3.091 OCW Scholar – Fall 2010

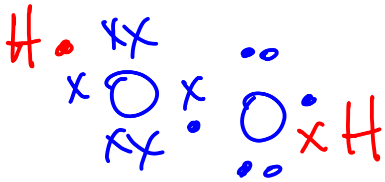
Final Exam - Solutions Key

Prof. Donald R. Sadoway, Instructor

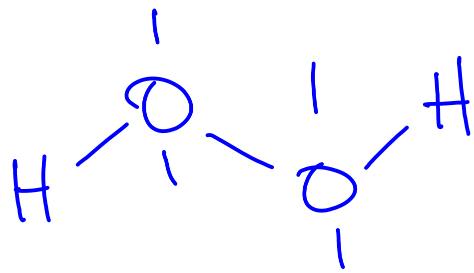
Problem #1 (20 points)

Answer the following questions about the hydrogen peroxide (H_2O_2).

(a) Draw the Lewis structure of H_2O_2.

3 

(b) Draw a 3-dimensional representation of the molecular geometry of the molecule.

3 

(c) Name the geometry of the electron distribution about the oxygen atoms.

1 tetrahedral

(d) Determine the per cent ionic character of the O–H bond.

3 $\chi_O = 3.44 \quad \chi_H = 2.20 \quad \therefore \Delta\chi = 1.24 \Rightarrow$

% ionic character $= \left[1 - \exp\left\{-\frac{1}{4}(\Delta\chi)^2\right\}\right] \times 100 = 32\%$

(e) Is the molecule polar or nonpolar? Explain.

3 non polar – symmetric disposition of polar bonds

(f) Calculate the maximum wavelength of a beam of α-particles (He nuclei) capable of breaking the O–H bond in H_2O_2.

DATA: Average Bond Energies (kJ/mol)

O–O	142
H–H	432

7 $E_{OH} = \sqrt{E_{O-O} \times E_{H-H}} + 96.3(\chi_O - \chi_H)^2 = \sqrt{(142 \cdot 432)} + 96.3(1.24)^2$

$= 248 + 148 = 396 \text{ kJ/mol} / N_{AV} = 6.57 \times 10^{-19} \text{ J/bond}$

$E_\alpha = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = E_{bond} \Rightarrow \lambda = \frac{h}{(2mE)^{1/2}}$

$\therefore \lambda_\alpha = \frac{6.6 \times 10^{-34}}{\left(2 \times \frac{4 \times 10^{-3}}{6.02 \times 10^{23}} \times 6.57 \times 10^{-19}\right)^{1/2}} = 7.06 \times 10^{-12} \text{ m}$

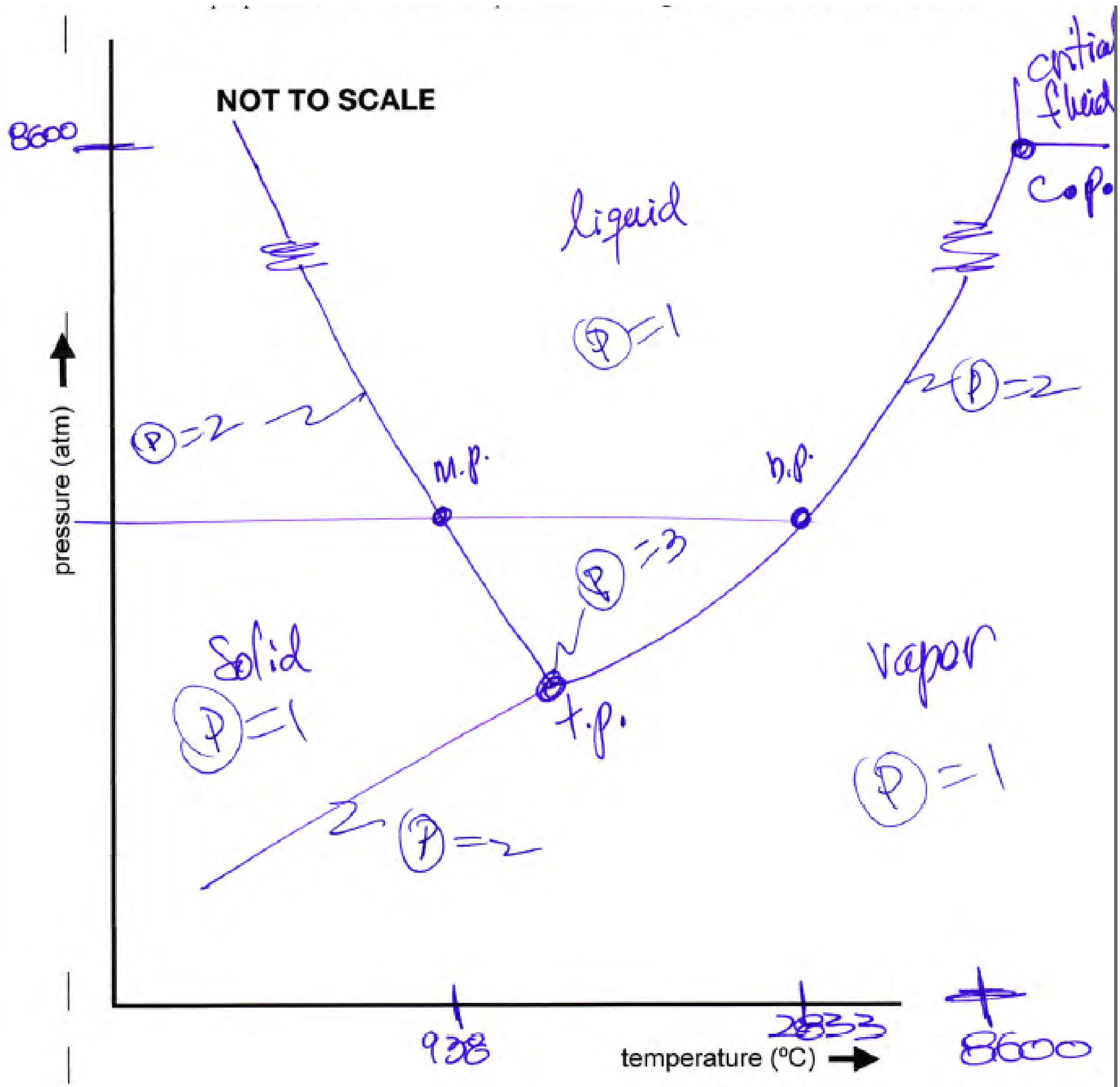
Problem #2 (9 points)

(a) Sketch the unary phase diagram (pressure *vs* temperature) of germanium (Ge). Indicate the normal melting point (P = 1 atm), normal boiling point, triple point, and critical point. Label all phase fields. On the diagram label ***one example of each***: (i) one-phase stability; (ii) two-phase coexistence; (iii) three-phase coexistence. For clarity, do not draw to scale.

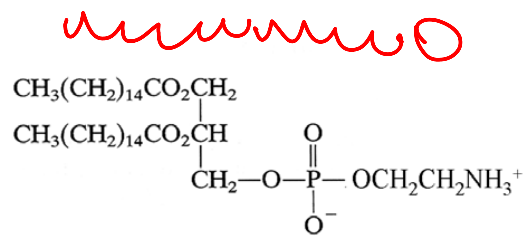
DATA: at the melting point, the density of the solid, $\rho_s = 5.32 \text{ g cm}^{-3}$
the density of the liquid, $\rho_\ell = 5.63 \text{ g cm}^{-3}$

critical point: P = 8600 atm, T = 8600ºC

triple point: no data – estimate its position on the diagram based on available information

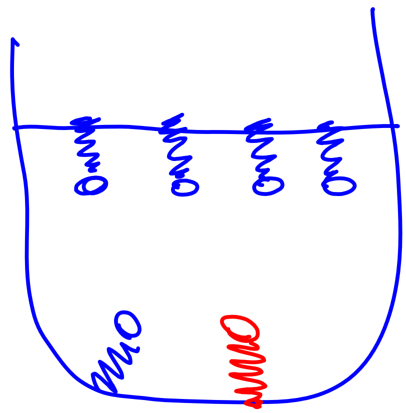


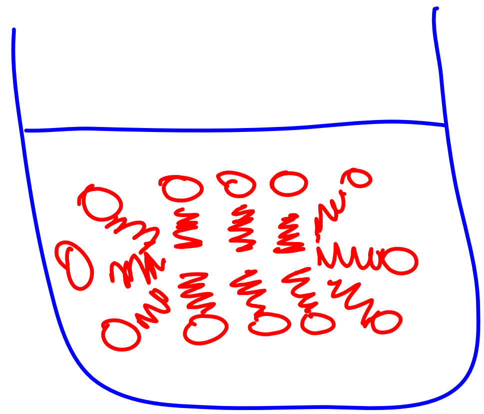
Problem #3 (10 points)



(a) To a beaker containing water at neutral pH the phospholipid, phosphatidylethanolamine, (chemical formula given at right) is added in sufficient quantity to enable interaction between phospholipid molecules. Draw a cartoon depicting one possible molecular arrangement that results. You may stylize parts of the phosphatidylethanolamine molecule, e.g., let  represent a hydrocarbon chain.

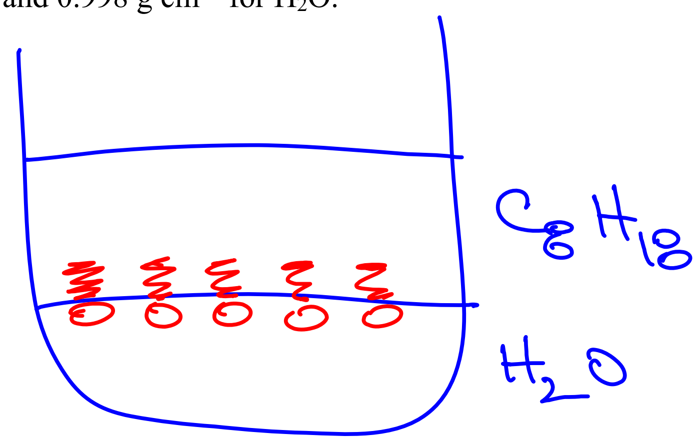
3





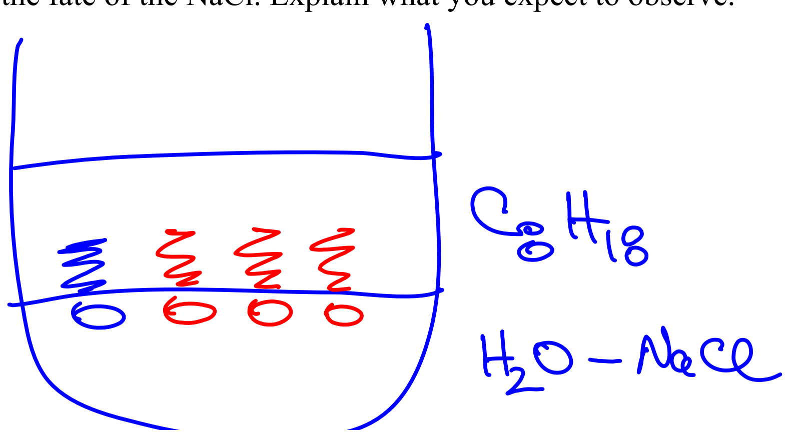
(b) To the beaker described in part (a) an equal volume of octane (C_8H_{18}) is added. The mixture of H_2O - C_8H_{18} containing the phosphatidylethanolamine is then subjected to vigorous agitation for several minutes and then allowed to equilibrate. Draw a schematic representation depicting one possible molecular arrangement that results. At 20ºC the values of density are 0.912 g cm^{-3} for C_8H_{18} and 0.998 g cm^{-3} for H_2O.

3

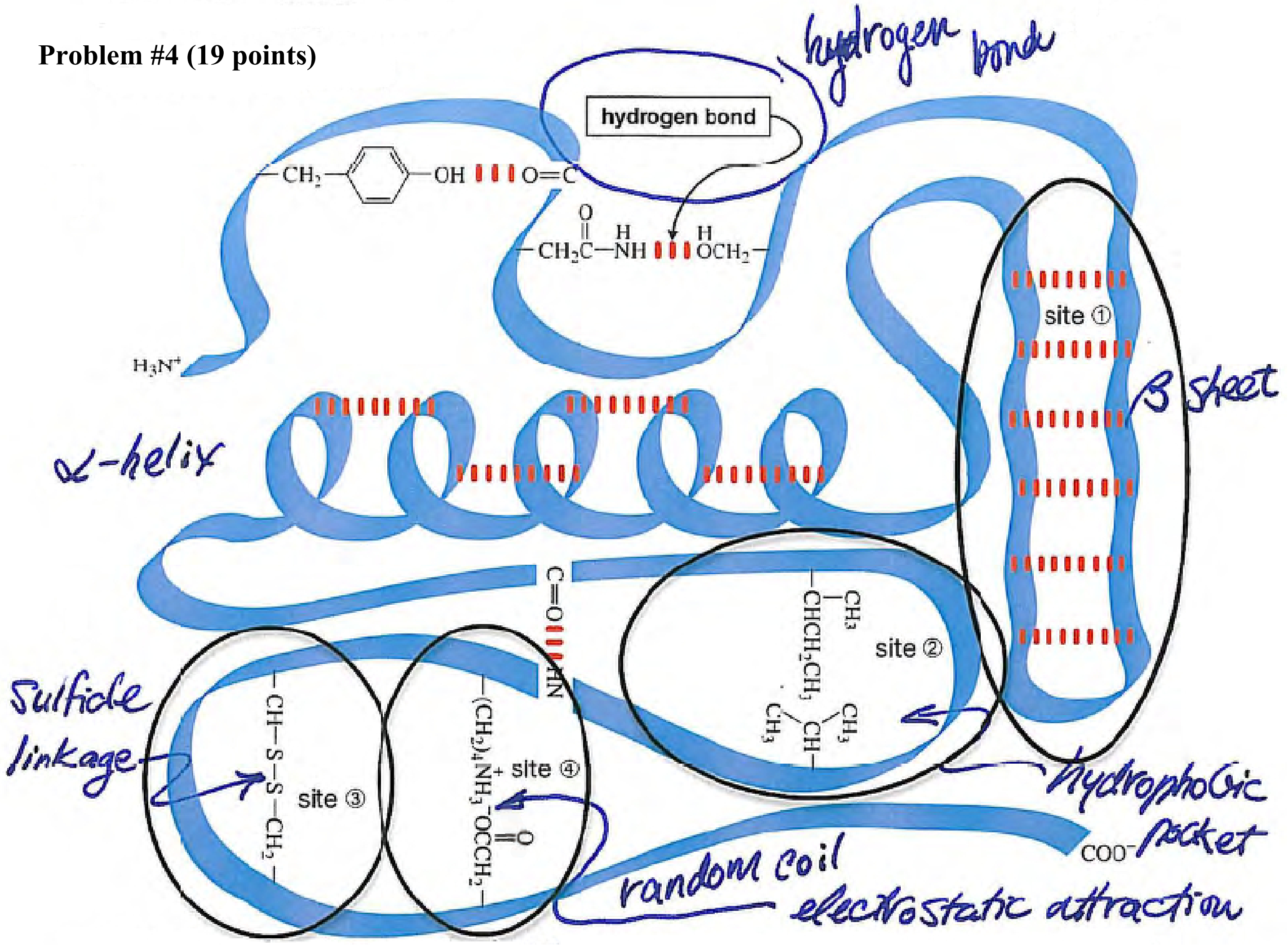


(c) To the beaker described in part (b) a small amount of sodium chloride (NaCl) is added and the mixture is then subjected to vigorous agitation for several minutes and then allowed to equilibrate. Draw a schematic representation depicting one possible molecular arrangement that results. Indicate the fate of the NaCl. Explain what you expect to observe.

4



Problem #4 (19 points)



(a) The sketch above is a schematic of a protein. On the sketch, label one example of each of the ***three*** types of secondary protein structures.

3

(b) On the sketch, label one example of each of ***four*** types of interactions that establish the tertiary structure of this protein.

4

(c) At each numbered site, name one ***chemical*** change to the environment (no change of temperature) of the protein that would destabilize the associated feature of the tertiary structure. Explain the relevant chemistry.

① Change of pH. Addition of protons would break the H-bonds and release the connection.

12

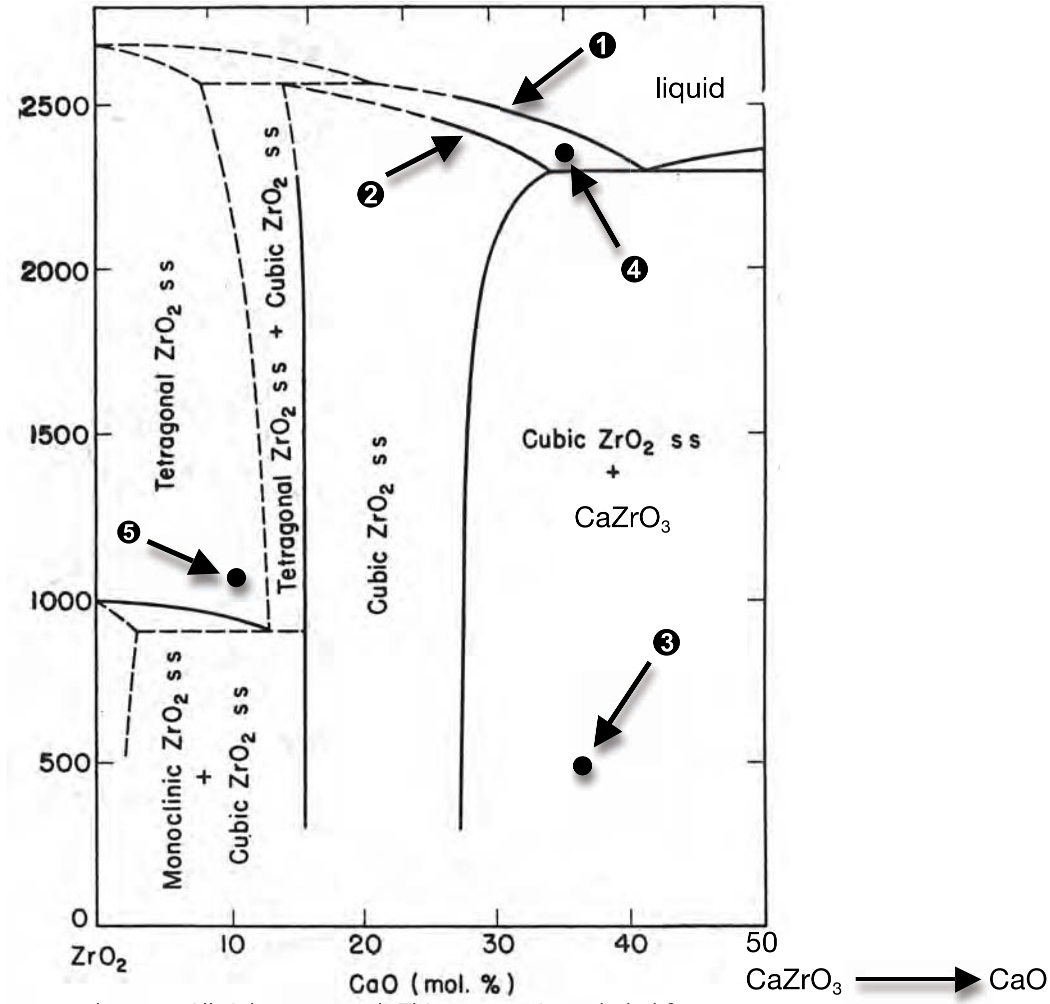
② Introduction of detergents. Hydrophobic tails bond to aliphatic groups while hydrophilic heads bond to water. This destablilizes the hydrophobic pocket and opens up the hairpin turn in the backbone.

③ Introdcution of reducing agents that would break the disulfide linkage.

④ Introduction of salts that would dissociate into ions which break the electrostatic attraction at the site.

Problem #5 (23 points)

The phase diagram of the binary system, zirconia - calcia (ZrO_2 - CaO) is given below.



6 (a) For the lines labeled on the diagram above as ❶ and ❷ (i) name the line, and (ii) write the equilibrium it represents.

❶ liquidus: liquid → liquid + solid cubic ZrO_2 ss

❷ solidus: solid cubic ZrO_2 ss → solid cubic ZrO_2 ss + liquid

9 (b) At each of the temperature-composition pairs labeled on the diagram above, (i) identify all phases present at equilibrium and (ii) give the composition of each phase present, expressed in mole % CaO.

❸ cubic ZrO_2 ss + $CaZrO_3$: cubic ZrO_2 ss (27% CaO) + $CaZrO_3$ (50% CaO)

❹ liquid + cubic ZrO_2 ss: liquid (38% CaO) + cubic ZrO_2 ss (30% CaO)

❺ tetragonal ZrO_2 ss: 10% CaO

Problem #5 (continued from previous page)

(c) The phase diagram on the previous page shows only the ZrO_2-rich half of the composition range. Rationalize the fact that the melting point of ZrO_2 exceeds that of CaO.

DATA:	ion	Ca^{2+}	Zr^{4+}	O^{2-}
	ionic radius (Å)	1.00	0.88	1.38

4

m.p. scales w/ binding energy which here is the ionic bond or Madelung energy or xtallization E

$\Rightarrow E_{ZrO_2}$ vs E_{CaO} : compare $\frac{z_1 z_2}{4\pi\epsilon_0(r_+ + r_-)}$

let $z_2 = 2-$ for O^{2-}

so ~~for~~ CaO $\frac{(2)(-2)}{4\pi\epsilon_0(1.00+1.38)}$ ①

~~for~~ ZrO_2 $\frac{(4)(-2)}{4\pi\epsilon_0(0.88+1.38)}$ ②

② more negative than ①

$\therefore$ ② has higher m.p.

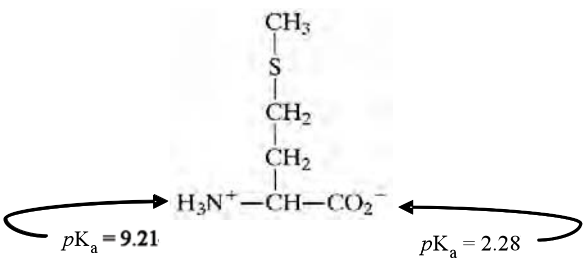
(d) The dominant defect in ZrO_2 is the Schottky disorder. Write the defect incorporation reaction associated with the dissolution of CaO into ZrO_2.

4

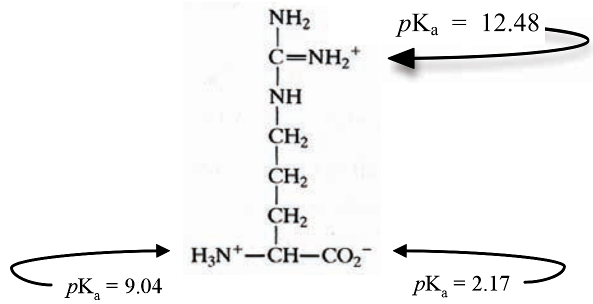
$$CaO \xrightarrow{ZrO_2} Ca_{Zr}'' + O_O^{\times} + V_O^{\bullet\bullet}$$

Problem #6 (22 points)

The skeletal structures of the two amino acids, methionine and arginine, are given below along with the values of the relevant acid dissociation constants (pK$_a$).



methionine (Met)



arginine (Arg)

(a) For an aqueous solution of methionine (Met) alone, calculate the value of pH at which the ratio of the concentration of neutral Met zwitterion to the concentration of protonated cation is 3.091×10^2.

4

$HA + H^+ = HAH^+$

$K_{a_1} = \frac{[H^+][HA]}{[HAH^+]}$

$\therefore pK_{a_1} = pH + \log_{10} \frac{[HAH^+]}{[HA]}$

$\therefore pH = pK_a + \log_{10} [HA]/[HAH^+]$

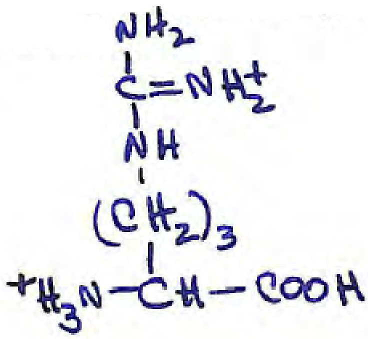
$pH = 2.28 + \log_{10}(3.091 \times 10^2)$

$= 2.28 + 2.49$

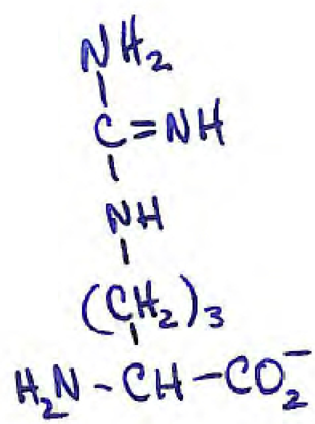
$= 4.77$

(b) Draw the skeletal structure of arginine (Arg) when it is solvated in an aqueous solution under each of the following conditions.

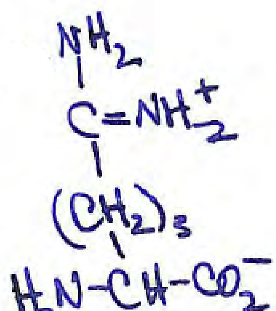
6 (i) pH = 1.5



(ii) pH = 14



(iii) pH = pI, the isoelectric point



Problem #6 (continued)

(c) Calculate the value of *p*H at which arginine (Arg) exists as the neutral zwitterion.

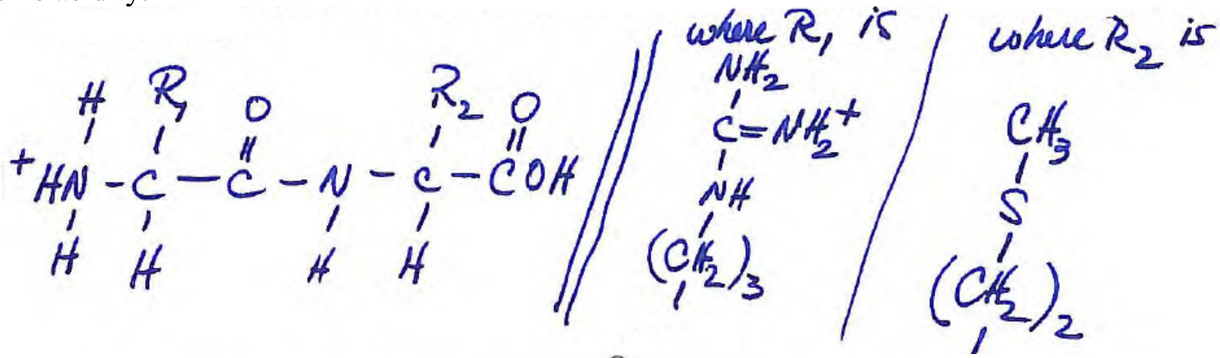
with a titratable R-group, the pH must be set at the midpoint between pKa values of the two amino groups

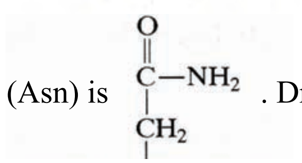
5 in order to get a net charge of +1 which balances the charge of −1 on the COO$^-$

$$\Rightarrow pI = \frac{12.48 + 9.04}{2} = 10.76$$

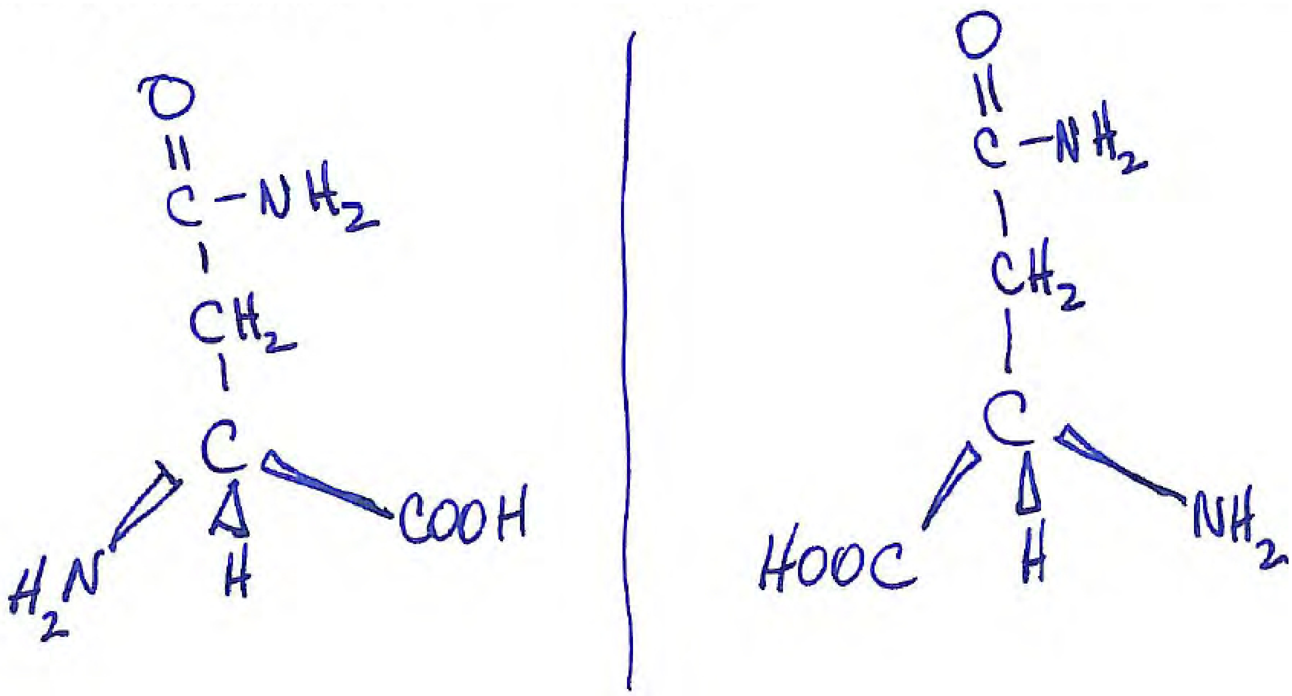
(d) Draw the skeletal structure of the dipeptide, Arg-Met, when it is solvated in an aqueous solution of extreme acidity.

3



(e) The substituent or R-group of asparagine (Asn) is  . Draw both enantiomers of Asn. You need not be able to label them.

4



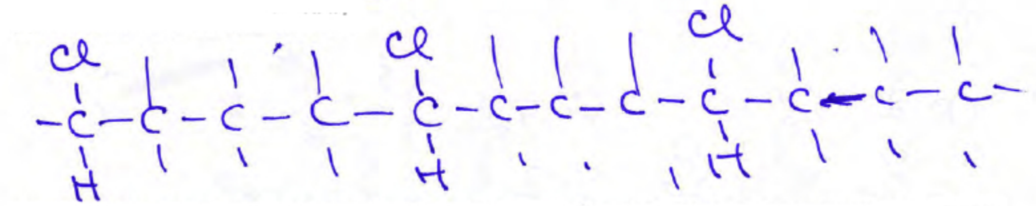
Problem #7 (13 points)

2-Chlorobutene, $ClHC{=}CH{-}CH_2{-}CH_3$, can be reacted to form isotactic polychlorobutene (PCB).

(a) Does the reaction occur by addition or condensation? Circle your answer.

1 (b) Draw a trimer of isotactic PCB.

2



(c) What is the value of the degree of polymerization, n, of isotactic PCB with a molecular weight of 3.091×10^5 g mol^{-1}?

3

$4C = 4 \times 12 = 48$
$7H = 7 \times 1 = 7$
$1Cl = 35.45 = 35.45$
$\overline{90.45}$

$n = \dfrac{3.091 \times 10^5}{90.45} = \underline{3417}$

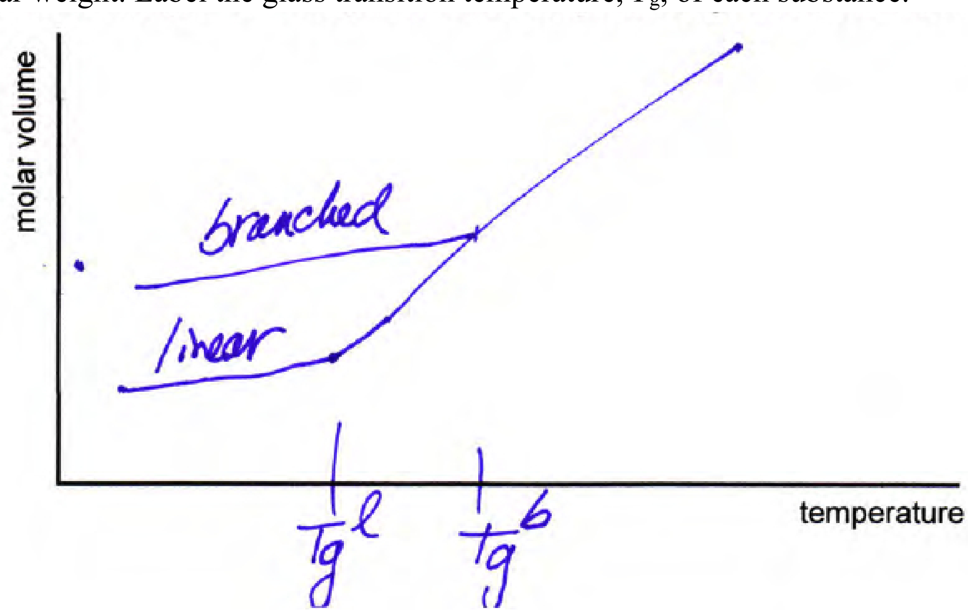
(d) Is isotactic PCB a thermoset or a thermoplastic? Explain.

Thermoplastic. Weak van der Waals bonds connect strands.

3

(e) On the graph below, draw a schematic representation of the temperature dependence of the molar volume of linear isotactic PCB and of branched isotactic PCB, assuming both to be of comparable molecular weight. Label the glass transition temperature, T_g, of each substance.

4



Problem #8 (12 points)

For each of the following types of defect, (1) give one example, (2) name one material property that is affected, and (3) briefly explain how the chosen defect causes the effect.

(i) 0-dimensional defect

Vacancy -- diffusivity

Impurity -- strength, electrical conductivity

(ii) 1-dimensional defect

Dislocation -- strength

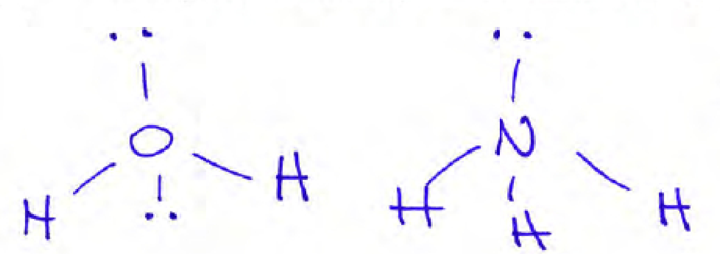
(iii) 2-dimensional defect

Grain boundary -- strength

Problem #9 (11 points)

(a) The normal boiling point is 100°C for H_2O and –33.3°C for NH_3, even though the two molecules have almost identical atomic weights. Explain this discrepancy, using narrative or cartoons or both, making reference to the operative chemical bonding.

6



H_2O has 2 NB pair
NH_3 has 1 NB pair
∴ H_2O has more H-bonding capability ⇒ higher b.p.

(b) Indium antimonide (InSb) is a compound semiconductor with a band gap energy, E_g, of 0.17 eV. The value of E_g can be increased by forming a solid solution of InSb and a compound semiconductor that has a larger band gap energy. Name one such compound semiconductor and justify your choice by making reference to the operative chemical bonding.

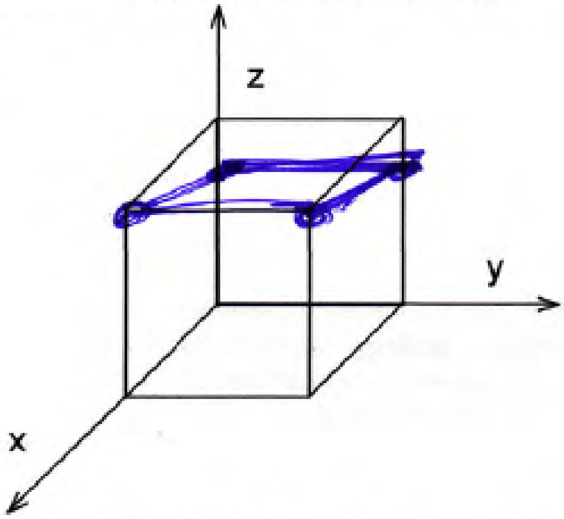
5

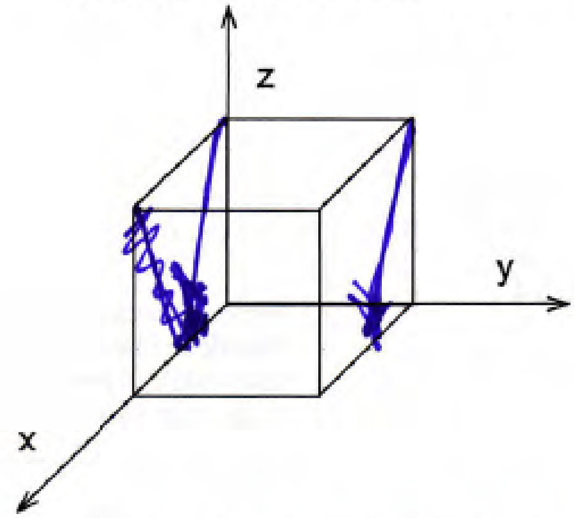
Choose InAs or InP.
As and P are smaller; thus the bond with In is stronger, so E_g is greater.

Problem #10 (12%)

(a) (i) In the cubic unit cell below sketch $(10\bar{3})$. (ii) In the cubic unit cell below sketch $[10\bar{3}]$.

6

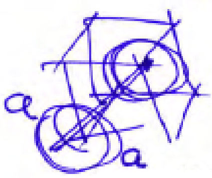




(b) Named after Salvadore Dali, dalium (Da) is BCC. Its molar volume is 9.99 cm^3 mol. Calculate the linear packing density along [011] in Da. Express your answer in atoms cm^{-1}.

6

$$\frac{2}{a^3} = \frac{N_{Av}}{V_m} \therefore a = \left(\frac{2V_m}{N_{Av}}\right)^{1/3} = \left(\frac{2\times 9.99}{6.02\times10^{23}}\right)^{1/3} = 3.21\times10^{-8}\text{ cm}$$

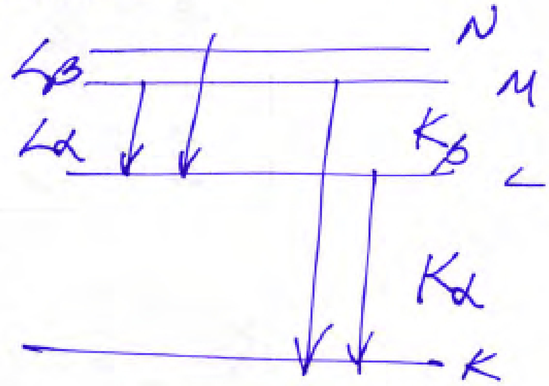


$$\frac{1\text{ atom}}{\sqrt{2}a} = \frac{1\text{ atom}}{\sqrt{2}\times 3.21\times10^{-8}\text{ cm}} = 2.20\times10^{7}\text{ atom/cm}$$

Problem #11 (13%)

(a) Draw the energy-level diagram of the target (anode) of an x-ray tube operating at a plate voltage great enough to generate the characteristic lines. Indicate the features associated with emission of ❶ K_α, ❷ K_β, ❸ L_α, and ❹ L_β radiation. The drawing need not be to scale but should reflect qualitative distinctions in magnitudes of transition energies.

8



(b) An x-ray tube fitted with tantalum (Ta) target is emitting radiation at a wavelength of 1.52×10^{-10} m. Is this the wavelength of the K_α line or the L_α line? Support your answer with calculations.

5

use Moseley's Law: $\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)(Z-\sigma)^2$

for K_α $\frac{1}{\lambda} = R\frac{3}{4}(Z-1)^2 \Rightarrow \lambda = \left(1.1\times10^7\times\frac{3}{4}(73-1)^2\right)^{-1} = 2.34\times10^{-11}$ — no good

for L_α $\frac{1}{\lambda} = R\frac{5}{36}(Z-7.4)^2 \Rightarrow \lambda = \left(1.1\times10^7\times\frac{5}{36}(73-7.4)^2\right)^{-1} = \underline{1.52\times10^{-10}\text{ m}}$