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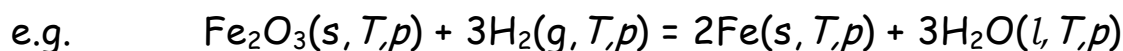
5.60 Thermodynamics & Kinetics
Spring 2008

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Thermochemistry

- Goal: To predict ΔH for every reaction, even if it cannot be carried out in the laboratory

The heat of reaction ΔH_{rx} is the ΔH for the *isothermal* reaction at constant pressure.



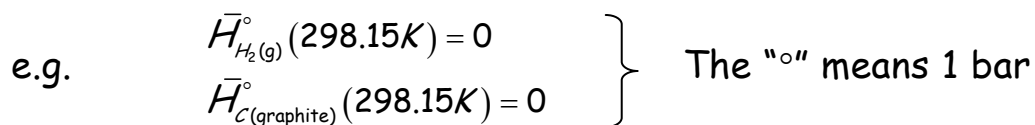
$$\Delta H_{rx}(T, p) = 2\bar{H}_{\text{Fe}}(T, p) + 3\bar{H}_{\text{H}_2\text{O}}(T, p) - 3\bar{H}_{\text{H}_2}(T, p) - \bar{H}_{\text{Fe}_2\text{O}_3}(T, p)$$

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

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

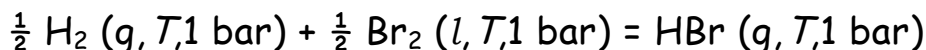
- Define a reference scale for enthalpy

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



- $\Delta H_f^\circ(298.15\text{K})$: 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 $T = 298.15 \text{ K}$)

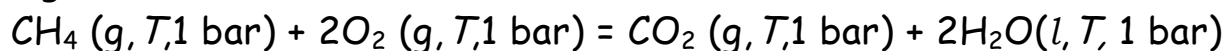


$$\begin{aligned} \Delta H_{rx} &= \Delta \bar{H}_f^\circ (\text{products}) - \Delta \bar{H}_f^\circ (\text{reactants}) \\ &= \Delta \bar{H}_{f, \text{HBr}}^\circ (\text{g}, T) - \underbrace{\left(\frac{1}{2} \Delta \bar{H}_{f, \text{H}_2}^\circ (\text{g}, T) + \frac{1}{2} \Delta \bar{H}_{f, \text{Br}_2}^\circ (\text{l}, T) \right)}_{0 - \text{elements in most stable forms}} = \Delta \bar{H}_{f, \text{HBr}}^\circ (\text{g}, T) \end{aligned}$$

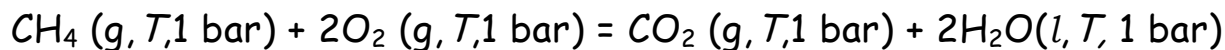
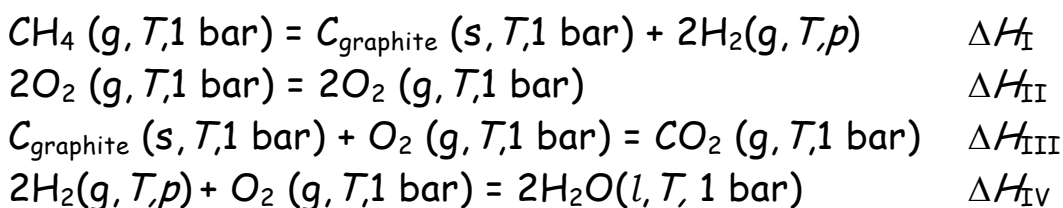
We can tabulate $\Delta \bar{H}_f^\circ (298.15 \text{ K})$ values for all known compounds.

We can calculate $\Delta \bar{H}_{rx}^\circ (T)$ 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 ΔH '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

- ΔH 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)

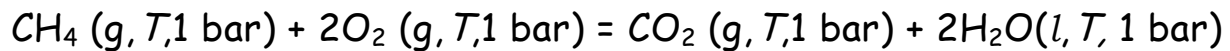
If $\Delta H_{rx} > 0$, $q_p > 0$ heat flows into the reaction from the surroundings (endothermic)

Temperature dependence of ΔH_{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.



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

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

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

Especially simple when ΔC_p is T -independent