

# Test #3A

Wednesday, November 17, 2004

11:05 a.m. - 11:55 a.m.

Name: \_\_\_\_\_  
(please print in UPPER CASE)

Recitation Instructor: \_\_\_\_\_

**A complete test consists of 4 questions.**

**Write your answers on these pages.**

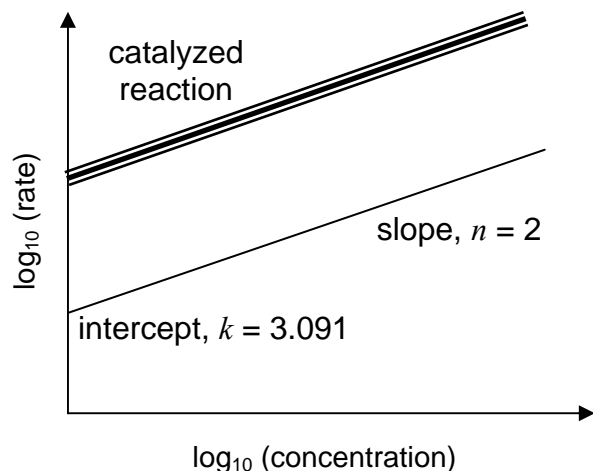
**State your assumptions and show calculations that support your conclusions.**

**RESOURCES PERMITTED: PERIODIC TABLE OF THE ELEMENTS, TABLE OF CONSTANTS,  
AN AID SHEET (ONE PAGE 8½" × 11"), AND A CALCULATOR.**

**NO BOOKS OR OTHER NOTES ALLOWED.**

**USE OF WIRELESS COMMUNICATIONS DEVICES STRICTLY FORBIDDEN.**

<b>#1</b>	24%	
<b>#2</b>	28%	
<b>#3</b>	28%	
<b>#4</b>	20%	
<b>TOTAL</b>	<b>100%</b>	

**Problem #1 (24%)**

The fictitious compound, pandemonium fluoride ( $\text{Pd}_2\text{F}_3$ ), decomposes readily at temperatures exceeding  $765^\circ\text{C}$ . The figure above shows the kinetics of the reaction conducted at  $800^\circ\text{C}$ . The reaction is second order in concentration of  $\text{Pd}_2\text{F}_3$ . The value of the specific chemical rate constant,  $k$ , is  $3.091 \text{ L mol}^{-1} \text{ s}^{-1}$ .

- 4% (a) On the graph above, label the slope and the intercept, indicating the numerical value of each.
- (b) Calculate how long it takes at  $800^\circ\text{C}$  for the concentration of  $\text{Pd}_2\text{F}_3$  to fall from  $1.11 \text{ mole L}^{-1}$  to 10% of that value. Express your answer in seconds.

14% *for second order rxns*

$$\frac{1}{c} = \frac{1}{c_0} + kt$$

$$\therefore \frac{1}{c} - \frac{1}{c_0} = kt$$

$$\therefore t = \frac{1}{k} \left( \frac{1}{c} - \frac{1}{c_0} \right)$$

$$= \frac{1}{3.091} \left( \frac{1}{0.111} - \frac{1}{1.11} \right) = \underline{\underline{2.625}}$$

- (c) The same reaction is now conducted under the influence of a catalyst. On the graph above, which shows the reaction as it proceeds in the absence of a catalyst, draw the line associated with the catalyzed reaction.

6%

**Problem #2 (28%)**

Composition A: 5% MgO – 95% SiO<sub>2</sub>;

Composition B: 20% MgO – 80% SiO<sub>2</sub>

- (a) Two glass-forming melts, A and B as specified above, are each cooled at the same rate down to room temperature. Identify which melt, A or B, exhibits the higher glass transition temperature and explain why.

8%

Melt A.

Melt A contains less MgO, i.e., less modifier → a more intact silicate network → higher viscosity

Higher viscosity means lower atom mobility → hence as temperature falls the melt has lower capacity to rearrange itself.

This quenches in a higher amount of free volume and effectively immobilizes the system at a higher temperature.

- (b) The two glasses formed in part (a) are soaked in molten calcium chloride (CaCl<sub>2</sub>) at the same temperature for a period of time long enough to allow for equilibration between glass and molten salt. Identify which melt, A or B, exhibits a greater improvement in strength and explain why.

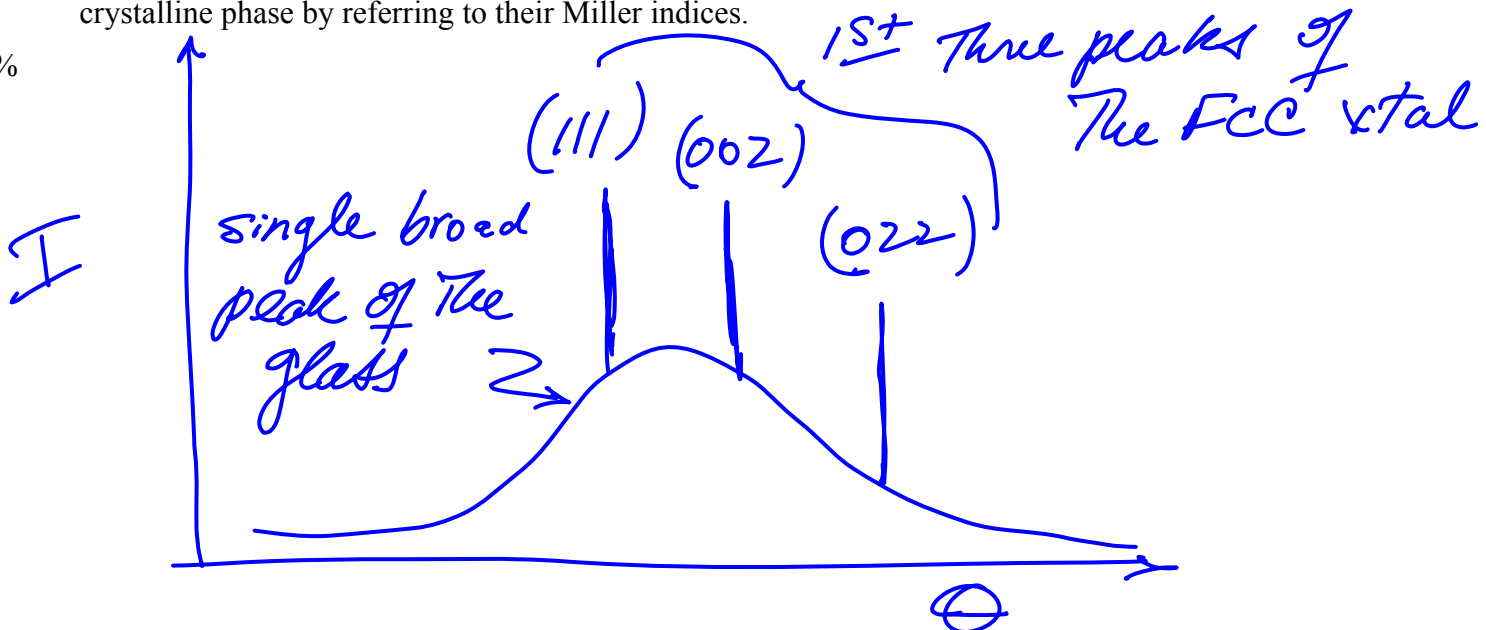
8%

Glass B.

The operative strengthening mechanism here is ion exchange which requires that the glass contain cations that can be replaced with larger cations donated by the molten salt. The only such cations present in either Glass A or B are Mg<sup>2+</sup> which can be exchanged for the larger Ca<sup>2+</sup> from the molten salt. Since Glass B contains more MgO, the degree of infusion of Ca<sup>2+</sup> is greater in that material with the result that it experiences a greater improvement in strength.

- (c) Glass B formed in part (a) is placed in an environment that causes devitrification. Sketch the x-ray diffraction pattern (*intensity (I) vs angle of reflection (θ)*) you would expect to measure for a specimen of glass B that was 50% amorphous and 50% crystalline. Assume that both phases are the same composition and that the crystalline phase is FCC. Label any three peaks associated with the crystalline phase by referring to their Miller indices.

12%



**Problem #3 (28%)**

To reduce the loss of helium, a pressure vessel is lined with a membrane made of a material through which the diffusivity of helium at 25°C is  $D_{\text{He}} = 3.091 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . The concentration at the inner surface of the membrane is maintained constant at  $4.00 \times 10^{-6} \text{ kg m}^{-3}$ . The concentration at the outer surface of the membrane is maintained constant at  $2.00 \times 10^{-6} \text{ kg m}^{-3}$ .

(a) How much helium, in kg, escapes per hour through the membrane?

DATA: membrane thickness,  $\delta = 3.091 \times 10^{-6} \text{ m}$ ; membrane area,  $A = 2.50 \text{ m}^2$

Error Function Values (provided without prejudice as to whether you need them for this question)

for values of  $\xi < 0.6$ , use the approximation  $\text{erf}(\xi) = \xi$ ;  $\text{erf}(1.0) = 0.843$   $\text{erf}(2.0) = 0.998$

14% because we have a membrane of finite thickness and concentration of diffusing species fixed at both surfaces of the membrane, assume steady state and use Fick's First Law to calculate the flux of helium through the membrane

$$\text{mass of He, } m = J A t = \left( -D \frac{dc}{dx} \right) (A) (t)$$

at steady state  $dc/dx$  can be represented by  $\Delta C / \delta$

$$\therefore m = \frac{3.091 \times 10^{-10} (4.00 - 2.00) \times 10^{-6} \times 2.50 \times 3600}{3.091 \times 10^{-6}} \quad \text{all in SI units}$$

$$= 1.80 \times 10^{-6} \text{ Kg He per hour}$$

(b) If the temperature were -20°C instead of 25°C, how would you expect the amount of leakage to differ qualitatively from what you calculated in part (a)? Explain. No calculation required.

7% the parameter affected by drop in temperature is the diffusion coefficient,  $D$ , which decreases according to the Arrhenius relationship,  $D = D_0 \exp(-Q/RT)$ .

at the lower temperature we expect the amount of leakage to be less than what was calculated in part (a)

(c) If the gas inside the pressure vessel were neon instead of helium, all other things being equal to the specification of part (a) how would you expect the amount of leakage to differ qualitatively from what you calculated in part (a)? Explain. No calculation required.

7% expect the diffusivity of Ne to be less than that of He in the same material owing to the larger atomic volume of Ne than that of He which would express itself in a lower value of diffusion coefficient for Ne than that of He

thus expect the amount of leakage with Ne to be less than that calculated in part (a)

**Problem #4 (20%)**

- (a) Which specimen, A or B, can be plastically deformed at lower applied stress? With reference to the relevant atomistics, explain why this is so.

Sample A: polycrystalline aluminum (Al) with average grain size 100  $\mu\text{m}$

Sample B: polycrystalline aluminum (Al) with average grain size 1  $\mu\text{m}$

8%

**Sample A.**

Owing to the misregistry of atoms in grain boundaries, they arrest the motion of dislocations. Thus the material with the higher density of grain boundaries will be more difficult to deform. Grain boundary density scales inversely with grain size. Thus, Sample A with its much higher grain size will be easier to deform and will require a lower applied stress for this to occur.

- (b) X-ray diffraction patterns are measured for pure silicon (Si) and the silicon - germanium alloy with the composition 80% Si - 20% Ge on an atomic basis.

(i) Do you expect to see in the pattern of the Si - Ge alloy differences in the positions of the peaks (angles of reflection) from those in the pattern of pure Si? Explain.

6%

Yes. Both Si and Ge have the same crystal structure, and the atomic size of Ge is greater than that of Si. So, alloying Si with 20% Ge is expected to result in no change of crystal structure but cause an increase in the lattice constant,  $a$ . Since the angles of reflection are determined by Bragg's Law,  $\lambda = 2d \sin \theta$ , and  $d = a/\sqrt{(h^2+k^2+l^2)}$ , it is clear that the change in lattice constant will cause a shift in peak positions.

(ii) Do you expect to see in the diffraction pattern of the Si - Ge alloy new peaks that are not present in the pattern of pure Si? Explain.

6%

No. Both Si and Ge have the same crystal structure, so alloying Si with 20% Ge will not change the crystal structure and therefore will not change the selection rules for Bragg reflection. Put another way, unless alloying with Ge can be shown to result in the addition of new planes to the parent Si crystal thereby creating new reflections or canceling existing reflections, we can expect no change in the pattern of peaks.