

Chem 115 POGIL Worksheet - Week #6
Oxidation Numbers, Redox Reactions, Solution Concentration,
Titrations, First Law, and Enthalpy

Why?

In addition to metathetical reactions, electron transfer reactions often occur in solutions. When electrons are transferred from one chemical species to another oxidation and reduction are said to have occurred. These kinds of reactions are very important in natural and synthetic processes. One way of tracking these changes is to look at assigned oxidation numbers on each element in the chemical species involved in the reaction.

To round out our discussions of solution reactions, we need to address the quantitative relationships between reactants and products. Up to now, we have used the connection between mass and moles to do this. When dealing with solutions, it is usually more convenient to analyze the stoichiometry in terms of mole-based solution concentration terms. An important application of this is the analytical technique of titration, used to determine the amount of a substance, such as an acid or base, in a solution. It is based on the quantitative relationships between volume and the mole-based solution concentration molarity.

In addition to mass changes, chemical reactions involve heat changes. Like mass-based stoichiometry, these heat changes are quantitative. One of the most important physical relationships governing heat 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 and chemical reactions. Considerations of heats of chemical reactions are important in many fields, ranging from nutrition to the search for more efficient fuels.

Learning Objectives

- Understand the rules for assigning oxidation numbers
- Understand the concepts of oxidation and reduction in terms of oxidation numbers
- Understand solution concentration in terms of molarity
- Know the connection between molarity, volume, and moles or millimoles of solute
- Understand the difference between analytical concentration and actual species concentration
- Understand the techniques of titration and the quantitative relationships on which it is based
- Know the First Law of Thermodynamics
- Understand the relationships between heat, work, internal energy, and enthalpy

Success Criteria

- Be able to assign oxidation numbers to elements in chemical species
- Be able to identify when a species is being oxidized or reduced
- Be able to calculate molarity of a solution
- Be able to convert between molarity, volume, and moles or millimoles
- Be able to assess the actual ion concentrations in a strong electrolyte solution
- Be able to carry out stoichiometry calculations using molarities and volumes of solutions

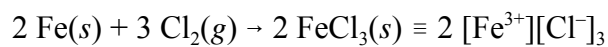
- Be able to carry out titration calculations
- Be able to calculate heat and temperature changes
- Be able to apply the First Law of Thermodynamics

Prerequisite

- Have read sections 4.4 through 4.6 in the text.
- Have read sections 5.1 through 5.4 in the text.

Information (Redox and Oxidation Numbers)

A reaction in which one species transfers electrons to another is called an **oxidation-reduction reaction**, also called a **redox reaction**. For example, consider the reaction of metallic iron with chlorine gas to form ionic iron(III) chloride:



We can think of this as the net transfer of six electrons from two iron atoms to three chlorine molecules:



In essence, the Fe "pushes" electrons and the Cl₂ "pulls" electrons, thereby effecting electron transfer. On this basis, we have the following definitions:

Oxidation - loss of electrons by a substance

Reduction - gain of electrons by a substance

Oxidation and reduction always involve transfer of electrons. Therefore, *there is never oxidation without reduction and vice versa in a redox reaction*. Oxidizing something must cause something else to be reduced and vice versa. Therefore, the substance oxidized is seen to be the agent of the other substance's reduction, and the substance reduced is seen to be the agent of the other substance's oxidation. This leads to the following definitions:

Oxidizing agent (oxidant) a substance that causes another substance to be oxidized and is itself reduced.

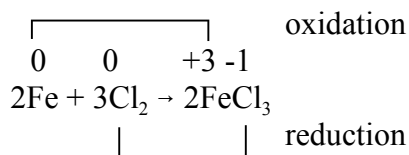
Reducing agent (reductant) a substance that causes another substance to be reduced and is itself oxidized.

The transfer of electrons from one species to another changes the electron count and distribution about the atoms in both. One way of reflecting this is through changes in assigned **oxidation numbers**. Oxidation numbers are real or hypothetical charges on atoms, assigned by the following rules:

- Atoms in elements are assigned 0.

- All simple monatomic ions have oxidation numbers equal to their charges. (e.g., all Group IA ions are +1; all group IIA ions are +2; all the following ions have oxidation numbers given by their charges - Fe^{2+} , Al^{3+} , S^{2-} , N^{3-})
- Fluorine is always -1 in its compounds.
- Halogens are usually -1, except when a central atom or when combined with a more electronegative¹ element (e.g., assign I as -1 in NI_3 , but +3 in ICl_3).
- Oxygen is -2 in most of its compounds, except in peroxides (H_2O_2 , Na_2O_2) where it is -1.
- Hydrogen is usually +1, except in hydrides with electropositive elements, particularly with metal cations, where it is -1 (e.g., NaH , CaH_2 , BH_4^-).
- The sum of all oxidation numbers for a neutral compound is zero; the sum is the charge on the species for a complex ion.

When a species is oxidized, one of its atoms goes to a higher (more positive or less negative) oxidation number. When a species is reduced, one of its atoms goes to a lower (less positive or more negative) oxidation number. For example, in the reaction between metallic iron and gaseous chlorine, the oxidation state of Fe goes from 0 to +3, making this an oxidation, and the oxidation number of each Cl goes from 0 to -1, making this a reduction.



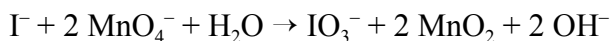
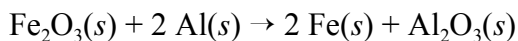
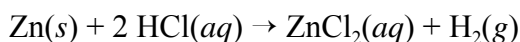
Key Questions

1. Assign the oxidation numbers of each element in the following chemical species: HCl , H_2O , NH_3 , NO_3^- , $\text{K}_2\text{Cr}_2\text{O}_7$, Hg_2Cl_2 , HgCl_2 , $\text{Al}(\text{OH})_3$, Na_3PO_4

¹We will discuss electronegativity in more detail later. For now, electronegativity can be defined as the ability of an atom in a compound to attract electrons to itself. In the periodic table, electronegativity increases left to right and bottom to top; e.g., $\text{O} < \text{F}$, $\text{I} < \text{Cl}$, $\text{Cl} < \text{O}$. Overall, the most electronegative elements are in the upper right, and the least electronegative elements are in the lower left of the periodic table.

Exercises

2. Which element is oxidized and which element is reduced in the following reactions?



Information (Solution Concentration)

Solution concentration is a statement of the amount of solute present in a solution relative to either the amount of solvent or the amount of solution. The most frequently used expression of concentration in chemistry is **molarity** (symbol M). Molarity is defined numerically by:

$$\text{Molarity} = \mathbf{M} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Sometimes it is more convenient to think of molarity in terms of millimoles of solute (10^{-3} mole) and milliliters of solution (10^{-3} L). These units are both 0.001 of the units used to define molarity as shown above, so the ratio of millimoles of solute to milliliters of solution will be numerically the same. Therefore, when convenient, we can define the molarity of a given solution alternatively as

$$\text{Molarity} = \mathbf{M} = \frac{\text{millimoles of solute}}{\text{milliliters of solution}}$$

By either definition, the numerical value of the molarity of a particular solution is the same.

Solutions of a certain molarity are most often prepared by using a **volumetric flask**. If the solute can be obtained in high purity ("analytical reagent grade"), the needed amount can be weighed on an analytical balance and then quantitatively transferred (no loss) to the volumetric flask. Solvent, usually water, is then added until the level reaches the calibration mark for the flask's volume. The stoppered flask must be shaken thoroughly to ensure proper mixing.

The advantage of knowing solution concentration in molarity is the direct relationship between the volume of a sample of the solution and the number of moles of solute it contains. If we take the product of a solution's molarity times its volume in liters, we can see by dimensional analysis that the resulting units will be moles of solute:

$$\mathbf{M} \times V_L = \left(\frac{\text{mol solute}}{\text{L soln}} \right) (\text{L soln}) = \text{mol solute}$$

Similarly, the product of a solution's molarity times its volume in milliliters gives the number of millimoles (abbreviated mmol) in the sample:

$$M \times V_{\text{mL}} = \left(\frac{\text{mmol solute}}{\text{mL soln}} \right) (\text{mL soln}) = \text{mmol solute}$$

These two relationships are used routinely when dealing with solution concentrations in molarity.

Another way of preparing a solution of a certain molarity is to start with a measured volume (an **aliquot**) of a more concentrated solution of known molarity and dilute to the desired concentration. The number of moles of solute in the aliquot of the concentrated solution can be calculated from $M \times V$. Regardless of the dilution, this will be the number of moles in the new solution. Therefore, we can write

$$M_{\text{initial}} V_{\text{initial}} = M_{\text{final}} V_{\text{final}}$$

or more simply

$$M_i V_i = M_f V_f$$

Exercises

3. Describe how you would go about making exactly 500 mL of 0.100 M $\text{NaNO}_3(aq)$ solution, using reagent grade $\text{NaNO}_3(s)$ (f.w. = 85.0 u).
4. Starting with a 0.100 M NaNO_3 solution, how would you go about preparing exactly 100 mL of 0.0250 M NaNO_3 solution?
5. How many milliliters of 0.0250 M CuSO_4 solution contain 1.75 g of solute? (f.w. $\text{CuSO}_4 = 159.6$ u)

Information (Analytical Concentration vs. Actual Species Concentration)

No molecular dissociation occurs when a nonelectrolyte is dissolved in water. In a nonelectrolyte solution, the molarity reflects the actual concentrations of solute molecules. Thus a 0.10 M sugar solution contains 0.10 mole of sugar molecules per liter of solution. The situation is different with electrolytes, because they break up to some extent to give ions in solution. The concentrations of those ions in solution depends upon (a) the amount of electrolyte that is dissolved, (b) whether the solute is a strong or weak electrolyte, and (c) the formula of the electrolyte. In order to talk about the concentrations of ions in weak electrolyte solutions, we will need to have some way of assessing the extent of dissociation of the solute. We will delay that topic until later. For now we will only consider predicting the concentrations of ions in solutions of strong electrolytes.

Many chemists call the number of moles of solute dissolved per liter of solution the **analytical concentration** of solute, given the symbol C . This is essentially a statement of the moles of solute per liter of solution that we dissolved, without regard to the concentrations of the species

that are actually present in the solution (only ions, a mixture of molecules and ions, or only molecules). For solutions of strong electrolytes, the concentrations of ions can be taken as whole number multiples of the analytical concentration. We will indicate the **actual concentration** of a species X by writing its symbol in square brackets, [X], meaning moles per liter of solution. For example, suppose we make a 0.10 M NaCl solution; i.e., $C = 0.10$ M. All of the NaCl(s) breaks up to dissolve as $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$ ions:

	$\text{NaCl}(s)$	\rightarrow	$\text{Na}^+(aq)$	$+$	$\text{Cl}^-(aq)$
Add	0.10 M		0 M		0 M
Result	0 M		0.10 M		0.10 M

From this we can say, $[\text{Na}^+] = 0.10$ M, $[\text{Cl}^-] = 0.10$ M, and the concentration of all ions (both cations and anions) is 0.20 M. Consider the same analytical concentration of Na_3PO_4 .

	$\text{Na}_3\text{PO}_4(aq)$	\rightarrow	$3\text{Na}^+(aq)$	$+$	$\text{PO}_4^{3-}(aq)$
Add	0.10 M		0 M		0 M
Result	0 M		0.30 M		0.10 M

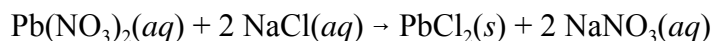
From, this we can say, $[\text{Na}^+] = 0.30$ M, $[\text{PO}_4^{3-}] = 0.10$ M, and the concentration of all ions (both cations and anions) is 0.40 M. Notice that this means that the 0.10 M solution of Na_3PO_4 has twice the concentration of ions (0.40 M) as the 0.10 M solution of NaCl (0.20 M).

Exercises

- Which of the following has the highest concentration of sodium ion: 0.20 M NaCl, 0.13 M Na_2SO_4 , 0.080 M Na_3PO_4 ?
- Indicate the concentrations of all ions in a solution prepared by mixing 45.0 mL of 0.200 M Na_2SO_4 and 65.0 mL of 0.300 M $\text{Al}_2(\text{SO}_4)_3$.

Problem

- How many grams of PbCl_2 (f.w. = 278.1 u) are produced by the reaction

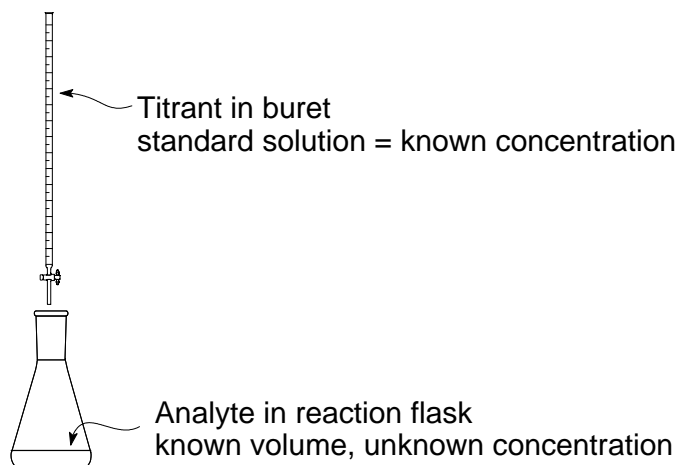


when 25.00 mL of 0.4567 M $\text{Pb}(\text{NO}_3)_2$ solution and 25.00 mL of 0.9876 M $\text{NaCl}(aq)$ solution are mixed?

Information (Titration)

An important application of the relationships $MV_L = \text{mol}$ and $MV_{\text{mL}} = \text{mmol}$ is **volumetric analysis**, which uses precise measurement of the volume of a solution of known concentration, called a **standard solution**, as a means of carrying out chemical analysis. In **titration**, the most commonly used type of volumetric analysis, a standard solution (the **titrant**) with known concentration is added to a measured volume of a solution to be analyzed (the **analyte**) having

unknown concentration. The titrant and analyte react with one another according to a known stoichiometry. By measuring the volume of titrant that completely consumes the analyte, it is possible to calculate the amount of analyte originally present in the sample solution (and therefore its concentration), using the known stoichiometric relationship between the two reactants.



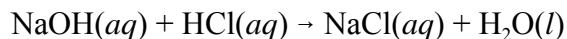
In most cases, the stoichiometric relationship between the analyte and titrant is 1:1, or less frequently 1:2 or 1:3. The volume of the analyte is usually measured and dispensed into a reaction flask with a pipet. The titrant is added to this sample from a buret, which measures the amount of titrant delivered. The volume at which the stoichiometrically correct amount of titrant has been delivered to completely consume the analyte is called the **equivalence point**. Some means must be used to detect the equivalence point. One common method is to add a small amount of an **indicator** solution to the reaction flask. The indicator is chosen so that it will undergo a pronounced color change very near the equivalence point. The volume of titrant needed to cause the indicator to change color is called the **end point** of the titration. Ideally the end point and the equivalence point should be the same, but in most real situations there is a small difference between the two, which introduces a small error into the measurement. This error will be negligible if the indicator has been correctly chosen for the system being analyzed.

Titration is often used to determine the concentration of a solution of an acid or base, employing the stoichiometry of a neutralization reaction. If the analyte is a weak or strong base, the titrant will be a standard solution of a strong acid, such as hydrochloric acid, $\text{HCl}(aq)$. If the analyte is a weak or strong acid, the titrant will be a standard solution of a strong base, such as sodium hydroxide, $\text{NaOH}(aq)$. The number of millimoles of titrant added to the analyte to reach the equivalence point is given by the product of the concentration of the standard solution in molarity times the volume delivered from the buret in milliliters:

$$\text{millimol titrant} = M_t \times V_t$$

At the equivalence point, the stoichiometric relationship between the millimoles of titrant added and the millimoles of analyte initially present, based on the balanced neutralization equation, can be used to find the solution concentration of the sample. For example, if the analyte is a monoprotic acid and the titrant is a standard solution of $\text{NaOH}(aq)$, the millimoles of acid

initially present will be equal to the millimoles of NaOH(aq) added to reach the equivalence point, because the stoichiometry between moles of analyte and moles of titrant is 1:1. For example, in the titration of a sample of HCl(aq) with NaOH(aq) titrant, the titration equation is



and at the equivalence point we would have

$$\text{mmol NaOH} = \text{mmol HCl}$$

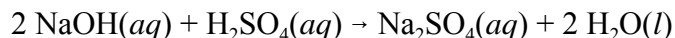
$$M_{\text{NaOH}} V_{\text{NaOH}} = M_{\text{HCl}} V_{\text{HCl}}$$

If the analyte is polyprotic ($n = 2, 3, \dots$), n millimoles of titrant will be required for every millimole of analyte to reach the equivalence point:

$$\text{mmol titrant} = n \times \text{mmol analyte}$$

$$M_t V_t = n M_a V_a$$

For example, in the titration of a sample of H₂SO₄(aq) with NaOH(aq), the titration equation is

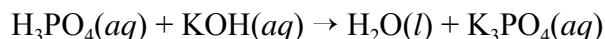
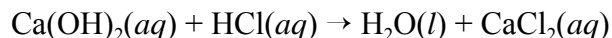
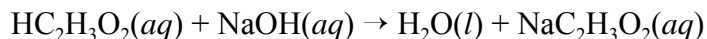


and at the equivalence point for consuming all the H₂SO₄ we would have

$$M_{\text{NaOH}} V_{\text{NaOH}} = 2 \times M_{\text{H}_2\text{SO}_4} V_{\text{H}_2\text{SO}_4}$$

Key Questions

9. Define the following terms: analyte, titrant, equivalence point, end point.
10. The following represent *skeletal* reaction equations for some possible titrations. For each, assume that the first species is the analyte and the second species is the titrant. Balance each equation. For each millimole of analyte, how many millimoles of titrant are needed for complete reaction in each case?



Exercises

11. A 25.00-mL sample of an unknown monoprotic acid is titrated to an equivalence point with 32.42 mL of 0.1000 M NaOH solution. What was the original concentration of acid in the sample?
12. How many milliliters of 0.1200 M HCl solution are needed to completely neutralize 50.00 mL of 0.1012 M Ba(OH)₂ solution?
13. A 20.00-mL sample of a chloride-containing solution was titrated with 0.4000 M AgNO₃ solution, requiring 28.62 mL to reach the equivalence point. Write the balanced reaction equation for this titration. What was the concentration of Cl⁻ ion in the original sample? How many grams of precipitate were formed?

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), defined as follows:

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

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, ΔE , defined as

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

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

$$\Delta E = q + w$$

(We will see other changes in properties, indicated by delta functions, which will always be defined as final value minus initial value; e.g., $\Delta x = x_f - x_i$.) 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 it 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, the heat content at the end of the process will be less. 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

14. In what ways can an object possess energy? How do these ways differ from one another?

15. If a system loses heat, where does it go?
16. Describe the following processes as exothermic or endothermic:
- an ice cube melts on a warm surface
 - water freezes
 - calcium chloride is mixed with water, resulting in a very hot solution
 - 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

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

from which it follows

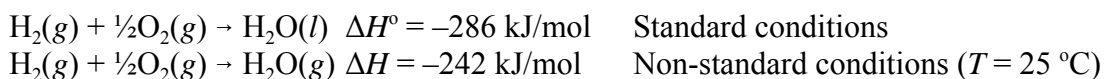
$$\Delta H = \Delta E - w$$

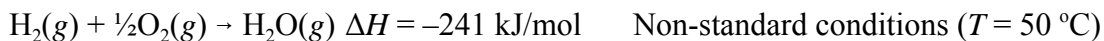
Note that if no work is done ($w = 0$), $\Delta H = \Delta E$. This means that the enthalpy change is the internal energy change when no work is done.

The amount of heat transferred in a chemical or physical process depends upon (1) physical conditions, (2) amount 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). Therefore, we must be careful when quoting values of q or ΔH to be sure to specify these conditions. To avoid confusion, we define

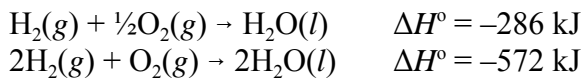
Standard conditions: $T = 25\text{ }^\circ\text{C}$; $P = 1\text{ atm} = 760\text{ mm Hg} = 29.9213\text{ in. Hg}$; all substances in their usual states for these conditions (the **standard state**).

Inasmuch as physical state is important, it is common practice to note the states (s , l , g) 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 ΔH° . Note the differences in the following thermochemical reactions, due to subtle changes in conditions:

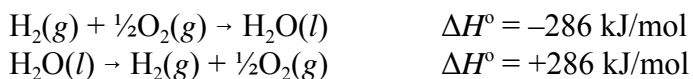




Enthalpy depends upon the amount of substance; i.e., it is an *extensive property*. Since thermochemical equations are read with the understanding that the coefficients are numbers of moles, changing the coefficients by multiplying through the equation also multiplies the value of the enthalpy. Compare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

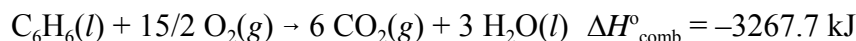


Reversing the direction of a reaction reverses the sense of the heat transfer. As we have seen, an exothermic process in one direction will be an endothermic process in its reverse direction. The heat transferred is the same in both cases, but the direction changes, as indicated by a sign change on the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



Exercises

17. 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. $\text{C}_6\text{H}_6 = 78.11 \text{ u}$)