# **ART EXAM**

WUCT 2019

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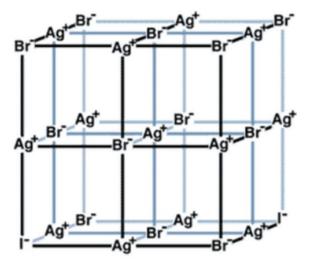
### **Instructions & Rules**

Clearly write your name and ID number above. Your exam will not be graded if these cannot be read. Write darkly on your exam, and box your answers. Two students will work on this exam for 60 minutes; a copy of the test will be provided to each student, but only one copy of the exam will be graded. Only work written on the front pages of this copy will be graded. No electronics of any kind can be used during the exam, except for a non-programmable scientific calculator. Cell phones must be turned off, and watches must be removed. The time will be projected and/or announced in the exam rooms. Necessary equations, constants, and a periodic table will be provided. Explanations must be in complete sentences, diagrams must be labeled, and units must be shown throughout calculations for full credit. Partial credit will be awarded where appropriate. Proctors may answer procedural questions, but they will not answer content-specific problems. Cheating will NOT be tolerated. Refer to proctor(s) for further questions.

#### Question 1 (30 points)

Before the days of digital pictures and iPhones, photographs were taken on film and developed in dark rooms. This question will look into this process in chemical detail.

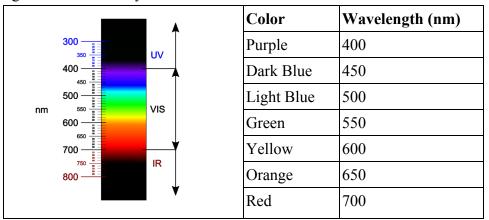
a. Film consists of a gelatin emulsion layered onto a base. The molecular structure of this emulsion is shown below.



i. (2 pts) What are the ions in this lattice? Name their elements and charges.

Iodine -1, Bromine -1, and Silver +1. (2 points for all 3, 1 point for 2 correct)

ii. **(4 pts)** When photons hit the ions in the lattice, an electron is ejected. If the minimum energy required to release an electron from the film,  $\varphi$ , is 2.20 eV, and the maximum kinetic energy of the emitted electrons is 7.05 x 10<sup>-20</sup> J, what color light was absorbed by the lattice?



7.05x10<sup>-20</sup> J = 0.44 eV Energy of light (+1): 2.20 eV+ 0.44 eV = 2.64 eV =  $4.23x10^{-19}$  J Wavelength of light (+2): E = hc/ $\lambda$ , so  $4.23x10^{-19}$  = E, and  $\lambda$  =  $4.7x10^{-7}$  m The wavelength is 470 nm, which is blue (any shade is acceptable) (+1). (4 points for getting right answer)

iii. (2 pts) When an electron is released, it is captured by an ion in the lattice.Explain which ion is most likely to capture this electron and what happens when it does.

Silver, as it will reach its neutral charge by obtaining an electron. When it captures the electron, it converts from ions to neutral atoms and precipitates out, which is what gives photos their definition. (2 points) (+1 for correct ion, +1 for precipitation explanation)

iv. (2 pts) How will areas on photos that receive more light appear on the translucent film compared to areas that received less light before the film is developed?

Areas that received more light will have more reduced silver atoms and higher amounts of precipitated silver, causing them to appear darker and more opaque on the film. (2 points) (+1 for light increasing reduction of ions, +1 for connecting to opacity)

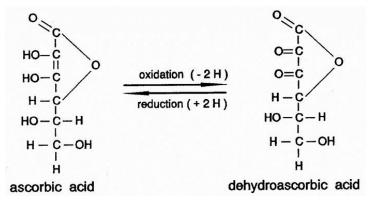
- b. During the development process, electrons are transferred from the developing agent to the lattice.
  - i. (1 pt) What is happening to the developing agent and lattice?

The developing agent is being oxidized, and the lattice is being reduced. (1 point)

ii. (2 pts) Why do regions that have received more light on a photo develop more quickly?

Areas with more light will already have some reduced silver atoms that have precipitated, meaning that the developing agent will not have to act as a reducing agent for as much on those regions. (2 points) (+1 for stating light has already begun reduction, +1 for stating developer will not have to do as much work because of that)

iii. (3 pts) A reaction involving ascorbic acid, otherwise known as Vitamin C, is shown below. Write out the reaction equation for this process to provide a reason why Vitamin C can be used as a developer. (the number of H lost will be obscured)



 $C_6H_8O_6 \leftrightarrow C_6H_6O_6 + 2H^+ + 2e^-$ Vitamin C gets oxidized, so it can act as a reducing agent. (3 points) (+2 for reaction, +1 for explanation)

iv. **(3 pts)** How many grams of Vitamin C will be needed to develop a photo that has 2.0 grams of silver ions on it?

Full redox equation:  $C_6H_8O_6 + 2Ag^+ \rightarrow C_6H_6O_6 + 2Ag + 2H^+$  (make sure charges are balanced)

2.0 g Ag = 0.0185 mol Ag, so 0.00927 mol Vitamin C is needed. Molar mass of vitamin C is 176.12 g/mol, so 1.632 g of Vitamin C will be used.
(3 points) (+1 for reaction, +1 for moles, +1 for mass)

v. (5 pts) The half-reaction cell potential for the Vitamin C reaction was found to be +0.38 V. What is the equilibrium constant for developing a photo at 25 °C?

Ag<sup>+</sup> + e<sup>-</sup> → Ag E=0.80 V(reduction potentials will be provided) 0.38 + 0.80 = 1.18 V-RTlnK = -nFE

8.314\*298\*lnK=2\*96500\*1.18  $\Delta G = -227.7 \text{ kJ/mol}$ K = 8.33x10<sup>39</sup> Photo development is a highly spontaneous process. (5 points)(+1 silver half-reaction, +1 total potential, +1 solving for delta G, +2 solving for K)

c. (3 pts) How can changes in pH affect the rate of development?

When base is added, it will react with the H+ and shift the equilibrium to the right, accelerating the reduction of Ag ions and increasing the rate of development. Conversely, adding an acidic solution will accept free electrons from reducing agents, slowing development. (3 points) (+1 base accelerates reduction, +1 acids slow reduction, +1 connect to dev.)

- d. After development, fixer will be added to the mixture to dissolve any leftover substances on the film. The majority of film is made of an emulsion of silver bromide, which is insoluble. Ammonia solubilizes this compound by coordinating with silver to form a charged coordination complex. This complex will have silver bonded to two ammonia molecules with no remaining electrons.
  - i. (2 pts) Why are ions generally soluble in water?

Ions are soluble because water is a polar substance that contains partially positive and partially negative components. These partially charged regions of water will interact with the charged ions and bring them into solution. (2 points) (+1 water is polar, +1 ions are polar and dissolve)

ii. (2 pts) Draw the VSEPR molecular structure of this silver coordination ion and state its geometry relative to the silver atom.

$$\begin{bmatrix} H & H \\ I & I \\ H - N - Ag - N - H \\ I & I \\ H & H \end{bmatrix}^{\dagger}$$

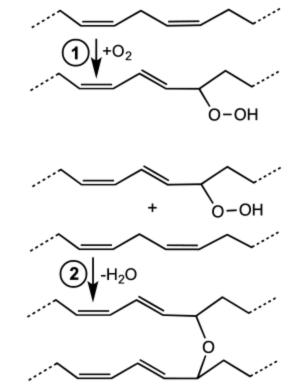
Linear (2 points) (+1 for structure, +1 for geometry)

#### Question #2 (30 points)

Over time, works of art will lose their vibrancy and quality as the chemicals they were made of interact with the environment. However, restoration scientists can carefully apply other chemicals to stop or even reverse this process.

a. While water-based paintings dry through the simple process of vaporization, oil paintings dry through a different process. As oils are composed of fatty acid chains, drying occurs when the fatty acids undergo oxidation with  $O_2$  to form tight crosslinks with each other, forming a hardened layer. This reaction is shown below:

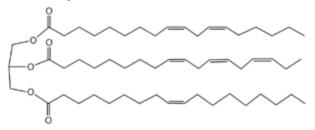
*Note:* Lines that do not have elemental symbols indicate bonds between carbon atoms. Bonds between carbon and hydrogen are not shown in the diagram, but are still present as all carbons in the molecule have four total bonds.



i. (2 pts) Identify the oxidizing and reducing agents.

Oxidizing agent: O<sub>2</sub> Reducing agent: Fatty acid (2 points) (+1 for ox. agent, +1 for red. agent)

ii. (2 pts) Shown below is an example of a fatty acid that would make up an oil paint. Order, from fastest to slowest, how quickly the top, middle, and bottom chains would dry.

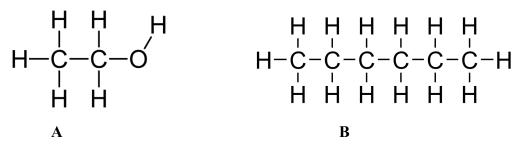


Middle, top, bottom (most double bonds gives faster drying) (2 points) (+1 if 2 are correct)

iii. (1 pt) If an oil painting was stored in an airtight preservation chamber immediately after completion, how would it feel (to touch) when removed?

It would still be wet, as oil requires oxygen to dry. (1 point)

- b. Many painters of the 17th century made the artistic choice to coat their works in varnish to enhance the colors and shine of the final painting.
  - i. (2 pts) Over time, varnish oxidizes, and it becomes brittle and yellow. Eventually, the varnish must be removed. Which solvent would you expect to be a more effective cleaner? Circle the letter of your choice and provide a short explanation.



A would be a better choice, as it is polar and aged varnish, which will have high oxygen content and many polar bonds, will dissolve better in a polar solvent (2 points) (+1 for correct choice, +1 for explanation involving polarity)

ii. (2 pts) As varnishes must be reapplied, scientists may opt to use a synthetic varnish that does not experience the effects of oxidation over time so that the coating does not have to be continually cleaned and reapplied. Assuming the oils in varnish behave similarly to those in oil paint, shown in section a.ii., hypothesize how you could modify a natural varnish to produce a synthetic varnish that would be a more stable alternative to natural varnishes.

As oxidation occurs on the double bonds of varnish, a more stable varnish could be made by hydrogenating all the double bonds to produce single-bonded carbons bonded to hydrogens. This would not oxidize and become brittle. (2 points) (+1 for noting oxidation occurs on double bonds so they must be removed, +1 for explaining how they would be removed (eg. hydrogenation))

In the 19th and 20th centuries, a new compound called nitrocellulose was developed as the first artificial plastic material and soon found use in inks and films. Due to its instability, media made from nitrocellulose must be precisely treated (even modern art may need preservation!).

c. (4 pts) Nitrocellulose is made from the partial nitration of cellulose, a polymeric sugar that can be represented with the chemical symbol  $[C_6H_7(OH)_3O_2]_n$ . Cellulose is reacted with nitric acid and a sulfuric acid catalyst to produce water and nitrocellulose, which has the symbol  $[C_6H_7(NO_3)_3O_2]_n$ . If 500 g of cellulose polymers composed of 100 monomers (n = 100) is reacted with excess nitric acid, how many grams of water will be produced?

[C<sub>6</sub>H<sub>7</sub>(OH)<sub>3</sub>O<sub>2</sub>]<sub>n</sub> + 3nHNO<sub>3</sub> → [C<sub>6</sub>H<sub>7</sub>(NO<sub>3</sub>)<sub>3</sub>O<sub>2</sub>]<sub>n</sub> + 3nH<sub>2</sub>O
[C<sub>6</sub>H<sub>7</sub>(OH)<sub>3</sub>O<sub>2</sub>]<sub>100</sub> + 300HNO<sub>3</sub> → [C<sub>6</sub>H<sub>7</sub>(NO<sub>3</sub>)<sub>3</sub>O<sub>2</sub>]<sub>100</sub> + 300H<sub>2</sub>O
Molar mass of cellulose: 16200 g/mol
0.03086 mol cellulose reacts to form 9.26 mol H<sub>2</sub>O
9.26mol\*18.015g/mol = 166.8 g water
(4 points) (+1 for balanced reaction, +1 for scaling for n, +1 for finding amount of water produced, +1 for correct mol to g conversions)

d. (1 pt) Nitrocellulose initially decomposes very slowly, releasing NO<sub>3</sub><sup>-</sup> from the molecule. However, plastic sculptures created in the past century already require restoration work, indicating that the rate of decomposition accelerates over time. How could you explain the acceleration of decomposition in nitrocellulose?
The NO<sub>3</sub><sup>-</sup> ions released catalyze further decomposition.

(1 point)

- e. More dangerously, film made of nitrocellulose is highly unstable, and several incidents have occurred in the past where nitrate films have burst into flames if exposed to even low amounts of heat. For this reason, the film industry has switched to safer alternatives, and old film must be stored separately in cold, fireproof chambers.
  - i. (2 pts) For the combustion of one monomer of nitrocellulose, the reaction can be written as  $4 C_6 O_{11} N_3 H_7 + 9 O_2 \rightarrow 24 CO_2 + 14 H_2 O_2 + 6 N_2$ . What is change in entropy of this reaction?

Species	$\mathbf{S}^{\mathbf{o}}\left(\frac{J}{mol\cdot K}\right)$
$C_{6}O_{11}N_{3}H_{7}(s)$	112.1
$O_2(g)$	205.1
$\rm CO_2(g)$	213.7
$H_2O(g)$	188.8
$N_{2}(g)$	191.6

 $\Delta S^{\circ} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$ 24\*213.7 + 14\*188.8 + 6\*191.6 - (4\*112.1 + 9\*205.1) 6627.3 J/mol·K (2 points) (+1 using correct entropy values, +1 for correct calculation)

ii. (1 pt) If the change in enthalpy for this combustion is -12,500 kJ/mol, when is this reaction spontaneous?

Since  $\Delta H^{\circ}$  is negative and  $\Delta S^{\circ}$  is positive,  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$  states that the change in Gibbs will always be negative, so the reaction is spontaneous at any temperature. (1 point)

iii. **(3 pts)** If the reaction runs at 298 K, approximately how much nitrocellulose will remain unreacted?

-12500 - 298\*6.6273 $-1.4 \times 10^4 \text{ kJ/mol}$  $\Delta G^\circ = -RTlnK$  $K = e^{5.84} = 345$ 

Because of the high K, there would be essentially no unreacted nitrocellulose. (3 points) (+1 Calculating  $\Delta G^{\circ}$ , +1 converting  $\Delta G^{\circ}$  to K, +1 explanation with K) Possible solution 2: The reaction is an irreversible combustion, so all the nitrocellulose reacts. (3 pts)

iv. (2 pts) Are the values you calculated in parts i-iii enough evidence to explain nitrocellulose's instability at low temperatures? Explain why or why not.

No, as the reactivity at room temperature is explained by a low activation energy, meaning that temperature does not have to be very high to reach the sufficient energy to begin the combustion reaction. Though the reaction proceeds favorably, the values of Gibbs free energy and K only indicate that products are favored in the reaction, not how easily the reaction can be initiated. (2 points) (+1 for explanation involving activation energy, +1 for saying values are insufficient)

In addition to restoring old works, chemistry can also be used to discover forgeries. In order to find forgeries created after 1945, scientists can actually detect significantly increased levels of carbon-14, a radioactive isotope that is created in high amounts after a nuclear explosion, compared to paintings created before 1945.

f. (1 pt) C-14 is created when neutrons released from atomic bombs collide with nitrogen-14 atoms. What else is released? Show an equation to support your answer.

 $714N + 01n \rightarrow 614C + 11p$ A proton is released. (1 point)

g. (1 pt) C-14 very slowly decays back to N-14. From the particle released, what kind of decay would this undergo?

An electron is released, so it is beta (beta minus) decay. (1 point)

h. (2 pts) How effective would you predict this technique to be a thousand years into the future, assuming that the Nuclear Non-Proliferation Treaty is never broken?

This technique would gradually decrease in effectiveness as C-14 decays and no nuclear detonations occur to replenish the amount of C-14. Over a long enough time, most C-14 will have all decayed and paintings created before and after 1945 would have similar amounts of the isotope.

(2 points) (+1 effectiveness would decrease over time, +1 C-14 will have decayed)

C-14 isn't just produced by nuclear bombs. In the atmosphere, it is also created at a regular rate by cosmic rays from the sun that produce neutrons which bombard nitrogen atoms in a similar way neutrons from bombs do. As a result, scientists can still use it to detect older forgeries by comparing the amount of C-14 present in the forgery in question to the amount of C-14 present at the time the actual painting was created.

 (4 pts) You are presented with a supposed painting dating back to 1310 AD. Records show that paintings created during that time had 0.0600 mg of C-14. Given that C-14 undergoes first order decay with a half-life of 5730 years, how much C-14 should be present currently for the painting to be considered genuine if the painting was perfectly preserved?

$$\begin{split} t_{1/2} &= 0.693/k \\ k &= 3.83 \times 10^{-12} \, \text{s}^{-1} \\ \ln(A_0/A) &= kt \\ t &= 2019 - 1310 = 709 \text{ years} = 2.24 \times 10^{10} \, \text{s} \\ A_0/A &= 1.089 \\ A_0 &= 0.060 \text{ mg, so } A = 0.055 \text{ mg} \\ (4 \text{ points}) \ (+1 \text{ for finding } k, +2 \text{ for using correct equation, } +1 \text{ for correct calculations}) \end{split}$$

#### Question #3 (15 points)

David was assigned to draw a mural with chalk. Not knowing the composition of the chalk, he guessed that the main component of chalk might be a combination of one or two chemicals from A. CaCO<sub>3</sub>; B. Ca(OH)<sub>2</sub>; C. Ca(HCO<sub>3</sub>)<sub>2</sub>. He got a handful of different chalks and carried out a set of double indicator titration experiments with phenolphthalein and methyl orange.

Indicator	pH range	
Phenolphthalein	Colorless 8.4 – 10 Pink	
Methyl Orange	Red 3.1 - 4.4 Orange	

He added phenolphthalein first and titrated each solution with HCl to the point where phenolphthalein turned from pink to colorless. The amount of HCl used is recorded as  $V_1$ . He then added methyl orange and titrated with HCl again. The amount of HCl needed to make the final solution red is recorded as  $V_2$ . The following reactions may occur between chalk and HCl.

 $\begin{aligned} & \operatorname{CaCO}_{3\,(s)} + \operatorname{HCl}_{(aq)} \notin \operatorname{CaCl}(\operatorname{HCO}_{3})_{(aq)} \\ & \operatorname{CaCl}(\operatorname{HCO}_{3})_{(aq)} + \operatorname{HCl}_{(aq)} \notin \operatorname{CaCl}_{2\,(aq)} + \operatorname{H}_{2}\operatorname{CO}_{3\,(aq)} \\ & \operatorname{Ca}(\operatorname{OH})_{2\,(s)} + 2 \operatorname{HCl}_{(aq)} \notin \operatorname{CaCl}_{2\,(aq)} + 2\operatorname{H}_{2}\operatorname{O}_{(1)} \\ & \operatorname{Ca}(\operatorname{HCO}_{3})_{2\,(s)} + 2 \operatorname{HCl}_{(aq)} \notin \operatorname{CaCl}_{2\,(aq)} + 2\operatorname{H}_{2}\operatorname{CO}_{3\,(aq)} \\ & \operatorname{The} K_{a} \text{ of } \operatorname{H}_{2}\operatorname{CO}_{3} \text{ is } 4.3 \times 10^{-7}, \text{ and the } K_{a} \text{ of } \operatorname{HCO}_{3}^{-1} \text{ is } 4.8 \times 10^{-11} \end{aligned}$ 

- The pH of an amphiprotic salt solution is calculated as  $pH = \frac{1}{2}(pKa_1 + pKa_2)$ 
  - a. (7 pts) Listed below are his results. Analyze the composition of each sample. (Write the capitalized letter for each chemical: A. CaCO<sub>3</sub>; B. Ca(OH)<sub>2</sub>; C. Ca(HCO<sub>3</sub>)<sub>2</sub>) Samples 4 and 5 contain 2 distinct compounds of the 3 given.

Sample	1	2	3	4	5
$V_{1}$ and $V_{2}$	$V_1>0, V_2$ very small	$V_1 = 0, V_2 > 0$	$V_{1}, V_{2} > 0$	$V_1 > V_2 > 0$	V <sub>2</sub> >V <sub>1</sub> >0
Composition	В	С	Α	A&B or B&C	A&C or B&C

A:  $CaCO_3$  forms a weakly basic solution. Addition of acid creates  $HCO_3^-$ , which forms a weakly basic buffer solution. More acid must be added to acidify this solution.

B:  $Ca(OH)_2$  forms a strongly basic solution. Addition of enough acid neutralizes this solution, so very small amounts are necessary to acidify it further.

C:  $Ca(HCO_3)_2$  forms a weakly basic buffer at pH 8.3, so the solution will initially be colorless. Addition of acid will be needed to acidify the solution.

Assign 1 point for every correct answer (+1 if 1-3 are ALL correct, +1 if 4 and 5 are BOTH correct) 7 points if all are correct (explanations not necessary)

b. (6 pts) David did the titration again with Sample 4 to test the purity. He took 1.200 g of Sample 4 and made a 100.0 mL solution with water. He then took 20.0 mL of it and titrated with 0.1 M HCl. V<sub>1</sub> = 30 mL, V<sub>2</sub> = 5mL. Calculate the impurity of Sample 4.

Two possible compositions of Sample 4:  $CaCO_3 + Ca(OH)_2$  -or-  $Ca(OH)_2 +$  $Ca(HCO_3)_2$ If the Sample 4 is  $CaCO_3 + Ca(OH)_2$ ,  $V_1: 2CaCO_3 + 2HCl \rightarrow CaCl_2 + Ca(HCO_3)_2$  $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$  $V_2$ : Ca(HCO<sub>3</sub>)<sub>2</sub> + 2HCl  $\rightarrow$  CaCl<sub>2</sub> + 2H<sub>2</sub>O + CO<sub>2</sub> From V<sub>2</sub> = 5ml,  $n_{HCl} = 0.0005 \text{ mol}$ ,  $n_{Ca(HCO_3)_2} = 0.00025 \text{ mol}$ Since all Ca(HCO<sub>3</sub>)<sub>2</sub> comes from CaCO<sub>3</sub>,  $n_{CaCO_3} = 0.0005$ mol  $K_{sn}$  of (CaCO<sub>3</sub>) = 6\*10<sup>-9</sup>, the max molarity of the CaCO<sub>3</sub> can only be  $\sqrt{(6*10^{-9})}$ , which is 7.74\*10<sup>-5</sup>, in this case there would only be  $1.55*10^{-6}$  mol of CaCO<sub>3</sub> in the solution, which is much smaller than the mols of CaCO<sub>3</sub> we calculated. So this composition of  $CaCO_3 + Ca(OH)_2$  is not possible. If Sample 4 is  $Ca(OH)_2 + Ca(HCO_3)_2$ , (Note: for this composition,  $n_{(Ca(OH)_2)}$  has to be greater than  $n_{(Ca(HCO_3)_2)}$  since  $V_1 > V_2$ )  $V_1: Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$  $V_2$ : Ca(HCO<sub>3</sub>)<sub>2</sub> + 2HCl  $\rightarrow$  CaCl<sub>2</sub> + 2H<sub>2</sub>O + CO<sub>2</sub> mass percentage of  $Ca(OH)_2 = (0.03L \text{ HCl } *0.1M *0.5*74 \text{ g/mol})/(1.2 \text{ g}*20.0 \text{ ml}/100.0 \text{ ml})$ ml)=46.25%  $Ca(HCO_3)_2 = (0.005L HCl * 0.1M * 0.5*163 g/mol)/(1.2g*20.0 ml/100.0 ml)=16.87\%$ Impurity = 100% - 46.25% - 16.87% = 36.88%(6 points) (+1 for identifying 1 correct reaction, +1 for 2 rxns, +1 for identifying correct composition, +1 for identifying that  $n_{(Ca(OH)_2)}$  has to be greater than  $n_{(Ca(HCO_3)_2)}$  +1 for calculating amount of  $Ca(HCO_3)_2$ , +1 for math)

c. (2 pts) David chose to draw with a CaCO<sub>3</sub>-based chalk. He was drawing his art piece when he accidentally chipped some chalk into a liter of water and got a cup of saturated solution. Supposing the chalk has no impurities and no solid chalk remained, what would be the mass percentage of dissolved chalk in this solution? (Approximate the density of the solution 1 g/mL).

 $CaCO_3 \neq Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)}$   $K_{sp} = 6 \times 10^{-9}$  at room temperature

The K<sub>sp</sub> of (CaCO<sub>3</sub>) = 6\*10<sup>-9</sup>, so the molarity of the CaCO<sub>3</sub> is  $\sqrt{(6*10^{-9}=7.74*10^{-5} \text{ M})^{-5} \text{ M}}$  (7.74\*10<sup>-5</sup> M\*100 g/mol\*1 L)/1000 g = 0.0008%

(2 points) (+1 calculating molarity from Ksp, +1 finding correct percentage)

#### **Question 4 (25 points)**

Ancient Grecians discovered that the corrosion of copper produces a green pigment named Verdigris, which many artists used as a pigment for paint. Grecians also discovered that copper corroded through different environmental processes produced pigments with different shades of green. One such method of corrosion produces a pale green pigment called nantokite by exposing copper metal to acetic acid and chlorine. The net ionic equation for this corrosion of copper metal is shown below:

$$2Cu_{(s)} + 2H^{+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow 2CuCl_{(s)} + H_{2(g)}$$
  
Nantokite

- a. Given that corrosion of metals usually denotes a redox reaction, answer the following questions using the above net ionic equation
  - i. (2 pts) Label the oxidation state for each reactant and product. Using this answer, explain why this corrosion is a redox reaction.

$$\begin{array}{c} 2Cu_{(s)} + 2H^{+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow 2CuCl_{(s)} + H_{2(g)} \\ 0 + 1 - 1 + 1 - 1 0 (+1) \end{array}$$
  
Cu is getting oxidized, H is getting reduced (+1) (2 points)

ii. (2 pts) Complete the half reactions for the corrosion of copper.

 $\begin{array}{l} Cu_{(s)} + Cl^{-}_{(aq)} \rightarrow CuCl_{(s)} + 2e^{-} \\ 2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \\ (2 \text{ points}) \ (+1 \ \text{for each half reaction}) \end{array}$ 

iii. (2 pts) A pH below 2.5 can be very corrosive to skin, and Greeks had not yet invented protective equipment, like gloves. If 1 L of solution is used, what is the maximum grams of nantokite that can be produced at one time without extremely harming any Grecian attempting to collect the nantokite product out of solution?

```
pH 2.5 = 10^{2.5} M H<sup>+</sup> = 3.2 \times 10^{-3} mol in 1 L
3.2x10<sup>-3</sup> * (2 mol CaCl/2 mol H<sup>+</sup>) * (99 g/1 mol CuCl) = 0.31 g CuCl
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(2 points) (+1 finding mol of H<sup>+</sup> from pH, +1 correct calculation of mass of CuCl)

iv. (6 pts) At 25°C the  $pK_a$  of acetic acid is 4.74. If a Grecian wanted to collect the produced nantokite without extremely corroding his hands ( $pH \le 2.5$ ) calculate the maximum amount (in grams) of acetic acid that can be added to 500mL of pure water at 25°C (assuming the addition of solid acetic acid does not change the volume).

 $K_a = 10^{4.74} = 1.82 \times 10^{-5}$ pH = 2.5  $3.2^{-3} M H^+$  $HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2 + H_3O^+$ Ι 0  $+_{\rm X}$ C +x-X  $32x10^{-3}$ E ?-x X  $X = 3.2 \times 10^{-3}$  $1.82 \times 10^{-5} = (3.2 \times 10^{-3})^2 / (?-3.2 \times 10^{-3})$ ? = 0.55 M  $HC_{2}H_{3}O_{2} = 0.55 \text{ M} - 3.2 \text{ x} 10^{-3} = 0.55 \text{ M}$ 0.55 mol/L \* 0.5 L = 0.27 mol \* 60.05 g/mol = 16.5 g(6 points) (+1 for finding pH, +4 for setup ICE/correct equation, +1 for calculations)

- b. Unfortunately, Grecians found it somewhat difficult to maintain products colored with nantokite. This is because exposing these products to water (eg. rain) would cause a red crust would form on the surface of the nantokite. Upon further investigation, the Grecians discovered that, alongside a red crust, completely submerging nantokite in water would create a very acidic solution.
  - i. (2 pts) Given that the red crust has molecular formula  $Cu_2O$ , write a chemical reaction that demonstrates its formation from nantokite.

 $2CuCl + H_2O \rightarrow 2HCl + Cu_2O$ (2 points)

ii. (3 pts) It was later discovered that the corrosion of copper by water often produced a noticeably larger amount of bubbles in solution than performing the reaction without water as a solvent. Explain this phenomenon based on the

products and reactions in both the original chemical equation for the corrosion of copper and the chemical equation of the reaction of water and nantokite.

 $2\text{CuCl} + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{Cu}_2\text{O}$ Formation of HCl drives following reaction which produces H<sub>2</sub>:  $2\text{Cu} + 2\text{HCl} \rightarrow 2\text{CuCl} + \text{H}_2$  (3 points) (+2 for reactions, +1 for explanation)

c. Answer the following questions assuming both the original reaction for corrosion of copper and the reaction of water with nantokite proceed to completion. Examine the following two methods for producing nantokite

A - Mix 40 g copper metal and 200 mL of 2M HCl in CCl<sub>4</sub>

**B** - Mix 40 g copper metal and 200 mL of 2M HCl in  $CCl_4$  with 3 mL of water

Given: the density of water is 1.0 g/mL, and CCl<sub>4</sub> is a nonreactive, anhydrous solvent.

- i. **(6 pts)** Which method would produce more nantokite? Calculate the amount (in grams) of nantokite produced through the selected method.
- 40 g Cu/(63.546 g/mol) = 0.63 mol Cu 2 M HCl \* 0.2 L = 0.4 mol HCl (limiting) (+1 identification of limiting reagent)

0.4 mol HCl \* (2 mol CuCl/2 mol HCl) = 0.4 mol CuCl 0.4 mol CuCl \* 99 g/mol = 39.6 g CuCl 3 mL H<sub>2</sub>O/(1 g/mL H<sub>2</sub>O\*18 g) = 0.167 mol H<sub>2</sub>O Limiting reaction with CuCl (+1 id.) 0.167 mol H<sub>2</sub>O \* (2 mol HCl/1 mol H<sub>2</sub>O) = 0.33 mol HCl (+1 rxn lowers CuCl) 0.62 mol Cu - 0.4 mol Cu reacted = 0.22 mol Cu remaining (HCl replenished) 0.22 mol Cu \* (2 mol HCl/2 mol Cu) = 0.22 mol CuCl (+1 remaining Cu rxn) 0.4 mol CuCl originally created - 0.167\*2 mol CuCl reacted with H<sub>2</sub>O to form (Cu<sub>2</sub>O + HCl) + 0.22 mol CuCl from replenished reaction = 0.286 mol 0.286 mol CuCl \* 99 g/mol CuCl = 28.32 g CuCl (+1 calcs of yield) (B) 28.32 g < (A) 39.6 g (+1 comparison) Method A (6 points)

ii. (1 pt) If we actually produce 30 g of nantokite, calculate the percent error for the method you selected in part I.
% Error = |Actual - Experimental|/Experimental \* 100%
= |30 g - 39.6 g|/39.6.8 g \* 100% = 24% (1 point)
Accept based on correct calculations, not numbers

iii. (1 pt) Which method would produce a more acidic product solution? Justify your answer in two to three sentences.

B, as method A uses all the HCl, while B leaves some HCl remaining since not enough Cu is present to react with all the HCl. (1 point)