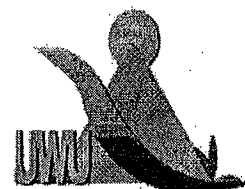


Uva Wellassa University, Sri Lanka
End Semester Examination - March 2011
MRT 321-2 Basic Water Chemistry



Time: Two (02) hour

Total 06 questions

Answer all questions

You may use standard symbols/ abbreviations without a definition

$$R = 8.314 \text{ J/mol.K}; H = 1.000; O = 16.000$$

- 1) (i) State two concentration scales used in the field of water industry. (25 marks)
- (ii) Assume that water behaves ideally in a solution that contains 2 mol NaCl per kg of water. What is the activity of water in this solution? Assume that NaCl dissociates completely to Na^+ and Cl^- ions in the solution and you may neglect the small amounts H^+ and OH^- that will be present ($H = 1.001; O = 16.000$). (25 marks)
- (iii) When both $\{H^+\}$ and $\{OH^-\}$ are expressed on the molal scale (i.e. m scale), and when H_2O is expressed on the mole fraction scale, the value of the acidity constant for water K_w at 298 K and 1 atm. is $1.01 \times 10^{-14} m^2$. What would be the constant equal at the same pressure and temperature conditions if we were to adopt the molal scale for expressing (H_2O)? (25 marks)
- (iv) At 298 K and 1 atm. $H_2O = H^+ + OH^-$ $K_w = 1.01 \times 10^{-14} m^2$. At 298 K and 1 atm. the enthalpy values for H_{aq}^+, OH_{aq}^- and H_2O are 0, -230.0 and -285.83 kJ.mol⁻¹, respectively. Estimate the value of K_w at 293 K? Hint: $\ln \left(\frac{K_1}{K_2} \right) = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$. (25 marks)
- 2) (i) The mathematical definition of the buffer capacity is $\beta = \frac{d(C_b - C_a)}{dpH}$. Based on this definition plus the intuitive understanding of the aqueous solutions explain why the value of β can never be zero for any solution. (25 marks)
- (ii) Schematically illustrate the variation of β of pure water as a function of pH (1 - 14). No derivation is needed. Briefly explain your answer. (25 marks)
- (iii) Estimate the buffer capacity of water at following pH values:
(a) pH = 2 (b) pH = 7 (c) pH = 14 (25 marks)
- (iv) A water analyst working for you reports that at 298 K and 1 atm. that certain water was found to have a β value of 10^{-4} eq/L at pH 4. You say "nonsense". Explain briefly. (25 marks)

- 3) (i) Briefly explain following terms:
 (a) Intrinsic and conditional acidity constants (b) Saturation index (25 marks)
- (ii) A spring water sample was obtained from Spring Valley (Badulla) for chemical analysis. The water has a calcium ion activity $10^{-3.04}$ and carbonate ion activity $10^{-5.36}$ in molar scale. Is the Spring Valley water in equilibrium with calcite, if not, is calcite tending to dissolve or precipitate?
 Following energy data are given.
- | | G° (kJ/mol) |
|--------------------|--------------------|
| Ca^{2+} | -554 |
| CO_3^{2-} | -527 |
| $CaCO_3$ (calcite) | -1128 |
- (25 marks)
- (iii) Define alkalinity? Consider a distilled water sample exposed to ambient atmosphere. Derive an equation for alkalinity? (25 marks)
- (iv) What do you mean by conservative species/ ions in water industry? Give an example for a conservative ion. What happens to the alkalinity of a water sample upon addition of following ions/ species?
 (a) CO_2
 (b) Protons
 (c) Hydrochloric acid
 (d) NaOH (25 marks)

- 4) Figures A and B show the variation of carbonate species as a function of pH at ambient conditions. Answer following questions.

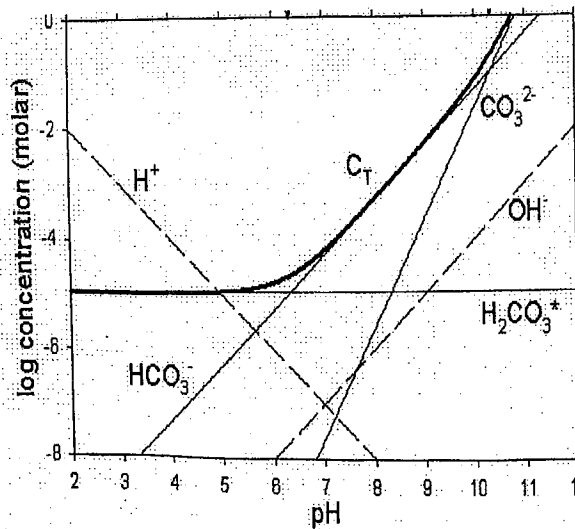


Figure A

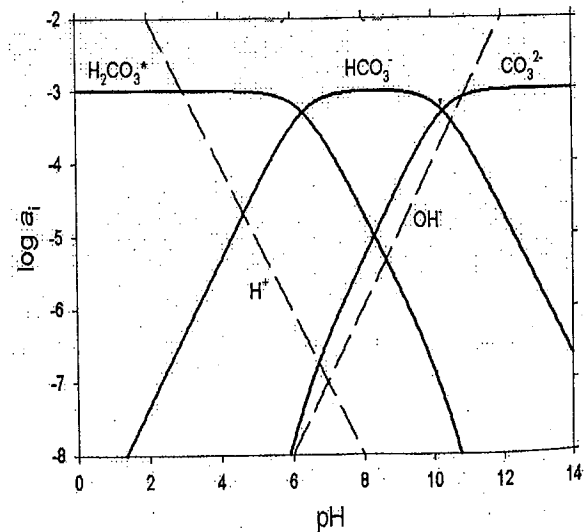


Figure B

- (i) State the initial conditions used in plotting these diagrams.

(25 marks)

- (ii) Write an expression for C_T in Figure A. Why is C_T curve not parallel to pH axis? (25 marks)
- (iii) Calculate the acidity constants of the carbonic acid using the data shown in the figures (25 marks)
- (iv) What is the pH of water in equilibrium with the atmospheric CO_2 at $25^\circ C$ assuming ideal behavior and no other dissolved solids or gases are present? The partial pressure of CO_2 in the atmosphere is 3.54×10^{-4} . If required use pK_1 , pK_2 and pK_w values from the graphs shown (Hint: Write a charge balance equation and assume that the activities of CO_3^{2-} and OH^- are much lower than that of the H^+ and HCO_3^-). (25 marks)

5) (i) Analysis of a spring water sample from Badulla gave following results:

Anion	mM	Cation	mM
HCO_3^-	5.436	Ca^{2+}	2.475
SO_4^{2-}	0.146	Mg^{2+}	0.663
NO_3^-	0.226	Na^+	0.223
Cl^-	0.231	K^+	0.036

Calculate the alkalinity of the water sample. (25 marks)

- (ii) What is a symmetric electrolyte? Calculate the ionic strength of the water sample shown in section (i). (25 marks)

- (iii) State a relationship between activity and concentration. How is activity coefficient of the calcium ion calculated? The activity models are shown below. Select the correct model for your calculation. Rationalize your selection.

Activity models and related data

$$\log \gamma = -Az^2 \sqrt{I}$$

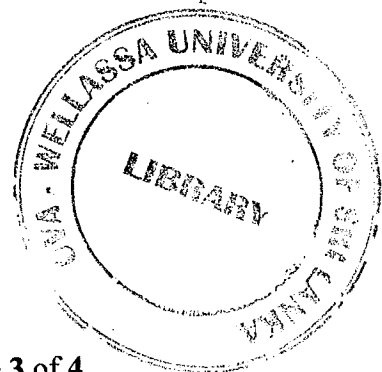
$$\log \gamma = -Az^2 \frac{\sqrt{I}}{1 + B a \sqrt{I}}$$

$$\log \gamma = -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

A, B Constants (for water $A = 0.5$ and $B = 0.33 \times 10^8$)
 Ca^{+2} , $a^0 = 4 \times 10^{-8} A^0$

- (iv) Calculate the activity of calcium ion in the water sample. Why it differs from the concentration of calcium ion? Rationalize your answer. (25 marks)

- 6) (i) Briefly define following terms:
 (a) Adsorption
 (b) Absorption
 (c) Precipitation
 (d) Ion exchange
 (e) Sorption



- (ii) According to surface complexation theory briefly describe the hydroxylation mechanism of gibbsite $[\text{Al}(\text{OH})_3]$ surface sites. (25 marks)
- (iii) What is pH_{zpc} of a solid? At this pH value state a relationship among charged surface species of gibbsite water suspension (hint: use the answer in section ii). (25 marks)
- (iv) A solid surface contains total of S_T surface sites. It interacted with a solution species A according to following empirical equation: $A + >S \rightarrow >AS$ where $>S$ is the free surface sites, and $>SA$ is the adsorbed surface species. Prove that $[>SA] = \frac{K_A[A][>S_T]}{1+K_A[A]}$ where $[A]$ is the equilibrium concentration of the solute species. K_A is a conditional constant related to the empirical equation shown. Indicate two assumptions made in deriving this relationship. (25 marks)