

## Chem 115 POGIL Worksheet - Week #7

### First Law, Enthalpy, Calorimetry, and Hess's Law

#### Why?

In addition to mass changes, chemical reactions involve heat changes associated with changes in the substances' *internal energy*. Like mass-based stoichiometry, these changes are quantitative. One of the most important physical relationships governing energy change is the First Law of Thermodynamics. Most often we will consider this in terms of a thermodynamic function called *enthalpy*. Knowing about the First Law and enthalpy is essential to understanding the relationship between heat change and chemical reactions.

Knowing how much heat is gained or lost in a chemical or physical process is important in many real-life applications, such as determining the caloric content of foods, the heat potential of fuels, and the heat required or liberated to produce useful materials. The heat associated with a process is an extensive property (related to amount) and often can be measured with an apparatus called a calorimeter. But in many cases, it is impractical (or downright dangerous!) to measure the heat of a certain process in a calorimeter. Fortunately, internal energy and enthalpy are *state functions*. This means their values depend solely on the physical state of the system, and not on how that state was reached. As a result, we can determine the enthalpy of a process from the values of any series of steps that add to give the desired overall process. In other words, we do not always need to measure heat change directly.

#### Learning Objectives

- Know the First Law of Thermodynamics
- Understand the relationships between heat, work, internal energy, and enthalpy
- Understand the concepts of heat capacity, molar heat capacity, and specific heat
- Understand the principles of calorimetry
- Understand Hess's Law and its use for calculating reaction enthalpies

#### Success Criteria

- Be able to calculate heat and temperature changes
- Be able to apply the First Law of Thermodynamics
- Be able to calculate heat or enthalpy from calorimeter data
- Be able to use Hess's Law to calculate reaction enthalpies

#### Prerequisite

- Have read sections 5.1 through 5.6 in the text

## Information (First Law of Thermodynamics)

Energy is the ability to do work or transfer heat. Work is the transfer of energy from one body to another. In a sense, work is energy in the process of transfer. This association between work and energy allows us to define a unit of energy as that quantity transferred when a unit of work is done. In other words, *energy and work have the same units*. The SI unit of energy is the joule (J), which is a derived unit defined as follows:

$$\text{joule (J)} \equiv \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$$

Because the SI unit of force, the newton, is defined as

$$\text{newton (N)} = \text{kg}\cdot\text{m}\cdot\text{s}^{-2}$$

we can also think of the joule as being a newton-meter:

$$\text{joule (J)} = \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2} \equiv (\text{kg}\cdot\text{m}\cdot\text{s}^{-2})(\text{m}) = (\text{newton})(\text{m})$$

Systems of chemical interest usually consist of certain amounts of substances undergoing physical or chemical change in a container of some type. The substances themselves constitute the **system**. Everything else, such as the container or the immediate laboratory environment, is considered part of the **surroundings**. The energy of either the system or surroundings can take many forms: thermal (heat), radiant (light), chemical, mechanical, electrical. But all of these forms of energy can be viewed in terms of equivalent amounts of **kinetic energy** ( $K$ , energy of motion) and **potential energy** ( $U$ , energy of position or composition). Thus, the total energy of a system may be defined as the sum of its kinetic and potential energies.

$$E_t = K + U$$

This energy is called the **internal energy**,  $E$ , of the system. As the system undergoes chemical or physical change, the forms of its energy may change, and some energy may be gained from or lost to the surroundings, but energy is neither created nor destroyed. This idea is the essence of the **First Law of Thermodynamics**:

Energy can be transferred from one object to another, and its forms can be interconverted, but energy can neither be created nor destroyed.

Consistent with the First Law of Thermodynamics, the energies of the system and surroundings can change only if they exchange energy with each other. Thus, if the energy of one increases, the energy of the other decreases by the same amount, or vice versa, maintaining a constant total energy.

In general, the potential and kinetic energies of a system, which make up its internal energy, cannot be evaluated on an absolute scale. However, we can observe and measure changes in the magnitude of the internal energy,  $\Delta E$ , defined as<sup>1</sup>

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_f - E_i$$

A system undergoing chemical or physical change can change its internal energy by transferring heat ( $q$ ), doing work ( $w$ ), or both:

$$\Delta E = q + w$$

If the system receives heat from its surroundings, the sign on  $q$  is positive ( $q > 0$ ); if it gives off heat the sign on  $q$  is negative ( $q < 0$ ). Likewise, if the surroundings do work on the system, the sign on  $w$  is positive ( $w > 0$ ); if the system does work on the surroundings, the sign on  $w$  is negative ( $w < 0$ ).

An example of a system doing work would be the expansion of a gas against a constant external pressure. This might be the result of a gas-producing chemical reaction. A simple example of heat transfer occurs when a hot object, such as a piece of metal, is placed in room-temperature water. If we consider the metal to be the system, as it transfers heat to its surroundings, the water, the temperature of the metal will go down and the temperature of the water will go up. After some time, a condition of **thermal equilibrium** will occur, at which point the temperature of both the metal and the water will be the same. This illustration raises the following general points about heat flow:

- (a) The sense of heat flow is always from the hotter object to the cooler object.
- (b) Thermal equilibrium occurs when both system and surroundings are at the same temperature.
- (c) The quantity of heat lost from the hotter object is equal to the heat gained by the cooler object.

The heat transferred between the system and surroundings represents a **change in heat content of the system**. If a system takes up heat from its surroundings, its heat content will be higher at the end of the process. Consequently,  $q$  will be positive. Such a process is **endothermic**. If the system gives off heat to its surroundings, its heat content at the end of the process will be less.

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<sup>1</sup>The symbol  $\Delta$  (Greek delta) indicates a change in some property. We will see other changes in properties, indicated by delta functions, which will always be defined as the difference between the final value minus the initial value; e.g.,  $\Delta x = x_f - x_i$ . This order of comparison (final minus initial) is crucial to imparting the correct sign on the value of the change.

Consequently,  $q$  will be negative. Such a process is **exothermic**. If a process is endothermic in one direction, it is exothermic in the opposite direction, and vice versa.

### Key Questions

1. What are the two major ways in which the internal energy of an object can be categorized? How do these ways differ from one another?
2. If a system loses heat, where does it go?
3. Describe the following processes as exothermic or endothermic:
  - a. an ice cube melts on a warm surface
  - b. water freezes
  - c. calcium chloride is mixed with water, resulting in a very hot solution
  - d. ammonium nitrate is mixed in water, resulting in a very cold solution

### Information (Enthalpy)

We will often be interested in the *heat content under constant pressure conditions*, called the **enthalpy**,  $H$ , of the system. Like internal energy,  $H$  cannot be measured directly, but we can measure the change in  $H$ , defined as

$$\Delta H \equiv H_f - H_i = q_p$$

where  $H_f$  and  $H_i$  are the final and initial heat content of the system, respectively, under constant pressure; and  $q_p$  is the heat transferred under constant pressure conditions. Under constant pressure conditions, we can rewrite the defining equation for internal energy as

$$\Delta E = q_p + w = \Delta H + w$$

from which it follows

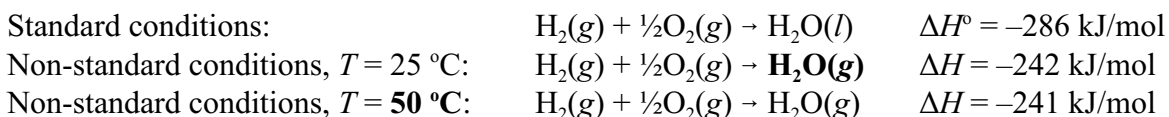
$$\Delta H = \Delta E - w$$

Note that if no work is done ( $w = 0$ ),  $\Delta H = \Delta E$ . This means that the enthalpy change is the internal energy change when no work is done.

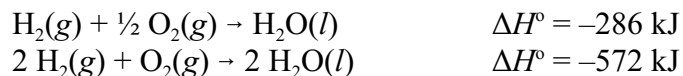
The amount of heat transferred in a chemical or physical process depends upon (1) physical conditions, (2) amounts of substances, and (3) direction of change. The *physical conditions* on which enthalpy depends are temperature ( $T$ ), pressure ( $P$ ), and physical state (i.e., solid, liquid, gas, aqueous solution). Therefore, we must be careful when quoting values of  $q$  or  $\Delta H$  to be sure to specify these conditions. To avoid confusion, we define

**Standard conditions:**  $T = 25\text{ }^\circ\text{C}$ ;  $P = 1\text{ atm} = 760\text{ mm Hg} = 29.9213\text{ in. Hg}$ ; all substances in their usual states for these conditions (the **standard state**).

Inasmuch as physical state is important, it is common practice to note the states (*s, l, g, aq*) along with the formulas of each chemical compound in a **thermochemical equation**. A thermochemical equation is an ordinary chemical equation written in conjunction with a thermochemical value (e. g., *q, ΔH*), where *the reactant and product coefficients are taken as numbers of moles*. When the value of the enthalpy is quoted for the reaction occurring under standard conditions, it is called the **standard enthalpy**, symbolized  $\Delta H^\circ$ . Note the differences in the following thermochemical reactions, due to subtle changes in conditions:



Enthalpy depends upon the amount of substance; i.e., it is an *extensive property*. Since thermochemical equations are read with the understanding that the coefficients are numbers of moles, changing the coefficients by multiplying through the equation also multiplies the value of the enthalpy. Compare the following:

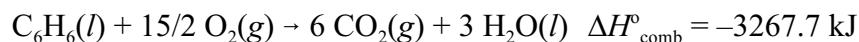


Reversing the direction of a reaction reverses the sense of the heat transfer. As we have seen, an exothermic process in one direction will be an endothermic process in its reverse direction. The heat transferred is the same in both cases, but the direction changes, as indicated by a sign change on the value of *q* or  $\Delta H$ . For example



## Exercises

4. The thermochemical equation for the burning of one mole of benzene under standard conditions is



- Is this reaction exothermic or endothermic?
- How much heat is released when a 5.00-g sample of benzene is burned in excess oxygen under standard conditions? (m.w.  $\text{C}_6\text{H}_6 = 78.11 \text{ u}$ )

## Information (Heat Capacity, Molar Heat Capacity, and Specific Heat)

The *heat capacity*, *C*, is the amount of heat, *q*, required to raise the temperature,  $\Delta T$ , of an object by 1  $^\circ\text{C}$ . The three variables are related by the equation

$$q = C\Delta T$$

The value of  $C$  in this equation, and likewise the magnitudes of  $q$  and  $\Delta T$ , pertain to a certain sample and depend on the amount. For example, if we compare a teaspoon of water with a swimming pool of water, the heat capacity of the swimming pool water is vastly larger. However, on a per mole or per gram basis, the heat capacities are the same. Thus, for pure substances, the heat capacity is usually defined on the basis of a one mole or one gram sample. The *molar heat capacity*,  $C_m$ , is the heat capacity per mole of substance, and the defining equation can be written

$$q = nC_m\Delta T$$

where  $n$  is the number of moles in the sample. Likewise, the *specific heat*,  $C_s$ , is the heat capacity per gram of substance, and the defining equation can be written

$$q = mC_s\Delta T$$

where  $m$  is the mass of substance in grams. In other words, for a specific sample of a pure substance,  $C = nC_m = mC_s$ . In using these relationships, realize that a change in temperature expressed in  $^{\circ}\text{C}$  is the same value if expressed in K units.

### Exercises

5. The specific heat of iron (at. wt. = 55.85 u) is 0.450 J/g·K. What is the heat capacity of a 23.5-g block of iron? What is the value of the molar heat capacity of iron?
6. How many joules of heat are required to raise the temperature of a 23.5-g block of iron from 25.0  $^{\circ}\text{C}$  to 96.2  $^{\circ}\text{C}$ ?

### Information (Calorimetry)

Heat absorbed or liberated by a chemical reaction can be determined with a calorimeter. The heat of the reaction is not directly observed, but rather its effect on an amount of water surrounding the reaction vessel in the calorimeter is measured. The heat capacity of the calorimeter,  $C_{\text{cal}}$ , can be experimentally determined or calculated, and with this and the observed temperature change the heat change of the calorimeter can be calculated:

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

*The heat change experienced by the calorimeter is equal in magnitude but opposite in sign to that for the reaction that caused it; i.e.,*

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

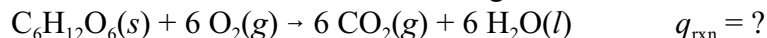
Thus, if the calorimeter experiences an endothermic heat change,  $q_{\text{cal}} > 0$ , characterized by a rise in its temperature, this must have been the consequence of an exothermic reaction, for which  $q_{\text{rxn}} < 0$  (negative). Conversely, if the calorimeter experiences an exothermic heat change,  $q_{\text{cal}} < 0$ ,

characterized by a fall in its temperature, this must have been the consequence of an endothermic reaction, for which  $q_{\text{rxn}} > 0$  (positive).

A simple calorimeter constructed from Styrofoam coffee cups (see Fig. 5.18 in the 12<sup>th</sup> edition of your book), such as you will use in the laboratory, measures reaction heats under constant pressure conditions; thus,  $q_{\text{rxn}} = \Delta H_{\text{rxn}}$ , the change in enthalpy of the reaction. This is often used to measure the heat change of a solution formed in the inner cup. The specific heat of the solution is generally assumed to be the same as that of pure water, 4.184 J/g·K. The heat capacity of the calorimeter is calculated as the product of the mass of the solution times 4.184 J/g·K. A bomb calorimeter (cf. Fig. 5.19 in the 12<sup>th</sup> edition of your book) measures heats under constant volume conditions; thus,  $q_{\text{rxn}} = \Delta E_{\text{rxn}}$ , the change in internal energy of the reaction. In most cases, the difference between  $\Delta H$  and  $\Delta E$  is small and is often ignored.

### Exercises

7. A 2.58-g sample of  $\text{KNO}_3$  (f.w. = 101.11 u) was added to 98.57 g of water in a coffee-cup calorimeter. The initial temperature of the water was 22.5 °C, and the temperature of the solution after mixing was 20.4 °C. On the basis of this experiment, what is the heat of solution per mole of  $\text{KNO}_3$  [f.w. = 101.11 u]? The specific heat of water is 4.184 J/g·K.
8. The combustion of 1.50 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  (m.w. = 180.0), caused the temperature of a bomb calorimeter to rise from 19.00 °C to 24.32 °C. The calorimeter had a heat capacity of 4.42 kJ/K. Calculate the heat of combustion of one mole of glucose:



### Information (Standard Conditions, State Functions and Hess's Law)

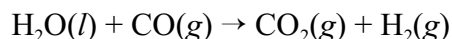
Remember that the measured value of  $\Delta H$  depends on the states of all reactants and products (*s*, *l*, *g*, *aq*) and the temperature and pressure under which the reaction occurs. Thus, as noted above, it is useful to define a set of **standard conditions**, defined as  $T = 25 \text{ °C}$ ,  $P = 1 \text{ atm}$ , and all substances in their usual states for these conditions (the **standard state**). The standard state of an element is its most stable state under standard conditions; e.g.,  $\text{H}_2(g)$ ,  $\text{C}(s)$  – graphite,  $\text{S}_8(s)$ ,  $\text{P}_4(s)$ . For compounds, the standard state is the most prevalent state under standard conditions; e.g.,  $\text{H}_2\text{O}(l)$ ,  $\text{CO}_2(g)$ ,  $\text{C}_2\text{H}_2(g)$ ,  $\text{C}_6\text{H}_6(l)$ .

Enthalpy is a **state function**, which only depends upon current conditions (the state of the system) for its value, not on how the current state was reached. As applied to  $\Delta H = H_f - H_i$ , the value of the enthalpy change for any process depends only on the difference between the final and initial states, not on the path taken to get from the initial to the final state. This means that any set of steps, whether real or imagined, that takes the system from the initial state to the final state of interest will have a sum of  $\Delta H$  values for all the steps that is identical to the value of  $\Delta H$  for the overall process if done directly. This principle, called **Hess's Law of Constant Heat Summation**, was first established by G. H. Hess in 1840:

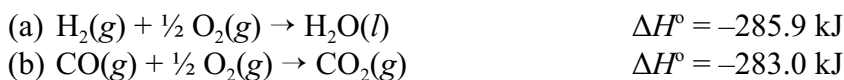
*The enthalpy change for a reaction is independent of path.*

In applying Hess's Law, a set of given thermochemical equations is manipulated such that they add to give a balanced thermochemical equation for the process of interest (the *target equation*). In doing this, whenever a given thermochemical equation is multiplied (usually by an integer, but sometimes by a rational fraction such as  $\frac{1}{2}$ ,  $\frac{1}{3}$ , etc.), its  $\Delta H$  is likewise multiplied. Whenever the direction of a given thermochemical equation is reversed, its  $\Delta H$  value changes sign.

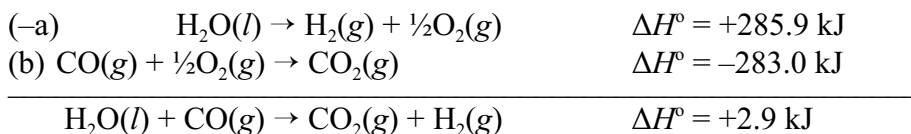
For example, suppose we wish to calculate  $\Delta H^\circ$  for the reaction,



given the following two thermochemical equations:

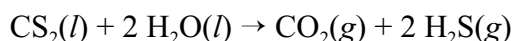


If we reverse equation (a) and keep equation (b) as given, we can add to get the desired overall reaction (the target equation):

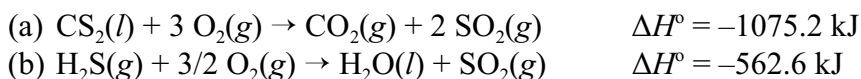


### Exercises

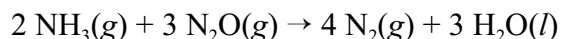
9. Calculate  $\Delta H^\circ$  for the reaction,



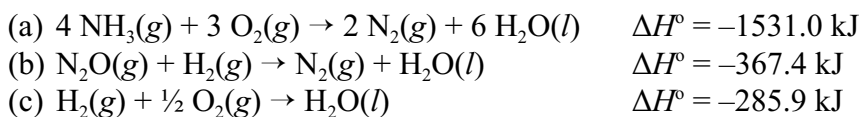
Given:



10. Calculate  $\Delta H^\circ$  for the reaction,



Given:





11. The **heat of combustion** for a compound composed of C and H, possibly with either or both O and N, is the heat liberated when *one mole* of the substance is burned with the stoichiometric amount of  $O_2(g)$  to produce,  $CO_2(g)$ ,  $H_2O(l)$ , and  $N_2(g)$ , as may be appropriate.

- i. Write the balanced equation for the combustion of one mole of  $C_2H_6(g)$ , which would be the basis for the thermochemical equation defining the heat of combustion of ethane.
- ii. Calculate the heat of combustion of  $C_2H_6(g)$  from the following data:

