Chapter 5 Part 3

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Internal Energy (U)

- Internal energy (U) is the sum of all kinds of energy present in a substance

$$\Delta U = q + w$$

  - ΔU is change in internal energy
  - q is heat
  - w is work

Internal energy

Heat Energy (q)

- q is positive when heat flows into the system (endothermic reaction)
- q is negative when heat flows out of the system (exothermic reaction)

Work (w)

- w is positive when the system has work done on it
- w is negative when the system does work on the surroundings

Internal Energy

A gas, while expanding, absorbs 25 J of heat and does 243 J of work. What is ΔU for the gas?

Internal Energy

Two gases, A(g) and B(g), are confined in a cylinder-and-piston arrangement. Gases A and B react to form a solid product C: A(g) + B(g) → C(s). As the reaction occurs, the system looses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

A. 1630 J
B. 670 J
C. −670 J
D. −1630J

Enthalpy (H)

- For processes that occur at a constant pressure, enthalpy is equal to heat
- For a chemical reaction:

$$\Delta H = \text{Energy of products} - \text{Energy of reactants}$$

- Enthalpy can be thought of as a measure of the thermal energy produced or absorbed by a chemical reaction
- If a reaction is endothermic, ΔH will be positive
- If a reaction is exothermic, ΔH will be negative

Burning Firewood

- If firewood is burned in the presence of oxygen gas, is thermal energy released or absorbed?

Burning Firewood

- If one increases the amount of firewood being burned, will the amount of thermal energy produced increase or stay the same?

Enthalpy as an extensive property

- Consider the following reaction:

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4;\ \Delta H = -385\ \text{kJ}$$

- When a chemical reaction is multiplied by a constant, the enthalpy change is also multiplied by that constant

$$3\,P_4O_{10} + 18\,H_2O \rightarrow 12\,H_3PO_4;\ \Delta H = 3(-385) = -1160\ \text{kJ}$$

$$\frac{1}{4}\,P_4O_{10} + \frac{3}{2}\,H_2O \rightarrow H_3PO_4;\ \Delta H = \frac{1}{4}(-385) = -96.3\ \text{kJ}$$

Enthalpy as an extensive property

- When the reactants and products in a chemical equation are reversed, the magnitude of ΔH is identical, by the sign of ΔH is reversed

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4;\ \Delta H = -385\ \text{kJ}$$

$$4\,H_3PO_4 \rightarrow P_4O_{10} + 6\,H_2O;\ \Delta H = +385\ \text{kJ}$$

State Functions

- State functions are functions that depend only on the state that a system is in and not the path to how that state was reached

State Functions

Examples of state functions	Examples path functions

- Altitude
- Enthalpy
- Entropy
- Free Energy

- Distance
- Heat
- Work

Hess's Law

- Hess's law states that if a process can be written as the sum of several stepwise processes. The enthalpy change of the total process equals the sum of the enthalpy changes of the various steps
- This is true because enthalpy is a state function

Hess's Law

Use Hess's Law to determine ΔH° for the reaction

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2\ (g), \text{ given that}$$

$$(1)\ C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -393\ kJ$$

$$(2)\ C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H^\circ = -110.\ kJ$$

Hess's Law

Use Hess's Law to determine ΔH° for the reaction

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2\ (g)\text{, given that}$$

$$(1)\ C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_1^{\circ} = -393\ \text{kJ}$$

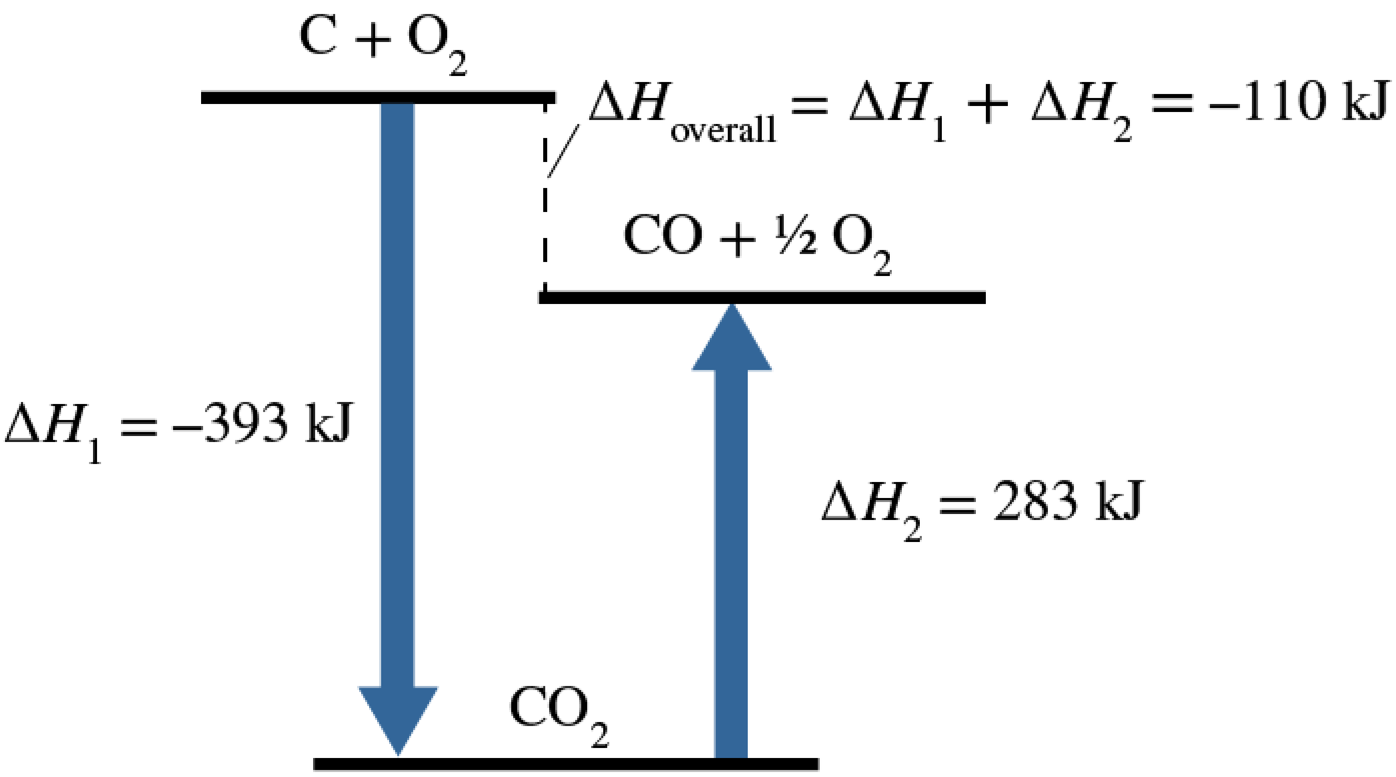
$$(2)\ C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H_2^{\circ} = -110.\ \text{kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_1^{\circ} = -393\ \text{kJ}$$

$$CO(g) \rightarrow C(s) + \frac{1}{2}O_2(g) \quad -\Delta H_2^{\circ} = 110.\ \text{kJ}$$

$$\Delta H_{rxn}^{\circ} = -393\ \text{kJ} + 110.\ \text{kJ} = -283\ \text{kJ}$$

Hess's Law



Hess's Law

Ammonia will burn in the presence of a platinum catalyst to produce nitric oxide, NO.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

What is the heat of reaction at constant pressure? Use the following thermochemical equations:

$$N_2 + O_2 \rightarrow 2NO;\ \Delta H = 180.6\ \text{kJ}$$

$$N_2 + 3H_2 \rightarrow 2NH_3;\ \Delta H = -91.8\ \text{kJ}$$

$$2H_2 + O_2 \rightarrow 2H_2O;\ \Delta H = -483.7\ \text{kJ}$$

Hess's Law

Given the following data

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H_1^\circ = -285.8 \text{ kJ}$$

$$C_3H_4(g) + 4\ O_2(g) \rightarrow 3\ CO_2(g) + 2\ H_2O\ (l) \qquad \Delta H_2^\circ = -1937 \text{ kJ}$$

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O\ (l) \qquad \Delta H_3^\circ = -2219.1 \text{ kJ}$$

Use Hess's Law to determine ΔH° for the reaction in kJ

$$C_3H_4(g) + 2H_2(g) \rightarrow C_3H_8(g)$$

Hess's Law

Determine

$$2\ N_2(g) + 5\ O_2(g) \rightarrow 2\ N_2O_5(g)$$

from these data

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O\ (l) \qquad \Delta H_1 = -571.66\ kJ$$

$$N_2O_5(g) + H_2O(l) \rightarrow 2\ HNO_3(g) \qquad \Delta H_2 = -92\ kJ$$

$$N_2(g) + 3\ O_2(g) + H_2(g) \rightarrow 2\ HNO_3(g) \qquad \Delta H_3 = -348.3\ kJ$$

Standard State Conditions (°)

- A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other conditions
- Standard states are denoted by a "°“ after the property symbol (H°)
- Since the enthalpy for a reaction varies with changes in experimental conditions such as temperature, pressure, and solution concentration, it is helpful to specify a standard state of conditions

Standard State Conditions (°)

- Standard state conditions
  - Gases, liquids, and solids must be in their pure form
  - Pressure is 1 bar
  - All solutions are 1 M
- Temperature for standard enthalpies are normally given at 25°C, but this is not a requirement

Standard Enthalpy of Formation

- Standard enthalpy of formation ($\Delta H_f°$) for a species is the enthalpy change of <u>one</u> mole of a species from its constituent elements in their most stable form

$$2\ N_{2(g)} + 5\ O_{2(g)} \rightarrow 2\ N_2O_5(s)$$

$$N_2(g) + \frac{5}{2}\ O_2(g) \rightarrow N_2O_5(s)$$

Standard Enthalpy of Formation

- Rules for standard heats of formation
  - $\Delta H_f°$ values have units of kJ/mol because each is the enthalpy change is for the formation of one mole of a chemical species.
  - The $\Delta H_f°$ value for an element in its standard state is equal to 0 kJ/mol.
  - Most $\Delta H_f°$ values are negative. This indicates that for most species, the formation from elements in their standard states is an exothermic process.

Standard enthalpies of reactions

Standard enthalpies of a reaction are the enthalpy change for a reaction under standard conditions and are found using the equation below

$$\Delta H^{\circ}_{rxn} = \sum \Delta H^{\circ}_{f}(\text{products}) - \sum \Delta H^{\circ}_{f}(\text{reactants})$$

Standard enthalpy of reaction

Hydrogen sulfide gas is a poisonous gas with the odor of rotten eggs. It occurs in natural gas and is produce during the decay of organic matter, which contains sulfur. The gas burns in oxygen as follows:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

Calculate the standard enthalpy change for this reaction using standard enthalpies of formation. The standard enthalpy of formation of H_2S, H_2O, and SO_2 are -20.50, -285.8, and -296.8 kJ/mol, respectively.

Standard enthalpy of reaction

The cooling effect of alcohol on the skin is due to its evaporation. Calculate the heat of vaporization of ethanol, C_2H_5OH.

$$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$$

The standard enthalpy of formation of $C_2H_5OH(l)$ is -277.7 kJ/mol and that of $C_2H_5OH(g)$ is -235.4 kJ/mol.

A. -277.7 kJ/mol
B. -235.4 kJ/mol
C. 42.3 kJ/mol
D. -42.3 kJ/mol