CHEM 301

Assignment #1

Provide solutions to the following questions in a neat and well organized manner.
Reference data sources for any constants and state assumptions, if any.
Due date: Thursday, Sept 27th, 2018

1. It is often said that 'one drop of motor oil will contaminate a million times it's volume in water'. Given that motor oil is a complex mixture of individual aliphatic and aromatic hydrocarbons with an average composition of $\mathbf{C_{20}H_{30}}$ and density of 0.87 kg/L, estimate the concentration of oil in this solution in units ppm and micromolar.

strategy: Start with some volume of oil and use the density to determine its mass. Dissolving this in one million volumes of water with its corresponding density of 1kg/L yields a mass ratio which can be expressed in ppm. Convert this conc. to molarity using the average $MW_{oil} \simeq 270$ g/mol.

Solution: Take 1.0 L of oil in 10^6 L of water.

$$1.0 \text{ L} \times 0.87 \frac{\text{kg}}{\text{L}} = 0.87 \text{ kg oil}$$

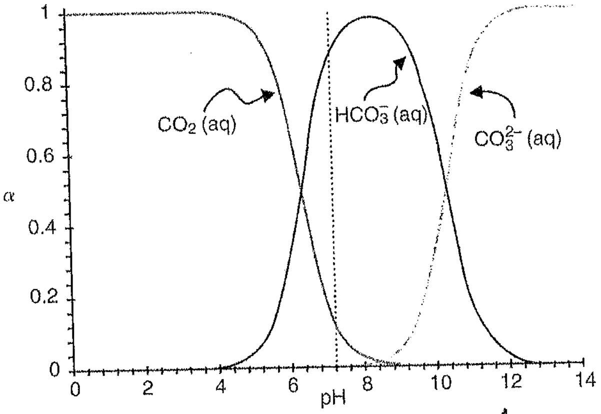
$\therefore$ in 10^6 L of water we have 0.87 kg oil

$$\frac{0.87 \text{ kg}}{10^6 \text{ kg}} \times 10^6 = 0.87 \text{ ppm}$$

Converting to molarity

$$\frac{0.87 \text{ mg}}{\text{L}} \times \frac{1 \text{ mol}}{270 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 3.2 \times 10^{-6} \frac{\text{mol}}{\text{L}}$$

2. Alkalinity of a freshwater sample is a measure of its acid neutralizing ability and is primarily due to the presence of hydrogen carbonate ion (**HCO_3^-**). A water sample obtained from an area of dolomitic limestone **$CaMg(CO_3)_2$** has a pH of 8.2 and a *total alkalinity* of 2.3 mM of **H^+**. If dolomite is the source of all of the major ions present, use your knowledge of chemical speciation of carbonic acid (Figure 1.2, textbook) and charge balance to calculate the concentration of the major ions.



Major Cations	Major Anions
Ca^{2+}	HCO_3^-
Mg^{2+}	CO_3^{2-} (minor)
H^+ (minor)	OH^- (minor)

Dissolution of dolomitic limestone;

$$CaMg(CO_3)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + Mg^{2+}_{(aq)} + 2\,CO_{3\,(aq)}^{2-}$$

at pH = 8.2 most CO_3^{2-} will be protonated via;

$$CO_3^{2-} + H^+ \longrightarrow HCO_3^-$$

$$[alk]_T = 2.3\times10^{-3}\ \frac{mol\ H^+}{L} \simeq [HCO_3^-]$$

Charge Balance Σ +ve = Σ -ve;

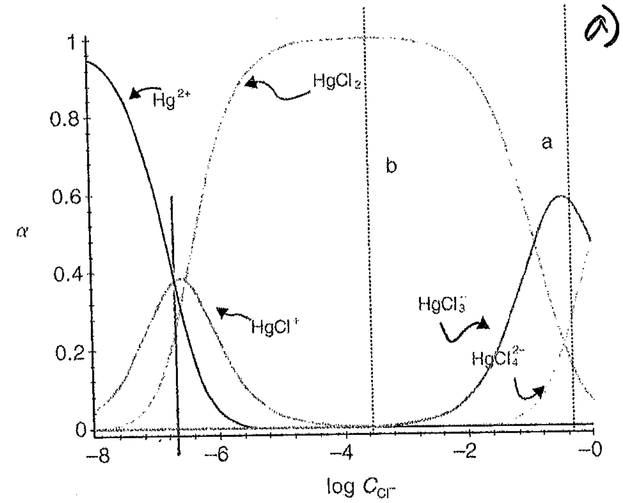
$\therefore\ 2[Ca^{2+}] + 2[Mg^{2+}] = [HCO_3^-]$ where # mols positive charge = 2× molar conc of Ca^{2+} and Mg^{2+}

and $[Ca^{2+}] = [Mg^{2+}]$ since they come from same source

Hence, $4[Ca^{2+}] = [HCO_3^-] = 2.3\times10^{-3}\ \frac{mol}{L}$

$$\therefore\ [Ca^{2+}] = \frac{2.3\times10^{-3}}{4} = 5.75\times10^{-4}\ \frac{mol}{L} = [Mg^{2+}]$$

3. a) Using the speciation diagram for mercury (II) chloro species (Figure 1.3, textbook), predict the aqueous chloride ion concentration in mg/L at which **Hg^{2+}** is no longer the dominant chemical speciation. Are these conditions more likely to be met in rain, surface, or groundwater?
b) The hydroxides, carbonates and sulfides of cadmium are insoluble and less likely to be mobile in the environment (Figure 1.6, textbook). However, their solubility is strongly influenced by pH and in the case of **CdS**(s) by the pe. Explain using balanced chemical equilibria to illustrate your answer.



a) Reading off x-axis where $\alpha_{Hg^{2+}}$ drops below that of $HgCl^+$ at $\log[Cl^-] = -6.7$

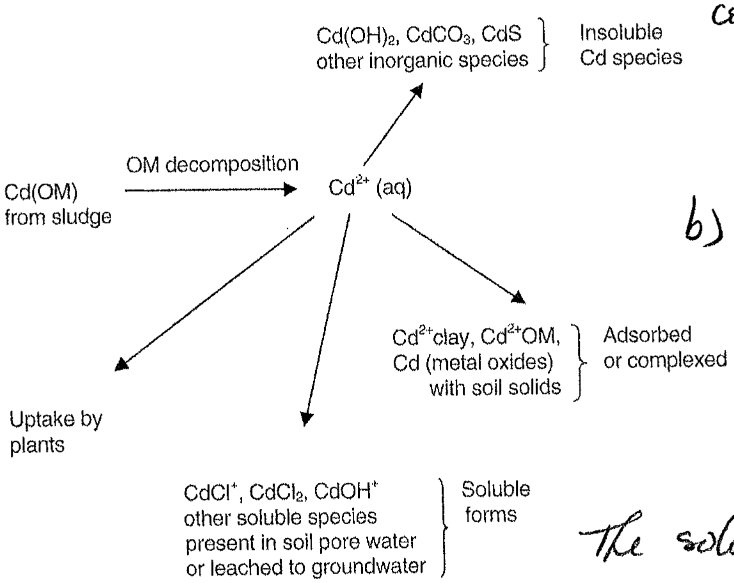
Therefore $[Cl^-] = 10^{-6.7} \doteq 2.0\times10^{-7}\ M$

Converting to mg/L:

$2.0\times10^{-7}\frac{mol}{L} \times \frac{35,450\ mg}{1\ mol} = 7.1\times10^{-3}\frac{mg}{L}$

or 7 ppb

May occur in some rain water, but generally chloride ion conc. in excess of this suggest $Hg^{2+}_{(aq)}$ will not be dominant speciation.



b) $Cd(OH)_{2(s)} + 2H^+ \rightleftharpoons Cd^{2+} + 2H_2O$

$CdCO_{3(s)} + 2H^+ \rightleftharpoons Cd^{2+} + H_2CO_3$

$CdS_{(s)} + 2H^+ \rightleftharpoons Cd^{2+} + H_2S$

$H_2S + 4H_2O \rightarrow SO_4^{2-} + 8e^- + 10H^+$

The solubility of $Cd(OH)_2$, $CdCO_3$ and CdS are increased in presence of acidity (i.e. H^+) since the basic anions produced react with H^+.

In the case of CdS, the oxidation of sulfide (ie $H_2S/HS^-/S^{2-}$) to sulfate further increases solubility.

4. Using the appropriate equilibrium constant/s, sketch a labeled pH speciation diagram for hypochlorous acid and calculate the ratio of hypochlorous acid (**HOCl**) to hypochlorite ion at pH 8.20. If an operator has determined that the total concentration of active chlorine (+I) is 1.00 ppm as **Cl_2**, what is the concentration the more powerful disinfecting form **HOCl**.

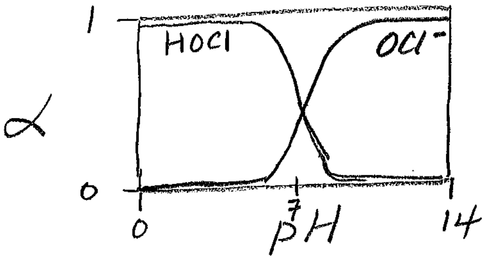
strategy: Use Ka (HOCl) to determine the fractional abundance HOCl.

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = 3.0 \times 10^{-8}$$

$$\therefore pK_a = 7.5$$

$$\alpha_{HOCl} = \frac{[HOCl]}{[HOCl]+[OCl^-]} = \left(\frac{1}{1+\frac{K_a}{[H^+]}}\right)$$

Solution;



Rearranging Ka expression

$$\frac{[HOCl]}{[OCl^-]} = \frac{[H^+]}{K_a}$$

$\therefore$ at $pH = 8.2$, $[H^+] = 10^{-8.2}$
$= 6.3 \times 10^{-9}\ M$

and $\frac{[HOCl]}{[OCl^-]} = \frac{6.3 \times 10^{-9}}{3.0 \times 10^{-8}} = 0.21$

$\therefore [HOCl] = 0.21\,[OCl^-]$

$$\alpha_{HOCl}^{pH=8.2} = \left(\frac{1}{1+\left(\frac{3.0 \times 10^{-8}}{6.3 \times 10^{-9}}\right)}\right)$$

$= 0.17$ (ie. 17% of the total active chlorine is in the form of HOCl)

$\therefore [HOCl] = 0.17\,[Cl_2]_T = 0.17$ ppm Cl_2

5. The following summarizes the concentrations in mg/L of species from the Colorado River. The pH was 8.3 and the *total alkalinity* was determined to be 140 mg/L as **$CaCO_3$**.

Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	SO_4^{2-}
77	29	98	88	250

Calculate the *total hardness* of this sample as mg/L of **$CaCO_3$** and determine the fraction of this which is said to be 'permanent' (i.e., remains after boiling).

$$Ca^{2+}_{(aq)} + 2HCO_{3\,(aq)}^{-} \rightleftharpoons CaCO_{3\,(s)} + CO_2 + H_2O$$

$$[alk]_T = T_{alk} \times \frac{1\ mol\ CaCO_3}{100.0\ g\ CaCO_3} \times \frac{2\ mol\ H^+}{1\ mol\ CaCO_3} \times \frac{1g}{10^3 mg}$$

$$= 140\ \frac{mg\ CaCO_3}{L} \times \frac{1\ mol\ CaCO_3}{100{,}000\ mg} \times \frac{2\ mol\ H^+}{1\ mol\ CaCO_3}$$

$$= 2.8_0 \times 10^{-3}\ \frac{mol\ H^+}{L} \simeq [HCO_3^-]\ at\ pH = 8.3$$

$$total\ hardness = \Sigma [M^{2+}] = [Ca^{2+}] + [Mg^{2+}]\ (M)$$

$$= \left(\frac{77\ mg\ Ca^{2+}}{L} \times \frac{1\ mol}{40{,}078\ mg}\right) + \left(29\ \frac{mg\ Mg^{2+}}{L} \times \frac{1\ mol}{24{,}305\ mg}\right)$$

$$= 1.9_2 \times 10^{-3} M + 6.8_5 \times 10^{-4} M$$

$$= 2.6_1 \times 10^{-3} M$$

Converting to $mg/L\ CaCO_3$

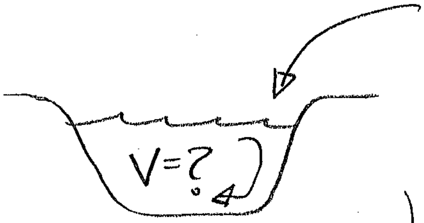
$$2.6_1 \times 10^{-3}\ \frac{mol}{L} \times \frac{100{,}000\ mg}{1\ mol} = 261\ \frac{mg\ CaCO_3}{L}$$

permanent hardness is equal to $[Ca^{2+}]$ after the reaction (above) have gone to completion. Since $[HCO_3^-] < 2 \times [Ca^{2+}]$ it will be limiting reagent, and only $1.4_0 \times 10^{-3}$ M of Ca^{2+} will react.

$\therefore [Ca^{2+}]$ remaining $= 2.6_1 \times 10^{-3} - 1.4_0 \times 10^{-3} = 1.2_1 \times 10^{-3} M$

Converting to $mg/L\ CaCO_3 = 121\ mg/L\ CaCO_3$

6. To measure the volume of a small lake, you add 5.0L of a 2.0M solution of a non-toxic dye which degrades by first order processes with a half-life of 3.0 days. After one week, in which the lake becomes well mixed, you take a 100. mL lake sample. The dye concentration in this sample is 2.9 x 10^{-6} M. Estimate the lake volume and state any assumptions.

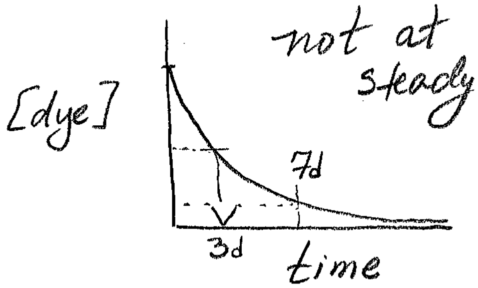


5.0 L of 2.0 M dye

$t_{1/2}$ (dye) = 3.0 days

$V_{sample} = 100.\ mL$

$[dye] = 2.9 \times 10^{-6} M$



not at steady-state

$$\tau = \frac{M}{F} \qquad t_{1/2} = \frac{\ln 2}{k}$$

given

$$\ln\left(\frac{[dye]_t}{[dye]_0}\right) = -kt$$

calculate $[dye]_0$ — from $t_{1/2}$ — 7. days

assumptions;
- well mixed
- residence time of water greater than residence time of dye ($\tau_w \gg \tau_{dye}$)

$$\ln([dye]_7) - \ln([dye]_0) = -\left(\frac{\ln 2}{3d}\right)(7d)$$

$$\ln(2.9\times10^{-6}) - \ln([dye]_0) = (-0.23_1 d^{-1})(7d) = 1.62$$

$$-12.7 - \ln([dye]_0) = 1.62$$

$$\therefore -\ln([dye]_0) = 14.3_7$$

$$\therefore [dye]_0 = e^{-14.3_7} = 5.7_4 \times 10^{-7} \frac{mol}{L}$$

$$\text{And, } [dye]_0 = \frac{\#\text{mols dye}}{\text{Volume lake}} = \frac{(5.0\,L)(2.0\,\frac{mol}{L})}{\text{Volume lake}} = \frac{10.0\text{ mol}}{\text{Vol. lake}}$$

$\therefore$ Volume of lake $= 1.7\times10^{7}$ L or $1.7\times10^{4} m^3$

7. Calculate the volume of water originally containing 10. mg O_2/L that would be completely depleted of O_2 if 100. kg of cane sugar (sucrose, $C_{12}H_{22}O_{11}$) is accidentally spilled into a water body. State any assumptions. Would you expect such an accident to have a greater or lesser impact in warmer waters? Explain.

$$C_{12}H_{22}O_{11} + 12\ O_2 \longrightarrow 12\ CO_2 + 11\ H_2O$$

$$\#\text{mols } C_{12}H_{22}O_{11} = 100.\text{ kg} \times \frac{10^3\text{ g}}{\text{kg}} \times \frac{1\text{ mol}}{342\text{ g}}$$
$$= 292\text{ mols}$$

$\therefore$ # mols O_2 consumed
$$= 12\ (292\text{ mol}) = 3.51 \times 10^3\text{ mol}$$

Hence, mass of O_2 consumed
$$= 3.51 \times 10^3\text{ mol} \times \frac{32,000\text{ mg}}{1\text{ mol}}$$
$$= 1.12 \times 10^8\text{ mg}$$

If each liter contains 10. mg O_2, this mass of sucrose can deplete

$$1.12 \times 10^8\text{ mg} \times \frac{1\text{ L}}{10.\text{ mg}} = 1.12 \times 10^7\text{ L}$$
$$= 1.12 \times 10^4\text{ m}^3$$

Warmer water contains less dissolved oxygen to begin with and degradation rates will be faster at higher temperature. Therefore, the impact of this spill will be more severe at higher temperature.

8. The following is an analysis report for a wastewater sample. The pH was not provided. Set up and use an Excel spreadsheet to answer the following.

Species	**Concentration (mg/L)**	**Units reported**
NH_3	0.08	as N
NO_2^-	0.008	as N
NO_3^-	2.0	as N
Na^+	227	as Na
K^+	18.3	as K
F^-	21.2	as F
Cl^-	24.1	as Cl
HCO_3-	15	as C
Ca^{2+}	1.7	as $CaCO_3$
SO_4^{2-}	20	as SO_4

a) Calculate the mequiv/L of positive and negative charge and express the charge balance as a % error. Comment.

$$\% \text{ error} = \frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}} \times 100\%$$

See attached

% error = 48%

b) Calculate the ionic strength (I) of this solution.

$I = 0.0072$ M

c) If H^+ and OH^- are the only ions missing from the analysis, what must the values of their activities be, given that K_{eq} for the dissociation of water is $10^{-14.0}$ at 25 °C. Calculate the activity co-efficients using the appropriate equation, based on the ionic strength.

Since there is a deficiency of anions, we set $[OH^-] = 6.76 \times 10^{-3}$ M to bring charge into balance. This increases the ionic strength to $I = 0.01$ M

Therefore, we calculate activity co-efficients using Debye-Huckel equation,

$$\log \gamma_{DH} = \frac{-Az^2\sqrt{I}}{1 + Ba_o\sqrt{I}}$$

$\therefore \gamma_{DH}(OH^-) = 0.912$ So $\{OH^-\} = \gamma \cdot [OH^-]$

$= 0.912\,[6.76 \times 10^{-3}]$

$= 6.17 \times 10^{-3}$

and $\{H^+\} = K_w / \{OH^-\}$

$= 1.0 \times 10^{-14} / 6.17 \times 10^{-3}$

$= 1.62 \times 10^{-12}$

Ions	conc (mg/L)	MW (g/mol)	conc (mol/L)	Z	meq/L	c_i*Z_i^2 (mol/L)	a_o (*10^{-8})	log γ_{DH}	γ_{DH}	log γ_{Davies}	γ_{Davies}
Calcium: Ca^{2+}	1.7	100.1	1.70E-05	2	3.40E-02	6.79E-05	6	-1.48E-01	0.711	-1.55E-01	0.700
Sodium: Na^+	227.0	23.0	9.87E-03	1	9.87E+00	9.87E-03	4	-3.89E-02	0.914	-3.88E-02	0.915
Potassium: K^+	18.0	39.1	4.60E-04	1	4.60E-01	4.60E-04	8	-3.54E-02	0.922	-3.88E-02	0.915
Fluoride: F^-	21.2	19.0	1.12E-03	1	1.12E+00	1.12E-03	3	-3.99E-02	0.912	-3.88E-02	0.915
Bicarbonate: HCO_3^-	15.0	12.0	1.25E-03	1	1.25E+00	1.25E-03	4	-3.89E-02	0.914	-3.88E-02	0.915
Sulfate: SO_4^{2-}	20.0	96.0	2.08E-04	2	4.17E-01	8.33E-04	4	-1.56E-01	0.699	-1.55E-01	0.700
Chloride: Cl^-	24.1	35.5	6.79E-04	1	6.79E-01	6.79E-04	3	-3.99E-02	0.912	-3.88E-02	0.915
Nitrate: NO_3^-	2.0	14.0	1.43E-04	1	1.43E-01	1.43E-04	3	-3.99E-02	0.912	-3.88E-02	0.915
Nitrite: NO_2^-	0.008	14.0	5.71E-07	1	5.71E-04	5.71E-07	5	-3.80E-02	0.916	-3.88E-02	0.915
					$\Sigma(+) - \Sigma(-)$	I = 0.5*$\Sigma c_i Z_i^2$					
					6.76E+00	7.21E-03					
					diff/sum *100						
					48.4%						

Ionic Strength and Activity Co-efficient Calculations

	INPUT
Temperature °C	25

A = 0.5097363

B = 32840000

Ions	conc (mg/L)	MW (g/mol)	conc (mol/L)	Z	meq/L	c_i*Z_i^2 (mol/L)	a_o (*10^{-8})	log γ_{DH}	γ_{DH}	log γ_{Davies}	γ_{Davies}
Calcium: Ca^{2+}	1.7	100.1	1.70E-05	2	3.40E-02	6.79E-05	6	-1.48E-01	0.711	-1.55E-01	0.700
Sodium: Na^+	227.0	23.0	9.87E-03	1	9.87E+00	9.87E-03	4	-3.89E-02	0.914	-3.88E-02	0.915
Potassium: K^+	18.0	39.1	4.60E-04	1	4.60E-01	4.60E-04	8	-3.54E-02	0.922	-3.88E-02	0.915
Fluoride: F^-	21.2	19.0	1.12E-03	1	1.12E+00	1.12E-03	3	-3.99E-02	0.912	-3.88E-02	0.915
Bicarbonate: HCO_3^-	15.0	12.0	1.25E-03	1	1.25E+00	1.25E-03	4	-3.89E-02	0.914	-3.88E-02	0.915
Sulfate: SO_4^{2-}	20.0	96.0	2.08E-04	2	4.17E-01	8.33E-04	4	-1.56E-01	0.699	-1.55E-01	0.700
Chloride: Cl^-	24.1	35.5	6.79E-04	1	6.79E-01	6.79E-04	3	-3.99E-02	0.912	-3.88E-02	0.915
Nitrate: NO_3^-	2.0	14.0	1.43E-04	1	1.43E-01	1.43E-04	3	-3.99E-02	0.912	-3.88E-02	0.915
Nitrite: NO_2^-	0.008	14.0	5.71E-07	1	5.71E-04	5.71E-07	5	-3.80E-02	0.916	-3.88E-02	0.915
Hydroxide: OH-			6.76E-03	1	6.76E+00	6.76E-03	3	-3.99E-02	0.912	-3.88E-02	0.915
					$\Sigma(+) - \Sigma(-)$	I = 0.5*$\Sigma c_i Z_i^2$					
					-8.62E-04	1.06E-02					
					diff/sum *100						
					0.0%						