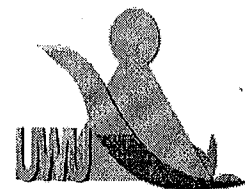




Uva Wellassa University, Sri Lanka
End Semester Examination – February 2012
MRT 422-3: Advanced Water Chemistry



Time: Three (03) hours

Answer all questions

All symbols carry standard meanings

Use of standard symbols without a definition is allowed

Answer to Question 6 (c) can be provided in the same sheet (page 5)

Question 1:

- (a) (20 marks) Define buffer capacity, β for a given system.
- (b) In order to calculate buffer capacity, β of distilled water we begin by deriving an equation for the acid-base titration curve. For distilled water assume that titrant is NaOH (i.e. $C_B = [Na^+]$).
- (i) (05 marks) Write charge balance equation substituting C_B for $[Na^+]$.
- (ii) (05 marks) If K_w is the ion activity product of water, obtain an expression for C_B in terms of $[H^+]$ and K_w .
- (iii) (10 marks) Write an expression for buffer capacity, β using the expression derived under (b).
- (iv) (20 marks) Prove that $\beta = 2.303[H^+] + [OH^-]$. Given $dH^+ = -2.303[H^+].dpH$
- (c) (20 marks) Determine the β at 298 K/ 1atm. For a solution of 10^{-1} M HA where the acidity constant for HA is $10^{-4.9}$.
- (d) (20 marks) Prove that the buffer capacity of any given aqueous solution cannot be zero.

Question 2:

(a) (25 marks) Define following terms as applied to natural waters.

- (i) Alkalinity (ii) Acidity

(b) (25 marks) Prove that the alkalinity is a conservative property for a given aqueous system. You may use $\text{H}_2\text{O}-\text{CO}_2$ system as an example.

(c) (25 marks) Calculate the alkalinity values of the solutions with following compositions:

- (i) Pure water (ii) 10^{-4} M HCl (iii) 10^{-3} M NaHCO_3 + 10^{-3} M HCl

(d) (25 marks) Does the alkalinity of a natural water (isolated from its surroundings) increase, decrease or stay constant upon addition of small quantities of the following?

- (i) HCl (ii) CO_2 (iii) Na_2SO_4

Explain your answer of the section (ii).

Question 3:

Part I

(a) (10 marks) What do you mean by open vs. closed $\text{CO}_2 - \text{H}_2\text{O}$ systems?

(b) (10 marks) How do these species differ: $\text{CO}_{2(\text{aq})}$, H_2CO_3 , and H_2CO_3^* .

Part II

Consider a calcite-water system in contact with a gas phase with a fixed p_{CO_2} .

(a) (20 marks) State equations of equilibrium chemistry of the systems (your answer should contain five mass action expressions).

(b) (20 marks) State the charge balance equation, and if the activities of H^+ , OH^- and CO_3^{2-} are negligible simplify it.

(c) (40 marks) Show that $a_{H^+}^3 = \frac{p_{CO_2} K_1^2 K_2^2 \gamma_{Ca^{2+}} K_2}{2K_{calcite} \gamma_{HCO_3}}$

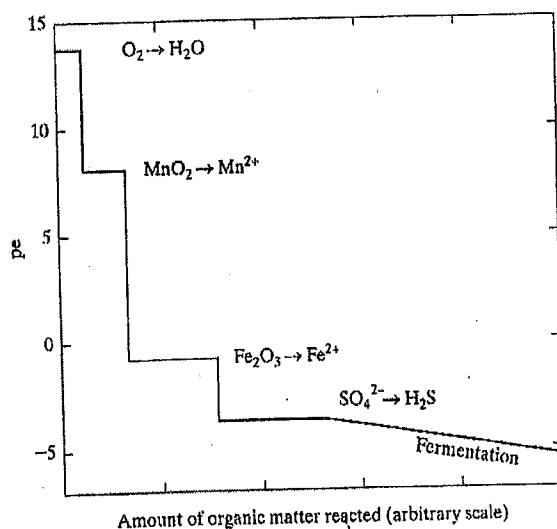
Question 4

(a) (25 marks) Define the terms pe and Eh. How are pe and Eh related?

(b) (25 marks) The concentrations of NO_3^- and NH_4^+ have been measured to be 10^{-5} M and 3×10^{-7} M, respectively, and $pH = 5$. What are the Eh and pe of this water?

Following data are given: $NO_3^- + 10H^+ + 8e^- \leftrightarrow NH_4^+ + 3H_2O(l)$; $\Delta_r G^\circ = -679.9 \text{ kJ mol}^{-1}$

(c) (25 marks) What do you mean by redox buffering and terminal electron acceptors (TEAP) in natural waters? Use the diagram shown below to answer:



(d) (25 marks) How is Eh of a water sample measured? Explain precautionary two steps that you take in Eh calculations.

Question 5

Part A

(a) (25 marks) Define following terms:

- (i) Partition coefficient
- (ii) Site density
- (iii) Specific surface area



- (b) (25 marks) A pesticide is added to soil slurry in a beaker containing 10.0 g of soil and 100 ml of 0.0050M CaCl₂ of a pesticide. Assume linear sorption calculate K_d . Predict the soil solution concentration if a soil contains 4.0 mg.kg⁻¹ of pesticide.

Part B

- (a) (10 marks) What is a non-variable charge surface?
- (b) (30 marks) A surface site is given as $\equiv S$ and the sorption of species M onto solid surface is shown as $\equiv S + M \rightarrow \equiv SM$.

Prove that $[\equiv SM] = K_L [M] [S_T] / (1 + K_L [M])$. K_L is Langmuir coefficient and $[S_T] = [\equiv SM] + [\equiv S]$.

- (c) (10 marks) List three assumptions made in deriving the Langmuir equation given in section (b).

Question 6

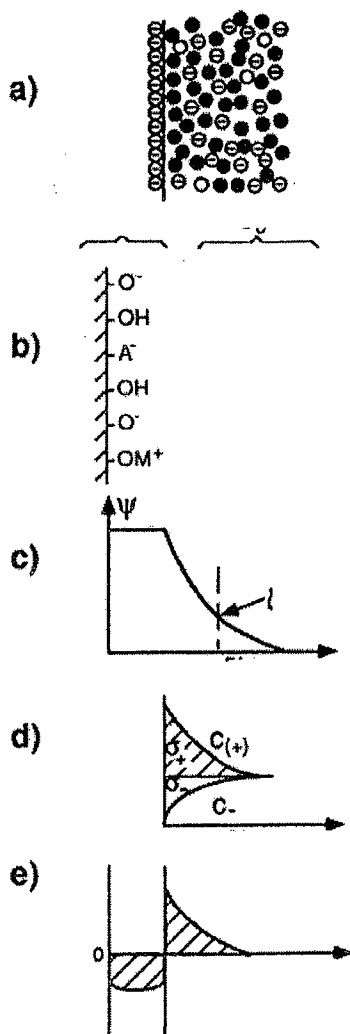
- (a) (20 marks) What is meant by variable charge surface?

- (b) (20 marks) Define following terms:

- (i) pH_{zpc} sphere (ii) Inner sphere complex (iii) Outer sphere
(iv) Ion pair



(c) (40 marks) Use the diagram shown to answer questions below.



(i). How are $-OH$ sites formed?

(ii). Label the diagrams (including both axes) (b), (c), (d), and (e).

(iii). What is the net area shown in diagrams (d) and (e)?

(d) (20 marks) State two assumptions made in Gouy Chapman theory.