Part I
Lead Acid Batteries

a)
Oxidation:
$PbSO_4 + H^+ + 2e^- \rightarrow Pb + HSO_4^-$
Reduction:
$PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$
b)

$$\begin{aligned} E &= E^o - \frac{RT}{nF} \log \frac{[HSO_4^-][Pb]}{[H^+][PbSO_4]} \\ &= E^o - 0.02958V \log_{10} \frac{[HSO_4^-]}{[H^+]} \end{aligned}$$

$$\begin{aligned} E = E^o - \frac{RT}{nF} \log \frac{[H_2O][PbSO_4]}{[H^+]^3[HSO_4^-][PbO_2]} \\ E^o - 0.02958V \log_{10} \frac{1}{[H^+]^3[HSO_4^-]} \end{aligned}$$

c)

$$\begin{aligned} E^o{}_{cell} &= E^o{}_{cathode} - E^o{}_{anode} \\ &= 1.685V - (-0.356V) \\ &= 2.041V \end{aligned}$$

$$Pb + HSO_4^- + PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + H^+ + 2e^- + PbSO_4 + 2H_2O$$
$$Pb + 2HSO_4^- + PbO_2 + 2H^+ \rightarrow 2PbSO_4 + 2H_2O$$
$$E = E^o - \frac{RT}{nF} \log \frac{1}{[H^+]^2[HSO_4^-]^2}$$

At low pH, the potential is high. From the Nernst equation, the lower the pH, the smaller the value subtracted from the standard potential. Alternately, from Le Chatelier's principle, the acid is in the reactants, and increasing the concentration of the reactants will drive the equilibrium forward.

Part II
Groundwater Contamination

$$SO_4^{2-} + 8e^- + 10H^+ \rightleftharpoons H_2S + 4H_2O \quad E^o = 0.3V$$

$$\begin{aligned} E &= E^o - \frac{RT}{nF} \log \frac{[SO_4^{2-}][H^+]^{10}}{[H_2S][H_2O]^4} \\ &= 0.3V - \frac{0.05916V}{8} \log_{10} \frac{10^{-4.15}}{10^{-5}(10^{-7.5*10})} \\ &= -0.260911 \\ 0 &> -0.26 \end{aligned}$$

The water is anoxic, so the groundwater is contaminated

Part III

Iron and Water Potentials

a)
Overall:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

Oxidation:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

b)

$$\begin{aligned}
\log_{10} k_{eq} &= -\frac{1}{2}\log_{10} pO_2 - 2\log_{10}\alpha_e - (-2\log_{10}\alpha_{H^+}) \\
&= -\frac{1}{2}\log_{10} pO_2 + 2pe + 2pH \\
41.54 &= 0.33889 + 2pe + 2pH \\
20.77 &= 0.169 + pe + 2pH \\
pe &= 20.60 - pH \\
\frac{20.77 - 20.60}{20.77} &= 0.00816
\end{aligned}$$

c)
From class:

$$\begin{aligned}
\log_{10} k &= \log_{10}[Fe^{2+}] + pe + 3pH \\
18.4 &= \log_{10}[Fe^{2+}] + pe + 3pH \\
pe &= 18.4 - 3pH - \log_{10}[Fe^{2+}] \\
pe &= 24.4|26.4 - 3pH
\end{aligned}$$

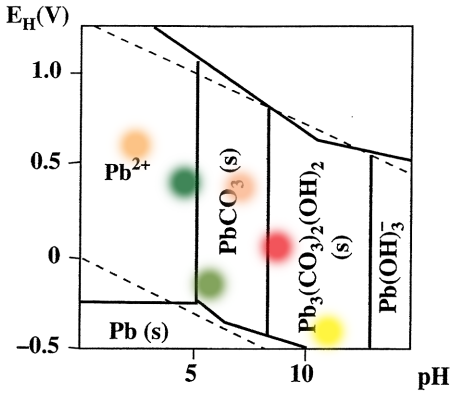
The pe of the water is either 24.4 or 26.4 $-3pH$ depending on the definition for the iron concentration.

Part IV

Aqueous Lead Oxidation-Reduction

Key	Water Type	Pb Species
▪	Surface ocean water	$Pb_3(CO_3)_2(OH)_2$ or $Pb(CO)_3$
▪	Normal stream water	$Pb(CO)_3$
▪	Aerobic acidic mine drainage waters	Pb^{2+}
▪	Anaerobic saline lake water	$Pb_3(CO_3)_2(OH)_2$
▪	Water logged soil	$Pb(CO)_3$ or Pb^{2+}
▪	Surface water of a New England lake severely affected by acid rain	Pb^{2+} or $Pb(CO)_3$

A pH in the acidic region (< 5) is most likely to mobilize Pb according to the stability field diagram.



Part V

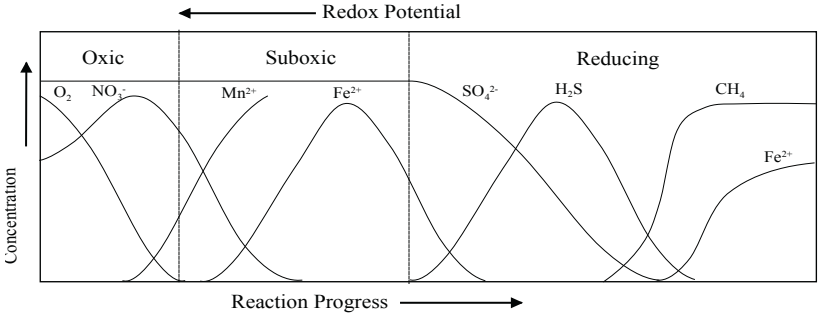
Redox Ladders

a)

Terminal electron acceptors are the last oxidizers in a sequence of reactions. In many biological reactions oxygen is the terminal electron acceptor. Others are NO_3^-, Mn^{4-}, Fe^{3+}, SO_4^{2-}, and CO_2.

b)

As water moves from recharge areas, it goes from oxic environments where dixoxygen as an oxidant is plentiful to suboxic environments where it is less abundant to anoxic environments which lack oxygen. As stronger oxidants are used up, bacteria use continually use up weaker and weaker electron acceptors. Dioxygen is the preferred oxidant, but it quickly runs out. While in environments where oxygen is plentiful, organic N is converted to ammonia, which is then oxidized to nitrate. When oxygen is low, nitrate is reduced instead, forming molecular nitrogen. After nitrate concentration declines, $Mn(IV)$ is reduced to $Mn(II)$, and further, $Fe(III)$ is reduced to $Fe(II)$. Sulfate is reduced, producing hydrogen sulfide, which has a characteristic smell. The reduction of the sulfate ion causes the decrease in the ferrous ion due to the formation of pyrite, FeS. Finally, carbon dioxide is reduced, creating methane; this is not very favorable, but carbon dioxide can be plentiful. Alternate pathways for methanogenesis involve the reduction of TEAs such as acetic or formic acids. As the sulfate ion is depleted, pyrite is no longer formed, and reduced ferrous ion concentrations begin to increase again.



Part VI

Arsenic

a)

The predominant species of As in groundwater is $As(III)$. Under oxidizing conditions, the predominant form of arsenic is $As(V)$, which is insoluble in water (Island et al. 2004).

b)
Iron oxide (with arsenic adsorbed on it) is the main direct source of dissolved arsenic groundwaters (Harvey et al. 2001).
c)
The negative correlation between sulfate and arsenic concentrations suggests that arsenopyrite is not the source of arsenic dissolved in the water. If pyrite dissolution played a large role in liberating arsenic, then the sulfate and arsenic concentrations would be positively correlation because dissolution of pyrite would yield both sulfate and arsenic. Instead, the negative correlation implies that both sulfate and $As(V)$ are both being reduced, which decreases the concentration of sulfate and increases that of $As(III)$.
Arsenic, ammonia, and calcium are positively correlated, which can be explained by respiration of dissolved organic carbon producing ammonia and carbon dioxide, which converts to carbonic acid and dissolves calcium (Harvey et al. 2001).
d)
The introduction of nitrate into the water causes the oxidation of $Fe(II)$ to $Fe(III)$ hydroxides which are able to sorb As in the water. In addition, the water soluble $As(III)$ is oxidized to insoluble $As(V)$. Both these processes decrease the measured concentrations of aqueous arsenic in the water.
e)
The inorganic carbon is composed of primarily materials of marine carbonate origin while the organic carbon is source from plant matter. Plants are more selective for the lighter carbon (Harvey et al. 2001) due to the kinetic isotope effect.
f)
Bacteria reduce $Fe(III)$ to $Fe(II)$, but when they run out of $Fe(III)$, the bacteria can reduce water insoluble $As(V)$ to the soluble $As(III)$. This is a dissimilative process where the bacteria don't take in the arsenic; the arsenic is released into the groundwater (Island et al. 2004).