

ESS 312 Geochemistry – sample final exam

This is an open book / open notes exam.

Time allowed: 2 hours.

Attempt as many questions as you can in the time allowed.

Look over the test before you begin working. Decide which questions you can answer easily and do them first.

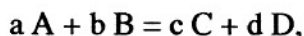
Think through each question and write a general answer before reaching for your calculator.

Show your working. We will give partial credit for partially correct answers, as long as we can follow your reasoning. Wherever possible, show us that you understand the concept behind the question.

Total points:

Equations and other material you may need:

- The dissociation constant of water at 25°C: $K_w = 1.00 \times 10^{-14}$
- For the reaction:



the Gibbs Free Energy change: $\Delta G = \Delta G^0 + RT \ln(a_C^c \cdot a_D^d / a_A^a \cdot a_B^b)$

- Temperature in degrees K = degrees C + 273.15
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Section (1)

10 short answer questions (typically these would be 5 points each, as indicated)

Provide short answers, definitions or explanations (using words or formulas as required):

- (a) List the four most abundant elements in: (i) the continental crust (2 pts) (ii) the mantle (2 pts).

(1) CRUST: O, Si, Al, (Fe, Mg, Ca)

(2) MANTLE: O, Si, Mg, (Fe, Al)

- (iii) List the two most abundant elements in the core (1 pt).

Fe, Ni

(iv) **Trick question (2 bonus pts):** List the third most abundant element in the core.

= ACTUALLY, WE DON'T KNOW ...

PROBABLY H, POSSIBLY O OR S

(b) Why is the ionization potential of Group I elements (the alkalis) much lower than group VII elements (the halogens)?

LOSS OF 1 OUTER SHELL ELECTRON FROM ALKALIS GIVES NOBLE GAS CONFIGURATION, HENCE ENERGETICALLY FAVORABLE.

(c) Which has a higher ionic strength - a 1 molal solution of RbCl or a 1 molal solution of BeSO₄? (2 pts) Explain why. (3 pts)

$$I = \frac{1}{2} \sum_i m_i z_i^2 = 1 \text{ FOR } 1 \text{ M RbCl}^+ \\ = 4 \text{ FOR } 1 \text{ M Be}^{2+} \text{SO}_4^{2-}$$

DOUBLY-CHARGED IONS WILL FORM COMPLEXES MORE READILY WITH H₂O AND EACH OTHER.

(d) Many elements have several stable (non-radioactive) isotopes - variants of their basic atomic structure in which the nucleus contains different numbers of neutrons. For example, oxygen has 3 stable isotopic forms, ¹⁶O₈, ¹⁷O₈ and ¹⁸O₈, each of which has 8 protons in the nucleus, but which have 8, 9 and 10 neutrons in the nucleus, respectively. Would you expect the different stable isotopes of O to have very similar, or very different ionic radii? Explain why (2 pts).

NUCLEUS ~ 1/1000 DIAMETER OF THE ATOM

ADDING UNCHARGED NEUTRONS TO THE

NUCLEUS WILL NOT CHANGE THE ATOMIC RADIUS

Explain whether you would expect stable isotope abundances to vary with pressure? (3 pts)

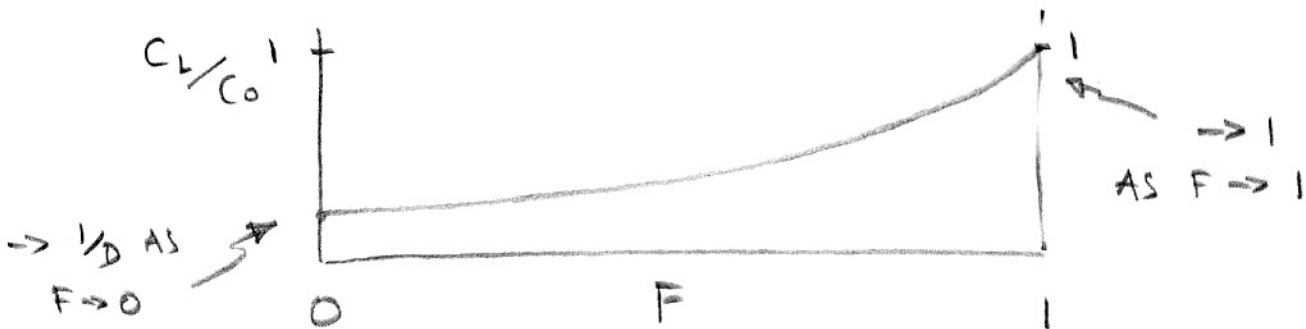
MOLAR VOLUMES OF 'ISOTOPICALLY-SUBSTITUTED' COMPOUNDS ARE SAME AS ISOTOPICALLY NORMAL COMPOUNDS, SO PRESSURE SHOULD NOT AFFECT STABLE ISOTOPE PARTITIONING

(e) The equation for the change in concentration of a trace element in the melt ($C_{i,L}$) during batch equilibrium partial melting is:

$$(C_{i,L}/C_{i,D}) = 1 / (F + D - FD)$$

In this equation, how does F change during partial melting? (2 pts) Explain qualitatively how the concentration of a compatible element in the melt changes as partial melting progresses? (3 pts)

F IS THE MELT FRACTION. IT INCREASES AS PARTIAL MELTING PROGRESSES.



(f) Suppose rainwater collected in Seattle has a pH of 6.2. What is the concentration of hydroxide ion (OH^-) in this water. Give units for your answer. Assume the water is at 25°C. (2 pts) From the pH alone, how do you know there must be other dissolved ions present in the rainwater? (3 pts)

$\text{pH} = -\log a_{\text{H}^+}$
 $\Rightarrow a_{\text{H}^+} = 10^{-6.2}$ FOR THIS RAINWATER
 $\Rightarrow a_{\text{OH}^-} = 10^{-7.8}$. IONIC STRENGTH IS LIKELY TO BE $< 10^{-3}$ SO $a_i \approx m_i$, HENCE
 $m_{\text{OH}^-} \approx 10^{-7.8}$ mol/kg . PURE WATER WOULD HAVE pH 7, THIS WATER LIKELY CONTAINS HCO_3^- , CO_3^{2-} AND OTHER IONS.

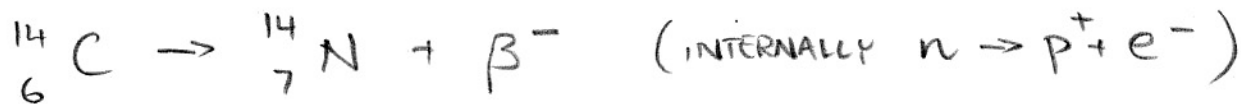
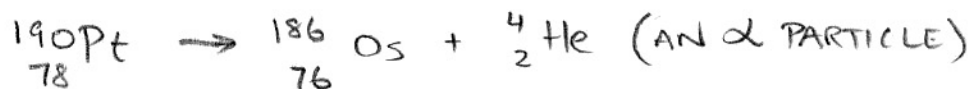
- (g) Why do gases generally have higher molar heat capacity than solids? (5 pts) **Bonus question (and hint):** Why do diatomic gases such as N_2 and CO have higher heat capacities than monatomic gases like Ar ? (2 bonus pts)

GASES HAVE TRANSLATIONAL DEGREES OF FREEDOM, \pm ROTATIONAL AND VIBRATIONAL DEGREES OF FREEDOM IF DIATOMIC OR POLYATOMIC. SOLIDS HAVE ONLY VIBRATIONAL DEGREES OF FREEDOM IN WHICH TO 'STORE' ENERGY.

- (h) Two saturated solutions of barite ($BaSO_4$) are prepared in separate beakers, by mixing an excess of the solid with distilled water, and with a strong $NaCl$ brine solution, respectively. Once equilibrium is reached, which beaker contains the higher concentration of Ba ? (2 pts) Explain your reasoning (3 pts) (Assume pH is the same in both solutions).

$[Ba^{2+}]$ IN THE BRINE BEAKER. HIGHER IONIC STRENGTH OF BRINE \Rightarrow GREATER COMPLEX FORMATION \Rightarrow LOWER $a_{Ba^{2+}}$ COMPARED TO $M_{Ba^{2+}}$ (ie $\gamma_{Ba^{2+}}$ IS LOWER IN THE BRINE SOLUTION).

- (i) Write expressions for the α decay of ${}^{190}_{78}Pt$ and the β^- decay of ${}^{14}_6C$, showing the element symbol, atomic weight (A) and atomic number (Z) of the product. (2 1/2 pts each)



- (j) The volume of the oceans is 1.37×10^{21} liters. The annual flow of rivers, glacier ice and groundwater into the oceans is 3.6×10^{16} liters/yr. Assuming the volume of the oceans is not changing, what is the residence time of water in the oceans? (5 pts)

$$\tau = \frac{A}{\frac{dA}{dt}} = \frac{1.37 \times 10^{21} \text{ l}}{3.6 \times 10^{16} \text{ l/yr}} = 3.8 \times 10^4 \text{ yr}$$

Section 2: Longer Questions (these would be worth 25 – 40 points each)

Stable Isotopes ASSUME $\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{SMOW}} = 0.0020052$

The equilibrium constant for the exchange of ^{18}O between calcite and liquid water, $\alpha_{\text{calcite-H}_2\text{O}}$, is given below for various temperatures between 0°C and 10°C :

T ($^\circ\text{C}$)	0	2	4	6	8	10
$\alpha_{\text{calcite-H}_2\text{O}}$	1.0345	1.0339	1.0333	1.0328	1.0323	1.0318

(i) What $\delta^{18}\text{O}_{\text{SMOW}}$ value do you expect for the calcite shells of ostracods living at 10°C in lake water with a $\delta^{18}\text{O}_{\text{SMOW}}$ value of -10‰ ? (Ostracods are small calcareous invertebrates, common in lakes).

$$\alpha = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{CALCITE}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{WATER}}} \quad \textcircled{1} \quad \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{LAKE WATER}} = \left(1 + \frac{\delta_{\text{LAKE}}}{1000}\right) \cdot \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{SMOW}}$$

$$\textcircled{2} \quad \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{CALCITE}} = 1.0318 \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{WATER}} = 0.99 \times 0.0020052 = 0.0019851$$

$$\textcircled{3} \quad \delta^{18}\text{O}_{\text{CALCITE-SMOW}} = 1000 \times \left(\frac{0.0019851}{0.0020052} - 1\right) = +21.5\text{‰}$$

(ii) What $\delta^{18}\text{O}_{\text{SMOW}}$ value do you expect for the calcite shells of foraminifera living in the ocean at 10°C ? Assume the α values given above apply equally to fresh water and seawater. (Foraminifera are calcite-shelled plankton that live at various depths in the oceanic water column).

$$1000 \ln \alpha_{\text{CALCITE-WATER}} \approx \delta_{\text{CALCITE-SMOW}} - \delta_{\text{WATER SMOW}}$$

$$1000 \ln (1.0318) = 31.3 = \delta_{\text{CALCITE-SMOW}} - 0\text{‰} \quad \text{OCEAN WATER}$$

CALCITE SHELLS SHOULD HAVE $\delta^{18}\text{O}_{\text{CALCITE-SMOW}} \approx +31.3\text{‰}$

(iii) What would be the $\delta^{18}\text{O}_{\text{SMOW}}$ value of the calcite shells of foraminifera living in a colder region of the ocean, where the water temperature is 2°C ?

SAME REASONING AS FOR (ii) ...

$$1000 \ln (1.0339) = 33.3 = \delta_{\text{CALCITE-SMOW}} - 0\text{‰}$$

FORAMINIFERA CALCITE SHELLS SHOULD HAVE $\delta^{18}\text{O}_{\text{CALCITE-SMOW}} \approx 33.3\text{‰}$

(iv) During ice ages, the build-up of large ice sheets lowers sea level by 120 meters worldwide. If the ice stored in the ice sheets has an average oxygen isotope value $\delta^{18O}_{ice-SMOW} = -33\text{‰}$, what would the $\delta^{18O}_{seawater-SMOW}$ value be in the ice-age oceans? Assume that the average depth of the oceans is 4000 m.

BY MASS BALANCE ...

$$\delta_{MODERN OCEANS} = f_{ICE} \delta_{ICE} + f_{ICE AGE SEAWATER} \delta_{ICE AGE SEAWATER}$$

$$0\text{‰} = \frac{120}{4000} \times -33\text{‰} + \frac{3880}{4000} \delta_{IA SW} \Rightarrow \delta_{ICE AGE SEAWATER} \approx +1\text{‰}$$

(v) Calculate the δ^{18O}_{SMOW} value of calcite shells of foraminifera living at a temperature of 2° C in the ice-age oceans.

$$1000 \ln(1.0339) = 33.3 = \delta_{CALCITE} - \delta_{ICE AGE OCEAN}$$

$$\Rightarrow \delta_{CALCITE-SMOW (ICE-AGE FORAMINIFERA)} \approx 33.3 + 1 = 34.3\text{‰}$$

Aqueous Geochemistry — solubility

6 a) Would you expect calcite to be more soluble in rainwater (ionic strength $\sim 10^{-4}$ mol/kg) or seawater (ionic strength 0.7 mol/kg)? Assume both solutions are at equilibrium with the same partial pressure of CO_2 .

MORE SOLUBLE IN SEAWATER. HIGH IONIC STRENGTH \Rightarrow MORE COMPLEXES
SEE PART 1 Q (h)

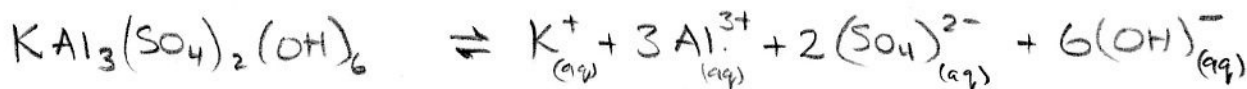
b) Define ionic strength. What is the ionic strength of a 1 molal solution of NaCl?
Of a 1 molal solution of $MgSO_4$?

$$I = \frac{1}{2} \sum_i m_i z_i^2 = 1 \text{ for } Na^+ Cl^-$$

$$= 4 \text{ for } Mg^{2+} SO_4^{2-}$$

SEE PART 1 Q (c).

c) Write an equation describing the dissolution of alunite $KAl_3(SO_4)_2(OH)_6$ in water.



d) Write the expression for the solubility product of alunite.

$$K_{sp} = a_{K^+} \cdot a_{Al^{3+}}^3 \cdot a_{SO_4^{2-}}^2 \cdot a_{OH^-}^6$$

e) How does formation of the relatively stable Al hydroxide complexes Al(OH)^{2+} , Al(OH)_2^+ and Al(OH)_3^0 in solution affect the solubility of alunite?

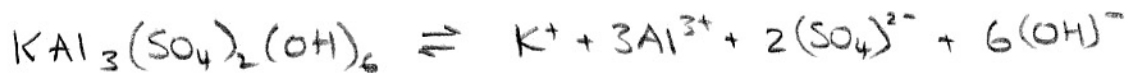
FORMATION OF THESE COMPLEXES REDUCES $a_{\text{Al}^{3+}}$, CAUSING MORE ALUNITE TO DISSOLVE

f) Given the following data:

Species	G_f° (298 K, 1 bar)	
K^+	-16.18	kJ / mol
Al^{3+}	-28.04	kJ / mol
OH^-	-8.99	kJ / mol
SO_4^{2-}	-42.48	kJ / mol
$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	-265.63	kJ / mol
	$R = 0.008314$	kJ / mol K

Calculate the solubility product (K_{sp}) of alunite. at 25°C.

FOR THE DISSOLUTION REACTION



$\Delta G = \Delta G^\circ + RT \ln(\text{IAP})$, BUT AT SATURATION ...

$$0 = \Delta G^\circ + RT \ln(K_{sp}) \quad G_{\text{PRODUCTS}} - G_{\text{REACTANTS}}$$

$$\Rightarrow K_{sp} = e^{-\Delta G^\circ / RT} \quad \Delta G^\circ = \begin{array}{l} -16.18 \\ +3(-28.04) \\ +2(-42.48) \\ +6(-8.99) \\ \hline -239.20 \end{array} - (-265.63) = +26.43 \text{ kJ/mol}$$

$$\begin{aligned} \Rightarrow K_{sp} &= e^{\frac{-26.43}{298 \times 0.008314}} \\ &= e^{-10.66} \\ &= 2.34 \times 10^{-5} \\ &(\approx 10^{-4.63}) \end{aligned}$$

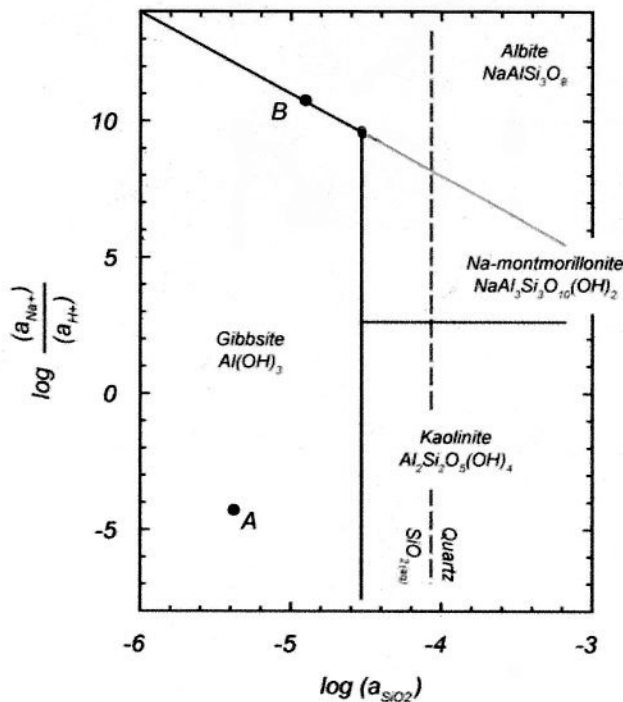
Aqueous Geochemistry — weathering

Q.2 Solubility and aqueous geochemistry (4 points)

a) (3 points) Define ionic strength. What is the ionic strength of a 1 molal solution of NaCl ?
Of a 1 molal solution of MgSO₄?

SEE PART 1 Q (h)
PART 2 Q (2b) ENOUGH ALREADY ...

The $\log_{10}(a_{\text{Na}^+}/a_{\text{H}^+})$ vs $\log_{10}(a_{\text{SiO}_2(\text{aq})})$ diagram is helpful for analyzing reactions involved in the weathering of plagioclase feldspars such as albite ($\text{NaAlSi}_3\text{O}_8$). A small incomplete portion of the diagram is shown below.



b) Briefly explain why we choose Na⁺, H⁺ and SiO₂ activities for plotting a phase diagram for albite. (4 pts)

FELDSPAR DISSOLUTION REACTIONS CONSUME H⁺,
AND PRODUCE Na⁺, AND PRODUCE SiO₂(aq). INCREASING
OR DECREASING ACTIVITIES OF THESE COMPONENTS WILL DECREASE
OR INCREASE FELDSPAR DISSOLUTION RATES.

c) Write a balanced reaction for the equilibrium between albite ($\text{NaAlSi}_3\text{O}_8$) and components in solution to produce Na-montmorillonite ($\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$), conserving Al in the solid phases. (4 pts)



The equilibrium constant for this reaction, $K_{\text{eq}} = 10^{-8}$. Using the equation you wrote above, calculate the slope of the boundary between the albite and Na-montmorillonite stability fields, and sketch it on the diagram (above). (4 pts)

$$K = \frac{a_{\text{Na}^+}^2 \cdot a_{\text{SiO}_2}^6}{a_{\text{H}^+}^2} \Rightarrow \log K = -8 = 2 \log\left(\frac{a_{\text{Na}^+}}{a_{\text{H}^+}}\right) + 6 \log a_{\text{SiO}_2(\text{aq})}$$

$$\Rightarrow \log\left(\frac{a_{\text{Na}^+}}{a_{\text{H}^+}}\right) = -3 \log a_{\text{SiO}_2(\text{aq})} - 4$$

$$Y = M X + B$$

STRAIGHT LINE, SLOPE -3
ON THE DIAGRAM.

Describe (without attempting to balance equations) what mineral reactions occur when a crystal of albite ($\text{NaAlSi}_3\text{O}_8$) is put into contact with the different solutions whose activities plot at points A and B on the diagram. (4 pts)

AT A ; FELDSPAR DISSOLVES TO PRODUCE GIBBSITE + Na^+ + DISSOLVED SILICA

AT B ; FELDSPAR IS IN EQUILIBRIUM WITH THIS SOLUTION. NO DISSOLUTION.

What happens when a crystal of quartz is brought into contact with solution A?

QUARTZ DISSOLVES.