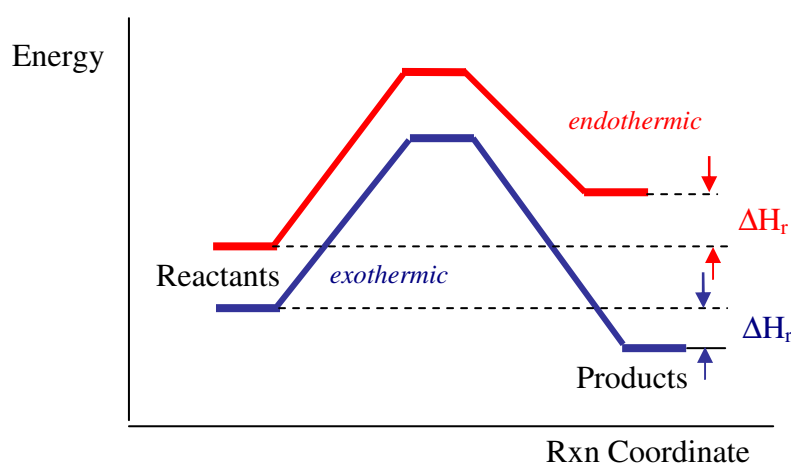


## THERMOCHEMISTRY

Thermochemistry deals with the amount of heat absorbed or emitted by the system during a chemical reaction. In chemical reactions, substances change their chemical structures. Some bonds are broken while some bonds are being formed. As



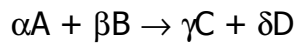
a result, sometimes the products of the reaction have lower energies than the reactants, in this case reaction system emits heat to the surroundings. We call such reactions "**exothermic**". Sometimes, the products have higher energies than the reactants, in this case the system absorbs heat from the surroundings and the reaction is called "**endothermic**".

The absorbed or emitted heat is called "**heat of reaction**". The heat of reaction is the heat absorbed/emitted from/to the surroundings in the transformation of the reactants at T and P to the products at the same T and P. Since P is constant;

$$Q_p = \Delta H_r$$

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heat of reaction is the change in enthalpy of the system due to chemical reaction at constant T and P. For a general reaction;



$$\begin{aligned}\Delta H &= H_{\text{final}} - H_{\text{initial}} = H_{\text{products}} - H_{\text{reactants}} \\ &= (\gamma \bar{H}_C + \delta \bar{H}_D) - (\alpha \bar{H}_A + \beta \bar{H}_B)\end{aligned}$$

$\bar{H}$  s are molar enthalpies of the substances at T and P. The absolute values of the molar enthalpies are unknown, they can not be measured. Molar enthalpy is a function of T and P;

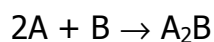
$$\bar{H} = \bar{H}(T, P)$$

In order to reduce the number of variables, P=1 atm is chosen as the Standard pressure. The molar enthalpy at 1 atm is the "Standard molar enthalpy" and designated by a zero superscript;

$$\bar{H}^\circ = \bar{H}(T, 1\text{atm})$$

For temperature t=25°C is chosen as the "reference temperature". Standard molar enthalpy at 25°C has a definite value. Since this value is unknown, Standard molar enthalpy for elements has been assumed to be zero at 25°C. The molar enthalpy of every element in its stable state at 1 atm pressure and 25°C is zero.

For compounds "**heat of formation**" is used instead of the molar enthalpy. In the formation reaction of a chemical compound, elements react to form 1 mole of the compound. The heat of reaction of the formation reaction at 1 atm pressure and 25°C is known as the "heat of formation" of the compound.



$$\Delta H_r = \bar{H}^o_{A_2B} - (2\bar{H}^o_A + \bar{H}^o_B)$$

Since A and B are elements in their stable states;

$$\bar{H}^o_A = \bar{H}^o_B = 0$$

$$\Delta H^o_f = \bar{H}^o_{A_2B}$$

Therefore, heat of formation is the standard molar enthalpy of the compound.

Heats of reaction are calculated by using heats of formation. For the general equation, we may write;

$$\begin{aligned} \Delta H_r &= H_{products} - H_{reactants} \\ &= (\gamma\Delta H^o_{f,C} + \delta\Delta H^o_{f,D}) - (\alpha\Delta H^o_{f,A} + \beta\Delta H^o_{f,B}) \end{aligned}$$

The unit for the heat of reaction is an energy unit only.

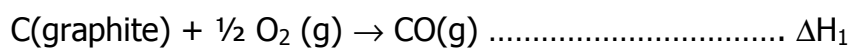
The heats of formation are measured calorimetrically. However, some formation reactions are unsuitable for calorimetric measurements. Either the reaction does not occur readily or the product is not pure, a mixture. In those cases, heats of combustion are used. "**Heat of combustion**" is the heat of the reaction in which 1 mole of the substance reacts with O<sub>2</sub>. The measurement of the heat of combustion is used to determine the heats of formation of all organic compounds which contain only carbon, oxygen and hydrogen.

### Hess's Law

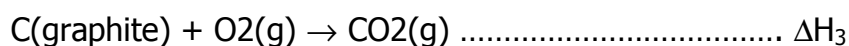
Heat of reaction is an enthalpy change. Since enthalpy is a state function, the change in enthalpy depends upon the initial and final states of the system. A chemical reaction can be carried out in different ways. If the reactants and the final

products are the same, the heat of reaction will be the same. It doesn't depend upon intermediate reactions.

In thermochemical calculations, chemical equations are considered as algebraic equations. They can be added, subtracted or multiplied by certain numbers. Heat of reaction does not depend upon the path between reactants and products.



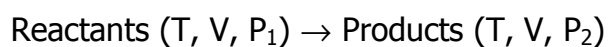
Net change:



$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

### Heat of Reaction at Constant Volume

For a constant volume case, the change may be shown as;



The final enthalpy is;

$$H_2 = E_2 + P_2V$$

And the initial enthalpy is;

$$H_1 = E_1 + P_1V$$

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Enthalpy change for the reaction may be written as;

$$\Delta H = H_2 - H_1 = (E_2 - E_1) + (P_2 - P_1)V$$

$$\Delta H = \Delta E + (P_2 - P_1)V$$

If the gases involving the reaction are assumed to be ideal;

$$P_1 = \frac{n_R RT}{V} \quad \text{and} \quad P_2 = \frac{n_P RT}{V}$$

$$\Delta H = \Delta E + \frac{RT}{V}(n_P - n_R)V$$

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

$\Delta H$  is the heat of reaction at constant pressure  $Q_P$ ;  $\Delta E$  is the heat of reaction at constant volume  $Q_V$ .

$$Q_P = Q_V + \Delta n R T$$