INDIV

INDIVIDUAL EXAM

WUCT 2019

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. Students will work individually on this exam for 60 minutes. Only work and answers written on the front of the page will be graded. Correct answers with reasonable supporting work will receive full credit, while correct answers without work will not receive full credit. If more than one answer is given when only one answer is asked for, that question will be marked as completely incorrect. Team members are not allowed to communicate with each other or their coaches during the exam. 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. Cheating will NOT be tolerated. Refer to proctor(s) for further questions.

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Question 1: (16 points)

The following question will have you evaluate two independent systems in equilibrium.

a) With the recent discoveries of ice deposits being found on Mars, the idea of colonizing it seems much more desirable. However, in order to get there a lot of rocket fuel is needed and an important component of it is N_2O_4. At 25 °C and 1 atm, N_2O_4 is a gas that partially dissociates into NO_2 according to the equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ with $K_c = 4.61*10^{-3}$ and is endothermic.

i) *(7 points)* For a system already in equilibrium at 25 °C and 1 atm, circle all the options below that would push the reaction to the right (towards NO_2).

A) Increase the temperature.

B) Decrease the temperature.

C) Increase pressure inside rigid container.

D) Decrease pressure inside rigid container.

E) A catalyst is added.

F) Introduce argon into the container at a constant pressure and variable volume.

G) Introduce argon into the container at a constant volume and variable pressure.

H) Introduce 3 additional moles of N_2O_4 into the container.

I) Introduce 3 additional moles of NO_2 into the container.

J) Remove 2g of both NO_2 and N_2O_4 from the container.

K) Add 2g of both NO_2 and N_2O_4 into the container.

1 point for each correctly circled answer **(5 points total)**

-1 point for each incorrectly circled answer

- **NOTE:** the student cannot receive negative points on this question or any other on the exam and therefore the minimum grade possible is **0 points**

2 additional points will be awarded **if and only if** the student correctly circles all the correct answers and no incorrect answers are circled

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ii) *(4 points)* Draw the Lewis Structure of N_2O_4 with lone pairs shown. Write all non-zero formal charges directly on the atom and draw all possible resonance structures.

1 point for correct connectivity of the Lewis structure
2 points for correct formal charges on all resonance
- If 1 atom is missing a formal charge/has incorrect formal charge **1 of 2 points** awarded
- If more that 1 formal charge is missing or incorrect **0 of 2 points** awarded
1 point for having 4 structures with correct bonds and electron combinations

b) The Haber-Bosch process is one of the most important discoveries of the modern world. It was the first process developed that allowed for people to mass-produce plant fertilizer due to the production of ammonia. The reaction is $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ with K = $4.61*10^8$ and the process is very exothermic.
(5 points) Given a system in equilibrium containing hydrogen, nitrogen and ammonia where nitrogen is in excess such that its mole fraction is 0.55, determine if adding a large amount of nitrogen to the system will increase, decrease or not effect the **mole fraction** of ammonia. Explain your answer in 2-3 sentences.

Given the K is so high means that the reaction favors the product (ammonia). This means that with the large amount of excess nitrogen that there is **almost** no hydrogen at all in the equilibrium system. This means that adding nitrogen will not push the reaction to the right enough to change the moles of ammonia substantially, but instead effectively dilutes the system This causes the mole fraction of ammonia to **decrease**.
1 point for saying that the the mole fraction of ammonia is **reduced.**
4 points for clearly demonstrating that they understand how nitrogen dilutes the system.
NOTE 1: If the student says that the addition of nitrogen will increase or not affect the mole fraction of ammonia the student will receive **0 points**.
NOTE 2: If the student says that there is no hydrogen in the system the max potential points awarded to student is **4 points.**

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Question 2: (21 points)

a) *(4 points)* The compound silver chloride, AgCl, is practically insoluble in water. To increase solubility, ammonia can be added to solution so the Ag^+ can form the complex, **$[Ag(NH_3)_2]^+$**. Name this complex **and** write the balanced net ionic equilibrium equation of the complex ion formation.

Diammine silver
1 point no partial credit

2 acceptable answers:
Ag^+ (aq) + 2NH$_3$ (aq) $\rightleftharpoons$ [Ag(NH$_3$)$_2$]$^+$ (aq)

AgCl (s) + 2NH$_3$ (aq) $\rightleftharpoons$ [Ag(NH$_3$)$_2$]$^+$ (aq) + Cl$^-$ (aq)

3 points for correct answer, no partial credit.

b) *(8 points)* When combining two equilibria equations, the net equilibrium constant (K) is the product of the two elementary equilibrium constants. If 0.50 moles of NH$_3$ is added to 2.0 L of a solution of water and then an excess of AgCl is added, how many <u>moles</u> of AgCl can dissolve in the solution given $K_{sp} = 1.8 \times 10^{-10}$ and $K_{formation} = 1.6 \times 10^7$? **Circle final answer.**

EQ#1: Ag^+ (aq) + 2NH$_3$ (aq) $\rightleftharpoons$ [Ag(NH$_3$)$_2$]$^+$ (aq)

EQ#2: AgCl (s) $\rightleftharpoons$ Ag^+ (aq) + Cl$^-$ (aq)

EQ Net: AgCl (s) + 2NH$_3$ (aq) $\rightleftharpoons$ [Ag(NH$_3$)$_2$]$^+$ (aq) + Cl$^-$ (aq)   K=?

$K = K_{sp} * K_f = 1.8 \times 10^{-10} * 1.6 \times 10^7 = 2.9 \times 10^{-3}$
0.50 mol / 2.0 L = 0.25 M of NH$_3$

	AgCl (s)	2NH$_3$ (aq)	$\rightleftharpoons$	[Ag(NH$_3$)$_2$]$^+$ (aq)	Cl$^-$ (aq)
I	EXCESS	0.25		0	0
C	-x	-2x		+x	+x
E	Excess - x	0.25 - 2x		x	x

$K = [Ag(NH_3)_2^+][Cl^-]/[NH_3]^2 = x * x / (0.25 - 2x)^2 = 2.9 \times 10^{-3}$
x / (0.25 - 2x) = 0.054

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x=0.012 M

0.012 M * 2 L = **0.024 moles of AgCl**

2 points for correct K calculation

2 points for correct ICE Table setup

2 points for correct molarity of AgCl calculation

1 point for correctly converting molarity of AgCl to moles of AgCl

1 point for correct final answer with units

Student will lose **1 point** for not circling final answer.
- Minimum score possible is 0 points.

c) *(6 points)* A different scenario has 50 mL of 1M HCl solution being to a 25 mL solution with a sodium hydroxide concentration of 2M. Next, excess AgCl was added to the solution. What is the concentration of $[Ag^+]$ after equilibrium is reached?

All HCl is neutralized by the NaOH, but there are Cl- ions present which does affect equilibrium.

Thus, we can assume the only **$[Ag^+]$** produced is from this equation:

$AgCl \leftrightharpoons Ag^+ (aq) + Cl^- (aq)$ $K_{sp} = 1.8*10^{-10}$

$[Cl]_{initial} = 0.05$ mol/0.075 L = 0.667M

	AgCl (s)	$\leftrightharpoons$	Ag$^+$ (aq)	Cl$^-$ (aq)
I	EXCESS		0	0.667M
C	-x		+x	+x
E	Excess - x		x	0.667+x

$K_{sp} = [Ag^+][Cl^-] = x(x+0.667M)$

$x = 2.7*10^{-10}$ M

$[Ag^+] = 2.7*10^{-10}$ M

1 point for recognizing all the HCl and NaOH is neutralized

3 points for recognizing that the Cl ions affect equilibrium of the process

1 point for correct ICE table setup, or correct K_{sp} expression

1 point for correct final answer with units

**Note:** If student does not recognize that chlorine ions affect the equilibrium of the system and receives a final answer of **$[Ag^+] = 1.34*10^{-5}$ M,** then **3 points** max will be awarded to student.

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d) ***(3 points)*** $[Ag(NH_3)_2]^+$ may be a familiar complex ion as it is also called Tollen's reagent used for the famous Tollen's test. This is a popular high school chemistry experiment where you can produce a "silver mirror" inside of a test tube. The tollens reagent is used to determine the presence of a aldehydes with the basic reaction given below:
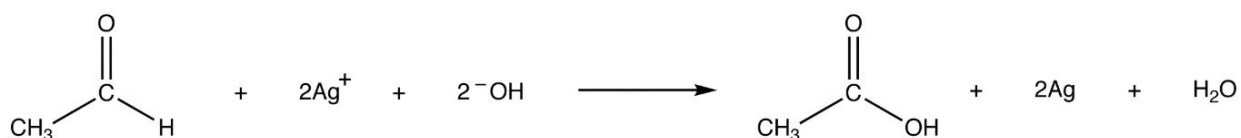
Given the Fischer projection of D-Glucose below, draw the fischer projection of what D-Glucose will be after reacting with Tollen's reagent and hydroxide ions.
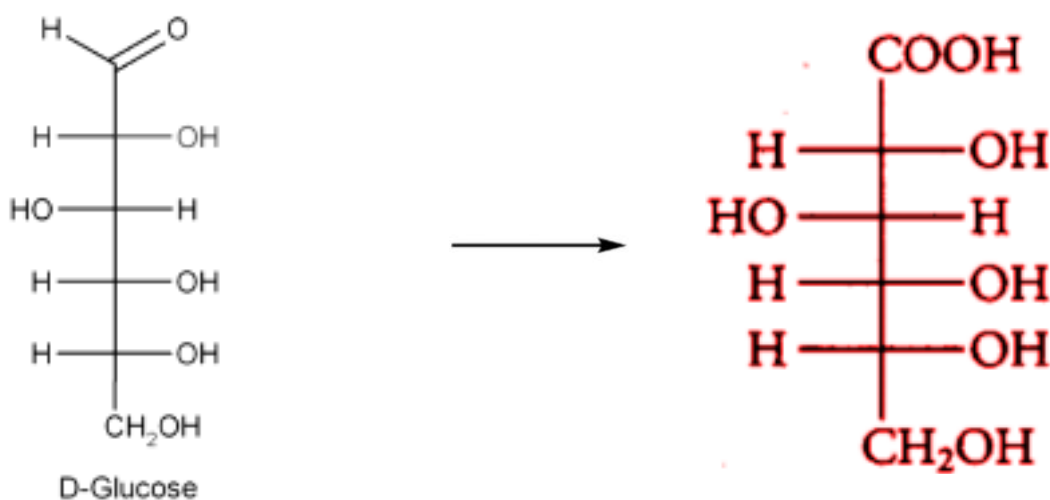
NOTE 1: This problem is all or nothing. This means if there are **any** changes to glucose structure below the keto group then no points awarded (If hydrogens not present = **1 point max**)
NOTE 2: Students can represent the carboxylic acid group in many ways. All of the ways listed below will be accepted:
  - COOH
  - CO_2H
  - A double bond between carbon and oxygen and a single bond to 1 OH group (electrons not needed)

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Question 3: (16 points)
Bromine is considered to be a very potent destroyer of ozone both in the stratosphere in both polar regions (Arctic and Antarctic). The following mechanism is known to cause ozone destruction:

$$BrO\cdot + ClO\cdot \xrightarrow{k_1} Br\cdot + Cl\cdot + O_2$$

$$Br\cdot + O_3 \xrightarrow{k_2} O_2 + BrO\cdot$$

$$Cl\cdot + O_3 \xrightarrow{k_3} ClO\cdot + O_2$$
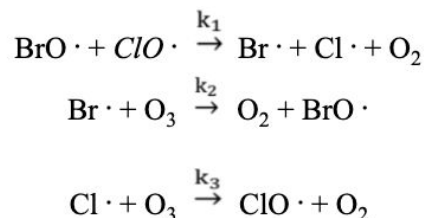
a. *(2 points)* Are free radicals paramagnetic or diamagnetic? **Circle one** of the options below and give a 1 sentence justification.

Paramagnetic   Diamagnetic

Free radicals are paramagnetic because they all have an odd amount of electrons or they have an unpaired electron

2 points for correct answer with explanation showing the <u>odd</u> number/presence of an unpaired of electrons is why radicals are paramagnetic

b. *(2 point)* Write the overall reaction for this mechanism.

$$2O_3 \rightarrow 3O_2$$

All or nothing

c. *(2 points)* Is the reaction mechanism above a "catalytic cycle"? Give a 1 sentence justification.

Yes there are no Br/BrO or Cl/ClO radical pairs in the net reaction and thus they can continue destroying ozone multiple times before being removed.

A correct answer with a reasonable explanation will receive full credit
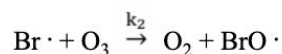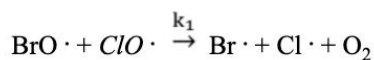
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Question 3 Continued:

    d. *(2 points)* Write the rate expression for ozone with respect to time, $d[O_3]/dt$, based on reactions (2) and (3).

$$d[O_3]/dt = -k_2 [Br \cdot][O_3] - k_3 [Cl \cdot][O_3] = -(k_2 [Br \cdot] + k_3 [Cl \cdot])[O_3]$$

2 points for correct answer (both answer with O_3 factored and unfactored will be accepted)

    e. *(8 points)* Assume that the radical chlorine (Cl ☐) and radical bromine (Br ☐) are consumed as fast as they form. This is called a pseudo steady state approximation (PSSA). Derive a relationship for $d[O_3]/dt$ in terms of the rate constants, BrO ☐ and ClO ☐ concentrations. The mechanism for this process has been copied below for convenience. **Circle your final answer.**

$$BrO \cdot + ClO \cdot \xrightarrow{k_1} Br \cdot + Cl \cdot + O_2$$

$$Br \cdot + O_3 \xrightarrow{k_2} O_2 + BrO \cdot$$

$$Cl \cdot + O_3 \xrightarrow{k_3} ClO \cdot + O_2$$
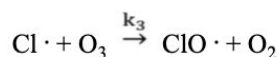
$$d[Br \cdot]/dt = k_1[BrO \cdot][ClO \cdot] - k_2 [Br \cdot][O_3] = 0 \rightarrow [Br \cdot] = k_1[BrO \cdot][ClO \cdot] / k_2[O_3]$$

$$d[Cl \cdot]/dt = k_1[BrO \cdot][ClO \cdot] - k_3 [Cl \cdot][O_3] = 0 \rightarrow [Cl \cdot] = k_1[BrO \cdot][ClO \cdot] / k_3[O_3]$$

$$d[O_3]/dt = - [(k_2(k_1[BrO \cdot][ClO \cdot] / k_2[O_3]) - k_3(k_1[BrO \cdot][ClO \cdot] / k_3[O_3]))][O_3]$$

$$d[O_3]/dt = -2k_1[BrO \cdot][ClO \cdot]$$

1 point for attempting to use rates to describe the quantity of Br ☐ and Cl ☐
2 points for setting $d[Br ☐]/dt$ and $d[Cl ☐]/dt$ relationships = 0
1 point for correct [Cl ☐] relationship
1 point for correct [Br ☐] relationship
3 point for correct final answer.
Student will lose **1 point** for not circling final answer.
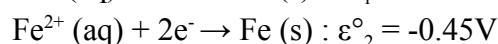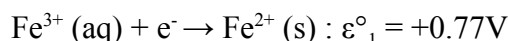   ● Minimum score possible is 0 points.

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Question 4: (11 points)

The production of pure iron from iron ore can be accomplished through smelting. The process however can have a large environmental impact and result in the release of thousands of tons of CO_2 into the atmosphere. A potential solution to this problem is electrolysis where about 2000 kWh of energy is needed to produce one tonne of iron. This problem will investigate the chemistry behind using electrolysis in order to purify iron. Faraday's constant = 96485 C/mol. For this entire problem assume all given information and all systems you are solving for occur at 25 °C and 1 atm.

a) *(3 points)* Given the information below determine the half cell potential for the reaction: **Fe^{3+} (aq) + 3e$^-$ → Fe (s). Circle final answer.**

$$Fe^{3+} \text{ (aq)} + e^- \rightarrow Fe^{2+} \text{ (s)} : \varepsilon^\circ_1 = +0.77V$$
$$Fe^{2+} \text{ (aq)} + 2e^- \rightarrow Fe \text{ (s)} : \varepsilon^\circ_2 = -0.45V$$

$$\Delta G^\circ = -nF\varepsilon^\circ = \Delta G_1^\circ + \Delta G_2^\circ \rightarrow -3F\varepsilon^\circ = -2F(-0.45V) - F(0.77V) \rightarrow$$
$$3\varepsilon^\circ = 2(-0.45V) + (0.77V) \rightarrow \varepsilon^\circ = \textbf{-0.043V or -0.04V}$$

2 points for correct setup ($\Delta G^\circ = -nF\varepsilon^\circ = \Delta G_1^\circ + \Delta G_2^\circ$), **1 point** for correct answer **with** units.
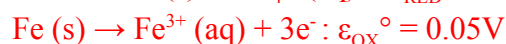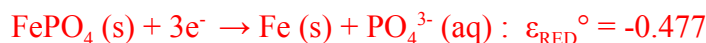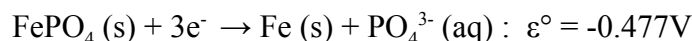**0 points** awarded for answer $\varepsilon^\circ = +/- 0.32V$
Student will lose **1 point** for not circling final answer.
■ Minimum score possible is 0 points.

b) *(8 points)* Your friend, Sloppy Joe, incorrectly solved part a) and received a reduction potential of $\varepsilon^\circ = -0.05V$. Using this incorrect value and the reaction below calculate what Joe will receive as the solubility constant of $FePO_4$. **Circle final answer.**

$$1V = J/C$$
$$FePO_4 \text{ (s)} + 3e^- \rightarrow Fe \text{ (s)} + PO_4^{3-} \text{ (aq)} : \varepsilon^\circ = -0.477V$$

$$FePO_4 \text{ (s)} + 3e^- \rightarrow Fe \text{ (s)} + PO_4^{3-} \text{ (aq)} : \varepsilon_{RED}^\circ = -0.477$$
$$Fe \text{ (s)} \rightarrow Fe^{3+} \text{ (aq)} + 3e^- : \varepsilon_{OX}^\circ = 0.05V$$
$$\varepsilon_{cell}^\circ = \varepsilon_{OX}^\circ + \varepsilon_{RED}^\circ = -0.427V$$
$$\Delta G^\circ = -nF\varepsilon^\circ = -RTln(K_{sp})$$
$$lnK_{sp} = nF\varepsilon^\circ/RT = (3 \text{ mol e}^- \text{ / mol rxn})(96485 \text{ C/mol e}^-)(-0.427V)/(8.314J/\text{mol rxn-K})(298K)$$
$$K_{sp} = \textbf{2.16} \cdot \textbf{10}^{\textbf{-22}}$$

3 points for ε_{cell}° calculation, **2 point** using both ΔG° equations, **3 points** for correct K_{sp} final answer.
Student will lose **1 point** for not circling final answer.

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Question 5: (20 points)
Dimensional analysis is a common tool used by engineers and scientist to both check their work as well as determine the relationship between different physical quantities by identifying their base quantities. The following question will ask for you to analyze the units of various situations. For simplicity please give all your final answers where you denote all units of length as **L**, all units of mass as **M**, and all units of time as **T**.

A useful example is that a Newton = kg-m/s² = MLT^{-2}

a. *(3 points)* Given the graph below shows a chemical reaction where [A] is concentration. Determine what the units for the **rate constant** are for this reaction. **Write your final answer in the box below.**
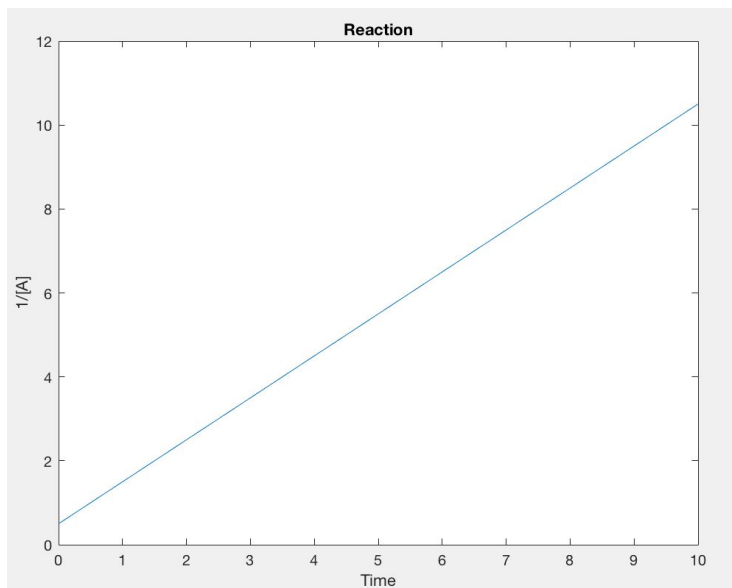
$$L^3M^{-1}T^{-1}$$

NOTE: Student will not be penalized in this part or the rest for expressing units in denominator with a fraction rather than a negative exponent.
From the graph student should identify that this is a second order reaction and that has units of molarity^{-1}s^{-1} (inverse molarity inverse seconds) which converts into $L^3M^{-1}T^{-1}$
Student could also identify that the slope of graph is k ∴ Δy/Δx= molarity^{-1}s^{-1} and convert that to proper units.

This question is all or nothing (no partial credit awarded)

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b. *(4 points)* An extremely important tool for analyzing fluid flow for engineers is the Reynolds number. Given the equation below determine the units for the Reynold's number for a viscous fluid in a pipe. **Write your final answer in the box below.**

$$Re = \frac{\rho v D}{\mu}$$

Re = Reynolds number $\quad\quad$ ϱ = fluid density

v = fluid velocity $\quad\quad$ μ = dynamic viscosity (Pressure·T)

D = pipe diameter

unitless

Pressure = Force/Area $\therefore$ P = N/L^2 = MLT^{-2}/L^2 = MT^{-2}L^{-1}

μ = Pa·T = MT^{-1}L^{-1}

v = LT^{-1}, ϱ = ML^{-3} , D = L

Re = (LT^{-1})(ML^{-3})(L)/(MT^{-1}L^{-1}) = unitless

2 points for Pressure = Force/Area equation, **2 points** for correct answer

NOTE: Just because the answer is unitless does not mean a blank answer in the box will be accepted.

c. *(3 points)* When analyzing mass transfer by diffusion a common relation is Fick's first law of diffusion. Given the equation below determine the units for the <u>diffusivity</u>. **Write your final answer in the box below.**

$$J = -D\frac{\Delta C}{\Delta x}$$

J = Flux $[\frac{M}{L^2-T}]$ $\quad\quad\quad$ D = Diffusivity

x = Distance $\quad\quad\quad$ C = Concentration

L^2T^{-1}

C = ML^{-3}, D = (J)(L)/(C) = (ML^{-2}T^{-1})(L)(L^{3}M^{-1}) = L^{2}T^{-1}

d. *(10 points)* The Avrami kinetics equation is used when describing how solids transform from one phase to another at a constant temperature. Given the data below and the Avrami equation determine the units of **k**. (Hint: create two simple independent equations based on data below to solve for n by using **all** of the natural log rules given). Write final answer in box below.

$$f = 1 - exp\{- k(t^n)\}$$

f = Fraction of mass transformed (unitless)　　　　k = rate

t = time　　　　　　　　　　　　　　n = constant (any positive real number)

State	Fraction Transformed	time (T)
1	0.25	320
2	0.62	445

Natural Log Rules:

$k(t^n) = $ unitless

$\ln(exp\{x\}) = x$,　$\ln(x^{-a}) = -a \cdot \ln(x)$ (where a is any real number),　$\ln(x \cdot y) = \ln(x) + \ln(y)$

Take ln() of both sides and apply rule #2: $-\ln(1-f) = kt^n$ **(1 point)**

Apply rule #3: $\ln(1/(1-f)) = kt^n$ **(1 point)**

Take ln() of both sides again: $\ln(\ln(1/1-f)) = \ln(kt^n)$

Apply rule #3 and #4: $\ln(\ln(1/1-f)) = \ln(k) + n*\ln(t)$ **(2 points)**

Create two independent equations by plugging in data: **(2 point)**

EQ#1: $-1.245899 = \ln(k) + 5.76832n$

EQ#2: $-0.032953 = \ln(k) + 6.09807n$

Solve for n by subtracting equations cancelling out ln(k) values: n = 3.68 **(2 point)**

k must have units of $1/(t^n)$ due to exp function being unitless $\therefore$ k has units of $T^{-3.68}$ **(2 points)**

$$T^{-3.68}$$

Note: If student has both EQ#1 and EQ#2 correct and makes an arithmetic error when solving for n, but their overall procedure is correct **and clearly visible to grader**, the student will be awarded **8 points**

Student will lose **1 point** for not writing final answer in box.
- Minimum score possible is 0 points.

Question 6: (16 points)

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"Freeze concentration" is a process used to create concentrated orange juice by removing frozen ice.

Juice is made up of pulp and liquid water. The feed juice (Stream 1, 10% wt pulp, 38563 kg/hr) is cooled in a freezer unit where ice crystals (of water) form. The resulting slurry of juice and ice (Stream 2) is filtered into two streams. Stream 3 consists of only juice (40% wt pulp). All of the ice crystals leave the process in Stream 4. This whole process is at **steady state.**

Approximate the heat capacity of the juice (liquid water & pulp) as a constant 4.184 kJ/(kgK). Approximate the heat capacity of the solid ice as a constant 2.108 kJ/(kgK).
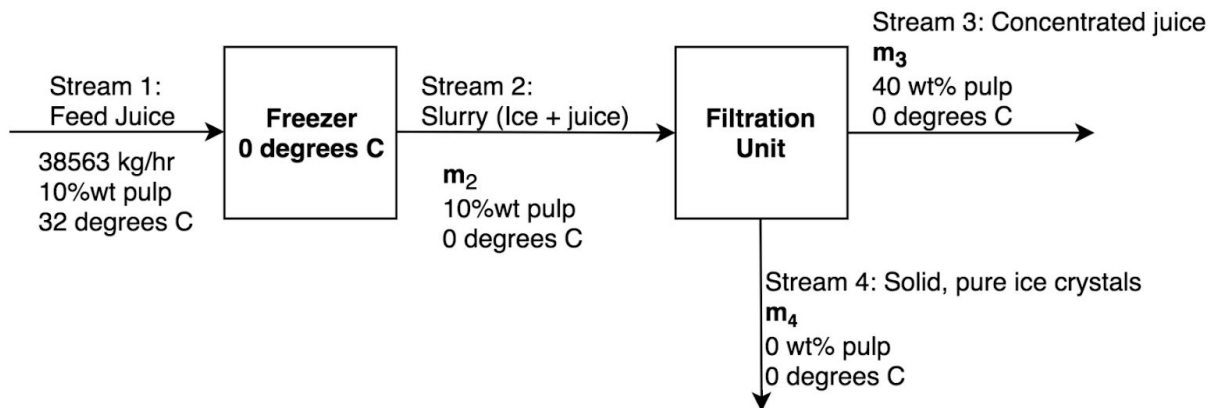
a. *(3 points)* How much ice is produced in the freezer? Give answer in units of (kg/hr) and write in provided box.

Need m_4
$m_1 = m_2$ ∴ $m_2 = 38563$ kg/hr
Overall Balance #1:
$m_2 = m_3 + m_4$

Pulp Balance #2:
$X_2 m_2 = X_3 m_3 + X_4 m_4$ where X_i is the wt fraction of pulp:
$(0.1)(38563$ kg/hr$) = (0.4)m_3$ ∴ $m_3 = 9641$ kg/hr
38563 kg/hr $= 9640.75 + m_4$ ∴ $m_4 = 28922$ kg/hr

$m_4 = 28922$ kg/hr

2 points for correct two starting mass balance equations with correct numbers plugged in
1 point for the correct final answer with units **written in box.**

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b. *(5 points)* If the heat of fusion is 6.00 kJ/mol for the juice, what does the minimum power of the freezer need to be? Give answers in units of (kW) and write in the given box. MW H_2O = 18g/mol.

$\hat{H}_1 = Cp\Delta T = 4.184*(0°C - 32°C) = -133.88$ kJ/kg

$\Delta\hat{H}_{Fus} = 6$ kJ/mol / $MW_{H20} = 333.4$ kJ/kg

$\hat{H}_2 = -\Delta\hat{H}_{Fus} = -333.4$ kJ/kg

$\Delta\hat{H} = (\hat{H}_1)*(38563$ kg/hr$) + (\hat{H}_2)*(28922$ kg/hr$)$

$\Delta\hat{H} = -5{,}163{,}483$ kJ/hr $- 9{,}642{,}595$ kJ/hr $= -14{,}803{,}657$ kJ/hr $= -4112$kJ/s

1 kJ/s = 1 kW $\therefore$ **-4112 kW or -4110 kW**

-4112 kW

1 point for correct $\hat{H}_1$ value, **1 point** for correct $\hat{H}_2$ value, **1 point** for correct $\Delta\hat{H}$ equation setup, **2 point** for correct final answer with units.
If student writes the correct answer but forgets negative sign then **4 points** will be awarded.
Student will lose **1 point** if answer is not written in box

NOTE 1: Alternate approach where student does $mCp\Delta T$ is equally as valid given they use the correct flow rates and final answer will receive full points.
**NOTE 2**: This problem relies on answers from part i) $\therefore$ if part i) was incorrect, but with those incorrect flow rates, part ii) is correct then full points for part ii) will be awarded.

c. *(5 points)* A common component in orange juice is vitamin C or ascorbic acid which has its structure given below. When this molecule loses a single acidic hydrogen (H^+) it is stabilized by resonance and has the largest amount of electron delocalization. Draw the lewis structure for this conjugate base of ascorbic acid including **all** non-zero formal charges and resonance if necessary.

2 points for correct hydrogen removed
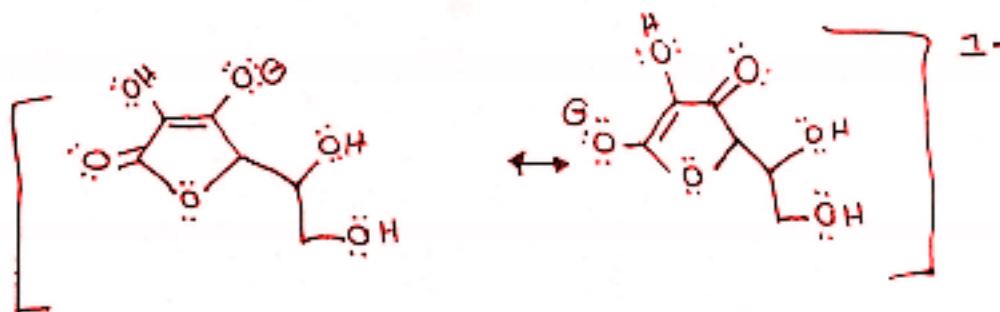**1 point** for leaving an extra electron when H^+ is removed
1 point for **correct** resonance structures
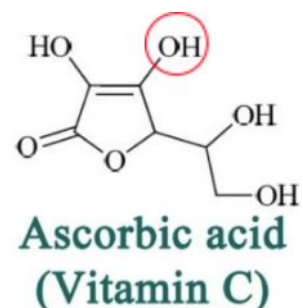
HO   OH
OH
O   O
        OH
Ascorbic acid
(Vitamin C)

5

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d. *(3 points)* You find that the juice plant you are working at is introducing 3 unknown pollutants into the environment and you separately titrate them separately with HCl. Given the list of 5 potential pollutants and their **conjugate acid** pKa values, determine the three pollutants by assigning them to their proper titration curve.

Pollutants Labeled A-E:

A - Na$_2$CrO$_4$: pKa = 6.5,   **B - NaHCO$_3$** : pKa = 10.25
C - NaH$_2$PO$_4$: pKa = 7.2, **D - NaOCl** : pKa = 7.6
E - C$_5$H$_5$N : pKa = 5.25

The graphs have very similar starting pH and equivalence point pH ∴ use half equivalence point where pH = pKa of conjugate acid.

A

C

D