Chapter 5: Energy Relationships in Chemistry: Thermochemistry

5.1 The Nature of Energy

-**Thermochemistry**: relationships between chemical reactions and energy changes
-**Force**: symbolized by *F*, any kind of push or pull exerted on an object
-**Work**: symbolized by *w*, movement of an object against some force
      $w = F \times d$ where *w* is work, *F* is force, and *d* is distance that the object is being moved
-**Heat**: energy that is transferred from one object to another because of difference in temperature
-**Energy**: the capacity to do work or to transfer heat

Kinetic and Potential Energy

-**Kinetic energy**: energy of motion
      $E_k = \frac{1}{2} mv^2$ where E_k is the kinetic energy, *m* is the mass, and *v* is the velocity.
-**Potential energy**: energy that an object possesses as a result of its composition or its position with respect to another object

Energy Units

-**Joule**: SI unit for energy, $1J = kg\text{-}m^2/s^2$
-**Calorie**: abbreviated *cal*, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C. 1 cal = 4.184 J

Systems and Surroundings

-**System**: portion singled out for study
-**Surroundings**: everything beyond the system
      Systems exchanges energy with surroundings in the form of heat and work, but not matter

Lowering the Energy of the System

Systems tend to attain as low an energy as possible. Systems with a high potential energy are less stable and more likely to undergo change than systems with a low potential energy.

5.2 The First Law of Thermodynamics

-**First law of thermodynamics**: aka **The Law of Conservation of Energy**; a statement of our experience that energy is conserved in any process. We can express the first law in many ways. One of the more useful expressions is that the change in internal energy, *ΔE*, of a system in any process is equal to the heat, *q*, added to the system, plus the work, *w*, done *on* the system by its surroundings: $\Delta E = q + w$.

Internal Energy

The total energy of a system is the sum of all the kinetic and potential energies of its components parts.
-**Internal energy**: total energy of the system (see above)
Because there are so many types of motion and interactions, we cannot determine the exact energy of any system. However, we can measure the changes *in internal energy that accompany chemical and physical processes.*

$$\Delta E = E_{final} - E_{initial}$$

$E_{final} > E_{initial}$ = system has gained energy
$E_{final} < E_{initial}$ = system has lost energy

Initial state refers to reactants, final state to products.

Relating ΔE to Heat and Work

The internal energy of a system changes in magnitude as heat is added to or removed from the system, or as work is done on it or by it.
$\Delta E = q + w$ where ΔE is internal energy, q is heat, and w is work

Heat added to the system is assigned a positive sign. Likewise, work on the system is positive. On the other hand, both the heat lost by the system and the work done by the system on its surroundings are negative; they reduce the internal energy.

Ex. A system absorbs 50 J of heat and does 10 J of work on its surroundings, $q = 50$ J and $w = -10$ J. Thus, $\Delta E = 50$ J + (-10 J) = 40 J.

State Functions

The total energy of a system is proportional to the total quantity of matter in the system; energy is an extensive property.
-**State function**: a property of a system that is determined by the state or condition of the system and not by how it got to that state; its value is fixed when temperature, pressure, composition, and physical form are specified. The internal energy of a system is a state function.
The value of a state function does not depend on the particular history of the sample, only on its present condition. Because E is a state function, ΔE depends only on the initial and final states of the system and not on how the change occurs.
However, the work done by a system in a given process is not a state function!!!

5.3 Heat and Enthalpy Changes

Heat flows between system and surroundings until *both are at the same temperature*.
-**Endothermic process**: a process in which a system absorbs heat from its surroundings
-**Exothermic process**: a process in which a system releases heat to its surroundings

Enthalpy

-**Enthalpy**: represented by *H*; deals with the amount of heat absorbed or released during a chemical reaction under constant pressure

The change in enthalpy, ΔH, equals the heat, q_p, added to or lost by the system when the process occurs under constant pressure:

$$\Delta H = q_p$$

(The subscript P on q is a reminder that we are considering a special case where pressures is constant)

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

$H_{\text{final}} > H_{\text{initial}}$ = positive ΔH; system has gained heat from surroundings (endothermic)
$H_{\text{final}} < H_{\text{initial}}$ = negative ΔH; system has lost heat to the surroundings (exothermic)

5.4 Enthalpies of Reaction

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

-**Thermochemical equations**: balanced chemical equations that show the associated enthalpy change

1. Enthalpy is an *extensive* property (depends on amount of matter present). *This fact means that the magnitude of ΔH is directly proportional to the amount of reactant consumed in the process*
2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. *When we reverse a reaction, the reactants become the products, and vice-versa. Reversing the products and reactants leads to the same magnitude but a change in sign for ΔH.*
3. The enthalpy change for a reaction depends on the state of the reactants and products.

5.5 Calorimetry

-**Calorimetry**: measurement of heat flow
-**Calorimeter**: apparatus that measures heat flow

Heat Capacity and Specific Heat

-**Heat capacity**: amount of energy required to raise the temperature of a given object by 1°C. The greater the capacity of a body, the more heat it requires to raise its temperature.
-**Molar heat capacity**: when referring to pure substances; heat capacity of 1 mol of substance
-**Specific heat**: heat capacity of 1 g of a substance (as opposed to a mole)

Specific heat= quantity of heat transferred / (grams of substance) X (temperature change)
$$= q / m \text{ X } \Delta T$$
$$q = (\text{specific heat}) \text{ X (grams of substance) X } \Delta T$$

Constant-Pressure Calorimetry

Calorimeters are simple instruments to control pressure. Because the calorimeter prevents the gain or loss of heat from its surroundings, the heat released by the reaction, $-q_{rxn}$, equals that gained by the solution, q_{soln}. Thus,

$$q_{rxn} = -q_{soln} = -(\text{specific heat}) \times (\text{grams of solution}) \times \Delta T$$
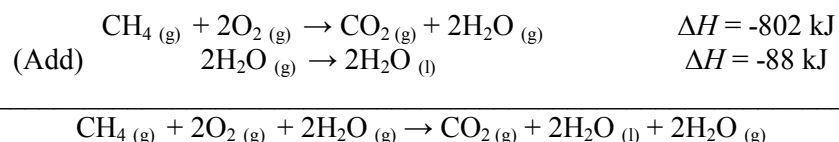
Bomb Calorimetry

-**Bomb calorimeter**: device for measuring the heat evolved in the combustion of a substance under constant-volume conditions. Most used for combustion reactions.
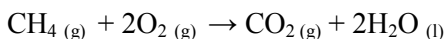
$$q_{evolved} = -C_{calorimeter} \times \Delta T, \text{ where } C_{calorimeter} \text{ is the heat capacity of the calorimeter}$$

5.6 Hess's Law

-Because enthalpy is a state function, the enthalpy change, ΔH, associated with any chemical process depends only on the *amount of matter that undergoes change*, and on the nature of the *initial state of the reactants* and the *final state of the products*.

$$CH_{4\ (g)} + 2O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2H_2O_{\ (g)} \qquad \Delta H = \text{-}802 \text{ kJ}$$
$$\text{(Add)} \qquad 2H_2O_{\ (g)} \rightarrow 2H_2O_{\ (l)} \qquad \Delta H = \text{-}88 \text{ kJ}$$
$$\overline{CH_{4\ (g)} + 2O_{2\ (g)} + 2H_2O_{\ (g)} \rightarrow CO_{2\ (g)} + 2H_2O_{\ (l)} + 2H_2O_{\ (g)}}$$

Net equation:

$$CH_{4\ (g)} + 2O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2H_2O_{\ (l)}$$

To obtain the net equation, the sum of the reactants of the two equations is placed on one side of the arrow, and the sum of the products on the other side. Because $2H_2O_{\ (g)}$ occurs on both sides of the equation, it can be cancelled.

-**Hess's law**: states that *if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for individual steps.* The overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out.

The first law of thermodynamics, in the form of Hess's law, teaches us that we can never expect to obtain more (or less) energy from a chemical reaction by changing the method of carrying out the reaction.

5.7 Enthalpies of Formation

Enthalpies of vaporization (ΔH for converting liquids to gas)
Enthalpies of fusion (ΔH for melting solids)
Enthalpies of combustion (ΔH for combusting a substance in oxygen)

-**Enthalpy of formation**: aka **Heat of formation**; enthalpy change that accompanies the formation of a substance from the most stable forms of its component elements. Labeled ΔH_f, where the subscript *f* indicates that the substance has been formed from its elements.

The magnitude of any enthalpy change depends on the conditions of temperature, pressure, and state (gas, liquid, solid) of the reactants and product.

-**Standard state**: for a substance is the form most stable at the particular temperature of interest and at standard atmospheric pressure.

-**Standard enthalpy of formation**: $\Delta H°_f$. chang in enthalpy that accompanies the formation of 1 mol of that substance from its elements, with all substances in their standard states.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

$$\Delta H°_{rxn} = \sum n\Delta H°_f \text{ (products) } - \sum m\Delta H°_f \text{ (reactants)}$$

$\sum$ = the sum of
m and n = stoichiometric coefficients of the chemical reaction

$$C_3H_{8\,(g)} + 5O_{2\,(g)} \rightarrow 3CO_{2\,(g)} + 4H_2O_{\,(l)}$$
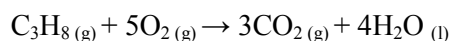
$$\Delta H°_{rxn} = [3\Delta H°_f\,(CO_2) + 4\Delta H°_f\,(H_2O)] - [\Delta H°_f\,(C_3H_8) + 5\Delta H°_f\,(O_2)]$$
$$\Delta H°_{rxn} = [(3 \text{ mol } CO_2)\,(-393.5 \text{ kJ/mol}) + (4 \text{ mol } H_2O)\,(-285.5 \text{ kJ/mol})]$$
$$= (-2324 \text{ kJ}) - (-103.85 \text{ kJ})$$
$$= -2220 \text{ kJ}$$

5.8 Foods and Fuels

-**Fuel value**: energy released when 1g of a material is combusted

Foods

-Main sources of energy for the body are from carbohydrates and fat
-Breakdown of carbohydrates is rapid, so energy is quickly supplied to the body
-Fats are well suited for the body because (1) they are insoluble in water, which permits their storage in the human body. (2) they produce more energy per gram thatneither proteins or carbohydrates.

Fuels

-**Fossil fuels**: coal, petroleum, and natural gas
-**Natural gas**: consists of gaseous hydrocarbons, compounds of hydrogen and carbon
-**Petroleum**: liquid composed of hundreds of compounds
-**Coal**: solid; contains hydrocarbons of high molecular weight as well as compounds containing sulfur, oxygen, and nitrogen. Most abundant fossil fuel
-**Syngas**: synthetic gas abbreviation