**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

**Terms You Should Know:** solubility, Ksp, precipitation, Ka, fractional composition

**Background Reading**: Atkins, Jones, & Laverman, Chapter 13, Sections 13.7, 13.8, 13.9, 13.10, 13.11; Chapter 12, Sections 12.14, 12.16, 12.17.

**After Completing this Exercise, Textbook Problems You Should be Able to Answer**:

12.81, 12.84, 12.91, 13.51, 13.53, 13.57, 13.63, 13.70, 13.73, 13.75

This is a two-day activity. On Monday, November 30, you will work in groups to determine likely causes for failure of the device on the ISS. On Wednesday, December 2, you will continue your work and make recommendations to NASA to improve the device.

**Day 1 Recap**

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 2.5·10-3 M, while [PO43-] was 13.3·10-3 M, and therefore Qsp = 2.7·10-12 which is greater than Ksp which = 1·10-26. You should have predicted the following precipitates: Ca3(PO4)2, and Mg3(PO4)2. This does (should) not make sense with personal experience.

Second: we looked at speciation in order to determine whether the values in the table were correct. Most groups found this calculation difficult, so we will repeat it today, with a slight variation. However, you should have found that either magnesium phosphate or calcium phosphate was the precipitate causing the problem in the water reclamation device.

So, lets begin!

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

|  |  |  |  |
| --- | --- | --- | --- |
| **component** | **Concentration (mM) on Earth** | **Concentration (mM) on ISS** | **% change** |
| *Urea* | 155 | 155 |  |
| *Na+* | 128 | 225 |  |
| *K+* | 60 | 115 |  |
| *Mg2+* | 7.5 | 14.7 |  |
| *Ca2+* | 2.5 | 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

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.

1) What are the biggest changes in concentrations comparing the earth and ISS urine samples?

Revisiting the concepts from Monday’s class, remember that urine and blood are both buffered near pH 7.4 with the carbonate buffer. Free phosphate refers to the concentration of the PO43- anion, free sulfate refers to the SO42- anion and free carbonate refers to the CO32- anion. Using the table of pKas below and the concentrations of the ions in table 1 above, calculate the concentration of free sulfate and carbonate in a solution buffered at pH 7.4. Phosphate is done for you as an example.

 **Table S1. Solubility equilibrium constant values**

|  |  |
| --- | --- |
| CaSO4 Ksp | 7.1·10-5 |
| Ca3(PO4)2 Ksp | 1·10-26 |
| CaCO3 Ksp | 8.7·10-9 |
| MgCO3 Ksp | 1.0·10-5 |
| Mg3(PO4)2 Ksp | 1.0·10-24 |
| MgSO4 Ksp | 4.7 |

**Table 3: Ka values**

|  |  |
| --- | --- |
| H2SO4 pKa1 | ~-3 |
| H2SO4 pKa2 | 1.92 |
| H3PO4 pKa1 | 2.12 |
| H3PO4 pKa2 | 7.21 |
| H3PO4 pKa3 | 12.68 |
| H­2CO3 pKa1 | 6.3 |
| H2CO3 pKa2 | 10.33 |

Example: What is the [PO43-] in a solution buffered at pH 7.4 when [PO43-]t = 13.3mM?

At this pH, we are in the region where H2PO4- is being deprotonated to for HPO42-: pKa2. Using the Henderson-Hasselbalch equation, we can calculate the ratios of each conjugate acid base pair:

pKa1: pH = pKa + log[H2PO4-]/[H3PO4]; 7.4 = 2.12 + log[H2PO4-]/[H3PO4];

 [H2PO4-]/[H3PO4] = 1.9·105

pKa2: 7.4 = 7.21 + log[HPO42-]/[H2PO4-]; [HPO42-]/[H2PO4-] = 1.5

pKa3: 7.4 = 12.68 + log[PO43-]/[HPO42-]; [PO43-]/[HPO42-] = 5.2·10-6

given those three ratios, and the fact that the total phosphate concentration (sum of all 4 possible species) is 13.3 mM, what is the concentration of free phosphate in the sample?

We can set up simultaneous equations. we know that:

[H3PO4] + [H2PO4-] + [HPO42-] + [PO43-] = 1.33·10-2M

[H2PO4-]/[H3PO4] = 1.9·105

[HPO42-]/[H2PO4-] = 1.5

[PO43-]/[HPO42-] = 5.2·10-6

rearranging and solving, we find [PO43-] = 4.2·10-8 M; there is essentially no free phosphate.

2a) What is the [SO42-] in a solution buffered at pH 7.4 when [SO42-]t = 16.5 mM?

2b) What is the [CO32-] in a solution buffered at pH 7.4 when [CO32-]t = 25 mM?

2c) Now, based on the concentrations of free phosphate, sulfate, and carbonate present in the Earth Sample at pH 7.4, propose what the precipitate is. There may be more than one predicted precipitate.

Importantly, 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, and making some simplifying assumptions, decide if that changes our answer.

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.

3a) what is the pH of a solution of 1.00 L water added to 20. mL of 1.0 M H2SO4? 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 to determine if any additional reactions occur.

3b) at this pH, calculate the free [PO43-] when [PO43-]t = 13.3mM

3c) at this pH, calculate the free [SO42-] when [SO42-]t originally in the solution 16.5 mM. Make sure to account for any additional sulfate added from H2SO4 that you calculated in part a!!

3d) at this pH, calculate the free [CO32-] when [CO32-]t = 25 mM

3e) Do you expect a precipitate to from from the sample collected on earth? If so, what do you predict the precipitate to be? If you make an assumption (ie, that [PO43-] = 0) then state it, with a phrase justifying your assumption.

3f) Do you expect a precipitate to from from the sample collected on the ISS? If so, what do you predict the precipitate to be? If you make an assumption (ie, that [PO43-] = 0) then state it, with a phrase justifying your assumption.

Water reclamation handout, day 2.

Once you have agreed on your answers to the problems, fill out this sheet with your answers and submit it to the instructor. This sheet is due at the start of class on Friday, December 4

Group members: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_,

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

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