

Name:

Student no.:

Aquatic Chemistry (AW-4007) 2003

Final Examine

13-11-03

9 – 12 h

The exam contains 9 questions.

The maximum number of points for each question is 10.

You are allowed to use two A4 pages of your own notes during the exam.

Do not forget to write your name and student no. on each additional sheet of paper you want to hand in.

FUNDAMENTAL CONSTANTS

Constant	Symbol	SI	CGS
Avogadro's constant	N_0	$6.022 \times 10^{23} \text{ mol}^{-1}$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's constant	k	$1.381 \times 10^{-23} \text{ J K}^{-1}$	$1.381 \times 10^{-16} \text{ erg deg}^{-1}$
Molar gas constant	$R = N_0 k$	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	$8.314 \times 10^7 \text{ erg mol}^{-1} \text{ deg}^{-1}$
Electronic charge	$-e$	$1.602 \times 10^{-19} \text{ C}$	$4.803 \times 10^{-10} \text{ esu}$
Faraday constant	$F = N_0 e$	$9.649 \times 10^4 \text{ C mol}^{-1}$	$9.649 \times 10^4 \text{ C mol}^{-1}$
Planck's constant	$h (h = 2\pi\hbar)$	$6.626 \times 10^{-34} \text{ J s}$	$6.626 \times 10^{-27} \text{ erg s}$
Permittivity of free space	ϵ_0	$8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$	1
Mass of $\frac{1}{12}$ of ^{12}C atom*	u	$1.661 \times 10^{-27} \text{ kg}$	$1.661 \times 10^{-24} \text{ g}$
Mass of hydrogen atom	m_H	$1.673 \times 10^{-27} \text{ kg}$	$1.673 \times 10^{-24} \text{ g}$
Mass of electron	m_e	$9.109 \times 10^{-31} \text{ kg}$	$9.109 \times 10^{-28} \text{ g}$
Gravitational constant	G	$6.670 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$	$6.670 \times 10^{-8} \text{ g}^{-1} \text{ cm}^3 \text{ s}^{-2}$
Speed of light in vacuum	c	$2.998 \times 10^8 \text{ m s}^{-1}$	$2.998 \times 10^{10} \text{ cm s}^{-1}$

* Atomic mass unit (also denoted by a.m.u. and a.u.).

- 1) To pure water 7 mM Na_2CO_3 and 10 mM NaOH are added. Assume Na_2CO_3 dissolves completely and Na^+ does not form dissolved complexes
- Select components, write tableaux and mole balance equations for this solution.
 - What is the alkalinity of the solution?
 - Estimate the pH of the solution (do not calculate explicitly!) and give reasons for your estimation.
 - The solution is subsaturated with respect to the CO_2 pressure of the atmosphere. What will be the effect of CO_2 dissolution on alkalinity, pH, and the concentration of dissolved inorganic carbon?
 - Assume Na_2CO_3 and NaOH are added to 0.7 M NaCl . What will be the effect on alkalinity and on pH compared to the solution prepared with pure water?



2) The protonation and deprotonation of hematite can be described by (Liger et al. 1999):



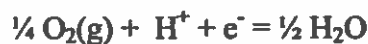
In a suspension of 0.8 g/L hematite at pH 8 the concentration of the three surface species: $\equiv \text{FeOH}_2^+$, $\equiv \text{FeOH}$, and $\equiv \text{FeO}^-$ is 54,9 μM , 107 μM , and 38 μM , respectively. The ionic strength of the suspension is 0.1 M and the specific surface area of hematite is 125 m^2/g .

- Calculate the surface charge density.
- Calculate the surface potential.
- Calculate the apparent constants for the protonation and deprotonation of the surface sites by using the diffuse double layer model.
- Are the calculated apparent constants consistent with the species distribution?
- At which pH are the intrinsic constants and the apparent constants equal?

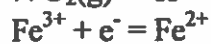
3) Water pumped from a well close to Zwolle has a pH of 7.00 and an iron concentration of 15.0 mg/L ($MW(Fe) = 55.845 \text{ g/mol}$). Assume that all dissolved iron occurs as Fe^{2+} and that goethite ($\alpha\text{-FeOOH}$) is the dominant Fe(III) hydroxide in the aquifer.

- Derive an expression for calculating the pe for the redox couple $Fe^{2+}/\alpha\text{-FeOOH}$?
- Calculate the pe of the redox couple $Fe^{2+}/\alpha\text{-FeOOH}$ in the groundwater.
- What will be the concentration of Fe^{2+} in equilibrium with goethite if the groundwater is pumped to the surface and the pe of the solution is controlled by the oxygen pressure in the atmosphere ($P(O_2)=0.20 \text{ atm}$)? Neglect pH changes due to iron oxidation and precipitation.
- What is the potential energetic gain of oxidizing 15.0 mg/L Fe^{2+} with oxygen at atmospheric pressure at pH 7?
- Discuss whether bacteria can make a living from catalysing the oxygenation of Fe^{2+} . Such bacteria have been isolated from acidic environments but can hardly be found in environments with neutral pH. Why could this be?

Use the following set of equations for your calculations



$$pe^0 = 20.75$$



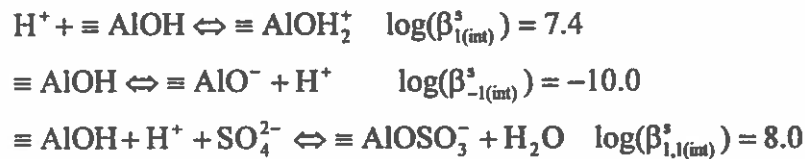
$$pe^0 = 13.0$$



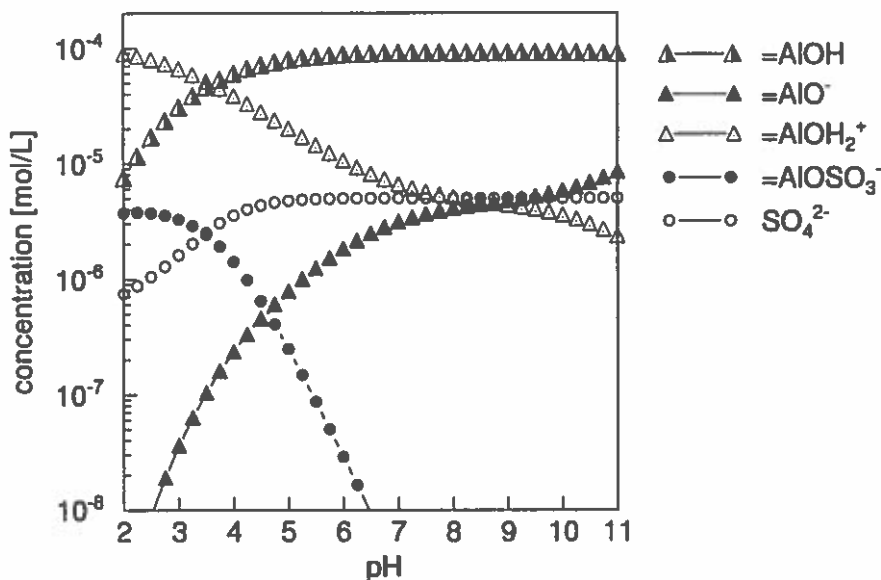
$$\log K = -0.5$$

- 4) In the lectures we discussed the energies of interactions between ions, atoms, and molecules involved in dissolving NaCl(s) in water.
- a) Which interactions have we taken into consideration for calculating the pair potential between Na and Cl for deriving the lattice energy of NaCl(s)?
 - b) K^+ and Br^- are larger than Na^+ and Cl^- . What will be the difference between the lattice energy of KBr(s) compared to NaCl(s)?
 - c) Which interactions contribute most to the energy of hydration of Na^+ and Cl^- ?
 - d) Why is the solubility of AgCl(s) much smaller compared to NaCl(s)? Do you think this is due to differences in lattice energy or caused by different energies of hydration of Ag^+ and Na^+ ?

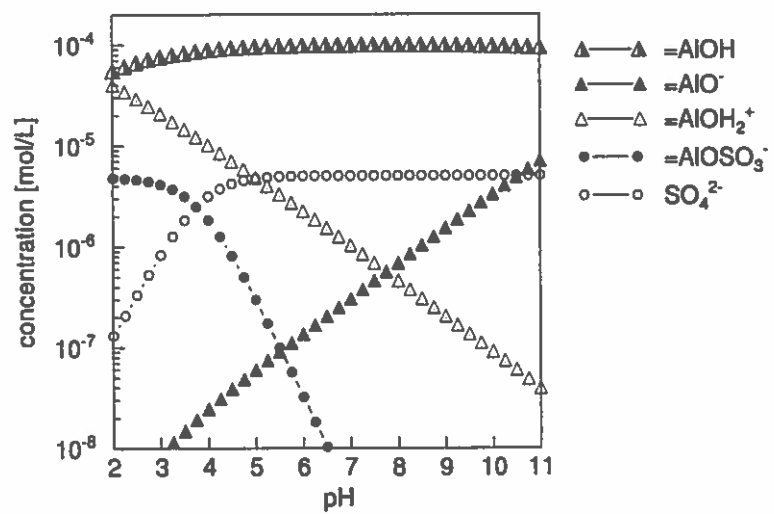
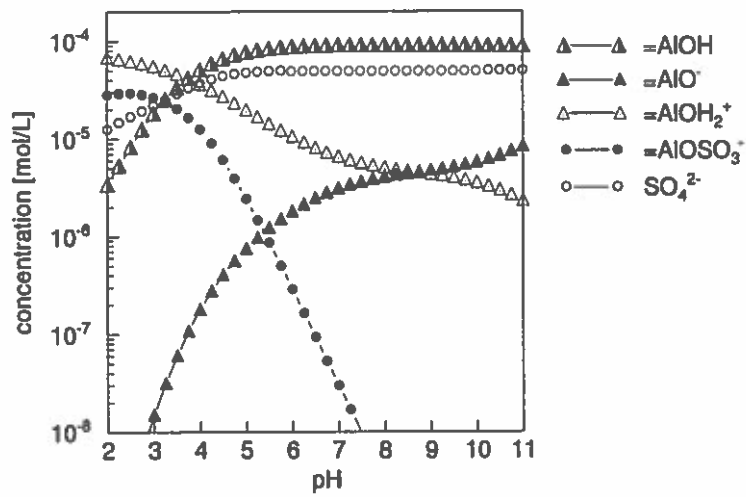
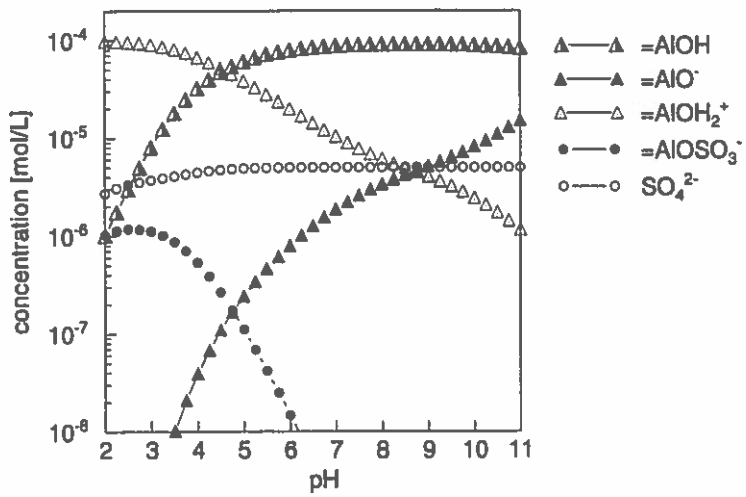
5) Sulfate adsorption onto aluminum oxide can be described by the following simplified formalism (Stumm, 1992)



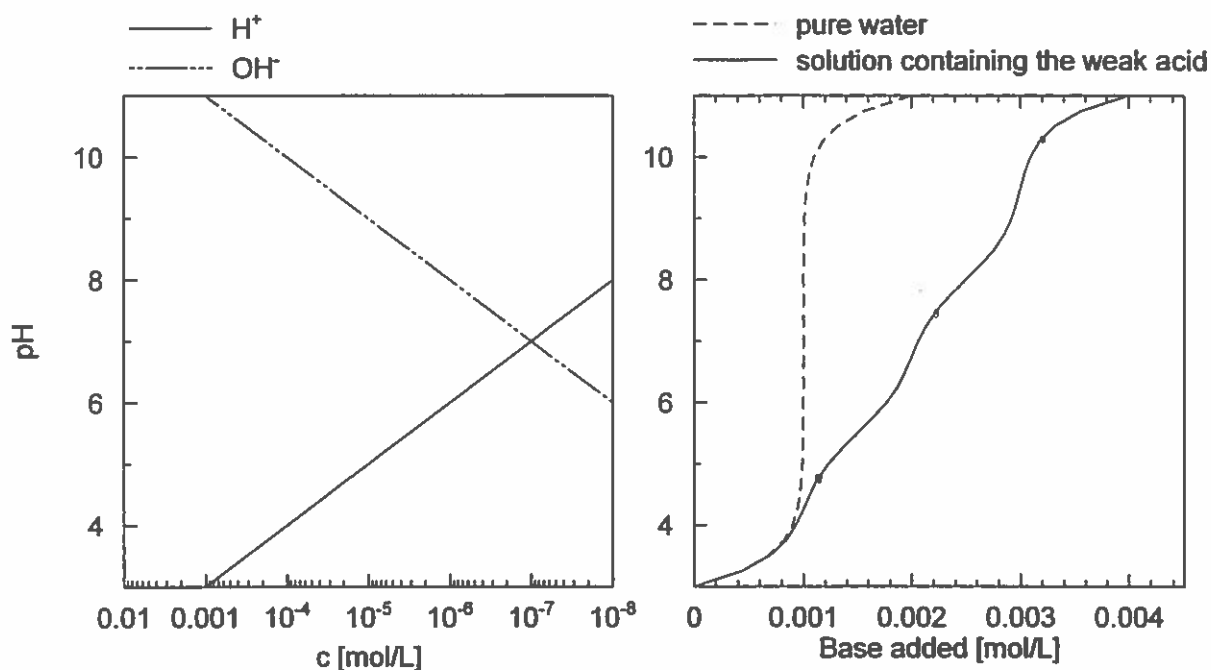
The graph below shows the concentrations of sulfate and the different surface species of aluminum oxide as function of pH. The calculations were performed using following set of parameters: $I=0.01$ M, concentration of aluminum oxide 1 g/L, specific surface area $10 \text{ m}^2/\text{g}$, concentration of surface sites 0.1 mM, sulfate concentration $50 \text{ }\mu\text{M}$.



- a) Comment on the strength of sulfate adsorption onto aluminum oxide and the mechanism of adsorption (inner-sphere / outer-sphere).
- b) In the following three graphs one parameter in the calculations has been changed. Select one of the following options for each graph and give reasons for your choice:
- sulfate concentration $5 \text{ }\mu\text{M}$
 - sulfate concentration $500 \text{ }\mu\text{M}$
 - $I = 1 \text{ mM}$
 - $I = 0.1 \text{ M}$
 - $\log(\beta_{1(\text{int})}^s) = 8.5$
 - $\log(\beta_{1(\text{int})}^s) = 5.5$
 - $\log(\beta_{-1(\text{int})}^s) = -8.5$
 - $\log(\beta_{-1(\text{int})}^s) = -11.5$



- 6) The right graph shows the titration curve of a solution containing a weak acid in comparison with the titration curve of pure water. Both solutions were adjusted to pH 3 with a strong acid before performing the titration.



- How many deprotonation steps can be discovered in the titration curve?
- What are the pK_a values of the acid?
- What is the concentration of the acid?
- Sketch the concentration of the different species of the acid as a function of pH in the left graph.
- Mark the equivalence points.

- 7) Plummer et al. (*Hydrogeochemistry of Bermuda: A case history of ground-water diagenesis of biocalcarenes* by L. N. Plummer et al. *Geol. Soc. Am. Bull.* 1976, 87, 1301-1316) discuss in their article the relevance of several processes for the composition of groundwater in Bermuda.
- a) Which are the most important processes controlling the composition of meteoric water infiltrating into the Bermudian soil and flowing through the aquifer towards the ocean?
 - b) How become these processes reflected in the composition of the groundwater?
 - c) Plummer et al. conclude that many of the waters contain significant rock contributions of magnesium. Which minerals might release Mg in the Bermudian aquifer? How can you determine whether the Bermudian groundwater is in equilibrium with those minerals?

- 8) *Acid Neutralizing Capacity, Alkalinity, and Acid-Base Status of Natural Waters Containing Organic Acids* by Harold F. Hemond. *Environ. Sci. Technol.* **1990**, *24*, 1486-1489. Hemond discussed in his paper the contribution of dissolved organic matter to the acid/base buffering in natural waters.
- a) In which type of waters is the contribution of dissolved organic matter to the neutralization intensity and capacity relevant?
 - b) How can the acid neutralization capacity in these waters be determined (more than one possibility)?
 - c) Traditionally the p-value is determined and taken as an estimate for the alkalinity. The p-value is determined by titration until pH 4.3. Another approach was suggested by Wilander et al. (1998). He suggested to air-equilibrate the sample by flushing air through the sample and subsequently performing a titration until pH 5.6. What is the conceptual idea behind the two different methods? Discuss the applicability of the two methods for determining the alkalinity depending on water composition.
Hint: include the dependency of the equivalence points on the total concentration of carbonate in your discussion.

- 9) *Mechanism of arsenic release to groundwater, Bangladesh and West Bengal* by R.T. Nickson et al.. In general, elevated arsenic concentrations in groundwaters are either attributed to the oxidative dissolution of arsenic rich pyrite (FeS_2) or to the reductive dissolution of iron oxy hydroxides with adsorbed arsenic.
- a) Discuss which information can be used to differentiate between the two processes?
 - b) Which of the two processes is according to Nickson et al. the most relevant in Bangladesh?
 - c) Suggest simple methods to remove arsenic from contaminated groundwaters.