Improving Air Quality with Electric Vehicles
Electrochemistry Experiment

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Key Concepts:

- Components of Photochemical Smog
- Why High Levels of Ozone in the Air are Undesirable
    - Antioxidants in the Lungs
    - Ozone as an Oxidizing Agent
- Automobile Emissions Increase Ozone Concentrations
    - Incomplete Combustion of Gasoline Produces Volatile Organic Hydrocarbons (VOC)
    - Combustion at High Temperatures Produces NO
    - VOC, NO and Sunlight Result in Ozone Formation
- Reducing Nitrogen Oxides and VOC Emissions
    - Catalytic Converters
    - Zero Emissions Vehicles (ZEVs): Electric Vehicles
- Current Technology for Electric Vehicles
    - How Lead-Acid Batteries Work
    - Drawbacks to Lead-Acid Batteries
- Vanadium Redox Flow Battery: A Possible Alternative to Lead-Acid Batteries for Electric Vehicles

Introduction: Photochemical Smog

Good air quality is important to public health. Several studies have linked high levels of air pollution to increased hospital admissions for respiratory and heart disease. Autopsies reveal more lung and airway damage in people exposed to high levels of air pollution. This tutorial will discuss the harmful components of polluted air, describe the important sources of air pollution in the United States, and examine several strategies for reducing air pollution. Redox reactions, where electrons are transferred from one compound to another, are the foundation for understanding each of these subjects redox reactions are involved in creating the molecules that comprise pollution, they are central to understanding why polluted air poses a health threat, and they are at the heart of strategies to reduce air pollution. Thus, to understand air pollution and its effects, we must understand electrochemistry, the study of the connection between chemical and electrical energy, and redox reactions.

In the modern industrial world, photochemical smog is the most common air-quality problem. Smog is a mixture of pollutants including nitrogen oxides, ozone, aldehydes, peroxyacetyl nitrate, particulates and volatile organic hydrocarbons (see Table 1).

Molecule Name and Formula	Two-Dimensional Representation	Three-Dimensional Representation
Nitric Oxide, NO	N═O	

Nitrogen Dioxide, NO_2		
Ozone, O_3		
Acetaldehyde, C_2H_4O (an example of an aldehyde)		
Peroxyacetyl Nitrate, $C_2H_3O_5N$		
1,3-Butadiene, C_4H_6 (an example of a volatile organic hydrocarbon)		

Table 1

The 2D representations shown in this table were drawn using CS ChemDraw Pro. In the 3D representations, carbon atoms are gray, hydrogen atoms are light blue, oxygen atoms are red, and nitrogen atoms are dark blue. The coordinates for the 3D representations were obtained from molecular-modeling calculations using ChemDraw 3D, and the images were rendered using SwissPDB Viewer and POV-Ray (see References).

These small molecules confer a variety of characteristics on the atmosphere. Nitrogen dioxide (NO_2) is a brownish color, and is responsible for the visible "brown cloud" associated with smog. Many people notice eye irritation when smog is severe because peroxyacetyl nitrate is a lachrymator (irritates the eyes), and some people experience difficulty breathing. In addition, visibility is impaired on smoggy days. Figure 1, below, shows the difference in visibility on high-pollution *vs.* low-pollution days in St. Louis, Missouri.

Figure 1a. Low Pollution Day

Figure 1b. High Pollution Day

Figure 1

Figure 1a is a picture of downtown St. Louis on a clear (low pollution) day. Figure 1b is a similar picture on a smoggy day. Notice that it is difficult to see the arch in Figure 1b. These pictures were taken by the Missouri Department of Natural Resource's Visual Air Pollution Camera. Click on the preceding link to see these pictures as well as a photo of today's visibility conditions.
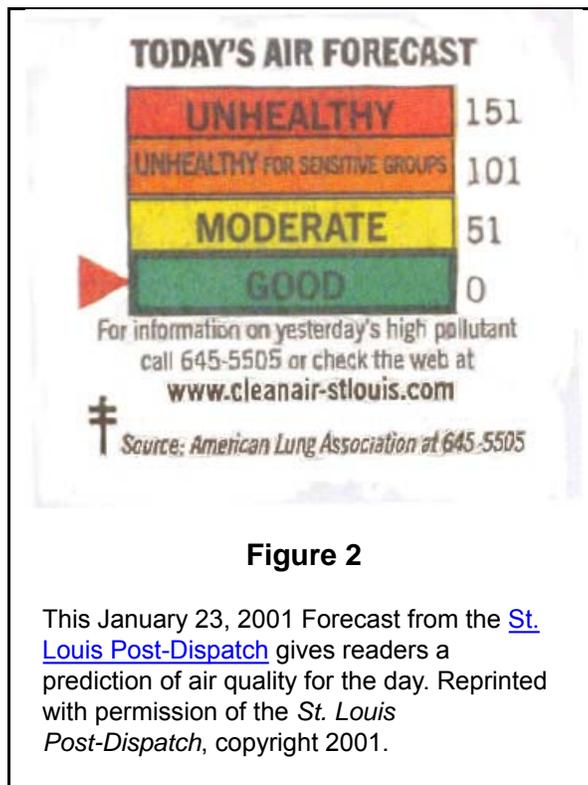
In the United States, the Environmental Protection Agency (EPA) is charged with monitoring air quality and ensuring that air pollution is not allowed to become so severe that it endangers public health. How does the EPA evaluate air quality?

Monitoring Air Quality and Communicating Air-Quality Information to the Public

The Environmental Protection Agency sets National Ambient Air Quality Standards (NAAQS). Air-quality data (which include concentrations of nitrogen oxides, ozone, etc.) are collected at monitoring stations, and reported to the EPA. When levels of air pollution exceed legal limits, the state must develop a plan to reduce emissions. St. Louis, Missouri is slightly out of compliance on ozone levels, but has attained NAAQS for the other major outdoor pollutants. (Hey! I thought ozone was a good thing! Click here for a discussion of when and where ozone is beneficial.) St. Louis is typical of many urban areas; ozone concentrations above the levels set by the EPA are the most prevalent air-quality problem in the U.S.

You may have noticed that the local news in the summer includes an "air-quality forecast." (See Figure 2 for an example from the *St. Louis Post-Dispatch* and click here for air-quality forecasts of many U.S. cities, compiled by the EPA.) The air-quality rating is essentially a predictor of how much smog (and, hence ozone) could be formed

that day. (Both concentrations of pollutants and weather patterns are used in air-quality forecasting.) Especially on poor air-quality days, people are encouraged to carpool, use public transportation or postpone non-essential car trips. We are discouraged from refueling cars and using lighter fluid on outdoor grills. Besides publicizing the times when citizens should make an extra effort not to contribute to air pollution, the air-quality forecasts also serve as a warning for people whose health is especially sensitive to poor air quality. On "bad air" days, some people need to avoid outdoor activities or use medications.

Figure 2

This January 23, 2001 Forecast from the St. Louis Post-Dispatch gives readers a prediction of air quality for the day. Reprinted with permission of the *St. Louis Post-Dispatch*, copyright 2001.

The limits set by the EPA for the components of air pollution differ. For example, the EPA has set the limit for ozone at 0.12 parts per million (ppm), measured as the average concentration over a one-hour period. This means that in one gram of air, the amount of ozone should not exceed 1.2×10^{-7} grams, or 2.5×10^{-9} moles, on average. The density of air varies with temperature and humidity, but is on the order of 0.001 g/mL. This means that one gram of air will occupy a volume of about 1 L. Therefore, the maximum concentration of ozone is about 3×10^{-9} moles/L. From your experience with solutions in lab, you will recognize this as a very small concentration. Why is the acceptable limit for ozone so low?

Why Is Ozone In Our Air a Problem?

The EPA regulates substances in the environment that pose a threat to public health. Ozone is toxic because it is a powerful oxidizer (which means it can easily gain electrons from another substance). Click here to learn about why ozone is such a strong oxidizing agent. Ozone can react with cell-membrane lipids or proteins to form peroxide (also a strong oxidizer). These oxidizing agents can damage lung tissue.

Your body is capable of handling small doses of strong oxidizers like ozone. The surface of your lungs is covered with epithelial lining fluid. This thin layer of fluid over the epithelial surface of the respiratory tract has several antioxidants dissolved in it, including Vitamin C (ascorbic acid) and glutathione, shown in Figure 3. (Refer to the tutorial, Nutrients and Solubility, for more information on Vitamin C.) If the antioxidant solution covering the lung surface was not present, oxidizing agents (such as ozone) would react with the lung tissue itself, damaging the lungs.

Molecule Name and Formula	Two-Dimensional Representation	Three-Dimensional Representation

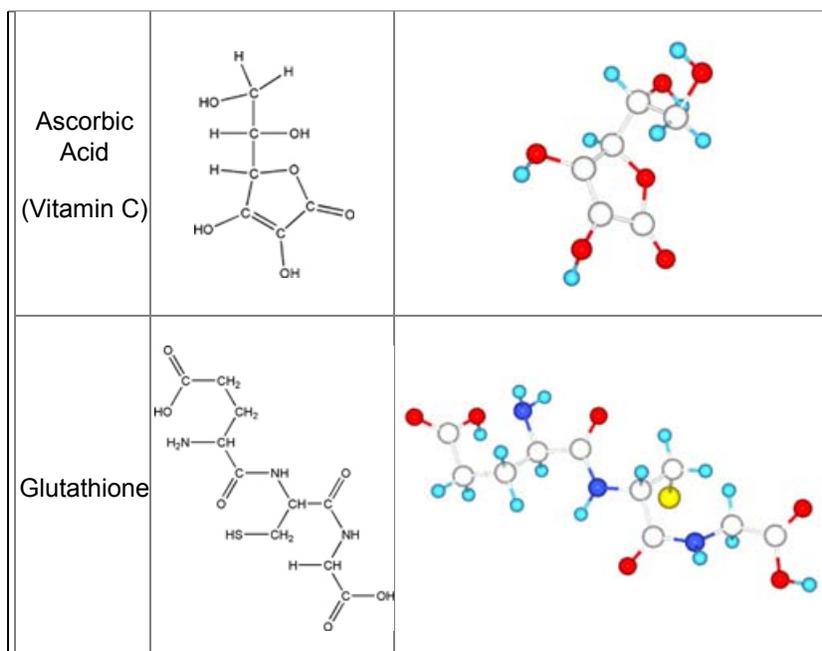|		
Ascorbic Acid (Vitamin C)		
Glutathione		

Figure 3

This figure contains two- and three-dimensional representations of ascorbic acid and glutathione. Note that glutathione is a tripeptide, a molecule composed of three amino acids (in this case, glutamic acid, cysteine and glycine).

The 2D representations shown in this table were drawn using CS ChemDraw Pro. The coordinates for the 3D representations were obtained from molecular-modeling calculations using CS Chem3D Pro, and the images were rendered using SwissPDB Viewer and POV-Ray (see References).

Antioxidants react with oxidizing agents like peroxide and ozone to form harmless products, as shown in Equation 1 below. (Recall, various peroxides are formed in the lungs when O_3 reacts with cell membranes. The simplest peroxide, hydrogen peroxide (H_2O_2), is used in the example below in Equation 1. Also note that dehydroxyascorbic acid is a nontoxic product.) See Box 1, below, for more details on the oxidation-reduction reactions that protect your lungs.
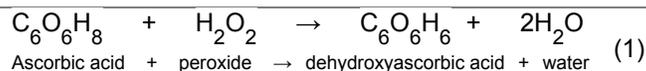
$$\text{Ascorbic acid} + H_2O_2 \rightarrow \text{dehydroxyascorbic acid} + 2H_2O \quad (1)$$
(anti-oxidant) (oxidizing agent) (harmless products)
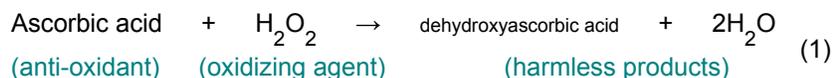
Box 1
Oxidation-Reduction Reactions in Your Lungs

Equation 1 shows ascorbic acid (Vitamin C) from the epithelial lining fluid of the lungs reacting with an oxidizing agent (peroxide) to form harmless products, thus preventing lung damage. What is being reduced and what is being oxidized?

Recall, oxidized means that the substance is losing electrons and reduced means that it is gaining electrons. In this example, hydrogen peroxide ($H_2O>_2$) is being reduced as it is converted to water because the oxygen has a (-1) oxidation state in the reactants and a (-2) oxidation state in the products.

$$C_6O_6H_8 \quad + \quad H_2O_2 \quad \rightarrow \quad C_6O_6H_6 \quad + \quad 2H_2O \quad (1)$$

Ascorbic acid + peroxide → dehydroxyascorbic acid + water

(oxidized)   (reduced)   (harmless products)

If hydrogen peroxide is being reduced, then obviously ascorbic acid is being oxidized. How can we verify that with oxidation numbers? Since the carbons in ascorbic acid are not equivalent, and therefore have different oxidation numbers, we need to look at a Lewis structure to see the corresponding change in oxidation numbers between the species that is oxidized (ascorbic acid) and the products. Lewis structures for the reduced form of Vitamin C (ascorbic acid) and the oxidized form (dehydroxyascorbic acid) are shown in Figure 4, below. The atoms that participate in the oxidation are circled.
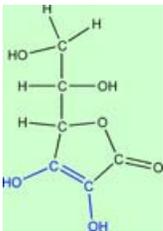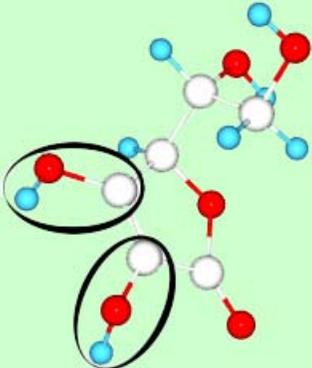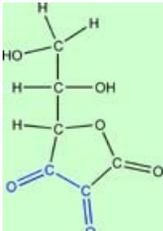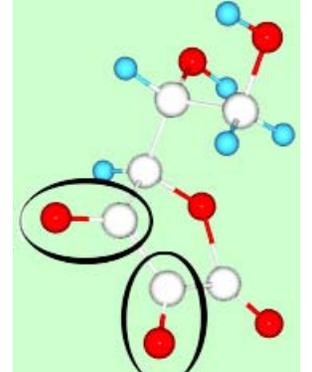
Molecule Name	Two-Dimensional Representation	Three-Dimensional Representation
Ascorbic Acid (reduced Vitamin C)		
Dehydroxyascorbic Acid (oxidized Vitamin C)		

Figure 4

These representations of the reduced and and oxidized forms of Vitamin C show how Vitamin C functions as an antioxidant. The atoms and bonds that participate in oxidation are shown in blue in the two-dimensional representation, and the atoms involved are circled in the three-dimensional representation.

Note: The coordinates for the 3D representations were obtained from molecular-modeling calculations using ChemDraw 3D, and the images were rendered using SwissPDB Viewer and POV-Ray (see References).

Recall: to determine oxidation numbers from Lewis structures, we begin by assigning electrons in bonds to the more electronegative

element. Lone-pair electrons are assigned to the atom on which they reside. The oxidation number is equal to the number of valence electrons for that element minus the number of assigned electrons.

Looking at the carbons highlighted in blue in the Lewis structures in Figure 4, we can see that the oxidation number for carbon changes from (+1) in ascorbic acid to (+2) in dehydroxyascorbic acid.

When the concentrations of strong oxidizing agents are high enough, the antioxidants in the epithelial lining fluid can be used up faster than they can be replaced by the body. Like any other biological characteristic, the composition of the epithelial lining fluid varies from one person to another. Some people secrete smaller amounts of antioxidants into the protective fluid that covers the lung. This may help explain why some people are more sensitive to high levels of ozone (an oxidizing agent) in the air than others.

Because ozone is a strong oxidizing agent and could be a possible health threat, the EPA has regulated its presence in the atmosphere we breathe. Data show that the combustion of fossil fuels raises ozone concentrations. (That is why we are cautioned to limit driving on poor air-quality days.) But ozone itself is not a product of combustion, so how is ozone formed from the gases released by our automobiles?

Questions on Oxidizing Agents

- Using your knowledge of Lewis structures and periodic trends, explain whether oxygen (O_2) can be more easily oxidized or reduced.

- Determine which compound in the following pairs would be the more effective oxidizing agent. (Hint: compare oxidation numbers between the compounds.)

   a. iodine (I_2) *vs.* the iodide ion (I^-)

   b. H_2O *vs.* H_2O_2

   c. Zinc (Zn) *vs.* the zinc ion (Zn^{2+})

- Does ascorbic acid gain or lose electrons when it reacts with ozone? Would you expect ascorbic acid to gain or lose any atoms when it reacts with ozone? Briefly explain your answers.

Automobile Emissions Increase Ozone Concentrations

Two common emissions products from our automobiles contribute to the formation of ozone: volatile organic hydrocarbons and nitrogen oxides. This section will explore how these ozone precursors are produced and how they lead to the formation of ozone.

Gasoline and other fossil fuels are a mixture of hydrocarbons (compounds containing carbon and hydrogen). Complete combustion of hydrocarbons produces water and carbon dioxide. The balanced equation for combustion of octane (one component of gasoline) appears below in Equation 2.

$$2\ C_8H_{18} + 17\ O_2 \rightarrow 18\ H_2O + 16\ CO_2 \qquad (2)$$

Incomplete combustion releases volatile organic hydrocarbons (VOCs), because the hydrocarbons are not completely converted to CO_2. The combustion products we are most concerned with in this tutorial are VOCs and nitrogen oxides (recall Table 1). Nitrogen oxides are produced during combustion even when the nitrogen content of the fuel is low, because nitrogen is always present in the air used for combustion (see Box 2, below).

Box 2
Nitrogen Oxide Emissions from Combustion of Fossil Fuels

Fossil fuels vary in their nitrogen content. Fuels that have a high nitrogen content produce more NO and NO_2 when they are burned than fuels with low nitrogen content. This accounts for some of the variation of nitrogen-oxide emissions in different regions of the country. (Click here http://www.epa.gov/acidrain/scorcard/nox95.gif, for an Environmental Protection Agency map of nitrogen-oxide emissions for coal-fired utilities throughout the U.S.)

You might expect methane, which contains essentially no nitrogen in the fuel itself, to have no nitrogen-oxide emissions, but this is not the case. In fact, some NO is formed any time nitrogen and oxygen are in contact at the high temperature of an engine. (This is because air is about 78% nitrogen and 21% oxygen by volume.) Equations 3 and 4, below show the reaction between nitrogen and oxygen in the air, and the equilibrium expression for the reaction.

$$N_2 \ + \ O_2 \ \rightarrow \ 2\,NO \qquad (3)$$
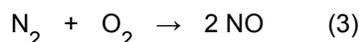
$$K_{eq} = \frac{[NO]^2}{[N_2][O_2]} \qquad (4)$$

Recall that the value of the equilibrium constant, K_{eq}, varies with temperature. For the reaction in Equation 3, $K_{eq} = 5 \times 10^{-7}$ at 298 K; hence, the equilbrium lies to the left. However, as temperature increases, K_{eq} changes and the equilibrium shifts to the right. Thus, the equilibrium concentration of NO increases. At 675 K (a realistic temperature for the exhaust manifold in a car), $K_{eq} = 0.01$ and the ratio of NO to O_2 and N_2, while still small, is no longer negligible. In fact, at 675 K, about 3% of the nitrogen in the air will be converted to NO.

We must conclude that any time we have nitrogen and oxygen in contact at high temperatures, some NO will be produced as a result. Since nitrogen and oxygen are always present together in the air we use to burn gasoline or coal, some NO emissions are inevitable.

In the U.S., fossil fuels are mostly burned to operate motor vehicles and to produce electricity. As a result, car emissions are a substantial source of VOCs and nitrogen oxides across the nation. In parts of the midwest, most of our electricity comes from burning coal, which results in relatively high nitrogen-oxide emissions. When concentrations of nitrogen oxides are large, noncombustion VOCs can also make a noticeable contribution to total ozone levels. Noncombustion VOCs include gasoline released into the air during refueling and solvents such as paint thinner or charcoal lighter fluid that are allowed to evaporate. Therefore, there are always nitrogen oxides and VOCs present in our atmosphere today. Before strategies can be developed to reduce ozone concentration in the lower atmosphere, we must first understand how VOCs and nitrogen oxides react to form ozone.

How Does Ozone Form?

Chemists frequently describe a complicated reaction in a step-by-step sequence of events or simpler reactions. There are many combinations of simple reactions that will form ozone. The series of reactions, or steps, presented below describe one scheme for ozone formation from nitrogen oxides and VOCs. This scheme can be separated into two stages: initiation and nitrogen-oxide cycling. Nitrogen-oxide cycling is diagrammatically represented in Figure 5, below.

Initiation

Ironically, the formation of ozone can begin with the destruction of an ozone molecule. When ozone (O_3) is photodissociated by ultraviolet light , it can react with water to form two OH radicals ($HO^\bullet$) as shown below in STEP 1, Equation 5. (A radical is a compound with an unpaired electron, which is represented with a dot "$^\bullet$" in the chemical formula.) Radicals are generally very reactive.

**STEP 1** $O_3 + Hn + H_2O \rightarrow O_2 + 2HO\bullet$ (5)
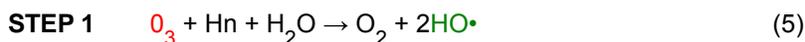
When volatile organic hydrocarbons are present in the air from car exhaust, or other sources, each OH radical reacts with a volatile organic hydrocarbon (represented as R-H) and O_2 to produce peroxy radicals ($RO_2\bullet$, where R represents the rest of the volatile-organic-hydrocarbon molecule). The production of peroxy radicals is shown in STEP 2, Equation 6, below.

STEP 2 $2HO\bullet + 2R\text{-}H + 2O_2 \rightarrow 2RO_2\bullet + 2H_2O$ (6)
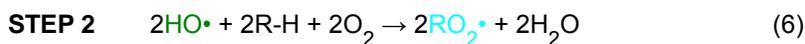
Nitrogen-Oxide Cycling and Ozone Production

Car exhaust also contains nitric oxide (see Box 2, above). Peroxy radicals react with nitric oxide (NO) to form nitrogen dioxide (NO_2):

STEP 3 $2RO_2\bullet + 2NO \rightarrow 2NO_2 + 2RO\bullet$ (7)
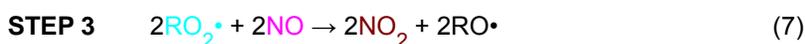
Nitrogen dioxide is photodissociated by sunlight, reforming nitric oxide (STEP 4, Equation 8).

STEP 4 $2NO_2 + hn \rightarrow 2NO + 2O$ (8)

Finally, oxygen atoms formed in Step 4 combine with molecular oxygen in the presence of an inert molecule like N_2, to form ozone. (N_2 stabilizes the product by removing excess energy through collisions.)

STEP 5 $2O_2 + 2O \rightarrow 2O_3$ (9)

Since NO is produced in Step 4, Steps 3-5 are repeated as long as VOCs are present. This cycling of nitrogen oxides is diagrammatically represented below in Figure 5. An animation of Steps three through five of the mechanism above can be viewed by clicking on the pink button in Figure 5.
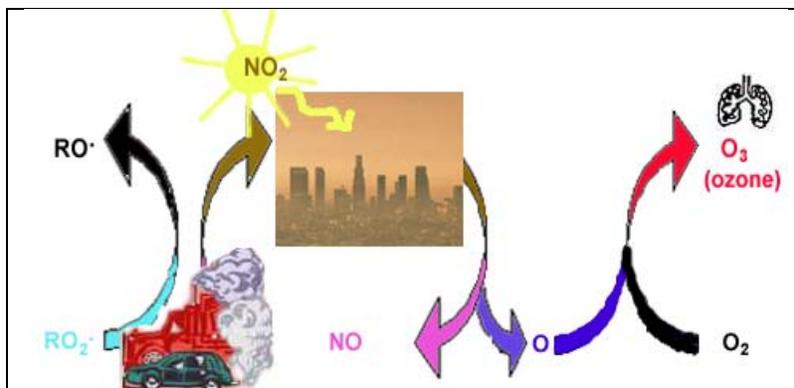

Figure 5

This is a diagrammatic illustration of Steps 3-5 of the mechanism for ozone formation described above. Note: Steps 1 and 2 are not represented in this diagram.

Volatile organic hydrocarbons (VOCs) and **NO** are both byproducts of fossil fuel combustion (pollution). VOCs form peroxy radicals ($RO_2\bullet$). $RO_2\bullet$ and **NO_2(Step 3).** In sunlight, NO_2

dissociates into O and NO **(Step 4)**. The O reacts with O_2 to produce ozone **(Step 5)**. Unfortunately, NO_2 can be regenerated from NO and $RO_2\bullet$ **(Step 3)**. The cycling of NO_2 and **(Steps 3 and 4)** means that even small concentrations of nitrogen oxides (NO and NO_2) can produce large amounts of ozone when VOCs are present.

Click on the pink button below to view an animation of the formation of ozone.

In summary, nitrogen dioxide, sunlight and oxygen produce ozone and nitric oxide. Nitric oxide (NO) is converted back to nitrogen dioxide (NO_2) by peroxy radicals ($RO_2\bullet$) from VOCs. Notice that even though STEP 1 uses ozone, there is still a net production of ozone: one molecule of ozone produces two hydroxy radicals which, through a series of reactions, form two molecules of nitrogen dioxide, and eventually produce two molecules of ozone. (This is an example of a chain reaction.) Therefore, in order to reduce ozone levels, we need to reduce levels of nitrogen oxides and volatile organic hydrocarbons.

Questions on Ozone Formation

- According to the simplified mechanism presented above, what must be present in order for NO and NO_2 to cycle in the atmosphere?
- What molecules do automobile exhaust contain that contribute to ozone formation? Are there other sources of these molecules in the atmosphere?

Reducing Nitrogen Oxides and VOC Emissions

As Box 2, above, indicates, any fossil-fuel combustion will produce some NO. This NO can then be converted to NO_2 if volatile organic hydrocarbons are also present, and in turn increases ozone production in the lower atmosphere. At the present time, there are essentially two strategies for reducing NO emissions: 1) removing pollutants such as NO from the post-combustion emission gases, and 2) finding alternatives to power cars that do not require the combustion of fossil fuels.

Catalytic Converters

Our main strategy until now for reducing NO emissions (and, hence, ozone levels) has been to remove NO from post-combustion emissions gases. Advances in catalytic converter technology have allowed steady progress on this front. The EPA's emissions standards for vehicles manufactured in 1980 are 6 grams/mile of nitrogen oxides and 2 grams/mile of hydrocarbons. Improved catalytic converters have made it possible to lower the maximum level of emissions for cars manufactured after 1996 to 2 grams/mile of nitrogen oxides and 0.8 grams/mile of hydrocarbons. The catalytic converter provides a noble metal (platinum or iridium) catalyst surface that promotes oxidation of VOCs and reduction of nitrogen oxides to yield innocuous products. For more detail about how catalytic converters work, click here.

California: A Model For Successful Pollution Reduction

Although improved catalytic converters are helping, the persistence of ozone levels that exceed the NAAQS indicate that they are not enough. What else needs to be done? The answer depends on the particular situation. Different regions of the country have different air-quality challenges. California, for example, has already reduced its reliance on fossil fuels to provide electricity. In December 2000, none of the electricity produced in California came from burning coal or oil, and two thirds of the electricity produced was derived from hydroelectric, nuclear and renewable energy sources. The remaining third was produced by burning natural gas. In California, cars cause more smog than does electricity generation, although some nitrogen oxides are produced when natural gas is burned. (See Box 2 for more details.)

California's efforts to improve air quality have not been limited to changes in the way it produces electricity. Legislation sets maximum emission levels for motor vehicles and industry, and the state sponsors public education for voluntary consumer choices that promote clean air. These efforts have paid off: in 1970 there were 148 air-quality alerts, but in 1997 there was only one. Nevertheless, the growing population of California, and the growing number of automobiles, continue to put pressure on air quality. In 1999, seven of the ten highest areas of ozone concentration in the U.S. were in the state of California.

Therefore, in response to the growing demand for automobiles, California is attempting to implement a second strategy to reduce NO emissions: finding alternative methods to power cars. The California legislature has required auto manufacturers to manufacture a mix of vehicles that meet progressively more stringent standards for emissions. In addition, legislation exists that requires a certain percentage of the vehicles manufactured to be zero-emission vehicles (ZEVs). The ZEV requirement was suspended for all years prior to model year 2003. It remains to be seen whether car manufacturers will be expected to comply with the existing targets for ZEVs in 2003. The answer will depend, at least in part, on the technology that is available for ZEVs. In the next section, we take a look at the current technology for ZEVs.

Current Technology for Electric Vehicles

The only ZEVs at this point are electric vehicles. Several car manufacturers sell electric vehicles to fleet buyers, and kits are available for individuals who want to convert ordinary cars into electric vehicles. For example, the Honda Insight and the Toyota Prius are hybrid gasoline/electric vehicles that do not require external charging. Although they are superior to ordinary gasoline vehicles in terms of both gas mileage and emissions, they are not ZEVs. Battery technology is the key to making electric vehicles. Some commercially available and most home-built electric vehicles use lead-acid batteries, similar to ordinary car batteries. To understand how to improve electric vehicles, we must first understand how batteries work.

Batteries in Electric Vehicles

Batteries are one of the most common applications of electrochemistry. Batteries harness oxidation-reduction, or redox, reactions to produce energy. Redox reactions involve the transfer of electrons from one substance to another. The electrochemical cell is the basis of every battery. In an electrochemical cell, electrons are transferred between two substances, even though the reactants are not in physical contact with each other. This electron transfer produces a current. If the cell is galvanic, the reaction proceeds spontaneously and the resulting current can be used to do work such as driving an electrical motor, or illuminating a flashlight. The tin(II)/ferricyanide cell you constructed in Experiment 5, "Electrochemistry: Cells and Redox Reactions" is a good example of a cell-based electrochemical reaction.

All redox reactions can be separated into two half-reactions. Figure 6 is a schematic of a lead-acid battery (an ordinary car battery). In the lead-acid battery, Pb is oxidized to Pb^{2+} at the anode (negative battery terminal) as shown in Equation 10 and Pb^{4+} is reduced to Pb^{2+} at the cathode (positive battery terminal) as shown in Equation 11.
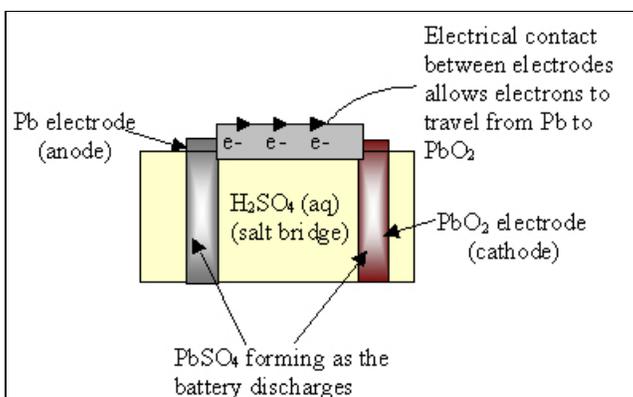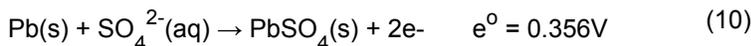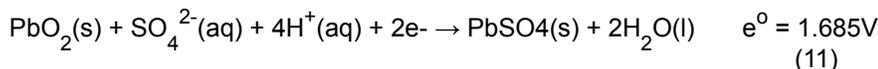

Figure 6

This schematic of a lead-acid battery shows the oxidation-reduction reaction between lead and lead (IV)

> oxide, mediated by sulfuric acid. Pb is the anode and PbO_2 is the cathode.

Oxidation half-reaction:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e\text{-} \qquad e^o = 0.356V \qquad (10)$$

Reduction half-reaction:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e\text{-} \rightarrow PbSO4(s) + 2H_2O(l) \qquad e^o = 1.685V$$
$$(11)$$

During discharge (when the battery is being used to generate electricity), the sum of the two half-reactions is the following **cell reaction:**

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow PbSO_4(s) + 2H_2O(l) \qquad e^o = 2.04V \qquad (12)$$
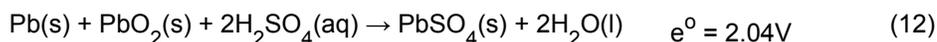
Notice that as the cell reaction proceeds, $PbSO_4$ precipitate forms on both electrodes.

Recall, from the Nernst Equation (see Experiment 5), that
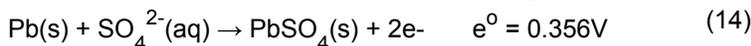
$$\varepsilon_{nm} = \varepsilon^o - \frac{RT}{nF} \ln Q$$

For the lead-acid battery, e^o = 2.04 volts. See Box 3, below, for a review of electrochemical potentials.) In the lead-acid battery,

$$Q = \frac{1}{[H_2SO_4]^2}$$

because all the reactants and products other than H_2SO_4 are solids or liquids that do not appear in the

equilibrium expression. This means that the actual battery voltage depends on the concentration of sulfuric acid, which is consumed as the battery discharges. (During discharge when $e > 0$, the cell is galvanic and the reaction occurs spontaneously, since $\Delta G < 0$.) Common car batteries are twelve-volt batteries, because they are actually six lead-acid cells (each of which has e^o = 2.04 volts as seen in Equation 12, above) connected in series and housed in a single container.

Box 3
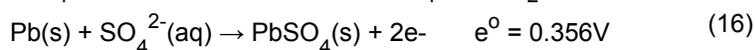**Electrical Potentials in Lead-Acid Batteries**

Every half-reaction has a standard electrical potential, designated as e^o. By convention, we write the half-reactions as reductions; i.e., the addition of electrons to the oxidized form of the substance. The two half reactions that comprise the redox reaction in a lead-acid battery are the following (written as reduction reactions):

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e\text{-} \rightarrow PbSO4(s) + 2H_2O(l) \qquad e^o = 1.685V \qquad (13)$$
$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e\text{-} \qquad e^o = 0.356V \qquad (14)$$

e^o is a measure of the tendency of the reactant in the half-reactiopn to accept electrons relative to $H^+ + e\text{-} \rightarrow {}^1/_2H_2$ (every species in its standard state). We obtain the e^o for the whole cell or reaction by adding together the standard potentials for the half reactions.

$$e^o{}_{cell} = e^o{}_{cathode} + e^o{}_{anode} \qquad (15)$$

Note that the anode half-reaction must be written in the reverse direction from Equation 14 above (as an oxidation reaction), and that the sign of e^o changes when the reaction is reversed. Rewriting Equations 13 and 14, and adding them together gives:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e- \rightarrow PbSO_4(s) + 2H_2O(l) \qquad e^o = 1.685V \qquad (13)$$

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e- \qquad e^o = 0.356V \qquad (16)$$

$$e^o_{cell} = 1.685 + 0.356 = 2.04V \qquad (17)$$

Recall, a potential of 2.04 V will only be measured if all the reactants and products are in their standard state, which means a concentration of 1 M for aqueous solutions. The Nernst Equation (Equation 18, below) allows us to calculate the potential when we have conditions other than the standard state.

$$\varepsilon_{rxn} = \varepsilon^o - \frac{RT}{nF} \ln Q \qquad (18)$$

Here, R is the gas constant, 8.314 J/mol-K; T is the Kelvin temperature; n is the number of moles of electrons transferred in the cell reaction; F is the value of the Faraday constant, 9.65×10^4 C/mol (i.e., the absolute value of the electric charge of one mole of electrons); and Q is the reaction quotient, a quantity of the same form as the equilibrium constant but employing activities actually present in the cell rather than those at equilibrium.

To recharge the lead-acid battery, the redox reaction (Equation 12) must be run in reverse. The electrical potential for this reverse reaction is negative ($e^o < 0$); therefore, the reaction is nonspontaneous. This means that energy is needed to drive the reaction (*i.e.*, recharge the battery). Notice that during recharging the $PbSO_4$ precipitate on the electrodes is oxidized and reduced to PbO_2 and Pb, respectively. Once recharging is complete, the forward reaction can run spontaneously again and create electrical work.

The main drawbacks to lead-acid batteries is that they are heavy and must be recharged over a period of hours. Depending on the weight of the vehicle and driving conditions, twenty batteries may be required to power the car for forty miles before recharging. The batteries weigh up to eighty pounds each, and they take up quite a bit of space. Although the weight and volume of the internal combustion engine is eliminated, electric vehicles are still heavier than their gasoline counterparts and often sacrifice trunk space for battery storage. In addition, the discharged batteries must be plugged into a battery charger for six or more hours for recharging.

What is the Effect of Recharging on Air Pollution?

Batteries in all-electric vehicles must be externally recharged. (Hybrid gasoline/electric vehicles continuously recharge the batteries during normal operation of the vehicle. Although hybrid vehicles are not ZEVs, they are an extremely efficient use of gasoline-derived energy.) Usually lead-acid batteries in electric vehicles are connected to a charger that plugs into an ordinary source of 110-V electricity. A complete analysis of how "clean" an electric vehicle is would have to take into account the emissions produced by electric companies to generate the electricity used in recharging. As discussed above, emissions from electricity production depend on the method used to generate electricity and vary from one region of the country to another. In parts of the midwest where high-nitrogen-content fuel is burned to generate electricity (see Box 2), the benefits of electric vehicles are debatable. Many researchers believe that the most practical long-term answer to our air-quality problems is widespread use of electric vehicles, coupled with a transition to electricity that is generated from renewable resources. (Click on http://www.edf.org/programs/energy/green_power/index.html for more details about "green electricity.")

Battery technology is the bottleneck that limits widespread electric vehicle use today. Advances in battery design may yield batteries that are smaller, lighter and can be recharged faster. A large range of possibilities are being explored by researchers in universities, government labs and industrial R&D programs.
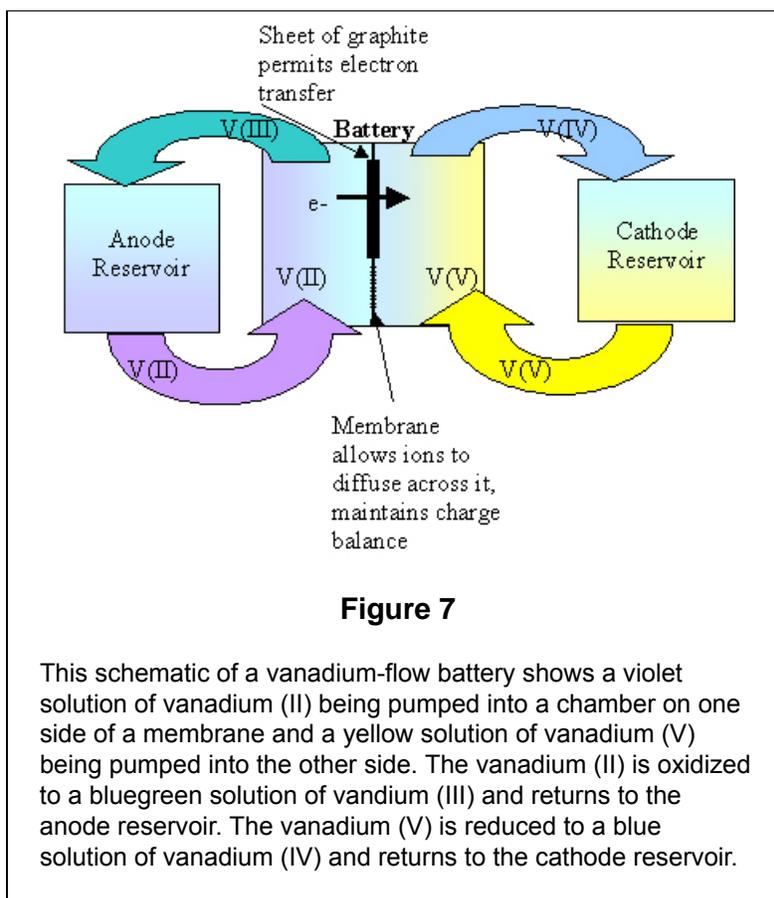
Questions on Lead-Acid Batteries

- How can one substance ($PbSO_4$) be the product of both an oxidation half-reaction and a reduction half-reaction in the lead-acid battery?
- Why is H_2SO_4 described as the salt bridge in Figure 6?

Improving Battery Technology for Electric Vehicles

One interesting approach has been developed by Professor Maria Skylass-Kazacos and her team at the University of New South Wales, Australia. Skylass-Kazacos has developed a vanadium-flow battery. A schematic of the vanadium-flow battery is shown in Figure 7. In a flow battery, the reactants are in solution instead of in solid plates (as in the lead-acid battery). On one side of the battery is a solution of vanadium (V) ions dissolved in sulfuric acid. The solution on the other side is vanadium (II) ions in sulfuric acid. (Note: Vanadium (V) ions produce yellow solutions and solutions of vanadium (II) ions are violet.) Just as in the lead-acid battery, electron flow produces a current.

$$\textbf{Oxidation half-reaction:} \qquad V^{2+} \rightarrow V^{3+} + e\text{-} \qquad (19)$$

$$\textbf{Reduction half-reaction:} \qquad V^{5+} + e\text{-} \rightarrow V^{4+} \qquad (20)$$

The solutions are separated by a sheet of graphite. The graphite is chemically inert and conducts electrons well. (You used graphite rods as electrodes for the same reasons in Experiment 5.) A semi-permeable membrane serves to complete the circuit and functions as a salt bridge. Without the membrane, as electrons flow from the anode (V^{2+} solution) to the cathode (V^{5+} solution), excess positive spectator ions would build up in the anode solution and the reaction would stop prematurely. Hydrogen ions may be the species that crosses the membrane to maintain charge balance, but this has not been experimentally verified. The cell has a potential of 1.6 volts when fully charged (assuming an electrolyte concentration of 2 M vanadium at 25°C).

Figure 7

This schematic of a vanadium-flow battery shows a violet solution of vanadium (II) being pumped into a chamber on one side of a membrane and a yellow solution of vanadium (V) being pumped into the other side. The vanadium (II) is oxidized to a bluegreen solution of vandium (III) and returns to the anode reservoir. The vanadium (V) is reduced to a blue solution of vanadium (IV) and returns to the cathode reservoir.

The vanadium battery is not the only flow-redox battery known. A flow-redox battery that uses iron and chromium ions was developed by NASA, for instance. However, the all-vanadium battery has a significant advantage over other flow-redox cells because mixing the electrolyte solutions does not damage the battery. If some of the

vanadium "leaks" through the membrane, the only disadvantage is energy that would have been generated from the transfer of electrons through the graphite is squandered. Once the battery is recharged, the vanadium ions will return to their charged oxidation states. The electrolyte solution is not permanently contaminated.

The vanadium-flow-redox battery may be an excellent alternative to lead-acid batteries for electric vehicles. The vanadium battery should be lighter and have a longer lifetime, and the vanadium compounds in the battery are less toxic than lead compounds. (The volume of solution required, although lighter than lead plates, may not result in significant space savings over lead-acid batteries.) Most importantly, though, for electric-vehicle applications, is that the vanadium-flow cell can be recharged in two ways. Just like lead-acid batteries, a vanadium battery can be plugged into a charger and recharged over a period of hours. However, if one doesn't want to wait several hours for the battery to recharge, the discharged electrolyte solutions can simply be drained and replaced with fully charged electrolyte solutions. This process would not be much more time consuming than refilling a standard car with gasoline. Will urban areas of the future be dotted with "vanadium-electrolyte filling stations?" If electric-vehicle use is coupled with electricity production from renewable energy sources, the vanadium battery may help us all breathe easier.

Questions on Flow Batteries

- Imagine a small tear in the membrane in Figure 7 that allows vanadium ions to slowly leak between the compartments. What ions will cross the membrane, and what will happen to them?
- Imagine, now, a large tear in the membrane in Figure 7, so that there are no longer separate compartments for the anode and cathode solutions. Can you predict the color of the solution a substantial time after mixing? Why or why not? What color(s) would you expect?

Summary

Good air quality is important to public health. Photochemical smog, a mixture of pollutants including ozone, is the most common air-quality problem. Background in electrochemistry and redox reactions can help us understand the causes of air pollution, its effects on our health and strategies to reduce air pollution.

The Environmental Protection Agency (EPA) is responsible for monitoring the air quality around the country. Many urban areas have ozone concentrations that exceed the standards set by the EPA. Ozone is harmful because it is a strong oxidizing agent, which can reduces the antioxidants found on the surface of the lung and can lead to lung damage.

Although ozone is a major component of photochemical smog, it is not directly produced by automobile emissions or by producing electricity (the two main activities that burn fossil fuels). Volatile organic hydrocarbons (VOCs) and nitrogen oxides, which result from the burning of fossil fuels, react in the lower atmosphere to produce ozone. Ozone concentrations are especially difficult to lower, because the mechanism for the formation of ozone contains cyclic steps, which regenerate nitrogen oxides and lead to production of additional ozone.

In the past, the focus for reducing automobile emissions has been on removing the pollutants from the post-combustion emission gases. The main strategy has been the development of more efficient catalytic converters. Catalytic converters provide noble metal surfaces that promote the reaction of nitrogen oxides with other exhaust components to yield innocuous products. However, the goal is now becoming the development of zero-emissions vehicles.

The current ZEV are electric vehicles and their feasibility is dependent on battery technology, where energy is produced by an oxidation-reduction reaction. At the heart of all batteries is an electrochemical cell. Most electric vehicles use the lead-acid battery (which is the conventional car battery), but there are a number of drawbacks to this battery, namely the weight and the recharging time. Hence, many researchers are studying battery technology. One interesting new design is a vanadium-flow battery, in which the redox reaction consists of solutions instead of solid material. A current is produced through electron transfer from the vanadium (II) ions in solution on one side of the battery to the vanadium (V) ions on the other side. This design looks promising, but it is in its infancy. Battery technology is still an active area of research.

Additional Links:

- More details on the vanadium-redox battery can be found at the [University of New South Wales'](#) web site

and the Vanadium Page.
- More detail on automotive-emissions control, courtesy of the Weekend Mechanics Club.
- The Environmental Protection Agency Office of Children's Health Protection maintains an informative site about air quality and its importance to childrens' health.
- The California Air Resouces Board web site will include recent information on ZEV quotas for car manufacturers. The site also includes data on California air-quality status and trends.
- Environmental Defense tracks national progress in producing clean, "green" energy. Their web site also includes a calculator that lets you estimate how much air pollution is created by the electricity you use, based on your electricity bill.
- Companies including Mazda and Corning provide information about their new developments in catalytic converters.
- Washington University's Science Outreach developed this curriculum on ozone for use in high schools.

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