Chem 115 POGIL Worksheet - Week 8
Thermochemistry (Continued), Electromagnetic Radiation, and Line Spectra

Why?

As we saw last week, enthalpy and internal energy are state functions, which means that the sum of the heats of any set of steps that adds to give an overall reaction will have the same heat as doing the reaction directly. This is Hess's Law. We will revisit this today and go on to see that if we use a special kind of thermochemical reaction, called the standard enthalpy of formation, we can calculate enthalpies of reactions without having to manipulate a series of individual thermochemical equations for each step.

To understand the modern model of atomic structure, we need to look at the nature of light and other forms of electromagnetic radiation. One of the most important ideas to emerge at the start of the twentieth century was that energy of subatomic particles and electromagnetic radiation is not continuous, but rather is quantized in discrete allowable values. An understanding of the basic relationships among the characteristic properties of electromagnetic radiation and an appreciation of the nature of state-to-state transitions in quantized systems will lay a foundation for understanding the modern quantum mechanical model of the atom.

Learning Objective
- Understand Hess's Law
- Understand the definition and use of standard enthalpy of formation
- Understand the fundamental relationships of electromagnetic radiation and the electromagnetic spectrum
- Understand the relationship between line spectra and the quantum concept

Success Criteria
- Be able to calculate enthalpy of a target reaction from a series of given reactions
- Be able to apply standard enthalpies of formation to calculate the enthalpy of a reaction
- Be able to do conversions between energy, wavelength, and frequency of electromagnetic radiation
- Be able to correlate state-to-state transitions with region of the electromagnetic spectrum and calculate the energy of a state-to-state transition

Prerequisite
- Have read sections 5.6 and 5.7
- Have read sections 6.1 through 6.3

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

Remember that the measured value of ΔH depends on the states of all reactants and products (s, l, g, aq) and the temperature and pressure under which the reaction occurs. In order to make meaningful direct comparisons, it is useful to define a set of standard conditions. By international agreement, **standard conditions** are defined as $T = 25\ °C$; $P = 1$ atm; all substances in their usual states for these conditions (the **standard state**). The standard state of an element is its most stable state; e.g., $H_2(g)$, $C(s)$ – graphite, $S_8(s)$, $P_4(s)$. For compounds, the standard state is the most prevalent state under standard conditions; e.g., $H_2O(l)$, $CO_2(g)$, $C_2H_2(g)$, $C_6H_6(l)$.
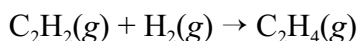
Enthalpy is a **state function**, which only depends upon current conditions (the state of the system) for its value, not on how the current state was reached. As applied to $\Delta H = H_f - H_i$, the value of the enthalpy change for any process depends only on the difference between the final and initial states, not on the path chosen. This means that any set of steps, whether real or imagined, that take the system from the initial state to the final state of interest will have a sum of ΔH values for all the steps that is equal to the value of ΔH for the overall process done directly. This principle, called **Hess's Law of Constant Heat Summation**, was first established by G. H. Hess in 1840:

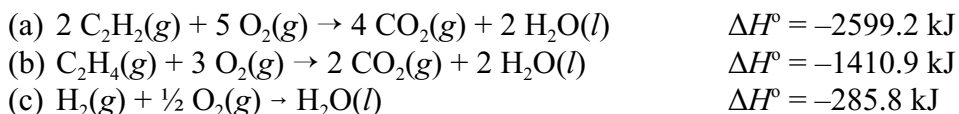*The enthalpy change for a reaction is independent of path.*

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 or rational fraction), its ΔH is likewise multiplied. Whenever the direction of a given thermochemical equation is reversed, its ΔH value changes sign.

Review Exercise

1. Calculate $\Delta H°$ for the reaction,

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$

Given:

(a) $2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$ $\Delta H° = -2599.2$ kJ
(b) $C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(l)$ $\Delta H° = -1410.9$ kJ
(c) $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l)$ $\Delta H° = -285.8$ kJ
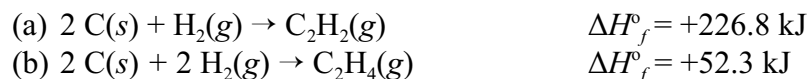
Information (Standard Enthalpies of Formation, $\Delta H°_f$)

Hess's Law calculations are done so frequently that it is convenient to have tabulated data for a large number of reactions. The most generally useful data for these kinds of calculations are **standard enthalpies of formation**.

The standard enthalpy of formation, $\Delta H°_f$, of a compound is the enthalpy change for the reaction in which *one mole* of the compound in its standard state is made from the stoichiometric amounts of its elements in their standard states. For all elements in their standard states, $\Delta H°_f \equiv 0$, by definition.

For example, the following thermochemical equations define standard enthalpies of formation for $C_2H_2(g)$ and $C_2H_4(g)$, respectively.

$$\text{(a) } 2 C(s) + H_2(g) \rightarrow C_2H_2(g) \qquad\qquad \Delta H°_f = +226.8 \text{ kJ}$$
$$\text{(b) } 2 C(s) + 2 H_2(g) \rightarrow C_2H_4(g) \qquad\qquad \Delta H°_f = +52.3 \text{ kJ}$$
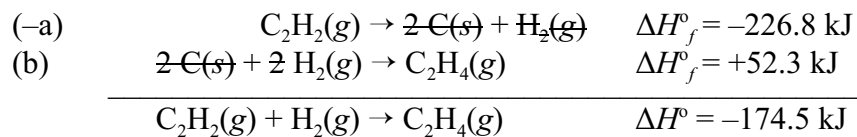
Notice that each of these equations gives the heat produced when exactly *one mole* of the product compound is made. There are no thermochemical equations for the formation of substances such as $C(s)$ as graphite or $H_2(g)$ as the gaseous element, because these are their normal elemental states. Their standard enthalpies of formation are set as zero by definition.

Let's use the two enthalpy of formation equations given above to calculate the enthalpy of the following reaction:
$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g) \qquad\qquad \Delta H° = ?$$
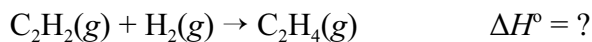
You calculated the enthalpy of this reaction in Review Exercise 1, but now we are going to do it with the thermochemical equations that define $\Delta H°_f$ for $C_2H_2(g)$ and $C_2H_4(g)$. To do this, we simply need to take the reverse of equation (a) with the negative of its given enthaply, and add it to equation (b), using its given enthalpy. The resulting sum is:

$$(-a) \qquad\qquad C_2H_2(g) \rightarrow \cancel{2 C(s)} + \cancel{H_2(g)} \qquad \Delta H°_f = -226.8 \text{ kJ}$$
$$(b) \qquad \cancel{2 C(s)} + 2 H_2(g) \rightarrow C_2H_4(g) \qquad\qquad \Delta H°_f = +52.3 \text{ kJ}$$
$$\overline{ C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g) \qquad\qquad \Delta H° = -174.5 \text{ kJ}}$$

This is the same answer you obtained in exercise 1 (if you did it correctly), as expected on the basis of Hess's Law. But notice that the answer we obtain here is the following sum, where $\Delta H°_f$ $(H_2) = 0$, because $H_2(g)$ is an element in its standard state:

$$\Delta H°_{rxn} = \Delta H°_f(C_2H_4) - \{\Delta H°_f(C_2H_2) + \Delta H°_f(H_2)\}$$
$$= \{+52.3 \text{ kJ}\} - \{-226.8 \text{ kJ} + 0 \text{ kJ}\}$$

This is the sum of the enthalpies of formation of the products, multiplied by their stoichiometric coefficients (here, 1), minus the sum of the enthalpies of formation of the reactants, multiplied by their stoichiometric coefficients (here again, both 1). This is a general result, which we can summarize as
$$\Delta H°_{rxn} = \Sigma n_p \Delta H°_p - \Sigma n_r \Delta H°_r$$

where n_p and n_r are the stoichiometric coefficients of each of the products and each of the reactants, respectively. [The Σ (Greek sigma) means "take the sum of".] Note that this relationship can *only* be used if all the data are enthalpies of formation. For a general reaction

$$aA + bB \rightarrow cC + dD,$$
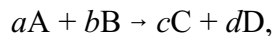
we would have

$$\Delta H^{\circ}_{rxn} = [c\Delta H^{\circ}_f(C) + d\Delta H^{\circ}_f(D)] - [a\Delta H^{\circ}_f(A) + b\Delta H^{\circ}_f(B)]$$
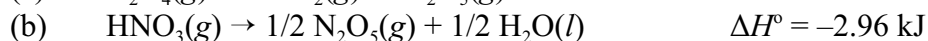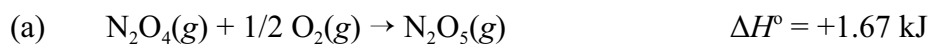
Key Questions

2. Write the balanced thermochemical equations that pertain to the standard enthalpies of formation of the given compounds.
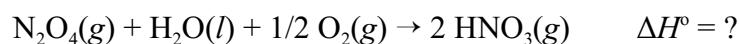
Compound	ΔH°_f (kJ/mol)	Thermochemical Equation
$CCl_4(g)$	−106.7	
$Fe_2O_3(s)$	−822.16	
$HNO_3(g)$	−134.31	
$NaHCO_3(s)$	−947.7	

Exercises

3. i. Given:

(a) $N_2O_4(g) + 1/2\ O_2(g) \rightarrow N_2O_5(g)$ $\Delta H^{\circ} = +1.67$ kJ
(b) $HNO_3(g) \rightarrow 1/2\ N_2O_5(g) + 1/2\ H_2O(l)$ $\Delta H^{\circ} = -2.96$ kJ

Calculate ΔH° for the reaction

$$N_2O_4(g) + H_2O(l) + 1/2\ O_2(g) \rightarrow 2\ HNO_3(g) \qquad \Delta H^{\circ} = ?$$

ii. Given following standard enthalpy of formation data:

Compound	ΔH°_f (kJ/mol)
$N_2O_4(g)$	+9.66
$HNO_3(g)$	−134.31
$H_2O(l)$	−285.83

Calculate ΔH° for the reaction

$$N_2O_4(g) + H_2O(l) + 1/2\ O_2(g) \rightarrow 2\ HNO_3(g) \qquad \Delta H^{\circ} = ?$$
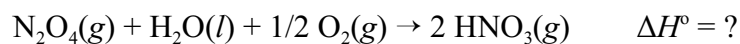
Compare your answer to your answer in part i.

4. Calculate the heat of combustion of methane, $CH_4(g)$, defined by the following thermochemical equation:

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \qquad\qquad \Delta H°_{rxn} = ?$$
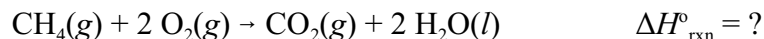
Given the following standard enthalpies of formation:

Compound	$\Delta H°_f$ (kJ/mol)
$CH_4(g)$	−74.85
$CO_2(g)$	−393.5
$H_2O(l)$	−285.8 kJ

5. Calculate the enthalpy of formation, $\Delta H°_f$, for benzene, $C_6H_6(l)$, given that the heats of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 kJ and −285.8 kJ, respectively, and that the heat of combustion of $C_6H_6(l)$ is −3267.7 kJ. To do this, carry out the following steps.

   i. Write the balanced thermochemical equation that defines the enthalpy of formation of benzene, $C_6H_6(l)$.

   ii. Write the balanced thermochemical equation for the heat of combustion of benzene, $C_6H_6(l)$.

   iii. Based on your answer to question ii, write an expression for the heat of combustion of benzene, $\Delta H°_{comb}$, in terms of the enthalpies of formation of the reactants and products. Using the data given in the problem, solve this for the unknown value of $\Delta H°_f(C_6H_6)$, the enthalpy of formation of benzene.

Information (Electromagnetic Radiation)
Light and other forms of radiant energy can be thought of a being propagated as a wave of oscillating electric and magnetic components. Hence, we call radiant energy **electromagnetic radiation**. Electromagnetic radiation is characterized by its energy (E), wavelength (λ – Greek lambda), and frequency (ν – Greek nu). The speed of propagation in a vacuum, commonly called the speed of light (c), is 2.9979×10^8 m·s^{-1}. The relationships between E, λ, and ν are

$$\nu = c/\lambda$$

$$E = h\nu = hc/\lambda$$

where h is Plank's constant, equal to 6.626×10^{-34} J·s. These equations apply to all kinds of electromagnetic radiation. The units of wavelength are usually nanometers (nm), where 1 nm = 10^{-9} m, although other length units may be used, depending on the radiation. An older unit called the Ångstrom (Å) is sometimes used with light and with x-rays, where 1 Å = 10^{-10} m = 0.1 nm.

Frequency usually has units of sec^{-1}, called the hertz (Hz). This means the number of waves that pass a reference point per second, but the word "wave" is not part of the unit and does not factor into the dimensional analysis.

The following chart shows the wavelength ranges of the various kinds of electromagnetic radiation.
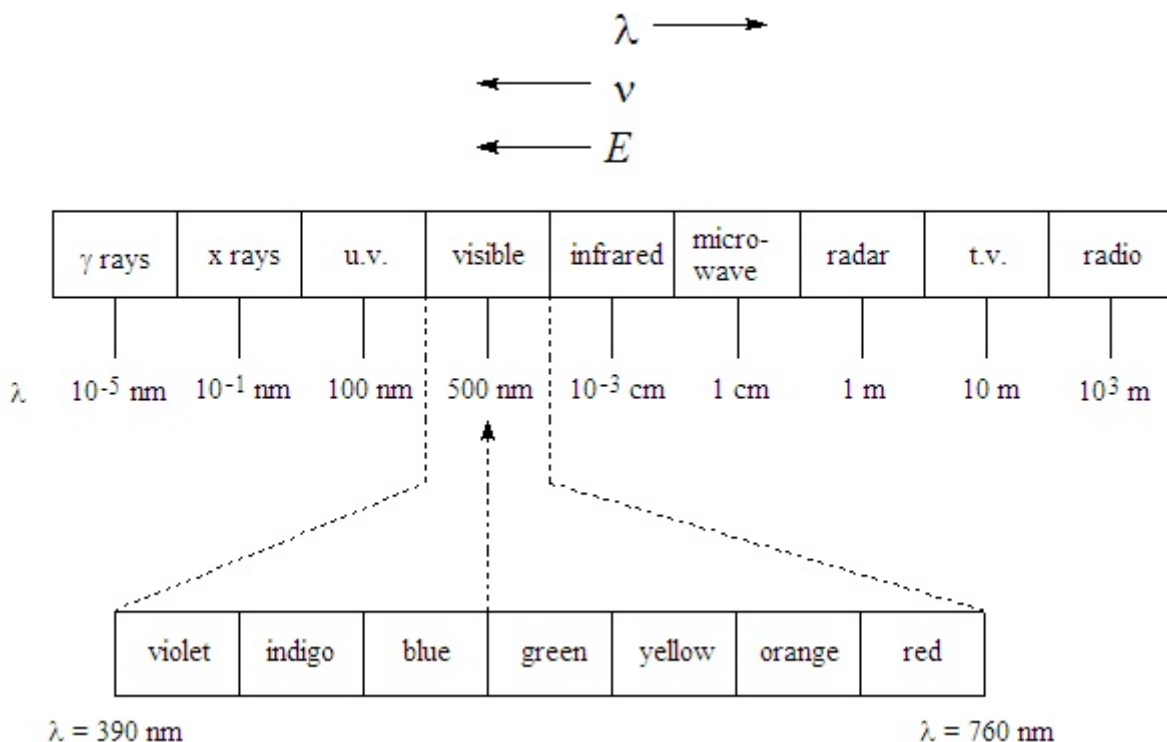
Key Questions

6. For each of the following, indicate which kind of radiation has higher energy.
   red light or blue light
   infrared radiation or radio waves
   x-rays or visible light

7. For each of the following, indicate which has higher frequency
   light with $\lambda = 490$ nm or light with $\lambda = 520$ nm
   light with energy of 3.0×10^{-19} J or light with energy of 4.5×10^{-19} J

Exercise

8. An argon laser emits green light with a wavelength of 514.5 nm. Calculate the following for this light: (a) the wavelength in Å; (b) the frequency in Hz (s^{-1}); (c) the energy in joules, J.

Information (Line Spectra and the Bohr Model)

Electrons bombarding hydrogen gas (H_2) in a discharge tube cause the formation of monatomic H atoms, some of which are in high energy states (*excited states*). The atoms can lose a portion of their excess energy by emitting electromagnetic radiation. Rather than a continuous spectrum containing all wavelengths within a range, the emitted radiation of hydrogen and other monatomic gasses consists of only certain characteristic wavelengths, which are typically observed as discrete lines in the spectrum, falling in the range from the ultraviolet region through the infrared region. Hence, these spectra are called *line spectra*. For hydrogen, four of these wavelengths fall in the visible region (where they can be seen by a human eye) and give lines that are violet (410 nm), blue (434 nm), blue-green (486 nm), and red (656 nm). In 1885, Balmer determined that these lines fit a relatively simple equation that relates the reciprocal of their wavelength ($1/\lambda$) to pairs of integers (n_1 and n_2). When additional lines in the invisible infrared and ultraviolet regions were discovered, they and Balmer's visible lines were all found to fit the following general equation:

$$\frac{1}{\lambda} = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad n = 1, 2, 3, ...; \ n_2 > n_1$$

where $\Re$, the *Rydberg constant*, is 1.096776×10^7 m^{-1}, and the n values are integers with $n_2 > n_1$. This equation was only valid for the emissions from hydrogen, a one-electron atom. In the case of the visible lines of the Balmer series, the value of n_1 is 2. When $n_1 = 1$, the associated lines fall in the ultraviolet region (the Lyman series). Values of $n_1 \geq 3$ correspond to successive series that fall in the infrared region (the Paschen, Brackett, and Pfund series), with increasing wavelength and decreasing frequency and energy as n_1 increases.

Neils Bohr, inspired by the Balmer equation and Max Plank's ideas of quantized energy, devised a model for the hydrogen atom. In Bohr's model the single electron is thought to be confined to certain orbits around the nucleus, where each orbit corresponds to a particular, quantized energy, given by the equation

$$E = (-hc\Re)\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18} \text{ J})\left(\frac{1}{n^2}\right)$$

Here n, the *principal quantum number*, can take on integer values from 1 to ∞. This equation can be extended to other one-electron atoms (e.g., He$^+$, Li^{2+}) in the form

$$E = -BZ^2/n^2 \qquad n = 1, 2, 3, ...$$

where B is a constant similar to the Rydberg constant and Z is the atomic number (number of protons). In either form, the Bohr equation predicts that the energy of the one-electron atom is inversely proportional to the square of the quantum number of its state. This gives rise to the energy level diagram shown on the last page of this work sheet, in which the spacing between energy states gets smaller as n increases.

In Bohr's model, as n increases, the electron is in an orbit that is further from the nucleus and therefore has a higher (less negative) energy. Note that the zero of energy corresponds to $n = \infty$, which has the electron an infinite distance away from the nucleus. Any lower value of n places the negative electron closer to the positive nucleus to which it is attracted, giving rise to a more favorable (negative) energy. The atom absorbs or emits energy in the form of electromagnetic radiation by changing from an initial state (E_i) with a value n_i to a final state (E_f) with a value n_f. These changes in state are called *transitions*. With absorption, the atom acquires energy, resulting in a higher energy state. Thus, for an absorption transition, $n_f > n_i$. With emission, the atom loses energy, resulting in a lower energy state. Thus, for emission, $n_f < n_i$. It is transitions from higher energy states to lower energy states that give rise to the observed line spectra. For any transition, the energy of the electromagnetic radiation (a photon) absorbed or emitted must exactly match the energy difference between the two states; i.e.,

$$\Delta E = E_f - E_i = E_{photon} = h\nu$$

Using the Bohr equation for the allowed energies in states n_f and n_i, we can write an equation to calculate the photon's energy as

$$\Delta E = E_{photon} = h\nu = \frac{hc}{\lambda} = (-2.18 \times 10^{-18}\,\text{J})\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

This equation has the same form as the experimentally determined Balmer equation, if we assume n_f and n_i of the Bohr equation correspond to n_1 and n_2 of the Balmer equation. Regardless of whether absorption or emission is involved, the energy of a photon is always taken as a positive number, so any sense of sign to the energy calculated from this equation is routinely dropped.

As the diagram on the last page shows, the Balmer series, which gives rise to the four lines in the visible spectrum, corresponds to transitions from higher states down to $n_f = 2$ (i.e., $3 \rightarrow 2$, $4 \rightarrow 2$, $5 \rightarrow 2$, $6 \rightarrow 2$). The energy gaps between $n_f = 2$ and $n_i > 2$ are such that the wavelengths of the emitted photons fall in the visible region. In the Lyman series (see diagram), the transitions are from upper states down to the lowest state ($n_f = 1$), called the *ground state* of the atom. The gaps between $n = 1$ and $n > 1$ states are bigger, and so the emitted photons have higher energies, falling in the ultraviolet region. By contrast, in the Paschen series (see diagram), the transitions are from higher states down to $n_f = 3$. Because the energy separations between states with higher n values are smaller, the transitions have lower energies, falling in the infrared region. The energy differences are even smaller when the transitions are from upper states to either $n_f = 4$ or $n_f = 5$, making the emitted radiation fall even further into the infrared region for these series (cf. Brackett and Pfund series on the diagram).

Key Questions

9. Is energy emitted or absorbed when the following transitions occur in hydrogen: (a) from $n = 1$ to $n = 3$, (b) from $n = 5$ to $n = 2$, (c) an H^+ ion acquires an electron into the $n = 2$ state.

10. The four visible lines of the Balmer series in the emission spectrum of hydrogen are violet (410 nm), blue (434 nm), blue-green (486 nm), and red (656 nm). Assign these as state-to-state transitions of the type $n_i \rightarrow n_f$, giving the n values involved for each line.

Exercise

11. Calculate the energy of the first line in the Lyman series for the hydrogen atom, which arises from a transition from $n_i = 2$ to $n_f = 1$. What is the wavelength of the radiation emitted? In what region of the electromagnetic spectrum does it fall?

Energy Level Model for a One-Electron Atom
(Named series are for the hydrogen atom.)

$n = \infty$ Pfund series $E_\infty = 0$

$n = 6$ $E_6 = -B/6^2$

$n = 5$ $E_5 = -B/5^2$

Brackett series $E_4 = -B/4^2$

$n = 4$

Paschen series

$n = 3$ $E_3 = -B/3^2$

Balmer series

$n = 2$ $E_2 = -B/2^2$

Lyman series

$n = 1$ $E_1 = -B/1^2$