

1. The following data was obtained from Buttertubs marsh on October 17, 2002.

Temp. = 15°C	
pH = 7.84	* derived values
ORP = 210 mV	$E_h^* = 0.452 \text{ V}$
Conductivity = 106 $\mu\text{S/cm}$	TDS* = 68 mg/L (as NaCl)
D.O. = 6.2 mg/L O₂	
Total Alkalinity = 37 mg/L CaCO₃	
Total Hardness = 57 mg/L CaCO₃	
Nitrate nitrogen = 0.08 mg/L NO₃-N	
Reactive phosphate phosphorous = 0.01 mg/L PO₄-P	
Sulfate = 2 mg/L SO₄²⁻	
Total sulfide = 0.004 mg/L S²⁻	

Answer each of the following:

- What is the concentration of nitrate ion expressed as ppb of **NO₃⁻**. [2]
- Given that K_H for **O₂** = $1.52 \times 10^{-3} \text{ M atm}^{-1}$ at 15°C, what is the % saturation of **O₂**? [3]
- Calculate the molar concentrations of **OH⁻**, **HCO₃⁻** and **CO₃²⁻**. [4]
- Calculate the ratio of **[H₂PO₄⁻]/[HPO₄²⁻]** in this sample. [2]
- Does the data suggest sources of calcium ion other than **CaCO₃**? Explain. [2]
- Based on your knowledge of the factors affecting chemical speciation, do you expect to find appreciable concentrations of **NH₄⁺** in this sample? Explain. [2]
- Using the Total Dissolved Solids (TDS) value expressed as mg/L of **NaCl**, calculate the ionic strength of the sample. [2]

2. Define and state the *environmental significance* of **TWO** of the following. [6]

- Oxidation Reduction Potential (ORP)
- Total Organic Carbon (TOC)
- Sodium Tripolyphosphate (STP)

3. Define each of the following in terms of explicit expressions involving the concentrations of species involved. [3]

- a) total carbonates, $[\text{CO}_3^{2-}]_T$
- b) calcium ion activity, $\{\text{Ca}^{2+}\}$
- c) fractional abundance of selenate ion, $\alpha_{\text{SeO}_4^{2-}}$

4. Provide balanced chemical equations to illustrate **TWO** of the following. [4]

- a) sodium tripolyphosphate ($\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$) acting as a base
- b) dissolution of CaCO_3 in the presence of aqueous carbon dioxide
- c) aerobic degradation of biomass in aquatic
(use $\{\text{CH}_2\text{O}\}$ to represent carbohydrate biomass)

5. With reference to the iron and manganese pe-pH diagrams, explain why well water rich in Fe^{2+} and Mn^{2+} will produce a precipitate on exposure to the atmosphere. [2]

6. The solubility of $\text{CdCO}_3(\text{s})$ is greatly affected by affected by the pH and the concentration of chelating agents, such as NTA. Use the equilibrium constants provided on the data sheet to determine the value of the equilibrium constant for the reaction below. [4]

Note: the pH speciation of NTA is represented as $\text{H}_3\text{T}/\text{H}_2\text{T}^-/\text{HT}^{2-}/\text{T}^{3-}$ (see attached diagram).



7. The US EPA has recommended lowering the maximum contaminant level (MCL) from 50 ppb As to 5 ppb. Arsenic occurs naturally in two oxidation states: As(III) and As(V). It is acidic in both oxidation states, but much more so as As(V), in which case it is chemically similar to phosphoric acid [i.e., P(V)]. The pK_a values of arsenous acid, H_3AsO_3 and arsenic acid, H_3AsO_4 are shown below and indicate that most of the H_3AsO_3 remains fully protonated at pH 7, whereas H_3AsO_4 is extensively deprotonated. Because of this difference in ionic charge on the dominant species, it is easier to remove As(V) than As(III) from solution by adsorption and ion-exchange processes that might be employed at a water treatment plant.

- a) Sketch a fully labeled pH speciation diagram for the As(V) species and a block pe-pH diagram for arsenic (slopes of all pe/pH boundaries = 0 or ∞). [4]
- b) Workers at a water treatment plant want to ensure that > 99% of the total arsenic in the water is in the oxidized form prior to feeding it to an ion-exchange process (i.e., $[As(III)] = 0.01 [As(V)]$). Assuming the arsenic species equilibrate rapidly in response to solution pe, what is the minimum target pe required to achieve if the pH is known to be 7.6 ? [6]

Acidity Constants for As(III) and As(V) species

	pK_{a1}	pK_{a2}	pK_{a3}
H_3AsO_3	9.23	12.10	13.41
H_3AsO_4	2.24	6.76	11.60

Standard Free Energy of Formation (ΔG_f°) in kJ/mol

e^- (aq)	H^+ (aq)	OH^- (aq)	$H_2O(l)$	$H_3O^+(aq)$	H_3AsO_4 (aq)	$H_2AsO_4^-$ (aq)	$HAsO_4^{2-}$ (aq)	$H_3AsO_3(aq)$	$H_2AsO_3^-$ (aq)
0	0	-157.3	-237.2	-237.2	-769.3	-748.8		-640.0	-587.7



Information Provided

Formula Sheet (including Ionic Strength etc)

Universal and Specific Constants (K_a 's, K_{sp} 's, K_f 's)

pe – pH for iron, manganese, selenium

pe – pH for carbon, sulfur, nitrogen

pH speciation for H_2S , H_2CO_3 , H_3PO_4

pH speciation for NTA