**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, complexation reaction, fractional composition, activity, ionic strength

**Background Reading**: Atkins, Jones, & Laverman, Chapter 13, Sections 13.7, 13.8, 13.9, 13.10, 13.11, 13.13; 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, 13.82, 13.86

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

**Background Information**

Space exploration is expensive. It costs approximately $10,000 to send *one pound* of material into earth orbit. Any method for reducing waste and recycling essential materials will result in significant cost savings. One of the long term goals of the international Space Station (ISS) is to develop and improve upon technologies to sustain life in a closed environment. As part of this effort, Russian scientists and engineers developed a water reclamation system that dehumidifies air on the ISS and returns potable water. An average person loses about 1800 mL of water per day from sweat and respiration. NASA sought to improve upon this system by reclaiming potable water from urine. This would lead to a substantial improvement in water recycling as the average person produces about 2 L of urine, which is 95% water, per day.

The system was tested on earth and was designed to take human urine to pure drinking water by a series of chemical reactions to sterilize and oxidize organics, followed by low pressure centrifugal distillation to purify the water and leave behind a concentrated brine solution. The process, in simplified form, is outlined below:

* Urine is collected
* For every liter of urine, 20 mL of 1.0 M sulfuric acid is added
* The treated urine is distilled to remove water, leaving behind organics and salts as a brine solution
* The distilled water is further purified and returned to the drinking water supply
* The brine is returned to earth in a “sacrificial return vessel,” i.e., it burns up in the earth’s atmosphere

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.

The next series of questions will help guide you to answer the question of what the precipitate is, and to propose one or more remediations that NASA can use to fix this problem. But first, a review of the important concepts you will need to solve the problems.

**i) polyprotic acids**

unlike monoprotic acids, like HNO3 or acetic acid (CH3CO2H), polyprotic acids have more than one ionizable proton. As such, determining the pH of such an acid can be complicated. Lets look in some detail at the pH of a carbonic acid solution.

Carbonic acid, H2CO3, has two ionizable protons, and two Ka values, shown below:

H2CO3 (*aq*) + H2O (*l*) = HCO3- (*aq*) + H3O+ (*aq*); Ka1 = 4.3·10-7

HCO3 (*aq*) + H2O (*l*) = CO32- (*aq*) + H3O+ (*aq*); Ka2 = 5.6·10-11

What if we wanted to determine the relative ratios (the speciation) of H2CO3, HCO3-, and CO32- in a solution at a given pH? If we write the expression for Ka1, we find:

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

And

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

the pKa1 for carbonic acid is 6.37. what would happen at a pH below 6.37, say, 5.37?

6.37 = 5.37 - log[HCO3-]/H2CO3]

log[HCO3-]/H2CO3] = -1.00

[HCO3-]/H2CO3] = 0.1

as the pH drops below the pKa of the acid, the composition moves to favor the *acidic species.* Notably, for every pH unit drop below the pKa, the relative concentrations of the acidic and basic forms change by 10-fold. Similarly, at a pH > pKa2 (which is 10.25), the speciation will favor carbonate anion over bicarbonate.

Note, when rearranged to pH = pKa + log[conjugate base]/[conjugate acid], this equation is known as the Henderson-Hasselbalch equation which is used extensively in the study of biochemistry and buffers.

Determining the pH of a polyprotic acid solution between the pKa values involves either multiple simultaneous equations or simplifications. For this unit, you will only need to determine the speciation of an acidic species given a pH.

**ii) solubility product constant, Ksp**

given a table of solubility product constants, you can predict whether or not a precipitate will form. For example, the Ksp for BaF2 is 1.7·10-6. If the [Ba2+] = 0.050 M and [F-] = 0.20 M, we expect a precipitate to form because [Ba2+][F-]2 = (0.050)(0.20)2 = 2·10-3 which is > Ksp.

The following table contains both 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+* | 2.5 |
| *[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

Exercise:

What are the likely precipitates that could form from this mixture? (Class discussion)

To verify, calculate the Qsp for the various concentrations for a sample; should a precipitate form?

Do your calculated values agree with personal experience?

In order to begin to understand what is going on, lets look at the speciation diagram for phosphate (found in section 12, Figure 12.22 of the text). 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 2.12, the first pKa for phosphoric acid, we expect equal concentrations of H3PO4 and H2PO4-.

{{Figure 12.22 from Atkins, Jones, & Laverman showing the speciation of phosphoric acid from pH 0-14}}

exercise:

a) verify mathematically that the concentrations of H3PO4 and H2PO4- are equal at pH 2.12.

b) calculate the concentrations of H3PO4 and H2PO4- in a solution at pH 3.12 if the original concentraton of phosphoric acid was 0.100 M.

c) does your answer make physical sense? Explain.

**Table 2: 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 | 6.3 |
| H2CO3 pKa2 | 10.33 |

It is reasonable to assume that the pH of urine is buffered 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.

Exercise

at pH 7.4, what is the approximate speciation (give ratio of the two largest contributors) of the phosphate ion?

Of sulfate?

Of carbonate?

how do these calcuations help us?

recalculate the Qsp values you did previously with the corrected values for the anions present in solution. Based on your new calculations, propose what the precipitate clogging the port in the water recycler is. Once you have a proposal, write it on the chalkboard and be prepared to defend your choice during a …

… Class discussion

Water reclamation handout, day 1.

Once you have agreed on your answers to the problems, fill out this sheet with your answers and submit it to the instructor.

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

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1) calculate the concentrations of H3PO4 and H2PO4- in a solution at pH 3.12 if the original concentraton of phosphoric acid was 0.100 M.

2a) pH 7.4, what is the approximate speciation (give ratio of the two largest contributors) of the phosphate ion?

2b) Of sulfate?

2c) Of carbonate?

3) Propose what the precipiate is. Back up your answer with a few sentences (on back if necessary) describing your calculations and logic.