

# Chapter 5. Thermochemistry

## Common Student Misconceptions

- Students confuse power and energy.
- Students fail to note that the first law of thermodynamics *is* the law of conservation of energy.
- Students have difficulty in determining what constitutes the system and the surroundings.
- Sign conventions in thermodynamics are always problematic.
- Students do not realize that a chemical reaction carried out in an open container occurs at constant pressure.
- Students do not realize that Hess's law is a consequence of the fact that enthalpy is a state function.
- Students should be directed to Appendix C of the text for a list of standard enthalpy values. (They are unlikely to find this information on their own!)

## 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.

$$w = F \times d$$

**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:

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

**Potential energy** is the energy an object possesses by virtue of its position or composition.

Electrostatic energy is an example (Lattice Energy)

It arises from interactions between charged particles.

$$LE = \frac{kQ_1Q_2}{d}$$

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**, abbreviated with a J.

$$\text{From } KE = \frac{1}{2}mv^2 \quad \text{J} = \text{kg} \times \frac{\text{m}^2}{\text{s}^2}$$

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<sub>2</sub> and O<sub>2</sub> in the cylinder form the 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.

$$w = F \times d$$

**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).

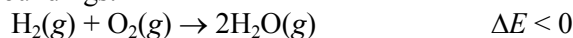
### Internal Energy

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.

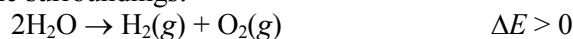
Change in internal energy,  $\Delta E = E_{\text{final}} - E_{\text{initial}}$ .

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,  $\Delta E < 0$ , indicating that the system has lost energy to the surroundings:



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,  $\Delta E > 0$ , indicating that the system has gained energy from the surroundings:



### 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 liberated from 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,  $q > 0$ .

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  $\text{H}_2\text{O}(l)$  at  $25^\circ\text{C}$  does not depend on whether we cool 50 g of  $\text{H}_2\text{O}(l)$  from  $100^\circ\text{C}$  to  $25^\circ\text{C}$  or heat 50 g of  $\text{H}_2\text{O}(l)$  at  $0^\circ\text{C}$  to  $25^\circ\text{C}$ .

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 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  $P\text{-}V$  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,  $\Delta H$ .

Mathematically,

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = \Delta E + P\Delta V$$

Since  $w = -P\Delta V$  and  $\Delta E = q + w$

then  $\Delta H = \Delta E + P\Delta V = (q_p + w) - w = q_p$

**This holds true at constant pressure only. Also, in reactions where volume is constant,  $P\Delta V = 0$ , so  $\Delta H = \Delta E$ .**

Heat transferred *from surroundings to the system* has a positive enthalpy (i.e.,  $\Delta H > 0$ ) **endothermic**

Heat transferred *from the system to the surroundings* has a negative enthalpy (i.e.,  $\Delta H < 0$ ) **exothermic**

**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. (or  $F = P \times A$ )

The volume of gas expands through  $\Delta V$  while the piston moves a height,  $\Delta h = h_f - h_i$  (distance)

The magnitude of work ( $w = F \times d$ ) done =  $F \times \Delta h = P \times A \times \Delta h = P \times \Delta V$ . (by substitution)

Since work is being done by the system *on the surroundings*, then it is negative

$$w = -P\Delta V.$$

Using the first law of thermodynamics,  $\Delta E = q + w$ , and  $w = -P\Delta V$

$$\Delta E = q - P\Delta V.$$

If the reaction is carried out under constant volume,

$\Delta V = 0$  and  $\Delta E = q_v$ . **At constant volume, heat is equal to change in energy.**

If the reaction is carried out under constant pressure,

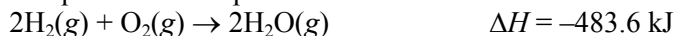
$$\Delta E = q_p - P\Delta V, \text{ or } \Delta H = q_p = \Delta E + P\Delta V \quad \text{and } \Delta E = \Delta H - P\Delta V$$

## 5.4 Enthalpies of Reaction

For a reaction,  $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$ .

The enthalpy change that accompanies a reaction is called the **enthalpy of reaction** or *heat of reaction* ( $\Delta H_{\text{rxn}}$ ).

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.

$\Delta H$  noted at the end of the balanced equation depends on the number of moles of reactants and products associated with the  $\Delta H$  value.

These equations are called *thermochemical equations*.

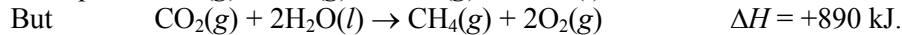
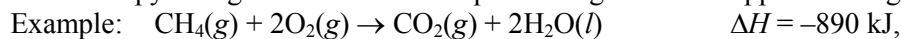
Enthalpy diagrams are used to represent enthalpy changes associated with a reaction.

In the enthalpy diagram for the combustion of  $\text{H}_2(\text{g})$ , the reactants,  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ , have a **higher** enthalpy than the products  $2\text{H}_2\text{O}(\text{g})$ ; this reaction is exothermic.

**KEY POINT:** Enthalpy is an extensive property. Therefore, the *magnitude* of enthalpy is directly proportional to the amount of reactant consumed. Example:  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ ;  $\Delta H = -890 \text{ kJ}$ ,

If **one mol of  $\text{CH}_4$**  is burned in oxygen to produce  $\text{CO}_2$  and water, **890 kJ of heat are released** to the surroundings. If **two mol of  $\text{CH}_4$  are burned**, then 1780 kJ of heat are released. The sign of  $\Delta H$  depends on the direction of the reaction.

The enthalpy change for a reaction is equal in magnitude but opposite in sign to  $\Delta H$  for the reverse reaction.



Enthalpy change depends on state.



## 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  $1^\circ\text{C}$ .

**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,  $q = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T$ .

Be careful of the sign of  $q$ .

### Constant-Pressure Calorimetry

The most common technique is to use atmospheric pressure as the constant pressure.

Recall  $\Delta H = q_p$ .

The easiest method is to use a coffee cup calorimeter.

$$q_{\text{soln}} = -q_{\text{rxn}}$$

$$q_{\text{soln}} = m_{\text{soln}} C_{\text{soln}} \Delta T$$

$$q_{\text{soln}} = \text{heat of solution} = (\text{grams of solution})(\text{specific heat of solution})(\text{change in temperature})$$

For dilute aqueous solutions, the specific heat of the solution will be close to that of pure water = 1.0 cal

### 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,

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T.$$

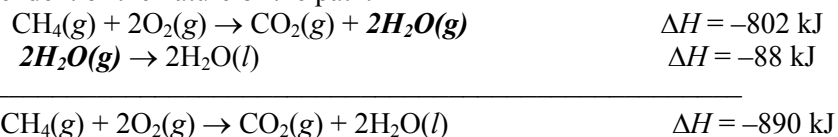
Since the reaction is carried out under constant volume,  $q$  relates to  $\Delta E$ .

## 5.6 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  $\Delta H$  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.



Therefore, for the reaction  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ ,  $\Delta H = -890 \text{ kJ}$ .

Note that  $\Delta H$  is sensitive to the states of the reactants and the products.

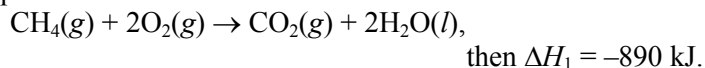
Hess's law allows us to calculate enthalpy data for reactions that are difficult to carry out directly:  $\text{C}(\text{s}) + \text{O}_2(\text{g})$  produces a *mixture* of  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$ .

## 5.7 Enthalpies of Formation

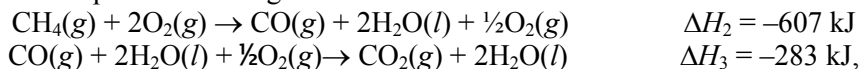
Hess's law states that if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of the  $\Delta H$ s for each of the individual steps.

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:



However, if the reaction proceeds through a CO intermediate:



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

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

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 state* (standard conditions) refer to the substance at: 1 atm and  $25^\circ\text{C}$  (298 K).

**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 more stable state is used. Example:

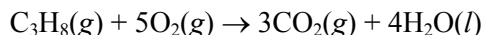
When dealing with carbon we use graphite because graphite is more stable than diamond or  $\text{C}_{60}$ .

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



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.

Decomposing into elements (note  $\text{O}_2$  is already elemental, so we concern ourselves with  $\text{C}_3\text{H}_8$ ):



Next we form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from their elements:



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:

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

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.

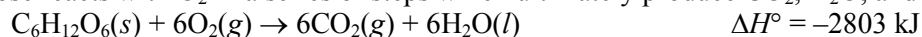
### Foods

Fuel value is usually measured in Calories (1 nutritional Calorie, 1  $\underline{\text{Cal}}$  = 1000  $\underline{\text{cal}}$ ).

Most energy in our bodies comes from the oxidation of carbohydrates and fats.

In the intestines, carbohydrates are converted into glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , or blood sugar.

In the cells glucose reacts with  $\text{O}_2$  in a series of steps which ultimately produce  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and energy.



Fats, for example tristearin, react with  $\text{O}_2$  as follows:



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  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$  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.