Soil Equilibria: What Happens to Acid Rain?

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CONTENTS

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Introduction

Session 1. How is acid rain formed?

Session 2. What is an acid?

Session 3: What is the pH of normal rain?

Soil Equilibria: What Happens to Acid Rain?

BRIEF DESCRIPTION

An important principle of science is that matter is neither created nor destroyed in a chemical reaction. Everything goes somewhere. Chlorofluorocarbons are useful and apparently safe because they are chemically inert gases but “What eventually happens to chlorofluorocarbons?” is a crucial question in understanding the formation of the ozone hole. Similar questions asked about DDT, PCBs, and lead in gasoline have resulted in societal decisions not to use those materials in some countries.

This module asks: *What happens to the oxides of sulfur and nitrogen produced during combustion?* Where do they go and how do they affect the environment? Are any effects significant? How can any effects be overcome or mitigated?

The effects of acid rain are more profound than just changes in pH. As illustrated in Figure 1, “What happens to acid rain?” involves soil chemistry, biology, shifts in multiple soil equilibria and the ecosystem response to those shifts. This module primarily considers the response of soil equilibria.

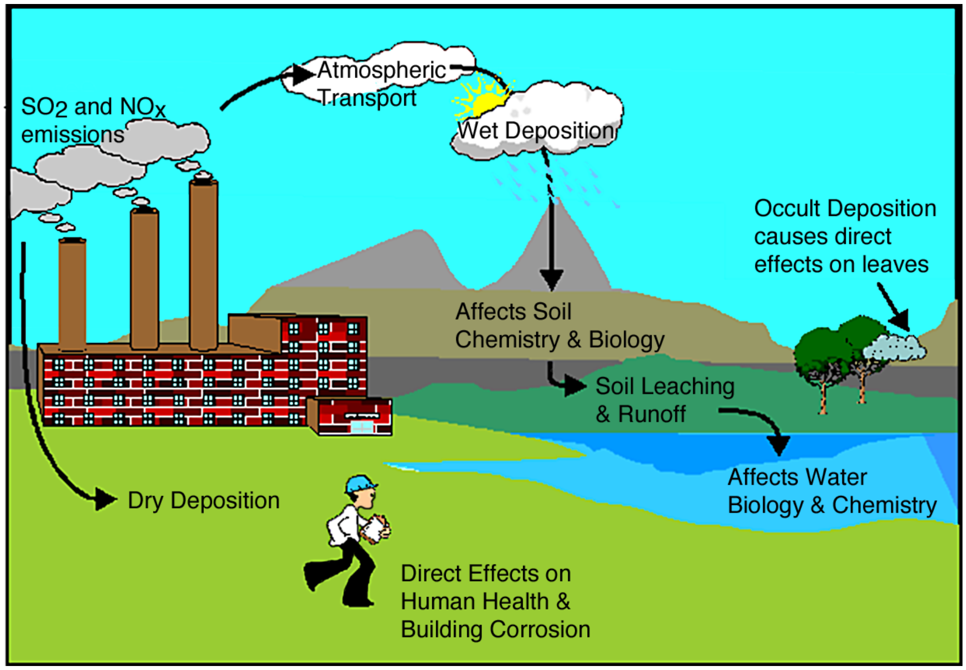


Figure 1. What happens to the oxides of sulfur and nitrogen produced by combustion?
Figure originally from http://www.york.ac.uk/inst/sei/sei/acidrain.html

Other than farmers and engineers, few people give much thought to soil unless they track it into the house or get stuck in the mud. Yet soil harbors much of the earth’s genetic diversity by sheltering organisms from the sun and by providing water, air and nutrients. Soil is the home of over half of all living things including bacteria, fungi, insects, small mammals and reptiles. Trees, shrubs, flowers and grasses are all anchored by soil and have half of their total biomass underground. Soil is also the source of our food and building materials and is used as an engineering medium in the foundation for homes and roads. Furthermore, soil is critical in regulating water supply by controlling the rate at which rainfall reaches rivers and by purifying and storing water. Soil is also the site of nature's recycling – organic wastes are processed into humus, mineral nutrients are made available and carbon is returned to the atmosphere as carbon dioxide.

What is soil? What chemical species are important in the soil system charge balance? What equilibria are involved? How are changes in pH, solubility, and ion-exchange interlinked with ion distributions and concentrations? How does the chemical system shift and the ecosystem respond to acid deposition? How resistant is a given soil and how much has it been altered? Instead of many simple problems where individual equilibria are separately studied, you are asked to question and investigate facets of a more complex problem through laboratory measurements of model and natural systems, supplemented by literature data.

Because the natural environment and the deposition varies from place to place different effects may result in different places. How relevant are the effects of geology, geographic location, time, and political boundaries?

INTERDISCIPLINARY ASPECTS

Aspects of this geochemistry module belong to geology, biology, and chemistry. "What happens to acid rain?" is an international question and studies and data from outside the US are extensively used in the initial and final activities.

PREREQUISITES

We assume that you are familiar with Lewis structures, ions, moles, molarity and chemical equations.

CHEMISTRY CONTENT

- Equilibria (Le Châtelier's Principle, acids and bases, buffers, distribution and ion exchange equilibria)
- Laboratory Procedures (analytical methods, instrumental techniques)

SCIENTIFIC THINKING

This module will also ask you to develop your skills in
- Experimental Design (sampling, controls/calibration)
- Data Analysis (analysis of the impact of the results on society)
- Critical Thinking/Problem Solving
- Systems Modeling (simulations, computation of complex interactions)
- Communicating Results (writing, speaking)

What can you learn from our modular approach?

General Approach

Our modular approach involves a series of questions, starting with the Module Question “What Happens to Acid Rain?” that provides a context for understanding and exploring chemistry concepts.

Learning in Context

You may wonder about the necessity of a context for learning chemistry. You may feel that you could just learn the concepts and not bother learning all the contextual information. Research in cognitive science has shown, however, that we retain knowledge better when appropriate background material is available. As an example, try the following experiment. Read the next paragraph once, close this manual, and write down as much as you remember.

> The procedure is not difficult. First, bring 1 liter of water to a state where it has undergone partially a phase transition in which the vapor pressure of the steam that is formed is equal to the pressure of the atmosphere. Then add 1.0 g of the mixture of chemicals known as *camilla thea*. The important ingredient in this mixture is 3,7-dihydro-1,3,7-trimethy-1H-purine-2,6-dione. Allow the mixture to steep for 5 minutes. Finally, filter the undissolved solids and collect the liquid.

If you are unfamiliar with the technical language, you may not be able to recall much of these instructions. However, if you are told that the passage is about making tea, suddenly you can figure out much of the new vocabulary and enhance your retention of the instructions. The context has helped you use background knowledge to comprehend the passage.

We have built a context surrounding the chemistry concepts and the problem-solving skills that we hope you will learn in this module. We hope that this context will help you make links to your background knowledge, to important societal issues, and to experiences from your everyday life. We believe that making these connections will aid your comprehension and enhance your retention. In addition to learning core chemistry concepts and gaining experience with scientific thinking skills, you will be able to answer a number of important and modern questions, increasing your overall scientific literacy about the world around you.

Transforming knowledge

As part of this module, you will also be encouraged to find solutions to problems that cannot be solved by simply “telling” facts you have memorized because solving new problems requires transforming your knowledge. As an example, consider a patient being examined by Dr. Rosario. The doctor realizes that she has never encountered this set of symptoms before, or at least she doesn’t remember having encountered them. Imagine Dr. Rosario giving one of the following responses to the patient:

> “Sorry, I can’t help you. I can’t find the answer in my textbook.”
>
> “Sorry, I can’t help you. There is something wrong with your blood chemistry but I can’t remember what I learned in my classes.”

> "Sorry, I can't help you. I wasn't told about symptoms like yours in medical school."

Clearly, doctors or scientists cannot be familiar with every case or remember all the information they learned in their training. In this module, we hope to give you experience with approaches used by scientists to solve problems, especially those for which an answer is not immediately obvious and for which multiple solutions are possible.

You will find that real-life problem solving is an iterative process. When you do not know how to solve a problem, you start by exploring your best ideas. If these ideas do not lead you toward a solution, you may have to back-track, rethink your ideas, and try something else. This process of generating and then refining your ideas allows you to define the problem more clearly. Eventually, you may reach an acceptable solution.

ORGANIZATION OF THE MODULE

Sessions begin with a Session Question which focuses on one aspect of the Module Question and raises issues you need to consider.

Explorations begin with a question that considers the Session Question in more depth and in different ways. *Your instructor will choose which Explorations to use* depending on her or his goals and the needs of your class. Explorations have a common organization:

1. **Creating the Context** asks the Exploration Question, discusses why the question is important, and reminds you of information discussed previously.
2. **Preparing for Inquiry** includes any background reading, activities, and/or questions that will help you prepare on your own for the main activities in the Exploration.
3. **Developing Ideas** describes how to gather information you will need to respond to the Session and Exploration questions. Activities include many types types of guided inquiry. *Demonstrations* or data provided by your instructor, this manual, or the computer resources that accompany the module. You will need to understand the purpose of the data or experiment, make detailed observations, and attempt to explain these observations. *Small group problem solving and class discussion* will help you formulate responses to questions, gather data from other groups, and give you different perspectives. *Laboratory explorations* ask you to design and carry out experiments to respond to a specific question.
4. **Applying Your Ideas** helps you explore the observations and data you have collected. Your instructor will choose which of these questions to use for interactive discussion, small group work, or homework.

Making the Link ends each Session. This section gives you a chance to look at your work in three ways: Looking Back reminds you of the Session goals, Checking Your Progress assesses your status in answering the module question, and Thinking Further provides review questions that may also asks you to extend what you have learned in a new context.

Culminating Project. As the Module ends, you will do a project that will integrate everything you have learned. Try to keep the Session Question in mind as you generate and refine your ideas along the way.

How is acid rain formed?

EXPLORATION 1A, COMBUSTION

CREATING THE CONTEXT

An important principle of science is that matter can neither be created nor destroyed by a chemical reaction. Everything goes somewhere. Gases being emitted as by-products of industry or from the tailpipes of automobiles do not disappear into the atmosphere. This module looks at what happens to the gaseous products of combustion, specifically at the oxides of sulfur (SO_2) and nitrogen (NO and NO_2). Where do they go? How do they affect our environment?

PREPARING FOR INQUIRY

Sulfur dioxides and the oxides of nitrogen are the major contributors to acid precipitation and deposition. Although some of these gases come from natural sources, about 80% of sulfur dioxide emissions and 60% of nitrogen oxide emissions are the result of human activities.

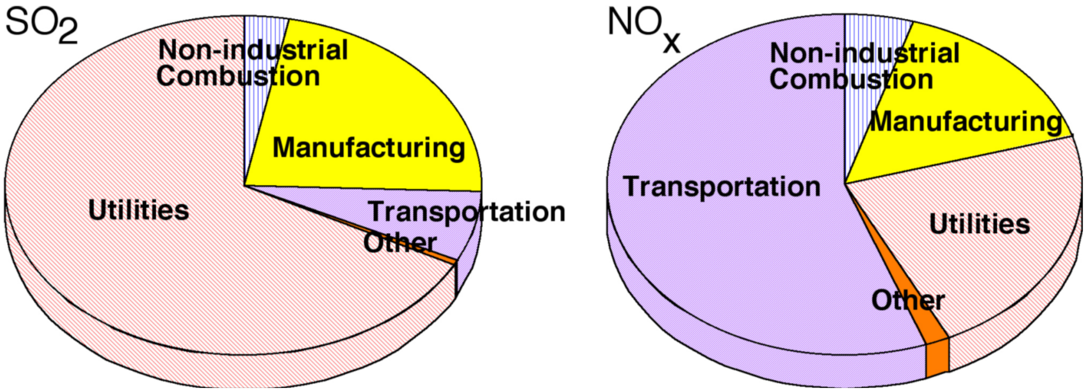


Figure 1A-1. United States SO_2 and NO_x anthropogenic emissions by source, 1999. Data originally from http://projects.dnmi.no/~emep/areas/index.html

Sulfuric Acid Formation

Most of the anthropogenic sulfur dioxide (SO_2) released into the atmosphere comes from the burning of sulfur-containing fuels such as coal, which typically contains 1 to 3% sulfur in the form of pyrite (FeS_2). Note that sulfur is not part of what is needed for the fuel, but is present as an impurity. Combustion of fuel in coal-fired power plants used to generate electricity is the major source of SO_2 emission.

$$4\ FeS_2(s) + 11\ O_2(g) \longrightarrow 2\ Fe_2O_3(s) + 8\ SO_2(g)$$

The smelting industry is also a major source of SO_2 when sulfide ores of lead, copper, and zinc are oxidized or roasted to produce the metal.

$$Cu_2S(s) + O_2(g) \longrightarrow 2\ Cu(s) + SO_2(g)$$

$$3\ PbS + 3\ O_2(g) \longrightarrow 3\ Pb(l) + 3\ SO_2(g)$$

The SO_2 generated by such reactions will then follow one of many possible pathways to eventually produce sulfuric acid, H_2SO_4. Some potential mechanisms for the formation of sulfuric acid are listed below.

(1) SO_2 is oxidized to sulfur trioxide, SO_3, by oxygen or nitrogen dioxide:

$$2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$$

$$SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g)$$

This reaction occurs in the atmosphere and is catalyzed by dusty, wet air. The SO_3 then dissolves in water to form sulfuric acid:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

(2) SO_2 dissolves in water to form sulfurous acid, H_2SO_3:

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$

Sulfurous acid is then oxidized to sulfuric acid by ozone, O_3 or hydrogen peroxide, H_2O_2:

$$H_2SO_3(aq) + O_3(g) \longrightarrow H_2SO_4(aq) + O_2(g)$$

$$H_2SO_3(aq) + H_2O_2(g) \longrightarrow H_2SO_4(aq) + H_2O(l)$$

(3) SO_2 is also oxidized directly to sulfuric acid by hydrogen peroxide:

$$SO_2(g) + H_2O_2(l) \longrightarrow H_2SO_4(aq)$$

Nitric Acid Formation

As seen in Figure 1A-1, the majority of the nitric oxide arising from human activities is emitted by cars and other vehicles powered by internal combustion engines. The great majority of such engines are fueled with gasoline, which is a mixture of hydrocarbons containing no nitrogen. The source of nitrogen is air itself. Under the conditions of high temperature and pressure that exist in the cylinders of automobile engines, atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$$

Nitric oxide reacts readily with additional oxygen to form nitrogen dioxide, which then dissolves in water to form both nitrous and nitric acid.

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$

$$2\ NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$$

Both the nitrogen and oxygen gas needed for the formation of nitrogen monoxide are very abundant in the atmosphere. As a consequence, NO and NO_2 are frequently found together and are collectively known as NO_x. (Similarly SO_2 and SO_3 are referred to as SO_x. Acid precipitation is thus largely a matter of “nox” and “sox.”)

Converters and Scrubbers

Catalytic converters, part of the automobile exhaust system, provide a surface on which much of the nitrogen oxides are reduced to nitrogen gas.

$$2\ NO(g) \longrightarrow N_2(g) + O_2(g)$$

Scrubbers installed in the exhaust stream of a power plant or smelter can remove much of the $SO_2(g)$ by conversion to a slurry of $CaSO_4(s)$.

$$CaCO_3(s) + SO_2(g) + 1/2\ O_2(g) \longrightarrow CaSO_4(s) + CO_2(g)$$

Assignment to be done before class

You will be assigned as a member of a particular regional group. Gather information to familiarize yourself with the sources of acid rain and the problems caused by acid rain in your assigned geographic area. See *http://chemistry.beloit.edu/Rain/pages/links.html* for sites (mostly in English) from governmental environmental protection agencies and non-governmental agencies in most of the countries.

Norway/Sweden

Germany/Poland/Czech Republic

England/Scotland

Canada/US

China/Japan/Korea

India

DEVELOPING IDEAS

Break into small groups by geographic region and based on your reading discuss the sources and effects of acid rain. Save your lists for later.

1A-1 What activities or industries (sectors) are the largest chemical sources of acid rain within your region?

1A-2 What are the largest geographical sources of acid rain within your region? Is the acid rain that falls on your area locally produced or does it come from another area? (The answer determines whether your area can solve the problem or whether additional international cooperation will be required.)

1A-3 What are the emission trends? Is the emission of SO_2 increasing or decreasing within your region? Is emission of NO_2 increasing or decreasing within your region?

1A-4 Which is the larger source of acid rain emissions within your region, SO_2 or NO_2?

1A-5 What are the effects of acid rain within your geographic area? How significant is each effect? What problems cause the most concern in your assigned region?

What more will you need to know in order to answer the above questions? Material from these initial readings will be needed for the culminating activity for this module, Session 6. As you work through this module, keep in mind that the goal is to apply what you have learned to evaluate the situation in your assigned geographic region.

APPLYING YOUR IDEAS

1A-6 Chemical treatment of fuels can remove its sulfur and thus prevent formation of SO_2. Alternatively, SO_2 can be chemically removed (“scrubbed”) from exhaust gas after the fuel is burned. Are both these options available for NO_x? Explain.

1A-7 When acid rain was first noticed as a problem in local environments, taller smokestacks were introduced. Does this solve the problem of acid rain? (A spectacular example of this effect occurred at the nickel smelter in Sudbury, Ontario.)

1A-8 If you smelted 1000 kg of PbS
- a. How many grams of SO_2 would be released into the atmosphere?
- b. How many grams of H_2SO_4 would be formed?

1A-9 Based on Figure 1A-1
- a. Propose a strategy to reduce sulfuric acid rain.
- b. Propose a strategy to reduce nitric and nitrous acid rain.
- c. How would a strategy to reduce acid rain in the United States differ for the coal-rich midwest compared to the hydroelectric-rich northwest?

1A-10 For what chemicals would you test if you wanted to evaluate the effectiveness of an automobile catalytic converter?

1A-11 The largest quantity industrial chemical produced in the United States is H_2SO_4, with over 10^{11} pounds produced annually. How would you synthesize H_2SO_4?

How do power plants and automobile emissions affect lakes and cities?

EXPLORATION 1B, EXPERIMENTAL DESIGN

CREATING THE CONTEXT

Production of SO_2 and NO

In these experiments, you will observe the simulated environmental effects of SO_2 and NO_x. Your "world" will be a covered Petri dish containing drop-sized "lakes," small chunks of "buildings," pieces of metal "bridges" and sources of $SO_2(g)$ and NO(g). Rather than producing these gases by combustion, you will generate them with chemical reactions that are not representative of how they are formed during combustion:

$$3\ NO_2^{-} + 3\ H^{+} \longrightarrow 3\ HNO_2 \longrightarrow 2\ \mathbf{NO(g)} + HNO_3 + H_2O$$

$$SO_3^{-2} + 2\ H^{+} \longrightarrow \mathbf{SO_2(g)} + H_2O$$

The SO_2 and NO you produce will then undergo all the same reactions as SO_2 and NO generated by combustion. For example, the NO will react with the oxygen in the air to form NO_2 as you saw in Exploration 1A.

Chemical Probes

In this activity, the "lakes," "buildings," or "bridges" placed at various distances from the pollution source will absorb some of the SO_2 and NO_x. The presence of these gases will be detected by **probes** – chemicals specifically dissolved in water to react with SO_2, NO, NO_2, or their products.

The acid-base indicator bromocresol green is sensitive to the acidic properties of sulfurous, nitrous, and nitric acids. As you know from Exploration 1A, SO_2 reacts with water to yield sulfurous acid,

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq) \longrightarrow 2H^{+} + SO_3^{-2},$$

and NO_2 reacts with water to form nitrous acid and nitric acid,

$$2\ NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq) \longrightarrow 2H^{+} + NO_2^{-} + NO_3^{-}.$$

Bromocresol green is yellow in acidic solutions and blue in basic solutions.

Aqueous potassium iodide, KI, serves as a probe for the presence of NO_2 since NO_2 the oxidizes the iodide ion, I^{-}, to brown, elemental iodine, I_2:

$$2\ NO_2(g) + 2\ I^{-}(aq) \longrightarrow 2\ NO_2^{-}(aq) + I_2(aq).$$

A solution of barium chloride, $BaCl_2$, serves as a probe for the sulfate ion, SO_4^{-2}. Here, the reaction requires several steps. First, SO_2 is oxidized by NO_2 to form SO_3,

$$SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g),$$

the $SO_3(g)$ reacts with water to yield sulfuric acid, which dissociates into H^{+} and SO_4^{-2} ions,

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq),$$

$$H_2SO_4(aq) \longrightarrow 2\ H^{+}(aq) + SO_4^{-2}(aq),$$

and the sulfate ions then react with the barium ions to form white, insoluble barium sulfate,

$$SO_4^{-2}(aq) + Ba^{+2}(aq) \longrightarrow BaSO_4(s).$$

PREPARING FOR INQUIRY

You will be designing experiments that allow you to observe the transport of SO_2 and NO_x as well as their effects on buildings and lakes of various sizes and distances from the “pollution source” located in the center of the dish.

- To generate SO_2 gas, add a drop of sulfuric acid (H_2SO_4, the “initiator”) to a drop of sodium sulfite (Na_2SO_3, the “SO_2 source”).
- To generate NO gas, add a drop of H_2SO_4 (again, the “initiator”) to a drop of sodium nitrite ($NaNO_2$, the “NO source”).

Once the reaction has been initiated, the Petri dish should be covered immediately to contain the gases.

For each experiment, plan the placement of the probe drops in the Petri dish carefully. Ideally, **the gas source should be in the center, only one gas source and effect should be tested at a time, and *small* drops or fractions of a drop should be used**. You will have an acid-base probe (bromocresol green), a NO_2 probe (KI), and an SO_4^{-2} probe ($BaCl_2$). Think about whether you wish to place your probes at the same distance from the source or at a variety of distances. You may wish to place a grid such as Figure 1B-1 under the Petri dish. Some reactions can be observed best over a black background and some over a white background. When you are timing changes, decide whether you want to measure when the change starts or when the change is complete. (Which will be easier to record?)

Make sure you sketch your experimental set-up in your laboratory notebook for *each* trial.

Available Materials

NO source
    0.5 M $NaNO_2$
SO_2 source
    0.5 M Na_2SO_3
initiator
    2 M H_2SO_4
acid probe
    bromocresol green
redox probe
    0.5 M KI
sulfate probe
    0.5 M $BaCl_2$
imported water
    0.01 M $NaHCO_3$
buildings
    $CaCO_3$ chips
bridges
    Mg chips

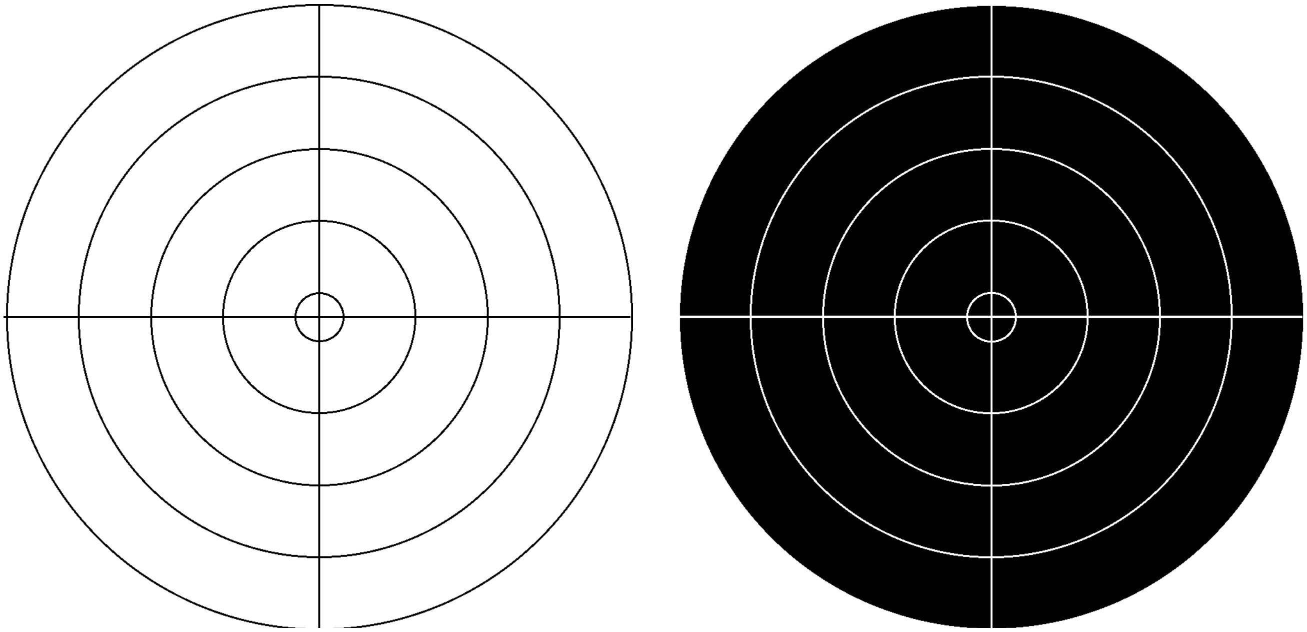


Figure 1B-1. Grids for use under a Petri dish.

Safety Precautions

Please be careful! Ingested or inhaled sulfites can cause allergic reactions. NO_x and SO_2 gases are toxic, so keep the cover on the Petri dish. Dilute to stop production of the SO_2 and NO gas.

DEVELOPING IDEAS

1. Does SO_2 or NO affect lakes?

Use $NaNO_2$ solution *or* Na_2SO_3 solution as the source. Be sure to use only one source at a time. Use H_2SO_4 solution as the initiator. Use bromocresol green solution as an acid-base probe that represents “lakes.”

a. Does invisible SO_2 or NO gas move through the air? How can you tell?

b. What effect does SO_2 or NO have on the lakes? How can you tell?

c. How does the time vary to observe effects for equal-sized lakes at different distances from the source?

d. How does the time vary to observe effects for different-sized lakes at equal distances from the source?

e. Do both SO_2 and NO sources give the same results?

f. What reaction(s) must have occurred to explain your observations?

2. Is NO_2 produced?

Use $NaNO_2$ solution as the source and H_2SO_4 solution as the initiator. Use KI solution as a redox probe that represents “lakes.”

a. Does NO or NO_2 gas move through the air? How can you tell?

b. Does NO_x have any effect on the lakes? How can you tell?

c. The source plus initiator makes NO(g). The probe tests for NO_2. From where does NO_2 come? What reaction(s) must have occurred to explain your observations?

3. Does geographic location matter?

Use $NaNO_2$ solution *or* Na_2SO_3 solution as the source. Use H_2SO_4 solution as the initiator. In this experiment you will produce solutions with varying concentrations of sodium bicarbonate, $NaHCO_3$, representing lakes from different geographical regions.

a. In a multiwell culture dish, mix four different solutions as follows:

$NaHCO_3$ solution	Bromocresol green solution
1 drop	9 drops
2 drops	8 drops
3 drops	7 drops
4 drops	6 drops

Use drops of these prepared solutions as "lakes" representing regions having different geology. Keep your lakes small and all the same size and the same distance from the source.

b. How does time vary to observe effects with lakes made from each mixture? Include a graph of time as a function of the relative $NaHCO_3$ concentration in your lab notebook.

4. Will SO_2 affect buildings and bridges?

Use Na_2SO_3 solution as the source and H_2SO_4 solution as the initiator. Place a small piece of $CaCO_3$ or Mg metal in the Petri dish. Add a drop of bromocresol green solution onto each sample to serve as a probe. Three minutes after starting SO_2 generation, remove the "pollution source" with a Kimwipe, replace the cover and continue to observe. (Flood the Kimwipe with water to stop gas generation before discarding.)

a. Is $CaCO_3$ acid or base? What do you observe before SO_2 is generated and after the SO_2 generation is stopped? What reaction(s) must have occurred to explain your observations?

b. The reactions of buildings exposed to acid rain also include

$$SO_2(g) + 1/2\ O_2(g) + CaCO_3(s) \longrightarrow CaSO_4(s) + CO_2(g)$$

$$H_2SO_4(aq) + CaCO_3(s) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$$

$CaSO_4$ occupies more space than $CaCO_3$. How will this affect the structural integrity of marble or limestone objects?

c. The reaction of the magnesium metal is:

$$2H^+(aq) + Mg(s) \longrightarrow Mg^{+2}(aq) + H_2(g)$$

How will this affect the structural integrity of metallic objects?

5. Is SO_4^{-2} produced?

Use Na_2SO_3 solution as the source and H_2SO_4 solution as the initiator. Use $BaCl_2$ solution as an SO_4^{-2} probe that represents "lakes."

a. Does SO_2 gas move through the air? How can you tell?

b. Does SO_2 gas have any effect on the lakes? How can you tell?

c. What if your world had both cars and power plants? Use $NaNO_2$ solution as one source *and* Na_2SO_3 solution as a second source in the arrangement shown in Figure 1B-2. Use H_2SO_4 solution as the initiator for both. Use $BaCl_2$ solution as a SO_4^{-2} probe that represents a "lake." Does using cars *and* power plants change your answers when using the SO_4^{-2} probe?

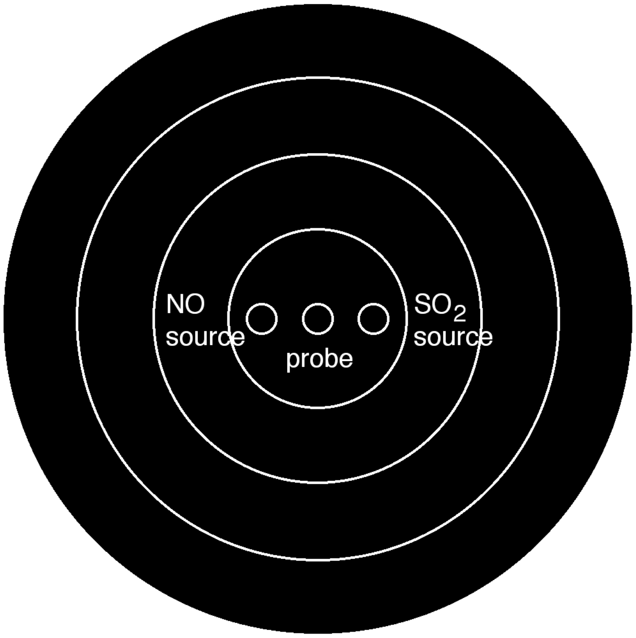


Figure 1B-2. Placement of cars and power plants around a probe.

d. What reaction(s) must have occurred to explain your observations?

APPLYING YOUR IDEAS

1B-1 You cannot see colorless gases. Summarize your evidence that colorless gases were produced at the source.

1B-2 One source produced NO(g). What color indicated a positive test for NO_2? What reaction sequences would account for the positive NO_2 test?

1B-3 One source produced SO_2(g). What reaction sequences must have occurred to produce a positive test for H^+?

1B-4 When your sources produced SO_2(g) and NO(g), what color indicated a positive test for SO_4^{-2}? What reaction sequences would account for a positive SO_4^{-2} test?

1B-5 Is $CaCO_3$ acidic or basic? What color do you observe before SO_2(g) is generated and after the SO_2(g) generation is stopped? What reaction(s) must have occurred to explain your observations?

1B-6 Does the geology of a region matter when assessing the impact of acid rain?

1B-7 If you were designing an environmental study to test the effects of acid rain on a lake, would you select a small or large lake? Explain.

1B-8 Classify each of the following reactions from this exploration as either a precipitation, acid-base, or oxidation-reduction reaction and explain why you decided what you did.

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$

$$2\ NO_2(g) + 2\ I^-(aq) \longrightarrow 2\ NO_2^-(aq) + I_2(s)$$

$$H_2SO_4(aq) + BaCl_2(aq) \longrightarrow BaSO_4(s) + 2\ HCl(aq)$$

$$2\ NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$$

What are the problems caused by acid rain?

Exploration 1C, Literature Research

Creating the Context

You have done some preliminary reading on the effects of acid rain in different geographical regions. It is now time to focus more in depth on specific problems caused by acid rain.

Preparing for Inquiry

You will be assigned as a member of one of the following problem groups.

Forests/trees

Lakes/fish

Cities/buildings

Health/people

Soil/agriculture

Find information about your assigned problem for your own geographical area at *http://chemistry.beloit.edu/Rain/pages/links.html*. What is the problem or concern? Some effects you may wish to consider include economics, aesthetics, ethics, tourism, historical importance and biodiversity. Can you quantify the problem? What are the important chemicals and their concentrations? Are there any trends – is it getting better or worse?

Developing Ideas

Meet in problem groups to compare information. Are the same problems found in all countries? Are the trends the same? Does research about effects in one location clarify or contradict information you obtained from your region?

Applying Your Ideas

Report back to regional groups from Exploration 1A. Share additional information you have learned from your problem group. Your regional group is relying on your expertise about the problem on which you have focused.

Now may be a good time to check your progress and organize your efforts toward Session 6. What will you need to know?

What happens to the oxides of sulfur and nitrogen formed by combustion?

Session 1, Making the Link

Looking Back

Session Goals

- Identify the sources of oxides of sulfur and nitrogen
- Identify the effects of acid rain on the environment

Checking Your Progress

You should be familiar with the following:

- Chemical and geographical sources of acid rain in your assigned region.
- Problems caused by acid rain in your assigned region.
- Effects of time, distance, and volume on the significance of acid rain.

Thinking Further

1-1 With your regional group, outline the information you will need to find to prepare for your presentation or paper in Session 6.

5-minute Writing Questions

1-2 Give a concise response to the session question, “How is acid rain formed?” From where does it chemically come?

1-3 What’s the problem with acid rain?

What household products behave like acid rain?

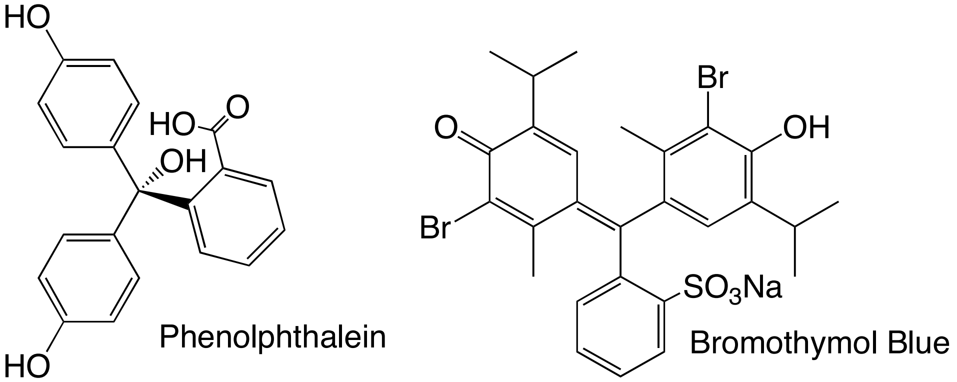
Exploration 2A, Chemical Classification

Creating the Context

In order to explain their observations, chemists often look for ways to group or classify them. One historical classification is “sour” or “slimy.”

Preparing for Inquiry

In class we will use water and either a blender or beaker and hotplate to extract a probe from purple cabbage. We will also use some chemical probes, Figure 2A-1, that you will encounter again in this module.



Phenolphthalein

Bromothymol Blue

Figure 2A-1. Some probes used in this experiment.

This experiment requires you to organize, systematize, and interpret a set of observations. Although the experiment appears to ask you just to categorize common household products as sour or slimy, it also requires that you do so in an iterative way. Based on *past* experience, do any of the products on the next page taste sour? (Never taste anything in a laboratory.) How do the chemical probes respond to those items? Based on *past* experience, do any of the products on the next page feel slimy? (Never touch chemicals in a laboratory.) Do the chemical probes respond differently to these products?

Developing Ideas

- Work in pairs.
- Record your observations using the table on the next page.
- Make a note of your past experiences (slimy or sour) with each chemical.
- Place a few drops of a household product in a spot plate well. Record your initial observations of color in the table.
- Add a drop of indicator and record any *changes* in the solution *other than those due to dilution*. For example, if the final solution is yellow, is the color the same or lighter yellow as the original? If so, record “no change.” (A lighter yellow color could simply be due to dilution.) If the yellow is different, for example record “darker yellow.”
- Which household chemicals give the same responses to the probe solutions?

Chemical	Past experience Sour? Slimy?	Initial color observation	Phenolphthalein probe	Bromothymol blue probe	Cabbage juice probe
Lemon Juice					
Formula 409 Cleaner					
Dill Pickle Juice					
Pineapple Juice					
Vinegar					
Household Ammonia					
Baking Soda (in water)					
Ivory Liquid Hand Soap					
Windex with ammonia-D					

APPLYING YOUR IDEAS

2A-1 What color changes are observed for phenolphthalein?

2A-2 What color changes are observed for bromothymol blue?

2A-3 What color changes are observed for cabbage juice?

2A-4 Which household chemicals give the same color responses to the probe solutions?

2A-5 Are the color changes consistent? Does a particular color of bromothymol blue always correspond to some other color of phenolphthalein or cabbage juice?

2A-6 What color is the sour form for each indicator used?

2A-7 What color is the slimy form for each indicator used?

2A-8 For the products where you left past experience blank, which would you expect to taste sour or feel slimy?

2A-9 Do any of the indicators give conflicting results for a particular household product? What does that tell you about the character of that product?

Putting it together

You have classified some chemicals as belonging to two different groups, sour or slimy, based on chemical properties. Instead of this original historical classification, the sour group is now called **acidic** and the soapy/slimy group is called **basic**. The original terminology lingers in the German language since the word for acid and for sour is säure. An English word with the same root is sauerkraut. The English word “acid”, the French word “acide”, and the Spanish word “ácido” come from the Latin word acidus, meaning sour or tart. In the next exploration we will focus on the portion of the molecule that makes something acidic or basic.

2A-10 Which chemicals would you describe as acids, and which would you describe as bases?

How do we identify acids from a chemical formula?

Exploration 2B, Strong and Weak Acids and Bases

Creating the Context

What do we mean by the term “acid rain”? How does it differ from normal rain? What exactly is an acid? We need to know more about acids chemically in order to understand what happens to acid rain.

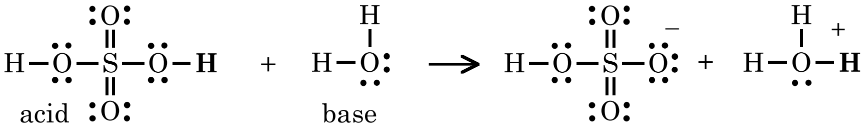
In Exploration 2A we saw that you can use probes to classify chemicals in groups: acids are sour and bases are slimy. However, this is not a good method for future use. What portion of a molecule makes something acid or base? In this exploration we will examine the chemical structure of acids and bases.

Preparing for Inquiry

Definition of Acids and Bases

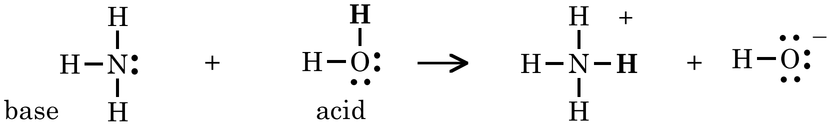
By the Brønsted-Lowry definition of acids and bases, an **acid** is any substance that can donate a proton, H^+, to another substance. By the same definition, a **base** is any substance that can accept a proton. For example, when sulfuric acid dissociates in water H_2SO_4 is the acid because it donates a proton to H_2O and H_2O is the base because it accepts a proton from H_2SO_4.

$$H_2SO_4 + H_2O \longrightarrow HSO_4^- + H_3O^+$$



In the case of ammonia in water, water is the proton donor (the acid) and ammonia is the proton-acceptor (the base).

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$



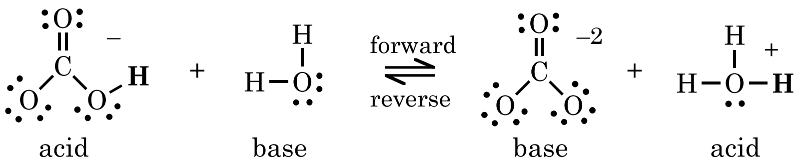
Notice that water acted as a base in the reaction with sulfuric acid and as an acid in the reaction with ammonia. Since water has the ability to act as either an acid or a base, we say that it is **amphoteric** (derived from *amphoteros*, Greek for “either of two”). Another example of an amphoteric substance is the bicarbonate ion, HCO_3^-.

$$\underset{\text{acid}}{HCO_3^-} + \underset{\text{base}}{H_2O} \rightleftharpoons CO_3^{-2} + H_3O^+ \qquad \underset{\text{base}}{HCO_3^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons H_2CO_3 + OH^-$$

As an acid, bicarbonate donates a proton to form carbonate ion, CO_3^{-2}. As a base, bicarbonate accepts a proton to form carbonic acid, H_2CO_3.

Notice that the reactions involving bicarbonate are written with double-arrows. This indicates that the reaction is capable of moving in either the left or right direction. Consider the reaction of bicarbonate as an acid:

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{-2} + H_3O^+$$



For the forward reaction, we have identified HCO_3^- as the acid and H_2O as the base. For the reverse reaction, CO_3^{-2} is the base and H_3O^+ is the acid.

More specifically, for the forward reaction we call CO_3^{-2} the **conjugate base** of HCO_3^- and H_3O^+ is the **conjugate acid** of H_2O. For the reverse reaction we call H_2O the conjugate base of H_3O^+ and HCO_3^- is the conjugate acid of CO_3^{-2}. Notice that acid-base **conjugate pairs** differ from each other by a proton!

Problem 2B-1

One of the components of acid rain is nitrous acid, HNO_2. For the dissociation of HNO_2, identify the acid and base on each side of the equation and identify the conjugate pairs.

$$HNO_2 + H_2O \rightleftharpoons NO_2^- + H_3O^+$$

You should write answers to boxed problems before going on in your reading.

✓ In this reaction, HNO_2 donates a proton to H_2O. Therefore, HNO_2 is the acid and H_2O is the base. NO_2^- is the conjugate base because it is formed when HNO_2 donates a proton. H_3O^+ is the conjugate acid because it is the result of H_2O accepting a proton.

In summary, an acid is a proton donor and it loses a proton to become its conjugate base; a base is a proton acceptor and it gains a proton to become its conjugate acid.

Polyprotic Acids

Acids that are capable of donating more than one proton are called **polyprotic** acids. H_2CO_3 is an example of a polyprotic acid:

$$\text{First proton: } H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

$$\text{Second proton: } HCO_3^- + H_2O \rightleftharpoons CO_3^{-2} + H_3O^+$$

Strong and Weak Acids and Bases

By definition, a **strong acid** is one whose reaction is complete. Nitric acid, HNO_3, is an example of a strong acid present in acid rain:

$$HNO_3(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$

Essentially all HNO_3 dissociates to give NO_3^- and H_3O^+ ions in water. Since HNO_3 is a strong acid, NO_3^- has no tendency to react with H_3O^+.

TABLE 2B-1: THE STRONG ACIDS

ACID	NAME
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydroiodic acid
HNO_3	nitric acid
H_2SO_4	sulfuric acid (first proton)
$HClO_4$	perchloric acid

TABLE 2B-2: THE STRONG BASES

BASE	NAME
LiOH	lithium hydroxide
NaOH	sodium hydroxide
KOH	potassium hydroxide
RbOH	rubidium hydroxide
CsOH	cesium hydroxide
R_4NOH	

Any acid not listed in Table 2B-1 is a **weak acid**, one that does not completely dissociate in water. The extent of reaction for a weak acid with water can be to the right or left, depending on the weakness of the acid. Very weak acids have an extent of reaction far to the left; as the strength of the acid increases, the extent of reaction shifts towards the right. The stronger the acid, the weaker it's conjugate base and vice versa.

Strongest Acid ↑ Weakest Acid

Weakest Base ↓ Strongest Base

$$
\begin{array}{rcl}
HClO_4 + H_2O & \longrightarrow & H_3O^+ + ClO_4^- \\
HCl + H_2O & \longrightarrow & H_3O^+ + Cl^- \\
H_3PO_4 + H_2O & \rightleftharpoons & H_3O^+ + H_2PO_4^- \\
Al^{+3} + H_2O & \rightleftharpoons & H_3O^+ + AlOH^{+2} \\
CH_3COOH + H_2O & \rightleftharpoons & H_3O^+ + CH_3COO^- \\
H_2PO_4^- + H_2O & \rightleftharpoons & H_3O^+ + HPO_4^{-2} \\
NH_4^+ + H_2O & \rightleftharpoons & H_3O^+ + NH_3 \\
H_2O + H_2O & \rightleftharpoons & H_3O^+ + OH^-
\end{array}
$$

HCl is a strong acid and therefore the H_3O^+ in solution will be equal to the initial concentration of the HCl to a first approximation. CH_3COOH is a weak acid and therefore the H_3O^+ in solution will be much less than the initial concentration of CH_3COOH. Note that strong and weak refers to the extent of the reaction with water; it does not refer to concentration or the number of moles in a given volume.

Developing Ideas

2B-2 What happens when you dissolve a strong acid or base in water? For each strong acid in Table 2B-1 and for each strong base in Table 2B-2, write a balanced chemical equation showing the dissolution of the acid or base in water.

HCl

HBr

HI

HNO_3

H_2SO_4

$HClO_4$

LiOH

NaOH

KOH

RbOH

CsOH

$(CH_3)_4NOH$

2B-3 Based on the reactions in problem 2B-2, list the ionic species other than OH^- and H_3O^+ in solutions of strong acids and bases. Except for HSO_4^-, these ions are *spectator ions* and they do not react as acids and bases in aqueous solution.

2B-4 Label the acid and base on each side of the following reactions:

$$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$$

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{-2} + H_3O^+$$

$$Al^{+3} + H_2O \rightleftharpoons Al(OH)^{+2} + H^+$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Strong and weak, concentrated and dilute

2B-5 In small groups, sketch a diagram of one of the following aqueous solutions from the atomic/molecular viewpoint. Explain your diagram to the rest of the class, including any assumptions and definitions that you made, and including all chemical species.

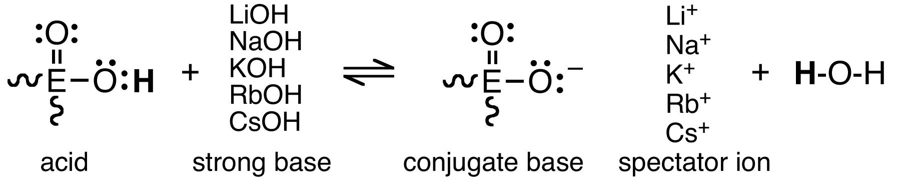
	strong acid	weak acid
concentrated acid		
dilute acid		

APPLYING YOUR IDEAS

Finding Acids and Bases from Neutral Compounds

Acids and bases react with each other to form an ionic compound. Sometimes it can be difficult to identify the conjugates because spectator ions are included in the formula of these neutral compounds. (There is no such thing as a solution of only acetate ions, CH_3COO^-; you must have a positive ion present to balance the charge of the negative ion.) Examples of these reactions are shown in the table below.

Acid Neutralization



$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$

sulfuric acid   sodium bisulfate

$CH_3COOH + KOH \longrightarrow CH_3COOK + H_2O$

acetic acid   potassium acetate

$H_2SO_3 + LiOH \longrightarrow LiHSO_3 + H_2O$

sulfurous acid   lithium bisulfite

E is a nonmetal element. ∿ may or may not be a bond, depending on the element and whether additional bonds are required by Lewis dot theory. Higher oxidation states of E and more electronegative substituents (-Cl, -F, $-CF_3$, =O) make the acid stronger. For example, the acidity of $H_2SO_4 > H_2SO_3 > CH_3COOH$.

Aqua Acid Dissociation

$Fe^{+3} + H_2O \rightleftharpoons Fe(OH)^{+2} + H^+$

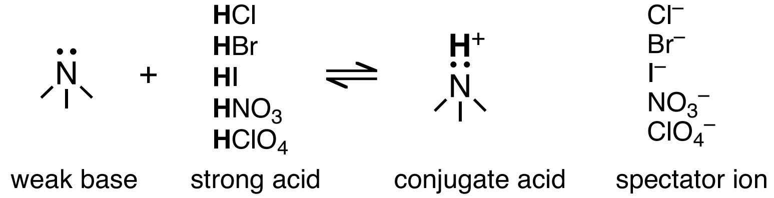
$Al^{+3} + H_2O \rightleftharpoons Al(OH)^{+2} + H^+$

$Al(OH)^{+2} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+$

acid   conjugate base

Smaller ions and larger positive charges make the acid stronger.

Base Neutralization



$CH_3NH_2 + HBr \longrightarrow CH_3NH_3Br$

methylamine   methylammonium bromide

$C_6H_5N + HCl \longrightarrow C_6H_5NHCl$

pyridine   pyridinium chloride

Monoprotic and polyprotic acids and bases

2B-6 Fill in the formulas that exist in water. Label each species as acid, base, or amphiprotic. (Many of the boxes will be empty!)

Dication (gained 2 protons)	Cation (gained 1 proton)	Neutral	Anion (lost 1 proton)	Dianion (lost 2 protons)
		NH_3		
			CH_3COO^-	
	$H_2NCH_2CH_2NH_3^+$			
				$^-OOC\text{-}COO^-$
		H_3NCH_2COO		

2B-7 In small groups (A, B, C, or D) identify each species as acid, base, or both and give the formula of its conjugate(s).

	A	**B**	**C**	**D**
1.	CH_3COOH	C_5H_5NHBr	C_6H_5COOK	$C_6H_5NH_3ClO_4$
2.	NH_4Cl	$ClCH_2COOH$	KH_2AsO_4	H_2CO_3
3.	H_3BO_3	H_2SO_4	$HONH_3Cl$	C_6H_5OH
4.	CH_3COONa	C_5H_5N	C_6H_5COOH	$C_6H_5NH_2$
5.	NH_3	$ClCH_2COOLi$	H_3AsO_4	$LiHCO_3$
6.	NaH_2BO_3	$RbHSO_4$	$HONH_2$	C_6H_5OK
7.	Al^{+3}	$Fe(OH)_2^+$	Fe^{+3}	$Al(OH)^{+2}$

What is pH?

EXPLORATION 2C, PH

CREATING THE CONTEXT

Most people have heard of the word “pH”. We talk about “acidic” foods and about “neutralizing” harmful substances. But what do these terms mean? This Exploration will define pH and the pH scale.

A proton in water is closely associated with one water molecule (the hydronium ion, H_3O^+), which is less closely associated with three more water molecules (see Figure 2C-1), which are less closely associated with even more water molecules in a hydrogen-bonded network. What is the proper formula for a proton in water, H^+ or H_3O^+ or $H_9O_4{}^+$ or $H^+(H_2O)_n$? We will abbreviate the formula for a proton in water as H^+ for the remainder of this module.

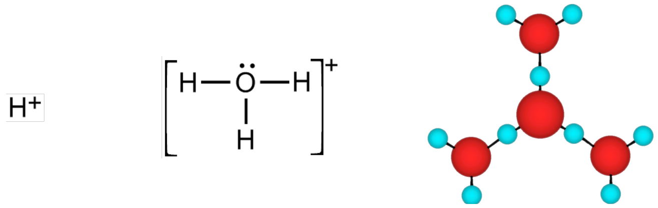


Figure 2C-1. Should we represent a proton in water as H^+, H_3O^+, $H_9O_4{}^+$ or $H^+(H_2O)_n$?

The pH of a substance is determined by the H^+ concentration, represented as $[H^+]$. Because the hydrogen ion concentration is often small and varies widely, it is often described by its negative log or “p” value.

$$pH = -\log[H^+] \qquad [H^+] = 10^{-pH}$$

Acidic solutions have high $[H^+]$ and low pH values ($pH < 7$) whereas basic solutions have low $[H^+]$ and high pH values ($pH > 7$).

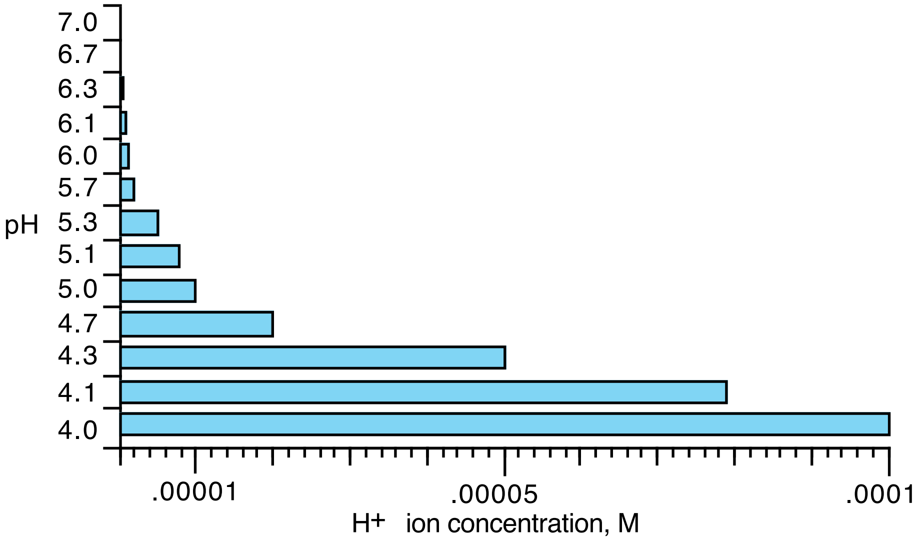


Figure 2C-2. Relationship between pH and H^+ ion concentration.

PREPARING FOR INQUIRY

Problem 2C-1

Calculate the pH of a 1.5×10^{-3} M solution of HCl:

✓ Since pH is related to $[H^+]$ our first step is to determine the $[H^+]$ of the solution. From table 2B-1 we know that HCl is a strong acid and will completely dissociate in solution:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

In a 1.5×10^{-3} M solution of HCl, $[H^+] = 1.5 \times 10^{-3}$ M. Plugging this into the pH equation gives:

$$pH = -\log[H^+] = -\log(1.5 \times 10^{-3}) = 2.82$$

This seems reasonable; HCl is an acid and should have a pH below 7.

Problem 2C-2

Calculate $[H^+]$ of a pH 3.3 solution of HCl:

✓ $[H^+] = 10^{-3.3} = 5.0 \times 10^{-4}$ M

In the problems above, you practiced finding the pH of a strong acid. Calculating the pH of a weak acid, however, is not as straightforward. Since weak acids do not completely dissociate we cannot use simple stoichiometry to determine $[H^+]$. Methods for calculating the pH of weak acids will be explored in the next session.

Autoionization of water

An important reaction in acid-base chemistry is the **autoionization** of water, which is simply the transfer of a proton from one water molecule to another:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$\text{or } H_2O \rightleftharpoons H^+ + OH^-$$

The product of the hydrogen ion concentration times the hydroxide concentration, $[H^+] \times [OH^-]$, has been experimentally determined to be a constant, K_w. At laboratory temperatures (assume 24°C),

$$\mathbf{K_w = [H^+]\ [OH^-] = 1.00 \times 10^{-14}}$$

Both the proton and hydroxide concentrations are 10^{-7} M in pure water (since K_w varies slightly with temperature the pH of neutral water also varies slightly with temperature). This corresponds to about 1 dissociated water molecule per billion, 10^9.

Because the product of $[H^+]$ and $[OH^-]$ is a constant in water, as one gets bigger the other gets smaller (Figure 2C-3.)

$$K_w = [H^+][OH^-] = 10^{-14}$$

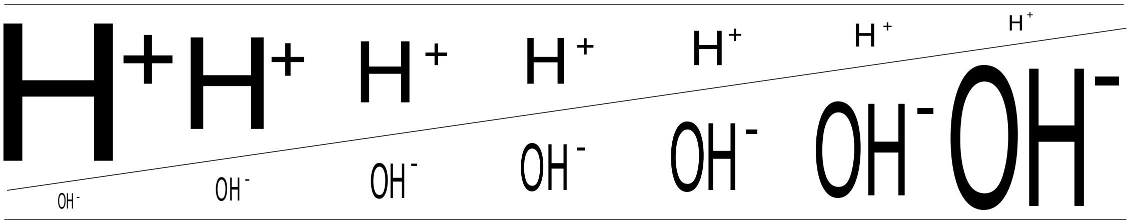


Figure 2C-3. Font size representing concentration of H^+ and OH^-. The product of $[H^+]$ and $[OH^-]$ in water is a constant. As one gets bigger the other must get smaller.

How are pH and pOH related?

$$K_w = [H^+][OH^-] = 10^{-14}$$

$$\log K_w = \log [H^+][OH^-] = \log(10^{-14})$$

$$\log K_w = \log [H^+] + \log[OH^-] = -14$$

$$pK_w = pH + pOH = 14$$

Since the sum of pH and pOH is a constant, as one gets bigger the other gets smaller (Figure 2C-4.) Both are equal when pH = pOH = 7.

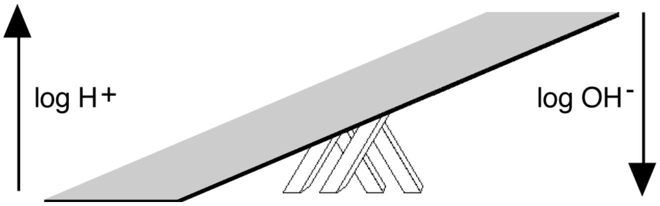


Figure 2C-4. Logarithmic seesaw for pH and pOH in water. The sum of pH and pOH in water is a constant. As one gets bigger the other must get smaller.

Developing Ideas

2C-3 Work in groups to determine one of the following. Any member of your group should be able to report your result to the class.

a. What is the pH of 0.10 M HCl? How much water must be added to 1.0 mL of 0.10 M HCl to change the pH by 1? by 2?

b. What is the pH of 0.10 M CH_3COOH? How much water must be added to 1.0 mL of 0.10 M CH_3COOH to change the pH by 1? by 2?

c. What is the pH of 0.00010 M NaOH? How much water must be added to 1.0 mL of 0.00010 M NaOH to change the pH by 1? by 2?

d. What is the pH of 0.00010 M NH_3? How much water must be added to 1.0 mL of 0.00010 M NH_3 to change the pH by 1? by 2?

e. Dilute a mixture of 1.0 mL of 0.10 M HCl and 1.0 mL of 0.10 M NH_3 with water. How much water is needed to change the pH by 1?

f. Dilute a mixture of 1.0 mL of 0.10 M NaOH and 1.0 mL of 0.10 M CH_3COOH with water. How much water is needed to change the pH by 1?

You might find it interesting to also measure the pH of the solutions from Exploration 2A.

APPLYING YOUR IDEAS

2C-4 Predict the pH for 0.10 M HCl, 0.010 M HCl, 0.0010 M HCl, and 0.00010 M HCl.

2C-5 What is the [H^+] for a solution of HNO_3 with pH 6, pH 2.3, and pH 0.9?

2C-6 Estimate the pH at which the probes in Exploration 2A change color.

2C-7 A bottle of (cheap) wine was tested for acidity, and its pH was found to 2.96 at 25 °C. What is the hydrogen ion [H^+] concentration? Is the solution acidic, basic or neutral?

2C-8 If the pH changes by 2 by what factor does the [H^+] change?

2C-9 The label on a shampoo bottle reads:

> *Original Apple Pectin Shampoo Concentrate*
> *- thoroughly cleans as it strengthens hair -*
> *pH 5.5*

a. What is the hydrogen ion concentration of the shampoo?

b. Is the shampoo acidic or basic?

c. The back label on the shampoo reads:

> ***FOR PROFESSIONAL USE ONLY***
> *APPLE PECTIN Shampoo Concentrate containing carbohydrate-rich apple pectin is a high-lathering, acid-balanced conditioning shampoo which aids in binding the inner fibers of hair, adding to its structure and substance.*

Why do you think the manufacturer has put words like “pH” and “acid-balanced” on the label of this product?

2C-10 You have a stock bottle containing an aqueous solution that is labeled as 0.050 M $Ba(OH)_2$.

a. Is the solution acidic or basic?
b. What are the molar concentrations of ions in the solution?
c. What is the pH of the solution?

2C-11 HCl is a strong acid while CH_3COOH is a weak acid. If you are given solutions of these acids with identical molarities which solution would have the lowest pH?

What is an acid?

SESSION 2, MAKING THE LINK

LOOKING BACK

Session Goals

- Identify acids, bases, conjugate acids and conjugate bases
- The difference between strong and weak acids
- How to calculate the pH from the molarity of a strong acid or strong base
- How to calculate the $[H^+]$ from pH

CHECKING YOUR PROGRESS

What is an acid?

2-1 A general equation for the reaction of any acid in water is:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

HA represents any acid and A^- represents its conjugate base. Using this equation as a guideline, write a general equation for the reaction of any base in water.

2-2 Describe the relationship between the strength of an acid and the strength of its conjugate base.

2-3 Differentiate between the terms “strength” and “concentration” as they apply to acids and bases.

2-4 When is HCl concentrated? Dilute? Strong? Weak?

2-5 Which has the largest pH in each pair?

a. 0.10 M HI or 0.10 M CH_3CH_2COOH?

b. 0.10 M $HONH_2$ or 0.10 M RbOH?

c. 0.10 M HCl or 0.0010 M HCl?

THINKING FURTHER

5-minute Writing Questions

2-6 Give a concise response to the session question, “What is an acid?”

2-7 Why are logarithmic scales used in science? Why does a log scale for $[H^+]$ make sense?

How do systems respond to stress?

EXPLORATION 3A, EQUILIBRIA AND LE CHÂTELIER'S PRINCIPLE

CREATING THE CONTEXT

In Exploration 2B, we gave an equation for the dissociation of the bicarbonate ion in water,

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{-2} + H_3O^+,$$

and stated that the double arrows indicate two reactions are taking place.

$$\text{forward reaction: } HCO_3^- + H_2O \longrightarrow CO_3^{-2} + H_3O^+$$

$$\text{reverse reaction: } CO_3^{-2} + H_3O^+ \longrightarrow HCO_3^- + H_2O$$

This system will eventually reach a state of dynamic **equilibrium** where both reactions are occurring at a constant rate. This makes it *appear* as if no reaction is taking place when in fact both reactions are still occurring. When a system in equilibrium has a greater concentration of products than reactants, we say that its position of equilibrium lies to the right. When the concentration of reactants is greater than products, the position of equilibrium lies to the left.

For acids and bases, the position of equilibrium is directly related to acidic or basic strength. Think of an acid-base equilibrium as a competition between the acids on opposite sides. For example, consider carbonic acid dissociating in water:

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

In this situation, H_2CO_3 is a stronger acid than H_3O^+. As a result, H_2CO_3 is a better proton donor and the dominant reaction is the one in which H_2CO_3 donates protons. For this reaction, we say that the position of equilibrium lies to the right since that is the direction of the dominant reaction.

When the stronger acid is on the right, as in the case of

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{-2} + H_3O^+$$

where H_3O^+ is a stronger acid than HCO_3^-, the dominant reaction is the one in which H_3O^+ donates protons and the equilibrium lies to the left.

In 1864, Cato Gulberg and Peter Waage formulated a powerful mathematical expression for describing the relationship of concentrations in equilibrium reactions. For a general reaction in equilibrium:

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

where A, B, C, and D are chemical species and *a, b, c,* and *d* are their stoichiometric coefficients, the expression

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

is a constant at constant temperature and pressure. The same definition in words is that at equilibrium the ratio of product concentrations raised to their stoichiometric coefficients to reactant concentrations raised to their stoichiometric coefficients is a constant at constant temperature. This ratio is called an **equilibrium expression** and it is equal to an **equilibrium constant, *K***. No matter what the starting concentrations, whether starting from only reactants, only products, or a mixture of both, you end up with the same value of *K*. This equilibrium law, sometimes called the law of mass action, is an ideal law that assumes ions and molecules act independently. The square brackets represent concentrations. Concentration units used in equilibrium

- Concentration units for solutes in solution are moles/liter.
- The concentration of pure liquids and solids is 1.

constant expressions are moles/liter for solutes, mole fraction for immiscible liquids and solids, and partial pressure in atmospheres for gases. (The mole fraction for a pure liquid or solid is 100% so concentrations of liquids and solids are often assumed to be 1.)

When the equilibrium constant describes the reaction of an acid with water it is given the subscript "a" for "acid." As an example, consider chlorous acid in water:

$$HClO_2 + H_2O \rightleftharpoons ClO_2^- + H_3O^+$$

The equilibrium expression for this reaction is given as:

$$K_a = \frac{[ClO_2^-]^1[H_3O^+]^1}{[HClO_2]^1[H_2O]^1} = \frac{[ClO_2^-][H_3O^+]}{[HClO_2][H_2O]} = \frac{[ClO_2^-][H^+]}{[HClO_2]}.$$

In the last term, water is omitted from the equilibrium expression because it is assumed to be a pure liquid and $[H_3O^+]$ has been written as $[H^+]$. In this form the equilibrium constant expression is the same as for the dissociation reaction:

$$HClO_2 \rightleftharpoons ClO_2^- + H^+$$

Problem 3A-1

Write an equilibrium expression for the dissociation of anilinium ($C_6H_5NH_3^+$) in water.

✓ The first step is to write a balanced equation. Anilinium is an acid so it will donate a proton to water:

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

From this we can write the equilibrium expression:

$$K_a = \frac{[H^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$

Strong and weak acids and bases

Let's revisit our discussion of strong and weak acids and bases, and relate them to the equilibrium constant. A weak acid incompletely dissociates in water (there is an equilibrium and an equilibrium constant).

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

A strong acid completely dissociates in water (there is not an equilibrium or an equilibrium constant for the acids and bases in Tables 2B-1 and 2B-2).

$$HCl \longrightarrow Cl^- + H^+ \text{ and } NaOH \longrightarrow Na^+ + OH^-$$

Polyprotic acids are capable of donating more than one proton and have a K_a value for the dissociation of each proton. K_{a1} corresponds to the dissociation of the first proton, K_{a2} corresponds to the dissociation of the second proton and K_{a3} corresponds to the dissociation of the third proton.

Values for some equilibrium constants are given in Appendix 1.

The magnitude of the K_a value is an indication of the acid strength. Larger values mean the species on the right side (and appearing in the numerator) are relatively larger and that the acid is relatively stronger. As indicated above for these weak acids, H_2CO_3 ($K_a = 3.2 \times 10^{-4}$) is stronger than H_3O^+ ($K_a = 10^{-7}$) is stronger than HCO_3^- ($K_a = 4.7 \times 10^{-11}$).

Le Châtelier's principle

Chemical equilibrium is a dynamic process in which reactants continually combine to give products and products continually combine to give reactants. Eventually a steady state situation is achieved where the production of products from the remaining reactants matches the rate of production of reactants from the remaining products.

Since equilibria are dynamic, if you change conditions such as concentrations, temperature, or pressure then the balance shifts. An increase in concentration shifts the balance toward the opposite side of the reaction. An increase in temperature alters the concentrations in the direction that absorbs heat. An increase in pressure alters the concentrations to favor the side with the smallest volume. The direction of the shift can be predicted by **Le Châtelier's principle**: a system at equilibrium responds to stress in a way that *partially* counteracts that stress.

As an example, consider the ionization of ammonia as a base:

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Suppose we add some NH_4Cl, a soluble salt that produces NH_4^+ and Cl^- ions. The equilibrium will shift to the left, consuming NH_4^+ and OH^- and producing NH_3 and H_2O. (The NH_4^+ concentration will still be higher than it was before the extra NH_4^+ was added, but not as high as simple addition would predict.)

Reactions whose balances can be shifted are the basis of gravimetric, chromatographic, titrimetic, and potentiometric methods in analytical chemistry.

Preparing for Inquiry

3A-2 In small groups (A, B, C, or D) write out the K_a expressions involving each species. Is this given species acid or base?

	A	**B**	**C**	**D**
1.	CH_3COOH	C_5H_5NHBr	C_6H_5COOK	$C_6H_5NH_3ClO_4$
2.	NH_4Cl	$ClCH_2COOH$	KH_2AsO_4	H_2CO_3
3.	H_3BO_3	H_2SO_4	$HONH_3Cl$	C_6H_5OH
4.	CH_3COONa	C_5H_5N	C_6H_5COOH	$C_6H_5NH_2$
5.	NH_3	$ClCH_2COOLi$	H_3AsO_4	$LiHCO_3$
6.	NaH_2BO_3	$RbHSO_4$	$HONH_2$	C_6H_5OK
7.	Al^{+3}	$Fe(OH)_2^+$	Fe^{+3}	$Al(OH)^{+2}$

DEVELOPING IDEAS

Model a system reaching equilibrium by placing 30 red beans, 30 pinto beans, 30 white beans, and 30 black-eyed peas in a paper cup. You will also need some additional beans to exchange when a successful reaction occurs. Without looking, withdraw three beans from the reaction vessel. Exchange your beans according to the reaction:

$$\text{Red} + \text{Pinto} \rightleftharpoons 2\ \text{White} + \text{Black-eyed.}$$

Put successful reactants aside; replace products and unused reactants back in reaction vessel. For example, if the three beans selected were 2 white and a black-eyed you would exchange them for one red and one pinto bean. For example, if a red, white and pinto bean were withdrawn you would return a black-eyed and three white beans. Keep a running tally of the number of each kind of beans in the cup. Also record whether the reaction proceeded to the right or left (→ and ←). If no reaction occurs, replace and try again. ***Do not record unsuccessful reactions.*** Repeat until about half of your last ten reactions go each way.

Trial	Direction	Red beans	Pinto beans	White beans*	Black-eyed	K
0		30	30	30	30	
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

*Actually, these are Great Northern beans.

Has the color of the overall mixture changed? Calculate the *K* value for your last few trials. Does your value for the equilibrium constant agree to the nearest power of ten with that found by other class members? (To improve the statistics you could start with a mole of each kind of beans and then run the reaction billions of times.)

Next you will investigate how this system responds to stress. Copy the last line of the table on the previous page to the first line of this page. Add an additional 10 more of one kind of bean to the reaction vessel and update your bean count.

Withdraw three beans from reaction vessel and react as before. Repeat until about half of your last ten reactions go each way.

Trial	Direction	Red beans	Pinto beans	White beans*	Black-eyed	*K*
0						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

Reference: P. D. Dickinson and W. Erhardt, *J. Chem. Ed.*, **68**, 930, (1991).

Did the initial reactions mainly go in the direction predicted by Le Châtelier's principle?

Calculate the *K* value for your last few trials. Is the same value of K obtained as before? Compare your results with other class members who chose a different stress to apply to the system.

APPLYING YOUR IDEAS

3A-3 What value did you obtain for the equilibrium constant in the bean experiment? Do your values from the first and second page agree?

3A-4 Explain your observations of the stressed bean systems in terms of Le Châtelier's Principle. What stress was applied? How did concentrations change in response to that stress?

3A-5 Explain your observations of the stressed bean systems in terms of the equilibrium constant. Was stress applied to the numerator or the denominator? How did the concentrations change to maintain the equilibrium expression as a constant?

3A-6 Consider the reaction between nitrogen gas and oxygen gas to form nitric oxide gas.

$$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g) \qquad \Delta H° = +181\ kJ$$

a. How is this process involved in acid rain formation?

b. Which way will the equilibrium shift if $O_2(g)$ is added to the system?

c. How will the system at equilibrium respond if $NO(g)$ is added to the system?

d. Which way will the equilibrium shift if heat is added to the system? (Recall exothermic and endothermic reactions)

e. How will the system at equilibrium respond if $N_2(g)$ is removed from the system?

3A-7 Consider the formation of sulfur trioxide, SO_3 from the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H° = -198\ kJ$$

a. How is this process involved in acid rain formation?

b. Which way will the equilibrium shift if $O_2(g)$ is added to the system?

c. How will the system at equilibrium respond if $SO_3(g)$ is added to the system?

d. Which way will the equilibrium shift if heat is added to the system?

e. How will the system at equilibrium respond if $SO_2(g)$ is removed from the system?

3A-8 For each of the following, write out a balanced equation and equilibrium expression for the acid dissociation in water:

HCN

H_2CO_3

C_5H_5N

$HONH_2$

HPO_4^{-2}

$H_2PO_4^-$

3A-9 Describe the relationship between the strength of an acid and its K_a value.

3A-10 Arrange the following acids in order of increasing acid strength:

HF HBr $H_2PO_4^-$ NH_4^+

3A-11 Describe the relationship between the strength of an acid and the strength of its conjugate base.

3A-12 Arrange the following bases in order of increasing base strength:

F^- NH_3 $LiOH$ CN^-

3A-13 A chemist found a container with an unknown weak acid and determined its K_a value to be about 2×10^{-5}. Suggest the identity of the unknown.

3A-14 A 1.0 M solution of $Ca(NO_3)_2$ has a pH of 6.9 while a 1.0 M solution of $Al(NO_3)_3$ has a pH of 3.5. Compare the pKa values for the relevant acid producing equilibria. Would $Fe(NO_3)_3$ have a higher or lower pH than $Ca(NO_3)_2$ and $Al(NO_3)_3$?

What is the pH of normal rain?

EXPLORATION 3B, EQUILIBRIUM CALCULATIONS

CREATING THE CONTEXT

To determine if rainwater has been affected by acid, it is necessary to know the pH of normal rain. The pH of pure distilled water is 7.0, so it would be tempting to assume that rain unaffected by acid rain would also have a pH of 7.0. However, rainwater is in equilibrium with the carbon dioxide in the atmosphere; carbon dioxide reacts with water to form carbonic acid.

Carbonic acid is a weak acid. As discussed in Session 2, weak acids do not completely dissociate so we cannot use simple stoichiometry to determine $[H^+]$. In this Exploration we will investigate algebraic techniques for finding the pH of a weak acid and then calculate the pH of normal rain in the absence of nitrogen or sulfur oxides.

PREPARING FOR INQUIRY

What are the general principles that can be used to calculate the pH of any acid or base? A first step in solving this type of equilibrium problem is to *write a balanced chemical equation and the corresponding equilibrium expression.* The concentration of each substance will be the given concentration before dissociation modified by the equilibrium chemical reaction.

Let us calculate the pH of a 0.10 M solution of CH_3COOH as an example. CH_3COOH is a weak acid that incompletely dissociates in solution.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5}$$

Starting from 0.10 M CH_3COOH gives $0.10 = [CH_3COOH] + [CH_3COO^-]$ or $[CH_3COOH] = 0.10 - [CH_3COO^-]$. In water $[H^+] = [OH^-]$ and $[H^+]$ will increase as CH_3COO^- is formed so $[H^+] = [OH^-] + [CH_3COO^-]$ is the proton balance and $[CH_3COO^-] = [H^+] - [OH^-]$.

Substitute these concentrations into the equilibrium constant expression:

$$K_a = 1.75 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]([H^+] - [OH^-])}{0.10 - ([H^+] - [OH^-])}.$$

CH_3COOH is an acid so it is likely that $[OH^-] << [H^+]$, but the value of K_a suggests a weak acid with $[OH^-] << 0.10$ M and $[H^+] << 0.10$ M. Making these approximations gives an equation with one unknown,

$$K_a = 1.75 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]([H^+] - \cancel{[OH^-]})}{0.10 - \cancel{([H^+] - [OH^-])}} \approx \frac{[H^+]^2}{0.10},$$

that solves to yield $[H^+] = 1.3 \times 10^{-3}$. Checking the assumptions gives $[CH_3COO^-] = 0.0013 - 10^{-14}/0.0013 \approx 0.0013$ and $[CH_3COOH] = 0.10 - 0.0013 + 10^{-14}/0.0013 \approx 0.10$ which are both true within significant digits. The pH is $-\log[H^+] = -\log(0.0013) = 2.88$.

Assumptions are not crossing things out; they are simply applying the answer to an addition or subtraction step. Be careful to not cross out all terms in a factor.

As a second example, what is the pH of a 0.50 M solution of $NaHSO_4$? The balanced chemical equation for the reaction is:

$$HSO_4^- \rightleftharpoons SO_4^{-2} + H^+$$

Starting from 0.50 M HSO_4^- gives $0.50 = [HSO_4^-] + [SO_4^{-2}]$ or $[HSO_4^-] = 0.50 - [SO_4^{-2}]$. In water $[H^+] = [OH^-]$ and $[H^+]$ will increase as SO_4^{-2} is formed so $[H^+] = [OH^-] + [SO_4^{-2}]$ is the proton balance and $[SO_4^{-2}] = [H^+] - [OH^-]$.

Substitute these concentrations into the equilibrium constant expression:

$$K_a = 1.2 \times 10^{-2} = \frac{[H^+][SO_4{}^{-2}]}{[HSO_4{}^-]} = \frac{[H^+]([H^+] - \cancel{[OH^-]})}{0.50 - ([H^+] - \cancel{[OH^-]})}$$

The value of K_a indicates that HSO_4^- is not a particularly weak acid so it is likely that that $[OH^-] << [H^+]$ and $[OH^-] << 0.50$ M. Rearranging and then using the quadratic equation to solve for $[H^+]$ gives:

$$(1.2 \times 10^{-2})(0.50 - [H^+]) = [H^+]^2$$
$$[H^+]^2 + 1.2 \times 10^{-2}\,[H^+] - 6.0 \times 10^{-3} = 0$$
$$[H^+] = 7.2 \times 10^{-2}$$

Checking the assumptions gives $[SO_4^{-2}] = 0.072 - 10^{-14}/.072 \approx 0.072$ and $[HSO_4^-] = 0.50 - 0.072 + 10^{-14}/.072 \approx 0.50 - 0.072$ is true within significant digits. The pH is $-\log[H^+] = -\log(7.2 \times 10^{-2}) = 1.14$

The quadratic formula says the solution to $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

When solving for concentrations they will always be the + answer!

Note that also trying the approximation that $[H^+] << 0.50$ M gives

$$K_a = 1.2 \times 10^{-2} = \frac{[H^+][SO_4{}^{-2}]}{[HSO_4{}^-]} = \frac{[H^+]([H^+] - \cancel{[OH^-]})}{0.50 - \cancel{([H^+] - [OH^-])}} \approx \frac{[H^+]^2}{0.50}$$

to yield $[H^+] = 0.077$ M.

In this case we find $[HSO_4^-] = 0.50 - 0.077 + 10^{-14}/.077 \approx 0.50$ is not a good assumption within significant digits. The pH is not $-\log(0.077) = 1.11$

As a third example, what is the pH of 0.10 M CH_3COONa? The balanced chemical equation for the acid-base reaction with water is:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Starting from 0.10 M CH_3COO^- gives $0.10 = [CH_3COO^-] + [CH_3COOH]$ or $[CH_3COO^-] = 0.10 - [CH_3COOH]$. In water $[H^+] = [OH^-]$ and $[OH^-]$ will increase as CH_3COOH is formed so $[OH^-] = [H^+] + [CH_3COOH]$ is the proton balance and $[CH_3COOH] = [OH^-] - [H^+]$.

Substitute these concentrations into the equilibrium constant expression:

$$K_a = \frac{\cancel{[H^+]}[CH_3COO^-]}{[CH_3COOH]}\,\frac{K_w}{\cancel{[H^+]}[OH^-]} = \frac{\big(0.10 - ([OH^-] - [H^+])\big)K_w}{\big([OH^-] - [H^+]\big)[OH^-]} = 1.75 \times 10^{-5}$$

(Since $[H^+]$ is hard to estimate, K_a was multiplied above by $1 = \dfrac{K_w}{[H^+][OH^-]}$.)

We can again make some approximations, rearrange and solve:

$$K_a = \frac{\cancel{[H^+]}[CH_3COO^-]}{[CH_3COOH]}\,\frac{K_w}{\cancel{[H^+]}[OH^-]} = \frac{\big(0.10 - (\cancel{[OH^-] - [H^+]})\big)K_w}{\big([OH^-] - \cancel{[H^+]}\big)[OH^-]} = 1.75 \times 10^{-5}$$

$$\frac{(0.10)K_w}{[OH^-]^2} = 1.75 \times 10^{-5}$$

$$[OH^-] = \sqrt{\frac{(0.10)(10^{-14})}{1.75\times10^{-5}}} = 7.56 \times 10^{-6}.$$

Checking assumptions gives $[CH_3COOH] = 7.56 \times 10^{-6} - 10^{-14}/(7.56 \times 10^{-6}) \approx 7.56 \times 10^{-6}$ and $[CH_3COO^-] = 0.10 - (7.56 \times 10^{-6} - 10^{-14}/(7.56 \times 10^{-6})) \approx 0.10$. These are both good within significant digits so pH = 14 – log([OH⁻]) = 8.88.

Problems

3B-1 Write the concentration expression, proton balance, and K_a equations for 0.100 M solutions in water and solve for pH.

	A	**B**	**C**	**D**
1.	CH_3COOH	C_5H_5NHBr	C_6H_5COOK	$C_6H_5NH_3ClO_4$
2.	NH_4Cl	$ClCH_2COOH$	KH_2AsO_4	H_2CO_3
3.	H_3BO_3	H_2SO_4	$HONH_3Cl$	C_6H_5OH
4.	CH_3COONa	C_5H_5N	C_6H_5COOH	$C_6H_5NH_2$
5.	NH_3	$ClCH_2COOLi$	H_3AsO_4	$LiHCO_3$
6.	NaH_2BO_3	$RbHSO_4$	$HONH_2$	C_6H_5OK
7.	Al^{+3}	$Fe(OH)_2^+$	Fe^{+3}	$Al(OH)^{+2}$

DEVELOPING IDEAS

3B-2 The equilibrium of $CO_2(g)$ with rainwater takes place in several steps. These steps are described in words below. *Translate the words into chemical equations.* (Hint: see Appendix 1 under carbon.)

a. Gaseous carbon dioxide dissolves in water to form an aqueous carbon dioxide solution.

b. The aqueous carbon dioxide reacts with water to make aqueous carbonic acid.

c. Carbonic acid is a polyprotic weak acid and its first proton partially dissociates in water.

d. Bicarbonate (hydrogen carbonate) is a very weak acid and it only slightly dissociates in water.

e. Based on the K_a equilibrium constants for carbonic acid (K_{a1}) and bicarbonate (K_{a2}), which of these weak acids is stronger? According to Le Châtelier's Principle how will the production of H^+ by the stronger acid affect the dissociation of the weaker acid?

Problem 3B-3

Write the one reaction from Appendix 1 that is the primary overall source of H^+ produced from $CO_2(g)$. (This equation is the sum of the reactions in questions a-c in 3B-2) What is the equilibrium constant expression for this reaction?

✓ The appropriate equilibrium constant expression is $K = 10^{-7.820} = \dfrac{[H^+][HCO_3^-]}{[CO_2(g)]}$.

The pH will depend on the concentration of $CO_2(g)$. Figure 3B-1 and 3B-2 show the partial pressure in atmospheres for carbon dioxide gas as a function of year. (Combustion of fossil fuels results in an increasing concentration of $CO_2(g)$ in the atmosphere.) The present value for $[CO_2(g)]$ can be estimated from the graphs and substituted into the equilibrium constant expression.

Problem 3B-4

What is the pH of natural rainwater at equilibrium with CO_2 in the atmosphere? Assume no nitrogen or sulfur oxides are present.

✓ From examining the chemical equation you wrote in Problem 3B-2, you should notice that one $[HCO_3^-]$ is produced for every $[H^+]$. If this reaction is the primary source of $[H^+]$, then $[HCO_3^-] = [H^+]$. Substituting into the equilibrium constant gives:

$$10^{-7.820} = \frac{[H^+]^2}{[CO_2(g)]}$$

Remember that the units normally used in equilibrium constant expressions are moles/liter for solutes, mole fraction for immiscible liquids and solids, and partial pressure in atmospheres for gases.

APPLYING YOUR IDEAS

3B-5 Collect some rainwater and measure its pH. How does this value compare with your calculated value from Problem 3B-4?

3B-6 What was the pre-industrial $[H^+]$ and pH of rain in 1800. Compare your answer to Problem 3B-4. Why are the answers different? Also predict the CO_2 concentration and calculate the pH of rain in 2050.

3B-8 Rain falling in industrialized regions is more acidic than that falling naturally. In eastern North America, the average pH of rainwater is about 4.2. Consider a small lake about 1 km × 1 km and 10 meters deep with a volume of 10^{10} L filled with average eastern US rainwater. Assume that the extra acidity is due entirely to sulfuric acid and that you would like to bring the pH to that of normal rainwater, which you calculated in a previous problem. One way to accomplish this is to dump limestone ($CaCO_3$) into the lake by helicopter, a method used in Sweden to compensate for the acid rain arriving from Britain.

a. How many times more concentrated is [H^+] in this lake than in a lake filled with normal rainwater? Hint: Compare with Problem 3B-4.

b. Write a balanced chemical equation for the reaction of sulfuric acid with limestone.

c. How many kilograms of limestone will it take to change the pH of the lake to that of normal rain? Show your work with units. Hint: this is a mole calculation, not an equilibrium calculation.

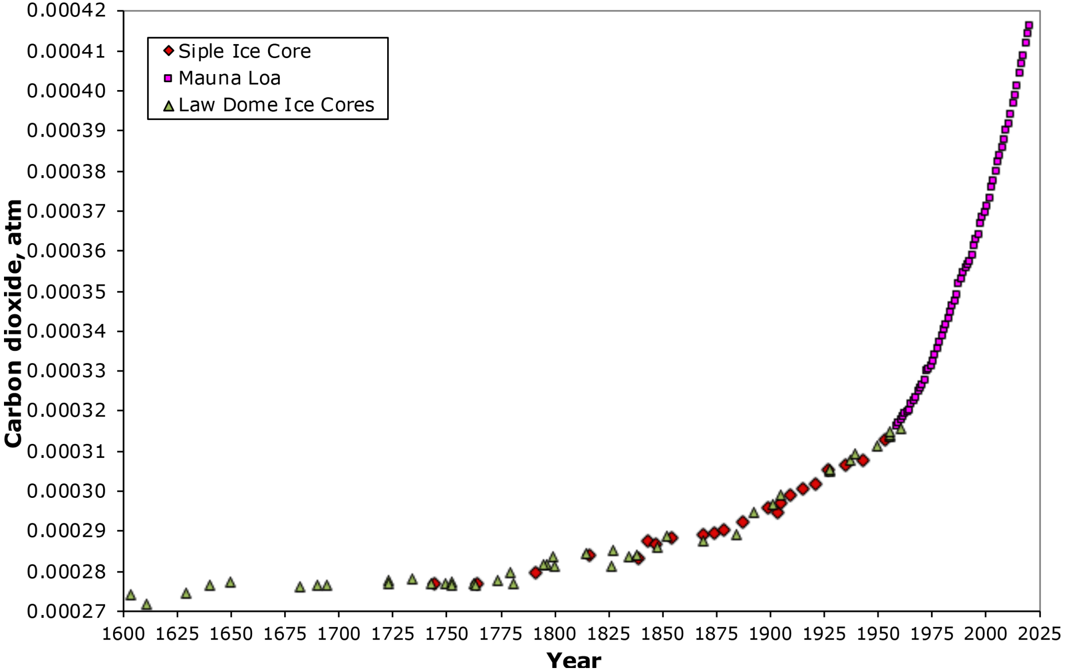


Figure 3B-1. Experimental partial pressure in atmospheres for carbon dioxide gas.

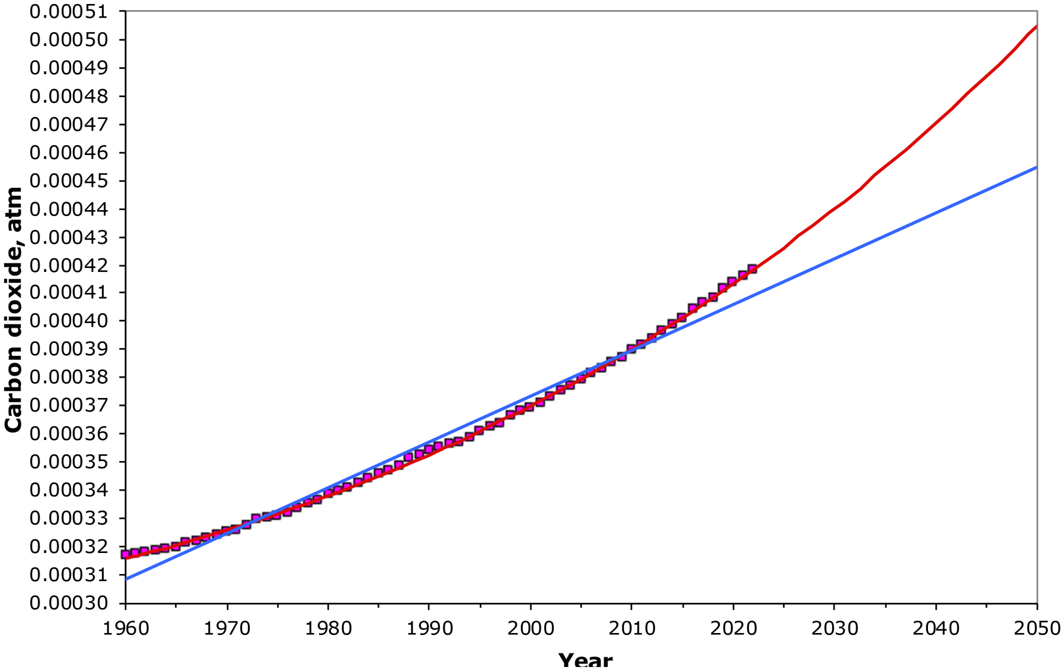


Figure 3B-2. Linear extrapolation and curve-fit extrapolation of partial pressure in atmospheres for carbon dioxide gas. Mauna Loa data through 2022 in 3B-1 and 3B-2.

How can we solve any equilibrium problem?

Exploration 3C, Systematic Method

Creating the Context

Lets formally review the procedure used in Exploration 3B for finding the pH of 0.50 M $NaHSO_4$. We identified three unknowns: $[HSO_4^-]$, $[SO_4^{-2}]$, and $[H^+]$. To make it mathematically possible to solve for three unknowns, three equations describing the system are required. One equation was the equilibrium expression:

$$K_a = \frac{[H^+][SO_4^{-2}]}{[HSO_4^-]}.$$

Another equation came from the total moles of HSO_4^- and SO_4^{-2} available,

$$0.50\ M = [HSO_4^-] + [SO_4^{-2}],$$

since the original HSO_4^- can lose a proton to become SO_4^{-2}. The third equation can come from the moles of H^+ available,

$$[OH^-] + 0.50\ M = [HSO_4^-] + [H^+],$$

or from the positive charges being equal to the negative charges,

$$[Na^+] + [H^+] = [OH^-] + [HSO_4^-] + 2\ [SO_4^{-2}].$$

For more complicated systems, especially those involving multiple equilibria or if the autoionization of water is included, it is useful to have a systematic method for obtaining as many equations as unknowns.

Preparing for Inquiry

Systematic Method for Obtaining Equilibrium Equations

1. Identify the species whose concentrations are unknown. You will need as many equations as there are unknowns. Because K^+, Na^+, NO_3^- and ClO_4^- are usually not significantly involved in equilibria, these ions are often used as spectator ions in problems and in the laboratory.
2. Write out the equilibrium constant expressions for balanced chemical equations for all reactions and look up the ***K*** values. *See* the appendix at the end of this module. Equilibrium constant expressions hold even in the presence of other equilibria.
3. Write the **charge** balance equation with coefficients equal to charge. For a real solution the sum of the [positive charges] equals the sum of the [negative charges]. There will only be one charge balance equation.
    a. If the only source of $[H^+]$ and $[OH^-]$ is $H_2O \rightleftharpoons H^+ + OH^-$, then $[H^+] = [OH^-]$ and they drop out of the charge balance expression.
    b. Be sure to include Li^+, Na^+, K^+, Rb^+ in the charge balance for the conjugate base of a weak acid (e. g., CH_3COONa).
    c. Be sure to include NO_3^-, ClO_4^-, Cl^-, Br^-, I^- in the charge balance for the conjugate acid of a weak base (e. g., NH_4Cl).
4. Write **mass** balance equations based on how the solution was prepared. The sum of all forms of a species must equal the total amount added. There may be more than one conservation of mass equation for a system if conservation equations are written for different elements.

Remember *K*, charge, mass!

5. **Solve and check** that you obtained a chemically reasonable answer.
    Acid solution: $[OH^-] << [H^+]$?
    Base solution: $[H^+] << [OH^-]$?
    Strong or weak?

   Any mathematical method of solving equations may be used.
6. Have you answered the original question?

Lets try using the systematic method on some strong acid and base problems. While these do not always require this level of sophistication, they do give us a chance to try the method on familiar problems.

Simple Examples

3C-1 What is $[H^+]$ in 0.10 M NaOH?

No K for strong acids and bases
Charge balance: $[H^+] + [Na^+] = [OH^-]$
Mass balance: $[Na^+] = 0.10$
One unknown: $[H^+] + 0.10 = [OH^-]$
Solve: $\cancel{[H^+]} + 0.10 = [OH^-]$
Answer question: $[H^+] = K_w/[OH^-] = 10^{-13}$
Check: $10^{-13} + 0.10 \approx 0.10$ *OK*

3C-2 What is $[H^+]$ in 0.10 M HCl?

No K for strong acids and bases
Charge balance: $[H^+] = [OH^-] + [Cl^-]$
Mass balance: $[Cl^-] = 0.10$
One unknown: $[H^+] = [OH^-] + 0.10$
Solve: $[H^+] = \cancel{[OH^-]} + 0.10$
Check: $10^{-13} + 0.10 \approx 0.10$ *OK*

3C-3 What is $[H^+]$ in 10^{-7} M HBr

No K for strong acids and bases
Charge balance: $[H^+] = [OH^-] + [Br^-]$
Mass balance: $[Br^-] = 10^{-7}$
One unknown: $[H^+] = [OH^-] + 10^{-7}$
Solve: $[H^+] = K_w/[H^+] + 10^{-7}$
clear fractions $[H^+]^2 - 10^{-7}[H^+] - K_w = 0$
quadratic formula $[H^+] = 1.62\times10^{-7}$
Is this the answer you expected?

3C-4 What is $[H^+]$ in 0.20 M HCl and 0.30 M NaOH

No K for strong acids and bases
Charge balance: $[Na^+] + [H^+] = [OH^-] + [Cl^-]$
Mass balance: $[Na^+] = 0.30$; $[Cl^-] = 0.20$
One unknown: $0.30 + [H^+] = [OH^-] + 0.20$
Solve: $[OH^-] = \cancel{[H^+]} + 0.10$
Answer question: $[H^+] = K_w/0.10 = 10^{-13}$
Check: $10^{-13} + 0.10 \approx 0.10$ *OK*

DEVELOPING IDEAS

Weak Acids and Bases

Weak acid and base problems can also be solved by the systematic method. First collect as many equations as there are unknowns. These examples illustrate combining the equations and solving using various chemical assumptions to simplify the mathematics.

3C-5 What is $[H^+]$ in 0.10 M CH_3COOH?

K: $Ka = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75\times10^{-5}$

Charge balance: $[H^+] = [OH^-] + [CH_3COO^-]$

Mass balance: $0.10 = [CH_3COOH] + [CH_3COO^-]$

From charge $[CH_3COO^-] = [H^+] - [OH^-]$

From mass $[CH_3COOH] = 0.10 - [CH_3COO^-] = 0.10 - [H^+] + [OH^-]$

Substitute into the equilibrium constant expression

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]([H^+]-[OH^-])}{0.10-[H^+]+[OH^-]} = 1.75\times10^{-5}$$

This gives us one equation and one unknown (realizing that $[H^+]$ and $[OH^-]$ can be converted using $K_w = [H^+]\,[OH^-]$). It is usually easier if you convert only when needed to solve the equation.

Solve

Assume acid

$$\frac{[H^+]([H^+]-\cancel{[OH^-]})}{0.10-[H^+]+\cancel{[OH^-]}} = 1.75\times10^{-5} \approx \frac{[H^+][H^+]}{0.10-[H^+]}$$

$$[H^+]^2 + 1.75\times10^{-5}[H^+] - 1.75\times10^{-5}(0.10) = 0$$

$$[H^+] = \frac{-1.75\times10^{-5} + \sqrt{(1.75\times10^{-5})^2 + 4(0.10)(1.75\times10^{-5})}}{2} = 1.31\times10^{-3}$$

pH = 2.88 *Check:* $[H^+] \pm [OH^-] \approx [H^+]$ *OK*

Assume weak

$$\frac{[H^+]([H^+]-[OH^-])}{0.10-\cancel{[H^+]}+\cancel{[OH^-]}} = 1.75\times10^{-5} \approx \frac{[H^+]([H^+]-[OH^-])}{0.10}$$

$$[H^+]\,([H^+] - K_w/[H^+]) = 1.75\times10^{-5}(0.10)$$

$$[H^+]^2 - K_w = 1.75\times10^{-5}(0.10)$$

$$[H^+]^2 = 1.75\times10^{-5}(0.10) + 10^{-14};\ [H^+] = 1.32\times10^{-3}$$

pH = 2.88 *Check:* $0.10 - [H^+] + [OH^-] = 0.099 \approx 0.10$ *OK*

Assume acid and weak

$$\frac{[H^+]([H^+]-\cancel{[OH^-]})}{0.10-\cancel{[H^+]}+\cancel{[OH^-]}} = 1.75\times10^{-5} \approx \frac{[H^+][H^+]}{0.10}$$

$$[H^+]^2 = 1.75\times10^{-5}(0.10);\ [H^+] = 1.32\times10^{-3}$$

pH = 2.88 *Check:* $[H^+] - [OH^-] \approx [H^+]$ and $0.10 - [H^+] + [OH^{-}] \approx 0.10$

Assumptions are not crossing things out; they are simply applying the answer to an addition or subtraction step. Be careful to not cross out all terms in a factor.

3C-6 What is $[H^+]$ in 0.10 M CH_3COONa?

K: $$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75\times10^{-5}$$

Charge balance: $[Na^+] + [H^+] = [CH_3COO^-] + [OH^-]$

Mass balances: $0.10 = [CH_3COOH] + [CH_3COO^-]$

$0.10 = [Na^+]$

From charge $[CH_3COO^-] = 0.10 + [H^+] – [OH^-]$

From mass $[CH_3COOH] = 0.10 – [CH_3COO^-] = [OH^-] – [H^+]$

Substitute into the equilibrium constant expression

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+](0.10+[H^+]-[OH^-])}{[OH^-]-[H^+]} = 1.75\times10^{-5}$$

Solve. (Notice that this is a basic solution. You will get a negative concentration for $[H^+]$ if you assume an acid solution.)

Assume basic

$$\frac{[H^+](0.10+\cancel{[H^+]}-[OH^-])}{[OH^-]-\cancel{[H^+]}} = 1.75\times10^{-5} \approx \frac{[H^+](0.10-[OH^-])}{[OH^-]}$$

$(0.10 – [OH^-])\ K_w/[OH^-]^2 = 1.75\times10^{-5}$

$1.75\times10^{-5}\ [OH^-]^2 + K_w\ [OH^-] - K_w\ (0.10) = 0$

$$[OH^-] = \frac{-K_w+\sqrt{K_w{}^2+4(1.75\times10^{-5})(K_w)(0.10)}}{2(1.75\times10^{-5})} = 7.60\times10^{-6}$$

$[H^+] = K_w/[OH^-] = 1.33\times10^{-9}$

pH = 8.88 *Check:* $[OH^-] \pm [H^+] \approx [OH^-]$ *OK*

Assume weak

$$\frac{[H^+](0.10+\cancel{[H^+]}-\cancel{[OH^-]})}{[OH^-]-[H^+]} = 1.75\times10^{-5} \approx \frac{[H^+](0.10)}{[OH^-]-[H^+]}$$

$$\frac{0.10\ [H^+]}{K_w/[H^+]-[H^+]} = \frac{0.10\ [H^+]^2}{K_w-[H^+]^2} = 1.75\times10^{-5}$$

$(0.10 + 1.75\times10^{-5})[H^+]^2 = K_w(1.75\times10^{-5})$

$[H^+] = 1.33\times10^{-9}$

pH = 8.88 *Check:* $0.10 + [H^+] – [OH^-] \approx 0.10$ *OK*

Assume basic and weak

$$\frac{[H^+](0.10+\cancel{[H^+]}-\cancel{[OH^-]})}{[OH^-]-\cancel{[H^+]}} = 1.75\times10^{-5} \approx \frac{[H^+](0.10)}{[OH^-]}$$

$$\frac{0.10\ [H^+]}{K_w/[H^+]} = \frac{0.10\ [H^+]^2}{K_w} = 1.75\times10^{-5}$$

$[H^+]^2 = (1.75\times10^{-6})(1.01\times10^{-14})/0.10$

$[H^+] = 1.33\times10^{-9}$

pH = 8.88 *Check:* $[H^+] – [OH^-] \approx [OH^-]$ and $0.10 + [H^+] – [OH^-] \approx 0.10$

3C-7 What is $[H^+]$ in 0.10 M oxalic acid, HOOC–COOH?

$$\text{HOOC-COOH} \rightleftharpoons H^+ + \text{HOOC-COO}^- \rightleftharpoons 2H^+ + \text{OOC-COO}^{-2}$$

K: $$Ka_1 = \frac{[H^+][HOOCCOO^-]}{[HOOCCOOH]} = 5.36\times10^{-2}$$

$$Ka_2 = \frac{[H^+][OOCCOO^{-2}]}{[HOOCCOO^-]} = 5.42\times10^{-5}$$

Charge balance: $[H^+] = [OH^-] + [\text{HOOC-COO}^-] + 2[\text{OOC-COO}^{-2}]$

Mass: $0.10 = [\text{HOOC-COOH}] + [\text{HOOC-COO}^-] + [\text{OOC-COO}^{-2}]$

Solve. *Assume* first dissociation stresses the system and depresses the second dissociation. (You can generally ignore Ka_2 if $Ka_1 >> Ka_2$ and the mass balance value >> Ka_1 and Ka_2).

$[H^+] = [OH^-] + [\text{HOOC-COO}^-] + 2\,\cancel{[\text{OOC-COO}^{-2}]}$

$0.10 = [\text{HOOC-COOH}] + [\text{HOOC-COO}^-] + \cancel{[\text{OOC-COO}^{-2}]}$

Substitute into the equilibrium constant expression

$[\text{HOOC-COO}^-] = [H^+] - [OH^-]$

$[\text{HOOC-COOH}] = 0.10 - [\text{HOOC-COO}^-] = 0.10 - [H^+] + [OH^-]$

$$Ka_1 = \frac{[H^+]([H^+]-[OH^-])}{0.10-[H^+]+[OH^-]} = 5.36\times10^{-2}$$

Assume acid and weak

$$\frac{[H^+]([H^+]-\cancel{[OH^-]})}{0.10-\cancel{[H^+]}+\cancel{[OH^-]}} = 5.36\times10^{-2} \approx \frac{[H^+][H^+]}{0.10}$$

$[H^+]^2 = 5.36\times10^{-2}(0.10)$; $[H^+] = 0.0732$

pH = 1.14 *Check:* $[H^+] - [OH^-] \approx [H^+]$ *OK*

but $0.10 - [H^+] + [OH^-] = 0.03 \approx 0.10$ *not great*

Assume acid

$$\frac{[H^+]([H^+]-\cancel{[OH^-]})}{0.10-[H^+]+\cancel{[OH^-]}} = 5.36\times10^{-2} \approx \frac{[H^+][H^+]}{0.10-[H^+]}$$

$$[H^+]^2 + 5.36\times10^{-2}[H^+] - 5.36\times10^{-2}(0.10) = 0$$

$$[H^+] = \frac{-5.36\times10^{-2} + \sqrt{(5.36\times10^{-2})^2 + 4(0.10)(5.36\times10^{-2})}}{2} = 0.0511$$

pH = 1.29 *and we already know the acid assumption is OK*

What about the assumption ignoring Ka_2?

$[\text{HOOC-COO}^-] = [H^+] = 5.36\times10^{-2}$

$$Ka_2 = \frac{[H^+][OOCCOO^{-2}]}{[HOOCCOO^-]} = 5.42\times10^{-5} \text{ gives } [\text{OOC-COO}^{-2}] = 5.42\times10^{-5}$$

$[\text{HOOC-COO}^-] + 2[\text{OOC-COO}^{-2}] = .0512 \approx 0.0511$ *OK*

Notice that in problems with assumptions about addition and subtraction results, about as much effort must be made checking those assumptions as in setting up the problem. Exploration 3D will present a graphical method of doing problems where assumption checking is simplified.

3C-8 What is $[H^+]$ in water with excess $Zn(OH)_2(s)$?

$Zn(OH)_2(s) \rightleftharpoons Zn^{+2} + 2OH^-$

K: $Ks = [Zn^{+2}]\,[OH^-]^2 = 10^{-15.80}$

$[H^+]\,[OH^-] = 10^{-14}$

Charge balance: $2[Zn^{+2}] + [H^+] = [OH^-]$

Solve: $2\,\dfrac{10^{-15.80}}{[OH^-]^2} + \cancel{\dfrac{10^{-14}}{[OH^-]}} = [OH^-]$

Assume the solution will be basic.

$[OH^-] = \sqrt[3]{3.17\times10^{-16}} = 6.82\times10^{-6}$

$[H^+] = 1.5\times10^{-9}$ (*OK* since $6.82\times10^{-6} + 1.5\times10^{-9} = 6.82\times10^{-6}$)

3C-9 What is $[H^+]$ in water with excess $Pb(OH)_2(s)$?

$Pb(OH)_2(s) \rightleftharpoons Pb^{+2} + 2OH^-$

K: $Ks = [Pb^{+2}]\,[OH^-]^2 = 10^{-19.85}$

$[H^+]\,[OH^-] = 10^{-14}$

Charge balance: $2[Pb^{+2}] + [H^+] = [OH^-]$

Solve: $2\,\dfrac{10^{-19.85}}{[OH^-]^2} + \cancel{\dfrac{10^{-14}}{[OH^-]}} = [OH^-]$

Assume the solution will be basic.

$[OH^-] = \sqrt[3]{2.83\times10^{-20}} = 3.05\times10^{-7}$.

$[H^+] = 3.3\times10^{-8}$ (*Check* $3.05\times10^{-7} + 3.3\times10^{-8} = 3.38\times10^{-7} \approx 3.05\times10^{-7}$)

No assumptions gives $[OH^-] = 3.16\times10^{-7}$ and $[H^+] = 3.17\times10^{-8}$.

APPLYING YOUR IDEAS

3C-10 Write as many equations as unknowns and find the pH to ±0.001 for 0.100 M solutions in water.

	A	**B**	**C**	**D**
1.	CH_3COOH	C_5H_5NHBr	C_6H_5COOK	$C_6H_5NH_3ClO_4$
2.	NH_4Cl	$ClCH_2COOH$	KH_2AsO_4	H_2CO_3
3.	H_3BO_3	H_2SO_4	$HONH_3Cl$	C_6H_5OH
4.	CH_3COONa	C_5H_5N	C_6H_5COOH	$C_6H_5NH_2$
5.	NH_3	$ClCH_2COOLi$	H_3AsO_4	$LiHCO_3$
6.	NaH_2BO_3	$RbHSO_4$	$HONH_2$	C_6H_5OK
7.	Al^{+3}	$Fe(OH)_2^+$	Fe^{+3}	$Al(OH)^{+2}$

Is there a faster way to calculate pH?

Exploration 3D, Logarithmic Concentration Diagrams

Creating the Context

In Explorations 3B and 3C you learned how to calculate the pH of weak acids and weak bases using an algebraic method. Even for simple systems this method often requires the use of the quadratic equation. For more complicated systems other mathematical solution methods are required.

In this Exploration you will learn how to use **logarithmic concentration diagrams** to graphically solve equilibrium equations and pH problems. Once familiar with this method, you will be able to solve very complex equilibrium equations knowing only the pK_a values and the initial concentrations. To learn more about the origin and use of the log C method, see Butler, J. N.; Cogley, D. R. *Ionic Equilibrium: Solubility and pH Calculations*, Wiley, New York, 1998.

Preparing for Inquiry

A logarithmic concentration diagram plots y = log(concentration) for each species as a function of x = pH. To make the diagram we need to know how the concentration of each species present depends on pH.

Derivation

Mark pH on the x-axis and log concentration on the y-axis. Since we will be plotting small concentrations (negative values of y), place the origin of the graph ($x = 0$, $y = 0$) near the top of the y-axis. The y-scale must extend past –7 but does not need to go to –14 since concentrations of less than 10^{-7} M will be negligible. The pH scale (x-axis) should span the pH range. Use equal spacing on both axes.

Lets begin by graphing $[H^+]$ and $[OH^-]$. How does $\log[H^+]$ depend on pH? Recalling the definition $pH = -\log[H^+]$, $\log[H^+] = -pH$. This line will have a slope of –1 and a y-intercept of 0. How does $\log[OH^-]$ depend on pH? Recall

$$K_w = [H^+][OH^-] = 10^{-14}$$

Taking the log of both sides of the equation, we can also write:

$$\log K_w = \log([H^+][OH^-]) = \log 10^{-14}$$

$$\log[H^+] + \log[OH^-] = -14$$

$$\log[OH^-] = -14 - \log[H^+] = -14 + pH$$

This line will have a slope of +1. Where will the $\log[H^+]$ and $\log[OH^-]$ lines meet? They will be equal in concentration at pH 7 (the pH of neutral water at 24°C). Label the species for the lines in Figure 3D-1.

In all aqueous solutions, regardless of what acid, base or salt has been added, these two lines always describe the relationship between $[H^+]$ and $[OH^-]$. Therefore, they are always part of log C diagrams for aqueous systems.

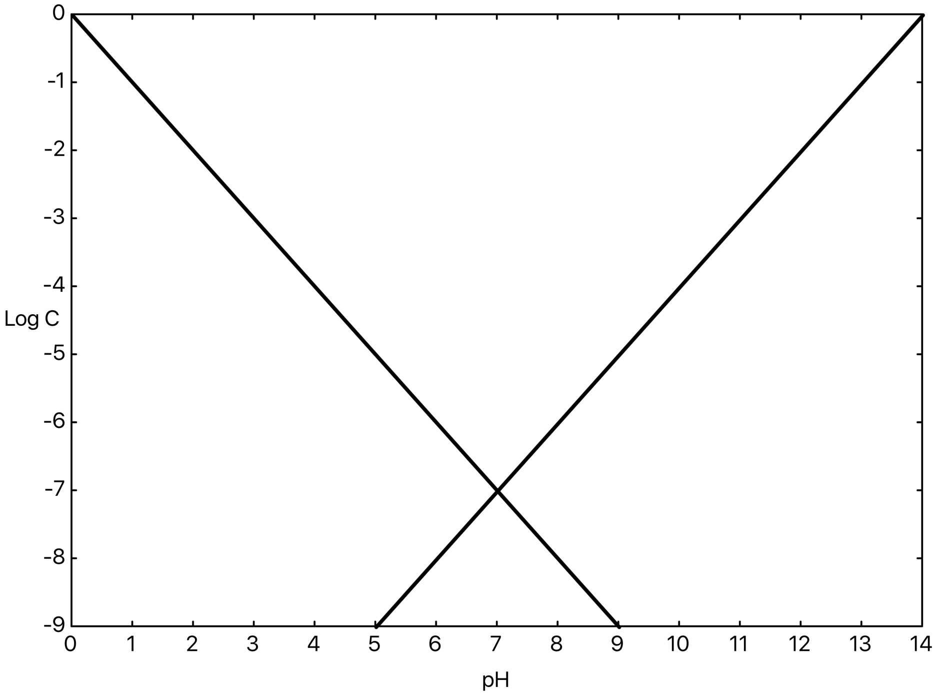


Figure 3D-1. Log C diagram for pure water. Label the lines with the species they represent.

When you add a weak acid, HA, to an aqueous system, some of it will dissociate to form H^+ and A^-.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

While A^- and HA can be interconverted by respectively gaining or losing a proton, the total amount present in the system, C_A, will remain constant and is given by the mass balance equation:

$$C_A = [A^-] + [HA]$$

Furthermore, the concentrations at equilibrium are related by the equilibrium expression:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Using the mass balance equation and equilibrium expression, we can solve for $[A^-]$ and [HA], Table 3D-1, and simplify for conditions of high and low pH, Table 3D-2.

Sketching the curves for $\log[A^-]$ and $\log[HA]$ from Table 3D-2 gives Figure 3D-2. The horizontal portions are at the mass balance value. For low pH “all” the A^- will be protonated and for high pH “all” the HA will be deprotonated. The total concentration of A^- plus HA can never exceed the total amount, C_A. The ±1 slope portions and the horizontal portions meet at pK_a = pH and 0.30 below $\log C_A$.

Table 3D-1. Solving for $[A^-]$ and $[HA]$ concentrations as a function of $[H^+]$

	Solve for $[A^-]$	Solve for $[HA]$
Rearrange mass balance equation	$[HA] = C_A - [A^-]$	$[A^-] = C_A - [HA]$
Substitute into equilibrium expression	$K_a = \frac{[H^+][A^-]}{C_A - [A^-]}$	$K_a = \frac{[H^+](C_A - [HA])}{[HA]}$
Rearrange	$K_a C_A - K_a [A^-] = [H^+][A^-]$ $\mathbf{[A^-] = \frac{K_a C_A}{[H^+] + K_a}}$	$K_a [HA] = [H^+] C_A - [H^+][HA]$ $\mathbf{[HA] = \frac{[H^+] C_A}{[H^+] + K_a}}$

Table 3D-2. $\log[A^-]$ and $\log[HA]$ for high and low pH

If $[H^+] << K_a$, i.e. high pH values	$[A^-] = \frac{K_a C_A}{\cancel{[H^+]} + K_a} \approx \frac{\cancel{K_a} C_A}{\cancel{K_a}} =$ C_A $\mathbf{\log[A^-] = \log C_A}$ horizontal line at mass balance	$[HA] = \frac{[H^+] C_A}{\cancel{[H^+]} + K_a}$ $\mathbf{\log[HA] = \log C_A + pK_a - pH}$ slope –1, intersects mass balance where $pK_a = pH$
If $[H^+] >> K_a$, i.e. low pH values	$[A^-] = \frac{K_a C_A}{[H^+] + \cancel{K_a}}$ $\mathbf{\log[A^-] = \log C_A - pK_a + pH}$ slope +1, intersects mass balance where $pK_a = pH$	$[HA] = \frac{[H^+] C_A}{[H^+] + \cancel{K_a}} \approx \frac{\cancel{[H^+]} C_A}{\cancel{[H^+]}} = C_A$ $\mathbf{\log[HA] = \log C_A}$ horizontal line at mass balance
If $[H^+] = K_a$	$[A^-] = \frac{K_a C_A}{K_a + K_a} = \frac{C_A}{2}$ $\log[A^-] = \log C_A - \log 2$ $\log[A^-] = \log C_A - 0.30$	$[HA] = \frac{[H^+] C_A}{[H^+] + [H^+]} = \frac{C_A}{2}$ $\log[HA] = \log C_A - \log 2$ $\log[HA] = \log C_A - 0.30$
	lines cross when $\log[A^-] = \log[HA]$ at 0.30 below $\log C_A$	

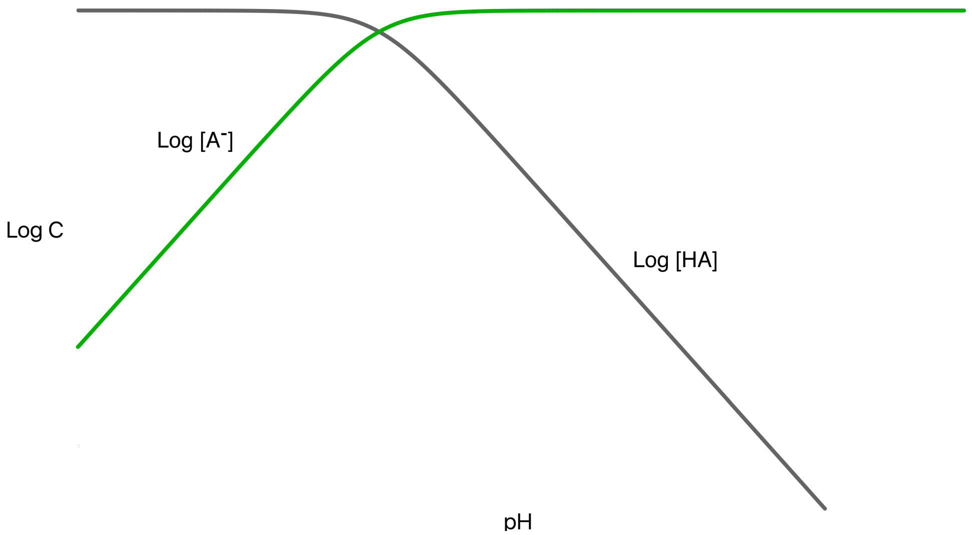


Figure 3D-2. Shape of the $\log[HA]$ and $\log[A^-]$ curves as a function of pH. The maximum value is $\log C_A$.

DEVELOPING IDEAS

Sketching Diagrams

a. Draw axes, x = pH, y = log c.

b. Draw and label H^+ and OH^- lines through (7,–7) with slopes +1 and –1.

c. Sketch curve for HA and A^- for each K_a. We can sketch the curve since we know both extremes and the crossing point (see derivation). Mark where pH = pK_a on mass balance line ("the system point"). Draw lines with slopes +1 and –1 through system point. Connect sloping lines with horizontal mass balance lines at 0.3 units below system point as in Figure 3D-2.

d. Label species present at high and low pH.

Problem 3D-1

Sketch the logarithmic concentration diagram for 0.1 M acetic acid in water. Be sure to include $[H^+]$ and $[OH^-]$ and to label all lines.

✓ Can you label the lines in Figure 3D-3 with the chemical species?

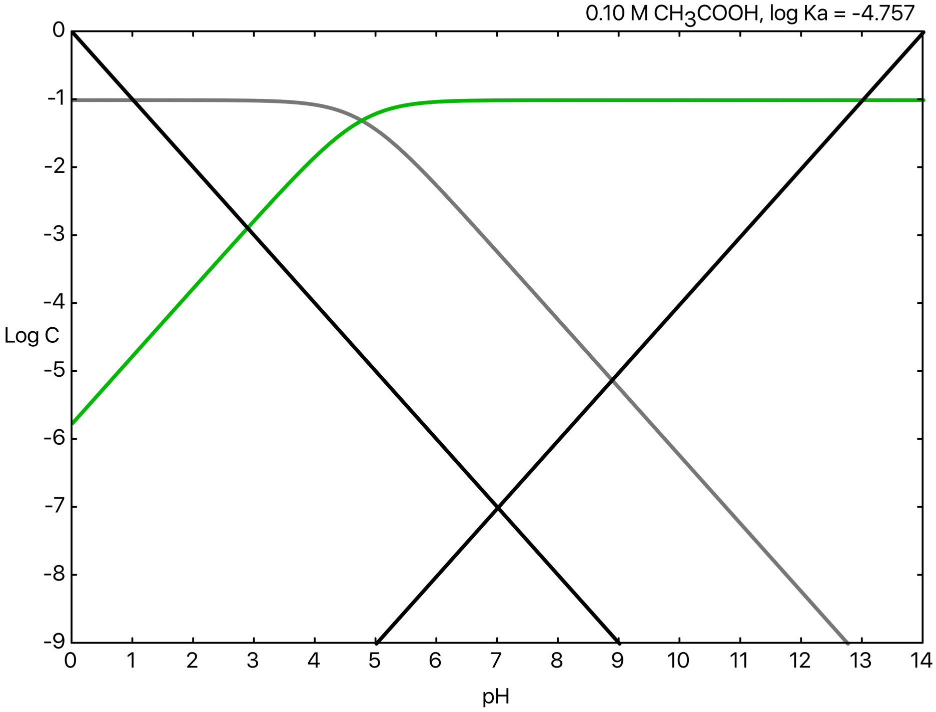


Figure 3D-3. Log C diagram for 0.1 M acetic acid. Other acids are similar since all HA and A^- lines will have the same shape and will merely shift up or down with concentration and shift left or right with changes in pK_a.

Investigations using *http://chemistry.beloit.edu/classes/Chem220/logconc*

3D-2 Change the mass balance concentration, C. How does the logarithmic concentration diagram shift?

3D-3 Change one of the K_a values. How does the logarithmic concentration diagram shift? Mark the pK_a on the pH axis. With what part of the graph do these points line up?

Proton Mass Balance

A logarithmic concentration diagram plots the log of the species concentration as a function of pH. At low pH nearly all will be present as the most protonated form and at high pH nearly all will be present as the least protonated form; in between each species takes a turn at being the predominate species over some pH range.

Logarithmic concentration diagrams can be used as a graphical method of doing acid/base problems whose advantage is the ease of checking main species (this is especially worthwhile for multiple equilibria). There will only be one pH at which the **proton mass balance** will be true and this equation is used to calculate the pH of the system.

To write the proton mass balance equation, start with $[H^+]$ on one side and $[OH^-]$ on the other side. Any species that has more protons than the starting species joins the $[H^+]$ side. Any species that has fewer protons than the starting species joins the $[OH^-]$ side. For example, the proton mass balance equation for acetic acid, CH_3COOH, is

$$[H^+] = [OH^-] + [CH_3COO^-]$$

Note that $[CH_3COOH]$ is the starting species and does not appear in the proton mass balance equation since CH_3COOH does not have fewer protons than CH_3COOH and CH_3COOH does not have more protons than CH_3COOH.

Problem 3D-4

Write the proton mass balance equation for 0.1 M sodium acetate, CH_3COONa.

✓ There are no forms of CH_3COO^- that have fewer protons. CH_3COOH has one more proton than the starting species, CH_3COO^-. The proton mass balance equation is thus:

$$[CH_3COOH] + [H^+] = [OH^-]$$

Problem 3D-5

Write the proton mass balance equation for 0.1 M ammonium acetate, CH_3COONH_4.

✓ There are no forms of CH_3COO^- that have fewer protons. CH_3COOH has one more proton than the starting species, CH_3COO^-. There are no forms of NH_4^+ that have more protons. NH_3 has one fewer proton than NH_4^+. The proton mass balance is:

$$[CH_3COOH] + [H^+] = [OH^-] + [NH_3]$$

Reading Log C Diagrams

Consider the log C diagram you prepared for 0.1 M acetic acid (Figure 3D-3). To find the pH, first write the proton balance equation:

$$[H^+] = [OH^-] + [CH_3COO^-]$$

At what point on the graph is this equation true? The simplest case will be when one term on each side dominates. Which is the better assumption?

$$[H^+] = [OH^-] + \cancel{[CH_3COO^-]}$$
$$[H^+] = \cancel{[OH^-]} + [CH_3COO^-]$$

At the intersection of the H^+ and OH^- lines, the concentration of CH_3COO^- is not small compared to OH^- so the top assumption is not true. At the intersection of the H^+ and CH_3COO^- line, the concentration of OH^- is so small that it is off the scale of the graph. Since $[OH^-] << [CH_3COO^-]$ at this point, we can neglect the $[OH^-]$ in the proton balance equation. The proton balance equation becomes:

$$[H^+] = \cancel{[OH^-]} + [CH_3COO^-]$$

The pH of the solution is found at the intercept of $[H^+]$ and $[CH_3COO^-]$. On the log C diagram prepared in Figure 3D-3 this intercept is at pH = 2.8.

Problem 3D-6

Estimate the pH of 0.1 M sodium acetate, CH_3COONa.

✓ The log C diagram prepared in Figure 3D-3 can also be used for this problem. The proton balance equation is:

$$[CH_3COOH] + [H^+] = [OH^-]$$

At what point on the graph is the proton balance equation true?

Which is the better assumption for 0.1 M CH_3COONa?

$$\cancel{[CH_3COO^-]} + [H^+] = [OH^-]$$
$$[CH_3COOH] + \cancel{[H^+]} = [OH^-]$$

At the intersection of the H^+ and OH^- lines, the concentration of CH_3COOH is not small compared to H^+ so the top assumption is not true. At the intersection of the CH_3COOH and OH^- lines, the concentration of H^+ is many orders of magnitude smaller. Since $[H^+] << [CH_3COOH]$ at this point, we can neglect the $[H^+]$ in the proton balance equation. The pH of the solution is found at the intercept of $[CH_3COOH]$ and $[OH^-]$, approximately 8.9.

APPLYING YOUR IDEAS

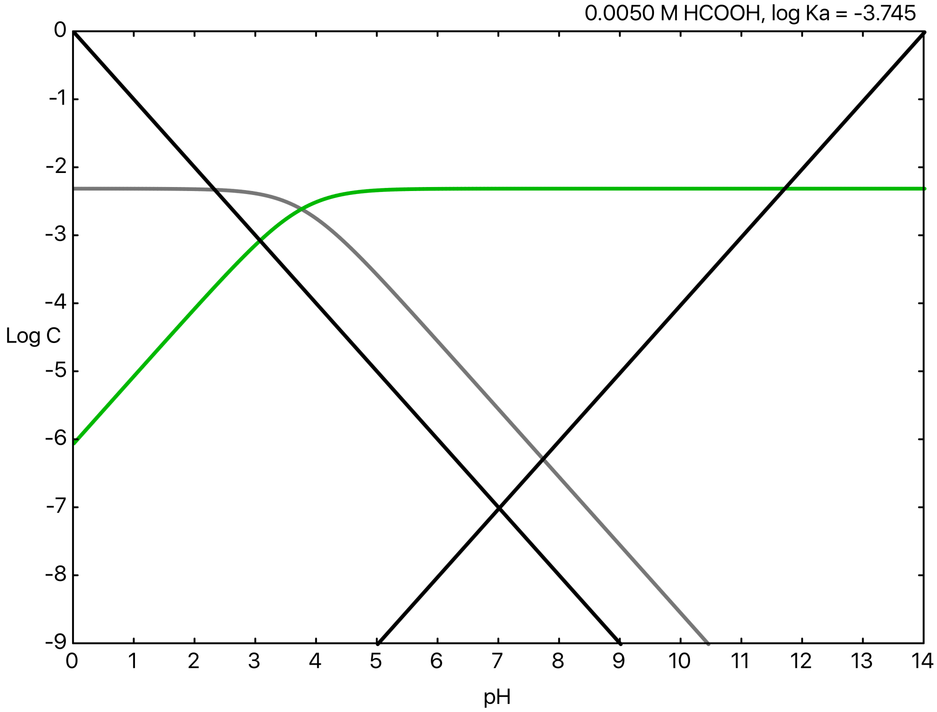
Problems

3D-7 Examine the logarithmic concentration diagram movies at *http://chemistry.beloit.edu/classes/Chem220/logconc.* How does the calculated logarithmic concentration diagram change with mass balance concentration? How does the logarithmic concentration diagram change with K_a?

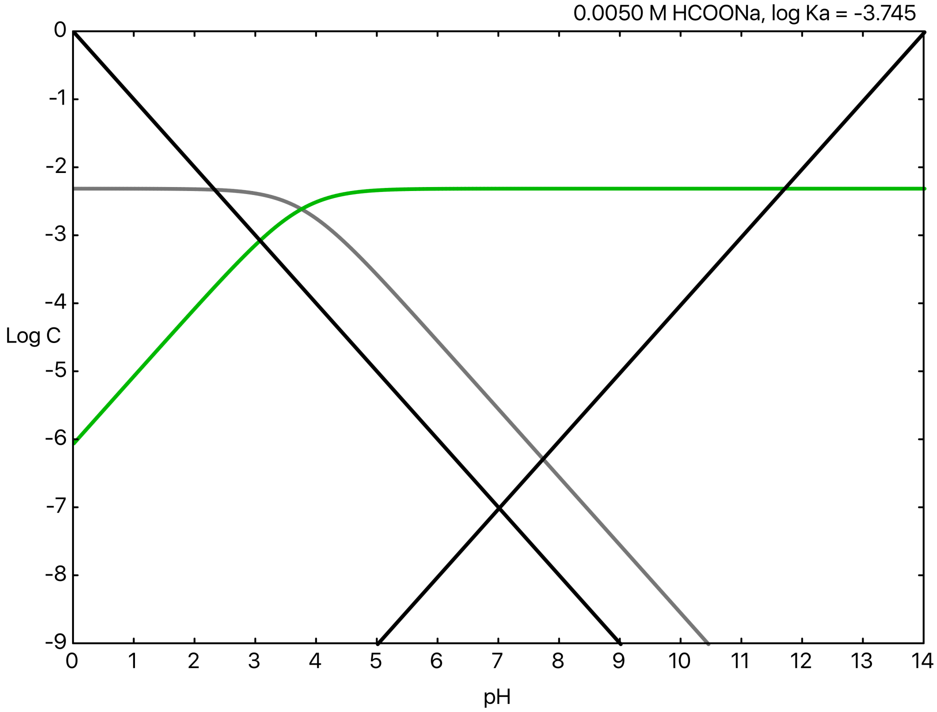
3D-8 Label each species on the logarithmic concentration diagram for 0.005 M HCOOH. The proton mass balance equation is:

$$[H^+] = [OH^-] + [HCOO^-]$$

At what pH will the proton mass balance be true?



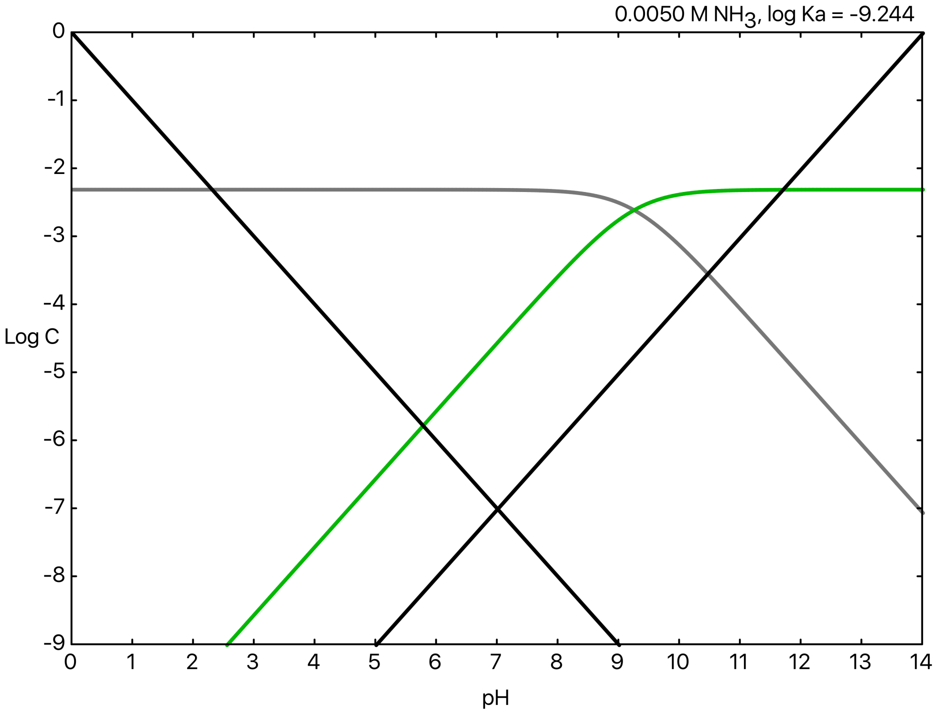
3D-9 Label each species on the logarithmic concentration diagram for 0.005 M HCOONa. Write the proton mass balance equation. At what pH will the proton mass balance be true?



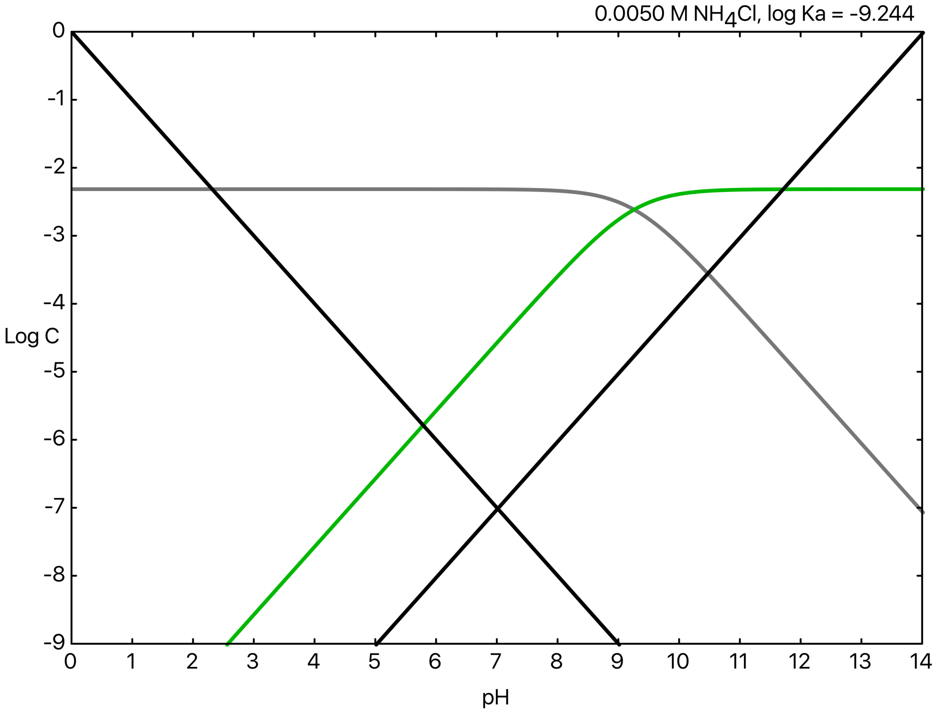
3D-10 Label each species on the logarithmic concentration diagram for 0.005 M NH_3. The proton mass balance equation is:

$$[NH_4^+] + [H^+] = [OH^-]$$

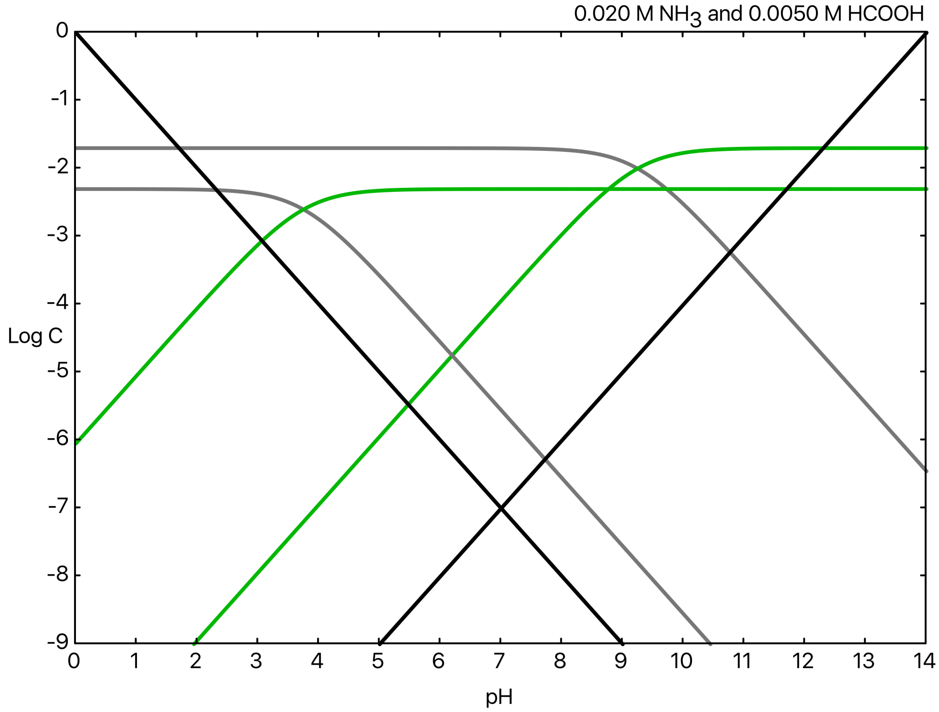
At what pH will the proton mass balance be true?



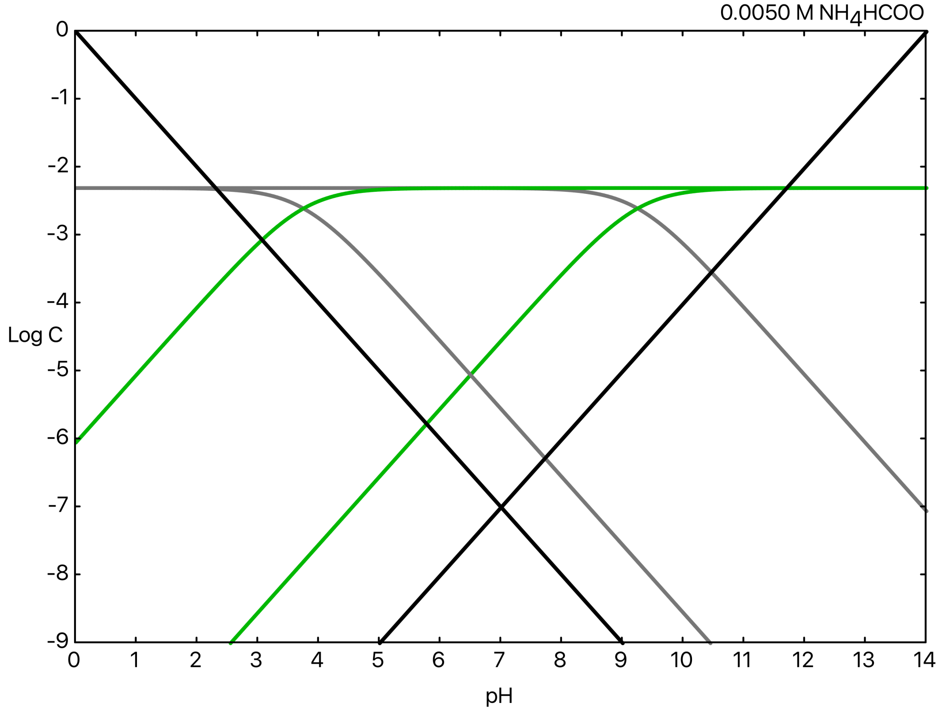
3D-11 Label each species on the logarithmic concentration diagram for 0.005 M NH_4Cl. Write the proton mass balance equation. At what pH will the proton mass balance be true?



3D-12 Label each species on the logarithmic concentration diagram for 0.02 M NH_3 and 0.005 M HCOOH. (Hint: What is log(0.02) and log(0.005)?) Write the proton mass balance equation. At what pH will the proton mass balance be true?



3D-13 Label each species on the logarithmic concentration diagram for 0.005 M NH_4HCOO. Write the proton mass balance equation. At what pH will the proton mass balance be true?



3D-14 Either sketch or calculate the logarithmic concentration diagram for 0.1 M ammonium acetate solution. Write out the proton mass balance equation and indicate the pH of the solution.

3D-15 Examine the logarithmic concentration diagram movies at *http://chemistry.beloit.edu/classes/Chem220/logconc*. How does the calculated logarithmic concentration diagram change when an acid has more than one K_a? Estimate the minimum difference in K_{a1} and K_{a2} values required in order to use a simple sketch to produce a logarithmic concentration diagram.

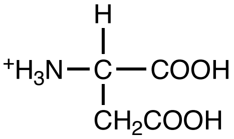
3D-16 Either sketch or calculate the logarithmic concentration diagram for 0.01 M calcium carbonate, $CaCO_3$. Note that there will be two system points since carbonate, CO_3^{-2}, will pick up first one proton to form bicarbonate, HCO_3^-, and then a second proton to form carbonic acid, H_2CO_3. Write out the proton mass balance equation and indicate the pH of the solution.

3D-17 Either sketch or calculate the logarithmic concentration diagram for 0.10 M oxalic acid. Write out the proton mass balance equation and indicate the pH of the solution.

3D-18 Estimate the pH of a solution which is 0.010 M acetic acid and 0.020 M ammonium chloride.

3D-19 Estimate the pH of a 0.10 M $(NH_4)_2HPO_4$ solution.

3D-20 Estimate the pH of a 0.10 M aspartic acid solution.

The p*Ka* for  ${}^{+}H_3N-\overset{H}{\underset{CH_2COOH}{C}}-COOH$ are 1.990, 3.900, and 10.002.

3D-21 At 0°C, $pK_w = 14.94$. Graph pH versus $\log[H^+]$ and $\log[OH^-]$ for water at 0°C. At what pH value does $\log[OH^-] = 0$? At what pH value do the two lines intersect? What is the slope of the $[H^+]$ line? The $[OH^-]$ line? What is the pH of pure water at 0°C?

How do you predict the pH of a weak acid?

SESSION 3, MAKING THE LINK

LOOKING BACK

Session Goals

- Understand the concept of equilibrium
- Writing equilibrium expressions to describe acid and base dissociation
- Writing as many equations as unknowns for a system at equilibrium
- How to use log C diagrams

CHECKING YOUR PROGRESS

3-1 Show your work by writing out the equations to be solved, giving as many equations as unknowns. Chemical formulas should be correct and show proper charges.

a. 0.1 M acetic acid solution

b. 0.1 M sodium acetate solution

c. 0.1 M ammonia solution

d. 0.1 M ammonium chloride solution

e. 0.180 M butylamine, $CH_3CH_2CH_2CH_2NH_2$

f. 0.180 M butylammonium chloride, $CH_3CH_2CH_2CH_2NH_3Cl$

g. 0.180 M oxalic acid, HOOC-COOH

3-2 What is the pH of a 0.10 M solution of

A	**B**	**C**	**D**
1. CH_3COOH	C_5H_5NHBr	C_6H_5COOK	$C_6H_5NH_3ClO_4$
2. NH_4Cl	$ClCH_2COOH$	KH_2AsO_4	H_2CO_3
3. H_3BO_3	H_2SO_4	$HONH_3Cl$	C_6H_5OH
4. CH_3COONa	C_5H_5N	C_6H_5COOH	$C_6H_5NH_2$
5. NH_3	$ClCH_2COOLi$	H_3AsO_4	$LiHCO_3$
6. NaH_2BO_3	$RbHSO_4$	$HONH_2$	C_6H_5OK
7. Al^{+3}	$Fe(OH)_2^{+}$	Fe^{+3}	$Al(OH)^{+2}$

THINKING FURTHER

5-minute Writing Questions

3-3 Give a concise response to the question, "How do you predict the pH of a weak acid?"

3-4 Explain what is meant by "dynamic equilibrium."

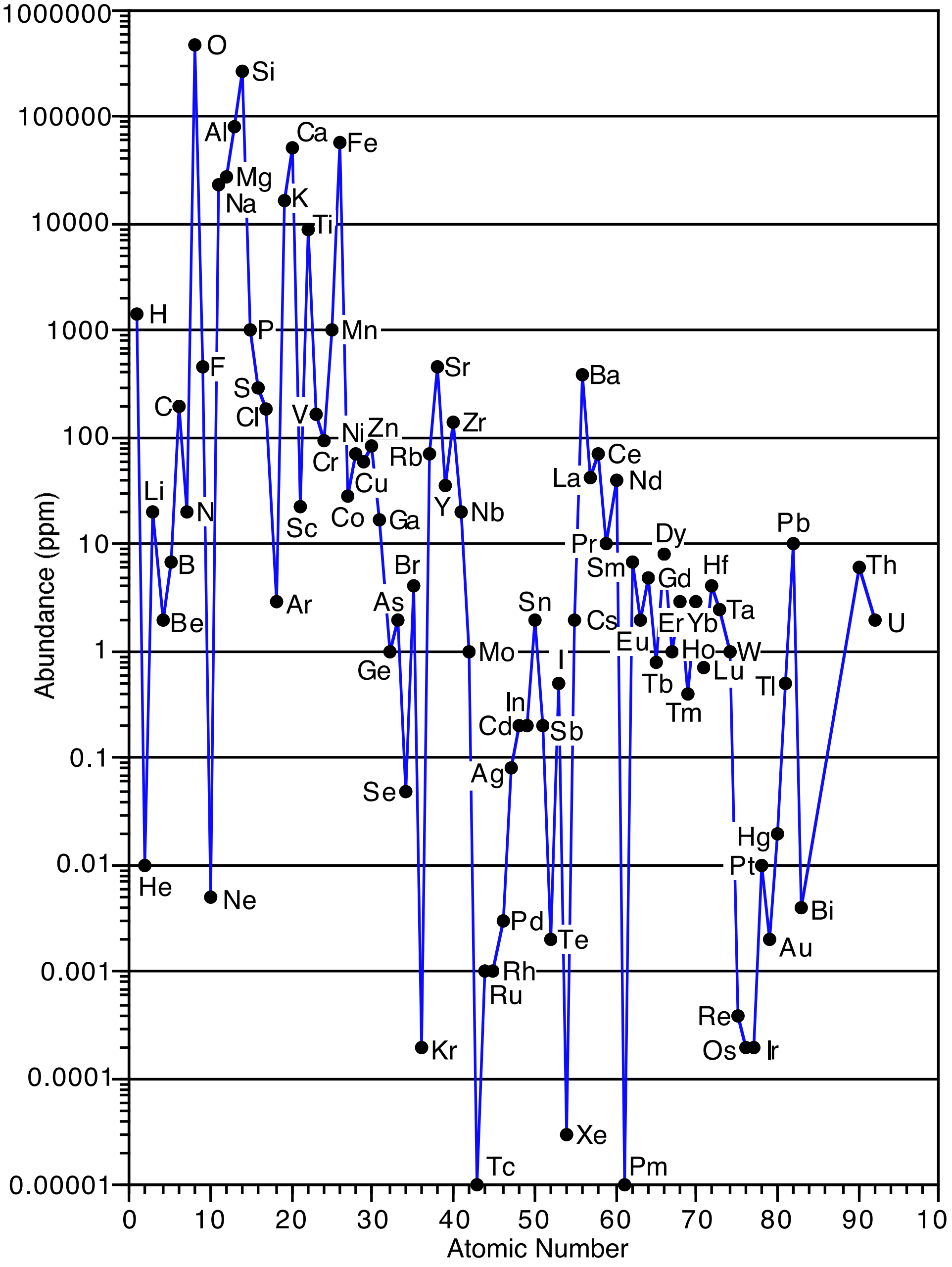
3-5 What are the advantages or disadvantages of solving equilibrium problems algebraically, with logarithmic concentration diagrams, or with a computer equation solver?

How does acid rain interact with soil?

EXPLORATION 4A, ION EXCHANGE OF ACIDIC AND BASIC CATIONS

CREATING THE CONTEXT

The formation of soil begins with the decomposition of rocks and minerals. Figure 4A-1 shows the abundance of elements available from the earth's crust. What elements will be found in soil?



100,000 ppm = 10%
10,000 ppm = 1%
1000 ppm = 0.1%

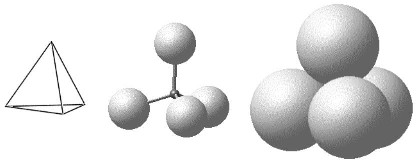
Figure 4A-1. Elemental Abundance in the Earth's Crust
(Data from Porterfield, *Inorganic Chemistry*, Table 1.1)

Problem 4A-1

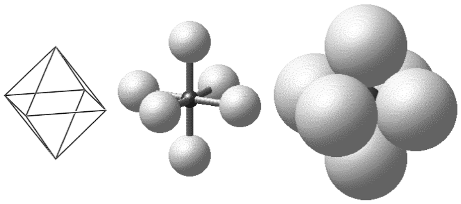
What elements are present at greater than 1% abundance in the earth's crust and available as a significant component for soil formation from the underlying rock?

✓ In order of abundance, O > Si > Al > Fe > Ca > Mg > Na > K

In ionic compounds of these elements, O^{-2} is the only anion. The other elements are found as cations: Si^{+4}, Al^{+3}, Fe^{+3}, Ca^{+2}, Mg^{+2}, Na^{+} and K^{+}. Si^{+4} is always found surrounded by four O^{-2} in a tetrahedron. The other cations are found surrounded by tetrahedra or octahedra of O^{-2} (Si^{+4} is too small to keep an octahedral arrangement of O^{-2} from touching each other.)

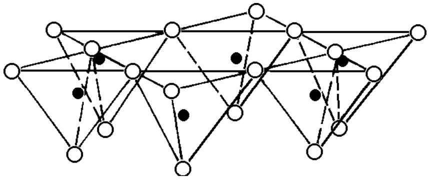


Si^{+4} surrounded by 4 O^{-2}

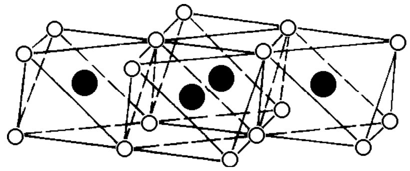


Al^{+3} surrounded by 6 O^{-2}

When adjacent tetrahedra share a corner O^{-2}, the tetrahedra link together to form tetrahedral sheets. When adjacent octahedra share a pair of O^{-2} on an edge, the octahedra link together to form octahedral sheets.

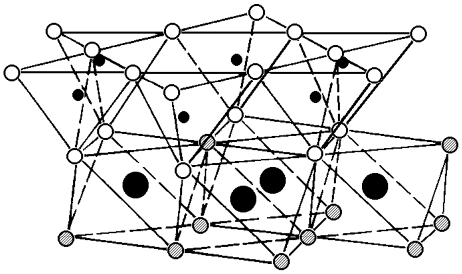


A tetrahedral sheet



An octahedral sheet

An octahedral and tetrahedral sheet can also link together. In the aluminum silicates the octahedral sheet O^{-2} that are not shared with the tetrahedral sheet (shown shaded at right) are protonated to give OH^{-}. Some important examples for soil are shown in Table 4A-1.



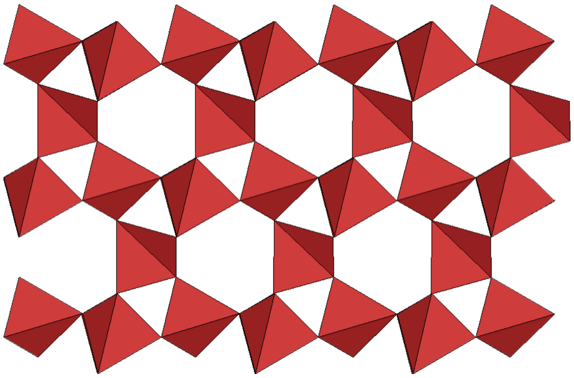
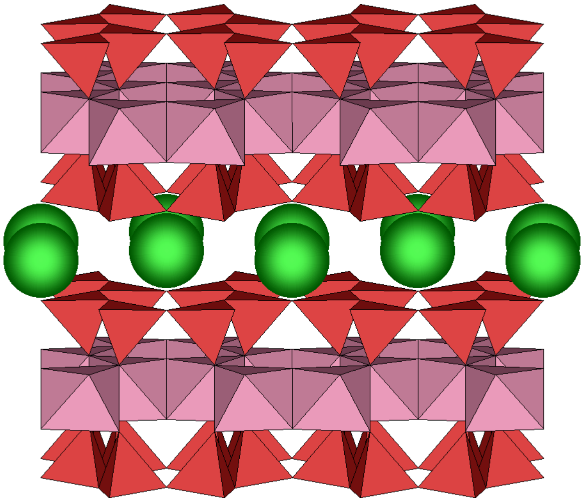
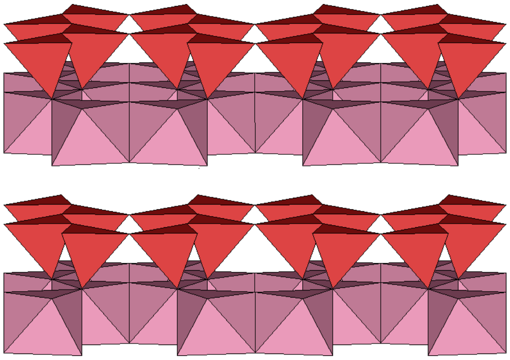
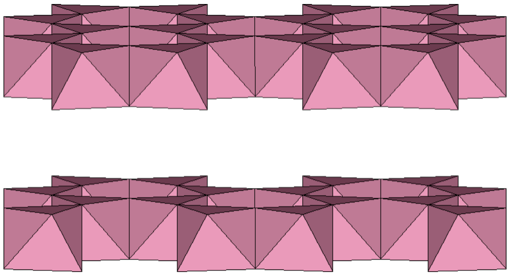
Linked tetrahedral and octahedral sheets.

Problem 4A-2

Verify that feldspar, muscovite, montmorillonite, kaolinite, and gibbsite are neutral species by summing the charges of the component ions.

✓	feldspar	muscovite	montmorillonite	kaolinite	gibbsite
K^{+}	+1	+1	0	0	0
Al^{+3}	+3	3(+3)	2(+3)	2(+3)	+3
OH^{-}	0	2(–1)	2(–1)	4(–1)	3(–1)
Si^{+4}	3(+4)	3(+4)	4(+4)	2(+4)	0
O^{-2}	8(–2)	10(–2)	10(–2)	5(–2)	0
total charge	0	0	0	0	0

Table 4A-1. Some Mineral Structures Important in Soil.

mineral	edge-shared octahedral sheets	corner-shared tetrahedral sheets	structure
quartz SiO_2	corner shared tetrahedral framework		
feldspar KSi_3AlO_8			
muscovite $KAl_2(OH)_2[Si_3AlO_{10}]$ (K^+ ions in space between tetrahedral sheets)	$Al_2(OH)_2$	$[Si_{1.5}Al_{0.5}O_5]_2$	
montmorillonite $Al_2(OH)_2[Si_2O_5]_2 \cdot nH_2O$ (H_2O in space between tetrahedral sheets)	$Al_2(OH)_2$	$[Si_2O_5]_2$	
kaolinite $Al_2(OH)_4[Si_2O_5]$	$Al_2(OH)_4$	$[Si_2O_5]$	
gibbsite $Al(OH)_3$	$Al_2(OH)_6$	–	

Preparing for Inquiry

The Formation of Soil

Some components of soils are formed through **weathering**, the physical and chemical breakdown of rocks and minerals which takes place under natural conditions. Physical weathering, including wind abrasion and rock fragmentation by the freezing of water, reduces the size of the particles. Chemical weathering further reduces the size of the rock and mineral particles and changes their chemical composition. Aluminum silicate clays are produced, excess silicon leaves as H_4SiO_4 which remains protonated at $pH<9$, and alkali metals and alkaline earth elements form nutrient ions in solution. Which weathering reactions in Table 4A-2 require rain? Which weathering reactions in Table 4A-2 require acid? Are the products or reactants favored at equilibrium?

Table 4A-2. Some chemical weathering reactions.

$Al_2(OH)_2[Si_2O_5]_2 + 5\ H_2O \rightarrow$ Montmorillonite	$Al_2(OH)_4[Si_2O_5] + 2\ H_4SiO_4$ Kaolinite	 log K = –7.06
$Al_2(OH)_4[Si_2O_5] + 5\ H_2O \rightarrow$ Kaolinite	$2\ Al(OH)_3 + 2\ H_4SiO_4$ Gibbsite	 log K = –8.78
$3\ KAlSi_3O_8 + 12\ H_2O + 2\ H^+ \rightarrow$ Feldspar	$KAl_2(OH)_2[Si_3AlO_{10}] + 2K^+ + 6\ H_4SiO_4$ Muscovite	 log K = –6.32
$2\ KAl_2(OH)_2[Si_3AlO_{10}] + 3\ H_2O + 2\ H^+ \rightarrow$ Muscovite	$3\ Al_2(OH)_4[Si_2O_5] + 2\ K^+$ Kaolinite	 log K = +3.10
$KAl_2(OH)_2[Si_3AlO_{10}] + 9\ H_2O + H^+ \rightarrow$ Muscovite	$3\ Al(OH)_3 + K^+ + 3\ H_4SiO_4$ Gibbsite	 log K = –11.63
$2\ KAlSi_3O_8 + 9\ H_2O + 2\ H^+ \rightarrow$ Feldspar	$Al_2(OH)_4[Si_2O_5] + 2\ K^+ + 4\ H_4SiO_4$ Kaolinite	 log K = –3.18
$Al_2(OH)_4[Si_2O_5] + 6\ H^+ \rightarrow$ Kaolinite	$2\ Al^{+3} + 2\ H_4SiO_4 + H_2O$ Aluminum ion	 log K = +7.44
$Al(OH)_3(s) + 3\ H^+ \rightarrow$ Gibbsite	$Al^{+3} + 3\ H_2O$ Aluminum ion	 log K = +8.11

Problem 4A-3

Weathering rates are greater for solutions in soils where abundant carbon dioxide is produced by decay of organic matter since this carbon dioxide provides a continuous source of hydrogen ion. Write a chemical equation showing carbon dioxide as a source of hydrogen ion.

✓ $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

Problem 4A-4

How will the reactions in Table 4A-2 respond to an increased concentration of dissolved silica, H_4SiO_4? to an increased concentration of K^+?

✓ By Le Châtelier's Principle an increased concentration of dissolved silica favors montmorillonite relative to kaolinite and to gibbsite. An increased concentration of K^+ favors feldspar relative to muscovite and to kaolinite.

The last three entries of Table 4A-1 correspond to the mineral weathering sequence of Figure 4A-2 involving sequential losses of a tetrahedral layer.

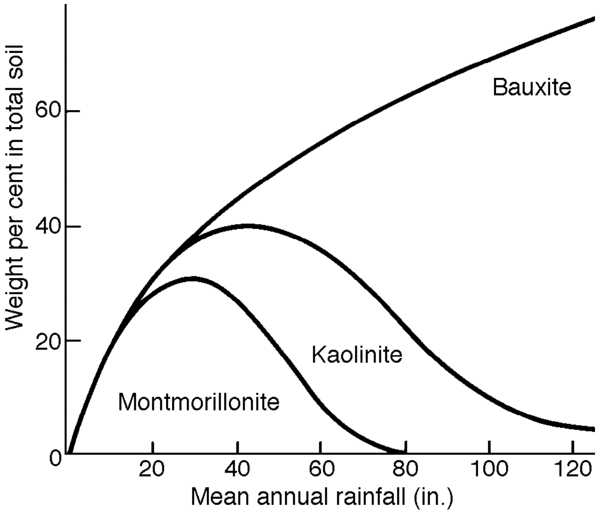


Figure 4A-2. Weathering of Hawaiian soil versus mean annual rainfall. Bauxite minerals such as gibbsite, $Al(OH)_3$, tend to form in areas of high rainfall and high relief, since these areas would have a high water flow rate. Montmorillonite, on the other hand, is usually formed in areas with low rainfall and low relief. Intermediate conditions favor the formation of kaolinite, normally the primary product of chemical weathering of silicate minerals. (Figure from A. H. Brownlow, *Geochemistry*, Prentice-Hall, 1979.)

The ideal chemical formulas in Tables 4A-1 and 4A-2 are usually more complex in natural materials with other elements partially substituting for silicon or aluminum. Such **isomorphic substitution** is shown in a chemical formula as a comma: for example, $(Al,Si)_4$ means a total of four Al and Si in some combination. When Al^{+3} replaces Si^{+4} in a tetrahedral sheet, the tetrahedral layer gains a –1 charge for every substitution. When Mg^{+2} replaces Al^{+3} in an octahedral sheet, the octahedral layer gains a –1 charge for every substitution.

For example, montmorillonite usually has intersheet water layers and extensive substitution by magnesium and iron(II) in the octahedral sheets. Aluminum may substitute for silicon in the tetrahedral sheets. Thus the formula for montmorillonite might be represented as

$$(Al,Mg,Fe)_2(OH)_2[(Si,Al)_4O_{10}]\cdot nH_2O.$$

Because of the isomorphic substitution, montmorillonite often has a deficiency of positive charge, and this causes extensive adsorption of cations like Ca^{+2} and Na^+ and K^+ and H^+ *on the surface and edges of the sheets*. These cations can easily be exchanged for other cations since they are present only for charge balance, and montmorillonite shows a high degree of ion exchange with adjacent solutions. Montmorillonite expands and contracts as the amount of water between the layers changes.

The charge on the mineral also depends on the pH since the OH^- groups can lose a proton to form O^{-2}.

Another component of good soil called **humic acid** is formed from the breakdown of plants by microorganisms and by the subsequent synthesis of new organic compounds. During soil formation the organic polymers of plant material are broken down to lower molecular weight monomers and the aliphatic portions are preferentially degraded, enriching the aromatic ring components. Enzymatic radical polymerization of free phenolic substances gives the structural backbone of humic acids. The organic soil matter undergoes continuous partial degradation and repolymerization. Humic acid does not have a well-characterized chemical formula, but a simplified representation is shown in Figure 4A-3.

Locate all the nutrient Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+} ions represented by M in Figure 4A-3. What element is attached to M? What functional group contains that element? Is that functional group an acid or base or a conjugate acid or base? In the absence of the metal ions, would you describe a humic substance as being positively charged or negatively charged?

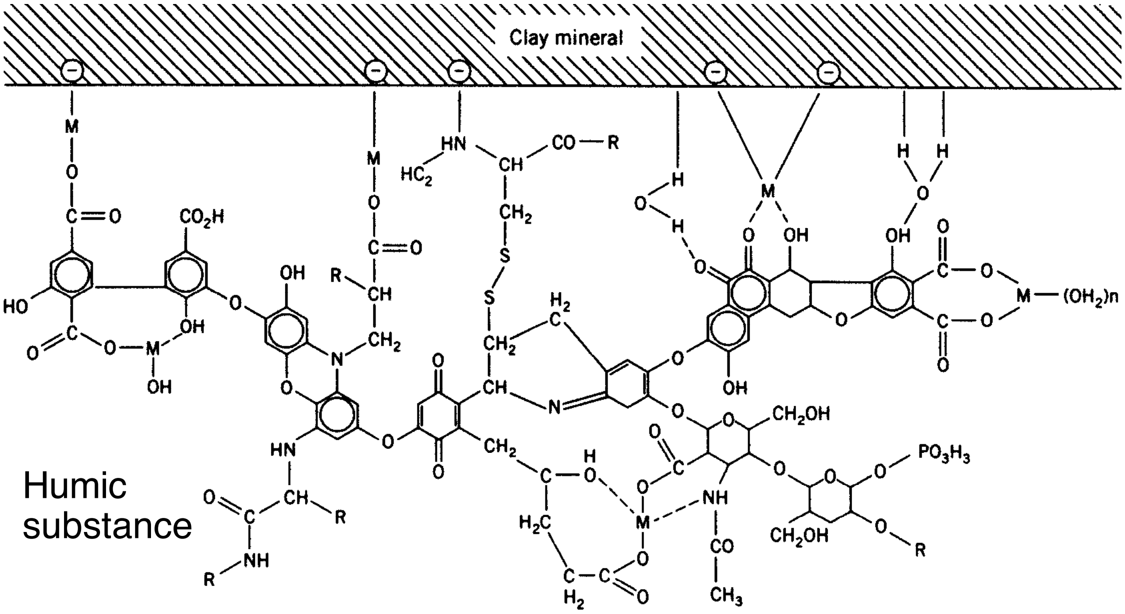
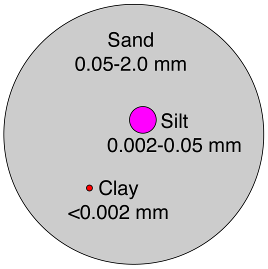


Figure 4A-3. A simplified humic substance (Figure from J. Eichhorn and A. Hüttermann, "Humus Disintegration and Nitrogen Mineralization" in *Effects of Acid Rain on Forest Processes*, D. L. Godbold and A. Hüttermann, eds., Wiley-Liss, New York, 1994.)

Weathering and the movement of soil particles create different layers of soil, or **horizons**. Most of the organic matter resulting from the growth of plants is added to the upper layers or horizons of the soil (the topsoil). For reference, some of the soil horizon designations are given in Table 4A-3.

DEVELOPING IDEAS

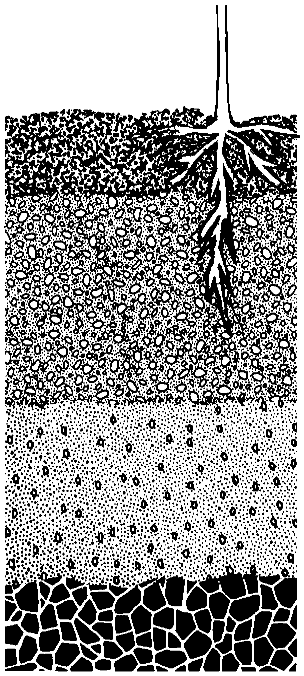
"The fertility of the soil lies in large part on the ability of clay minerals to absorb and release water and several cations that are indispensable for plant nutrition. This process is fundamental to the life of higher plants and, based on these, to the life of those animals which, in turn, feed upon the plants." F. Liebau, *Structural Chemistry of Silicates*, Springer-Verlag, Berlin, 1985.



Relative sizes of sand, silt, and clay. Sand feels gritty, like sand paper. Silt feels floury, soft, or smooth. Clay feels sticky or slick. *Know Soil Know Life*, SSSA (2012)

Soil Particles

The exchange of ions that occur between soil particles and growing plant roots is vital to plant and animal life. Moreover, soil particles are the sites for most chemical, physical, and biological properties of soils. An important property of soil particles is their small size; clay particles are smaller than 2 micrometers (μm). They are too small to be seen with a light microscope and can only be seen with an electron microscope. Because of their small size, soil particles expose a large external surface area per unit mass.



Wisconsin Cooperative Extension

Table 4A-3. Names of Soil Horizons

O horizon: The surface layer consists primarily of organic matter and only a small amount of mineral matter by volume. This layer is black or dark brown in color due to humic material.

A horizon: A mineral layer of soil enriched in organic matter that accumulates from the decomposition of plant material.

B horizon: A layer enriched in clay minerals, gypsum, calcium carbonate, and oxides and hydroxides of iron, aluminum, and manganese by leaching from the topsoil.

C horizon: Broken up parent material from which the soil is developed.

R horizon: Hard bedrock.

Another property of soil particles is their **surface charge**. The external surfaces of soil particles characteristically carry negative charges. One consequence of this negative charge is the attraction of hundreds of thousands of cations such as H^+, Ca^{+2}, Mg^{+2}, and Al^{+3} to the particle surface. We can think of the soil particle as essentially a huge anion, with a swarm of cations **adsorbed** or held to the particle surface. In addition to the adsorbed cations, many water molecules are associated with soil particles, and are attracted to the adsorbed cations.

Clay soil particles are characterized by their layered structure and their mineral (inorganic compounds of metals like Al, Ca, Mg) composition. Each particle is composed of a series of layers, much like a book. These layers are comprised of sheets of aluminum, silicon, magnesium, and iron atoms surrounded and held together by oxygen and hydroxy (OH) groups. Isomorphic substitution with cations of lower charge and unsatisfied valencies of the broken oxygen bonds at the edge of the lattice give rise to negative surface charge.

The organization of humus is similar to that of clay in that a negatively charged particle is surrounded by many cations. (See Figure 4A-3). The negative charges of humus particles are associated with the conjugate bases from ionized carboxylic acids and phenol groups as shown in Figure 4A-4.

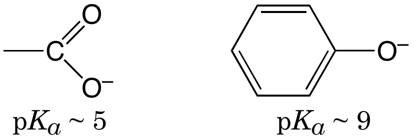


Figure 4A-4. Carboxylate and phenolate conjugate bases.

Cation Exchange in Soils

We have seen that particles of soil involve fixed negative charges, both in clay mineral soil and in organic soil. Thus, *soil charge balance tends to occur between fixed negatively charged groups and relatively mobile positively charged cations.* When water moves through a soil, it forms a **soil solution**, which consists of ions dissociated from the surface of soil particles and other trace elements from the water. Cations are exchanged between soil particles and the soil solution. The **cation exchange capacity** of a soil is a measure of the quantity of negatively charged sites to which cations can be held by ionic bonds.

How does cation exchange affect the pH of the soil solution?

Problem 4A-5

Examine the magnitude of the equilibrium constants in Appendix I. Which ions expected to be present in soil are weak acids and react with water to produce H^+? Hint: you may wish to prepare a logarithmic concentration diagram to help visualize the behavior of these acids.

✓ H^+, Al^{+3}, $Al(OH)^{+2}$, Fe^{+3}, $Fe(OH)^{+2}$, are acid cations.
Ca^{+2}, Mg^{+2}, Mn^{+2}, K^+, and Na^+ are not acid cations.

Nutrient forms used by plants, listed by elemental amounts needed.

H	H_2O
C	CO_2
O	O_2
N	NO_3^- NH_4^+
K	K^+
P	$H_2PO_4^-$ HPO_4^{-2}
Ca	Ca^{+2}
Mg	Mg^{+2}
S	SO_4^{-2}
Cl	Cl^-
Fe	Fe^{+2} Fe^{+3}
B	H_3BO_3
Mn	Mn^{+2}
Zn	Zn^{+2}
Cu	Cu^+ Cu^{+2}
Ni	Ni^{+2}
Mo	MoO_4^{-2}

Know Soil Know Life, SSSA (2012)

In acid soils, the cations that are present will be mainly acid cations. In alkaline soils, the cations that are present will not be mainly acid cations and these are called “base” cations. Neutral soils will be balanced by the presence of both acid and base cations.

The calcium, magnesium, potassium, and sodium cations are called the base cations because as acid is added to the soil solution, hydrogen can exchange with any of these cations, thus removing the hydrogen cations from the soil solution (just as a base would react with added hydrogen cations). When strong acids are added by acid rain, the solution pH doesn't change much as long as there are more basic soil cations than added H^+.

For most plants, optimum growth occurs when sodium, calcium, magnesium, and potassium ions occupy 80% of the cation exchange sites. This occurs when the pH of the soil is somewhere between 6.3 and 6.7. Hydrogen cations in the soil compete for binding sites with these four cations. When the pH of the soil drops by one unit, the hydrogen ion concentration of the soil solution is increased by a factor of ten. Thus, many more hydrogen ions are competing for exchange sites. This results in a higher concentration of hydrogen cations on the exchange sites and a lower concentration of calcium, magnesium, potassium, and sodium cations on the exchange sites. The cations are displaced into the soil solution where they are leached away by rainwater if not promptly taken up by plants. The loss of these cations due to leaching is one of the principle long-term effects of acid rain.

APPLYING YOUR IDEAS

4A-6 What are the top 9 abundant elements in the earth’s crust?

4A-7 What is the ionic charge of each of these elements?

4A-8 What is the geometry usually found around these ions?

4A-9 Spend some time investigating and deciding what is illustrated in Table 4A-1 by using the polyhedral models page at

http://chemistry.beloit.edu/edetc/pmks

See the trioctahedral sheets. How do the ball and stick versus polyhedral representations compare? You can turn the different representations on and off as you interact with the structure. Try to identify tetrahedral silicon sheets and octahedral aluminum sheets.

4A-10 Spend some time investigating and deciding what is illustrated in Figure 4A-3 by using the Virtual Museum of Minerals and Molecules *https://virtual-museum.soils.wisc.edu/display/soil-organic-matter/* for a model with humic acid, soil protein, and soil saccharides. Turn various functional groups on and off. Which groups are acids or bases?

4A-11 If each of the following were independent ions made of Si^{+4} and O^{-2}, how many H^+ would be needed for charge balance?

_____ two corner-shared tetrahedra
_____ two edge-shared tetrahedra
_____ two face-shared tetrahedra.
_____ two corner-shared octahedra
_____ two edge-shared octahedra
_____ two face-shared octahedra

4A-12 Describe the structural changes that occur as montmorillonite weathers to kaolinite to gibbsite.

4A-13 Estimate the pH for a solution containing equal amounts of the following pairs. What assumption(s) must you make? Can you always ignore the dissociation of water?

a. Al^{+3} and $Al(OH)^{+2}$

b. Ca^{+2} and $CaOH^+$

c. Fe^{+3} and $Fe(OH)^{+2}$

d. Mg^{+2} and $Mg(OH)^+$

e. Mn^{+2} and $Mn(OH)^+$

f. K^+ and KOH

g. Na^+ and NaOH

4A-14 Draw a cartoon of a soil particle at pH = 6.5 and at pH = 5.5, including the surface charge of the particle and any other ions associated with the particle.

4A-15 Aluminum is considered to be an acid component of the soil. Why should this be true?

4A-16 Sea water has much higher Mg^{+2}/Ca^{+2} and Na^{+}/K^{+} ratios than river water. How will small particles of a clay mineral moving in a river change when the river reaches the sea?

4A-17 Cations are important components of soil, not only because they are essential plant nutrients but also because of their ability to buffer the effects of acid rain. Silicon and aluminum are considerably more abundant than sodium, calcium, magnesium and potassium, but the latter are the most active participants in cation exchange. Table 4A-4 represents the energy needed to remove a given ion from a solid lattice such as those found in soil. Figure 4A-5 shows the relative ionic radii of these same ions.

Table 4A-4. Energies of formation of oxides of various cations

Ion	kcal/mole	Ion	kcal/mole
K^+	299	Al^{+3} (non-framework)	1793
Na^+	322	Al^{+3} (framework)	1878
H^+	515	Ti^{+4}	2882
Ca^{+2}	839	Si^{+4} (SiO_4^{-4} tetrahedra)	3142
Mn^{+2}	895	Si^{+4} ($Si_4O_{12}^{-8}$, single chain)	3131
Mg^{+2}	912	Si^{+4} ($Si_4O_{11}^{-6}$, double chain)	3127
Fe^{+2}	919	Si^{+4} ($Si_4O_{10}^{-4}$ sheets)	3123
Fe^{+3}	~1500	Si^{+4} (SiO_2 framework)	3110

M. L. Huggins, K. H. Sun, *J. Phys. Chem.*, **50**, 319-28 (1945).

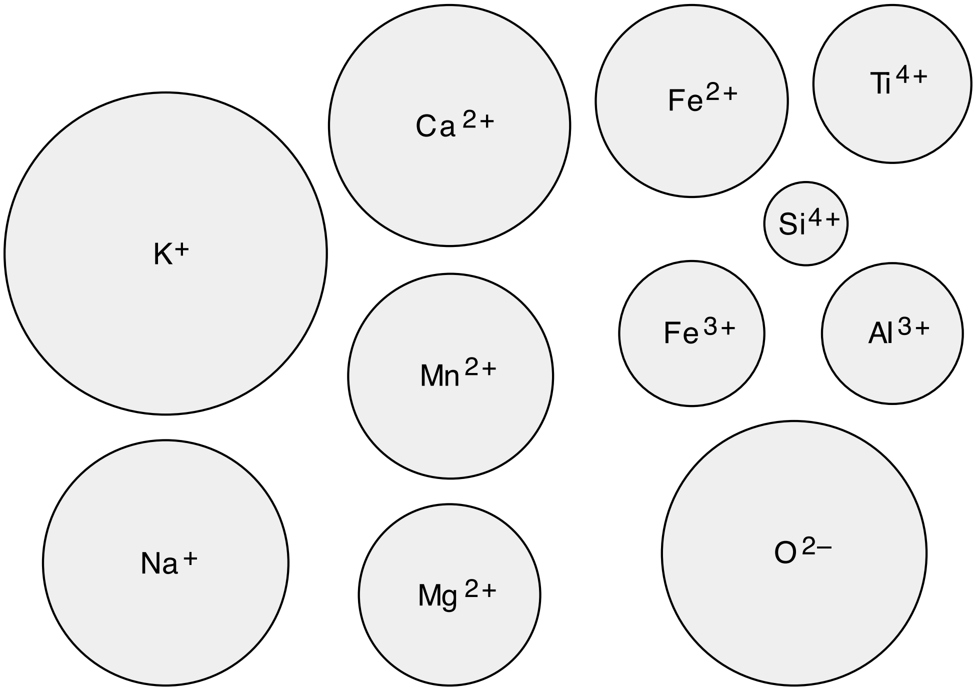


Figure 4A-5. Relative Ion Radii

Use Table 4A-4 and Figure 4A-5 to propose an explanation for why the most abundant cations do not participate in cation exchange as frequently as sodium, calcium, magnesium and potassium. What other ions in soil should also exchange relatively easily?

4A-18 Clay minerals and organic matter in natural waters often occur in the colloidal state, having particle diameters that are intermediate between that of dissolved molecules and that of particles that can settle out of solution. Such colloids are very, very small and their overall surface area is very, very large.

a. Calculate the surface area of a mineral particle with the volume of a 1mm cube (a sand grain).

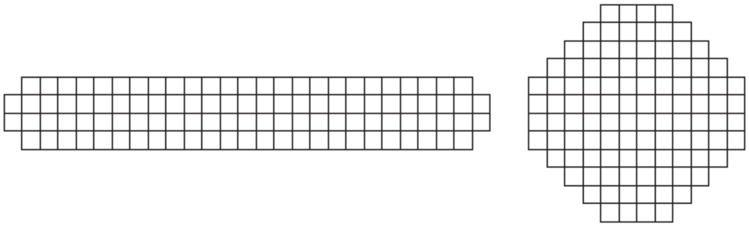
b. Break the mineral particle down into silt particles that are each 0.01 mm cubes. Calculate the surface area of each silt particle. (Hint: You will have 10^6 particles.)

c. Now break the mineral particle down into clay particles. For simplicity, assume 0.001 mm cubes. Calculate the surface area of each clay particle.

d. Compare the relative surface areas of equal amounts (by weight) of sand, silt and clay that you calculated in parts a-c. In this example we considered sand, silt and clay particles as simple cubes. That assumption is pretty good for sand but silt and especially clay tend to be composed of thin plates and so have surface areas of five to ten times higher than the values you calculated.

4A-19 The main factors in soil development are vegetation, climate, parent material, topography, and time. The discussion in this exploration has mainly concerned the weathering of parent material. What are some ways the other factors affect the weathering of parent material?

4A-20 Small particles of most minerals are soluble, but the layered minerals found in clays are an exception. One reason concerns the energy of formation, as illustrated in Table 4A-4. Another reason has to do with particle shape since defect sites are more reactive. Which two-dimensional shape has more blocks with two exposed sides?



How does ion exchange work?

EXPLORATION 4B, ION-EXCHANGE COLUMN

THE CONTEXT

We would like to determine the amount of copper in a sample of copper sulfate by a simple titration. In this procedure, the copper ions are exchanged for hydrogen ions and the analysis is then done by acid-base titration.

You will be using a cation exchange resin in this experiment. This is a type of polymer (plastic) with attached sulfonic acid groups, $R\text{–}SO_3^-$, where R stands for part of the resin. Ions of opposite charge must also be present to ensure charge balance. These positive ions (cations) are not permanently bound to the resin and can be exchanged by appropriate adjustment of equilibrium conditions. You will be starting with the resin in the acid form, where the positive ion present is hydrogen ion. Addition of a copper solution then replaces the hydrogen ions with copper ions,

$$2\ R\text{–}SO_3H + Cu^{+2} \rightleftharpoons (R\text{–}SO_3)_2Cu + 2\ H^+$$

freeing the hydrogen ions for analysis by titration with NaOH.

A similar process is involved in the “deionization” of water; cations are exchanged for hydrogen ions on a cation exchange resin and anions are exchanged for hydroxide ions on an anion exchange resin. Water softeners similarly exchange Na^+ for Ca^{+2} and Mg^{+2}.

PREPARING FOR INQUIRY

Preparation of the Ion Exchange Column

Obtain a chromatography column. (It looks like a short buret). A small plug of cotton should be placed in the bottom of the barrel to keep resin in the tube and out of the stopcock. The cotton should not be packed so tight as to impede water flow. Fill the column with water.

Put about 15 mL of cation exchange resin in water in a small beaker and transfer the suspension into the water-filled column in one continuous pour with the aid of a wash bottle. The final column should be filled to less than half with resin. Liquid may be removed through the stopcock as necessary, but do not worry about spilling water while pouring resin into the column. Return any unused beads.

For good results always keep the liquid level above the resin. If the liquid drains below the resin, it will cause air bubbles and subsequent uneven drainage. (If you have a problem you can try to remove air bubbles by holding a stopper in the top of the column and inverting the column many times to re-suspend the resin, but usually you have to start over.)

The next step is to make sure that all the cations in the column are hydrogen ions. A cation-exchange column is regenerated by percolating a solution of about 3 M HCl through the column. A volume of acid about 3 times that of the resin is usually sufficient. It should be passed through the column at a rate not greater than 2 to 3 mL/min. (The slow passage ensures equilibrium will be established at each point as the solution passes down the column.) Use a timer and graduated cylinder to check. The column will need to be regenerated again after three or four exchanges have been made on it, or if a color change caused by use reaches the bottom of the column.

Wash the column with pure water until the water leaving the column is the same pH as the entering wash water as determined by litmus paper. Fill the column with water, and then let it flow out until the water level is within 0.5 cm of the surface of the resin. Repeat several times. The rate of water flow can be as fast as possible, but do not let the liquid level go below the surface of the resin. Remember: **slow for exchange**, **fast for rinse**.

Use of the Ion Exchange Column

Prepare three or four copper sulfate samples by accurately weighing out approximately 0.2 g of copper sulfate to the nearest 0.0001 g and *dissolving* in a small amount of pure water.

For each exchange, lower the water level in the column to about 0.5 cm above the resin. Place one entire copper solution at the top of the column and a clean titration flask under the column to receive the effluent. Use a 50 mL Erlenmeyer for a weight titration or the balance capacity may be exceeded. *Slowly* run the copper solution through the column at a rate of about 1 drop per second. Allow the liquid level to fall to about 0.5 cm above the resin. Rinse out the original copper solution container several times with a few mL of water and run the rinse solution through the column at about one drop per second until the liquid level falls to about 0.5 cm above the resin.

All the copper ions in the sample should now have displaced hydrogen ions from the resin. The hydrogen ions can be rinsed from the column at a much faster rate. Fill the column with pure water and collect the solution at the maximum rate. Do not let the liquid go below the surface of the resin. Keep adding water to the column and collecting the effluent into the titration flask, until the pH of the effluent is the same as that of the added pure water when tested by litmus paper. Where is the copper? Where is the sulfate? Save the solution in the flask for the next part.

Repeat with additional copper samples until you have three or four separate samples ready to titrate. Before starting each sample, you will need to decide if your column needs to be regenerated. If so, repeat starting with the HCl washing above or the sample concentration investigation below.

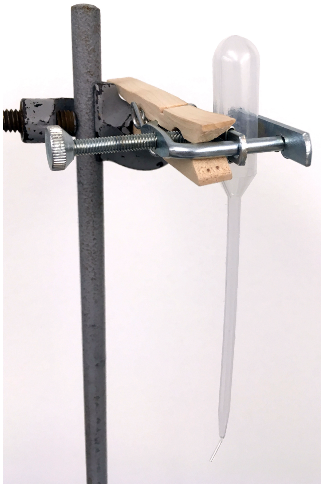
Titrate the Collected Hydrogen Ions with NaOH

In this titration a measured amount of an NaOH solution of known concentration is added to your acidic solution of unknown concentration. At the **equivalence point** or **stoichiometric point**, the number of moles of base added is equivalent to the number of moles of acid in the original solution.

Add 2 drops of phenolphthalein indicator solution to each titration flask and mix well by swirling the contents of the flask.

Weight Titration

Rinse and fill a plastic microtip pipet with approximately 1.0 M NaOH. Record the g NaOH/kg of the standard solution and the initial weight of the *flask* containing sample and indicator. Turn the Hoffman screw clamp on the pipet to add NaOH solution. Be sure to stop adding NaOH solution when the titration solution changes color, and the color remains after swirling. When the mixed solution stays pink for at least 20 seconds, record the final weight of the flask. Do not go beyond the equivalence point of the titration!



Microtip pipet and Hoffman clamp used for weight titration

Sample Concentration

Another use of ion exchange columns is for concentrating samples. No matter how dilute your original copper solution was, all copper was stored on the column. Put 5 mL of 3 M HCl on the top of the column and allow it to run through slowly into a clean container. Follow this with pure water. Where is the copper now? The hydrogen ions will replace the copper ions and you will get a solution of copper(II) chloride. In a fume hood, add some NH_3 solution (enough to neutralize the acid) to the receiving flask. You should first see a $Cu(OH)_2$ precipitate. Keep adding NH_3 to obtain the color of the $Cu(NH_3)_x^{+2}$ complex. Record your observations.

Clean Up

Ion exchange resins do not wear out rapidly and can be regenerated a number of times. *Do not throw your resin away* but put it in the available container for future use. The resin is relatively expensive and should not be wasted. An easy way to wash out your column is to invert it over the used resin container, and squirt water from a wash bottle into the tip.

DEVELOPING IDEAS

Calculations

Calculate the number of moles of hydrogen ion in the sample. Convert this to the number of moles of copper ion. From the known sample mass and the calculated moles, find the experimental molar mass of copper sulfate. What is the expected molar mass of $CuSO_4$? Assume water of hydration makes up the rest of the experimental molar mass. Based on the molar mass of water, how many waters of hydration are in the copper sulfate sample?

APPLYING YOUR IDEAS

Questions

Why do we use a column rather than just treating the solution with ion exchange resin in a beaker, and filtering to separate the resin from solution? (We could filter much faster in a regular filtration set up.) Note that it is not a matter of contact time since you could leave the solution in the beaker as long as you want.

Are there any limitations on the type of sample that can be used in this method?

What kind of equilibria are involved in this analysis?

How does ion-exchange protect soils from acid rain?

EXPLORATION 4C, BUFFERS

CREATING THE CONTEXT

In Exploration 4A, you discovered that a high cation exchange capacity was a crucial factor in a soil's ability to maintain pH. Soils with high cation exchange capacity are also said to have high **buffering capacity**, which means they can absorb a significant amount of acid or base without a notable change in pH. By definition, a **buffer** resists a change in pH when an acid or base is added.

Consider an NH_3/NH_4^+ buffer system formed by an aqueous solution of NH_3 and NH_4Cl. Since Cl^- is a spectator ion, the important equilibrium is:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

A buffer resists pH change by exchanging stronger acids and bases for weaker acids and bases. When OH^- is added, NH_4^+ is converted to NH_3. NH_3 is a weaker base than hydroxide so the pH change is not as drastic as when OH^- is added to water. When H^+ is added, NH_3 is converted to NH_4^+. NH_4^+ is a weaker acid than hydronium ion (dissociates less) so the pH change is not as drastic as when H^+ is added to water.

Problem 4C-1

Suggest at least four *pairs* of chemicals from the following list that can be used to make a buffer. Explain your reasoning for each pair.

HCl, $NaOH$, CH_3COOH, CH_3COONa, NH_3, NH_4Cl.

✓ Some possible answers include:

1. A mixture of CH_3COONa and CH_3COOH (a conjugate base of a weak acid with a weak acid.)
2. A mixture of NH_4Cl and NH_3 (a conjugate acid of a weak base and a weak base.)
3. Addition of HCl to excess NH_3 (a strong acid and excess weak base generates the conjugate of the base to give NH_4Cl and NH_3.) There must be excess NH_3 since addition of HCl to an equivalent number of moles of NH_3 gives only NH_4Cl which is not a buffer. Addition of excess HCl to NH_3 gives HCl and NH_4Cl which is not a buffer.
4. Addition of NaOH to excess CH_3COOH (a strong base and excess weak acid generates the conjugate of the acid to give CH_3COONa and CH_3COOH.) There must be excess CH_3COOH since addition of NaOH to an equivalent number of moles of CH_3COOH gives CH_3COONa which is not a buffer. Addition of excess NaOH to CH_3COOH gives NaOH and CH_3COONa which is not a buffer.
5. Addition of HCl to excess CH_3COONa (a conjugate base of a weak acid with a strong acid generates the weak acid to give CH_3COONa and CH_3COOH.) There must be excess CH_3COONa since addition of HCl to an equivalent number of moles of CH_3COONa gives CH_3COOH which is not a buffer. Addition of excess HCl to CH_3COONa gives HCl and CH_3COOH which is not a buffer.

6. Addition of NaOH to excess NH_4Cl (a strong base and the conjugate acid of a weak base generates the weak base to give NH_3 and NH_4Cl.) There must be excess NH_4Cl since addition of NaOH to an equivalent number of moles of NH_4Cl gives NH_3 which is not a buffer. Addition of excess NaOH to NH_4Cl gives HCl and NH_4Cl which is not a buffer.

PREPARING FOR INQUIRY

The Buffer Equation

What is $[H^+]$ in 0.10 M CH_3COOH with 0.20 M CH_3COONa? Set up this problem in general for M_{HA} and M_{NaA}.

1. Equilibrium constant $K_a = \frac{[H^+][A^-]}{[HA]}$
2. Mass balances $M_{HA} + M_{NaA} = [HA] + [A^-]$

   $M_{NaA} = [Na^+]$
3. Charge balance $[H^+] + [Na^+] = [A^-] + [OH^-]$
4. Substitute to obtain one equation and one unknown.

   From charge $[A^-] = M_{NaA} + [H^+] - [OH^-]$.

   From mass $[HA] = M_{HA} + M_{NaA} - M_{NaA} - [H^+] + [OH^-]$

   Substitute into the equilibrium constant expression.

   $$K_a = \frac{[H^+](M_{NaA} + [H^+] - [OH^-])}{M_{HA} - [H^+] + [OH^-]}$$
5. Solve. What if $[H^+]$ and $[OH^-]$ are both << M_{NaA} and M_{HA}?

   $$K_a = \frac{[H^+](M_{NaA} + \cancel{[H^+]} - \cancel{[OH^-]})}{M_{HA} - \cancel{[H^+]} + \cancel{[OH^-]}} \approx \frac{[H^+]M_{NaA}}{M_{HA}}$$

   Using the values for this problem: $1.75\times10^{-5} \approx \frac{[H^+](0.20)}{0.10}$

   $[H^+] = 8.8\times10^{-6}$; $[OH^-] = 1.1\times10^{-9}$ *Yes*, 10^{-5} and 10^{-9} << 0.10 and 0.20

Note that we are not canceling terms but simply adding a small number to a much larger number to leave the large number unchanged within significant digits.

The buffer equation for conjugate acid/base pairs:

$$\boxed{K_a = \frac{[H^+]M_{NaA}}{M_{HA}} \text{ if } [H^+] \text{ and } [OH^-] << M_{NaA} \text{ and } M_{HA}}$$

Notice that this looks like the K_a expression, but the restrictions are an important part of the equation. If the restrictions fail, you will need to use the complete systematic method to solve the problem.

In biological and biochemical fields, the buffer equation is used in log form and is called the **Henderson-Hasselbalch** equation:

$$[H^+] = K_a \frac{M_{HA}}{M_{NaA}}; \text{ pH} = \text{p}K_a - \log\frac{M_{HA}}{M_{NaA}} = \text{p}K_a + \log\frac{M_{NaA}}{M_{HA}}$$

The same restrictions apply, $[H^+]$ and $[OH^-]$ << M_{NaA} and M_{HA}.

The pH of a buffer solution is not changed by dilution (within buffer assumption limits). Examine the buffer equation to see the effect on the pH of the same dilution in both numerator and denominator.

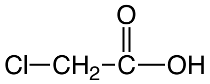
A buffer resists pH change when strong acids or bases are added since they are consumed by the buffer. As the buffer is used up, it becomes less resistant to changes in pH.

Developing Ideas

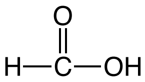
Class Activity

(*J. Chem. Ed.*, **71**, A7 (1994))

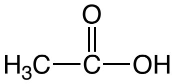
Each group should obtain a small beaker and dropper, a dropper bottle of 0.01 M NaOH solution, half a petri dish, and a dropper bottle containing a dilute solution of one of the following acids:


$Cl{-}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}OH$

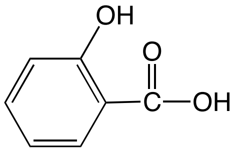
Chloroacetic Acid


$H{-}\overset{\overset{\large O}{\|}}{C}{-}OH$

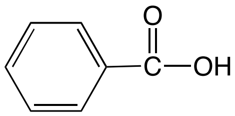
Formic Acid


$H_3C{-}\overset{\overset{\large O}{\|}}{C}{-}OH$

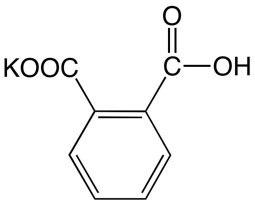
Acetic Acid



Salicylic Acid



Benzoic Acid



Potassium Biphthalate

Put 30 drops of the acid solution in a small beaker. (Be sure to record which acid you are using!)

Add 1 drop of phenolphthalein indicator. Phenolphthalein is colorless in acidic solutions and pink in basic solutions.

Add 0.01 M NaOH from the dropper just until the solution in the beaker turns colored. What does the color change tell you about the relationship between the original moles of acid and the moles of NaOH added?

Add another 30 drops of the original acid solution to the beaker. You have just made a buffer by mixing the conjugate base of an acid with an equal amount of the same acid. How is the pH of the solution related to the pKa of the acid? (Hint: Examine the buffer equation for equal amounts of acid and conjugate base.)

Transfer drops of the buffer mixture to a petri dish to make four puddles. Add one drop of a different indicator solution to each puddle. With the help of a reference color table, estimate the pH of each mixture. Put your results in the table below and exchange data with other groups to fill in the table.

Table for class results

	Chloroacetic	Formic	Acetic	Salicylic	Benzoic	Biphthalate
Erythrosin B color						
Methyl orange color						
Bromocresol green color						
Congo red color						
estimated solution pH						
estimated pK_a						

Soil Buffering

Several buffering mechanisms are present in the soil. Each mechanism is predominant at a different pH range. Consider a soil having equal amounts of carbonates, such as $CaCO_3$, and clays. Initially the pH stays around 8 due to the carbonate buffer system.

$$CaCO_3(s) + H^+ \rightleftharpoons Ca^{+2} + HCO_3^-$$

$$HCO_3^- + H^+ \rightleftharpoons CO_2(g) + H_2O$$

When fine carbonate particles are distributed evenly, the soil has the buffering capacity to withstand large inputs of strong acid.

If the carbonate rock is depleted or absent, the next mechanism of the cation exchange reactions in clay minerals takes over and the pH stays around 5.5. H^+ displaces the "base" cations Ca^{+2}, Mg^{+2}, Na^+, K^+ from ion exchange sites, removing H^+ from the soil solution. This buffer capacity is limited because it depends on the availability of exchangeable sites occupied by base cations.

When weathering of rocks and minerals is insufficient to replenish base cations lost during acidification, a third buffering mechanism, that of aluminum ion, becomes important. The solubility of aluminum hydroxide governs the pH in a buffer range from 4.2 to 3.8.

$$Al(OH)_3(s) + 3\ H^+ \rightleftharpoons Al^{+3} + 3\ H_2O$$

Since aluminum compounds are abundant in soils, buffer capacity in this range is rarely depleted. If the pH drops still further, H^+ is neutralized by the dissolving of iron oxides.

APPLYING YOUR IDEAS

4C-2 In what ways are some soils like conjugate acid-base buffers in their ability to moderate acid rain?

4C-3 In what ways are conjugate acid-base buffers and soil different?

4C-4 How can we protect soil from acid rain?

4C-5 In soils affected by acid rain, H+ displaces other cations on the surface of soil particles, occupying more of the cation exchange sites on the particle. What happens to the displaced cations, and how might this affect plant growth?

Problems Using the Buffer Equation

4C-6 Find the pH of a solution containing 0.75 M lactic acid and 0.25 M sodium lactate. Lactic acid, $CH_3CH(OH)COOH$, $K_a = 1.4 \times 10^{-4}$, is a common constituent of biologic systems. For example, it is found in milk and is present in human muscle tissue during exertion.

4C-7 A buffered solution contains 0.25M NH_3 and 0.40M NH_4Cl. What is the pH of this solution?

4C-8 A scientist needs to prepare a solution buffered at pH 4.30 and plans to use benzoic acid. Calculate the ratio of sodium benzoate to benzoic acid that will produce a buffer at this desired pH.

4C-9 What is the pH of 70 g NH_4Cl and 600 mL concentrated aqueous NH_3 (14.5 M) diluted to 1 L? What is the pH if 5 mL of this mixture is then diluted to 500 mL by adding water? (This mixture is used in Exploration 5D.)

4C-10 How does the pH of 400 mL of water change when

a. 100 mL 0.0500 M NaOH is added?

b. 100 mL 0.0500 M HCl is added?

4C-11 How does the pH of 400 mL of a 0.200 M NH_3 and 0.300 M NH_4Cl solution change when

a. 100 mL 0.0500 M NaOH is added?

b. 100 mL 0.0500 M HCl is added?

4C-12 What is the pH of 20.00 mL 0.0800 M NH_3 added to

a. 40.00 mL of water?

b. 40.00 mL of 0.0300 M HCl?

c. 40.00 mL of 0.0300 M NH_4Cl?

d. 40.00 mL of 0.0400 M HCl?

e. 40.00 mL of 0.0400 M NH_4Cl?

f. 40.00 mL of 0.0400 M NaOH?

4C-13 A chemist starts with a 25.0 mL sample of 0.10 M acetic acid, to which 0.10 M NaOH is added.

a. What is the initial pH, before any NaOH is added?

b. What is the pH after 5.0 mL NaOH is added?

c. What is the pH after 10.0 mL NaOH is added?

d. What is the pH after 15.0 mL NaOH is added?

e. What is the pH after 20.0 mL NaOH is added?

f. What is the pH after 25.0 mL NaOH is added?

g. What is the pH after 30.0 mL NaOH is added?

h. What is the pH after 35.0 mL NaOH is added?

What happens when the buffer runs out?

EXPLORATION 4D, TITRATIONS

CREATING THE CONTEXT

You have made use of acid-base titrations as an analytical technique in Exploration 4B. What can equilibrium calculations tell us about titrations?

A plot of the pH of a solution as a function of the amount of added **titrant** gives a sigmoidal shape called a pH titration curve. Titration curves have a relatively flat buffer region, followed by concentrations changing rapidly near the equivalence point, and then another flat region as the concentration of the titrant in the flask approaches the concentration in the buret. When a sharp and easily located endpoint is observed from small additions of titrant causing large changes in relative concentration, titration is useful as a laboratory analysis technique.

We have already encountered calculations that correspond to each portion of a titration curve:

	Weak acid titrated with strong base	Weak base titrated with strong acid
Before addition	Weak acid	Weak base
Before equivalence	Buffer	Buffer
Half equivalence	pH = pKa	pH = pKa
Equivalence	Weak base	Weak acid
After equivalence	Strong base	Strong acid

As a review, consider the calculations involved for the titration of 50.0 mL 0.100 M CH_3COOH (in the flask) with 0.200 M NaOH (in the buret).

0.00 mL added (a solution of acetic acid)

K_a $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75\times10^{-5}$

Charge: $[H^+] = [OH^-] + [CH_3COO^-]$

Mass: $0.100 = [CH_3COOH] + [CH_3COO^-]$

Solve: $K_a = \frac{[H^+]([H^+] - \cancel{[OH^-]})}{0.100 \quad [H^+] + [OH^-]}$; $[H^+] = 0.00132$; pH = 2.878

10.00 mL added (a buffer)

Dilution! $\frac{50}{50+10}0.100$ M CH_3COOH = 0.0833 M CH_3COOH

$\frac{10}{50+10}0.200$ M NaOH = 0.0333 M NaOH

Reaction! Strong base will convert CH_3COOH to CH_3COONa to give 0.0500 M CH_3COOH and 0.0333 M CH_3COONa.

Buffer! $K_a = \frac{[H^+]0.0333}{0.0500}$; $[H^+] = 2.63\times10^{-5}$; pH = 4.581

Yes, 0.00003 and $3.8\times10^{-10} << 0.0500$ and .0333

12.50 mL added (a buffer)

Dilution! $\frac{50}{50+12.5}0.100\text{ M }CH_3COOH = 0.0800\text{ M }CH_3COOH$

$\frac{12.5}{50+12.5}0.200\text{ M NaOH} = 0.0400\text{ M NaOH}$

Reaction! Strong base will convert CH_3COOH to CH_3COONa to give 0.0400 M CH_3COOH and 0.0400 M CH_3COONa.

Buffer! $K_a = \frac{[H^+]0.0400}{0.0400}$; $[H^+] = 1.75\times10^{-5}$; pH = 4.757

Yes, 0.0000175 and $5.71\times10^{-10} << 0.0400$

25.00 mL added (a solution of sodium acetate)

Dilution! $\frac{50}{50+25}0.100\text{ M }CH_3COOH = 0.0667\text{ M }CH_3COOH$

$\frac{25}{50+25}0.200\text{ M NaOH} = 0.0667\text{ M NaOH}$

Reaction! Strong base will convert CH_3COOH to CH_3COONa to give 0.0000 M CH_3COOH and 0.0667 M CH_3COONa.

K_a $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75\times10^{-5}$

Charge: $[Na^+] + [H^+] = [OH^-] + [CH_3COO^-]$

Mass: $0.0667 = [CH_3COOH] + [CH_3COO^-]$

$0.0667 = [Na^+]$

Solve: $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}\frac{K_w}{[H^+][OH^-]}$

$$= \frac{(0.0667 + \cancel{[H^+]} - \cancel{[OH^-]})K_w}{(\cancel{0.0667} - \cancel{0.0677} - \cancel{[H^+]} + [OH^-])[OH^-]}$$

$[OH^-] = 6.17\times10^{-6}$; pH = 8.790

30.00 mL added (a strong base and a weak base)

Dilution! $\frac{50}{50+30}0.100\text{ M }CH_3COOH = 0.0625\text{ M }CH_3COOH$

$\frac{30}{50+30}0.200\text{ M NaOH} = 0.0750\text{ M NaOH}$

Reaction! Strong base will convert CH_3COOH to CH_3COONa to give 0.0125 M NaOH and 0.0625 M CH_3COONa.

Mass balance on hydroxide:

$0.0125 + [CH_3COOH] + [H^+] = [OH^-]$

but we expect $[CH_3COOH] + [H^+] << .0125$ since

neither water or CH_3COO^- are significantly protonated.

$[OH^-] = 0.0125$; pH = 14 – pOH = 12.097

40.00 mL added (a strong base and a weak base)

Dilution! $\frac{50}{50+40}0.100\text{ M }CH_3COOH = 0.0556\text{ M }CH_3COOH$

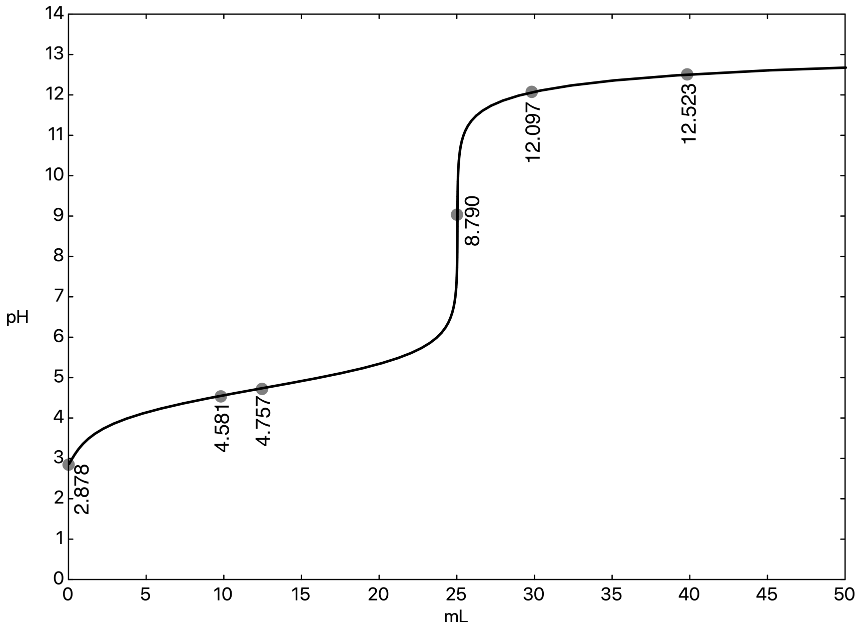
$\frac{40}{50+40}0.200\text{ M NaOH} = 0.0889\text{ M NaOH}$

Reaction! Strong base will convert CH_3COOH to CH_3COONa to give 0.0333 M NaOH and 0.0556 M CH_3COONa.

Mass balance on hydroxide:

$0.0333 + \cancel{[CH_3COOH]} + \cancel{[H^+]} = [OH^-]$

$[OH^-] = 0.0333$; pH = 14 – pOH = 12.523



Calculated points on the titration curve

Preparing for Inquiry

The object of the rest of Exploration 4D is to gain experience in interpreting titration curves. For each of the problems, first move the movie slider bar on the module web site and then answer the questions.

4D-1 What are the main species at each point in the titration curve in Figure 4D-1?

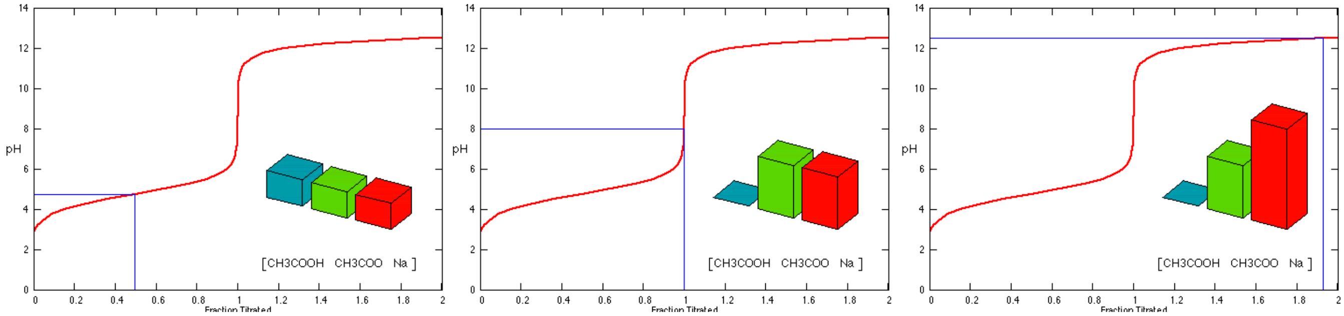


Figure 4D-1. Halfway to equivalence the concentrations of HA and A^- and Na^+ are equal. At the equivalence point $[A^-]$ and $[Na^+]$ are equal. At double the equivalence point $[Na^+] = 2\,[A^-]$.

4D-2 What happens to the titration curve if you change the value of K_a for the analyte (Figure 4D-2)? Why?

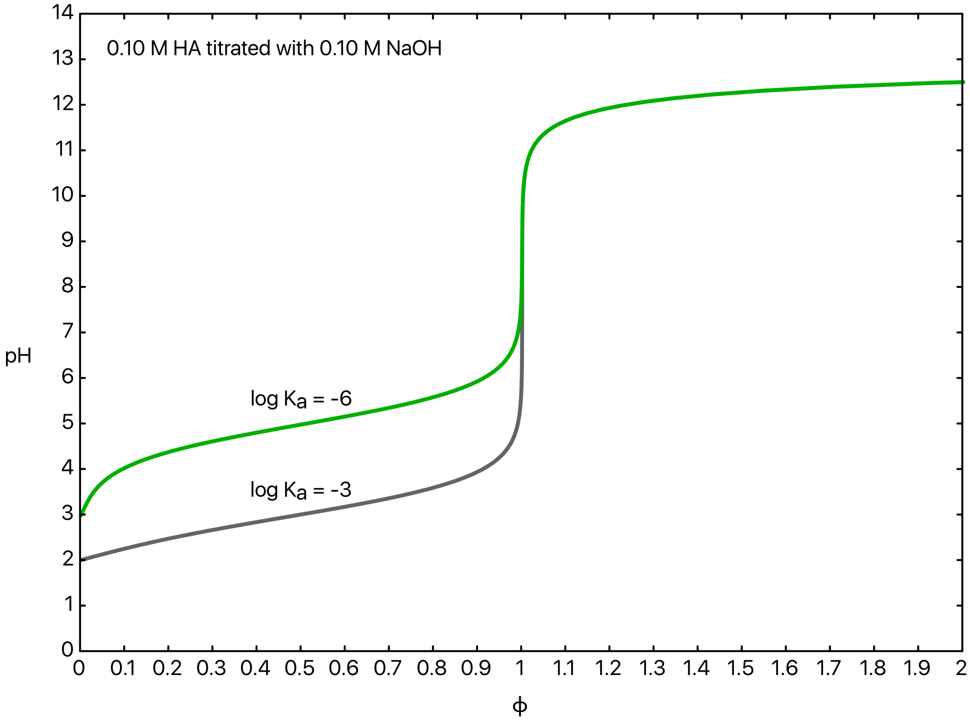


Figure 4D-2. Before equivalence, H^+ is controlled by the K_a equilibrium.

4D-3 What happens to the titration curve if you change the concentration of NaOH in the buret (Figure 4D-3)? Why?

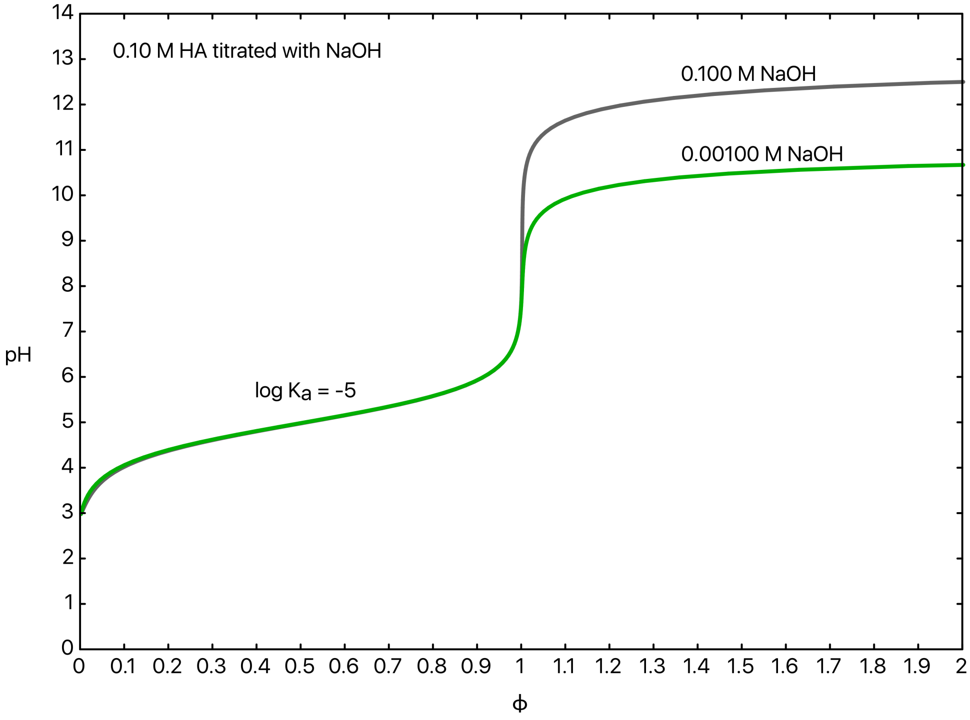


Figure 4D-3. After equivalence, H^+ approaches the molarity of titrant (in buret).

4D-4 What happens to the titration curve if you dilute the solutions (Figure 4D-4)? Why?

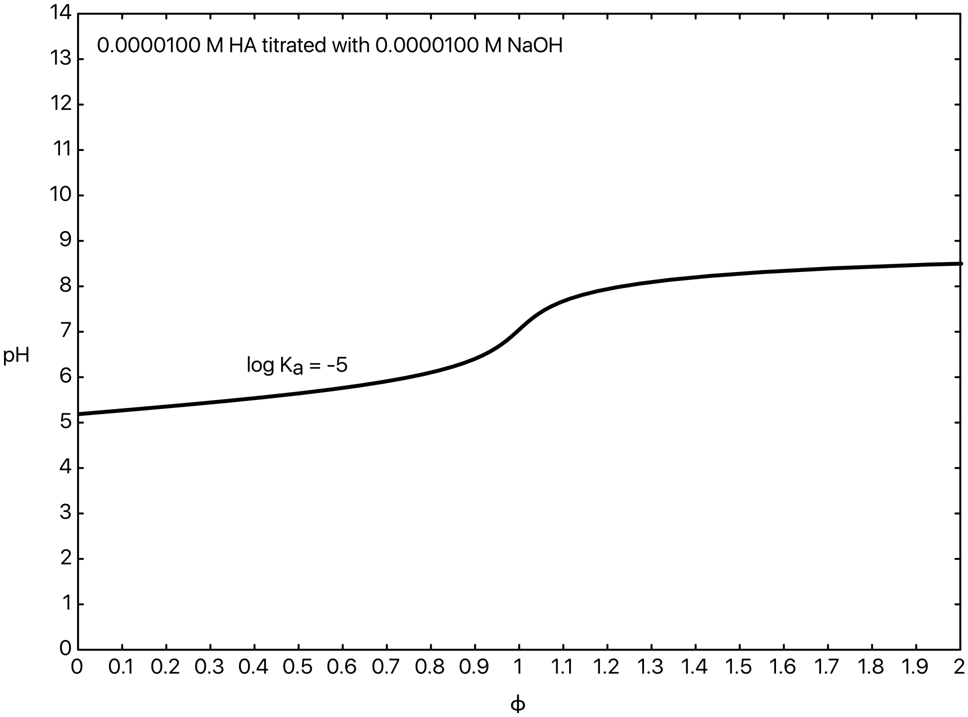


Figure 4D-4. The endpoint becomes less sharp as the solutions are diluted.

4D-5 What happens to the titration curve if you change K_{a2} for a diprotic acid (Figure 4D-5)? Why?

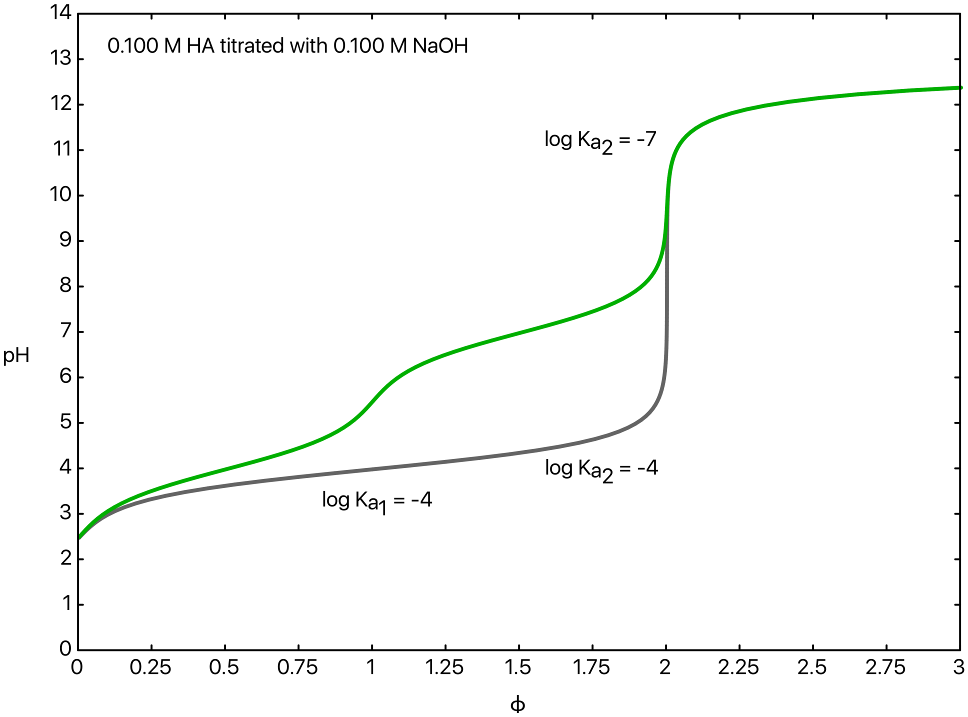


Figure 4D-5. Only the first endpoint is affected when K_{a2} is changed.

DEVELOPING IDEAS

Indicators

Consider an indicator with different colored acid and base forms:

$$HIn \rightleftharpoons H^+ + In^- \qquad K_a^{In} = \frac{[H^+][In^-]}{[HIn]}.$$

If $\frac{[In^-]}{[HIn]} < 0.1$, normally the color of HIn will be observed. This corresponds to $[H^+] > 10\ K_a$. If $\frac{[In^-]}{[HIn]} > 10$, normally the color of In^- will be observed. This corresponds to $[H^+] < 0.1\ K_a$. For $0.1\ K_a < [H^+] < 10\ K_a$, a mixture or intermediate color will be observed. The color change interval for the indicator is thus approximately $pH = pK_a^{In} \pm 1$.

We want an observable, sharp, change that comes at the molar equivalence point of the titration. The difference between the equivalence point and the observed endpoint is called the **indicator error**. For a minimum indicator error, the indicator color change should occur during the vertical part of the titration curve. *Small amounts of indicator are normally used since the indicator must also be titrated to reach the endpoint.*

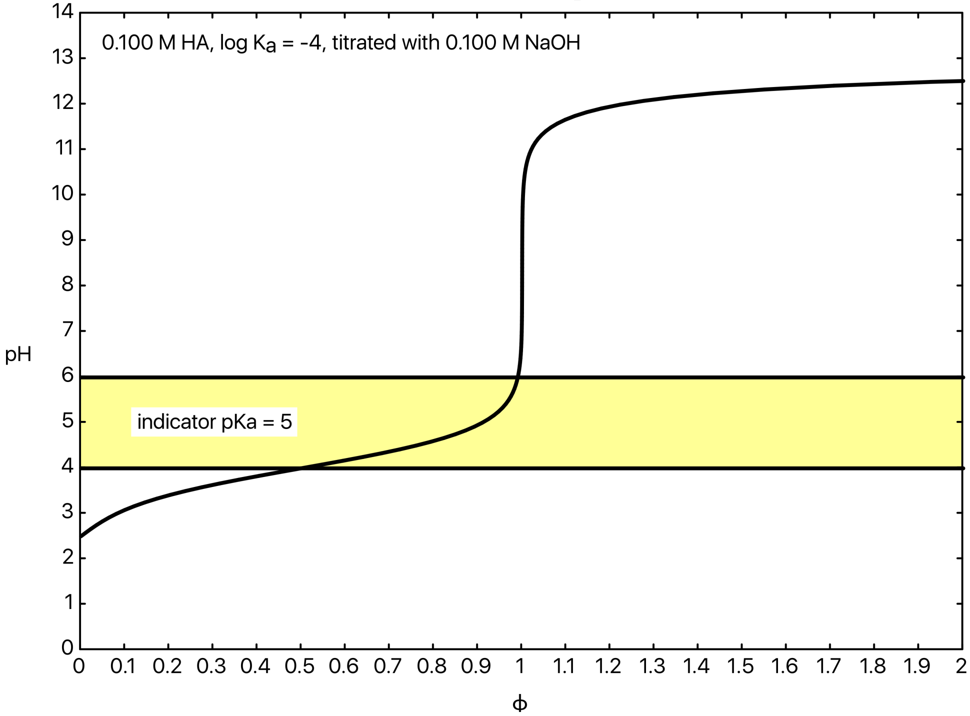


Figure 4D-6. Would an indicator with pK_a 5 or pK_a 7 be a better choice for this titration? (Over how many mL does the color transition occur?)

Soil

During chemical weathering of rocks, acids formed from carbon dioxide and the oxides of sulfur and nitrogen titrate the bases of the minerals. Whether the titration proceeds past the endpoint determines whether the soil solution will be acidic or basic.

Figure 4D-7 shows the results of a model calculation for the release of aluminum ion from soil as a function of time. What does the shape of these curves imply? To what does the x-axis correspond? Why does the soil depth change the endpoint?

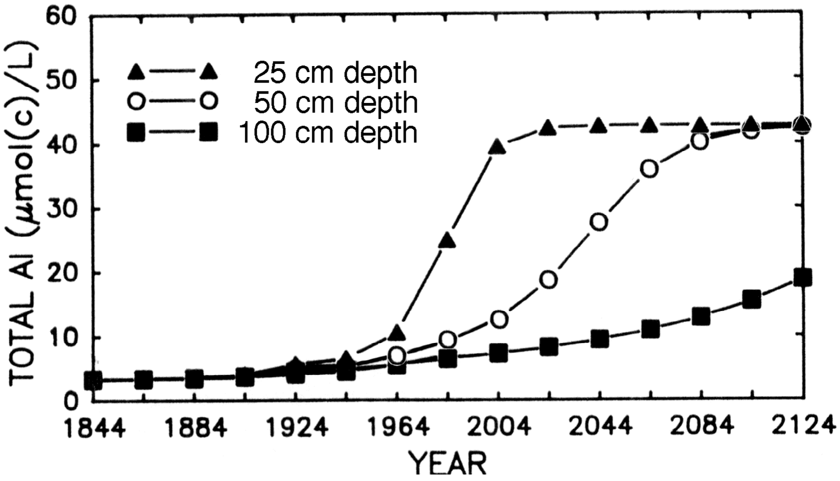


Figure 4D-7. Model calculations of aluminum concentration in soil solution for generic clayey poorly drained soil as a function of soil depth (25 cm, 50 cm and 100 cm). D. Binkley, C. T. Driscoll, H. L. Allen, P. Schoeneberger, and D. McAvoy, "The Nature of Soil Acidity and H^+ Budgets," *Acidic Deposition and Forest Soils: Context and Case Studies of the Southeastern United States*, Springer-Verlag, New York, Ecological Studies Vol. 72, 1988.

APPLYING YOUR IDEAS

4D-6 A chemist adds 20.3 mL of 0.1 M NaOH to 25.0 mL of an unknown concentration of HCl until phenolphthalein just turns pink, indicating that all of the acid has been neutralized.

a. How many moles of HCl were initially present before any base was added?

b. What is the original molarity of the HCl solution?

c. What was the pH of the original solution?

4D-7 Consider the titrations of 100 mL of 0.1M HCl with 0.1 M NaOH and the titration of 100 mL of 0.1 M CH_3COOH with 0.1 M NaOH. Which of the following would be the same for both titrations? Circle all true answers.

a. The initial pH

b. The pH at the halfway point

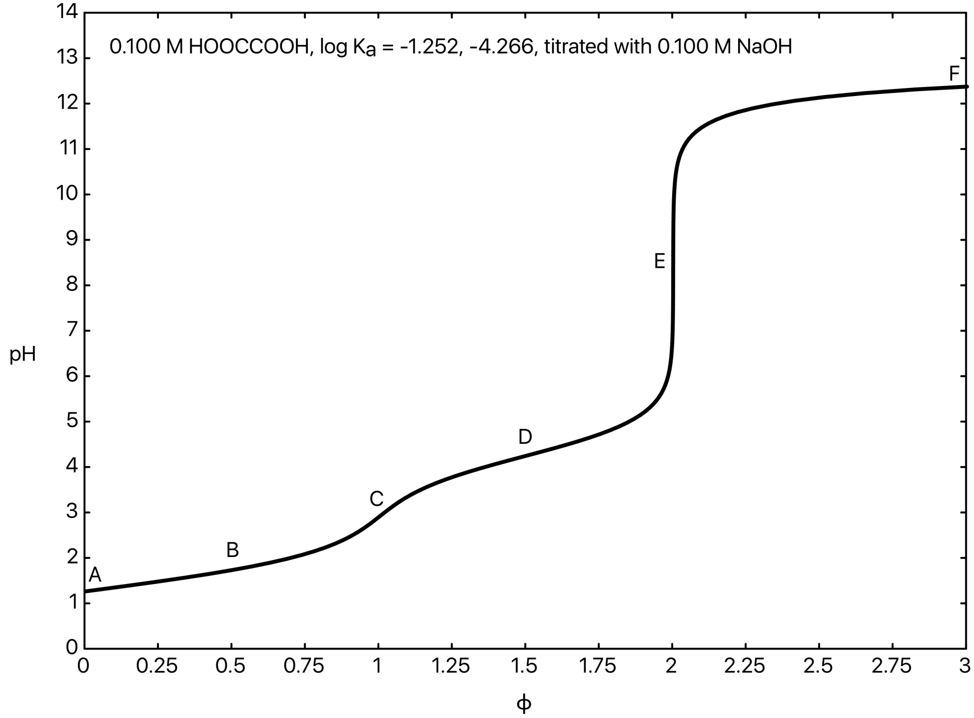
c. The volume of NaOH required to reach the equivalence point

d. The pH at the equivalence point

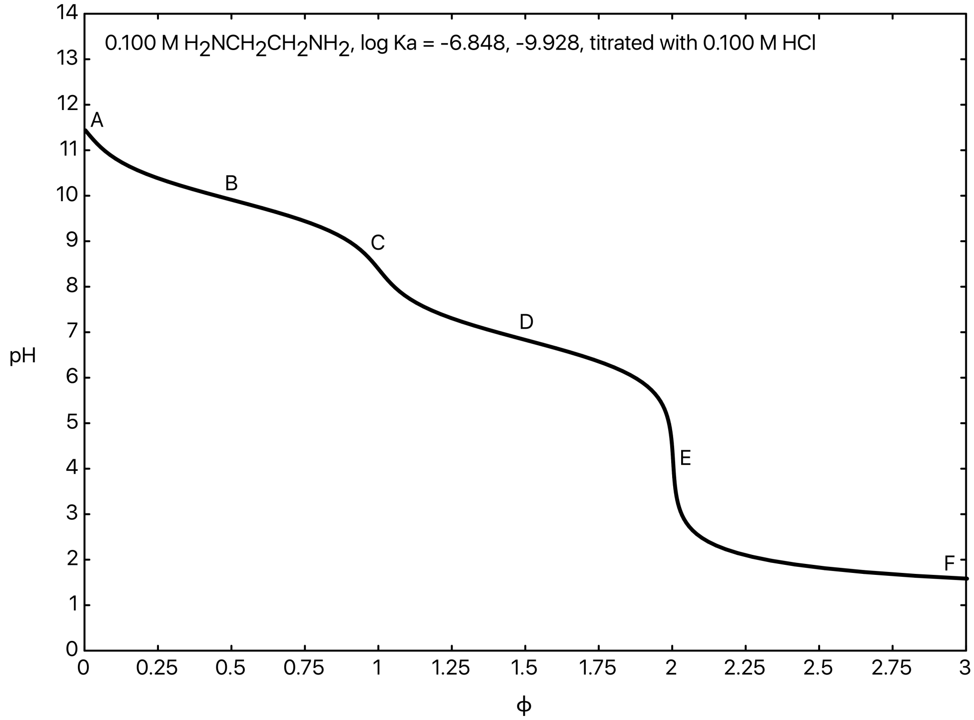
e. The pH after 120 mL added

4D-8 Label the main species present for each portion of the titration curve.

a. 0.10 M HOOCCOOH titrated with 0.10 M strong base



b. 0.10 M $H_2NCH_2CH_2NH_2$ titrated with 0.10 M strong acid



4D-9 An indicator with what pK_a would work best for the titrations in problem 4D-8?

a. 0.10 M HOOCCOOH titrated with 0.10 M strong base

b. 0.10 M $H_2NCH_2CH_2NH_2$ titrated with 0.10 M strong acid

4D-10 Buffer capacity can be used to quantify the ability of solutions to resist changes in pH when acids or bases are added. The charge balance, the mass balance *C*, and the equilibrium constant expressions can be combined to calculate the amount of added acid or base for a given [H$^+$] concentration:

$$n = \frac{K_w}{[\mathrm{H}^+]} - [\mathrm{H}^+] + \frac{C\,K_a}{K_a + [\mathrm{H}^+]}$$

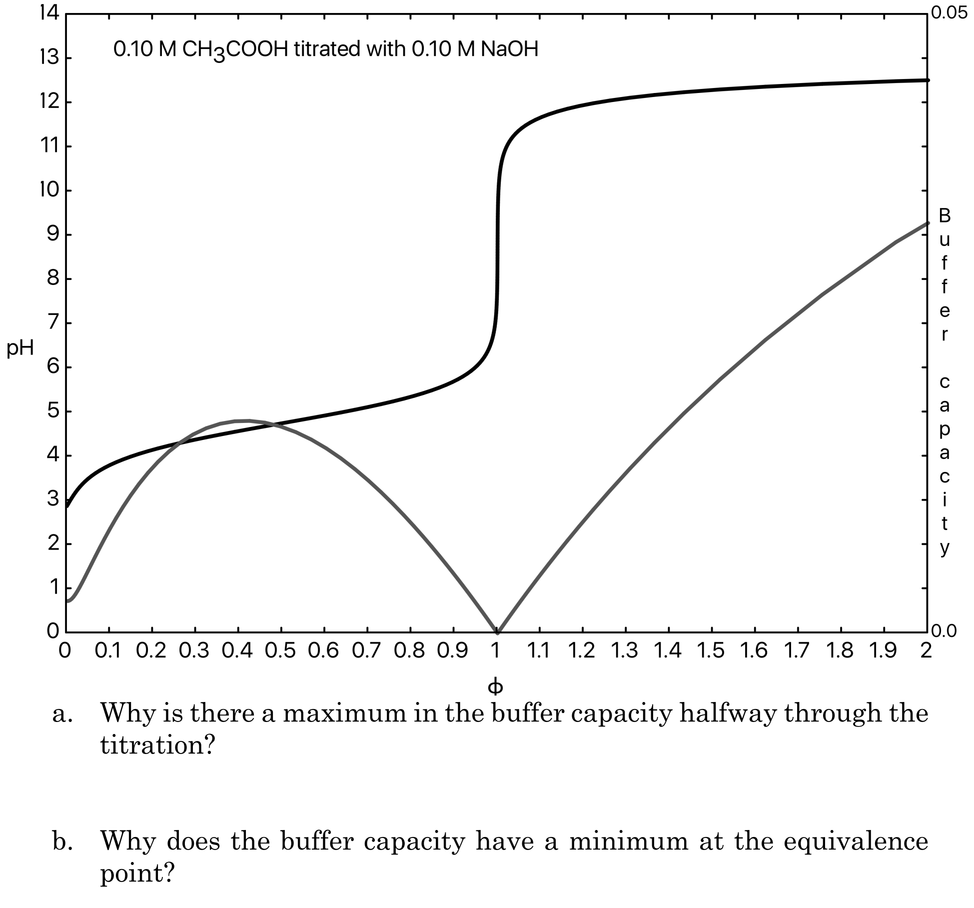
The buffer capacity is then the derivative of *n* with respect to pH,

$$\frac{dn}{d(pH)} = \frac{dn}{d[\mathrm{H}^+]}\frac{d[\mathrm{H}^+]}{d(pH)} = \left(-\frac{K_w}{[\mathrm{H}^+]^2} - 1 - \frac{C\,K_a}{(K_a + [\mathrm{H}^+])^2}\right)(-2.303[\mathrm{H}^+]).$$

Multiplying out the terms and extending for polyprotic acids yields a general expression for the buffer capacity:

$$2.303\left(\frac{K_w}{[\mathrm{H}^+]} + [\mathrm{H}^+] + \sum \frac{C\,K_a[\mathrm{H}^+]}{(K_a + [\mathrm{H}^+])^2}\right).$$

The titration curve for 0.10 M CH_3COOH with 1.0 M NaOH is shown below along with the buffer capacity at each point in the titration.



a. Why is there a maximum in the buffer capacity halfway through the titration?

b. Why does the buffer capacity have a minimum at the equivalence point?

c. Why does the buffer capacity steadily increase after the equivalence point?

Polyprotic Acids and Bases

EXPLORATION 4E, GRAPHS AND SOLUTIONS BASED ON α-FRACTIONS

CREATING THE CONTEXT

Consider a polyprotic molecule with four acidic protons, H_4A. Possible *A*-containing species are H_4A, H_3A^-, H_2A^{-2}, HA^{-3}, and A^{-4}. Which are the major components and what fraction of the total concentration is present as each of the species (the α-fraction)?

Derivation of Acid α-Fractions

Consider the acid *dissociation* equilibria of a tetraprotic acid, H_4A.

$$H_4A \rightleftharpoons H^+ + H_3A^- \qquad K_{a1} = \frac{[H^+][H_3A^-]}{[H_4A]}$$

$$H_3A^- \rightleftharpoons H^+ + H_2A^{-2} \qquad K_{a2} = \frac{[H^+][H_2A^{-2}]}{[H_3A^-]}; \; K_{a1}K_{a2} = \frac{[H^+]^2[H_2A^{-2}]}{[H_4A]}$$

$$H_2A^{-2} \rightleftharpoons H^+ + HA^{-3} \qquad K_{a3} = \frac{[H^+][HA^{-3}]}{[H_2A^{-2}]}; \quad K_{a1}K_{a2}K_{a3} = \frac{[H^+]^3[HA^{-3}]}{[H_4A]}$$

$$HA^{-3} \rightleftharpoons H^+ + A^{-4} \qquad K_{a4} = \frac{[H^+][A^{-4}]}{[HA^{-3}]}; \quad K_{a1}K_{a2}K_{a3}K_{a4} = \frac{[H^+]^4[A^{-4}]}{[H_4A]}$$

Dissociation equilibrium constants are numbered according to the number of protons that have been lost.

The mass balance for the acid with total concentration, C_A, is:

$$C_A = [H_4A] + [H_3A^-] + [H_2A^{-2}] + [HA^{-3}] + [A^{-4}]$$

Substitute the above overall equilibrium constant expressions into the mass balance expression to obtain:

$$C_A = [H_4A] + \frac{K_{a1}[H_4A]}{[H^+]} + \frac{K_{a1}K_{a2}[H_4A]}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}[H_4A]}{[H^+]^3} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}[H_4A]}{[H^+]^4}$$

Factoring out $[H_4A]$ yields:

$$C_A = [H_4A]\left\{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[H^+]^4}\right\} = [H_4A]\, D_o$$

where the *dissociation function*, D_o, is defined as:

$$\boxed{D_o = 1 + \frac{K_{a1}}{[H^+]^1} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[H^+]^4} + \dots} = \frac{C_A}{[H_nA]}$$

Now, what fraction of the total acid is present as each species?

$$\alpha_0 = \text{fraction that has lost 0 } H^+ = \frac{[H_4A]}{C_A} = \frac{1}{D_o}$$

$$\alpha_1 = \text{fraction that has lost 1 } H^+ = \frac{[H_3A^-]}{C_A} = \frac{K_{a1}[H_4A]}{[H^+]C_A} = \frac{K_{a1}}{[H^+]D_o}$$

$$\alpha_2 = \text{fraction that has lost 2 } H^+ = \frac{[H_2A^{-2}]}{C_A} = \frac{K_{a1}K_{a2}[H_4A]}{[H^+]^2 C_A} = \frac{K_{a1}K_{a2}}{[H^+]^2 D_o}$$

$$\alpha_3 = \text{fraction that has lost 3 H}^+ = \frac{[\mathrm{HA}^{-3}]}{\mathrm{C_A}} = \frac{K_{a1}K_{a2}K_{a3}[\mathrm{H_4A}]}{[\mathrm{H}^+]^3\mathrm{C_A}} = \frac{K_{a1}K_{a2}K_{a3}}{[\mathrm{H}^+]^3\mathrm{D_o}}$$

$$\alpha_4 = \text{fraction that has lost 4 H}^+ = \frac{[\mathrm{A}^{-4}]}{\mathrm{C_A}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}[\mathrm{H_4A}]}{[\mathrm{H}^+]^4\mathrm{C_A}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[\mathrm{H}^+]^4\mathrm{D_o}}$$

Note that the α-fractions are successive terms of D_o divided by D_o!

PREPARING FOR INQUIRY

The α-fractions are dependent only on the hydrogen ion concentration. If we know the $[H^+]$ then we can calculate the α-fraction (as in Table 4E-1) and we can use $[H^+]$ as a master variable to plot how the distribution changes with pH (as in Figure 4E-1.)

Table 4E-1. α-fraction dependence on pH for phosphoric acid

	pH 2	pH 4	pH 6	pH 8	pH 10	pH 12
α_0	0.5844	0.0139	0.0001	0.0000	0.0000	0.0000
α_1	0.4156	0.9855	0.9404	0.1365	0.0016	0.0000
α_2	0.0000	0.0006	0.0595	0.8634	0.9914	0.5855
α_3	0.0000	0.0000	0.0000	0.0001	0.0070	0.4145
Total α	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Distribution (α) diagrams

An acid-base distribution diagram plots the species fraction present as a function of pH (Figure 4E-1). At low pH nearly all will be present as the most protonated form and at high pH nearly all will be present as the least protonated form; in between each species takes a turn at being the predominate species over some pH range.

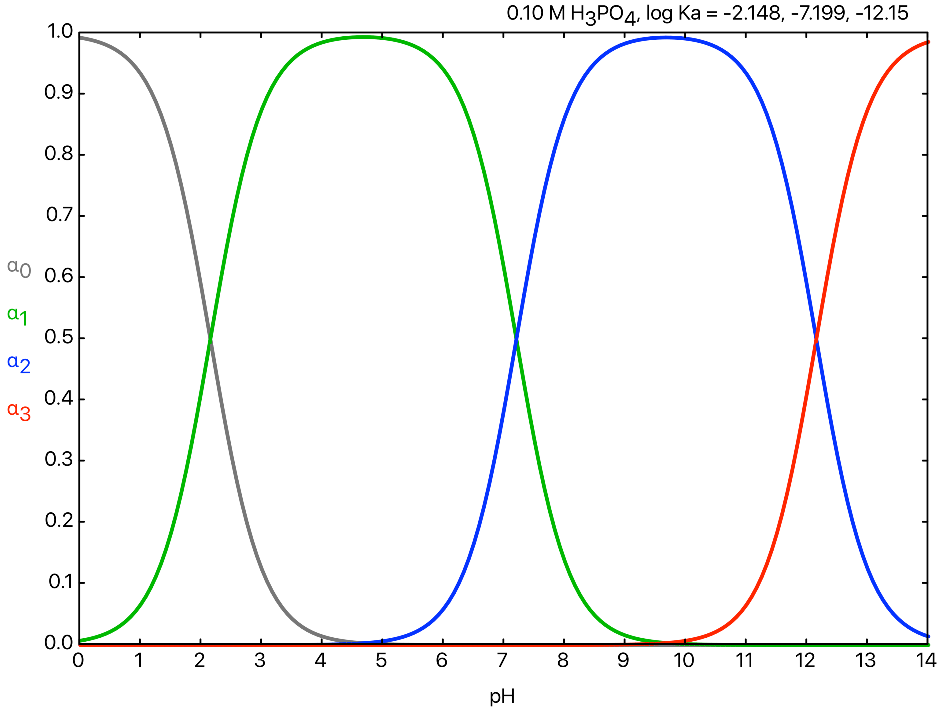


Figure 4E-1. Distribution Diagram for phosphoric acid. Can you label the phosphoric species present at different pH values?

Logarithmic Concentration Diagrams

Since the concentration of each species is its α-fraction times the total acid concentration C_A, logarithmic concentration diagrams can be calculated from α-fractions. Compare the distribution diagram in Figure 4E-1 with the logarithmic concentration diagram in Figure 4E-2.

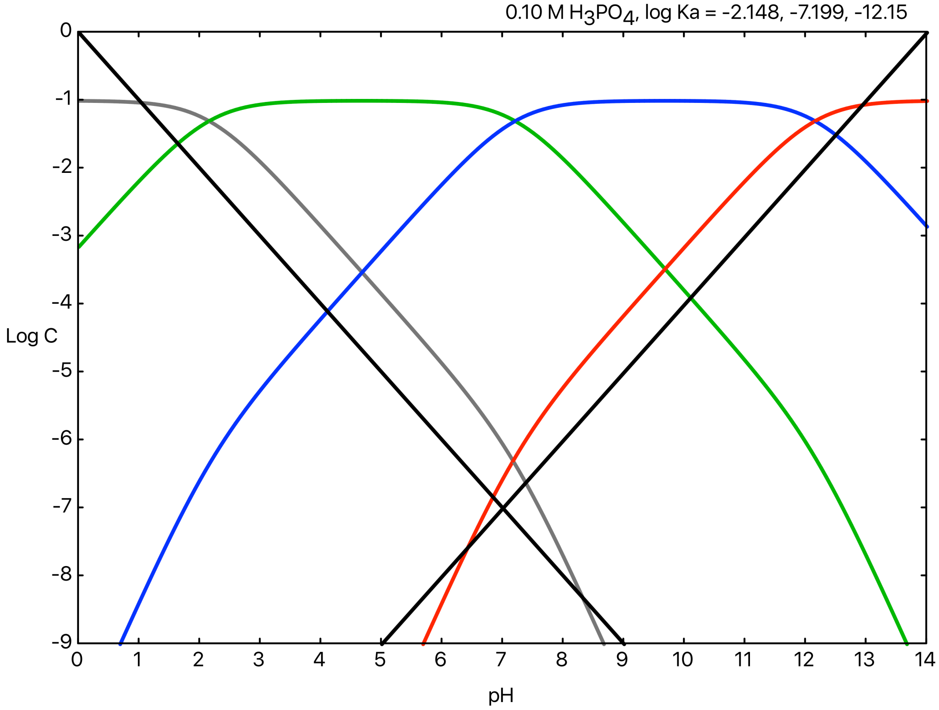


Figure 4E-2. The logarithmic concentration diagram for 0.10 M phosphoric acid. Can you label each curve with the phosphoric species it represents?

DEVELOPING IDEAS

Solving for pH

By using the mass and charge balance information along with the α-fraction definitions, an equation with one unknown is obtained and the pH of the system can be calculated.

To find the pH of NaH_2PO_4, write the charge balance equation.

$$[Na^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2\,[HPO_4^{-2}] + 3[PO_4^{-3}]$$

If C_A is the total molarity of all phosphoric acid species, then concentrations of individual phosphoric acid species are fractions of the total. Combining the mass balance equations (including $[Na^+] = C_A$) and the charge balance equation yields

$$[H^+] = \frac{10^{-14}}{[H^+]} + \{\alpha_1 + 2\,\alpha_2 + 3\,\alpha_3 - 1\}\,C_A$$

This is an equation with one unknown that can be solved for $[H^+]$.

To find the pH of $H_2NCH_2CH_2NH_3Cl$, replace the ethanediammonium species with the α-fraction times the total in the charge balance equation to give an equation with one unknown.

$$[H^+] + 2\,[H_3NCH_2CH_2NH_3^{+2}] + [H_2NCH_2CH_2NH_3^+] = [OH^-] + [Cl^-]$$

$$[H^+] = \frac{10^{-14}}{[H^+]} - \{2\alpha_0 + \alpha_1 + 1\}\ C_A$$

To find the pH of H_3NCH_2COO, replace the glycine species with the α-fraction times the total in the charge balance equation to give an equation with one unknown.

$$[H^+] + [H_3NCH_2COOH^+] = [OH^-] + [H_2NCH_2COO^-]$$

$$[H^+] = \frac{10^{-14}}{[H^+]} + (\alpha_2 - \alpha_0)\ C_A$$

Finally consider a general acid with molarity C_A and n values of K_a where the fully protonated acid contributes a charge of p and whose associated counter ions contribute a charge of q to the charge balance equation. Some examples are given in Table 4E-2. The one equation with one unknown can be written as

$$\boxed{[H^+] = \frac{10^{-14}}{[H^+]} + \{(0-p)\,\alpha_0 + (1-p)\,\alpha_1 + (2-p)\,\alpha_2 + \dots + (n-p)\,\alpha_n - q\}\ C_A}$$

p is the charge on the fully protonated acid and *q* is the charge on the associated counter ions.

Table 4E-2. Describing charges in acids and bases

	n	p	q
CH_3COOH	1	0	0
CH_3COONa	1	0	+1
NH_4Cl	1	+1	-1
NH_3	1	+1	0
H_3PO_4	3	0	+0
NaH_2PO_4	3	0	+1
Na_2HPO_4	3	0	+2
Na_3PO_4	3	0	+3
$H_3NCH_2CH_2NH_3Cl_2$	2	+2	-2
$H_2NCH_2CH_2NH_3Cl$	2	+2	-1
$H_2NCH_2CH_2NH_2$	2	+2	0
$NH_3CH_2COOHCl$	2	+1	-1
NH_3CH_2COO	2	+1	0
NH_2CH_2COONa	2	+1	+1
HCl	0	0	-1
NaOH	0	0	+1

Strong acids and bases have $p = 0$ since $[H^+]$ and $[OH^-]$ are always present in the charge balance equation.

Titration of H_4A with NaOH

The α-fractions are also helpful when calculating titration curves for polyprotic acids and bases. The charge balance equation for each point in the titration of H_4A with NaOH is:

$$[Na^+] + [H^+] = [OH^-] + [H_3A^-] + 2\,[H_2A^{-2}] + 3\,[HA^{-3}] + 4\,[A^{-4}]$$

Using the definitions $[H_3A^-] = \alpha_1\ C_A$, $[H_2A^{-2}] = \alpha_2\ C_A$, $[HA^{-3}] = \alpha_3\ C_A$, and $[A^{-4}] = \alpha_4\ C_A$ gives:

$$[Na^+] + [H^+] = \frac{K_w}{[H^+]} + (\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4)\ C_A.$$

C_A or C_B is the mass balance concentration and it changes during the titration. M_A or M_B is the unchanging initial molarity in flask or buret.

The total volume will be different at each point of the titration and this affects the concentrations. When titrant volume V_B of base with concentration M_B is added to the initial volume V_A of acid with initial concentration M_A, the new volume will be V_A+V_B and mass balances are:

$$C_A = \frac{V_A\,M_A}{V_A+V_B} \text{ and } [Na^+] = C_B + q\,C_A = \frac{V_B\,M_B}{V_A+V_B} + q\,\frac{V_A\,M_A}{V_A+V_B}$$

Combine the equations and C_A terms:

$$\frac{V_B\,M_B}{V_A+V_B} + [H^+] = \frac{K_w}{[H^+]} + (\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 - q)\,\frac{V_A\,M_A}{V_A+V_B}$$

Multiply by the total volume ($V_A + V_B$):

$$V_B\,M_B + [H^+]\,(V_A + V_B) = \frac{K_w}{[H^+]}(V_A + V_B) + (\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 - q)\,V_A\,M_A.$$

Collect V_B terms on one side and V_A terms on the other:

$$V_B\,M_B + [H^+]\,V_B - \frac{K_w}{[H^+]}V_B =$$

$$- [H^+]\,V_A + \frac{K_w}{[H^+]}V_A + (\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 - q)\,V_A\,M_A.$$

Factor out the moles of acid and base on each side:

$$V_B\,M_B\left(1 + \frac{[H^+] - K_w/[H^+]}{M_B}\right) =$$

$$V_A\,M_A\left(\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 - q - \frac{[H^+] - K_w/[H^+]}{M_A}\right).$$

Divide moles of added strong base by moles of acid to find the fraction titrated.

$$\text{Fraction titrated} = \phi = \frac{V_B\,M_B}{V_A\,M_A} = \frac{\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 - q - \dfrac{[H^+] - K_w/[H^+]}{M_A}}{1 + \dfrac{[H^+] - K_w/[H^+]}{M_B}}.$$

If you step through H^+ values, you can calculate a titration curve as in Figure 4E-3 for phosphoric acid titrated with strong base. This titration curve is a plot of $y = \text{pH}$ and $x = \phi = \text{fraction titrated}$. If you prefer the more traditional x-axis with volume of base added, plot $x = V_B = \phi\,V_A\,M_A/M_B$.

Similar derivations give the general fraction titrated formula for H_iA,

$$\boxed{\phi = \frac{\text{moles}_{\text{flask}}}{\text{moles}_{\text{buret}}} = \frac{\left\{\left(\sum_{i=0}^{n}(i-p)\alpha_i\right) - q\right\}_{\text{flask}} - \dfrac{[H^+] - K_w/[H^+]}{M_{\text{flask}}}}{\dfrac{[H^+] - K_w/[H^+]}{M_{\text{buret}}} - \left\{\left(\sum_{i=0}^{n}(i-p)\alpha_i\right) - q\right\}_{\text{buret}}},}$$

where fully protonated p and counter q charges are defined as in Table 4E-2. For strong acids and bases, $\{\ldots\} = -q$ or -1 for NaOH and $+1$ for HCl.

The general formula works for the titration of ethanediamine with strong acid as in Figure 4E-4.

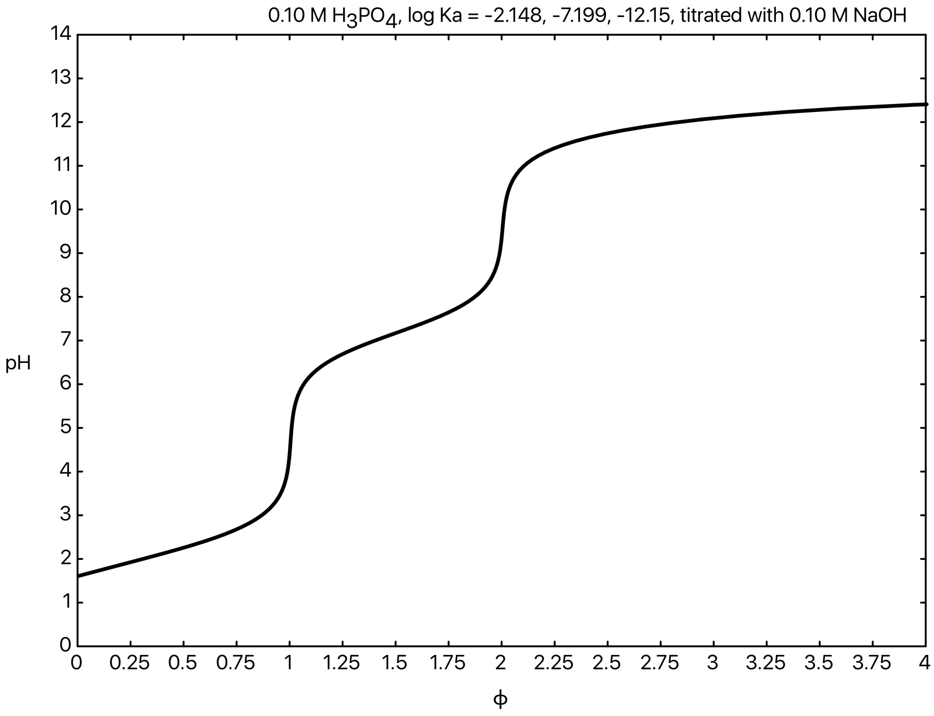


Figure 4E-3. Do you see the endpoints at ϕ = 1 and ϕ = 2? Can you identify the phosphoric acid species titrated at each equivalence point? At what pH should the indicator change to detect each endpoint?

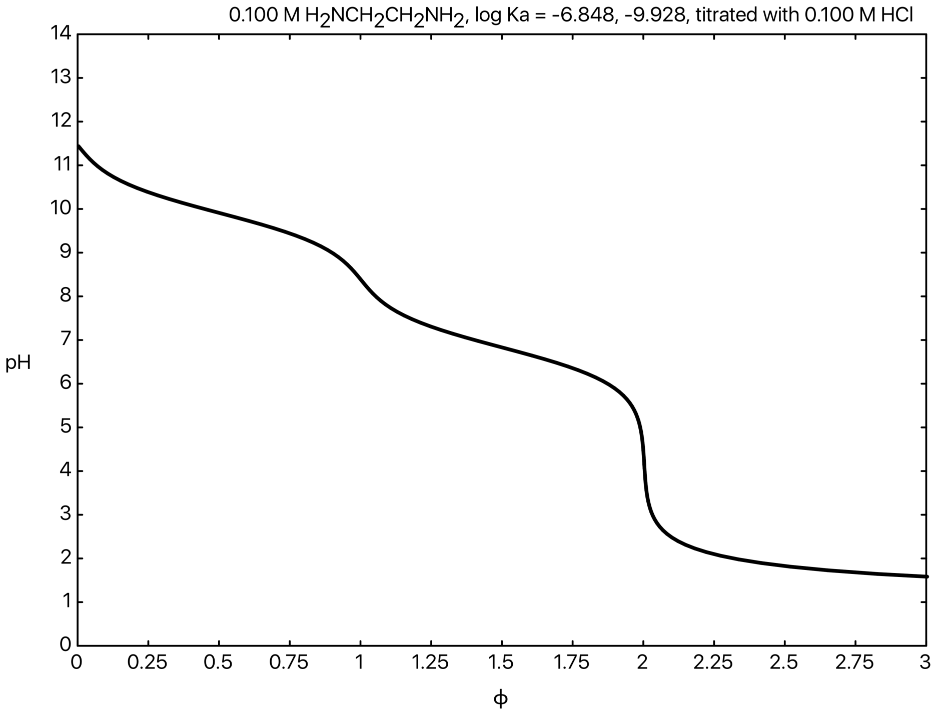


Figure 4E-4. Do you see the endpoints at ϕ = 1 and ϕ = 2? Can you identify the ethanediamine species titrated at each equivalence point? At what pH should the indicator change to detect each endpoint?

APPLYING YOUR IDEAS

pH Problems

4E-1 What is the pH of 0.10 M oxalic acid?

4E-2 What is the pH of 0.15 M Na_2HPO_4?

4E-3 What is the pH of 0.17 M glycine?

4E-4 What is the pH of 0.05 M ethanediamine, $H_2NCH_2CH_2NH_2$?

4E-5 What is the pH of 0.0018 M H_4SiO_4? (This is the concentration in equilibrium with amorphous SiO_2.)

Graphs

4E-6 What fraction of phosphoric acid is present as each species at pH 6.5?

4E-7 Prepare the distribution diagram for oxalic acid and label each curve with the species it represents.

4E-8 Prepare the distribution diagram for the amino acid glycine and label each curve with the species it represents. What is the predominate form of the amino acid glycine at pH 7?

4E-9 Prepare the distribution diagram for H_4SiO_4. What is the predominate form at pH 6?

4E-10 Prepare the logarithmic concentration diagram and estimate the pH.
a. 0.10 M oxalic acid

b. 0.10 M glycine

c. 0.10 M H_4SiO_4.

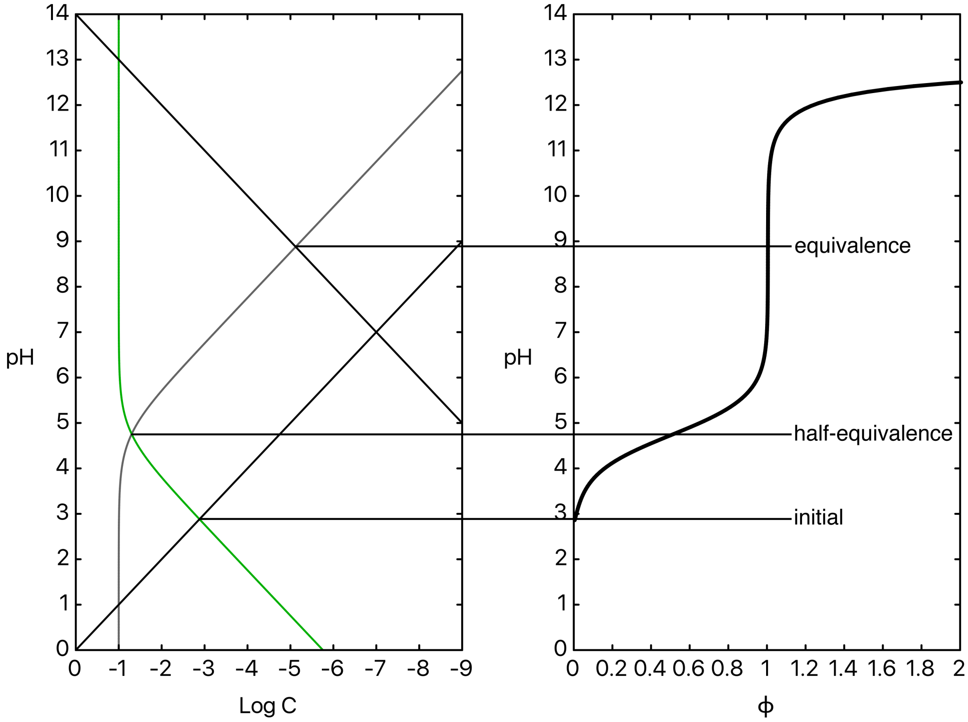
4E-11 Prepare the titration curve for 0.10 M acid with 0.12 M NaOH. Label each area of the curve with the predominate species present.
a. 0.10 M oxalic acid

b. 0.10 M glycine

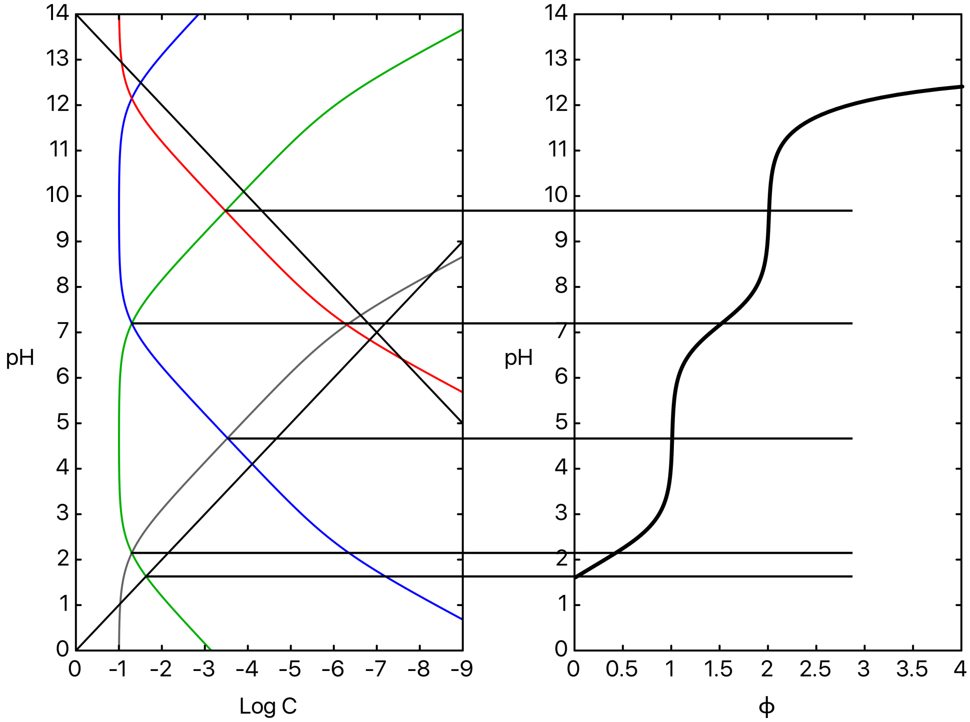
d. 0.10 M H_4SiO_4.

4E-12 The figure on the right shows a titration curve (y = pH, x = fraction titrated). The figure on the left shows a rotated logarithmic concentration diagram for the same chemical. What are the principal species for each horizontal line?

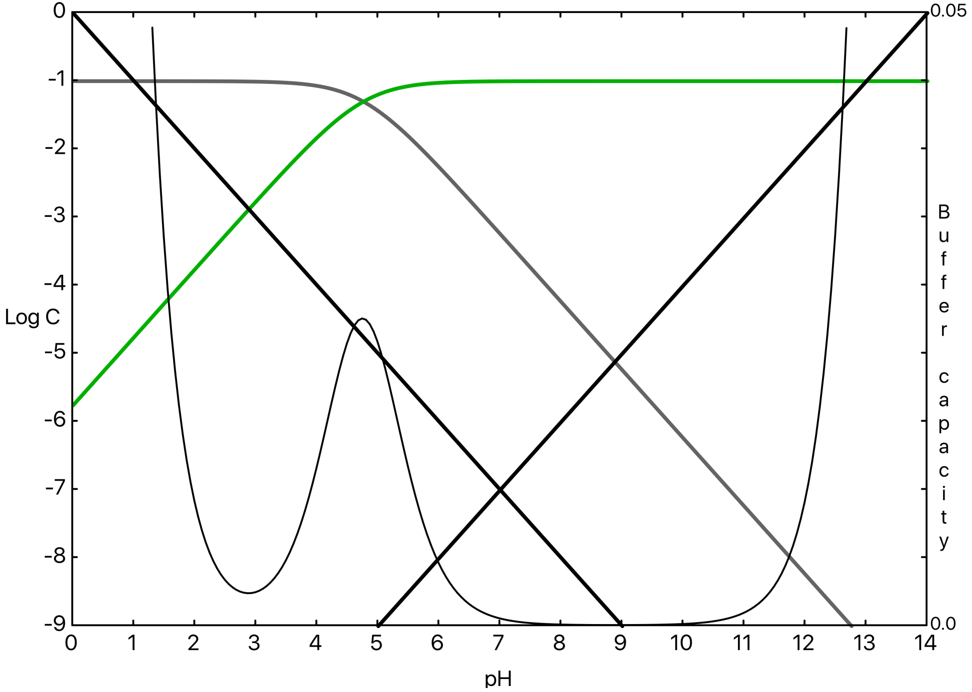
a. 0.10 M CH_3COOH titrated with 0.10 M strong base



b. 0.10 M H_3PO_4 titrated with 0.10 M strong base



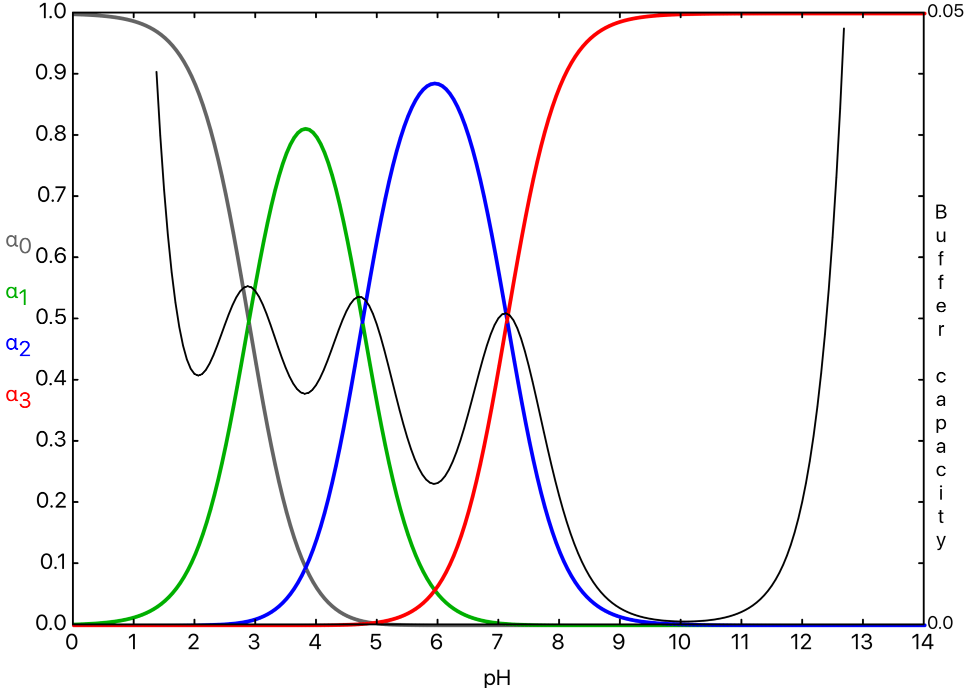
4E-13 The logarithmic concentration diagram for 0.1 M CH_3COOH is shown below along with the buffer capacity at each pH.



a. Why is there a maximum in the buffer capacity near pH 5?

b. Why is the buffer capacity highest at high and low pH?

4E-14 The distribution diagram for 0.1 M $C_6H_3(COOH)_3$ is shown below along with the buffer capacity at each pH. Why are there three humps for the buffer capacity?



Has this area been affected by acid rain?

Session 4, Making the Link

Looking Back

Session Goals

- Develop an understanding of soil composition
- Understand the concept of cation exchange and how it can protect soil from the damaging effects of acid rain
- Learn about buffers and how they can protect soil from acid rain

Checking Your Progress

4-1 Explain the concept of weathering. What occurs during this process? Why are some minerals more resistant to weathering than others? How is this related to soil formation?

4-2 What is soil organic matter? Why is it important to know something about this material? What components of the soil organic matter are most important in soil chemistry?

4-3 Assign Fe^{+3}, Al^{+3}, Ca^{+2}, and Na^{+} as acid or base cations according to the value of the equilibrium constant for their reaction with water. Hint: Toward which side does the equilibrium lie?

$$M^{+n} + H_2O \rightleftharpoons M(OH)^{n-1} + H^{+}?$$

4-4 Read “Acid Rain's Dirty Business: Stealing Minerals from the Soil,” *Science*, **272**, 198 (12 April 1996).
Will stopping deposition of H_2SO_4 solve the problem of acid rain?

THINKING FURTHER

4-5 Which of the soils in Figure 4-1 can best resist acid rain? Which of these soils has the least resistance to acid rain?

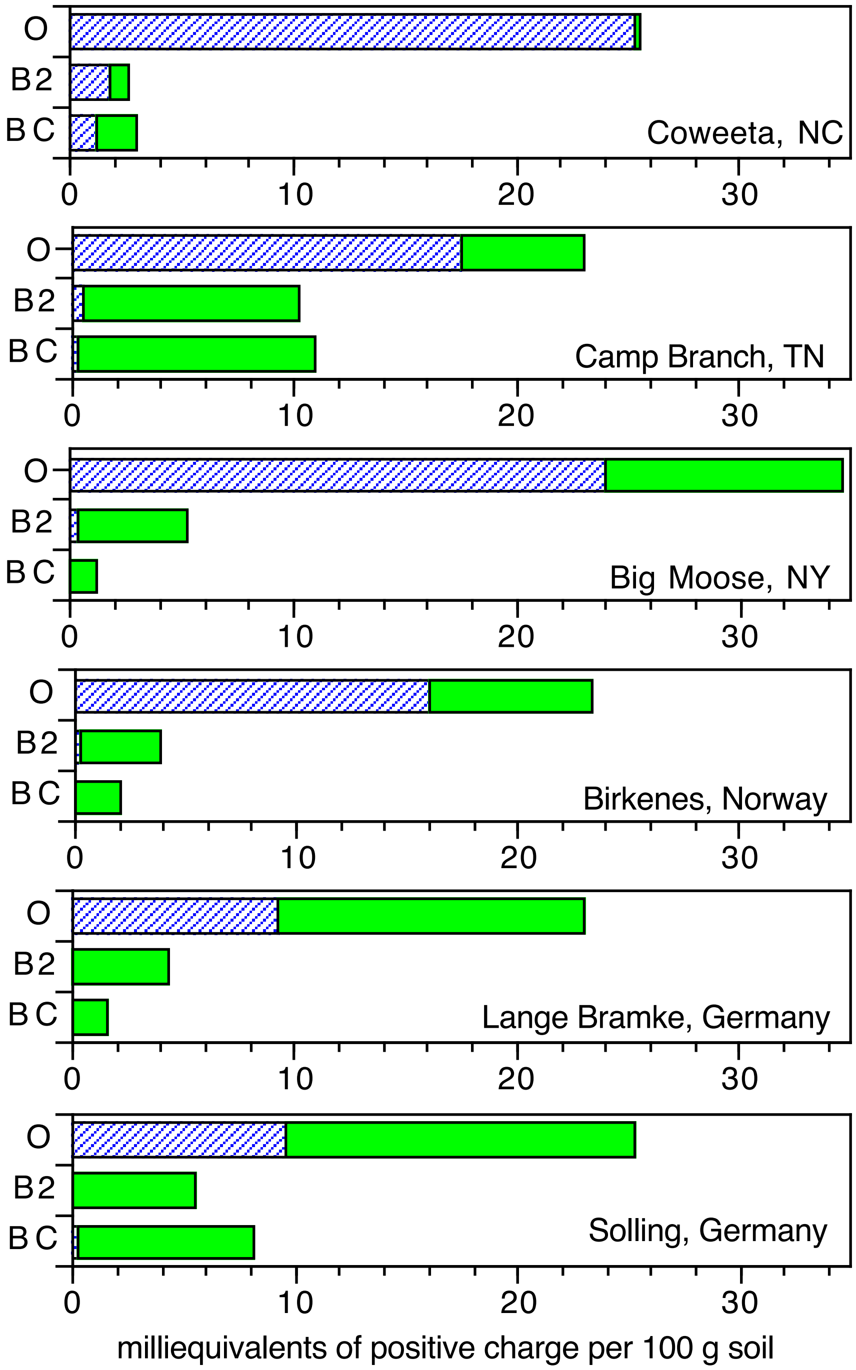
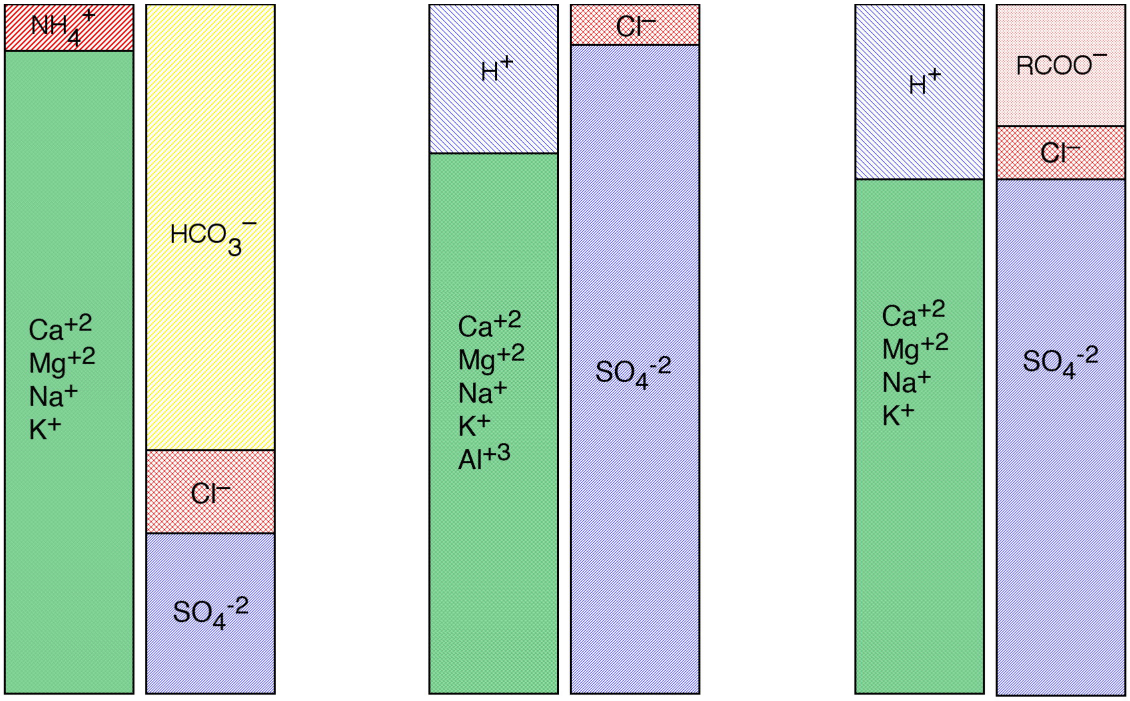


Figure 4-1. Comparison of soil exchange chemistry for different soil horizons and forest ecosystems. O and B refer to soil horizons (*see* Table 4A-3).
▨ exchangeable $Ca^{+2} + Mg^{+2} + K^{+} + Na^{+}$ 🟩 exchangeable $Al^{+3} + H^{+}$.

Figure based on C. S. Cronan, “Aluminum Biogeochemistry in the ALBIOS Forest Ecosystems: The Role of Acidic Deposition in Aluminum Cycling” in *Effects of Acid Rain on Forest Processes*, D. L. Godbold and A. Hüttermann, eds., Wiley-Liss, New York, 1994, pp 51-81.

4-6 Use the information below to describe how can you tell whether a soil or lake has been affected by acid deposition. Measuring pH alone will not answer the question since there are naturally acidic organic materials. What will you need to measure?

Cations and Anions Found in Lakes



Well-Buffered Lakes
- Ions primarily from soluble minerals, e.g., carbonates
- Positively charged ions are mostly base cations such as Ca^{+2} and Mg^{+2}
- Major negatively charged ion is HCO_3^-

Clear-Water Acid Lakes
- acidic from acid rain
- mineral acids from human sources (sulfuric and nitric acids)
- clear water
- high transparency
- low dissolved organic C

Bog Acid Lakes
- naturally acidic
- weak organic acids (humic and tannic acid) plus mineral acids
- colored or stained reddish brown or copper
- low transparency
- high dissolved organic C

Data from Wisconsin Cooperative Extension

4-7 Which of the following will make soil more acidic? Explain your reasoning.
- organic matter accumulation
- decrease in mineral particle size (increase in surface area)
- weathering of silicates
- plant growth
- remove plants by fire
- remove plants by harvest

5-minute Writing Questions

4-8 Give a concise response to the session question, “How does acid rain interact with soil?”

Are all soils the same?

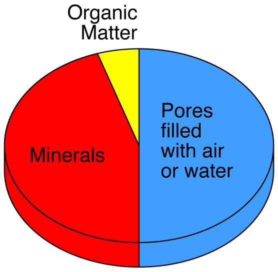
Exploration 5A, CEC and Base Saturation

Creating the Context

What it takes for a plant to thrive in soil is comparable to what it takes to make a good cup of coffee. Imagine a large coffee urn of freshly brewed coffee. You start with freshly ground coffee beans still full of flavor (freshly ground rocks still full of calcium, magnesium, potassium and trace elements). The glass side arm with the tap from which you fill your cup represents cations in the soil solution. The coffee in the pot represents the cations bound on the surface of the soil colloids and the coffee grounds in the percolator basket represent the soil and the bound cations. You can quickly empty the small sidearm of the coffee pot, but almost as fast as you empty it, the sidearm is replenished from the coffee in the body of the pot. But once the coffee in the pot is used up you must take time to brew a new batch, and if the coffee is to be any good, you need to add some fresh coffee grounds (fertilizer or freshly ground rocks).

In the coffee pot analogy, the vast majority of the nutrients are bound up internally in the soil particles in the basket of the coffee urn. These nutrients are not readily removed as water percolates through the soil column (they become available by physical and chemical weathering as physical processes grind the soil and expose new surfaces for dissolution by water). The overwhelming majority of the readily available nutrients are lightly bound to the surface of the soil particles at cation exchange sites (represented by the body of the coffee pot). A small but quickly renewable quantity of the nutrients is actually dissolved in the water surrounding the soil particles (represented by the coffee in the glass side-arm).

The ability to supply base cations (how many cups of coffee you can get out of the coffee pot) is going to depend on a combination of how full is the coffee pot and how big is the coffee pot.



Relative amounts in soil. A well-structured soil has pores for water and air. During rainfall water will penetrate rather than running off.
Know Soil Know Life, SSSA (2012)

Preparing for Inquiry

The **cation exchange capacity** of a soil, **CEC**, is a measure of the number of exchangeable positive ions per mass of soil (the strength of the coffee grounds in the analogy above). CEC is normally expressed in units of millimole of positive charge per 100 grams of soil (mmol$_c$/100g) or centimole of positive charge per kilogram of soil (cmol$_c$/kg). These units are numerically equivalent. Since CEC counts the number of charges, 1/2 mmol of Ca^{+2}, 1/3 mmol of Al^{+3} or 1 mmol of K^+ will bind to 1 mmol$_c$/100g soil.

The cation exchange capacity of a soil is made up of a number of components:

a. Negative sites on clay surfaces that arise due to isomorphous substitution within the clay lattice. These are unaffected by pH and the magnitude of the charge is dependent on the degree of isomorphous substitution.
b. Ionized functional groups on humic material, mainly carboxylate (-COO^-) and phenolate (-O^-). While this charge is always negative in

soil, its magnitude depends on pH. Carboxylate has a pK_a in the range 3–5 and phenolate has a pK_a in the range 7–8. In very acid soils the negative charge on the organic matter is due entirely to carboxylate since phenolate remains largely unionized. In slightly acid soils (pH 6–7) all the carboxylate groups have been ionized and phenolate groups are beginning to contribute significantly to CEC.

c. Hydrous oxide and clay edge sites with variable charge due to unsatisfied valences of the broken bonds at the edge of the lattice. The magnitude of the charge varies with pH.

The **base saturation** is the fraction of the cation exchange sites occupied by base cations (how full the coffee pot in the analogy above.) Base saturation is usually expressed in %.

Problem 5A-1

In an soil ideal for plant growth, 40-50% of the cation exchange sites will be occupied by calcium, 5-15% occupied by magnesium, 2-5% by potassium and 20-30% by hydrogen. To what range of base saturation does this correspond?

✓ The range of base saturation is from 40% + 5% + 2% = 47% to 50% + 15% + 5% = 70%. Hydrogen ion is not a base cation.

Different constituents of soils vary widely in their cation exchange capacity. Furthermore, some types of soil particles have highly pH dependent cation exchange sites and other types of soil particles have largely pH independent cation exchange capacity. Sand and silt have negligible CEC and thus are very sensitive to acid deposition regardless of their % base saturation or the soil pH. Particles of soil organic matter have the highest CEC of all soil particles (200-750 mmol_c/100g soil) but their CEC is also the most highly dependent on pH.

Table 5A-1. Soil Properties

	Sheets	Surface area	Water capacity	CEC
Kaolinite $Al_4(OH)_8[Si_4O_{10}]$	Layers held tightly by hydrogen bonding	Low (10-30 m^2/g)	Low	Low: mostly pH dependent with little isomorphous substitution, <10 mmol_c/100g
Muscovite $K_2Al_4(OH)_4[AlSi_3O_{10}]_2$	Layers strongly bound by K^+	Moderate (100 m^2/g)	Moderate	Moderate: mostly isomorphous replacement of Al^{+3} for Si^{+4}, ~40 mmol_c/100g
Montmorillonite $Al_4(OH)_4[Si_4O_{10}]_2$	Water swells between layers	High (600-800 m^2/g)	High	High: mostly isomorphous replacement of Fe^{+2} and Mg^{+2} for Al^{+3}, ~100 mmol_c/100g
Humic substances		High	High	High: pH dependent, >200 mmol_c/100g

Clay particles make a significant contribution to the CEC of soils. However, there are many types of clays. Old soils from warm humid regions are clays made of hydrous oxides of iron and aluminum and have the lowest CEC. Layer silicate clays are highly variable, as seen in Table 5A-1. Kaolinite has a low CEC of 2-5 mmol_c/100 g soil, montmorillonite and vermiculite have a high CEC ranging from 80-180 mmol_c/100 g soil, while fine-grained micas are low to moderate at 15-40 mmol_c/100 g soil.

The CEC can vary with the pH of the soil as seen in Figure 5A-1. What chemical features would give rise to a pH dependent negative charge? What features would give rise to a pH independent negative charge? Of what does the shape of the variable charge portion of the curve remind you?

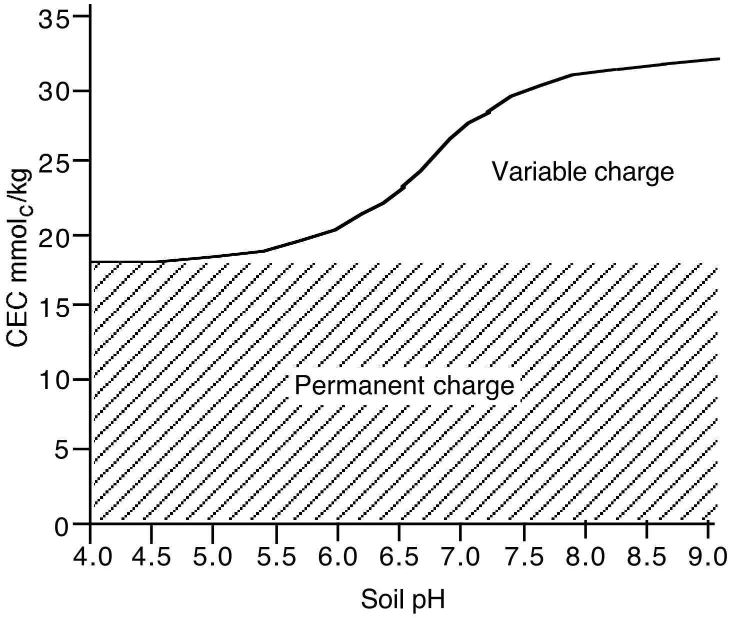


Figure 5A-1. Typical Variation of CEC with pH.

Because natural soils differ so widely both in CEC and % base saturation, there is a corresponding variability in ecosystem sensitivity to acidic deposition.

Well-buffered soils have pH>6.5 and a corresponding base saturation in excess of 80%. These soils are dominated by the presence of carbonates. Cation exchange becomes the dominant buffering agent in the absence of adequate carbonate buffering. As the calcium, magnesium and potassium are used up due to exchange with added acid, the pH drops. When pH levels below pH 5 and base saturation under 10% are achieved, aluminum becomes the dominant cation exchanging with H^+. This is important because aluminum ions are toxic to plant roots and in lakes the aluminum is toxic to fish and other aquatic organisms. Exploration 5B considers aluminum in more detail. At low pH the availability of phosphates, base cations, and molybdenum drop to levels insufficient for healthy plant growth and manganese, iron and aluminum all reach toxic levels.

There are many different types of soil, including sand, silt, clay, and organic soil. Each different type of soil varies in both physical structure and chemical composition, both of which are important features of soil. A soil must be strong enough and cohesive enough to support a tree in a windstorm, yet porous enough to hold water and air. A soil must also be able to supply the necessary nutrients for plant growth, including both anions such as nitrates, phosphates and sulfates and cations such as ammonium, potassium, calcium, magnesium and trace elements.

For plants, the ideal soil is formed from a mixture of sand, silt and clay particles. The optimum blend of these particles is 25-52% sand (0.05 to 2.0 mm in diameter), 28-50% silt (0.002 to 0.05 mm in diameter) and 7-27% clay (less than 0.002 mm in diameter). This combination provides a nearly equal mixture of large air-holding pores and small water-holding pores. Soil meeting these specifications is called a **loam**.

You will examine the pH of several different types of soil before and after a simulated acid rain event. Wash each soil with a solution of nitric acid of concentration similar to that of acid rain. You will also examine the effects of acid rain on the soil after adding the amount of **lime** ($CaCO_3$) that a farmer would typically add to prepare the soil for growing vegetables. Your observations will include an examination of how well limed soils buffer the effects of acid rain in comparison to the unlimed soils.

At the atomic level, the H^+ cations in the simulated acid rain will compete with the metal or nutrient cations bound to the negatively charged cation exchange sites of the soil. A soil with a high cation exchange capacity (CEC) will absorb most of the added H^+ at the exchange sites and release metal cations into the soil solution. A soil with a low CEC will not have as many cations available for exchange with H^+ and therefore most of the added H^+ will remain in solution. Consequently, the pH of a soil with a high CEC should not drop nearly as much as the pH of a soil with a low CEC as a result of acid rain.

DEVELOPING IDEAS

The soil samples have been dried and sieved through a 2 mm soil sieve to remove rocks. Half of each soil sample has been treated with lime at a ratio of 0.5 g $CaCO_3$ per 100 g dry soil. Ideally, a sandy soil, a silt loam, at least one type of clay soil, and a high organic matter soil will be available.

Distinguish soil types

You can roughly distinguish soil types by a simple “feel test.” Take a golf ball-size sample of soil and add just enough water to thoroughly wet the soil. Then squeeze the soil between your thumb and forefinger. If you can make a long, flexible ribbon, you have a *clay* soil. A *clay loam* makes a short ribbon that breaks easily. A *silt loam* will make a very short ribbon with a broken appearance. A loam, sandy loam and sandy soil will not form a ribbon at all. *Loam* will form a moderately stable ball, the *sandy loam* will barely form a ball, and the sandy soil will not even stick together in a ball when wet. *Determine and record the type of soil used* as clay, clay loam, silt loam, loam, sandy loam, or sandy.

Measure the pH of each limed and unlimed soil

To measure a soil pH, place 10 g of dried soil in a 50 mL beaker and add 10 mL of distilled water. Stir to form a paste and let the sample sit for five to ten minutes. Measure and record the pH of each soil sample.

Measure the effect of a simulated acid rain event

Place 50 mL of 0.001 M HNO_3 in a small beaker and add 10 g of a soil sample. Stir thoroughly and let sit for five minutes. While waiting, assemble a vacuum filter apparatus. Start the vacuum and add a little water to the filter paper. This will adhere the filter paper to the bottom of the funnel. Pour the soil/dilute acid slurry into the funnel and filter using vacuum filtration. Rinse your small beaker with 25 mL of distilled water and pour onto the soil in the filter to rinse. Repeat this rinsing with a second 25 mL portion of distilled water.

Transfer the rinsed soil to a 50 mL beaker and add 10 mL of distilled water. Stir to form a paste and let the sample sit for five to ten minutes. Measure and record the pH of each soil sample.

APPLYING YOUR IDEAS

Experimental Conclusions

5A-2 Prepare a data table showing the pH of each soil (limed and unlimed) before and after treatment with simulated acid rain.

5A-3 What types of soils are most affected by acid rain? What types of soils show the most benefit from liming? What types of soils show the least benefit from liming?

5A-4 If you tested more than one type of clay soil, did they behave in a similar fashion or did you observe any differences?

Problems

5A-5 Application of calcium carbonate (liming) increases soil pH. How does adding Ca^{+2} increase soil pH? How does adding CO_3^{2-} increase soil solution pH?

5A-6 What other compounds besides calcium carbonate could be added to soil to minimize the detrimental effects of acid rain on soil?

5A-7 Why do soils with a high CEC require more limestone to increase their pH than does a soil with a low CEC?

5A-8 Does the CEC of an organic soil increase or decrease with increasing pH? Explain your reasoning.

5A-9 What soil types are most susceptible to acid rain? Where in the world are these soil types found? (See world soil types in the *ChemConnections Media Resources* .)

5A-10 Raising the pH may precipitate metal ions as hydroxides. Which metal ions in Appendix I have the least soluble hydroxides?

5A-11 Soil A has a CEC of 25 $mmol_c$/100g of soil and a 40% base saturation. Soil B has a CEC of 10 $cmol_c$/kg of soil and a base saturation of 80%.

a. Which soil is better buffered against acid rain?

b. In typical soils, toxic levels of aluminum begin to be encountered when the % base saturation drops below 10%. How many equivalents of acid deposition will soil A and soil B tolerate before they begin to show symptoms of aluminum toxicity?

5A-12 Over the course of a year, 100 cm of rain with an average pH of 4 falls on a 1 hectare field (10^4 m^2).

a. How many moles of H^+ fall on the field? If the acid rain was entirely due to H_2SO_4, how many tons of sulfuric acid would have been deposited?

b. How many tons of calcium carbonate would you have to add to the field to prevent a pH change?

c. Assume the field has an initial CEC of 10 mmolc/100g and an initial base saturation of 80%, that the top 100 cm of the soil will be uniformly affected (due either to mixing by plowing or transport by root activity), and that the soil density is 2.5g/cm^3. If you did not protect the field by adding lime, how much would the % base saturation of the field change?

5A-13 For each of the following substances, indicate whether isomorphic substitution or ionizable functional groups is most important in determining the cation exchange capacity.

a. kaolinite

b. soil organic matter

c. montmorillonite

d. talc

e. muscovite

5A-14 Is application of lime an effective way of combating acid rain? Consider the data in Figure 5A-2 as part of your answer.

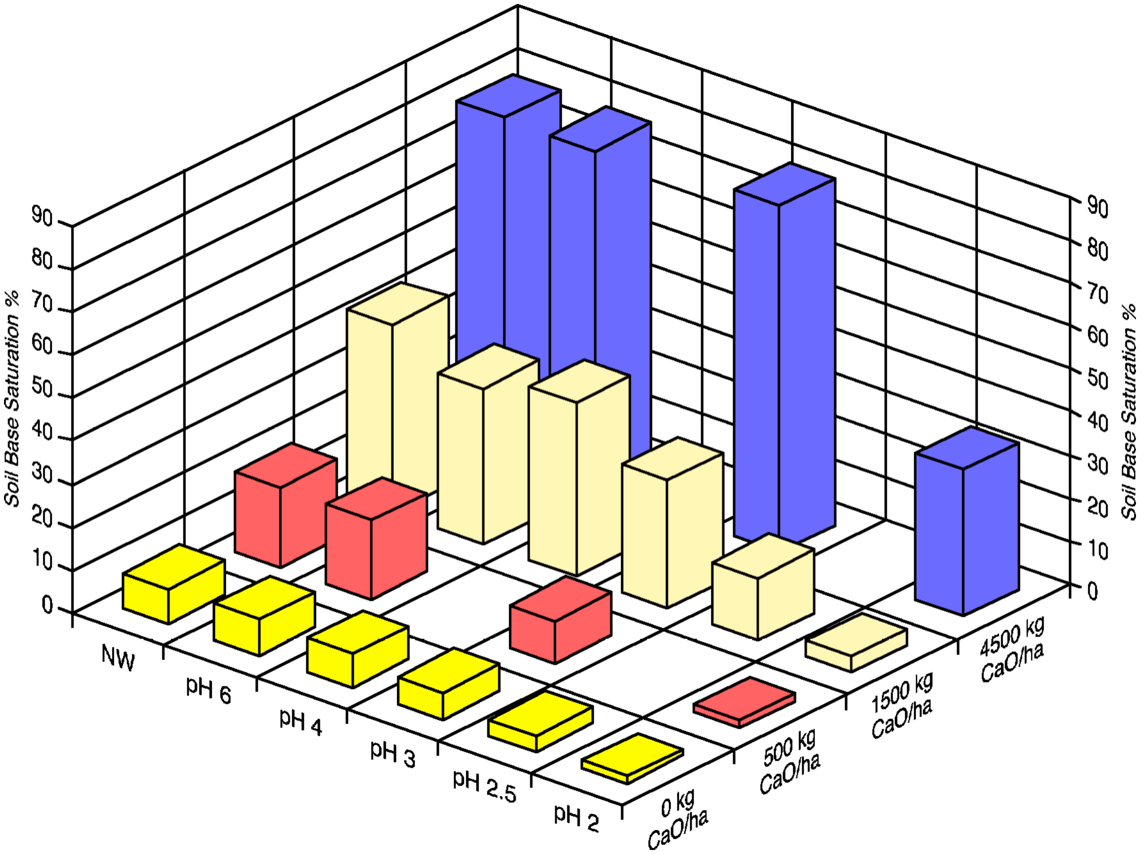


Figure 5A-2. Effects of lime (kg/ha) and acid “rain” (specified pH applied by sprinkler or not watered) on soil base saturation for O horizon. Monthly 50mm waterings May to September, 1988, with artificial rain of different acidities were applied by boom sprinkler. Liming was a single dose of $CaCO_3$ applied to the soil at the beginning of the treatment. The initial base saturation was 8.3% and the soil also received any natural precipitation.

Data from Gunnar Abrahamsen, Arne O. Stuanes, Bjørn Tveite *Long-Term Experiments with Acid Rain in Norwegian Forest Ecosystems,* Springer-Verlag, New York, Ecological Studies Vol. 104, 1994.

Will aluminum be mobilized?

Exploration 5B, Aluminum Toxicity

Creating the Context

As predicted by equilibrium calculations, lower calcium ion concentrations and higher aluminum ion concentrations are observed for lower pH waters. Figure 5B-1 shows an example from UK streams.

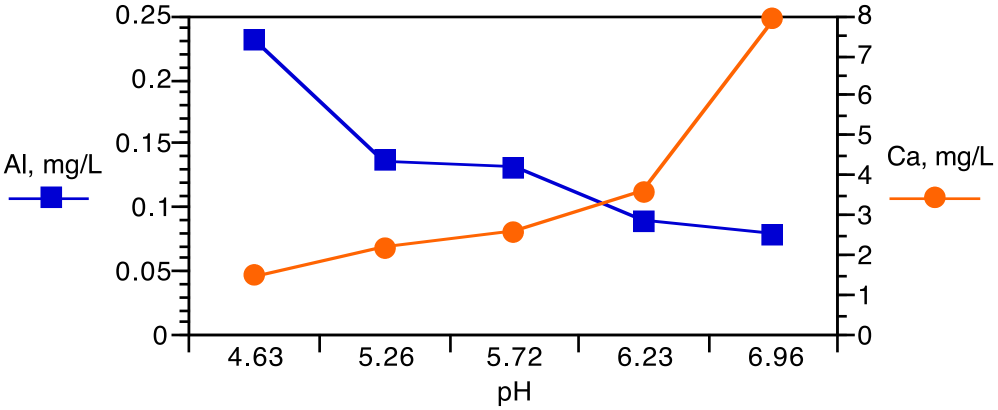


Figure 5B-1. Aluminum and calcium in 181 Welsh and Pennine streams grouped by pH. Data from A. W. H. Turnpenny, "Field studies on fisheries in acid waters in the United Kingdom" from *Acid Toxicity and Aquatic Animals*, R. Morris, E. W. Taylor, D. J. A. Brown, and J. A. Brown Eds., Cambridge University Press, 1989, p 55.

Unfortunately, aluminum ion is detrimental to aquatic life as seen in Figure 5B-2. LT_{50} is the number of days it takes for 50% of trout to die (at the highest aluminum concentration half the fish died in 5 days). Thus the *y*-axis, $1/LT_{50}$, is a measure of the mortality rate of fish.

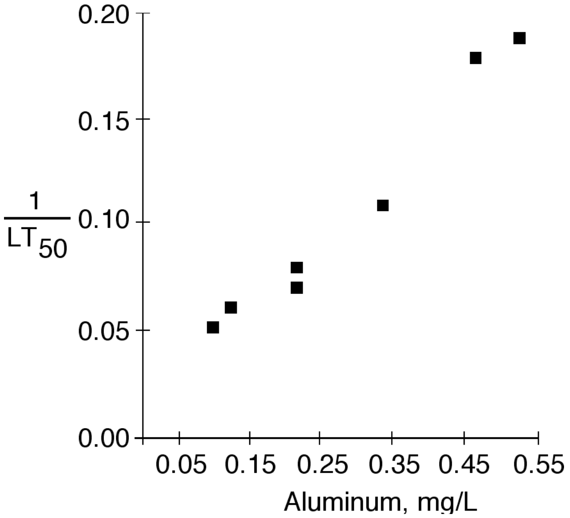


Figure 5B-2. Mortality of caged trout per day in River Tywi headwater streams, Wales, as a function of added aluminum. Data from J. H. Stoner and A. S. Gee, *J. Inst. Wat. Engrs. Sci.*, 39, 27-45, (1985) from *Acid Toxicity and Aquatic Animals*, R. Morris, E. W. Taylor, D. J. A. Brown, and J. A. Brown Eds., Cambridge University Press, 1989, p 51.

Aluminum has also been implicated in plant growth inhibition. Since roots are in direct contact with the soil solution, the initial effect is on root growth. Aluminum ion affects the growing regions of roots and interferes with cell elongation. Root hairs stop growing within minutes. Because Al^{+3} is smaller and more highly charged than Ca^{+2}, it interferes with Ca^{+2} signal transduction and replacement of Ca^{+2} with Al^{+3} makes cell walls and membranes more rigid. Poor nutrient uptake leads to additional symptoms listed in Table 5B-1. Defense mechanisms used by plants in response to Al^{+3} include production of citric acid to complex the aluminum ions.

Table 5B-1. Observed Symptoms Associated With Aluminum Toxicity

Root Responses	Shoot Responses
Increased tissue Al	Delay in budbreak and leaf expansion
Reduced plant water uptake	Decreased stem and leaf production
Decreased root biomass	Decreased shoot biomass
Decreased fine root branching	Decreased tissue Mg and Ca
Decreased terminal root elongation	Increased tissue Al concentration
Decreased tissue Mg and Ca	Altered tissue P concentrations
Altered tissue P	
Cellular Responses	
Inhibition of cell division and mitotic activity	
Decreased water permeability in cell membranes	

From C. S. Cronan , R. April, R. Bartlett, P. Bloom, C. Driscoll, S. Gherini, G. Henderson, J. D. Joslin, J. M. Kelly, R. Newton, R. Parnell, H. Patterson, D. Raynal, M. Schaedle, C. Schofield, B. Sucoff, H. Tepper, and F. Thornton, "Aluminum toxicity in forests exposed to acidic deposition: the ALBIOS results," *Water, Air, Soil Pollut.* 48:181-192 (1989).

The presence of high levels of calcium ion seems to mitigate the effects of aluminum, as seen using the criteria of fish or no fish in Norwegian lakes in Figure 5B-3.

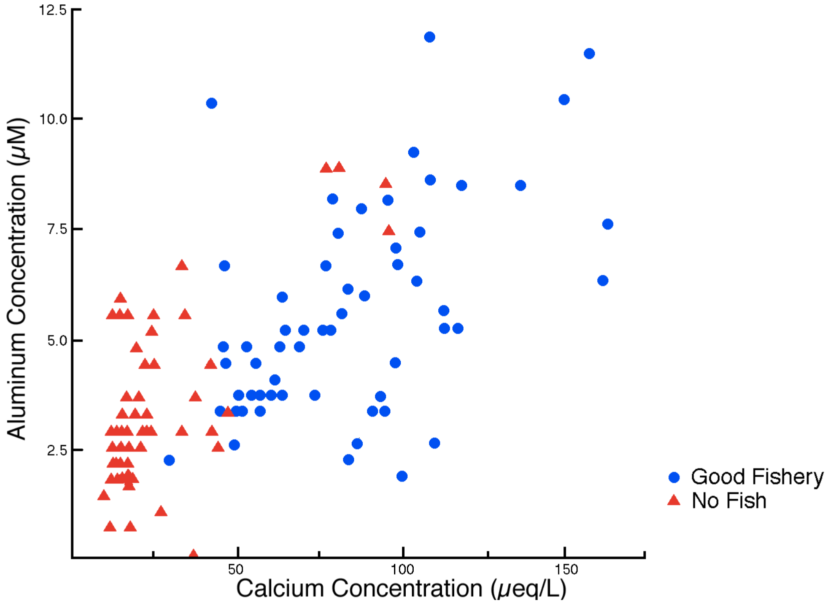


Figure 5B-3. Fishery status of southern Norwegian lakes with a pH greater than 5.0. R. F. Wright and E. Snekvik, "Acid precipitation - chemistry and fish populations in 70 lakes in southernmost Norway," *Verh. Internat. Verein. Limnol.*, 20, 765-75 (1978) from *Acid Toxicity and Aquatic Animals*, R. Morris, E. W. Taylor, D. J. A. Brown, J. A. Brown Eds., Cambridge University Press, 1989, p 33.

What aluminum species are in solution and how do their concentrations depend on pH? How does base saturation affect aluminum and calcium concentrations? How are these related to acid rain? The next section uses equilibrium calculations to examine these and other relationships.

PREPARING FOR INQUIRY

Aluminum ion in solution has serious consequences for plant and animal life. Aluminum in soil solution comes from dissolved minerals:

$$\mathrm{Al(OH)_3(s) + 3\,H^+ \underset{K_{H/Al}}{\rightleftharpoons} Al^{+3} + 3\,H_2O}$$

The value of $K_{H/Al}$ depends on the soil type but a widely used value is log $K_{H/Al}$ = 8.0 (If both the pH and pAl are known from field measurements then an approximate value for the local geology can be calculated using log $K_{H/Al}$ = 3 pH – pAl.)

Table 5B-2. Gibbsite Equilibrium Constant

Soil Organic Matter	Horizon	log $K_{H/Al}$
>70%	O	6.5
15-30%	A	7.6
5-15%	B	8-9
<5%	C	8.5-9.5

From *Manual on methodologies and criteria for modeling and mapping critical loads and levels and air pollution effects, risks and trends*, Chapter V, *Mapping Critical Loads for Ecosystems*, Table V.9 (2017), UNECE-CLRTAP, www.icpmapping.org

Al^{+3} ion reacts with water to produce a series of aluminum hydroxy species:

$$\begin{array}{lll}
\mathrm{Al^{+3} + H_2O \rightleftharpoons Al(OH)^{+2} + H^+} & \log K_{a1} = & -5.0 \\
\mathrm{Al(OH)^{+2} + H_2O \rightleftharpoons Al(OH)_2^{+} + H^+} & \log K_{a2} = & -5.1 \\
\mathrm{Al(OH)_2^{+} + H_2O \rightleftharpoons Al(OH)_3(aq) + H^+} & \log K_{a3} = & -6.8 \\
\mathrm{Al(OH)_3(aq) + H_2O \rightleftharpoons Al(OH)_4^{-} + H^+} & \log K_{a4} = & -5.8 \\
\mathrm{2\,Al^{+3} + 2\,H_2O \rightleftharpoons Al_2(OH)_2^{+4} + 2\,H^+} & \log K_{a22} = & -7.7 \\
\mathrm{3\,Al^{+3} + 4\,H_2O \rightleftharpoons Al_3(OH)_4^{+5} + 4\,H^+} & \log K_{a34} = & -13.94
\end{array}$$

Which are the main aluminum species in water and how do the relative concentrations of aluminum species change with pH? One way to answer this question is to prepare a logarithmic concentration diagram. To do that, we need to rearrange the equilibrium constant expressions to see how the concentration of each species depends on the pH.

$$K_{H/Al} = \frac{[Al^{+3}]}{[H^+]^3} = 10^{9.0}; \qquad [Al^{+3}] = 10^{9.0}\,[H^+]^3$$

$$K_{a1} = \frac{[Al(OH)^{+2}][H^+]}{[Al^{+3}]}; \qquad [Al(OH)^{+2}] = \frac{10^{-5.00}[Al^{+3}]}{[H^+]} = 10^{4.0}\,[H^+]^2$$

$$K_{a1}K_{a2} = \frac{[Al(OH)_{2+}][H^+]^2}{[Al^{+3}]}; \qquad [Al(OH)_2^{+}] = \frac{10^{-10.1}[Al^{+3}]}{[H^+]^2} = 10^{-1.1}\,[H^+]$$

$$K_{a1}K_{a2}K_{a3} = \frac{[Al(OH)_3][H^+]^3}{[Al^{+3}]}; \qquad [Al(OH)_3] = \frac{10^{-16.9}[Al^{+3}]}{[H^+]^3} = 10^{-7.9}$$

$$K_{a1}K_{a2}K_{a3}K_{a4} = \frac{[Al(OH)_4^-][H^+]^4}{[Al^{+3}]}; \qquad [Al(OH)_4^-] = \frac{10^{-22.7}[Al^{+3}]}{[H^+]^4} = \frac{10^{-13.7}}{[H^+]}$$

$$K_{a22} = \frac{[Al_2(OH)_2^{+4}][H^+]^2}{[Al^{+3}]^2}; \qquad [Al_2(OH)_2^{+4}] = \frac{10^{-7.7}[Al^{+3}]^2}{[H^+]^2} = 10^{10.3}\,[H^+]^4$$

$$K_{a34} = \frac{[Al_3(OH)_4^{+5}][H^+]^4}{[Al^{+3}]^3}; \quad [Al_3(OH)_4^{+5}] = \frac{10^{-13.94}[Al^{+3}]^3}{[H^+]^4} = 10^{13.06}\,[H^+]^5$$

Taking the log of each expression, for example log $[Al^{+3}] = 9.0 - 3$ pH, gives log concentrations that depend linearly on pH with slopes of –5, –4, –3, –2, –1, 0, and +1.

Problem 5B-1

Label each line in Figure 5B-4 with the appropriate species. What happens to the concentration of aluminum species in solution as the H^+ increases or decreases from the concentration found in normal rain?

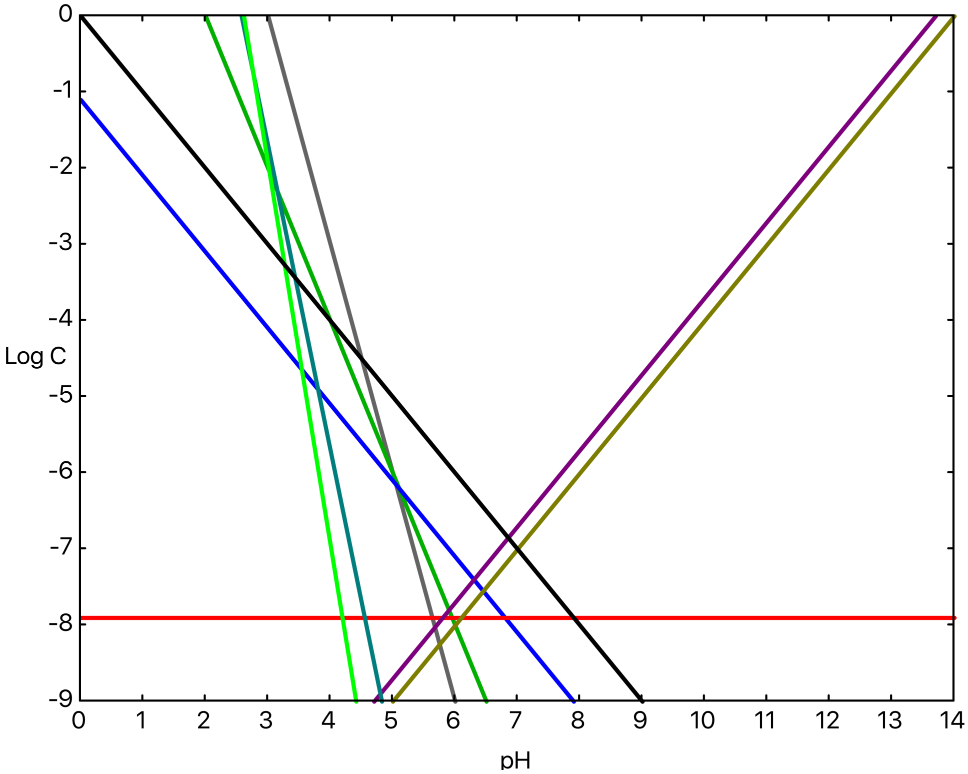


Figure 5B-4. Logarithm of the concentration of each aluminum containing species, H^+, and OH^-, as a function of pH.

Developing Ideas

As noted above, the effect of aluminum on living organisms depends on the relative concentrations of calcium and aluminum in solution. Solution calcium is derived from the calcium-aluminum ion exchange equilibrium between aluminum ions in solution, Al^{+3}, the fraction of the ion exchange sites containing calcium, CaX_2, calcium ions in solution, Ca^{+2}, and the fraction of the ion exchange sites containing aluminum, AlX_3.

$$2\ Al^{+3} + 3\ CaX_2 \rightleftharpoons 3\ Ca^{+2} + 2\ AlX_3$$

The value of this equilibrium constant varies with mineral structure and soil type. See Table 5B-3. Soil texture is identified by the size of the soil particles and the feel of a moist sample. Sandy soil will feel gritty, silt will feel smooth or slippery, and a predominately clay soil will feel sticky. Soils with high organic content (>15%) are considered peat.

Table 5B-3. Log K_d for ion exchange equilibria* where X^- is an exchange site.

Soil Type	$2\ Al^{+3} + 3\ CaX_2 \rightleftharpoons 3\ Ca^{+2} + 2\ AlX_3$ $K_{Al/Ca}$	$2H^+ + CaX_2 \rightleftharpoons Ca^{+2} + 2HX$ $K_{H/Ca}$
Sand	2.31	5.24
Silt	0.88	5.39
Clay	0.39	6.73
Peat	0.98	4.62

Values for top 30 cm of soil from *Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends*, Section VI.2.3.1 *Cation Exchange* and Tables VI.4 and VI.5 (2015), UNECE-CLRTAP, www.icpmapping.org
*G. L. Gaines and H. C. Thomas, *J. Chem. Phys.* 21: 714-718 (1953)

If Al^{+3} and Ca^{+2} and H^+ are the only exchangeable cations then the fraction of ion exchange sites containing aluminum ions plus the fraction of ion exchange sites containing calcium ions plus the fraction of ion exchange sites containing hydrogen ions totals 100%. For such a system where calcium is the only base cation, then CaX_2 is the base saturation value. Changes in solution concentration do not immediately affect the much larger pool of exchange ions so CaX_2 may be taken as constant for a given problem.

If CaX_2 is known and $[Al^{+3}] = K_{H/Al}[H^+]^3$ then using the three equations

$$AlX_3 + CaX_2 + HX = 1$$

$$K_{Al/Ca} = \frac{[Ca^{+2}]^3 AlX_3{}^2}{[Al^{+3}]^2\ CaX_2{}^3} \qquad K_{H/Ca} = \frac{[Ca^{+2}]HX^2}{[H^+]^2\ CaX_2}$$

it is possible to eliminate $[Ca^{+2}]$ and solve for pH independent values of HX and AlX_3. (An even simpler assumption is that calcium and aluminum are the only exchanging species so $AlX_3 + CaX_2 = 1$.)* In either case,

$$[Ca^{+2}] = \left\{ \frac{(K_{Al/Ca})(K_{H/Al})^2(CaX_2)^3}{(AlX_3)^2} \right\}^{1/3} [H^+]^2.$$

---

*J. O. Reuss and D. W. Johnson, *Acid Deposition and the Acidification of Soils and Waters*, Springer Verlag: New York, Ecological Studies Vol. 59, 1986, pp 1-120. J. O. Reuss, “Implications of the calcium aluminum exchange system for the effect of acid precipitation on soils,” *Journal of Environmental Quality* 12(4): 591-595 (1983).

APPLYING YOUR IDEAS

Problems

5B-2 Rationalize the trends in Figure 5B-1 based on soil cation exchange.

5B-3 Extrapolate the relationship in Figure 5B-2 to estimate a safe level of aluminum for river trout. Using this value and Figure 5B-1, what minimum pH should be considered safe?

5B-4 A soil profile has these pH values:

Depth from surface (cm)	pH
0-5	3.6
5-8	3.8
8-12	4.1
12-28	4.9
28-55	5.0
55-80	5.1
80-110	5.1

At what depth would you expect to find the most Al in solution? The least Al in solution? Why?

5B-5 The polymerization of phenols is part of the process in organic soil building. Speculate on the consequences of the effect observed in Figure 5B-5.

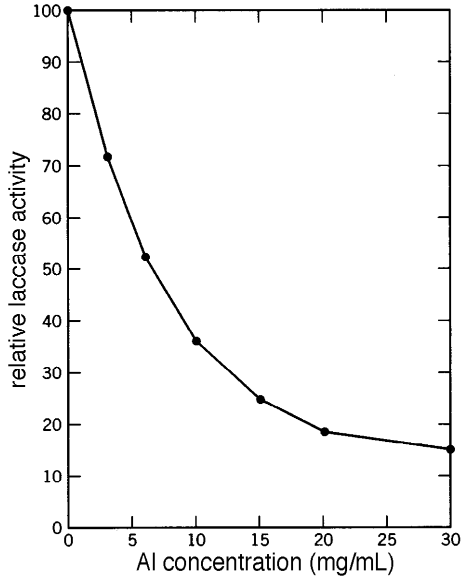


Figure 5B-5. Effect of the presence of Al^{+3} ions on the laccase catalyzed oxidation of phenols. Figure from J. Eichhorn, A. Hüttermann, “Humus Disintegration and Nitrogen Mineralization” in *Effects of Acid Rain on Forest Processes*, D. L. Godbold and A. Hüttermann, eds., Wiley-Liss, New York, 1994.

5B-6 Plot the concentration of Ca^{+2} and of each aluminum species in natural waters relative to the total concentration of metal species in solution as a function of pH. Use a value of CaX_2 appropriate for soil at some location in your assigned country from Session 1.

a. Report the CaX_2 and K values. How did you determine what values to use? (Cite your references.)

b. Label each line with its correct chemical species (proper formula and charge).

c. Based on Figure 5B-3 the [Ca^{+2}] in healthy water should be greater than 10 times the concentration of any Al species. What pH range has fraction $Ca^{+2} > 0.9$? Mark this pH range on your graph.

d. Describe how the results change for differing values of CaX_2. What do your conclusions imply for soil with your value of CaX_2?

5B-7 Figure 5B-6 shows trends in ion concentration measured by SEM/EDS for an archaeological window glass sample from the Greene Farm in Warwick, RI. The sample has distinct corrosion layers that vary in composition from the bulk glass. Composition trends between corrosion layers reveal an influx of aluminum toward the glass and an outflux of calcium and potassium from the sample.

Based on the observed ion mobility, estimate the pH of soil in which the glass was buried.

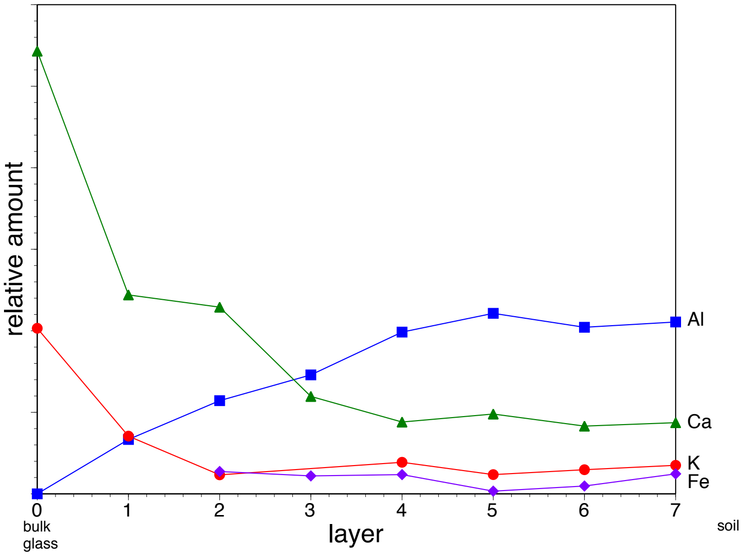


Figure 5B-6. Change in relative ion concentration in each layer going from bulk glass at the left to the surface exposed to soil at right. Values are not on an absolute scale: trends are for each element but do not show relative concentrations between elements. Data from C. G. Cooper, “Glass Corrosion: Diagnostic uses of 17th Century Archaeological Window Glass,” Beloit College Senior Thesis, May 2011.

What is my soil's exchangeable basicity?

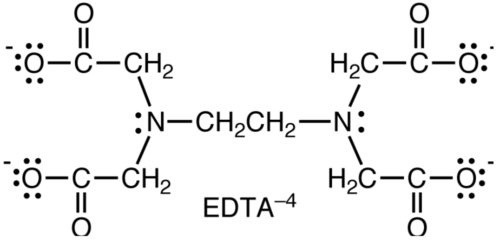
EXPLORATION 5C, EDTA TITRATIONS & ATOMIC EMISSION SPECTROSCOPY

CREATING THE CONTEXT

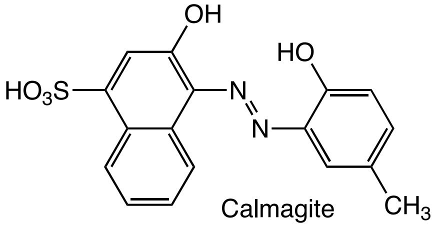
Ca^{+2}, Mg^{+2}, K^+ and Na^+ are collectively called base cations. In more acidic soils these ions are replaced by Al^{+3} and H^+, which are called acid cations. To determine which base cations are available in a soil, all the exchangeable ions are replaced by NH_4^+ using ion exchange as 1.0 M ammonium acetate passes through a soil column. The freed Ca^{+2} and Mg^{+2} ions are then measured by EDTA titration and the K^+ and Na^+ are measured by flame atomic emission spectroscopy. Exploration 5D will measure the exchangeable acidity.

Determination of Calcium plus Magnesium

The method of analysis is a "complexometric" titration at pH 10 for calcium with ethanediaminetetraacetic acid (abbreviated H_4EDTA). $EDTA^{-4}$ wraps around metal ions to hold or complex them in a 1:1 ratio. Why does the pH have to be high for this method to work?



$EDTA^{-4}$



Calmagite

The indicator for this titration is an organic dye, 1-(1-hydroxyl-4-methyl-2-phenylazo)-2-napthol-4-sulfonic acid, called Calmagite (named for CALcium MAGnesium indicator). Calmagite is blue in its free form and pink when it is complexed to magnesium.

The reactions involved in detecting the endpoint are:

$$Ca^{+2} + EDTA^{-4} \rightleftharpoons CaEDTA^{-2}$$

$$\underset{\text{red}}{MgIn} + EDTA^{-4} \rightleftharpoons MgEDTA^{-2} + \underset{\text{blue}}{In^{-2}} \quad (\text{In} = \text{indicator})$$

After all the calcium ions have been titrated with $EDTA^{-4}$ ions, the magnesium ions are titrated and the endpoint is seen. Magnesium ions are guaranteed to be present because a small amount has been added to the stock EDTA solution.

Leaching Columns

PREPARING FOR INQUIRY

Sample Preparation

Sign up for a specific soil sample and measure its exchangeable basicity for three replicates.

Using a rough balance, weigh out accurately approximately 10 g (to 0.01 g) of dry soil into a clean, dry beaker. If soil is wet, dry in an oven before weighing. Add about a teaspoon of acid-washed sand to the soil and mix well. Clay soils may require more sand so start one first to see if the amount of sand is correct. Plug a clean, dry leaching column with cotton (sufficient to retain the soil, but not to inhibit the flow of solution). Use less than one cotton ball (e.g., divide one ball among the three samples). Pour into the column a layer of acid-washed sand (less than a *level* teaspoon) and level. Pour in all the soil/sand mixture, making sure it is evenly mixed.

Run 100 mL of 1.0 M ammonium acetate solution (pH 7) through the column at about 1 drop/sec, collecting all of the leachate in a 100 mL volumetric flask. After checking solution flow through your first column, decide if you need more or less sand for your next two columns. Since it should take 15-20 minutes for the entire 100 mL, start the next two columns before the first one has finished. When the leaching is complete, make each flask to volume with 1 M ammonium acetate solution and mix well. Discard the used sand/soil mixture in solid waste, not in the sink.

Standardize the EDTA

Standardize the EDTA solution by titrating a known calcium chloride solution. The standard calcium chloride solution has been prepared for you by dissolving a weighed amount of primary standard calcium carbonate in a small amount of HCl to give calcium chloride and then diluting to volume.

Rinse and fill your buret with the available approximately 0.01 M EDTA solution. Pipet a 10 mL aliquot of the approximately 0.03 M calcium chloride standard into a clean Erlenmeyer flask, add about 30 mL of pure water, about 2 mL of ammonia buffer and a few drops of indicator. *Leave the concentrated ammonia buffer in the fume hood and measure it out there. Try not to breathe any ammonia.* How accurate does the 2 mL of concentrated ammonia buffer need to be? Does the Erlenmeyer flask need to be dry? Titrate fairly rapidly until the wine red color of the complexed Calmagite indicator starts to change to the blue of the free indicator. When the color becomes purple, add EDTA dropwise until the color is pure blue, with no tinge of red remaining.

Water is added here so that the sample volume will be the same as when you titrate 40 mL of leachate solution. You will not need to add water to the 40 mL of leachate to make its volume 40 mL.

Unlike some titrations, the color will not continue to change or darken after the endpoint. Once the color has changed, further addition of titrant will only change the color through dilution. The color can best be observed by looking at the highlights in the solution, and the endpoint is a little tricky since you are using very dilute solutions. If the color is difficult to see, try adding more indicator. Spend some time getting this procedure to work for you. Some people can see the change better when the shades are paler and some when the shades are darker. Some people see the change better if some methyl red is added as an inert dye to produce an orange color before the endpoint and a green color after the endpoint. Before going on, decide how many drops of indicator you will consistently use for all trials.

You should be able to *obtain three results that agree to at least within 0.1 mL* for the same standard calcium solution. You may only discard results for which you have recorded in your notebook that something was wrong (“first trial”, “darker”, “missed the flask”, etc.).

Titrate Leachate Solution

Be sure to standardize the EDTA *before* titrating the dirt sample solutions so you can perfect your technique and decide on the amount of indicator that works best for you.

Keep practicing with the standard until your results are repeatable to less than 0.1 mL of titrant.

Titrate 40 mL samples following the same method so that the indicator will have the same concentration as you used for the EDTA standardization. Do two titrations for each of the three samples but remember to keep some solution for atomic absorption analysis.

Hardness of Tap Water

While you have your buret set up with EDTA solution, do a determination of the "hardness" of tap water. Measurement of hardness is the most frequently performed water analysis.

Hardness in water is caused by dissolved minerals, primarily Ca(II) and Mg(II). Hardness is usually expressed as parts per million calcium carbonate equivalent. *Parts per million, or ppm, is the same as mg/L.* "Equivalent" means that even though a variety of ions with various counterions may be present to cause hardness, we pretend for calculation purposes that they are all calcium carbonate.

Water Classification	ppm $CaCO_3$
Soft	0 to 60
Moderately Hard	61 to 120
Hard	121 to 180
Very Hard	More than 180

Large amounts of hardness are undesirable for aesthetic and economic reasons in the beverage, food, laundry, textile, or paper industries. Calcium and magnesium ions form a precipitate with soap, and with detergents to a lesser extent. Levels above 500 ppm hardness are undesirable for domestic use. Most drinking water supplies average about 250 mg/L. Hardness may be removed by water softening (exchange of these ions for Na^+).

Rinse and fill a 400 or 600 mL beaker with water from a faucet. Tap water is not necessarily well mixed, so you want to take all you will need at one time. Record whether the faucet is for hot or cold water. Follow the same procedure you used before but use 100.0 mL tap water samples carefully measured with a graduated cylinder and double the amount of indicator.

Groups of 2 or 3 people should share a run of standards.

Check that no soil is present in any of the solutions so you all get usable results.

Determination of Potassium and Sodium

The concentrations of K^+ and Na^+ are usually much smaller than that of Ca^{+2} and Mg^{+2}. Use your remaining sample to measure the K^+ or Na^+ concentration in solution using a flame photometer and standards made up in 1.0 M ammonium acetate. By aspirating a solution sample into an acetylene torch, the atoms get excited and give off light with a wavelength characteristic for the element. To analyze for Na set the spectrometer wavelength to 589.0 nm; to analyze for K set the wavelength to 766.5 nm.

The sample and standard solutions must all be run at the same time. If the found concentration is greater than the range of the standard curve, dilute your sample solution by 5 mL into 50 mL with 1 M ammonium acetate and remeasure. If the instrument does the dilution, record the dilution factor.

Make a plot of emission as a function of the standard concentrations, in order to calculate the concentration of the unknown solution in ppm (mg/L).

Is Beer's Law followed for the used concentration range?

Flame emission photometer

DEVELOPING IDEAS

Calculations

What is the concentration of the EDTA based on your standardization?

How many moles of Ca^{+2} plus Mg^{+2} were found by titration? The moles were displaced from a known volumetric fraction of a known mass of soil. Calculate the concentration of Ca^{+2} plus Mg^{+2} in the soil in units of millimole of charge/100 g soil.

From the ppm (mg/L) determined by flame emission, use the volume of the solution to find the mass of the ion displaced from the soil. Convert this amount to moles. The moles were displaced from a known mass of soil. Calculate the concentrations of K^+ and of Na^+ in the soil in units of millimole of charge/100 g soil.

What are the mean and standard deviation for each ion?

What is the total concentration of exchangeable base charges in your soil?

Calculate the equivalent ppm $CaCO_3$ in your tap water sample by substituting values for the terms printed in italics:

$$\frac{\textit{endpoint}\ \text{mL}\,\dfrac{\textit{known}\ \text{mol EDTA}}{\text{L}}\,\dfrac{1\ \text{mol CaCO}_3}{1\ \text{mol EDTA}}\,\dfrac{\textit{MW}\ \text{g CaCO}_3}{\text{mol CaCO}_3}}{100\ \text{mL}}\;\frac{\text{milli}}{0.001}$$

APPLYING YOUR IDEAS

Conclusions

Compare your results with others who studied the same soil. How similar are the values for exchangeable basicity?

Compare your results with others who studied different soil. How do the values for exchangeable basicity vary with soil color?

How hard is the water you tested? What does water hardness indicate about the localities ability to moderate the effects of acid rain?

What is my soil's exchangeable acidity?

Exploration 5D, Titration and Complexation

Creating the Context

Ca^{+2}, Mg^{+2}, K^{+} and Na^{+} are collectively called base cations. In more acidic soils these ions are replaced by Al^{+3} and H^{+}, which are called acid cations. Soil acidity is among the important environmental factors that can influence plant growth. To determine which acid cations are available in a soil, all the exchangeable ions are replaced by K^{+} using ion exchange as 1.0 M potassium chloride passes through a soil column. Titration of the freed cations with sodium hydroxide gives the total exchangeable acidity. At this point the aluminum ions will be in the form of $Al(OH)_3(H_2O)_3$. Addition of fluoride complexes the aluminum ion to give AlF_6^{-3} and 3 OH^{-}. The now free OH^{-} ions are titrated with HCl and the amount indicates the quantity of exchangeable Al^{+3}. The remainder of the exchangeable acidity is assumed to be H^{+}.

Preparing for Inquiry

Procedure

Use the same soil you studied in Exploration 5C and measure the exchangeable acidity for three replicates.

Using a rough balance, weigh out accurately approximately 10 g (to 0.01 g) of dry soil into a clean, dry beaker. If soil is wet, dry in an oven before weighing. Add about a teaspoon of acid-washed sand to the soil and mix well (clay soils may require more sand). Plug a clean, dry leaching column with cotton (sufficient to retain the soil, but not to inhibit the flow of solution). Use less than one cotton ball (e.g., divide one ball among the three samples). Pour into the column a layer of acid-washed sand (less than a *level* teaspoon) and level. Pour in all the soil/sand mixture, making sure it is evenly mixed.

Run 100 mL of 1.0 M KCl solution through the column at about 1 drop/sec, collecting all of the leachate in a 100 mL volumetric flask. At one drop/second this should take 15-20 minutes for the 100 mL so run three columns at once. When the leaching is complete, make the flask to volume with water and mix well. Discard the used sand/soil mixture in solid waste, not in the sink.

Titrate 40 mL leachate with 0.01 M NaOH using phenolphthalein as an indicator. The first permanent pink endpoint tells you the total exchangeable acidity, H^{+} plus Al^{+3}. Do not discard the contents of the titration flask.

Add 10 mL 1.0 M KF and titrate the same flask with 0.01 M HCl until the pink color *disappears*. This titration tells you the quantity of aluminum ion present. Solutions containing fluoride ion must be placed in a waste container for proper disposal. Discard the used sand/soil mixture in the solid waste, not in the sink.

Do two NaOH titrations for each of the three samples but if no aluminum ion is found in the first trial it is not necessary to repeat the HCl titration.

DEVELOPING IDEAS

Calculations

From the endpoint for the NaOH titration find the moles of acid displaced from the column. These moles were displaced from a known volumetric fraction of a known mass of soil. What would be the millimoles of exchangeable acid charge in 100 g soil?

From the endpoint for the HCl titration find the moles of hydroxide released when NaF was added. To how many moles of Al^{+3} does that correspond? These moles were displaced from a known volumetric fraction of a known mass of soil. What would be the millimoles of exchangeable aluminum ion in 100 g soil?

What would be the millimoles of exchangeable hydrogen ion in 100 g soil?

Cation exchange capacity is the total exchangeable acidity and basicity.

$$\text{CEC} = \text{Exchangeable } (3Al^{+3} + H^{+} + 2Ca^{+2} + 2Mg^{+2} + K^{+} + Na^{+})$$

What would be the millimoles of exchangeable positive charge in 100 g soil?

Cation exchange capacity is expressed as millimole charge / 100 g soil = centimole charge / kg soil.

Finally, base saturation is the fraction of the cation exchange sites that are occupied by Ca^{+2}, Mg^{+2}, K^{+} and Na^{+}.

$$\text{Base saturation} = \frac{\text{Exchangeable } (2Ca^{+2} + 2Mg^{+2} + K^{+} + Na^{+})}{\text{Exchangeable } (3Al^{+3} + H^{+} + 2Ca^{+2} + 2Mg^{+2} + K^{+} + Na^{+})}$$

What is the CEC and % base saturation for your soil?

APPLYING YOUR IDEAS

Conclusions

Compare your results with others who studied the same soil. How similar are the values for exchangeable acidity?

Compare your results with others who studied different soil. How do the values for exchangeable acidity vary with soil color?

How far has your soil been titrated by acid rain?

Would exchange with KCl work to find exchangeable bases? Would exchange with NH_4CH_3COO work to find exchangeable acids? Another method uses $BaCl_2$ for cation exchange. Would the $BaCl_2$ method be useful to find exchangeable bases or to find exchangeable acids?

References

- Soil and Plant Analysis Council, "Determination of Exchangeable Acidity and Exchangeable Aluminum Using 1 N Potassium Chloride", *Soil Analysis Handbook of Reference Methods*, 1999.
- U. Jönsson, U. Rosengren, B. Nihlgård, and G. Thelin, "A Comparative Study of Two Methods for Determination of pH, Exchangeable Base Cations and Aluminum," *Communications in soil science and plant analysis*, **33**, p. 3809-3824 (2002).
- UNECE ICP, "Soil Analysis Method 10: Determination of Exchangeable Cations (Al, Ca, Fe, K, Mg, Mn, Na), Free H+ and Exchangeable Acidity," Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests (2010).

Metals and Ligands

Exploration 5E, Graphs and Solutions Based on δ-Fractions

Creating the Context

Metal ions usually do not have enough electrons to form covalent bonds by sharing one electron from the metal ion with one electron from the bonded atom. Since ligands have a lone pair of electrons (and a full Lewis octet), metals and ligands form coordination bonds where both electrons come from the ligand.

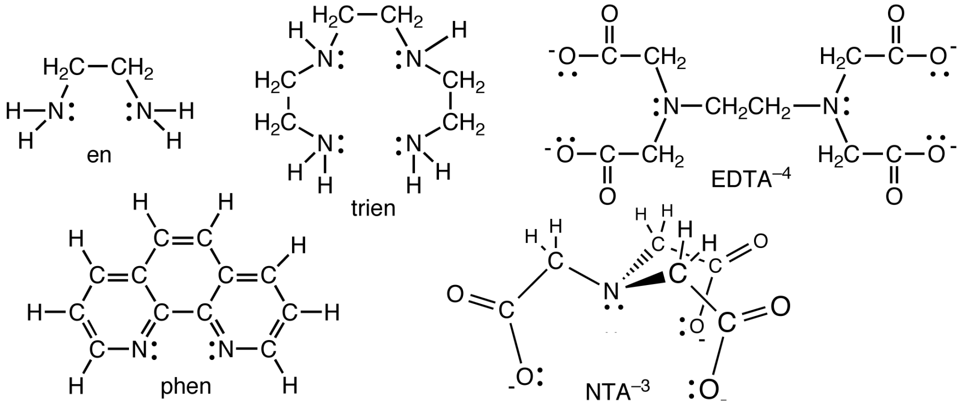
$$M^{+n} + :L \rightleftharpoons M:L^{+n}$$

These equilibria are quite similar to that between H^+ and a weak base.

$$HA \rightleftharpoons H^+ + :A^-$$

Similar techniques are used to solve both types of equilibrium problems.

Examples of ligands include $:NH_3$, $:OH_2$, $:Cl^-$, $:OCOCH_3^-$ and



Examples of metals include Ag^+, Al^{+3}, Cu^{+2}, or Fe^{+3}. Metals may bond with 0 to 9 ligands (4 and 6 being the most common coordination numbers).

Charge balance can be achieved in solution using spectator ions so *you can not tell from the metal charge how many ligands will coordinate!* For this module rely instead on the table of equilibrium constants, Appendix 1, to determine what species will occur. Equilibria are often not well separated and significant amounts of more than one species may be present simultaneously.

Consider the metal ligand *formation* equilibria for Cu^{+2} with NH_3.

$$Cu^{+2} + NH_3 \rightleftharpoons CuNH_3^{+2} \qquad K_{f1} = \frac{[ML]}{[M][L]}$$

$$Cu(NH_3)^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_2^{+2} \qquad K_{f2} = \frac{[ML_2]}{[ML][L]};\; K_{f1}K_{f2} = \frac{[ML_2]}{[M][L]^2}$$

$$Cu(NH_3)_2^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_3^{+2} \qquad K_{f3} = \frac{[ML_3]}{[ML_2][L]};\; K_{f1}K_{f2}K_{f3} = \frac{[ML_3]}{[M][L]^3}$$

$$Cu(NH_3)_3^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_4^{+2} \qquad K_{f4} = \frac{[ML_4]}{[ML_3][L]};\; K_{f1}K_{f2}K_{f3}K_{f4} = \frac{[ML_4]}{[M][L]^4}$$

Formation equilibrium constants are numbered according to the number of ligands that have formed coordinate bonds with the metal ion.

The mass balance for the metal with total concentration, C_M, is:

$$C_M = [M] + [ML] + [ML_2] + [ML_3] + [ML_4].$$

Substitute the above overall equilibrium constant expressions into the mass balance expression to obtain

$$C_M = [M] + K_{f1}[M][L] + K_{f1}K_{f2}[M][L]^2 + K_{f1}K_{f2}K_{f3}[M][L]^3 + K_{f1}K_{f2}K_{f3}K_{f4}[M][L]^4.$$

Factoring out [M] yields

$$C_M = [M]\ \{1 + K_{f1}[L] + K_{f1}K_{f2}[L]^2 + K_{f1}K_{f2}K_{f3}[L]^3 + K_{f1}K_{f2}K_{f3}K_{f4}[L]^4\} = [M]\ F_o$$

where the *formation function*, F_o, is defined as

$$\boxed{\begin{gathered} F_o = 1 + K_{f1}[L] + K_{f1}K_{f2}[L]^2 + K_{f1}K_{f2}K_{f3}[L]^3 + K_{f1}K_{f2}K_{f3}K_{f4}[L]^4 + \ldots \\ F_o = 1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4 + \ldots \text{ where } \beta_i = K_{f1}K_{f2}\ldots K_{fi} \end{gathered}}$$

Now, what fraction of the total metal is present as each species?

$$\delta_0 = \text{fraction of M with 0 L} = \frac{[M]}{C_M} = \frac{1}{F_o}$$

$$\delta_1 = \text{fraction of M with 1 L} = \frac{[ML]}{C_M} = \frac{K_{f1}[M][L]}{C_M} = \frac{K_{f1}[L]}{F_o}$$

$$\delta_2 = \text{fraction of M with 2 L} = \frac{[ML_2]}{C_M} = \frac{K_{f1}K_{f2}[M][L]^2}{C_M} = \frac{K_{f1}K_{f2}[L]^2}{F_o} = \frac{\beta_2[L]^2}{F_o}$$

$$\delta_3 = \text{fraction of M with 3 L} = \frac{[ML_3]}{C_M} = \frac{K_{f1}K_{f2}K_{f3}[M][L]^3}{C_M} = \frac{K_{f1}K_{f2}K_{f3}[L]^3}{F_o} = \frac{\beta_3[L]^3}{F_o}$$

$$\delta_i = \text{fraction of M with } i \text{ L} = \frac{[ML_i]}{C_M} = \frac{\beta_i[L]^i}{F_o}$$

Note that the δ-fractions are successive terms of F_o divided by F_o!

The average number of ligands *gained* is $\overline{n} = 0\delta_0 + 1\delta_1 + 2\delta_2 + 3\delta_3 + \ldots$

PREPARING FOR INQUIRY

The δ-fractions are dependent only on the equilibrium free ligand concentration, [L]. If we know the [L] then we can calculate the δ-fraction (as in Table 5E-1) and we can use [L] as a master variable to plot how the distribution varies with pL (as in Figure 5E-1).

Table 5E-1. δ-fraction dependence on pNH_3 for Cu^{+2}

	pL = 1	pL = 2	pL = 3	pL = 4	pL = 5	pL = 6
δ_0	0.0000	0.0000	0.0165	0.4149	0.8988	0.9891
δ_1	0.0000	0.0040	0.1808	0.4549	0.0985	0.0108
δ_2	0.0039	0.1081	0.4865	0.1224	0.0027	0.0000
δ_3	0.2478	0.6819	0.3070	0.0077	0.0000	0.0000
δ_4	0.7483	0.2059	0.0093	0.0000	0.0000	0.0000
Total δ	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Distribution (δ) diagrams

A metal-ligand distribution diagram plots the species fraction present as a function of pL (Figure 5E-1). At low pL nearly all metal will be present with the maximum number of ligands and at high pL nearly all the metal will be present without ligands; in between each species takes a turn at being the predominate species over some pL range.

Logarithmic Concentration Diagrams

Since the concentration of each metal species is its δ-fraction times the total metal concentration, C_M, logarithmic concentration diagrams can be prepared from the δ-fractions. Compare the distribution diagram in Figure 5E-1 with the logarithmic concentration diagram in Figure 5E-2.

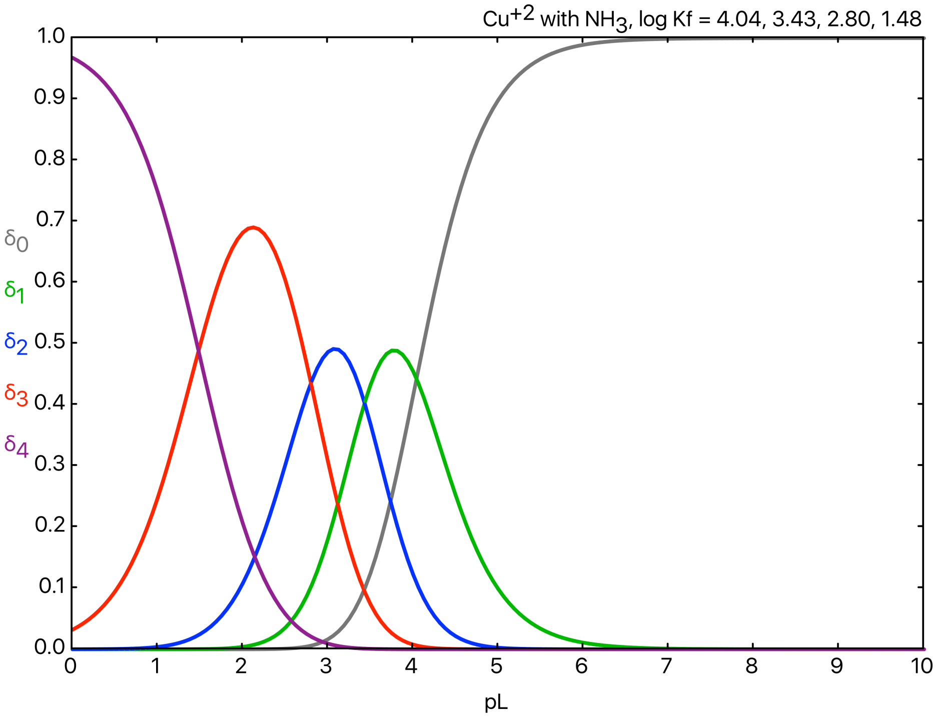


Figure 5E-1. Distribution diagram for copper(II) and ammonia. Can you label the copper(II) ammonia species present at different pNH_3 values?

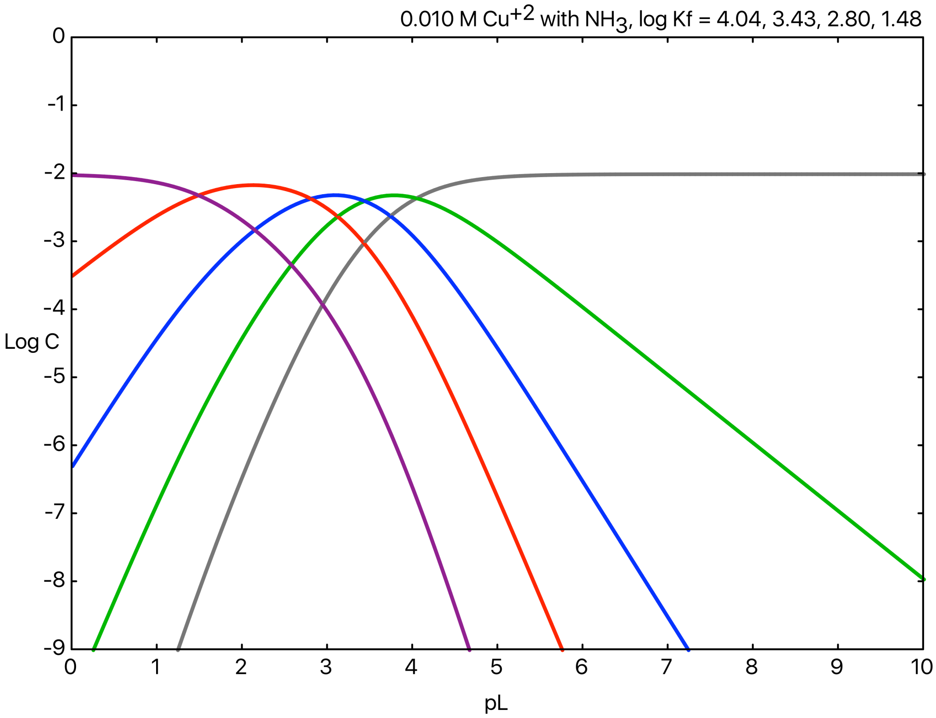


Figure 5E-2. The logarithmic concentration diagram for 0.001 M Cu^{+2} with NH_3. Can you label each curve with the copper(II) ammonia species it represents?

DEVELOPING IDEAS

Finding free L from given total C_L and C_M

Using the mass balance for the total ligand, C_L,

$$C_L = [ML] + 2[ML_2] + 3[ML_3] + 4[ML_4] + ... + [L] + [HL] + [H_2L] + ...,$$

the δ-fraction definitions of $[ML] = \delta_1 C_M$, $[ML_2] = \delta_2 C_M$, $[ML_3] = \delta_3 C_M$, and the α-fraction for the fully deprotonated ligand (Exploration 4E) gives:

$$C_L = (\delta_1 + 2\delta_2 + 3\delta_3 + 4\delta_4 + ...)\, C_M + \frac{[L]}{\alpha_n} = \bar{n}\, C_M + \frac{[L]}{\alpha_n}$$

This equation with one unknown can be solved for [L]. For the simplest case when none of the ligand is protonated, $\alpha_n = 1$. Sometimes a buffer is used to create a solution with a given pH and then α_n can be calculated for that pH.

Types of calculation problems

Given the **uncomplexed ligand** concentration, $[L]/\alpha_n$, find [L].

Given concentrations of **total ligand**, $C_L = \bar{n}\, C_M + [L]/\alpha_n$, and **total metal**, C_M, find [L].

Given **[L]**, the concentration of ligand with no protons and no metal,

a. Find the fraction of metal that has gained ligands, δ_0, δ_1, δ_2, ...
   or prepare a distribution diagram by indexing L (see Figure 5E-1).

b. Find the average number of ligands gained by the metal ion, $\bar{n}$.

c. Find the concentrations of ligand species, $\alpha_1[L]/\alpha_n$, $\alpha_2[L]/\alpha_n$, ...

Given [L] and the total metal concentration, C_M,

a. Find concentrations of metal containing species,
   $[M] = \delta_0 C_M$, $[ML] = \delta_1 C_M$, $[ML_2] = \delta_2 C_M$, $[ML_3] = \delta_3 C_M$

b. Find the total ligand concentration, $C_L = \bar{n}\, C_M + [L]/\alpha_n$

Titration of M with L

The δ-fractions are also helpful when calculating titration curves for metals and ligands. The total volume will be different at each point of the titration and this affects the concentrations. When titrant volume V_L of ligand with concentration M_L is added to the initial volume V_M of metal ion with initial concentration M_M, the new volume will be $V_L + V_M$ and mass balances are:

$$C_L = \frac{V_L\, M_L}{V_L + V_M} \text{ and } C_M = \frac{V_M\, M_M}{V_L + V_M}.$$

C_M or C_L is the mass balance concentration and it changes during the titration. M_M or M_L is the unchanging initial molarity in flask or buret.

Combining these with the mass balance equation, $C_L = \bar{n}\, C_M + \frac{[L]}{\alpha_n}$, gives:

$$\frac{V_L\, M_L}{V_L + V_M} = \bar{n}\frac{V_M\, M_M}{V_L + V_M} + \frac{[L]}{\alpha_n}.$$

Multiply by the total volume $(V_L + V_M)$:

$$V_L\, M_L = \bar{n}\, V_M\, M_M + \frac{[L]}{\alpha_n}(V_L + V_M).$$

Collect V_L terms on one side and V_M terms on the other:

$$V_L\, M_L - \frac{[L]}{\alpha_n}V_L = \bar{n}\, V_M\, M_M + \frac{[L]}{\alpha_n}V_M.$$

Factor out the moles of metal and ligand on each side:

$$V_L\, M_L\, (1 - \frac{[L]}{\alpha_n\, M_L}) = V_M\, M_M\, (\,\bar{n} + \frac{[L]}{\alpha_n\, M_M}).$$

The ratio of the moles is the fraction titrated.

$$\text{Fraction titrated} = \phi = \frac{V_L\, M_L}{V_M\, M_M} = \frac{\bar{n} + \dfrac{[L]}{\alpha_n\, M_M}}{1 - \dfrac{[L]}{\alpha_n\, M_L}}.$$

$$\text{Free metal} = [M] = \delta_0\, C_M = \delta_0\, \frac{V_M\, M_M}{V_L + V_M} = \frac{\delta_0\, M_M\, M_L}{\phi\, M_M + M_L}.$$

If you step through the L values, you can calculate a titration curve as in Figure 5E-3 for Cu^{+2} titrated with NH_3. A titration curve is a plot of y = pM and x = fraction titrated, ϕ. If you prefer the more traditional x-axis with volume of ligand added, plot $V_L = \phi\, \frac{V_M\, M_M}{M_L}$ as x.

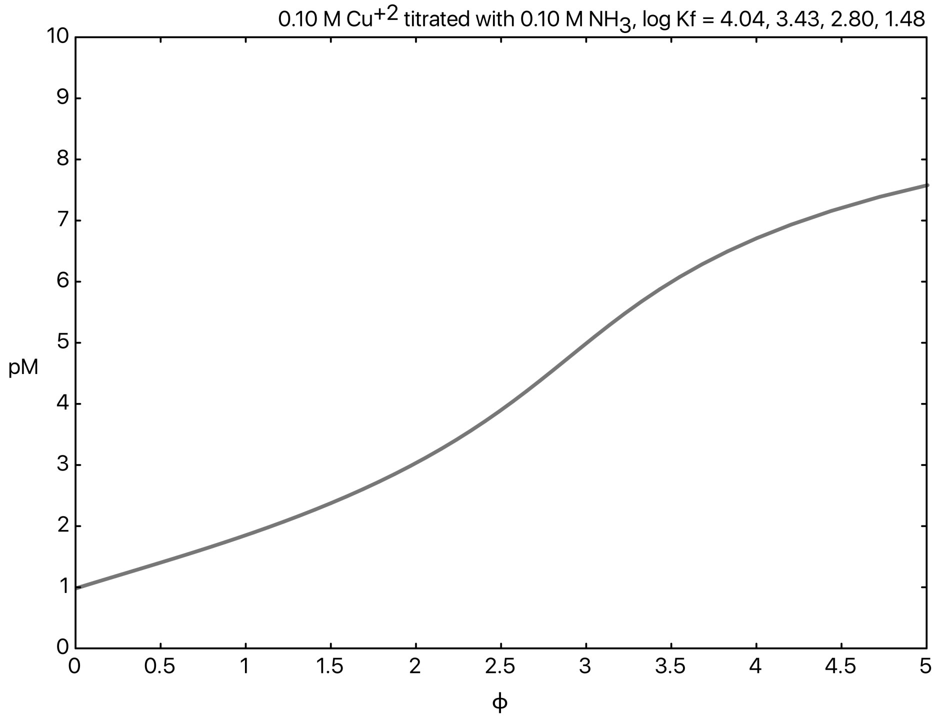


Figure 5E-3. Can you identify the four endpoints in the titration of Cu^{+2} with NH_3? How well would an indicator work?

Ammonia is a *monodentate* ligand since it forms one coordination bond with a metal. Reacting with Cu^{+2} requires 4 NH_3 (and 4 K_f) to get four coordination. With 4 K_f and overlapping equilibria, the titration curve in Figure 5E-3 does not have a sharp endpoint.

Ethanediamine, en, is a *bidentate* ligand since it forms two coordination bonds with a metal. Reacting with Cu^{+2} requires 2 en (and 2 K_f) to get four coordination. The equilibria are better separated and the titration curve in Figure 5E-4 has a sharper endpoint.

Triethanetetramine, trien, and nitrilotriacetic acid, NTA, are *tetradentate* ligands. Ethanediaminetetraacetate, $EDTA^{-4}$, is a *hexadentate* ligand.

Reacting with Cu^{+2} requires 1 $EDTA^{-4}$ (and 1 K_f) to get four coordination. The titration curve in Figure 5E-5 has an extremely sharp endpoint (change in metal concentration of over 10^{15})!

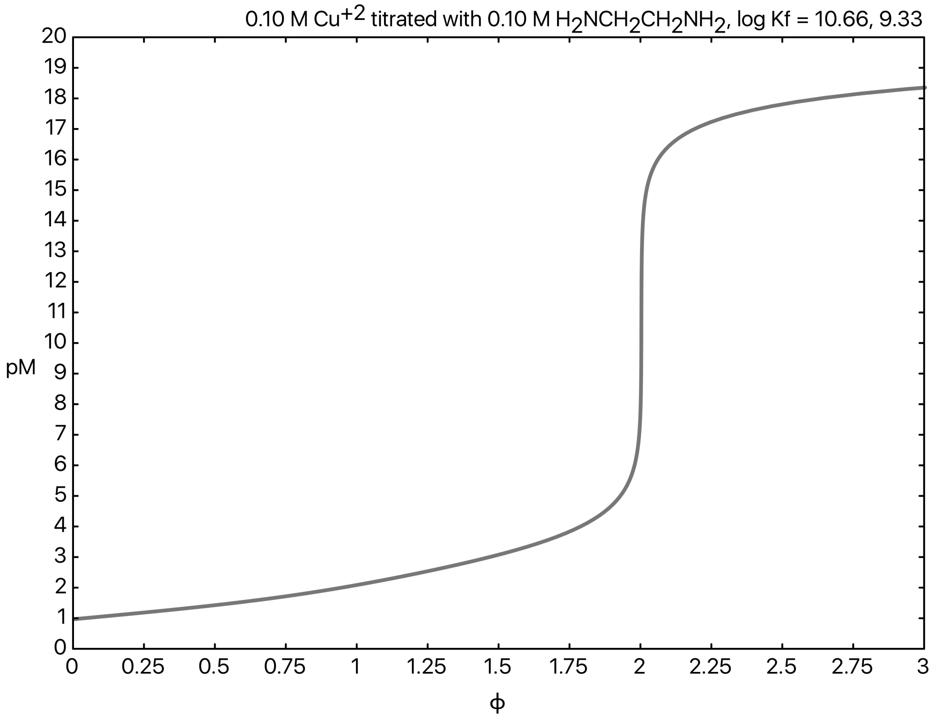


Figure 5E-4. Can you identify the two endpoints in the titration of 0.10 M Cu^{+2} with 0.10 M $NH_2CH_2CH_2NH_2$?

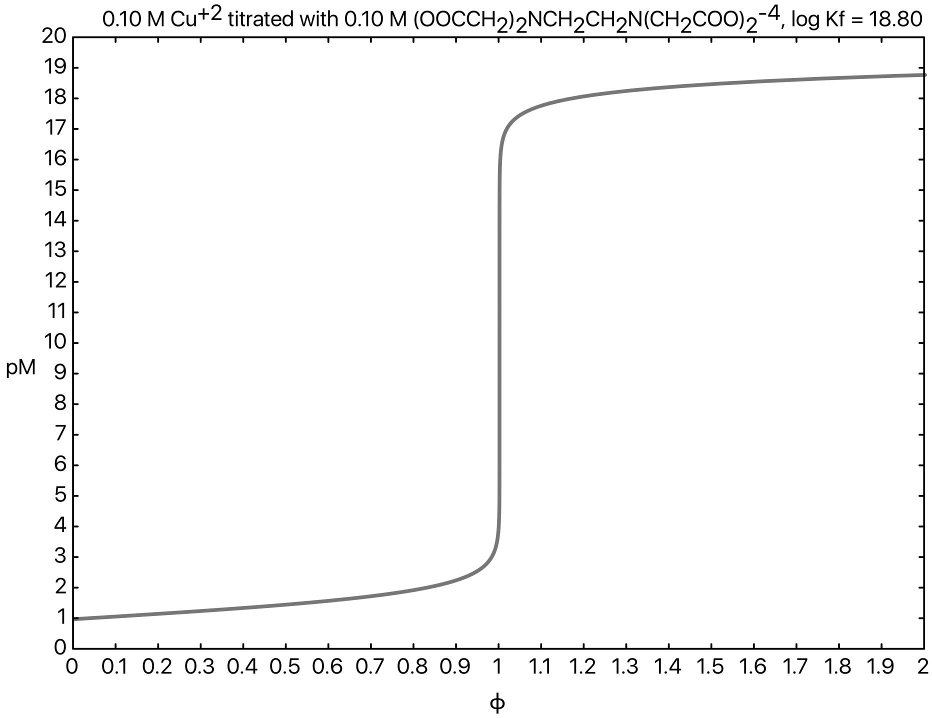


Figure 5E-5. Can you identify the single endpoint in the titration of 0.10 M Cu^{+2} with 0.10 M $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2{}^{-4}$?

For the Cu^{+2} NH_3 equilibria, we have $1K_a$, $4K_f$, mass balance on Cu^{+2}, and mass balance on NH_3, giving seven equations and seven unknowns.

For the Cu^{+2} $EDTA^{-4}$ equilibria, we have $4K_a$, $1K_f$, mass balance on Cu^{+2}, and mass balance on $EDTA^{-4}$, giving seven equations and seven unknowns.

This may not seem like much of an advantage when doing calculations, but we can pH buffer the solution to simplify the K_a equilibria, and benefit from one (large) K_f with a sharp titration endpoint.

Conditional Titrations

The titrations in Figures 5E-3, 5E-4, and 5E-5 assume that the pH is high enough that protonation of the titrant does not occur. The pH of a solution can be adjusted by the use of a buffer, but the base form of the buffer may then also act as a ligand and form complexes with the metal ion. How does the titration curve of M with Y change with pH and in the presence of a constant amount of L/HL^+ buffer?

The mass balance for the metal is:

$$C_M = [M] + [ML] + [ML_2] + [ML_3] + \ldots + [MY] + [MY_2] + \ldots$$

The *conditional formation function*, F_o', will be:

$$\boxed{F_o' = 1 + K_{f1L}[L] + K_{f1L}K_{f2L}[L]^2 + K_{f1L}K_{f2L}K_{f3L}[L]^3 + \ldots + K_{f1Y}[Y] + K_{f1Y}K_{f2Y}[Y]^2 + \ldots}$$

Now, what fraction of the total metal is present as each species?

$$\delta_0 = \begin{array}{l}\text{fraction of M}\\ \text{with 0 L and 0 Y}\end{array} = \frac{[M]}{C_M} = \frac{1}{F_o'}$$

$$\delta_{1L} = \begin{array}{l}\text{fraction of M}\\ \text{with 1 L and 0 Y}\end{array} = \frac{[ML]}{C_M} = \frac{K_{f1L}[M][L]}{C_M} = \frac{K_{f1L}[L]}{F_o'}$$

$$\delta_{2L} = \begin{array}{l}\text{fraction of M}\\ \text{with 2 L and 0 Y}\end{array} = \frac{[ML_2]}{C_M} = \frac{K_{f1L}K_{f2L}[M][L]^2}{C_M} = \frac{K_{f1L}K_{f2L}[L]^2}{F_o'}$$

$$\delta_{1Y} = \begin{array}{l}\text{fraction of M}\\ \text{with 0 L and 1 Y}\end{array} = \frac{[MY]}{C_M} = \frac{K_{f1Y}[M][Y]}{C_M} = \frac{K_{f1Y}[Y]}{F_o'}$$

$$\delta_{2Y} = \begin{array}{l}\text{fraction of M}\\ \text{with 0 L and 2 Y}\end{array} = \frac{[MY_2]}{C_M} = \frac{K_{f1Y}K_{f2Y}[M][Y]^2}{C_M} = \frac{K_{f1Y}K_{f2Y}[Y]^2}{F_o'}$$

Note that the δ-fractions are terms of F_o' divided by F_o'!

The average number of Y *gained* is $\bar{n}_Y = 0\delta_0 + 1\delta_{1Y} + 2\delta_{2Y} + \ldots$

The mass balance for the titrant Y without metal is:

$$\frac{[Y]}{\alpha} = [Y] + [HY] + [H_2Y] + [H_3Y] + \ldots + [H_nY],$$

so the mass balance for the total titrant is $C_Y = \bar{n}_Y\, C_M + \frac{[Y]}{\alpha}$.

As before the ratio of the moles is the fraction titrated:

$$\boxed{\begin{array}{c}\text{Fraction titrated} = \phi = \dfrac{V_Y\, M_Y}{V_M\, M_M} = \dfrac{\bar{n}_Y + \dfrac{[Y]}{\alpha_n\, M_M}}{1 - \dfrac{[Y]}{\alpha_n\, M_Y}} \\[2em] \text{Free metal} = [M] = \delta_0\, C_M = \delta_0\, \dfrac{V_M\, M_M}{V_Y + V_M} = \dfrac{\delta_0\, M_M\, M_Y}{\phi\, M_M + M_Y}\end{array}}$$

The F_o' corrects for decreased free metal concentration due to buffer complexation and the α_n corrects for protonation of Y at a finite pH. Figure 5E-6 shows a titration curve for system where the buffer determines the pH, the fraction of available $EDTA^{-4}$ and the fraction of uncomplexed free metal ion.

For additional examples of how titrations are affected by metal concentration, $EDTA^{-4}$ concentration, pH, and buffer concentration see the *ChemConnections Media Resources*.

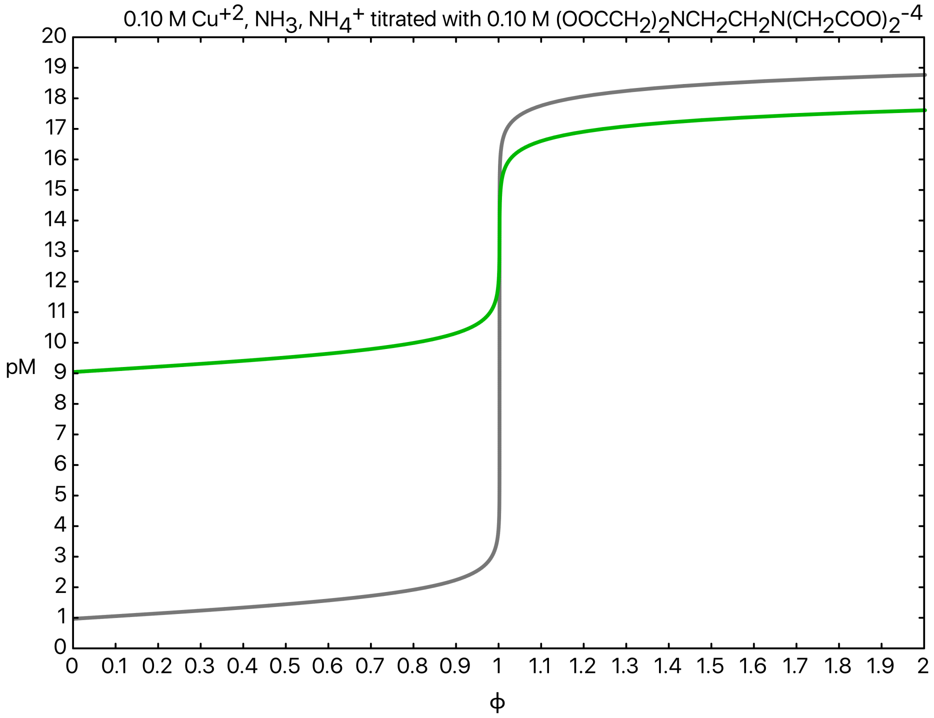


Figure 5E-6. Buffer complexation and pH effects of 0.1 M NH_3 and 0.1 M NH_4^+ on the titration curve for 0.10 M Cu^{+2} with 0.10 M $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{-4}$.

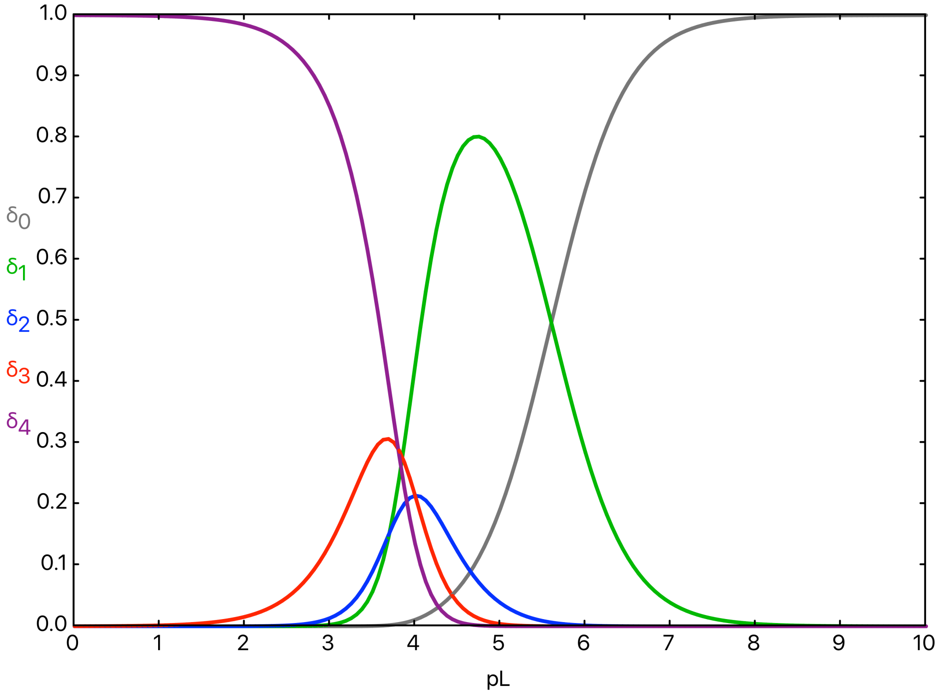
APPLYING YOUR IDEAS

Problems

5E-1 A defense mechanism used by some plants to prevent aluminum ion toxicity is to excrete citric acid. Write the equilibrium reactions involved in decreasing the concentration of aluminum ion.

5E-2 For 0.10 M total F^- and 0.0010 M total Al^{+3}, ignoring pH and reactions with water, give the correct chemical formula and molarity for each chemical species that is present.

5E-3 The plot shows a distribution diagram for CH_3COO^- with Hg^{+2}. Label each curve with the chemical formula of the species it represents.



5E-4 Consider the titration of Ca^{+2} with $EDTA^{-4}$ in the presence of NH_3/NH_4Cl buffer. The titration reaction is a metal ligand formation equilibrium of Ca^{+2} with $EDTA^{-4}$.

$$Ca^{+2} + EDTA^{-4} \rightleftharpoons CaEDTA^{-2-} \quad K_f = \frac{[CaEDTA^{-2}]}{[Ca^{+2}][EDTA^{-4}]}.$$

a. What other equilibrium reactions of Ca^{+2} will occur?

b. What other equilibrium reactions of $EDTA^{-4}$ will occur?

Assigned Metal Ions for Problems 5E-5 through 5E-9

If your last name begins with A-G use Zn^{+2} for problems 5E5-9.
If your last name begins with H-M use Cd^{+2} for problems 5E5-9.
If your last name begins with N-R use Cu^{+2} for problems 5E5-9.
If your last name begins with S-Z use Ni^{+2} for problems 5E5-9.

Hints and Constants for Problems 5E-7 and 5E-8

a. What is the pH of the buffer?

b. What fraction of the titrant ligand is fully deprotonated?

c. What fraction of the untitrated metal is uncomplexed by the buffer?

d. Log K_f equilibrium constant values for NH_3 are

Zn^{+2}	2.18, 2.25, 2.31, 1.96
Cd^{+2}	2.51, 1.96, 1.30, 0.79
Cu^{+2}	3.99, 3.34, 2.73, 1.97
Ni^{+2}	2.67, 2.12, 1.61, 1.07, 0.63, -0.09

e. Log K_a equilibrium constant values for H_6EDTA^{+2} are
0.00, –1.49, –2.00, –2.66, –6.16, –10.24
Log K_f equilibrium constant values for $EDTA^{-4}$ are
Zn^{+2} 16.50, Cd^{+2} 16.46, Cu^{+2} 18.80, Ni^{+2} 18.62

f. Log K_a equilibrium constant values for H_4trien^{+4} are
–3.320, –6.670, –9.200, and –9.921
Log K_f equilibrium constant values for trien are
Zn^{+2} 14.0, Cd^{+2} 10.8, Cu^{+2} 20.1, Ni^{+2} 14.0

5E-5 For 1.00×10^{-2} M total metal ion with acetate as a ligand and pH 6.00, give the correct formula and molarity for each chemical species that is present if the uncomplexed acetate concentration, $[L]/\alpha_N(H^+)$, is (a) 1.00 M (b) 0.10 M (c) 0.010 M (d) 0.0010 M

5E-6 For 1.00×10^{-2} M total metal ion and 0.10 M total acetate, C_L, as a ligand, give the correct formula and molarity for each chemical species that is present if the pH is (a) 3.12 (b) 4.27 (c) 5.31 (d) 6.48

5E-7 Hand in a plot of the –log of the free metal concentration as a function of the fraction titrated for the titration of 0.0010 M metal ion with 0.0020 M $EDTA^{-4}$ in the presence of 0.30 M NH_3 and 0.10 M NH_4Cl.

5E-8 Hand in a plot of the –log of the free metal concentration as a function of the fraction titrated for the titration of 0.0020 M metal ion with 0.0025 M trien in the presence of 0.10 M NH_3 and 0.05 M NH_4Cl.

5E-9 For *your* metal ion, does $EDTA^{-4}$ or trien give a sharper endpoint?

5E-10 Sketch (*not* a computer printout) a before and after view that shows how the titration curve changes if you
a. increase the value of titrant K_f?
b. increase the buffer concentration?
c. increase the buffer K_f?
d. increase the hydrogen ion concentration?
e. increase the metal ion concentration?

Is this soil nutritious or toxic?

SESSION 5, MAKING THE LINK

LOOKING BACK

Do all soils react to acid rain in the same manner? Can we protect soils from being damaged by acid rain? Can we treat damaged soils?

Session Goals

- Concepts of cation exchange capacity and base saturation
- Observe the benefits of liming soil
- Recognize the problems of aluminum toxicity

CHECKING YOUR PROGRESS

5-1 What is pH-dependent cation exchange capacity and what causes it?

5-2 The pH of a soil with a high CEC is less affected by acid rain than the pH of a soil with a low CEC. Why?

5-3 Analysis of a 100 g soil sample found 14 mmol H^+, 5 mmol Ca^{+2}, 4.5 mmol Mg^{+2}, 1 mmol K^+, and 2 mmol Al^{+3}. What is the base saturation of the soil?

5-4 Examine Table 5.1 concerning probable causes for forest decline in areas thought to be affected by acid rain. Based on your studies would you add to or cross out anything on this list?

Table 5-1. Hypotheses for the Main Causes of Forest Decline

- A. Air Pollution
  - 1. Direct effects of gaseous pollutants and acidic rain, alone or in combination
  - 2. Indirect effects via soil acidification
    - a. Reduced availability of certain plant nutrients (increased leaching of Ca, Mg, or K would gradually lead to soil deficiencies)
    - b. Toxic effects of aluminum (increased solubility).
      - i. may negatively affect root growth, reducing the uptake of water and nutrients, and shifting root distribution toward the surface
      - ii. may cause needle yellowing by blocking Mg uptake
      - iii. may slow down soil nutrient recycling by reducing the activity of decomposers
  - 3. Excess availability of nitrogen (enhanced deposition of NH_4^+ and NO_3^- ions).
    - a. Boreal forests normally have a shortage of N and increased inorganic nitrogen deposition might increase forest production. Increased growth rates increase the demand for other nutrients and may make trees less resistant to wind, drought, and parasites.
    - b. Leaching of Ca and Mg as nitrate salts would increase soil acidity
- B. Bad Forestry Practices
  - 1. Planting species outside natural distribution areas
  - 2. Harvesting practices
- C. Natural Factors (but the natural prepollution situation is unknown)
- D. Multiple Stresses (one or more of the above)

Table based on Gunnar Abrahamsen, Arne O. Stuanes, Bjørn Tveite, *Long-Term Experiments with Acid Rain in Norwegian Forest Ecosystems*, Springer-Verlag, New York, Ecological Studies Vol. 104, 1994.

5-5 It has been observed that the dissolution of mica is three times faster in 10^{-4} M H_2SO_4 than in water, but eight times faster in 10^{-4} M HOOC-COOH. (M. Robert, M. K. Razzaghe, M. A. Vincente, and G. Veneau, "Rôle au facteur biochimique dans l'altération des minéraux silicatés," *Sci. Sol* 2-3:153-174 (1979).) Propose an explanation for these observations.

5-6 As pH increases, Ca, K and Mg become more available to plants but Fe, Mn, Zn, and Cu becomes less available. Why?

THINKING FURTHER

Soils play a very important role in **nutrient cycling**, the continuous circulation of nutrients such as carbon, nitrogen, magnesium, iron, calcium and phosphorous. Figure 5-1 illustrates how various nutrients are cycled within a forest. For instance, when a plant dies it returns nutrients to the soil as it decomposes. This recycling process prevents nutrients from getting held up somewhere in the forest.

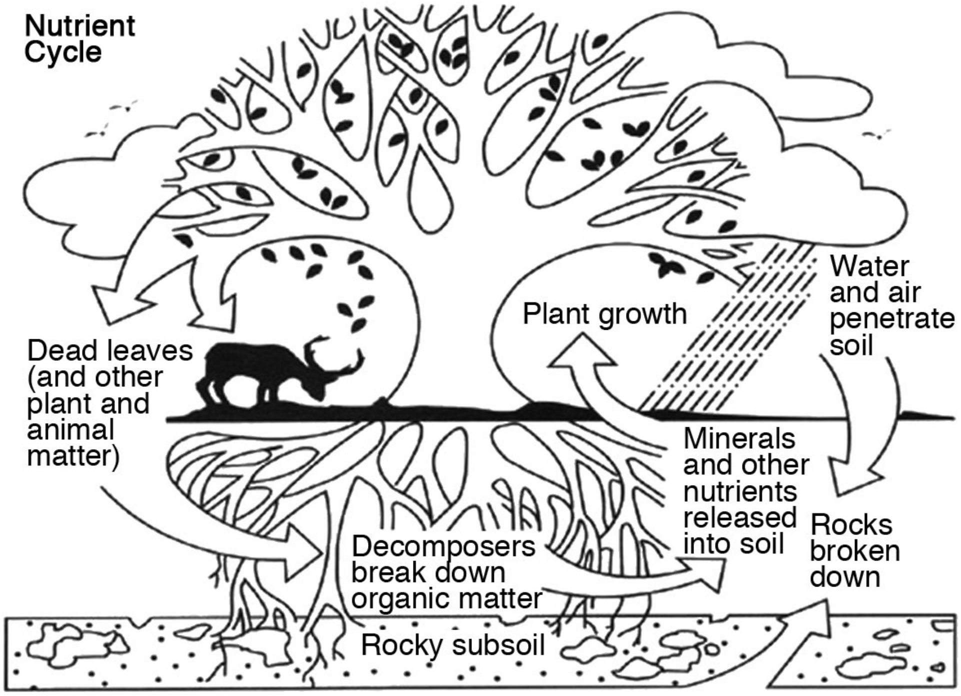


Figure 5-1. Nutrient cycling in a forest ecosystem, from USDA Soil Quality Issue Brief (1995) https://www.nrcs.usda.gov/wps/portal/nrcs/detail/national/technical/nra/rca/?cid=nrcs143_014198

5-7 Describe the fate of a carbon atom that enters the soil and participates in a full nutrient cycle.

5-8 How might acid rain disrupt nutrient cycling?

Acid Rain Poses a Previously Unrecognized Threat to Great Lakes Sugar Maples

ScienceDaily (Dec. 15, 2011) — The number of sugar maples in Upper Great Lakes forests is likely to decline in coming decades, according to University of Michigan ecologists and their colleagues, due to a previously unrecognized threat from a familiar enemy: acid rain.

Over the past four decades, sugar maple abundance has declined in some regions of the northeastern United States and southeastern Canada, due largely to acidification of calcium-poor granitic soils in response to acid rain.

Sugar maple forests in the Upper Great Lakes region, in contrast, grow in calcium-rich soils. Those soils provide a buffer against soil acidification. So sugar maple forests here have largely been spared the type of damage seen in mature sugar maples of the Northeast.

But now, a U-M-led team of ecologists has uncovered a different and previously unstudied mechanism by which acid rain harms sugar maple seedlings in Upper Great Lakes forests.

The scientists have concluded that excess nitrogen from acid rain slows the microbial decay of dead maple leaves on the forest floor, resulting in a build-up of leaf litter that creates a physical barrier for seedling roots seeking soil nutrients, as well as young leaves trying to poke up through the litter to reach sunlight.

"The thickening of the forest floor has become a physical barrier for seedlings to reach mineral soil or to emerge from the extra litter," said ecologist Donald Zak, a professor at the U-M School of Natural Resources and Environment and co-author of an article published online Dec. 8 in the *Journal of Applied Ecology*. Zak is also a professor of ecology and evolutionary biology.

"What we've uncovered is a totally different and indirect mechanism by which atmospheric nitrogen deposition can negatively impact sugar maples," Zak said.

The new findings are the latest results from a 17-year experiment at four sugar maple stands in Michigan's lower and upper peninsulas.

By the end of this century, nitrogen deposition from acid rain is expected to more than double worldwide, due to increased burning of fossil fuels. For the last 17 years at the four Michigan sugar maple test sites, Zak and his colleagues have added sodium nitrate pellets (six times throughout the growing season, every year) to three 30-meter by 30-meter test plots at each of the four Michigan maple stands. Adding the pellets was done to simulate the amount of nitrogen deposition expected by the end of the century.

Seedling-establishment data from the nitrogen-spiked test plots were compared to the findings from a trio of nearby control plots that received no additional nitrogen. Most of the fieldwork and analysis was done by 2010 SNRE graduate Sierra Patterson, who conducted the study for her master's thesis.

Patterson and her colleagues found that adding extra nitrogen increased the amount of leaf litter on the forest floor by up to 50 percent, causing a significant reduction in the successful establishment of sugar maple seedlings.

When the number of seedlings on nitrogen-supplemented treatment was compared to the number of seedlings on the no-nitrogen-added treatment, the mean abundance of second-year seedlings was 13.1 stems per square meter under ambient nitrogen deposition and 1.6 stems per square meter under simulated nitrogen deposition.

The mean abundance of seedlings between three and five years of age also significantly declined under simulated nitrogen deposition: 10.6 stems per square meter grew under ambient nitrogen deposition, compared to 0.6 stems per square meter under simulated nitrogen deposition.

"Increasing nitrogen deposition has the potential to lead to major changes in sugar maple-dominated northern hardwood forests in the Great Lakes region," said Patterson, who now works as a botanist for the Huron-Manistee National Forests in Michigan.

"In terms of regeneration, it looks like it'll be difficult for new seeds to replace the forest overstory in the future," she said "So the populations of sugar maples in this region could potentially decline."

Funding for the study has been provided by grants from the National Science Foundation and the U.S. Department of Energy's Division of Environmental Biology.

"The surprising results reported in this study are an example of the value of long-term research," said Saran Twombly, program director in the National Science Foundation's Division of Environmental Biology, which funded the work.

"Uncovering the unexpected link between nitrogen deposition and sugar maple seedling success depended on the ability to simulate increased nitrogen deposition year after year," Twombly said. "The manipulations used to reveal the details of this link could not have worked in other than a long-term study."

References

1. "Acid rain poses a previously unrecognized threat to Great Lakes sugar maples." *ScienceDaily*. (2011, December 15) http://www.sciencedaily.com/releases/2011/12/111215135933.htm
2. Sierra L. Patterson, Donald R. Zak, Andrew J. Burton, Alan F. Talhelm, Kurt S. Pregitzer. "Simulated N deposition negatively impacts sugar maple regeneration in a northern hardwood ecosystem." *Journal of Applied Ecology*, 2011; http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2664.2011.02090.x/abstract
3. Jim Ericson, "Acid rain poses a previously unrecognized threat to Great Lakes sugar maples." University of Michigan News Service (2011, December 15). http://ns.umich.edu/new/20128-acid-rain-poses-a-previously-unrecognized-threat-to-great-lakes-sugar-maples

What are the critical problems in your region?

SESSION 6, CULMINATING PROJECT

LOOKING BACK

The effects of acid deposition are not uniform with respect to location, depending both on the amount of deposition and on the local geology. What are the critical problems in your region?

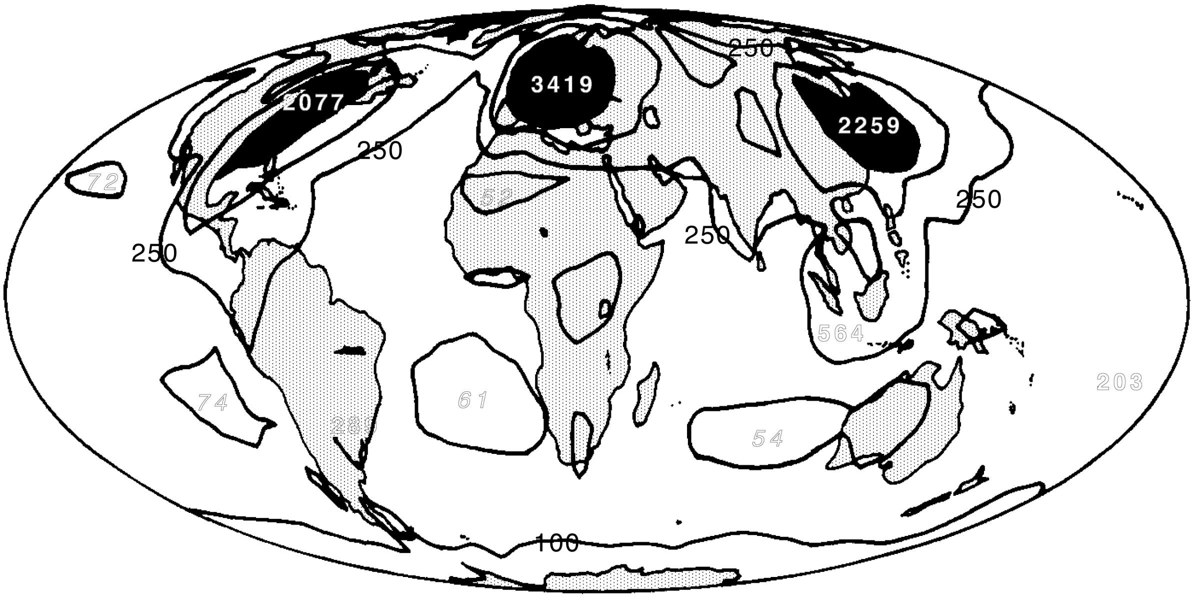


Figure 6-1. Annual deposition of sulfur, (mg S)/(m^2 year). Contours drawn at 100, 250, and 500. Values shown are maxima or minima. Map from J. N. Galloway and H. Rodhe, "Regional atmospheric budgets of S and N fluxes: how well can they be quantified," *Proceedings of the Royal Society of Edinburgh*, **97B**, 61-80 (1991).

CHECKING YOUR PROGRESS

Regional Group Project

Your instructor will indicate whether you should prepare and defend a poster or hand in a several page typed report. This project should include contributions from each member of your regional group.

You should include answers to most of the following questions:

a. What are the sources of acid rain in your region?
b. Do the inputs come from within the country or from across the border?
c. What are the trends for emission or deposition in the area?
d. What are the cation exchange capacity and base saturation for the area?
e. Is acid deposition affecting the area? Are the forests/trees, lakes/fish, cities/buildings, health/people, or soil/agriculture effects significant?
f. Should we intervene to restore the soil? How?
g. What are the prospects for the future?

Much useful material and links can be found on the course web page.

Incorporate the graphs from problems 5B-6 as an integral part of the *discussion* of your answers to the questions above.

Provide references for the figures and facts you include in your report. It should be clear if you are citing values from a particular location or whether you are estimating values based on general soil types. **For web resources give the web address and the author or sponsoring organization**. All the links on the course web page indicate the sponsoring organization. You should cite the original page when possible rather than citing the class link. For print articles give the author, title, journal or newspaper, date, volume, and page number.

THINKING FURTHER

6.1 Where do we go from here? Are you optimistic or pessimistic about controlling acid rain or its effects? Explain your answer. How does Figure 6-2 influence your answer?

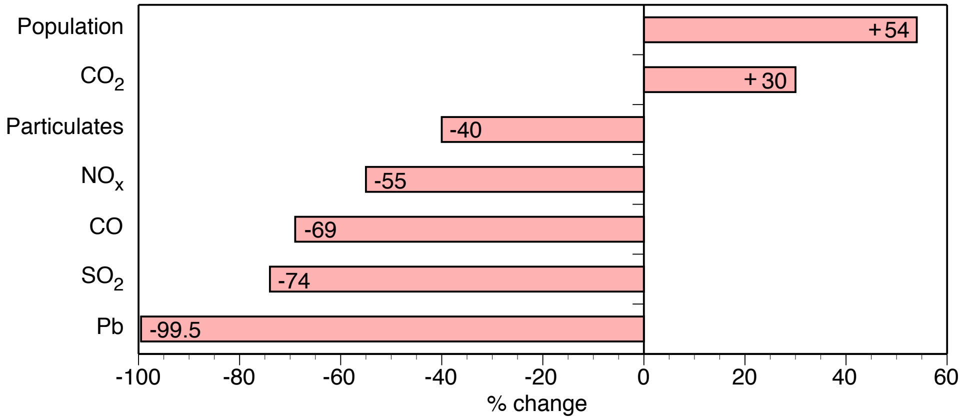


Figure 6-2. US percentage change in emissions between 1970 and 2011.
Data from US EPA, which was founded in 1970.
https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data

6.2 The pH of acid rain found in industrialized areas would increase if the release to the atmosphere of which of the following were decreased? Circle your answer(s) and then explain.

SO_2 CaO N_2 NO CO_2

6.3 Various hypotheses concerning acid rain have suggested the adverse effects on plants and animals are due to

a. increased H^+ concentration

b. decreased Ca^{+2} concentration

c. increased Al^{+3} concentration.

What causes each of the above? Which do you think is the greater problem?

6.4 This module tends to ignore plant processes that affect soils. How do each of the items in Table 6-1 change the abiotic situation?

Table 6-1. Rhizosphere* Events

Excretion of H^+ that exchanges for nutrient Mg^{+2}, Ca^{+2}, NH_4^+, K^+
Release of CO_2 by respiration
Oxidation of nitrogen and sulfur to NO_3^- and SO_4^{2-}
Excretion of organic acids which complex metals and increase mobility of Al^{+3} and Fe^{+3}
Depletion of O_2 that reduces the redox potential and favors Fe^{+2} over Fe^{+3}
Removal of water through root uptake and transpiration
Alteration of soil permeability

*Fine roots and associated microorganisms.

Table based on Y. Lucas, "The Role of Plants in Controlling the Rates and Products of Weathering: Importance of Biological Pumping," *Annu. Rev. Earth Planet. Sci.,* **29**, 135-163 (2001)

Equilibrium Constants

APPENDIX 1

Acids (See text for a larger list)

$H_2O \rightleftharpoons H^+ + OH^-$	$\log K_w = -14.00$	water
$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	$\log K_{a1} = -2.24$	arsenic
$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{-2}$	$\log K_{a2} = -6.96$	"
$HAsO_4^{-2} \rightleftharpoons H^+ + AsO_4^{-3}$	$\log K_{a3} = -11.50$	"
$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	$\log K_{a1} = -9.237$	boric
$H_2BO_3^- \rightleftharpoons H^+ + HBO_3^{-2}$	$\log K_{a2} = -12.74$	"
$HBO_3^{-2} \rightleftharpoons H^+ + BO_3^{-3}$	$\log K_{a3} = -13.80$	"
$HClO_2 \rightleftharpoons H^+ + ClO_2^-$	$\log K_a = -1.96$	chlorous
$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$	$\log K_a = +0.20$	chromic
$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{-2}$	$\log K_a = -6.51$	"
$HOCl \rightleftharpoons H^+ + OCl^-$	$\log K_a = -7.53$	hypochlorous
$HF \rightleftharpoons H^+ + F^-$	$\log K_a = -3.17$	hydrofluoric
$HF + F^- \rightleftharpoons HF_2^-$	$\log K_{f2} = 0.58$	
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$\log K_{a1} = -2.148$	phosphoric
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$	$\log K_{a2} = -7.198$	"
$HPO_4^- \rightleftharpoons H^+ + PO_4^{-3}$	$\log K_{a3} = -12.375$	"
$HSO_4^- \rightleftharpoons H^+ + SO_4^{-2}$	$\log K_{a2} = -1.987$	sulfuric
$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	$\log K_{a1} = -1.857$	sulfurous
$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	$\log K_{a2} = -7.172$	"
$HCOOH \rightleftharpoons H^+ + HCOO^-$	$\log K_a = -3.744$	formic
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	$\log K_a = -4.756$	acetic
$ClCH_2COOH \rightleftharpoons H^+ + ClCH_2COO^-$	$\log K_a = -2.865$	chloroacetic
$Cl_2CHCOOH \rightleftharpoons H^+ + Cl_2CHCOO^-$	$\log K_a = -1.10$	dichloroacetic
$CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$	$\log K_a = -4.874$	propanoic
$CH_3(CH_2)_2COOH \rightleftharpoons H^+ + CH_3(CH_2)_2COO^-$	$\log K_a = -4.818$	butanoic
$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	$\log K_a = -4.202$	benzoic
$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$	$\log K_a = -9.997$	hydroxybenzene (phenol)
$4\text{-}NO_2C_6H_4OH \rightleftharpoons H^+ + NO_2C_6H_4O^-$	$\log K_a = -7.149$	4-nitrophenol
$2,4\text{-}(NO_2)_2C_6H_3OH \rightleftharpoons H^+ + (NO_2)_2C_6H_3O^-$	$\log K_a = -4.114$	2,4-dinitrophenol
$HOOC\text{-}COOH \rightleftharpoons H^+ + HOOC\text{-}COO^-$	$\log K_{a1} = -1.250$	oxalic
$HOOC\text{-}COO^- \rightleftharpoons H^+ + OOC\text{-}COO^{-2}$	$\log K_{a2} = -4.266$	"
$1,2\text{-}C_6H_5(COOH)_2 \rightleftharpoons H^+ + C_6H_5COOHCOO^-$	$\log K_{a1} = -2.950$	phthalic
$1,2\text{-}C_6H_5COOHCOO^- \rightleftharpoons H^+ + C_6H_5(COO^-)_2$	$\log K_{a2} = -5.408$	"
$NH_3(g) \rightleftharpoons NH_3(aq)$	$\log K_H = 1.77$	ammonia

$NH_4^+ \rightleftharpoons H^+ + NH_3$	$\log K_a =$	–9.245	ammonium
$CH_3CH_2NH_3^+ \rightleftharpoons H^+ + CH_3CH_2NH_2$	$\log K_a =$	–10.673	ethylammonium
$CH_3(CH_2)_3NH_3^+ \rightleftharpoons H^+ + CH_3(CH_2)_3NH_2$	$\log K_a =$	–10.640	butylammonium
$HONH_3^+ \rightleftharpoons H^+ + HONH_2$	$\log K_a =$	–5.960	hydroxylammonium
$C_6H_5NH_3^+ \rightleftharpoons H^+ + C_6H_5NH_2$	$\log K_a =$	–4.601	anilinium
$C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N$	$\log K_a =$	–5.229	pyridinium
$H_3N(CH_2)_2NH_3^{+2} \rightleftharpoons H^+ + H_2N(CH_2)_2NH_3^+$	$\log K_{a1} =$	–6.848	ethanediammonium
$H_2N(CH_2)_2NH_3^+ \rightleftharpoons H^+ + H_2N(CH_2)_2NH_2$	$\log K_{a2} =$	–9.928	"
$H_3NCH_2COOH^+ \rightleftharpoons H^+ + H_3NCH_2COO$	$\log K_{a1} =$	–2.350	glycinium
$H_3NCH_2COO \rightleftharpoons H^+ + H_2NCH_2COO^-$	$\log K_{a2} =$	–9.778	glycine

Aluminum

$Al^{+3} + H_2O \rightleftharpoons H^+ + AlOH^{+2}$	$\log K_{a1} =$	–5.00	
$AlOH^{+2} + H_2O \rightleftharpoons H^+ + Al(OH)_2^+$	$\log K_{a2} =$	–5.10	
$Al(OH)_2^+ + H_2O \rightleftharpoons H^+ + Al(OH)_3(aq)$	$\log K_{a3} =$	–6.70	
$Al(OH)_3(aq) + H_2O \rightleftharpoons H^+ + Al(OH)_4^-$	$\log K_{a4} =$	–5.90	
$2\ Al^{+3} + 2\ H_2O \rightleftharpoons Al_2(OH)_2^{+4} + 2\ H^+$	$\log K_{22} =$	–7.70	
$3\ Al^{+3} + 4\ H_2O \rightleftharpoons Al_3(OH)_4^{+5} + 4\ H^+$	$\log K_{34} =$	–13.94	
$Al(OH)_3(s) + 3\ H^+ \rightleftharpoons Al^{+3} + 3\ H_2O$	$\log K =$	8.11	gibbsite
		10.80	amorphous
$Al(OH)_3(s) \rightleftharpoons Al^{+3} + 3\ OH^-$	$\log K_s =$	–33.89	gibbsite
		–31.20	amorphous
$Al^{+3} + F^- \rightleftharpoons AlF^{+2}$	$\log K_{f1} =$	7.0	
$AlF^{+2} + F^- \rightleftharpoons AlF_2^+$	$\log K_{f2} =$	5.7	
$AlF_2^+ + F^- \rightleftharpoons AlF_3(aq)$	$\log K_{f3} =$	4.1	
$AlF_3(aq) + F^- \rightleftharpoons AlF_4^-$	$\log K_{f4} =$	2.6	
$AlF_4^- + F^- \rightleftharpoons AlF_5^{-2}$	$\log K_{f5} =$	1.2	
$AlF_5^{-2} + F^- \rightleftharpoons AlF_6^{-3}$	$\log K_{f6} =$	0.0	
$Al^{+3} + OOC\text{-}COO^{-2} \rightleftharpoons Al(OOC\text{-}COO)^+$	$\log K_{f1} =$	6.1	
$Al(OOC\text{-}COO)^+ + OOC\text{-}COO^{-2} \rightleftharpoons Al(ox)_2^-$	$\log K_{f2} =$	5.0	
$Al(OOC\text{-}COO)_2^- + OOC\text{-}COO^{-2} \rightleftharpoons Al(ox)_3^{-3}$	$\log K_{f3} =$	4.0	
$Al^{+3} + HSO_4^- \rightleftharpoons AlHSO_4^{+2}$	$\log K_f =$	0.46	
$Al^{+3} + SO_4^{-2} \rightleftharpoons AlSO_4^+$	$\log K_{f1} =$	3.02	
$AlSO_4^+ + SO_4^{-2} \rightleftharpoons Al(SO_4)_2^-$	$\log K_{f2} =$	1.90	

Barium

$Ba^{+2} + H_2O \rightleftharpoons H^+ + BaOH^+$	$\log K_a =$	–13.36	
$Ba^{+2} + HCO_3^- \rightleftharpoons BaHCO_3^+$	$\log K_f =$	0.98	
$Ba^{+2} + CO_3^{-2} \rightleftharpoons BaCO_3(aq)$	$\log K_f =$	2.71	
$BaCO_3(s) \rightleftharpoons Ba^{+2} + CO_3^{-2}$	$\log K_s =$	–8.57	witherite
$Ba^{+2} + SO_4^{-2} \rightleftharpoons BaSO_4(aq)$	$\log K_f =$	2.70	
$BaSO_4(s) \rightleftharpoons Ba^{+2} + SO_4^{-2}$	$\log K_s =$	–9.98	barite

Cadmium

$Cd^{+2} + H_2O \rightleftharpoons H^+ + CdOH^+$	$\log K_{a1} = -10.10$	
$CdOH^+ + H_2O \rightleftharpoons H^+ + Cd(OH)_2(aq)$	$\log K_{a2} = -10.20$	
$Cd(OH)_2(aq) + H_2O \rightleftharpoons H^+ + Cd(OH)_3^-$	$\log K_{a3} = -12.21$	
$Cd(OH)_3^- + H_2O \rightleftharpoons H^+ + Cd(OH)_4^{-2}$	$\log K_{a4} = -14.78$	
$2\ Cd^{+2} + H_2O \rightleftharpoons Cd_2OH^{+3} + H^+$	$\log K_{21} = -9.40$	
$Cd(OH)_2(s) \rightleftharpoons Cd^{+2} + 2OH^-$	$\log K_s = -14.36$	
$Cd^{+2} + Cl^- \rightleftharpoons CdCl^+$	$\log K_{f1} = 1.98$	
$CdCl^- + Cl^- \rightleftharpoons CdCl_2(aq)$	$\log K_{f2} = 0.62$	
$CdCl_2(aq) + Cl^- \rightleftharpoons CdCl_3^-$	$\log K_{f3} = -0.20$	
$CdCl_3^- + Cl^- \rightleftharpoons CdCl_4^{-2}$	$\log K_{f4} = -0.70$	
$Cd^{+2} + F^- \rightleftharpoons CdF^+$	$\log K_{f1} = 0.46$	
$CdF^- + F^- \rightleftharpoons CdF_2(aq)$	$\log K_{f2} = 0.07$	
$Cd^{+2} + CO_3^{-2} \rightleftharpoons CdCO_3(aq)$	$\log K_{f1} = 4.36$	
$CdCO_3(aq) + CO_3^{-2} \rightleftharpoons Cd(CO_3)_2^{-2}$	$\log K_{f2} = 2.87$	
$CdCO_3(s) \rightleftharpoons Cd^{+2} + CO_3^{-2}$	$\log K_s = -12.00$	otavite
$Cd^{+2} + HCO_3^- \rightleftharpoons CdHCO_3^+$	$\log K_f = 0.36$	
$Cd^{+2} + SO_4^{-2} \rightleftharpoons CdSO_4(aq)$	$\log K_{f1} = 2.37$	
$CdSO_4(aq) + SO_4^{-2} \rightleftharpoons Cd(SO_4)^{-2}$	$\log K_{f2} = 1.13$	
$CdSO_4(s) \rightleftharpoons Cd^{+2} + SO_4^{-2}$	$\log K_s = -0.11$	

Calcium

$Ca^{+2} + H_2O \rightleftharpoons H^+ + CaOH^+$	$\log K_a = -12.70$	
$Ca(OH)_2(s) \rightleftharpoons Ca^{+2} + 2\ OH^-$	$\log K_s = -5.20$	portlandite
$Ca^{+2} + OH^- \rightleftharpoons CaOH^+$	$\log K_f = 1.30$	
$Ca^{+2} + HCO_3^- \rightleftharpoons CaHCO_3^+$	$\log K_f = 1.27$	
$Ca^{+2} + CO_3^{-2} \rightleftharpoons CaCO_3(aq)$	$\log K_f = 3.22$	
$CaCO_3(s) \rightleftharpoons Ca^{+2} + CO_3^{-2}$	$\log K_s = -8.48$	calcite
	-8.30	aragonite
$CaMg(CO_3)_2(s) \rightleftharpoons Ca^{+2} + Mg^{+2} + 2\ CO_3^{-2}$	$\log K_s = -16.54$	dolomite
$Ca^{+2} + F^- \rightleftharpoons CaF^+$	$\log K_f = 1.00$	
$CaF_2(s) \rightleftharpoons Ca^{+2} + 2\ F^-$	$\log K_s = -10.50$	fluorite
$Ca^{+2} + PO_4^{-3} \rightleftharpoons CaPO_4^-$	$\log K_f = 6.46$	
$Ca^{+2} + HPO_4^{-2} \rightleftharpoons CaHPO_4(aq)$	$\log K_f = 2.74$	
$Ca^{+2} + H_2PO_4^- \rightleftharpoons CaH_2PO_4^+$	$\log K_f = 1.41$	
$Ca^{+2} + HSO_4^- \rightleftharpoons CaHSO_4^+$	$\log K_f = 1.08$	
$Ca^{+2} + SO_4^{-2} \rightleftharpoons CaSO_4(aq)$	$\log K_f = 2.36$	
$CaSO_4(s) \rightleftharpoons Ca^{+2} + SO_4^{-2}$	$\log K_s = -4.36$	anhydrite
$CaSO_4(H_2O)_2(s) \rightleftharpoons Ca^{+2} + SO_4^{-2}$	$\log K_s = -4.61$	gypsum

Carbon

$CO_2(g) + H_2O \rightleftharpoons H^+ + HCO_3^-$	$\log K = -7.82$
$CO_2(g) \rightleftharpoons CO_2(aq)$	$\log K_H = -1.47$
$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq)$	$\log K = -2.80$
$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-$	$\log K_{a1} = -3.50$
$CO_2(aq) + H_2O \rightleftharpoons H^+ + HCO_3^-$	$\log K_a = -6.351$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$	$\log K_{a2} = -10.329$

Cobalt

$Co^{+2} + H_2O \rightleftharpoons H^+ + CoOH^+$	$\log K_{a1} = -9.70$
$CoOH^+ + H_2O \rightleftharpoons H^+ + Co(OH)_2(aq)$	$\log K_{a2} = -9.10$
$Co(OH)_2(aq) + H_2O \rightleftharpoons H^+ + Co(OH)_3^-$	$\log K_{a3} = -12.70$
$Co(OH)_3^- + H_2O \rightleftharpoons H^+ + Co(OH)_4^{-2}$	$\log K_{a4} = -14.70$
$2\ Co^{+2} + H_2O \rightleftharpoons Co_2OH^{+3} + H^+$	$\log K_{21} = -11.00$
$Co^{+2} + Cl^- \rightleftharpoons CoCl^+$	$\log K_{f1} = 0.54$
$CoCl^+ + Cl^- \rightleftharpoons CoCl_2(aq)$	$\log K_{f2} = 1.77$
$Co^{+2} + CO_3^{-2} \rightleftharpoons CoCO_3(aq)$	$\log K_f = 4.23$
$Co^{+2} + HCO_3^- \rightleftharpoons CoHCO_3^+$	$\log K_f = 1.89$
$Co^{+2} + SO_4^{-2} \rightleftharpoons CoSO_4(aq)$	$\log K_f = 2.30$

Copper

$Cu^{+2} + H_2O \rightleftharpoons H^+ + CuOH^+$	$\log K_{a1} = -7.50$
$CuOH^+ + H_2O \rightleftharpoons H^+ + Cu(OH)_2(aq)$	$\log K_{a2} = -8.70$
$Cu(OH)_2(aq) + H_2O \rightleftharpoons H^+ + Cu(OH)_3^-$	$\log K_{a3} = -10.68$
$Cu(OH)_3^- + H_2O \rightleftharpoons H^+ + Cu(OH)_4^{-2}$	$\log K_{a4} = -13.10$
$2\ Cu^{+2} + 2\ H_2O \rightleftharpoons Cu_2(OH)_2^{+2} + 2\ H^+$	$\log K_{22} = -10.59$
$Cu^{+2} + Cl^- \rightleftharpoons CuCl^+$	$\log K_{f1} = 0.20$
$CuCl^- + Cl^- \rightleftharpoons CuCl_2(aq)$	$\log K_{f2} = -0.46$
$CuCl_2(aq) + Cl^- \rightleftharpoons CuCl_3^-$	$\log K_{f3} = -2.03$
$CuCl_3^- + Cl^- \rightleftharpoons CuCl_4^{-2}$	$\log K_{f4} = -2.30$
$Cu^{+2} + CO_3^{-2} \rightleftharpoons CuCO_3(aq)$	$\log K_{f1} = 6.77$
$CuCO_3(aq) + CO_3^{-2} \rightleftharpoons Cu(CO_3)_2^{-2}$	$\log K_{f2} = 3.43$
$Cu^{+2} + HCO_3^- \rightleftharpoons CuHCO_3^+$	$\log K_f = 1.80$
$Cu^{+2} + SO_4^{-2} \rightleftharpoons CuSO_4(aq)$	$\log K_f = 2.36$

Iron (II)

$Fe^{+2} + H_2O \rightleftharpoons H^+ + FeOH^+$	$\log K_{a1} = -9.40$
$FeOH^+ + H_2O \rightleftharpoons H^+ + Fe(OH)_2(aq)$	$\log K_{a2} = -11.10$
$Fe(OH)_2(aq) + H_2O \rightleftharpoons H^+ + Fe(OH)_3^-$	$\log K_{a3} = -8.50$
$Fe(OH)_2(s) \rightleftharpoons Fe^{+2} + 2\ OH^-$	$\log K_s = -14.44$
$Fe^{+2} + F^- \rightleftharpoons FeF^+$	$\log K_f = 1.00$
$Fe^{+2} + Cl^- \rightleftharpoons FeCl^+$	$\log K_f = 0.14$
$Fe^{+2} + HCO_3^- \rightleftharpoons FeHCO_3^+$	$\log K_f = 1.10$

$Fe^{+2} + CO_3^{-2} \rightleftharpoons FeCO_3(aq)$	$\log K_f =$	4.38	
$FeCO_3(s) \rightleftharpoons Fe^{+2} + CO_3^{-2}$	$\log K_s =$	–10.24	siderite
$Fe^{+2} + HSO_4^{-} \rightleftharpoons FeHSO_4^{+}$	$\log K_f =$	1.08	
$Fe^{+2} + SO_4^{-2} \rightleftharpoons FeSO_4(aq)$	$\log K_f =$	2.39	
$Fe^{+2} + HPO_4^{-2} \rightleftharpoons FeHPO_4(aq)$	$\log K_f =$	3.60	
$Fe^{+2} + H_2PO_4^{-} \rightleftharpoons FeH_2PO_4^{+}$	$\log K_f =$	2.70	

Iron (III)

$Fe^{+3} + H_2O \rightleftharpoons H^{+} + FeOH^{+2}$	$\log K_{a1} =$	–2.19	
$FeOH^{+2} + H_2O \rightleftharpoons H^{+} + Fe(OH)_2^{+}$	$\log K_{a2} =$	–2.41	
$Fe(OH)_2^{+} + H_2O \rightleftharpoons H^{+} + Fe(OH)_3(aq)$	$\log K_{a3} =$	–7.97	
$Fe(OH)_3(aq) + H_2O \rightleftharpoons H^{+} + Fe(OH)_4^{-}$	$\log K_{a4} =$	–9.03	
$2\ Fe^{+3} + 2\ H_2O \rightleftharpoons Fe_2(OH)_2^{+4} + 2\ H^{+}$	$\log K_{22} =$	–2.85	
$3\ Fe^{+3} + 4\ H_2O \rightleftharpoons Fe_3(OH)_4^{+5} + 4\ H^{+}$	$\log K_{34} =$	–3.43	
$Fe(OH)_3(s) + 3\ H^{+} \rightleftharpoons Fe^{+3} + 3\ H_2O$	$\log K =$	3-5	varies with geology
$Fe(OH)_3(s) \rightleftharpoons Fe^{+3} + 3\ OH^{-}$	$\log K_s =$	–38.8	amorphous
$Fe^{+3} + F^{-} \rightleftharpoons FeF^{+2}$	$\log K_{f1} =$	6.04	
$FeF^{+2} + F^{-} \rightleftharpoons FeF_2^{+}$	$\log K_{f2} =$	4.43	
$FeF_2^{+} + F^{-} \rightleftharpoons FeF_3(aq)$	$\log K_{f3} =$	3.15	
$Fe^{+3} + Cl^{-} \rightleftharpoons FeCl^{+2}$	$\log K_{f1} =$	1.48	
$FeCl^{+2} + Cl^{-} \rightleftharpoons FeCl_2^{+}$	$\log K_{f2} =$	0.65	
$FeCl_2^{+} + Cl^{-} \rightleftharpoons FeCl_3(aq)$	$\log K_{f3} =$	–1.00	
$Fe^{+3} + HSO_4^{-} \rightleftharpoons FeHSO_4^{+2}$	$\log K_f =$	2.48	
$Fe^{+3} + SO_4^{-2} \rightleftharpoons FeSO_4^{+}$	$\log K_{f1} =$	4.04	
$FeSO_4^{+} + SO_4^{-2} \rightleftharpoons Fe(SO_4)_2^{-}$	$\log K_{f2} =$	1.34	
$Fe^{+3} + HPO_4^{-2} \rightleftharpoons FeHPO_4^{+}$	$\log K_f =$	5.43	
$Fe^{+3} + H_2PO_4^{-} \rightleftharpoons FeH_2PO_4^{+2}$	$\log K_f =$	5.43	

Lithium

$Li^{+} + H_2O \rightleftharpoons H^{+} + LiOH$	$\log K_a =$	–13.64	
$Li^{+} + SO_4^{-2} \rightleftharpoons LiSO_4^{-}$	$\log K_f =$	0.64	

Lead

$Pb^{+2} + H_2O \rightleftharpoons H^{+} + PbOH^{+}$	$\log K_{a1} =$	–7.60	
$PbOH^{+} + H_2O \rightleftharpoons H^{+} + Pb(OH)_2(aq)$	$\log K_{a2} =$	–9.50	
$Pb(OH)_2(aq) + H_2O \rightleftharpoons H^{+} + Pb(OH)_3^{-}$	$\log K_{a3} =$	–11.00	
$Pb(OH)_3^{-} + H_2O \rightleftharpoons H^{+} + Pb(OH)_4^{-2}$	$\log K_{a4} =$	–11.61	
$2\ Pb^{+2} + H_2O \rightleftharpoons Pb_2OH^{+3} + H^{+}$	$\log K_{21} =$	–6.40	
$3\ Pb^{+2} + 4\ H_2O \rightleftharpoons Pb_3(OH)_4^{+2} + 4H^{+}$	$\log K_{34} =$	–23.89	
$4\ Pb^{+2} + 4\ H_2O \rightleftharpoons Pb_4(OH)_4^{+4} + 4H^{+}$	$\log K_{44} =$	–19.99	
$Pb(OH)_2(s) \rightleftharpoons Pb^{+2} + 2OH^{-}$	$\log K_s =$	–19.85	
$Pb^{+2} + Cl^{-} \rightleftharpoons PbCl^{-}$	$\log K_{f1} =$	1.55	
$PbCl^{-} + Cl^{-} \rightleftharpoons PbCl_2(aq)$	$\log K_{f2} =$	0.65	

$PbCl_2(aq) + Cl^- \rightleftharpoons PbCl_3^-$	log K_{f3} =	–0.40	
$PbCl_3^- + Cl^- \rightleftharpoons PbCl_4^{-2}$	log K_{f4} =	–0.34	
$Pb^{+2} + F^- \rightleftharpoons PbF^-$	log K_{f1} =	1.85	
$PbF^- + F^- \rightleftharpoons PbF_2(aq)$	log K_{f2} =	1.29	
$PbF_2(aq) + F^- \rightleftharpoons PbF_3^-$	log K_{f3} =	0.28	
$PbF_3^- + F^- \rightleftharpoons PbF_4^{-2}$	log K_{f4} =	–0.32	
$Pb^{+2} + HCO_3^- \rightleftharpoons PbHCO_3^+$	log K_f =	2.87	
$Pb^{+2} + CO_3^{-2} \rightleftharpoons PbCO_3(aq)$	log K_{f1} =	7.24	
$PbCO_3(aq) + CO_3^{-2} \rightleftharpoons Pb(CO_3)_2^{-2}$	log K_{f2} =	3.40	
$PbCO_3(s) \rightleftharpoons Pb^{+2} + CO_3^{-2}$	log K_s =	–13.13	cerrusite
$Pb^{+2} + SO_4^{-2} \rightleftharpoons PbSO_4(aq)$	log K_{f1} =	2.69	
$PbSO_4(aq) + SO_4^{-2} \rightleftharpoons Pb(SO_4)^{-2}$	log K_{f2} =	0.78	
$PbSO_4(s) \rightleftharpoons Pb^{+2} + SO_4^{-2}$	log K_s =	–7.79	anglesite

Magnesium

$Mg^{+2} + H_2O \rightleftharpoons H^+ + MgOH^+$	log K_a =	–11.40	
$Mg(OH)_2(s) \rightleftharpoons Mg^{+2} + 2\ OH^-$	log K_s =	–11.16	brucite
$Mg^{+2} + F^- \rightleftharpoons MgF^+$	log K_f =	2.05	
$Mg^{+2} + HCO_3^- \rightleftharpoons MgHCO_3^+$	log K_f =	1.01	
$Mg^{+2} + CO_3^{-2} \rightleftharpoons MgCO_3(aq)$	log K_f =	2.92	
$MgCO_3(s) \rightleftharpoons Mg^{+2} + CO_3^{-2}$	log K_s =	–7.46	magnesite
$CaMg(CO_3)_2(s) \rightleftharpoons Ca^{+2} + Mg^{+2} + 2\ CO_3^{-2}$	log K_s =	–16.54	dolomite
$Mg^{+2} + SO_4^{-2} \rightleftharpoons MgSO_4(aq)$	log K_f =	2.26	
$Mg^{+2} + PO_4^{-3} \rightleftharpoons MgPO_4^-$	log K_f =	6.59	
$Mg^{+2} + HPO_4^{-2} \rightleftharpoons MgHPO_4(aq)$	log K_f =	2.87	
$Mg^{+2} + H_2PO_4^- \rightleftharpoons MgH_2PO_4^+$	log K_f =	1.51	

Manganese

$Mn^{+2} + H_2O \rightleftharpoons H^+ + MnOH^+$	log K_a =	–10.60	
$Mn(OH)_2(s) \rightleftharpoons Mn^{+2} + 2\ OH^-$	log K_s =	–12.81	pyrochroite
$Mn^{+2} + F^- \rightleftharpoons MnF^+$	log K_f =	0.84	
$Mn^{+2} + Cl^- \rightleftharpoons MnCl^+$	log K_{f1} =	0.61	
$MnCl^+ + Cl^- \rightleftharpoons MnCl_2(aq)$	log K_{f2} =	–0.36	
$MnCl_2(aq) + Cl^- \rightleftharpoons MnCl_3^-$	log K_{f3} =	–0.56	
$Mn^{+2} + HCO_3^- \rightleftharpoons MnHCO_3^+$	log K_f =	1.30	
$Mn^{+2} + CO_3^{-2} \rightleftharpoons MnCO_3(aq)$	log K_f =	4.90	
$MnCO_3(s) \rightleftharpoons Mn^{+2} + CO_3^{-2}$	log K_s =	–10.58	rhodocrosite
$Mn^{+2} + SO_4^{-2} \rightleftharpoons MnSO_4(aq)$	log K_f =	2.25	

Nickel

$Ni^{+2} + H_2O \rightleftharpoons H^+ + NiOH^+$	log K_{a1} =	–9.90	
$NiOH^+ + H_2O \rightleftharpoons H^+ + Ni(OH)_2(aq)$	log K_{a2} =	–9.10	
$Ni(OH)_2(aq) + H_2O \rightleftharpoons H^+ + Ni(OH)_3^-$	log K_{a3} =	–11.00	
$Ni^{+2} + Cl^- \rightleftharpoons NiCl^+$	log K_{f1} =	0.41	
$NiCl^+ + Cl^- \rightleftharpoons NiCl_2(aq)$	log K_{f2} =	–2.30	
$Ni^{+2} + CO_3^{-2} \rightleftharpoons NiCO_3(aq)$	log K_f =	4.57	
$Ni^{+2} + HCO_3^- \rightleftharpoons NiHCO_3^+$	log K_f =	2.09	
$Ni^{+2} + SO_4^{-2} \rightleftharpoons NiSO_4(aq)$	log K_{f1} =	2.30	
$NiSO_4(aq) + SO_4^{-2} \rightleftharpoons Ni(SO_4)_2^{-2}$	log K_{f2} =	–1.48	

Potassium

$K^+ + H_2O \rightleftharpoons H^+ + KOH$	log K_a =	–14.46	
$K^+ + SO_4^{-2} \rightleftharpoons KSO_4^-$	log K_f =	0.85	
$K^+ + HPO_4^{-2} \rightleftharpoons KHPO_4^-$	log K_f =	0.29	

Silicon

$SiO_2(s) + 2H_2O \rightleftharpoons H_4SiO_4(aq)$	log K =	–2.71 –3.98	amorphous quartz
$H_4SiO_4(aq) \rightleftharpoons H^+ + H_3SiO_4^-$	log K_{a1} =	–9.83	
$H_3SiO_4^- \rightleftharpoons H^+ + H_2SiO_4^{-2}$	log K_{a2} =	–13.17	

Sodium

$Na^+ + H_2O \rightleftharpoons H^+ + NaOH$	log K_a =	–14.18	
$NaCl(s) \rightleftharpoons Na^+ + Cl^-$	log K_s =	1.60	halite
$Na^+ + F^- \rightleftharpoons NaF(aq)$	log K_f =	–0.20	
$Na^+ + HCO_3^- \rightleftharpoons NaHCO_3(aq)$	log K_f =	–0.25	
$Na^+ + CO_3^{-2} \rightleftharpoons NaCO_3^-$	log K_f =	1.27	
$Na^+ + HPO_4^{-2} \rightleftharpoons NaHPO_4^-$	log K_f =	0.29	
$Na^+ + SO_4^{-2} \rightleftharpoons NaSO_4^-$	log K_f =	0.73	

Strontium

$Sr^{+2} + H_2O \rightleftharpoons H^+ + SrOH^+$	log K_a =	–13.18	
$Sr^{+2} + F^- \rightleftharpoons SrF^+$	log K_f =	0.55	
$Sr^{+2} + CO_3^{-2} \rightleftharpoons SrCO_3(aq)$	log K_f =	2.81	
$SrCO_3(s) \rightleftharpoons Sr^{+2} + CO_3^{-2}$	log K_s =	–9.27	strontianite
$Sr^{+2} + HCO_3^- \rightleftharpoons SrHCO_3^+$	log K_f =	1.21	
$Sr^{+2} + SO_4^{-2} \rightleftharpoons SrSO_4(aq)$	log K_f =	2.30	
$SrSO_4(s) \rightleftharpoons Sr^{+2} + SO_4^{-2}$	log K_s =	–6.62	celestite

Vanadium (III)

$V^{+3} + H_2O \rightleftharpoons H^+ + VOH^{+2}$	log K_{a1} =	–2.30
$VOH^{+2} + H_2O \rightleftharpoons H^+ + V(OH)_2^+$	log K_{a2} =	–3.98
$V(OH)_2^+ + H_2O \rightleftharpoons H^+ + V(OH)_3(aq)$	log K_{a3} =	–5.19
$2\ V^{+3} + 2\ H_2O \rightleftharpoons V_2(OH)_2^{+4} + 2\ H^+$	log K_{22} =	–3.79
$2\ V^{+3} + 3\ H_2O \rightleftharpoons V_2(OH)_3^{+3} + 3\ H^+$	log K_{23} =	–10.12
$V^{+3} + SO_4^{-2} \rightleftharpoons VSO_4^+$	log K_f =	2.67

Zinc

$Zn^{+2} + H_2O \rightleftharpoons H^+ + ZnOH^+$	log K_{a1} =	–9.00	
$ZnOH^+ + H_2O \rightleftharpoons H^+ + Zn(OH)_2(aq)$	log K_{a2} =	–8.80	
$Zn(OH)_2(aq) + H_2O \rightleftharpoons H^+ + Zn(OH)_3^-$	log K_{a3} =	–10.30	
$Zn(OH)_3^- + H_2O \rightleftharpoons H^+ + Zn(OH)_4^{-2}$	log K_{a4} =	–12.40	
$Zn(OH)_2(s) \rightleftharpoons Zn^{+2} + 2OH^-$	log K_s =	–15.80	
$Zn^{+2} + Cl^- \rightleftharpoons ZnCl^-$	log K_{f1} =	0.40	
$ZnCl^- + Cl^- \rightleftharpoons ZnCl_2(aq)$	log K_{f2} =	0.20	
$ZnCl_2(aq) + Cl^- \rightleftharpoons ZnCl_3^-$	log K_{f3} =	–0.10	
$ZnCl_3^- + Cl^- \rightleftharpoons ZnCl_4^{-2}$	log K_{f4} =	–0.30	
$Zn^{+2} + HCO_3^- \rightleftharpoons ZnHCO_3^+$	log K_f =	1.50	
$Zn^{+2} + CO_3^{-2} \rightleftharpoons ZnCO_3(aq)$	log K_{f1} =	5.30	
$ZnCO_3(aq) + CO_3^{-2} \rightleftharpoons Zn(CO_3)_2^{-2}$	log K_{f2} =	4.33	
$ZnCO_3(s) \rightleftharpoons Zn^{+2} + CO_3^{-2}$	log K_s =	–10.00	smithsonite
$Zn^{+2} + SO_4^{-2} \rightleftharpoons ZnSO_4(aq)$	log K_{f1} =	2.34	
$ZnSO_4(aq) + SO_4^{-2} \rightleftharpoons Zn(SO_4)_2^{-2}$	log K_{f2} =	0.94	

Values above are taken from

- A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum, NY, 1974.
- W. Stumm and J. Morgan, *Aquatic Chemistry*, Wiley, Appendix 1, 3rd ed., 1996, who cite D. K. Nordstrom, L. N. Plummer, D. Langmuir, E. Busenberg, H. M. May, B. F. Jones, and D. L. Parkhurst, "Revised Chemical Equilibrium Data from Major Mineral Reactions and Their Limitations," in *Chemical Modeling of Aqueous Systems II*, D. C. Melchior and R. L Bassett, Eds., ACS Ser. 416, American Chemical Society, Washington, DC, 1990.
- *MINTEQA2: A Geochemical Assessment Model*, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division (1999), https://www.epa.gov/ceam/minteqa2-equilibrium-speciation-model, who cite *Critical Stability Constants of Metal Complexes Database*, National Institute of Standards and Technology, (NIST Standard Reference Database 46).

Soil Sampling

APPENDIX 2

Collecting Soil Samples

Collect several handfuls of each type of soil in a large ziplock bag or plastic bucket. Label the bag for future reference, describing where you collected the soil. Try as much as possible to preserve the collecting area, and carefully fill in the small hole your sampling will leave.

Ideally, it would be best for you to have soils with a variety of pH's and buffering capacities. This helps demonstrate the natural range of lake acidity, and the range of different effects that acid rain can have on lakes...

It would be most advantageous to include a rock-like or granite sample to simulate high mountain lakes with little or no buffering capacity, a soil sample high in carbonate such as limestone to demonstrate soils with a high level of natural buffering capacity, and several other soils, such as: rich garden loam, pine forest floor, soil from a burned area, maple woods, oak woods, redwood forest, ocean beach, eucalyptus woods, and so on. If you do not have access to a forest of a certain kind of tree, get a sample from directly under a tree or small grove of that type of tree...

It is ironic that soils high in carbonate (buffer) are found in arid regions, places that receive little rain (and, therefore, little acid rain). These soils are high in carbonate because it has not been leached (washed) out of the soil by water...

Perhaps the simplest approach to collecting soil samples is to look for dramatic differences in environment. Collect a soil that is affected by a variable, and one that is not affected by that variable. Following are some suggested quick strategies for finding soils of differing pH:

- Soils of different wetness: from a very wet area, from a continuously dry area, and from a somewhat moist area.
- Soils affected by different plants: under perennial plants, under annual plants (collect these two soils at the same measured depth from the surface); soil under a deciduous tree, under a coniferous tree, soil that has no large plants growing on it.
- Soil from beneath a very young tree, soil from beneath an older tree.
- Soil that is under a post in or a yard that neighborhood dogs frequent, soil that is not affected by dog urine.
- Soils affected by human use: in a fertilized field, in a fallow field, in a range land, in a uncultivated field, in an area built on fill transported from another area; soil near a parking lot, garage, or other area where internal combustion engine exhaust would settle.
- Soils on very different slopes: at the apex of a hill, at the backslope, at the toeslope.
- Potting soils, sand from sandboxes, kitty litter, vermiculite from packing. Call companies listed under “Soils” in the Yellow Pages. They may have different soils or fill dirt available.

Soil Histories

Many of the quick strategies for obtaining different types of soil mentioned above are based on finding soils with a variety of soil histories. A brief summary of how soil histories vary many be helpful to you. Soil histories can differ due to variations in these soil-forming factors: parent material, climate, organisms, topography, and time. These factors act in concert to form any given soil. To find soils with different pH's, locate distinct variations in these factors.

Parent material is the geologic deposit from which a soil is weathered. Examples of different geologic deposits are: volcanic ash, volcanic rock, deposits of sediments via wind or water, glacial deposits, or bedrock. Soils weathered from different parent geological material can differ widely in pH. For example, a soil weathered from a sedimentary sandstone rock has a markedly different acidity than a soil weathered from a limestone rock.

Climate refers to the average of cyclical differences in temperature and the amount and patterns of precipitation. To find soils affected by changes in climatic temperature, look for a soil in an open, sunny field and one under the cool shade of a building or a tree. To find soils subjected to different patterns of precipitation, look for soils on the dry and moist sides of a hill.

Organisms are the people, other animals, and plants that live in and on the soil environment. Organisms add some material to the soil and take other away from it, thereby cycling nutrients. By cycling nutrients, organisms affect the soil pH. Likewise, organisms are affected by the pH of the soil around them. When looking for samples with different pH's, due to the action of soil organisms, try: soils found under different plants, such as agricultural crops, tree roots, shrubs, grasses, or flowers; soils found in a wild field and soil found in a rangeland, soil in a lawn or park and soil found in an empty lot.

Topography is the lay of the land; how flat or hilly it is. Topography will affect the water table and erosion. A soil at a hill crest will have a different water table that one found in a creek bed or river bed, and so is likely to have a different pH.

Time is how long the soil has been forming, how long it has been undergoing chemical and physical changes. If a soil has been in place for a long time, it will have different properties than one that has been there for less time. An older soil tends to have smaller particles than one that is younger soil (an indication of how much clay there is). Often, older soils also have a reddish color. Soils on a shoulder slope have not been in place as long as soils at a toeslope, and so may have different acidities.

This appendix was taken from the Explorer Databases developed jointly by the University of Kansas UNITE group and the Great Lakes Collaborative. It was previously online at
http://unite2.tisl.ukans.edu/UNITEResource/783749568-447DED81.rsrc

Corrections for Ionic Strength

APPENDIX 3

CREATING THE CONTEXT

The equilibrium law,

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D} \qquad K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b},$$

is an *ideal* law and only holds in the ideal case where ions and molecules act independently of each other. Solutions must either be very dilute or involve no ions. Interactions between ions of opposite charge shift the position of equilibrium for all types of equilibria involving ions (K_s, K_a, K_f, etc.). The higher the charges on the ions, the greater the effect.

These effects are independent of the kind of electrolyte for moderately concentrated solutions (under 0.1 M), and dependent upon a concentration parameter called *ionic strength*,

$$\mathrm{I} = \frac{1}{2}\left\{\mathrm{c}_1 z_1^2 + \mathrm{c}_2 z_2^2 + \mathrm{c}_3 z_3^2 + \ldots\right\},$$

where c is the molarity and z is the charge on the ion. Ionic strength is a measure of how many ions are in the solution, or how non-ideal the solution. Examples:

0.1 M NaCl	$\mathrm{I} = \frac{1}{2}\{[0.1](+1)^2 + [0.1](-1)^2\} = 1(0.1) = 0.1\ \mathrm{M}$
0.1 M Na_2SO_4	$\mathrm{I} = \frac{1}{2}\{[0.2](+1)^2 + [0.1](-2)^2\} = 3(0.1) = 0.3\ \mathrm{M}$
0.1 M $MgSO_4$	$\mathrm{I} = \frac{1}{2}\{[0.1](+2)^2 + [0.1](-2)^2\} = 4(0.1) = 0.4\ \mathrm{M}$
0.1 M $Al(OH)_3$	$\mathrm{I} = \frac{1}{2}\{[0.1](+3)^2 + [0.3](-1)^2\} = 6(0.1) = 0.6\ \mathrm{M}$

Ionic strengths are additive; if a solution is both 0.04 M KOH and 0.02 M Na_2SO_4, the ionic strength is 0.04 + 3(0.02) = 0.10 M.

Corrections for non-ideal behavior when the ionic strength is not zero involve multiplying the true concentration in solution by an activity coefficient, f, in equilibrium constant expressions. The same f applies to any equilibria involving that species in a given solution, to solution conductivity, and to colligative properties (freezing point depression, etc.).

As seen in Figure A3-1, f is about 1 for uncharged species. For charged species, the activity coefficient is a function of the ionic strength, of the ion charge, and at increasing ionic strength of the ion size. In very dilute solutions, f approaches 1. In moderate ionic strength solutions, $f < 1$ due to ion pairing. In high ionic strength solutions $f > 1$ due to loss of water to ion solvation. The high ionic strength interactions are highly specific and harder to predict.

The Davies equation lets us calculate an approximate value for f:

$$f = 10^{-z^2\left\{\frac{0.51\sqrt{\mathrm{I}}}{1+\sqrt{\mathrm{I}}} - 0.15\ \mathrm{I}\right\}}.$$

Equations with more parameters have been developed but the Davies equation is sufficient for introducing the idea of activity corrections.

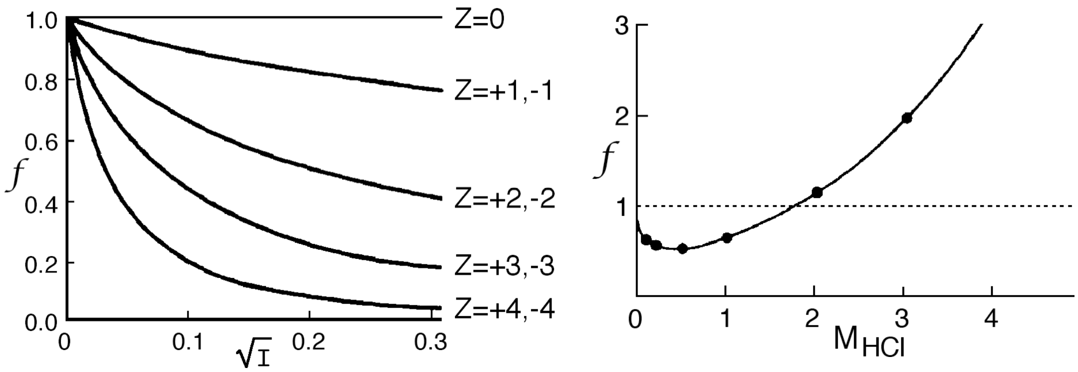


Figure A3-1. The activity coefficient, f, depends on the ion charge, Z, and the ionic strength, I, of the solution. At low ionic strength $f<1$. At very high ionic strength $f>1$ as shown for HCl.

Preparing for Inquiry

Tabulated equilibrium constants for $a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$ are normally defined in terms of activities, $K° = \dfrac{(f_\mathrm{C}[\mathrm{C}])^c(f_\mathrm{D}[\mathrm{D}])^d}{(f_\mathrm{A}[\mathrm{A}])^a(f_\mathrm{B}[\mathrm{B}])^b}$. Note that if the ion concentration is raised to a power then so is the activity coefficient.

One way to view this correction is that the tabulated values of $K°$ must be adjusted to apply to a specific ionic strength, $K' = \dfrac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = \dfrac{K°}{\dfrac{f_\mathrm{C}{}^c f_\mathrm{D}{}^d}{f_\mathrm{A}{}^a f_\mathrm{B}{}^b}}$.

In practice, an equilibrium problem is first solved without activity corrections. The ionic strength is then computed based on the preliminary concentrations and the definition of ionic strength. As needed, calculate

$$f_1 = 10^{-1\left\{\frac{0.51\sqrt{\mathrm{I}}}{1+\sqrt{\mathrm{I}}} - 0.15\,\mathrm{I}\right\}} \quad \text{for ion charge} = \pm 1$$

$$f_2 = 10^{-4\left\{\frac{0.51\sqrt{\mathrm{I}}}{1+\sqrt{\mathrm{I}}} - 0.15\,\mathrm{I}\right\}} \quad \text{for ion charge} = \pm 2$$

$$f_3 = 10^{-9\left\{\frac{0.51\sqrt{\mathrm{I}}}{1+\sqrt{\mathrm{I}}} - 0.15\,\mathrm{I}\right\}} \quad \text{for ion charge} = \pm 3$$

to adjust the value of K. The equilibrium problem is then solved again and the process repeated until a consistent result is obtained.

Do not change the charge balance or the mass balance equations. These equations are independent of ionic strength effects.

Developing Ideas

A3-1 What is $[\mathrm{H^+}]$ in 0.10 M $\mathrm{CH_3COOH}$?

Equilibria: $\dfrac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = \dfrac{1.75\times10^{-5}}{f_1^2}$, $[\mathrm{H^+}][\mathrm{OH^-}] = \dfrac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[\mathrm{H^+}] = [\mathrm{OH^-}] + [\mathrm{CH_3COO^-}]$

Mass balance: $0.10 = [\mathrm{CH_3COOH}] + [\mathrm{CH_3COO^-}]$

Ionic Strength: $I = \frac{1}{2}\left\{[H^+] + [OH^-] + [CH_3COO^-]\right\}$

For an initial estimate since the concentrations are unknown, use I = 0.0 and $f_1 = 1.00$. Substitute into the *Ka* expression,

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]([H^+]-[OH^-])}{0.10-[H^+]+[OH^-]} = \frac{1.75\times10^{-5}}{f_1^2},$$

to find $[H^+] = 1.32\times10^{-3}$ so $[OH^-] \approx 10^{-11}$, $1.32\times10^{-3} = [CH_3COO^-] = I$ and $f_1 = 10^{-1\left\{\frac{0.51\sqrt{I}}{1+\sqrt{I}}-0.15\,I\right\}} = 0.960$. A better equilibrium constant is then $\frac{1.75\times10^{-5}}{(0.960)^2} = 1.90\times10^{-5}$. Repeating the problem with this new value gives $[H^+] = [CH_3COO^-] = I = 1.37\times10^{-3}$ and $f_1 = 0.959$. Another round won't change anything so we are finished.

As expected the corrections are minimal (4%) for modest ionic strength.

The $pH = -\log f_1[H^+] = 2.881$

pH is the value measured by pH meters. This means $pH = -\log f_1[H^+]$ and $pH = 14 + \log f_1[OH^-]$

A3-2 What is $[H^+]$ in 0.10 M CH_3COOH and 1.0 M $NaNO_3$?

Equilibria: $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{1.75\times10^{-5}}{f_1^2}$, $[H^+][OH^-] = \frac{1.00\times10^{-14}}{f_1^2}$

Charge balance: $[H^+] + [Na^+] = [OH^-] + [CH_3COO^-] + [NO_3^-]$

Mass balance: $0.10 = [CH_3COOH] + [CH_3COO^-]$

$0.10 = [NO_3^-]$, $0.10 = [Na^+]$

Ionic Strength: $I = \frac{1}{2}\left\{[H^+] + [Na^+] + [OH^-] + [CH_3COO^-] + [NO_3^-]\right\}$

This time we can start with I = 1.0 from the $NaNO_3$, so $f_1 = 0.785$. Substitute into the *Ka* expression,

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]([H^+]-[OH^-])}{0.10-[H^+]+[OH^-]} = \frac{1.75\times10^{-5}}{f_1^2}.$$

$[H^+] = [CH_3COO^-] = 1.67\times10^{-3}$, $I = 1.00167$, and $f_1 = 0.785$ so we are done. Note that $[H^+]$ is 25% higher in the presence of the 1.0 M $NaNO_3$ but the pH $= -\log f_1[H^+] = 2.882$ is almost unchanged!

A3-3 What is the $[H^+]$ and pH in 0.10 M oxalic acid?

We could use the Ka_1, Ka_2, charge, mass, and ionic strength equations

$$\frac{[H^+][HOOC\text{-}COO^-]}{[HOOC\text{-}COOH]} = \frac{5.36\times10^{-2}}{f_1^2},$$

$$\frac{[H^+][OOC\text{-}COO^{-2}]}{[HOOC\text{-}COO^-]} = \frac{5.42\times10^{-5}}{f_2}$$

$$[H^+] = [OH^-] + [HOOC\text{-}COO^-] + 2\,[OOC\text{-}COO^{-2}]$$

$$0.10 = [HOOC\text{-}COOH] + [HOOC\text{-}COO^-] + [OOC\text{-}COO^{-2}]$$

$$I = \frac{1}{2}\left\{[H^+] + [OH^-] + [HOOC\text{-}COO^-] + 2\,[OOC\text{-}COO^{-2}]\right\}$$

Alternatively you could start with the species equation (Exploration 4E)

$$[H^+] = \frac{10^{-14}}{[H^+]f_1^2} + \{\alpha_1 + 2\,\alpha_2\}\,C_A \text{ with corrected } Ka \text{ values}$$

Either gives $[H^+] = [HOOC\text{-}COO^-] = 0.0511 = I$ and $f_1 = 0.820$, $f_2 = 0.451$,
which gives $[H^+] = [HOOC\text{-}COO^-] = 0.0580 = I$ and $f_1 = 0.812$, $f_2 = 0.435$,
which gives $[H^+] = [HOOC\text{-}COO^-] = 0.0583 = I$ and $f_1 = 0.812$, $f_2 = 0.435$.
The pH would be $-\log f_1[H^+] = 1.325$.

A3-4 What is the $[H^+]$ and pH of excess $Th(OH)_4(s)$ in water?

$$\frac{4\times10^{-43}}{f_4\,f_1^{\,4}} = K_s = [Th^{+4}][OH^-]^4 \text{ and } \frac{1.01\times10^{-14}}{f_1^{\,2}} = K_w = [H^+][OH^-]$$

Charge balance is ~~$4\,[Th^{+4}]$~~ $+ [H^+] = [OH^-]$ if assume small solubility.
For I=0, $[OH^-] = 1.0\times10^{-7}$; $f_1 = 0.9996$, $f_4 = 0.9941$ and $[OH^-] = 1.0\times10^{-7}$

$$[Th^{+4}] = \frac{4\times10^{-43}}{f_4\,f_1^{\,4}[OH^-]^4} = 3.9\times10^{-15} \text{ so assumption was good. pH} = 7.00$$

Applying Your Ideas

A3-5 Calculate the ionic strength of a solution that contains

a. 0.210 M Na_2SO_4

b. 0.053 M KCl, 0.0372 M $Sr(ClO_4)_2$, and 0.218 M $La(NO_3)_3$

c. 0.623 M Na_2SO_4, 0.250 M NaBr, and 0.0236 M $Al_2(SO_4)_3$

d. 750 mL 0.0854 M $CaCl_2$ added to 250 mL 0.0032 M KIO_3 (dilution!)

A3-6 Using activity corrections according to the Davies equation, determine the ionic strength, activity coefficients, the $[H^+]$ and the pH that results for a solution of

a. 0.048 M $Na_2C_2O_4$ in distilled water

b. 0.048 M $Na_2C_2O_4$ in 0.00076 M $KClO_4$

c. 0.048 M $Na_2C_2O_4$ in 0.00076 M $HClO_4$

A3-7 Solve these problems using activity corrections according to the Davies equation.

a. 3C-6

b. 4E-2

c. 4E-3

d. 4E-4

Redox and the Nernst Equation

APPENDIX 4

CREATING THE CONTEXT

Most of this module has concerned chemical equilibrium or occasionally the direction a reaction will proceed to reach equilibrium. Non-equilibrium systems where components are separated by a semipermeable membrane are also of interest. In these cases an electrochemical voltage develops across the membrane based on how far the system is from equilibrium. Important examples are chemical batteries and action potentials due to ionic concentration gradients across a cell membrane.

We describe these systems by the oxidation reduction reaction occurring on each side, writing half reactions in the reduction direction (IUPAC convention) with e^- *always on left side*: $a\text{A} + b\text{B} + ... + ne^- \rightleftharpoons c\text{C} + d\text{D} + ...$

The Nernst Equation

The Nernst equation is used to find the voltage of the half-reactions:

$$E = E° - \frac{RT}{nF}\ln\left\{\frac{(f[\text{C}])^c(f[\text{D}])^d}{(f[\text{A}])^a(f[\text{B}])^b}\right\} = E° - \frac{RT}{nF}\ln(10)\log\left\{\frac{(f[\text{C}])^c(f[\text{D}])^d}{(f[\text{A}])^a(f[\text{B}])^b}\right\}$$

$E°$ is the standard reduction potential, the voltage when all $f[\ \ ]=1$. Similar to looking up K in a table you often look up $E°$ in a table. Note that { } has same form as K for the half-reaction but the expression is not a constant since the system is usually not at equilibrium. As for K, any solvents, pure liquids, and pure solids do not appear in the expression.

$R = \dfrac{8.31446261815324 \text{ volt coulomb}}{\text{K mole}}$
(volt coulomb = Joule)
T = temperature in K
n = number of electrons
(activity of electron is 1)
F = 96485.3321233 coulombs/mole
(F is Faraday's constant)

For 25°C, $\dfrac{RT}{F} = 0.02569$ volts and $\dfrac{RT}{F}\ln(10) = 0.05916$ volts.

Electrochemical Cells

Two half-reactions are combined in an electrochemical cell:

left electrode | left electrolyte || right electrolyte | right electrode

Slashes or vertical lines are phase boundaries where charge carriers change and the combined voltage is $E_{CELL} = E_{RIGHT} - E_{LEFT}$. The minus sign acknowledges that the left electrode reaction will be an oxidation. If the redox reaction does not involve a solid metal, Pt is often used as an inert electrode.

Problem A4-A

Find E_{CELL} for Ag | $f[\text{Ag}^+] = 0.010$ || $f[\text{Fe}^{+3}] = 0.0050$, $f[\text{Fe}^{+2}] = 0.0030$ | Pt

$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$ $E° = +.7993$ V $\qquad$ $\text{Fe}^{+3} + e^- \rightleftharpoons \text{Fe}^{+2}$ $E° = +.771$ V

$E_{LEFT} = .7993 - 0.05916 \log\dfrac{1}{.01} = .6810$ $\qquad$ $E_{RIGHT} = .771 - 0.05916\log\dfrac{.003}{.005} = .7841$

$$E_{CELL} = E_{RIGHT} - E_{LEFT} = 0.7841 - 0.6810 = 0.1031$$

Some Reference Electrodes

If you are only interested in one redox reaction then a well known reaction might be used for one of the half reactions.

The SHE potential of $2\,H^+ + 2\,e^- = H_2(g)$ is defined as zero, $E^o = 0$ V

$$\text{Pt} \,|\, f\,[H^+] = 1.000\text{ M},\ H_2(g) = 1.000\text{ atm} \,\|$$

A desirable feature of a reference electrode is for the electrode potential to remain unchanged even if some current flows. Common and more practical reference electrodes (no hydrogen tank) use K_s to buffer concentrations:

SCE electrode, $E_f = 0.241$	Ag/AgCl electrode, $E_f = 0.197$
$\text{Hg} \,|\, \text{KCl(s)}, \text{Hg}_2\text{Cl}_2\text{(s)} \,\|$	$\text{Ag} \,|\, \text{KCl(s)}, \text{AgCl(s)} \,\|$
Calomel is an old name for mercury chloride	

PREPARING FOR INQUIRY

Relating E to K_a, K_f, K_s

1. For each half cell reaction, write the Nernst equation involving the element and dependent on M^{+n} or H^+.
2. M^{+n} or H^+ is found from the K_a, K_f, or K_s expression.
3. Substitute in given conditions
   a. Equilibrium constant value
   b. For $E°$, all activities (concentrations) equal one.
   c. Given E or E_{CELL} for specified concentrations.

Some Example Redox Problems

A4-B. Find $E°$ for $Pb(OH)_2(s) + 2e^- \rightleftharpoons Pb(s) + 2OH^-$.

A4-C. Find K_s for $Hg_2(CH_3COO)_2$ given $E_{CELL} = 0.596$ V for
SHE $\|$ $0.0100 = [CH_3COO^-]$, saturated $Hg_2(CH_3COO)_2$ $|$ Hg

A4-D. Find $E°$ for $Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$

A4-E. Find K_a for CH_3COOH given $E_{CELL} = 0.445$ V for
Pt $|$ 1.00 atm H_2, 0.0100 M CH_3COOH $\|$ SCE

Answers (with steps numbered)

A4-B. Find $E°$ for $Pb(OH)_2(s) + 2e^- \rightleftharpoons Pb(s) + 2OH^-$.

1. $Pb^{+2} + 2e^- \rightleftharpoons Pb \quad E° = -.126;\ E = -.126 - \dfrac{0.05916}{2}\log\dfrac{1}{[Pb^{+2}]}$

2. $[Pb^{+2}]$ is found from $K_s = [Pb^{+2}][OH^-]^2 = 8{\times}10^{-16}$

   $[Pb^{+2}] = \dfrac{8\times10^{16}}{[OH^-]^2};\ E = -.126 - \dfrac{0.05916}{2}\log\dfrac{[OH^-]^2}{8\times10^{16}}$

3. $E°$ for $Pb(OH)_2(s) + 2e^- \rightleftharpoons Pb(s) + 2OH^-$ means the potential when $[OH^-] = 1.00$. $[Pb^{+2}] \neq 1.00$ since it is not a species in the $E°$ equation.

   $E°_{Pb(OH)_2} = -.126 - \dfrac{0.05916}{2}\log\dfrac{1}{8\times10^{16}} = -.57$ V

A4-C. Find K_s for $Hg_2(CH_3COO)_2$ given $E_{CELL} = 0.596$ V for
SHE $\|$ $0.0100 = [CH_3COO^-]$, saturated $Hg_2(CH_3COO)_2$ $|$ Hg

1. $Hg_2^{+2} + 2e^- \rightleftharpoons 2Hg(l) \quad E° = 0.796;\ E = 0.796 - \dfrac{0.05916}{2}\log\dfrac{1}{[Hg_2^{+2}]}$

2. $[Hg_2^{+2}]$ is found from $K_s = [Hg_2^{+2}][CH_3COO^-]^2$

$$[Hg_2^{+2}] = \frac{K_s}{[CH_3COO^-]^2};\ E = 0.796 - \frac{0.05916}{2}\log\frac{[CH_3COO^-]^2}{K_s}$$

3. When $[CH_3COO^-] = 0.0100$ M, we know $E_{CELL} = E_{RIGHT} - E_{LEFT} = E_{RIGHT} - 0$ V

$$0.596 = 0.796 - \frac{0.05916}{2}\log\frac{(.0100)^2}{K_s};\ 10\ \frac{2(.596 - .788)}{-0.05916} = \frac{.01^2}{K_s};\ K_s = 1.73\times10^{-11}$$

A4-D. Find $E°$ for $Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$

1. $Ag^+ + e^- \rightleftharpoons Ag\ \ E° = .7993;\ E = .7993 - 0.05916\log\frac{1}{[Ag^+]}$

2. $[Ag^+]$ is found from $K_{f1}K_{f2} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 10^{3.31+3.92}$

$$[Ag^+] = \frac{[Ag(NH_3)_2^+]}{10^{7.23}[NH_3]^2};\ E = .7993 - 0.05916\log\frac{10^{7.23}[NH_3]^2}{[Ag(NH_3)_2^+]}$$

3. $E°$ for $Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$ means the potential when
$[NH_3] = [Ag(NH_3)_2^+] = 1.00$. $[Ag^+] \neq 1.00$ since it is not in the $E°$ equation.
$E = .7993 - 0.05916\log 10^{7.23} = 0.372$

A4-E. Find K_a for CH_3COOH given $E_{CELL} = 0.445$ V for
Pt | 1.00 atm H_2, 0.0100 M CH_3COOH || SCE

1. $2H^+ + 2e^- \rightleftharpoons H_2\ \ E° = 0;\ E = 0 - \frac{0.05916}{2}\log\frac{[H_2(g)]}{[H^+]^2}$
2. $[H^+]$ is found from $K_a = [H^+][CH_3COO^-]/[CH_3COOH]$
3. When $C_a = 0.0100$ M, we know $0.445 = E_{RIGHT} - E_{LEFT} = 0.241 - E_{LEFT}$
$E_{LEFT} = -.204 = 0.05916\log[H^+];\ [H^+] = 3.56\times10^{-4}$
From charge balance $[H^+] = [CH_3COO^-] + [OH^-]$, $[CH_3COO^-] = 3.56\times10^{-4}$
From mass balance $C_a = [CH_3COOH] + [CH_3COO^-]$, $[CH_3COOH] = 0.00964$
$K_a = [H^+][CH_3COO^-]/[CH_3COOH] = 1.31\times10^{-5}$

DEVELOPING IDEAS

Since redox reactions can be related to equilibria, many of the same types of graphical representations are useful.

Redox Distribution Diagrams

E can be used as a master variable to determine relative concentrations.

$V^{+2} + 2\,e^- \rightleftharpoons V(s)$ E° = –1.125 V
$V^{+3} + e^- \rightleftharpoons V^{+2}$ E° = –0.255 V
$VO^{+2} + e^- + 2\,H^+ \rightleftharpoons V^{+3} + H_2O$ E° = 0.337 V
$VO_2^+ + e^- + 2\,H^+ \rightleftharpoons VO^{+2} + H_2O$ E° = 1.001 V

$$E = -1.125 - \frac{0.05916}{2}\log\frac{[V(s)]}{[V^{+2}]}; \qquad \frac{[V^{+2}]}{[V(s)]} = 10^{\frac{2(E+1.125)}{0.05916}}$$

$$E = -0.255 - \frac{0.05916}{1}\log\frac{[V^{+2}]}{[V^{+3}]}; \qquad \frac{[V^{+3}]}{[V^{+2}]} = 10^{\frac{E+.255}{0.05916}}$$

$$E = +0.337 - \frac{0.05916}{1}\log\frac{[V^{+3}]}{[VO^{+2}][H^{+}]^{2}}; \qquad \frac{[VO^{+2}]}{[V^{+3}]} = 10^{\frac{E-.337}{0.05916} + 2\text{ pH}}$$

$$E = +1.001 - \frac{0.05916}{1}\log\frac{[VO^{+2}]}{[VO_2^{+}][H^{+}]^{2}}; \qquad \frac{[VO_2^{+}]}{[VO^{+2}]} = 10^{\frac{E-1.001}{0.05916} + 2\text{ pH}}$$

$$C_V = [V^{+2}] + [V^{+3}] + [VO^{+2}] + [VO_2^{+}]$$

$$C_{V(aq)} = [V^{+2}]\left\{1 + \frac{[V^{+3}]}{[V^{+2}]} + \frac{[V^{+3}]}{[V^{+2}]}\frac{[VO^{+2}]}{[V^{+3}]} + \frac{[V^{+3}]}{[V^{+2}]}\frac{[VO^{+2}]}{[V^{+3}]}\frac{[VO_2^{+}]}{[VO^{+2}]}\right\}$$

(If vanadium metal is present, $C_{V(aq)}$ becomes voltage dependent and the mass balance is not a constant!)

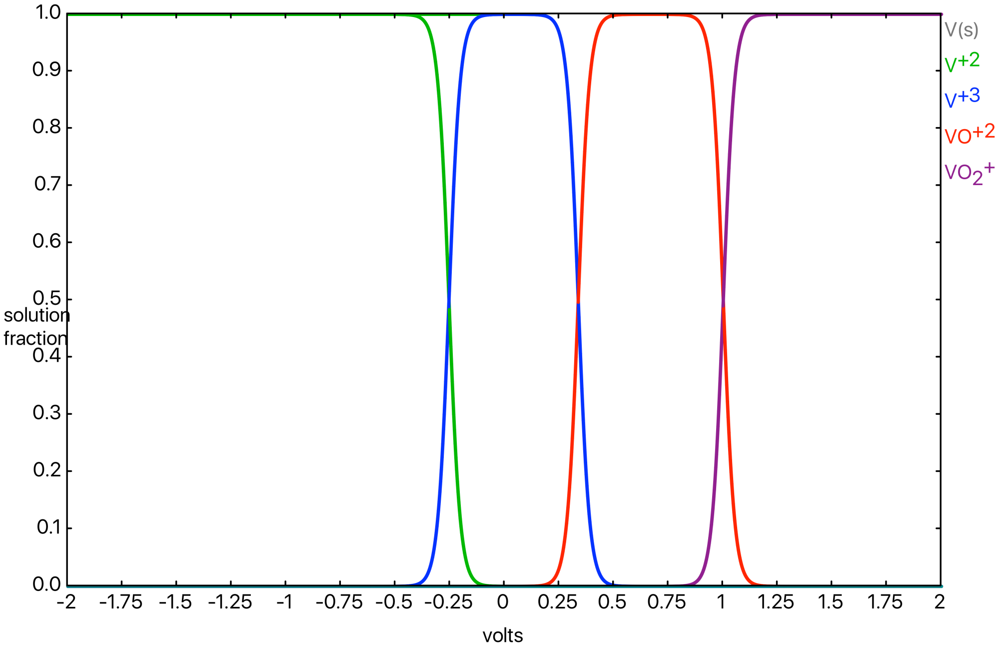


Figure A4-1. Distribution Diagram for the oxidation states of vanadium.

Problem A4-F

Label the curves with the proper chemical formula.

At what voltages do the species switch?

- ✓ At large positive voltages species have lost electrons and oxidized forms predominate (or oxidizing agents have large positive voltages.)
- ✓ At large negative voltages species have gained electrons and reduced forms predominate (or reducing agents have negative voltages.)

Calculating equivalence point potentials

Equal voltage for half reactions in the same beaker or they would react further.

$$\mathbf{Fe^{+2} + Ce^{+4} \rightleftharpoons Fe^{+3} + Ce^{+3}}$$

$$E = 0.68 - .05916 \log \frac{[Fe^{+2}]}{[Fe^{+3}]} = 1.44 - .05916 \log \frac{[Ce^{+3}]}{[Ce^{+4}]}$$

Add the two Nernst equations to put the concentrations all in one term.

$$E = 0.68 - .05916 \log \frac{[Fe^{+2}]}{[Fe^{+3}]} \text{ for } Fe^{+3} + e^- \rightleftharpoons Fe^{+2}$$

$$\underline{E = 1.44 - .05916 \log \frac{[Ce^{+3}]}{[Ce^{+4}]} \text{ for } Ce^{+4} + e^- \rightleftharpoons Ce^{+3}}$$

$$2E = 0.68 + 1.44 - .05916 \log \frac{[Fe^{+2}][Ce^{+3}]}{[Fe^{+3}][Ce^{+4}]}$$

By electron balance (species that lose electrons must equal species that gain electrons, all relative to the starting materials), $[Ce^{+3}] = [Fe^{+3}]$.

At equivalence point $[Fe^{+2}] = [Ce^{+4}]$, so $E = \frac{0.68 + 1.44}{2} = 1.06$ V

$$\mathbf{MnO_4^- + 8\,H^+ + 5\,Fe^{+2} \rightleftharpoons Mn^{+2} + 5\,Fe^{+3} + 4\,H_2O}$$

$$E = 0.68 - \frac{0.05916}{1} \log \frac{[Fe^{+2}]}{[Fe^{+3}]} = 1.51 - \frac{0.05916}{5} \log \frac{[Mn^{+2}]}{[MnO_4^-][H^+]^8}$$

Add the two Nernst equations to put the concentrations all in one term.

$$E = 0.68 - .05916 \log \frac{[Fe^{+2}]}{[Fe^{+3}]} \text{ for } Fe^{+3} + e^- \rightleftharpoons Fe^{+2}$$

$$\underline{5\left\{ E = 1.51 - \frac{.05916}{5} \log \frac{[Mn^{+2}]}{[MnO_4^-][H^+]^8} \right\} \text{ for } MnO_4^- + 8H^+ + 5\,e^- \rightleftharpoons Mn^{+2} + 4\,H_2O}$$

$$6\,E = 0.68 + 5\,(1.51) - .05916 \log \frac{[Fe^{+2}][Mn^{+2}]}{[Fe^{+3}][MnO_4^-][H^+]^8}$$

By electron balance, $5\,[Mn^{+2}] = [Fe^{+3}]$.

At equivalence point $[Fe^{+2}] = 5\,[MnO_4^-]$, so $E = \frac{0.68 + 5(1.51) + .05916 \log[H^+]^8}{6}$.

$$\mathbf{U^{+4} + 2\,Ce^{+4} + 2\,H_2O \rightleftharpoons UO_2^{+2} + 4\,H^+ + 2\,Ce^{+3}}$$

$$E = 1.44 - .05916 \log \frac{[Ce^{+3}]}{[Ce^{+4}]} = 0.334 - \frac{0.05916}{2} \log \frac{[U^{+4}]}{[UO_2^{+2}][H^+]}$$

Add the two Nernst equations to put the concentrations all in one term.

$$E = 1.44 - .05916 \log \frac{[Ce^{+3}]}{[Ce^{+4}]} \text{ for } Ce^{+4} + e^- \rightleftharpoons Ce^{+3}$$

$$\underline{2\left\{ E = 0.334 - \frac{.05916}{2} \log \frac{[U^{+4}]}{[UO_2^{+2}][H^+]^4} \right\} \text{ for } UO_2^{+2} + 4\,H^+ + 2\,e^- \rightleftharpoons U^{+4} + 2\,H_2O}$$

$$3E = 1.44 + 2\,(0.334) - .05916 \log \frac{[Ce^{+3}][U^{+4}]}{[Ce^{+4}][UO_2^{+2}][H^+]^4})$$

By electron balance, $[Ce^{+3}] = 2\,[UO_2^{+2}]$.

At equivalence point $[Ce^{+4}] = 2\,[U^{+4}]$, so $E = \frac{1.44 + 2(0.334) + .05916 \log[H^+]^4}{3}$.

Problem A4-G

$$Fe^{+2} + Ce^{+4} \rightleftharpoons Fe^{+3} + Ce^{+3}$$
$$MnO_4^{-} + 8\ H^{+} + 5\ Fe^{+2} \rightleftharpoons Mn^{+2} + 5\ Fe^{+3} + 4\ H_2O$$
$$U^{+4} + 2\ Ce^{+4} + 2\ H_2O \rightleftharpoons UO_2^{+2} + 4\ H^{+} + 2\ Ce^{+3}$$

For which of these reactions does the equivalence point depend on pH?

For which of these reactions is the equivalence point an inflection point of the titration curve?

Since indicators respond to changes in potential rather than direct changes in activity of a species, what indicator should be used for each of these titrations?

Redox Titration Calculations

Consider the titration of 50.0 mL of 0.0500 M Fe^{+2} with 0.020 M MnO_4^{-} versus an SCE electrode where both solutions are also 1.0 M H_2SO_4.

1. What is the titration reaction?

$$MnO_4^{-} + 8H^{+} + 5Fe^{+2} \rightleftharpoons Mn^{+2} + 5Fe^{+3}$$

2. Which Nernst equation should be used?

For half reactions in the same beaker the voltage must be equal or they would react further. Use the one whose concentrations are easiest to calculate.

$$E_{RIGHT} = 0.68 - \frac{0.05916}{1}\log\frac{[Fe^{+2}]}{[Fe^{+3}]} = 1.51 - \frac{0.05916}{5}\log\frac{[Mn^{+2}]}{[MnO_4^{-}][H^{+}]^8}$$

3. Calculate E_{RIGHT} for various mL added.

0 mL added

$$E_{RIGHT} = 0.68 - .05916\log\frac{[Fe^{+2}]}{[Fe^{+3}]}$$

Can't do calculation since $[Fe^{+3}]$ is very small and unknown.

$$E_{RIGHT} = 1.51 - \frac{0.05916}{5}\log\frac{[Mn^{+2}]}{[MnO_4^{-}][H^{+}]^8}$$

Can't do calculation since $[Mn^{+2}]$ and $[MnO_4^{-}]$ both very small and unknown.

The Nernst equation can not be evaluated for 0 mL added since the voltage depends on impurities. In lab we do not record the voltage for 0 mL added.

10 mL MnO_4^{-} added

Before equivalence $[Fe^{+2}]$ is decreased by reacting with added $[MnO_4^{-}]$ and the missing moles go to make $[Fe^{+3}]$ and $[Mn^{+2}]$ according to balanced reaction. *Dilution and reaction! Calculate new concentrations.*

$$\frac{50.0}{10.0+50.0}\,0.0500\ M\ Fe^{+2} - \frac{10.0}{10.0+50.0}\,0.0200\ M\ MnO_4^{-}\,\frac{5\ mol\ Fe^{+2}}{1\ mol\ MnO_4^{-}} = 0.02500\ M\ Fe^{+2}$$

$$\frac{10.0}{10.0+50.0}\,0.0200\text{ M MnO}_4^-\,\frac{5\text{ mol Fe}^{+3}}{1\text{ mol MnO}_4^-}=0.01667\text{ M Fe}^{+3}$$

Redox Buffer! $[Fe^{+2}] = 0.02500$ and $[Fe^{+3}] = 0.01667$.

$$E_{RIGHT} = E°_{Fe} - .05916\log\frac{[Fe^{+2}]}{[Fe^{+3}]} = .67\text{ V}$$

$$E_{CELL} = E_{RIGHT} - E_{LEFT} = 0.67 - 0.24 = 0.43\text{ V}$$

15 mL MnO_4^- added

Same method. $[Fe^{+2}] = 0.01538$ and $[Fe^{+3}] = 0.07692$.

$$E_{CELL} = E_{RIGHT} - E_{LEFT} = 0.72 - 0.24 = 0.48\text{ V}$$

25 mL MnO_4^- added

Add both Nernst equations. Equivalence at inflection point only for 1:1 titrations!

$$E_{RIGHT} = E°_{Fe} - \frac{0.05916}{1}\log\frac{[Fe^{+2}]}{[Fe^{+3}]}$$

$$5\left\{E_{RIGHT} = E°_{Mn} - \frac{0.05916}{5}\log\frac{[Mn^{+2}]}{[MnO_4^-][H^+]^8}\right\}$$

$$\overline{6\,E_{RIGHT} = E°_{Fe} + 5\,E°_{Mn} - .05916\log\frac{[Fe^{+2}][Mn^{+2}]}{[Fe^{+3}][MnO_4^-][H^+]^8}}$$

By electron balance, $5\,[Mn^{+2}] = [Fe^{+3}]$; at equivalence point $[Fe^{+2}] = 5\,[MnO_4^-]$.

$$E_{RIGHT} = \frac{E^{\circ}_{Fe} + 5\,E^{\circ}_{Mn} + .05916\log[H^+]^8}{6} = \frac{.68 + 5(1.51) + .05916\log(1)^8}{6}$$

$$E_{CELL} = E_{RIGHT} - E_{LEFT} = 1.37 - 0.24 = 1.13\text{ V at pH 0}$$

40 mL MnO_4^- added

After equivalence $[MnO_4^-]$ is decreased by reacting with initial $[Fe^{+2}]$ and the missing moles go to make $[Fe^{+3}]$ and $[Mn^{+2}]$ according to balanced reaction. *Dilution and reaction! Calculate new M.*

$$\frac{40.0}{40.0+50.0}\,0.0200\text{ M MnO}_4^- - \frac{50.0}{40.0+50.0}\,0.0500\text{ M Fe}^{+2}\,\frac{1\text{ mol MnO}_4^-}{5\text{ mol Fe}^{+2}} = 0.003333\text{ M MnO}_4^-$$

$$\frac{50.0}{40.0+50.0}\,0.0500\text{ M Fe}^{+2}\,\frac{1\text{ mol Mn}^{+2}}{5\text{ mol Fe}^{+2}} = 0.02778\text{ M Mn}^{+2}$$

Redox Buffer! $[MnO_4^-] = 0.003333$ and $[Mn^{+2}] = 0.005556$.

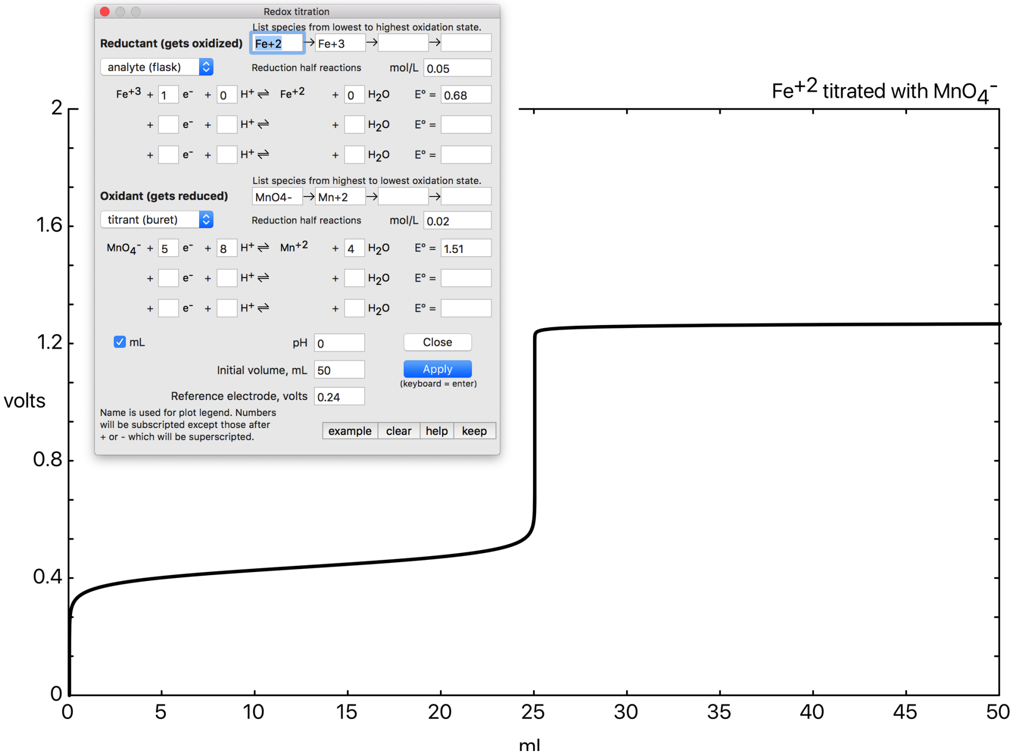
$$E_{RIGHT} = E°_{Mn} - \frac{0.05916}{5}\log\frac{[Mn^{+2}]}{[MnO_4^-][H^+]^8} = 1.51\text{V}$$

$$E_{CELL} = E_{RIGHT} - E_{LEFT} = 1.51 - 0.24 = 1.26\text{ V at pH 0.}$$

45 mL MnO_4^- added

Same method. $[MnO_4^-] = 0.004211$ and $[Mn^{+2}] = 0.005263$.

$$E_{CELL} = E_{RIGHT} - E_{LEFT} = 1.51 - 0.24 = 1.26\text{ V}$$



Redox titration

List species from lowest to highest oxidation state.

Reductant (gets oxidized) Fe+2 → Fe+3 → →

analyte (flask) — Reduction half reactions — mol/L 0.05

Fe^{+3} + 1 e^- + 0 $H^+ \rightleftharpoons$ Fe^{+2} + 0 H_2O E° = 0.68

List species from highest to lowest oxidation state.

Oxidant (gets reduced) MnO4- → Mn+2 → →

titrant (buret) — Reduction half reactions — mol/L 0.02

MnO_4^- + 5 e^- + 8 $H^+ \rightleftharpoons$ Mn^{+2} + 4 H_2O E° = 1.51

☑ mL

pH 0

Initial volume, mL 50

Reference electrode, volts 0.24

Name is used for plot legend. Numbers will be subscripted except those after + or - which will be superscripted.

Figure A4-2. The equivalence point is not at the inflection point but is at 1.13 V vs SCE.

APPLYING YOUR IDEAS

Many redox reactions are slow (much slower than acid-base reactions). There may be localized zones from imperfections in mixing or diffusion and from varying biological activities. However, equilibrium reactions do provide boundary conditions for natural waters.

$$O_2(g) + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \quad E° = +1.229\ V$$

$$E = E° - \frac{0.05916}{4}\log\frac{1}{[H^+]^4 p_{O_2}} = 1.229 - 0.05916\ pH + \frac{.05916}{4}\log pO_2$$

The partial pressure of oxygen in the atmosphere is 0.2 atmosphere so the maximum voltage obtained versus SHE is E = 1.229 – 0.05916 pH. This is the equation for the upper limit line in Figure A4-3.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \quad E° = 0.00\ V$$

$$E = E° - \frac{0.05916}{2}\log\frac{p_{H_2}}{[H^+]^2} = -0.05916\ pH - \frac{0.05916}{2}\log pH_2$$

The lowest possible value for E would be when hydrogen is at atmospheric pressure giving E = –0.05916 pH. This is the equation for the lower limit line.

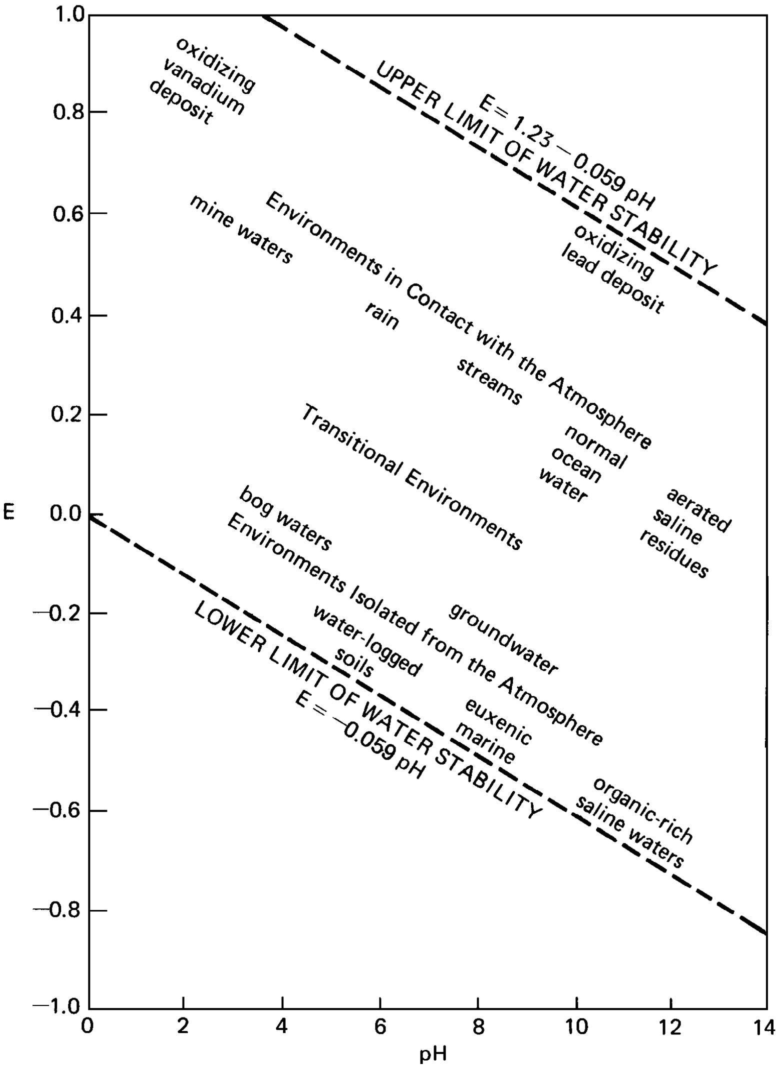


Figure A4-3. E vs pH for natural waters (Arthur H Brownlow, *Geochemistry*, Prentice-Hall, 1979, Chapter 4.)

The oxidation potential of natural material can be measured by immersion of a reference electrode (assumed to be a standard hydrogen electrode) and an inert electrode (usually made of platinum). If the material contains a large amount of one or more reducing agents, a large, negative E value will be obtained. Similarly, if the material contains a large amount of one or more oxidizing agents, a large, positive E value will be obtained. Measurements of E have been made on soils and sediments as well as on natural water solutions. Soils and sediments are either measured directly (if they contain water) or a sample of the material is suspended in water. In either case, what is being measured is the potential of a water solution, which may or may not be directly related to the composition of the soil or sediment.

There are a number of problems in measuring E in natural materials. The equipment is sensitive, particularly to temperature changes. Inserting the electrodes into a material can change the chemical environment, particularly if air is introduced to material normally out of contact with the atmosphere.

We can think of E as reflecting the abundance of electrons in the environment. A large number of available electrons would give a reducing environment. An absence of available electrons would give an oxidizing environment. Similarly, we can think of pH as representing the abundance of protons. A large number of available protons would give an acid environment, and a scarcity of available protons would give a basic environment. Since protons and electrons have opposite charges, we might expect that when we have an abundance of one we would have a shortage of the other. In other words, we would expect that an oxidizing environment (high E) would tend to be acidic (low pH), and a reducing environment (low E) would tend to be basic (high pH). Note that both of the limiting lines in the figure slope down to the right. These and other reaction lines plotted on E-pH diagrams usually slope to the right because the reactions occur at a lower E when the pH is raised.

The major natural controls on E and pH are (1) the organic processes of photosynthesis, respiration, and decay; (2) oxidation-reduction reactions involving iron, sulfur, and carbon; and (3) the balance between dissolved CO_2 and calcium carbonate in natural waters.

Suppose that we are interested in whether the copper dissolved in a stream is mainly in the form of Cu^+ or Cu^{+2}. The standard potential for the reduction is +0.16 volt. Assume that the measured E of the stream is +0.40 volt. This is a more oxidizing potential than that of the copper half-reaction. Therefore, we would expect Cu^{+2} to be the dominant ion. We can even determine the ratio Cu^{+2}/Cu^+ by applying the Nernst equation:

$$0.40 = 0.16 - \frac{0.059}{1}\log\frac{[Cu^+]}{[Cu^{+2}]};\ \log\frac{[Cu^+]}{[Cu^{+2}]} = \frac{0.24}{-0.059} = -4.1;\ \frac{[Cu^{+2}]}{[Cu^+]} = 10^{4.1}$$

Thus there are over a ten thousand times as many Cu^{+2} ions in our stream as there are Cu^+ ions.

LOOKING FURTHER

This module started with the problem of sulfur-containing fuels. Combustion oxidizes the sulfur and eventually produces sulfuric acid. Acid deposition affects soils and metal-ion dissolution that then impacts fish and trees.

A related problem is that of acid rock drainage. Abandoned mines, exposed mine tailings, or road cuts can provide a source of sulfur-containing minerals. Exposure to air and water, with the help of bacteria, again produces sulfuric acid.

Some cases have been quite severe. “Extremely acidic mine waters with pH values as low as −3.6, total dissolved metal concentrations as high as 200 g/L, and sulfate concentrations as high as 760 g/L, have been encountered underground in the Richmond Mine at Iron Mountain, CA. These are the most acidic waters known.” (*Environ. Sci. Technol.*, **2000**, *34*(2), 254–258.)

Acidic waters readily dissolve some minerals. When the pH is raised past 3, either through dilution with fresh water or neutralizing minerals, previously soluble Fe^{+3} ions precipitate as a yellow-orange iron oxide and $Fe(OH)_3$. This precipitate can smother plant and animal life on the streambed, further disrupting stream ecosystems. (http://en.wikipedia.org/wiki/Acid_mine_drainage)

Iron in water can cause yellow, red, or brown stains on laundry, dishes, and sinks. In addition, iron can clog wells, pumps, sprinklers, and other devices such as dishwashers, which can lead to costly repairs. Iron gives a metallic taste to water, and can affect foods and beverages–turning tea, coffee, and potatoes black. (https://www.health.state.mn.us/communities/environment/water/wells/waterquality/iron.html)

Understanding these processes require the same skills you have developed looking at acid precipitation.