**Module 5 – Water reclamation on the ISS: “Houston, we have a problem.”**

**It costs approximately $10,000 per pound to ship supplies to the international space station in orbit around the earth. One way to minimize costs and provide additional life support options for the astronauts is to recycle wastewater back to drinkable water. Russia developed a dehumidifier-type device that reclaimed moisture from the air from sweat and breathing, and this was used on the Mir space station in the 1990s. Scientists and engineers at NASA developed a water reclamation device that improves overall water efficiency on the ISS by reclaiming water from urine. This unit was installed in 2009. However, the device is not working up to specifications and it is your job to figure out what is going wrong and make recommendations to improve it.**

**Learning Objectives**: Upon completion of this exercise, you should be able to:

1. Read and interpret tabular data
2. Determine which precipitates might form from a complex mixture of ions
3. Calculate the maximum solubility of a species in solution
4. Determine the effect of acid/base chemistry on solubility
5. Examine the use of EDTA as a complexing agent

**Review (material you should know or learn prior to this exercise):** equilibrium and equilibrium constants, Le Châtelier’s principle, coupled equilbria, solubility product (Ksp), pH, Ka, Acids and Bases (Fundamentals J).

**Terms you should learn while doing this exercise:** complexation reaction, fractional composition, activity, ionic strength

**Relevant reading**: Atkins, Jones, & Laverman 7th Ed, Topics6E.1, 6E.4, 6G.1, 6G.2, 6I.1, 6I.3 (some of this reading will be review from the last module), and two publications from the NASA Marshall Space Flight Center.

**After completing this 3-day module, you should practice your skills on these relevant problems**: 6E.1 and 6E.2 (assume complete dissociation of the first proton), 6E.13 and 6E.17 (assume solutions are buffered at the given pH), 6G.1, 6G.3, 6G.7 (pH only), 6G.12, 6I.1, 6I.12

These reading assignments, and the assigned exercises, serve as a *general introduction* to concepts that you will need in order to work on the activities in the coming periods. Your conceptual understanding and quantitative application of these topics will be assessed during homework, concept quizzes, and exams.

**Guided Reading Part 1, Sakai assignment due by class time Monday Oct 31, 2016**

Read the document “main\_eclss.pdf” (posted on Sakai) from the George C. Marshall Space Flight Center (a NASA facility) that describes the Environmental Control and Life Support System, focusing on the Water Recovery System. Why is NASA interested in developing renewable means for providing crew life support?

Read the document “day 1 reading.pdf,” also from the Marshall Space Flight Center that reports the failure of the water recovery system after approximately one year in orbit. The system failed on two separate occasions; one failure was mechanical (described on the bottom of page 4 and all of page 5) while the other was chemical. You can skip over the mechanical failure section, though it is interesting to see the creativity the astronauts displayed to solve the problem. Using both documents as your sources, describe in a few sentences how urine and evaporative water (sweat) is processed back into drinking water on the International Space Station.

Read Topic 6E.1, Table 6E.1, Topic 6E.4 and Figure 6E.2. You do NOT need to know how to calculate the fractions as shown in the “How is that done?” section of 6E.2. When we know the relative ratios of all the possible protonated forms of a polyprotic acid (SO42-, HSO4- and H2SO4 for example), then we have determined the speciation of that acid at a given pH. A pKa expression can be arranged to pH = pKa + log[conjugate base]/[conjugate acid] (shown in Topic 6G.2); this equation is known as the Henderson-Hasselbalch equation which is used extensively in the study of biochemistry and buffers. Note that it is a base 10 log. Rewrite the Ka expressions as log expressions for the following chemical reactions. Use the example shown for the first Ka of carbonic acid as your guide:

H2CO3 (*aq*) + H2O (*l*) = HCO3- (*aq*) + H3O+ (*aq*); pKa1 for carbonic acid

Ka1 = [H3O+][HCO3-]/[H2CO3]

**pKa1, carbonic = pH - log[HCO3-]/H2CO3]**

HCO3-(*aq*) + H2O (*l*) = CO32- (*aq*) + H3O+ (*aq*); pKa2 for carbonic acid

H2SO4 (*aq*) + H2O (*l*) = HSO4- (*aq*) + H3O+ (*aq*); pKa1 for sulfuric acid = -3 (value not in the table)

HSO4-(*aq*) + H2O (*l*) = SO42- (*aq*) + H3O+ (*aq*); pKa2 for sulfuric acid

H3PO4 (*aq*) + H2O (*l*) = H2PO4- (*aq*) + H3O+ (*aq*); pKa1 for phosphoric acid

H2PO4-(*aq*) + H2O (*l*) = HPO42- (*aq*) + H3O+ (*aq*); pKa2 for phosphoric acid

HPO42-(*aq*) + H2O (*l*) = PO43- (*aq*) + H3O+ (*aq*); pKa3 for phosphoric acid

Using these equations and the corresponding pKa values, determine the relative ratio of the following species at different pH values, and the concentration of species 1 and 2 if the total concentration of species 2 and species 1 was 0.100 M. The first line is done as an example.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| pH | species 1 | species 2 | pKa value | [species 2]/[species 1] | [species 2] | [species 1] |
| 4 | H2CO3 | HCO3- | 6.37 | 4.27·10-3 | 4.25·10-4 M | 0.0996 M |
| 4 | HSO4- | SO42- |  |  |  |  |
| 11 | HPO42- | PO43- |  |  |  |  |
| 8 | HCO3- | CO32- |  |  |  |  |

from Table 6E.1, pKa1 for carbonic acid is 6.37.

pKa1 = pH - log[HCO3-]/H2CO3]

[HCO3-]/[H2CO3] = 104-6.37 = 4.27·10-3

but, [HCO3-] + [H2CO3] = 0.100 M; we have 2 equations and 2 unknowns. Plugging in:

[HCO3-] = 4.27·10-3·(0.100 – [HCO3-])

[HCO3-] = 4.25·10-4 M; [H2CO3] = 0.0996 M

Note: I strongly recommend using Wolfram alpha (or your favorite program for solving simultaneous equations) to solve these problems! Check out this link: <http://www.wolframalpha.com/input/?i=x%2Fy+%3D+0.00427;+x%2By%3D.1>

Read Topic 6I.1 and Table 6I.1. Given your answers to the previous question, determine if a precipitate forms in the following solutions buffered at constant pH.

pH 4, [sulfate]total = 0.100 M, [Ba2+] = 0.0100 M

pH 11, [phosphate]total = 0.100 M, [Li+] = 1.00·10-2 M; Ksp for Li3PO4 = 3.2·10-9

pH 8, [carbonate]total = 0.100 M, [Ag+] = 0.0100 M

**In class activity Day 1**

For the purposes of this class, we are going to assume the following simplified procedure for urine processing on the international space station:

* Urine is collected
* For every liter of urine, 20 mL of 1.0 M sulfuric acid is added
* A filtration step removes particulates and organic matter
* The treated urine is distilled at low pressure, leaving behind a brine solution
* The distilled water tested for purity and returned to the drinking water supply

The system was designed (and tested) to allow for 85% of the water to be removed from the urine before the brine was discarded. However, after installation in the ISS, the system failed. Parts were returned to Earth for analysis, and it was found that a precipitate had clogged some of the drain ports, leading to electrical failures and leaking.

During the next two days, the in-class and out-of-class exercises and questions will help guide you to answer the question of what the precipitate is, and to propose one or more strategies for remediation that NASA can use to fix this problem.

The following table contains actual and estimated values for various species present in urine.

**Table 1. Major components of human urine.**

|  |  |
| --- | --- |
| **Component** | **Concentration (mM) on Earth** |
| *Urea* | 155 |
| *Na+* | 128 |
| *K+* | 60 |
| *Mg2+* | 7.5 |
| *Ca2+* | 1.2 |
| *[PO43-]tot†* | 13.3 |
| *[SO42-]tot†* | 16.5 |
| *Cl-* | 52.7 |
| *[CO32-]tot†* | 25 |
| *pH* | 7.40 |

 †These values refer to total concentration of all protonation states

Looking at Table 1 and Table 2 on the next page, discuss in your group and predict what precipitates could form in urine.

To verify your guesses, calculate the Qsp for the various concentrations shown for a urine sample. Each member of your group should calculate one or two values only… divide and conquer!

Using the values in Table 2 shown below, determine if Qsp is greater than Ksp.

 **Table 2. Solubility equilibrium constant values**

|  |  |
| --- | --- |
| CaSO4 Ksp | 2.4·10-5 |
| Ca3(PO4)2 Ksp | 1·10-26 |
| CaCO3 Ksp | 8.7·10-9 |
| MgCO3 Ksp | 1.0·10-5 |
| Mg3(PO4)2 Ksp | 1.0·10-25 |
| MgSO4 Ksp | 4.7 |

Should a precipitate form in urine?

Does this conclusion agree with your own personal experience?

In order to begin to understand what is going on, why we predict a precipitate when none should be present, lets look at the speciation diagram for phosphate (found in Topic 6E.4, Figure 6E.2). A speciation diagram shows the varying concentration profile for the various protonation states for a polyprotic acid as a function of pH. For example, at pH 7.21, the second pKa for phosphoric acid, we expect equal concentrations of H2PO4- and HPO42-.

{a Figure showing the speciation of phosphoric acid}

**Figure 6E.2** The variation of the fractional composition (the speciation) of the species in phosphoric acid with pH.

a) Verify mathematically that the concentrations of H2PO4- and HPO42- are equal at pH 7.21.

b) Calculate the concentrations of H2PO4- and HPO42- in a solution at pH 7.40 if the total concentraton of all the forms of phosphate is 0.0133 M.

c) Estimate the concentration of PO43- at pH 7.40 from that of HPO42- calculated above. Note: think carefully about the easy way to solve this problem…

It is reasonable to assume that the pH of urine is buffered (we will read about buffers for the next class) with carbonate/bicarbonate, as there is approximately 25-50 mM of that ion in solution (similar to concentrations in blood) and the pH is similar to that of blood. Interestingly, the pH of urine is usually lower (6-6.5) in the morning due to decreased food intake (starvation) and the pH rises up to almost 7.5-8 in the evening. However, urine pH is highly dependent on what foods are consumed, and we will assume pH 7.4 for now.

Given the *total* concentration of phosphate of 13.3 mM as shown in Table 1, at pH 7.4, what is the concentration of PO43-? (you already did this calculation!)

Of sulfate (given its total concentration of 16.5 mM)? (Hint: the first proton of sulfuric acid is very strong, with a negative pKa value. You can assume that as a strong acid, it completely dissociates to form HSO4-)

Of carbonate (total concentration of 25 mM)? (Hint: ignore the 2nd pKa value at first, why?)

 **Table 3: Ka values for various acids**

|  |  |
| --- | --- |
| H2SO4 pKa1 | ~-3 |
| H2SO4 pKa2 | 1.92 |
| H3PO4 pKa1 | 2.12 |
| H3PO4 pKa2 | 7.21 |
| H3PO4 pKa3 | 12.68 |
| H2CO3 pKa1 | 6.37 |
| H2CO3 pKa2 | 10.25 |

Now, recalculate the Qsp values you did previously with the corrected values for the anions present in solution. Each member of your group should calculate the same one or two values as previously… divide and conquer! Should a precipitate form in urine?

Does this conclusion agree with your own personal experience?

**Guided Reading Part 2, Sakai assignment due by class time Wednesday Nov 2, 2016**

Review your calculations from day 1 to ensure you got the right values on the key. Understand how to setup the WolframAlpha calculations. You are free to use another simultaneous equation solver such as your calculator, a program you write, Maple or Mathematica if you are more familiar or comfortable with that. After you have reviewed your answers, just write “reviewed” as the answer on the Sakai homework.

Optional: Predicting values from pH/pKa review. If you want to review how to calculate speciation, here is an additional practice problem.

Oxalic acid, HO2C-CO2H has two pKa values, 1.23 and 4.19. For ease of represntation, lets call oxalic acid H2Ox. For each of the following pH values. 1.00, 2.00, 5.00, 8.00:

a) Determine the two highest concentration species of H2Ox, HOx-, and Ox2-

b) Calculate the ratio of HOx- and Ox2-.

Read Topics 6G.1-6G.2 on buffers.

Write the definition of a buffer in your own words[[1]](#footnote-1)†.

Determine the pH of water (pH 7.00) if 1.00 mL of 1.00 M HCl was added to 100. mL of water. You can use a procedure similar to that outlined in Example 6B.1.

In the last class activities, we assumed that the pH of the various solutions we studied were buffered at various pH values so that the pH of the solution would remain essentially constant. Assume that blood, pH 7.40, is a carbonic acid/bicarbonate (HCO3-/H2CO3) solution at 25 mM total concentration. What is the ratio of carbonic acid to bicarbonate in that solution?

Determine the pH of the solution if 1.00 mL of 1.00 M HCl was added to 100. mL of *blood*. Use a procedure similar to that in Example 6G.2.

Does blood resist pH changes?

**Challenge reading (not required):** Activity.

In the last class, we predicted that a precipitate (calcium phosphate, calcium carbonate, and magnesium phosphate) should form in urine at pH 7.4. However, this does not actually happen. The reason is that we are dealing with a solution with high ionic strength: a solution with high concentrations of ions. In these solutions, the *effective* concentration (the activity) of the ionic species is lower than we would predict, because of attractive ionic forces between all the different counter ions. For example, we expect calcium phosphate to precipitate since [Ca2+] = 0.0012 M and [PO43-] = 4.24·10-8 M, the Qsp = 3.11·10-22 which is greater than Ksp = 1·10-26. However, in a solution that is about 0.015 M in ions (lets assume Na+ and Cl- for simplicity), you can imagine that the Mg2+ might be attracted to the Cl- ions, and the PO43- ions might be attracted to the Na+ ions. These other ions “block” the Ca2+ and PO43- ions from coming into contact with each other and precipitating. Chemists include a term called an activity coefficient (gamma) to more accurately model concentrations in salt solutions. In high ionic strength solutions, like urine, the activity coefficients are on the order of 0.2 for PO43- to 0.4 for Ca2+; these depend strongly on the ionic strength and on the charge of the ion. The activity of a species is determined by multiplying the activity coefficient, , by the molarity. Using these values, we can calculate a corrected Qsp for calcium phosphate, as shown:

Qsp = {activity Ca2+}3·{activity PO43-}2 = {[Ca2+]}3·{[PO43-]}2

= (0.4(0.0012 M))3·(0.2(4.24·10-8 M))2 = 8.0 ·10-27

this value is below the Ksp so we do not expect a precipitate to form. You will not need to know about activities for the exam or homework.

**In class activity Day 2**

What did we learn in the last class? Let’s recap.

First: we determined that based on simple Qsp calculations, we should expect a precipiate in urine. For example, from the table of ions, we saw that [Ca2+] was 1.2·10-3 M, while [PO43-] was 4.24·10-8 M, and therefore Qsp = 3.12·10-24 which is greater than Ksp which = 1·10-26. You should have predicted the following precipitates: Ca3(PO4)2, CaCO3, and Mg3(PO4)2. This does not (should not) make sense with personal experience. However, we were able to fix that prediction using the concept of activity (in the optional pre-class reading), and we do not expect a precipitate to form. That being said, Qsp is not very much higher than Ksp for any of those 3 species, so even if a precipitate did form, not very much of it would form; certainly not enough to cause a breakdown of the water purifier on the space station.

Second: we looked at speciation in order to more deeply examine the values in the table showing the components of urine.

So, lets begin!

Table one is repeated here, with the addition of composition data for urine collected on the International Space Station. Calculate the percent change in each species.

**Table 1. Major components of human urine.**

|  |  |  |  |
| --- | --- | --- | --- |
| **component** | **Concentration (mM) on Earth** | **Concentration (mM) on ISS** | **% change** |
| *Na+* | 128 | 225 |  |
| *K+* | 60 | 115 |  |
| *Mg2+* | 7.5 | 14.7 |  |
| *Ca2+* | 1.2 | 9.0 |  |
| *[PO43-]tot†* | 13.3 | 22 |  |
| *[SO42-]tot†* | 16.5 | 29.5 |  |
| *Cl-* | 52.7 | 106 |  |
| *[CO32-]tot†* | 25 | 48 |  |
| *pH* | 7.40 | 7.60 |  |

 †These values refer to total concentration of all protonation states

Based on the percent change, do you forsee any likely candidates for the precipitate?

If you look back at the procedure NASA uses for treating the urine (first paragraph of in-class day 1), the first step is to add sulfuric acid (a strong acid) to prevent bacterial growth. We have thus far completely neglected the actual procedure used by NASA in forming our recommendation as to what the precipitate is. Lets now look to the procedure, making some simplifying assumptions, to decide if that changes our recommendation.

The first step in purifying the urine collected on the ISS is to treat every liter of urine with 20 mL of 1.0 M H2SO4. To simplify the calculations, lets assume that urine is water.

a) What is the pH of a solution of 20. mL of 1.0 M H2SO4 added to 1.00 L water? To determine this, given that the first pKa of sulfuric acid is ~-3, you can safely assume that 100% of the H2SO4 reacts to form H3O+ and HSO4- ions. Use pKa2 (1.92) to determine if any more protons are added to the solution from HSO4-.

b) At pH 1.58 (this should be the same pH you found in part a), calculate the free [PO43-] when [PO43-]t = 22 mM. As we saw in the last class, you can either solve 4 simultaneous equations to solve this problem for [H3PO4], [H2PO4-], [HPO42-] and [PO43-], or simply calculate the ratio of the two highest concentration species at the pH of the solution, and then calculate [PO43-] from those values. What are the two highest concentration species at pH 1.58?

c) At pH 1.58 (this should be the same pH you found in part a), calculate the free [CO32-] when [CO32-]t = 48 mM. As we saw in the last class, you can either solve 3 simultaneous equations to solve this problem for [H2CO3], [HCO3-] and [CO32-], or simply calculate the ratio of the two highest concentration species at the pH of the solution, and then calculate the [CO32-] from those values. What are the two highest concentration species at pH 1.58?

d) At pH 1.58 (this should be the same pH you found in part a), calculate the free [SO42-] when [SO42-]t originally in the solution 29.5 mM. Make sure to account for any additional sulfate added from H2SO4 that you calculated in part a. To make this problem easier to solve, assume that all of the sulfate is present as HSO4- at the beginning of the problem. Then, use pKa2, sulfuric to determine how much SO42- forms from the sulfate (and how much additional H3O+ forms).

e) Using your newly calculated values, determine if a precipitate should form from the sample collected on the ISS. If so, what do you predict the precipitate to be?

**Guided Reading Part 3, Sakai assignment due by class time Monday Nov 4, 2016**

Was our prediction correct? Read the document “day 3 reading.pdf,” the continuation of the day 1 document from the Marshall Space Flight Center that reports the failure of the water recovery system after approximately one year in orbit. The whole document is provided for your interest, but you need only read pages 6-7 (pages 2 and 3 of the pdf).

What was the precipitate? What were the main causes of the precipitate on the space station compared to on earth?

The authors claim that “lower pH levels inhibit precipitation.” Explain how this is true using information from the previous 2 days of this module.

The units used by NASA for concentration are mg/L, and they report calcium as 283 mg/L in the urine collected on the international space station. What is this value in M?

What was NASA’s solution to the problem? Given the information in the article, how much does this problem cost NASA per year?

Read Topic 6I.3 on complex ion formation. Does the solublity of AgCl depend on pH? Why or why not?

In the last class, you determined that a precipitate of calcium sulfate formed with [Ca2+] = 9.0·10-3 M and SO42- = 4.76·10-3 M. Assuming that one could form a metal complex with a ligand and calcium, would you predict that to increase or decrease the chances of precipitation?

The ligand L reacts with Ca2+ in solution according to the following chemical equation, with its equilibrium constant:

Ca2+ (aq) + L (aq) 🡪 CaL2+ (aq); Kf = 1.0·104

Write the Kf expression in terms of molar solubilities of ions in solution.

If [L] was 0.010 M, what would the [Ca2+] be given the initial [Ca2+] = 9.0·10-3? Set up an ICE table to solve the problem, but you need only submit the final result on Sakai.

Does a precipitate of CaSO4 form from this solution?

Finally, learn a little bit about EDTA, a common metal complexing agent, by skimming through the following website. Focus on the sections entitled “uses,” and “coordination chemistry principles.” <https://en.wikipedia.org/wiki/Ethylenediaminetetraacetic_acid>

There are a lot of pages on the web that discuss the hazards of EDTA. I found many of these web pages while searching for facts about EDTA. For example many sites claim that since EDTA is prepared from ethylenediamine (a caustic irritant), formaldehyde (highly toxic and carcinogenic), and sodium cyanide (highly toxic to respiration), it must also be toxic. In fact, the LD50 (the dose that causes death to 50% of the test animals) is on the order of 2 g/kg of body weight, which is considered “low acute toxicity.” To put this in context, this is the 10 times less toxic than Aspirin, 15 times less toxic than caffeine, and 1/6th the toxicity of table salt. Just because a chemical is synthesized from toxic chemicals does not make it toxic.

EDTA is used in chelation therapy to treat lead and other heavy metal poisoning, and in dental treatments. It is known to have some toxicity when fed to animals in relatively high doses, but the amounts used in foods and soaps are miniscule. The World Health Organization lists it as one of the top essential medicines needed for a national health program. As you continue your education at HMC and beyond, remember the science you have learned and help educate the public against scientific misinformation. Here is a website from a journal of toxicology with scientific information, not hearsay claims. <http://ijt.sagepub.com/content/21/2_suppl/95>

Bonus material: Read these websites about calcium leaching in space.

Astronauts lose about 1% of bone density per *month* in space; contrast this value to the estimate of 1% loss per *year* in the eldery. Scientists aren’t 100% sure why. Originally they thought that it was due to lack of stress on the bones, and added exercise regimens to astronauts spending time in space. However, the results of these studies were inconclusive. If we are going to Mars, we need to figure this out!

<https://en.wikipedia.org/wiki/Spaceflight_osteopenia>

<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3546622/>

<https://science.nasa.gov/science-news/science-at-nasa/2001/ast01oct_1>

**In class activity Day 3**

Our goal today is to develop a recommendation to NASA that they could use to solve their problem. Lets first examine different acids that NASA could have used besides sulfuric acid, as the sulfate generated from that acid was part of the problem. Consult the following properties of strong acids and make a recommendation to NASA as to which other acid they might consider.

Hydrochloric acid (HCl) is volatile, meaning it can evaporate readily, though it is highly soluble in water. It reacts with oxidizers to form chlorine (a chemical weapon) even when dilute.

Nitric acid (HNO3) is non-volatile acid but decomposes on prolonged storage both thermally and due to light absorption to give off corrosive and toxic NOx gas. This decomposition is accelerated when nitric acid is treated with organics, though it occurs more slowly when dilute.

Perchloric acid is non-volatile, but is highly reactive with metals like aluminum. It can readily form explosive mixtures upon contact with organics. Perchlorate salts (especially of organic compounds) tend to be shock sensitive.

Sulfuric acid has a very low vapor pressure. When concentrated, it reacts with organics to form HCl and SO2, but when dilute, it does not react with organic compounds as readily.

As a group, discuss the following questions for 3-5 minutes before moving on.

1) Is a strong acid needed? Why or why not?

2) Are any of the other common strong acids more suitable for the space station than sulfuric? Why or why not?

We will next investigate EDTA, ethylenediamine tetraacetate, an extremely common complexing agent. Check your bottle of shampoo. Most shampoos and many food products contain “tetrasodium EDTA” or “disodium EDTA.” EDTA has four carboxylate groups and two amines and all 6 groups can bind to a metal ion in an octahedral shape to sequester the metal ion from being free in solution. This aids by preventing mold or bacterial growth, serves as an antioxidant (to prevent those *cis* double bonds in natural oils from oxidizing and turning rancid) and, by removing calcium or magnesium from hard water (like that in Claremont…), prevents soap scum from forming (soap scum is the calcium or magnesium salt of a fatty acid and is rather insoluble in water). EDTA is also used to remove scale, calcium carbonate, which deposits in pipes or on cooking pots. The chemical reaction that shows the chelation of calcium to the tetra-anionic form of EDTA is shown. What is the charge on the Ca(EDTA) complex?



The equilibrium constant for this chemical reaction (as shown using the tetraanion of EDTA) is 4.47·1010; the related reaction for Mg2+ has an equilibrium constant of 6.17·108. What does this suggest about using EDTA to help solve the solubility problem?

One problem exists with this chemical equation. Considering the structure of EDTA, and the pH of the treated solution (we found it to have a pH of about 1.5 last time), what is a likely stucture for EDTA at this pH? Discuss this as a group before turning the page.

The effective concentration of EDTA4- is *highly* pH dependent. The speciation diagram for EDTA (Y, in the diagram) as a function of pH is shown to the right. Clearly, at acidic pH, the effective concentration of EDTA4- is very low. In fact, it can be calculated just like you calculated the speciation of PO43-, SO42-, and CO32- in class. The fraction of the total EDTA in solution present as EDTA4- as a function of pH is shown below.

{Figure from Harris showing the fractional composition of EDTA as a function of pH}

pH fraction present as EDTA4-

1 1.4·10-18

2 2.6·10-14

3 2.1·10-11

4 3.0·10-9

5 2.90·10-7

6 1.80·10-5

7 3.80·10-4

We can still complex metal ions at low pH, but the effective equilibrium constant is much lower since the concentration of free EDTA4- is much lower. Calculate K’eq, the effective Keq which equals Keq·(fraction EDTA4-) for the Ca(EDTA) complex at pH 2, 3, 4, and 5. This would be a good place to divide and conquer within your group, since each calculation takes the same form.

At those same pH values, determine the free [Ca2+] if the initial concentration is 9.0·10-3 M (the concentration on the international space station) and the total amount of added EDTA is 0.100 M. If you use the fraction of EDTA present as the tetraanion as a multiplier in front of the Keq value, as you just calculated, then you can use the total EDTA concentration in your ICE table.

What is the minimum pH necessary to reduce the [Ca2+] by a factor of 10?

What is your final recommendation to NASA?

1. † <https://www.youtube.com/watch?v=BoJI1p7cHhc>; note, I want you to actually use English words, just in your own *arrangement*. [↑](#footnote-ref-1)