

Chapter 5

Thermochemistry

Chapter 5 suggested problems -

10th Ed.: 37, 39, 45, 49, 51, 61, 63, 67, 69, 71, 73, 75, 101

11th Ed.: 41, 43, 45, 49, 51, 61, 63, 67, 69, 71, 73, 101, 105

Class Notes

- I. Energy: the capacity to do work
 - A. The first law of thermodynamics - the conservation of energy: energy can neither be created nor destroyed in chemical reactions, although it can be transferred (heat, light) or transformed (from heat to light, etc.)
 - B. Potential energy: the energy a body has based on its position (gravitational potential energy)
 1. Chemical potential energy: energy stored in chemical bonds
 - C. Kinetic energy: energy associated with motion - translational, rotational, vibrational, spin
 - D. Internal energy: total energy, sum of potential and kinetic energies
 - E. Measured in calories and Joules ($4.184 \text{ J} = 1 \text{ cal}$)
- II. Thermodynamics 101 - four important thermodynamic values
 - A. During the course of a chemical reaction the internal energy changes
 1. $\Delta U = U_{\text{final}} - U_{\text{initial}}$
 2. $\Delta U = q + w = q - P\Delta V$
 3. Definitions
 - a. System: the part of the world in which we have an interest
 - b. Surroundings: everything else

- i. Open system: a system that can exchange matter and energy with the surroundings
 - ii. Closed system: a system that can exchange energy but not matter with the surroundings
 - iii. Isolated system: a system that cannot exchange either matter or energy with the surroundings
 - c. Work: a transfer of energy that can be used to the change the height of a weight somewhere in the surroundings
 - i. In chemical reactions most work is PV work (expansion work), work done by an expanding gas
 - d. Heat: a transfer of energy as a result of a temperature difference between the system and the surroundings
 - e. Given $\Delta U = q + w = q - P\Delta V$ work and heat are equivalent ways of the changing the internal energy of the system
 - f. Sign conventions
 - i. From system to surroundings: (-)
 - ii. From surroundings to system: (+)
- B. Enthalpy: in a system at constant pressure the heat associated changes in internal energy is called enthalpy
 - 1. $H = U + PV$
 - a. $H_i = U_i + PV_i$
 - b. $H_f = U_f + PV_f$
 - c. $\Delta H = H_f - H_i = (U_f - U_i) + P(V_f - V_i) = \Delta U + P\Delta V$
 - d. Since $\Delta U = q - P\Delta V$ in a system that does only PV work on its surroundings, then
 - e. $\Delta H = q + P\Delta V - P\Delta V = q$
 - f. Sign conventions
 - i. Exothermic (-) - heat flows from system to surroundings
 - ii. Endothermic (+) - heat flows from surroundings to system
 - g. Types of enthalpy (different processes that, at constant pressure, lead to changes in internal energy with consequent releases or absorbing of energy)

- i. Enthalpy of reaction
- ii. Enthalpy of formation
- iii. Enthalpy of physical change (phase change)
- iv. Enthalpy of ionization and enthalpy of electron gain

C. Gibbs Free Energy - the energy available to do useful work changes during the course of chemical reactions - depends on enthalpy, entropy, and temperature

- 1. $\Delta G = \Delta H - T\Delta S$
- 2. $-\Delta G =$ spontaneous reaction; $+\Delta G =$ nonspontaneous reaction
 - a. $S =$ entropy - a measure of disorder, usually increases during reactions (+) and is usually about 1% or less the size of ΔH
 - b. Usually: if $-\Delta H$ then $-\Delta G$; if $+\Delta H$, then $+\Delta G$

III. Enthalpy of reaction (heat of reaction or ΔH_{rxn})

A. General

- 1. Since $\Delta H_{\text{rxn}} = H_{\text{final}} - H_{\text{initial}}$, then $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$
- 2. Thermochemical equations: the coefficients of the balanced equation represent the number of moles of reactants and products producing the associated enthalpy change
 - a. $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \Rightarrow 2 \text{H}_2\text{O}(\text{g}); \Delta H_{\text{rxn}} = -483.6 \text{ kJ}$

B. The enthalpy of substances varies with their state of matter, it is essential that the state of each reactant and product be specified

C. Enthalpy is an extensive property - depends on the masses (the extent of the samples) involved in the reaction (as compared to intensive properties such as boiling point and melting point, which are independent of mass)

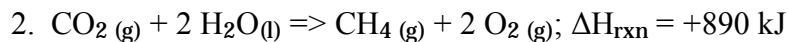
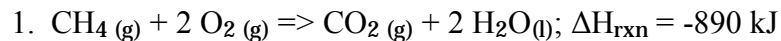
- 1. $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \Rightarrow 2 \text{H}_2\text{O}(\text{g}); \Delta H_{\text{rxn}} = -483.6 \text{ kJ}$
- 2. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \Rightarrow \text{H}_2\text{O}(\text{g}); \Delta H_{\text{rxn}} = -241.8 \text{ kJ}$
- 3. $20 \text{H}_2(\text{g}) + 10 \text{O}_2(\text{g}) \Rightarrow 20 \text{H}_2\text{O}(\text{g}); \Delta H_{\text{rxn}} = -4836 \text{ kJ}$
- 4. "Molar" enthalpy values and fractional coefficients

D. Enthalpy is an state function, i.e., the enthalpy change for a phase change or for a chemical reaction does not depend on the path taken from initial conditions to the final conditions

- 1. A path function depends on the way in which the final conditions are reached from the initial conditions

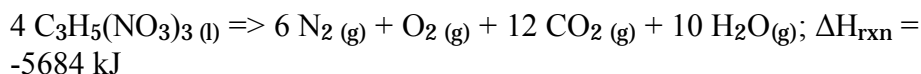
- The road to the top of Pike's Peak: elevation vs. the length of the road to the top

E. ΔH_{rxn} is equal in magnitude but opposite in sign for the reverse reaction



F. Stoichiometry

- Nitroglycerin (NG) is a powerful explosive that creates four different gaseous products when detonated:



Calculate the enthalpy of reaction when 10.0 g of NG is detonated:

$$(10.0 \text{ g NG}) \times (1 \text{ mol NG} / 227.1 \text{ g NG}) \times (-5684 \text{ kJ} / 4 \text{ mol NG}) = -62.6 \text{ kJ}$$

- Calculate the enthalpy of reaction for the combustion of 100.0 g of methane gas:

$$(100.0 \text{ g CH}_4) \times (1 \text{ mole CH}_4 / 16.04 \text{ g CH}_4) \times (-890 \text{ kJ} / \text{mole CH}_4) = -5549 \text{ kJ}$$

IV. Measuring enthalpy

A. Specific heat and heat capacity

- Specific heat: the amount of heat required to raise the temperature of 1.00 g of a substance by 1 K
- The greater the specific heat the more energy required to raise the temperature of a substance
 - The specific heats of solid aluminum, solid iron, and liquid water are 0.90 J/g·K, 0.45 J/g·K, and 4.18 J/g·K respectively. A 1.00 g sample of each substance is placed in identical glass test tube. The test tubes are immersed for 5 minutes in boiling water. At the end of the 5 minutes, the temperature of the three substances is measured. Which of the three will be the warmest? Which will be the coolest?
- Heat capacity: the amount of heat required to raise the temperature of a substance by 1 K
- Molar heat capacity: the amount of heat required to raise the temperature of 1 mole of a substance by 1 K

B. Calculating heat flow: $q = (SH) \times (m) \times (\Delta T)$

1. How much heat is required to raise the temperature of 250.0 g of liquid water from 22°C to a temperature of 100°C?

$$q = (4.18 \text{ J/g} \cdot \text{K}) \times (250.0 \text{ g}) \times (100^\circ\text{C} - 22^\circ\text{C} / 1 \text{ K} / 1^\circ\text{C}) = 81588 \text{ J} = 81.5 \text{ kJ}$$

2. An aluminum pan weighing 750.0 g is filled with boiling water. The pan is emptied and placed in a freezer until it reaches the ambient temperature of 0°C. How much heat does the pan emit?

$$q = (0.90 \text{ J/g} \cdot \text{K}) \times (750.0 \text{ g}) \times (-100 \text{ K}) = -67500 \text{ J} = -67.5 \text{ kJ}; \text{ since the heat is emitted the correct value is } -67.5 \text{ kJ}$$

C. Calorimetry (qualitative)

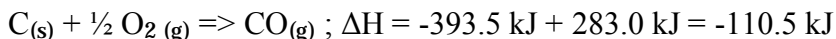
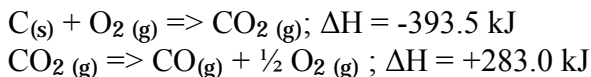
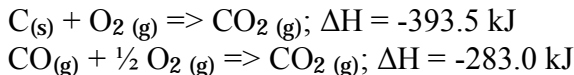
- V. Hess's Law: if a reaction can be written as the sum of a series of two or more reactions, the overall enthalpy of reaction is equal to the sum of the enthalpies of reactions for each member of the series

- A. $A + B \Rightarrow C + D$; $\Delta H_{\text{rxn}} = X \text{ kJ}$
 $C + D \Rightarrow E + F$; $\Delta H_{\text{rxn}} = Y \text{ kJ}$
 $E + F \Rightarrow G + H$; $\Delta H_{\text{rxn}} = Z \text{ kJ}$

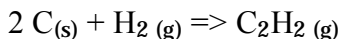
$$\text{overall: } A + B \Rightarrow G + H; \Delta H_{\text{rxn}} = X + Y + Z \text{ kJ}$$

- B. $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \Rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$; $\Delta H_{\text{rxn}} = -802 \text{ kJ}$
 $2 \text{H}_2\text{O}(\text{g}) \Rightarrow 2 \text{H}_2\text{O}(\text{l})$; $\Delta H_{\text{rxn}} = -88 \text{ kJ}$
 $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \Rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$; $\Delta H_{\text{rxn}} = -890 \text{ kJ}$

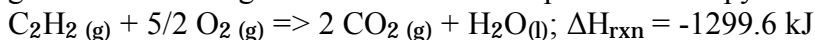
- C. The molar enthalpy of combustion of solid carbon to carbon dioxide gas is -393.5 kJ / mole of carbon and the molar enthalpy of combustion of carbon monoxide gas to carbon dioxide gas -283.0 kJ / mole of carbon monoxide. Using these data calculate the enthalpy change for the combustion of solid carbon to carbon monoxide.

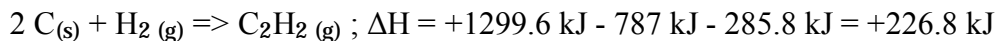
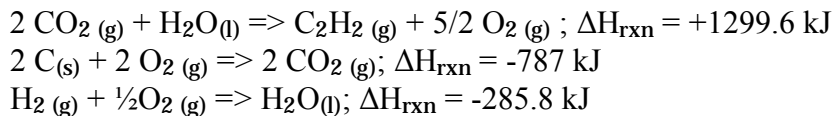
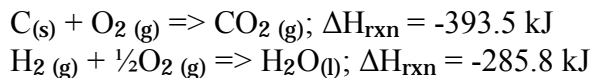


- D. Calculate ΔH for the reaction



given the following reactions and their respective enthalpy changes:





VI. Enthalpy of formation

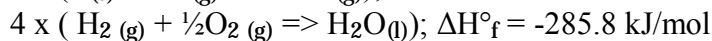
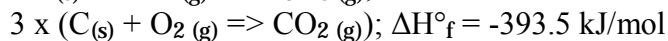
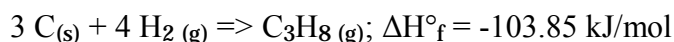
A. ΔH°_f for a compound is the enthalpy change for the reaction that forms one mole of the compound from its elements with all elements in their standard states

1. "°" indicates that calculations were made with the substances in their standard states
2. Usually 298 K and 1 atm
3. If an element exists in two or more forms under standard conditions the most stable form is used in the calculation of ΔH°_f
4. The stoichiometry is always for the formation of one mole of compound (product)
5. ΔH°_f are always in units of kJ/mol of substance formed
6. ΔH°_f of the most stable form of an element in the standard state is 0 kJ/mol; no formation reaction is needed if the element already exists in the standard state

B. Using Hess's Law if we know ΔH°_f for the participants in a reaction (all of the reactants and all of the products) we can calculate ΔH_{rxn}

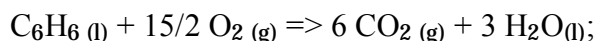
$$1. \Delta H^\circ_{\text{rxn}} = E(n)(\Delta H^\circ_{f \text{ prod}}) - E(n)(\Delta H^\circ_{f \text{ rxt}})$$

C. Examples



$$\Delta H^\circ_{\text{rxn}} = [(3 \text{ moles}) \times (-393.5 \text{ kJ/mol}) + (4 \text{ moles}) \times (-285.8 \text{ kJ/mol})] - [(1 \text{ mole}) \times (-103.85 \text{ kJ/mol})] = -2219.85 \text{ kJ}$$

2. Calculate the standard enthalpy change for the combustion of 1 mole of liquid benzene to carbon dioxide gas and liquid water.



$$\Delta H^{\circ}_{\text{rxn}} = [(6 \text{ moles}) \times (\Delta H^{\circ}_{\text{f}} \text{CO}_2 (\text{g})) + (3 \text{ moles}) \times (\Delta H^{\circ}_{\text{f}} \text{H}_2\text{O}(\text{l}))] - [(1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{C}_6\text{H}_6 (\text{l})) + (15/2 \text{ moles}) \times (\Delta H^{\circ}_{\text{f}} \text{O}_2 (\text{g}))]$$

$$\Delta H^{\circ}_{\text{rxn}} = [(6 \text{ moles}) \times (-393.5 \text{ kJ/mol}) + (3 \text{ moles}) \times (-285.8 \text{ kJ/mol})] - [(1 \text{ mole}) \times (+49.0 \text{ kJ/mol}) + (15/2 \text{ moles}) \times (0 \text{ kJ/mol})] = -3267 \text{ kJ}$$

3. The standard enthalpy change for the reaction



If the $\Delta H^{\circ}_{\text{f}}$ for solid calcium oxide is -635.5 kJ/mol and for carbon dioxide gas is -393.5 kJ/mol, what is the standard enthalpy of formation of solid calcium carbonate?

$$\Delta H^{\circ}_{\text{rxn}} = [(1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CaO}(\text{s})) + (1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CO}_2 (\text{g}))] - [(1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CaCO}_3 (\text{s}))]$$

$$[(1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CaCO}_3 (\text{s}))] = [(1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CaO}(\text{s})) + (1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CO}_2 (\text{g}))] - [(1 \text{ mole}) \times (\Delta H^{\circ}_{\text{f}} \text{CaCO}_3 (\text{s}))] - \Delta H^{\circ}_{\text{rxn}}$$

$$\Delta H^{\circ}_{\text{f}} \text{CaCO}_3 (\text{s}) = [(1 \text{ mole}) \times (-635.5 \text{ kJ/mol}) + (1 \text{ mole}) \times (-393.5 \text{ kJ/mol})] - [+178.1 \text{ kJ}] = -1207.1 \text{ kJ}$$

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