

Q1

$$a) \quad 50 \times 10^{-9} \frac{\text{mol}}{\text{L}} \text{ Cu} \times \frac{63.54 \text{ g}}{\text{mol}} \times \frac{10^6 \mu\text{g}}{\text{g}} \\ = 3.2 \mu\text{g/L}$$

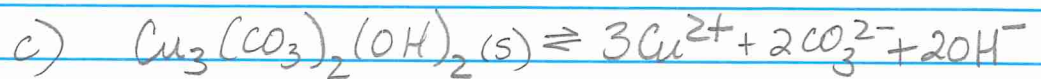
∴ Exceeds criteria

$$b) \quad 1 \text{ mM HCO}_3^- = 10^{-3} \text{ M HCO}_3^-$$

$$\therefore \log [\text{HCO}_3^-] = -3$$

pH seawater ~ 8.2

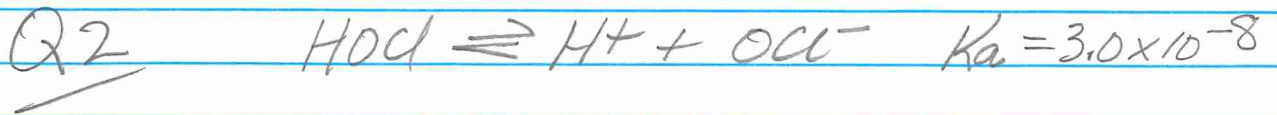
∴ $\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s})$ dominant



$$K_{sp} = [\text{Cu}^{2+}]^3 [\text{CO}_3^{2-}]^2 [\text{OH}^-]^2$$

The precipitation of azurite occurs when $Q_{sp} > K_{sp}$ which is defined by conditions that given $[\text{OH}^-]$ (i.e. pH) and $[\text{CO}_3^{2-}]$ (i.e. HCO_3^- and pH) and finally $[\text{Cu}^{2+}]$.

At a given pH, the conc of HCO_3^- required to result in $Q_{sp} > K_{sp}$ will depend on the conc. of Cu^{2+} ion.



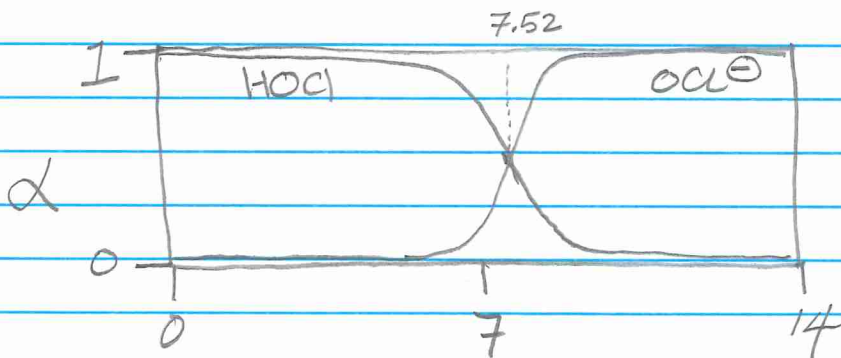
$\therefore pK_a = 7.52$

$$\alpha_{\text{HOCl}} = \frac{[\text{HOCl}]}{[\text{HOCl}]_T} = \frac{[\text{HOCl}]}{[\text{HOCl}] + [\text{OCl}^-]}$$

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

So $\alpha_{\text{HOCl}} = \frac{[\text{HOCl}]}{[\text{HOCl}] + \frac{K_a [\text{HOCl}]}{[\text{H}^+]}}$

$$= \frac{1}{1 + \frac{K_a}{[\text{H}^+]}} \quad \text{OR} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a}$$



At $\text{pH} = 7.31$, $\alpha_{\text{OCl}^-} \approx 0.4$

CHECK

$$\alpha_{\text{HOCl}} (\text{at pH } 7.31) = \frac{10^{-7.31}}{10^{-7.31} + 3.0 \times 10^{-8}} = \frac{4.90 \times 10^{-8}}{7.90 \times 10^{-8}} = 0.62$$

$$\alpha_{\text{OCl}^-} = (1 - \alpha_{\text{HOCl}}) = 1.00 - 0.62 = 0.38$$

Q3

a) Ionic strength is given by

$$I = \frac{1}{2} \sum C_i z_i^2$$
 which is the half of

sum of molar conc of each ion multiplied by the square of ionic charge.

Higher ionic strength reduces the chemical activity (effective conc) of ions in aqueous solution.

b) Total organic carbon is a measure of all oxidizable carbon in a water sample (i.e. biomass $\{CH_2O\}$).

Higher TOC will result in a greater demand on oxygen as it decomposes under aerobic conditions to yield inorganic carbon (i.e. CO_2 / HCO_3^- / CO_3^{2-}).

c) Degradation half-life ($t_{1/2}$) the time required for the conc of a substance to drop to $1/2$ of original value.

related to first order rate constant

$$t_{1/2} = \frac{0.693}{k} \quad (\text{i.e. larger } k, \text{ shorter } t_{1/2})$$

As $t_{1/2}$ increases the residence will increase as well

$$\tau = \frac{1}{k}$$

Q4

a) covalent oxides (e.g. CO_2 , SO_2 etc) react with water to form acidic solution and lower the pH

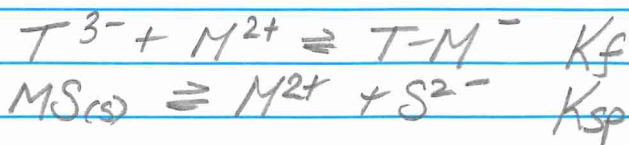
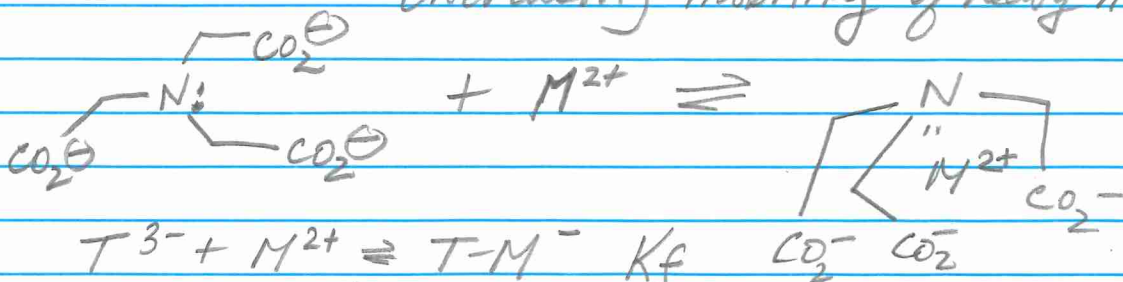


b) CO_2 (g) partial pressure increases the conc of $[\text{CO}_2(\text{aq})] = K_H \cdot P_{\text{CO}_2}$

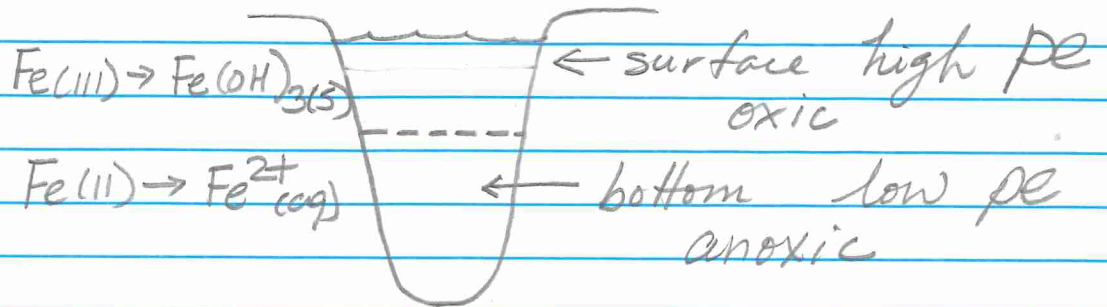
and this in turn increases the solubility of $\text{CaCO}_3(\text{s})$ which dissociates to yield a basic anion (e.g. CO_3^{2-})



c) nitrido triacetate (NTA) is a powerful chelating agent, which has a large formation constant, to yield a complex ion increasing mobility of heavy metals.



Q5



At surface (high pe), chromium is in a soluble Cr(VI) oxyanion $\text{CrO}_4^{2-}(\text{aq})$. Whereas, iron (III) is present in an insoluble $\text{Fe(OH)}_3(\text{s})$ form and therefore not observed in dissolved metal fraction. Similarly, manganese will be in oxidized (IV) present as $\text{MnO}_2(\text{s})$.

At depth (low pe), chromium will be a soluble Cr(III) form $\text{CrO}^+(\text{aq})$ below ~80 m. Similarly, iron will be present in soluble Fe(II) - $\text{Fe}^{2+}(\text{aq})$ and manganese as soluble Mn(II) - $\text{Mn}^{2+}(\text{aq})$.

Q6.



$$E^\circ = 1.005 \text{ V (data sheet)}$$

$$\therefore pe^\circ = 17.0$$

$$pe = pe^\circ - \frac{3}{1} \text{pH} + \frac{1}{1} \log [\text{Fe}^{2+}]$$

↑
1M (std. conditions)

$$\therefore pe = 17.0 - 3(9.0) \\ = -10.0$$



(data sheet)

$$pe = 4.2 - \frac{9}{8} \text{pH} - \frac{1}{8} \log \frac{[\text{HS}^-]}{[\text{SO}_4^{2-}]}$$

$$pe^\circ = 4.20$$

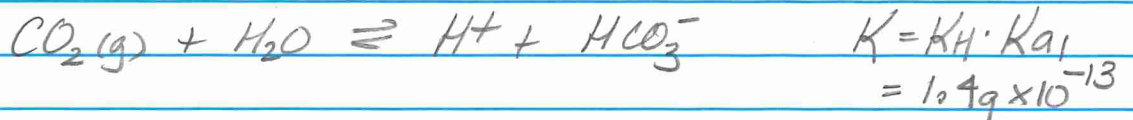
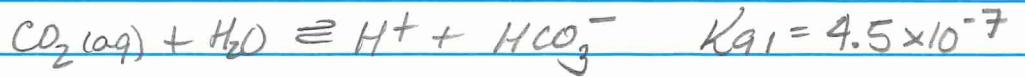
$$\therefore pe = -5.9$$

↑
1M (std. conditions)

More positive pe value indicates greater driving force to occur in direction written. Therefore, under these conditions the reduction of $\text{Fe}(\text{OH})_3(\text{s}) \rightarrow \text{Fe}^{2+}$ does NOT bring about the oxidation of $\text{HS}^- \rightarrow \text{SO}_4^{2-}$

(Note the solution to this question in textbook chap 10, 76) does not adjust to pH 9 which introduces an error)

Q7



$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{P_{\text{CO}_2(\text{g})}}$$

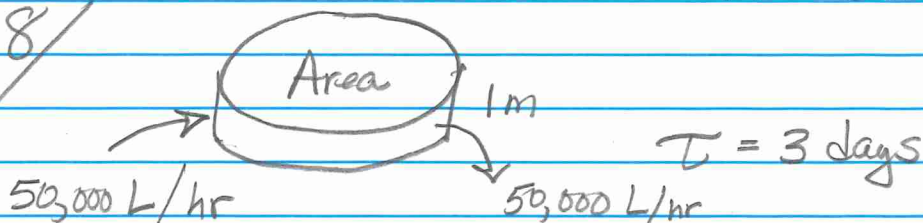
$$\therefore P_{\text{CO}_2} = \frac{[\text{H}^+][\text{HCO}_3^-]}{K}$$

$$= \frac{(10^{-6.5} \text{ M})(6.25 \times 10^{-3} \text{ M})}{1.49 \times 10^{-13} \text{ M}^2/\text{Pa}}$$

$$= 13,300 \text{ Pa}$$

or 0.131 atm

Q8



$$\tau = \frac{M}{F}$$

$$\therefore M = \tau \cdot F$$

$$= (3 \text{ day})(50,000 \frac{\text{L}}{\text{hr}} \times 24 \frac{\text{hr}}{\text{day}})$$

$$= 3.6 \times 10^6 \text{ L}$$

$$\text{Area} = \frac{\text{Volume}}{\text{Depth}}$$

$$= 3.6 \times 10^3 \text{ m}^3 \text{ (Volume of tank)}$$

$$= \frac{3.6 \times 10^3 \text{ m}^3}{1 \text{ m}} = 3.6 \times 10^3 \text{ m}^2$$

Q9



$$pe^\circ = 1.83$$

$$pe = pe^\circ - \frac{2}{2} pH - \frac{1}{2} \log \frac{[\text{SO}_3^{2-}]}{[\text{SO}_4^{2-}]}$$

at boundary = 0

$$\therefore pe = 1.83 - 8 = -6.2$$

+13 — O₂/H₂O

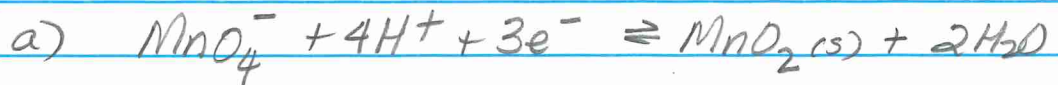
-4 — SO₄²⁻/HS⁻
 -6 — SO₄²⁻/SO₃²⁻
 -8 — H₂O/H₂

The reduction of SO₄²⁻ → SO₃²⁻ occurs at pe below the reduction of SO₄²⁻ → HS⁻

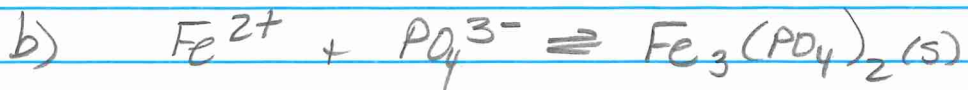
pH = 8

Therefore, SO₃²⁻ is not thermodynamically stable in water at pH = 8

Q 10/

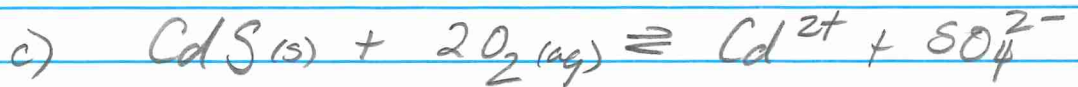


Adding CaCO_3 (basic) will react with H^+ and shift equilibrium to LEFT (reactant side), which will in turn increase $\{e^-\}$ and lower pe (more reducing)



Increasing pH, increases the conc of PO_4^{3-} (relative to other protonation states)

thus shifting equilibrium to RIGHT (product side), favouring precipitation of $\text{Fe}_3(\text{PO}_4)_2(\text{s})$



Decrease in pe favours reduced form of sulfur, favouring formation of S^{2-} which forms highly insoluble $\text{CdS}(\text{s})$, thus reducing its mobility.