

CHEM 20B Week 4

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Thermochemistry

Thermochemistry: study of heat transfer during chemical reactions.

- Chemical reactions are usually studied at constant pressure, heat transfers in reactions are measured at constant pressure

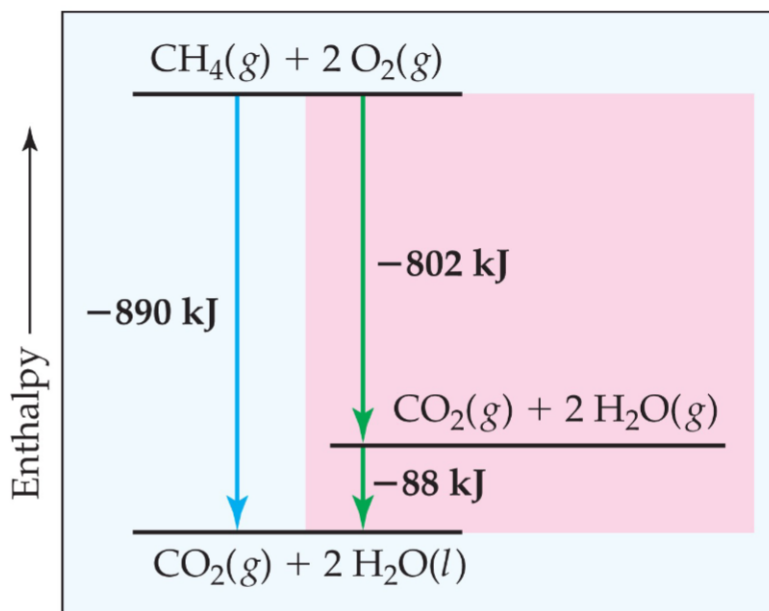
$$q_p = \Delta H = H_f - H_i = H_{products} - H_{reactants} = \Delta H_{reaction}$$

- $\Delta H_{reaction}$ is called the **reaction enthalpy**

- $\Delta H_{reaction} > 0$: endothermic
- $\Delta H_{reaction} < 0$: exothermic

Hess's Law

- If a reaction is carried out in a series of steps, ΔH for the reaction is the sum of ΔH for each of the steps.
- Enthalpy is a state function:
 - ΔH is sensitive to the states of the reactants and products
 - Depends on the amount of matter
- If a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps



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Standard Enthalpy of Formation ΔH_f^0

- The most useful thermochemical data are tables of the standard enthalpy of formation ΔH_f^0 for compounds, defined as the enthalpy of formation of a compound in its standard state from the elements in their standard states at **1 atm** and **298.15 K**.
- The enthalpy of each element at the standard state, in its most stable form at the standard state, is assigned to be zero.
- For example:
 - ΔH_f^0 (O₂ gas, 298K, 1atm) = 0
 - ΔH_f^0 (C, graphite, 298K, 1atm) = 0

- Enthalpy of formation of molecules is then defined as the enthalpy of reaction to make the molecules from their atomic ingredients in their stable form.

- For example:

$$\Delta H_f^0(H_2O(l)) \equiv \Delta H_{reaction} \left(H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), T = 298.15 \text{ K} \right) = -285.8 \frac{kJ}{mol}$$

- The change in standard state enthalpy for any reaction can be calculated from the standard state enthalpy of formation of its products and reactants as

$$\Delta H^0 = \sum_{i=1}^{prod} n_i \Delta H_i^0 - \sum_{j=1}^{react} n_j \Delta H_j^0$$

- For the general reaction of the form $aA + bB \rightarrow cC + dD$, the standard enthalpy change is:

$$\Delta H^0 = c\Delta H_f^0(C) + d\Delta H_f^0(D) - a\Delta H_f^0(A) - b\Delta H_f^0(B)$$

Reversible Processes in Ideal Gases - Isothermal processes:

- In this case, heat will flow (in either direction) to offset the cost of PV work, whereas T remains constant.

$$dw = -PdV$$
$$w = - \int_{V_1}^{V_2} PdV$$

- For an ideal gas, $P = nRT/V$. Because T is constant it comes outside the integral to give:

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$
$$w = -nRT \ln \left(\frac{V_2}{V_1} \right)$$
$$q = +nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta U = 0$$

$$\Delta H = 0$$