

Chemical Consequences of Burning Fossil Fuels SPN LESSON #30



TEACHER INFORMATION

LEARNING OUTCOME: After completing chemical reactions such as adding oxides of nonmetals to water to form acids, the students are able to understand that fossil fuel combustion produces acid-forming oxides and to provide examples of the effects of acids on metals and carbonate-containing substances.

LESSON OVERVIEW: The purpose of this lesson is to introduce students to the chemical consequences of burning fossil fuels. The underlying theme is that fossil fuel combustion leads to the formation of oxides of three nonmetals: carbon, nitrogen, and sulfur. When each of these oxides is added to water, an acid forms. In addition to threatening wildlife in our streams, lakes, and rivers, acids are shown in this lesson to react with such building materials as carbonate-containing rocks and some metals. An extension for Advanced Placement chemistry students investigates the equilibria of such weak acids as carbonic and sulfurous. The chemical consequences of burning fossil fuels provide another reason to shift from relying on fossil fuels to using alternative sources of energy such as photovoltaic electricity.

GRADE-LEVEL APPROPRIATENESS: This Level III Physical Setting lesson is intended for use in high school chemistry or Advanced Placement chemistry classrooms.

MATERIALS: Red and blue litmus paper, beakers, water and drinking straws or dry ice, seltzer water, dilute nitric acid, marble chips or shells, pieces of zinc, small test tubes

SAFETY: Students <u>must</u> wear goggles while performing chemistry experiments. They should not touch dilute nitric acid or dry ice directly with their hands.

TEACHING THE LESSON: Ask students whether they know the products of burning fossil fuels. If they have completed the School Power...Naturally ^(sm) lesson *Avoiding Carbon Dioxide Emissions from Burning Fossil Fuels*, they should be able to identify the products of burning hydrocarbons as carbon dioxide and water. Continue by pointing out that coal and, to a lesser extent, oil also contain sulfur impurities that lead to the emission of sulfur oxides and that the high temperatures of fossil fuel combustion cause nitrogen and oxygen in the atmosphere to react to form nitrogen oxides. The reason to be concerned about the formation of carbon, sulfur, and nitrogen oxides is that oxides of nonmetals, when added to water, form acids. The purpose of this lesson is not only to teach students that fossil fuel combustion produces acid-forming oxides but also to show them the effects of acids—on metals and carbonate-containing rocks. When you debrief students following performance of the laboratory work, you can elicit from them the

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equations for the chemical reactions they have observed or present them, as described in the Acceptable Responses section below. An extension of the lesson for Advanced Placement chemistry students investigates the equilibria of such weak acids as carbonic and sulfurous, formed by the addition of water to carbon and sulfur dioxides, respectively.

The Caryatid statue was photographed first in 1919 and then again in 1981. The photographs are reproduced with permission: © The Field Museum, Chicago, #CSGN40263 and #GN83213 6c (www.fieldmuseum.org)





ACCEPTABLE RESPONSES FOR DEVELOP YOUR UNDERSTANDING SECTION:

<u>Answer to Question</u>: Alternative sources of energy that depend on providing heat to produce electricity will still cause formation of nitrogen oxides if the temperature is high enough. If the temperature is *not* high enough, the efficiency with which the electricity is produced will be reduced. The most common fossil fuel alternative that relies on heat to produce electricity is nuclear fission.

When added to both a marble chip and a piece of zinc, dilute nitric acid will show the effect of bubbling almost immediately. This indicates that a gas is being released. In the case of the marble chip—calcium carbonate, or limestone—the gas is carbon dioxide:

 $2 \text{ HNO}_3 + \text{CaCO}_3 \mathbf{7} \text{ Ca}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2.$

Carbon dioxide can be detected by its ability to extinguish a flame (the reverse of the reaction of burning organic matter). In the case of zinc, the gas emitted is hydrogen:

 $2 \text{ HNO}_3 + \text{Zn} 7 \text{Zn}(\text{NO}_3)_2 + \text{H}_2$.

A flame causes hydrogen gas to react with oxygen in the air to form water. This reaction produces a popping sound, which can become loud enough to warrant covering one's ears if the hydrogen concentration is sufficiently great.

In contrast with the reaction of marble and zinc with dilute nitric acid, these materials will show little reaction with seltzer water. Even though seltzer water contains more dissolved carbon dioxide than will dissolve in water at atmospheric pressure, this excess carbon dioxide will soon bubble away. This will leave only a saturated solution of carbon dioxide like that calculated to have a pH of almost 4 in the Advanced Placement extension of the lesson.

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The solubility of sulfur dioxide in water at 0°C is 22.8 grams per 100 mL of water. For a saturated solution of carbon dioxide, this translates into a molar concentration of 22.8 g x (1 mol/64 g) = 0.356 mol/0.1 L = 3.56 mol/L. This would also be the molar concentration of H₂SO₃ before it dissociates. Assume that *x* represents the number of moles per liter of H₂SO₃ which dissociate into H⁺ and HSO₃⁻. Then the number of remaining moles per liter of H₂CO₃ is 3.56 - x. Substituting these values into the equilibrium equation gives

 $x^*x/(3.56 - x) = 1.54 \times 10^{-2}$.

If we further assume that $x \ll 3.56$, then it can be neglected in the denominator, and we obtain

 $x = \sqrt{3.56 \times 1.54 \times 10^{-2}} = 2.34 \times 10^{-1} = 10^{-0.631}$, which is definitely << 3.56. This corresponds to a pH of 0.631, which is far more acidic than a saturated solution of carbon dioxide.

What about the dissociation of the second H⁺ from HSO₃⁻? Of the $x = 2.34 \times 10^{-1}$ moles per liter of HSO₃⁻, assume the number of moles dissociating is *y*. Then substitution into the second equilibrium equation gives

 $(x+y)*y/(x+y) = 1.02 \times 10^{-7}$.

If we can assume that $y \ll x$, we then can neglect y relative to x and obtain $y = 1.02 \times 10^{-7}$, which is clearly $\ll x = 2.34 \times 10^{-1}$. We can also see that, as in the case of carbonic acid, the second dissociation makes no measurable contribution to the concentration of H⁺ in sulfurous acid.

ADDITIONAL SUPPORT FOR TEACHERS

SOURCE FOR THIS ACTIVITY: Activity is not adapted.

BACKGROUND INFORMATION: The name for the element oxygen means "acid former," and Lavoisier originally identified acids as solutions of nonmetallic oxides. The equations whereby nonmetallic oxides form acids are given in the student handout. The equations for the reactions of dilute nitric acid and calcium carbonate and zinc are given above in the Acceptable Responses section. Additional background information is provided in the Advanced Placement extension of the lesson, which investigates the chemical equilibria of such weak acids as carbonic and sulfurous.

REFERENCES FOR BACKGROUND INFORMATION: Buell, Phyllis and James Girard. *Chemistry: An Environmental Perspective*. Prentice Hall, Englewood Cliffs, NJ, 1994.

Handbook of Chemistry and Physics. CRC Publishing, annually.

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Should you have questions about this activity or suggestions for improvement, please contact Bill Peruzzi at billperuz@aol.com

(STUDENT HANDOUT SECTION FOLLOWS)

Name			_
Date			

Chemical Consequences of Burning Fossil Fuels

Most of our energy needs are met by burning fossil fuels. Burning is a chemical reaction of the molecules of the fuel with molecules of oxygen in the air. Among the by-products of this burning are molecules containing this oxygen. They are called *oxides*.

Of special concern are oxides formed when atoms of three elements combine with oxygen atoms: carbon, sulfur, and nitrogen. Because all fossil fuels contain carbon, oxides of carbon will form when fossil fuels are burned. Two possible oxides can form: carbon monoxide (CO) and carbon dioxide (CO₂). Carbon monoxide forms only when there is a limited amount of oxygen present, such as in an enclosed area. Carbon monoxide is dangerous to humans because its molecules are similar to oxygen molecules (O₂), and molecules of carbon monoxide bind more strongly than oxygen needed to metabolize food and provide energy to the body. But in the presence of sufficient oxygen, molecules of carbon monoxide will react with additional oxygen molecules to form carbon dioxide:

 $2 \text{ CO} + \text{O}_2 \mathbf{7} 2 \text{ CO}_2.$

The burning of fossil fuels occurs at temperatures of several hundreds of degrees. At these high temperatures nitrogen molecules (which comprise 78% of Earth's atmosphere) react with molecules of oxygen (comprising 21% of Earth's atmosphere) to form oxides of nitrogen:

 $N_2 + O_2$ **7**2 NO2 NO + O₂ **7** 2 NO₂.

The latter gas, nitrogen dioxide, is brown in color and known as smog.

Oxides of sulfur are formed when there are sulfur impurities in fossil fuels that are burned. Sulfur is found as an impurity in coal and, to a lesser extent, in oil. It reacts with oxygen in the air to form sulfur dioxide. Molecules of sulfur dioxide can subsequently react with additional oxygen molecules to form sulfur trioxide:

 $S + O_2 7 SO_2$ 2 SO₂ + O₂ 7 2 SO₃.

The problem resulting from the formation of oxides of carbon, nitrogen, and sulfur is a problem common to the oxides of all nonmetals: when added to water, they form acids:

 $CO_2 + H_2O$ **7** H_2CO_3 (carbonic acid) 4 $NO_2 + O_2 + 2$ H_2O **7** 4 HNO_3 (nitric acid) $SO_2 + H_2O$ **7** H_2SO_3 (sulfurous acid)

$SO_3 + H_2O 7 H_2SO_4$ (sulfuric acid)

(In fact, the name oxygen means "acid former.")

DEVELOP YOUR UNDERSTANDING

<u>Question</u>: Some alternatives to fossil fuels are used to produce electricity in the same way as fossil fuel combustion. They provide a source of heat, which boils water to make steam that turns a turbogenerator. Which of the oxides (those of carbon, sulfur, or nitrogen) are produced by fossil fuel alternatives that rely on producing heat?

NOTE: You <u>must</u> wear goggles to protect your eyes when performing the following lab work. If you handle dry ice, do not touch it directly with your hands.

You can demonstrate that adding carbon dioxide to water makes it acidic by adding carbon dioxide to water in either of two ways: exhaling into it through a drinking straw (your body produces carbon dioxide in the process of digesting food), or by putting a small piece of dry ice (frozen carbon dioxide) in it. In either case, start with pieces of red and blue litmus paper in the water and observe what happens to them when the carbon dioxide is added: acids cause blue litmus paper to turn red (actually pink). If you add carbon dioxide by exhaling into the water through a drinking straw, you will need to be patient—you will need to exhale a lot of air to add enough carbon dioxide to the water to make the litmus paper change color.

Why is there concern that burning fossil fuels produces oxides of carbon, nitrogen, and sulfur in the air? Acids are widely known for their chemical properties of reacting with rocks containing carbonate—for example, limestone—and with metals. To witness these reactions, place a small marble chip in a small test tube and a small piece of zinc in another. Add enough dilute nitric acid to cover the solids in both test tubes. What do you observe?

Next, place another small marble chip in a small test tube, and another small piece of zinc in another. Add seltzer water to cover the solids in both test tubes. What do you observe now? Allow the seltzer test tubes to stand overnight. Do you observe any difference the next day?

Seltzer water is carbon dioxide dissolved in water under pressure. It is therefore also carbonic acid. But you should have noticed that the reaction of the seltzer water with the marble chip and piece of zinc was not nearly as rapid as the reaction of the dilute nitric acid with the same materials. This difference in reaction rate is attributed to a difference in the strength of these acids. Nitric acid is a *strong* acid; carbonic acid is a *weak* acid.

NOTE: The remainder of this lesson, dealing with equilibrium constants, is intended for Advanced Placement chemistry students.

The *strength* of an acid is determined by the degree to which its molecules are dissociated into hydrogen (more correctly, hydronium) ions. As a strong acid, nitric acid in solution consists predominantly of the hydrogen and nitrate ions— H^+ and NO₃, respectively. But carbonic acid is a weak acid, dissociating its hydrogen ions in two stages:

 H_2CO_3 **7** H^+ + $HCO_3^ HCO_3^-$ **7** H^+ + CO_3^{2-}

The arrows are written in both directions here, because with weak dissociation there is an equilibrium between the reactant on the left side and the products on the right. These equilibria are described by equilibrium constants, as follows:

 $[H^+][HCO_3^-]/[H_2CO_3] = K_1 = 4.30 \times 10^{-7} (18^{\circ}C)$

 $[H^+][CO_3^{2-}]/[HCO_3^{-}] = K_2 = 5.61 \times 10^{-11} (25^{\circ}C),$

where [X] means the molar concentration of chemical X, in moles per liter.

The solubility of carbon dioxide in water at 25°C is 0.145 grams per 100 mL of water. For a saturated solution of carbon dioxide, this translates into a molar concentration of 0.145 g x (1 mol/44 g) = 0.0033 mol/0.1 L = 0.033 mol/L. This would also be the molar concentration of H₂CO₃ before it dissociates. Equilibrium calculations are usually done in approximation, and that is the case here. Assume that *x* represents the number of moles per liter of H₂CO₃ which dissociate into H⁺ and HCO₃⁻. Then the number of remaining moles per liter of H₂CO₃ is 0.033 – *x*. Substituting these values into the equilibrium equation gives

 $x^*x/(0.033 - x) = 4.30 \times 10^{-7}$.

If we further assume that $x \ll 0.033$, then it can be neglected in the denominator, and we obtain

 $x = \sqrt{3.3 \times 4.3 \times 10^{-9}} = 1.9 \times 10^{-4} = 10^{-3.721}$, which is definitely << 0.033. Note that this corresponds to a pH of 3.721.

What about the dissociation of the second H⁺ from HCO₃⁻? Of the $x = 1.9 \times 10^{-4}$ moles per liter of HCO₃⁻, assume the number of moles dissociating is *y*. Then substitution into the second equilibrium equation gives

 $(x+y)^*y/(x+y) = 5.61 \times 10^{-11}$.

If we can assume that $y \ll x$, we then can neglect y relative to x and obtain $y = 5.61 \times 10^{-11}$, which is clearly $\ll x = 1.9 \times 10^{-4}$. We can also see that the second dissociation makes no measurable contribution to the concentration of H⁺ in carbonic acid.

The equilibrium conditions for the dissociation of sulfurous acid (another weak acid) are

 H_2SO_3 **7** H^+ + $HSO_3^ HSO_3^-$ **7** H^+ + SO_3^{2-} These equilibria are described by equilibrium constants, as follows:

 $[H^+][HSO_3^-]/[H_2SO_3] = K_1 = 1.54 \text{ x } 10^{-2} (18^{\circ}\text{C})$ $[H^+][SO_3^{2^-}]/[HSO_3^-] = K_2 = 1.02 \text{ x } 10^{-7} (18^{\circ}\text{C}).$

<u>Question</u>: The solubility of sulfur dioxide in water at 0° C is 22.8 grams per 100 mL of water. Using the above example of carbonic acid, find the hydrogen ion concentration of a saturated solution of sulfurous acid.