HLWYM HEmails

From: Murphy, William [WMurphy@csuchico.edu]
Sent: Wednesday, August 17, 2005 3:50 PM
To: jprikryl@swri.edu
Cc: dpickett@swri.edu
Subject: uranophane
Attachments: Comments on Reversal.doc

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Jim (David),

Please see the attached comments on Jim's experiments and calculations.

Bill

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Subject: uranophane
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"dpickett@swri.edu" <dpickett@swri.edu>
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MESSAGE	99	8/17/2005 3:51:32 PM
Comments on Reversal.doc	22592	

Options
Priority: Standard
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Jim,

Your uranophane work is outstanding. If you haven't started preparing a paper for Geochimica, then you should.

For the GSA calculations/talk, I'm tempted now to use the log K = 5.35 for soddyite from Giammar's reinterpretation of Nguyen. What do you think?

Here are some comments on the precipitation data and free energy calculations you sent me recently.

-Bill

The uranium data are still a little jumpy. Is it real? (I doubt it.) What are possible explanations? Colloids, sorption, analytical uncertainty? The whole story is so coherent and convincing that the jumpiness doesn't seem to be critical. But considering that uranium jumpiness was a clue we used to discern the invalidity of the data set from several years ago, it's worth thinking about likely explanations.

The moles of U released/precipitated vs. time plots are fantastic and strongly supportive of the reversal. Because the calculations of moles released depends slightly on preceding analyses and moles removed in samples, then the curves might be touched up by inferring that the precipitation data at 350 hours for 2A and 2B and at 800 and 1000 hours for 1B are a little bit wrong because of analytical errors. Estimating more realistic values for these samples to use in calculating moles released at subsequent times could actually improve the accuracy of the subsequent moles released data. It looks a little like data massaging, and it is, but I think its valid. I think we did a little of this kind of adjustment for the analcime data. If the consequences of the massaging seem to be insignificant, then it's not worth while. Mainly moles released data affect calculations of kinetics. There is a kinetics story in your data, too, which could be another paper.

Log K = 10.93 seems like a good estimate to me. I suggest estimating a minimum uncertainty in this number by looking at the value for the 1A experiment that seems most undersaturated relative to this value and for the 7B experiment that seems to be most supersaturated. You can see these points on the wrong side of the plane in the 3-D figure. (That figure is wonderful.) Maybe these anomalous data could be reasonably qualified if they look like they appear to be affected by analytical uncertainties such as the 350, 800, and 1000 hour data noted in the previous comment.

The log Q's you calculate depend on the aqueous speciation in EQ3, right? Do aqueous complexes have a significant effect. For example, do sodium silicate or calcium carbonate aqueous species have significant effects on the calcium or silica activities?

EQ3 uses SiO2(aq) instead of Si(OH)4(aq). They are the same species, but they have different standard state free energies of formation. I suspect we've been through this

difference in conventions before, and confirmed that there are no problems with the log Q's.

I checked your calculations and differed slightly in the last digits, which are insignificant, but we should make it all consistent. Here are some of the picky details:

Guillamont's free energy for Si(OH)4 is –1307.735 kJ/mole. Apparently you used –1307.74. Of course the uncertainty is vastly bigger than this difference, but it shows up in number checking.

Your value of R is 8.3145 kJ/K mole. I've seen 8.314 used a lot, and I've used 8.31426, I think. Perhaps you could check a recent edition of the Handbook of Chemistry and Physics.

I suggest using 298.15 K for 25 C instead of 298.