

## 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.

### 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.
- Potential energy can be converted into kinetic energy.
  - Example: a ball of clay dropping off a building.

### Units of Energy

- SI unit is the **joule**, J.
- From  $E_k = \frac{1}{2}mv^2$ ,  $1 J = 1 kg \times \frac{m^2}{s^2}$
- Traditionally, we use the **calorie** as a unit of energy.
- The nutritional Calorie, Cal = 1000 cal.

### 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 not involved in the system).
- Example: If we are interested in the interaction between hydrogen and oxygen in a cylinder, then the H<sub>2</sub> and O<sub>2</sub> 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 amount of force applied to an object over a distance:  
 $w = F \times d$
  - **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**.
- Absolute internal energy cannot be measured, only changes in internal energy.
- Change in internal energy;
- Example: A mixture of H<sub>2</sub> (g) and O<sub>2</sub> (g) has a higher internal energy than H<sub>2</sub>O (g)
- Going from H<sub>2</sub> (g) and O<sub>2</sub> (g) to H<sub>2</sub>O (g) results in a negative change in internal energy.
$$\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta E < 0$$
- Going from H<sub>2</sub>O (g) to H<sub>2</sub> (g) and O<sub>2</sub> (g) results in a positive change in internal energy.
$$2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta E > 0$$

### Relating $\Delta E$ 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 absorbed by the system plus the work done on or by the system:  $\Delta E = q + w$
- Heat flowing from the surroundings to the system is positive (i.e., the system feels fold to the touch because it is absorbing heat from your hand),  $q > 0$ .
- 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) at 100°C or heat 50 g of H<sub>2</sub>O (l) at 0°C.
- 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 is used to produce heat and work. The change in internal energy of the battery is the same in both cases.

## 5.3 Enthalpy

- The heat transferred between the system and the surroundings during a chemical reaction carried out under constant pressure is called **enthalpy**,  $H$ .
- Again, we can only measure the change in enthalpy,  $\Delta H$ .
- Mathematically,  $\Delta H = H_{\text{final}} - H_{\text{initial}} = q_p$
  
- Heat transferred from the surroundings to the system has a positive enthalpy (i.e.,  $\Delta H > 0$  for an endothermic reaction).
- Heat transferred from the system to the surroundings has a negative enthalpy (i.e.,  $\Delta H < 0$  for an exothermic reaction).
- Enthalpy is a state function.

### **Energy, Enthalpy, and P – V Work**

- Consider:
  - A cylinder of cross-sectional area  $A$ ,
  - A piston exerting a pressure,  $P = F/A$ , on a gas inside the cylinder,
  - The volume of gas expanding through  $\Delta V$  while the piston moves a height  $\Delta h = h_f - h_i$ ,
  - Since work is being done by the system on the surroundings,  $w = -P\Delta V$
  - From the first law of thermodynamics,
    - $\Delta E = q - P\Delta V$
  - If the reaction is carried out under constant volume,
    - $\Delta V = 0$  and  $\Delta E = q_v$
  - If the reaction is carried out under constant pressure,
    - $\Delta E = q_p - P\Delta V$  or
    - $q_p = \Delta H =$
    - and  $\Delta E = \Delta H - P\Delta V$

## 5.4 Enthalpies of Reaction

- The enthalpy change that accompanies a reaction is called the **enthalpy of reaction**.
- For a reaction,  $\Delta H_{\text{rxn}} = H(\text{products}) - H(\text{reactants})$ .
- Consider the thermochemical equation for the production of water:
- The equation tells us that 483.6 kJ of energy is released to the surroundings when water is formed.
- In an enthalpy diagram, the reactants,  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$ , have a higher enthalpy than the product  $2 \text{H}_2\text{O}(\text{g})$ .
  
- Enthalpy is an extensive property.
  - Therefore the *magnitude* of enthalpy is directly proportional to the amount of reactant consumed.
  - Example: If 1 mol of  $\text{CH}_4$  is burned in oxygen to produce  $\text{CO}_2$  and water, 890 kJ of heat is released to the surroundings. If 2 mol of  $\text{CH}_4$  is burned, then 1780 kJ of heat is released.
  
- The sign  $\Delta H$  depends on the direction of the reaction.
  - The enthalpy changes for a reaction and its reverse reaction are equal in magnitude but opposite in sign.
  - Example:  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \quad \Delta H = -890 \text{ kJ}$
  - but  $\text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \quad \Delta H = +890 \text{ kJ}$
  
- Enthalpy change depends on state.
  - $2 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \quad \Delta H = -88 \text{ kJ}$

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

### Constant-Pressure Calorimetry

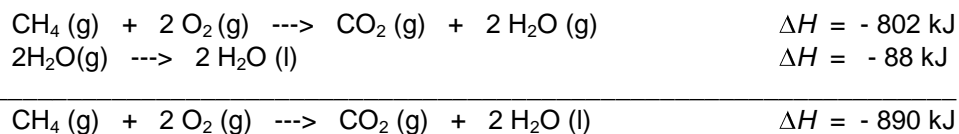
- Most common technique: use atmospheric pressure as the constant pressure.
- Recall that  $\Delta H = q_p$
- Easiest method: use a coffee-cup calorimeter.  
$$q_{\text{soln}} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T = -q_{\text{rxn}}$$

### 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,  $C_{\text{cal}}$ , then the heat of reaction,  
$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T$$
- Since the reaction is carried out under constant volume,  $q$  corresponds to  $\Delta E$  rather than  $\Delta H$ .
  - For most reactions the difference between  $\Delta E$  and  $\Delta H$  is small.

## 5.5 Hess's Law

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



- Therefore, for the reaction  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ ,  $\Delta H = -890 \text{ kJ}$
- Note that  $\Delta H$  is sensitive to the states of the reactants and products.
- Hess's law allows us to calculate enthalpy data for reactions that are difficult to carry out directly:  
 $\text{C}(\text{s}) + \text{O}_2(\text{g})$  produces a *mixture* of  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$

## 5.7 Enthalpies of Formation

- Hess's law states that if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of the  $\Delta H$ s for each of the individual steps.
- Consider the formation of  $\text{CO}_2(\text{g})$  and  $2 \text{H}_2\text{O}(\text{l})$  from  $\text{CH}_4(\text{g})$  and  $2 \text{O}_2(\text{g})$ 
  - If the reaction proceeds in one step:
$$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$$
then  $\Delta H_1 = -890 \text{ kJ}$
  - However, if the reaction proceeds through a CO intermediate:
$$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \quad \Delta H_2 = -607 \text{ kJ}$$
$$\text{CO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \quad \Delta H_3 = -283 \text{ kJ}$$
Then  $\Delta H$  for the overall reaction is:
$$\Delta H_3 + \Delta H_2 = -607 \text{ kJ} - 283 \text{ kJ} = -890 \text{ kJ} = \Delta H_1$$
- If a compound is formed from its constituent elements, then the enthalpy change for the reaction is called the **enthalpy of formation**,  $\Delta H_f$
- Standard conditions** (*standard state*) refer to the substance at:
  - 1 atm and  $25^\circ\text{C}$
- Standard enthalpy**,  $\Delta H^\circ$ , is the enthalpy measured when everything is in its standard state.
- Standard enthalpy of formation** of a compound,  $\Delta H_f^\circ$  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 most stable state is used. Example: When dealing with carbon we use graphite because graphite is more stable than diamond or  $\text{C}_{60}$ .
- 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  $\Delta H$  for
$$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$$
- We start with the reactants, decompose them into elements, then rearrange the elements to form products. The overall enthalpy is the sum of the enthalpy changes for each step.
- Decomposing into elements (note  $\text{O}_2$  is already elemental, so we concern ourselves with  $\text{C}_3\text{H}_8$ ); we have:
$$\text{C}_3\text{H}_8(\text{g}) \rightarrow 3 \text{C}(\text{s}) + 4 \text{H}_2\text{O}(\text{l}) \quad \Delta H_1 = \Delta H_f^\circ [\text{C}_3\text{H}_8(\text{g})]$$
  - Next we form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from their elements:
$$3 \text{C}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) \quad \Delta H_2 = 3\Delta H_f^\circ [\text{CO}_2(\text{g})]$$
$$4 \text{H}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 4 \text{H}_2\text{O}(\text{l}) \quad \Delta H_3 = 4\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})]$$
  - We look up the values and add:
$$\Delta H_{\text{rxn}}^\circ = -1(-103.85 \text{ kJ}) + 3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ}) = -2220 \text{ kJ}$$
- In general:
  - 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.

### Foods

- Fuel value is usually measured in Calories (1 nutritional Calorie, 1 Cal = 1000 cal).
- 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.
  - In the cells glucose reacts with  $O_2$  in a series of steps which ultimately produce  $CO_2$ ,  $H_2O$ , and energy.
$$C_6H_{12}O_6 (g) + 6 O_2 (g) \rightarrow 6 CO_2 (g) + 6 H_2O (l) \quad \Delta H^\circ = -2803 \text{ kJ}$$
- Fats, for example, tristearin, react with  $O_2$  as follows:
$$2 C_{57}H_{110}O_6 (s) + 163 O_2 (g) \rightarrow 114 CO_2 (g) + 110 H_2O (l) \quad \Delta H^\circ = -75,250 \text{ kJ}$$
- 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  $1.0 \times 10^6$  kJ of energy 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.
- Common fuels have typical fuel values around 30 kJ/g.
- Hydrogen has great potential as a fuel with a fuel value of 142 kJ/g.

### Other Energy Sources

- Nuclear energy: energy released in 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.



