Tentamen: GEO3-1304, Structure and Properties of Earth Materials
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Datum: 8-11-2013, 13:30-16:30, Educatorium-Theatron

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

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}
$\log_a x = \log_b x / \log_b a$ with $\log_{10} e = 0.43429448$ and $\log_e 10 = 2.30258509$
1 kbar = 100 MPa;
1 Ma $\approx 3.15576 \times 10^{13}$ s
(*Note:* "erf^{-1}" is the inverse error function not "1/erf")

Questions:
1.
  a) You are given a set of hand specimens of mantle rocks. How would you identify the depths of origin of the different samples? What clues would you look for to identify their mode of emplacement into the crust? Give as much information as you can about mineralogy, alteration and textures.
  b) Describe how you would distinguish olivine from clinopyroxene in a petrographic thin-section of a mantle rock. In your answer describe how the mineralogical properties (*e.g.* relief, colour, cleavage *etc.*) are linked to crystal structure.
  c) What transformation takes place to garnet at pressures greater than 14 GPa. Give the name of the new mineral formed, and describe how elements occupy different sites as the structure changes. This mineral is not metastable and cannot be observed in rocks exhumed to the surface. What textures would be present in the surface rocks to help you identify that this mineral had originally been present?

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.
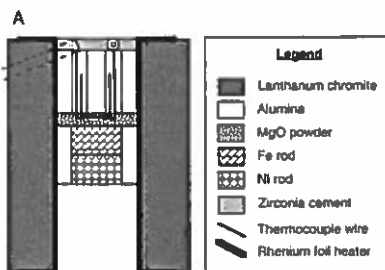
b) How does the elastic shear modulus relate to the S-wave velocity in minerals and rocks? What can seismic S-wave detection tell us about the Earth's deep structure?

c) Where is heat stored in a crystal and explain why liquid water has such a high heat capacity (3× most crystalline metals), despite being a fluid?

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

e) What is the Fermi level in electronic semiconductors and metallic-conductors?

3. The Spinel (AB_2O_4) and Perovskite (ABO_3) structure types become important at the high pressures encountered in the deep mantle. Choose one of these structures and answer the following questions:

a) Sketch the unit cell of your chosen structure type. Show which elements occupy different structural sites.

b) Give an example of a mineral that adopts this structure and describe where it could be found within the Earth. Sketch a phase diagram for the system $(Mg,Fe)_2SiO_4$ from a depth of 100 km in the upper mantle, through the transition zone to a depth of 750 km in the lower mantle and show on this diagram where your chosen mineral is stable.

c) Which phase(s) would form as this mineral breaks down on moving to even higher pressures? Give the names and briefly describe the structure of the new minerals formed.

4.

a) What kinds of high pressure apparatus can be used to synthesise Earth materials and experimentally investigate their properties under i) Earth's upper mantle conditions (<50GPa) and ii) Earth's core conditions (~300 GPa)?

b) What analytical techniques are often employed to determine which phases are present during such experiments?

c) Experiments carried out by M.L. Yunker and J.A. Van Orman (*EPSL*, **254**, pp203-213, 2007) on the solid state inter-diffusion of nickel and iron at high pressure, are useful for the interpretation of planetary interiors. Simple diffusion couples of pure nickel and iron were placed in a multi-anvil cell capable of confinement pressures to 23GPa (230kbar). The confined magnesium oxide octahedron, of just 8mm edge length, contained an assembly shown in figure A. The iron / nickel diffusion couple (centre of assembly) was just 1mm diameter surrounded by alumina, within a rhenium-foil/lanthanum chromite electrical furnace.

A

Legend
- Lanthanum chromite
- Alumina
- MgO powder
- Fe rod
- Ni rod
- Zirconia cement
- Thermocouple wire
- Rhenium foil heater

The results of a run at 1600°C for 10 hours are given as a concentration versus depth profile in figure B.

The analysis was achieved after the run, using an electron microprobe instrument with 1 micrometre (or 1 micron, *i.e.* 1×10^{-6}m) resolution.

The initial concentrations may be assumed to be 100% Fe in contact with 100% Ni.

The simplest solution of the diffusion equation $\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} = 0$ with the symmetric boundary conditions of the diffusion couple is:

$$c_{(x,t)} = \frac{c_0}{2}\left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] = \frac{c_0}{2}\left[\text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

Assuming D is independent of concentration and position.

Concentration c_0, is the initial concentration at time, $t <= 0$ for $x < 0$. The concentration, $c_{(x,t)}$ for $x > 0$ at $t <= 0$ is 0. **Use the above solution and the data below to calculate the diffusion coefficient for iron in nickel at 1600°C.**

Figure B.

Diffusion profile after 10 hours at 1600°C.
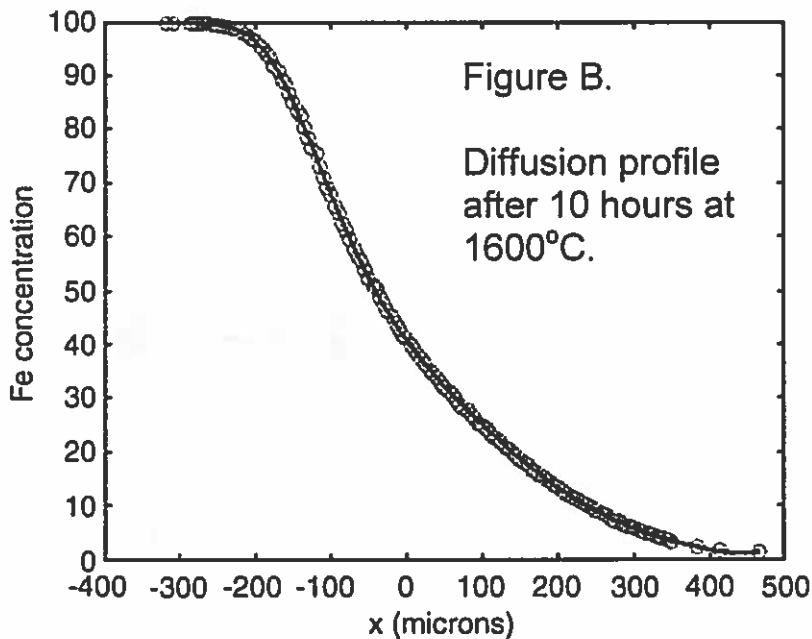
x (microns)

Tip: Take the inflexion point at 50% Fe to be $x = 0$ (at -40 micron from original interface on the printed scale). Then use these shifted data, tabulated here, for the calculation of the diffusivity of Fe into Ni.

x (micrometre)	$c_{(x,t)}$Fe (Atom %)
0	50
40	41
140	25
240	14
340	6

d) Why does the interface drift during diffusion?
e) The diffusion coefficients of Fe in Ni and Ni in Fe both fall to about 10^{-20} m^{2}s^{-1} at the temperatures where characteristic exsolution lamellae formed in meteoritic iron (<900°C). Estimate how long (in Ma), a typical lamella of the order of 1mm would take to form by diffusion with this diffusivity?

x	erf(x)	erfc(x)
0	0	1
0.05	0.056372	0.943628
0.1	0.112463	0.887537
0.15	0.167996	0.832004
0.2	0.222703	0.777297
0.25	0.276326	0.723674
0.3	0.328627	0.671373
0.35	0.379382	0.620618
0.4	0.428392	0.571608
0.45	0.475482	0.524518
0.5	0.5205	0.4795
0.55	0.563323	0.436677
0.6	0.603856	0.396144
0.65	0.642029	0.357971
0.7	0.677801	0.322199
0.75	0.711156	0.288844
0.8	0.742101	0.257899
0.85	0.770668	0.229332
0.9	0.796908	0.203092
0.95	0.820891	0.179109
1	0.842701	0.157299
1.1	0.880205	0.119795
1.2	0.910314	0.089686
1.3	0.934008	0.065992
1.4	0.952285	0.047715
1.5	0.966105	0.033895
1.6	0.976348	0.023652
1.7	0.983791	0.01621
1.8	0.989091	0.01091
1.9	0.99279	0.00721
2	0.995322	0.004678
2.1	0.997021	0.00298
2.2	0.998137	0.001863
2.3	0.998857	0.001143
2.4	0.999312	0.000689
2.5	0.999593	0.000407
2.6	0.999764	0.000236
2.7	0.999866	0.000134
2.8	0.999925	0.000075
2.9	0.999959	4.11E-05
3	0.999978	2.21E-05
3.1	0.999988	1.16E-05
3.2	0.999994	0.000006
3.3	0.999997	3.1E-06
3.4	0.999999	1.5E-06
3.5	0.999999	7E-07

5.

   a) Write out the formula that links Gibbs free energy to enthalpy and entropy. How does each of these parameters vary with temperature in a mineral?

   b) Consider two phases α and β. Phase α is stable at low temperature and phase β is stable at high temperature. Describe what happens to the Gibbs free energy as the mineral transforms on heating from α to β. If the transformation is reversed, would you expect to see the same magnitude of change in Gibbs free energy and if not why not?

   c) The variation of heat capacity with temperature is a key parameter required so that thermodynamic data can be applied to geological problems. Describe a simple calorimetry experiment that could be used to determine heat capacity and its variation with temperature. What measurements would you make and how would you link this to heat capacity? How precise should the results of this experiment be in order for the results to be geologically useful? Why is water a good liquid to use in the calorimeter?

   d) Why are some minerals metastable? Which thermodynamic parameter is this linked to?

6.

   a) Explain why graphs of log (diffusion rate, D) *versus* $1/T_{abs}$, for polycrystalline materials often show a kinked plot, with the low temperature negative slope steepening rapidly above a certain temperature to a well defined steeper slope at high temperatures. What sort of graphs are these? Draw one with labels to explain the underlying reasons for the changes in slope in terms of diffusive processes that occur in the polycrystalline material.

   b) Give a general formula for the temperature dependence of diffusion, in order to explain the significance of the magnitude of the slope in such graphs.

   c) What probability distribution underlies the thermal behaviour seen in these graphs?

   d) Explain the role of defects in assisting solid state diffusion?

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

7.

   a) Exsolution can occur through two different mechanisms. Describe the different mechanisms and show how a phase diagram can be derived from the Gibbs free energy of mixing across a range of different temperatures and for a solid solution between two end-member compositions A and B. Show the position of the solvus and the spinodal curves on your phase diagram.

   b) Experiments were performed to measure the kinetics of coarsening exsolution lamellae. Two rate laws could be written, both of which fit within the range of experimental error:

$$\lambda = \lambda_0 + k\,t^{1/3}$$
$$\lambda = \lambda_0 + (kt)^{1/3}$$

   Which of the above equations could be used give the correct solution for activation energy E_a and why?

8.

a) What work is required to create two fresh crystal surfaces, each of unit area, by cleavage under a vacuum? $W = \gamma_1$

b) 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.

c) Describe what additional energy terms need to be considered in a full description of the total energy involved in solid-state crystalline growth of new phases, as a result of free energy driven exsolution or chemical reaction, within preexisting crystals. How will these terms affect nucleation?

d) What is disjoining pressure and where is it likely to be encountered in minerals?

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

9.

a) Manganese oxide minerals are often observed growing in a distinctive two-dimensional form on the surface of bedding planes in limestone. What are the mineralogical and chemical controls on the shape of the crystals and how do the diffusion and crystallization rates interact to give their distinctive shape?

b) How would the crystal form change as the diffusion rate increased relative to the crystal growth rate? (Initially to be just below the growth rate, then to exceed the growth rate).

c) Why are manganese oxide minerals important for element sequestration in river water? In your answer explain how this is linked to crystal structure.

10.

a) The energy of an electron is related to its wavelength via the De Broglie relation: $\lambda = h/p$, where the momentum $p = (2m_e eV)^{\frac{1}{2}}$, and h = Planck's constant. What is the wavelength of electrons produced in a 1MeV transmission electron microscope? If a cubic magnetite crystal viewed in this microscope has a unit cell lattice parameter of 840pm, then by what angle will such a beam of electrons be diffracted?

b) What advantage does neutron diffraction have over electron and x-ray diffraction, in measurement of crystal unit cell dimensions?

c) What are colour centres in ionic crystals and why do they cause colouration?

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

e) Explain contact potential between dissimilar metals in terms of Fermi level and explain the thermoelectric effect seen in thermocouples, commonly used for laboratory high temperature measurement.

Good luck!