NAME: ____________________

Key

CHEM 584 "Materials Chemistry"
Fall 2008

Professor Kenneth S. Suslick

Midterm Exam

8 Questions on 7 Pages, including this one.

100 points as indicated. Look through the exam first to balance your time allocations. Try to use the space provided; short but complete answers are best.

Mark all answers directly on the test itself.

atomic number → 26
Fe
55.85 ← atomic mass

1A	2A											3A	4A	5A	6A	7A	8A
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac† (227)	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

lanthanides*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
actinides†	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Supplementary Information

$1\ \text{Å} = 10^{-10}$ m

$c = \lambda\nu$

$E = h\nu$

$h = 6.626 \times 10^{-34}$ J s

$V = IR$

$e = 1.6 \times 10^{-19}$ C

$\mu = 2.83\ (\chi_m T)^{1/2}$ BM $= [n(n+2)]^{1/2}$ BM

$1\ \text{eV} = 1.6 \times 10^{-19}$ J

R(Hall) = 1/ne

C = A s

E(eV) = (1242 eV nm)/(λ nm)

Bragg equation: $2d\sin\theta = n\lambda$

Cu radiation wavelength = 1.5418 Å

$t(\text{Å}) = 0.9\lambda/(B\cos\theta)$

Radius Ratio Rule

coordination	ratio range	Possible structures
4	0.225 to 0.414	zinc blende, wurtzite
6	0.414 to 0.732	sodium chloride, rutile, nickel arsenide
8	0.732 to 1.0	cesium chloride, fluorite

Ionic radii (Å)

Zr^{4+}	0.87	O^{2-}	1.32
Se^{2-}	1.91	Ni	1.15
Al	1.25	Si	1.17
Ge	1.22		

1. a) **Explain the difference between Physical Vapor Deposition and Chemical Vapor Deposition. (5 pts)**

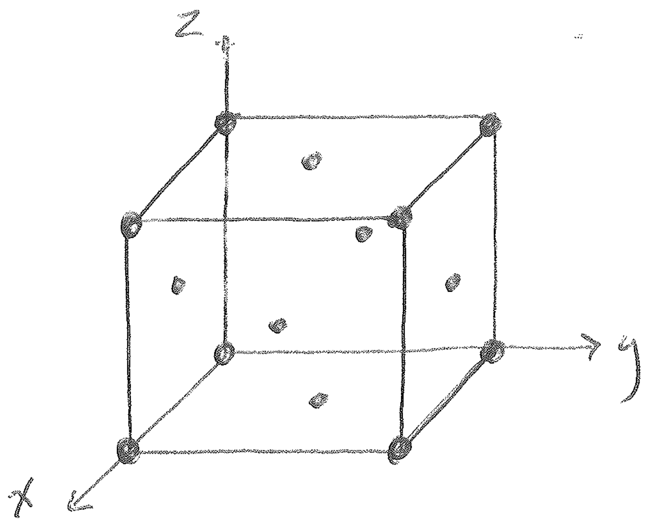
Physical vapor deposition relies on atoms from the source material being physically removed whether by sputtering or evaporation. Consequently, deposition of the material does not rely on chemical reactions and the chemical composition of the source material remains unchanged as it is deposited on the target substrate.

Chemical vapor deposition relies on a reactive precursor that is introduced into the system. The precursor is activated and relies on the subsequent reaction with the surface of the target substrate.

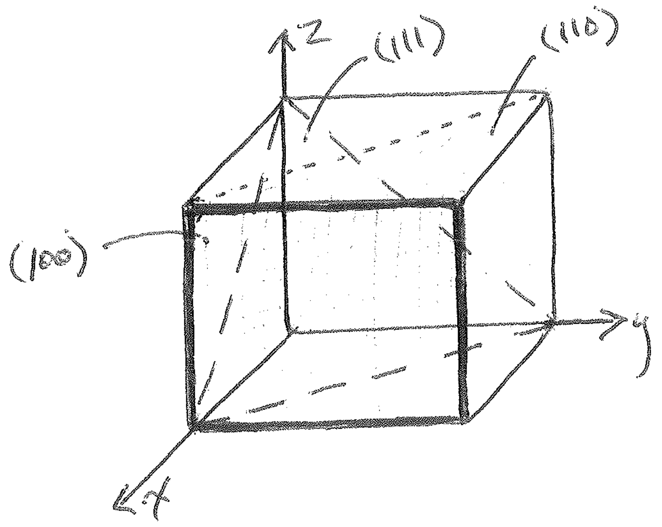
b) **Name one type of CVD, describe how it works, and provide a labeled drawing of the apparatus. (5 pts)**

c) **Name one type of PVD, describe how it works, and provide a labeled drawing of the apparatus. (5 pts)**

2) a) Draw the unit cell of an FCC crystal structure clearly identifying all axes. (5 pts)



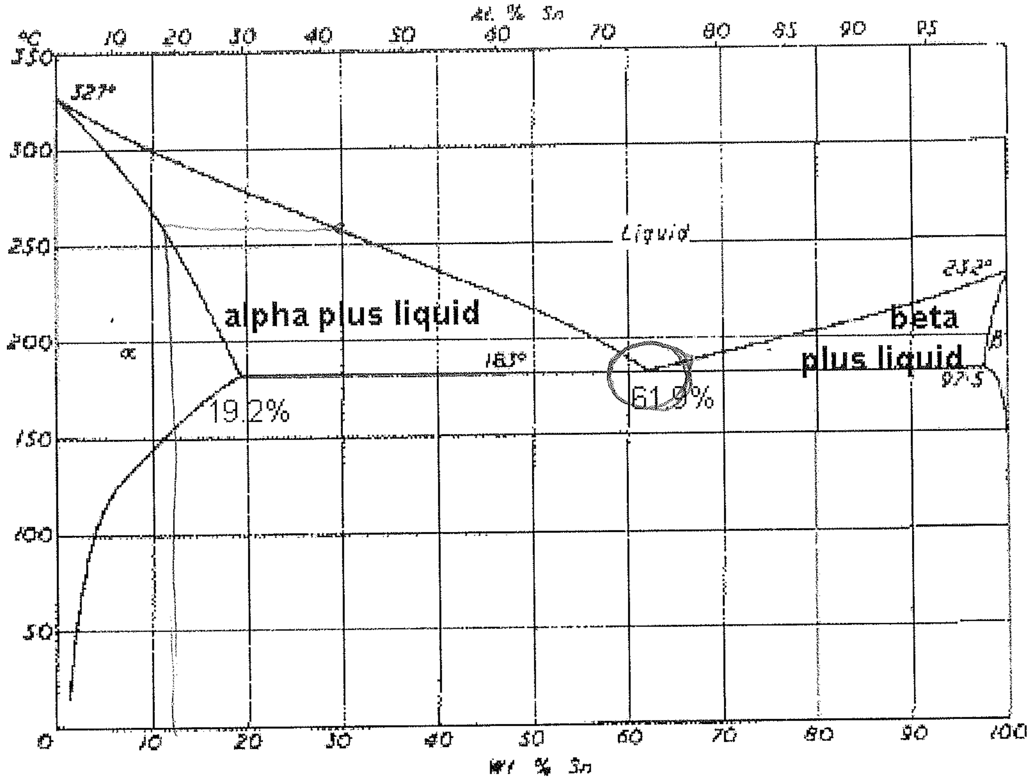
b) Separately show the planes (100), (110), and (111). (6 pts)



c) Based on your knowledge of planar density, state which plane you expect to be more reactive and why. (4 pts)

The surface energy for a crystallographic plane will depend on its packing density – that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in the plane that are satisfied, and, consequently, the lower the surface energy. The (110) plane has the lowest planar density resulting in the highest surface energy therefore it is the most reactive.

3. For the following questions use the lead tin phase diagram shown below. The starting temperature of each question below is 350 °C. If you have to calculate an answer, show your work. If you read the answer directly from the phase diagram, just say so.

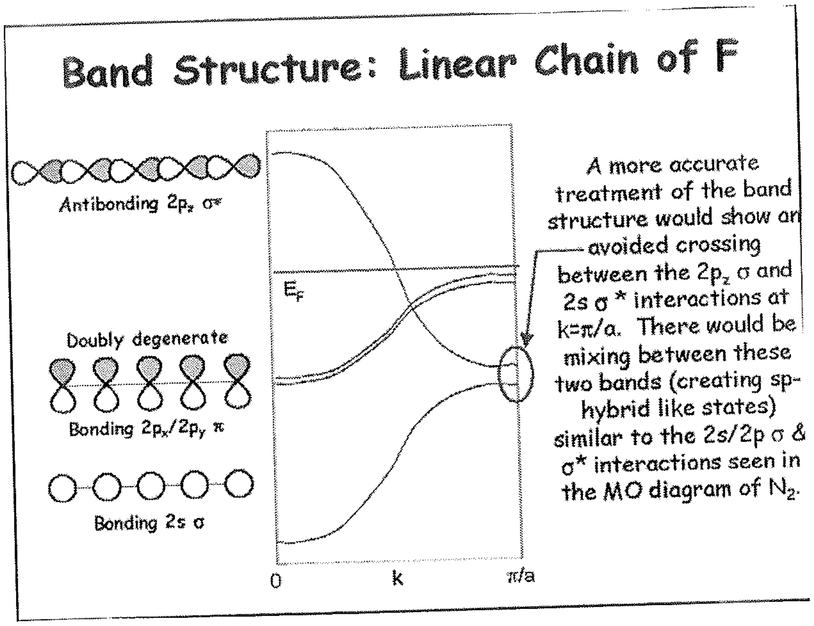


a) Consider a sample that is 30 wt% Sn: upon cooling, what will be the composition of the first solid phase that appears? [7 pts]

Cooling a 30 wt% Sn/ 70 wt% Pb sample results in the formation of the first solid phase, α, at ~255°C. This phase will contain ~12 % Sn.

b) Circle the eutectic point(s) on the above phase diagram. [3 pts]

4. **Draw the valence band structure of a linear chain of fluorine atoms. Be sure to label each band. (16 pts).**



Band Structure: Linear Chain of F

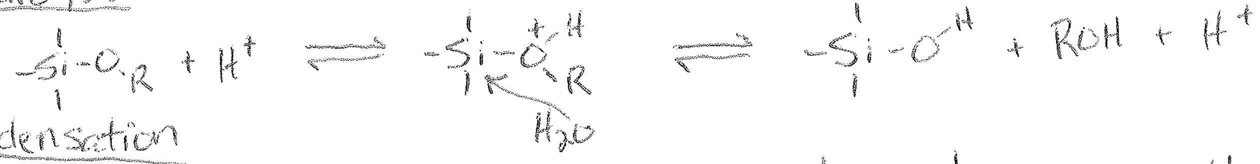
A more accurate treatment of the band structure would show a avoided crossing between the $2p_z$ σ and 2s σ* interactions at k=π/a. There would be mixing between these two bands (creating sp-hybrid like states) similar to the 2s/2p σ & σ* interactions seen in the MO diagram of N_2.

5. **For sol-gel chemistry, what are the two competing mechanisms in metal oxide formation from metal alkoxides and how do their rates compare? Draw the chemical reactions. (16 pts)**

The two competing mechanisms in metal oxide formation from metal alkoxides are acid catalysis and base catalysis. Base catalysis results in faster reactions due to OH^- and R_3SiO^- being better nucleophiles. As a result, base catalyzed systems form dense, highly branched networks while acid catalyzed systems form porous, bushy networks.

Acid Catalyzed

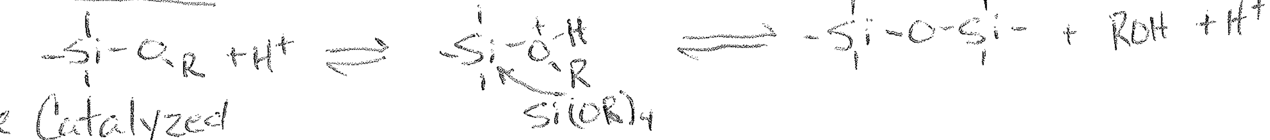
Hydrolysis



$$\mathrm{-Si-O-R + H^+ \rightleftharpoons -Si-\overset{+}{O}(H)-R \rightleftharpoons -Si-O-H + ROH + H^+}$$

H_2O

Condensation

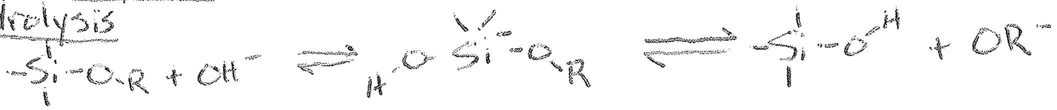


$$\mathrm{-Si-O-R + H^+ \rightleftharpoons -Si-\overset{+}{O}(H)-R \rightleftharpoons -Si-O-Si- + ROH + H^+}$$

$Si(OR)_4$

Base Catalyzed

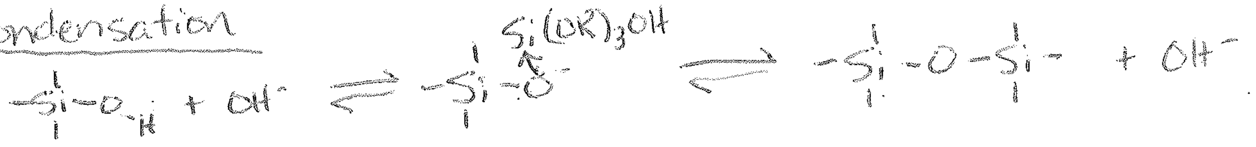
Hydrolysis



$$\mathrm{-Si-O-R + OH^- \rightleftharpoons H-O-Si-O-R \rightleftharpoons -Si-O-H + OR^-}$$

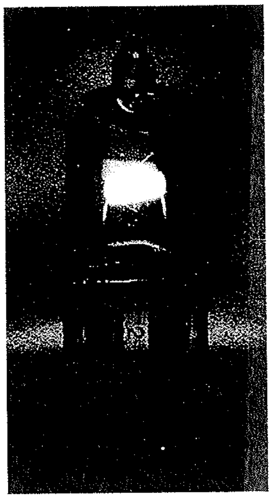
Condensation

$Si(OR)_3OH$



$$\mathrm{-Si-O-H + OH^- \rightleftharpoons -Si-O^- \rightleftharpoons -Si-O-Si- + OH^-}$$

6. What is the role of halogen in a tungsten halogen light bulb? Write the appropriate chemical reactions. **(8 pts)**



The tungsten filament will sublimate upon resistive heating thereby shortening the lifetime of the bulb. Halogen present in the bulb will react with the gaseous tungsten forming a volatile tungsten halide. The halide will decompose upon contact with the hot filament releasing solid tungsten and regenerating the halogen, making the system catalytic in halogen.

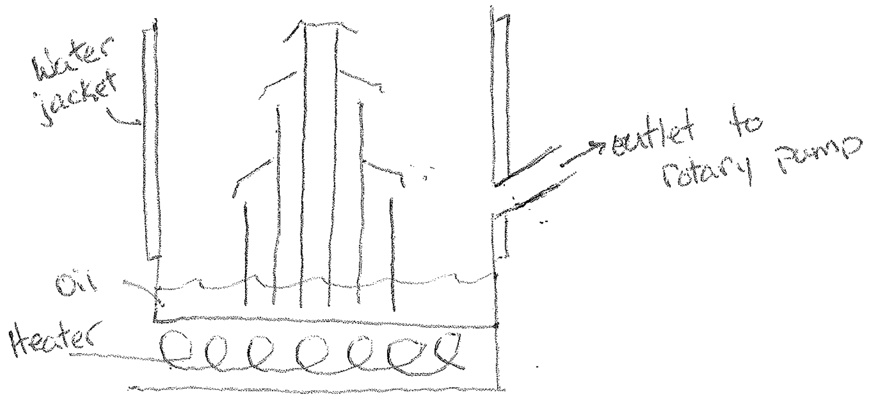
$$W_{(s)} \xrightarrow{heat} W_{(g)}$$

$$W_{(g)} + I_2 \longrightarrow WI_{2(g)}$$

$$WI_{2(g)} \xrightarrow{heat} W_{(s)} + I_2$$

7. How does a diffusion pump work? Sketch and describe. (10 pts)

A diffusion pump utilizes a heavy oil that is heated. Upon heating, the oil evaporates and the oil vapor moves up a set of concentric tubing and is redirected downward. The vapor collides with lighter gas molecules in the chamber and transfers downward momentum to the small molecules. The gas molecules are then pumped from the system by a secondary pump as the oil vapor is condensed on the side walls where it can then be reused.



8. Given the data in the table below:

Diffusing Species	*Host Metal*	$D_0(m^2/s)$	*Activation Energy* Q_d	
			kJ/mol	*eV/atom*
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94
C	α-Fe	6.2×10^{-7}	80	0.83
C	γ-Fe	2.3×10^{-5}	148	1.53

a) In which phase of Fe does carbon diffuse more quickly and why? (5 pts)

Carbon diffuses more quickly in the γ-Fe phase which has an FCC structure. The FCC structure has octahedral holes that are of the right size (Fe – C distance all equal to 1.7 Å) to accommodate carbon where the sites in the BCC structure have two distances that are too short (~1.4 Å) or too long (~2.0 Å). Due to a high energy cost to fit the carbon in the BCC structure, carbon diffusion in FCC is faster.

b) What is the mechanism of carbon diffusion in solid iron? (5 pts)

Carbon diffuses in iron via interstitial diffusion. The FCC structure has octahedral holes that are of the right size (Fe – C distance all equal to 1.7 Å) to accommodate carbon.