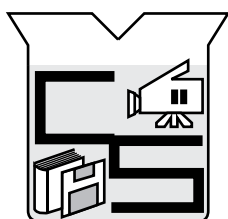
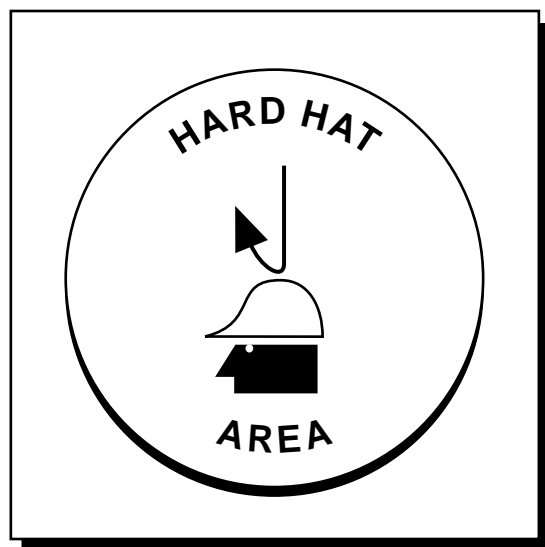


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*ChemSource Project Principal Investigator:
Mary Virginia Orna, OSU
Department of Chemistry
College of New Rochelle
New Rochelle, NY 10805
Phone: (914) 654-5302
FAX: (914) 654-5387*

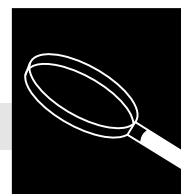


ChemSource

*Instructional Resources for Preservice and
Inservice Chemistry Teachers*

**INDUSTRIAL INORGANIC
CHEMISTRY**

Topic Overview



CONTENT IN A NUTSHELL

Industrial chemistry includes the application of chemistry to the manufacture of chemical substances. The processes used in industry frequently differ significantly from those used in the laboratory. Often the conditions that exist on a small scale when reactions are carried out in beakers and flasks are not the same as are encountered when a reaction is attempted in large vats. Today most chemicals are manufactured in continuous processes. Frequently this requires that a different reaction be used because the laboratory preparation cannot be adapted to the requirements of industry.

Industrial chemicals are produced in large quantities. If a substance is manufactured in only small quantities, it is referred to as a **fine chemical**. The Appendix contains a list of the top chemicals in terms of quantity manufactured. (This information is published annually by the American Chemical Society in *Chemical and Engineering News*.) This list contains many substances familiar to the beginning chemistry student. Sulfuric acid heads the list of inorganic chemicals. It is widely used in the manufacture of other chemicals. Ethylene is always near the top, if not at the top, of the list of organic chemicals. It is used extensively in the plastics industry as well as in the manufacture of a wide variety of organic chemicals. Ammonia, nitric acid, and phosphoric acid are important in the fertilizer industry. (Sulfuric acid is also important in the fertilizer industry, but it has many other industrial applications as well.)

Because of the importance of fertilizers to world food production and the utilization of several of the top chemicals in that industry, the activities and demonstrations in this module focus on the fertilizer industry. Even if there is no fertilizer industry nearby, students can relate to this because of the importance of food in their lives. (Most teenagers love to eat!) Many areas have nearby agricultural regions where the application of fertilizers can be observed and knowledgeable individuals can be found to discuss this important topic with students.

Metallurgy is another important facet of the application of industrial chemistry. The extraction of metals from their ores involves a number of processes. Some steps in the separation procedure are physical processes while others involve chemical reactions. Because of the emphasis in many areas on recycling of aluminum and the energy savings accompanying aluminum recycling, aluminum is a particularly good model for study. The importance of iron (steel) to the economy and its widespread use make iron production another interesting metallurgical process.

Quality control (or quality assurance) is an important aspect of a chemical manufacturing plant. Many chemists and chemical engineers are employed in this support group within a chemical manufacturing plant, testing industrial products to insure that they meet the specifications desired. Raw materials are tested to see that the starting materials are of the proper quality to give the desired product. Finished products are tested before distribution to insure that they meet standards claimed by the manufacturer.

Industrial chemistry is the point at which chemistry, chemical engineering, business, and many other areas begin to overlap. In this module, there is ample opportunity for students to utilize many other disciplines. The history of industrial chemistry provides insight into the lives of many chemists and those who were not chemists but were drawn to chemistry because of economic or other reasons. For example, Leopold Godowsky and Leopold Mannes were professional musicians who had an interest in photography. In high school they began to experiment with color photography. They continued their collaboration for many years, finally developing the process for making Kodachrome™ film, which remains one of the best color processes.

The impact of economic or political conditions on chemical manufacturing also provides a fascinating study. For example, the manufacture of ammonia in the U.S. increased rapidly at the end of World War I due to the urgent war-time need for nitrates. The first full-size plant for the production of HNO_3 from NH_3 was built in Muscle Shoals, Alabama in 1917. The ammonia industry also expanded during the 1940s and 1950s due to World War II and the Korean Conflict.

Social issues related to industrial chemistry include problems related to waste disposal from large chemical plants as well as disposal of chemicals by individuals (*e.g.*, pesticides). The responsibility of the government to regulate manufacturing practices (*e.g.*, air quality in the vicinity of chemical plants) provides an opportunity for students to discuss the impact of governmental regulations on industry and *vice versa*.

This is an enrichment topic. Since the background material comes from many modules, different sections can be used throughout the course. In order to use all the material, this module should be placed late in the course. The activities in this module illustrate practical applications of stoichiometry, qualitative analysis, and pH measurements.

1. Industrial production and use of fertilizers
2. Metallurgy
3. Scaling up
4. Contribution of the chemical industry to agriculture
5. Impact of the chemical industry on the economy and world trade

1. Mole
2. Balancing equations
3. Stoichiometry
4. Redox reactions
5. Kinetics
7. Electrochemistry
8. Thermochemistry
9. Acids and bases
10. Percent composition

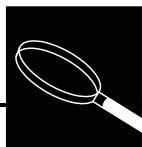
1. Qualitative analysis skills
2. pH measurement
3. Mass and volume measurements
4. Problem solving strategies (dimensional analysis, *etc.*)
5. Algebraic manipulations
6. Observation

PLACE IN THE CURRICULUM

CENTRAL CONCEPTS

RELATED CONCEPTS

RELATED SKILLS



PERFORMANCE OBJECTIVES

After completing their study of industrial inorganic chemistry, students should be able to:

1. describe several industrial processes.
2. discuss the process of scaling up reactions for industrial use.
3. express an appreciation for the role of chemistry and chemical manufacturing processes in food production and other areas of their everyday life.
4. discuss the relationship of the chemical industry to the economy.



Concept/Skills Development

Activity 1: Physical and Chemical Examination of Soil

LABORATORY ACTIVITY: STUDENT VERSION

Introduction

The successful American society and our comfortable lifestyle is largely a result of the ability of our nation to feed its population. Without maintaining American soils, this food supply will dwindle. This activity is designed to examine only a few of the characteristics that farmers and soil scientists must understand and control.

Purpose

To illustrate the relevance of chemistry in the agricultural industry by examining the oxygen level, humus content, and pH of soil.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Do not touch hot crucibles. They look just like cool ones.
3. Follow proper procedures for lighting burners.
4. Follow usual safety procedures for handling equipment and chemicals.
5. Dispose of waste as directed by your teacher.

Part A. Oxygen Level in Soil

Procedure

1. Place about 200 g bright red clay type soil in a flask or jar that can be closed tightly.
2. Add about 50 g sucrose (table sugar) and mix thoroughly with the soil.
3. Add enough water to cover the soil to a depth of about 3-5 cm.
4. Close the container tightly. It should be kept at room temperature or warmer for about 2 weeks. During this time, the color of the soil should begin to change. Carefully note the color of the soil at the beginning and end of the activity.
5. Thoroughly wash your hands before leaving the laboratory.

Implications and Applications

1. To what is the red color of the soil primarily due?
2. What did the sugar have to do with the processes taking place over the two-week period?
3. Why is a proper level of oxygen necessary for plants?
4. Based on your observations in this activity, describe a technique you could use to compare relative amounts of iron content of various samples of soil.

Part B. Humus Content in Soil

Your teacher will supply you with either a local soil sample or a commercial potting material.





Procedure

1. Weigh a clean, dry crucible and cover.
2. Fill the crucible about half full with soil and reweigh the crucible and cover. Note the color of the soil. Dry the crucible and contents overnight in a drying oven at about 60 °C.
3. Record the mass of the soil and crucible after drying. (The soil is referred to as “dry soil” throughout *Part B* of the activity.) Note the color of the soil.
4. Place the crucible in a clay triangle on a ring stand. Heat it with a hot flame for 30 min. Stir the soil with a glass stirring rod occasionally while heating. Be sure to use a hot flame.
5. Allow the crucible and soil to cool. Weigh the crucible, cover, and soil.
6. Record the color of the soil and general appearance before drying, after drying, and after heating strongly for 30 min.
7. Repeat the procedure using a commercial potting soil or peat moss.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

Data Chart

- | | |
|---|-------|
| A. Mass of empty crucible and cover. | _____ |
| B. Mass of crucible, cover, and soil before drying overnight. | _____ |
| C. Mass of crucible, cover, and soil after drying overnight. | _____ |
| D. Mass of dry soil after overnight heating at 60°C. (C-A) | _____ |
| E. Mass of crucible, cover, and soil after strongly heating for 30 min. | _____ |
| F. Mass of soil after heating strongly for 30 min. (E-A) | _____ |
| G. Mass of humus lost during 30 min heating. (D-F) | _____ |

Using the mass of the “dry soil” before it was strongly heated (D) and the mass loss as a result of strongly heating the “dry soil” (G) calculate the percent by mass humus in the original sample of soil (B-A). (This calculation assumes that the mass loss during the 30 min of intense heating is due to the burning of the humus.)

Implications and Applications

1. Why is it desirable to dry the soil overnight before the intense heating process?
2. During the 30 min of heating strongly, why does only the humus volatilize?
3. How do the results for the commercial potting material compare with the other soil sample? Why are the results different?
4. Why is humus important for plant growth?
5. Composting organic wastes is strongly encouraged. Explain what composting is and how it would be useful in efforts to protect the environment and improve the soil.

Extension

Use the mass of the soil before and after drying overnight at 60 °C (C-B) to determine the percent water by mass in the original sample.

Part C. Soil pH

Part C1. Measuring the pH

1. Allow several soil samples to air-dry for two or three days.
2. Weigh 10 g of a sample of air-dried soil and mix it thoroughly with 10 mL of distilled water. Stir and let it sit for 15-20 min.
3. Stir the mixture again. Measure the pH using a pH meter, pH test papers, or pH indicator solutions provided by your teacher. Record your pH measurement.
4. Follow Steps 2 and 3 for each soil sample.
5. Thoroughly wash your hands before leaving the laboratory.

Data Analysis, Observations, and Concept Development

Note the source of the soil for each sample. Record the pH. Observe the color and odor, if any, for each sample. Compare the pH, color, and odor for the different samples.

Part C2. Changing the pH

1. Weigh 50 g air-dried soil and place it in a beaker or flask.
2. You will be assigned a substance to be tested for pH. Carefully add 0.5 g of the assigned substance to the soil sample and mix thoroughly.
3. Slowly add just enough water to moisten the soil (about 20-30 mL).
4. Repeat Steps 2 and 3 for each material to be tested for its effect on soil pH.
5. Cover the samples and allow to stand for one to two weeks, keeping the sample moist *but not saturated* throughout this time.
6. After this period of time, weigh 10 g of each treated soil and add 10 mL of water. Stir and allow to stand for 15-20 min.
7. Stir again and measure and record the pH.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Prepare a data chart showing the substance(s) you used and the resulting pH measured. How much did each substance change the pH from the pH measured before the substance was added (as measured in *Part C1*)?

Implications and Applications

1. If the pH changed, how is the direction of change related to the chemical properties of the substance added?
2. In a reference source, find the most desirable pH for optimal growth of several types of plants.
 - a. Do all these plants have the same optimum soil pH?
 - b. What type of plant would be best suited to the soil sample you tested?
 - c. For a plant that would not grow as well in your soil sample, what could you use to treat the soil to provide more appropriate growing conditions?



**LABORATORY
ACTIVITY:
TEACHER
NOTES**

***Activity 1: Physical and Chemical
Examination of Soil***

Major Chemical Concept

This activity helps show the relevance of mass percent calculations, pH determinations, oxidation-reduction reactions, and Brønsted-Lowry acid-base reactions. This activity could be substituted for more traditional laboratory activities to illustrate the application of chemical principles such as pH or oxidation-reduction.

Level

All levels

Expected Student Background

Part A requires an understanding of simple oxidation-reduction reactions (see *Oxidation-Reduction* module). For *Part B*, students should be able to calculate percent by mass. *Part C* requires an understanding of the concept of pH and the use of pH paper, pH indicators or a pH meter to measure pH (see *Acids and Bases* module). Familiarity with standard laboratory procedures is assumed.

Time

Preparation of the soil sample in *Part A* requires about 15 min. The samples should be observed every few days over the following two weeks. Observations require only a few minutes since the only data to be collected is color change.

Part B may be done in one class period (50 min). *NOTE: Pre-drying overnight is required before this activity.*

If soil samples have been air-dried for two to three days, the sample can be prepared (Step 1 of *Part C1*) prior to beginning *Part B* and the pH measurement in *Part C1* can be made while students are waiting for complete combustion of the soil sample in *Part B*. There may also be sufficient time during the intense heating of the soil sample in *Part B* to prepare the samples for *Part C2*. Again, the observations during the one to two-week incubation period do not require much time. The pH measurements require only a few minutes.

Safety

Read the *Safety Considerations* in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

- Balance
- 12 Burners
- 12 Graduated cylinders, 10-100-mL
- 12 Flasks (or some type of container that can be closed)
- 12 Crucibles
- 12 Crucible tongs
- 12 Ring stand set ups with clay triangles
- 12 Wire gauze
- pH meter (optional)
- Drying oven

Consumables

Soil samples [NOTE: If red clay soil is not available in your area, it can be simulated by thoroughly mixing a few grams of finely powdered Fe_2O_3 with local soil.]

Commercial potting soil, 600-900 g

Distilled water

pH paper, indicator solutions or pH meter

Sucrose (table sugar), 600 g

Substances to affect pH—5 g each of one or more of these:

Calcium carbonate, CaCO_3

Calcium oxide, CaO

Calcium sulfate, CaSO_4

Commercial "lime"

Ammonium chloride, NH_4Cl

Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$

Advance Preparation

1. All equipment and supplies should be available to students. This saves much time in set up. Equipment should be checked to insure proper working condition.
2. For *Part B*, soil samples should be predried overnight at about 60 °C.
3. For *Part C* students will need 100-500 g or more of each soil sample, depending on the moisture content of the soil and how many substances you will be testing for their effect on pH of the soil. If you use a pH meter, standardize the meter before the laboratory period.

Pre-Laboratory Discussion

1. If this is used as an activity replacing more traditional activities, demonstrate the technique for measuring pH using the method you have chosen for this measurement. If you use a pH meter, it is important to explain that meters are standardized and should not be arbitrarily adjusted during the activity.
2. Safety should be stressed especially with emphasis on hot and cold porcelain looking the same.

Part A

Proper levels of oxygen in the soil are needed for plant growth and microorganism activity. Many chemical reactions in the soil are carried out aerobically by microorganisms. One of the most important of these is the decomposition of plant and animal material by bacteria and fungi. The release and conversion of nitrogen contained in organic substances is dependent on a well aerated soil. The level of oxygen in the soil can be examined by observing its color. Oxygen rich soils generally have bright-colored red subsoils. Soils that have gray subsoils are usually deficient in oxygen.

The oxidation state of iron is responsible for the color of the soil. A red, oxygen-rich soil contains iron(III) oxide, Fe_2O_3 . A gray subsoil contains iron largely as iron(II) oxide. In the case of the gray subsoil, the iron has been reduced from iron(III) to iron(II). This reaction occurs because the microorganisms could not obtain oxygen from the air in the soil, usually because the soil is too wet. Thus the microorganisms use the oxygen bonded to the iron in the iron(III) oxide converting the iron(III) to iron(II). Sugar is added in this activity to supply the energy needed by these microorganisms.

This activity provides a real-life illustration of oxidation-reduction.



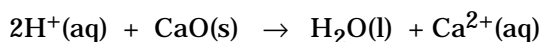
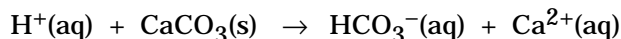
Part B

Plant and animal material returned to the soil after the death of the organism forms the humus content of soils. Humus is a source of nutrients that can replenish what is removed by growing plants. Many of these nutrients (*e.g.*, carbon and nitrogen) are cycled through our ecosystems and are a subject of much study (see *Biogeochemical Cycles* module). These cycles could be presented during the pre-laboratory discussion.

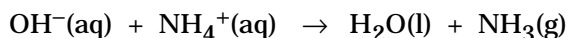
Part C

Many factors affect pH of soils such as fertilizers, type of soil, rainfall, season, type of crop grown the previous season or the type of plants (trees, shrubs, *etc.*) found in the area. Because optimum growth conditions for different plants occurs at different pH values, soil samples may be too acidic or too basic depending on the types of plants one wishes to grow. (For example, most vegetables prefer a pH between 6 and 8.) A good gardener will know the optimum pH for the plants and will adjust the soil pH accordingly. "Lime" is commonly used to raise soil pH. Anhydrous or aqueous ammonia will also raise soil pH. However, continued use of ammonia (and fertilizers containing ammonium ion) leads to an increase in soil acidity by microbial oxidation of NH_4^+ to NO_3^- . Crop fertilization can increase soil acidity because many fertilizers contain ions (*e.g.*, NH_4^+) that tend to lower the pH of the soil. Also rainfall leaches neutral and basic substances more readily than acids, increasing surface soil acidity. These factors increase the tendency of cultivated soils to be acidic unless treated with lime. If soil is too basic, pine needles or almost any type of tree leaves can be added to lower the pH.

Brønsted-Lowry bases increase soil pH by reacting with excess H^+ ions in acidic soils. Calcium carbonate, calcium oxide, and commercial "lime" are examples of substances that can neutralize acidic soils.



If equal masses are used, CaO will cause a larger pH increase than will CaCO_3 . Commercial "lime" is frequently a mixture of substances such as CaCO_3 and MgCO_3 . Since CaSO_4 is the salt of a strong acid and strong base, it will not neutralize acid and thus will not affect the soil's pH. Brønsted-Lowry acids decrease soil pH by reacting with excess OH^- ions in basic soils. Ammonium salts (*e.g.*, NH_4NO_3) can neutralize basic soils.



Teacher-Student Interaction

1. The degree of supervision required will depend upon whether this activity is used as an alternate to other activities to illustrate the concepts of percent by mass and pH or as an enrichment activity. During long periods of heating crucibles, discuss observations with students.
2. Discuss with students how materials in *Part C2* are responsible for affecting pH.
3. Do not be concerned that variations in results are obtained when the same soil samples are used since no attempt has been made to provide uniform soil samples. Differences may also be greater if a visual method (pH paper or indicator) is used to measure pH.

Anticipated Student Results

Don't expect student data to agree closely for these activities. Interest is generated, however, by having students analyze local soil samples. Use this opportunity to discuss reasons for differences in student results.

Part A

Within two weeks, the bright red soil should begin to turn gray as the microorganisms use the combined oxygen, reducing iron(III) to iron(II).

Part B

It is not possible to predict the mass percent humus you will obtain due to the variations among soil types and to nonuniformity of samples. It is better to collect class data and compare. The commercial potting soil should be more consistent.

Part C

Results will vary with the soil samples. For *Part C2*, the following pH values are typical results for the various compounds used to affect the soil pH. These are not absolute values, just possible results. Allow for differences among soil samples and student interpretation of colors if indicators are used.

Calcium carbonate	6.8
Calcium oxide	7.0
Calcium sulfate	4.5
Commercial lime	6.0

Always keep a sample of the original untreated soil to use as a control for comparison.

Answers to Implications and Applications

Part A

1. The red color of the soil is primarily due to presence of iron(III) compounds.
2. The sugar was an energy source for the microorganisms during the activity.
3. The proper level of oxygen is necessary because plant roots and other tissues must carry on respiration, which requires oxygen. (Other answers are acceptable.)
4. Student answers will vary. One answer could be to compare relative amounts of iron content of various samples of soil by establishing a color scale like pH indicator scales.

Part B

1. Drying the soil overnight before the intense heating process is necessary so that the humus will burn easily and completely (see also answer to *Question 1* in *Assessing Laboratory Learning*).
2. During the 30 min of heating strongly, only the humus volatilizes because organic matter will oxidize at lower temperatures. The oxidation products are CO_2 and H_2O , which are volatile at the temperatures used. Most inorganic compounds are not volatile at the temperatures reached in the activity and will not be converted to volatile compounds under the conditions of the activity. For example, silicon dioxide, a component of soils, is already fully oxidized.
3. Typically, commercial potting soils will have higher humus amounts because humus is added to provide the nutrients and the mulching effect to aid in aeration.
4. Humus is important for plant growth because it is a source of needed nutrients.
5. Student answers will vary. Composting involves returning waste plant (and sometimes animal) materials to the soil. Compost provides nutrients, principally carbon and nitrogen, to the soil.



Part C

1. The direction of change related to the acid/base nature of the substance added. Substances that are Brønsted-Lowry bases raise pH. Substances that are Brønsted-Lowry acids lower pH.
2.
 - a. There is variation in optimum soil pH for different plants.
 - b. Answer will depend on soil pH.
 - c. Answer will depend on soil pH.

Post-Laboratory Discussion

1. Collect class data for all activity parts and discuss similar and dissimilar findings. Identify the source of all soil samples to facilitate this discussion. Is there a correlation between the source of the soil sample and the color (oxygen content), percent humus, and/or pH?
2. Ask if students noticed large pieces of material in soil samples that might cause variations in experimental data if not removed. In commercial analysis, careful drying and sieving of samples is used to provide sample uniformity. Although results show much more variation without this treatment, most high school laboratories are not equipped to prepare samples in this manner. Also, the time required can be considerable.
3. Questions should be posed about the chemical reasons behind the pH values obtained in *Part C2*. Discuss Brønsted-Lowry acid-base reactions for species such as CaCO_3 , CaSO_4 , and CaO (plus any other substances used) and their effect on pH.
4. Ask questions about the role of chemistry in agriculture and discuss the effect on the food industry and the economy.

Extensions

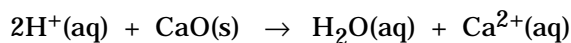
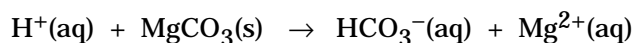
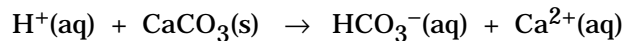
1. Invite someone from the county agricultural extension service to talk with your classes about fertilizers, *etc.*
2. Discuss fertilizers and their components.
3. Include the major industrial processes that are involved in making the raw materials from which fertilizers are made such as the Haber process, the Ostwald process, the contact process, *etc.* in a class discussion.
4. Grow some plants in different pH soils and watch the effects of pH.
5. Contact a nursery and arrange for a tour of their facilities with an expected emphasis on soil chemistry.

Assessing Laboratory Learning

Because results will vary, discussion of data is the most effective way of assessing this laboratory activity. The following questions could be used as a basis for the discussion.

1. If a sample is not dried overnight at 60°C before combustion, what would be the effect on the percent humus? Explain. [*Percent humus would be greater because the mass loss would include loss of water as well as loss of organic matter due to combustion.*]
2. Ammonium nitrate (NH_4NO_3) is used as a fertilizer. How does adding NH_4NO_3 affect soil pH? [*Decrease pH*]

3. Which will be more effective in raising soil pH, 1.0 g CaCO₃, 1.0 g MgCO₃, or 0.50 g CaO? (Assume all reactions go to completion.)



[CaO will be most effective. 1.0 g MgCO₃ will neutralize 0.012 g H⁺. 1.0 g CaCO₃ will neutralize 0.010 g H⁺. 0.50 g CaO will neutralize 0.018 g H⁺.]

References See texts by Jacobs *et al.*, 1971; Kleiss, 1986; and Tocci, 1987 in *References* section of this module.



**LABORATORY
ACTIVITY:
STUDENT
VERSION**

Activity 2: The Solvay Process

Purpose

To illustrate reactions in the Solvay Process, and to produce sodium carbonate by an industrial process.

Safety



1. Wear protective goggles throughout the laboratory activity.
2. Gloves for handling dry ice.
3. Thoroughly wash your hands before leaving the laboratory.

Procedure

Part I. Preparation of NaHCO₃

1. Obtain a 250-mL gas collection bottle and stopper, 25 X 300-mm test-tube with a stopper assembly, and a length of rubber tubing (see Figure 1).
2. Measure 60 mL 3 M NH₃ in a graduated cylinder and pour into a 250-mL Erlenmeyer flask. Weigh out 20 g NaCl to 0.1 g and add it to the NH₃ solution. Stopper tightly, and shake the solution for several minutes to saturate it with NaCl. If all the NaCl dissolves, add a bit more. When the solution appears to be saturated, filter out the excess solid, using a long-stemmed funnel and filter paper, letting the clear liquid drain into the test-tube.
3. Assemble the apparatus shown in Figure 1. The long rubber tubing should be connected to the bent tube on the stopper assembly. The short straight tube is fitted with a small valve, called a Bunsen valve, which will vent CO₂ if the pressure becomes excessive. A Bunsen valve consists of a short length of rubber tubing containing a short lengthwise slit. The valve lets gas out, but not in.

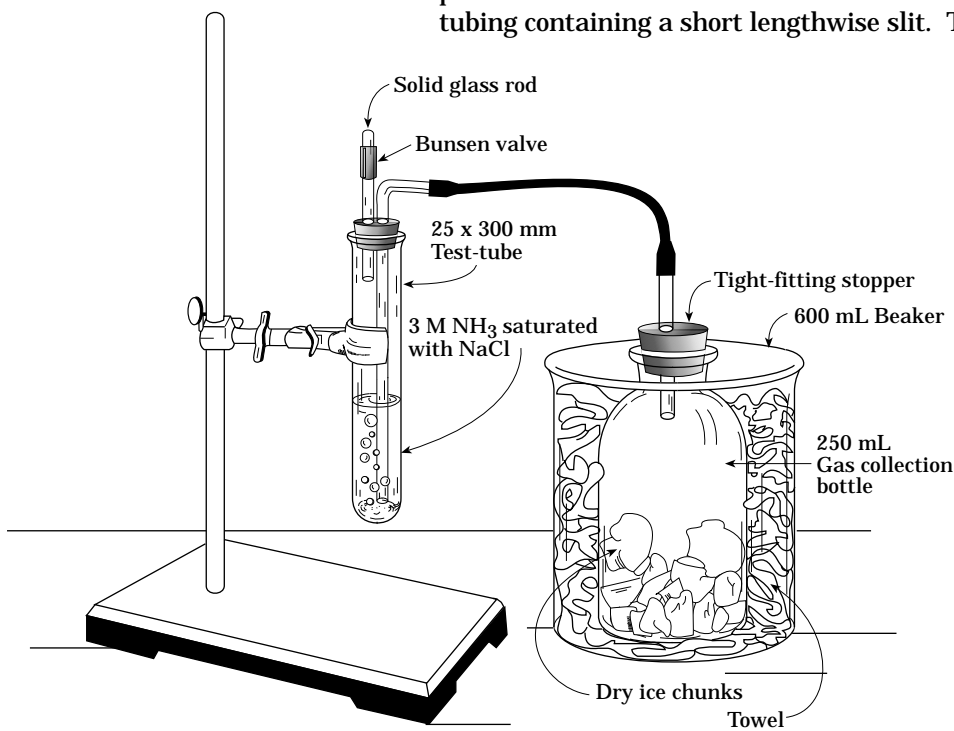


Figure 1. Apparatus for making NaHCO₃

Fill the gas collection bottle about half full with crushed solid CO₂ (dry ice). Wrap the bottle with a towel or several paper towels for insulation, and put it into a 600-mL beaker. Insert the stopper firmly in the gas collection bottle.

If your apparatus is tight, you will observe bubbles of CO₂ in the NH₃-NaCl solution; they should be produced at a vigorous rate, and as they bubble up through the solution they will react with NH₃ and become somewhat smaller. As the reaction goes on, the concentration of HCO₃⁻ ions will gradually increase. While the reaction is proceeding, begin *Part II* of the experiment. However, check the stoppers occasionally to make sure they haven't popped out.

Finally, after about 30 min of bubbling, you should observe a slight cloudiness in the solution as small crystals of NaHCO_3 start to form. Continue the bubbling for 30 min more, during which time an appreciable amount of NaHCO_3 should form. During the last 15 min cool the large test-tube in an ice bath, which will decrease the solubility of the NaHCO_3 , and hence, produce more product.

3. Disconnect the stopper from the large test-tube and unclamp it carefully. Cool the tube in an ice bath for several minutes. Filter the NaHCO_3 , using a Buchner funnel with suction.
4. When all the liquid has been sucked into the suction flask, turn off the suction. Add 3 mL *ice-cold* distilled water to the crystals, wait 10 sec, and then turn on the suction. This should remove most impurities in the NaHCO_3 . Repeat the procedure with an additional 3 mL of *ice-cold* water.
5. Turn off the suction and pour 5 mL 95% ethanol onto the crystals. Again, wait about 10 seconds and then turn on the suction. Repeat with another 5 mL of ethanol. Then leave the suction on for 2 min to dry the crystals. Turn off the suction, remove the filter paper from the funnel, and with a spatula transfer the crystals to a piece of filter paper weighed to 0.1 g.
6. Weigh the crystals on the paper to 0.1 g. Place a small portion of the product into a small test-tube. Add a few drops of 6 M HCl. The effervescence of CO_2 is indicative of the presence of the HCO_3^- anion in the solid and shows that the solid is not just NaCl.

Part II. Preparation of Na_2CO_3

1. Heat a small evaporating dish to redness. Allow it to cool to room temperature, and weigh it to 0.001 g.
2. Add about one gram of your NaHCO_3 product, which should be dry by now, and weigh again to 0.001 g.
3. Heat the evaporating dish and NaHCO_3 again to redness, holding it at red heat for about 10 min. Let the sample cool to room temperature and weigh it.
4. Rinse out all equipment and return it to the stockroom.

Data Analysis and Concept Development

Explain why:

1. NaHCO_3 is the product obtained from solution made from NaCl, NH_3 , and CO_2 .
2. It takes about 30 min for the first NaHCO_3 to appear.
3. One cannot make Na_2CO_3 directly by reaction of CaCO_3 and NaCl.

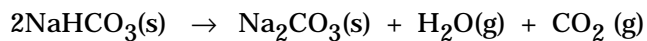
Data Table

Mass of filter paper	_____ g
Mass of filter paper + NaHCO_3	_____ g
Mass of NaHCO_3 formed	_____ g
Mass of evaporating dish	_____ g
Mass of evaporating dish + NaHCO_3	_____ g
Mass of evaporating dish + Na_2CO_3	_____ g
Mass of NaHCO_3 decomposed	_____ g
Mass of Na_2CO_3 produced	_____ g



Implications and Applications

Given the reaction shown, answer the following:

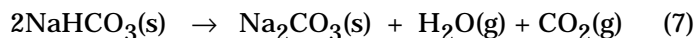
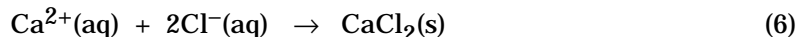
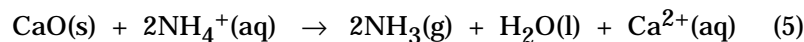
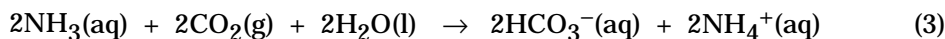
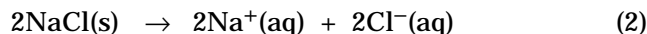
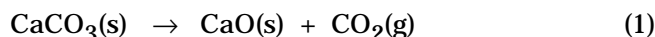


1. How many grams of Na_2CO_3 would be produced from 1.00 g NaHCO_3 ?
2. How many grams of Na_2CO_3 were obtained from one gram of NaHCO_3 in the sample you decomposed?
3. How would you explain the difference between the results of Questions 1 and 2?

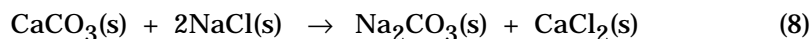
Activity 2: The Solvay Process**Introduction**

Sodium carbonate, Na_2CO_3 , ranks in the top twenty industrial chemicals in amount produced in the United States. It is used to make glass, soap, paper, and other substances. Two hundred years ago, before chemistry was a science, sodium carbonate, then called soda ash since it was obtained from wood ashes, was in short supply, and the French government offered a prize for a synthetic method for its manufacture. In 1791 Leblanc developed a process using common salt, limestone, coal, and sulfuric acid. Salt was heated with sulfuric acid and converted to salt cake, Na_2SO_4 . Salt cake was heated to about 900°C with a mixture of coal and limestone, producing a mixture of Na_2CO_3 , CaS, and impurities called black ash. The sodium carbonate was leached from the solid with water and recrystallized. It was a rather messy process, but at least it worked! The Leblanc process was used to make Na_2CO_3 during much of the nineteenth century. Following its development in 1865, the Solvay process gradually replaced the Leblanc process and became the source of most of the Na_2CO_3 produced during this century. In 1938, some large deposits of the mineral trona, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, were discovered near Green River, Wyoming and have been extensively mined. They now furnish over half the sodium carbonate needs of this country.

This experiment illustrates some of the reactions used in the Solvay process for making Na_2CO_3 . The reactants are table salt (NaCl), ammonia (NH_3), and carbon dioxide (CO_2). A moderately concentrated NH_3 solution is first saturated with NaCl. Carbon dioxide is then bubbled through the resulting solution. It reacts with NH_3 and H_2O to form HCO_3^- and NH_4^+ ions. Among the possible ionic products, sodium hydrogen carbonate, NaHCO_3 , has by far the lowest solubility in water and crystallizes out (solubility in moles/liter at 0°C : NaHCO_3 , 0.82; NH_4Cl , 5.5; NaCl, 6.1; NH_4HCO_3 , 1.5). The solubility of NaHCO_3 is lower at low temperatures, so the mixture is cooled to about 0°C to obtain the maximum product yield. The CO_2 for the process is made by heating limestone, CaCO_3 , with CaO formed as the other product. The NH_3 used is regenerated from the NH_4^+ ions present in the solution, by reaction with CaO. The final products of the first part of the process are NaHCO_3 and CaCl_2 . Sodium carbonate is then made from NaHCO_3 by heating the latter to about 300°C , where it decomposes. The key reactions in the overall Solvay process are summarized below:



Net reaction (sum of Reactions 1-7):

**Major Chemical Concepts**

Solubility, stoichiometry, thermodynamics

**LABORATORY
ACTIVITY:
TEACHER
NOTES**



Level

General or Basic

Expected Student Background

Students should be able to solve stoichiometry and solubility problems.

Time

Part I 45 to 55 min

Part II 35 to 45 min

Safety

Read the *Safety Considerations* in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

Part I. Preparation of NaHCO₃

12 Beakers, 600-mL

12 Gas collection bottles, 250-mL

12 Rubber tubing pieces

12 Test-tube clamps

12 Ringstands

12 Test-tubes, 25- x 300-mm

12 Stoppers, Size 2, two-hole

12 Stoppers, Size 6, one-hole

24 Glass tubing, 10 cm

12 Glass bends (A in Figure 1)

12 Lab towel

12 Bunsen valves (short piece of rubber tubing with 1 cm longitudinal slit with one end fitted with small piece of solid glass rod as a stopper)

Part II. Preparation of Na₂CO₃

12 Evaporating dishes

12 Burners

12 Ringstand, ring, wire gauze set-ups (for heating evaporating dish)

Consumables

3 M NH₃ solution, 1 L [dilute 200 mL conc. NH₃ (15 M) to 1 L]

Sodium chloride, NaCl, 240 g

Dry Ice, 2 lbs (available from grocery or ice cream stores)

Advance Preparation

Glass elbows must be prepared for the apparatus shown in Figure 1. Follow standard glass forming procedures. Heat the center of the glass tubing, slowly rotating it until it glows a yellow color and becomes flexible. Slowly bend until a right angle is formed. Fire polish all ends. Make sure that the glass tube extends to near the bottom of the test-tube (32 cm from end to bend).

Assemble the apparatus, including the Bunsen valve, as described in *Part I* of the procedure and shown in Figure 1.

Pre-Laboratory Discussion

Possible pre-laboratory discussion questions are:

1. What is the purpose of the Solvay process? [*To prepare Na₂CO₃*]
2. What raw materials are actually used up in the overall process? [*CaCO₃ and NaCl*]
3. What are the final products? [*Na₂CO₃ and CaCl₂*]
4. If 20 g of NaCl were dissolved in 60 mL 3 M NH₃, assuming 100% yield according to the Solvay process, how much NaHCO₃ would crystallize out of the final solution at 0 °C? Assume that NaCl is the limiting reactant, and that the solubility of NaHCO₃ is 0.82 moles per liter. (HINT: Moles NaCl = Moles NaHCO₃ produced; find moles NaHCO₃ remaining in solution and subtract from moles produced.) [*24.6 g NaHCO₃*]
5. In the reaction, 2NaHCO₃(s) → Na₂CO₃(s) + H₂O(g) + CO₂(g):
 - a. How many grams of Na₂CO₃ would be produced from 1.000 g NaHCO₃? [*0.631 g Na₂CO₃*]
 - b. How would the mass of Na₂CO₃ per gram NaHCO₃, as observed in your experiment, vary from the theoretical value if:
 - (1) The NaHCO₃ were wet when it was weighed? [*Lower mass of Na₂CO₃*]
 - (2) The NaHCO₃ contained NaCl as an impurity? [*Higher mass of Na₂CO₃*]

Teacher-Student Interaction

This activity provides an opportunity for students to perform a synthesis using common industrial substances. As the reaction bubbles, ask students why it takes so long before crystals of NaHCO₃ begin to form, and why it is necessary to rinse the crystals with water many times. The concepts of saturation and removal of impurities by differences in solubility can be amplified. In *Part II* students can be asked while heating NaHCO₃, why it changes to Na₂CO₃. Driving off water and CO₂ by heating is a common process both in the laboratory and in industry.

Anticipated Student Results

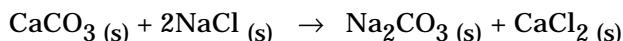
Mass of filter paper	1.1 g
Mass of filter paper + NaHCO ₃	21.1 g
Mass of NaHCO ₃ formed	20.0 g
Mass of evaporating dish	52.500 g
Mass of evaporating dish + NaHCO ₃	72.500 g
Mass of evaporating dish + Na ₂ CO ₃	64.500 g
Mass of NaHCO ₃ decomposed	20.000 g
Mass of Na ₂ CO ₃ produced	12.000 g

Answers to Data Analysis and Concept Development

1. Of all the compounds (NaHCO₃, NH₄Cl, NaCl, NH₄HCO₃) possible to make NaHCO₃ has the lowest solubility in water.



- The concentration of NaHCO_3 must exceed 0.82 mol/liter before solid NaHCO_3 will begin to appear. It also takes some time for the ammonia solution to cool down. The lower the temperature, the lower the solubility of NaHCO_3 .
- We need an indirect method of making Na_2CO_3 because the overall reaction shown is not spontaneous:



Answers to Implications and Applications

- 1.00 g NaHCO_3 x
$$\frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g NaHCO}_3} \times \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol NaHCO}_3} \times \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} = 0.631 \text{ g Na}_2\text{CO}_3$$
- 12.00g Na_2CO_3 / 20.00g NaHCO_3 = 0.600 g Na_2CO_3 per gram of NaHCO_3 .
- If the mass of Na_2CO_3 is too low possible errors include that NaHCO_3 was not dry when heating began, or that splattering occurred during the heating process. If the mass of Na_2CO_3 is too high possible errors include impurities in NaHCO_3 and not heating NaHCO_3 long enough to drive off all water and CO_2 .

Post-Laboratory Activities

Discussion might center around whether the majority of the class has larger or smaller masses of Na_2CO_3 than expected and what could have been done to increase the yield.

Extension

Some students may want to research how sodium bicarbonate and sodium carbonate are made industrially, what quantities are produced annually, and what are their major industrial uses.

Assessing Laboratory Learning

- If 5.00 g of NaCl is dissolved in 60.0 mL of 3 M NH_3 , how much NaHCO_3 will crystallize out of the final solution at 0°C after CO_2 has been bubbled through. The molar solubility of NaHCO_3 is 0.82 mole/liter. [3.05 g]
- If 7.05 g of NaHCO_3 is recovered, what is the percent yield of NaHCO_3 ? [7.05g/6.83g x 100 = 103%]
- Which experimental errors could be responsible for this percent yield:
 - The temperature of the ammonia solution is above 0 °C?
 - The NaHCO_3 was weighed while it was still wet?
 - There were impurities in the NaHCO_3 ?
 - Some NaHCO_3 was lost in the filtration process?

Answer: [b, c]

References

This activity is adapted from Slowinski, E. J., Wolsey, W. C., and Masterton, W. J. (1984). *Chemical principles in the laboratory (3rd Ed.)*, pp. 85-91. Philadelphia, PA: CBS College Publishing, Saunders College Publishing. Background information is found in *Chemical Technology: An Encyclopedic Treatment*, 1968; Faith, Keyes, and Clark's *Industrial Chemicals*, 1975; and *Kirk-Othmer Encyclopedia of Chemical Technology*, 1978-84 (in References).

CAUTION: Use appropriate safety guidelines in performing demonstrations.

DEMONSTRATIONS

Demonstration 1: Reaction of Metals with Acid and Base

Purpose

To illustrate the reactions of metals with acid and base.

Materials

6 Test-tubes
 6 M Hydrochloric acid, HCl, 100 mL (50 mL 12 M HCl diluted to 100 mL)
 25% Sodium hydroxide, NaOH (dissolve 25 g NaOH in 75 g water)
 Aluminum (in small pieces, aluminum foil can be used)
 Iron filings (or small pieces of iron)
 Copper (copper wire or copper tubing can be used)

Safety

Use care in handling the acid and base solutions. Be careful that the mouth of the test-tube is directed away from all people to avoid injury if bumping of the solution occurs during heating.

Procedure

Add 6 M HCl to half-fill three test-tubes. Add 25% NaOH to half-fill the remaining three test-tubes. Add a few iron filings to a tube containing acid and observe. If the reaction is too slow, the tube can be heated gently. [*Iron dissolves as is evidenced by coloration of the acid and formation of bubbles of hydrogen gas.*] Then add a few iron filings to a tube containing the base and observe. When no reaction is observed, the tube can be heated gently. [*No reaction should occur. Heating should have no effect.*] Repeat for copper and aluminum. [*Aluminum and iron should dissolve in acid with evolution of hydrogen gas. Only aluminum will dissolve in base. You may have to heat to observe the reaction, depending on the size of aluminum pieces.*]

Remarks

This demonstration illustrates the amphoteric nature of aluminum. It can be used to explain why aluminum is not a good container to use for highly basic substances. Drano™ contains a mixture of NaOH and aluminum, which react in the drain to generate large amounts of heat and hydrogen gas, causing the “gurgling” action that breaks up clogs in drains. The NaOH is also effective in reacting with fats to “make soap” if greasy foods comprise the mixture clogging the drain. Since many fertilizers contain acidic substances, metal containers should not be used to store fertilizers. Also it is important to wash buckets (galvanized pails are zinc coated) if they are used to transport fertilizer. Although copper will not react with acids, copper alloys (e.g., brass and bronze) contain metals (brass: copper and zinc; bronze: copper and tin and/or other metals such as lead, zinc, aluminum) that do react with acid.

Demonstration 2: Brown Bottle Reaction

Purpose

This demonstration illustrates reactions involved in the synthesis of nitric acid (Ostwald Process).

Materials

Gas generating apparatus (side-arm flask with stopper or Erlenmeyer flask and one-hole stopper fitted with glass tube, rubber tubing, pneumatic trough or plastic tray—see diagram)
 Bottle or flask (for collecting NO) with stopper, 200-300 mL



Copper wire, 1-2 g is probably sufficient (or penny minted before 1982)
Nitric acid, HNO₃, concentrated
Litmus paper, red and blue
Glass plate, 3" x 3"

Safety

Oxides of nitrogen are toxic. This demonstration should be done in a hood. Be careful not to spill HNO₃ on your skin. Concentrated nitric acid can cause severe burns. Nitric acid reacts with skin to produce yellow stains.

Procedure

Set up the gas generating apparatus as shown in Figure 2 to collect NO (nitrogen monoxide) over water.

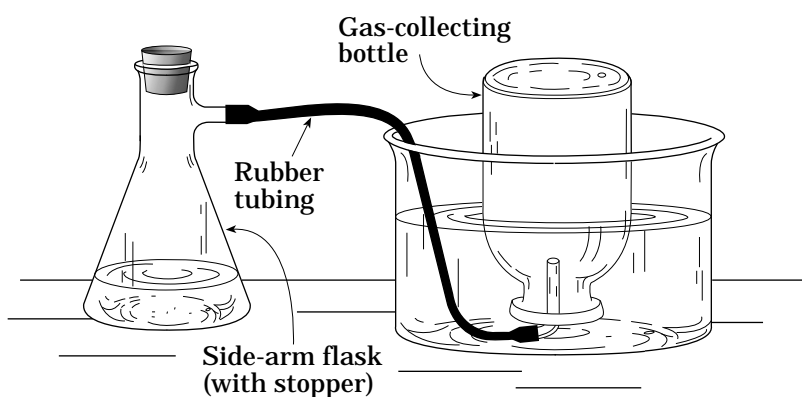


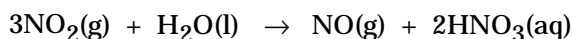
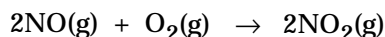
Figure 2. Gas generating apparatus.

Fill the collection bottle with water, cover with glass plate and invert in the pneumatic trough so that the neck of the bottle is below the surface of the water. Remove the glass plate. Place the delivery tube into the collection bottle. Place the copper in the side-arm flask. Add about 5 mL concentrated nitric acid and quickly stopper the flask. The reaction will generate NO. When the bottle is full of NO (colorless gas, but may be slightly colored due to presence of NO₂), remove the bottle and quickly stopper it. [A small amount of water should remain in the bottle. In removing the bottle and stoppering it, enough O₂ will be admitted

to oxidize NO to NO₂ (nitrogen dioxide), and the gas in the bottle should turn red-brown due to NO₂.] Shake the bottle and the color disappears as NO₂ dissolves in water. Open the bottle to air briefly and usually enough NO remains to see the color change to red-brown again. Again stopper the bottle and shake until the color disappears. Drop a piece of blue litmus paper into the water in the bottom of the bottle and observe the color change to red (indicating that an acid has been formed). Red litmus should not change color.

Remarks

This demonstration simulates part of the Ostwald Process for formation of nitric acid. Equations for reactions taking place are:



Discuss the Ostwald process and the commercial importance of nitric acid in conjunction with this demonstration. *NOTE: NO is generated by the oxidation of NH₃ in the Ostwald process (see Biogeochemical Cycles module).*

Demonstration 3: Electrolysis of Aqueous CuCl

Purpose

Electrolysis is used in the industrial preparation and purification of metals and other substances. This demonstration illustrates the electrolytic preparation of copper by reduction of Cu²⁺ in CuCl₂(aq).

Materials

- Beaker
- 9-V Battery and clip
- 2 Pencils
- 2 Wires with alligator clamps on each end (for connecting battery to pencils)
- 0.1 M Copper(II) chloride, CuCl_2 (1.3 g CuCl_2 or 1.7 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 mL solution)

Safety

Observe the usual safety precautions for handling solutions. Properly dispose of the CuCl_2 solution. Since Cl_2 is formed at the anode, the electrolysis should not be allowed to proceed for lengthy time periods unless it is done in a hood. Avoid contact with the closed electrical circuit or with electrical connections before completing the circuit.

Procedure

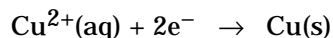
Set up the electrolysis apparatus as shown in Figure 3. The U-tube can be taped to an inverted cup that serves as a stand. Place the copper chloride solution in the U-tube. Sharpen the pencils (or otherwise expose the graphite) on **both** ends. Using the alligator clamp, attach a wire to one end of each pencil. Immerse the other end of the pencil in the copper chloride solution placing one pencil in each arm of the U-tube. Attach the wires to the electrodes of the battery.

Electrolyze the copper chloride solution until the color begins to fade and Cu(s) begins to form on one electrode (a red copper-colored coating will be visible when the pencil is removed from the solution.)

Remarks

Mechanical pencil “lead” can be used instead of pencils for the electrodes. Attach alligator clamps to one end of the “lead”. Immerse the other end in the solution. Failure to react could be due to microfractures in the pencil “lead.”

Electrolysis of CuCl_2 will produce copper metal at the cathode. The reduction reaction is:



The fading of the blue color is due to the removal of Cu^{2+} ions from the solution as Cu^{2+} is reduced. (The anode reaction produces chlorine. The odor of chlorine can be detected at the anode. This reaction is not pertinent to the purpose of this demonstration, but could be mentioned.)

Although copper is not produced electrolytically, metallurgy of reactive metals such as magnesium and sodium requires electrolysis to obtain the uncombined element. Copper is purified by electrolysis. Impure copper is the anode while pure copper is used for the cathode. During the electrolysis, copper dissolves at the anode and by carefully controlling the electrical potential pure copper is redeposited at the cathode. Other metallic impurities that are less easily oxidized than copper fall to the bottom of the container during electrolysis. This residue is the anode sludge. In copper purification, the anode sludge can contain such precious metals as silver and gold. Sometimes recovery of these metals can actually pay for the electricity required for the purification.

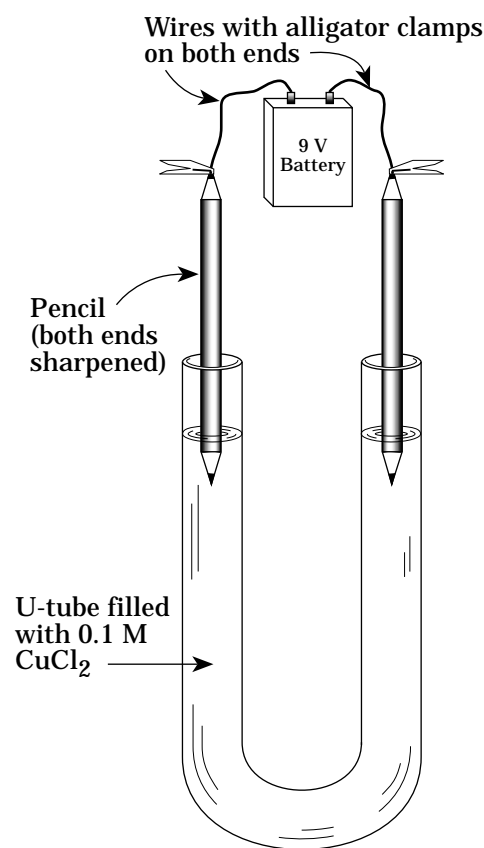


Figure 3. Electrolysis apparatus.



Demonstration 4: Properties of Fertilizers

Purpose

To illustrate conductivity and pH of fertilizers.

Materials

Fertilizer samples (such as 8-8-8, “plant food”)
Distilled water
Conductivity apparatus (see *Instrumentation* section)
pH paper or pH meter

Procedure

“Dissolve” a spoonful of fertilizer in 50 mL distilled water. Observe that many commercial fertilizers (such as 8-8-8) are not completely soluble in water. Test for electrolytes by observing conductivity of the solution. Test solution pH using pH paper or a pH meter.

Safety

Observe the usual safety precautions for handling substances.

Remarks

This demonstration leads to discussing differences in fertilizer composition. Fertilizers such as 8-8-8 could be added to water in the same proportions as plant foods or you could simply add “a spoonful” to a small beaker (50 mL) of water. This is a qualitative demonstration and is intended only to illustrate that fertilizers are not neutral and that they are generally conductors because they contain soluble ionic substances. In addition to fertilizers, lime (calcium oxide, CaO) could also be tested.

Extensions

Qualitative tests for several ions could be performed on the fertilizers. Most fertilizers will contain nitrate and phosphate ions. Many also contain calcium and ammonium ions. Plant foods formulated for house plants frequently contain many ions. Read the label to see which ions are present and experiment to see which ones will give “good” tests with your fertilizer sample (see *Inorganic Qualitative Analysis* module or a standard text on qualitative analysis for reagents needed to test for these ions).

Demonstration 5: Soil pH

Part A. Measurement of Soil pH

Purpose

This demonstration illustrates the measurement of soil pH.

Materials

Beaker, 50 mL
Soil sample(s)
Distilled water
pH meter (calibrated with buffers of known pH)

Safety

Use normal safety precautions.

Procedure

Place 10 g of a soil sample in a 50-mL beaker. Add distilled water to form a soft paste. Stir several times during a 30 min period. After 30 min, measure the pH with a calibrated pH meter.

Remarks

This is one method used to measure soil pH. (Usually the soil sample would undergo careful mixing to insure uniformity and would be sieved to remove large particles such as gravel. This could be done if a sieve is available or large particles could be removed upon inspection of the sample.) The pH of the soil is used to determine whether lime needs to be added before growing crops that do not thrive in soils of low pH. If possible, it would be helpful to measure the pH of several soil samples of different types to show how soil pH varies. Students could be asked to bring a sample of soil for measurement. This demonstration could be expanded to a student activity, if desired.

Part B. Reserve vs. Active Acidity of Soils*Purpose*

Soils contain “free” H^+ ions (active acidity) and H^+ ions that can be released by ion exchange (reserve acidity). This demonstration illustrates a method of measuring both types of acidity.

Materials

Filter paper
2 Funnels
2 Beakers, 50-mL
Soil sample(s)
Distilled water
pH meter (calibrated with buffers of known pH)
0.2 M Potassium nitrate, KNO_3 , 20 mL (0.4 g KNO_3 in 20 mL aqueous solution)
Supports for funnels

Safety

Use normal safety precautions.

Procedure

Fold filter paper in fourths and place in funnel. Moisten the filter paper with distilled H_2O and press firmly against the funnel. Add 10 g of soil to each. *Slowly* pour 20 mL of distilled water through one sample and collect the filtrate in a 50-mL beaker. *Slowly* pour 20 mL of 0.2 M KNO_3 through the second sample and collect the filtrate. Measure the pH of both solutions, being careful to rinse the electrode between measurements.

Remarks

Some of the hydrogen ions in the soil are not ionizable when the soil is simply wet with water; however, they can be removed by ion exchange. When the potassium ion replaces these hydrogen ions, they contribute to the acidity of the soil. The pH may be lower in the sample that was extracted with potassium nitrate. (Potassium nitrate solution should be neutral if distilled water is used to prepare the solution. You may want to prepare additional 0.2 M KNO_3 so you can measure the pH of the KNO_3 solution to demonstrate that the effect is not due to the potassium nitrate.)

Reference

See Jacobs *et al.*, 1971, in *References* section.

Other Demonstration Ideas**The Can Ripper**

An aluminum can is weakened by treatment with 0.1 M $CuCl_2$ so that it can be torn apart (see directions in the *Group and Discussion Activities* section of the *Oxidation-Reduction* module).

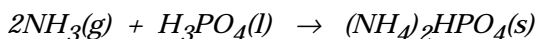
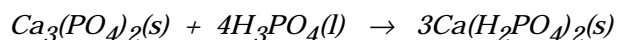
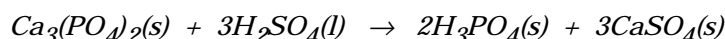
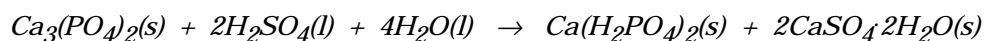
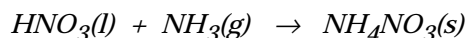
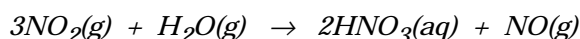
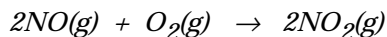
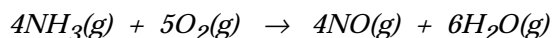
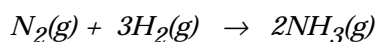


GROUP AND DISCUSSION ACTIVITIES

Key Questions

Key questions for this module will depend upon the emphasis you choose. Suggested questions include:

1. Give the reaction(s) used in some important commercial processes. *[Responses to this question will vary depending upon the processes you discuss. See Background Notes for suggestions.]*
2. List some of the chemicals produced in largest quantity worldwide. *[The list of the top chemicals is given in the Appendix. Of those, the ones discussed in the background material for this module include H_2SO_4 , NH_3 , HNO_3 .]*
3. What are some important commercial reactions used in the production of fertilizers? *[Responses may vary. Some of the major reactions include:]*



4. Why does the production of aluminum require the use of electricity while carbon (usually in the form of coke) is used in the production of iron? *[Aluminum is much more easily oxidized than iron; thus, it requires a stronger reducing agent. The only chemical reducing agents that will reduce aluminum (e.g., Mg, Na, etc.) also require electricity in their production; thus, it is more practical to produce aluminum directly.]*
5. List some important steps in scaling up from laboratory (bench) scale to industrial scale. *[First the most favorable conditions are sought on the laboratory scale. Then the reaction is tried in a small-sized model of the industrial process. After optimizing conditions on a small scale, the process is tried in a large-sized or developmental unit. The next step is the semi-commercial plant scale and finally the full-scale commercial plant. At any step the reaction may prove to be "unworkable" and require further investigation to find more suitable conditions (perhaps a different catalyst or different temperature or pressure) or even require substituting another reaction to achieve the desired product.]*

Counterintuitive Examples

A bottle of NO containing a small amount of water will develop a red color when the bottle is briefly opened to the air. Shaking the bottle causes the color to disappear. This reaction is involved in the commercial process for nitric acid production (Ostwald process; see *Demonstration 2: Brown Bottle Demonstration*).

Analogies and Metaphors

The human body is sometimes described as a chemical manufacturing plant. Many chemicals are produced from “raw materials” in the body. For example, complex carbohydrates are broken up into simple sugars, which are in turn metabolized to CO_2 and H_2O with the generation of energy. Proteins are decomposed into amino acids and then reassembled to form tissue. (Students may study some of these reactions in biology courses. For an elementary discussion some of these reactions, refer to an introductory college chemistry text designed for allied health students.)

Pictures in the Mind

In the Frasch process three concentric pipes are inserted into a hole drilled down to the sulfur deposit. Superheated water is forced down the outer pipe into the sulfur, causing it to melt. Molten sulfur is then forced up the middle pipe by compressed air.

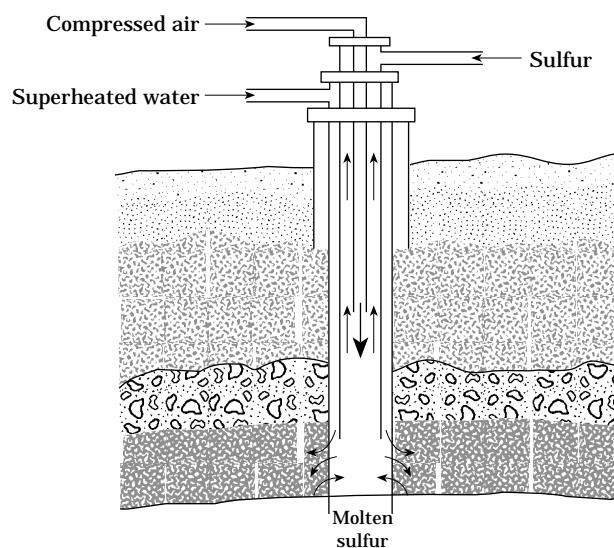


Figure 4. The Frasch process.

Background Notes

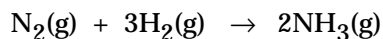
Industrial chemistry includes a broad range of manufacturing processes including petroleum refining, preparation of metals from their ores (metallurgy), and production of pharmaceuticals. Industrial chemistry is a broad field, and the discussion in this module is restricted to industrial processes associated with the production of synthetic inorganic fertilizers and the preparation of aluminum from bauxite ore as representative industrial processes. Other commercial processes are discussed in the modules on *Alkali Metals* (Solvay process for sodium carbonate) and *Chemistry in Medicine* (synthesis of aspirin).

The principal ingredients of inorganic (or mineral) fertilizers furnish the elements nitrogen, phosphorus, and potassium in forms that can be utilized by plants. The analysis (or grade) of inorganic fertilizers is expressed as % N, % P (as P_2O_5), and % K (as K_2O). If a fertilizer contains only one of these essential elements, it is referred to as a straight fertilizer. If it contains all three elements, it is said to be a complete fertilizer. Although the nitrogen in mineral fertilizers is generally in the form of ammonium or nitrate salts, anhydrous ammonia, and urea are also used as straight nitrogen fertilizers. The principal substance used as a source of phosphorus is $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Potassium is generally present as potassium chloride (muriate of potash).

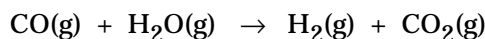
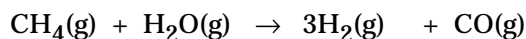
TIPS FOR THE TEACHER



Ammonia is prepared by the Haber-Bosch process, developed by Fritz Haber and adapted for industrial-scale use by Carl Bosch in 1913 (see *History*). Nitrogen from the air is reacted with hydrogen at elevated temperatures (500-700 °C) and high pressures (about 200 atm) in the presence of a mixed Fe₃O₄-Mn catalyst.



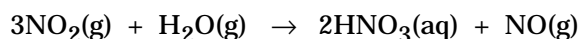
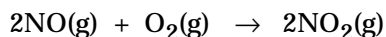
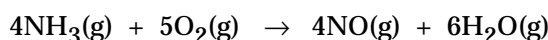
The hydrogen needed for the reaction is usually produced by steam reforming, the reaction of steam with natural gas (methane, CH₄) or petroleum products such as propane (C₃H₈) using an iron oxide-chromium oxide catalyst.



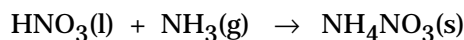
These processes tie the cost of fertilizer production, and hence the cost of food production, to the cost of petroleum and natural gas (see *History*).

The largest single use for ammonia is direct application of anhydrous ammonia as a fertilizer. There are several advantages of using anhydrous ammonia as a fertilizer, such as the ability to apply it prior to or after planting. Anhydrous ammonia combines with clay and organic matter to resist leaching loss, a significant problem with nitrate fertilizers.

Because anhydrous ammonia requires special equipment to apply, solid fertilizers are desirable. One such fertilizer can be prepared by oxidation of ammonia to nitric acid followed by reaction of the resultant nitric acid with ammonia to form ammonium nitrate. Almost all the nitric acid commercially produced is prepared by the Ostwald process. Ammonia is oxidized in air over a platinum catalyst at 850 °C and atmospheric pressure to form nitrogen monoxide (nitric oxide, NO), which is further oxidized to NO₂ by reaction with oxygen. Reaction of NO₂ with water produces nitric acid and NO, which is recycled to produce more nitric acid.

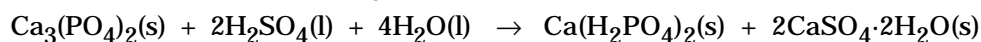


The largest use for nitric acid is in the manufacture of ammonium nitrate for fertilizers.



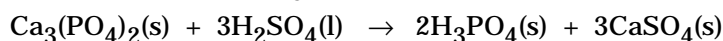
The other major use for nitric acid is in making explosives.

Phosphorus fertilizers are generally prepared by the reaction of sulfuric acid with phosphate rock, principally Ca₃(PO₄)₂.

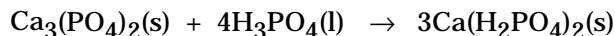


Although Ca₃(PO₄)₂ can be used directly as a phosphate fertilizer, its limited solubility renders it marginally effective. Reaction of phosphate rock with sulfuric acid produces Ca(H₂PO₄)₂, which is soluble and hence a more effective phosphorus fertilizer. The mixture of Ca(H₂PO₄)₂ and CaSO₄·2H₂O formed by the above reaction is known as “superphosphate”.

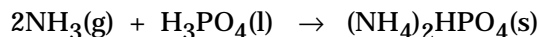
Currently, 85% of the fertilizer phosphate produced in the U.S. is based on phosphoric acid. Rather than producing a mixture of Ca(H₂PO₄)₂ and CaSO₄·2H₂O, additional sulfuric acid is added to produce H₃PO₄.



The phosphoric acid produced by this method is known as “wet-process” phosphoric acid and is contaminated with impurities from the phosphate rock. Usually these impurities do not significantly affect the use of the acid in fertilizer production. If “wet-process” phosphoric acid (instead of sulfuric acid) is added to phosphate rock, “triple superphosphate” is produced.



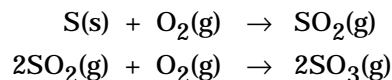
“Wet process” phosphoric acid is also used to prepare $(\text{NH}_4)_2\text{HPO}_4$, diammonium hydrogen phosphate or DAP, by direct reaction of ammonia and phosphoric acid.



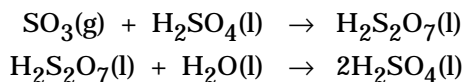
In 1977, 64% of the phosphate fertilizer used in the U.S. was diammonium hydrogen phosphate.

Sulfuric acid, required for the production of “wet-process” phosphoric acid and “superphosphate”, is the chemical produced in largest quantity world-wide. Until recently, sulfuric acid production was used as a measure of the economic strength of a nation. Because of its extensive use in the production of phosphate fertilizers (2/3 of the annual production is used for this purpose), and because large quantities of phosphate fertilizers are produced in eastern Europe and other countries lacking other industries, sulfuric acid production is no longer an accurate measure of the economy.

In the production of sulfuric acid, sulfur is reacted with oxygen from the air in the presence of a V_2O_5 catalyst at 410-430 °C to form SO_3 .



SO_3 reacts with sulfuric acid to form pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$. Pyrosulfuric acid is reacted with water to form sulfuric acid.



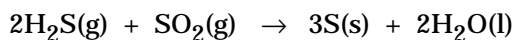
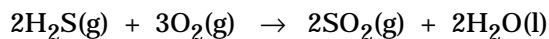
This indirect method of reaction of SO_3 with water is used because the amount of heat generated in the process is extremely large. (Also SO_3 is not very soluble in water.) The two-step process facilitates the dissipation of heat. The large quantity of thermal energy accompanying the reaction may be used to produce steam for the generation of power via turbines. This synthesis for sulfuric acid is known as the Contact process.

Sulfuric acid is used in many industrial processes in addition to fertilizer production. It is used extensively in the manufacture of other substances as well as in the paper industry. Over 70% of the sulfuric acid produced annually is used directly by the producers to make other materials. Because production costs are small compared to shipping costs, most sulfuric acid is produced close to the site of use.

More than 85% of the sulfur consumed worldwide is converted to sulfuric acid. The sulfur required for the Contact process is obtained from two principal sources. Formerly most sulfur was obtained from native sulfur deposits and was mined by the Frasch process. In the Frasch process, three concentric pipes are drilled to the level of the sulfur deposit. Superheated water at 160 °C is forced down the outer pipe. The hot water melts the sulfur. Compressed air is forced down the center pipe. The compressed air mixes with the water-sulfur slurry, aerating the liquid sulfur and causing it to rise to the surface through the middle pipe (see diagram in *Pictures in the Mind*). The sulfur thus obtained is a liquid and is usually shipped as a liquid (rather than solid). In 1980, the output of sulfur by the Frasch process was about 8.1 million tons.



Currently about half of the world's elemental sulfur production is recovered sulfur. Most of the recovered sulfur is obtained from "sour" natural gas and petroleum by the Claus process. "Sour" natural gas contains hydrogen sulfide (or organic sulfides) which on burning produces SO_2 , a primary air pollutant. Thus, the Claus process serves two purposes: to reduce pollution that would result from combustion of the untreated gas and to produce sulfur. The principal reactions in the Claus process are:

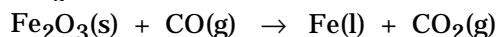


These reactions are carried out at atmospheric pressure in the presence of a bauxite (aluminum oxide) catalyst.

In addition to nitrogen and phosphorus, the third major element in fertilizers is potassium. About 90% of potassium fertilizer is potassium chloride, KCl. Prior to 1965, New Mexico furnished most of the KCl used in fertilizers. Today KCl is mined extensively in Canada. Several methods of purification are used to concentrate the potassium chloride and remove undesirable impurities, principally NaCl. One of these is the "thermal method". At 100°C , KCl is more soluble than NaCl in a saturated KCl/NaCl solution while at 30°C , NaCl is more soluble. (At 100°C , the mass percent solubility of KCl in saturated KCl/NaCl is 21.65% while the solubility of NaCl is 16.90%. At 30°C , the mass percent solubility of KCl in saturated KCl/NaCl is 11.70% while the solubility of NaCl is 20.25%.) Advantage is taken of this difference in solubility to separate the two substances. The disadvantage of fractional crystallization is the high energy requirement. For this reason other methods of separation are more commonly used today.

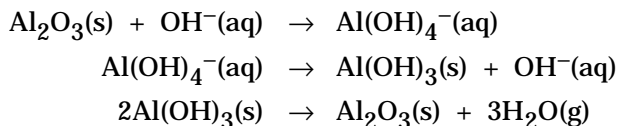
In addition to the primary elements found in fertilizers (N, P, and K), the secondary elements Ca, Mg, and S as well as micronutrients (*e.g.*, Fe, Mn, Mo, and B) are needed for plant growth. "Lime", usually in the form of CaCO_3 , is frequently applied to acid soils to raise the pH and is a source of calcium. Dolomitic limestone (a mixture of CaCO_3 and MgCO_3) is a source of both Ca and Mg. Sulfate salts, including superphosphate, are sources of sulfur for soils deficient in this element. Micronutrients are also added to fertilizers to improve plant growth.

Metallurgy, extraction of metals from their ores, is an important facet of industrial chemistry. There are several general methods used in the production of metals from their ores. All involve the reduction of metal compounds, since very few metals are found free (uncombined) in nature. The most reactive metals require electrolytic reduction, whereas, less reactive metals may be reduced chemically by such reducing agents as C, CO, or H_2 . Because C is inexpensive and readily available (as coke), carbon is used directly or partially oxidized to CO and reacted with metal oxides at high temperatures to form CO_2 and the free molten metal. Iron is produced by this method.

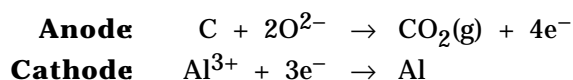


Some metals, such as cobalt, germanium, and tungsten, are reduced chemically by hydrogen to give the metal. As mentioned above, hydrogen is produced from natural gas and petroleum products, a more expensive process than carbon reduction used only if less expensive reducing agents are unavailable or if undesirable products result when other reduction methods are used.

The more reactive metals, such as aluminum and the alkali and alkaline earth metals, must be produced electrolytically. Bauxite, the principal aluminum ore, contains hydrated aluminum oxide. Impurities are removed from the ore by dissolution of Al_2O_3 in NaOH, dilution to precipitate $\text{Al}(\text{OH})_3$, and dehydration to Al_2O_3 .



Aluminum is produced by the electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6 (cryolite) using carbon electrodes. The electrode reactions are:



(Note that the carbon anode is consumed during electrolysis.) This process for the production of aluminum was developed independently by Charles Hall in the United States and Paul-Louis Héroult in France in 1886 (see *History*).

Because of the expense of using electricity in aluminum production and the fact that aluminum does not readily oxidize like iron on exposure to air, extensive efforts are being made to recycle aluminum. The cost of recycling aluminum is 5% of the cost of producing aluminum from bauxite ore. This fact has led to a significant increase in the recycling of aluminum. In 1972, only 15.4% of the aluminum beverage cans produced were recycled. By 1982, 55.5% of the aluminum beverage cans produced were recycled. Aluminum is also reclaimed from automobile parts and construction materials.

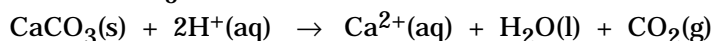
A discussion of industrial chemistry must include reference to the distinction between chemical reactions as carried out in the laboratory and industrial processes. Prior to 1900, most industrial processes were “batch” processes involving the same reactions used in the laboratory, but on a larger scale using larger containers. When a reaction is carried out on a large scale sometimes the course of the reaction is changed by introducing different conditions, such as the generation of excessive quantities of heat that is not effectively dissipated because of poor heat exchange or altering the rate of reaction, making a batch process impractical. Sometimes the starting materials for laboratory-scale reactions are too expensive to be practical industrially, but different, less-expensive raw materials can be used to prepare the desired product using a different reaction. This different reaction may involve more steps or reaction conditions that are impractical in the laboratory, but economic considerations are the driving force in selection of processes for industrial chemical syntheses. Today most industrial processes are continuous or semi-continuous, many being carried out under much different conditions and generally employing a different reaction from those a chemist would use in the laboratory. The continuous process has contributed to reduction in cost of many chemicals and has increased large scale synthesis of many important chemicals.

In “scaling up” from laboratory scale to commercial scale several steps are required. After the reaction conditions have been optimized on the laboratory scale, the reaction is tried in a small-sized model of the industrial process. After this, a large-sized or developmental unit is utilized to optimize reaction conditions. The process is then ready for semi-commercial plant scale and finally is adapted for the full-scale commercial plant. Computer simulation is used for modeling the process as a means of predicting potential problem areas. Computer modeling also assists in designing the lay-out and control systems for large-scale plants. Throughout the process of scaling up, the industrial chemist works closely with engineers to monitor production and product quality. Frequently, reactions that occur readily and with good yield on a laboratory level must be significantly modified for industrial-scale conditions. Sometimes the reaction itself must be modified or a completely different reaction used. Sometimes the reaction conditions or plant design can be adapted. In either case, a knowledge of chemistry as well as the principles of engineering is essential to the development of a successful industrial process.

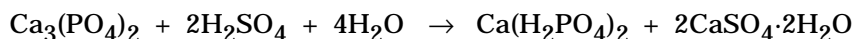


Language of Chemistry

1. Historically lime meant calcium oxide, CaO (also called “quicklime” or “burned lime”). Slaked lime (or “hydrated lime”) refers to calcium hydroxide, Ca(OH)₂. In the fertilizer industry, lime is used to refer to both of these substances and to other calcium or magnesium salts of weak acids, such as calcium carbonate, CaCO₃:



2. “Sour” petroleum or natural gas contains H₂S or sulfur-containing hydrocarbons.
3. Superphosphate (sometimes called superphosphate of lime) is a mixture of Ca(H₂PO₄)₂ and CaSO₄·2H₂O formed by the reaction:



4. Triple superphosphate (sometimes called triple superphosphate of lime) is Ca(H₂PO₄)₂ formed by the reaction:



Names of relevant commercial processes:

5. In the Claus process, sulfur is produced by oxidation of H₂S in “sour” natural gas and petroleum products.
6. In the Contact process for sulfuric acid, SO₂ is oxidized to SO₃ in the presence of V₂O₅ catalyst. SO₃ is dissolved in H₂SO₄ and the resulting H₂S₂O₇ is hydrolyzed or diluted to produce H₂SO₄.
7. The Frasch process is one method of obtaining sulfur from native deposits. Super-heated water and compressed air are forced into the underground deposit to melt the sulfur and bring it to the surface, where it is collected in almost pure form.
8. The catalyzed reaction of nitrogen and hydrogen to produce ammonia at high pressure (200 atm) and temperature (500 °C) is known as the Haber-Bosch process.
9. The Hall process is an electrolytic method for production of Al from bauxite (Al₂O₃·2H₂O). After a pretreatment process to remove some impurities such as iron compounds, Al₂O₃ dissolved in Na₃AlF₆ is electrolyzed between carbon electrodes to produce Al and O₂, which reacts with the carbon anode to produce CO and CO₂.
10. In the Ostwald process, nitric acid is made by the oxidation of NH₃ to NO followed by oxidation of NO to NO₂ and dissolution of NO₂ in water to give HNO₃.

Common Student Misconceptions

1. **“Algal bloom from fertilizer run-off produces oxygen.”**

Actually algal bloom from fertilizer run-off reduces the oxygen content of the water rather than enhances it (as expected, since algae produce O₂ by photosynthesis). The algae block sunlight to plants below them. These plants and the organisms that depend on them die and decay. This increase in decay uses O₂ at a faster rate than the algae can produce it.

2. **“The main use of NH₃ is in household cleaners (or maybe chemistry laboratories).”**

Most ammonia is used in the fertilizer industry; however, there are many industrial uses for NH₃. Use of ammonia in household cleaners constitutes a very minor use for ammonia.

3. **“Most of the H_2SO_4 produced industrially is used in chemistry laboratories.”**

H_2SO_4 is one of the most important industrial chemicals and is used in the fertilizer industry as well as in other commercial processes. (Examples are the paper industry, paints and pigments, refineries, metal plants, *etc.*)

4. **“The use of fertilizers is ‘bad’.”**

Although ‘organic gardening’ has increased and new farming methods are being developed and encouraged that utilize “natural fertilizers” (*e.g.*, no-till farming), the world’s food needs cannot presently be met without the use of commercial fertilizers. It is important to emphasize the close link between food production and the use of commercial fertilizers.

5. **“All industries are big contributors to pollution.”**

Most industries try to work out chemical reactions and production protocols for the least polluting method.

6. **“Chemical industries are an unsafe environment in which to work.”**

Chemical industries have a high safety record. Working in the chemical industry is no more dangerous than in any other industry.

Problem Solving

1. This is a good place to review balancing equations, stoichiometry, equilibrium, *etc.* It is important to emphasize the relationship of chemistry to other disciplines in discussing this material with students.
2. This fictitious case history illustrates the impact of chemistry on society by outlining the factors to be considered in locating an industry: lead smelting.

Problem

Imagine that you are the managing director of a chemical firm that extracts lead metal from its ore, lead sulfide (galena). A new smelter is to be built in the small coastal town of Plumbton, and a number of sites, lettered A to E on the map (shown at the end), have been proposed by the local council.

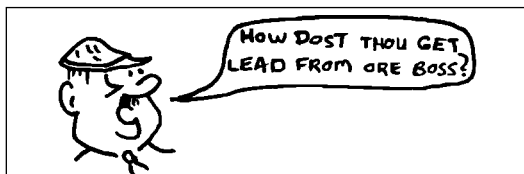
What are the good and bad points of each site? As managing director, which site would you choose? To help you arrive at a decision, an information sheet about Plumbton and lead smelting is given that must be completed first.





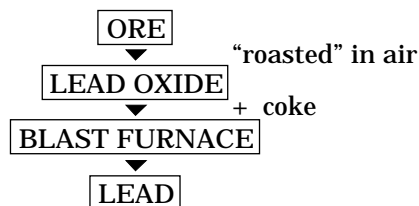
Plumbton

Plumbton is a coastal town with a population of 60,000 situated in an area of outstanding natural beauty. In the recent past, its main industry was fishing, and it is still well known for its oysters. More recently tourists have provided most of the town's employment, but this is only seasonal, and the town's unemployment figures are 10% above the national average. The only light industry is a small factory manufacturing lead-acid car batteries.



Lead Smelting

In this process, lead sulfide (the ore galena) is changed into lead oxide by heating strongly in plenty of air ("roasting" it with plenty of oxygen). Lead metal is obtained from lead oxide by a process of reduction similar to that used in the extraction of iron. The lead oxide is mixed with carbon in the form of coke and heated in a current of hot air in a blast furnace.



Write out and answer the following questions:

1. What is the common name of the ore from which lead is extracted?
[Galena]
2. Write an equation to show what happens when the ore is roasted.
 $[2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)]$
3. Name the waste product formed in this reaction. [Sulfur dioxide gas]
4. What is meant by the word *reduction*? [Gain of electrons]
5. Write an equation to show how the lead oxide is reduced.
 $[2PbO(s) + C(s) \rightarrow 2Pb(s) + CO_2(g)]$
6. What is the reducing agent in this reaction? [Coke, C]
7. What is the waste product in this reaction? [$CO_2(g)$]

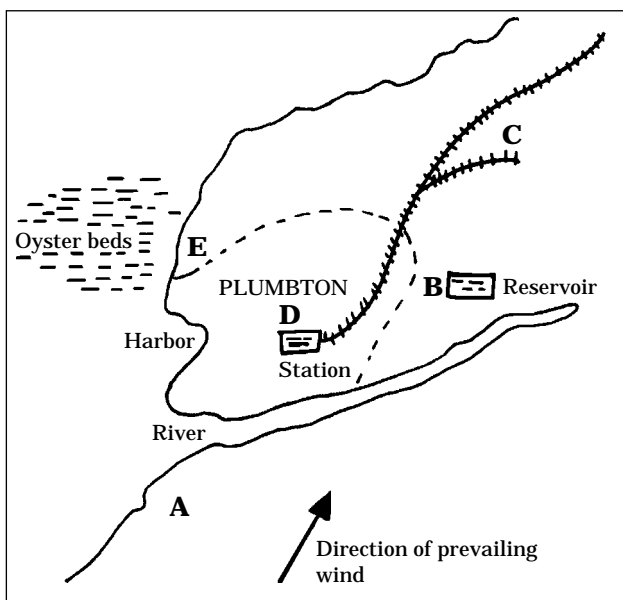
As well as the waste products listed above, there is also solid waste called *slag* that has to be disposed of by the company.

Points to Consider

1. Society needs lead (to make lead-acid batteries, for example).
2. Profit and employment
3. Transport ... large amounts (about one million tons) of galena and coke will have to be brought into the town by rail or boat, and similarly the lead will have to leave the town.
4. Nearness to the town...
 - a. for convenience of the work force, but
 - b. an industrial site within an urban area may disturb local residents.

5. Removal of *all* waste products.
6. Pollution. Lead is a poisonous element. There will be some lead in the solid waste, and despite strict controls some lead may escape into the atmosphere from the blast furnace; this may combine with other gases in the atmosphere and rainwater, thus entering streams, the river, and the sea.

Oysters do not suffer from lead poisoning but can store large quantities of lead in their bodies. Humans can take in lead directly from the atmosphere or by eating contaminated food.



Study the map and the points to consider when choosing a site; then complete the following table in your notebook.

SITE	ADVANTAGES (for)	DISADVANTAGES (against)

As managing director, which site would you choose? [C]

Why? [Site C is upwind from the town.]

What other factors would you take into account? [If Site C is higher elevation than the town, contamination of the water table could occur.]

CHEM 13 NEWS, December 1980, p. 10.



Decision Making

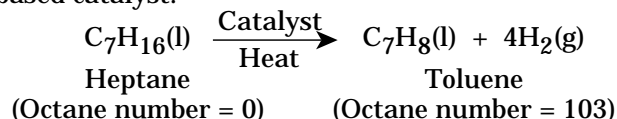
Students can assume they are managers in a chemical manufacturing plant and discuss factors to be considered in their responsibilities to their employer and society. Factors include: alternative manufacturing processes (different chemical reactions with different starting materials to produce the same product—stoichiometry and energy consumption as well as economics are important issues here), source and consumption of raw materials (including possible exploitation of natural resources of underdeveloped nations), pollution and waste disposal and public health issues. Students should be guided to see that there is not a simple “right answer.” As with other decisions in our lives there are tradeoffs. As responsible citizens, we must make informed decisions concerning complex issues. The study of chemistry helps us prepare to make those decisions.

Pollution problems, waste disposal problems, *etc.*, facing our communities and nations are linked to consumer use of chemical products (*e.g.*, fertilizer run off, waste water treatment, recycling paper and metals) as well as to commercial production of chemicals. It is important that students realize that chemical reactions can be used to change the form of matter but that it is impossible to make pollution or waste “disappear.” Factors that must be considered in addition to the feasibility of the process are the cost (economics), the environmental effect of the clean-up, public perception of the problem and the proposed solution.

HISTORY: ON THE HUMAN SIDE

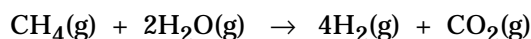
1. Although one of the most abundant metals, aluminum was considered a precious metal until the late 1800s. Many chemists tried to find a practical method for isolating aluminum from its ores, but it was 1886 before Charles Martin Hall, in Oberlin, Ohio, and Paul Héroult, in France, independently discovered the same method for electrolytic reduction of aluminum from bauxite ore. Both of these men were only 22 years old when they made this discovery. Hall went on to found the Aluminum Corporation of America (ALCOA). In a day when aluminum beverage cans present a litter problem along our highways, it is difficult to believe that before the 1880s aluminum was more precious than gold!
2. Fritz Haber first prepared ammonia from its elements in 1903, but years of experimentation were required before the synthesis became practical on an industrial scale. In 1908, he approached BASF regarding financial backing to develop his ammonia synthesis for industrial production. Carl Bosch, an engineer, was assigned to help him optimize conditions to facilitate the industrial synthesis of ammonia from nitrogen and hydrogen. There were several problems faced in adapting Haber's synthesis to an industrial scale. The osmium catalyst Haber used in the laboratory scale reaction was rare and difficult to handle. After much experimentation an iron catalyst containing oxides of aluminum, potassium, and calcium was found suitable. The catalyst is now generated *in situ* by the hydrogen reduction of Fe_3O_4 containing small amounts of the other oxides. Because high pressures were required, new equipment had to be developed. In 1913, the first plant opened. Essentially the same process is used today. The industrial synthesis of ammonia from the elements is frequently called the Haber process, but should be referred to as the Haber-Bosch process. Haber developed the reaction on a laboratory scale, but Bosch translated it into an industrial process.

3. In the early 1950s most large refineries were installing catalytic reformers for improving the octane number of their gasoline. Catalytic reforming units could convert low octane gasoline to high octane gasoline in a single pass over a platinum-based catalyst.



Along with the aromatic products, catalytic reformers produced huge amounts of hydrogen (four moles per mole of aromatic hydrocarbon). There was some demand for hydrogen, but not for the enormous amounts that were rolling out of these hydroformers. Most of the hydrogen was burned off in giant flares.

Refiners needed a use for all that hydrogen. After looking into various ways to use hydrogen, the production of ammonia looked most promising. Ammonia could be used as fertilizer, a large-volume product. Farmers at that time were using only solid fertilizers and would not know how to handle ammonia. Although refiners could use ammonia to make ammonium nitrate, ammonium sulfate, or ammonium phosphate, why not put ammonia directly into the soil? The refiners convinced farmers that they could improve yields by fertilizing with liquid ammonia solution, or even with pure anhydrous ammonia. They succeeded in selling farmers on fertilizing with ammonia and needed to increase the size of their ammonia plants to meet the new demand. Consequently, new plants had to be built to make more hydrogen from natural gas, by steam reforming.

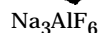


4. In the early 1900s, Wilhelm Ostwald developed a method of producing nitric acid starting with ammonia. The oxidation of ammonia using a platinum catalyst had been reported earlier by Charles Frederic Kuhlmann in France. Ostwald perfected the process and obtained patents in several countries, but Germany refused to grant him a patent. Prior to World War I, Germany had stockpiled Chilean nitrate of soda (NaNO_3) apparently intending to use an older method to prepare nitric acid (needed for the manufacture of gunpowder) by distilling nitric acid from a mixture of sodium nitrate and sulfuric acid.

1. Message on bumper stickers:
 a. Don't like farmers? Don't complain with your mouth full.
 b. What in the world isn't chemistry?

2. **CHEMTOON**

Let me help you out of your coat



CHEM 13 NEWS, December 1983, p. 16

3. A chemistry student from Birmingham
 Found his shirt cuffs so handy, he cribbed on 'em;
 But the elements ran
 As he wrote his exam
 Forming steel from Fe, C, and molybdenum.
 Adapted from *CHEM 13 NEWS, March 1965, p. 882*
4. Oxide: a favorite substance for making shoes.
CHEM 13 NEWS, November 1976, p. 1106

**HUMOR: ON
 THE FUN SIDE**



5. Word Search (see *Appendix* for master copy)

M C W V P K R E H W W M B L S X L
U N I K U M X U L J E X V C S J I
N Z E T A H P S O H P R E F U S P
I K X T G L Y M Z O E Y H A L U E
M U Q W T J U T E U T O D C F C L
U B O W H I J G E T S J K Y U I V
L I L X C J U Q J P A H B C R R T
A S H L Z R G L H D D L P F I T S
F R A S C H G O B E X D L P C I A
R C F X V X R S U L F U R U M N F
A C Y Y M U M I A Z D O I K R C N
G B C T S Y L A T A C E Y C J C P
U K K S A C A P V A X G K B O R Y

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Quicklime, burned lime, or just lime—its the oxide of this metal.
2. Process of extracting sulfur through use of superheated water and compressed air.
3. Acid made from the Ostwald process.
4. A mixture of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.
5. A complete fertilizer contains the elements nitrogen, potassium and this element.
6. An oxide of vanadium serves this function in the Contact process.
7. This acid is the substance produced in largest quantities in the United States.
8. Process of extraction of metals from their ores.
9. This metal is obtained from bauxite.
10. Sour petroleum or natural gas contains compounds of this yellow solid.

Answers: 1. CALCIUM 2. FRASCH 3. NITRIC 4. SUPERPHOSPHATE
5. PHOSPHORUS 6. CATALYST 7. SULFURIC 8. METALLURGY
9. ALUMINUM 10. SULFUR

6. See relevant cartoons at end of module.

MEDIA Because it is impossible to demonstrate industrial processes adequately in the classroom, it is strongly recommended that you obtain videos or films of industrial processes to view with your class. A few of these are listed below:

1. The *World of Chemistry* videotapes “No. 16: The Busy Electron,” “No. 17: The Precious Envelope,” “No. 18: The Chemistry of the Earth,” “No. 19: Metals,” “No. 20: On the Surface,” and “No. 25: Chemistry and the Environment” are particularly appropriate for this module. *World of Chemistry Videocassettes*. Annenberg/CPB Project, P.O. Box 1922, Santa Barbara, CA 93116-1922; (800) 532-7637; *World of Chemistry Series*, Atlantic Video, 150 South Gordon Street, Alexandria, VA 22304; (703) 823-2800 or QUEUE Educational

- Video, 338 Commerce Drive, Fairfield, CT 06430; (800) 232-2224.
2. *Chemical Equilibrium*, Program 6 of TV Ontario Videotape Series. This tape highlights the Haber Process. Free previews are available from TV Ontario Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516; (919) 380-0747.
 3. "Chemistry in Action" Videotape Series is published by Films for the Humanities and Sciences, P.O. Box 2053, Princeton, NJ 08543; (800) 257-5126.
 - a. *Aluminum* (#NB-1108).
 - b. *Chemicals from NaCl* (#NB-1110).
 4. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
 - a. *Lake Study* for Windows, by David Whisnant and James McCormick. Vol. V B, No. 1, for IBM PS/2, PC-compatible computers.
 - b. *BCTC* for Windows, by David Whisnant and James McCormick. Vol. V B, No. 2, for IBM PS/2, PC-compatible computers.
 5. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).
 - a. For the Apple II computer running on ProDOS: AR 801, AR 802.
 - b. For the Apple II computer: AP 801, AP 803, AP 805, AP 806, AP 807.
 - c. For IBM PCs and PC-compatibles: PC 3702, PC 3702, PC 3705.
 - d. For the Apple Macintosh computer: MC 801.
 6. Videodiscs published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
 - a. "Making Aspirin," "Perkin's Experiment," and "Making Polyethylene," three chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc II (double sided, 60 min.), Special Issue 4.
 - b. "Polymers," and "Dyes," two chapters on the videodisc *Demonstrations in Organic Chemistry* (double sided, 60 min.), Special Issue 6.

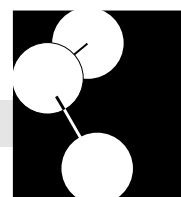
A simple electrolysis apparatus is described in *Demonstration 3*.

A simple conductivity apparatus is described in the articles by Gadek (1987) and Russo (1986) in the *References* section.

Almost all topics are related to this module: acids and bases, balancing equations, chemical equilibrium, descriptive chemistry of elements, electrochemistry, kinetics, mole, redox reactions, stoichiometry, and thermochemistry.

INSTRUMENTATION

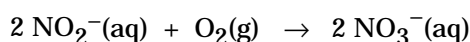
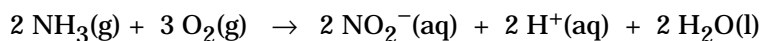
Links/Connections



WITHIN CHEMISTRY

Biology

A natural connection is the use of artificial nitrates from fertilizers to supplement the usable nitrates in the soil. Since most plants are not legumes and consequently incapable of fixing nitrogen, they must have a source of nitrate to insure proper growth and production needs are met. Removal of plant materials from farming areas greatly reduces the return of nitrates made from ammonia or ammonium salts by bacteria. Approximately 10% of nitrates added to the soil each year are artificial fertilizers, while the remainder is a result of nitrogen fixation by symbiotic bacteria in the nodules on roots of legume plants.



The oxidation of ammonia (or ammonium ion) is an exergonic process, and the energy released is used by bacteria as a primary energy source.

Earth Science

Metallurgy results in the production of useful and needed materials for industry. Most metals are not readily available but are also contained in ores with many other materials that must be eliminated. Major metals and their sources are shown in the following chart.

Since the United States is dependent on the availability of such metals, these metals are considered strategic. As a result, these metals are stockpiled.

Obtaining metals from their ores involves several steps: (1) mining, (2) preparing the ore by concentrating it, (3) reducing the metal ions in the ore to produce the free metals as atoms, (4) refining or purifying the metal, and if needed (5) producing alloys. Every metal has its own unique processes and reactions involving these steps.

Chemical Engineering

Commercial chemical manufacturing processes such as the Contact, Ostwald, and Haber processes involved in fertilizer production.

Metal	Mineral	Composition
Al	Bauxite	Al ₂ O ₃
Cr	Chromite	FeCr ₂ O ₄
Cu	Chalcocite	Cu ₂ S
	Malachite	Cu ₂ CO ₃ (OH) ₂
Fe	Hematite	Fe ₂ O ₃
	Magnetite	Fe ₃ O ₄
Pb	Galena	PbS
Mn	Pyrolusite	MnO ₂
Mo	Molybdenite	MoS ₂
Hg	Cinnabar	HgS
Sn	Cassiterite	SnO ₂
Ti	Rutile	TiO ₂
	Ilmenite	FeTiO ₃
Zn	Sphalerite	ZnS

Materials Engineering

A major consideration in construction is the strength of the alloys used. A natural consequence of metallurgy is the study of ductility, tensile strength, conductivity, *etc.* associated with alloys.

Personal

Possible careers are agronomist, chemical engineer, environmental scientist or environmental hygienist, industrial chemist, recycling engineer (resource management), research chemist, sanitation or water chemist, soil scientist, metallurgist.

Community

1. **Field trips** agricultural extension service, chemical manufacturing plant, environmental testing lab, health department, industrial chemical sales company
2. **Knowledgeable individuals** agronomists, chemical engineers, environmental scientists (environmental hygienists), industrial chemists, pharmacists, recycling engineers (resource management), research chemists, sanitation department chemists, water chemists, soil scientists, metallurgist

Fertilizer run-off is an environmental problem generated by the use of fertilizers to increase food production.

Food production *versus* world economy is an important issue related to this module. Fertilizer use increases food production and is therefore directly related to the economy of a country. Use of fertilizers and subsequent environmental impact *vs.* food production needs should be discussed. Furnishing fertilizers to underdeveloped countries and education of those involved in farming concerning the proper use of fertilizer are important issues.

In spite of extensive production in a few less-industrialized nations, sulfuric acid production is still considered by many to be one of the ten leading economic indicators. Ammonia is also important to national economy. A comparison of production of various substances and national prosperity is an interesting exercise that provides an opportunity for students to see that elements and compounds they have studied are directly related to current economic issues.

The danger of ammonium nitrate (there are frequent reports of fires caused by improper use or storage) or other chemicals can be discussed if newspaper clippings are saved as the accidents occur. Incorrect, or incomplete, explanations that imply chemical errors are frequently given in news accounts. Again if clippings are saved, students will have the opportunity to see that science literacy is important for everyone—including journalists.

Recycling of metals, particularly aluminum, fits logically here. Recycling aluminum is particularly important because of decreasing reserves of bauxite and the need to conserve energy. By recycling one aluminum beverage can, it can save enough energy to burn a 75-W light bulb for three hours. In the United States, 20% of the energy used is consumed in the Hall Process to produce aluminum from bauxite ore.

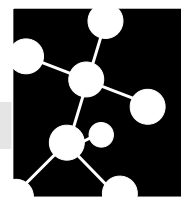
Determination of soil moisture and pH activity can be extended to include a comparison of the soil analyses from different locations.

Compare the effect of different fertilizer formulations (8-8-8 *vs.* 6-12-6, *etc.*) on plant growth.

**TO THE
CONTEMPORARY
WORLD**

**SOCIETAL
(SCIENCE/
TECHNOLOGY/
SOCIETY)**

Extensions



Studies have shown that phosphate rock can be used directly as fertilizer. This fact has significant implications for developing nations because it does not require a sophisticated chemical industry to produce fertilizer. Research this idea and, if a source of phosphate rock can be located, students can grow plants using commercial fertilizer (such as superphosphate) and phosphate rock and compare the results (see Worthy, 1986, in *References* section).

Investigate hydroponic plant growth and nutrients needed for different plants. Experiment with growing different plants hydroponically.

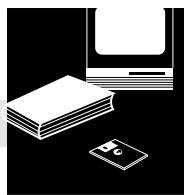
Compare the annual production of various industrial chemicals for different countries.

Industrial processes for various substances (*e.g.*, Solvay process for Na_2CO_3 , Downs process for sodium, *etc.*) and the lives of individuals associated with industrial processes provide interesting library research topics.

Several projects are referred to in the *Societal Links and Connections* section.

Module developed by Caroline L. Ayers, Philip Dail, and Carolyn Morse, the North Carolina team.

The following individuals provided information and/or references used in the preparation of this module:



References

John Jernigan, Texasgulf, Aurora, NC

James M. Lucas, Applied Statistics Group, E. I. Du Pont de Nemours and Company, Wilmington, DE

Horace Mann, Fertilizer Division, Tennessee Valley Authority, Muscle Shoals, AL

H. Joseph Kleiss, Department of Soil Science, North Carolina State University, Raleigh, NC

Bohn, H. L., McNeal, B. L., and O'Connor, G. A. (1971). *Soil chemistry*. New York, NY: Wiley-Interscience.

This standard soil chemistry text contains information such as acidity of soils, oxidation-reduction processes in soils, and the role of various ions in soil chemistry and plant growth.

Chang, R. (1991). *Chemistry* (4th Ed.). New York, NY: McGraw Hill.

Chapter 26 is devoted to Industrial Chemistry. A table of the top 50 chemicals from 1982-1988 is on p. 1057. The components of petroleum and their uses are shown in a diagram on p. 1055.

Chang, R., and Tikkanen, W. (1988). *The top 50 industrial chemicals*. New York, NY: Random House.

Chemecology.

This magazine, published by Chemical Manufacturers Association (2501 M Street, N.W., Washington, DC 20037, Phone 202-887-1100), is a valuable resource for both teachers and students. Articles on health, safety and the environment are included in each issue. Call or write to obtain issues for use in your classroom.

Chemical and Engineering News.

This news magazine is published weekly by the American Chemical Society and sent to all ACS members. It carries news related to industrial chemistry in each issue. Frequent feature articles describe industrial chemical processes, environmental issues related to industrial chemistry or economic or business issues in chemistry. If you're not an ACS member, find a chemist who is and request back issues for use in your classroom.

Chemical technology: An encyclopedic treatment. (1968). New York, NY: Barnes & Noble.

This reference work contains information about manufacturing processes. Volume 1 contains information about the industrial production of Na_2CO_3 .

Faith, Keyes, and Clark's Industrial Chemicals (4th Ed.). (1975). New York, NY: Wiley.

This is a good source of information about industrial chemical processes. For example, the mining and processing of trona are described.

Gadek, F. J. (1987). Easily made electronic device for conductivity experiments. *Journal of Chemical Education*, 64, 628-629.



This article gives directions for a simple conductivity apparatus.

Heitmann, J. A., and Rhees, D. J. (1984). *Scaling up*. Philadelphia, PA: Chemical Heritage Foundation, 3401 Walnut Street.

This pamphlet provides concise information about adaptation of reactions for industrial production. It accompanies a multi-panel traveling exhibit; information regarding the exhibit and its whereabouts can be obtained from CHF.

Hileman, B. (1990, March 5). Alternative agriculture. *Chemical and Engineering News*, pp. 26-40.

The special report includes information on fertilizer consumption by crop as well as pesticide/herbicide use and farming methods. There is also a discussion of government and economic issues related to farming.

International Fertilizer Development Center. *Fertilizer manual*. Muscle Shoals, AL.

This is a revision of *UN fertilizer manual* published in 1967 and contains a history of fertilizers plus information concerning the manufacture of fertilizers.

Jacobs, H. S., Reed, R. M., Thien, S. J., and Withee, L. V. (Eds.). (1971). *Soil laboratory exercise source book*. Madison, WI: American Society of Agronomy.

This reference contains laboratory exercises related to soil chemistry. (Address: American Society of Agronomy, 677 South Segoe Road, Madison, WI 53711)

Jones, M. M., Johnston, D. O., Netterville, J. T., Wood, J. L., and Joesten, M. D. (1987). *Chemistry and society* (5th Ed.). Philadelphia, PA: Saunders.

This text includes a chapter on agricultural chemistry as well as sections discussing various industrial processes. Many references to societal issues related to various chemistry topics are included.

Kirk-Othmer encyclopedia of chemical technology (3rd Ed.). (1978-1984). New York, NY: Wiley.

This 24-volume work provides a wealth of information about industrial processes. Information about the industrial production of Na_2CO_3 is found in Volume 1.

Kleiss, H. J. (1986). *Applications of the basic sciences in soil science*. Raleigh, NC: Author.

This work describes soil science laboratory activities.

New developments in fertilizer technology. (1983). Muscle Shoals, AL: National Fertilizer Development Center, Tennessee Valley Authority.

This contains extensive material on the manufacture of fertilizers. Order from publisher.

Pearson, R. W., and Adams, F. (Eds.). (1967). *Soil acidity and liming* Madison, WI: American Society of Agronomy.

This work provides information on agricultural studies of the effects of soil acidity and liming on plant growth. Functions and deficiency characteristics in plants for various elements is given.

Reisch, M. S. (1993, April 12). Top 50 chemical production resumed growth last year. *Chemical and Engineering News*, p. 17.

This article lists the top 50 chemicals and quantities produced in the U.S. in 1991, a comparison with production in 1990, and growth over last ten years. A similar article appears each April.

Russo, T. (1986). A low-cost conductivity apparatus. *Journal of Chemical Education*, 63, 981-982.

Construction of a simple conductivity apparatus is described in this article.

Selinger, B. (1989). *Chemistry in the marketplace* (4th Ed.). Marrickville, Australia: Harcourt.

This reference provides information on uses of a wide range of substances. (Can be purchased from ACS Education Office.)

Slowinski, E. J., Wolsey, W. C., and Masterton, W. L. (1984). The Solvay process. In *Chemical principles in the laboratory* (3rd Ed., pp. 85-91). Philadelphia, PA: Saunders.

The Solvay Process activity was adapted from the experimental procedure described here.

Tocci, S. (1987). *Chemistry around you*. New York, NY: Prentice Hall.

This book describes chemistry activities suitable for use with students.

Ullmann's encyclopedia of industrial chemistry (5th Ed.). (1985-). Weinheim: VCH.

Extensive information on industrial chemicals and manufacturing processes is contained in this reference. New volumes are published annually. (19 of 36 planned volumes had been published in 1990.)

Worthy, W. (1986, September 22). Fertilizing by ion exchange promising. *Chemical and Engineering News*, 64, 29.

This article describes the use of phosphate rock as fertilizer.

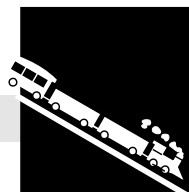
- **Transparency Masters**

1. Top 50 Chemicals in 1991 and 1992

This list is taken from a *C&EN* article (Reisch, 1993). An updated list is reported each April, (See *References*).

2. Interrelation of Industrial Processes in the Fertilizer Industry

Appendix

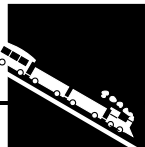


3. Word Search

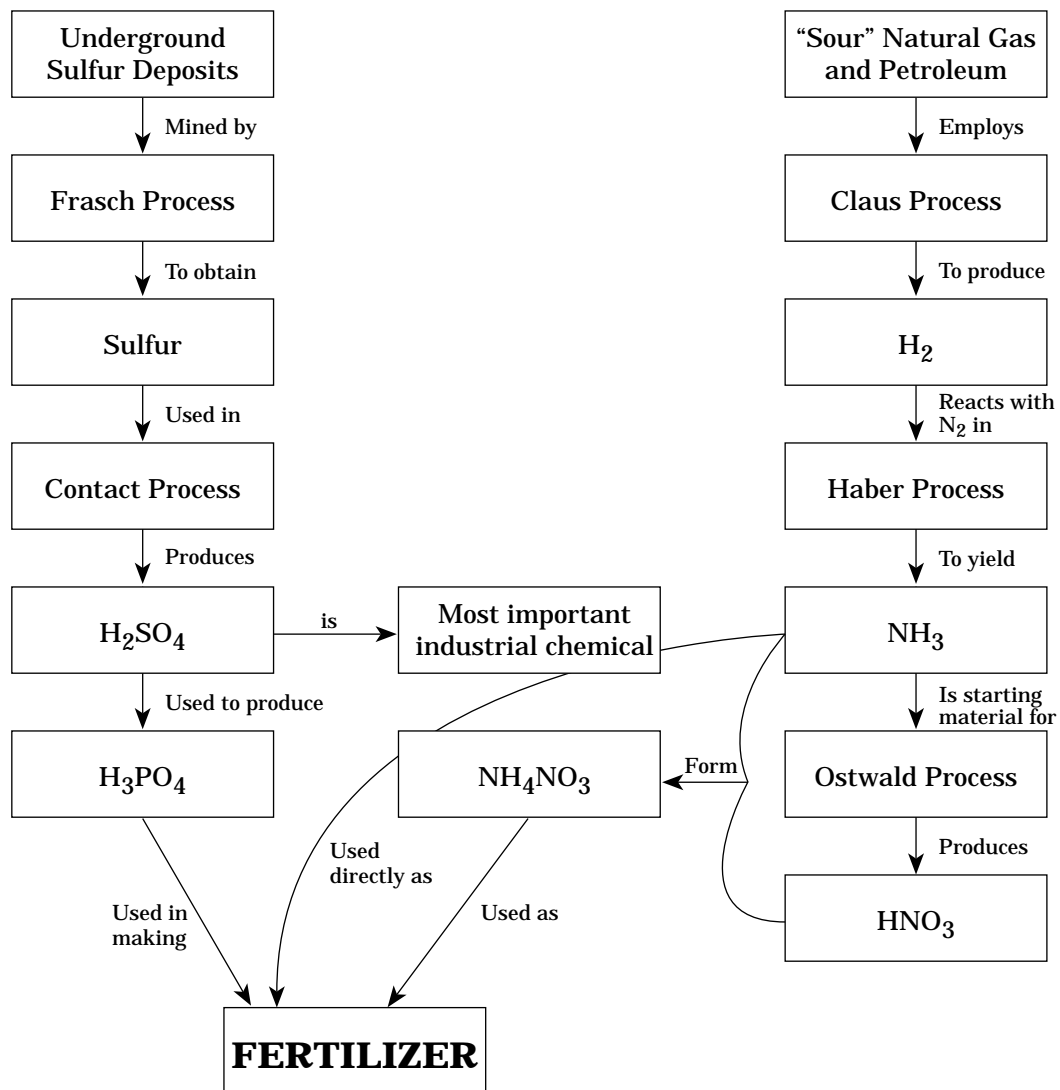
- **Humor**

Top 25 Chemicals in 1991 and 1992

Rank		
1991	1992	
1	1	Sulfuric acid
2	2	Nitrogen
3	4	Ethylene
4	3	Oxygen
5	5	Ammonia
6	6	Lime
7	7	Phosphoric acid
8	8	Sodium hydroxide
9	10	Chlorine
10	9	Propylene
11	11	Sodium carbonate
12	12	Urea
13	13	Nitric acid
14	15	Ammonium nitrate
15	14	Ethylene dichloride
16	17	Benzene
17	16	Vinyl chloride
18	20	Carbon dioxide
19	19	Methyl <i>tert</i> -butyl ether
20	18	Ethylbenzene
21	21	Styrene
22	22	Methanol
23	28	Terephthalic acid
24	23	Formaldehyde
25	27	Toluene



Interrelation of Industrial Processes in the Fertilizer Industry

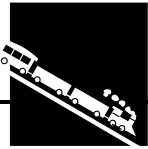


Word Search

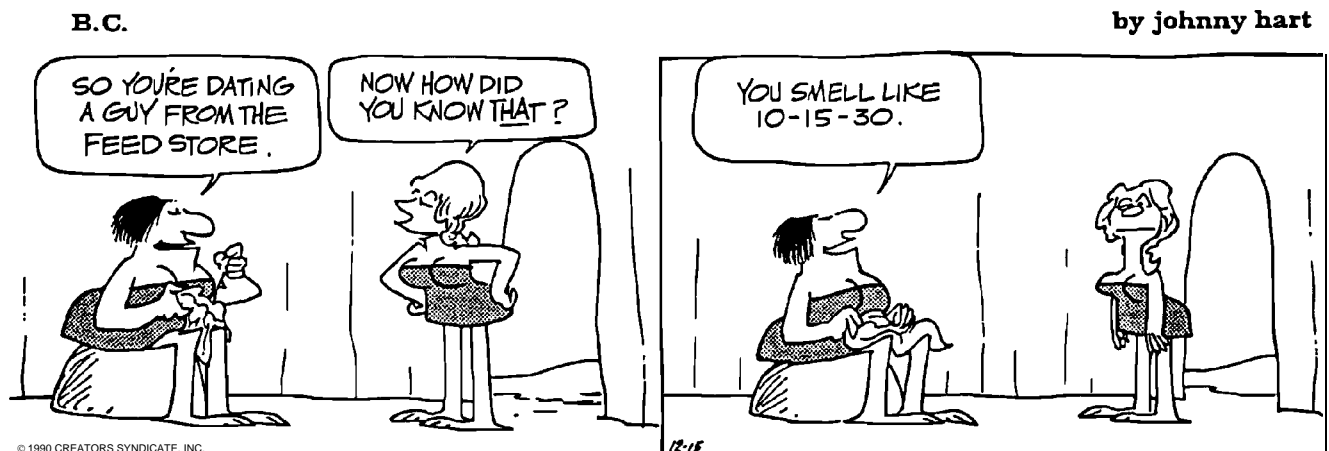
M C W V P K R E H W W M B L S X L
U N I K U M X U L J E X V C S J I
N Z E T A H P S O H P R E P U S P
I K X T G L Y M Z O E Y H A L U E
M U Q W T J U T E U T O D C F C L
U B O W H I J G E T S J K Y U I V
L I L X C J U Q J P A H B C R R T
A S H L Z R G L H D D L P F I T S
F R A S C H G O B E X D L P C I A
R C F X V X R S U L F U R U M N F
A C Y Y M U M I A Z D O I K R C N
G B C T S Y L A T A C E Y C J G P
U K K S A C A P V A X G K B O R Y

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

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3. Acid made from the Ostwald process.
4. A mixture of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.
5. A complete fertilizer contains the elements nitrogen, potassium, and this element.
6. An oxide of vanadium serves this function in the Contact process.
7. This acid is the substance produced in largest quantities in the United States.
8. Process of extraction of metals from their ores.
9. This metal is obtained from bauxite.
10. Sour petroleum or natural gas contains compounds of this yellow solid.



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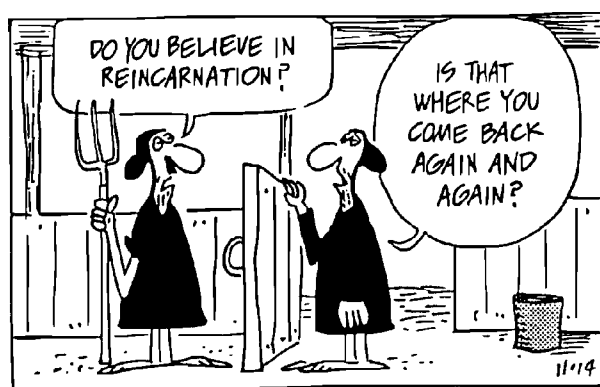


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THE WIZARD OF ID



Brant parker and Johnny hart



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