Mercury: Oxidation and Reduction

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NC SCOS Objective:

5.05 – Analyze oxidation/reduction reactions with regard to the transfer of electrons.

- Assign oxidation numbers to elements in REDOX reactions
- Identify the elements oxidized and reduced
- Write simple half reactions
- Assess the practical applications of oxidation and reduction

This unit is designed to assess bullets 1, 2 and 4. I have found that the ability to "write simple half reactions" is not assessed on the NC E.O.C. test.

Lesson Outline: Day 1

- Gallery walk – Minamata Bay disaster, 1950s Japan
  - Where is the Hg coming from?
- Learning oxidation and reduction – guided notes, PowerPoint
  - Oxidation
  - Reduction
  - Oxidizing/reducing agent
  - Oxidation state
  - Redox reaction equations
- Determining Oxidation State Activity
  - Using trends to discover rules for determining oxidation state
- Looking at Hg in the body
  - How does it get in? (In what forms is it?)
  - What happens, chemically, once it's in?
  - What effects do we see? (infants, children, adults)

Lesson Outline: Day 2

- Review
- Video clip – *Kilowatt Ours*
  - Energy
  - Where does coal come from?
  - Hg in coal
- Looking at redox in the combustion of coal
  - Mapping the path of Hg – from the earth to the atmosphere and through the food chain
  - Four reaction equations – ID oxidation states, ox/reducing agents, ox/reduced elements
- Homework – Saving ourselves: what can we do? (choose 1)
  - Hg in fish - http://www.epi.state.nc.us/epi/fish/safefish.html
  - Alternative energy - http://www.kilowattours.org/script_chapter8b.php
  - Reducing energy use (and cost) at home - http://www.kilowattours.org/script_chapter7.php
  - Duke Energy and Progress Energy's plans to accommodate increasing demands
    http://www.newsobserver.com/opinion/columns/story/1555992.html
    http://www.duke-energy.com/about-us/coal.asp
    http://www.southernstudies.org/2009/03/nc-oks-dukes-massive-new-coal-fired-plant-as-minor-pollution-source.html
    http://www.duke-energy.com/news/releases/2008060901.asp

Lesson Sequence – Day1

Gallery Walk (20 minutes)
Students will silently observe a sequence of images. After observation, the following questions will be answered individually to allow time for student reflection, and then discussed as a group. In particular, question # 3 will be answered in this class, and students' thoughts should be written where they can be accessed later.

Gallery Walk Questions

1. What appears to have happened here (what is the sequence of events)?
2. In this case, the contaminant was mercury – where did it come from?
3. How do you think mercury was able to get into the people's bodies?
4. Could something like this happen again?

Instruction: Oxidation and Reduction (30 minutes, including activity)
Accompanying PowerPoint presentation will be used to instruct students on the basics of oxidation and reduction. Slide 2 is the emphasis for student note-taking purposes. Slides 1-5 will be discussed in brief prior to the Oxidation State group activity.

Oxidation State Activity (10 minutes, suggested time)

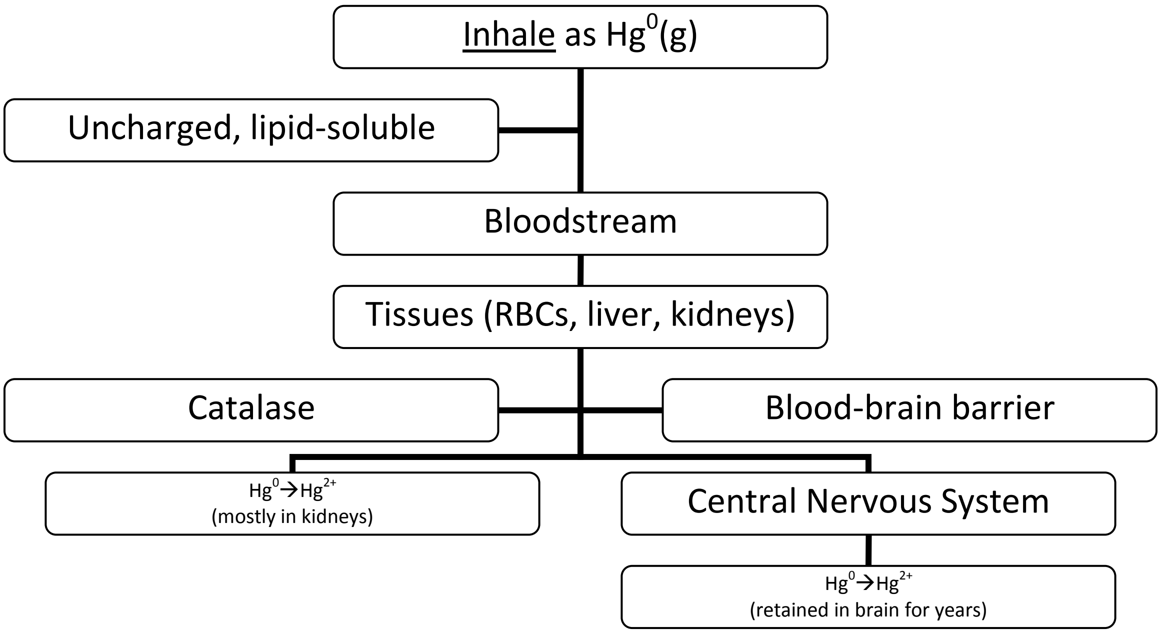
In groups, students will discover guidelines for determining oxidation state. Groups will be given an envelope with color-coded groups of chemical species – each color corresponds to a different guideline. Based on the patterns exhibited by each substance group and the guiding questions on the Handout, students should be able to deduce the guidelines for determining oxidation state. Each student should have a copy of the accompanying handout to keep for notes following the activity.

Slides 6-10 are useful for going over the Oxidation State activity as a class to ensure students are on track. Slides 11-13 tie oxidation state and the processes of oxidation and reduction together, and introduce oxidizing and reducing agents. Students should take notes on these slides. Slide 14 offers a flow-chart summary of REDOX.

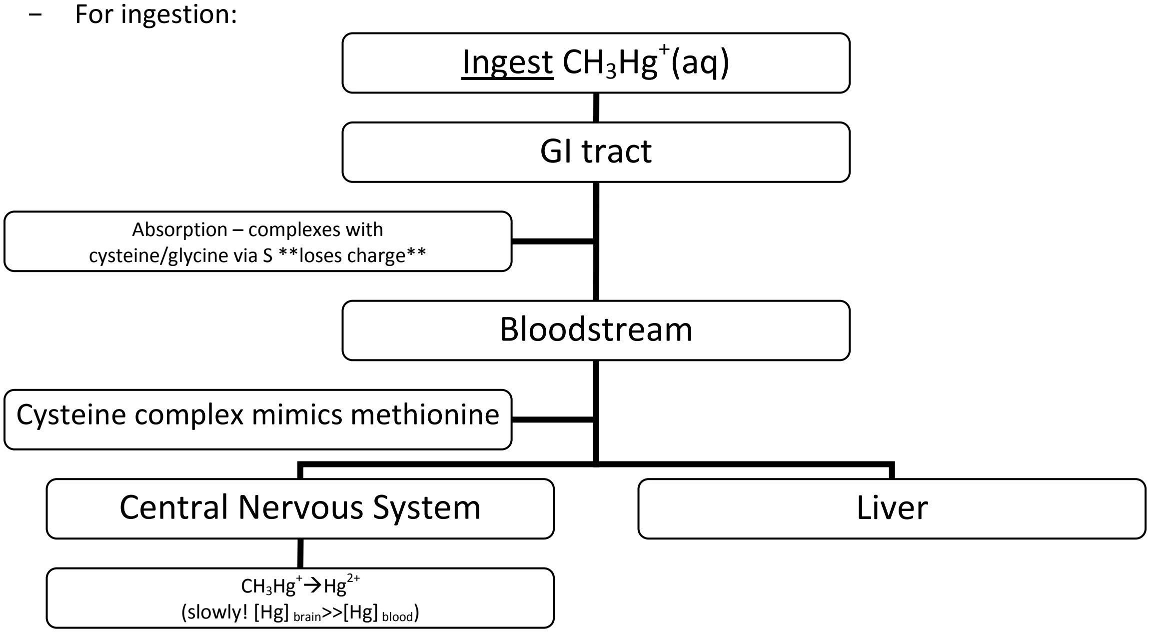
Looking at Mercury in the Body (40 minutes)
After learning the basic tenets of REDOX, students will re-examine the case of Minamata Bay within the frame of mercury oxidation and reduction. The format is a class discussion under the umbrella question "What do we need to know about mercury to keep this from happening?" Students should be led to ask the following questions and arrive at these key points:

- Where does it come from? – to be answered *tomorrow*
- What forms is it in?
  - Hg^0(l, g)
  - Hg^{2+}(aq)
  - CH_3Hg^+(aq)
- How does it get inside the body?
  - Physically:
    - inhale (lungs)
    - touch (skin)

        - ingest (GI tract)
    - Chemically:
        - Inhale – must be volatile to get inside, uncharged to get into blood (Hg^0)
        - Touch – liquid, uncharged and lipid-soluble to get through skin into blood (Hg^0)
        - Ingest – can be charged/uncharged, any phase, but if charged, it must bind to a protein to transport it out of the GI tract into the blood (Hg^0, Hg^{2+}, CH_3Hg^+)
- What does it do once inside the body? (Emphasis should be placed on which oxidation state is necessary for the mercury to travel from one place to another.)
    - For inhalation:



    - For ingestion:



- What are symptoms of mercury poisoning?
  Students will read *The Dancing Cats of Minamata Bay* (Aronson).

- Stumbling gait, confusion, fever of unknown origin, convulsions
- Stupor deepening to irreversible coma
- Death

Ask, what about the chemistry of mercury in the brain may help you determine why one would show these types of symptoms?

Final Individual Assessment

Students should draw – individually – what happens to the electrons when mercury is oxidized from Hg to Hg^{2+}.

If time, have them label oxidation states and identify what is oxidized/reduced and the oxidizing/reducing agents in the following equation:

$$Hg_2^{2+}(aq) + H_2S(s) \longrightarrow Hg(l) + HgS(s) + 2H^+(aq)$$

Lesson Sequence – Day 2

Review: (10 minutes)
Students will review from Day 1 – What are the oxidation states of mercury? How does it get into the body? What does it do once its inside?

Mercury in Coal – Video Clips from *Kilowatt Ours:* (10 minutes)
Students will watch 3 segments from the documentary *Kilowatt Ours*, available online (http://www.kilowattours.org/script.php, with YouTube access) or DVD. Sections include Introduction, Chapter 1 and Chapter 5. The video will introduce students to some specific problems in science that affect them directly (growing energy demand, global warming, rising fuel costs, and specifically the use of coal for energy), address the source of coal and how mercury poisoning is connected to burning coal. Students may take notes. They will need to know: where the mercury comes from, where it goes (its path from the ground to our bodies), and how it affects us.

Preparation for Mapping Activity: (10 minutes)
As a class, students should answer the following questions:

1. How is mercury a threat for us here?
   - Mercury burned in power plants is carried through the air and inhaled.
   - Mercury from coal combustion is deposited in bodies of water where it travels up the food chain into fish that we eat. Ask – Why does it show up in water and not other places?
   - Mercury can travel long distances from where it was emitted from a power plant and get deposited.
2. Where does mercury come from?
   - Mercury comes from combustion of coal, which comes from the ground.
   - Coal is harvested in the Appalachian mountains.
   - Mercury can also come from other sources – manufacturing plants, electronics, medical equipment, etc.
3. What is mercury's path through the atmosphere and food chain? What places should we include on our maps? What oxidation states would you anticipate for each?
   - Point sources (power plants, manufacturing plants as volatiles and runoff) – $Hg^0(g)$, $Hg^{2+}(g)$, CH_3Hg^+
   - Atmosphere (volatile and bonded to particulate matter) – $Hg^0(g)$, Hg^{2+} (divalent form travels short distances over short periods of time and is deposited; elemental form travels long distances over long periods of time – years – before it is oxidized to the divalent form and then deposited)
   - Ground – $Hg^0(l)$ (elemental mercury is extracted from the ground in coal as seen in the video)
   - Water – $Hg^0(l)$, Hg^{2+}, CH_3Hg^+ (deposition from the atmosphere is in the divalent form and no longer volatile; runoff from point sources can be any form)
   - Benthos – $Hg^0(l)$, Hg^{2+}, CH_3Hg^+ (bottom-feeding microbes in bodies of water absorb divalent and methyl mercury from sediments – divalent forms become methylated; elemental form is absorbed at a much slower rate through skin)
   - Fish – Hg^0, Hg^{2+}, CH_3Hg^+ (fish absorb small amounts of elemental mercury through their skin, but mainly take in divalent and methylated forms by eating smaller organisms)
   - Animals/Humans – $Hg^0(g)$, Hg^{2+}, CH_3Hg^+ (similar to fish, humans may inhale elemental mercury from the air or near bodies of water in small amounts, or in large amounts from a point source such as a manufacturing plant if they were working there; liquid elemental mercury can be absorbed through the skin in small amounts; the main uptake of mercury occurs from eating

fish that have eaten smaller fish/organisms where divalent and methylmercury have been able to “bioaccumulate” as they traveled up the food chain)

Mapping Mercury Through the Atmosphere and Food Chain: (40 minutes)
Using the information compiled in point 3 (above), students will map the path of mercury through the atmosphere and food chain. They should illustrate each location and include the oxidation state of mercury there. A one-paragraph explanation of the path and accompanying oxidation states, or one sentence per point for # 3 (above) should be included. This can be done in small groups or individually. The following diagram, taken from *Mercury Pollution: Integration and Synthesis* (Copyright Lewis Publishers, an imprint of CRC Press, available online via http://wi.water.usgs.gov/mercury/mercury-cycling.html#references) shows a sample diagram.

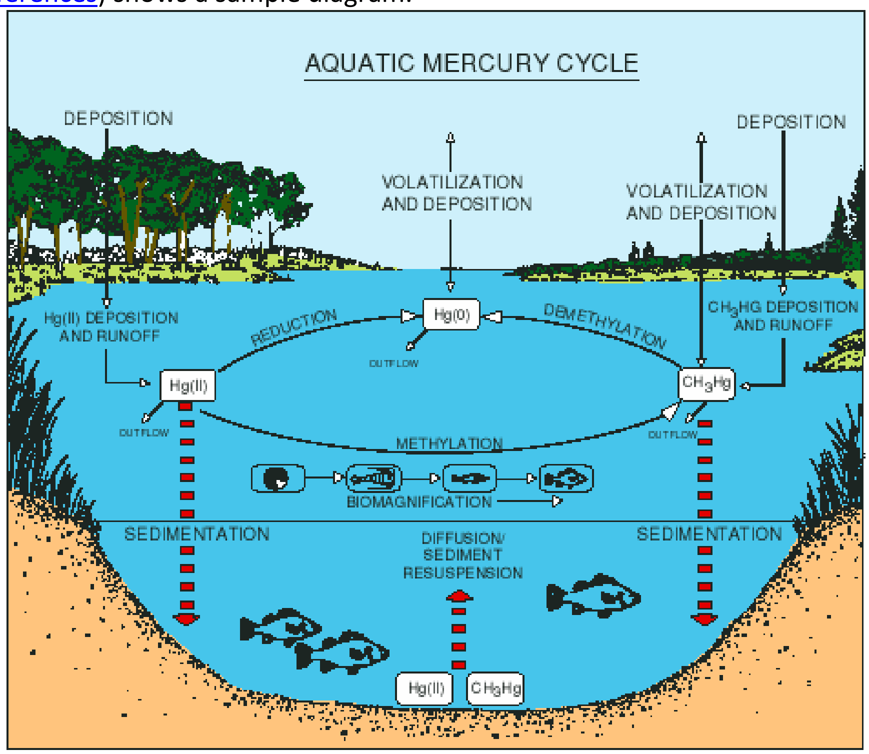


Figure 6. Mercury cycling pathways in aquatic environments are very complex. The various forms of mercury can be converted from one to the next; most important is the conversion to methylmercury (CH_3Hg^+), the most toxic form. Ultimately, mercury ends up in the sediments, fish and wildlife, or evades back to the atmosphere by volatilization. Reprinted with permission from Mercury Pollution: Integration and Synthesis. Copyright Lewis Publishers, an imprint of CRC Press.

Review Activity: (20 minutes)
Students will review REDOX reactions by labeling the following equations with oxidation states, what is oxidized/reduced and oxidizing/reducing agents.

1. $HgO(g) \longleftrightarrow Hg(g) + 2O_2(g)$
2. $HgCl_2(g) + H_2O(g) \longleftrightarrow HgO(g) + 2HCl(g)$
3. $HgSO_4(s) \longleftrightarrow HgO(g) + SO_2(g) + \frac{1}{2}O_2(g)$
4. $HgSO_4(s) + Cl_2(g) \longleftrightarrow HgCl_2(g) + SO_2(g) + O_2(g)$

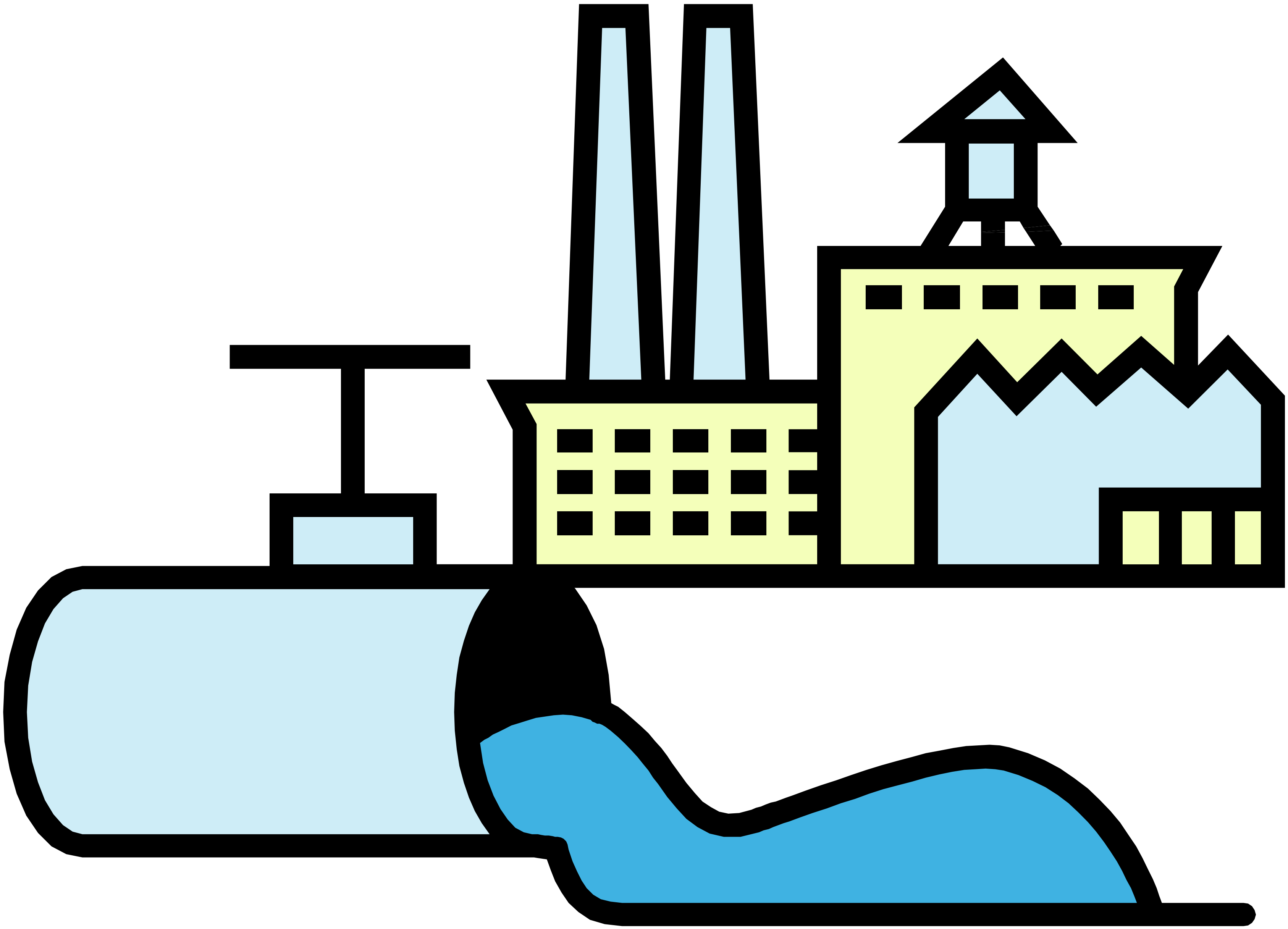
Homework Assignment:
Students will explore the answer to the question: How can we protect ourselves from Mercury and its effects? They may choose to present on any of the following options:

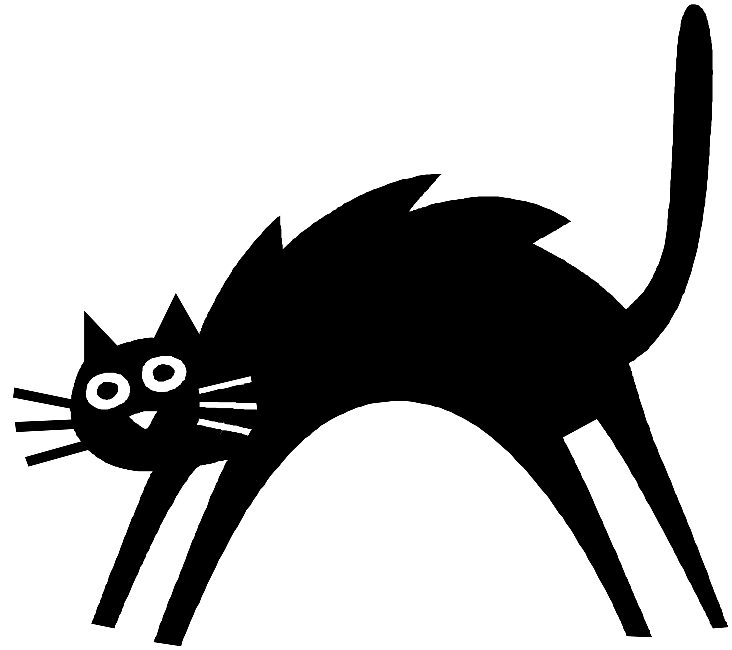
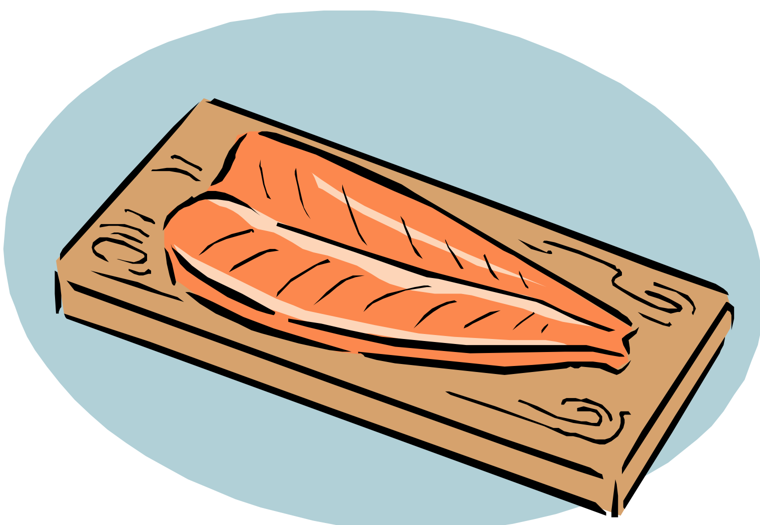
- Hg in fish - http://www.epi.state.nc.us/epi/fish/safefish.html
- Alternative energy - http://www.kilowattours.org/script_chapter8b.php
- Reducing energy use (and cost) at home - http://www.kilowattours.org/script_chapter7.php
- Duke Energy and Progress Energy's plans to accommodate increasing demands
  http://www.newsobserver.com/opinion/columns/story/1555992.html
  http://www.duke-energy.com/about-us/coal.asp
  http://www.southernstudies.org/2009/03/nc-oks-dukes-massive-new-coal-fired-plant-as-minor-pollution-source.html
  http://www.duke-energy.com/news/releases/2008060901.asp

Students should develop an 8 ½ x 11 poster explaining the danger of mercury to humans chemically (What forms? Where does it come from? What does it do inside the body?), and what they found can be done to help reduce its threat to us. They should try to make the language accessible to the general public.

***The first website – with information on mercury in local fish – can be printed for students who may not have access to the internet at home.

Gallery Walk





RIP

The Dancing Cats of Minamata Bay

Minamata had been a peaceful little Japanese village supporting itself by fishing within its neighboring bay, by harvesting salt in one of its shallow coves and by some subsistence rice farming. Salt production, their only source of negotiable funds, was shortly to become a government monopoly and so the leaders of this coastal community sought alternate sources of income.

Following the Russo-Japanese War [1904 – 05], Japan underwent a rapid expansion of its industrial base. Minamata, on the southwest coast of Kyushu, eagerly agreed to donate land as the price for attracting a new industrial plant manufacturing carbide. The demand for carbide, however, diminished during the next decade and so the factory switched its production line to ammonium sulphate, an agricultural fertilizer. During World War I, the importation of fertilizers to Japan was halted and thus the company [now called Nippon Chisso] achieved great prosperity since it held a near monopoly on the manufacture of fertilizers.

Following World War I, Nippon Chisso [*Chisso* is the Japanese word for nitrogen] aggressively expanded its operations into Japan's Asiatic colonies, particularly Korea, where it established massive factories powered by cheap hydro-electric power. In 1927, through the use of a high-pressure gas process, Nippon Chisso grew to become one of Asia's most powerful chemical manufacturing corporations.

A crucial change took place at the Minamata plant complex in 1930. It was discovered that a variety of organic chemical compounds could be elaborated by passing acetylene [derived from the calcium carbide] over mercuric sulphate. Among these newly synthesized products was vinyl acetylene, an essential ingredient for the manufacture of plastics.

As the Chisso production facility in Minamata expanded, so did the village. From a small, anonymous community, Minamata grew to become a town and then, during the second World War, into a prosperous city. But from the beginning it was a city wholly dependent upon a single industry. Indeed, the civic leadership of Minamata was always controlled by Chisso and criticism of Chisso or the working conditions within its plants was regarded as tantamount to heresy.

Japan in the 1930s was transformed into an industrial-military nation. By 1938, in association with the German chemical corporation, I.G. Farben, the Minamata complex augmented its output of vinyl chloride and other components essential for military use.

The local fishermen were the first to declare that something was amiss. They noted dead fish floating on the surface of Minamata's bay. And, to their increasing dismay, their fishing yield progressively diminished. The local association of fishermen sent a delegation to Nippon Chisso claiming that the loss of fish was caused by industrial wastes emptied into the bay. The company vehemently denied the charges and declared the fishermen to be unpatriotic. Nonetheless, in 1927 and again in 1943 Chisso quietly provided a meager stipend to the fishermen, with the stipulation that there be no further requests for compensation.

The Nippon Chisso factories in Minamata were destroyed by American air strikes in 1944, leaving the community without a source of income. But during the extended occupation of Japan by Allied Forces, and prompted by extensive unemployment, the Minamata complex was allowed to be rebuilt in 1949 for the production of polyvinyl chloride. By 1953 Minamata became the major Asiatic source for the production of PVCs. The Nippon Chisso factories now provided 60% of Minamata's tax-base; and the city's mayor and most of its Municipal Council were either current or past employees of the company.

By the mid-1950s yet another disturbing event surfaced. Citizens noticed that many of the town's cats behaved strangely. For no apparent reason they exhibited frenzied behavior, throwing themselves against stone walls, prancing or staggering as though intoxicated, and frequently hurling themselves into Minamata Bay, where many drowned. What may have been faintly amusing at first rapidly produced much concern by the more thoughtful people of Minamata.

In May 1956, the Minamata City Hospital [managed and funded by Nippon Chisso] admitted four patients with essentially similar presenting signs and symptoms. These four had been healthy until they experienced the sudden onset of stumbling gait, confusion, fever of unknown origin, convulsions, stupor which deepened into irreversible coma and death. Within weeks there were a total of 17 deaths. A hasty epidemiologic inquiry found two things which all of these dead patients shared: They were all longtime citizens of Minamata and their principal diet had been fish derived from the Bay.

The yield of fish in the Bay diminished so drastically that on November 2, 1959, 4,000 desperate fishermen stormed the Chisso factory demanding compensation for the loss of their income. The public denounced the action of the fishermen, the leaders of whom were duly punished, but a feeling of disquiet became pervasive in Minamata as the number of unexplained deaths increased. The chief physician of the city hospital, Dr. Hosokawa, fed some of the factory waste products to a few cats, saw them develop a frenzied behavior, and at autopsy, exhibited the characteristic signs of mercury poisoning. He was, however, forbidden to publish his findings.

Years later, a careful toxicological survey disclosed that the fish and shellfish of the Minamata Bay were heavily contaminated with methyl mercury, as were the internal organs of the frenzied cats and the local fish-eating citizens. Thus far, 1,760 victims have been identified but a local university places the victims at over 10,000.

Nippon Chisso ceased manufacturing products requiring mercury in 1969, concentrating now on the synthesis of fertilizers and other industrial chemicals. The sediment of the Bay is still heavily contaminated with methyl mercury, earth fill has covered the shallow inlets of the Bay, a memorial park has been established and local fishing has long since been prohibited. The victims have been financially compensated but the unhappy incident is rarely discussed locally.

Stanley M. Aronson, MD

Source: Aronson, Stanley M., MD. "The Dancing Cats of Minamata Bay." Rhode Island Medicine and Health. 88.7 (2005): 209.

Name:______________________

Determining Oxidation State

Background: There are a few guidelines to determining the oxidation state of an element. For the most part, it's rather simple and consistent with what you already know about the natural ionic charge of elements. There are also a few exceptions…but nothing you can't figure out!

Objective: By looking at trends amongst several different groups of substances, you will come up with the guidelines for determining an element's oxidation state.

Guideline 1: Write the substances in this group in the box below. Answer the following questions to help you come up with the first guideline for determining oxidation state.

1. In a few words, give a general description of the substances in this group.
2. What is consistent about the oxidation state of substances in this group?
3. Using your answers to questions 1 and 2, rewrite the guideline below for assigning oxidation state to this type of substance.

Guideline 2: Write the substances in this group in the box below. Answer the following questions to help you come up with the second guideline for determining oxidation state.

1. In general, how would you describe the overall charge on the substances in this group?
2. What is the relationship between the oxidation states given for each element and the overall charge on the substance? [Hint: make sure to take note of subscripts.]
3. Rewrite the guideline below for assigning oxidation state to this type of substance.

Guideline 3: Write the substances in this group in the box below. Answer the following questions to help you come up with the third guideline for determining oxidation state.

1. In general, how would you describe the substances in this group with regard to their charge?

2. What is the relationship between the oxidation states given for each element and the overall charge on each substance?

3. Rewrite the guideline below for assigning oxidation state to this type of substance.

Guideline 4: Write the substances in this group in the box below. What do you notice about the relationship between the oxidation state assigned and the electronegativity of each element within the substances?

Name:_______________________

Determining Oxidation State KEY

Background: There are a few guidelines to determining the oxidation state of an element. For the most part, it's rather simple and consistent with what you already know about the natural ionic charge of elements. There are also a few exceptions…but nothing you can't figure out!

Objective: By looking at trends amongst several different groups of substances, you will come up with the guidelines for determining an element's oxidation state.

Guideline 1: Write the substances in this group in the box below. Answer the following questions to help you come up with the first guideline for determining oxidation state.

0	0	0	0
$Na(s)$	$H_2(g)$	$Hg(l)$	$S_8(s)$

1. In a few words, give a general description of the substances in this group.
   Pure, uncombined elements
2. What is consistent about the oxidation state of substances in this group?
   They are all zero.
3. Using your answers to questions 1 and 2, rewrite the guideline below for assigning oxidation state to this type of substance.
   Pure, uncombined elements have an oxidation state of zero.

Guideline 2: Write the substances in this group in the box below. Answer the following questions to help you come up with the second guideline for determining oxidation state.

-4 +1	+4 -2	+2 +6 -2	+2 -2
$CH_4(g)$	$CO_2(g)$	$CuSO_4(s)$	$HgO(g)$

1. In general, how would you describe the overall charge on the substances in this group?
   Neutral (zero).
2. What is the relationship between the oxidation states given for each element and the overall charge on the substance? [Hint: make sure to take note of subscripts.]
   The sum of the oxidation states is equal to the overall charge (zero).
3. Rewrite the guideline below for assigning oxidation state to this type of substance.
   For neutral compounds, the sum of the oxidation states is equal to zero.

Guideline 3: Write the substances in this group in the box below. Answer the following questions to help you come up with the third guideline for determining oxidation state.

+3	-2 +1	+4 -2	+4 -2
$V^{3+}(aq)$	$OCl^{-}(aq)$	$CO_3^{2-}(aq)$	$VO^{2+}(aq)$

1. In general, how would you describe the substances in this group with regard to their charge?
   Charged (ionic).

2. What is the relationship between the oxidation states given for each element and the overall charge on each substance?
   The sum of the oxidation states is equal to the overall charge.

3. Rewrite the guideline below for assigning oxidation state to this type of substance.
   For ions, the sum of the oxidation states is equal to the overall charge.

Guideline 4: Write the substances in this group in the box below. What do you notice about the relationship between the oxidation state assigned and the electronegativity of each element within the substances?

-1 +2	+1 -1	+1 -2 +1
$F_2O(g)$	$H_2O_2(aq)$	$NaOH(aq)$

The negative oxidation state is assigned to the most electronegative element, and the positive oxidation state is assigned to the less electronegative elements.

Oxidation State Activity Substances

For Guideline 1:

0

$Na(s)$

0

$H_2(g)$

0

$Hg(l)$

0

$S_8(s)$

For Guideline 2:

4 +1

$CH_4(g)$

+4 -2

$CO_2(g)$

+2 +6 -2

$CuSO_4(s)$

+2 -2

$HgO(g)$

For Guideline 3:

+3 -2 +1

$V^{3+}(aq)$ $OCl^{-}(aq)$

+4 -2

$CO_3^{2-}(aq)$

For Guideline 4:

-1 +2

$F_2O(g)$

Sources:

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