Tentamen: GEO3-1304, Structure and Properties of Earth Materials
Docenten: dr. C.J. Peach & dr. P.R.D. Mason
Datum: 04-11-2009, 13:00-16:00, C.008 & C.010

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) $= 1.602 \times 10^{-19}$ 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 $\approx$ 100 MPa

Questions:
1.
a) Describe what would happen to the mineral Olivine $(Mg,Fe)_2SiO_4$ if it were to sink through the Earth's mantle from a depth of 100 km in the upper mantle, through the transition zone to a depth of 750 km in the lower mantle. Illustrate you answer with a sketch of a phase diagram with corresponding pressures of 0-150 kbar (upper mantle), 150-250 kbar (transition zone) and >250 kbar (lower mantle).

b) What are the two possible mechanisms of transition from olivine into its higher pressure phases? Why is it important to know what this mechanism is?

2.
a) Wet diffusion experiments on Titanite $[CaTi(O)SiO_4]$ (*Sphene*) using oxygen isotopes were carried out by Zhang *et al.*, (*Chemical Geology*, 235, pp.105-123, 2006), to determine the oxygen diffusivity under hydrothermal conditions. Crystals of pure Titanite were surrounded by [18]O enriched water, in capsules that were heated to 800°C under a pressure of 70MPa. The diffusion of [18]O into the crystal followed the predictions of the "diffusion equation" when solved for the semi-infinite half-space boundary conditions, with the surface concentration held constant. This yielded the "error function" solution below:

$$C_{(x,t)} = C_0\left(1 - \text{erf}\,\frac{x}{\sqrt{4Dt}}\right)$$

Where, C_0 is the initial concentration of ^{18}O maintained at the crystal surface. $C_{(x,t)}$ is the concentration with position x, measured from the surface, after time t.

The **erf** $[\eta]$ is the Gaussian error function and **erfc** $[\eta]$ is its compliment *i.e.* (1 - **erf** $[\eta]$). (Both are tabulated below for reference). (*Note:* "**erf** $^{-1}$" is the inverse error function not "1/**erf**").

Rearrangement of the solution gives:

$$\text{erfc}^{-1}\left[\frac{C_{(x,t)}}{C_0}\right] = \frac{x}{\sqrt{4Dt}}$$

Use the solution above to calculate the diffusion coefficient for ^{18}O diffusion in Titanite using the experimentally determined profile "sph31" that was produced using the above conditions after a run lasting 1.555×10^6 s, (shown below, on plot of results as the smoothed line):
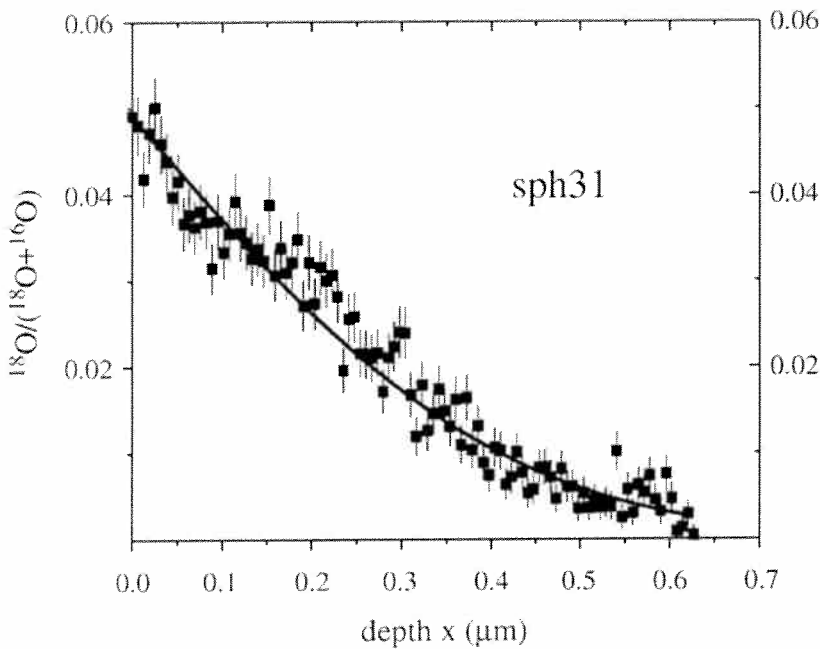

η	erf η	erfc η
0	0	1.0
0.02	0.022565	0.977435
0.04	0.045111	0.954889
0.06	0.067622	0.932378
0.08	0.090078	0.909922
0.10	0.112463	0.887537
0.15	0.167996	0.832004
0.20	0.222703	0.777297
0.25	0.276326	0.723674
0.30	0.328627	0.671373
0.35	0.379382	0.620618
0.40	0.428392	0.571608
0.45	0.475482	0.524518
0.50	0.520500	0.479500
0.55	0.563323	0.436677
0.60	0.603856	0.396144
0.65	0.642029	0.357971
0.70	0.677801	0.322199
0.75	0.711156	0.288844
0.80	0.742101	0.257899
0.85	0.770668	0.229332
0.90	0.796908	0.203092
0.95	0.820891	0.179109
1.0	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	0.983790	0.016210
1.8	0.989091	0.010909
1.9	0.992790	0.007210
2.0	0.995322	0.004678
2.2	0.998137	0.001863
2.4	0.999311	0.000689
2.6	0.999764	0.000236
2.8	0.999925	0.000075
3.0	0.999978	0.000022

Tip: Take the constant surface $^{18}O/(^{18}O+^{16}O)$ concentration to be 0.05 and the original (deep) concentration to be zero.

b) With what scientist's name is the "diffusion equation" associated?

c) Write down his first law, explaining the terms?

d) What steps are necessary, at the atomic scale, for solid state diffusion to occur in crystals?

e) Why is solid state diffusion temperature dependent?

3. Three different crystal structures, that are widely-adopted by a large range of minerals, have been described in detail during the course. These are Spinel (AB_2O_4), Perovskite (ABO_3) and Rutile (MO_2) types. Choose one of these structures and answer the following questions:

   a) Sketch the unit cell of your chosen structure type.

   b) Give an example of a mineral that adopts this structure and describe where it could be found within the Earth.

   c) **EITHER** - (*i*) How does this mineral reflect or respond to temperature and pressure conditions in the part of the Earth you just described in part (b) above?

   OR - (*ii*) How does your chosen mineral help to create or remediate environmental problems?

4. The results of single crystal diffusion experiments for the diffusion of the tracer ^{26}Mg into two olivines are given, below, as a function of absolute temperature. Both experimental sets were carried out under similar low oxygen atmospheres to prevent oxidation of the iron from Fe^{2+} to Fe^{3+}. Melt-grown crystals of pure forsterite (Mg_2SiO_4) and natural single crystals of olivine with composition (Mg:92%,Fe:8%)$_2SiO_4$ picked from San Carlos peridotite nodules (xenoliths in a basalt), are represented in the two plots (a) and (b) respectively, below:

a.

b
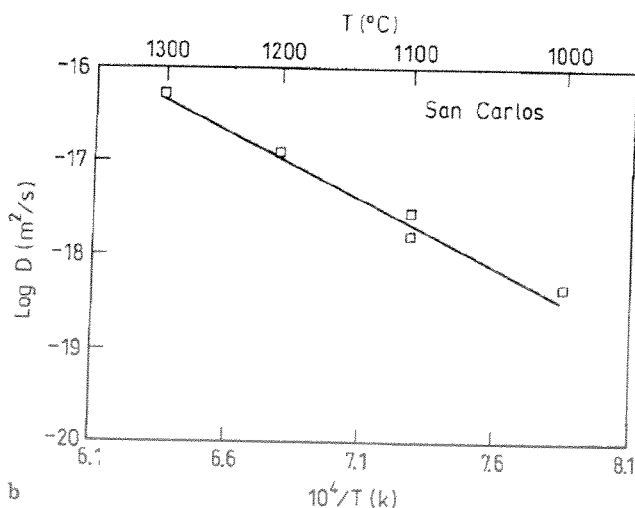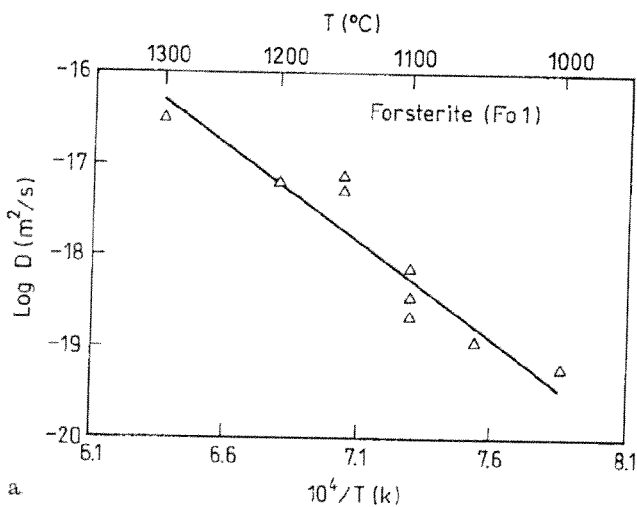
a) What kind of diagrams are these?

b) Write an equation relating diffusion coefficient to absolute temperature, based on these diagrams.

c) What does the slope of these plots represent?

d) At 1100°C, in which type of olivine is the diffusion of ^{26}Mg easiest?

e) In both materials, what is the significance of only a single slope being visible over the temperature range?

f) Estimate the activation energy for diffusion of ^{26}Mg, in each olivine type, based on the presented data. Note: $log_{10}D$ is plotted against 10000/T, (T in kelvin; *i.e.* 1000 celsius will plot as (1/1273.15) × 10000 = 7.854 on the horizontal axis.

g) If both crystals had similar crystallographic orientation for diffusion, then suggest what processes could be responsible for the difference in the measured slopes?

5.

a) 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. How precise should the results of this experiment be in order for the results to be geologically useful?

b) How does the Gibbs free energy of a mineral vary with temperature?

c) 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?

6.

a) Briefly describe 3 instruments that may be used to show the characteristic atomic-scale regularity of crystals and explain how these instruments provide that information?

b) 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 elasticity and thermal expansion.

c) Where is heat stored in a crystal?

d) Why do metals have higher heat capacities than non-metallic elements?

e) Why do metals conduct electricity better than silicates at room temperature?

f) Why is the activation energy for high temperature diffusion in crystals often similar to the activation energy for ionic electrical conduction, under similar experimental conditions?

7.

a) What are the three main types of *solid solution* observed in minerals? Give examples of specific minerals in each part of your answer.

b) How do the enthalpy and entropy of mixing in a solid solution interact to give *exsolution*? Sketch a diagram to show ΔH_{mix}, $-T\Delta S_{mix}$ and ΔG_{mix} vary in a binary system consisting of atoms A and B (i.e. over a composition from 100%A to 100%B). How can this information be used to construct a phase diagram with a solvus that gives two stable compositions at one temperature T?

8.

a) Explain what is physically or structurally responsible for 3 of the many extraordinary physical properties of water and indicate any significant effect these properties have on the present state of our planet.

b) Explain how the physical properties of water make it a good solvent for ionic solids such as sodium chloride. Why does the solubility fall dramatically as water becomes a super critical fluid near $375°C$ and 20 MPa?

c) Why does water absorb infrared radiation?

d) What minerals could contain water in the Earth's deep mantle?

e) What effects does water have on the fracture strength of minerals?

9.
  a) How do the rate of *crystal growth* and rate of *diffusion* (in the solution surrounding the crystal) interact to control the shape of a crystal in the cubic crystal class? Give examples for the crystallization of metallic silver from silver nitrate solution and sodium chloride from a saturated solution. In your answer describe the angles between crystal faces that are formed and how they are related to the internal structure of the mineral.
  b) During dissolution of NaCl crystals in water which crystallographic sites would you expect to be most active? How would you expect the presence or absence of bacteria in solution to affect the dissolution rate?

10.
  a) What is Bragg's law and how may it be used to understand crystal structure?
  b) What are the advantages of neutron diffraction over x-ray and electron diffraction in the characterization of atomic structures?
  c) 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 crystal viewed in this microscope has an atomic spacing of 564pm, then by what angle will such a beam of electrons be diffracted?
  d) What is such a microscope usually used for in materials studies of deformed crystals?

Good luck!