

Unit 7

Toxic Heavy Metals

Overview

In ancient Rome wine was stored in lead vessels, which would make the wine somewhat sweet. The lead would leach into the wine and react to form lead acetate, which added sweetness, but unbeknownst to the Romans also made the wine poisonous. Metals—especially heavy metals—pose a unique environmental pollution problem. Heavy metals are especially toxic because their ions are water-soluble and readily taken up by the body. Once in the body they can incorporate and combine with vital enzymes to interfere with their proper function. They bioaccumulate and surprisingly small amounts can cause substantial physiological and neurological damage. In addition, unlike many other pollutants, metals cannot be destroyed or rendered completely harmless. Although there are several “problem” metals, this Unit 7 deals with the more notorious metals: mercury, lead, cadmium and arsenic.

Introduction and Common Features

Objectives

After completing this section, you should be able to

1. explain the difference between a heavy metal and a light metal.
2. describe how most heavy metals are transported from place to place.

Key Terms

heavy metal
mercury (Hg)
lead (Pb)
cadmium (Cd)
arsenic (As)

Reading Assignment

Read pages 381–382 in the textbook.

Study Notes

There are no study notes for this section.

Exercises

No exercises have been assigned for this section.

Common Features—Toxicity of the Heavy Metals

Objectives

After completing this section, you should be able to

1. explain the biochemical toxicology of heavy metals and their interaction with sulfhydryl groups.
2. describe the medical treatment for acute heavy metal poisoning.
3. explain the role of speciation and chemical form on the level of toxicity of a metal.

Key Terms

sulfhydryl groups (-SH)

British Anti-Lewisite (BAL)

ethylenediaminetetraacetic acid (EDTA)

speciation

blood-brain barrier

Reading Assignment

Read pages 382–383 in the textbook.

Study Notes

You should be able to describe how heavy metal cations interfere with metabolic reactions within the body by reacting with sulfhydryl groups found in enzymes to form metal-sulfur bonds (Objective 1). Over a longer period of time heavy metals can incorporate themselves into various structures in the body. For example, Pb^{2+} is similar in size and charge to Ca^{2+} so it incorporates well into bones. However, acute heavy metal poisoning assumes that most of the metal is still in the blood. In this case, chelation therapy is the preferred medical treatment, using compounds like BAL or EDTA to complex the metal (Objective 2).

Warning: Chelation therapy carries a real risk. Organic ligands in the blood can potentially chelate and effectively remove other non-harmful or in fact necessary metal ions. The treatment is usually closely monitored and often blood serum is supplemented to offset the removal of essential ions.

It is important for you to realize that all metals are a natural part of the environment. Heavy metals are widely distributed, mostly in forms and amounts that do no harm (i.e., in rocks). These heavy metals only become a health and environmental hazard when they are found in high concentrations in or near biological systems. The chemical form (speciation) of a metal is also important in determining its toxicity (Objective 3). For example, C_2H_5HgCl is approximately 250 times more toxic than its inorganic analog $HgCl_2$.

The type of exposure also determines the amount of harm the metal can inflict on an organism. Large amounts of elemental liquid mercury can be digested without detrimental effects, because the digestive tract cannot absorb mercury well in its elemental form. In fact, ancient Romans used to drink liquid mercury as a cure for constipation. It is the vapours from liquid mercury that are dangerous. When breathed in they can work their way into the blood stream past the blood-brain barrier directly into the central nervous system. A more modern example is the use of the so-called “barium meal,” which is a suspension of barium sulfate used as a contrasting agent in diagnostic x-ray work. Although barium is toxic, the barium sulfate has a solubility product in the order of 10^{-10} , which means it releases virtually no Ba^{2+} ions. The barium sulfate itself cannot be absorbed in the digestive tract so, as with the elemental mercury example, it too shall pass.

Exercise

Do Problem 7-1 within the chapter.

Common Features—Bioaccumulation of the Heavy Metals

Objectives

After completing this section, you should be able to

1. state which heavy metals undergo bioconcentration and/or biomagnification.
2. relate (mathematically) average lifetime and half-life of a substance.
3. calculate the steady-state concentration of a substance (C_{ss}) in an organism given the rate of intake (R) and rate constant for elimination (k) for that substance.

Key Terms

biomagnification

steady-state concentration (C_{ss})

half-life ($t_{1/2}$)

average lifetime (T_{avg})

Reading Assignment

Read pages 384–386 in the textbook.

Study Notes

By now, you should be able to make a clear distinction between terms such as bioconcentration, biomagnification, and bioaccumulation. Many aquatic organisms show evidence of bioconcentrating heavy metals. However, it is only mercury that really exhibits biomagnification (Objective 1).

To perform your calculations remember to use the formulae $C_{ss} = \frac{R}{k}$ and $T_{avg} = 1.44t_{1/2}$ (Objectives 2 and 3). You should also recall the concept of steady state, which we discussed in the Study Notes of the section entitled “The Chemistry of the Ozone Layer—Catalytic Processes of Ozone Destruction” in Unit 2. The two schematics below illustrate the similarity between a steady-state system in a chemical reaction where there is an intermediate species and a steady-state system in an organism exposed to a substance.

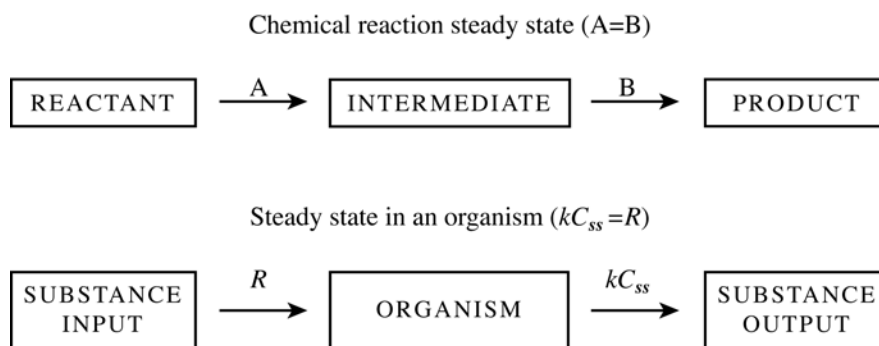


Figure 7.1

Exercises

Do Problems 7-2 and 7-3 within the chapter.

Do Additional Problems 1 and 2 found at the end of the chapter on page 416.

Correction: In the answer to Additional Problem 1, replace 138 and 276 with 69 and 138, respectively (p. AN-5 in the textbook).

Mercury—The Free Element

Objectives

After completing this section, you should be able to

1. list at least three commercial uses of elemental mercury.
2. differentiate between the toxicity of mercury liquid and gas.
3. state three sources of mercury vapor in the environment.

Key Terms

fluorescent light
blood-brain barrier
mercury vapor (gas)

Reading Assignment

Read pages 386–387 in the textbook.

Study Notes

The toxicity of mercury coupled with its general use has made it a serious environmental concern. Even though many of the health problems have long been known, they have often been ignored because mercury is a useful and versatile substance. Some of the more major commercial uses of elemental mercury include fluorescent light tubes and arc lamps, electrical contacts and switches, and mercury batteries (Objective 1).

We already alluded to the difference in toxicity between gaseous and liquid mercury (Objective 2). The mechanism of entry into the blood and eventually the brain is increased by breathing in vapors as opposed to ingesting the element. You should note that in very young children the blood-brain barrier has not yet fully developed and so they are more susceptible to poisoning by lead and mercury.

The textbook mentions input of mercury into the atmosphere from volcanic eruptions. However, anthropogenic sources such as coal and fuel oil combustion, as well as discarded batteries (Objective 3).

Exercises

No exercises have been assigned for this section.

Mercury—Mercury Amalgams

Objective

After completing this section, you should be able to explain what a mercury amalgam is and give two examples.

Key Terms

amalgam
dental amalgam
porcelain filling
extraction
Amazon River

Reading Assignment

Read pages 387–388 in the textbook.

Study Notes

There are no study notes for this section.

Exercises

No exercises have been assigned for this section.

Mercury—Mercury and the Chloralkali Process

Objectives

After completing this section, you should be able to

1. describe the traditional chloralkali process.
2. explain improvements made to this process using fluorocarbon-based membranes.
3. explain the risks and environmental damage associated with the chloralkali process.

Key Terms

sodium-mercury amalgam
chloralkali plant
electrolysis
fluorocarbon membrane

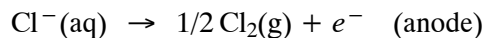
Reading Assignment

Read pages 388–389 in the textbook.

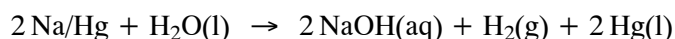
Study Notes

In describing each of the processes involved, you should be able to describe which electrochemical reaction occurs at both the anode and cathode (Objectives 1 and 2). You are not responsible for knowing the concept of overvoltage.

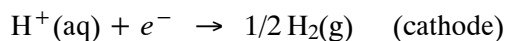
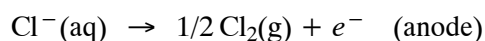
A. Chloralkali process with mercury



The $\text{Na}^{+}(\text{aq})$ rather than $\text{H}^{+}(\text{aq})$ is reduced due to large overvoltage for reduction of $\text{H}^{+}(\text{aq})$ at the mercury cathode, because of the lowering of free energy for the formation of the sodium amalgam. After electrolysis, the mercury is recovered and sodium hydroxide and hydrogen gas are generated.



B. Chloralkali process with a fluorocarbon membrane



Note the $\text{Na}^{+}(\text{aq})$ does not react at the cathode in this case and merely forms an aqueous NaOH solution with the $\text{OH}^{-}(\text{aq})$.

During the fluorocarbon membrane process chemists must take care not to let the chlorine and hydrogen gases mix as they will violently explode in the presence of light. In the case of the mercury cathode process, the hydrogen gas is generated in a completely different part of the process during treatment of the sodium amalgam after electrolysis. This eliminates the need for keeping the gases in the electrolytic cell completely separate. However, in the recycling of the mercury from the amalgam some mercury is lost to the environment through cooling water or escapes in gaseous form. Once in the environment, the mercury can oxidize and be taken up by fish in natural water systems. The mercury would eventually poison any food chain dependent on those fish (Objective 3).

Exercises

No exercises have been assigned for this section.

Mercury—Ionic Mercury

Objectives

After completing this section, you should be able to

1. state two uses for mercury in batteries.
2. list at least three symptoms of mercury poisoning.

Key Terms

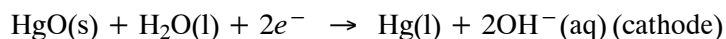
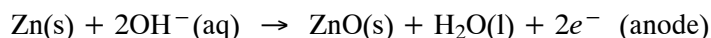
mercury (II) ion (mercuric ion or Hg^{2+})
nervous disorder
mercury cell battery

Reading Assignment

Read pages 389–390 in the textbook.

Study Notes

Mercury cell batteries (developed by Ruben-Mallory in the 1930s) has the advantage that it can maintain a constant voltage (1.3 V) for up to 95% of the battery's total capacity. The half reactions involved are given below showing the involvement of the mercuric paste in the cathode.



However, in an ordinary flashlight battery (a dry cell) the anode is zinc and the cathode is a carbon rod. Mercury had been used on the zinc electrode to prevent corrosion. You are not responsible to remember the half reactions in detail, but you should know in general terms how the mercury is being used in each of these two different batteries (Objective 1).

Some mercury poisoning symptoms were mentioned earlier in the section entitled “Mercury—The Free Element.” The symptoms including loss of eyesight, muscle tremors, depression, memory loss, paralysis, and insanity are all essentially nervous disorders (Objective 2).

Aside: Lewis Carroll did not invent the phrase “mad as a hatter.” By the time *Alice in Wonderland* (1865) was published, it was already well known. One

of the first written examples of its use is from a work by Thomas Chandler Haliburton (aka Judge Haliburton), of Nova Scotia, who was well known in the 1830s for his comic writings about the character Sam Slick. In *The Clockmaker* (1836) he wrote: “Father he larfed out like any thing; I thought he would never stop—and sister Sall got right up and walked out of the room, as mad as a hatter.” It would seem that since Thomas Haliburton found no need to explain this phrase, it was already in use in his part of the world at that time.

Exercise

Do Problem 7-4 within the chapter.

Mercury—Methylmercury Formation

Objectives

After completing this section, you should be able to

1. describe, in general terms, how and where dimethylmercury and methylmercury are formed.
2. state the major source of methylmercury exposure in humans.
3. explain why mercury vapor and methylmercury compounds are more toxic to humans than other mercury species.

Key Terms

dimethylmercury ($\text{Hg}(\text{CH}_3)_2$)
methylmercury ion (CH_3Hg^+)
blood-brain barrier
human placental barrier

Reading Assignment

Read pages 390–392 in the textbook.

Study Notes

Keep Figure 7-3 in mind when you describe the formation of dimethylmercury and methylmercury in the mud of natural water systems (Objective 1). Please note that these formation processes are necessarily anaerobic in nature. It is not surprising then to know that the consumption of fish constitutes the main source of methylmercury for humans (Objective 2). You should appreciate the small concentrations and the toxicity levels involved. It does not take much of these organomercury compounds to pose a health concern.

Aside: To illustrate this point, Dr. Karen E. Wetterhahn, an experienced chemist at Dartmouth College (USA), died from mercury poisoning in June 1997. In August 1996, during transfer of dimethylmercury in a fume hood, one to several drops spilled on her disposable latex gloves. Approximately three months later, Dr. Wetterhahn began experiencing nausea and vomiting episodes. She then began to lose her balance, then her hearing and eyesight, went into a coma and died 10 months after the initial exposure. This recent

incident was well publicized and is mentioned briefly in the next section of the textbook.

The concept of speciation is key to the accessibility of mercury. The fact that ionic species (Hg^{2+} and Hg_2^{2+}) are not readily transported across biological membranes, greatly reduces their toxicity compared with non-ionic elemental mercury and methylmercury compounds (Objective 3).

Exercises

No exercises have been assigned for this section.

Mercury—Methylmercury Toxicity

Objectives

After completing this section, you should be able to

1. describe Minamata disease and the history surrounding it.
2. state at least three of the symptoms of methylmercury poisoning.
3. state at least two symptoms of offspring of the mothers of methylmercury poisoning.

Key Terms

catalyst
polyvinyl chloride
Minamata disease
cerebral palsy
mental retardation

Reading Assignment

Read pages 392–393 in the textbook.

Study Notes

You should be able to give a general description of the disaster that occurred at Minamata Bay and the “disease” that was named after this small Japanese fishing village of 1300 people (Objective 1). About 200 people died and blood mercury levels of clinical patients were in the 70–900 ppm range. Although Minamata Bay was one of the worst examples, similar poisonings occurred to a lesser degree in other parts of the world. Take for example, the Reed Paper controversy in Dryden, Ontario. A chloralkali plant used to generate chemicals to bleach pulp lost approximately 10 tonnes of mercury to the environment between 1962 and 1970. Two local native bands fished extensively in the water system associated with the paper and chloralkali plants. Their diet included a substantial amount of fish from these waters and some members of these bands had mercury tissue levels of 600 ppb (just on the lower cusp of clinical mercury poisoning range). After 1970 mercury use was limited and after 1975 it was discontinued.

Methylmercury poisoning is very similar to mercury poisoning. Note the symptoms listed on page 393 (Objective 2). Notice that since methylmercury readily passes through the human placental barrier the fetus of an afflicted mother is also subject to methylmercury poisoning. In the case of infants exposed during development, the symptoms are even more extreme (Objective 3). You should be able to list these symptoms.

Exercises

Do Problems 7-5 and 7-6 within the chapter.

Mercury—Other Sources of Methylmercury and Other Forms of Mercury

Objective

After completing this section, you should be able to list three commercial uses of organomercury compounds.

Key Terms

fungicide

World Health Organization's "safe limit"

phenylmercury ion ($C_6H_5Hg^+$)

slimicide

Reading Assignment

Read pages 393–395 in the textbook.

Study Notes

The toxicity of mercury coupled with its general use has made it a serious environmental concern. Even though many of the health problems have long been known, they have often been ignored because mercury is a useful and versatile substance. Despite the introduction of mercury to the environment by a variety of sources, there is little evidence of worldwide contamination on the same scale as has occurred with lead. It should also be noted that introduction of mercury to the environment by all routes has dramatically decreased in the last 30 years. Stringent control of mercury emissions can be attributed to public awareness of the problem brought about by much publicized events such as the Reed Paper controversy or the Minamata Bay disaster.

Exercises

Do Problem 7-7 within the chapter.

Lead—The Free Element

Objectives

After completing this section, you should be able to

1. describe the two physical features of lead that make it a functional material.
2. state at least two uses of elemental lead.

Key Terms

Roman

Renaissance

solder (low-melting tin/lead alloy)

tin

lead shot

Reading Assignment

Read pages 395–396 in the textbook.

Study Notes

Lead is both malleable and has a relatively low melting point (327°C), which makes it easy to work with and shape (Objective 1). In addition, it also has a relatively high density (11.35 g mL^{-1}), which is why it is used in ammunition. Other uses for lead have included water ducts, piping, cooking vessels, solder, roofing, flashing, and soundproofing (Objective 2).

Exercises

No exercises have been assigned for this section.

Lead—Ionic 2+ Lead

Objectives

After completing this section, you should be able to

1. state the two common ionic forms of lead.
2. explain how lead can dissolve in water stating the required conditions and the relevant chemical equation.
3. explain why lead contamination is less common in hard water areas than in soft water areas.
4. list three common commercial past uses for lead(II) salts.

Key Terms

galena
lead storage battery
lead solder
lead carbonate (PbCO_3)
lead(II) oxide (PbO)
lead-glazed pottery
lead pigment
lead chromate (PbCrO_4)
red lead (Pb_3O_4)
white lead ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$)
titanium dioxide (TiO_2)
PVC stabilizer
lead arsenate ($\text{Pb}_3(\text{AsO}_4)_2$)

Reading Assignment

Read pages 396–401 in the textbook.

Omit “Environmental Instrumental Analysis 7-1” (pp. 398–400 in the textbook).

Study Notes

Lead is commonly found in Pb(II) and Pb(IV) oxidation states (Objective 1). We will deal with the lead(IV) species in a later section in this unit. Similar to

mercury, many of these lead species are aqueous inorganics. Elemental lead can oxidize in the presence of air (oxygen) if it is in an acidic aqueous medium as suggested by the chemical equation shown on page 396 (Objective 2). The oxygen is necessary for the oxidation to occur, lead will not oxidize to lead(II) with dilute acids on its own. Also, keep in mind that hard water containing dissolved carbonates can form a protective insoluble PbCO_3 layer (in the presence of oxygen) on the surface of lead (Objective 3). Although the formation of PbCO_3 drastically reduces availability of lead(II) ions in the water, we will see in the next section that this “protective” layer is not completely insoluble.

Applications that involve lead(II) have included lead-acid batteries found commonly in automobiles, lead arsenate pesticides, and polymeric stabilizers in some PVC mini-blinds to name a few. However, exploitation of colours formed from lead(II) salts has been one of the oldest and more universal applications that includes pottery glazes, as well as an array of paint pigments (Objective 4).

Exercise

Do Problem 7-8 within the chapter.

Lead—The Solubilization of “Insoluble” Lead Salts

Objectives

After completing this section, you should be able to

1. explain why PbS and PbCO₃ are more soluble in water of low pH.
2. perform basic solubility and equilibrium calculations.

Key Terms

lead sulfide (PbS)

lead carbonate (PbCO₃)

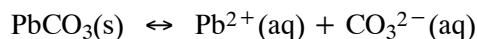
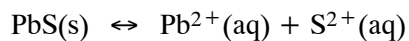
solubility

Reading Assignment

Read pages 401–403 in the textbook.

Study Notes

Read through the equilibrium equations on page 402 carefully and make sure you understand how the relationship $[\text{Pb}^{2+}] = 2.5 \times 10^{-4} [\text{H}^+]$ was derived. Another qualitative way of looking at this process is to think of Le Châtelier’s Principle. Consider the two solubility equilibria at the top of page 402.



As H⁺ is added it will react with S²⁻ (or CO₃²⁻) to go on and produce other products (i.e. H₂S or H₂CO₃). To compensate this loss on the products side, the equilibria move to the right, so more PbS and PbCO₃ dissolves and re-establishes the S²⁻ and CO₃²⁻ concentrations (Objective 1).

You may wish to review both equilibrium and acid-base topics in your first-year chemistry course to help refresh your memory to do basic K_{sp} calculations (Objective 2).

Exercises

Do Problem 7-9 within the chapter.

Do Additional Problem 3 at the end of the chapter on page 416.

Lead—Ionic 4+ Lead

Objectives

After completing this section, you should be able to

1. recognize lead(II), lead(IV) and mixed lead(II/IV) species given the chemical formula.
2. explain the operation of a lead storage battery.

Key Terms

highly oxidizing environment

mixed oxide

red lead (Pb_3O_4)

lead storage battery

Reading Assignment

Page 403 in the textbook.

Study Notes

Lead has + 2 and + 4 as common valence states and you should be able to recognize this within any chemical formula of a given lead compound (Objective 1). In some cases you may also find mixed oxides (see Problem 7-A below).

The lead storage battery or lead-acid battery is a secondary cell (a chemical cell that can be recharged) and is commonly found in automobiles. The first two chemical equations on page 403 represent the half reactions in a lead storage battery at the anode and cathode, respectively (Objective 2).

Exercise

Question 7-A

Identify how many lead(II) and lead(IV) are in the paint pigment red lead (Pb_3O_4).

Lead—Tetravalent Organic Lead

Objectives

After completing this section, you should be able to

1. identify the two common anti-knock agents added to leaded gasoline.
2. explain the purpose of adding organohalide compounds to leaded gasoline.

Key Terms

tetravalent

tetramethyllead (TML, $\text{Pb}(\text{CH}_3)_4$)

tetraethyllead (TEL, $\text{Pb}(\text{CH}_2\text{CH}_3)_4$)

neurotoxin

Reading Assignment

Read page 404 in the textbook.

Study Notes

Tetramethyl- and tetraethyllead were common antiknock agents for gasoline (Objective 1). They are now banned in most developed countries to curb contamination of the environment by lead. To prevent lead build up in the engines organohalides were also added to the gasoline to produce various lead halides that are removed in the exhaust of the automobile (Objective 2).

Exercise

Do Additional Problem 6 at the end of the chapter on page 417.

Lead—Lead in the Environment and Its Health Effects

Objectives

After completing this section, you should be able to

1. state at least three symptoms of lead poisoning.
2. explain why children are more susceptible to lead poisoning.
3. describe the medical treatment for acute lead poisoning.

Key Terms

catalytic converter
blood-brain barrier
safe level
threshold level

Reading Assignment

Read pages 404–408 in the textbook.

Study Notes

Lead has many similarities to mercury. It is a toxic heavy metal that in high enough concentrations attacks the central nervous system. It is a cumulative poison and because it is a useful substance there has been widespread use and subsequently also widespread pollution of the environment. (In fact, lead has caused much more environmental contamination than has mercury.) However, unlike mercury it does not undergo biomagnification.

Lead is a cumulative poison with a whole body half-life of about six years. Because Pb^{2+} and Ca^{2+} are similar in ionic radius, lead can replace calcium in calcium-containing tissue (skeleton, teeth, hair) of the body. Symptoms and effects of lead poisoning include mental retardation of young children, lower birthweights for newborns, higher risk of premature birth, blindness, cerebral palsy, interference with hemoglobin synthesis, growth inhibition and hypertension (Objective 1). The most important biochemical effect of lead is interference in the synthesis of heme. It inhibits key enzymes involved in heme production and results in the accumulation of metabolic intermediates, which the body eventually eliminates. The net result is

impairment of synthesis of hemoglobin and other respiratory pigments such as cytochromes that require heme. Because of the blood-brain barrier in young children has not fully developed they are especially susceptible to lead poisoning (Objective 2).

In cases of acute lead poisoning a similar technique to mercury poisoning is used. That is, the free ionic species in the blood is chelated before it can pass the blood-brain barrier. For lead ethylenediaminetetraacetic acid (EDTA) is used to complex Pb^{2+} ions in the blood (Objective 3).

Exercises

Do Problem 7-10 within the chapter.

Do Additional Problem 4 at the end of the chapter on page 416.

Cadmium—The Free Element

Objectives

After completing this section, you should be able to

1. list three sources of cadmium release into the environment.
2. explain how a nicad battery works.

Key Terms

zinc smelting

nicad (nickel-cadmium) battery

cadmium hydroxide ($\text{Cd}(\text{OH})_2$)

Reading Assignment

Read pages 408–409 in the textbook.

Study Notes

Sources of environmental cadmium include release during zinc, copper, or lead smelting, burning coal, and incineration of waste materials (Objective 1). You should know that nicad batteries are secondary cells (i.e., rechargeable) and commonly used calculators, video cameras, and other portable electronic devices. You do not have to memorize the half reactions, but you should know that cadmium metal is oxidized (anode) as shown at the top of page 409 and that nickel(III) is reduced (cathode) to nickel(II) to produce a charge (Objective 2). The reverse reactions occur during recharging.

Aside: Nicad batteries have a so-called memory effect. The chemical reactions are reversible, but the physical changes in the electrodes may not be. If a recharge is started before the battery is completely discharged, the next discharge may stop at that point and fail to provide further energy.

Exercises

No exercises have been assigned for this section.

Cadmium—Environmental Cadmium

Objectives

After completing this section, you should be able to

1. list at least three commercial uses for cadmium compounds.
2. state the main source of cadmium exposure for humans.
3. describe itai-itai disease.
4. explain what metallothionein is and its function in the human body.

Key Terms

cadmium pigment
photovoltaic device
photoelectric cell
itai-itai disease
metallothionein
cumulative poison

Reading Assignment

Read pages 409–411 in the textbook.

Study Notes

If you are a painter, you will immediately recognize cadmium yellow as being a unique brilliant yellow paint. Similar to lead, cadmium is important in pigments for paints and plastics. Cadmium is also used in electronic devices such as photovoltaic devices, nicad batteries, specialty alloys, and as phosphors in TV screens (Objective 1). We are exposed to cadmium from various sources including those already mentioned in the previous section (i.e., zinc, copper, or lead smelting, burning coal, and incineration of waste materials), but also through cigarette smoke. If you are not a smoker or do not live near a smelter your exposure through breathing air or drinking water is minimal. The major source of cadmium exposure for most people is seafood and organ meats (Objective 2).

Itai-itai disease is described in detail on page 410 and rests on the principle that Cd^{2+} ions are similar in size and charge to Ca^{2+} . Replacement of

calcium by cadmium in bone material destroys some of the structural integrity of the bone (Objective 3).

Metallothionein protein is used normally to control zinc levels in the body, but is also the body's first defense against cadmium poisoning (Objective 4).

Exercise

Do Additional Problem 8 at the end of the chapter on page 417.

Arsenic

Objectives

After completing this section, you should be able to

1. state the two common valences of arsenic.
2. list three sources of arsenic release into the environment.
3. state the major source for human arsenic exposure.
4. explain why exposure to organic arsenic in food is not a serious health hazard.
5. describe the most toxic species of arsenic and the mechanism of the toxicity.
6. describe the symptoms of acute arsenic poisoning.

Key Terms

valence shell

trivalent arsenic (As(III))

pentavalent arsenic (As(V))

leachate

lead arsenate ($\text{Pb}_3(\text{AsO}_4)_2$)

calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$)

sodium arsenite (Na_3AsO_3)

Paris Green ($\text{Cu}_3(\text{AsO}_3)_2$)

synergistic

death by wallpaper

arsine gas (AsH_3)

trimethyl arsine ($\text{As}(\text{CH}_3)_3$)

Reading Assignment

Read pages 411–414 in the textbook.

Omit “Box 7-1 Organotin Compounds” (p. 413 in the textbook)

Study Notes

Arsenic is found in either the +3 or +5 valence state (Objective 1). There are many minor uses of arsenic like GaAs electronics (see Unit 5 on solar cells) or producing glass. In the past it was heavily used in pesticides, before organic products were available (see Unit 6). Arsenic was even present in early medications like Salvarsan® (arsphenamine) which was used to cure syphilis. Its present release into the environment includes use of arsenic pesticides, wood preservatives, mining (lead, gold, copper, and nickel), producing iron and steel, and combustion of coal (Objective 2). Most people are exposed to arsenic through drinking water (Objective 3) and through foods they eat. However, foods will most contain organic arsenic sources that are water-soluble and excreted (i.e., not readily taken up by the body). In addition, any absorbed organic arsenic can be readily methylated and excreted by the body (Objective 4).

Arsines (e.g. AsH_3 and $\text{As}(\text{CH}_3)_3$) are the most toxic arsenic compounds, because of their tendency to bond strongly to sulfhydryl groups of enzymes in the body (Objective 5). Acute poisoning can result in damage to the digestive tract and produces symptoms like vomiting and diarrhea (Objective 6). Similar to acute mercury poisoning, the treatment for acute arsenic(III) poisoning is chelation therapy with BAL.

Aside: It had long been rumoured that Napoleon died in 1821 of deliberate arsenic poisoning during his exile on St. Helena. However, it is a more likely scenario that trimethyl arsine gas produced by moulds on wallpaper containing the arsenic pigment Scheele's green (copper arsenite) which was not uncommon in Napoleon's time, lead to eventual "death by wallpaper." Hair samples from Napoleon show a slow buildup of arsenic (arsenic accumulates in the keratin of hair and fingernails), which is consistent with chronic exposure and bioaccumulation rather than an acute poisoning.

Exercises

Do Problem 7-11 within the chapter.

Do Additional Problems 5 and 7 at the end of the chapter on pages 416 to 417.

Answer to Extra Exercise

Note: the following is an answer to an extra question posed within this *Study Guide*. Short answers to in-chapter problems can be found at the end of the textbook. In addition, detailed solutions for all problems in the textbook are available in the accompanying *Solutions Manual for Environmental Chemistry* by Colin Baird.

Answer 7-A

Red lead (Pb_3O_4) is a mixed oxide with three lead atoms and four oxygen atoms. Assume all the oxygen atoms are -2 in charge, for a total of -8 charge. The lead atoms must balance this to obtain a neutral Pb_3O_4 compound. This can only be achieved by two lead(II) atoms plus one lead(IV) atom within the compound.

$$2\text{Pb(II)} + 1\text{Pb(IV)} + 8\text{O(II)} = \text{Total Charge}$$

$$2(2+) + 1(4+) + 8(2-) = 0$$

Review Procedure

1. Review the unit objectives and make sure that you can define, and use in context, the key terms introduced in this unit.
2. Go over the Review Questions (pp. 415–416 textbook) to test your factual knowledge of the material covered this unit.
3. Do some of the Supplementary Exercises for Chapter 7 for additional practice or examination preparation. Supplementary Exercises (with answers) can be found on the resource Web pages that accompany the textbook.

<http://www.whfreeman.com/ENVCHEM/INDEX.HTM>

4. Do the tutor-marked assignment for Units 6 and 7 (TMA 3), make a photocopy for yourself and send the original to your tutor. Then proceed to Unit 8.