Chemistry 20B, Winter 2017, Sections 2 & 3, Midterm #2
2 March 2017
5 questions + 2 small extra credit problems, 8 pages.
Answer on these sheets only. Additional space on last page.
If you need extra sheets, please ask your proctor or TA.
If you continue a problem on an additional page, please indicate that on the original problem page.
Note: Only these papers can be used; no other notes are allowed.

1) 8
2) 20
3) 22
4) 17
5) 16
EC1+2) 1

Please answer each question concisely. Show your calculations.
You may (and in some cases, must) draw explanatory diagrams.
Label all axes and features on graphs and diagrams.

You may not use a calculator, computer, watch, smart device, or electronics of any sort.
Irrelevant and/or incorrect material will result in loss of points.
➔ **Only exam answers in pen will be considered for regrading.**

Table of constants and conversions
Speed of light: $c = 3 \times 10^8$ m/s
Faraday constant = 96500 coul/mole
Electron charge magnitude: $e = 1.6 \times 10^{-19}$ C
Plank's constant: $\hbar = 1.1 \times 10^{-34}$ J-s
Gas constant: R = 0.08206 L-atm/mol-K = 8.314 J/mol-K = 1.987 cal/mol-K
Boltzmann constant: $k_B = 1.4 \times 10^{-23}$ J/K
Electron rest mass: $m = 9.1 \times 10^{-31}$ kg
Proton rest mass: $M = 1.7 \times 10^{-27}$ kg
1 mole = 6.02×10^{23}

Energy Conversion Table

	eV	cm^{-1}	kcal/mol	kJ/mol	K	J	Hz
eV	1	8 065.73	23.060 9	96.486 9	11 604.9	1.602 10 x 10^{-19}	2.418 04 x 10^{+14}
cm^{-1}	1.239 81 x 10^{-4}	1	0.002 859 11	0.011 962 7	1.428 79	1.986 30 x 10^{-23}	2.997 93 x 10^{+10}
kcal/mol	0.043 363 4	349.757	1	4.18400	503.228	6.95 x 10^{-21}	1.048 54 x 10^{+13}
kJ/mol	0.010 364 10	83.593	0.239001	1	120.274	1.66 x 10^{-21}	2.506 07 x 10^{+12}
K	0.000 086 170 5	0.695 028	0.001 987 17	0.008 314 35	1	1.380 54 x 10^{-23}	2.083 64 x 10^{+10}
J	6.241 81 x 10^{+18}	5.034 45 x 10^{+22}	1.44 x 10^{+20}	6.02 x 10^{+20}	7.243 54 x 10^{+22}	1	1.509 30 x 10^{+33}
Hz	4.135 58 x 10^{-15}	3.335 65 x 10^{-11}	9.537 02 x 10^{-14}		4.799 30 x 10^{-11}	6.625 61 x 10^{-34}	1

$\Delta G° = -nFE° = -2.303\ RT \log_{10}K_{eq}$

$pH = pK_a - \log_{10}([HA]/[A^-])$

You will find a periodic table for your reference on the next page.

Name ______________ Section # ____

Question 1 (10 points):

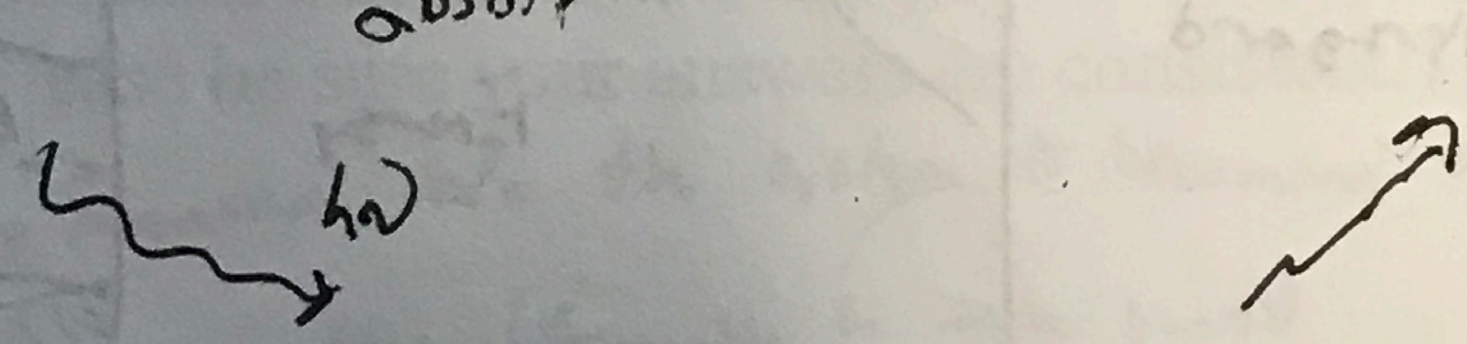
a) Which of the following photons have sufficient energy to break typical covalent chemical bonds? (8 points)
X-rays, microwaves, visible, infrared

X-rays carry enough energy (≈ 1000 eV) to break covalent bonds which usually exist from 1-10 eV (usually smaller)

+8

b) With what molecular transitions are the photons you selected in (a)? (2 points)
associated with

absorptions



An X ray photon will have the energy of ≈ 1000 eV (1 keV) which pertains to its transition.

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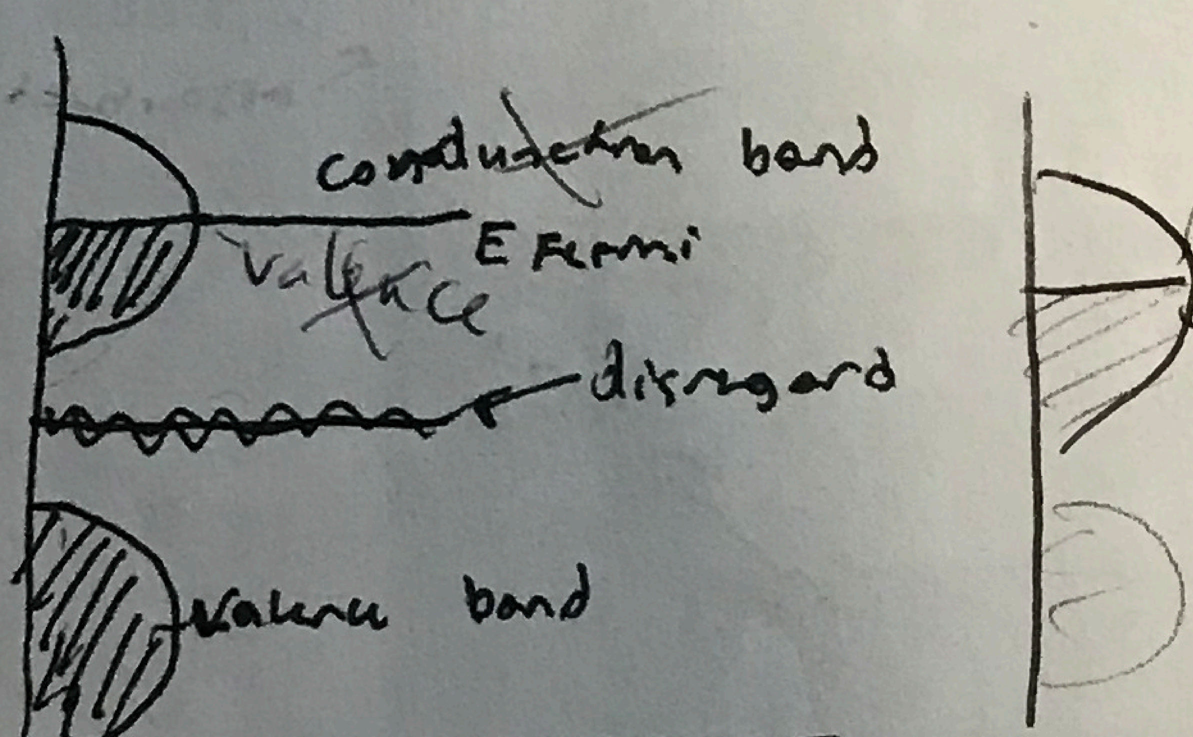
Name ______________________

Question 2 (20 points):
Silicon can be reacted to form SiO_2 (an insulator) or metal silicides such as Ni_2Si that are metallic.
Draw and concisely compare simple energy level (band) diagrams for Si, SiO_2, and Ni_2Si. metal
(It may be helpful to draw the three diagrams on one line.)
Indicate where bands are filled and where they are empty. 2
Indicate the Fermi energy on each diagram. 2
Label your axes. 1
You do not need to include dopants in any of the above, just the pure material (which is call "intrinsic").

(colored in means filled)

Homo and Lumo are same so no band gap
↓
Ni_2Si acts as metal



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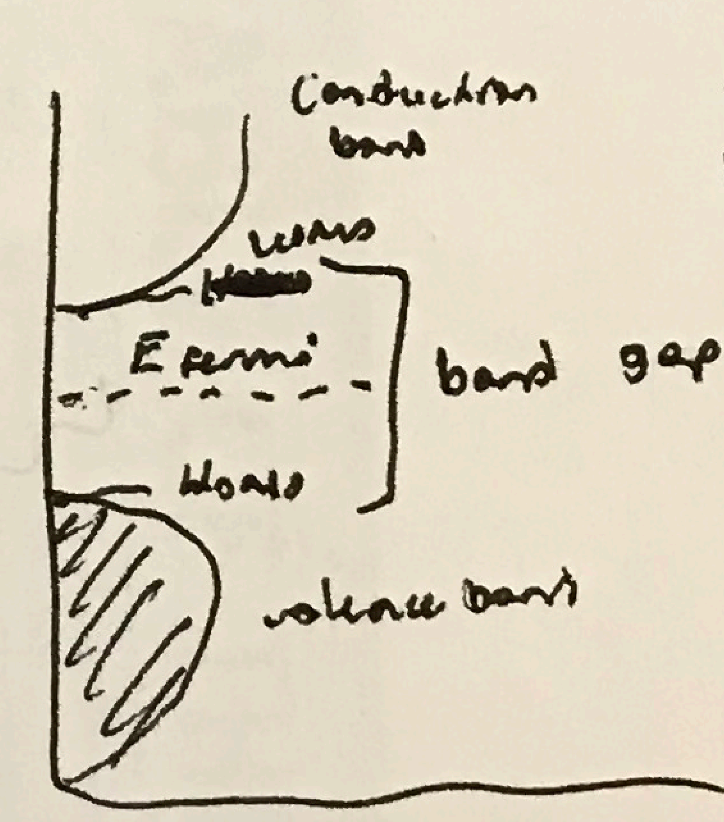
SiO_2 (insulator)
↑
has larger band gap than semiconductor (Si)



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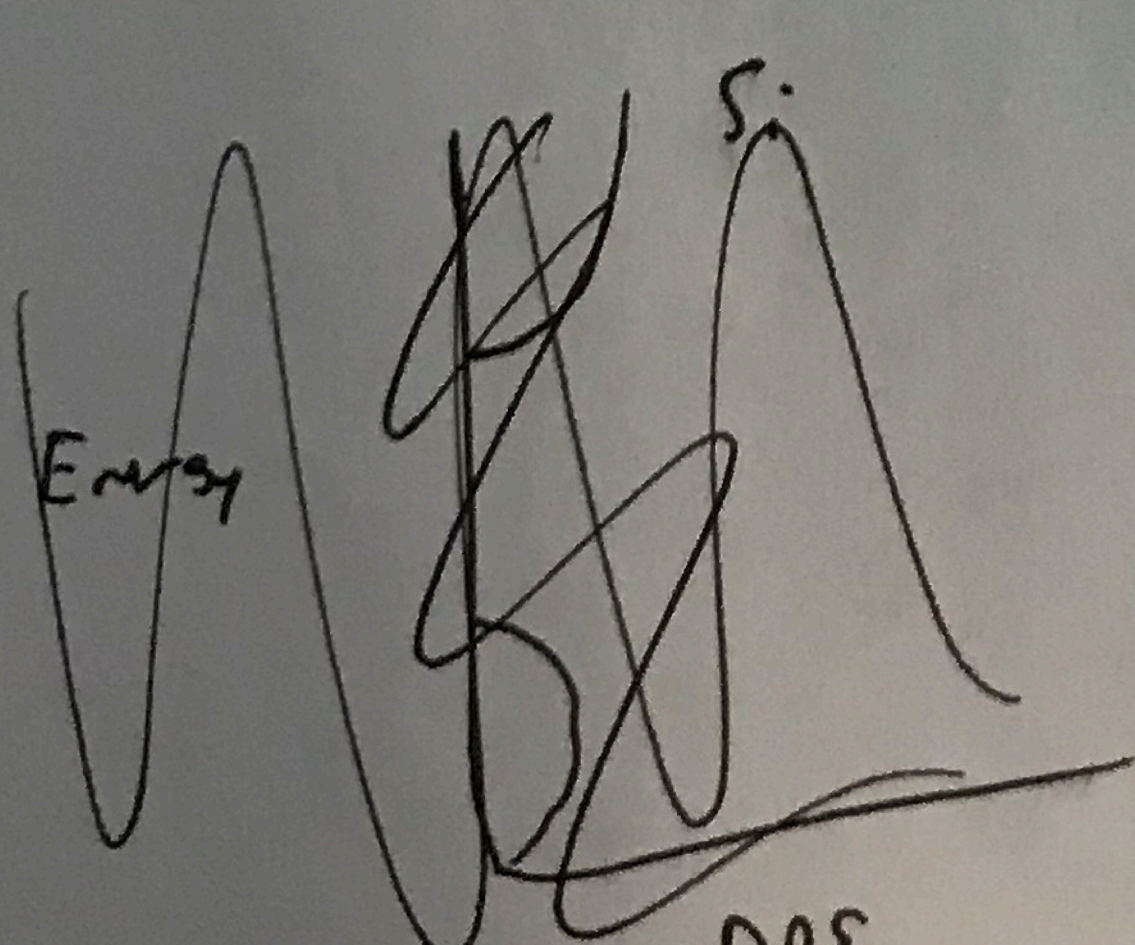
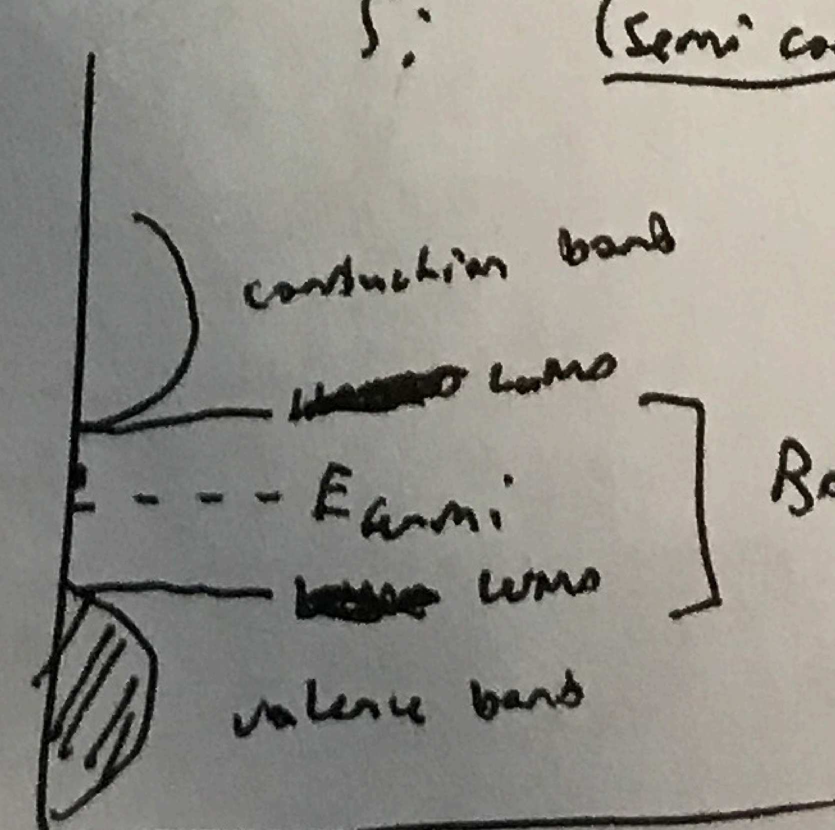
Si (semiconductor)





Band gap (smaller than insulator)

* band gaps not perfectly to scale

note: band gap is larger in the insulator than the semiconductor

Name ____________________

Question 3 (25 points):

For the transition metal complex $Ag(NH_3)_2^+$:

a) Identify the Lewis acid(s) and Lewis base(s). (5 points)

electron pair acceptor ↑ ... ↑ electron pair

NH_3 is the electron pair donor (Lewis base)

−1 Ag^{+} is the electron pair acceptor (Lewis acid)

b) Write the formation reaction from the (aqueous) metal ion and the ligands. Give the formation (equilibrium) constant (in terms of concentrations). (5 points)

$$Ag^+_{(aq)} + 2(NH_3)_{(aq)} \rightarrow Ag(NH_3)_2^+{}_{(aq)} \qquad K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

c) Give the signs of ΔH, ΔS, and ΔG for the reaction that you wrote above. Indicate what you expect for the formation constant (*i.e.*, is it greater or less than some number?) Is the reaction spontaneous? (Please be sure your answers are consistent!) (10 points)

$\Delta G = \Delta H - T\Delta S$

ΔS is negative b/c the system is becoming more ordered

ligands are entropically favorable

ΔH is negative (favorable to make bonds)

ΔG is negative b/c this is spontaneous

therefore $K_f > 1$ (products > reactants)

d) Do you expect the reduction half-cell potential of the metal ion or that of the complex to be larger (reduction to the solid metal)? Explain your answer concisely. (5 points)

which one is more likely to reduce?

~~Ag^+~~ $Ag^{+} \rightarrow Ag^{3+} + 2e^-$ reduce potential

$2NH_3 + 2e^- \rightarrow 2NH_3$ reduc potential

~~The reduction half cell potential will be larger the~~

$\Delta G = -nFE^\circ$ Not

reduce $Ag^+ + e^- \rightarrow Ag$ $\Delta E^\circ_{reduc} = +$

$2NH_3 \rightarrow 2NH_3^+ + 2e^-$ $\Delta E^\circ_{ox} = -$

reduction potentials (options)

~~The reduction to the~~ −2

$e^- + Ag^+ \rightarrow Ag$

$e^- + Ag(NH_3)_2^+ \rightarrow Ag(NH_3)_2$

~~because it will require less energy~~ to

22

The reduction of the metal ion ~~should be greater~~ b/c 5 according to ~~above~~, $e^- + Ag^+ \rightarrow Ag$ (Ag is reduced) spontaneously meaning that in $\Delta G = -nFE^\circ$, the $E_{reduction}$ is greatest for the metal ion that is spontaneous.

Midterm 1

H&AE 105
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Name ____________________

Question 4 (25 points):
For phosphoric acid, H_3PO_4, the pK_as are:
$pK_{a1} = 2.2$
$pK_{a2} = 7.2$
$pK_{a3} = 12.7$

$H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$
K_{a1}

a) Write the reaction associated with K_{a2}. (10 points)

K_{a2}

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightarrow HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

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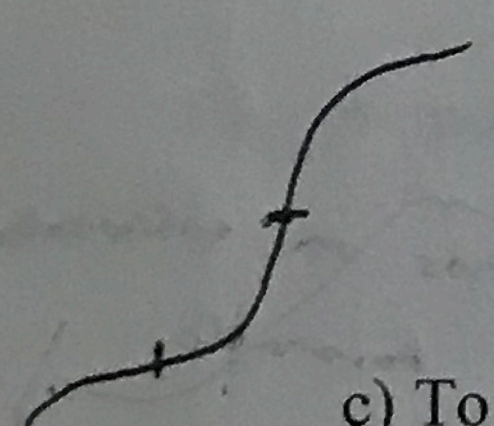
b) Write K_{a2} in terms of concentrations of the reactants and products in the reaction above? (5 points)

$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$$



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c) To make a buffer that is close to neutral pH, how would you use some of the following. Be precise in terms of what you would use and how much of each. (10 points)
(You do *not* have to use all of these chemicals. Assume that you have glassware to measure volumes and scales to measure weights.)
0.001 M HCl, 1 M HCl, 10 M HCl
0.001 M H_3PO_4, 1 M H_3PO_4 weak acid
0.001 M NH_3, 1 M NH_3 weak base
Water
Solids: Fe, Na, NaCl, NaH, NaOH

pH ≈ 7

* buffer = weak acid + conj base
or base + conj acid
(adding strong acid to buffer buffer)

$pK_a = pH - \log\left[\frac{(HA)}{(A^-)}\right]$

H_3PO_4 ← 1L 1M
gen equation
1 mol NaOH
40 g/mol

7.2

$pH = pK_{a1} - \log\left[\frac{H_3PO_4}{[H_2PO_4^-]}\right]$

$pH = pK_{a2} - \log\left[\frac{(HPO_4^{2-})}{(PO_4^{3-})}\right]$

$7 = 7.2 - \log[\quad]$

2

· For a buffer, it will have a larger capacity if more of each component is added

· One could use 100 mL of the 1M H_3PO_4 and then add to it 300 mL of NH_3 (which will act as base).

Name ____________________

Question 5 (20 points):

For $Cu(OH)_2$, $K_{sp}=2.2\times10^{-20}$

Also, for $Cu(NH_3)_4^{2+}$, $K_F=5\times10^{12}$

a) Write the equilibrium expression for K_{sp} in terms of concentrations (5 points)

$Cu(OH)_{2\,(s)} \rightarrow Cu^{2+}_{(aq)} + 2OH^-_{(aq)}$

$K_{sp} = \frac{[Cu^{2+}][OH^-]^2}{[Cu(OH)_2]} = [Cu^{2+}][OH^-]^2$

b) Rank the order from highest to lowest in which $Cu(OH)_2(s)$ will dissolve and concisely explain your answers. (15 points)

Water, 1 M $Cu(NO_3)_2$, 1 M NaOH, 1 M NH_3

common ion ↑ ↑ metal complex

	$Cu(OH)_2$ →	Cu^{2+} +	$2OH^-$
I		0	0
C		+x	+2x
E		x	2x

using eq from above

high → low

1 M NH_3 , 1 M $Cu(NO_3)_2$, 1 M NaOH

NH_3 will form complex metal ions with the Cu^{2+}, therefore driving down the concentration of Cu^{2+}, by removing it, the solubility will shift right and dissolve more

Also, the K_F for $Cu(NH_3)_4^{2+}$ is very high

adding Cu^{2+} ions create the common ion effect in which the concentration of Cu^{2+} ions increase. To balance back out the solubility moves to the left and decreases solubility

By dissolving $Cu(OH)_2$ in $Cu(NO_3)_2$, Cu^{2+} ions are already present which alters the ICE table.

adding OH^- increases the $[OH^-]$ which is squared in the K_{sp} equation meaning that the reaction will move even further left and dissolve less

By dissolving the solid in NaOH, OH^- ions become already present which change the Ice table

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Name ____________________

Extra credit #1 (2 points):
ZnO is a colorless semiconductor that is used in sunscreen.
What can you say about its bandgap? ____ for ZnO

Its band gap is larger (in eV) than the eV of UV light, that way it blocks the UV light which cannot overcome this band gap

The sunscreen blocks UV light

Extra credit #2 (2 points):
What combinations of the chemicals in 4c could you use to start a fire and how would each combination you name react?

* Solid Na (pure element) put into water would create a violent reaction (and even make flames) showing the kind of group one metals strong reaction with water (that is why pure Na must be stored in oil)

NaH and water would react to form H_3O^+ ~~and pure Na~~, and as shown above, Na is very reactive

Continue any answers below if you need more room.

Continuation of problem #_____