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UNIVERSITY OF PRETORIA / UNIVERSITEIT VAN PRETORIA  
DEPARTMENT OF PLANT PRODUCTION AND SOIL SCIENCE /  
DEPARTEMENT PLANTPRODUKSIE EN GRONDKUNDE

GKD 320  
SOIL CHEMISTRY / GRONDCHEMIE

Internal examiner / Interne eksaminator: Mr P.C. de Jager  
External examiner / Eksterne eksaminator: Mr Teunis Vahrmeijer

Semester test / *Semestertoets*  
August / Augustus 2011  
Time / *Tyd*: 90 min  
Marks / *Punte* : 45

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**Question 1 / Vraag 1**

Define the activity of the following with reference to their appropriate standard states: / *Definieer die aktiwiteit van die volgende met verwysing die gepaste standaard toestande:*

- a) Solvent / *Oplosmiddel*; (3)
  - b) Solid / *Vastestof*; (3)
  - c) Solute / *Opgeloste stof*. (3)
- (9)**

a) Activity is expressed as molar fractions. (1 mark). The standard state is a pure solvent (1 mark) where the mole fraction of water is unit (1).  $(H_2O) = n_{(water)} / \sum n_{(water)} + n_{(solutes)}$  (1 mark)

b) a) Activity is expressed as molar fractions. (1 mark). The standard state is a pure solid phase (1 mark) where the mole fraction of water is unit (1 mark).  $(Solid) = n_{(solid)} / \sum n_{(solid)} + n_{(impurities)}$  (1 mark)

c) Infinite dilution reference state. (1 mark) At standard state if there is so few other solutes in solution that it's translational freedom is unaffected – behaving ideally (1 mark).  $(Solute) = \text{activity coefficient} \times \text{molar concentration}$  (1 mark).

**Question 2 / Vraag 2**

2.1) Do you expect gypsum ( $CaSO_4 \cdot 2H_2O$ ) to be more or less soluble in deionised water compared to a 10 mM NaCl solution? Elaborate on your answer. *Verwag jy dat gips ( $CaSO_4 \cdot 2H_2O$ ) minder of meer oplosbaar is in gede-ioniseerde water of in 'n 10 mM NaCl oplossing? Verduidelik jou antwoord.* (5)

2.2) Will the additions of an organic ligand that strongly complex with Ca in solution (for example,  $EDTA^{4-}$ ) increase or decrease gypsum solubility compared to deionised water? Elaborate on your answer. *Sal die toevoeging van 'n organiese ligand wat sterk komplekseer met Ca in oplossing (byvoorbeeld  $EDTA^{4-}$ ), gips se oplosbaarheid verhoog of verlaag in vergelyking met gede-ioniseerde water. Verduidelik jou antwoord.* (4)

2.3) Will the additions of an organic ligand that strongly complex with Ca in solution (for example,  $EDTA^{4-}$ ) increase or decrease gypsum solubility compared to a 10 mM NaCl solution? Elaborate on your answer. *Sal die toevoeging van 'n organiese ligand wat sterk komplekseer met Ca in oplossing (byvoorbeeld  $EDTA^{4-}$ ) gips se oplosbaarheid verhoog of verlaag in vergelyking met 10 mM NaCl oplossing. Verduidelik jou antwoord.* (4)

2.1) It will be higher in the 10 mM NaCl solution. (2 mark) The higher salinity / ionic strength of the solution will lower the activity of both  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (1 mark). Chemical equilibrium is driven by activity and not concentration (1 mark). This lowering in activity will result in the dissolution of more gypsum in an attempt to reach equilibrium again (1 mark).

2.2) The addition of the organic ligand will increase the solubility relative to water (2 mark). Strong complexation will further decrease concentration and therefore the activity of free  $\text{Ca}^{2+}$  (1 mark). As a result of the Le Chatelier effect gypsum will again dissolve to reach an equilibrium again (1 mark)

2.3) It is expected that gypsum solubility would be the greatest in the EDTA solution (2 mark) The specific interaction as a result of complexation will decrease  $\text{Ca}^{2+}$  activity more than the nonspecific interaction of the saline solution. (1 mark). As a result of the Le Chatelier effect gypsum will again dissolve to reach equilibrium again (1 mark).

### Question 3 / Vraag 3

Define the following (with appropriate illustration and / or examples if needed) / *Definieer die volgende (met gepaste illustrasies en / of voorbeelde waar nodig):*

- a) Solution complex / *Oplossingskompleks*; (3)
  - b) Ion pair / *loonpaar*; (3)
  - c) Hydroxo-cation / *Hidroksi-katioon*; (3)
- (9)**

- a) Complexes – Stronger / more stable association between anions and cations (1 mark)
  - Innersphere complexation – direct bonding between anion and cations (1mark)
  - Example:  $\text{CuSO}_4^0$  (aq) (1 mark)
- b) Ion pairs - Weakly association between a cation and ligand (anion) (1 mark)
  - Outersphere complexation water molecule is present between cation and ligand (1 mark)
  - Example:  $\text{CaSO}_4^0$  (1 mark)
- c) Hydroxocation - ( $3 < \text{Charge density} < 8.5$ ) (1 mark). Examples  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  (1 mark).  
Coordinated to at least one hydroxyl  $\text{Fe}(\text{H}_2\text{O})\text{OH}^{+2}$  (1mark)

#### Question 4 / Vraag 4

Differentiate between an A type and a B type cation and give two examples of each. / Onderskei tussen A en B tipe katione en gee twee voorbeelde van elk. (8)

##### B type or "soft cation"

- Has 10 - 12 outer shell electron
- Electron sheaths easily deformed by electronic field ("soft sphere")
- More easily polarisable
- Complexes with "soft bases", for example, ligands with S and N are donor atoms
- With respect to halogens it prefers to form chloro and iodo complexes in solution rather than fluoro
- Readily complexes with  $S^{2-}$ ,  $HS^-$  in solution
- Forms sparingly soluble precipitates with sulphites
- Complexes readily with organic material and generally more environmentally toxic.
- Anthropogenic activities are increasingly enriching the environment with B type metals:
- Examples :  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$ ,  $Cu^{2+}$

##### A type or "hard cation"

- Has the inert gas type electron configuration ( $d^0$ )
- Electron sheaths not easily deformed by electronic field ("hard sphere")
- Not easily polarisable
- Complexes with "hard bases" for, example, F and ligands with oxygen as donor atom
- With respect to halogens it prefers to form fluoro rather than chloro and iodo complexes in solution
- Does not readily associate (complex and precipitate) with sulphites
- Multi - and polyvalent cations (except  $Mg^{2+}$ ) tend to form sparingly soluble precipitates with  $CO_3^{2-}$ ,  $PO_4^{3-}$  and  $OH^-$
- Examples:  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Al^{3+}$

### Question 5 / Vraag 5

You received the following analysis of the soil solution: / oplossing. Ignore solution complexation and calculate the activity of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  in this solution. Jy het die volgende analises ontvang van 'n grond. Ignoreer oplossingskompleksering en bereken die aktiwiteit van  $\text{Na}^+$  en  $\text{SO}_4^{2-}$  in hierdie oplossing. (6)

Mark allocation: Conversion from mg to mol (1 mark)  
Ionic strength calculation (1mark)  
Correct activity coefficient calculations for Na and  $\text{SO}_4$  (2 marks)  
Correct activity calculations for Na and  $\text{SO}_4$  (2 marks)

As discussed in class for ionic strength calculations you have to sum ( $z^2 \times \text{concentration}$ ) for all the ions to obtain the ionic strength.

Ion / ioon	Concentration / Konsentrasie mg / l
$\text{Ca}^{2+}$	80
$\text{Mg}^{2+}$	25
$\text{Na}^+$	10
$\text{K}^+$	12
$\text{SO}_4^{2-}$	169
$\text{HCO}_3^-$	200

### Information sheet / Informasieblad

$I = \frac{1}{2} \sum z_i^2 C_i$ <p> <math>I</math> = ionic strength  <math>z_i</math> = charge of ion <math>i</math>  <math>C_i</math> = concentration of ion <math>i</math> </p>	$\log \gamma_i = -Az_i^2 \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right]$ <p> <math>\gamma_i</math> = activity coefficient of ion <math>i</math>  <math>A</math> = constant related to dielectrical constant of water  <math>= 0.5</math> at 298 K         </p>
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### Molar mass of the various

Ion / ioon	Molar mass ( $\text{g mol}^{-1}$ )
$\text{Ca}^{2+}$	40.08
$\text{Mg}^{2+}$	24.3
$\text{Na}^+$	22.99
$\text{K}^+$	39.1
$\text{SO}_4^{2-}$	96.056
$\text{HCO}_3^-$	61