## **Chapter 5. Thermochemistry**

## **Lecture Outline**

## 5.1 The Nature of Energy

- Thermodynamics is the study of energy and its transformations.
- **Thermochemistry** is the study of the relationships between chemical reactions and energy changes involving heat.
- Definitions:
  - **Energy** is the capacity to do work or to transfer heat.
  - Work is energy used to cause an object with mass to move.

$$w = F x d$$

- Heat is the energy used to cause the temperature of an object to increase.
  - A force is any kind of push or pull exerted on an object.
  - The most familiar force is the pull of gravity.

## **Kinetic Energy and Potential Energy**

• **Kinetic energy** is the energy of motion:

$$E_k = \frac{1}{2}mv^2$$

- **Potential energy** is the energy an object possesses by virtue of its position or composition.
  - Electrostatic energy is an example.
    - It arises from interactions between charged particles.

$$E_{el} = \frac{kQ_1Q_2}{d}$$

- Potential energy can be converted into kinetic energy.
  - An example is a ball of clay dropped off a building.

### **Units of Energy**

- SI unit is the **joule**, J.
- From  $E_k = \frac{1}{2}mv^2$ ,  $1J = 1 \text{kg x} \frac{\text{m}^2}{\text{s}^2}$
- Traditionally, we use the **calorie** as a unit of energy.
  - 1 cal = 4.184 J (exactly)
- The nutritional Calorie, Cal = 1,000 cal = 1 kcal.

## System and Surroundings

- A system is the part of the universe we are interested in studying.
- **Surroundings** are the rest of the universe (i.e., the surroundings are the portions of the universe that are not involved in the system).
- Example: If we are interested in the interaction between hydrogen and oxygen in a cylinder, then the  $H_2$  and  $O_2$  in the cylinder form a system.

# **Transferring Energy: Work and Heat**

- From physics:
  - Force is a push or pull on an object.
  - Work is the energy used to move an object against a force.

$$w = F \times d$$

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- **Heat** is the energy transferred from a hotter object to a colder one.
- Energy is the capacity to do work or to transfer heat.

## 5.2 The First Law of Thermodynamics

- The first law of thermodynamics states that energy cannot be created or destroyed.
- The first law of thermodynamics is the law of conservation of energy.
  - That is, the energy of system + surroundings is constant.
  - Thus, any energy transferred from a system must be transferred to the surroundings (and vice versa).

## **Internal Energy**

- The total energy of a system is called the **internal energy**.
- It is the sum of all the kinetic and potential energies of all components of the system.
- Absolute internal energy cannot be measured, only changes in internal energy.
- Change in internal energy,  $\infty E = E_{\text{final}} E_{\text{initial}}$ .
- Example: A mixture of  $H_2(g)$  and  $O_2(g)$  has a higher internal energy than  $H_2O(g)$ .
- Going from  $H_2(g)$  and  $O_2(g)$  to  $H_2O(g)$  results in a negative change in internal energy, indicating that the system has lost energy to the surroundings:

$$H_2(g) + O_2(g) \Box 2H_2O(g) \qquad \qquad \infty E < 0$$

• Going from  $H_2O(g)$  to  $H_2(g)$  and  $O_2(g)$  results in a positive change in internal energy, indicating that the system has gained energy from the surroundings:

### Relating ∞*E* to Heat and Work

- From the first law of thermodynamics:
  - When a system undergoes a physical or chemical change, the change in internal energy is given by the heat added to or liberated from the system plus the work done on or by the system:

$$\infty E = q +$$

- Heat flowing from the surroundings to the system is positive, q > 0.
- Work done by the surroundings on the system is positive, w > 0.

### **Endothermic and Exothermic Processes**

- An endothermic process is one that *absorbs* heat from the surroundings.
  - An endothermic reaction feels cold.
  - An **exothermic** process is one that *transfers* heat to the surroundings.
  - An exothermic reaction feels hot.

### **State Functions**

- A state function depends only on the initial and final states of a system.
  - Example: The altitude difference between Denver and Chicago does not depend on whether you fly or drive, only on the elevation of the two cities above sea level.
  - Similarly, the internal energy of 50 g of H<sub>2</sub>O(*l*) at 25□C does not depend on whether we cool 50 g of H<sub>2</sub>O(*l*) from 100□C to 25□X or heat 50 g of H<sub>2</sub>O(*l*) at 0□C to 25□X.
- A state function does not depend on how the internal energy is used.
  - Example: A battery in a flashlight can be discharged by producing heat and light. The same battery in a toy car is used to produce heat and work. The change in internal energy of the battery is the same in both cases.

# 5.3 Enthalpy

- Chemical changes may involve the release or absorption of heat.
- Many also involve work done on or by the system.

- Work is often either electrical or mechanical work.
- Mechanical work done by a system involving expanding gases is called **pressure-volume work** or *P-V* work.
- The heat transferred between the system and surroundings during a chemical reaction carried out under constant pressure is called **enthalpy**, *H*.
- Again, we can only measure the change in enthalpy,  $\infty H$ .
- Mathematically,

$$\infty H = H_{\text{final}} - H_{\text{initial}} = \infty E + P \infty V$$
$$w = -P \infty V; \ \infty E = q + w$$
$$\infty H = \infty E + P \infty V = (q_{\text{p}} + w) - w = q_{\text{p}}$$

- For most reactions  $P \propto V$  is small thus  $\infty H = \infty E$
- Heat transferred from surroundings to the system has a positive enthalpy (i.e.,  $\infty H > 0$  for an endothermic reaction).
- Heat transferred from the system to the surroundings has a negative enthalpy (i.e.,  $\infty H < 0$  for an exothermic reaction).
- Enthalpy is a state function.

### A Closer Look at Energy, Enthalpy, and P-V Work

- Consider:
  - A cylinder has a cross-sectional area *A*.
  - A piston exerts a pressure, P = F/A, on a gas inside the cylinder.
  - The volume of gas expands through  $\infty V$  while the piston moves a height  $\infty h = h_f h_i$ .
  - The magnitude of work done =  $F \ge \infty h = P \ge A \ge \infty h = P \ge \infty V$ .
  - Since work is being done by the system on the surroundings, then •  $w = -P \infty V$ .
  - Using the first law of thermodynamics,
    - $\infty E = q P \infty V.$
  - If the reaction is carried out under constant volume,
  - $\infty V = 0$  and  $\infty E = q_v$ .
  - If the reaction is carried out under constant pressure,
    - $\infty E = q_p P \infty V$ , or
    - $q_{\rm p} = \infty H = \infty E + P \infty V$
    - and  $\infty E = \infty H P \infty V$

### **5.4 Enthalpies of Reaction**

- For a reaction,  $\infty H_{\text{rxn}} = H_{\text{products}} H_{\text{reactants}}$ .
- The enthalpy change that accompanies a reaction is called the **enthalpy of reaction** or *heat of* reaction ( $\infty H_{rxn}$ ).
- Consider the thermochemical equation for the production of water:

- The equation tells us that 483.6 kJ of energy are released to the surroundings when water is formed.
- $\infty H$  noted at the end of the balanced equation depends on the number of moles of reactants and products associated with the  $\infty H$  value.
- These equations are called *thermochemical equations*.
- Enthalpy diagrams are used to represent enthalpy changes associated with a reaction.
- In the enthalpy diagram for the combustion of  $H_2(g)$ , the reactants,  $2H_2(g) + O_2(g)$ , have a higher enthalpy than the products  $2H_2O(g)$ ; this reaction is exothermic.
- Enthalpy is an extensive property.
  - Therefore, the *magnitude* of enthalpy is directly proportional to the amount of reactant consumed.

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• Example: If one mol of CH<sub>4</sub> is burned in oxygen to produce CO<sub>2</sub> and water, 890 kJ of heat are released to the surroundings. If two mol of CH<sub>4</sub> are burned, then 1780 kJ of heat are released. The sign of ∞*H* depends on the direction of the reaction.

 $\infty H = -88 \text{ kJ}$ 

- The enthalpy change for a reaction is equal in magnitude but opposite in sign to  $\infty H$  for the reverse reaction.
- Example:  $CH_4(g) + 2O_2(g) \square CO_2(g) + 2H_2O(l)$   $\infty H = -890 \text{ kJ},$
- But  $CO_2(g) + 2H_2O(l) \square CH_4(g) + 2O_2(g)$   $\infty H = +890 \text{ kJ}.$
- Enthalpy change depends on state.
  2H<sub>2</sub>O(g) □ 2H<sub>2</sub>O(l)

### 5.5 Calorimetry

- **Calorimetry** is a measurement of heat flow.
- A **calorimeter** is an apparatus that measures heat flow.

#### Heat Capacity and Specific Heat

- Heat capacity is the amount of energy required to raise the temperature of an object by  $1\Box C$ .
  - Molar heat capacity is the heat capacity of 1 mol of a substance.
    - Specific heat, or specific heat capacity, is the heat capacity of 1 g of a substance.
- Heat,  $q = (\text{specific heat}) \times (\text{grams of substance}) \times \infty T$ .
- Be careful of the sign of q.

#### **Constant-Pressure Calorimetry**

- The most common technique is to use atmospheric pressure as the constant pressure.
- Recall  $\infty H = q_p$ .
- The easiest method is to use a coffee cup calorimeter.

 $q_{\rm soln} =$  (specific heat of solution) x (grams of solution) x  $\infty T = -q_{\rm rxn}$ 

• For dilute aqueous solutions, the specific heat of the solution will be close to that of pure water.

### Bomb Calorimetry (Constant-Volume Calorimetry)

- Reactions can be carried out under conditions of constant volume instead of constant pressure.
- Constant volume calorimetry is carried out in a **bomb calorimeter**.
- The most common type of reaction studied under these conditions is combustion.
- If we know the heat capacity of the calorimeter,  $C_{cal}$ , then the heat of reaction,

$$q_{\rm rxn} = -C_{\rm cal} \ge \infty T$$

• Since the reaction is carried out under constant volume, q relates to  $\infty E$ .

### 5.6 Hess's Law

- Hess's Law: If a reaction is carried out in a series of steps,  $\infty H$  for the reaction is the sum of  $\infty H$  for each of the steps.
- The total change in enthalpy is independent of the number of steps.
- Total  $\infty H$  is also independent of the nature of the path.

$CH_4(g) + 2O_2(g) \square CO_2(g) + 2H_2O(g)$ $2H_2O(g) \square 2H_2O(l)$	$\infty H = -802 \text{ kJ}$ $\infty H = -88 \text{ kJ}$
$CH_4(g) + 2O_2(g) \square CO_2(g) + 2H_2O(l)$	$\infty H = -890 \text{ kJ}$

- Therefore, for the reaction  $CH_4(g) + 2O_2(g) \square CO_2(g) + 2H_2O(l), \infty H = -890$  kJ.
- Note that  $\infty H$  is sensitive to the states of the reactants and the products.
- Hess's law allows us to calculate enthalpy data for reactions that are difficult to carry out directly:  $C(s) + O_2(g)$  produces a *mixture* of CO(g) and  $CO_2(g)$ .

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## **5.7 Enthalpies of Formation**

- Hess's law states that if a reaction is carried out in a number of steps,  $\infty H$  for the overall reaction is the sum of the  $\infty H$ s for each of the individual steps.
- Consider the formation of  $CO_2(g)$  and  $2H_2O(l)$  from  $CH_4(g)$  and  $2O_2(g)$ .
  - If the reaction proceeds in one step:

$$\operatorname{CH}_4(g) + 2\operatorname{O}_2(g) \Box \operatorname{CO}_2(g) + 2\operatorname{H}_2\operatorname{O}(l),$$

then  $\infty H_1 = -890$  kJ.

• However, if the reaction proceeds through a CO intermediate:

Then  $\infty H$  for the overall reaction is:

$$\infty H_2 + \infty H_3 = -607 \text{ kJ} - 283 \text{ kJ} = -890 \text{ kJ} = \infty H_1$$

- If a compound is formed from its constituent elements, then the enthalpy change for the reaction is called the **enthalpy of formation**,  $\infty H_{f}$ .
- Standard state (standard conditions) refer to the substance at:
  - 1 atm and 25 C (298 K).
- Standard enthalpy,  $\infty H\Box$ , is the enthalpy measured when everything is in its standard state.
- Standard enthalpy of formation of a compound,  $\infty H \square_{\phi}$ , is the enthalpy change for the formation of 1 mol of compound with all substances in their standard states.
- If there is more than one state for a substance under standard conditions, the more stable state is used. Example: When dealing with carbon we use graphite because graphite is more stable than diamond or  $C_{60}$ .
- The standard enthalpy of formation of the most stable form of an element is zero.

### Using Enthalpies of Formation to Calculate Enthalpies of Reaction

- Use Hess's law!
- Example: Calculate  $\infty H$  for

$$C_{3}H_{8}(g) + 5O_{2}(g) \Box 3CO_{2}(g) + 4H_{2}O(l)$$

- We start with the reactants, decompose them into elements, then rearrange the elements to form products. The overall enthalpy change is the sum of the enthalpy changes for each step.

  - Next we form CO<sub>2</sub> and H<sub>2</sub>O from their elements:  $3C(s) + 3O_2(g) \square 3CO_2(g)$  $4H_2(g) + 2O_2(g) \square 4H_2O(l)$
- $\infty H_2 = 3 \ \infty H \square_{\mathbf{f}} [\operatorname{CO}_2(g)]$  $\infty H_3 = 4 \ \infty H \square_{\mathbf{f}} [\operatorname{H}_2 O(l)]$
- We look up the values and add:  $\infty H \Box_{rxn} = -1(-103.85 \text{ kJ}) + 3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ}) = -2220 \text{ kJ}$
- In general:

 $\infty H \square_{\text{rxn}} = \times n \infty H \square_{\text{f}} (\text{products}) - \times m \infty H \square_{\text{f}} (\text{reactants})$ 

• Where *n* and *m* are the stoichiometric coefficients.

### **5.8 Foods and Fuels**

- Fuel value is the energy released when 1 g of substance is burned.
- The fuel value of any food or fuel is a positive value that must be measured by calorimetry.

#### Foods

- Fuel value is usually measured in Calories (1 nutritional Calorie,  $1 \underline{C}al = 1000 \underline{c}al$ ).
- Most energy in our bodies comes from the oxidation of carbohydrates and fats.
- In the intestines, carbohydrates are converted into glucose,  $C_6H_{12}O_6$ , or blood sugar.

#### Thermochemistry

• In the cells glucose reacts with O<sub>2</sub> in a series of steps which ultimately produce CO<sub>2</sub>, H<sub>2</sub>O, and energy.

$$C_6H_{12}O_6(s) + 6O_2(g) \square 6CO_2(g) + 6H_2O(l)$$
  $\infty H \square = -2803 \text{ kJ}$ 

• Fats, for example tristearin, react with O<sub>2</sub> as follows:

$$2C_{57}H_{110}O_6(s) + 163O_2(g) \square 114CO_2(g) + 110H_2O(l)$$
  $\infty H \square = -75,250 \text{ kJ}.$ 

• Fats contain more energy than carbohydrates. Fats are not water soluble. Therefore, fats are good for energy storage.

## Fuels

- In the United States we use about  $1.03 \times 10^{17}$  kJ/year ( $1.0 \times 10^{6}$  kJ of fuel per person per day).
- Most of this energy comes from petroleum and natural gas.
- The remainder of the energy comes from coal, nuclear, and hydroelectric sources.
- Coal, petroleum, and natural gas are fossil fuels. They are not renewable.
- Natural gas consists largely of carbon and hydrogen. Compounds such as  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$  and  $C_4H_{10}$  are typical constituents.
- **Petroleum** is a liquid consisting of hundreds of compounds. Impurities include S, N, and O compounds.
- **Coal** contains high molecular weight compounds of C and H. In addition, compounds containing S, O, and N are present as impurities that form air pollutants when burned in air.
- Syngas (synthesis gas): a gaseous mixture of hydrocarbons produced from coal by coal gasification.

# **Other Energy Sources**

- Nuclear energy is the energy released in the splitting or fusion of nuclei of atoms.
- Fossil fuels and nuclear energy are *nonrenewable* sources of energy.
- **Renewable energy** sources include:
  - solar energy.
  - wind energy.
  - geothermal energy.
  - hydroelectric energy.
  - biomass energy.
  - These are virtually inexhaustible and will become increasingly important as fossil fuels are depleted.

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