

Question 1 / Vraag 1

1.1. Calculate the activity of Ca^{2+} and SO_4^{2-} in a solution of 0.050 M $\text{Ca}(\text{NO}_3)_2$ and 0.010 M MgSO_4 . Use the Davies equation, assume $A = 0.5$. / Bereken die aktiwiteit van Ca^{2+} en SO_4^{2-} in 'n 0.050 M $\text{Ca}(\text{NO}_3)_2$ en 0.010 M MgSO_4 oplossing. Gebruik die Davies vergelyking, neem aan $A = 0.5$. (8)

1.2. Define chelation with reference to the specific ligands involved in the soil solution and discuss the influence it has on the plant availability of trace elements and also soil forming processes. / Definieer chelatie met verwysing na die spesifieke ligande betrokke in die grondoplossing en die invloed op die plantbeskikbaarheid van spoorelemente en ook grondformasie. (10)

1.1 $I = \frac{1}{2} \sum c_i z_i^2$ IF units were missing: -1 mark
 $= \frac{1}{2} (0,05 \text{ M} \cdot 2^2 + 0,1 \text{ M} \cdot 1^2 + 0,01 \text{ M} \cdot 2^2 + 0,01 \text{ M} \cdot 2^2)$
 $= 0,19 \text{ mol l}^{-1}$ (2 marks)

$\log f_i = -AZ_i^2 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0,3 I \right)$
 $= -0,5 \cdot 2^2 \left(\frac{0,19^{\frac{1}{2}}}{1 + 0,19^{\frac{1}{2}}} - 0,3 \cdot 0,19 \right)$
 $\log f_i = -0,49 \rightarrow f_{\text{Ca}^{2+}} = f_{\text{SO}_4^{2-}} = 0,32$ (2 marks)

$(\text{Ca}^{2+}) = f_{\text{Ca}^{2+}} [\text{Ca}^{2+}]$ (2 marks)
 $= 0,32 \text{ mol}^{-1} \cdot 0,05 \text{ mol l}^{-1}$
 $= 0,016$ dimensionless or mol mol⁻¹

$(\text{SO}_4^{2-}) = f_{\text{SO}_4^{2-}} [\text{SO}_4^{2-}]$
 $= 0,32 \text{ mol}^{-1} \cdot 0,01 \text{ mol l}^{-1}$
 $= 0,003$ (2 marks)

1.2. Chelation is the strong complexation (1 mark) of a cation, for example ferric iron (1 mark), in solution (1 mark) with a ligand (1 mark). The ligand forms multiple bonds / multidentate complex with the central cation (1 mark). Chelation is characterised by a large formation constants (K_f) (1 mark) of greater than 10. This indicates a very stable complex in solution (1 mark). The chelation of, for example, aqueous ferric iron increases the solubility of ferric (oxy) hydroxide minerals (1 mark), leading to an increase in the plant availability of iron (1 mark). In the soil, organic ligand (1 mark), for example, humates (1 mark) and fulvates (1 mark) are known natural chelates. Chelation by organic ligands (ligand promoted dissolution) (1 mark), along with redox and proton promoted dissolution, plays a role during weathering especially in environments with high organic material turnover (hot and wet climates) (1 mark). A specific soil forming process chelation is involved in is podzolisation (1 mark).

Question 2 / Vraag 2

The presence of arsenic in ^{the} soil environment is of great concern and enters the soil system through pesticide use. The toxicity of arsenic in the soil environment is dependent on its speciation. Arsenate (AsO_4^{3-}) is not as toxic as arsenite (AsO_3^{3-}) and also not as mobile in the soil environment. / Die teenwoordigheid van arseen in die grondomgewing is 'n groeiende kommer en beland in die sisteem deur die toediening van sekere gifstowwe wat

gebruik word. Die toksisiteit van arseen in die omgewing is 'n funksie van sy spesiëring. Arsenaat (AsO_4^{3-}) is nie so toksies soos arseniet (AsO_3^{3-}) nie en minder mobiel in die grondomgewing.

Answer the following questions with the information below: / Antwoord die volgende vrae met die informasie wat hieronder gegee is:

Fe(III) reduction



Goethite



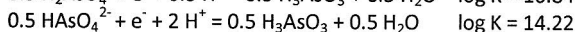
Arsenate speciation



Arsenite speciation



Arsenate reduction



Fe(III) hydrolysis species

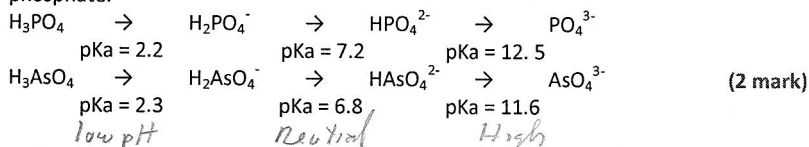


2.1. Which of these two As species chemistry is close to that of phosphate? Give sufficient proof. / Watter een van die As spesies se chemie is naby aan die van fosfaat? Gee genoegsame bewyse. (6)

2.2. Give the dominant arsenate and arsenite species at pH 7? / Gee die dominante arsenaat en arsenite spesies by pH = 7 (6)

2.3. Can goethite prevent the reduction of arsenate to arsenite in the soil at pH = 7? Use above information to derive the appropriate chemical equation. / Kan goethiet die reduksie van arsenaat verhoed by 'n pH = 7. Gebruik bogenoemde informasie om gepasde reaksie vergelyking uit te werk. (10)

2.1. Arsenate (1 mark). The speciation, as well as the pKa values for the various deprotonation, is similar to phosphate:

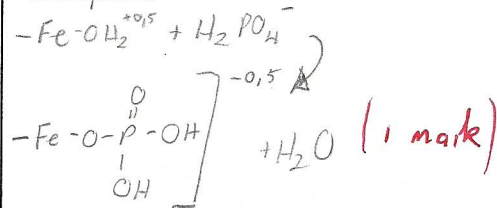


Both arsenate and phosphate are strongly sorbed by ferric (oxy) hydroxides forming inner-sphere complexes (1 mark).

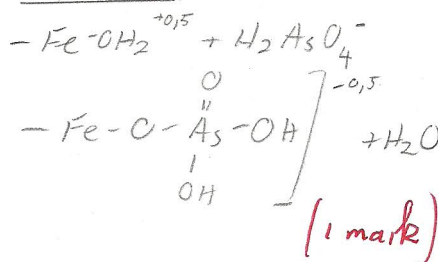
Two marks were also given for illustration of phosphate and arsenate sorption

with single coordinated - Fe₂(OH)₂^{+0.5} functional group

Phosphate



Arsenate



2.2. Arsenate: H_2AsO_4^- (1 mark) and $\text{HA}_2\text{O}_4^{2-}$ (1)
This is shown by the pKa of the second deprotonation of 6.8:

$$\frac{(\text{HA}_2\text{O}_4^{2-})(\text{H}^+)}{(\text{H}_2\text{AsO}_4^-)} = 10^{-6,8}$$

$$\frac{(\text{HA}_2\text{O}_4^{2-})}{(\text{H}_2\text{AsO}_4^-)} = 10^{-6,8} (10^{-7})^{-1}$$

$$= 10^{0,2} \text{ total (3)}$$

Arsenite: H_3AsO_3 (1 mark).
The pKa for the first deprotonation is 9.2:

$$\frac{(\text{H}_2\text{AsO}_3^-)(\text{H}^+)}{(\text{H}_3\text{AsO}_3)} = 10^{-9,2}$$

$$\frac{(\text{H}_2\text{AsO}_3^-)}{(\text{H}_3\text{AsO}_3)} = 10^{-9,2} (10^{-7})^{-1}$$

$$= 10^{-1,8} \text{ total (3)}$$

also same method:

$$\frac{[\text{H}_2\text{AsO}_4^-][\text{H}^+]}{[\text{H}_3\text{AsO}_4^-]} = 10^{-6,8}$$

$$\frac{[\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_4^-]} = 10^{-6,8} [10^{-7}]^{-1}$$

$$= 10^{0,2}$$

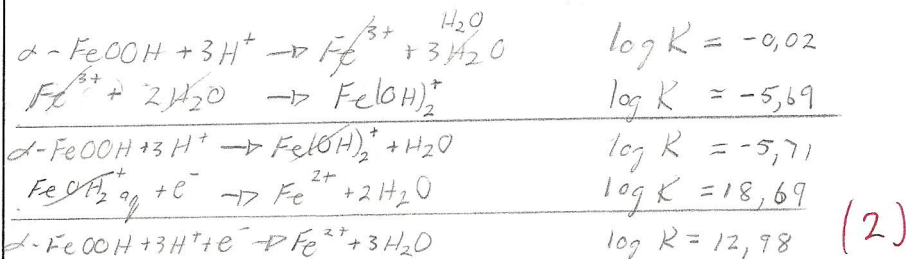
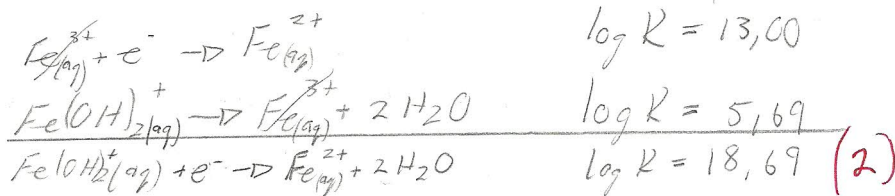
Exact multiplication at pH=7

$$\Delta \text{H}_2\text{AsO}_4^- = 0,61$$

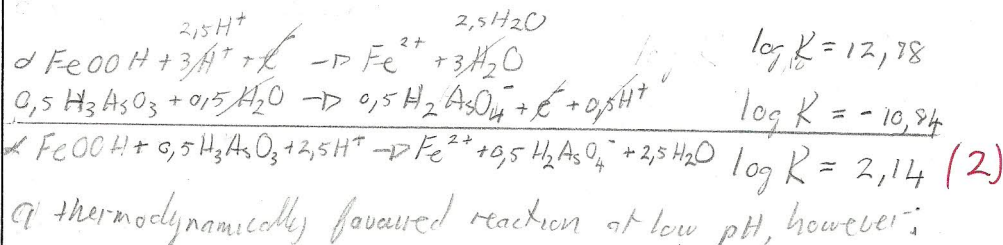
$$\Delta \text{H}_2\text{AsO}_3^- = 0,39$$

Just for marking not asked,

2.3. Assumptions: Activity of water and solid phases taken as unity (1 mark).
Dominant aqueous Fe(III) species: $\text{Fe}(\text{OH})_2^+$ (1 mark).



Or in other words can $\alpha\text{-FeOOH}$ oxidise Arsenite



$$\frac{(Fe^{2+})(H_2AsO_4^-)^{0.5}}{(H^+)^{2.5}(H_3AsO_3^0)} = 10^{2.14}$$

$$\frac{(H_2AsO_4^-)}{(H_3AsO_3^0)} = \left(10^{2.14} (H^+)^{2.5} (Fe^{2+})^{-1} \right)^2$$

$$\text{at } pH=7 =$$

$$\frac{(H_2AsO_4^-)}{(H_3AsO_3^0)} = 10^{4.28} (H^+)^5 (Fe^{2+})^{-2}$$

$$= 10^{4.28} (10^{-7})^5 (Fe^{2+})^{-2} \quad (2)$$

$$= 10^{-30.72} (Fe^{2+})^{-2} \quad \Rightarrow$$

For the less toxic $H_2AsO_4^-$ to be dominant in solution at pH 7: (2)

$$\frac{(H_2AsO_4^-)}{(H_3AsO_3^0)} > 1, Fe^{2+} \text{ activity must be } < 10^{-15.36} \text{ (very low)}$$

Question 3 / Vraag 3

3.1. Compare inner sphere complexation and outer sphere complexation on mineral surface on hand of appropriate illustration as well as the environmental relevance thereof. / Vergelyk binnesfeer en buitsfeer kompleksering op mineraaloppervlaktes aan hand van gepaste illustrations en ook die omgewings relevansie daarvan. (10)

3.2. Discuss the basic characteristics associated with cation exchange reactions. / Bespreek die basiese eienskappe wat ge-assosieer word met katioonuitruilingsreaksies. (5)

3.3. Humus has a myriad of functional groups including carboxylic (-COOH , $\text{pK}_a = 5$) and alcoholic functional groups (R-OH , $\text{pK}_a = 12$). What will be the net charge of organic material at a pH of 6? Substantiate your answer with appropriate reaction mechanism and calculations. / Humus het verskeie funksionele groepe insluitende carboksiel (-COOH , $\text{pK}_a = 5$) en alkohol (R-OH , $\text{pK}_a = 12$) groepe. Wat sal die net oppervlaklading wees van organiese materiaal by 'n pH (5)

3.1. Outer sphere complexation (max 4 marks)

- A water molecule is present between ion and the surface;
- Type of interaction: electrostatic / coulombic;
- Ions are weakly held and exchangeable;
- Anions: Outersphere complexes are usually formed by conjugated bases of strong monoprotic acid forms: NO_3^- , Cl^- , ClO_4^- , I^- , F^- etc.
- Hydrated cations usually form outersphere complexes, hence the name exchangeable cations.

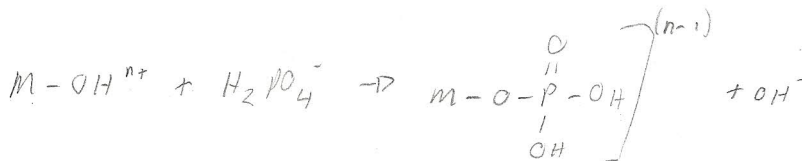
Illustration (1 marks)



Inner sphere complexation (max 4 marks)

- Direct bonding between metal cation and surface;
- Type of interaction: chemical bonding;
- Ions are strongly held and sorption reaction often not reversible;
- Innersphere complexation is less affected by pH, ionic strength and solution composition;
- Surface has a specific affinity for the ion – hence the term specific adsorption
- Anions: PO_4^{3-} , CO_3^{2-} , Si(OH)_4

Illustration (1 marks)



Innersphere complexed ions are strongly attenuated in the soil and therefore less mobile and plant available (2 marks)

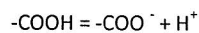
3.2. General characteristics of cation exchange (5 marks)

- Exchangeable cations are outersphere complexed;
- Reactions are completely reversible;
- Exchange reactions are rapid literary occurring in milli- and micro seconds;
- Diffusion controlled: The rate limiting step of exchange reaction is diffusion from and to the surface;
- Reactions are stoichiometric – cation exchanged is replaced by another of equal charge;

Outersphere complex ions more plant available. Pollutants
That are outersphere complexed pose a greater environmental danger. (1 mark)

3.3. The pKa is the deprotonation constant and it also shows the pH at which equal amount of acid and conjugated base is present. Therefore:

Carboxylic groups



$$\text{pKa} = 5$$

At pH = 6 (2 marks)

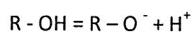
$$\frac{(\text{H}^+)(-\text{COO}^-)}{(-\text{COOH}^0)} = 10^{-5}$$

$$\frac{(-\text{COO}^-)}{(-\text{COOH}^0)} = 10^{-5} (10^{-6})^{-1}$$

$$\frac{(-\text{COO}^-)}{(-\text{COOH}^0)} = 10^1$$

Therefore more deprotonated $-\text{COO}^-$ than $-\text{COOH}^0$

Alcoholic groups



$$\text{pKa} = 12$$

At pH = 6 (2 marks)

$$\frac{(\text{H}^+)(\text{R}-\text{O}^-)}{(\text{R}-\text{OH}^0)} = 10^{-12}$$

$$\frac{(\text{R}-\text{O}^-)}{(\text{R}-\text{OH}^0)} = 10^{-12} (10^{-6})^{-1}$$

$$\frac{(\text{R}-\text{O}^-)}{(\text{R}-\text{OH}^0)} = 10^{-6} - \text{R}-\text{OH}^0 \text{ dominates}$$

Net charge is negative because $\text{R}-\text{OH}^0$ and $-\text{COOH}^0$ do not contribute to surface charge. The only ionised functional groups at this pH are: $-\text{COO}^-$. The amount of $\text{R}-\text{O}^-$ is negligible (1 mark).