Lecture #50

Redox Chemistry: Lead I
(Stumm & Morgan, Chapt. 8)

Benjamin; Chapter 9
Case study: Lead

• Regulations
  • 0.015 mg/L action level in drinking water

• Sources
  • Natural: lead minerals
  • Industrial: paints
  • Plumbing: service connections, solder, brass alloy faucets

• Health Effects
  • Kidney, nervous system damage
A short history of Lead

- Emperor Nero & others
  - a predilection to lead-tainted diets and suffered from gout and other symptoms of chronic lead poisoning
  - Not only did the Romans drink legendary amounts of wine, but they flavored their wines with a syrup made from simmered grape juice that was brewed in lead pots. The syrup was also used as a sweetener in many recipes favored by Roman gourmands.
  - "One teaspoon of such syrup would have been more than enough to cause chronic lead poisoning," Dr. Nriagu said.

NY Times: March 17, 1983

Peter Ustinov as Nero
Our continuing love affair with lead

- Used for some of the earliest pressurized water pipes
  - Malleable, plentiful
  - Plumbing and plumbers use Pb
- Used with modern urban water systems
  - Lead service lines – esp. 1920s-1940s
  - Lead solder: until 1986
  - Brass fittings with lead

David Reckhow
Then, Flint
Flint

- 31 January 2016; Boston Globe

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Flint worries are focused on children

by Abby Goodnough

FLINT, Mich. — Qayyana Towns’ 2-month-old daughter wriggled on an exam table last week as her pediatrician ticked off questions that have become essential for every parent of young children here.

“Do you have any concerns for her — for water — for what she’s drinking?” asked the doctor, Mona Hanna-Attisha. “I have a whole bunch of bottled water that I picked up,” said Towns, 26, assuring the doctor that the family had been drinking it for a few months, since the gravity of Flint’s water crisis came to light.

“And before that you were using tap water?”

“Yes,” Towns replied, as her other child, a 1-year-old, Kion, cuddled around.

Hanna-Attisha would wait no time adding King and his sister, Taeyana, to a new database of children under 6 who may have been exposed to lead in Flint’s water, a group she believes could number 8,000.

Of all the concerns raised by the contamination of Flint’s water supply, and the failures of the state and federal governments to promptly address the crisis after it began nearly two years ago, none is more chilling than the possibility that children in this tattered city may have suffered permanent damage to developing brains and nervous systems from exposure to lead.

Residents and advocates have accused the state of the government’s failure to protect Flint’s children, something many of them say would not have happened if the city were largely white. Adding to their injury, they say, are the harsh conditions of poverty that have already weighed obstacles in their young lives.

At the same time, many are turning their attention to the future, when the effects of consuming lead-laced water for months may be all too evident.

At the center of those efforts is Hanna-Attisha, whose research documenting a spike in children’s blood lead levels forced dismissive government officials to finally acknowledge the water crisis last fall. With her colleagues at Hurley Children’s Hospital, where she directs the pediatric residency program, she is at the forefront of the scramble to put in place the services and resources so that every child who needs extra help learning or overcoming medical problems will have support for years to come.

Decades of research have found that exposure to even low levels of lead can profoundly affect children’s growth, behavior, and intelligence over time. Studies have linked elevated lead levels in blood to learning disabilities, problems with attention and fine motor coordination, and even violent behavior.

Younger children and fetuses are especially vulnerable because of their developing brains and nervous systems, which is why the efforts here will focus on children 6 years and younger.

Releases by the office of Governor Rick Snyder last week referred to a resident who said she was told by a state nurse in January 2015, regarding her son’s elevated blood lead level, “It is just a few IQ points... it is not the end of the world.”

Hanna-Attisha and others who have studied lead poisoning have a sharply different view of lead exposure, for which there is no cure.

“If you were going to put something in a population to keep them down for generations to come, it would be lead,” Hanna-Attisha said.

Underlying the problem are the troubling conditions prevalent among low-income children and their families in cities like Flint: spotty access to doctors and health care services; a dearth of healthy foods; living conditions so poor that many of the children may have already been exposed to lead poisoning from the paint in their homes; parents with limited time and financial resources.

The doctors here said they will focus on improving the diets of affected children and expanding education programs like Head Start, the federally funded preschool program for low-income children, which already has a waiting list in Flint. Hanna-Attisha has submitted dozens of recommendations to the governor, state legislators and federal officials.

It remains a wish list at this point, but she and others believe that with Flint’s public health crisis in the national spotlight, the city’s chances of getting help are better than ever before.

Snyder and the state Legislature have so far allocated $28 million in emergency state spending for Flint. Some of the money will provide initial services, like health assessments and home visits from nurses, to lead-exposed children. Snyder has also asked the federal government to expand Medicaid to cover every Flint resident younger than 21, regardless of income level. And Democrats in Congress said Thursday that they would seek $600 million in federal aid for Michigan to help Flint.

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David Reckhow
CEE 680 #50
Blood Pb

- Children <5 yrs
- Levels in 2015; after change to Flint River

Hanna-Attisha et al., 2016
AJPH 106:2:283-290

Elevated Blood Levels
Flint Michigan Crisis

Timeline
- April 2014: the city stopped getting its water from Detroit as a cost-saving measure and began instead drawing water from the Flint River.
- High blood lead levels noted in children
- Water lead levels were above standard
- Oct 16, 2015: Flint switches back to Detroit Water

Sources
- VPI website: [http://flintwaterstudy.org/](http://flintwaterstudy.org/)
- 12/22/2015 Rachel Maddow video:
# Flint Water Quality – why?

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<td>0.45</td>
<td>1.6</td>
<td>mg/mg</td>
</tr>
<tr>
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WQ data From MOR and 2014 WQR  
CSMR = chloride to sulfate mass ratio  
Larson Ratio = ([Cl⁻] + 2[SO₄²⁻])/[HCO₃⁻]
The Flint case

- A cascade of actions and effects

Desire to Save $$

Stop buying water from Detroit

Higher Cl/SO4 ratio
Stopped adding PO4

Use local Flint River

Widespread corrosion in water pipes

Legacy of lead plumbing

Release of Pb into water

Other Metals too

Destruction of chlorine residual

More hazardous chlorinated compounds

Growth of microorganism (e.g., Legionella)

Sediment in water –some settled in water heaters

Decision to add more chlorine

Denial by public officials & Blame the innocent

Exposure
Water Quality

- **pH**

- **Cl₂**

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Flint Rash Investigation Report, August, 2016
Pb(II) solubility

- 3 mg/L DIC
- No phosphate

From: Internal Corrosion and Depositional Control, by Schock & Lytle, Chapt. 20 in Water Quality and Treatment (6th ed.), 2011
Control w/o Phosphate or high Redox

- Can only work for low carbonate waters
- Not as good as phosphate or high Redox

From: Mike Schock

David Reckhow
Flint Finished Water Quality – why?

Alkalinity was about the same; pH actually went up a bit

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WQ data from Edwards website

David Reckhow
IDWT
Consider galvanic corrosion

- Micro environments near surface can have very low pHs
  - Basic ligands like hydroxide and phosphate will be much less important
  - Weak base anions can become enriched

Nguyen et al., 2010; WRF Report

Figure 1.1 Reactions at lead anode and copper cathode surfaces
Sulfate and Chloride

- In bulk water neither sulfate nor chloride can compete well with hydroxide for lead.
- Near surface with active galvanic corrosion, pH drops and hydroxide is very low.
  - Sulfate forms insoluble PbSO\(_4\) precipitate
    \[ K_{s0} = [Pb^{+2}][SO_4^{-2}] = 1.54 \times 10^{-8} \]
  - Chloride forms soluble PbCl\(^+\) complex
    \[ K_1 = \frac{[PbCl^+]}{[Pb^{+2}][Cl^-]} = 59.5 \]

Nguyen et al., 2010; WRF Report
Pb(II): pH vs PO₄T; low CO₃T

- 6 mg/L DIC

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

AL = 15 μg/L = 10⁻¹.₈ mg/L

**Note:** Concentration units are log (mg Pb/L). The solid phase boundary lines are approximate.

**Figure 4-19:** Contour diagram for the impact of varying concentrations of orthophosphate and hydrogen ion, with DIC = 6 mg C/L, temperature = 25°C, and I = 0.005 mol/L
Pb(II); pH/PO₄₄ contour plot

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

\[ \text{AL} = 15 \, \mu\text{g/L} = 10^{-1.8} \, \text{mg/L} \]

Figure 4-21 Three-dimensional surface plot of lead concentration versus orthophosphate dose for 2.4 mg C/L DIC (DIC = 2 \times 10^{-4} M, I = 0.01 mol/L, temperature = 25°C)
Other issues

- Legionella

- Trihalomethanes

Flint Distribution system locations; data from WITAF, EPA and UMass
The press & public reaction

- Cites elevated DBPs in water heaters
- Ruffalo advises against bathing
- [video](#)

May 4, 2016
May 5, 2016
May 31, 2016
Public engagement

- Edwards slide
- Environmental justics issues
Washington, DC
Pb Increase Correlates with Chloramines

<table>
<thead>
<tr>
<th>Monitoring Period Start</th>
<th>Monitoring Period End</th>
<th>Lead (ppb) 90th percentile</th>
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<tbody>
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<td>January 1, 1992</td>
<td>June 30, 1992</td>
<td>18</td>
</tr>
<tr>
<td>July 1, 1992</td>
<td>December 31, 1992</td>
<td>15</td>
</tr>
<tr>
<td>January 1, 1993</td>
<td>June 30, 1993</td>
<td>11</td>
</tr>
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<td>July 1, 1993</td>
<td>December 31, 1993</td>
<td>37</td>
</tr>
<tr>
<td>January 1, 1994</td>
<td>June 30, 1994</td>
<td>14</td>
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<td>July 1, 1994</td>
<td>December 31, 1994</td>
<td>12</td>
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<td>January 1, 1997</td>
<td>June 30, 1997</td>
<td>6</td>
</tr>
<tr>
<td>July 1, 1997</td>
<td>December 31, 1997</td>
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<td>July 1, 1998</td>
<td>December 31, 1998</td>
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<td>January 1, 1999</td>
<td>June 30, 1999</td>
<td>5</td>
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<td>July 1, 1999</td>
<td>June 30, 2000</td>
<td>12</td>
</tr>
<tr>
<td>July 1, 2000</td>
<td>June 30, 2001</td>
<td>8</td>
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<tr>
<td>July 1, 2001</td>
<td>June 30, 2002</td>
<td>75</td>
</tr>
<tr>
<td>January 1, 2003</td>
<td>June 30, 2003</td>
<td>40</td>
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<tr>
<td>July 1, 2003</td>
<td>December 31, 2003</td>
<td>63</td>
</tr>
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</table>

pH Raised with CaO

NH3 added to give Chloramines

Grumbles & Welsh, WASA, House Testimony 3/5/04

David Reckhow
CEE 680  #51
Washington, DC Lead Service Lines

Low income households
Chloramines: a solution to the DBP problem?

- Inorganic chloramines are formed by the reaction of free chlorine with ammonia.
  \[
  \text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad (1)
  \]

- Monochloramine is formed very quickly (in minutes)

- Although it is not as powerful an oxidant or disinfectant as free chlorine, it does continue to provide some pathogen protection.

- It does not continue to produce THMs and most HAAs like free chlorine does.

- Therefore, many cities like DC have decided to convert their distribution system disinfectant to chloramines.
Washington DC

- Free chlorine and lime addition (high pH)
- Nov 2000, switch to chloramines

Edwards et al., 2009; *Environ. Sci. Technol.*, 43 (5), pp 1618–1623

David Reckhow
Chlorine to chloramines

Schock et al., 2007
What went wrong?

- Washington, DC
  - Change from chlorine to chloramines
  - Solubilization of lead (+IV)
- Flint, MI
  - Change from low Chloride water to high
  - No more phosphate inhibitor
  - Greater corrosion rates
How to avoid Lead problems

- Optimized corrosion control treatment
  - Control of pH and alkalinity
  - Addition of orthophosphate based corrosion inhibitors
  - Keep oxidized environment
- Minimize changes in distributed water chemistry
- Removal lead from system
  - Lead service lines
  - Lead in plumbing fixtures
2003 Lead crisis in Washington, DC
NY Times: 27 March 2016

- Lead is a neural toxin
- Especially serious in children
- EPA: Pb & Cu Rule Published in 1991
- If lead concentrations exceed an action level of 15 ppb in more than 10% of customer taps sampled (i.e., 90%ile), the system must undertake a number of additional actions to control corrosion.
Public Outrage

- 2003 in DC & elsewhere

The Great Lead Water Pipe Disaster
- Werner Troesken
- 2006 MIT Press
Why did the DC crisis happen?

- Unintended consequences of decisions made to protect public health
- Need to provide clean water to cities
  - Disinfect with chlorine
  - Lead is a great piping material
- Some secondary problems that need fixing - carcinogens
  - Solution: Convert chlorine to chloramines?
  - Oops

First, a short history of municipal drinking water
How to avoid Lead problems

- Optimized corrosion control treatment
  - Elevated pH and control of alkalinity
  - Addition of orthophosphate based corrosion inhibitors
- Other guidance
  - Keep oxidized environment
  - Keep chloride to sulfate ratio low
  - Minimize changes in distributed water chemistry
- Removal lead from system
  - Lead service lines
  - Lead in plumbing fixtures
Protection by a CaCO$_3$ film?

- Calcium carbonate will precipitate when the solubility product is exceeded
  - This occurs at elevated pHs where the equilibrium shifts toward more carbonate
  - Of course there has to be a certain amount of calcium (hardness present as well)
- This film has been shown to protect pipes from corrosion
  - for this reason, high pHs and high alkalinitities can help with corrosion control
  - How high should the pH be?
Me-Carbonate Equilibria

- From Pankow

\[
\begin{align*}
MCO_3(s) &= M^{2+} + CO_3^{2-} \\
M^{2+} + OH^- &= MOH^+ \\
MOH^+ + OH^- &= M(OH)_2^0 \\
M(OH)_2^0 + OH^- &= M(OH)_3^- 
\end{align*}
\]

\[
K_{s0} = \frac{[M^{2+}][CO_3^{2-}]}{} \quad (12.1)
\]

\[
K_{H1} = \frac{[MOH^+]}{[M^{2+}][OH^-]} \quad (12.2)
\]

\[
K_{H2} = \frac{[M(OH)_2^0]}{[MOH^+][OH^-]} \quad (12.3)
\]

\[
K_{H3} = \frac{[M(OH)_3^-]}{[M(OH)_2^0][OH^-]} \quad (12.4)
\]

\[\text{pH for initially-pure water (i.e., } (C'_B - C'_A) = 0\text{) in equilibrium @ 25}^\circ\text{C/1 atm with a divalent metal carbonate.}\]

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>(\log K_{s0})</th>
<th>(\log K_{H1})</th>
<th>(\log K_{H2})</th>
<th>(\log K_{H3})</th>
<th>exactly using Eq. (12.17)</th>
<th>approximately using Eq. (12.26)</th>
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<tr>
<td>Mg(^{2+})</td>
<td>-7.46</td>
<td>2.58</td>
<td>-</td>
<td>-</td>
<td>10.19</td>
<td>10.29</td>
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<tr>
<td>Ca(^{2+})</td>
<td>-8.30</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>9.96</td>
<td>10.01</td>
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<td>Ba(^{2+})</td>
<td>-8.30</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
<td>9.96</td>
<td>10.01</td>
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<td>Sr(^{2+})</td>
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<td>0.82</td>
<td>-</td>
<td>-</td>
<td>9.73</td>
<td>9.77</td>
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<td>Mn(^{2+})</td>
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<td>3.4</td>
<td>3.4</td>
<td>1.0</td>
<td>9.63</td>
<td>9.68</td>
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<td>Zn(^{2+})</td>
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<td>6.0</td>
<td>2.5</td>
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<td>9.44</td>
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<td>Fe(^{2+})</td>
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<td>2.6</td>
<td>8.93</td>
<td>9.22</td>
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<tr>
<td>Pb(^{2+})</td>
<td>-13.13</td>
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<td>4.6</td>
<td>3.0</td>
<td>8.20</td>
<td>8.40</td>
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<tr>
<td>Cd(^{2+})</td>
<td>-13.74</td>
<td>3.9</td>
<td>3.8</td>
<td>2.6</td>
<td>7.88</td>
<td>8.20</td>
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Me-carbonates

- Closed System with $C_T = 3 \times 10^{-3}$ M

Stumm & Morgan, 1996, Figure 7.8, pg. 374
Langelier Index (LI)

- A measure of the degree of saturation of calcium carbonate in water
  - When a water is exactly in equilibrium with CaCO₃ such that neither dissolution nor precipitation is occurring,
    - LI = 0
  - When CaCO₃ precipitation is occurring, the water is oversaturated and by definition:
    - LI > 0
  - So the extent of oversaturation (ie., the LI) is defined as the number of log units of the actual, measured, water pH \( (pH_{\text{act}}) \) above the theoretical value that gives perfect equilibrium \( (pH_{\text{sat}}) \)

\[
LI \equiv pH_{\text{act}} - pH_{\text{sat}}
\]
The saturation pH can be calculated using the solubility product constant (Kso) and knowing the water’s carbonate content from knowledge of the alkalinity.
No assumptions on mass balance

- Returning to the basic solubility, but not requiring that calcium and total carbonates be equal

\[ K_{SO} = [Ca^{+2}][CO_3^{-2}] \]

\[ K_{SO} = [Ca^{+2}] \alpha_2 C_T \]

\[ \alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1} \]

And so at pH = 6.3 – 10.3

\[ \alpha_2 \approx \frac{1}{\frac{[H^+]}{K_2}} = K_2/[H^+] \]

\[ K_{SO} = [Ca^{+2}] \frac{K_2}{[H^+]} C_T \]

\[ [H^+] = [Ca^{+2}] \frac{K_2}{K_{SO}} C_T \]
LI (cont)

- Continuing

\[
[H^+] = [Ca^{+2}] \frac{K_2}{K_{so}} C_T
\]

\[
\log [H^+] = \log[Ca^{+2}] + \log K_2 - \log K_{so} + \log C_T
\]

\[
pH_{sat} = -\log[Ca^{+2}] + pK_2 - pK_{so} - \log C_T
\]

- And now combining with the LI definition

\[
LI \equiv pH_{act} - pH_{sat}
\]

\[
LI = pH_{act} + \log[Ca^{+2}] - pK_2 + pK_{so} + \log C_T
\]
LI (cont)

- And since in the pH range below 10.3, the alkalinity is mostly due to bicarbonate, we can equate the $C_T$ to the alkalinity

\[ LI = pH_{act} + \log[Ca^{+2}] - pK_2 + pK_{so} + \log[Alk] \]

- And general practice has been to increase pH so that the LI is 0.2 to 1.0

- While CaCO$_3$ films have been found to inhibit iron corrosion, there is little evidence that a high LI can reduce the level of soluble Pb
Alkalinity was about the same; pH actually went up a bit

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Getting the lead out: Lead service lines (LSL) in US

Cornwall et al., 2016
JAWWA, April
Pb mitigation in Boston

- Karalekas study

Source: Karalekas et al. (1983).

Figure 4-2 Mean levels of lead in samples taken from Boston, Massachusetts, and Somerville, Massachusetts, 1976-1981

From: Internal Corrosion and Depositional Control, by Schock Chapt. 17 in Water Quality and Treatment (5th ed), 1999
Pb Mitigation

- Impacts on other corrosion byproducts

From: Karalekas et al., 1983 [J.AWWA 75:2:92]
Iron Scale

**Figure 17.1** Adjoining anodes and cathodes during the corrosion of iron in acidic solution. (Source: Water Chemistry, V. L. Snoeyink and D. Jenkins. Copyright © 1980, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

**Figure 2-6** Schematic of scale on a cast-iron distribution pipe
Pb: Equations

- **Redox**

\[
PbO_{2(s)} + 4H^+ + 2e^- = 2H_2O + Pb^{2+} \quad \log K = 49.2
\]

\[
Pb^{2+} + 2e^- = Pb_{(s)} \quad \log K = -4.26
\]

\[
PbO_{(s)} + 2H^+ = Pb^{2+} + H_2O
\]

\[
Pb^{2+} + H_2O = PbOH^+ + H^+
\]

\[
PbOH^+ + H_2O = Pb(OH)_2^o + H^+
\]

\[
Pb(OH)_2^o + H_2O = Pb(OH)_3^- + H^+
\]

- **Solubility**

\[
log *K_{s0} = 12.7
\]

\[
log *K_1 = -7.7
\]

\[
log *K_2 = -9.4
\]

\[
log *K_3 = -11.0.
\]

- **Mass Balance**

\[
Pb_T = [Pb^{+2}] + [PbOH^+] + [Pb(OH)_2^0] + [Pb(OH)_3^-]
\]

\[
= [Pb^{+2}] \left( 1 + \frac{K_1}{[H^+]^3} + \frac{K_1 K_2}{[H^+]^2} + \frac{K_1 K_2 K_3}{[H^+]^3} \right)
\]

\[
Pb_T = *K_{so} [H^+]^2 \left( 1 + \frac{K_1}{[H^+]^3} + \frac{K_1 K_2}{[H^+]^2} + \frac{K_1 K_2 K_3}{[H^+]^3} \right)
\]

Pb (+II): Solubility

- Red- PbO(s)

From: Aquatic Chemistry Concepts, by Pankow, 1991
Pb: Predominance Equations I

Again, in general

\[ Pb_T = *K_{so} [H^+]^2 \left( 1 + \frac{*K_1}{[H^+]} + \frac{*K_1 * K_2}{[H^+]^2} + \frac{*K_1 * K_2 * K_3}{[H^+]^3} \right) \]

Which can reduce to (depending on predominance):

- For Pb\(^{+2}\)
  \[ Pb_T \approx *K_{so} [H^+]^2 (1) = 10^{-12.7} [H^+]^2 \]

- For Pb(OH)\(_2\)\(^{\circ}\)
  \[ Pb_T \approx *K_{so} [H^+]^2 \left( \frac{*K_1}{[H^+]} \right) = *K_{so} * K_1 [H^+] = 10^{-20.4} [H^+] \]

- For Pb(OH)\(_2\)\(^{\circ}\)
  \[ Pb_T \approx *K_{so} [H^+]^2 \left( \frac{*K_1 * K_2}{[H^+]^2} \right) = *K_{so} * K_1 * K_2 = 10^{-29.8} \]
Oxidation Chemistry of Pb

- **Oxidation States**
  - 0, +II, +IV

- **Solubility**
  - 0 oxidation state: insoluble
    - Pb(s)
  - +II oxidation state: relatively soluble
    - PbO(s) (red & yellow), Pb(OH)$_2$(s)
  - +IV oxidation state: essentially insoluble
    - PbO$_2$(s)
Pb: Predominance Equations II

\[
2pe = 49.2 + \log\{\text{PbO}_2(s)\} - \log\{\text{Pb}^{2+}\} - 2\log\{\text{H}_2\text{O}\} - 4pH 
\]

From: Aquatic Chemistry Concepts, by Pankow, 1991
Pb Predominance

- \( \text{Pb}_T = 10^{-2} \text{ M} \)

From: Aquatic Chemistry Concepts, by Pankow, 1991 (pg. 468)
Pb Predominance

- \( \text{Pb}_T = 10^{-4} \text{ M} \)

Pb Predominance

- Combined

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Pb Predominance

- \( \text{Pb}_T = 10^{-6} \text{ M} \)

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• To next lecture