EDO UNIVERSITY IYAMHO
Department of Chemical Engineering
CHM 211: General Chemistry III

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Description: The course is designed to give the students an in-depth understanding of some areas in General Chemistry such as thermochemistry, electrochemistry etc.

Prerequisites: Students should be familiar with the concepts in theory of Heat of Reaction and Calorimetry, Work, First law of Thermodynamics, Hess's Law, Standard Enthalpies of Formation, Electrochemical cells, Nernst equation, Electrochemical Corrosion, writing and balancing stoichiometric equations (*e.g.,* reduction half-cell equation); understand how to read electromotive series table (*e.g.,* standard EMF value of metals); and have good skill in solving simultaneous equations.

Assignments: Students are expected to have a minimum four individual homework assignments in addition to a Quiz, Mid-Term Test and a Final Exam. Assignment and Quiz are prearranged and structured as preparation for the Mid-Term and Final Exam. They are designed to be a studying material for both exams.

Grading: Students will be evaluated by assigning 15% of this class grade to assignments/lecture attendance, 5% for quiz and 10% for the mid-term test. While 70% is to be assigned for the final semester exam. All continuous assessment exercises constitute 30% of the final grade and the final exam will be all-inclusive and thorough.

Textbook: Recommended textbooks for the course are as stated:
Title: *General Chemistry*
Authors: Darrel Ebbing and Steven D. Gammon
Publisher: Books/Cole; 10th edition
ISBN-13: 978-1285051376
Year: 2013

Title: *The Nature and Properties of Engineering Materials*
Author: Zbigniew D. Jastrzebski,
Publisher: John Wiley & Sons. Second Edition
ISBN-13: 978-0471022589
Year: 1997

Title: *"Chemistry, The Central Science"*,
Author: Theodore E. Brown, H. Eugene LeMay, Bruce E. Bursten, Catherine Murphy, Patrick Woodward and Matthew E. Stoltzfus
Publisher: Pearson Publishers. 13th Edition.

Lectures: Below is an extract of the lecture note.

Thermochemistry-Introduction: Natural gas consists mostly of Methane, CH_4 and the complete combustion of a hydrocarbon, such as methane, yields carbon dioxide and water as products. More important, however, is another "product" of this reaction, yet to be referred to: heat. This heat can be used to produce hot water in a water heater, to heat a house, or to cook food. Thermochemistry is the branch of chemistry concerned with the heat effects that accompany chemical reactions. To understand the relationship between heat and chemical and physical changes, we must start with some basic definitions. We will then explore the concept of heat and the methods used to assess the transfer of energy across boundaries. Another form of energy transfer is work, and, in combination with heat, we will define the first law of thermodynamics. At this point, we will establish the relationship between heats of reaction and changes in internal energy and enthalpy. We will see that the tabulation of the change in internal energy and change in enthalpy can be used to calculate, directly or indirectly, energy changes during chemical and physical changes. Finally, concepts introduced in this lesson will answer a host of practical questions, such as why natural gas is a better fuel than coal

What is Thermochemistry: Thermochemistry is the branch of chemistry concerned with the heat effects that accompany chemical reactions. It is the study of the energy and heat associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. In a simpler term it is the study of changes in energy (heat) associated with physical and chemical changes.

General Concepts and Terminology: This part will introduce and define some very basic terms.

A *system* is the part of the universe chosen for study, and it can be as large as all the oceans on Earth or as small as the contents of a beaker. Most of the systems we will examine will be small and we will look, particularly, at the transfer of energy (as heat and work) and matter between the system and its surroundings. The *surroundings* are that part of the universe outside the system with which the system interacts. Figure 1 picture three common systems: first, as we see them and, then, in an abstract form that chemists commonly use. An *open system* freely exchanges energy and matter with its surroundings (Fig. 1a). A *closed system* can exchange energy, but not matter, with its surroundings (Fig.1b). An *isolated system* does not interact with its surroundings (approximated in Fig1c).
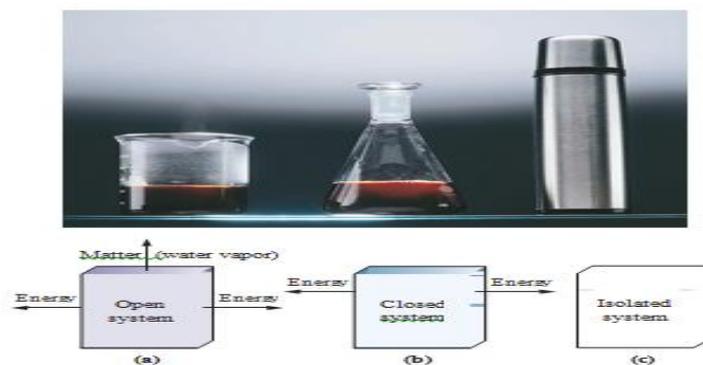
FIFURE 1: Systems and their surroundings (a) Open system. The beaker of hot coffee transfers energy to the surroundings—it loses heat as it cools. Matter is also transferred in the form of water vapor. (b) Closed system. The flask of hot coffee transfers energy (heat) to the surroundings as it cools. Because the flask is stoppered, no water vapor escapes and no matter is transferred. (c) Isolated system. Hot coffee in an insulated container approximates an isolated system. No water vapor escapes, and, for a time at least, little heat is transferred to the surroundings. (Eventually, though, the coffee in the container cools to room temperature.)

The remainder of this section says more, in a general way, about energy and its relationship to work. Like many other scientific terms, energy is derived from Greek. It means "work within." *Energy* is the capacity to do work. *Work* is done when a force acts through a distance. Moving objects do work when they slow down or are stopped. Thus, when one billiard ball strikes another and sets it in motion, work is done. The energy of a moving object is called *kinetic energy* (the word kinetic means "motion" in Greek). Whilst the energy possessed by virtue of its position or chemical composition (bonds) is referred to as *potential energy.*

Heat: Heat is energy transferred between a system and its surroundings as a result of a temperature difference. Energy that passes from a warmer body (with a higher temperature) to a colder body (with a lower temperature) is transferred as heat. At the molecular level, molecules of the warmer body, through collisions, lose kinetic energy to those of the colder body. Thermal energy is transferred—"heat flows"—until the average molecular kinetic energies of the two bodies become the same, until the temperatures become equal. Heat, like work, describes energy in transit between a system and its surroundings.

Not only can heat transfer cause a change in temperature but, in some instances, it can also change a state of matter. For example, when a solid is heated, the molecules, atoms, or ions of the solid move with greater vigor and eventually break free from their neighbors by overcoming the attractive forces between them. Energy is required to overcome these attractive forces. During the process of melting, the temperature remains constant as a thermal energy transfer (heat) is used to overcome the forces holding the solid together. A process occurring at a constant temperature is said to be isothermal. Once a solid has melted completely, any further heat flow will raise the temperature of the resulting liquid.

Although we commonly use expressions like "heat is lost," "heat is gained," "heat flows," and "the system loses heat to the surroundings," you should not take these statements to mean that a system contains heat. It does not. The energy content of a system is a quantity called the internal energy. Heat is simply a form in which a quantity of energy may be transferred across a boundary between a system and its surroundings.

It is reasonable to expect that the quantity of heat, q, required to change the temperature of a substance depends on

- ✓ how much the temperature is to be changed
- ✓ the quantity of substance
- ✓ the nature of the substance (type of atoms or molecules)

Historically, the quantity of heat required to change the temperature of one gram of water by one degree Celsius has been called the calorie (cal). The calorie is a small unit of energy, and the unit kilocalorie (kcal) has also been widely used. The SI unit for heat is simply the basic SI energy unit, the joule (J).

$$1 cal = 4.184 J \qquad\qquad Eq.1$$

While the joule is ordinarily used, the calorie is widely encountered in older scientific literature.

The quantity of heat required to change the temperature of a system by one degree is called the *heat capacity* of the system. If the system is a mole of substance, the term *molar heat capacity* is applicable. If the system is one gram of substance, the applicable term is *specific heat capacity*, or more commonly, *specific heat*. The specific heats of substances are somewhat *temperature dependent*. Over the range from 0 to 100 °C, the specific heat of water averages about

$$\frac{4.18 J}{g\ ^{o}C} = 4.18 J\ g^{-1}\ ^{o}C^{-1} \qquad\qquad Eq.2$$

The quantity of heat is related to the mass, specific heat and temperature change as follows.

$$quantity\ of\ heat = mass\ of\ substance\ \times specific\ heat\ \times temperature\ change$$
$$(where,\ mass\ of\ substance\ \times specific\ heat = heat\ capacity = C) \quad Eq.3$$

$q = m * \text{specific heat} * \Delta T = C * \Delta T \qquad\qquad Eq.4$

In above equation, the temperature change is expressed as $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature. When the temperature of a system increases ($T_f > T_i$), ΔT is positive. A positive q signifies that heat is absorbed or gained by the system. When the temperature of a system decreases ($T_f < T_i$), ΔT is negative. A negative q signifies that heat is evolved or lost by the system.

Another idea that enters into calculations of quantities of heat is the law of conservation of energy: In interactions between a system and its surroundings, the total energy remains constant—energy is neither created nor destroyed. Applied to the exchange of heat, this means that

$$q_{system} + q_{surroundings} = 0 \qquad\qquad Eq.5$$

Thus, heat gained by a system is lost by its surroundings, and vice versa.

$$q_{system} = -q_{surroundings} \qquad\qquad Eq.6$$

Experimental Determination of Specific Heats

Let us consider how the law of conservation of energy is used in the experiment outlined in Figure 2. The object is to determine the specific heat of lead. The transfer of energy, as heat, from the lead to the cooler water causes the temperature of the lead to decrease and that of the water to increase, until the lead and water are at the same temperature. Either the lead or the water can be considered the system. If we consider lead to be the system, we can write $q_{lead} = q_{system}$. Furthermore, if the lead and water are maintained in a thermally insulated enclosure, we can assume that $q_{water} = q_{surroundings}$. Then, applying equation (6), we have $q_{lead} = - q_{water}$
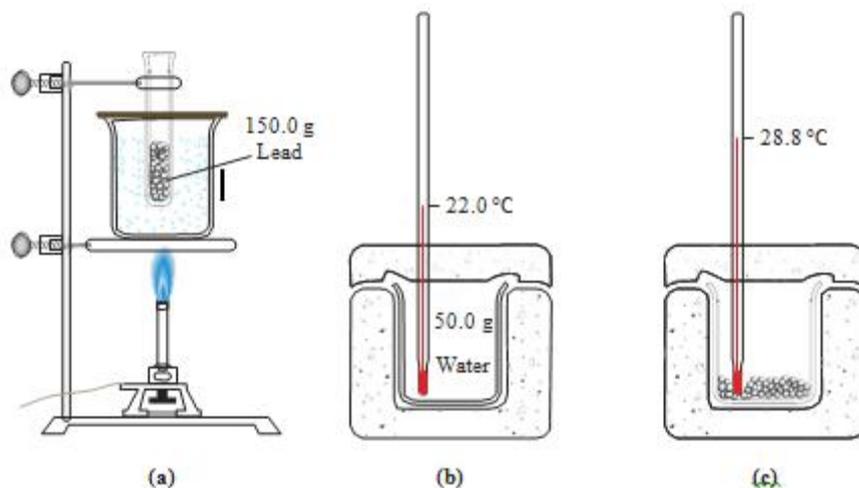
FIGURE 2: Determining the specific heat of lead

(a) A 150.0 g sample of lead is heated to the temperature of boiling water 100.0 °C. (b) A 50.0 g sample of water is added to a thermally insulated beaker, and its temperature is found to be 22.0 °C. (c) The hot lead is dumped into the cold water, and the temperature of the final lead water mixture is 28.8 °C.

EXAMPLE A1: Evaluating a Quantity of Heat

Question: How much heat is needed to raise the temperature of 7.35 g of water from 21.0 to 98.0 °C? (Assume the specific heat of water is 4.18 J g^{-1} °C^{-1} throughout this temperature range.)

Scrutinize: To answer this question, we begin by multiplying the specific heat capacity by the mass of water to obtain the heat capacity of the system. To find the amount of heat required to produce the desired temperature change we multiply the heat capacity by the temperature difference.

Solution:

The specific heat is the heat capacity of 1.00 g water:

$$\frac{4.18J}{g\ water\ {}^{o}C}$$

The heat capacity of the system (7.35 g water) is

$$7.35\ g\ water \times \frac{4.18J}{g\ water\ {}^{o}C} = 30.7\frac{J}{{}^{o}C}$$

The required temperature change in the system is

$$98.0 - 21.02\ °C = 77.0\ °C$$

The heat required to produce this temperature change is

$$30.7\frac{J}{{}^{o}C} \times 77.0^{o}C = 2.36 \times 10^{3}J$$

The objective in Example A1 is to calculate a quantity of heat based on the amount of a substance, the specific heat of that substance, and its temperature change. And the line of

reasoning used is summarized in Eq. 4, which relates a quantity of heat to the mass of a substance, its specific heat, and the temperature change.

EXAMPLE A2: Evaluating Specific Heat from Experimental Data

Question: Using the data presented in Figure 2, evaluate the specific heat of lead.

Study: Keep in mind that if we know any four of the five quantities—q, m, specific heat, T_f, T_i—we can solve equation 4 for the remaining one. We know from Figure 2 that a known quantity of lead is heated and then dumped into a known amount of water at a known temperature, which is the initial temperature. Once the system comes to equilibrium, the water temperature is the final temperature. For this question, we will use equation 4 to proffer solution.

Solution: First, use equation 4 to calculate for q_{water} i.e.

Recalling that: $q = m *$ specific heat $* \Delta T = C * \Delta T$ (Eq.4)

$$q_{water} = 50.0\,g\,water \times \frac{4.18J}{g\,water\ ^oC} \times 28.8 - 22.02^oC = 1.4 \times 10^3 J$$

From the equation $q_{system} = -q_{surroundings}$

$$q_{lead} = -q_{water} = -1.4 \times 10^3 J$$

Now, from equation 4 again, we obtain

$$q_{lead} = 150.0\,g\,lead \times specific\,heat\,of\,lead \times 28.8 - 100.0^oC = -1.4 \times 10^3 J$$

$$Specific\,heat\,of\,lead = \frac{-1.4 \times 10^3 J}{150.0\,g\,lead \times (28.8 - 100.0)\ ^oC} = 0.13 J\,g^{-1\,o}C^{-1}$$

PRACTICE EXAMPLE A1: How much heat, in kilojoules (kJ), is required to raise the temperature of 237 g of cold water from 4.0 to 37.0 °C (body temperature)?
PRACTICE EXAMPLE B1: How much heat, in kilojoules (kJ), is required to raise the temperature of 2.50 kg Hg (l) from - 20.0 to - 6.0 °C? Assume a density of 13.6 g>mL and a molar heat capacity of 28.0 J mol-1 °C-1 for Hg (l).
PRACTICE EXAMPLE A2: When 1.00 kg lead specific heat = 0.13 J g^{-1} °C^{-1} at 100.0 °C is added to a quantity of water at 28.5 °C, the final temperature of the lead–water mixture is 35.2°C. What is the mass of water present?

PRACTICE EXAMPLE B2: A 100.0 g copper sample specific heat = 0.385 J g^{-1} °C^{-1} at 100.0 °C is added to 50.0 g water at 26.5 °C. What is the final temperature of the copper–water mixture?

Heat of Reaction and Calorimetry: In this, we shall examine the notion of *thermal energy*—kinetic energy associated with random molecular motion. Another type of energy that contributes to the internal energy of a system is *chemical energy*. This is energy associated with chemical bonds and intermolecular attractions. If we think of a chemical reaction as a process in which some chemical bonds are broken and others are formed, then, in general, we expect the chemical energy of a system to change as a result of a reaction. Furthermore,

we might expect some of this energy change to appear as heat. A *heat of reaction, q_{rxn}*, is the quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system at constant temperature. One of the most common reactions studied is the combustion reaction. This is such a common reaction that we often refer to the heat of combustion when describing the heat released by a combustion reaction.

If a reaction occurs in an *isolated system, that is, one that exchanges no matter or energy with its surroundings*, the reaction produces a change in the thermal energy of the system—the temperature either increases or decreases. Imagine that the previously isolated system is allowed to interact with its surroundings. The heat of reaction is the quantity of heat exchanged between the system and its surroundings as the system is restored to its initial temperature (Fig. 3). In actual practice, we do not physically restore the system to its initial temperature. Instead, we calculate the quantity of heat that would be exchanged in this restoration. To do this, a probe (thermometer) is placed within the system to record the temperature change produced by the reaction. Then, we use the temperature change and other system data to calculate the heat of reaction that would have occurred at constant temperature.
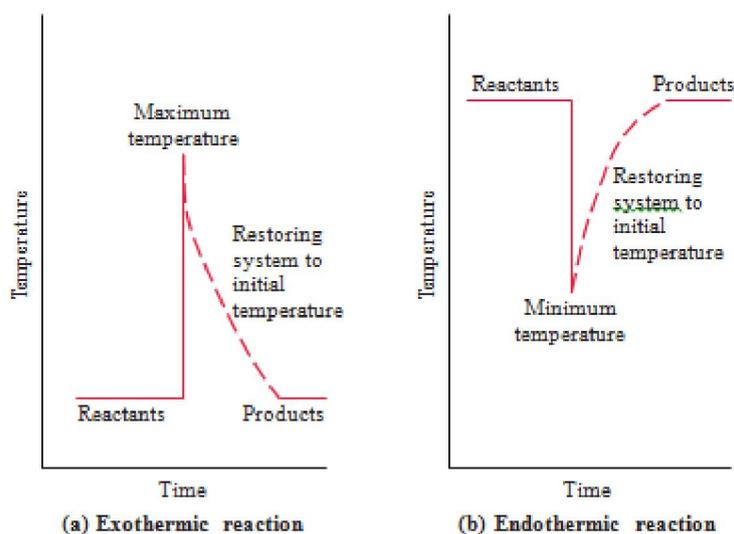

FIGURE 3: Conceptualizing a Heat of Reaction at Constant Temperature

The solid lines indicate the initial temperature and the (a) maximum and (b) minimum temperature reached in an isolated system, in an exothermic and an endothermic reaction, respectively. The broken lines represent pathways to restoring the system to the initial temperature. The heat of reaction is the heat lost or gained by the system in this restoration.


Figure 4: Exothermic and Endothermic reactions

Two widely used terms related to heats of reaction are exothermic and endothermic reactions. An *exothermic reaction* is one that produces a temperature increase in an isolated system or, in a non-isolated system, gives off heat to the surroundings. For an exothermic reaction, the heat of reaction is a negative quantity ($q_{rxn} < 0$). A good example of an exothermic reaction is that involving the production of a slaked lime, $Ca(OH)_2$, it is produced by the action of water on quicklime, CaO. The reactants are mixed at room temperature, but the temperature of the mixture rises to 40.5 ^oC. (See Fig. 4a)

$$CaO(s) + H_2 0(l) \rightarrow Ca(OH)_2(s)$$
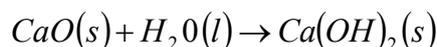
Also, in the reaction between hydrogen and oxygen gas where water and energy is being released exothermic process is said to occur ie,

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + energy$$

$$H_2O(g) \rightarrow H_2O(l) + energy$$
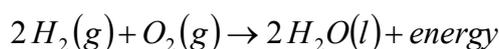
In an *endothermic reaction,* the corresponding situation is a temperature decrease in an isolated system or a gain of heat from the surroundings by a non-isolated system. In this case, the heat of reaction is a positive quantity ($q_{rxn} > 0$). An endothermic reaction, $Ba(OH)_2.8H_2O(s)$ and $NH_4Cl(s)$ are mixed at room temperature, and the temperature falls to 5.8^oC in the reaction. (See Fig. 4b)

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2.2H_2O(s) + 2NH_3(aq) + 8H_2O(l)$$

Likewise, in the reactions below endothermic process is said to occur ie,

$$energy + 2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

$$energy + H_2O(s) \rightarrow H_2O(l)$$
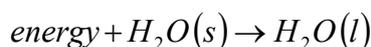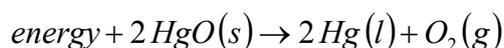
Heats of reaction are experimentally determined in a *calorimeter*, a device for measuring quantities of heat. We shall consider two types of calorimeters, namely the constant volume and constant pressure calorimetries respectively in this section, and we will treat both of them as isolated systems.

Bomb (Constant-Volume) Calorimetry: Figure 5 shows a bomb calorimeter, which is ideally suited for measuring the heat evolved in a combustion reaction. The system is everything within the double-walled outer jacket of the calorimeter. This includes the bomb and its contents, the water in which the bomb is immersed, the thermometer, the stirrer, and so on. The system is isolated from its surroundings. When the combustion reaction occurs, chemical energy is converted to thermal energy, and the temperature of the system rises. The heat of reaction, as described earlier, is the quantity of heat that the system would have to lose to its surroundings to be restored to its initial temperature. This quantity of heat, in turn, is just the negative of the thermal energy gained by the calorimeter and its contents ($q_{calorim}$).

$$q_{rxn} = -q_{calorim} \ (where \ q_{calorim} = q_{bomb} + q_{water}......) \qquad Eq.7$$
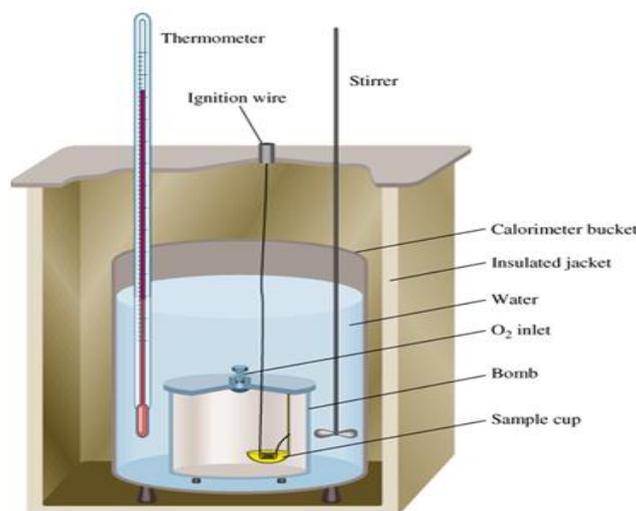
FIGURE 5: Bomb Calorimeter

An iron wire is embedded in the sample in the lower half of the bomb. The bomb is assembled and filled with O_2 (g) at high pressure. The assembled bomb is immersed in water in the calorimeter, and the initial temperature is measured. A short pulse of electric current heats the sample, causing it to ignite. The final temperature of the calorimeter assembly is determined after the combustion. Because the bomb confines the reaction mixture to a fixed volume, the reaction is said to occur at constant volume.

If the calorimeter is assembled in exactly the same way each time we use it— that is, use the same bomb, the same quantity of water, and so on—we can define a heat capacity of the calorimeter. This is the quantity of heat required to raise the temperature of the calorimeter assembly by one degree Celsius. When this heat capacity is multiplied by the observed temperature change, we get $q_{calorim}$. But on the contrary the heat capacity of a bomb calorimeter must be determined experimentally.

$$q_{calorim} = heat\ capacity\ of\ calorim \times \Delta T \qquad Eq.8$$

And from Equation 7, we can then establish q_{rxn}.

$$q_{rxn} = -q_{calorim} \qquad\qquad Eq.9$$

The "Coffee-Cup" (Constant-Pressure) Calorimeter: In the general chemistry laboratory you are much more likely to run into the simple calorimeter pictured in Figure 6 than a bomb calorimeter. We mix the reactants (generally in aqueous solution) in a Styrofoam cup and appraise the temperature change. Styrofoam is a good heat insulator, so there is very little heat transfer between the cup and the surrounding air. We treat the system—the cup and its contents—as an isolated system.

As with the bomb calorimeter, the heat of reaction is defined as the quantity of heat that would be exchanged with the surroundings in restoring the calorimeter to its initial temperature. But, again, the calorimeter is not physically restored to its initial conditions. We simply take the heat of reaction to be the negative of the quantity of heat producing the temperature change in the calorimeter. Considering Eq. 7, $q_{rxn} = -q_{calorim}$
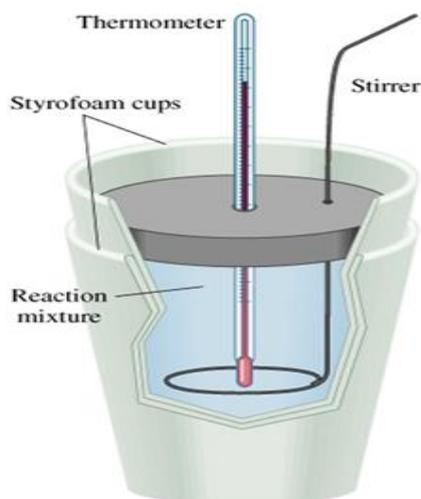
FIGURE 6: Styrofoam "Coffee-Cup" Calorimeter

The reaction mixture is in the inner cup. The outer cup provides additional thermal insulation from the surrounding air. The cup is closed off with a cork stopper through which a thermometer and a stirrer are inserted and immersed into the reaction mixture. The reaction in the calorimeter occurs under the constant pressure of the atmosphere.

Example A3: Using Bomb Calorimetry Data to Determine a Heat of Reaction

The combustion of 1.010 g sucrose, $C_{12}H_{22}O_{11}$, in a bomb calorimeter causes the temperature to rise from 24.92 to 28.33 °C. The heat capacity of the calorimeter assembly is 4.90kJ/°C. What is the heat of combustion of sucrose expressed in kilojoules per mole of $C_{12}H_{22}O_{11}$?

Solution: We are given a specific heat and two temperatures, the initial and the final, which indicate that we are to use equation 8. This means that

$$q_{calorim} = heat\ capacity\ of\ calorim \times \Delta T \qquad Eq.8$$

Thus,

$$q_{calorim} = 4.90\ kJ/^{\circ}C \times (28.33 - 24.92)^{\circ}C = (4.90 \times 3.41)kJ = 16.7kJ$$

Now, using equation 9, we get

$$q_{rxn} = -q_{calorim} = -16.7kJ$$

This is the heat of combustion of the 1.010 g sample.

Per gram $C_{12}H_{22}O_{11}$:

$$q_{rxn} = \frac{-16.7kJ}{1.010\ gC_{12}H_{22}O_{11}} = -16.5kJ/gC_{12}H_{22}O_{11}$$

Per mole $C_{12}H_{22}O_{11}$:

$$q_{rxn} = \frac{-16.7kJ}{gC_{12}H_{22}O_{11}} = \frac{342.3\ g\ C_{12}H_{22}O_{11}}{1\ mol\ C_{12}H_{22}O_{11}} = -5.65 \times 10^3\ kJ/molC_{12}H_{22}O_{11}$$

EXAMPLE A4   Determining a Heat of Reaction from Calorimetric Data

Question: In the neutralization of a strong acid with a strong base, the essential reaction is the combination of H^+ (aq) and OH^-(aq) to form water: *$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$*

Two solutions, 25.00 mL of 2.50 M HCl(aq) and 25.00 mL of 2.50 M NaOH(aq), both initially at 21.1 °C, are added to a Styrofoam-cup calorimeter and allowed to react. The temperature rises to 37.8 °C. Determine the heat of the neutralization reaction, expressed per mole of H_2O formed. Is the reaction endothermic or exothermic?

Solution: In addition to assuming that the calorimeter is an isolated system, assume that all there is in the system to absorb heat is 50.00 mL of water. This assumption ignores the fact that 0.0625 mol each of NaCl and H_2O are formed in the reaction, that the density of the resulting NaCl(aq) is not exactly 1.00 g/mL, and that its specific heat is not exactly 4.18 J g^{-1} °C^{-1}. Also, ignore the small heat capacity of the Styrofoam cup itself. Because the reaction is a neutralization reaction, let us call the heat of reaction q_{neutr}. Now, according to equation 9, q_{neutr} = - $q_{calorim}$, and if we make the assumptions described above, we can solve the problem.

Let begin with

$$q_{calorim} = 50.00 \; mL \times \frac{1.00 \, g}{mL} \times \frac{4.18 J}{g \; ^o C} \times (37.8 - 21.1) \, ^o C = 3.5 \times 10^3 \, J$$

$$q_{neutr} = -q_{calorim} = -3.5 \times 10^3 \, J$$

In 25.00 mL of 2.50 M HCl, the amount of H^+ is

$$mol \; H^+ = 25.00 \times \frac{1L}{1000 \, mL} \times \frac{2.50 \, mol}{1L} \times \frac{1 \, mol \; H}{1 \, mol \; HCl} = 0.0625 \, mol \; H^+$$

Similarly, in 25.00 mL of 2.50 M NaOH there is 0.0625mol OH^-. Thus, the H^+ and the OH^- combine to form 0.0625mol H_2O. (The two are in stoichiometric proportions; neither is in excess.)

The amount of heat produced per mole of H_2O is

$$q_{neutr} = \frac{-3.5 \times 10^3 \, J}{0.0625 \, mol \; H_2O} = -56kJ \, / \, mol \; H_2O$$

Because q_{neutr} is a negative quantity, the neutralization reaction is exothermic. In this example, relatively small quantities of acid and base were mixed yet a comparatively large temperature change occurred. The large temperature rise was due to the relatively large negative heat of neutralization.

Work: Heat effects generally accompany chemical reactions, meanwhile in some reactions, work is also involved—that is, the system may do work on its surroundings or vice versa. Consider the decomposition of potassium chlorate to potassium chloride and oxygen. Suppose that this decomposition is carried out in a weird vessel pictured in Figure 7 below.
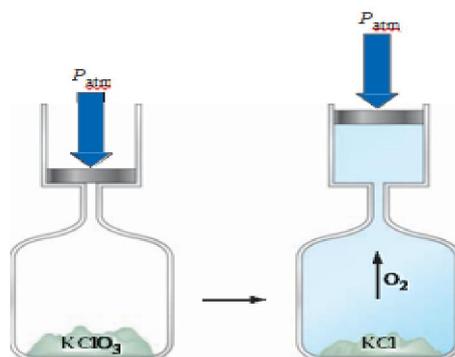
Figure 7: illustrating work (expansion) during chemical reaction.

$$2\,KClO_3\,(s) \longrightarrow 2\,KCl\,(s) + 3\,O_2\,(g)$$

The oxygen gas that is formed pushes back the weight and, in doing so, does work on the surroundings.

The walls of the container resist moving under the pressure of the expanding O_2 (g) except for the piston that closes off the cylindrical top of the vessel. The pressure of the O_2 (g) exceeds the atmospheric pressure and the piston is lifted—the system does work on the surroundings. Work involved in the expansion or compression of gases is called pressure–volume work.

Now let us switch to a somewhat simpler situation to see how to calculate a quantity of P–V work.
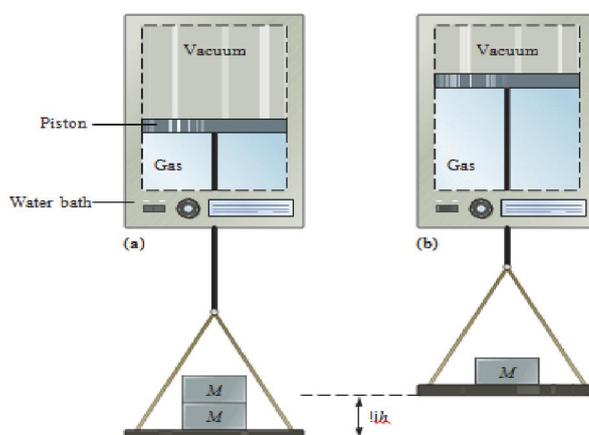

FIGURE 8: Pressure–Volume Work

(a) In this hypothetical apparatus, a gas is confined by a massless piston of area A. A massless wire is attached to the piston and the gas is held back by two weights with a combined mass of 2M resting on the massless pan. The cylinder is immersed in a large water bath in order to keep the gas temperature constant. The initial state of the gas is $P_i = 2Mg/A$ with a volume V_i at temperature, T. (b) When the external pressure on the confined gas is suddenly lowered by removing one of the weights the gas expands, pushing the piston up by the distance, Δh. The increase in volume of the gas (ΔV) is the product of the cross-sectional area of the cylinder (A) and the distance (Δh). The final state of the gas is $P_f = Mg/A$, V_f, and T.

In the hypothetical apparatus pictured in Figure 8(a), a weightless piston is attached to a weightless wire support, to which is attached a weightless pan. On the pan are two identical weights just sufficient to stop the gas from expanding. The gas is confined by the cylinder walls and piston, and the space above the piston is a vacuum. The cylinder is contained in a constant-temperature water bath, which keeps the temperature of the gas constant. Now imagine that one of the two weights is removed, leaving half the original mass on the pan. Let us call this remaining mass M. The gas will expand and the remaining weight will move against gravity, the situation represented by Figure 8(b). After the expansion, we find that the piston has risen through a vertical distance, Δh; that the volume of gas has doubled; and that the pressure of the gas has decreased. Now let us see how pressure and volume enter into calculating how much pressure–volume work the expanding gas does. First we can calculate the work done by the gas in moving the weight of mass M through a displacement Δh.

Recall that, *Work (w) = Force (M*g) ^ distance (Δh) = - M*g*Δh*   *Eq. 10*

The magnitude of the force exerted by the weight is M * g, where g is the acceleration due to gravity. The negative sign appears because the force is acting in a direction opposite to the piston's direction of motion.

Now recall, pressure = force (M * g)/area (A)—so that if the expression for work is multiplied by A/A we get

$$x = -\frac{M \times g}{A} \times \Delta h \times A = -P_{ext}\Delta V \qquad\qquad Eq.\,11$$

The "pressure" part of the Pressure–Volume Work is seen to be the external pressure (P_{ext}) on the gas, which in our thought experiment is due to the weight pulling down on the piston and is given by Mg/A. Note that the product of the area (A) and height (Δh) is equal to a volume—the volume change, ΔV, produced by the expansion.

Two significant features to note in Equation 11 are the negative sign and the term P_{ext}. The *negative sign* is necessary to conform to sign conventions. When a gas expands, ΔV is positive and w is negative, signifying that energy leaves the system as work. When a gas is compressed, ΔV is negative and w is positive, signifying that energy (as work) enters the system. The term P_{ext} is the external pressure—the pressure against which a system expands or the applied pressure that compresses a system. In many instances the internal pressure in a system will be essentially equal to the external pressure, in which case the pressure in equation 11 is expressed simply as P.

If pressure is stated in atmospheres and volume in liters, the unit of work is the *liter-atmosphere, L atm*; while the SI unit of work is the joule. The conversion factor between these two units of work can be obtained from the gas constant, R.

8.3145 m^3 Pa mol^{-1} K^{-1} = 8.3145 m^3 N m^{-2} mol^{-1} K^{-1} = 8.3145 kg m^2 $s^{-2}mol^{-1}$ K^{-1}

8.3145 J mol^{-1} K^{-1} = 0.082057 L atm mol^{-1} K^{-1} = 0.083145 L bar mol^{-1} K^{-1} and

$$\frac{8.3145\text{J}}{0.082057 \text{ L atm}} = 1.01.33 \frac{J}{L\ atm}$$

EXAMPLE 5   Calculating Pressure–Volume Work

QUESTION: Suppose the gas in Figure 8 is 0.100 mole Helium at 298 K, the two weights corresponds to an external pressure of 2.40 atm in Figure 8(a), and the single weight in Figure 8(b) corresponds to an external pressure of 1.20 atm. How much work, in joules, is associated with the gas expansion at constant temperature?

SOLUTION: We are given enough data to calculate the initial and final gas volumes (note that the identity of the gas does not enter into the calculations because we are assuming ideal gas behavior). With these volumes, we can obtain ΔV. The external pressure term in the pressure–volume work is the final pressure: 1.20 atm. The product - Pext * ΔV must be multiplied by a factor to convert work in liter-atmospheres to work in joules.

First, we calculate the initial volumes and final volumes.

$$V_{initial} = \frac{nRT}{P_i} = \frac{0.100 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{2.40 \text{ atm}} = 1.02 \text{ L}$$

$$V_{final} = \frac{nRT}{P_f} = \frac{0.100 \text{ mol} \times 0.0821 \text{ L atm } mol^{-1}K^{-1} \times 298\,K}{1.20\,atm} = 2.04\,L$$

Applying Equation 11 we have,

$$\mathbf{x = -P_{ext}\Delta V = -1.20 \text{ atm} \times (2.04 - 1.02) \text{ L} \times \frac{101.33 \text{ J}}{1 \text{ L atm}} = -1.24 \times 10^2 \text{ J}}$$

First law of Thermodynamics

Absorption or evolution of heat and the performance of work require changes in the energy of the system and its surroundings. When considering the energy of a system, we use the concept of internal energy and how heat and work are related to it. ***Internal energy, U,*** is the total energy (both kinetic and potential) in a system, including translational kinetic energy of molecules, the energy associated with molecular rotations and vibrations, the energy stored in chemical bonds and intermolecular attractions, and the energy associated with electrons in atoms.

A system contains only internal energy; it does not contain energy in the form of heat or work. Heat and work are the means by which a system exchanges energy with its surroundings. Heat and work exist only during a change in the system. The relationship between heat q, work w, and changes in internal energy ΔU is dictated by the law of conservation of energy, expressed in the form known as the first law of thermodynamics.

$$\Delta U = q + w \qquad\qquad Eq. 12$$

An isolated system is unable to exchange either heat or work with its surroundings, so that ***ΔU$_{isolated\ system}$ = 0*** and we can say, "***The energy of an isolated system is constant***"

In using Equation 12 we must keep these important points in mind:

1. Any energy entering the system carries a positive sign. Thus, if heat is absorbed by the system, q > 0. If work is done on the system, w > 0.
2. Any energy leaving the system carries a negative sign. Thus, if heat is given off by the system, q < 0. If work is done by the system, w < 0.
3. In general, the internal energy of a system changes as a result of energy entering or leaving the system as heat and/or work. If, on balance, more energy enters the

system than leaves, ΔU is positive. If more energy leaves than enters, ΔU is negative.

4. A consequence of $\Delta U_{isolated\ system} = 0$ is that $\Delta U_{system} = -\Delta U_{surroundings}$; that is, energy is conserved.

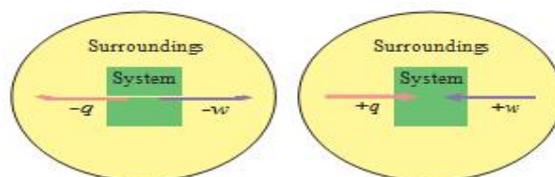Figure 9: Illustration of sign conventions used in thermodynamics

Example 6: Relating ΔU, q, and w Through the First Law of Thermodynamics

Question: A gas, while expanding (recall Figure 8), absorbs 25 J of heat and does 243 J of work. What is ΔU for the gas?

Solution: The key to problems of this type lies in assigning the correct signs to the quantities of heat and work. Because heat is absorbed by (enters) the system, q is positive. Because work done by the system represents energy leaving the system, w is negative. You may find it useful to represent the values of q and w, with their correct signs, within parentheses. Then complete the algebra.

$$\Delta U = q + w = (+25\,J) - (-243\,J) = 25\,J - 243\,J = -218\,J$$

The negative sign for the change in internal energy, ΔU, signifies that the system, in this case the gas, has lost energy.

Class Exercise:

1. In compressing a gas, 355 J of work is done on the system. At the same time, 185 J of heat escapes from the system. What is ΔU for the system?
2. If the internal energy of a system decreases by 125 J at the same time that the system absorbs 54 J of heat, does the system do work or have work done on it? How much?

State Function

To describe a system completely, we must indicate its temperature, its pressure, and the kinds and amounts of substances present. When we have done this, we have specified the state of the system. Any property that has a unique value for a specified state of a system is said to be a function of state, or a state function. For example, a sample of pure water at 20 °C (293.15 K) and under a pressure of 100 kPa is in a specified state. The density of water in this state is 0.99820 g/mL. We can establish that this density is a unique value—a function of state—in the following way: Obtain three different samples of water—one purified by extensive distillation of groundwater; one synthesized by burning pure H_2 (g) in pure O_2 (g); and one prepared by driving off the water of hydration from $CuSO_4$ 5 H_2O and condensing the gaseous water to a liquid. The densities of the three different samples for the state that we specified will all be the same: 0.99820 g/mL. Thus, the value of a function of state depends on the state of the system, and not on how that state was established.

The internal energy of a system is a function of state, although there is no simple measurement or calculation that we can use to establish its value. That is, we cannot write

down a value of U for a system in the same way that we can write d = 0.99820 g/mL for the density of water at 20 °C. Fortunately, we don't need to know actual values of U. Consider, for example, heating 10.0 g of ice at 0 °C to a final temperature of 50 °C. The internal energy of the ice at 0 °C has one unique value, U_1, while that of the liquid water at 50 °C has another, U_2. The difference in internal energy between these two states also has a unique value,

$\Delta U = U_2 - U_1$, and this difference is something that we can precisely measure. It is the quantity of energy (as heat) that must be transferred from the surroundings to the system during the change from state 1 to state 2. As a further illustration, imagine that a system changes from state 1 to state 2 and then back to state 1.

$$State\ 1\ (U_1) \overset{\Delta U}{\rightarrow} Sate\ 2\ (U_2) \overset{-\Delta U}{\longrightarrow} State\ 1\ (U_1)$$

Because U has a unique value in each state, ΔU also has a unique value; it is U_2-U_1. The change in internal energy when the system is returned from state 2 to state 1 is $-\Delta U = U_1 - U_2$. Thus, the overall change in internal energy is

$$\Delta U + (-\Delta U) = (U_2 - U_1) + (U_1 + U_2) = 0$$

This means that the internal energy returns to its initial value of U_1, which it must do, since it is a function of state. It is important to note here that when we reverse the direction of change, we change the sign of ΔU.

Heats of Reaction (ΔU and ΔH)

Consider the reactants in a chemical reaction as the initial state of a system and the products as the final state.

$$reactants\ (initial\ state\ U_i) \rightarrow products(final\ state\ U_f)$$
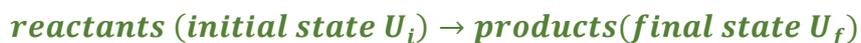
$$\Delta U = U_f - U_i$$

According to the first law of thermodynamics, $\Delta U = q + w$. We have heat of reaction as q_{rxn} and so we can write $\Delta U = q_{rxn} + w$

Now consider again a combustion reaction carried out in a bomb calorimeter. The original reactants and products are confined within the bomb, and we say that the reaction occurs at constant volume. Because the volume is constant, $\Delta V = 0$, and no work is done.

That is, $w = -P\Delta V = 0$. Denoting the heat of reaction for a constant-volume reaction as q_V, we see that $\Delta U = q_v$.

$$\Delta U = q_{rxn} + w = q_{rxn} + 0 = q_{rxn} = q_v$$

The heat of reaction measured in a bomb calorimeter is equal to ΔU.

Chemical reactions are not ordinarily carried out in bomb calorimeters. The metabolism of sucrose occurs under the conditions present in the human body. The combustion of methane (natural gas) in a water heater occurs in an open flame. This question then arises: How does the heat of a reaction measured in a bomb calorimeter compare with the heat of reaction if the reaction is carried out in some other way? The usual other way is in beakers, flasks, and other containers open to the atmosphere and under the constant pressure of the atmosphere.

The relationship between q_V and q_P can be used to devise another state function that represents the heat flow for a process at constant pressure. To do this, we begin by writing
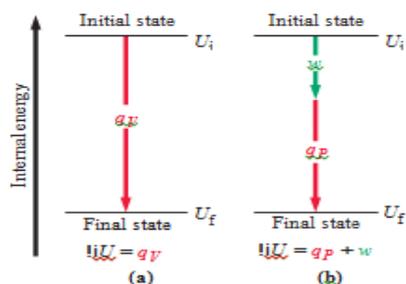

FIGURE 10: Two Different Paths Leading to same Internal Energy Change in a System

In path (a), the volume of the system remains constant and no internal energy is converted into work—think of burning gasoline in a bomb calorimeter. In path (b), the system does work, so some of the internal energy change is used to do work—think of burning gasoline in an automobile engine to produce heat

$$q_v = q_p + w$$

Now, using $\Delta U = q_v$, $w = -P\Delta V$ and rearranging terms, we obtain

$$\Delta U = q_p - P\Delta V$$

$$q_p = \Delta U + P\Delta V$$

The quantities U, P, and V are all state functions, so it should be possible to derive the expression ΔU + PΔV from yet another state function. This state function, called enthalpy, H, is the sum of the internal energy and the pressure–volume product of a system: H = U + PV. The enthalpy change, ΔH, for a process between initial and final states is

$$\Delta H = H_f - H_i = \left(U_f + P_f V_f\right) - (U_i + P_i V_i)$$

$$\Delta H = \left(U_f + U_i\right) + (P_f V_f - P_i V_i)$$

$$\Delta H = \Delta U + \Delta PV$$

If the process is carried out at a constant temperature and pressure ($P_i = P_f$) and with work limited to pressure–volume work, the enthalpy change is ΔH = ΔU + PΔV and the heat flow for the process under these conditions is

$$\boldsymbol{\Delta H = q_p} \qquad\qquad \boldsymbol{Eq.\,13}$$

Enthalpy (Δ H) and Internal Energy (Δ U) Changes in a Chemical Reaction

We have noted that the heats of reaction at constant pressure, ΔH, and the heat of reaction at constant volume, ΔU, are related by the expression

$$\boldsymbol{\Delta U = \Delta H - P\Delta V} \qquad\qquad \boldsymbol{Eq.\,14}$$

The last term in this expression is the energy associated with the change in volume of the system under a constant external pressure. To assess just how significant pressure–volume work is, consider the following reaction, illustrated in Figure 11 below.

$$2\,CO\,(g) + O_2\,(g) \rightarrow 2\,CO_2\,(g)$$

If the heat of this reaction is measured under constant-pressure conditions at a constant temperature of 298 K, we get -566.0 kJ, indicating that 566.0 kJ of energy has left the system as heat: ΔH = - 566.0 kJ. To evaluate the pressure–volume work, we begin by writing: $\quad P\Delta V = P(V_f - V_i)$

Then we can use the ideal gas equation to write this alternative expression.

$$P\Delta V = RT(n_f - n_i)$$

Here, n_f is the number of moles of gas in the products 2 mol CO_2 and n_i is the number of moles of gas in the reactants 2 mol CO + 1 mol O_2. Thus,

$$P\Delta V = 0.0083145\ kJ\ mol^{-1}K^{-1} \times 298K \times (2 - [2-1])mol = -2.5\ kJ$$

The change in internal energy is: $\qquad \Delta U = \Delta H - P\Delta V$

$$= -566.0\ kJ - (-2.5\ kJ)$$

$$= -563.5\ kJ$$

This calculation shows that the PΔV term is quite small compared to ΔH and that ΔU and ΔH are almost the same. An additional interesting fact here is that the volume of the system decreases as a consequence of the work done on the system by the surroundings.

$$C_{12}H_{22}O_{11}(s) + 12\,O_2(g) \longrightarrow 12\,CO_2(g) + 11\,H_2O(l) \quad \Delta H = -5.65 * 10^3\,kJ$$

In the combustion of sucrose at a fixed temperature shown in the stoichiometry above, the heat of combustion turns out to be the same, whether at constant volume (q_V) or constant pressure (q_P). Only heat is transferred between the reaction mixture and the surroundings; no pressure–volume work is done. This is because the volume of a system is almost entirely determined by the volume of gas and because 12 mol $CO_2(g)$ occupies the same volume as 12 mol $O_2(g)$. There is no change in volume in the combustion of sucrose: $q_P = q_V$

In thermochemistry, our chief interest is generally in heats of reaction, not pressure–volume work. And because most reactions are carried out under atmospheric pressure, it's helpful to have a function of state, enthalpy, H, whose change is exactly equal to something we can measure: q_P.

Standard States and Standard Enthalpy Changes: The measured enthalpy change for a reaction has a unique value only if the initial state (reactants) and final state (products) are precisely described. If we define a particular state as standard for the reactants and products, we can then say that the standard enthalpy change is the enthalpy change in a reaction in which the reactants and products are in their standard states. This so-called standard enthalpy of reaction is denoted with a degree symbol, $\Delta H°$.

The standard state of a solid or liquid substance is the pure element or compound at a pressure of 1 bar (10^5 Pa) and at the temperature of interest. For a gas, the standard state is the pure gas behaving as an (hypothetical) ideal gas at a pressure of 1 bar and the temperature of interest.

Although temperature is not part of the definition of a standard state, it still must be specified in tabulated values of ΔH°, because ΔH° depends on temperature.

Standard Enthalpy of Formation ΔH_f^0 is the heat change that results when one mole of a compound is formed from its elements at a pressure of 1 atm. The standard enthalpy of formation of any element in its most stable form is zero. The degree symbol denotes that the enthalpy change is a standard enthalpy change, and the subscript "f" signifies that the reaction is one in which a substance is formed from its elements.
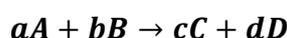
$$\Delta H_f^o(O_2) = 0 \qquad\qquad \Delta H_f^o(C, graphite) = 0$$

$$\Delta H_f^o(O_3) = 142\ kJ/mol \qquad\qquad \Delta H_f^o(C, diamond) = 1.90\ kJ/mol$$

Standard Enthalpy of Reaction ΔH_{rxn}^o is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \rightarrow cC + dD$$

$$\Delta H_{rxn}^o = \left[c\Delta H_f^o(C) + d\Delta H_f^o(D)\right] - \left[a\Delta H_f^o(A) + b\Delta H_f^o(B)\right]$$

$$\Delta H_{rxn}^o = \sum n\,\Delta H_f^o(products) - \sum m\,\Delta H_f^o(reactants)$$

Table 6.3 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f^o (kJ/mol)	Substance	ΔH_f^o (kJ/mol)
Ag(s)	0	$H_2O_2(l)$	−187.6
AgCl(s)	−127.04	Hg(l)	0
Al(s)	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	HI(g)	25.94
$Br_2(l)$	0	Mg(s)	0
HBr(g)	−36.2	MgO(s)	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
CO(g)	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	NO(g)	90.4
Ca(s)	0	$NO_2(g)$	33.85
CaO(s)	−635.6	$N_2O_4(g)$	9.66
$CaCO_3(s)$	−1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	0	O(g)	249.4
HCl(g)	−92.3	$O_2(g)$	0
Cu(s)	0	$O_3(g)$	142.2
CuO(s)	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
HF(g)	−268.61	$SO_2(g)$	−296.1
H(g)	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	ZnO(s)	−347.98
$H_2O(l)$	−285.8		

Thermochemical Equations

1. The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \, kJ$$

2. If you reverse a reaction, the sign of ΔH changes

$$H_2O(l) \rightarrow H_2O(s) \qquad \Delta H = -6.01 \, kJ$$

3. If you multiply both sides of the equation by a factor n, then ΔH must change by the same factor n.

$$2H_2O(s) \rightarrow 2H_2O(l) \qquad \Delta H = 2 \times 6.01 \, kJ = 12.02 \, kJ$$

Enthalpy change is directly proportional to the amounts of substances in a system.

4. The physical states of all reactants and products must be specified in thermochemical equations.
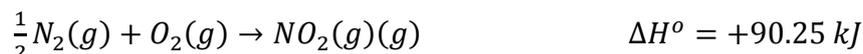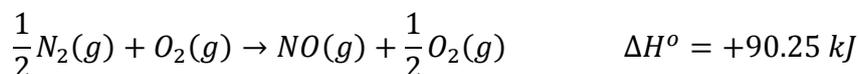
$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \, kJ$$
$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = 44.0 \, kJ$$

HESS'S LAW (INDIRECT DETERMINATION OF ΔH)

To describe the standard enthalpy change for the formation of NO_2 (g) from N_2 (g) and O_2 (g),

$$\frac{1}{2}N_2(g) \rightarrow O_2(g) \rightarrow NO_2(g) \qquad \Delta H^o =?$$
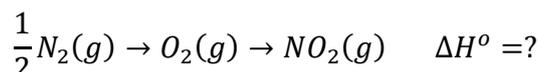
we can think of the reaction as proceeding in two steps: First we form NO(g) from $N_2(g)$ and $O_2(g)$, and then $NO_2(g)$ from NO(g) and $O_2(g)$. When the equations for these two steps are added together with their individual and distinctive ΔH° values, we get the overall equation and ΔH° value that we are seeking.

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^o = +90.25 \, kJ$$

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H^o = -57.07 \, kJ$$

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)(g) \qquad \Delta H^o = +90.25 \, kJ$$

Note that in summing the two equations NO (g), a species that would have appeared on both sides of the overall equation was canceled out.

Hess's law states the If a process occurs in stages or steps (even if only hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.

Hess' law is simply a consequence of the state function property of enthalpy. Regardless of the path taken in going from the initial state to the final state, ΔH (or ΔH° if the process is carried out under standard conditions) has the same value. It's of greatest value because it permits us to calculate ΔH values that we cannot measure directly through indirect calculation of ΔH.

Example 7: Applying Hess's Law

Use the heat of combustion data from page 268 to determine ΔH° for reaction (7.18) 3 C1graphite2 + 4 H₂(g) → C₃H₈(g)   ΔH° = ?

Fuels as Sources of Energy

One of the most important uses of thermochemical measurements and calculations is in assessing materials as energy sources. For the most part, these materials, called fuels, liberate heat through the process of combustion. We will briefly survey some common fuels,

Fossil Fuels: The bulk of current energy needs are met by petroleum, natural gas, and coal—so called fossil fuels. These fuels are derived from plant and animal life of millions of years ago. The original source of the energy locked into these fuels is solar energy. In the process of photosynthesis, CO_2 and H_2O, in the presence of enzymes, the pigment chlorophyll, and sunlight, are converted to carbohydrates. These are compound with formulas $C_m(H_2O)_n$, where m and n are integers. For example, in the sugar glucose $m = n = 6$, that is $C_6(H_2O)_6 = C_6H_{12}O_6$. Its formation through photosynthesis is an endothermic process, represented as

$$6CO_2(g) + 6H_2O(g) \xrightarrow{\text{"chlorophyll" } sunlight} C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H^o = +2.8 \times 10^3 \; kJ$$

When the above reaction is reversed, as in the combustion of glucose, heat is evolved. The combustion reaction is exothermic.

Problems Posed by Fossil Fuel Use: There are two fundamental problems with the use of fossil fuels. First, fossil fuels are essentially nonrenewable energy sources. The second problem with fossil fuels is their environmental effect. Sulfur impurities in fuels produce oxides of sulfur. The high temperatures associated with combustion cause the reaction of N_2 and O_2 in air to form oxides of nitrogen. Oxides of sulfur and nitrogen are implicated in air pollution and are important contributors to the environmental problem known as acid rain. Another inevitable product of the combustion of fossil fuels is carbon dioxide, one of the "greenhouse" gases leading to global warming and potential changes in Earth's climate.

Coal and Other Energy Sources: In the United States, reserves of coal far exceed those of petroleum and natural gas. Despite this relative abundance, however, the use of coal has not increased significantly in recent years. In addition to the environmental effects cited above, the expense and hazards involved in the deep mining of coal are considerable. Surface mining, which is less hazardous and expensive than deep mining, is also more damaging to the environment. One promising possibility for using coal reserves is to convert coal to gaseous or liquid fuels, either in surface installations or while the coal is still underground.

Gasification of Coal Before cheap natural gas became available in the 1940s; gas produced from coal (variously called producer gas, town gas, or city gas) was widely used in the United States. This gas was manufactured by passing steam and air through heated coal and involved such reactions as

ELECTROCHEMISTRY: INTRODUCTION

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte. A process of this kind can always be represented as a chemical reaction and is known generally as an electrode process. Electrode processes take place

within the double layer and produce a slight unbalance in the electric charges of the electrode and the solution. Much of the importance of electrochemistry lies in the ways that these potential differences can be related to the thermodynamics and kinetics of electrode reactions. In particular, manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction.

CHEMISTRY AND ELECTRICITY

The connection between chemistry and electricity is a very old one, going back to ALESSAN-DRO VOLTA'S discovery, in 1793, that electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper. In 1800, Nicholson and Carlisle, using Volta's primitive battery as a source, showed that an electric current could decompose water into oxygen and hydrogen. This was surely one of the most significant experiments in the history of chemistry, for it implied that the atoms of hydrogen and oxygen were associated with positive and negative electric charges, which must be the source of the bonding forces between them. By 1812, the Swedish chemist BERZELIUS could propose that all atoms are electrified, hydrogen and the metals being positive, the nonmetals negative. The use of electricity as a means of bringing about chemical change continued to play a central role in the development of chemistry. HUMPHREY DAVEY prepared the first elemental sodium by electrolysis of a sodium hydroxide melt. It was left to Davey's former assistant, MICHAEL FARADAY, to show that there is a direct relation between the amount of electric charge passed through the solution and the quantity of electrolysis products. JAMES CLERK MAXWELL immediately saw this as evidence for the "molecule of electricity".

2.1   Electro-neutrality

Nature seems to strongly discourage any process that would lead to an excess of positive or negative charge in matter. Suppose, for example, that we immerse a piece of zinc metal in pure water. A small number of zinc atoms go into solution as Zn ions, leaving their electrons behind in the metal: $Zn(s) \rightarrow Zn^{2+} + 2e^-$
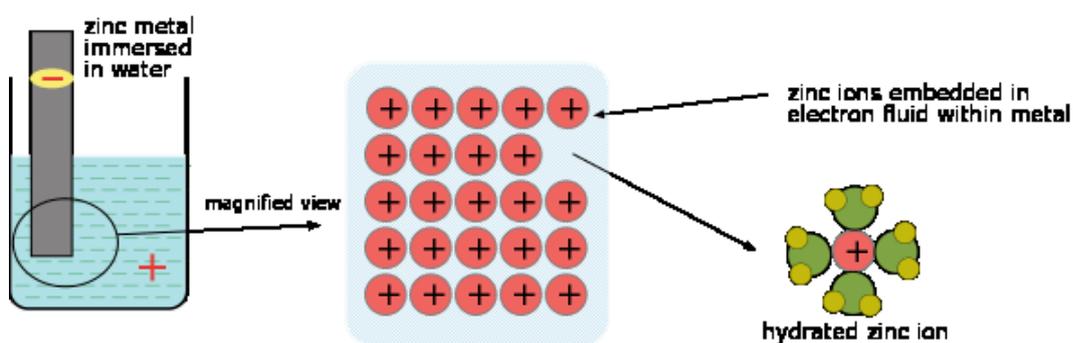

Fig. 1: Oxidation of metallic zinc in contact with water

As this process goes on, the electrons which remain in the zinc cause a negative charge to build up within the metal which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition. Very soon, therefore, the process comes to a halt, resulting in a solution in which the

concentration of Zn^{2+} is still too low (around 10^{-10} M) to be detected by ordinary chemical means.

There would be no build-up of opposing charges in the two phases

1. If the excess electrons could be removed from the metal or the positive ions consumed as the reaction proceeds. For example, we could drain off the electrons left behind in the zinc through an external circuit that forms part of a complete electrochemical cell.
2. Another way to remove electrons is to bring a good electron acceptor (that is, an oxidizing agent) into contact with the electrode. A suitable electron acceptor would be hydrogen ions; this is why acids attack many metals. For the very active metals such as sodium, water itself is a sufficiently good electron acceptor.

The degree of charge unbalance that is allowed produces differences in electric potential of no more than a few volts, and corresponds to unbalances in the concentrations of oppositely charged particles that are not chemically significant. There is nothing mysterious about this prevention, known as the electro neutrality principle; *it is a simple consequence of the thermodynamic work required to separate opposite charges, or to bring like charges into closer contact*. The additional work raises the free energy of the process, making it less spontaneous.

The only way we can get the oxidation of the metal to continue is to couple it with some other process that restores electroneutrality to the two phases. A simple way to accomplish this would be to immerse the zinc in a solution of copper sulfate instead of pure water. The reaction is a simple oxidation-reduction process, a transfer of two electrons from the zinc to the copper:

$$Zn(s) \rightarrow Zn^{2+} + 2e- \qquad\qquad Cu^{2+} + 2e- \rightarrow Cu(s)$$

The dissolution of the zinc is no longer inhibited by a buildup of negative charge in the metal, because the excess electrons are removed from the zinc by copper ions that come into contact with it. At the same time, the solution remains electrically neutral, since for each Zn ion introduced to the solution, one Cu ion is removed. The net reaction quickly goes to completion:

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$

1.2   Potential differences at interfaces

The transition region between two phases consists of a region of charge unbalance known as the electric double layer. As its name implies, this consists of an inner monomolecular layer of adsorbed water molecules and ions, and an outer diffuse region that compensates for any local charge unbalance that gradually merges into the completely random arrangement of the bulk solution. In the case of a metal immersed in pure water, the electron fluid within the metal causes the polar water molecules to adsorb to the surface and orient themselves so as to create two thin planes of positive and negative charge. If the water contains dissolved ions, some of the larger (and more polarizable) anions will loosely bond (chemisorb) to the metal, creating a negative inner layer which is compensated by an excess of cations in the outer layer.

The interfacial potential differences which develop in electrode-solution systems are limited to only a few volts at most. This may not seem like very much until you consider that this potential difference spans a very small distance. In the case of an electrode immersed in a solution, this

distance corresponds to the thin layer of water molecules and ions that attach themselves to the electrode surface normally only a few atomic diameters. Thus a very small voltage can produce a very large potential gradient. Interfacial potentials are not confined to metallic electrodes immersed in solutions; they can in fact exist between any two phases in contact, even in the absence of chemical reactions. In many forms of matter, they are the result of adsorption or ordered alignment of molecules caused by non-uniform forces in the interfacial region.
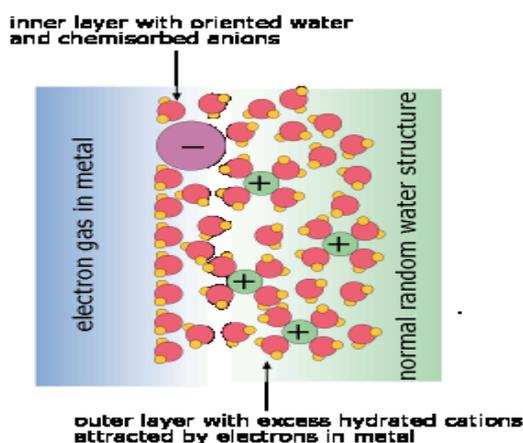

Fig. 2: Electric double layer at an electrode surface

ELECTROCHEMICAL CELLS

Although it is physically impossible to measure or manipulate the potential difference between a piece of metal and the solution in which it is immersed (the usual way of measuring a potential difference between two points is to bring the two leads of a voltmeter into contact with them. It's simple enough to touch one lead of the meter to a metallic electrode, but there is no way you can connect the other lead to the solution side of the interfacial region without introducing a second electrode with its own interfacial potential, so you would be measuring the sum of two potential differences. Thus single electrode potentials, as they are commonly known, are not directly observable), we can easily measure a potential difference between two such electrodes immersed in a solution. The result will be the sum of the two electrode potentials.
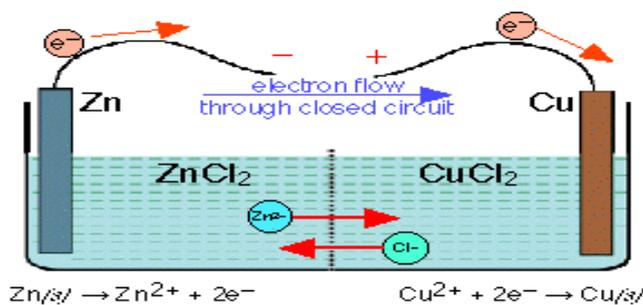

Fig. 3: A simple electrochemical cell:

The two compartments of this cell are separated by a porous barrier that allows ions to pass through while preventing gross mixing of the two solutions. When the two electrodes are

This arrangement is called a galvanic cell. A typical cell might consist of two pieces of metal, one zinc and the other copper; each immersed each in a solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through. metals, one, zinc and the other copper; each immersed each in a solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through.

If we simply left it at that, no significant amount of reaction would take place. However, if we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions go into solution in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the same as before— the oxidation of zinc by copper (II) ions:

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$

But this time, the oxidation and reduction steps take place in separate locations

Left electrode: $\quad Zn(s) \rightarrow Zn^{2+} + 2e^- \text{ oxidation}$

Right electrode: $\quad Cu^{2+} + 2e^- \rightarrow Cu(s) \text{ reduction}$

In the simplest cells, the barrier between the two solutions can be a porous membrane, but for precise measurements, a more complicated arrangement, known as a salt bridge, is used. With the salt bridge, we have two liquid junction potentials instead of one (that cause natural potential difference, known as the junction potential that develops when any two phases [such as two solutions] are in contact) but they tend to cancel each other out.

By connecting a battery or other source of current to the two electrodes, we can force the reaction to proceed in its non-spontaneous or reverse direction. And also by placing an ammeter in the external circuit, we can measure the amount of electric charge that passes through the electrodes, and thus the number of moles of reactants that get transformed into products in the cell reaction. Electric charge q is measured in coulombs. The amount of charge carried by one mole of electrons is known as the faraday, which we denote by F. For most purposes, you can simply use 96,500 coulombs as the value of the faraday.

Example: For the cell in the Fig. above, how much mass would the Zinc electrode lose if a current of 0.15 amps flows through the external circuit for 1.5 hours?

Solution, the amount of charge passing between the electrodes is:

$$(0.15 \, amp) \times (1.5 \times 60 \times 60)$$

$$(0.15 \, amp) \times (5400 \, sec) = 810c$$

$$\frac{(810c)}{(96500cF^{-1})} = 0.0084 \ F$$

Since the oxidation of one mole of Zn to Zn²⁺ results in the removal of two moles of electrons, the number of moles of Zn removed from the electrode is 0.0042, corresponding to a weight loss of $(0.0042 \ mol) \times (65.37 \ g \ mol^{-1}) = 0.273$

Cell description conventions

Special symbolic notations are adopted in describing a given electrochemical cell. Following this notation the cell of Fig.3 would be

Zn(s) | Zn²⁺(aq) || Cu²⁺(aq) | Cu(s)

The vertical bars indicate phase boundaries; the double vertical bar in the middle denotes the phase boundary between the two solutions. As a matter of convention, the chemical species that undergo reduction when the cell reaction proceeds to the right according to the net equation are shown on the right side, and those that undergo oxidation are shown on the left.

There are several other conventions relating to cell notation and nomenclature that you are expected to know:

•   The anode is where oxidation occurs, and the cathode is the site of reduction. In an actual cell, either electrode can have either identity, depending on the direction in which the net cell reaction is occurring.

•   If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be positive.

•   "Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

Electrodes and electrode reactions

The electron-transfer step that takes place at each electrode is known as the electrode reaction. The substances that receive and lose electrons are called the electro active species.

In the example of the Zn/Cu cell we have been using, the electrode reaction involves a metal and its hydrated cation; we call such electrodes metal-metal ion electrodes. There are a number of other kinds of electrodes which are widely encountered in electrochemistry and analytical chemistry they are

1. Ion-ion electrodes
2. Gas electrodes
3. Insoluble-salt electrodes

Standard half-cell potentials

When a net reaction proceeds in an electrochemical cell, oxidation occurs at one electrode (the anode) and reduction takes place at the other electrode (the cathode.) We can think of the cell as consisting of two half-cells joined together by an external circuit through which electrons flow and an internal pathway that allows ions to migrate between them so as to preserve electro neutrality.

Reduction potentials: Each half-cell has associated with it a potential difference whose magnitude depends on the nature of the particular electrode reaction and on the concentrations of the dissolved electro active species. The sign of this potential difference depends on the direction (oxidation or reduction) in which the electrode reaction proceeds. In order to express them in a uniform way; we adopt the convention that half-cell potentials are always defined for the reduction direction. Thus the half-cell potential for the Zn/Zn^{2+} electrode (or couple as it is sometimes called) is defined as the potential difference between a piece of metallic zinc and the solution when the reaction below takes place

$$Zn^{2+} + 2e^- \rightarrow Zn(s)$$
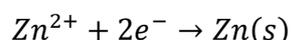
In the cell Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s) the zinc appears on the left side, indicating that it is being oxidized, not reduced. For this reason, the potential difference contributed by the left half-cell has the opposite sign to its conventional half-cell potential. More generally, we can define the cell potential or cell EMF as

$$E_{cell} = \Delta V = E_{right} - E_{left}$$

in *which "right" and "left" refer to the cell notation convention ("reduction on the right")* and not, of course, to the physical orientation of a real cell in the laboratory. If we expand the above expression we see that the cell potential is just the difference between the two half-cell potentials E $_{right}$ and E $_{left}$.

$$E_{cell} = V_{Cu} - V_{soln} + V_{soln} - V_{Zn}$$

Reference half-cells: The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. Although we cannot determine the absolute value of a half-cell potential, we can still measure its value in relation to the potentials of other half cells. In particular, if we adopt a reference half-cell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.

The reference cell we use for this purpose is the hydrogen half-cell in which hydrogen gas is allowed to bubble over a platinum electrode having a specially treated surface which catalyzes the reaction

$$\mathrm{Pt}/\frac{1}{2}\mathrm{H_2(g)}/\,\mathrm{H^+(aq)}//\,....$$

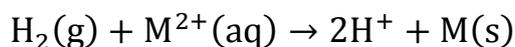$$\frac{1}{2}H_2(g) \rightarrow H^+ + e^-$$
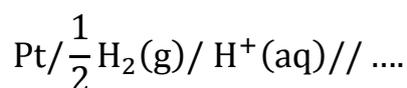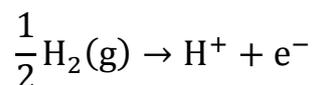
When this electrode is operated under standard conditions of 1 atm Hg pressure, 25°C, and pH = 0, it becomes the *standard hydrogen electrode, sometimes abbreviated SHE.*

In order to measure the relative potential of some other electrode couple M^{2+}/M, we can set up a cell

$$Pt/H_2(g)/H^+//M^{2+}(aq)/M(s)$$
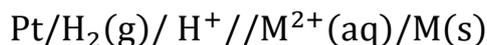
whose net reaction is

$$H_2(g) + M^{2+}(aq) \rightarrow 2H^+ + M(s)$$

In analogy with, $E_{cell} = V_{Cu} - V_{soln} + V_{soln} - V_{Zn}$

the potential difference between the platinum and M electrodes will be

$$\mathbf{E_{cell} = V_M - V_{soln} + V_{soln} - V_{Pt}}$$

but since the difference $V_{soln} - V_{Pt}$ is by definition zero for the hydrogen half-cell, the cell potential we measure corresponds to $\mathbf{E_{cell} = V_M - V_{soln}}$

which is just the potential (relative to that of the SHE) of the half-cell whose reaction is

$$M^{2+} + 2e^- \rightarrow M(s)$$
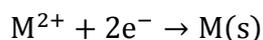
Standard [reduction] potentials for hundreds of electrodes have been determined (mostly in the period 1925-45, during which time they were referred to as "oxidation potentials") and are usually tabulated in order of increasing tendency to accept electrons. This ordering is also known as the "*electromotive series of the elements.*" As can be seen in the abbreviated version in the Table below, sodium is the most "active" of the metallic elements in the sense that its oxidation product Na^+ shows the smallest tendency (as indicated by the highly negative voltage) to undergo reduction.

Table 1: Some Standard Reduction Potentials

These couples (an oxidant and its conjugate reductant) are arranged in order of increasing tendency of the species in the leftmost column (oxidizing agents) to accept electrons.

oxidant (electron acceptor)	reductant (electron donor)	volts
Na^+	$Na(s)$	−2.71
Zn^{2+}	$Zn(s)$	−.76
Fe^{2+}	$Fe(s)$	−.44
Cd^{2+}	$Cd(s)$	−.40
Pb^{2+}	$Pb(s)$	−.126
2 H⁺	**H₂ (g)**	**0.000**
$AgCl(s)$	$Ag(s) + Cl^-(aq)$	+.222
$Hg_2Cl_2(s)$	$2\ Cl^-(aq) + \underline{Hg}(l)$	+.268
Cu^{2+}	$Cu(s)$	+.337
$I_2(s)$	$2\ I^-$	+.535
Fe^{3+}	Fe^{2+}	+.771
Ag^+	$Ag(s)$	+.799
$O_2(g) + 4\ H^+$	$2\ H_2O(l)$	+1.23
$Cl_2(g)$	$2\ Cl^-$	+1.36

Reference electrodes: In most electrochemical experiments our interest is concentrated on only one of the electrode reactions. Since all measurements must be on a complete cell involving two electrode systems, it is common practice to employ a reference electrode as the other half of the cell. *A reference electrode is an electrode which has a stable and well-known electrode potential.*

Electrodes selected for reference purposes have potentials that are stable and reproducible. They may be classified according to the nature of the electrochemical reactions that take place in them. The reactions must be highly reversible in order to avoid a change of potential when a small current flows through the reference electrode.

The reference electrodes that are most often used include calomel electrodes ($Hg/Hg_2Cl_2/KCl$ or HCl) calomel is, silver chloride electrodes (Ag|AgCl|KCl or HCl), mercuric sulphate electrodes (Hg|HgSO4|H2SO4), mercury oxide electrodes (Hg|HgO|KOH), and quinhydrone electrodes (Pt|hydro-quinone, quinone | HCl).

Example: Find the standard potential of the cell

$$Cu(s)/Cu^{2+}//Cl^{-1}/AgCl(s)/Ag(s)$$

and predict the direction of electron flow when the two electrodes are connected.

Solution: The net reaction corresponding to this cell will be

$$2Ag(s) + 2Cl^-(aq) + Cu^{2+}(aq) \rightarrow AgCl(s) + Cu(s)$$

Since this involves the reverse of the AgCl reduction, we must reverse the corresponding half-cell potential:

$$E_{cell} = \Delta V = E_{right} - E_{left}$$

$$E_{cell} = (0.337 - 0.222)V = 0.115V$$

Since this potential is positive, the reaction will proceed to the right; electrons will be withdrawn from the copper electrode and flow through the external circuit into the silver electrode. Note carefully that in combining these half-cell potentials, we did not multiply E° the for the Cu^{2+}/Cu couple by two.

Cell Potentials and the Electromotive Series

Tables containing the same sequence of reactions as in Table 1, but without the voltage data, were in common use long before electrochemical cells were studied and half-cell potentials had been measured. If you read down the central column, you will notice that it begins with the sequence of metals Na, Zn, Fe, etc. This sequence is known as the activity series of the metals, and expresses the decreasing tendency these species to lose electrons- that is, to undergo oxidation. The activity series has long been used to predict the direction of oxidation-reduction reactions. Consider, for example, the oxidation of Cu by metallic zinc that we have mentioned previously. The fact that zinc is near the top of the activity series means that this metal has a strong tendency to lose electrons. By the same token, the tendency of Zn to accept electrons is relatively small. Copper, on the other hand, is a poorer electron donor, and thus its oxidized form, Cu, is a fairly good electron acceptor. We would therefore expect the reaction to proceed in the direction indicated, rather than in the reverse direction.

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$
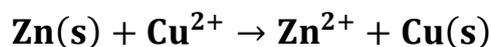
An old-fashioned way of expressing this is to say that "zinc will displace copper from solution".

Cell Potentials and Free Energy

From the above, it should be apparent that the potential difference between the electrodes of a cell is a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to the right. But we already know that the standard free energy change, expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. Thus and measure the same thing, and are related in a simple way:

$$\Delta G^o = -nFE^o$$

A few remarks are in order about this very fundamental and important relation:

- The negative sign on the right indicates that a positive cell potential (according to the sign convention discussed previously) implies a negative free energy change, and thus that the cell reaction will proceed to the right.

- Electrical work is done when an electric charge q moves through a potential difference ΔV. The right side of. Eq. 10 refers to the movement of n moles of charge across the cell potential E°, and thus has the dimensions of work.
- The value of $\Delta G°$ expresses the maximum useful work that a system can do on the surroundings. "Useful" work is that which can be extracted from the cell by electrical means to operate a lamp or some other external device. This excludes any P-V work that is simply a consequence of volume change (which could of course conceivably be put to some use!) and which would be per- formed in any case, even if the reactants were combined directly. This quantity of work $-\Delta G°$ can only be extracted from the system under the limiting conditions of a reversible change, which for an electrochemical cell implies zero current. The more rapidly the cell operates the less electrical work it can supply.
- If F is expressed in coulombs per mole, the electrical work is in joules per mole. To relate these units to electrical units, recall that the coulomb is one amp-sec, and that power, which is the rate at which work is done, is measured in watts, which is the product of amps and volts. Thus

$$1J = 1(amp - sec) \times \text{volts}$$

Example: For how many minutes could a Cu/Zn cell keep a 100-watt lamp lit, assuming that one mole of reactants are transformed to products, and that the cell voltage is 90 percent of the reversible value E°?

Solution: From Table 1, E° for the cell Zn(s) | Zn^{2+} (aq) || Cu^{2+} (aq) | Cu(s) is 1.10 V; 90% of this is 0.99 V. Substituting into

$$\Delta G° = -nFE°$$

With n = 2 (two electrons are transferred per mole of reaction), we have

$$\Delta G° = -(2 \text{ mol}) \times (96500 \text{ amp sec } mol^{-1}) \times 0.99 \text{ Volt} = 191070 \text{ watts} - sec$$
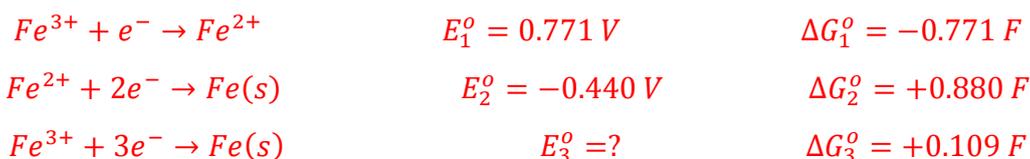
is the free energy change under these conditions, the cell can deliver 100 watts for (191070/100) = 1910.7 sec, or for about 1910.7/60 = 32 minutes approximately.

Example:

Calculate E^o for the electrode Fe^{3+}/Fe^{2+} from the standard electrode potential of the couples Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe as given in the standard electrode potential table.

Solution,

Tabulate the values and calculate the ΔG_s^o as follows:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E_1^o = 0.771 \, V$	$\Delta G_1^o = -0.771 \, F$
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	$E_2^o = -0.440 \, V$	$\Delta G_2^o = +0.880 \, F$
$Fe^{3+} + 3e^- \rightarrow Fe(s)$	$E_3^o =?$	$\Delta G_3^o = +0.109 \, F$

The free energy for the net half-reaction is 0.109 nF, so $E_3^o = -\frac{0.109}{3} \, V = -0.036 \, V$

NERNST EQUATION

The standard cell potentials we have been discussing refer to cells in which all dissolved substances are at unit activity, which essentially means an "effective concentration" of 1M. Similarly, any gases that take part in an electrode reaction are at an effective pressure (known as the fugacity) of 1 atm. If these concentrations or pressures have other values, the cell potential will change in a manner that can be predicted from the principles you already know.

Suppose, for example, that we reduce the concentration of Zn^{2+} in the Zn/Cu cell from its standard effective value of 1 Mt to a much smaller value:

$$Zn(s)/Zn^{2+}(aq, 0.01M)//Cu^{2+}(aq)/Cu(s)$$

This will reduce the value of the reaction quotient Q for the cell reaction

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$
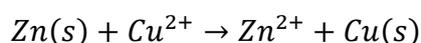
thus making it more spontaneous, or "driving it to the right" as the Le Châtelier principle would predict, and making its free energy change ΔG more negative than ΔG°, so that E would be more positive than E°. The relation between the actual cell potential E and the standard potential E° is developed in the following way. We begin with the Equation that relates the standard free energy change (for the complete conversion of products into reactants) to the standard potential

$$\Delta G^o = -nFE^o$$

By analogy we can write the more general equation

$$\Delta G = -nFE$$

which expresses the change in free energy for any extent of reaction- that is, for any value of the reaction quotient Q. We now substitute these into the expression that relates ΔG and ΔG° which you will recall from the chemical equilibrium:

$$\Delta G = \Delta G^o + RT \ln Q$$

This gives

$$-nFE = -nFE^o + RT \ln Q$$

which can be rearranged to

$$E = E^o - \frac{RT}{nF} \ln Q$$

This is the very important Nernst equation which relates the cell potential to the standard potential and to the activities of the electro-active species. Notice that the cell potential will be the same as E° only if Q is unity. The Nernst equation is more commonly written in base-10 log form and for 25°C:

$$E = E^o - \frac{0.059}{n} \log Q$$

BATTERIES AND FUEL CELLS

One of the oldest and most important applications of electrochemistry is to the storage and conversion of energy. You already know that a galvanic cell converts chemical energy to work; similarly, an electrolytic cell converts electrical work into chemical free energy. Devices that carry out these conversions are called batteries. In ordinary batteries the chemical components are contained within the device itself. If the reactants are supplied from an external source as they are consumed, the device is called a fuel cell.

The term battery derives from the older use of this word to describe physical attack or "beating"; Benjamin Franklin first applied the term to the electrical shocks that could be produced by an array of charged glass plates. In common usage, the term "call" is often used in place of battery.

ELECTROCHEMICAL CORROSION

Corrosion can be defined as the destruction of a solid body through an unintentional chemical or electrochemical action starting at its surface. This definition covers metallic and nonmetallic materials; generally, however, the term corrosion is invariably used to denote the destruction of metals. Nonmetallic materials are attacked only by certain chemical agents under specific conditions and are usually resistant to the action of mild corrosion media such as water and the atmosphere. All but a few metals, however, are corroded more or less by water and the atmosphere.

Furthermore, the attack on a metal occurs mostly by electrochemical action because of the characteristics structure of metals, which accounts for phenomena such as the free movement of electrons through their lattices. Most metals exist in nature in combined forms such as oxides, hydroxides, carbonates, sulfides, sulfates and silicates. The extraction of metals from their ores requires a considerable amount of energy. The isolated metals therefore can be regarded as being in a much higher energy state than in their corresponding ores, and they will show a natural tendency to return to their lower energy combined state (In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects are dissipated by a variety of different routes). Thus the corrosion of metals can be regarded as the reverse process of that of reducing metals from their ores.

Metal corrosion in an aqueous media can be illustrated by the following reactions:

In the absence of oxygen

$$M(s) + 2H_2O(l) \leftrightarrow M(OH)_2(s) + H_2(g)$$
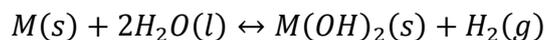
In the presence of oxygen

$$M(s) + \frac{1}{2}O_2(g) + H_2O(g) \leftrightarrow M(OH)_2(s)$$
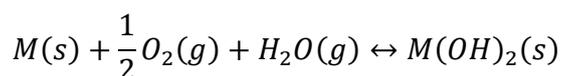
For the reaction to occur the change in the free energy (ΔG) must be negative. If ΔG is positive, then the reaction will not occur and corrosion will not take place

From thermodynamics

$$\Delta G - \Delta G^o = RT ln \frac{a_{pr}}{a_r}$$

Where ΔG is the free energy change of the reaction at chosen temperature and pressure, ΔG^o is the standard free energy change when the products and reactants are in the standard state, and $a_{pr} and\ a_r$ denote the activities of the products and reactants respectively. The ratio $\frac{a_{pr}}{a_r}$, is known as the equilibrium constant of the reaction, Q thus the above equation can be written as

$$\Delta G - \Delta G^o = RT ln Q$$

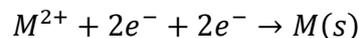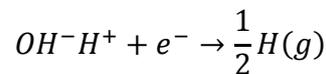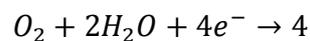If the activities of the reactants and products are equal to one, then $Q = 1\ and\ \Delta G = \Delta G^o$

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. In this sense the system can be regarded as an electrochemical cell in which;

the anodic process is something like

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$
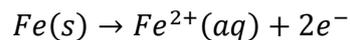
And the cathodic steps can be any of

$$O_2 + 2H_2O + 4e^- \rightarrow 4$$

$$OH^-H^+ + e^- \rightarrow \frac{1}{2}H(g)$$

$$M^{2+} + 2e^- + 2e^- \rightarrow M(s)$$

Where, M is a metal. A thin film of moisture on the surface of the metal can serve as the medium for the electrolyte. Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

Classification of Corrosion

1. Dry or Chemical Corrosion
2. Wet or Electrochemical corrosion

Dry or Chemical Corrosion: Occurs due to chemical attack of metal by the environment such as dry gas. It can also occur due to high temperature and without liquid phase. It is of two types:

a. Oxidation corrosion
b. Corrosion by gases

Oxidation Corrosion: is due to direct attack of oxygen on metals. Oxygen molecules are attracted to the surface by Vander Wall Force

Mechanism:

1. When temperature increases the metal undergoes oxidation and losses e^- as illustrated below:
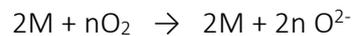
$$2M \rightarrow 2M^{+n} + 2ne^-$$

Metal Ion

2. Electron are gained by the oxygen molecules forms oxide ions

$$nO_2 + 4ne^- \rightarrow 2n\ O^{2-}$$

Oxide Ion

3. Scale of metal oxide formed

$$2M + nO_2 \rightarrow 2M + 2n\ O^{2-}$$

Metal Oxide

Corrosion by Gases: Carbon dioxide, Chlorine, Hydrogen Sulphide, Sulphur dioxide and Fluorine are examples of some gases that cause corrosion. Corrosion by gas depends on chemical affinity between metal and the gas.

Wet or Electrochemical Corrosion: Occurs when aqueous solution or liquid electrolytes are present. Wet corrosion takes place in environments where the relative humidity exceeds 60, it is most efficient in waters containing salts, such as NaCl (e.g. marine conditions), due to the high conductivity of the solution.

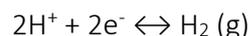### Mechanism of Electrochemical Corrosion

Anodic Reaction: Dissolution of metal takes place. As result metal ions are formed with the liberation of free electrons.
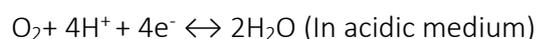
$$M \leftrightarrow M^{+n} + e^-$$

Metal Ion

Cathodic Reaction:

i.   Hydrogen Evolution: Occurs usually in acidic medium

$$2H^+ + 2e^- \leftrightarrow H_2\ (g)$$

ii.   Oxygen Absorption: Occurs when solution is aerated sufficiently.

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \text{ (In acidic medium)}$$

$$O_2 + 4H^+ + 4e^- \leftrightarrow 4OH^- \text{ (In basic medium)}$$

Forms of Corrosion

Galvanic Corrosion: When two different metals are present in contact with each other in conducting medium e.g. Electrolyte

Concentration Cell Corrosion: Same as Galvanic corrosion occurs when two different metals are exposed to different air concentrations.

Pitting Corrosion: Formed as a result of pit and cavities; localized attack and formed by cracking protective coating

Stress Corrosion: Occurs in the presence of tensile stress and corrosive environment. For example brass get corrode in traces of ammonia.

Factors Affecting Corrosion

1. Nature of the Metal
2. Nature of the environment.

Nature of Metal

(i) **Position in Galvanic Series:** If two metals are present in in electrolyte, the metal with less reduction potential undergoes corrosion. The greater the difference faster the corrosion.

(ii) **Over Voltage:** Due to high evolution of hydrogen, the rate is slow.

(iii) **Area and Distance:** When anodic metal area is smaller than cathodic area, rate of corrosion at anode is higher because of demand of electron by cathodic area.

(iv) **Physical and Mechanical properties of Metal**

+ Pure metals are more corrosion resistant.

+ Smaller grain size metals have high solubility and corrosion.

+ Uniform distribution of stress on metal reduces rate of corrosion.

+ Passive metals show higher corrosion resistance because of formation of protective oxide film on their surface.

+ Polycrystalline forms are more sensitive.

Nature of Environment

+ **Temperature:** Directly proportional to corrosion

+ **Humidity:** Corrosion is faster in humid conditions

+ **pH:** If less than 7 the rate of corrosion is high. Al, Zn, Sn, Pb, and Fe are affected by both acid and bases.

+ **Impurities and Suspended Particles:** When these will get dissolved in moisture, provides electrolyte for conductivity and hence corrosion increases.

Corrosion Control: The various means of controlling corrosion are enumerated below as follows:

1. **Proper Metal and Alloy Selection**

+ Using pure and noble metals

+ Practically not possible because of low strength of pure metal

+ Use of metal alloys which are homogeneous

2. **Proper design of metal**

+ Minimal contact with medium

+ Prevention from moisture

+ Adequate ventilation and drainage

+ Welding

+ Avoid cervices between adjacent parts

+ Bend should be smooth

+ Bimetallic contacts should be avoided

+ Paint cathodic portion

+ Prevent uneven stress

3. **Cathodic Protection:** in this protective measure the metal is forced to be protected to behave like cathode, the method employed are:

Sacrificial anodic protection

+ Metal to be protected from corrosion connected to more anodic metal

+ Commonly used metals Mg, Zn, Al and their alloys

Impressed current method

+ Direct current is applied in opposite direction to nullify the corrosion current

+ Converts the corroding metal from anode to cathode.

4. **Modifying Environment**

Eliminating dissolved oxygen:

+ De-aeration

+ By using chemical substances like sodium sulphite and hydrazine. Also called **Deactivation.**

Reducing Moisture:

+ Dehumidification by using silica gels

Reducing Acidity:

+ Neutralizing the acidic environment by adding lime, NaOH, Ammonia

+ Commonly used in refineries

5. **Protective coating:**

+ Application of coating

+ Coating material should be chemically inert under particular temp and pressure.

6. **Use of corrosion Inhibitor**

Anodic Inhibitor:

+ These are oxygen and oxidizing agent.

+ They combine the anodic metal forming an oxide film which reduce corrosion

Cathodic Protection:

+ Organic inhibitors like amines, mercaptans, urea and thiourea reduces the H ion diffusion by adsorption

+ Mercury, arsenic and antimony deposits films at cathodic area which raise the hydrogen over volume.

+ Eliminating Oxygen from the medium by adding sodium sulphate and hydrazine.

ELECTROLYTIC CELLS

This type of cell is formed when an external current is introduced into the system. It may consist of all the basic components of galvanic cells and concentration cells plus an external source of

electrical energy. Notice that anode has a (+) polarity and cathode has (-) polarity in an electrolytic cell, where external current is applied. This is the type of cell set up for electrically protecting the structures by Cathodic protection. The polarity of an electrolytic cell is opposite to that in a galvanic (corrosion) cell.