$498 \times 10^{-9} = 4 \times 10^{-7}$

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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

Typical bond: 3 − 4 eV, up to 8 eV

microwaves, visible, infrared are too low in energy

→ X-rays, ~~sometimes visible for very~~

+8

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

~~X-Rays are ionizing radiation, they knock free an electron from the~~

X-Rays are "ionizing radiation", their energy is high enough to break the bond energy and free an electron from the bond, causing the bond to dissociate.

0

Should be:
Excites core electrons

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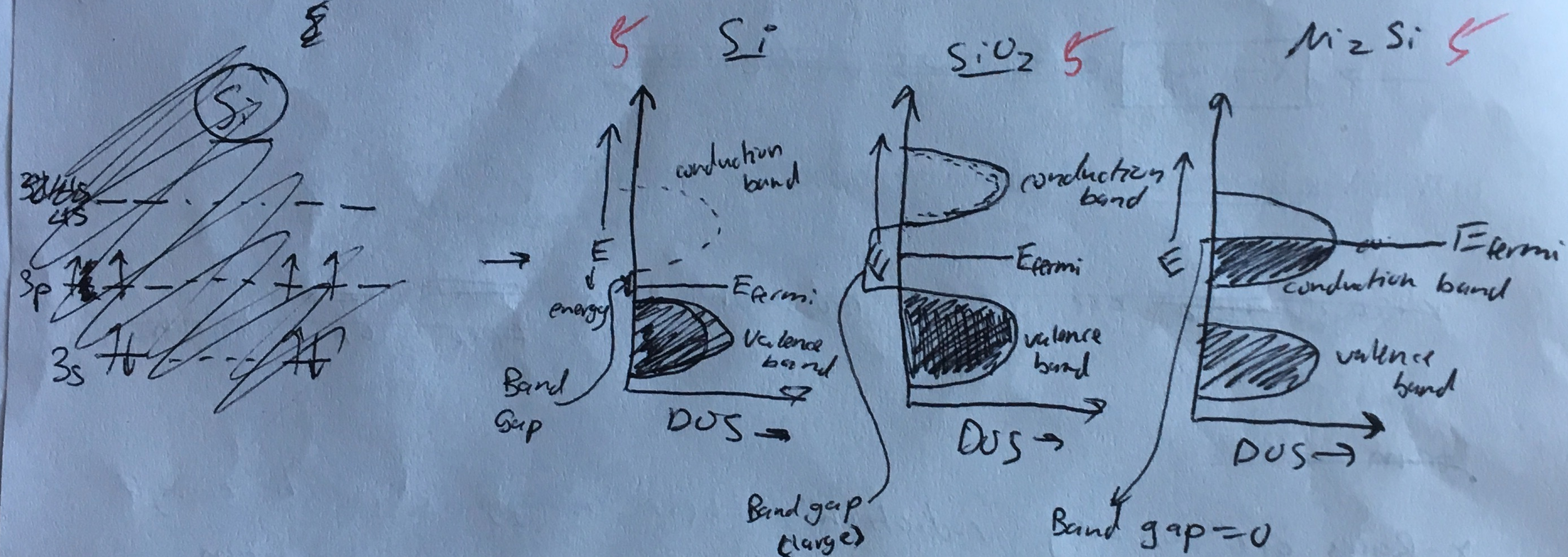
Question 2 (20 points):
Silicon can be reacted to form SiO_2 (an insulator) or metal silicides such as Ni_2Si that are metallic.
Draw and concisely compare simple energy level (band) diagrams for Si, SiO_2, and Ni_2Si.
(It may be helpful to draw the three diagrams on one line.)
Indicate where bands are 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 called "intrinsic").



Si has a band gap that allows for semi-conduction. Its E Fermi is lower than that of the insulator Ni_2Si and that of SiO_2.
The band gap of SiO_2 is largest because it is an insulator and does not conduct.

Ni_2Si does not have a band gap; it is a metal and the lack of a band gap makes its e^- easily excitable, which makes it very conductive.

1 1 → 1

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Acid: acceptor
Base: donor

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)

Ag^+ is the Lewis acid

NH_3 is the Lewis base

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

$$Ag^+_{(aq)} + 2(NH_3)_{(aq)} \longrightarrow [Ag(NH_3)_2^+]_{(aq)}$$

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

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

ΔG: −
ΔH: −
ΔS: −

$K_f >> 1$

metal complexes are very very stable and thus they are favored. The K_f for metal complexes are (much greater) always very large, usually $> 10^{10}$

Because $K > 1$, ΔG must be negative, as the reaction is favored and equilibrium lies on the right; $|\Delta H| > |T\Delta S|$; enthalpy outweighs entropy

Because bonds are being formed energy is released. therefore the reaction is exothermic, so $\Delta H_{prod} - \Delta H_{react}$ will be negative. ∴ ΔH = −

Because bonds are formed, and 3 molecules become 1 complex, there is less entropy in the system; ΔS is negative

The reaction is spontaneous, as $K_f > 1$ & ΔG are negative

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)

no Ecell

1) $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ E < 0

\+

2) $\{Ag(NH_3)_2^+\}_{(aq)} + e^- \longrightarrow Ag_{(s)} + 2NH_3$ E < 0

−1

3) $Ag^+ + Ag_{(s)} + 2(NH_3) \longrightarrow [Ag(NH_3)_2^+]_{eq} + Ag_{(s)}$ $E_{tot} > 0$

For reaction 3, which is the same as the formation of $[Ag(NH_3)_2^+]$ as well as a sum of reaction 1 and the inverse of reaction 2, Ecell is positive, because $\Delta G = -nFE$ & $\Delta G = -RT\ln(K)$ → $K > 1$, $\Delta G < 1$, $E > 0$.

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Because both reduction potentials should be less than 0 and equation 2 is the one that is flipped and made negative, then Ag^+ must have the less negative reduction half-cell potential, to keep Ecell > 0

this is also because $Ag(NH_3)_2^+$ is a very stable compound, thus reducing it and breaking the bonds would be very unfavorable, so $E_{Ag(NH_3)_2}$ would be more negative than E_{Ag^+}.

Ag wants to be oxidized, not reduced.

Therefore, $|E_{Ag}| < |E_{Ag(NH_3)_2}|$

23+17=40

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Question 4 (25 points):
For phosphoric acid, H_3PO_4, the pK_as are:
$pK_{a1} = 2.2$ $H_3PO_4 \rightarrow H_2PO_4$
$pK_{a2} = 7.2$ $H_2PO_4 \rightarrow HPO_4$
$pK_{a3} = 12.7$ $HPO_4 \rightarrow PO_4$

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

$$H_2PO_{4(aq)}^- + H_2O_{(l)} \rightleftarrows HPO_{4(aq)}^{2-} + H_3O^+_{(aq)}$$

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

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

$pK_a = -\log_{10} K_a$

$\frac{HA}{H_{+}A^-} = 1$

$pH = pK_a - \log_{10} \frac{HA}{A}$

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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
0.001 M NH_3, 1 M NH_3
Water
Solids: Fe, Na, NaCl, NaH, NaOH

10

At K_{a2}, $[H_2PO_4] = [HPO_4]$.

~~1 mol H_3PO_4~~ 1.5 mol NaOH needed to neutralize 1.5 equivalents of H_3PO_4

Take 1 mol of solid NaOH (≈40g) and dissolve it in 1 liter of H_2O to make a 1 molar stock solution of NaOH. Then, take 10mL of 1M H_3PO_4 and mix it with 15mL of 1M NaOH to obtain a buffered solution at pH = 7.2. For pH = exactly 7, use a little less NaOH. The buffer will be a solution of equal concentrations $[H_2PO_4]$ and $[HPO_4]$. The first 10mL of 1M NaOH will reach the first equivalence point* and the 5 mL more (to get to 15mL) will get to the buffer point $[H_2PO_4] = [HPO_4]$, where pH = pKa

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* at which all H_3PO_4 is converted to H_2PO_4

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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)

~~$Ksp = [Cu^{2+}][OH^-]^2$~~

$K_{sp} = [Cu^{2+}][OH^-]^2$ ✓

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

I TOTALLY FORGOT WATER. ITS ON NEXT PAGE good!

Highest

1M NH_3

The most will dissolve in 1M NH_3. In the presence of NH_3, Cu^{2+} will form an ion complex $Cu(NH_3)_4^{2+}$. This K_f is very high (5×10^{12}), so it happens with pretty much all the Cu^{2+} ions in solution.

$Cu^{2+} + 4NH_3 \rightarrow Cu(NH_3)_4^{2+}$ $K_f = 5\times10^{12}$

Because products are being removed in the dissolution of $Cu(OH)_2$

$Cu(OH)_2 \rightarrow Cu^{2+} + 2(OH^-)$

The equilibrium is driven to the right increasing the K to $\sim 1\times10^{-7}$

1M $Cu(NO_3)_2$

Because of the common ion effect, 1M $Cu(NO_3)_2$ will lower the molar solubility of Cu in $Cu(OH)_2$:

~~$2.2\times10^{-20} = [\ ][\ ]^2 \rightarrow$ molar solubity $= 2.2\times10^{-20}$~~

$2.2\times10^{-20} = [1+x][2x]^2 = 4x^2$ molar solubility $\rightarrow$ $\sim 10^{-10}$ mol/L

This value is lower than the original molar solubility of $\sim10^{-7}$ mol/L

$2.2\times10^{-20} = [x][2x]^2 = 4x^3$

1M NaOH

1M NaOH will lower the molar solubility of $Cu(OH)_2$ the most.

$2.2\times10^{-20} = [x][1+2x]^2$ (inital conc. of OH = 1

$2.2\times10^{-20} = x \rightarrow$ molar solubility $= 2.2\times10^{-20}$

This is a lower molar solubility than that of the 1M $Cu(NO_3)_2$ solution; and because the 1M NH_3 increases the solubility of $Cu(OH)_2$, it is above both other solutions ✓

lowest

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

The band gap is $> 3.2\,eV$ (should be around $\sim 3.3\,eV$). It is used in sunscreen because it absorbs UV light, which is just higher in energy than visible light. Bandgap is the E required to excite an e^- by absorbing the photon, so bandgap must be in the U-V range.

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?

~~$2Na_{(s)} + 2HCl \rightarrow 2NaH + Cl_{2(g)}$~~

$2Na_{(s)} + 2H_2O \rightarrow 2NaH^- + H_{2(g)} + O_{2(g)}$ (Na ignites/explodes on contact with H_2O, ~~[illegible]~~ enough heat is transfered to start a fire.)

H_2O can be found ~~replaced by~~ by using any of the solutions, as the solutions have H_2O in them.

$2Na_{(s)} + 2HCl \rightarrow 2NaH^- + Cl_{(2)}$ (Na explodes, heat made can start a fire) releases Cl_2 gas)

Continue any answers below if you need more room.

Continuation of problem # 5

Highest → 1M NH_3
↓
H_2O
↓
1M $Cu(NO_3)_2$
↓
1M NaOH
↓
lowest

~~The solubility of $Cu(OH)_2$ remains relatively unchanged, still OH⁻ is a common ion, sometimes the H^+ ions of water $[H^+] = 1.0\times10^{-7}$ react with the OH^- to form H_2O.~~

~~However, these effects are minimal and the solubility of $Cu(OH)_2$ will be [illegible] normal.~~

neutral — H_2O does not effect the solubility. The solubility is: $2.2\times10^{-20} = [x][2x]^2 = 4x^3 = \sim 10^{-7}$ moles/L

So, H_2O is below NH_3 (which increases solubility) but above $Cu(NO_3)_2$ and 1M NaOH (which decrease the solubility)