Name (Last, First): ___________________ ID Number: ________________________

Sample Question Solutions for the Team Round Test

1. The WUCT Question Writing Team has realized that they are losing muscle mass because they are spending much of their time coming up with difficult questions. To combat their muscle atrophy, they have all decided to start drinking protein shakes, WASHU-MAX, containing leucine hydrochloride, a common amino acid, in supplements. It is a diprotic acid with $\mathrm{pKa}_1 = 2.36$ and $\mathrm{pKa}_2 = 9.60$. To make the shake, 0.500M NaOH solution is slowly added to 50.00mL of a 0.100M leucine hydrochloride. Show all work for full credit.

a. What is the initial pH of the solution before any NaOH is added?

LeuH2+ in equilibrium with H+ and LeuH, Ka=4.4*10^-3
If x = [H+] = [LeuH], then [LeuH2+] = 0.100 – x
[LeuH][H+]/[LeuH2+] = [x]2/[0.100-x] = 4.4*10^-3
x=0.019M = [H+]
pH=-log[H+]=1.72

*only the first deprotonation calculation is required; however, if the second deprotonation calculation is performed, it will be accepted

b. Parts i and ii relate to the titration of leucine hydrochloride to a pH of 3.50.

i) What volume of NaOH solution must be added to the leucine hydrochloride to reach a pH of 3.50?

.50=2.36 + log [LeuH]/[LeuH2+]

[LeuH]/[LeuH2+]=13.8

mol LeuH + mol LeuH2+ = 5.00*10^-3

➔ 4.66*10^-3 mol LeuH, requiring 4.66*10^-3 mol NaOH

volume NaOH = (4.66*10^-3 mol)/(0.500M) = 9.32

ii) At this pH, what charge predominates on leucine ions?

Leucine starts at + because the amine group has three hydrogens, but at pH 3.5, it has lost the hydrogen on –OH, so the -O- and –NH3+ yield a net charge of 0.

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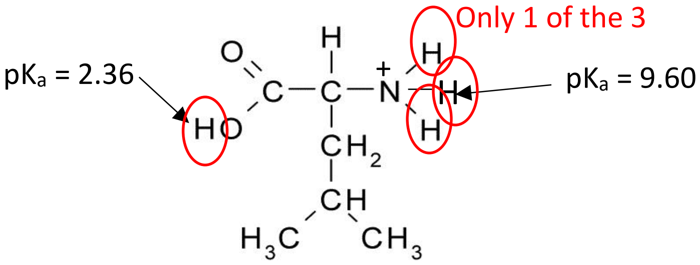
c. Since leucine hydrochloride is a diprotic acid, leucine hydrochloride will go through two deprotonation events in the course of this titration.

i) On the structure given below, circle one of the deprotonation sites.



ii) State with justification whether it is the first or second site of deprotonation.

Carboxylic acid (pKa = 2.36) will deprotonate first since it is more acidic than amine hydrogen (pKa = 9.60)

d. While writing this question, the WUCT questions writers decided to perform this titration in the lab. They decided to use phenolphthalein, a pH indicator, that changes from colorless to a bright pink color at the second equivalence point. However, while titrating, they overshot the equivalence point and the solution turned a bright pink color and then colorless again. **No** calculations are needed for part d.

i) Given that phenolphthalein (represented by "In") exists in the equilibrium given: $H_2In \rightarrow In^{2-} \rightarrow In(OH)^{3-}$, how might the team return the solution to the pink color they want since they cannot start over? Present one possible solution, and assume their lab professors have granted access to any chemicals that they might need.

The students could add an acid of known concentration to the solution to push it from the In(OH)3- back to the In2- form. Students need only say that they will add an acid of some kind. Names and chemical formulas are accepted.

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ii) Why do you think pH meters are used when possible, instead of chemical pH indicators?

pH meters will constantly measure the pH allowing a titration curve to be obtained. A pH indicator has a range of pH where it changes color, so the results will not be as accurate as reading off a graph would be. Additionally, the pH indicators sometimes hard to distinguish (ex. What shade of light pink phenolphthalein are you looking for).

e. As one may expect, these chemists are not the best in the laboratory. They made some errors during their titration other than overshooting the second equivalence point. For the errors below, indicate and explain—in 2-3 sentences—how each would affect the results.

i) There was a bubble of air in the tip of the burette before the titration was started

A bubble of air in the tip of the burette will lead the chemist to believe more of the titrant was added than actually was. This will effect results because the calculations will show that the solution being titrated is more acidic than it actually is.

ii) They left a drop of NaOH hanging on the tip of the burette when they were finished.

Similar thinking here, not all the titrant is actually dispensed into the solution into solution (that they measure to be added on the burette), so the solution being titrated is actually less acidic that calculated.

iii) A few drops of NaOH dripped into the burette because they left the funnel they used to fill the burette with NaOH on the top.

If some NaOH drips into the burette after the titration is started, then more NaOH will be added than the reading will show. This will cause the experimenter to calculate the pH to be less acidic because they believe that they added less NaOH than they actually did. Could also say here that if the titration had not been started, and the experimenter realized their mistake, that they could record a new volume from the side of the burette as the starting volume of titrant. Both answers are valid, both would be accepted, but only one is needed.

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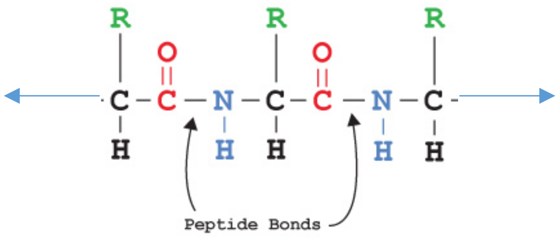
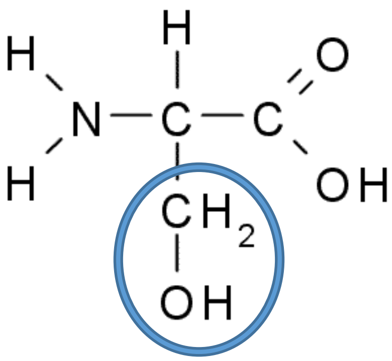
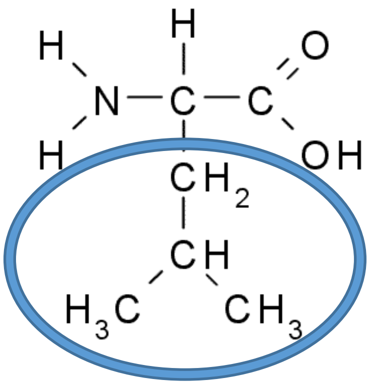
f. Pictured below is a section of a peptide chain (arrows represent a continuation of the chain). The green R’s represent the side chain groups of the three amino acids in the given chain. Also given below are the structures of two amino acids, Serine and Leucine, with their side chain groups (R groups) circled.

i) If a peptide chain has a long stretch of several hundred Serine amino acids linked together, and a long stretch of several hundred Leucine amino acids linked together, identify which stretch of amino acids likely be found in a polar (e.g. aqueous) environment, and which will likely be found in a nonpolar environment. Justifications should include discussion about the circled R-groups and their properties.





Serine



Leucine

Serine will likely be found in a polar environment because it is polar (has –OH or hydroxyl functinal group) . Likes dissolve likes. The –OH goup is highly polar compared to leucine’s isobutyl group. C-H bonds are considered essentially nonpolar, so leucine would likely be found in a nonpolar environment. *Concisely, but completely, explain the following interesting observations:*

2.

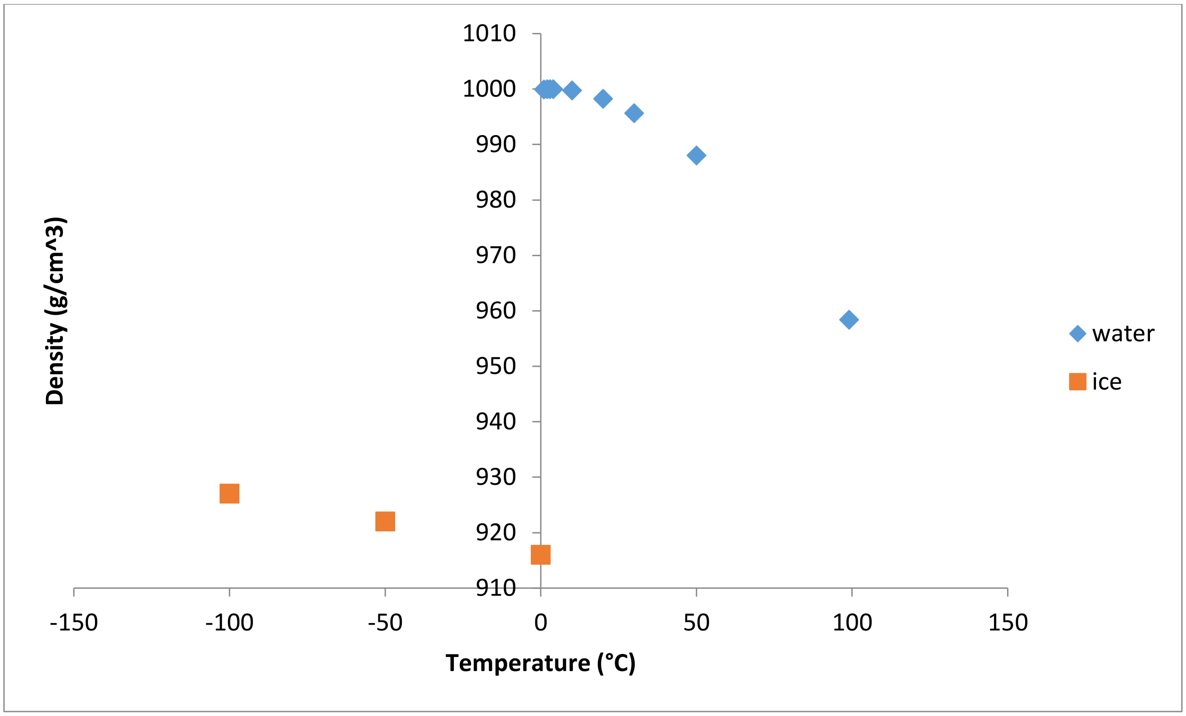


*Figure 1: Density of ice (**red squares**) and water (**blue diamonds**) as a function of temperature.*

a. As the temperature of ice increases to its melting point, a monotonic decrease in density is observed (**Figure 1**). On the other hand, as the temperature of water decreases to its freezing point, the density increases then decreases, reaching a peak density value at around 4 °C. Explanations should account for these observations at a qualitative level.

Density = mass divided by volume; in ice, hydrogen bonding network between water molecules is structured as a crystal lattice while in water hydrogen bonds are temporary and unstructured. Consequently, water molecules are more closely packed in the liquid state than as a solid (more mass / unit volume), so ice has a lower density than water. Increasing the temperature of ice causes more oscillation in the molecules, so each molecule occupies more volume from jostling its neighbors. Similarly, decreasing the temperature of when temperature is high relative to freezing temperature decreases the energy and thus the motion of water molecules, so each molecule occupies on average a lower volume. However, if temperature is increased close to heating, molecules will be sufficiently slow such that hydrogen bonding becomes more structured and rigid, increasing the volume between water molecules as the system approaches a lattice structure as seen in ice.

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b. Carbon dioxide sublimes at 194.7K and will not melt at atmospheric pressure (1 atm). However, when the pressure is increased to 5.12 atm, carbon dioxide will melt at 216.6 K.

Intermolecular forces between carbon dioxide molecules are weak London dispersion forces. At low temperatures, carbon dioxide forms a structured solid held together by a larger number of these weak interaction. However, molecules in a liquid have fewer interactions on average than those in a solid. At atmospheric pressure, the intermediate number of interactions found in liquid carbon dioxide is insufficient to allow it to exist as a liquid, so it sublimates. However, increasing the pressure allows the formation of more interactions in liquid carbon dioxide, so it can exist.

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c.

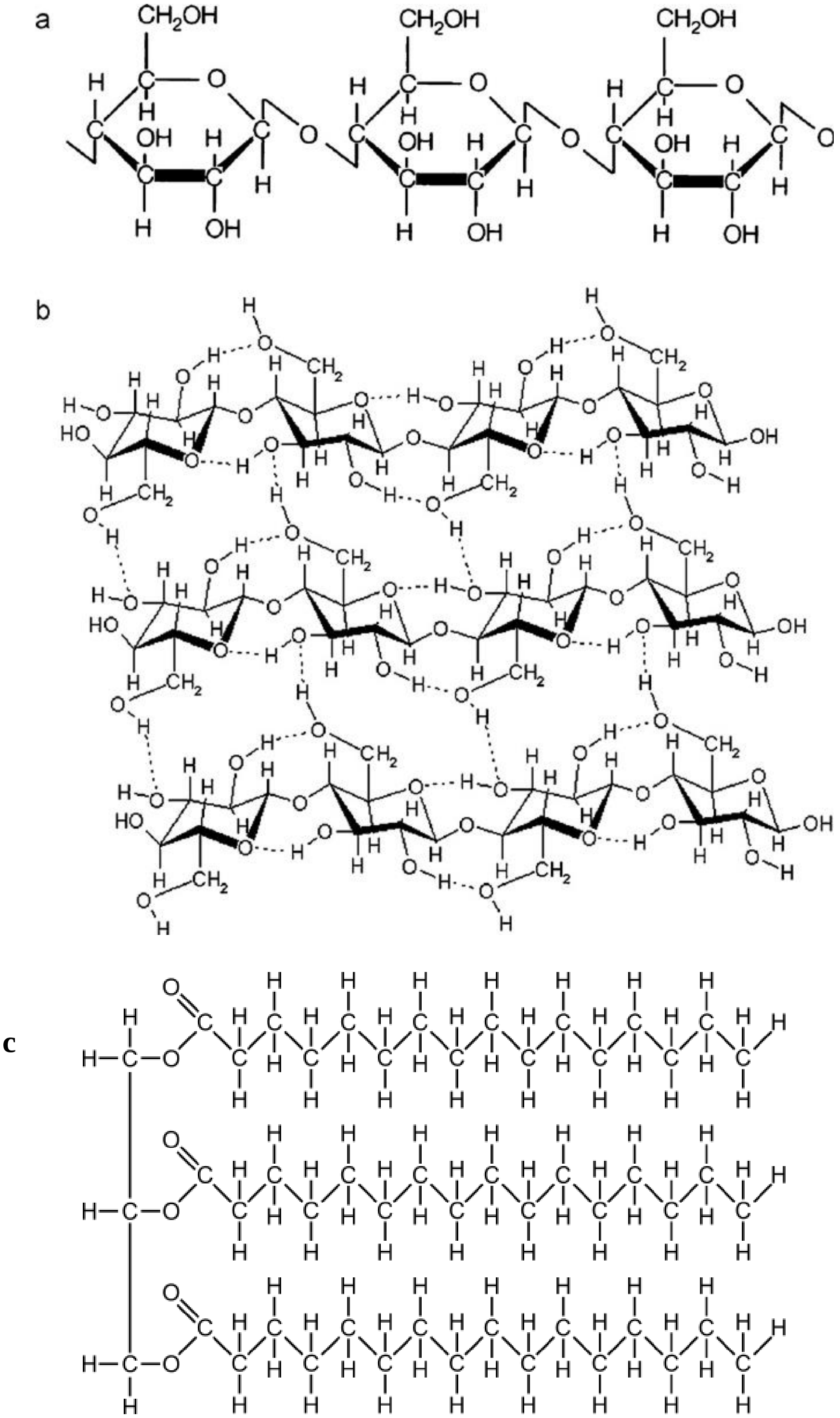

Figure 3: (a)(Top) A polymer of carbohydrates (b)(Middle) hydrogen bonding pattern of the carbohydrates that comprise paper (c)(Bottom) A triglyceride, the main component of oils. ***Note****: In (b), the carbons comprising the carbohydrate rings are not explicitly labeled but are present at the vertices of the rings.*

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Paper consists of a chain of sugars, as shown in Figure 3a and 3b. When paper is dipped in water, it loses its structural integrity (i.e. becomes “mushy”), but when it is dipped in oil, it does not. Use the information from **Figure 3** to support your explanation.

Cellulose is highly hydrophilic. Water molecules will compete with cellulose units for hydrogen bonds. Since there are many more water molecules than cellulose molecules in an aqueous environment, the cellulose-cellulose hydrogen bonding network will be replaced by water-cellulose hydrogen bonds. As a result, the individual long-chain cellulose fibers will separate and become completely hydrated, so paper will dissolve and lose its structural integrity. However, in oil, triglycerides have very few hydrogen bond donors or acceptors and cannot disrupt the hydrogen-bonding network of cellulose.

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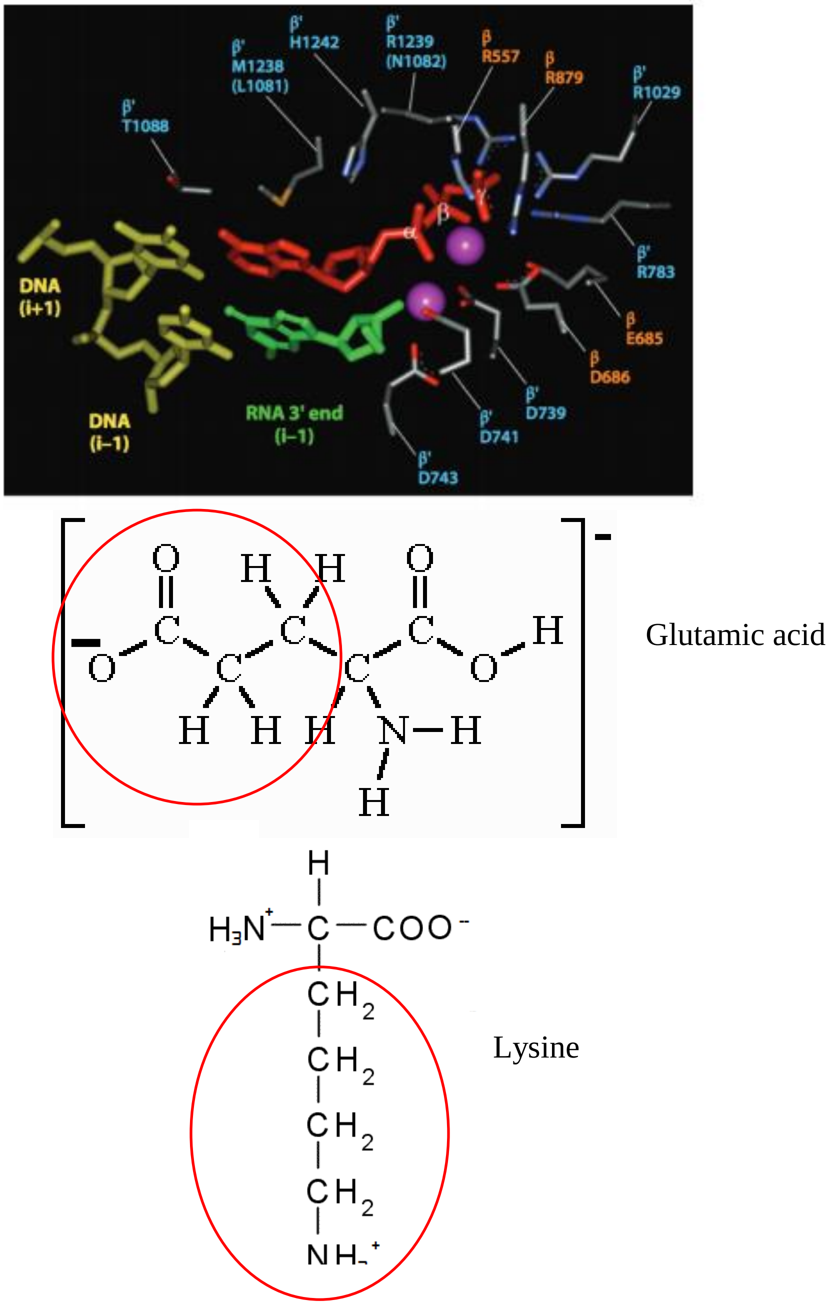

Figure 3. The active site of RNA polymerase, an enzyme that uses DNA to synthesize ribonucleic acids, long polymers of nucleotides that are the building blocks of life. Two magnesium ions (purple spheres) occupy part of the active site and are surrounded by glutamic acids D743, D741, D739, D686. Part of each glutamic residue is drawn as a stick model, with red portions at the tip indicating oxygen atoms. For your convenience, the structures of glutamic acid and lysine are provided, and the circled parts of each molecule are the parts that interact with magnesium.

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It has been found that the magnesium ions are critical catalysts for the nucleoaddition reaction through which the RNA molecule is extended (you do not have to explain this). It has also been found that mutations that change D739 from a glutamic acid into a lysine (structure above) prevent RNA polymerase from catalyzing the reaction.

The negative glutamic acid molecules chelate the magnesium, keeping it in the active site. The electrostatic interactions between the oxygen atoms on glutamic acid (which have a partial negative charge) and the positively charged magnesium ion are key for this. If a glutamic acid molecule is replaced by a lysine molecule, which is positively charge, the magnesium ion will be repelled instead of attracted and will not remain in the active site.

3. A beaker contains 1 L of water in surroundings of temperature -10 °C. 30 grams of NaCl is then added to the water. Assume NaCl dissociates completely. Show all work for full credit.

a. What is the concentration in mol/L of Na^+ and Cl^- ions in the solution?

30 grams NaCl *1 mole NaCl/58.4397grams=.5133 mole NaCl
.5133 mole/ 1L =.5133 mole/L Na+ and Cl- solution

b. How much of the water will turn into ice? (K_f of water is 1.853 K*kg/mol)

$\Delta T_F=K_{F*}b*i$
Solve for b
$\Delta T_F/(K_F*i)=b$
(10K)/(1.853Kkg/mol*2)=b
2.698mol/kg=b
30g NaCl*(1/58.4397g/mol)=.5133mole (could reference A)
$b=(.5133\text{ mole})/m_w$
$.5133\text{mole}/b=m_w$
$m_w=.190\text{kg}$
1kg-.190kg=.808kg water will freeze

c. If instead of NaCl, we add 30 grams of $CaCl_2$ how much of the water will turn into ice? Assume $CaCl_2$ dissociates completely in water.

$\Delta T_F=K_{F*b*i}$
Solve for b
$\Delta T_F/(K_F*i)=b$
(10K)/(1.853Kkg/mol*3)=b
1.799mol/kg=b
30g $CaCl_2$*(1/110.978g/mol)=.2703 mole
$b=(.2703\text{ mole})/m_w$
$.2703\text{mole}/b=m_w$
$m_w=.1503\text{kg}$
1kg-.1503kg=.845kg water will freeze

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d. If we now drop 30 grams of $AgNO_3$ into the solution of $CaCl_2$ how much of the water will be frozen after equilibrium is reestablished? (K_{sp} for AgCl is $1.77*10^{-10}$ at 10°C, for purposes of this question you can assume it is also $1.77*10^{-10}$ at -10°C). Assume $AgNO_3$ dissociates completely in water.

30g AgNO3*(1 mole/169.87g)=.177mole Ag+ and NO3-
.2703 mole CaCl2 *2 mole Cl-/mole CaCl2=.5406mole Cl-
Can assume reaction goes to completion.
.5406mole Cl--.177mole Cl-=.3636mole Cl-
.177 mole NO3
.2703 mole Ca
Add them up
.8109 mole solute
(10K)/(1.853Kkg/mol*1)=b
b=5.397mol.kg
b=(.8109mole)/mw
.8109mole/b=mw
mw=.15kg
no change!

e. If we now drop 30 grams of Hg_2SO_4 into the solution of $CaCl_2$, what mass (in g) of the water will be frozen after equilibrium is reestablished? (assume that K_{sp} for Hg_2Cl_2 is $1.43*10^{-18}$ at -10°C) Note: $Hg_2^{2+}$is a dimer and will not dissociate in water.

30g Hg_2SO_4*(1 mole/493.265g)=.060819mole Hg_2^{+2} and SO_4^{-2}
.2703 mole $CaCl_2$ *2 mole Cl^-/mole $CaCl_2$=.5406mole Cl^-
Can assume reaction goes to completion.
.5406mole Cl^--.12164mole Cl^-=.4200mole Cl^-
.060819 mole SO_4^{-2}
.2703 mole Ca
Add them up
.7511 mole solute
(10K)/(1.853Kkg/mol*1)=b
b=5.397mol.kg
b=(.7511mole)/m_w
.7511mole/b=m_w
mw=.1392kg
1-.1392kg=.86kg will be frozen
More water will freeze!