

Chapter Six Notes - Thermochemistry

6.1 The Nature of Energy

A. Definition

1. Energy is the capacity to do work (or to produce heat*)
 - a. Work is a force acting over a distance (moving an object)
 - b. *Heat is actually a form of energy.
 - (1) chemicals may store potential energy in their bonds that can be released as heat energy

B. Law of Conservation of Energy

1. Energy can be converted from one form to another, but cannot be created or destroyed
 - a. Potential energy
 - (1) energy due to position or composition
 - b. Kinetic energy
 - (1) energy due to the motion of an object

$$(2) \quad KE = \frac{1}{2} m v^2$$

C. Heat and Temperature

1. Temperature reflects random motion of particles in a substance
2. Temperature indicates the direction in which heat energy will flow
3. Heat is a measure of energy content
4. Heat is what is transferred during a temperature change

D. State Functions

1. A property of a system that depends only on its present state.
2. State functions do not depend on what has happened in the system, or what might happen in the system in the future
3. State functions are independent of the pathway taken to get to that state.

Example: a liter of water behind a dam has the same potential energy for work regardless of whether it flowed downhill to the dam, or was taken uphill to the dam in a bucket. The potential energy is a state function dependent only on the current position of the water, not on how the water got there.

E. Chemical Energy

1. Exothermic reactions
 - a. Reactions that give off energy as they progress
 - b. Some of the potential energy stored in the chemical bonds is converted to thermal energy (random KE) through heat
 - c. Products are generally more stable (stronger bonds) than reactants
2. Endothermic reactions
 - a. Reactions in which energy is absorbed from the surroundings
 - b. Energy flows into the system to increase the potential energy of the system

- c. Products are generally less stable (weaker bonds) than the reactants

F. Thermodynamics

1. System Energy

$$\Delta E = q + w$$

- a. q = heat

- (1) q is positive in endothermic reactions
- (2) q is negative in exothermic reactions

- b. w = work

- (1) w is negative if the system does work
- (2) w is positive if work is done on the system

2. Work done by gases

$$w = -P\Delta V$$

- a. by a gas (through expansion)

- (1) ΔV is positive
- (2) w is negative

- b. to a gas (by compression)

- (1) ΔV is negative
- (2) w is positive

6.2 Enthalpy and Calorimetry

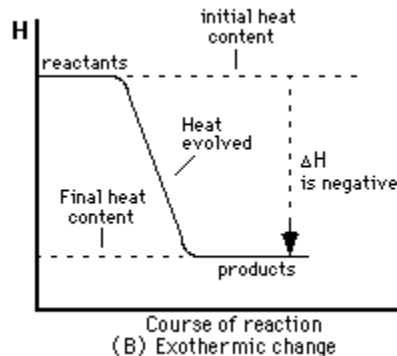
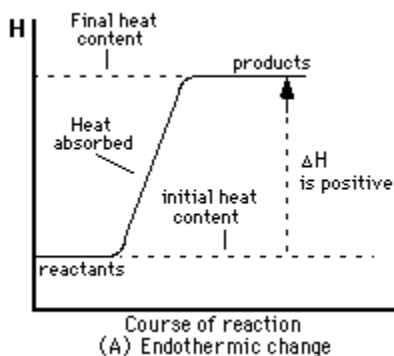
A. Enthalpy

$$H = E + PV$$

- 1. In systems at constant pressure, where the only work is PV, the change in enthalpy is due only to energy flow as heat (ΔH = heat of rxn)

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- a. ΔH is negative for exothermic rxns
- b. ΔH is positive for endothermic rxns



B. Calorimetry - science of measuring heat

1. Heat capacity (C)

- a. ratio of heat absorbed to increase in temperature

$$C = \frac{\text{heat absorbed}}{\text{Temperature increase}}$$

2. Specific Heat Capacity

- a. Energy required to raise the temp of 1 gram of a substance by 1 °C

3. Molar heat capacity

- a. Energy required to raise the temp of 1 mole of a substance by 1 °C

C. Constant Pressure Calorimetry (solutions)

1. Calculating Heat of Rxn, ΔH

- a. ΔH = specific heat capacity x mass of sol'n x increase in temp

$$\Delta H = s \times m \times \Delta T$$

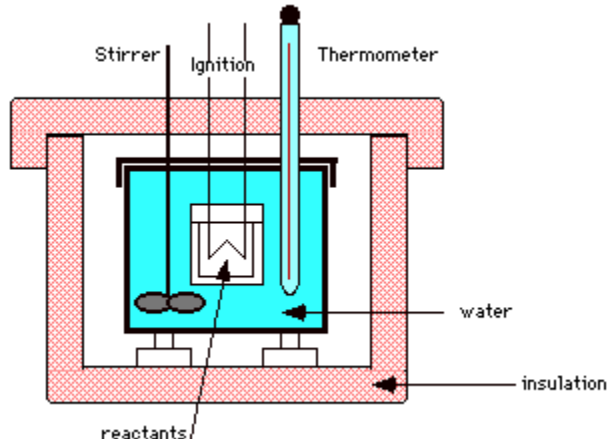
2. Heat of rxn is an extensive property - dependent on the amount of substance

- a. $\Delta H \propto$ moles of reactant

D. Constant Volume Calorimetry

1. Volume of bomb calorimeter cannot change, so no work is done

2. The heat capacity of the calorimeter must be known, generally in kJ/°C



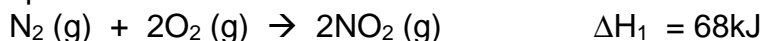
$$2. \quad \Delta E = q + w, \quad w = 0 \quad \therefore \Delta E = q$$

6.3 Hess's Law

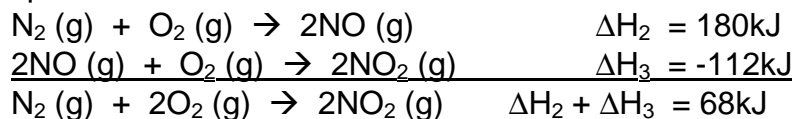
A. Statement of Hess's Law

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

One step:

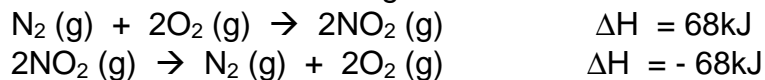


Two step



B. Characteristics of Enthalpy Changes

1. If a reaction is reversed the sign on ΔH is reversed



2. The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer

C. Using Hess's Law

1. Work backward from the final reaction
2. Reverse reactions as needed, being sure to also reverse ΔH
3. Remember that identical substances found on both sides of the summed equation cancel each other

6.4 Standard Enthalpies of Formation

A. Standard State

1. For a compound
 - a. Gaseous state
(1) pressure of 1 atm
 - b. Pure liquid or solid
(1) standard state is the pure liquid or solid
 - c. Substance in solution
(1) concentration of 1 M
2. For an element
 - a. the form in which the element exists at 1 atm and 25°C

B. Standard Enthalpy of Formation (ΔH_f°)

1. The change in enthalpy that accompanies the formation of one mole of a compound from its elements with all elements in their standard state

C. Calculating enthalpy change

1. When a rxn is reversed, the magnitude of ΔH remains the same, but its sign changes
2. When the balanced eqn for a rxn is multiplied by an integer, the value of ΔH must be multiplied by the same integer
3. The change in enthalpy for a rxn can be calculated from the enthalpies of formation of the reactants and products

$$\Delta H_{\text{reaction}}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

4. Elements in their standard states are not included
 - a. For elements in their standard state, $\Delta H_f^\circ = 0$

6.5 Present Sources of Energy

A. Fossil Fuels

1. Energy derived from these fuels was initially captured from solar energy by photosynthesis
2. Combustion of fossil fuels always produces H_2O and CO_2

B. Petroleum and Natural Gas

1. Petroleum
 - a. Thick, dark liquid composed of hydrocarbon
2. Natural gas
 - a. Methane, with smaller amounts of ethane, propane and butane

Some Common Hydrocarbons	
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

C. Petroleum Refining

1. Original refining isolated kerosene (gasoline was a waste product)
2. Tetraethyl lead added as an "anti-knock" agent

Petroleum Fraction	Major Uses
$\text{C}_5 - \text{C}_{10}$	Gasoline
$\text{C}_{10} - \text{C}_{18}$	Kerosene, Jet fuel
$\text{C}_{15} - \text{C}_{25}$	Diesel fuel, Heating oil, lubricating oil
$> \text{C}_{25}$	Asphalt

D. Coal

1. Four stages of Coal
2. Carbon content increases over time
3. Value of coal is proportional to carbon content

Type of Coal	Mass Percent of Each Element				
	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1

E. CO_2 and Earth's Climate

1. CO_2 is a by-product of cellular respiration
2. CO_2 is a by-product of burning fossil fuels
3. CO_2 is a greenhouse gas
4. Atmospheric CO_2 increased 16% from 1880 to 1980
5. Long-term climatic change seems imminent but is difficult to predict

6.6 New Energy Sources

A. Coal Conversion

1. Gasification
 - a. Reduce length of hydrocarbon molecules to create liquid or gaseous fuels
 - b. Produce Syngas (CO and H₂)
2. Coal Slurry
 - a. Coal dust suspended in water used as a heavy fuel oil replacement
3. Coal limitations
 - a. Mining of coal has a serious environmental impact

B. Hydrogen as a fuel

1. Freeing hydrogen from compounds requires substantial energy
 - a. $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 3\text{H}_2(\text{g}) + \text{CO}(\text{g}) \quad \Delta H = 206 \text{ kJ}$
 - b. $\text{H}_2\text{O}(\text{l}) + \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \quad \Delta H = 286 \text{ kJ}$
2. Hydrogen is difficult to transport
 - a. Hydrogen in contact with metal produces free hydrogen atoms
 - b. Hydrogen attempts penetrate the metal and make it brittle
3. Hydrogen is not dense
 - a. The fuel equivalent of 20 gallons of gasoline occupies a volume of 238,000 liters.
 - b. Liquid hydrogen is stored under great pressure and is potentially explosive

C. Other Energy Alternatives

1. Shale
 - a. Must be heated to extract fuel molecules, and produces immense amounts of waste rock
2. Ethanol from fermentation
 - a. Mixture of ethanol and gasoline - gasohol
 - b. Ethanol is renewable
3. Methanol
4. Seed oils
 - a. Renewable