Lecture 6 b

Spring 2022

General Chemistry II

Chem 102

Thermochemistry

Cont.

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Hess's Law

On going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2\,(g) \quad \Delta H_1 = ???\ kJ$$

$$N_2(g) + O_2(g) \rightarrow 2NO\,(g) \quad \Delta H_2 = 180\ kJ$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2\,(g) \quad \Delta H_3 = -112\ kJ$$

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2\,(g) \quad \Delta H_1 = \Delta H_2 + \Delta H_3 = 68\ kJ$$

Factors affecting $\Delta_r H^o$

- quantities of reactants and products.
- physical state of reactants and products

$$H_2O(g) \rightarrow H_2(g) + {}^{1}/_{2}\,O_2(g) \quad \Delta H = 241.8\ \text{kJ}$$

$$H_2O(l) \rightarrow H_2(g) + {}^{1}/_{2}\,O_2(g) \quad \Delta H = 285.8\ \text{kJ}$$

- If a reaction is reversed, the sign of ΔH is also reversed.
- If the coefficients in a balanced reaction are multiplied by a factor, the value of ΔH is multiplied by the same factor.

Exercise

Consider the complete combustion of ethanol:

$$\mathbf{C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta_rH^o = ???}$$

Knowing that

$$2C(graphite) + 3H_2(g) + {}^{1}/_{2}\,O_2(g) \rightarrow C_2H_5OH(l) \quad \Delta H_f^o = -277.7kJ$$

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_f^o = -282.8\ kJ$$

Reverse the first equation and the sign of ΔH

$$C_2H_5OH(l) \rightarrow 2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H_f^o = 277.7kJ$$

$$C_2H_5OH(l) \rightarrow 2C(graphite) + 3H_2(g) + {}^{1}/_{2}\,O_2(g) \quad \Delta H_f^o = 277.7kJ$$

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ kJ$$ **×2**

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_f^o = -282.8\ kJ$$ **×3**

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta_r H^o = ????$$

$$\boldsymbol{\Delta_r H^o} = (1)277.7 - (2)393.5 - (3)282.8$$

$$= -21357.7\ kJ$$

Exercise

How much heat is required to decompose calcium carbonate to calcium oxide and carbon dioxide?

Knowing that ΔH^o_f (kJ/mol) of $CaCO_3$ (s) = – 1207.1, CaO (s) = – 635.5, CO_2 (g) = – 393.5

Solution

$$Ca\,CO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta_r H^o = ??\ kJ$$

$$\Delta_r H^o = \sum_{products} v\Delta_f H^o_m - \sum_{reac\tan ts} v\Delta_f H^o_m$$

$$\Delta_r H^o = (-635.5 - 393.5) - (-1207.1) = +178.1\ kJ$$

Alternatively

$$Ca\ (s) + C\ (s) + {}^{3}/_{2}\, O_2\ (g) \rightarrow Ca\,CO_3(s) \quad \Delta H_f^o = -1207.1\ kJ$$

$$Ca\ (s) + {}^{1}/_{2}\, O_2(g) \rightarrow CaO(s) \quad \Delta H_f^o = -635.5\ kJ$$

$$C\ (s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ kJ$$

$$Ca\,CO_3(s) \rightarrow CaO(s) + CO_2(g) \quad \Delta_r H^o = ??\ kJ$$

$$Ca\,CO_3(s) \rightarrow Ca\ (s) + C\ (s) + {}^{3}/_{2}\, O_2\ (g) \quad \Delta H_f^o = +1207.1\ kJ$$

$$Ca\ (s) + {}^{1}/_{2}\, O_2(g) \rightarrow CaO(s) \quad \Delta H_f^o = -635.5\ kJ$$

$$C\ (s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ kJ$$

$$\Delta_r H^o = (1207.1) + (-635.5) + (-393.5) -= +178.1\ kJ$$

Exercise

Calculate the enthalpy change of formation of methane from solid carbon and hydrogen gas using

$$C\,(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ \text{kJ}$$

$$H_2(g) + {}^{1}/_{2}\,O_2\,(g) \rightarrow H_2O(l) \quad \Delta H_f^o = -285.8\ \text{kJ}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ \Delta H_f^o = -890.3\ \text{kJ}$$

Solution

$$C\,(s) + 2H_2(g) \rightarrow CH_4(g)\Delta_r H^o = ???\ \text{kJ}$$

$$C\ (s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ kJ$$

$$2H_2(g) + O_2\ (g) \rightarrow 2H_2O(l) \quad \Delta H_f^o = -571.6\ kJ$$

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) \Delta H_f^o = 890.3\ kJ$$

$$C\ (s) + 2H_2(g) \rightarrow CH_4(g) \Delta_r H^o = ???\ kJ$$

$$\Delta_r H^o = (-393.5) + (-571.6) + (890.3) -= -74.8\ kJ$$

Significance of knowing $\Delta_r H^o$

- Identifying the direction of heat transfer.
  - At room temperature, most exothermic reactions are product-favored.
- The heat of combustion of fuels can be calculated
- Taking precautions to prevent exothermic reactions from over-heating and possible damages when reactions are carried out on a large scale.