One of the most common ways of removing hexavalent chromium (Cr[VI]) from industrial wastewater is to reduce it to trivalent chromium (Cr[III]), which can be removed by precipitation and settling.
Consider a treatment system with a constant pH of 7.5 and an initial hexavalent chromium concentration of 1 μM.

a. Assume that all of the hexavalent chromium can be reduced to trivalent chromium. Predict the concentration of dissolved chromium after all of the $Cr(OH)_{3(s)}$ has settled.

b. It might be possible to use ammonia to reduce the hexavalent chromium provided that an appropriate catalyst can be found (e.g., ammonia oxidizing bacteria). Estimate the mass of ammonium chloride (MW = 53 gm/mol) needed to reduce 100 liters of a 1 μM of hexavalent chromium.

c. In terms of thermodynamics, is this process feasible under the conditions described above (i.e., pH 7.5, initial Cr[VI] concentration of 1 μM)? Provide a quantitative justification for your answer.

The following information might be useful to you in solving these problems.

$$H_2O = H^+ + OH^- \qquad\qquad K_w = 10^{-14}$$
$$Cr(OH)_{3(s)} = Cr^{3+} + 3\ OH^- \qquad K_{s0} = 10^{-33.1}$$
$$Cr^{3+} + OH^- = CrOH^{2+} \qquad \beta_1 = 10^{10.0}$$
$$Cr^{3+} + 2\ OH^- = Cr(OH)_2^+ \qquad \beta_2 = 10^{18.4}$$
$$Cr^{3+} + 3\ OH^- = Cr(OH)_3^0 \qquad \beta_3 = 10^{25.3}$$
$$Cr^{3+} + 4\ OH^- = Cr(OH)_4^- \qquad \beta_4 = 10^{28.2}$$
$$H_2CrO_4 = H^+ + HCrO_4^- \qquad K_{a1} = 10^{-0.86}$$
$$HCrO_4^- = H^+ + CrO_4^{2-} \qquad K_{a2} = 10^{-6.5}$$
$$HCrO_4^- + 7\ H^+ + 3\ e^- = Cr^{3+} + 4\ H_2O \qquad E_H^0 = 1.35\ V$$
$$NO_3^- + 10\ H^+ + 8\ e^- = NH_4^+ + 3\ H_2O \qquad E_H^0 = 0.88\ V$$
$$NH_4^+ = H^+ + NH_3 \qquad K_{a1} = 10^{-9.3}$$
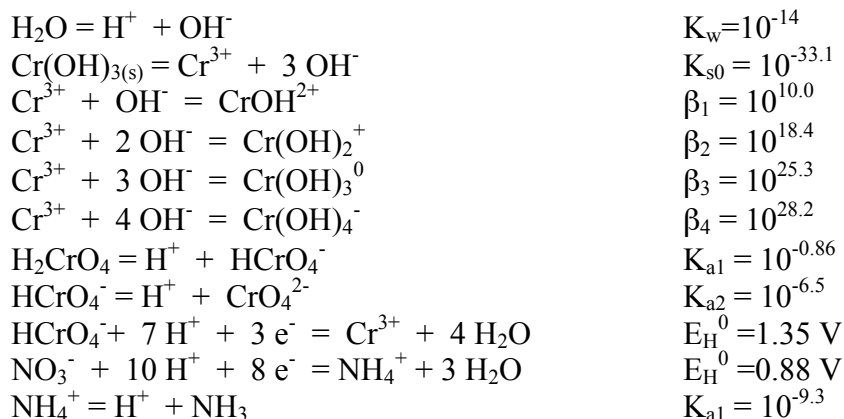
Assume $\gamma = 1.0$, $T = 25°C$; $P = 1$ bar, $P_{CO_2} = 10^{-3.5}$ bar
$F = 9.65 \times 10^4$ C mol^{-1}
$R = 8.314$ J K^{-1} mol^{-1}

A drinking water treatment plant that treats surface water has an alkalinity of 0.7 mEq/L and a Ca^{2+} concentration of 0.6 mM. Assume that the water is in equilibrium with the atmosphere when it enters the water treatment plant.

a. The first treatment step involves the addition of 0.1 mM NaOCl. Assuming that the water remains in equilibrium with the atmosphere and that no redox reactions occur during this step calculate the equilibrium pH.

b. The next step in the treatment process involves the addition of 1 mM $Na_2CO_{3(s)}$ (soda ash). Assuming that the water does not equilibrate with the atmosphere during this treatment step and that the NaOCl added in the first step disappears without altering the alkalinity, calculate the equilibrium pH before any precipitation or dissolution reactions occur.

c. After precipitation occurs, the particles are removed by flocculation and air is bubbling air through the water until it equilibrates with the atmosphere. The final pH after this process is 8.6. What is the equilibrium concentration of dissolved Ca^{2+}?

d. Write a one or two sentence explanation for what the operators of the drinking water treatment plant hoped to accomplish with the steps described in a, b and c.

The following information might be useful to you in solving these problems.

$$H_2O = H^+ + OH^- \qquad\qquad K_w = 10^{-14}$$
$$H_2CO_3^* = HCO_3^- + H^+ \qquad K_1 = 10^{-6.35}$$
$$HCO_3^- = CO_3^{2-} + H^+ \qquad K_2 = 10^{-10.33}$$
$$CO_{2(g)} + H_2O = H_2CO_3^* \qquad K_H = 10^{-1.48} \ M\ bar^{-1}$$
$$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-} \qquad K_{s0} = 10^{-8.48}$$
$$HOCl = H^+ + OCl^- \qquad\qquad K_a = 10^{-7.6}$$
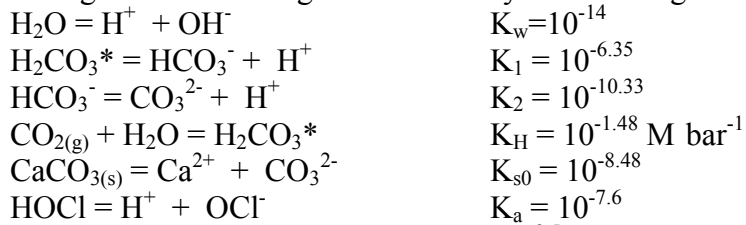
Assume $\gamma = 1.0$, $T = 25°C$; $P = 1\ bar$, $P_{CO_2} = 10^{-3.5}\ bar$

$$alpha\_1 = \frac{[HCO_3^-]}{[HCO_3^*] + [HCO_3^-] + [CO_3^{2-}]} \qquad\qquad alpha\_2 = \frac{[CO_3^{2-}]}{[HCO_3^*] + [HCO_3^-] + [CO_3^{2-}]}$$

pH	alpha 1	alpha 2
7.0	8.17E-01	3.82E-04
7.1	8.49E-01	5.00E-04
7.2	8.76E-01	6.49E-04
7.3	8.98E-01	8.38E-04
7.4	9.17E-01	1.08E-03
7.5	9.33E-01	1.38E-03
7.6	9.45E-01	1.76E-03
7.7	9.55E-01	2.24E-03
7.8	9.63E-01	2.84E-03
7.9	9.69E-01	3.60E-03
8.0	9.74E-01	4.55E-03
8.1	9.77E-01	5.75E-03
8.2	9.79E-01	7.26E-03
8.3	9.80E-01	9.14E-03
8.4	9.80E-01	1.15E-02
8.5	9.79E-01	1.45E-02
8.6	9.76E-01	1.82E-02
8.7	9.73E-01	2.28E-02
8.8	9.68E-01	2.86E-02
8.9	9.62E-01	3.57E-02
9.0	9.53E-01	4.46E-02

| pH	alpha 1	alpha 2
9.1	9.43E-01	5.55E-02
9.2	9.30E-01	6.89E-02
9.3	9.14E-01	8.53E-02
9.4	8.94E-01	1.05E-01
9.5	8.71E-01	1.29E-01
9.6	8.43E-01	1.57E-01
9.7	8.10E-01	1.90E-01
9.8	7.72E-01	2.28E-01
9.9	7.29E-01	2.71E-01
10.0	6.81E-01	3.19E-01
10.1	6.29E-01	3.71E-01
10.2	5.74E-01	4.26E-01
10.3	5.17E-01	4.83E-01
10.4	4.60E-01	5.40E-01
10.5	4.03E-01	5.97E-01

A treatment system has been designed for the removal of MTBE from contaminated groundwater. The treatment system relies upon the photolysis of hydrogen peroxide to produce hydroxyl radicals that react with the MTBE. A pilot study was conducted by dissolving 100 µg/L of MTBE (MW 88.1 gm/mol) in distilled water. The initial concentration of H_2O_2 was 0.2 mM. Under these conditions, the disappearance of MTBE follows first-order kinetics with a half-life of 6 minutes. The same treatment system is going to be used to treat water with the composition listed below.

Dissolved organic carbon (DOC) = 2 mg/L
Total dissolved inorganic carbon (i.e., C_T) = 1 mM
For H_2CO_3 pK_{a1} = 6.35; pK_{a2} = 10.33
pH = 8.0
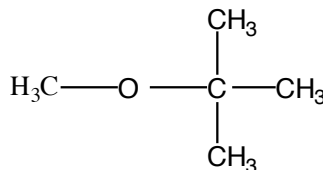
MTBE

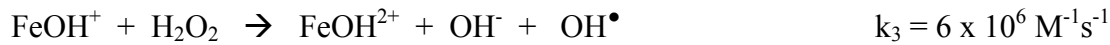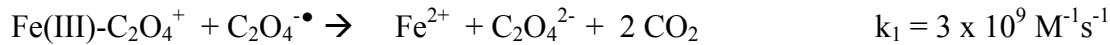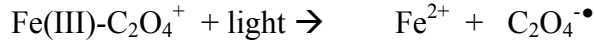Rate constants for hydroxyl radical reactions with:

MTBE:	1×10^8 M^{-1} s^{-1}
CO_3^{2-}:	4×10^8 M^{-1} s^{-1}
HCO_3^-:	9×10^6 M^{-1} s^{-1}
H_2O_2:	3×10^7 M^{-1} s^{-1}
DOC	2.5×10^4 L/mg s

a. Assuming that the absorption of light by the groundwater is negligible in comparison to light absorption by the hydrogen peroxide, estimate the half-life of MTBE in groundwater in the treatment system (initial concentration of MTBE = 100 µg/L). You can assume that a very small volume of concentrated hydrogen peroxide is added continuously to maintain a constant concentration of 0.2 mM without diluting the MTBE and solutes.

b. In reality, dissolved solutes might compete with H_2O_2 for adsorption of UV light. How much of the UV light is absorbed by species other than H_2O_2 under the initial conditions in part (a).
    Molar extinction coefficient (ε) at 254 nm for H_2O_2:   90 M^{-1} cm^{-1}
    Beam attenuation coefficient (α) at 254 nm for the
    groundwater sample before adding peroxide: 0.20 cm^{-1}

c. In addition to hydroxyl radicals, photolysis of groundwater will produce a variety of other reactive species. List two of the other reactive species that will be formed when groundwater is subjected to UV radiation. Do you expect these to react with MTBE? Explain your reasoning.

The photolysis of Fe(III)-oxalate complexes ($Fe(III)$-$C_2O_4^+$) in the presence of hydrogen peroxide has been proposed as an advanced oxidation process for treating water contaminated with organic pollutants. The reactions that occur in this system are listed below along with relevant chemical data. For simplicity, assume the initial conditions (*i.e.*, pH, $[O_2]$, $[H_2O_2]$) remain constant during the reaction.

$$Fe(III)\text{-}C_2O_4^+ + light \rightarrow \quad Fe^{2+} + C_2O_4^{-\bullet}$$

$$Fe(III)\text{-}C_2O_4^+ + C_2O_4^{-\bullet} \rightarrow \quad Fe^{2+} + C_2O_4^{2-} + 2\ CO_2 \qquad k_1 = 3 \times 10^9\ M^{-1}s^{-1}$$

$$Fe^{2+} + H_2O_2 \rightarrow \quad Fe^{3+} + OH^- + OH^\bullet \qquad k_2 = 1 \times 10^2\ M^{-1}s^{-1}$$

$$FeOH^+ + H_2O_2 \rightarrow FeOH^{2+} + OH^- + OH^\bullet \qquad k_3 = 6 \times 10^6\ M^{-1}s^{-1}$$

$$Fe^{2+} + O_2 \rightarrow \quad Fe^{3+} + O_2^{-\bullet} \qquad k_4 = 1 \times 10^{-5}\ M^{-1}s^{-1}$$

$$FeOH^+ + O_2 \rightarrow \quad FeOH^{2+} + O_2^{-\bullet} \qquad k_5 = 2 \times 10^0\ M^{-1}s^{-1}$$

$$Fe^{2+} + OH^- \leftrightarrow FeOH^+ \qquad K_6 = 3 \times 10^4\ M^{-1}$$

$$H_2O_2 + OH^\bullet \rightarrow \quad HO_2^\bullet + H_2O \qquad k_7 = 3 \times 10^7\ M^{-1}s^{-1}$$

For Fe(III)-$C_2O_4^+$:   *Initial Conditions:*
ε at 313 nm = 2000 $M^{-1}\ cm^{-1}$ $[Fe(III)\text{-}C_2O_4^+] = 1\ \mu M$
quantum yield for direct photolysis = 0.6 $[H_2O_2] = 1\ mM$
                                                $[O_2] = 0.25\ mM$
                                                pH = 5

d. To start the process, the Fe(III)-oxalate complex is photolyzed using monochromatic light from a laser. The flux of light at 313 nm is 10^{-6} mEi cm^{-2} s^{-1} and the path length for the photoreactor is 10 cm. Assuming that other solutes do not absorb light at this wavelength, estimate the half-life of the Fe(III)-oxalate complex.

e. Estimate the concentration of Fe^{2+} after steady state has been achieved.

f. Assume that the system is going to be used to treat water containing 0.5 μM of an organic contaminant that has a rate constant for reaction with $OH^\bullet$ of 5 x 10^9 M^{-1} s^{-1}. For every mole of oxalate consumed how many moles of the contaminant will be transformed? [Consider only the initial period, when the concentrations of all reactants are approximately equal to their initial values.]