

University of Canterbury

End of Year Examination 2006

Prescription Number(s): CHEM 324

Paper Title: Analytical & Environmental Chemistry

Time Allowed: THREE HOURS

Number of pages: ELEVEN

Answer **FIVE** of the SEVEN questions.

All questions are of equal value.

TURN OVER

1. ***Either:*** Write an essay on the environmental chemistry of Sn.

Your answer should discuss:

- (i) the use of Sn compounds in the marine environment;
- (ii) the properties and processes that lead to bioaccumulation of Sn compounds and their consequent environmental impact;
- (iii) methods for analysis of various Sn species, with particular reference to factors such as extraction and pre-concentration, species derivatisation, species fractionation, options for analytical detection, the optimization of analytical sensitivity and the significance of the “characteristic mass.”

- Or:*** Write an essay on the environmental chemistry of Hg.

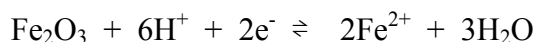
Your answer should discuss:

- (i) the use of Hg compounds, their toxicity and examples of their anthropogenic impact;
- (ii) the properties and processes that lead to bioaccumulation of Hg compounds in aquatic systems;
- (iii) methods for analysis of various Hg species, with particular reference to factors such as pre-concentration, species derivatisation, species fractionation, and the instrumental and chemical parameters that should be considered for optimization of analytical sensitivity;
- (iv) the use of methods, or reference materials for establishing the “recovery” of analyte in the adopted sample preparation protocol.

2. Answer any **THREE** of the following, (a) – (d):

(a) In relation to the redox properties of a natural water:

(i) Define electron activity in terms of K° for a redox process such as



(ii) Compare the term $p\epsilon$ for a redox system with pH for an acid-base system.

(iii) Indicate your understanding of the statement: “in a natural water the $p\epsilon$ value is poised (buffered) in a range that is determined by the ratio of available reducing agent to inorganic oxidising agents”. [It may be helpful to focus this answer around an example.]

(b) The $p\epsilon$ and $p\epsilon^{\circ}$ values for the redox system: $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$ are given by:

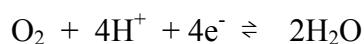
$$p\epsilon^{\circ} = (1/z) \log K^{\circ} = (1/z) (-\Delta G^{\circ}/2.3RT) = (1/z) (-\Delta G^{\circ}/5.71)$$

$$\text{and } p\epsilon = p\epsilon^{\circ} - \log ([\text{Fe}^{2+}]/[\text{Fe}^{3+}])$$

From the following values of ΔG°_f , calculate $p\epsilon$ for an interstitial water in which $[\text{Fe}^{3+}] = 10^{-8}$ M and $[\text{Fe}^{2+}] = 10^{-10}$ M.

$$\Delta G^{\circ}_f (\text{kJ mol}^{-1}): \text{e}^- (0.0), \text{Fe}^{3+} (-4.6), \text{Fe}^{2+} (-78.9)$$

Assuming that the system is in equilibrium with O_2 , calculate the partial pressure of O_2 in the interstitial water. The value of $p\epsilon^{\circ}$ for the reaction



is 20.75.

Question 2 continued on the following page

Question 2 continued

(c) An E_H - pH diagram for the system $O_2/H_2O/H_2$ is provided (**Figure 1**).

(i) Which labelled domain (1 through 6) in this diagram best represents the measured values of E_H for:

- a well aerated river water;
- a water-logged soil;
- water in contact with gold mine tailings.

Write an explanation for **two** of these assignments.

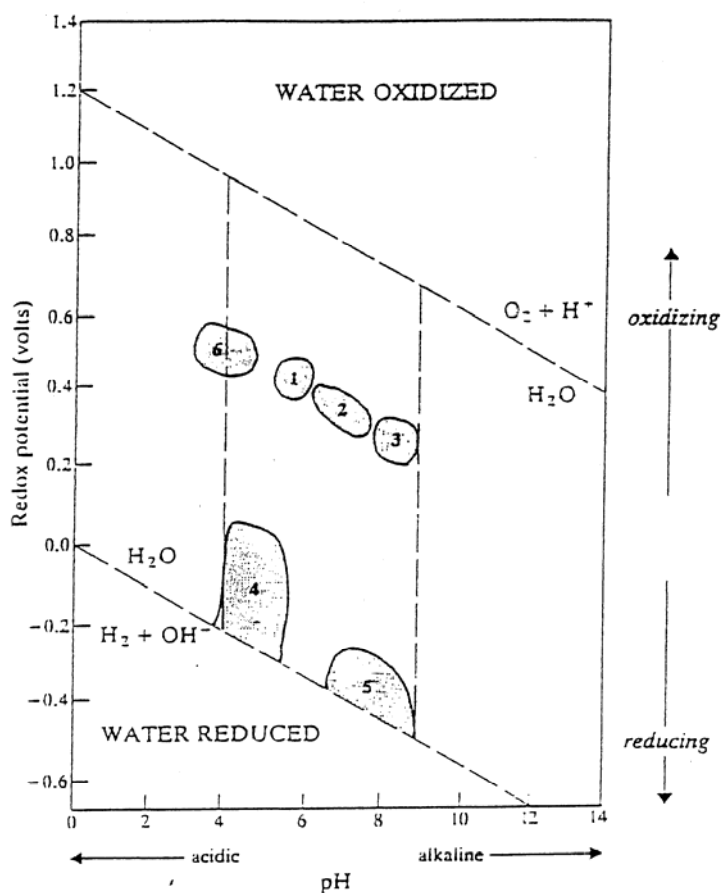
(ii) For which labelled domain (1 through 6) will there exist:

- the highest proportion of Fe as $Fe(H_2O)_6^{3+}$;
- the highest proportion of Fe as $Fe(H_2O)_6^{2+}$;
- the highest proportion of Fe as $Fe(OH)_3(s)$.

Write an explanation for **one** of these assignments.

Figure 1.

The E_H -pH conditions of some natural environments.



Question 2 continued

- (d) Write descriptive notes on the redox chemistry of arsenic in the Waikato river. Your answer should refer to **Figure 2**.

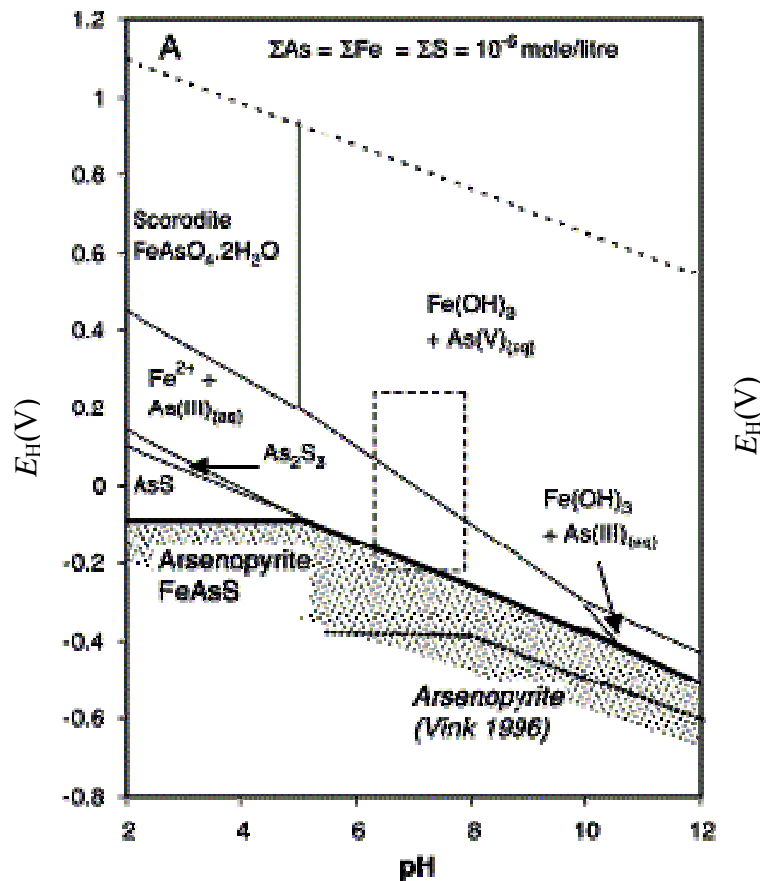


Figure 2.

E_H -pH diagram (25°C, 1 atm) for the As-Fe-O-S system showing the stability field of arsenopyrite (stippled; heavy lines). Dashed box in the centre of the diagram shows typical near-surface conditions. Diagram calculated for dissolved As, Fe, and S of 10^{-6} mol/L.

3. For an ion-selective electrode, $E_{\text{cell}} = E' + S \log(a_i + K_{ij}a_j^{n/z})$
- (a) Describe the processes that lead to the development of an electrical potential difference at the interface between a solution and the surface of an ion-selective electrode membrane. Explain how the measured potential enables the analyte activity to be determined.
 - (b) Explain why it is important to consider the ionic strength of standards and samples when determining analyte concentrations using ion-selective electrodes.
 - (c) A chloride ion-selective electrode was equilibrated in a solution of 1.0×10^{-4} M LiCl. The equilibrium potential was 95.4 mV. The electrode was then equilibrated in a separate solution of 1.0×10^{-3} M LiBr. The equilibrium potential was 109.6 mV.

Determine $K_{\text{Cl}^-, \text{Br}^-}$, assuming that the slope of the chloride calibration curve is -59.2 mV and that ion activities are proportional to concentrations.

- (d) Briefly outline the most important advantages and limitations of ion-selective electrode potentiometry for environmental analyses.

4. Write an essay on the diffusive gradients in thin films (DGT) technique, and its application to environmental chemistry.

Your answer should include a description of the components of DGT devices, an explanation of the function of each component, how the DGT technique may be used to determine time-averaged metal concentrations in an environmental water, other examples of applications of the DGT technique and its advantages and limitations for environmental use.

The expression below may be helpful when answering this question:

$$C_b = C_r \Delta g \Delta r / D t$$

5. The following entries are from a table giving total metal concentrations (C_{TOTAL}) and free metal concentrations (C_{FREE}) in filtered seawater samples.

Answer questions (a) - (f) with respect to entries in the table.

| Metal | Sample | Technique | C_{TOTAL} (nM) | C_{FREE} (nM) | Comments |
|-------|--------------|-------------------------------|----------------------------|---------------------------|--|
| Zn | Atlantic | ASV | 6.0 | 0.6 | C_{FREE} was independent of stirring rate |
| Cu | Sargasso Sea | ASV | 9.8 | 1.8 | Errors introduced by direct reduction of complexes |
| Fe | Pacific | AdSV (Ligand = pyrogallol) | | 0.5 | |

- (a) How might C_{TOTAL} be determined?
- (b) What is the meaning of C_{FREE} in the context of these measurements?
- (c) Briefly outline the principles of ASV (anodic stripping voltammetry).
Explain why ASV was not used to determine Fe.
- (d) Explain fully, with reference to the underlying principles, what information can be derived from the use of variable stirring rates in ASV. Explain the comment in the above table for zinc.
- (e) How might direct reduction of Cu complexes be detected and how might it be avoided?
- (f) Briefly describe the technique of AdSV (adsorptive stripping voltammetry).

6. Below is a list of terms used in connection with polymers. For each term:
- explain what you understand the term to mean;
 - name an associated method for polymer characterization; and
 - outline how the method works.
- (a) Molecular weight distribution
- (b) Number-average molecular weight
- (c) Weight-average molecular weight
- (d) Viscosity-average molecular weight
- (e) Z-average molecular weight
- (f) Glass transition temperature
- (g) Degree of crystallinity
- (h) End-to-end distance

7. (a) As in many other areas of chemistry, the following are useful tools for the polymer chemist:

(i) IR spectroscopy;

(ii) NMR spectroscopy;

(iii) mass spectrometry.

For **all three** of these methods, outline some of the polymer properties that can be characterized by them, in each case explaining the basis of the characterization.

(b) Discuss the following statement:

“To assess the environmental impact of polymers, it is necessary to consider all aspects of their production, use and disposal from the ‘cradle to the grave’, together with corresponding data for competing materials.

Production cannot be considered independently from either use or disposal, and vice versa. Only in this way can appropriate choices be made.”

END OF PAPER