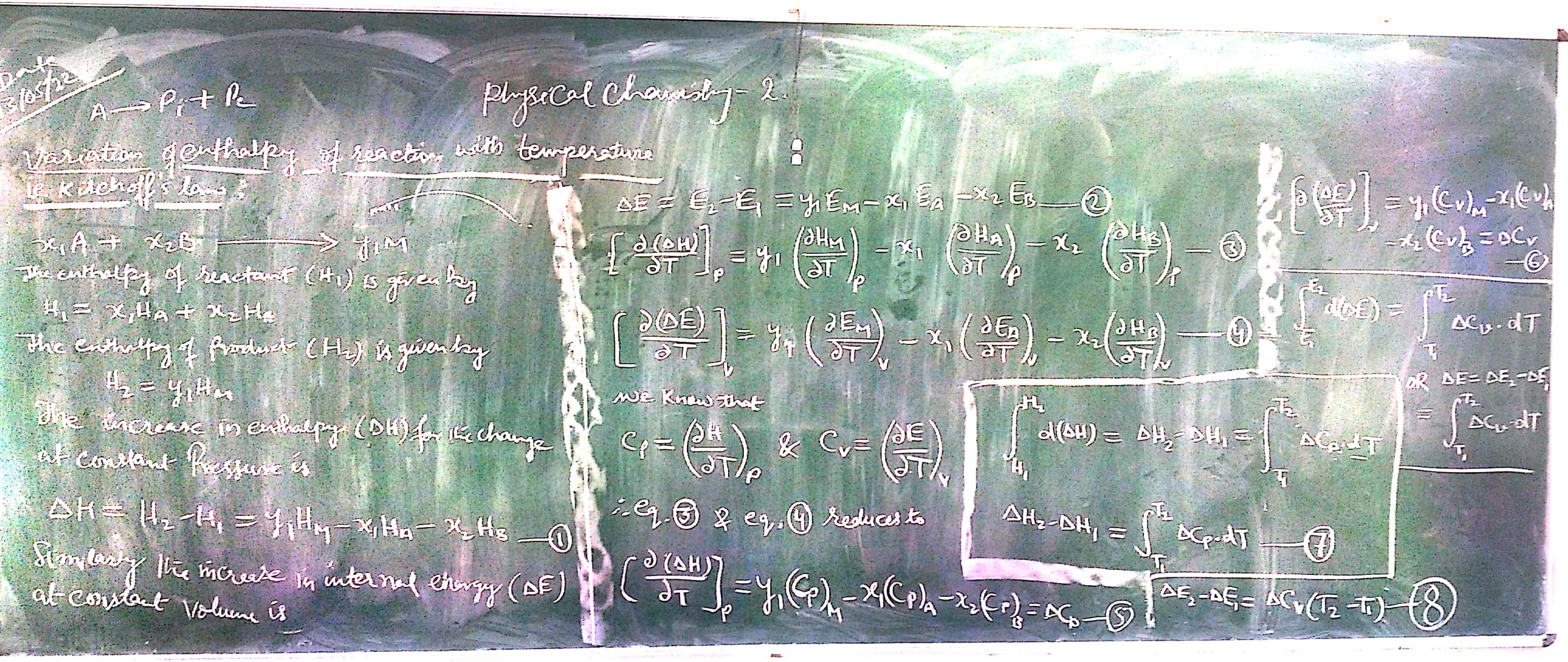

Date 3/05/22

$A \rightarrow P_1 + P_2$

Physical Chemistry - 2.

Variation of enthalpy of reaction with temperature i.e. Kirchhoff's law:

$$x_1 A + x_2 B \longrightarrow y_1 M$$

The enthalpy of reactant (H_1) is given by

$$H_1 = x_1 H_A + x_2 H_B$$

The enthalpy of product (H_2) is given by

$$H_2 = y_1 H_M$$

The increase in enthalpy (ΔH) for the change at constant Pressure is

$$\Delta H = H_2 - H_1 = y_1 H_M - x_1 H_A - x_2 H_B \text{ --- } ①$$

Similarly the increase in internal energy (ΔE) at constant Volume is

$$\Delta E = E_2 - E_1 = y_1 E_M - x_1 E_A - x_2 E_B \text{ --- } ②$$

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = y_1 \left(\frac{\partial H_M}{\partial T}\right)_p - x_1 \left(\frac{\partial H_A}{\partial T}\right)_p - x_2 \left(\frac{\partial H_B}{\partial T}\right)_p \text{ --- } ③$$

$$\left[\frac{\partial(\Delta E)}{\partial T}\right]_v = y_1 \left(\frac{\partial E_M}{\partial T}\right)_v - x_1 \left(\frac{\partial E_A}{\partial T}\right)_v - x_2 \left(\frac{\partial H_B}{\partial T}\right)_v \text{ --- } ④$$

We know that

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \& \quad C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

∴ eq. ③ & eq. ④ reduces to

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = y_1 (C_p)_M - x_1 (C_p)_A - x_2 (C_p)_B = \Delta C_p \text{ --- } ⑤$$

$$\left[\frac{\partial(\Delta E)}{\partial T}\right]_v = y_1 (C_v)_M - x_1 (C_v)_A - x_2 (C_v)_B = \Delta C_v \text{ --- } ⑥$$

$$\int_{H_1}^{H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT \text{ --- } ⑦$$

$$\int_{E_1}^{E_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_v \cdot dT$$

OR $\Delta E = \Delta E_2 - \Delta E_1$

$$= \int_{T_1}^{T_2} \Delta C_v \cdot dT$$

$$\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1) \text{ --- } ⑧$$

Variation of Enthalpy of reaction with temperature i.e., Kirchoff's equation: Enthalpy of reaction, in general, varies with temperature and its variation with temperature can be deduced as follows:

Let x_1 moles of substance A react with x_2 moles of B to form y_1 moles of M, at a constant temperature, each substance being in a certain specific state. Thus,

$$x_1 A + x_2 B \longrightarrow y_1 M$$

The enthalpy of the reactants (H_1) is given by,

$$H_1 = x_1 H_A + x_2 H_B$$

The enthalpy of the products (H_2) is given by,

$$H_2 = y_1 H_M$$

The increase in enthalpy (ΔH) for the change at constant pressure is,

$$\Delta H = H_2 - H_1 = y_1 \overset{H_M}{\cancel{E_M}} - x_1 \overset{H_A}{\cancel{E_A}} - x_2 \overset{H_B}{\cancel{E_B}} \quad ①$$

Similarly, the increase in internal energy (ΔE) at constant volume is,

$$\Delta E = E_2 - E_1 = y_1 E_M - x_1 E_A - x_2 E_B \quad ②$$

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where 'E' terms represent the respective internal energy.

Differentiating eq. ① with respect to temperature at constant pressure and ~~eq.~~ differentiating eq. ② w.r.t temperature at constant volume, we get,

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = y_1\left(\frac{\partial H_M}{\partial T}\right)_p - x_1\left(\frac{\partial H_A}{\partial T}\right)_p - x_2\left(\frac{\partial H_B}{\partial T}\right)_p \quad \text{③}$$

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_V = y_1\left(\frac{\partial E_M}{\partial T}\right)_V - x_1\left(\frac{\partial E_A}{\partial T}\right)_V - x_2\left(\frac{\partial H_B}{\partial T}\right)_V \quad \text{④}$$

we know that,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \& \quad C_v = \left(\frac{\partial E}{\partial T}\right)_V$$

∴ eq. ③ & eq. ④ reduces to

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = y_1(C_p)_M - x_1(C_p)_A - x_2(C_p)_B = \Delta C_p \quad \text{⑤}$$

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_V = y_1(C_V)_M - x_1(C_v)_A - x_2(C_v)_B = \Delta C_v \quad \text{⑥}$$

where, ΔC_p and ΔC_v refer to overall changes in heat capacities in the reaction, i.e., refer to their algebraic sum. Expressions ⑤ & ⑥ are mathematical forms of Kirchoff's law and represents that Variations of heat Content and internal energy of the reactants & Products with temperature.

Integrating eq. ⑤ & ⑥ between proper limits, we have,

$$\int_{H_1}^{H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p . dT$$

Assuming ΔC_p to be independent of temperature, we get. ~~eqn ⑦~~ $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$ — ⑦

Where ΔH_2 and ΔH_1 are the enthalpies of reactions at Contant pressure at temperature T_2 & T_1, respectively.

Integrating equation ⑥ between proper limits, we get.

$$\int_{E_1}^{E_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_v . dT$$

$$\Delta E = \Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v . dT$$

Assuming ΔC_v to be independent of temperature, we get $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$ — ⑧

where ΔE_2 and ΔE_1 are the enthalpies of reaction at constant volume, at temperature T_2 and T_1, respectively.

Kirchoff's law is valid for physical and chemical Changes and is independent of nature ~~of~~ and complexity of the systems.