CHAPTER 8
THERMOCHEMISTRY: CHEMICAL ENERGY

Chapter Learning Goals

Section 8.1 Define energy. Define and perform calculations involving potential and kinetic energy.

Section 8.2 State the First Law of Thermodynamics, and understand its application to thermochemistry. Differentiate between the concepts of heat and temperature.

Section 8.3 Identify a state function.

Section 8.4 Define and calculate *PV* work. Know whether work is being done by the system or on the system.

Section 8.5 Differentiate between energy and enthalpy, and perform calculations interconverting the two. From ΔH or ΔE, tell whether energy is being lost from or gained by the system.

Section 8.6 Define thermodynamic standard state. Calculate ΔE for a reaction.

Section 8.7 Given a balanced chemical equation and enthalpy change for a chemical reaction, calculate the enthalpy change per mole or per gram of each reactant and product.

Section 8.8 Perform calculations involving specific heat (or molar heat capacity), heat flow, and temperature change. Calculate ΔH or ΔE in a calorimetry experiment.

Section 8.9 Use Hess's law to calculate a standard heat of reaction.

Section 8.10 Use standard heats of formation to calculate a standard heat of reaction.

Section 8.11 Use bond dissociation energies to approximate a standard heat of reaction.

Section 8.12 Write balanced equations for combustion reactions. Use Hess's Law to calculate enthalpies of combustion.

Section 8.13 Predict whether entropy increases or decreases for a chemical reaction or physical change.

Section 8.14 Predict the signs of ΔH, ΔS and ΔG for a reaction. Use the equation $\Delta G = \Delta H - T\Delta S$ to determine whether the forward reaction or the reverse reaction is favored. Use ΔH and ΔS to determine the temperature at which a reversible system is at equilibrium.

Lecture Outline

8.1. Energy

A. Energy
   1. Capacity to do work or supply heat
   2. Energy = work + heat

B. Kinetic energy
   1. Energy of motion
   2. $E_K = 1/2mv^2$

C. Potential energy – stored energy

D. Joule
   1. SI unit for energy.
   2. 1 J = 1(kg·m^2)/s^2

E. Calorie
   1. Amount of energy necessary to raise the temperature of 1 g of water by 1°C
   2. 1 cal = 4.184 J
   3. Nutritional calorie (Calorie)
   4. 1 Cal = 1000 cal = 1 kcal = 4.184 kJ

8.2. Energy Changes and Energy Conservation

A. Law of Conservation of Energy
   1. Energy can be neither created nor destroyed.
   2. It can only be converted from one form into another.

B. Many forms of energy
   1. Thermal energy
      a. Kinetic energy of molecular motion
      b. Temperature – measure of the kinetic energy of molecular motion
   2. Heat
      a. Energy transferred from one object to another
      b. Result of a temperature difference between them
   3. Chemical energy
      a. A type of potential energy
      b. Chemical bonds of molecules act as the storage medium

C. First Law of Thermodynamics: The energy of the universe is constant.

8.3. Internal Energy and State Functions

A. System – everything we focus on in an experiment

B. Surroundings – everything other than the system

C. Internal energy – energy of the system

D. System isolated from the surroundings
   1. No energy transfer to surroundings
   2. $\Delta E = 0$
   3. First Law of Thermodynamics: The total internal energy of an isolated system is constant.

E. System is not isolated from surroundings
   1. Energy flows to or from surroundings
   2. $\Delta E = E_{final} - E_{initial}$

F. Energy changes measured from the point of view of the system
   1. Direction of heat flow related to observed temperature change.
   2. Energy flows out of system to surroundings – negative value
   3. Energy flows into system from surroundings – positive value
   4. Amount of energy released or gained in a reaction is dependent on amount of reactants and products involved in reaction.

G. State Function – function or property whose value depends only on the present state (condition) of the system, not on path used to arrive at that condition
   1. Reversible

2. Overall change is zero if system returns to its original condition

8.4. Expansion Work

A. Work
  1. Force (*f*) that produces movement of an object times distance moved (*d*)
  2. $w = F \times d$

B. Expansion work (*PV* work) - Gases do work when the molecules push against the walls of their container and the volume of the container increases.
  1. Work done as result of volume change in the system. If there is no volume change, no work is done.
  2. $w = -(P \times \Delta V)$
  3. Expansion of the system – Requires the output of energy
     a. System does work on surroundings
     b. ΔE is negative
     c. $w = -P\Delta V$
        i. Work is negative
        ii. ΔV is positive
  4. Contraction of the system – Requires the input of energy
     a. Surroundings do work on the system
     b. ΔE is positive
     c. $w = -P\Delta V$
        i. Work is positive
        ii. ΔV is negative

8.5. Energy and Enthalpy

A. Total energy change of a system
  1. $\Delta E = q + w$ (q = heat)
  2. $\Delta E = q + (-P\Delta V)$

B. Amount of heat transferred: $q = \Delta E + P\Delta V$

C. Reactions carried out with constant volume
  1. $\Delta V = 0$
  2. No *PV* work done
  3. $q_v = \Delta E$
  4. If the volume of the system does not change, the heat transferred to or from a system is the *energy change* of that system.

D. Reactions carried out at constant pressure
  1. $\Delta V \neq 0$
  2. Energy change due to both heat transfer and *PV* work
  3. $q_p = \Delta E + P\Delta V$.
  4. If the pressure of the system does not change, the heat transferred to or from a system is the *enthalpy change* of that system.

E. Heat of reaction, ΔH
  1. Enthalpy change of a system
  2. $\Delta H = \Delta E + P\Delta V$
  3. State function – value depends only on the current state of the system
  4. *Unless a gas is involved in the reaction*, volume changes are usually negligible and $\Delta H \approx \Delta E$.
  5. $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
  6. Amount of heat released in a specific reaction depends on actual amounts of reactants.

8.6. The Thermodynamic Standard State

A. Value of enthalpy change, ΔH, reported for a reaction represents amount of heat released when reactants converted to products in molar amounts represented by coefficients of the balanced equation.
  1. Total amount of heat involved in a reaction depends on actual amounts of reactants.
  2. Physical states of reactants and products must be specified.
  3. Temperature and pressure also must be reported.

B. Thermodynamic Standard State = 298.15 K (25°C), 1 atm pressure of each gas, 1 M concentration (for solutions)

1. Allows different reactions to be compared
2. Indicated by addition of a superscript ° to indicate enthalpy of standard state, $\Delta H°$
3. Standard conditions as defined for thermodynamics (P = 1 atm; T = 298.15 K) are different from standard conditions as defined for gas laws (P = 1 atm; T = 273.15 K).

C. Standard enthalpy of reaction – enthalpy change measured under standard conditions.

8.7. Enthalpies of Physical and Chemical Change

A. Enthalpies of physical change - Temperature does not change during a change of state.
1. Heat of fusion – amount of heat required for melting
2. Heat of vaporization – amount of heat required for evaporation
3. Sublimation
   a. Direct conversion of solid to vapor without going through a liquid state
   b. Heat of sublimation = Heat of fusion + Heat of vaporization

B. Enthalpies of chemical change
1. Heats of reaction – enthalpies of chemical change
2. Endothermic reactions
   a. $H_{products} > H_{reactants}$
   b. Heat flows into system from surroundings - *Endothermic*
   c. ΔH is positive
3. Exothermic reactions
   a. $H_{products} < H_{reactants}$
   b. Heat flows to surroundings from system - *Exothermic*
   c. ΔH is negative
4. $\Delta H°$ values for a given equation
   a. Equation balanced for number of moles of reactants and products
   b. All substances are in standard states
   c. Physical state of each substance specified
   d. Refers to reaction going in direction written
   e. Reversing direction of reaction changes sign of $\Delta H°$

8.8. Calorimetry and Heat Capacity

A. Calorimetry – experimental technique that allows energy change associated with a chemical or physical process to be determined
1. Temperature change observed when system gains or loses energy in the form of heat
2. Performed in a calorimeter
3. For an exothermic reaction: amount of heat released by reaction = amount of heat gained by calorimeter + amount of heat gained by solution.
4. The amount of heat transferred and, therefore, the temperature change depend on the amount of substance involved.

B. Heat capacity (C)

$$C = \frac{q}{\Delta T}$$

1. Amount of heat required to raise the temperature of an object or substance a given amount
2. Extensive property
3. Heat capacity links the flow of heat with temperature change, allowing conversion of one to the other.

C. Specific heat
1. Amount of heat necessary to raise the temperature of exactly 1 g of a substance by exactly 1°C
2. q = (specific heat) × (mass of substance) × (ΔT)
3. Intensive property of a substance – depends on the state of a substance.

D. Molar heat capacity (C_m)
1. Amount of heat necessary to raise the temperature of 1 mole of a substance by 1°C
2. $q_m = (C_m) \times$ (moles of substance) $\times (\Delta T)$
3. Intensive property of a substance – depends on the state of a substance.

8.9. Hess's Law

A. Hess's law

1. Overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for individual steps in the reaction
2. Reactants and products in the individual steps added and subtracted like algebraic quantities in determining the overall equation

B. Combine individual reactions so that their sums will be the desired reaction – textbook example 8.6
1. When an equation is reversed, Δ*H* must be multiplied by –1.
2. When an equation is multiplied by a coefficient, Δ*H* must be multiplied by the same coefficient.

8.10. Standard Heats of Formation

A. Standard heat of formation
1. Enthalpy change ΔH°_f for the hypothetical formation of 1 mole of a substance in its standard state from the most stable forms of it constituent elements in their standard states
2. The most stable forms of all elements in their standard state have $\Delta H^\circ_f = 0$.

B. Standard enthalpy change found by subtracting the sum of the heats of formation of reactants from the sum of the heats of formation of products:

$$\Delta H^\circ = \Sigma\ \Delta H^\circ_{\text{products}} - \Sigma\ \Delta H^\circ_{\text{reactants}}$$

1. When an equation is reversed, Δ*H* must be multiplied by –1.
2. When an equation is multiplied by a coefficient, Δ*H* must be multiplied by the same coefficient.

8.11. Bond Dissociation Enthalpies

A. Bond dissociation enthalpies – Energy added to break bonds
1. Enthalpy changes, Δ*H*°, for corresponding bond–breaking reactions
2. Δ*H*° = *D* = bond dissociation energy
3. Always positive
4. Always need energy to break a bond
5. Bond dissociation energies are defined for isolated gaseous-state molecules.

B. Δ*H*° = *D*(bonds broken) – *D*(bonds formed)

C. Bond order – not all bonds are equal and require different energy to dissociate.

8.12. Fossil Fuels, Fuel Efficiency, and Heats of Combustion

A. Heat of combustion (ΔH°_c) – amount of energy released on burning a substance

B. Fuel efficiency
1. Calculate ΔH°_c in kJ/g or kJ/mL
2. Can compare efficiency for different fuels

C. Fossil fuels
1. Decayed remains of organisms from previous geological eras
2. Coal, natural gas and petroleum
   a. Coal and petroleum – complex mixture of compounds
   b. Coal – vegetable origin, compounds structurally similar to graphite
   c. Petroleum – viscous liquid mixture of hydrocarbons, primarily marine origin

8.13. An Introduction to Entropy

A. Spontaneous process
1. Process that proceeds on its own without continuous external influence.
2. Need either a release of energy or an increase in disorder of the system, such as the mixing of two gases.

B. Entropy (*S*)
1. Amount of molecular disorder or randomness in a system
2. Larger the value of *S,* greater the molecular randomness
3. $\Delta S = S_{\text{final}} - S_{\text{initial}}$
4. $S_{\text{final}} > S_{\text{initial}}$
   a. Δ*S* is positive
   b. System has become more random
5. $S_{\text{final}} < S_{\text{initial}}$
   a. Δ*S* is negative
   b. System has become less random

C. Spontaneous process

1. Favored by decrease in *H* (negative ΔH)
2. Favored by increase in *S* (positive ΔS)

8.14. An Introduction to Free Energy

A. Gibbs free-energy change (ΔG); $\Delta G = \Delta H - T\Delta S$.

B. Sign of ΔG used as a criterion for determining spontaneity of a process

a. ΔG negative – spontaneous

b. ΔG positive ≠ nonspontaneous

C. Temperature dependence ($T\Delta S$) term for ΔG.

1. Spontaneity of some processes depends on temperature
2. Low temperatures – ΔH dominates and controls spontaneity
3. High temperatures – $T\Delta S$ dominates and controls spontaneity

D. $\Delta G = 0$

1. Process at equilibrium
2. Balanced between spontaneous and nonspontaneous
3. Temperature at which a nonspontaneous reaction becomes spontaneous

$$T = \frac{\Delta H}{\Delta S}$$