

## ***CHEM 110 Chapter 5: Thermochemistry***

Most of our energy comes from chemical reactions.

The study of energy and its changes is termed thermodynamics. Our study of thermodynamics will look at one branch in particular: thermochemistry.

**Thermochemistry consists of the energy changes involved in chemical reactions.**

### **Two Main Types of Energy**

- a. Kinetic: Commonly referred to as energy of motion

Formula:  $E_k = \frac{1}{2}mv^2$ , where  $m$  = mass of object and  $v$  = object's velocity (m/s)

- b. Potential: Commonly referred to as energy of position

Formula:  $E_p = mgh$ , where  $m$  = mass of object;  $g$  = gravitational constant  $9.8 \text{ m/s}^2$ ; and  $h$  = height of the object based on a reference height

Special Form for small charged objects:  $E_{el} = kQ_1Q_2 \div d$ , where  $k$  = a constant  $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$ ;  $Q$  represents charges 1 and 2 (typically that of an electron =  $1.60 \times 10^{-19} \text{ C}$ ), and  $d$  = distance in meters

### Units of Energy

- a. The joule (J) and the calorie (cal):  $1 \text{ cal} = 4.184 \text{ J}$  (exactly)

The joule is defined as the amount of energy a mass of 2 kg moving at a speed of 1 m/s possesses.

*How is this energy transferred between the system and the surroundings?*

### 2 Main Means: Work and Heat

**WORK:** A force ( $F$ , push or pull) applied over a distance ( $d$ ). *Since a distance is involved, in order for work to be done an object must be moved.*

Formula:  $w = F \times d$  for units of joules,  $F$  = newtons and  $d$  = meters

**HEAT:** Heat is energy being transferred from one object to another. This transfer occurs spontaneously for hotter to cooler objects due to a difference in temperature.

### **The 1<sup>st</sup> Law of Thermodynamics (Law of Conservation of Energy)**

Simply stated, the first law of thermodynamics states that during ordinary chemical and physical change, energy is neither created nor destroyed but rather *conserved*.

Any change in the internal energy ( $\Delta E$ ) can be described as the difference between the final and initial energies of the system:  $\Delta E = E_{\text{final}} - E_{\text{initial}}$

In addition,  $\Delta E$  can be defined as  $q + w$ , where  $q$  refers to heat gained or lost by the system and  $w$  refers to the work done on or by the system.

**IMPORTANT SIGN CONVENTIONS:** See Table 5.1 of text.

**For (+) values:**  $q$  = heat gained by system;  $w$  = work is done on the system

For (-) values:  $q$  = heat lost by system;  $w$  = work done by the system

If  $\Delta E$  is overall +, then the system has gained energy; - indicates the system has lost energy.

Also, the terms exothermic refer to heat being lost by the system while endothermic refers to heat being gained (absorbed) by the system.

Because we are not concerned with how the change in internal energy occurred within the system, only its value,  $\Delta E$ , energy is a state function.

Other state functions: temperature, pressure, volume, location. These do NOT depend on how they got the way they are. Only the fact that they have changed is of importance.

### ENTHALPY (H) (Section 5.3 of Text)

*Enthalpy is a thermodynamic property of a system (chemical or physical change) that is used to represent heat flow when only constant pressure–volume (P–V) work is performed.*

*P-V work occurs when gases expand or contract at constant pressure.*

*This work added to the internal energy (E) of the system = enthalpy (H)*

$$H = E + PV$$

$$\Delta H = \Delta E + P\Delta V$$

*Note that there is no  $\Delta$  in front of P since it is constant.*

*If  $\Delta E$  can also =  $q + w$  and  $-w = P\Delta V$ , then it follows with substitution that*

$$\Delta H = q + w - w = q_p$$

*Where the  $-w$  indicates work is done BY the system (it is losing internal energy) and  $+w$  indicates work is done ON the system (it is gaining internal energy)*

*Hence,  $\Delta H$  is the same as heat gained or lost by the system (chemical/physical reaction) at constant pressure.*

### Enthalpy Changes for Reactions

$\Delta H = H_{final} - H_{initial}$  OR since change in enthalpy for reactions can be represented by the reactants (initial) and products (final),

$$\Delta H = H_{products} - H_{reactants}$$

**Example:**  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}), \Delta H = -483.6 \text{ kJ}$

Guidelines for Enthalpy Change Equations (pg. 174 of text)

1. **Enthalpy is an extensive property. It does depend upon the amount of reactant(s) consumed and is directly proportional (increase reactant amount, increase thermal energy).**
2. **Reverse the reaction,  $\Delta H$  must also be reversed. Hence, if a reaction has a + enthalpy one way, it will have a - enthalpy the opposite way.**
3. **The enthalpy change depends upon the physical states of the reactants and products. Be attentive to this!**

**How can  $\Delta H$  be determined experimentally?**

**Answer: through calorimetry**

**Calorimetry is the measurement of heat flow through the use of a device called a calorimeter.**

**A simple calorimeter can be made using Styrofoam cups.**

Heat Capacity vs. Specific Heat

In order to do calculations using a calorimeter, it is helpful to know either the heat capacity or specific heat of substances involved.

Heat capacity = amount of heat required to raise the temperature of a certain mass of a substance or mixture by 1 K or 1°C. Hence, it is an extensive property. *It does depend upon the amount.*

**Specific heat** = amount of heat required to raise the temperature of a 1 gram of a substance by 1 K or 1°C. Hence, it is an **intensive property**. *It does NOT depend upon the amount.*

**Example:** 10 grams of water would have a heat capacity of 41.84 J/g°C; 1 gram of water would have a specific heat of 4.184 J/g°C.

$$\text{Specific Heat (s)} = q \div (m \times \Delta T)$$

Where  $q$  = quantity of heat gained or lost,  $m$  = mass of the substance or mixture, and  $\Delta T$  is the change in temperature

Typically, this equation is used in the rearranged form:

$$q = m \times s \times \Delta T$$

To find values of the specific heat for various substances, use a table like that found on pg. 176 of the text.

### **Constant-Pressure Calorimetry**

This type of calorimetry involves reactions in which the pressure is constant or nearly so, such as those occurring in solution. This is where a simple Styrofoam (coffee cup) calorimeter can be applied.

$$q = m \times s \times \Delta T$$

## Constant-Volume Calorimetry (Bomb Calorimetry)

This type of calorimetry is typically used to study combustion reactions and their stored chemical potential energy.

A small quantity of a substance is placed in a small cup termed “the bomb” followed by being sealed and pressurized with oxygen. A known mass of water is present and its change in temperature is measured before and after the combustion until a common temperature is reached. The heat evolved during the reaction can be measured using the below equation:

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T \text{ where } C_{\text{cal}} \text{ is the heat capacity of the calorimeter}$$

### Hess's Law

This very important enthalpy related law states that if the enthalpy change ( $\Delta H$ ) of an overall reaction is desired, it can be found by taking the sum of the enthalpy changes for the individual steps leading to that desired reaction.

*See example homework problems 61 and 63 from pg. 205.*

Enthalpies of Formation ( $\Delta H_f$ ): See Appendix C pgs. 1059–1061 for Table of Values

Enthalpy of Formation is defined as the enthalpy change that results when a particular compound is formed from its constituent elements.

Example:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$

Note that at ordinary temperatures  $\text{H}_2\text{O}$  does not exist as a gas but rather a liquid.

Hence, it is necessary to define a standard enthalpy change ( $\Delta H^\circ$ ) for a reaction.

This is defined as the change that occurs when all the reactants and products are in their standard states: typically 1 atmosphere pressure and 298.15 K (25°C).

So, the reaction for water's formation becomes:

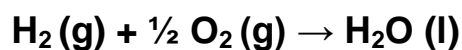


However, this does not define the quantity of the substances involved.

Standard Enthalpy of Formation ( $\Delta H^\circ_f$ ) = standard enthalpy change for 1 mole of a compound forming from its elements.

**See Table 5.3 of Text for Values along with Appendix C**

**For water,**



$$\Delta H^\circ_f = -285.8 \text{ kJ/mole}$$

These values of  $\Delta H^\circ_f$  can be used to calculate standard enthalpies of reaction ( $\Delta H^\circ_{\text{rxn}}$ ) similar to

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{products}) - \sum m \Delta H^\circ_f (\text{reactants})$$

Where the Greek letter sigma ( $\Sigma$ ) indicates “sum of” and “n” and “m” are coefficients from the balanced equation.

For instance:

$\Delta H^\circ_{\text{rxn}}$  for  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$ , “n” would equal 2 for  $\text{H}_2\text{O}(\text{l})$ , “m” would equal 2 for  $\text{H}_2(\text{g})$  and 1 for  $\text{O}_2(\text{g})$ .