

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

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Datum: 9-11-2012, 13:30-16:30, Educatorium-Megaron

### 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,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ ,

Planck's constant,  $h = 6.626 \times 10^{-34} \text{ J s}$ ,

Rest mass of electron,  $m_e = 9.10956 \times 10^{-31} \text{ kg}$ ,

Charge on electron,  $e = 1.60219 \times 10^{-19} \text{ C}$ ,

1 electron volt (eV) =  $1.602 \times 10^{-19} \text{ J}$ ,

Universal Gas Constant,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,

Boltzmann's constant,  $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$

$\log_a x = \log_b x / \log_b a$  with  $\log_{10} e = 0.43429448$  and  $\log_e 10 = 2.30258509$

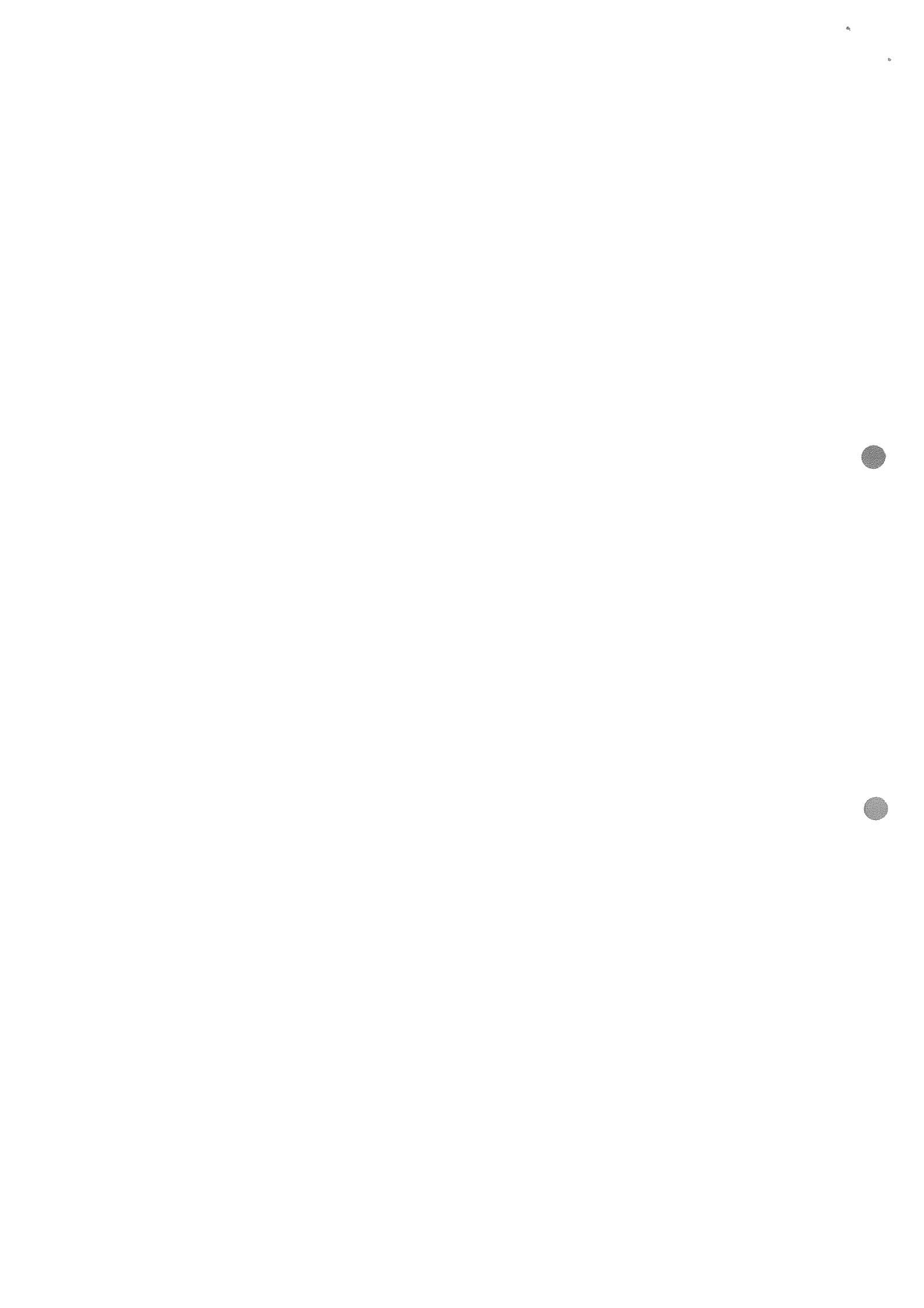
1 kbar  $\approx$  100 MPa; 1 Ma  $\approx$   $3.15576 \times 10^{13} \text{ s}$

(Note: "erf<sup>-1</sup>" is the inverse error function not "1/erf")

### Questions:

1.
  - a) Describe how you would identify the mineral Olivine under the optical microscope. In your answer explain as far as you can how the optical properties are related to the crystal structure of this mineral.
  - b) Which minerals could be used to indicate the depth of origin in a suite of mantle xenolith samples?
  - c) Describe what would happen to the mineral Olivine ( $\text{Mg,Fe}_2\text{SiO}_4$ ) 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 your 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).
  - d) 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) Diffusion is one of many transport processes. Give three examples of physical transport processes and show the similarity in form to Fick's first law of diffusion. Include the physical units for each of the parameters.
  - b) Explain why solid state diffusion is temperature dependent.

(continued)



- c) Explain the atomic-scale steps required for solid state diffusion and explain why ionic electrical conductivity often has similar activation energy to high temperature diffusion.
- d) What are colour centres in crystals? Give examples of minerals that exhibit colour due to these defects.
- e) What is the Fermi level in electronic semiconductors and metallic-conductors?
- f) 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.

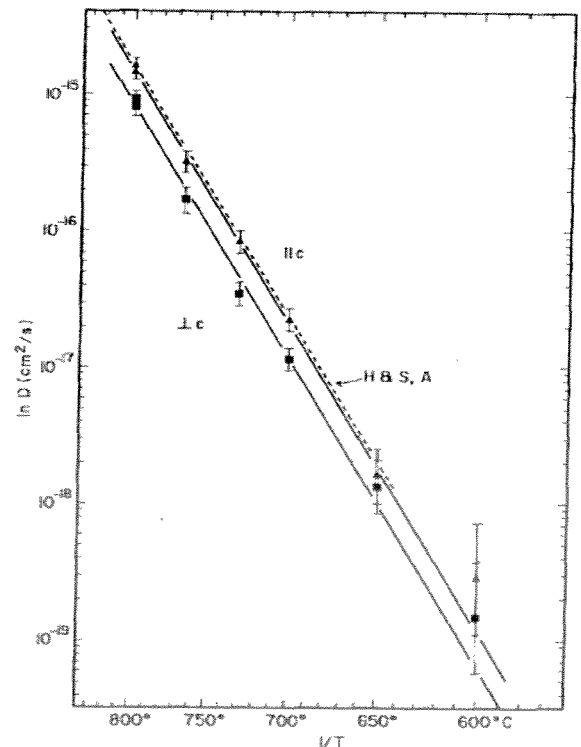
3.

- a) Write out the formula that links Gibbs free energy to enthalpy and entropy.
- b) Sketch diagrams to show how each of these parameters vary with temperature in a mineral at constant pressure.
- c) Consider two phases,  $\alpha$  and  $\beta$ . Phase  $\alpha$  is stable at low temperature and phase  $\beta$  is stable at high temperature. Describe what happens to the Gibbs free energy as the mineral transforms on heating from  $\alpha$  to  $\beta$ . If the transformation is reversed, would you expect to see the same magnitude of change in Gibbs free energy and if not why not?
- d) 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?

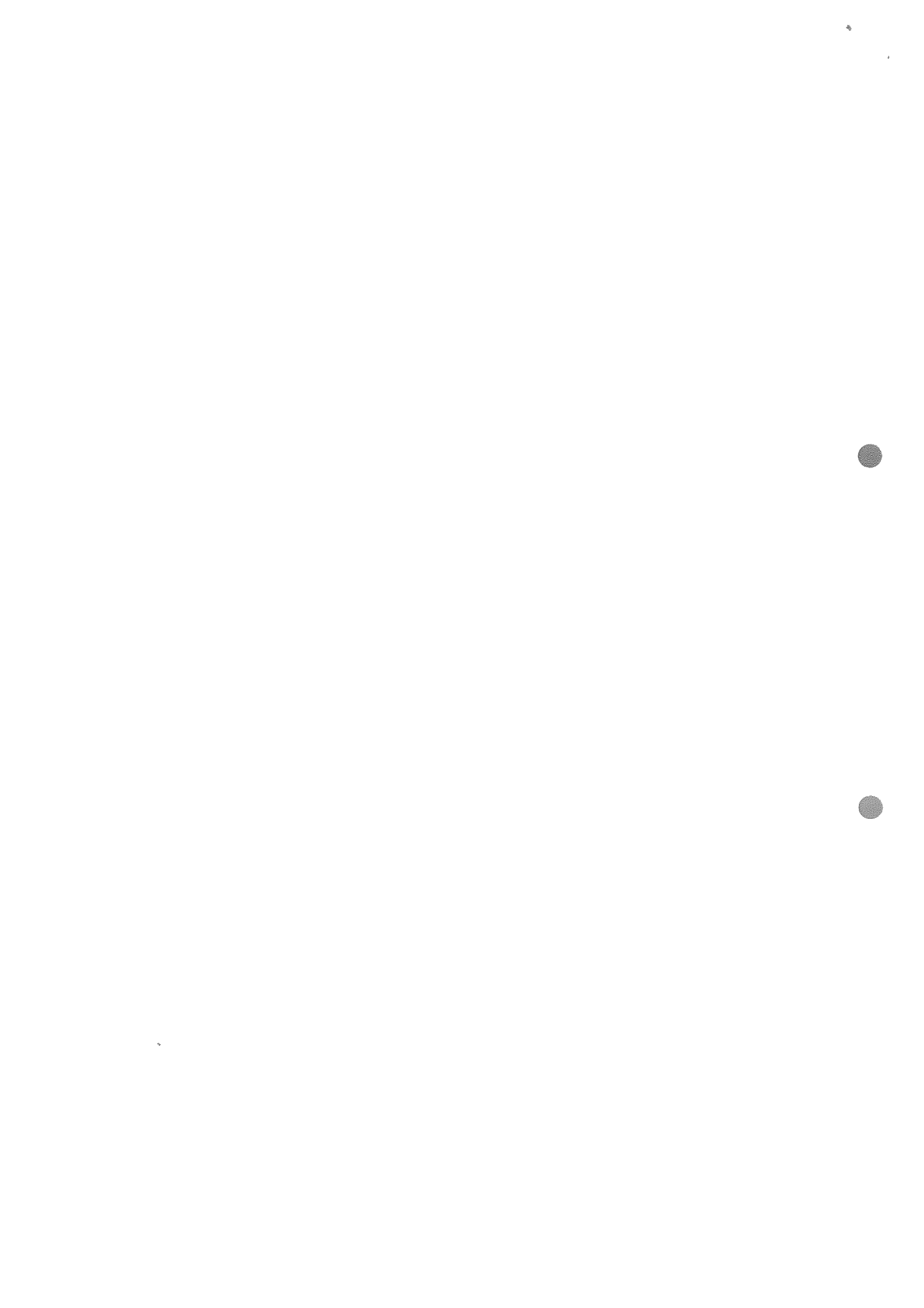
4.

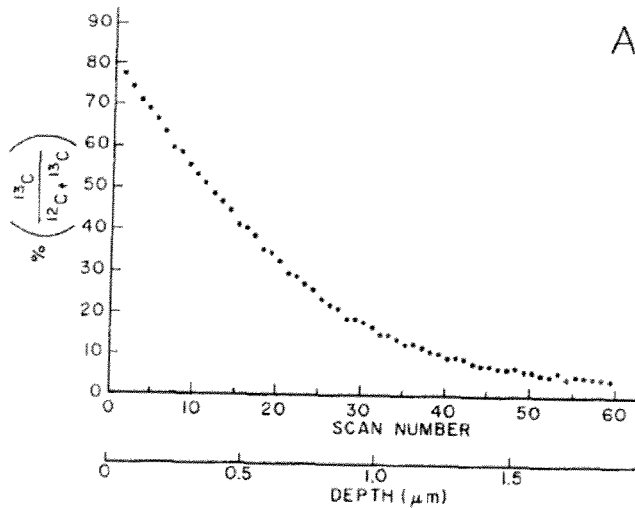
Experiments by Kronenberg, Yund and Giletti (*Phys. Chem. Min.*, 1984), on the diffusion of carbon into calcite ( $\text{CaCO}_3$ ) single crystals, parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the c-axis, revealed that carbon diffusion is almost crystallographically isotropic and has a simple temperature dependence on an Arrhenius diagram; see diagram on right where the diffusion coefficients are plotted for the two orientations (solid lines) and also compared with earlier data (H & S, A – dotted line).

- a) Suggest an expression relating diffusivity to absolute temperature that underlies these plots and give the name of the statistical thermodynamical distribution upon which it is based.
- b) Given, that the slope of these  $\log_{10}(D)$  vs.  $1/T$  plots, for the two extremes in crystallographic orientation, are almost the same, then take this negative slope to be  $-1.901 \times 10^4 \text{ K}$  and use it to estimate the molar activation energy for carbon diffusion in calcite. *Tip: take care with logarithms.*



(continued)





A The above experiments were carried out in capsules under high pressure and temperature.  $\text{CO}_2$  doped with the isotope  $^{13}\text{C}$  at constant concentration  $c_1$ , was used as a fluid in contact with the crystal surface during the experiment and the diffusive process modelled by assuming a semi-infinite medium with constant surface concentration. The solution of the "diffusion equation" came from Crank

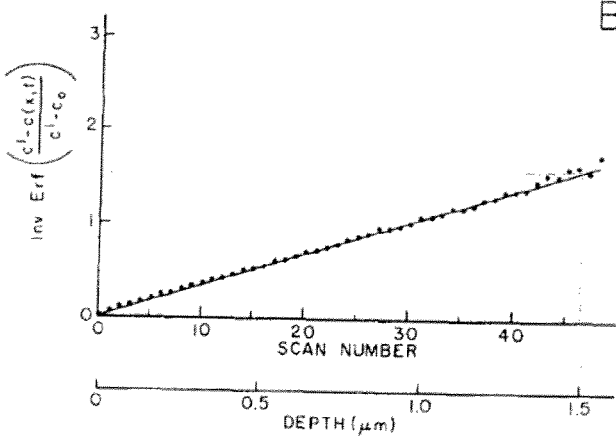
(1956), as  $\frac{c_1 - c(x,t)}{c_1 - c_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ , where

$c_0$  was the original concentration of  $^{13}\text{C}$  throughout the crystal.

A typical set of data for a run lasting  $1.25 \times 10^6$  s at  $800^\circ\text{C}$ ,  $p\text{CO}_2 = 1.39$  bar and  $p\text{H}_2\text{O} = 0.8$  bar is given to the left. The top figure (A), shows the diffusion profile and the lower figure (B) gives a plot of

$\text{inverse\_erf}\left(\frac{c_1 - c(x,t)}{c_1 - c_0}\right)$ , both *versus*

depth from the crystal surface in micrometres.



- c) Use the lower plot (B) to calculate the diffusion coefficient for carbon in calcite under the experimental conditions.

**Tip: take care to use the depth scale not scan number!**

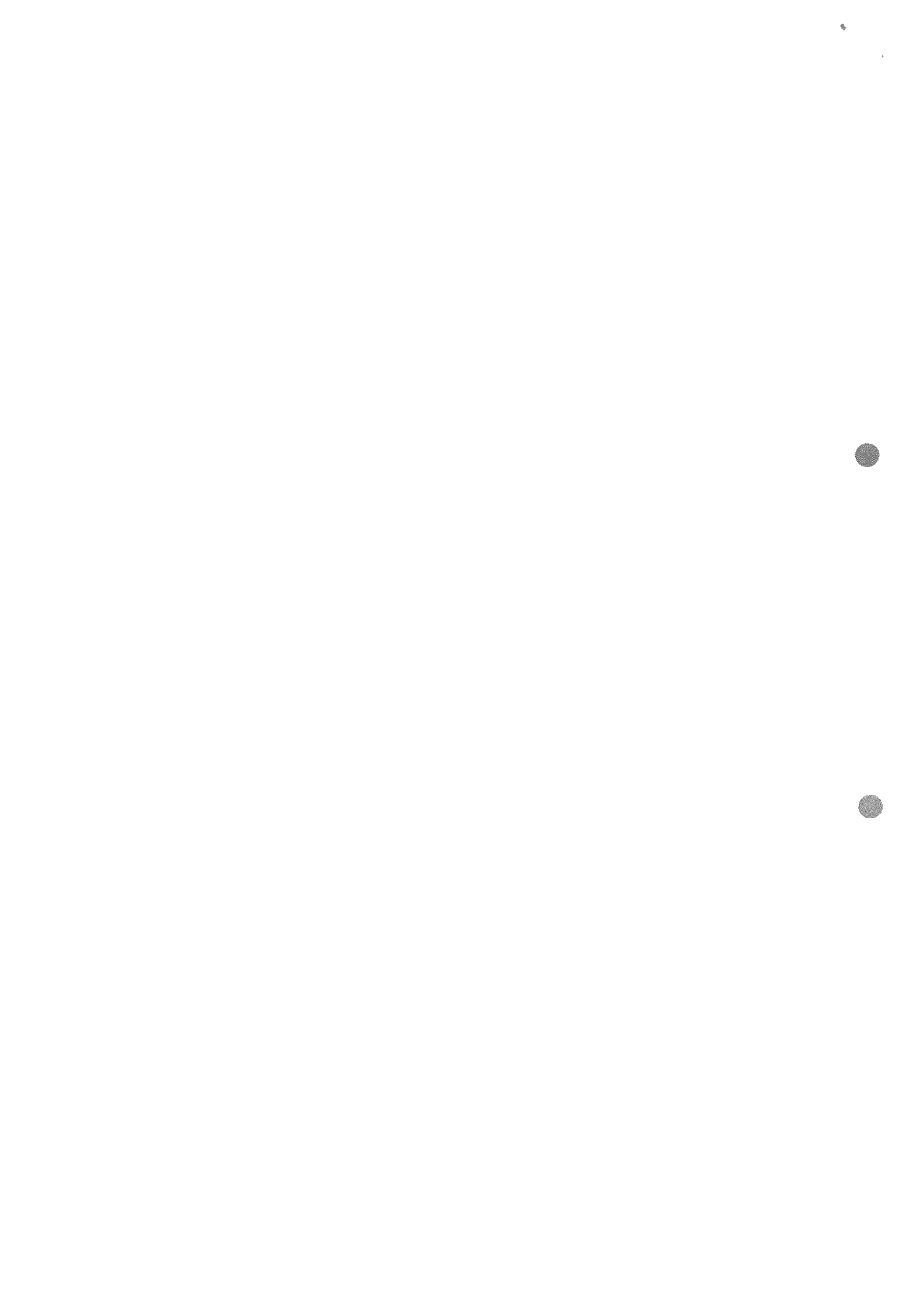
5.

- What are the three main types of *solid solution* observed in minerals? Give examples of specific minerals for each part of your answer.
- How do the enthalpy and entropy of mixing in a solid solution interact to give *exsolution*? Sketch a diagram to show  $\Delta H_{\text{mix}}$ ,  $-T\Delta S_{\text{mix}}$  and  $\Delta G_{\text{mix}}$  vary in a binary system consisting of atoms A and B (i.e. over a composition from 100%A to 100%B).
- Show how this information be used to construct a phase diagram with a solvus that gives two stable compositions at one temperature T?
- 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:

$$\lambda = \lambda_0 + kt^{1/3}$$

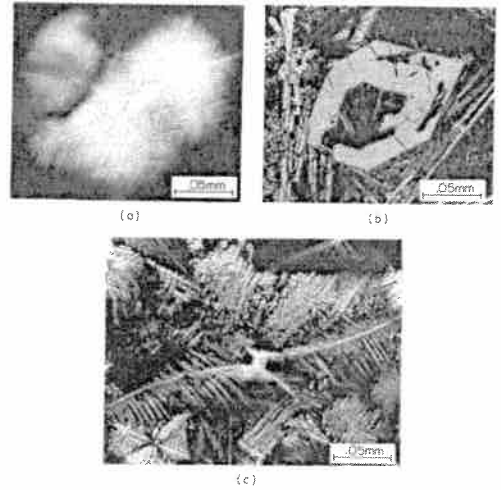
$$\lambda = \lambda_0 + (kt)^{1/3}$$

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

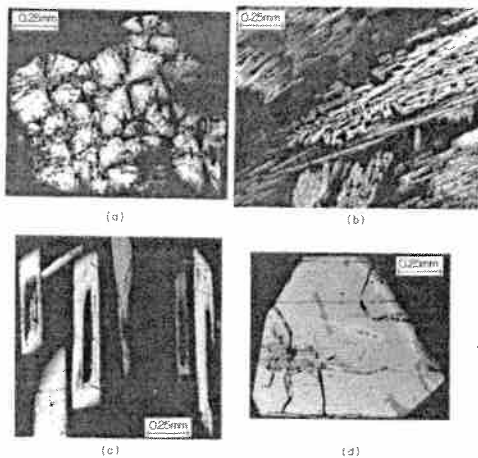


6.

Pillow basalts are formed when basaltic lava is erupted under water, deep enough to suppress water boiling. Cooled by the water, pillows solidify rapidly. Olivine crystals at their chilled margins are finely dendritic [Photo (a) - right photo trio from Bryan, 1972], whereas skeletal crystals are found at pillow centres [Photo (b)], open dendrites occur elsewhere in the pillow interiors [Photo (c)]. (All from Kirkpatrick, *Am. Min.* **60**, 1974).



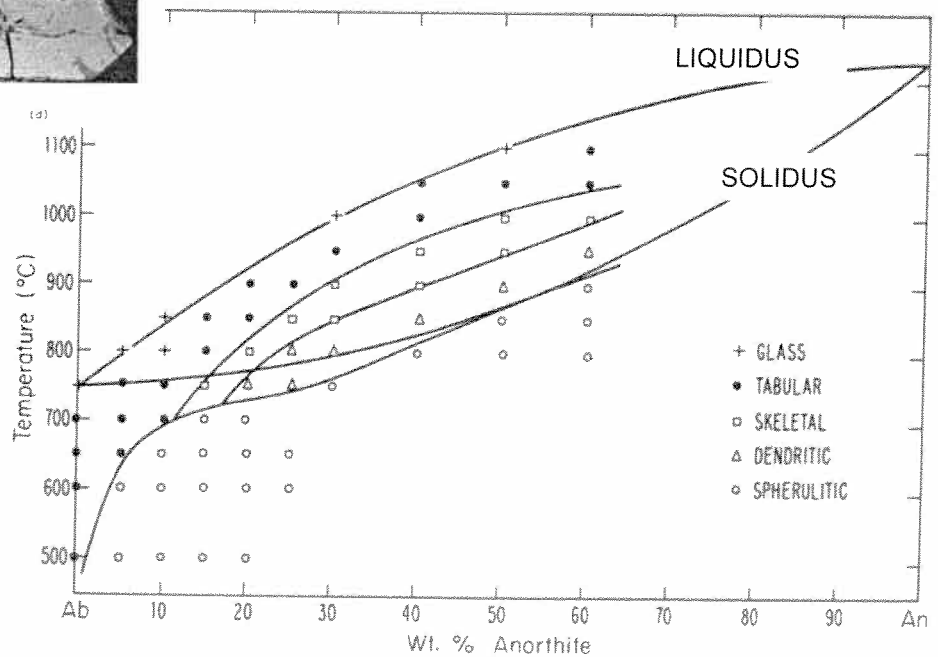
Experiments (Lofgren, 1974) on the growth of plagioclase crystals from melt also show a variety of crystal forms dependent on the degree of under cooling ( $\Delta T$ ) from the liquidus melting line.



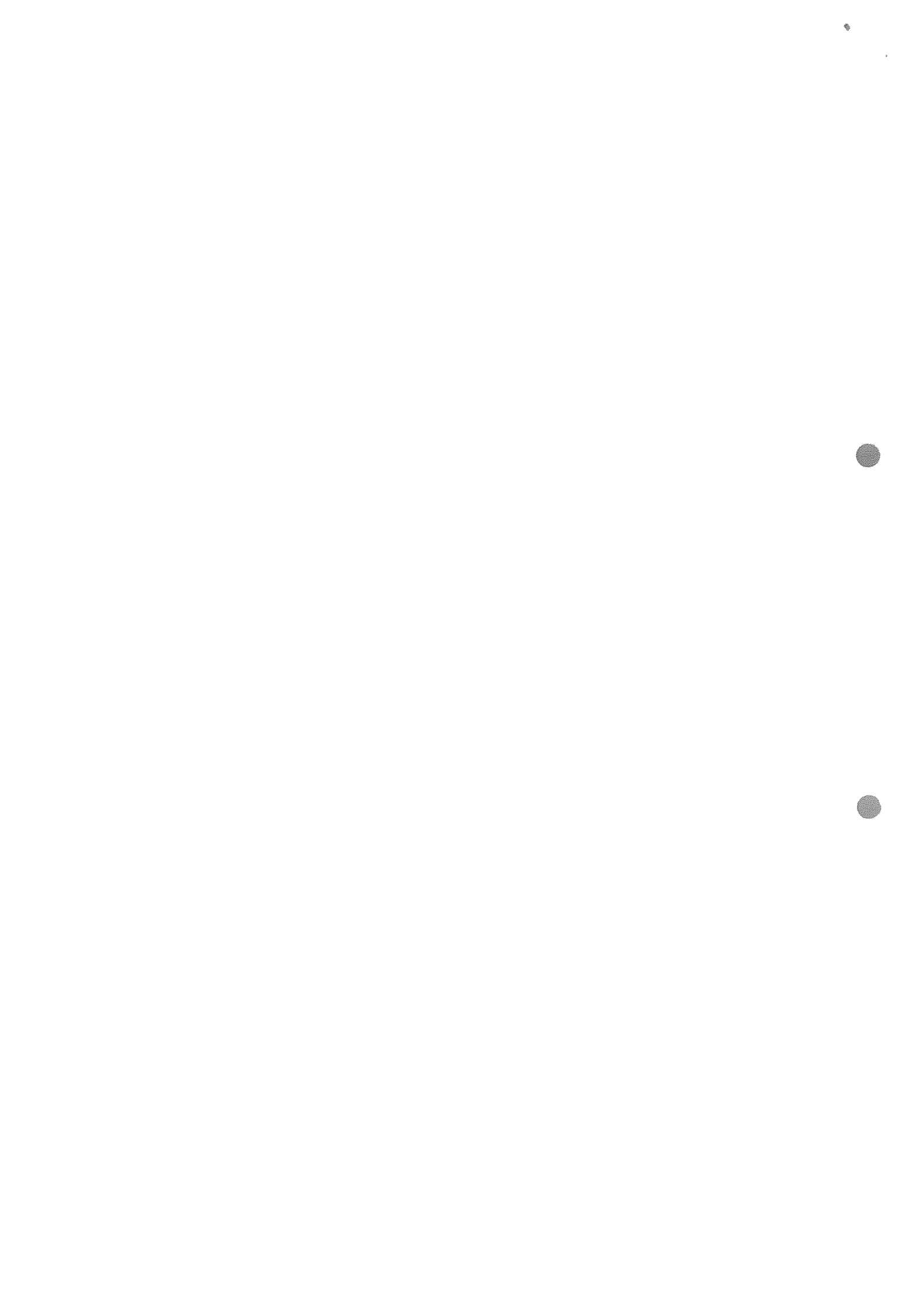
(Left) Plagioclase crystals grown at 5 kbar from water saturated plagioclase melts (from Lofgren, 1974)

- a) spherulitic crystals with  $\Delta T = 430^\circ\text{C}$ .
- b) dendritic crystals,  $\Delta T = 200^\circ\text{C}$ .
- c) skeletal crystals,  $\Delta T = 100^\circ\text{C}$ .
- d) tabular crystals,  $\Delta T = 50^\circ\text{C}$ .

The crystal forms found after the short experimental runs at different degrees of under cooling are mapped out on the phase diagram for plagioclase feldspar (right).



- a) Explain with the aid of free energy diagrams the problem of homogeneous nucleation and growth from a melt, with respect to crystal size and amount of under cooling.
- b) What is the significance of the glass along the liquidus?
- c) Suggest reasons for the different morphologies of crystal growth. Remembering that diffusion is strongly temperature dependent, then where on the phase diagram would clear effects of diffusion limited growth be expected to be found?
- d) What additional energy terms need to be considered in nucleation and crystallization of a new phase in the solid state?
- e) How can nucleation be assisted?





- 7.
- Sketch a diagram to show a cross-section through the crystal structure of the sheet silicate mineral chrysotile ( $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ ).
  - Explain what is meant by tetrahedral- octahedral mismatch.
  - Why is Chrysotile asbestiform? Sketch a diagram to illustrate your answer.
  - Which other silicate minerals can be asbestiform and why?
- 8.
- 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.
  - In a similar way, explain why the atoms in crystals have a regular structure, exhibit elasticity and thermal expansion. What is responsible for the forces between atoms in this case?
  - What work is required to create two fresh crystal surfaces, each of unit area, by cleavage under a vacuum?
  - 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.
- 9.
- Describe how a saturated solution of NaCl crystallizes at room temperature on a glass slide, at the edge of a small bubble of solution where flow is restricted. 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?
  - What happens in the middle of the bubble where flow is not restricted and the diffusion rate is faster than the crystal growth rate?
  - At which crystallographic sites would you expect dissolution to begin, as a mineral breaks down in a solution? Describe how dislocations in the structure may play a role.
  - What would you expect to happen to the dissolution process if bacteria were added to the solution?
- 10.
- The regularity of crystal structure may be shown by x-ray diffraction. Explain the basis for Bragg's law of x-ray diffraction by crystals and calculate the expected first order diffraction angle  $\theta$ , for a crystal with an atomic layer spacing  $d$ , of 500 pm using Cu- $K_\alpha$  x-rays of wavelength,  $\lambda = 154.4$  pm.
  - What advantage does neutron diffraction have over electron and x-ray diffraction, in measurement of crystal unit cell dimensions?
  - Where is heat stored in a crystal and explain why liquid water has such a high heat capacity ( $3\times$  most crystalline metals), despite being a fluid?
  - Why does water absorb infrared radiation?
  - Explain how the physical properties of water make it a good solvent for ionic solids such as sodium chloride?

*Good luck!*

