

CHEM 301

Assignment #1

SOLUTIONS

1. In an effort to relate some fundamental concepts in aquatic chemistry to your local politician, you realize that you need to use an appropriate analogy. Given that a typical Olympic sized swimming pool holds 2500 m³ of water, answer each of the following, showing your work and stating any assumptions;

- The number of teaspoons of a water soluble pollutant it would take to contaminate a pool to a level of 10 pptr.
- The number of days required to flush this pollutant to a concentration of 5 pptr with a garden hose (flowing at 25 liters per minute).

Strategy:

Part a) can be approached on the basis of the mass ratio (ie 10 pptr = 10 ng/kg). Given that the pool contains water with a density of 1.0 kg/L, and that 1 teaspoon equals roughly 6.0 mL, we can come up with a good analogy provided that we make a reasonable assumption about the density of the pollutant (let's say 1 g/mL).

Part b) involves residence times, where the key information is the stock (2500 m³) and the flux (25 L/min). Once we calculate the residence time, we can use this to get the first order rate constant, since $\tau = 1/k$. We will need a few assumptions here to solve this one. These include that; 1) the pool is well mixed and 2) the pollutant is lost only through flushing out with the water (ie is persistent over the time scale of the water residence time).

Solution:

Part a): Mass of pollutant in grams = 10 ng/kg \times 1g/10⁹ ng \times 2500 m³ \times 1000 kg/m³ = 0.25 g
Therefore, the number of teaspoons of pollutant = 0.25 g \times 1 tsp/6 g = **0.004 teaspoons**

Given the small fraction of a teaspoon that results, we may decide to modify the analogy (afterall, we are talking to a politician who may not relate to '0.004 of a tsp'. If we take 1 drop of pollutant as weighing ~25 mg, we could express this mixing ratio as, roughly 10 drops of pollutant in an Olympic sized swimming pool.

Part b): Residence time = stock/flux = (2500 m³ \times 10³ L/m³)/25 L/min = 10⁵ min = 69.4 days
Therefore, $k = 1.44 \times 10^{-2}$ days and $t_{1/2} = 0.694/k = \mathbf{48.2 \text{ days}}$

Recall, the integrated rate law for first order kinetics is given by;

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

and when $[A]_t/[A]_o = 1/2$, then $t = t_{1/2}$.

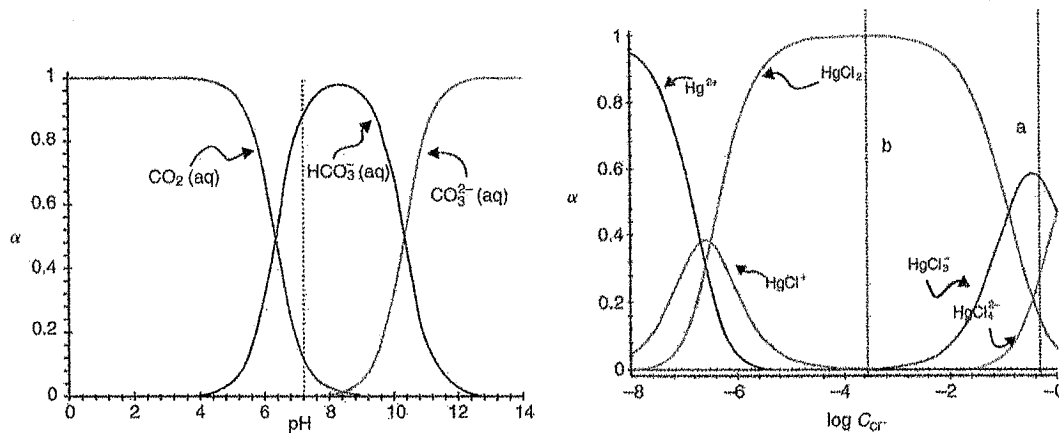
So, $\ln(0.693) = -k t_{1/2}$ and $t_{1/2} = 0.693/k$.

2. Refer to speciation diagrams (Figures 1.2 and 1.3, textbook) to answer each of the following.
- Estimate the concentration of individual inorganic carbon species at pH 6.8, if the total carbonate concentration, $[\text{CO}_3^{2-}]_T = 4.2 \text{ mM}$. Confirm these estimates using the acid dissociation constants for carbonic acid.
 - Estimate the fraction of mercury (II) present as HgCl_3^- in estuarine water (density = 1.02 g/mL) containing 3550 ppm chloride.

Strategy:

Using the speciation diagrams below, we draw a vertical line at pH = 6.8 and $C_{\text{Cl}^-} = 3550 \text{ mg/L} = 0.100 \text{ M}$ to identify the fractional abundance (α) of each species present. Once we know the fractional abundance, we can determine the concentration using the general equation;

$$[X] = \alpha_X [X]_T$$



Solution:

From Figure 1.2 at pH = 6.8, the inorganic dissolved carbon is predominantly bicarbonate ion (HCO_3^-) with a fractional abundance of ~ 0.80 . The remaining carbonate species present being $\text{CO}_2(\text{aq})$ with a fractional abundance of ~ 0.20 .

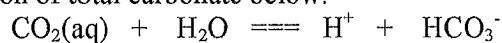
$$\text{So, } [\text{HCO}_3^-] = \alpha_{\text{HCO}_3^-} [\text{CO}_3^{2-}]_T = 0.80 (4.2 \times 10^{-3} \text{ M}) = \mathbf{3.4 \times 10^{-3} \text{ M}}$$

Similarly,

$$[\text{CO}_2] = \alpha_{\text{CO}_2} [\text{CO}_3^{2-}]_T = 0.15 (4.2 \times 10^{-3} \text{ M}) = \mathbf{0.84 \times 10^{-3} \text{ M}}$$

Note that $[\text{CO}_3^{2-}] \sim 0$ at this pH.

To calculate the carbonate concentration at pH 6.8, we use the following chemical equilibria and the definition of total carbonate below.



$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 4.5 \times 10^{-7} \text{ (textbook App. B4)}$$

$$[\text{CO}_3^{2-}]_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 4.2 \times 10^{-3} \text{ M}$$

At pH 6.8, it is clear that $[\text{CO}_3^{2-}] \sim 0$, so this simplifies to

$$[\text{CO}_3^{2-}]_T = [\text{CO}_2] + [\text{HCO}_3^-] = 4.2 \times 10^{-3} \text{ M}$$

Since we know $[\text{H}^+] = 10^{-6.8} = 1.58 \times 10^{-7} \text{ M}$, we have two equations and two unknowns and the problem can be solved.

Rearranging $[\text{CO}_2] = 4.2 \times 10^{-3} - [\text{HCO}_3^-]$ and substituting into K_{a1} expression yields,

$$4.5 \times 10^{-7} = \frac{(1.58 \times 10^{-7}) [\text{HCO}_3^-]}{(4.2 \times 10^{-3} - [\text{HCO}_3^-])}$$

Solving for $[\text{HCO}_3^-]$ gives, $[\text{HCO}_3^-] = 3.1_1 \times 10^{-3} \text{ M}$

Substituting back in to the total carbonate expression yields, $[\text{CO}_2(\text{aq})] = 1.0_9 \times 10^{-3} \text{ M}$

Which are close to our estimates based on interpolating from Figure 1.2.

b) In order to use Figure 1.3, we need to convert the chloride ion concentration from mg/L into mol/L and then express that on a \log_{10} scale.

$$3550 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mol}}{35.5 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ L}}{1.02 \text{ kg}} = 0.982 \text{ mol}$$

Therefore, $\log_{10}(0.100) = -1.01$

Reading from Figure 1.3, yields;

$$\alpha_{\text{H}_2\text{CO}_3^*} \sim 0.05$$

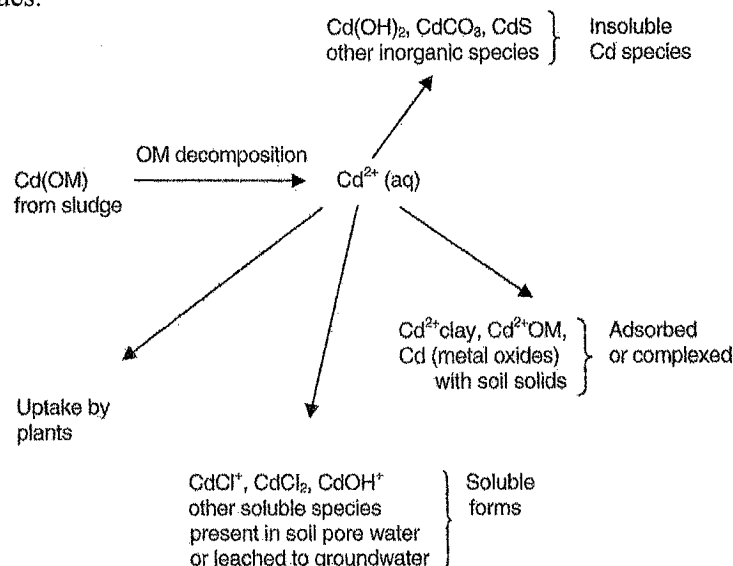
$$\alpha_{\text{HCO}_3^-} \sim \mathbf{0.40}$$

$$\alpha_{\text{CO}_3^{2-}} \sim 0.55$$

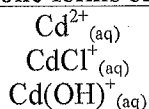
3. The hydroxides, carbonates and sulfides of most metals are insoluble and less likely to be mobile in the aquatic environment. Write chemical equations to describe/explain how the aqueous solubility of the following cadmium compounds will be affected;

- the influence of pH on $\text{Cd}(\text{OH})_2$ mobility
- the influence of pe on CdS mobility

Strategy: Figure 1.6 (textbook) below summarizes a number of cadmium species. The hydroxides, carbonates and sulfides are generally insoluble, as predicted by solubility rules and supported by relatively low K_{sp} values.

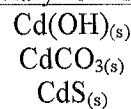


Mobile forms of Cd



Other aqueous forms, generally ions

Stationary forms of Cd

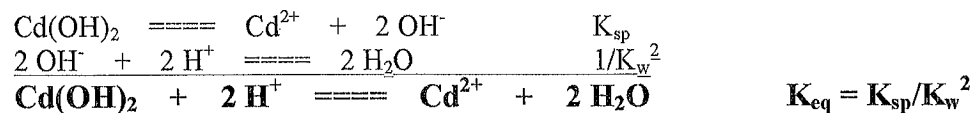


Adsorbed forms including Cd^{2+} -clay, Cd^{2+} -OM etc

Note: Most of the stationary forms of insoluble Cd species, become more water soluble in acidic solution. This is because the anions produced upon dissolution (e.g. OH^- , CO_3^{2-} and S^{2-}) are basic and therefore reaction with H^+ .

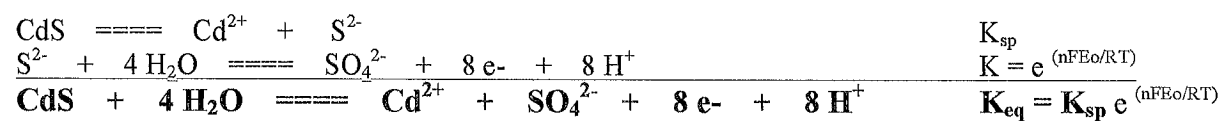
Solution:

a) In general, salts containing basic anions (e.g., OH^- , CO_3^{2-} , S^{2-}) will become increasingly soluble in acidic solution. This is a direct result of acid-base chemistry involving the anion, which effectively 'removes' the anion. The solubility increases as more salt dissolves to compensate.



Since $K_w \sim 10^{-14}$, $K_{eq} \sim 10^{28}$ times greater than K_{sp} .

b) CdS(s) will form when cadmium (II) is in the presence of the reduced sulfur species sulfide (-II) ion. This will predominate under reducing or low pe conditions. However, as sulfur has a number of higher available oxidation states (e.g., (IV) and (VI)), higher pe conditions will favour the sulfate ion, whose metal salts are markedly more soluble. Hence as the pe increases, the CdS(s) will become more soluble and consequently more mobile in the aquatic environment.



4. The concentrations of the major ions (ppm) in San Pellegrino Natural Mineral Water (Case Study #1, Friday, Sept 16th) are given below. Use this information to calculate each of the following:

SO ₄ ²⁻	HCO ₃ ⁻	Ca ²⁺	Cl ⁻	Mg ²⁺	Na ⁺	NO ₃ ⁻ (N)	K ⁺	F ⁻
430	245	170	52.0	51.4	33.3	2.6	2.2	0.5

- The charge balance and express as the % error = (difference/sum)*100.
- The total dissolved solids (TDS) and the temporary hardness (ppm CaCO₃).
- The ionic strength (molar) and use this to estimate the activity coefficients of the most dominant cation and anion, using the appropriate model.

Strategy: To determine the charge balance, all ionic concentrations need to be converted to moles of charge per liter (equivalents/L). The total dissolved solids is the sum of the masses of all dissolved species that will be left over after the water has been evaporated and the temporary hardness is that which is removed by boiling given by total hardness – total alkalinity (when both are expressed as an equivalent mass of CaCO₃). The ionic strength is given by ½ of the sum of all molar ion concentrations scaled by the square of their respective charge and the activity coefficients are estimated using an empirical relationship (depending on the ionic strength). I would recommend setting up and using a spreadsheet to handle the repetitive calculations.

$$\frac{\text{equiv}}{L} = \frac{\text{mass of ion}}{\text{mass of solution}} \times \frac{1 \text{ mol ion}}{\text{molar mass of ion}} \times \frac{\# \text{ mols of charge}}{1 \text{ mol of ion}}$$

$$\text{TDS} = \sum m_i (\text{for all ions})$$

$$\text{Temporary hardness} = \sum [M^{2+}] - 2[\text{alk}]_T (\text{for molar concentrations})$$

$$\text{or } T_{\text{hardness}} - T_{\text{alk}} (\text{in ppm CaCO}_3)$$

where the chemistry is described by,



$$I = 0.5 \sum [i] z_i^2 \quad (\text{where } [i] \text{ are molar concentrations})$$

$$\log \gamma_{\text{DH}} = \frac{-A z^2 \sqrt{I}}{1 + B a_0 \sqrt{I}} \quad \text{or} \quad \log \gamma_{\text{Davies}} = -A z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

Solution: (see attached spreadsheet results)

a) The sum of all positive charges is 14.2 mequiv/L and that for negative charges is 14.6 mequiv/L. Therefore the charge balance expressed as a percent error = -1.5%.

b) TDS = 987 mg/L

total hardness = (4.24 + 2.12) x 10⁻³ mol/L = 6.36 x 10⁻³ M or 636 mg/L of CaCO₃

total alkalinity = (4.02 + 0.02) x 10⁻³ mol/L = 4.04 x 10⁻³ M or 202 mg/L of CaCO₃

Therefore the temporary hardness is given by 434 mg/L of CaCO₃.

c) The ionic strength is given by 0.0253 M, so either the Debye Huckel or the Davies approximations can be used. Since calcium is the dominant cation (based on molar concentrations), we calculate $\gamma_{(\text{Ca}^{2+})}$.

$\gamma_{(\text{Ca}^{2+})} = 0.569$ using Debye-Huckel equation

and

$\gamma_{(\text{Ca}^{2+})} = 0.547$ using the Davies equation

Charge Balance, Ionic Strength and Activity Co-efficient Calculations

A = 0.50513
B = 32753000

Temperature °C 20

Ions	conc (mg/L)	MW (g/mol)	conc (mol/L)	Z	meq/L	$c_i Z_i^2$ (mol/L)	a_i ($\times 10^3$)	log γ_{DH}	γ_{DH}	log γ_{Davies}	γ_{Davies}
Calcium: Ca ²⁺	170.0	40.1	4.24E-03	2	8.48E+00	1.70E-02	6	-2.45E-01	0.569	-2.62E-01	0.547
Sodium: Na ⁺	33.3	23.0	1.45E-03	1	1.45E+00	1.45E-03	4	-6.65E-02	0.858	-6.55E-02	0.860
Magnesium: Mg ²⁺	51.4	24.3	2.12E-03	2	4.23E+00	8.46E-03	8	-2.27E-01	0.593	-2.62E-01	0.547
Potassium: K ⁺	2.2	39.1	5.63E-05	1	5.63E-02	5.63E-05	3	-6.94E-02	0.852	-6.55E-02	0.860
Bicarbonate: HCO ₃ ⁻	245.0	61.0	4.02E-03	1	4.02E+00	4.02E-03	4	-6.65E-02	0.858	-6.55E-02	0.860
Sulfate: SO ₄ ²⁻	430.0	96.0	4.48E-03	2	8.96E+00	1.79E-02	4	-2.66E-01	0.542	-2.62E-01	0.547
Chloride: Cl ⁻	52.0	35.5	1.46E-03	1	1.46E+00	1.46E-03	3	-6.94E-02	0.852	-6.55E-02	0.860
Nitrate: NO3-N	2.6	14.0	1.86E-04	1	1.86E-01	1.86E-04	3	-6.94E-02	0.852	-6.55E-02	0.860
Fluoride: F ⁻	0.5	19.0	2.63E-05	1	2.63E-02	2.63E-05	3	-6.94E-02	0.852	-6.55E-02	0.860
Carbonate: CO ₃ ²⁻	0.0	60.0	0.00E+00	2	0.00E+00	0.00E+00	5	-2.55E-01	0.556	-2.62E-01	0.547

$$\Sigma(+) - \Sigma(-) = 0.5^2 \Sigma c_i Z_i^2$$

-4.38E-01 2.53E-02

diff/sum *100
-1.5%

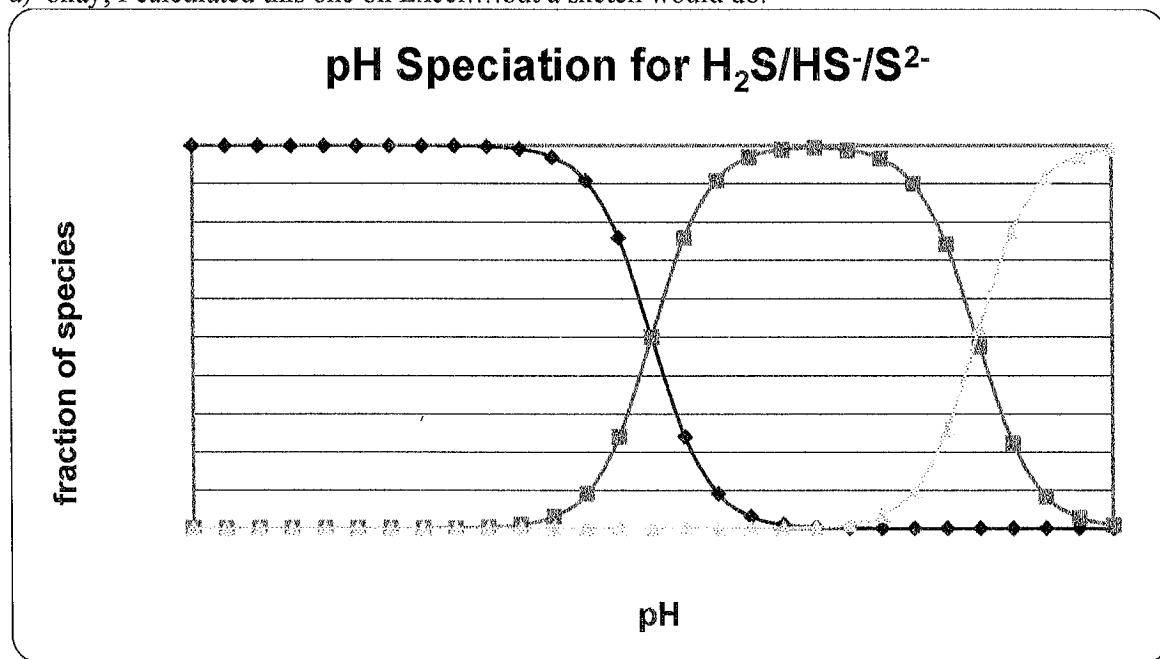
5. Using the appropriate equilibrium constant/s,
- Sketch a labeled pH speciation diagram for hydrogen sulfide.
 - Calculate the fraction of H_2S present in a water sample at pH 8.20.
 - Calculate the molar concentration of sulfide ion (S^{2-}), if the total reduced $[\text{S(-II)}]_{\text{T}}$ concentration has been determined to be 2.00 ppm in freshwater.
 - Calculate the concentration in ppm of sulphate ion, if this water were to become oxidic (high pe).

Strategy:

pH speciation diagrams can be sketched for well behaved acids/bases in which the pKa values are well separated such that no more than two chemical forms exist at any given pH. This is the case for the $\text{H}_2\text{S} - \text{HS}^- - \text{S}^{2-}$ system, where K_{a1} and K_{a2} are 1.0×10^{-7} and 1.1×10^{-12} , respectively. Use $\text{pKa} = \text{pH}$ at which the acid and conjugate base are present in equal portions (i.e., the fractional abundance, $\alpha = 0.5$).

Solution:

- okay, I calculated this one on Excel... but a sketch would do.



$$\text{b) } \alpha_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}]_{\text{T}}} = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]}$$

at pH = 8.2, it can be seen that $[\text{S}^{2-}] \sim 0$

$$\therefore \alpha_{\text{H}_2\text{S}} \cong \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{HS}^-]}$$

Since we want to calculate a value for this fractional abundance at a specific pH, we need to make a substitution with an expression that includes $[\text{H}^+]$.

Rearranging the K_{a1} expression yields, $[HS^-] = \frac{K_{a1} [H_2S]}{[H^+]}$

Substituting this into the fractional abundance expression gives;

$$\therefore \alpha_{H_2S} \cong \frac{[H_2S]}{[H_2S] + \frac{K_{a1}[H_2S]}{[H^+]}} = \frac{[H^+]}{[H^+] + K_{a1}}$$

Since at pH = 8.2, $[H^+] = 10^{-8.2} = 6.31 \times 10^{-9}$ M, we can calculate

$$\alpha_{H_2S} \cong \frac{6.31 \times 10^{-9}}{(6.31 \times 10^{-9}) + (1.0 \times 10^{-7})} = \mathbf{0.059}$$

c) $[S^{2-}] = \alpha_{S^{2-}} [S(-II)]_T$

where $[S(-II)]_T = 2.00$ ppm and the pH = 8.2

So we need an expression for the fractional abundance of S^{2-} as a function of $[H^+]$ as before. Following a similar process, we can derive

$$\alpha_{S^{2-}} = \frac{[S^{2-}]}{[H_2S] + [HS^-] + [S^{2-}]} = \frac{[S^{2-}]}{\frac{[H^+]^2[S^{2-}]}{K_{a1}K_{a2}} + \frac{[H^+][S^{2-}]}{K_{a2}} + [S^{2-}]} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\therefore \alpha_{S^{2-}} = 1.64 \times 10^{-4}$$

So, $[S^{2-}] = 1.64 \times 10^{-4} (2.00 \text{ ppm}) = 3.28 \times 10^{-4}$ ppm

Converting this to a molar concentration;

$$3.28 \times 10^{-4} \text{ ppm} = 3.28 \times 10^{-4} \text{ mg/kg} \times 1 \text{ mol}/32.06 \text{ g} \times 1 \text{ kg/L} = \mathbf{1.02 \times 10^{-5} \text{ mol/L}}$$

d) Under oxidizing conditions, all reduced sulfur (-II) would be oxidized to sulphate ion (VI).

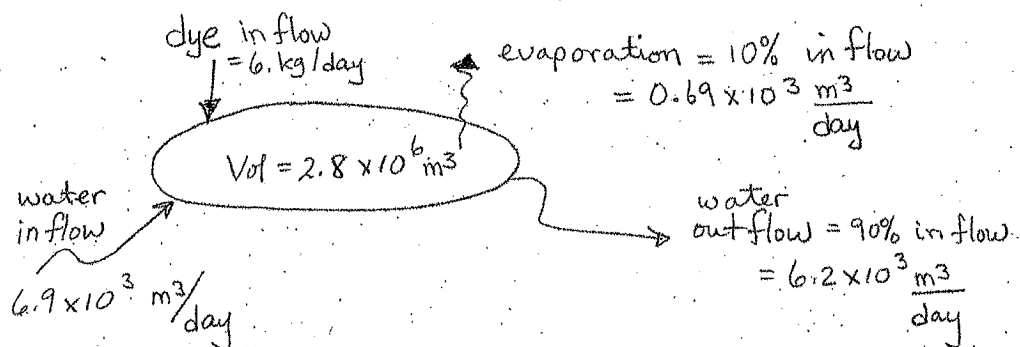
$$[SO_4^{2-}] = \frac{2.00 \text{ mg S}}{\text{kg}} \times \frac{1 \text{ mol S}}{32,000 \text{ mg}} \times \frac{96,000 \text{ mg}}{1 \text{ mol SO}_4^{2-}} = \mathbf{6.0 \text{ mg/kg}}$$

6. A non-volatile water soluble dye is released to a lake at a rate of 6.0 kg per day. The lake has a volume of $2.8 \times 10^6 \text{ m}^3$ and the average flow rate of the river feeding the lake is $6.9 \times 10^3 \text{ m}^3/\text{day}$. The lake is well mixed and 10% of the lake water is lost through evaporation.

- Draw a diagram of the system illustrating stocks and fluxes, where possible.
- What is the *steady state* concentration of the dye in the lake?

Strategy: A good start for these sort of questions is to sketch a diagram identifying the compartment/s, stock/s and various fluxes. The dye is non-volatile, so it is not lost by evaporation and instead stays in the aqueous phase. Since the water in the lake is lost by both evaporation and outflow, whereas the dye is only lost by outflow (assuming that it is persistent on the time scale of the residence time of the water), we can say τ_{dye} is not equal to the τ_{water} .

Solution:



$$\tau_w = \frac{\text{stock of water}}{\text{Flow of water}} = \frac{2.8 \times 10^6 \text{ m}^3}{6.9 \times 10^3 \text{ m}^3/\text{day}} = 406 \text{ days}$$

$\tau_p \neq \tau_w$ because evaporative loss of water does not include pollutant

$$\tau_p = \frac{\text{stock of dye}}{\text{outflow of dye}} = \frac{[\text{dye}] \times \text{Vol of lake}}{[\text{dye}] \times \text{outflow of water}} = \frac{2.8 \times 10^6 \text{ m}^3}{6.2 \times 10^3 \text{ m}^3/\text{day}} = 452 \text{ days}$$

$$\tau_p = \frac{\text{stock of dye}}{\text{in flow of dye}} = \frac{[\text{dye}] \times \text{Vol of lake}}{6.0 \text{ kg/day}}$$

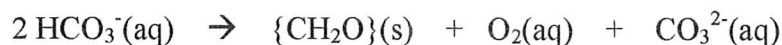
$$452 \text{ day} = \frac{[\text{dye}] \cdot 2.8 \times 10^6 \text{ m}^3}{6.0 \text{ kg/day}}$$

$$\therefore [\text{dye}] = \frac{452 \text{ day} \cdot 6.0 \text{ kg/day}}{2.8 \times 10^6 \text{ m}^3} = 9.7 \times 10^{-4} \frac{\text{kg}}{\text{m}^3} = 0.97 \text{ mg/L}$$

7. In temperate regions, lake sediments often show stratified layers that vary with season - dominated by the presence of lighter coloured metal carbonates in summer and darker metal sulfides in winter. Explain using the expected seasonal changes in pH and pe. *You may find it useful to refer to the pe-pH diagrams for aqueous carbon and sulfur species.*

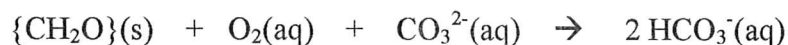
Strategy: Insoluble salts will precipitate from aqueous solution when the product of concentrations of the corresponding ions (Q_{sp}) exceeds the solubility product (K_{sp}).

Solution: In summer, photosynthesis and aeration keep lake surface waters relatively oxic (higher pe) and basic (higher pH) as a result of the following reaction.



Carbon and sulfur will be in their higher oxidation states (+IV) and (+VI), respectively. If the aqueous concentrations of common metal ions is high enough, metal carbonates (e.g. CaCO_3 , MgCO_3 , $\text{Fe}_2(\text{CO}_3)_3$, $\text{Mn}(\text{CO}_3)_2$ etc) may form and settle to the bottom giving rise to a lighter coloured sediment layer.

In the winter, lakes are often covered with ice and snow minimizing photosynthesis and aeration processes. Respiration and degradation will dominate and waters become relatively anoxic (lower pe) and acidic (lower pH).



Carbon and sulfur will be in their lower oxidation states (-IV) and (-II), respectively. If the aqueous concentration of metal ions is high enough, metal sulfides (e.g., FeS , MnS) will form giving rise to a darkly coloured sediment layer.

Such variations in colour can sometimes be used to visually date sediment cores.

8. One of the parameters used to characterize water supplies to discriminate between water influenced by sea-salt (Na^+ dominant), chemical weathering (dissolution of minerals, Ca^{2+} dominant) and evaporation is the weight ration of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$. Calculate the $\text{Na} / \text{Na} + \text{Ca}$ weight ratio and the TDS for the four major rivers listed below. Plot $\text{Na} / \text{Na} + \text{Ca}$ ($0 \rightarrow 1$) on the x-axis versus the log TDS (mg/L) on the y-axis and compare it to a similar plot appearing in *Science* 170, 1088-1090. Characterize each of these river waters as being dominated by rainfall, chemical weathering or evaporation. (See further *An Introduction to Environmental Chemistry* (2nd Ed) by J.E. Andrews et al., Blackwell Pubs, 2004 pp.145 – 151.)

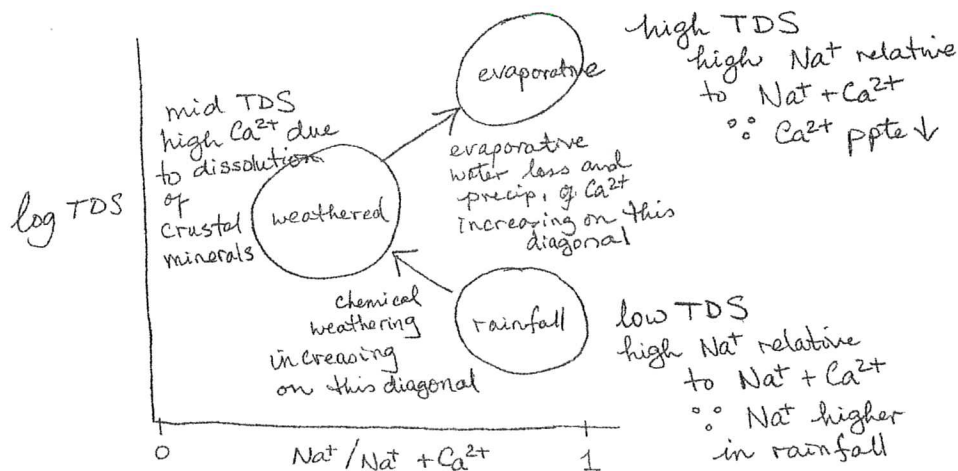
Major dissolved ion composition (mmol L^{-1}) of major rivers.

	MacKenzie (1)	Orinoco (2)	Ganges (3)	Rio Grande (4)
Ca^{2+}	0.82	0.08	0.61	2.72
Mg^{2+}	0.43	0.04	0.20	0.99
Na^+	0.30	0.06	0.21	5.10
K^+	0.02	0.02	0.08	0.17
Cl^-	0.25	0.08	0.09	4.82
SO_4^{2-}	0.38	0.03	0.09	2.48
HCO_3^-	1.82	0.18	1.72	3.00
SiO_2	0.05	0.19	0.21	0.50

Strategy: Surface waters dominated by rainfall contain relatively low concentrations of dissolved minerals (i.e., $\text{TDS} < 10 \text{ mg/L}$) and in general, have a higher relative abundance of Na^+ & Cl^- as these will dominate sea spray aerosols which are often entrained in rainwater.

Chemical weathering is a process whereby water in contact with continental crust slowly dissolves Earth abundant minerals such as those containing Ca^{2+} , HCO_3^- and SO_4^{2-} . Evaporation of surface waters leads to an enrichment of all dissolved minerals. As concentrations increase, some will exceed the saturation limit of certain minerals and precipitation occurs. This is true for Ca^{2+} and HCO_3^- , in particular.

Hence, we can use the $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio in conjugation with the TDS to characterize waters into three broad categories (rainfall, weathered or evaporative) or in transition between these extremes.



Solution: Using a spreadsheet and the data given in the question to calculate the TDS and the $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$ ratio for each of the four major river systems.

	Mackenzie		Orinoco		Ganges		Rio Grande	
	mmol L-1	mg L-1	mmol L-1	mg L-1	mmol L-1	mg L-1	mmol L-1	mg L-1
Ca ²⁺	0.82	32.88	0.08	3.21	0.61	24.46	2.72	109.07
Mg ²⁺	0.43	10.45	0.04	0.97	0.20	4.86	0.99	24.06
Na ⁺	0.3	6.90	0.06	1.38	0.21	4.83	5.1	117.30
K ⁺	0.02	0.78	0.02	0.78	0.08	3.13	0.17	6.65
Cl ⁻	0.25	8.84	0.08	2.83	0.09	3.18	4.82	170.39
SO ₄ ²⁻	0.38	36.52	0.03	2.88	0.09	8.65	2.48	288.33
HCO ₃ ⁻	1.82	111.02	0.18	10.98	1.72	104.92	3.00	183.00
SiO ₂	0.5	30.05	0.19	11.42	0.21	12.62	0.50	30.05
TDS		237.44		34.45		166.65		878.84
log TDS		2.38		1.54		2.22		2.94
Na/(Na+Ca)		0.17		0.30		0.16		0.52

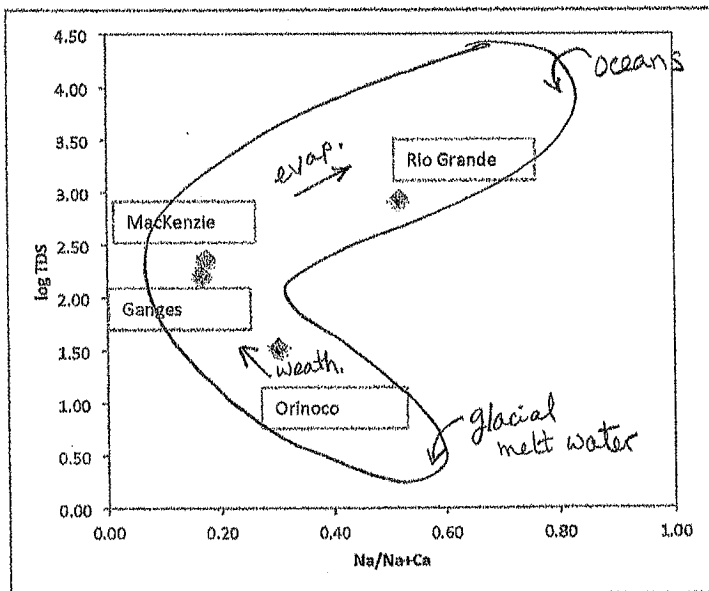
mid TDS
low Na/Na+Ca
weathering

low TDS
high Na/Na+Ca ratio
rainfall

mid TDS
low Na/Na+Ca
weathering

high TDS
high Na/Na+Ca ratio
evaporative

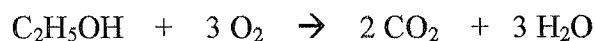
	Na/Na+Ca	log TDS
Mackenzie	0.17	2.38
Orinoco	0.30	1.54
Ganges	0.16	2.22
Rio Grande	0.52	2.94



9. In a police report last summer, it was revealed that approximately 400 L of alcoholic beverages were dumped into Cowichan river. Assuming an average ethanol content of 6% (v/v), estimate the mass of dissolved oxygen that would be consumed during biodegradation. How many cubic meters of river water (originally containing 10. mg O₂/L) would be completely depleted of O₂? What factors would mitigate the loss of dissolved oxygen? Would you expect such an incident to have a greater or lesser impact in warmer waters? Explain.

Strategy: We can use the number of moles of ethanol and stoichiometry from the degradation reaction to determine the number of moles of O₂ consumed. Since the water originally contains 10 mg/L, we can determine the number of liters of water that would theoretically be depleted of O₂.

Solution: The degradation of ethanol is given by the following balanced chemical reaction.



Given 400 L of beverages at 6% (v/v) = 400 L x (6/100) = 24 L of ethanol. Since the density of ethanol is 0.79 kg/L (text), we have 24 L x 0.79 kg/L x 10³ g/kg = 1.9 x 10⁴ g ethanol.

mols O₂ consumed = # mols ethanol x (3 mols O₂/1 mol ethanol)

$$= 1.9 \times 10^4 \text{ g} \times (1 \text{ mol}/46 \text{ g}) \times (3 \text{ mols O}_2/1 \text{ mol ethanol})$$

$$= 1.2 \times 10^3 \text{ mols O}_2$$

$$(\text{or } 3.8 \times 10^7 \text{ mg of O}_2)$$

Therefore, the volume of water depleted = 3.8 x 10⁷ mg x (1 L/10 mg) = 3.8 x 10⁶ L (or ~4000 m³).

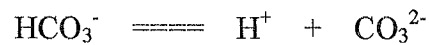
The loss of O₂(aq) by degradation will be mitigated to some extent by the rate of photosynthesis (primary producers/chlorophyll) and the aeration (turbulence at the surface).

In warmer waters, the rate of degradation would be faster making it more difficult for photosynthesis and aeration processes to keep up. Also, warmer waters can dissolve less oxygen to begin with, so this too can make the impact of biodegradable pollutants on the oxygen status greater.

10. In seawater the ions CO_3^{2-} and HCO_3^- are present in concentrations of 0.27 mM and 2.3 mM, respectively. However, in seawater the most of the carbonate ions are *complexed*, such that only 10% are 'free' in solution. Similarly, 75% of the hydrogen carbonate ions are 'free' in seawater. Furthermore, the *activity coefficients* of CO_3^{2-} and HCO_3^- are 0.20 and 0.60, respectively. Use K_a for HCO_3^- as 3.7×10^{-11} .

- Calculate the pH of seawater based on the molar concentrations of CO_3^{2-} and HCO_3^- .
- Repeat taking into account the effect of complexation and activity coefficients.
- How do your results compare to the observed global average pH of seawater?

Strategy: The $[\text{H}^+]$ and hence the pH, is controlled by the $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer system. Hence, we should consider the reaction that relates these two species, namely K_{a2} .



where,

$$K_{a2} = \frac{\{\text{H}^+\}\{\text{CO}_3^{2-}\}}{\{\text{HCO}_3^-\}} \quad \text{and} \quad \{\text{H}^+\} = \frac{K_{a2}\{\text{HCO}_3^-\}}{\{\text{CO}_3^{2-}\}}$$

Solution:

a) assuming $\{\text{HCO}_3^-\} = [\text{HCO}_3^-]$ and $\{\text{CO}_3^{2-}\} = [\text{CO}_3^{2-}]$

then
$$\{\text{H}^+\} = \frac{(3.7 \times 10^{-11})(2.3 \times 10^{-3})}{(0.27 \times 10^{-3})}$$

$$= 3.15 \times 10^{-10}$$

$\therefore \text{pH} = 9.50$

b) using additional information about activity co-efficients and tight ion pairing we can write

$$\begin{aligned} \{ \text{HCO}_3^- \}_f &= [\text{HCO}_3^-] \times \gamma_{\text{HCO}_3^-} \times \alpha_{\text{free}} \\ &\quad \uparrow \qquad \qquad \uparrow \qquad \qquad \uparrow \\ &\quad 2.3 \text{mM} \qquad 0.60 \qquad 0.75 \\ &= 1.04 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \{ \text{CO}_3^{2-} \}_f &= [\text{CO}_3^{2-}] \times \gamma_{\text{CO}_3^{2-}} \times \alpha_{\text{free}} \\ &\quad \uparrow \qquad \qquad \uparrow \qquad \qquad \uparrow \\ &\quad 0.27 \text{mM} \qquad 0.20 \qquad 0.10 \\ &= 5.4 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} \therefore \{ \text{H}^+ \} &= \frac{K_{a2} \{ \text{HCO}_3^- \}_f}{\{ \text{CO}_3^{2-} \}_f} \\ &= \frac{(3.7 \times 10^{-11})(1.04 \times 10^{-3})}{(5.4 \times 10^{-6})} \\ &= 7.13 \times 10^{-9} \\ &= 8.15 \end{aligned}$$

c) The global average pH of seawater is ~8.2 (text).