Name:	Student no.:

Aquatic Chemistry (Geo4-1406) 2005

Test Examination

The examination contains 7 questions. The maximum number of points for each question is different and is indicated at the top of the page.
You are allowed to use two A4 pages of your own notes during the examination.
Do not forget to write your name and student number 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	$2.998 \times 10^{8}\ \text{m s}^{-1}$	$2.998 \times 10^{10}\ \text{cm s}^{-1}$

1) To pure water 0.4 mM Na_2CO_3 and 0.4 mM H_2CO_3 are added. Assume Na_2CO_3 dissolves completely and Na^+ does not form complexes with bicarbonate or carbonate.

   a) Select components, write tableaux and mole balance equations for this solution.

   b) What is the alkalinity of the solution?

   c) 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 and pH?

   d) Estimate the pH of the solution (do not calculate!) and give reasons for your estimation.

   e) Comment on the buffer intensity of the solution.

$H_2CO_3 = HCO_3^- + H^+$, $pK_a = 6.3$; $HCO_3^- = CO_3^{2-} + H^+$, $pK_a = 10.3$

2) The protonation and deprotionation of gamma-alumina can be described by:

$$H^+ + \equiv AlOH \Leftrightarrow \equiv AlOH_2^+ \quad \log(\beta^s_{1,1(int)}) = 7.2$$

$$\equiv AlOH \Leftrightarrow \equiv AlO^- + H^+ \quad \log(\beta^s_{1,-1(int)}) = -9.5$$

In a suspension of 2 g/L gamma-alumina the concentration of the three surface species: $=AlOH_2^+$, $=AlOH$, and AlO^- is 29.3 μM, 524 μM, and 47 μM, respectively. The ionic strength of the suspension is 0.01 M and the specific surface area of gamma-alumina is 75 m^2/g.

a) Calculate the surface charge density.

b) Calculate the surface potential.

c) Calculate the apparent constants for the protonation and deprotonation of the surface sites by using the diffuse double layer model.

d) Are the calculated apparent constants consistent with the species distribution?

e) At which pH are the intrinsic constants and the apparent constants equal?

3) Following equation describes methanogenesis:

$CO_2(g) + 4\ H_2(g) = CH_4(g) + 2H_2O$ $\log K\ (10\ ^\circ C) = 25.25$

a) How many electrons are required to reduce CO_2 to methane? 8 e⁻

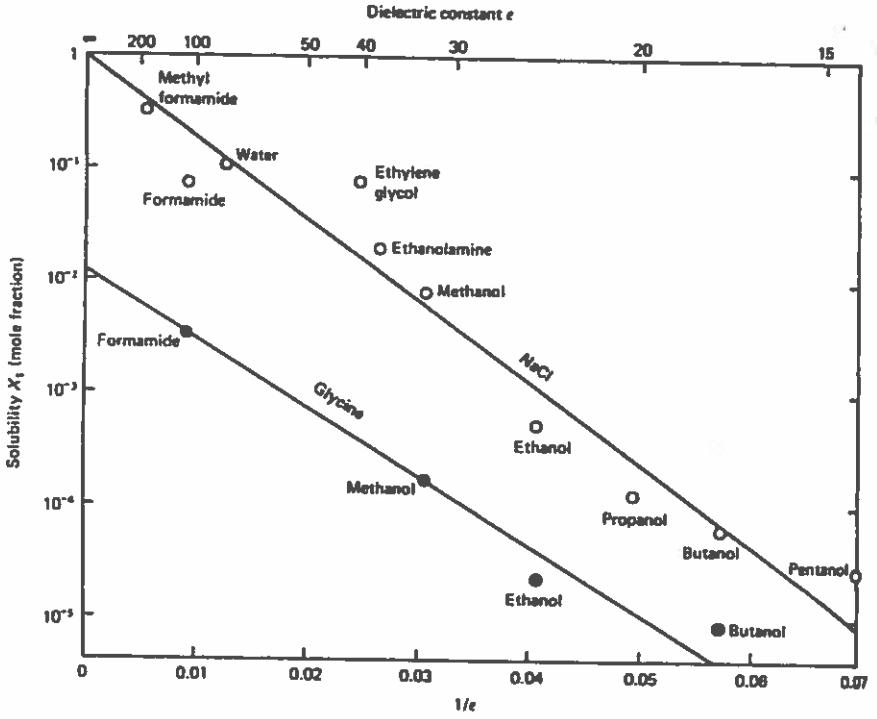
b) What might be a source for H_2 in anoxic sediments?

c) The porewater of a marine sediment has a CO_2 pressure of 0.07 atm and a CH_4 pressure of 2 atm and a H_2 pressure of $2x10^{-6}$ atm. What is the thermodynamically more favorable reaction, methanogenesis or methane oxidation?

d) What is the potential energetic gain of the reaction?

5,4 kJ/mol

4) Following graph shows the solubility of NaCl as a function of the dielectric constant of different solvents.



ion - dipole + dispersion + ~~dipole-induced dipole~~ + ion-induced dipole

a) Which intermolecular interactions have to be taken into consideration for calculating the pair potential between a dissolved ion and butanol?

b) Give an explanation why the solubility of NaCl depends on the dielectric constant of the solvent? $X_s = \exp(-\Delta u_i / kT)$ ε in Δu_i → larger

c) What would be the position of the line in the graph for KBr? Discuss the influence of the size of the ions on the enthalpy and the entropy of solution.

↳ΔH ↳ΔS

5) According to the model of Dzombak and Morel the reaction of the weak surface sites of HFO with protons and Cu(II) can be described by the following set of equations:

$$H^+ + \equiv FeOH \Leftrightarrow \equiv FeOH_2^+ \quad \log(\beta^s_{1(int)}) = 7.3$$

$$\equiv FeOH \Leftrightarrow \equiv FeO^- + H^+ \quad \log(\beta^s_{-1(int)}) = -9$$

$$\equiv FeOH + Cu^{2+} \Leftrightarrow \equiv FeOCu^+ + H^+ \quad \log(\beta^s_{-1,1(int)}) = 0.6$$

At pH 5.3 and I=0.1 M the concentration of protonated sites (=$FeOH_2^+$) and deprotonated sites (=FeO^-) is 1 mmol/L and 2.1 10^{-5} mol/L, respectively. When 10 µmol/L of a Cu(II) solution is added to the suspension about 2.5 µmol/L will remain in solution and about 7.5 µmol/L will be adsorbed.

a) Does Cu(II) form inner- or outer-sphere complexes with HFO? Give arguments for your decision. outer, only electrostatic attraction

b) Does Cu(II) adsorption decrease or increase with increasing pH? increase

c) Does Cu(II) adsorption decrease or increase with increasing I? I ↗ → γ ↙ → a_i ↙ → abs ↙

d) Does Cu(II) adsorption decrease or increase with increasing I at pH 9?

6) Water in lakes and rivers is frequently not in equilibrium with the CO_2 pressure in the atmosphere. In the course we discussed two processes, which can limit the rate of CO_2 dissolution or the outgassing of CO_2.

a) What are sinks and sources for CO_2 in surface waters?

b) Describe the two processes we included in our discussion about the rate limitation of CO_2 dissolution or outgassing.

c) Which one of the two processes is the most relevant with respect to the rate of CO_2 transfer between the atmosphere and surface waters?

7) Plummer et al. (*Hydrogeochemisty of Bermuda: A case history of ground-water diagenesis of biocalcarenites* 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 Bermudan soil and flowing through the aquifer towards the ocean?

b) Frequently the ion acitivity product IAP = $\{Ca^{2+}\}\{CO_3^{2-}\}$ in ground waters from aquifers containing calcite is not in agreement with the solubility product (K_{sp}) of pure crystalline calcite. What has to be taken into consideration when using K_{sp} values for pure crystals for describing the equilibrium between aqueous and solid phases in natural systems?

8) In chapter 2: *The Sedimentary Sink – Factors Influencing the Distribution of Sedimentary Constituents* in W.S. Broecker's and T.-H. Peng's book *Tracers in the Sea* we looked at the depth profile of the carbonate concentration in equilibrium with calcite.
   a) What is the "lysocline" the authors address in this chapter?
   b) Which corrections have to be done for calculating the carbonate concentration in deep ocean waters in equilibrium with calcite at given calcium concentration?
   c) Which fundamental equations are combined for deriving the Debye-Hueckel limiting law?
   d) For what type of interactions does the Debye-Hueckel limiting law account for?
   e) What other approaches or equations can be used for including these interactions in thermodynamic equilibrium calculations?

In the last project: *Mechanism of arsenic release to groundwater, Bangladesh and West Bengal* by R.T. Nickson et al., we investigated the possibility of removing arsenic from groundwaters with high arsenic concentrations by aeration and subsequent filtration.

a) Where does the arsenic in the ground water come from?

b) Which processes are involved in removing arsenic from the aqueous phase by aeration and filtration?

c) Which parameters would be important for the processes?

d) Do you think that aeration of ground water and subsequent filtration is a practical method for cleaning contaminated ground waters in Bangladesh?