Tentamen: GEO3-1304, Structure and Properties of Earth Materials

Docenten: dr. H.E. King & dr. C.J. Peach (coordinator)
Datum: 11-11-2016, 09:00-11:30, KBG-Cosmos

Instructions:

- Read all questions through, thoroughly, before answering.
- Answer any **6** from the **8** questions and clearly label your answers with the question number.
- Use S.I. units, unless stated otherwise.
- Show any calculation steps clearly and use annotated diagrams where appropriate.
- Write your name clearly on each separate answer sheet.
- Duration of examination: **2.5 hours**

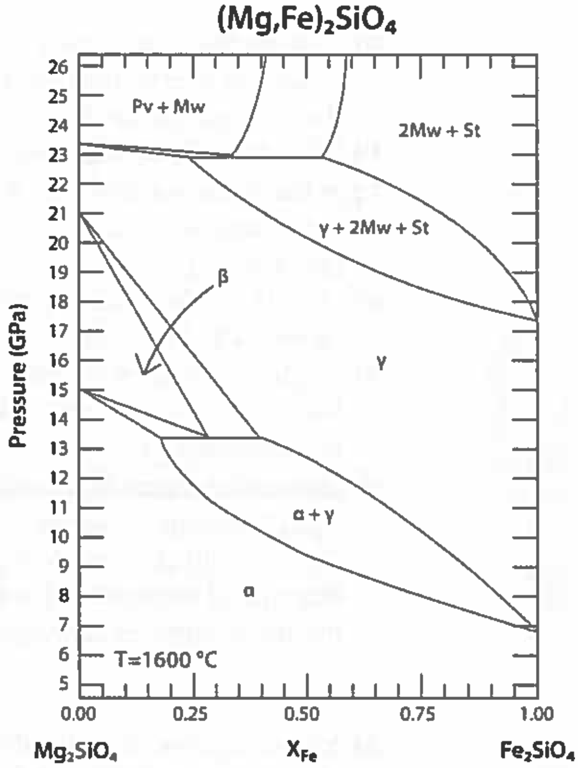
> ***Reminder:***
> Do not use reference books, notes and information sources other than what is given on this paper!
>
> Turn off all communications devices.
>
> You may use a standard scientific calculator.

Use the following where needed:

Avogadro's Constant, $N_A = 6.022 \times 10^{23}$ mol $^{-1}$;
Planck's constant, $h = 6.626 \times 10^{-34}$ J s ;
Rest mass of electron, $m_e = 9.10956 \times 10^{-31}$ kg ;
Charge on electron, $e = 1.60219 \times 10^{-19}$ C;
1 electron volt (eV) = 1.602×10^{-19} J;
Universal Gas Constant, $R = 8.314$ J mol $^{-1}$ K $^{-1}$;
Boltzmann's constant, $k = 1.381 \times 10^{-23}$ J K $^{-1}$;
$\log_e x = \log_{10} x / \log_{10} e$ with $\log_{10} e = 0.43429448$ *and* $\log_e 10 = 2.30258509$;
10 kbar = 1GPa.
(*Note:* "**erf** $^{-1}$" is the inverse error function not "**1/erf**")

Questions:

[*n*] indicates the marks allocated to each part question. All 8 questions carry equal weight.



1. The drive to reach thermodynamic equilibrium forces the minerals within the Earth's mantle to undergo various phase transitions as temperature and pressure increase with depth. One such phase transition occurs via reconstructive phase transformations between different polymorphs, labelled α, β, γ in the diagram on right.

a) What are the mineral names for α, β, γ? [3]

b) In 1984 Akaogi et al. conducted an experiment to determine the ΔH_{sol} for each of these phases at 975 K by dissolving the phase into a $2PbO.B_2O_3$ melt. Using the ΔH_{sol} for the different phases that are listed below, calculate the change in enthalpies associated with the complete phase transitions at 975 K that we would also expect to see in the mantle. [5]

$$\Delta_{sol}H^{\alpha}_{Mg_2SiO_4} = 67128\,Jmol^{-1}$$
$$\Delta_{sol}H^{\beta}_{Mg_2SiO_4} = 37158\,Jmol^{-1}$$
$$\Delta_{sol}H^{\gamma}_{Mg_2SiO_4} = 30338\,Jmol^{-1}$$

c) In addition to information about enthalpic changes during mineral reactions we also need information about the entropy of the system, particularly the different entropies associated with each mineral phase, to be able to evaluate whether a reaction will proceed or not. The entropy associated with each phase can be split into three separate components. Name and describe each of these components. [6]

d) Using the entropy values for each mineral at 975 K below, calculate the Gibb's free energy of each of the reactions from question b) using $\Delta G_r = \Delta H_r^{975} - T\Delta S_r^{975}$

$$S^{\alpha}_{Mg_2SiO_4} = 285.47\,Jmol^{-1}K^{-1}$$
$$S^{\beta}_{Mg_2SiO_4} = 268.65\,Jmol^{-1}K^{-1}$$
$$S^{\gamma}_{Mg_2SiO_4} = 266.44\,Jmol^{-1}K^{-1}$$

Which reaction is more likely to occur under the temperature conditions of the experiment and why. [6]

e) As can be seen from the phase diagram above these phases can form solid solutions between Mg and Fe-rich end members. Name the type of solid solution that these phases form. [1]

f) Which component of the overall entropy of the mineral phase will be most important for dictating the overall entropy associated with the solid solution phases in the phase diagram? Explain how this will affect the phase transition if the composition of the mantle minerals is changed within the solid solution? [4]

2.

a) Explain the forces that control the position of atoms in a crystal and, with the aid of force and energy diagrams, show the physical reasons behind linear elasticity and thermal expansion. [6]

b) Why does liquid water have a far higher heat capacity than most metals? [2]

c) What electrical property does liquid water possess that strongly enhances solvation of ionic substances such as sodium chloride and how does it act to help the solvation process? [2]

d) How does electrical conductivity vary with temperature in metals and semiconductors? [2]

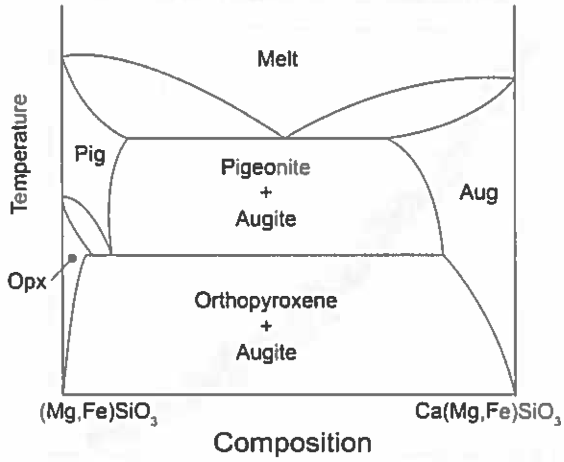
e) Explain contact potential and the thermoelectric Seebeck effect in the common laboratory thermocouple. Why must thermocouples be used in pairs to measure temperature? [3]

f) How is the Fermi level affected by impurities in the semiconductor silicon? Show, using band-gap diagrams, how a contact between two forms of impure silicon can produce a useful electronic component known as a junction diode which has a directional conductivity useful in rectification of alternating current to direct current in power supplies, amongst many other uses. [5]

3.

a) Majorite garnet is not stable at Earth surface conditions and exsolves pyroxene as temperature and pressure decrease. Such features can be observed in a petrographic microscope. What are the characteristics of these features under the microscope? [6]

b) We can observe these features in other minerals including pyroxenes. Look at the image below and use the exsolution features to describe what must have happened to this pyroxene crystal to produce the textures now visible in thin section. Recreate the pyroxene phase diagram below in your answer booklet and use it to show and help explain the four main stages of the path that the crystal has taken as temperature decreases to produce the features observed in the image. [8]



c) Describe the mechanism of <u>growth</u> for exsolutions in systems where there is a large difference in the structure of the minerals that are exsolved and the host mineral, such as pyroxene and garnet. Use diagrams to help you, think about diffusion and the role of changes in chemistry. [5]

d) When the exsolved mineral and the host mineral have similar structures a different type of process can occur that ends up forming larger exsolution features. Name this process. Is this mechanism or the one described in question **c)** kinetically easier to form exsolutions and why. [3]

e) Explain how we can use exsolutions to examine differences in cooling rates. [3]

4.

a) What is Fick's 1st law of diffusion? Give an expression for this with the physical units for each term. Also, give expressions for two other transport laws which share this form and describe the terms along with their physical units.[6]

b) Diffusion experiments were carried out by Cherniak, Watson and Wark (*Chemical Geology* **236**, 2007) to obtain the diffusion coefficient for titanium ions in quartz, (SiO_2). In the example given here, titanium-free quartz crystals were surrounded by titanium dioxide powder (TiO_2, rutile) in sealed capsules subjected to 1100°C for one hour, then quenched and analysed to yield diffusion profiles in the concentration of Ti with distance in from the surface of the quartz crystals. Such a profile is given in the figure 4a (below). The diffusive process was modelled for a semi-infinite half space, representing the initially titanium free quartz crystal, and an assumption of a constant concentration of titanium at its boundary with the rutile powder. The solution of Fick's second law $\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} = 0$, for these boundary conditions is of the form:

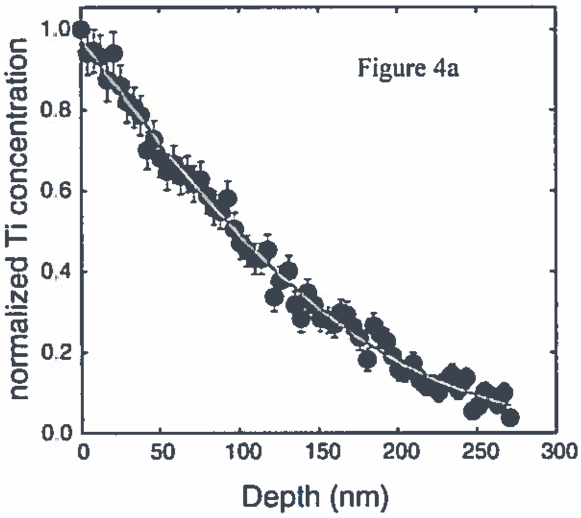
$$C_{(x,t)} = C_0 \mathbf{erfc}\,(x \,/\, (4Dt)^{1/2})$$

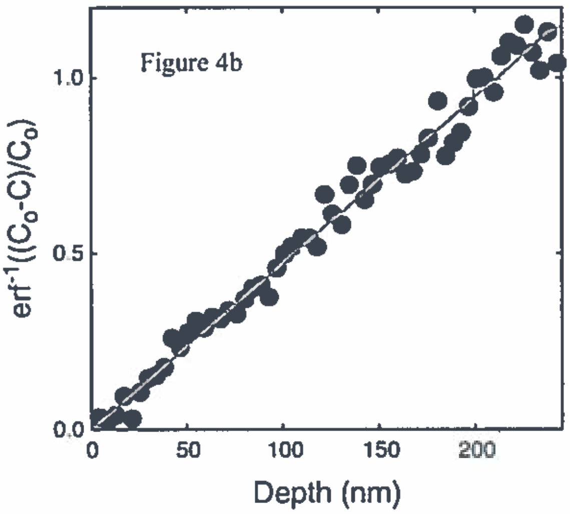
Where C_0 is the concentration at the quartz crystal boundary (at $x = 0$) and $C_{(x,t)}$ is the concentration at depth x into the crystal after time t. This may be rearranged as follows:

$$\frac{C_{(x,t)}}{C_o} = 1 - \mathbf{erf}\ (x\ /\ (4Dt)^{1/2})$$

$$\frac{C_o - C_{(x,t)}}{C_o} = \mathbf{erf}\ (x\ /\ (4Dt)^{1/2})$$

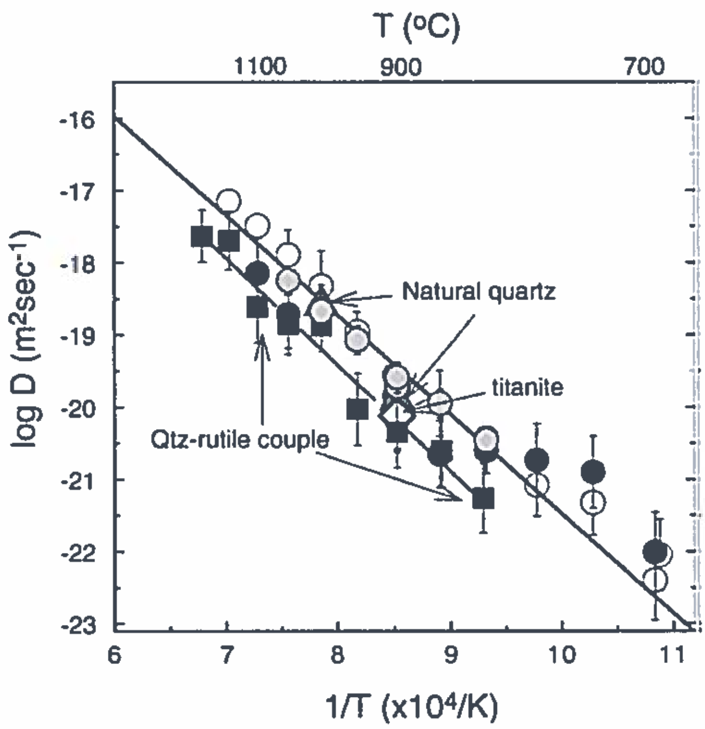
Figure 4b shows the profile data of 4a inverted and replotted using the last expression. Use the best-fit straight-line on this plot to determine the diffusion coefficient for Ti into quartz. [4]





c) The graph below, of $\log_{10}$(diffusion coefficient) *versus* reciprocal absolute temperature (with a multiplication factor of 10^4), shows a collection of diffusion data for Ti in quartz from various experiments like the above and also from diffusion couples. What do we call such graphs? Give a general formula for the temperature dependence of diffusion which can be used, graphically, to determine activation energy from the magnitude of the graph slope. On whose thermo-statistical probability distribution is the formula based? [3]

d) Use the full solid line through the circular data points to determine the activation



energy for Ti diffusion in quartz, in kJ mol^{-1}.[5]

e) The circular points represent powdered rutile against quartz whereas the squares represent crystals of rutile in contact with crystals of quartz as diffusion couples. Why are the diffusivities measured in crystal to crystal couples slower than from experiments involving compacted fine grained powders? [2]

5.

a) In the deepest regions of the mantle we observe indications that new phases, perovskite and ferropericlase, are present. Where can we observe these minerals at the Earth's surface. [1]

b) What two analytical techniques can we use to identify these phases both in natural examples and in experiments? Both of these techniques form spectra with peaks, but the peaks are related to different phenomenon. Briefly describe how the peaks arise in each of these techniques. [8]

c) At the very base of the mantle perovskite breaks down to form post-perovskite. What type of phase transition is described by this transformation and why? [3]

d) The area that contains post-perovskite is called the D'' layer and is seismically distinct from the areas that contain perovskite. Explain how seismic anisotropy can be related to the structure of post-perovskite. [4]

e) At the centre of the Earth we have the core that is comprised of a liquid outer and solid inner core. What type of observations do we have that allow us to estimate the chemistry of the Earth's core? [2]

f) Fe-Ni meteorites are proposed to be sections of planetesimal cores and show large exsolution textures. Explain how these textures are produced in these materials. [4]

g) The inner core also shows seismic anisotropy. What is the current hypothesis about why this anisotropy arises? [1]

h) Mercury is proposed to have no solid inner core. What chemical component that is likely to be present in the core could be the cause of this and why? [2]

6.

a) What is Bragg's law of diffraction and how may it be used to determine the lattice spacing of crystals? [3]

b) The tip of a stylus used in an Atomic Force Microscope (AFM) is usually an atomically-sharp silicon nitride crystal under a thin flexible silicon cantilever. Extremely small contact forces (of the order of 10^{-12} N), are sensed using the flexure of the silicon cantilever. Explain the nature of the forces experienced by the stylus tip as it is lowered steadily towards the surface of a crystal under vacuum. Use a force versus displacement diagram to explain the response during approach and retreat of the stylus from the surface. [3]

c) What basic limitation does the scanning tunnelling microscope have that affects the choice of material which can be observed? [1]

d) The energy of an electron is related to its wavelength via the De Broglie relation: $\lambda = h/p$, where the momentum $p = (2m_e eV)^{1/2}$, and h = Planck's constant. What is the wavelength of electrons produced in a 1MeV transmission electron microscope? If a cubic periclase crystal (MgO) viewed in this microscope has a unit cell lattice parameter of 421pm, then by what angle will such a beam of electrons be diffracted as a result of this lattice spacing? [3]

e) In tomographic experiments, which follow the internal compaction deformation of polycrystalline salts, using the synchrotron x-ray source at Grenoble, crystals of halite

(NaCl) become defective and coloured blue after exposure to the intense x-ray beam. Explain the source of this colour within the crystal structure? [2]

f) How can changes in chemical phase and reaction kinetics be monitored in very high pressure experiments? [2]

g) How can pressure be measured in the Diamond anvil cell? [2]

h) Why does water absorb infrared radiation? [2]

i) Why does solid state ionic electrical conductivity share similar activation energies to solid state diffusion in ionic crystals? [2]

7.

a) Mineral particles play an important role in atmospheric chemistry. The particles can be grouped into two categories based on <u>how</u> they are introduced to the atmosphere. Name the two groups, explain how they are different and provide an example of each type. [5]

b) What do mineral particles provide within the atmosphere that allows them to play an important role in atmospheric chemistry? Name and describe two processes that occur in these locations. [5]

c) Particles in the atmosphere can be hazardous to human health. This includes materials that we have introduced into our local environment such as asbestos. Name two types of asbestos minerals and their mineral group. [4]

d) What are the physical and chemical properties of asbestos that make it so hazardous? [4]

e) When are asbestos materials hazardous and why? Think about how they interact with the body and the three factors that affect toxicity. [7]

8.

a) Explain the interfacial contact angle formed by liquid droplets on a solid surface. How is this contact angle modified when the solid can deform easily? [3]

b) What physical processes compete in the nucleation and growth of new crystalline phases in the solid state? Illustrate your answer with energy diagrams of the main processes relating to solid-state nucleation and growth of new phases within typical crystals. Explain why considerable undercooling is often required before new phases appear and become accommodated within crystalline material despite favourable thermodynamic prediction of their chemical phase stability. [5]

c) What are chondrules in chondritic meteorites? What evidence do they show for their early thermal histories whilst in space? [3]

d) What work is required to create two fresh crystal surfaces, each of unit area, by cleavage under a vacuum? [1]

e) Is the work required to cleave a quartz crystal in a vacuum the same as when this is done submerged under water? Explain your answer. [2]

f) Explain the electrical structure near to mineral surfaces submerged in water. What is meant by the point of zero charge? [4]

g) Explain why fine particles of minerals can be suspended in fresh water but may become quickly flocculated and sedimented by mixing with sea water. [2]

Good luck!