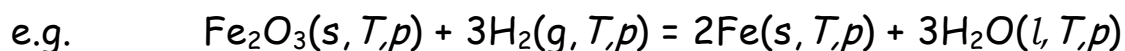


## Thermochemistry

- Goal: To predict  $\Delta H$  for every reaction, even if it cannot be carried out in the laboratory

The heat of reaction  $\Delta H_{rx}$  is the  $\Delta H$  for the *isothermal* reaction at constant pressure.



$$\Delta H_{rx}(T, p) = 2\bar{H}_{\text{Fe}}(T, p) + 3\bar{H}_{\text{H}_2\text{O}}(T, p) - 3\bar{H}_{\text{H}_2}(T, p) - \bar{H}_{\text{Fe}_2\text{O}_3}(T, p)$$

$$[\Delta H_{rx} = H(\text{products}) - H(\text{reactants})]$$

We cannot know  $\bar{H}$  values because enthalpy, like energy, is not an absolute scale. We can only measure differences in enthalpy.

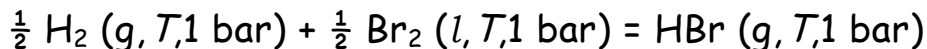
- Define a reference scale for enthalpy

$$\bar{H}(298.15\text{K}, 1\text{ bar}) \equiv 0 \quad \text{For every element in its most stable form at 1 bar and 298.15K}$$

e.g. 
$$\left. \begin{array}{l} \bar{H}_{\text{H}_2(g)}^\circ(298.15\text{K}) = 0 \\ \bar{H}_{\text{C(graphite)}}^\circ(298.15\text{K}) = 0 \end{array} \right\} \text{The "}\circ\text{" means 1 bar}$$

- $H_f^\circ(298.15\text{K})$ : We can now write reactions to form every compound from its constituent atoms. The heat of reaction is the heat of formation of 1 mole of that compound from the constituent elements in their most stable forms.

Example (let  $T = 298.15\text{ K}$ )



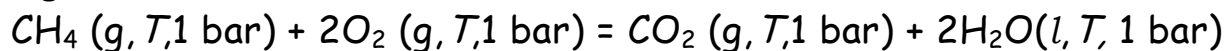
$$\Delta H_{rx} = \Delta \bar{H}_f^\circ (T) = \bar{H}_{\text{HBr}}^\circ (\text{g}, T) - \underbrace{\frac{1}{2} \bar{H}_{\text{H}_2}^\circ (\text{g}, T) - \frac{1}{2} \bar{H}_{\text{Br}_2}^\circ (\text{l}, T)}_{0 \text{ - elements in most stable forms}}$$

$$\therefore \Delta \bar{H}_f^\circ (T) = \bar{H}_{\text{HBr}}^\circ (\text{g}, T)$$

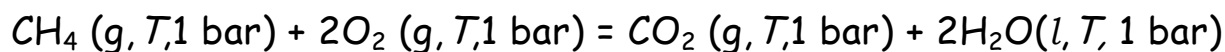
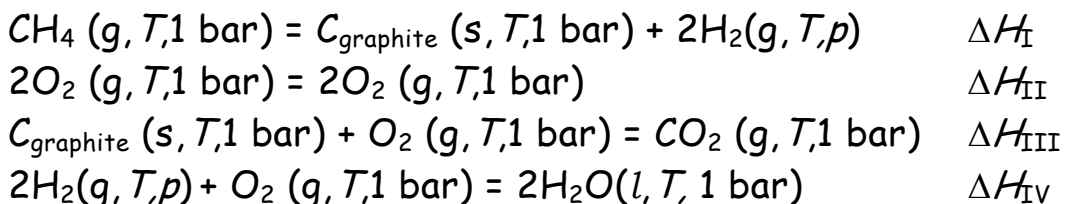
We can now tabulate  $\bar{H}_f^\circ (298.15\text{K})$  values for all known compounds.

We can calculate  $\bar{H}_{rx}^\circ (T)$  for any reaction ( $T = 298.15\text{K}$ ).

e.g.



- First decompose reactants into elements
- Second put elements together to form products
- Use Hess's law [A statement of the fact that because  $H$  is a function of state, we can add  $\Delta H$ 's around paths.]



$$\Delta H_{rx} = \Delta H_I + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV}$$

$$\Delta H_I = \bar{H}_C + 2\bar{H}_{H_2} - \bar{H}_{CH_4} = -\Delta H_{f,CH_4}^\circ$$

$$\Delta H_{II} = \bar{H}_{O_2} - \bar{H}_{O_2} = 0$$

$$\Delta H_{III} = \bar{H}_{CO_2} - \bar{H}_C - \bar{H}_{O_2} = \Delta H_{f,CO_2}^\circ$$

$$\Delta H_{IV} = 2\bar{H}_{H_2O} - 2\bar{H}_{H_2} - \bar{H}_{O_2} = 2\Delta H_{f,H_2O}^\circ$$

$$\therefore \Delta H_{rx} = 2\Delta H_{f,H_2O}^\circ + \Delta H_{f,CO_2}^\circ - \Delta H_{f,CH_4}^\circ$$

In general,

$$\Delta H_{rx} = \sum_i v_i \Delta H_{f,i}^\circ (\text{products}) - \sum_i v_i \Delta H_{f,i}^\circ (\text{reactants})$$

$v \equiv$  stoichiometric coefficient

- $\Delta H$  at constant  $p$  and for reversible process is  $\Delta H = q_p$

$\Rightarrow$  The heat of reaction is the heat flowing into the reaction from the surroundings

If  $\Delta H_{rx} < 0$ ,  $q_p < 0$  heat flows from the reaction to the surroundings (exothermic)

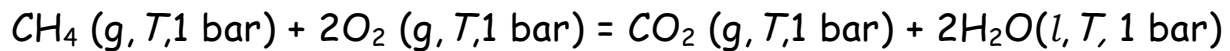
If  $\Delta H_{rx} > 0$ ,  $q_p > 0$  heat flows into the reaction from the surroundings (endothermic)

## Temperature dependence of $\Delta H_{rx}$

Recall 
$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

$$\therefore \left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p = \sum_i \nu_i C_{p,i}(\text{products}) - \sum_i \nu_i C_{p,i}(\text{reactants})$$

e.g.



$$\Delta C_p = \bar{C}_{p,\text{CO}_2}(\text{g}, T, 1 \text{ bar}) + 2\bar{C}_{p,\text{H}_2\text{O}}(\text{l}, T, 1 \text{ bar}) - \bar{C}_{p,\text{CH}_4}(\text{g}, T, 1 \text{ bar}) - 2\bar{C}_{p,\text{O}_2}(\text{g}, T, 1 \text{ bar})$$

$$\int_{T_1}^{T_2} \left(\frac{\partial \Delta H}{\partial T}\right)_p dT = \Delta H(T_2) - \Delta H(T_1)$$

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$\boxed{\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT}$$