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

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Datum: 6-11-2015, 09:00-12:00, Educatorium-Alpha

Instructions:

- Read all questions through, thoroughly, before answering.
- Answer **8** from the **10** 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: 3 hours

> ***Reminder:***
> Do not use reference books, notes and information sources other than your wonderful brains!
>
> 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 $\log_e 10 = 2.30258509$
1 kbar = 100 MPa;
(*Note:* "**erf** $^{-1}$" is the inverse error function not "**1/erf**")

Questions:

1.

a) Pyroxene undergoes what type of transformation with garnet as depth increases in the mantle?

b) Describe the structure of garnet. How does the composition of majorite garnet vary from upper mantle garnet? How is this related to the garnet structure?

c) Majorite garnet is not stable at Earth surface conditions. What happens to majorite garnet as it is brought to shallower depths?

d) A petrographic microscope can be used to find the stability features in **c**). What are the characteristics of these features under the microscope that are also present in other phases such as feldspars?

e) Using a diagram explain how these features are generated based on the Gibbs free energy of mixing and changes in temperature. Show how a phase diagram of these features can be generated assuming a solid-solution between two end-members A and B. Show the position of the solvus on the diagram.

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.

b) Why do metals generally have higher heat capacities, thermal conductivities and electrical conductivities than non-metallic elements, at low to moderate temperatures?

c) Name an ore mineral with a silver lustre which exhibits semiconduction?

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

e) 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.

3.

a) A major component of the mantle is olivine. Describe the chemistry and structure of olivine.

b) Olivine can form a solid solution. What type of solid solution is this?

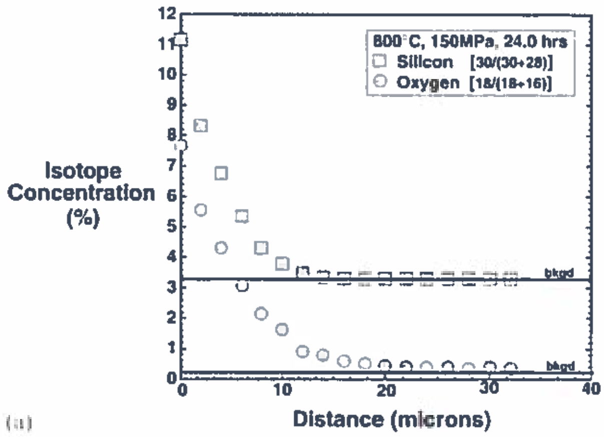
c) Produce a binary phase diagram for olivine solid solution crystallization using compositions between forsterite and fayalite. How is the composition of the melt related to that of a crystallizing olivine grain and why? How does further crystallization affect the composition of the olivine grains?

d) What are the other two forms of solid solution that are found in minerals? Use examples to describe the different forms of solid solution. How does temperature play a role in these solid solutions?

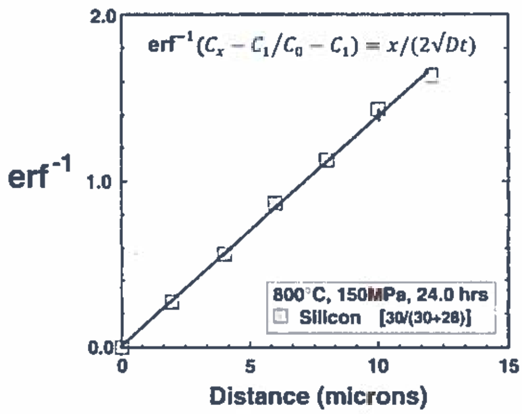
4.

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.

American scientists, John Farver and Richard Yund (*Tectonophysics* 325 (2000) pp.193-205), carried out silicon and oxygen diffusion experiments on fine grained quartz under hydrothermal and dry conditions. The experiments used a natural, very fine grained (1.2μm grain diameter) pure quartzite (Arkansas novaculite), with a low porosity and equilibrated structure. Rectangular pieces of this material were surrounded with ^{18}O enriched water and crushed ^{30}Si enriched SiO_2 then encapsulated in closed gold capsules. The charges were heated under pressure and temperature, for a day, to allow diffusion of the isotopically labelled oxygen and silicon into the novaculite.
The analysis of the diffusion profiles followed the solution of



(a)



(b)

Fick's second law, $\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} = 0$ with the boundary condition of a constant surface concentration on the novaculite. Assuming the novaculite is semi-infinite in extent at the scale of the profile and concentrations are measured inwards from the surface, then the solution (from Crank, 1975, *The Mathematics of Diffusion*) is:

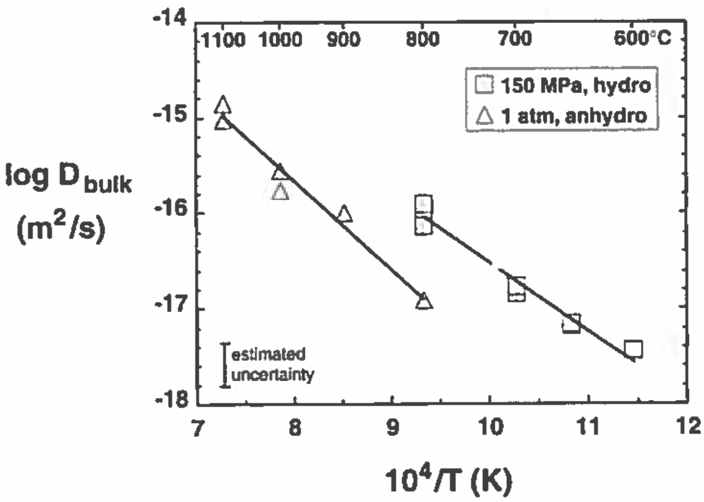
$$\frac{C_x - C_1}{C_0 - C_1} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Typical results for hydrothermal runs are given in the figures (a) & (b).

√ **b)** Use the graph in figure (b) to determine the diffusion coefficient for ^{30}Si in novaculite at 800°C, 150MPa for a run that took 24 hours. (1micron $=1\times10^{-6}$m).

√ **c)** 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. What do we call such graphs?

√ **d)** The combined results of hydrothermal (wet) and anhydrous (dry) runs gave the following graph (on right) of the type referred to in part **c)**. Use these two best-fit lines to determine the activation energies, in kJmol^{-1}, for hydrous (square symbols) and anhydrous (triangle symbols) bulk diffusion of silicon in the novaculite material.



√ **e)** What can the temperature dependence graph tell us about the effect of hydrous fluids on the diffusive transport in novaculite quartzite at elevated temperatures?

5.

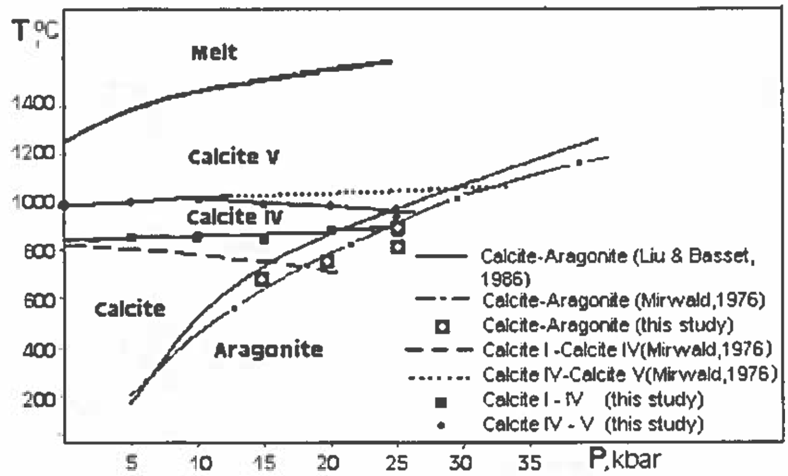
a) Using the ΔH_f° for calcite and aragonite (below) and Hess' law calculate the ΔH associated with the transformation of calcite to aragonite.

Calcite: $2Ca + 2C + 2O_2 \rightarrow 2CaCO_3$ -1207.37 kJmol^{-1}

Aragonite: $2Ca + 2C + 2O_2 \rightarrow 2CaCO_3$ -1207.74 kJmol^{-1}

b) Name the type of reaction that describes this change in enthalpy.

c) Which phase is expected to be stable at standard conditions based on your answer to **a)**? Using the phase diagram (right), does this correspond to what we see in nature and experiments? Describe why, based on the phase diagram.



d) What is the missing piece of information that we need to be able to predict whether a reaction will happen or not? Write the equation for Gibbs' free energy to highlight this.

e) The change in the missing information has a value of -3.7 $Jmol^{-1}$ for the calcite to aragonite transition. Use your equation from **d)** and the value you calculated for ΔH in **a)** to calculate the Gibbs' free energy at standard conditions (1 atm and 298.15 K) of this transformation. Does this correspond to what we observe in the phase diagram from **c)** and why?

f) Name and describe the three different components of our missing information.

g) Which component is important for solid solutions and when is it at a maximum?

6.

a) Explain how the physical properties of water make it a good solvent for ionic solids such as sodium chloride?

b) Why does water absorb infrared radiation?

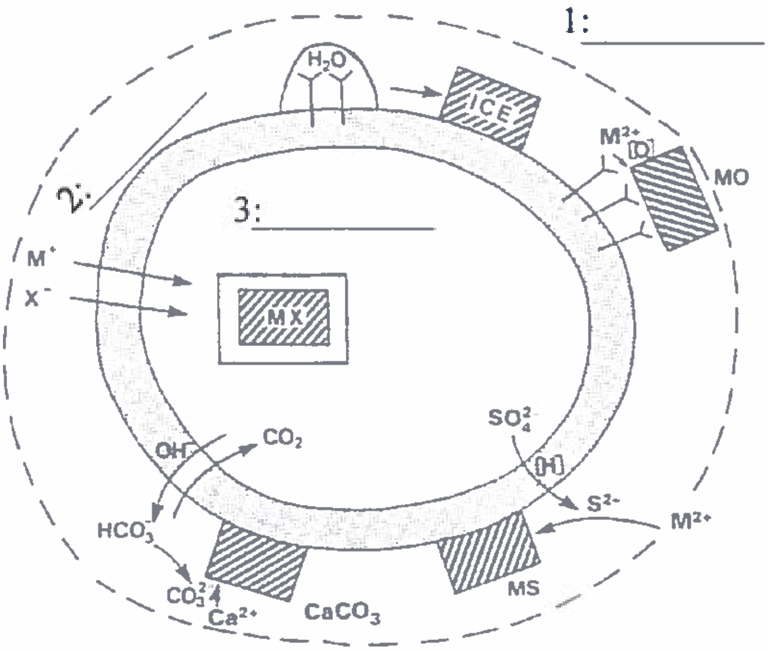
c) What is the role of defects in assisting solid state diffusion?

d) Why does solid state ionic electrical conductivity share similar activation energies to solid state diffusion in ionic crystals?

e) Explain how "clean" electricity may be generated from a fuel-cell using an ionic conductor like zirconia (ZrO_2) and hydrogen fuel? Describe the physical/chemical processes in operation, the transport of charge at each material interface and type of charge carriers transported in each material, including the connection wires. Why is this technology considered to be clean? Would such a fuel-cell operate at room temperature and if not then why not?

7.

a) The diagram below shows the different types of biomineralization that can occur due to the action of microbes. Name the <u>three</u> different types for the correct area of the diagram (indicated with a line and number, 1:___, 2:___ or 3:___), as 1: is ..., 2: is…and 3: is… on your answer sheet. The three types in the diagram are examples of biologically controlled biomineralization what is the name of the biomineralization that occurs due to the action of microbes in mines that produce acid mine drainage?



b) Bacteria can control the nucleation and growth of mineral precipitates by controlling the system in a number of different ways. Name four controls that the microbes can exert on the system.

c) Explain how these factors affect the nucleation and growth of minerals?

d) Name a type of bacteria that forms biomineral within their cell. What type of mineral is formed? Which of the controls described in **b)** are these types of bacteria using?

e) Name a type of bacteria that control biomineral formation outside their cell. What type of mineral is formed? Which of the controls described in **b)** are these types of bacteria using?

8.

a) Why do thermally equilibrated metamorphic rocks, like marbles and deep-crustal granulites, often have grain boundaries at 120°? Explain the role of surface/interface energetics.

b) Suggest reasons for the dendritic morphology of snow crystals grown in cold humid air and also for the basic characteristic hexagonal symmetry.

c) 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?

d) What process produced the Widmanstätten lamellae in the iron meteorites and how may these be used to find cooling rates of planetary core material?

e) What physical processes compete in the exsolution 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 in 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.

9.

a) What are the three modes of adsorption that a gas can adopt when it becomes attached to a crystal surface in vacuum (*i.e.* no solution is present)? Draw a diagram for each.

b) The situation in solution is quite different as there are additional energy barriers that an ion must overcome before it can attach to the surface. Describe the four energy barriers that an ion within a solution must overcome to finally attach as a growth unit to the surface (*e.g.* at a kink site). Use an energy diagram to show the different steps.

c) Draw a Kossel crystal and label the three different types of surfaces that are present.

d) How do the reactivities of each type of surface differ? Explain why this is in terms of dissolution and growth.

10.

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

b) Scanning probe microscopy has many variants. Describe the basics of the atomic force microscope (AFM) and outline the principles at work in producing an atomic scale image. If the probe is raised and lowered near a crystal surface explain how the cantilever will respond and outline the forces involved?

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

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 halite crystal (NaCl) viewed in this microscope has a unit cell lattice parameter of 564pm, then by what angle will such a beam of electrons be diffracted as a result of this lattice spacing?

e) In scanning electron microscopy (SEM) and transmission electron microscopy (TEM) crystals of halite (NaCl) become defective and coloured after exposure to an intense electron beam. Similarly exposure to intense gamma radiation photons also produces colouration of halite. Explain the source of this colour within the crystal structure?

Good luck!