Test #3B
Wednesday, November 17, 2004
1:05 p.m. - 1:55 p.m.

Name:_____

(please print in UPPER CASE)

Recitation Instructor:_____

A complete test consists of 4 questions.
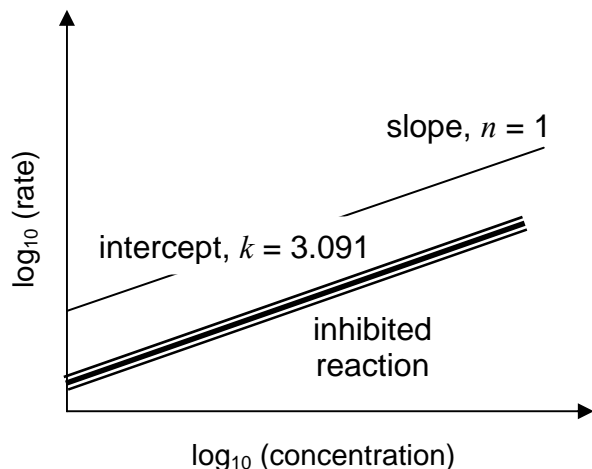
Write your answers on these pages.

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.

#1	24%	
#2	28%	
#3	28%	
#4	20%	
TOTAL	**100%**	

Problem #1 (24%)

The fictitious compound, administratium sulfide (Ad_2S), decomposes readily at temperatures exceeding 365°C. The figure above shows the kinetics of the reaction conducted at 400°C. The reaction is first order in concentration of Ad_2S. The value of the specific chemical rate constant, k, is 3.091 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 400°C for the concentration of Ad_2S to fall from 2.22 mole L^{-1} to 10% of that value. Express your answer in seconds.

14%

for a first-order rxn

$$\ln c/c_0 = -kt$$

$$\therefore t = -\frac{t}{k} \ln c/c_0$$

$$= -\frac{1}{3.091} \ln \frac{0.222}{2.22}$$

$$= 0.745 \text{ s}$$

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

6%

Problem #2 (28%)

Composition A: 25% Li_2O − 75% B_2O_3;   Composition B: 5% Li_2O − 95% B_2O_3

(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 B.

Melt B contains less Li_2O, 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 sodium chloride (NaCl) 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 A.

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 Li^+ which can be exchanged for the larger Na^+ from the molten salt. Since Glass A contains more Li_2O, the degree of infusion of Na^+ is greater in that material with the result that it experiences a greater improvement in strength.

(c) Glass A 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 A that was 50% amorphous and 50% crystalline. Assume that both phases are the same composition and that the crystalline phase is BCC. Label any three peaks associated with the crystalline phase by referring to their Miller indices.

12%
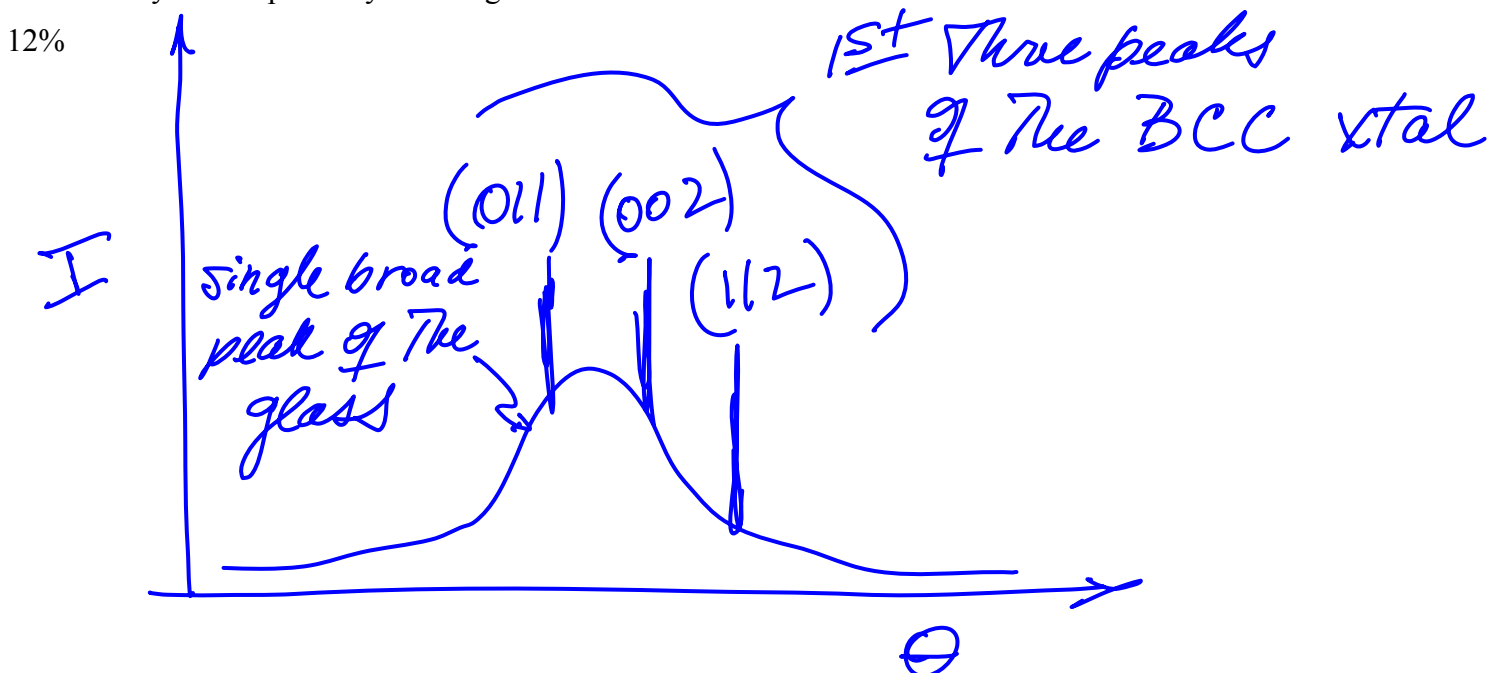
Problem #3 (28%)

To reduce the loss of argon, a pressure vessel is lined with a membrane made of a material through which the diffusivity of argon at 25°C is $D_{Ar} = 3.091 \times 10^{-11}$ m^2 s^{-1}. The concentration at the inner surface of the membrane is maintained constant at 5.00×10^{-6} kg m^{-3}. The concentration at the outer surface of the membrane is maintained constant at 1.00×10^{-6} kg m^{-3}.

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

  DATA: membrane thickness, $\delta = 3.091 \times 10^{-6}$ m;   membrane area, $A = 3.50$ 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 $erf(\xi) = \xi$; $erf(1.0) = 0.843$ $erf(2.0) = 0.998$

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 argon through the membrane

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

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

$$\therefore m = \frac{3.091 \times 10^{-11} \times (5.00 - 1.00) \times 10^{-6} \times 3.50 \times 3600}{3.091 \times 10^{-6}}$$

$$= 5.04 \times 10^{-7} \ kg \ Ar \ per \ hour$$

(b) If the temperature were 110°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 temperature rise is the diffusion coefficient, D, which increases according to the Arrhenius relationship, D = D$_o$exp(-Q/RT).

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

(c) If the gas inside the pressure vessel were neon instead of argon, 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 greater than that of Ar in the same material owing to the smaller atomic volume of Ne than that of Ar which would express itself in a higher value of diffusion coefficient for Ne than that of Ar

  thus expect the amount of leakage with Ne to be greater 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: iron - boron ($Fe_{80}B_{20}$) single crystal

  Sample B: amorphous iron - boron ($Fe_{80}B_{20}$) (metallic glass)

8%   Sample A.

Sample A is crystalline and therefore is endowed with slip systems populated with various defects including dislocations which allow slip to occur at values much lower than theoretical shear stress. In contrast, Sample B is amorphous and therefore lacks slip systems and dislocations. Thus, we expect that slip occurs in Sample B at higher value of applied shear stress in the absence of dislocations.

(b) X-ray diffraction patterns are measured for pure nickel (Ni) and the nickel - silver alloy with the composition 75% Ni - 25% Ag on an atomic basis.

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

6%   Yes. Both Ni and Ag have the same crystal structure, and the atomic size of Ag is greater than that of Ni (look at the atomic volume in the periodic table). So, alloying Ni with 25% Ag 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 Ni - Ag alloy new peaks that are not present in
    the pattern of pure Ni? Explain.

6%   No. Both Ni and Ag have the same crystal structure, so alloying Ni with 25% Ag will not change the crystal structure and therefore will not change the selection rules for Bragg reflection. Put another way, unless alloying with Ag can be shown to result in the addition of new planes to the parent Ni crystal thereby creating new reflections or canceling existing reflections, we can expect no change in the pattern of peaks.