

Name:

Student no.:

Aquatic Chemistry (AW-4007) 2003

Second-Chance Examination

to be solved at home

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 0.1 mM Na₂S is added and dissolves completely. (12 points)

a) Select components, write tableaux and mole balance equations for this solution by considering following reactions:



b) What is the alkalinity of the solution?

c) Estimate the pH of the solution (do not perform extensive calculations but base your estimation of some simple considerations!)

d) H₂S is a very toxic gas. How would you proceed to evaluate the risk of handling this solution in a laboratory without fume hood?

2) To a suspension containing 0.089g/L of HFO Cd²⁺ is added. In equilibrium following speciation of the =FeOH surface sites is obtained:

Species	Concentration [μM]
=FeOH	152.0
=FeO ⁻	19.7
=FeOH ₂ ⁺	26.7
=FeOCd ⁺	4.8

The ionic strength of the suspension is 0.1 M, the pH is 7.5, and the concentration of the free Cd²⁺ ion is 3.2 μM . The specific surface area of HFO is 600 m²/g. (12 points)

a) Does Cd²⁺ form inner-sphere or out-sphere complexes with HFO? Justify your conclusion.

b) Calculate the **apparent** constant of following reaction
 $\equiv \text{FeOH} + \text{Cd}^{2+} \rightleftharpoons \equiv \text{FeOCd}^+ + \text{H}^+$

c) Calculate the surface charge density of the HFO.

d) Calculate the surface potential by using the diffuse double layer model.

e) Calculate the **intrinsic** constant of following reaction by using the diffuse double layer model.

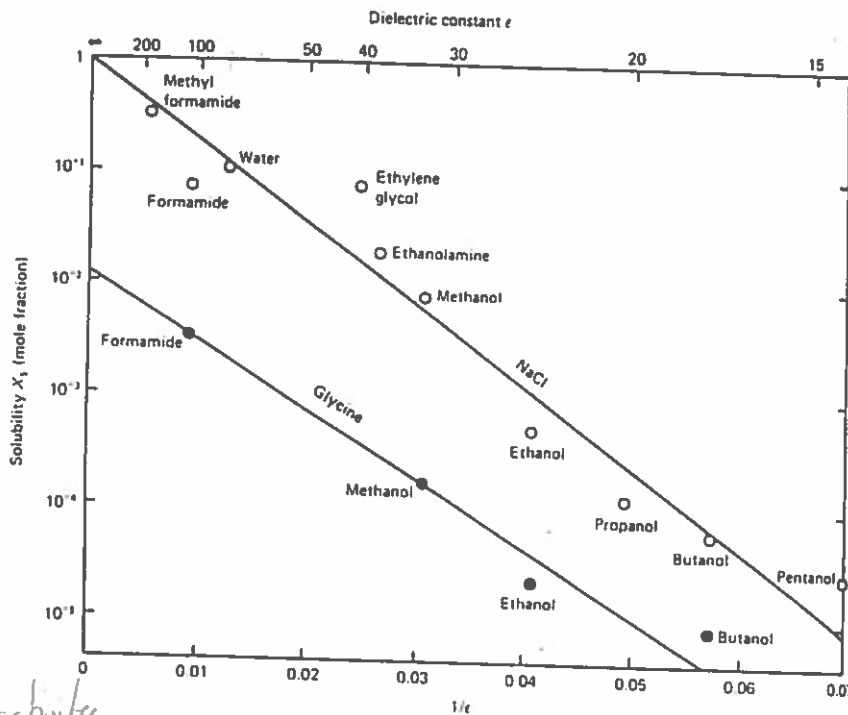


f) What would be the effect of decreasing the ionic strength on Cd²⁺ adsorption if the surface charge density would remain constant?

4) Comment on following statements I (16 points).

Statement	Correct Or wrong?	Explanation
Ar atoms in a gas phase do not interact because they are non-polar.	wrong	London (non polar - non polar)
The electronic polarizability of an atom or molecule increases with its size.	correct	when radius increases α_0 also increases.
The greater the electronic polarizability of two interacting molecules the greater their London-dispersive interaction.	correct	α_1, α_2 are on top of the equation
Dipole-dipole interactions contribute to the Van der Waals interactions	yes	its Keesom energy or Debye-Huckel Keesom
Van der Waals interactions are weak.	correct	because it is the sum of Keesom + London + Debye it is stronger than the other. But also largely distance dependent.
Whether a dipolar molecule will be orientated in a fixed position in the vicinity of an ion depends on the charge of the ion, its dipole moment, the distance between the ion and the molecule, and temperature.	Correct	rotating when $kT > \frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}$
It is impossible to calculate the self energy of an ion in water based on the pair potentials between the ion and surrounding water molecules	correct	$w(r)$ is not in the equation.
The lattice energy of NaCl is predominately controlled by coulombic interactions between the Na^+ and Cl^- ions.	Correct	$\frac{-Q_{\text{Na}} Q_{\text{Cl}}}{4\pi\epsilon_0 r^2} \rightarrow Q \rightarrow \text{coulomb.}$ $-\frac{nB}{r^{n+1}}$

5) Following graph shows the solubility of NaCl as a function of the dielectric constant of different solvents. (12 points)



- conc. / activity
 $\gamma = a$
 $a < m$
 $\gamma < 1$
- Give an explanation why the solubility of NaCl depends on the dielectric constant of the solvent? $= \frac{Q^2}{8\pi\epsilon_0\epsilon} \left(1 - \frac{1}{\epsilon}\right)$ low $\epsilon \rightarrow$ less soluble
 - The activity of dissolved ions in water is lower than their concentrations at moderate ionic strength. Is this effect stronger or weaker at the same ionic strength in ethanol? Explain why.
 - Does the solubility of N_2 in the different solvents also depend on the dielectric constant? Give arguments for your decision.

making the cavity uses pair potential, which has ϵ_0 in it.

ϵ gives whether you're a good soluble. this solubility depends on ϵ

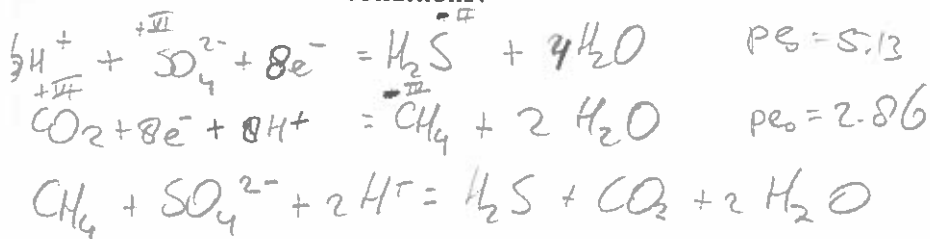
6) A Swedish lake has following pH and DIC / DOC contents. (12 points)

pH	DOC [mg/L]	DIC [μ M]
5.93	14.2	13.5

- a) Comment on the relative importance of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) for the acid neutralization capacity (ANC) of the lake water? *DOC and DIC are both important*
- b) How would you determine the ANC of this lake water? *charge balance \rightarrow excess - comes from DOC*
- c) Assume that the lake is supersaturated with respect to the CO_2 pressure of the atmosphere. What would be the effect of CO_2 evasion on the ANC and the pH of the lake water? *$\text{CO}_2 \rightarrow$ no ANC effect
pH effect*

3) Anaerobic oxidation of methane coupled to the reduction of sulfate is an important process for inhibiting the release of methane from sediments. In the pore water of a sediment in the vicinity of a so-called *cold seep* following partial pressures and concentrations are measured: $P(\text{CO}_2)=0.01$ atm, $P(\text{H}_2\text{S})=10^{-8}$ atm, $P(\text{CH}_4)=10^{-6}$ atm, $c(\text{SO}_4^{2-})=28.2$ mM, $\text{pH} = 8.2$ (12 points)

- a) Calculate the p_e value for the redox couple $\text{H}_2\text{S}(\text{g})/\text{SO}_4^{2-}$ ($p_e^0_{\text{SO}_4/\text{H}_2\text{S}(\text{g})} = 5.13$)
- b) Calculate the p_e value for the redox couple $\text{CH}_4(\text{g})/\text{CO}_2(\text{g})$ ($p_e^0_{\text{CO}_2(\text{g})/\text{CH}_4(\text{g})} = 2.86$)
- c) Is the oxidation of methane to carbon dioxide coupled to the reduction of sulfate to sulfide feasible in this sediment?
- d) What is the free energy of oxidizing one mole methane by sulfate under these conditions?



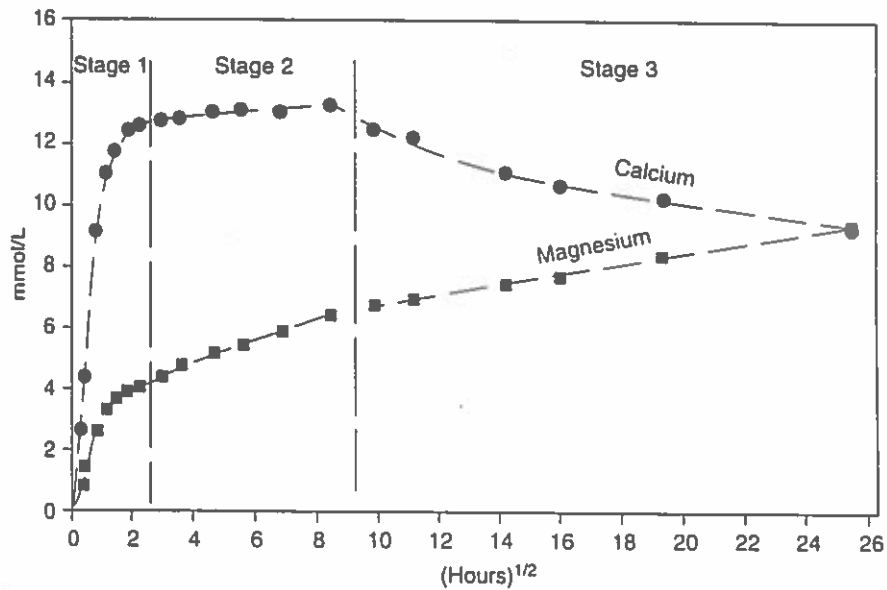
$$\begin{array}{r} p_e \\ p_e \rightarrow \\ \hline p_e \end{array}$$

calculate new K by p_{e0} and when K 's

7) Comment on following statements II. (12 points)

Statement	Correct Or wrong?	Explanation
Small mineral particles have a higher solubility than large mineral particles.	Correct	σ is below deviation line
A platinum redox electrode is suitable to measure the pe of a solution.	wrong	in natural solution, only account for one redox couple.
The transfer of CO ₂ between the atmosphere and the surface water in a lake is typically limited by the diffusion through the laminar film in the gas phase.	wrong	getting dissolved is more difficult.
The Boltzmann equation can be used to relate the potential of an electric field with the charge density		
		Poisson relation electric field - ions
The capacitance in the constant capacitance model depends on ionic strength and temperature.	correct	both in H
Enrichment of manganese in sediments indicates that the overlying water is anoxic.	wrong	Mn-oxides are precipitated, Mn ²⁺ is soluble
The pe value, at which ferric iron oxides are reductively dissolved to ferrous iron, depends on their solubility.		
Arsenate forms inner-sphere complexes at the surface of iron oxides.	correct	outer sphere complexes are impossible between two minus-species

8) The evolution of dissolved Ca^{2+} and Mg^{2+} concentrations over time due to the dissolution of a high Mg-calcite in distilled water is shown in the figure below. (12 points)



- Describe the change in Ca and Mg concentrations as a function of time in the stages 1-3?
- What happens in stage 3?
- Explain how this experiment is related to the hydrogeochemistry of Bermuda.
- What do the experimental results indicate with respect to the interchange energy of replacing Ca^{2+} by Mg^{2+} in calcite?