1) Sodium ferrocyanide, Na$_4$Fe(CN)$_6$ is routinely added to road salt, typically in the amount of $\frac{26 \mu \text{mol Na}_4\text{Fe(CN)}_6}{\text{kg salt}}$, as an anticaking agent. Despite it's worrisome name, this compound is non-toxic and has even been approved as a food additive. Reports have shown, however, that ferrocyanide in aqueous solution breaks down to form free cyanide (a highly toxic compound) in the presence of sunlight.

$$\text{Fe(CN)}_6^{4-} \rightarrow \text{FeCN}^+ + 5\text{CN}^-$$

In water CN$^-$ is in equilibrium with HCN:

$$\text{HCN} = \text{H}^+ + \text{CN}^- \quad K = 10^{-9} \text{ mol/L}$$

a) On a cold day in early November, freezing rain is expected, so the roads are salted. 5 cm of rain falls. The rain washes the salt from the roads, and the runoff (whose pH is 6.9) accumulates in ponds. Given a salt application rate of 0.10 kg salt/m of road, calculate concentration of Na$_4$Fe(CN)$_6$ in highway run-off. Assume road width of 15m.

b) What fraction of CN$_T$ is present as CN$^-$?

c) As the first step in estimating the risk due to inhalation of air above the puddles of runoff, calculate the initial flux density of HCN volatilizing from a puddle of runoff, given a "piston" velocity of 1 cm/hr, and a puddle depth of 10cm.
2) The Henry's constant for \( \text{O}_2 \) at a certain temperature is 540 (L-atm)/mol. Given that the atmosphere is about 1/5 oxygen:

a) What is dissolved \( \text{O}_2 \) concentration in the surface water of a lake at equilibrium with the air? (in part a, assume no \( \text{O}_2 \) sources or sinks exist in the lake.)

b) Now, assume phytoplankton are producing \( \text{O}_2 \) via photosynthesis at a rate of .005 mole per hour per \( \text{m}^2 \) of lake surface. Assume winds are calm. What would be the steady state dissolved \( \text{O}_2 \) concentration under these conditions?

c) What would be the steady state dissolved \( \text{O}_2 \) concentration for \( U_{10} = 2.5 \) m/s?

3) Certain bacteria can respire in anoxic environments using arsenic (V) as electron acceptor. The relevant half-reactions are:

\[
\frac{1}{2} \quad \text{H}_2 \text{AsO}_4^- + \frac{3}{2} \text{H}^+ + e^- \rightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}
\]

\[ \log K = 10.84 \]

\[ \Delta G^\circ = -14.5 \frac{\text{Kcal}}{\text{mol} \, e^-} \]

and:

\[
\frac{1}{4} \quad \text{CH}_2\text{O} + \frac{1}{4} \text{H}_2\text{O} \rightarrow e^- + \text{H}^+ + \frac{1}{4} \text{CO}_2 \, (g)
\]

\[ \log K = 1.2 \]

\[ \Delta G^\circ = -1.63 \frac{\text{Kcal}}{\text{mol} \, e^-} \]
a) What is the overall respiration reaction, standard free energy change \( \Delta G^\circ \), and equilibrium constant?
b) Is this process energetically more or less favorable than sulfate reduction? 
\( \Delta G^\circ \) for the reduction reaction for sulfate \( \rightarrow \text{HS}^- \) is \(-5.78 \text{ Kcal/mol e}^-\)
c) If \([\text{H}_2 \text{AsO}_4^-] = [\text{H}_3 \text{AsO}_3] = 0.5 \text{ mM and pH is 7, estimate pe of the system.}\)

4) A set of experimental channels is set up to test fish survival at various pH values, in an effort to help understand acid deposition effects on freshwater fisheries. Well water, as pumped directly from the well, has Alk = \(8 \times 10^{-4} \text{ eq/L and pH} = 6.5\). This water is amended with H\(_2\)SO\(_4\) to make waters having pH values of 6.0, 5.0, and 4.0, respectively, which are then pumped to the various experimental channels.
   a) How much H\(_2\)CO\(_3\)* is initially present in the well water?
b) The well water, while sitting in an open tank, will tend to equilibrate with the atmosphere. Explain in which direction the pH will change as the water equilibrates with air
   b) How much sulfuric acid (in equivalents/L) must be added to the original (non-air-equilibrated) well water to adjust it to pH 6.0?

5) BTEX (benzene, toluene, ethylbenzene, xylene; a mixture of compounds that is typical of gasoline) is found to be seeping into a small river, a result of leaking underground storage tanks at a nearby gasoline station. You are tasked with the job of figuring out how much of this material is lost to the atmosphere, vs. how much is lost to some other sink processes within the river.

Consider, for this problem, only the case of benzene, C\(_6\)H\(_6\) (MW=78 Daltons), which is found at 3.85 ppm in the river near the location of the seep. Your first job is to figure out how much benzene is lost to volatilization. From a tracer test using argon (MW=40 Daltons) you conclude that the water-side-controlled gas exchange velocity is 300 cm/hr
for Ar. The river is uniformly 0.3 meters deep and has a uniform width of 4 m. Its velocity is 50 cm/sec, and dilution by inflow of groundwater may be neglected over the region of interest.

a) If benzene were not degraded in this river, what would be its concentration 800 m downriver from the seep?

b) You measure actual benzene concentration 800m downriver a total of 3 times and find values of 0.69, 0.65, and 0.62. If you use the average of these three values, what overall first-order decay constant would best describe the loss of benzene?

c) extra credit. Briefly discuss whether the loss of benzene entirely explainable, or not, by volatilization only? (if not, then some bio- or maybe photo- degradation must be going on).

6) A point injection of a salt tracer is made in the above river, in order to directly measure a longitudinal dispersion coefficient. In order to decide how sensitive your analytical chemistry must be, and over what period of time you should sample downstream, you want to make a first guess of the longitudinal dispersion coefficient based on river hydraulics.

a) Assume a slope of 5 x 10^{-4}, and make your best estimate of D_L.

b) How long after the injection do you expect your salt pulse to be passing the sampling point, 800 m downriver? How wide (measured in the along-river direction) will it be at this time (use a 2 std. dev. criterion)?