Ye Olde Chemistry 112 Precipitation Kinetics Experiment

I. Introduction

Solubility and precipitation are much-discussed topics in Chemistry 102. The central ideas surround an equilibrium constant allied with a salt dissociation reaction taking place in water at a fixed temperature. For example, magnesium hydroxide ($Mg(OH)_2(s)$) is a basic salt with low solubility in water. Its dissociation reaction is given by:

$$(Mg(OH)_2(s)) \;=\; Mg^{2+}(aq) \;+\; 2\, OH^{-}(aq)$$

with a heterogeneous equilibrium constant

$$K_{sp} \;=\; [Mg^{2+}(aq)] \times [OH^{-}(aq)]^2$$

and reaction quotient

$$Q \;=\; [Mg^{2+}(aq)] \times [OH^{-}(aq)]^2$$

Chemistry Tables tell us that $K_{sp} \approx 6 \times 10^{-12}$ for magnesium hydroxide in water at temperature 298 K. We learn in Chemistry 102 that for an aqueous solution of magnesium hydroxide, if Q ever exceeds K_{sp}, then the reaction chemistry is turned on right-to-left. A solid precipitate of $Mg(OH)_2$ is thereby formed which remains in equilibrium with the ions remaining in solution. If on the other hand, Q is less than K_{sp}, the aqueous solution is less-than-saturated. No solid material falls out of solution and the system can remain at equilibrium as a homogeneous, single phase. If magnesium hydroxide solid were introduced to the solution, all or part of it would dissolve so long as $Q \leq K_{sp}$.

The above ideas are fairly straightforward and enable a chemist to make accurate predictions regarding the solubility and precipitation of a large number of salts. The ideas overlook, however, several kinetic properties and indeed, the precise chain of events in precipitation. The purpose of this Chemistry 112 experiment is to address a few of these properties via a series of observations and measurements.

II. A Few Important Ideas About Precipitation

Precipitation is the response of a liquid solution not at chemical equilibrium, i.e. when $Q \geq K_{sp}$. There are a few key things to note about the response and the events which lead up to it.

First and foremost is that precipitation entails three distinct stages. The initial one is referred to as the *fluctuation stage*. This is the time period in which parts of the liquid attain a supersaturated state of affairs--when Q first exceeds K_{sp} in various pockets of a given sample. In the supersaturated state, a liquid solution has dissolved more of a given salt than it can accommodate under equilibrium circumstances.

Second, fluctuations initiate a stage referred to as *nucleation*. This is the second stage where the tiniest of solid material is born. Nucleation can occur in one or several parts of a liquid sample over a short period of time different from-- but typically longer than--the fluctuation stage.

Nucleation precedes the third and final stage referred to as *growth*. Here solid material falls out of the liquid phase and attaches to one or more nuclei. The growth stage is the longest one of the three and can indeed transpire over several years in some cases of geochemical interest.

The above ideas drive home that the three stages of precipitation do not take place instantaneously. As with all physical processes, fluctuations, nucleation, and growth take time.

One is also reminded of the *motion* that salt ions undergo during the equilibration process. Ions must travel to a fluctuation site in order to form a nucleus. Still more salt family members must travel during the growth stage. The mode of travel is never like what we humans are used to--walking, biking, and airplane riding. Rather the ions bump and jerk their way through the host liquid, suffering numerous collisions--about 10^{13} every second--along the way. One says that ions *diffuse* in the liquid solution during the three stages.

But herein lies the tricky part. When ions diffuse toward a nucleus during the growth stage, this depletes the salt concentration in parts of the solution. In effect, a given nucleus robs the surrounding vicinity of dissolved salt. If another nucleus were introduced to this vicinity, it would not grow at all because there would be no salt to attach. The take-home point is that in precipitation, there are winner nuclei which grow happily. There are also losers which perish by starvation.

And herein lies the experiment. We will basically travel in the footsteps of two famous chemists, Raphael Liesegang and Wilhelm Ostwald. The research of these folks during the late 1800s and early 1900s independently established quite a bit of what we know about solutions and precipitation. To make matters simpler, we will carry out the precipitation experiments in one dimension--as opposed to three. Also to make things simpler, we will work with highly viscous solutions in which all of the precipitation events take place slowly. In such a way, we will observe and time the ion diffusion. We will also observe the locations of winner and loser nuclei.

III. Experimental

Important: Please read and understand all of the steps before doing. Please wear goggles and latex gloves at all times.

(1) Prepare a 25 cc solution of 0.4 molar aqueous magnesium sulfate ($MgSO_4(s)$) solution in a 100 cc beaker.

(2) To the 25 cc, add 2.2 grams of gelatin. By means of a hot plate, raise the solution temperature near the boiling point and allow the gelatin to dissolve completely. Hold the temperature near 100 C for three minutes. The high temperature conditions will cause extensive cross-liking of the protein which constitutes the gelatin.

(3) Allow the solution to cool for five - eight minutes. Then add several drops of metacresol purple indicator.

(4) Transfer the solution to a test tube and allow it to cool to room temperature. An ice bath will accelerate the cooling process.

(5) After the salt/gelatin solution has cooled and solidified, add 1 cc of the concentrated ammonium hydroxide solution to the top of the test tube. Note the time at which this solution is added.

Important: The ammonium hydroxide carries with it a powerful odor. This step may require use of one of the laboratory hoods. Please insert a cork or stopper into the test tube in order to reduce the amount of vapor admitted to the lab.

(6) Nucleation of magnesium hydroxide should begin to take place. This will cause parts of the solution to lose its transparency and instead become turbid or cloudy.

The turbidity edge locates the solution region where the fluctuation and nucleation events are taking place. Measure in centimeters the distance separating the turbidity edge and the gelatin level. Record the time of the measurement.

(7) As the hydroxide ions diffuse, the pH in the solution will begin to rise. This increase in pH will cause the indicator color to change from orange to a bluish-purple.

The edge of the purple cloud locates the boundary of the hydroxide ions which have yet to attach to a nucleus. The purple cloud is where the active players for the growth stage are found. Please measure in centimeters the distance between the purple cloud edge and the gelatin level. Record the time of the measurement.

(8) At five-minute intervals, record the positions of the turbidity edge and the purple cloud edge. Make sure that each distance measurement uses the top of the gelatin as a reference.

(9) Sooner or later, there will appear "winner" regions where nuclei prosper and grow to form solid magnesium hydroxide. Record the boundaries of these regions in centimeters.

(10) There will also appear "loser" regions where nuclei were unable to prosper and grow. Record the boundaries of these regions in centimeters.

IV. Calculations and Analysis

(1) Construct a high-quality, well-labeled plot of the turbidity edge position $P_{T\text{-edge}}$ in centimeters versus time t in minutes.

(2) Let the behavior of $P_{T\text{-edge}}$ be described by the following equation:

$$P_{T\text{-edge}} = A\,t^{\alpha}$$

Determine best-fit values of A and α. The latter is referred to as the *diffusion scaling coefficient* for the turbid edge. Carefully plot this function on the same graph constructed in (1).

(3) Construct a high-quality, well-labeled plot of the purple cloud edge position $P_{pc\text{-edge}}$ in centimeters versus time t in minutes.

(4) Let the behavior of $P_{pc\text{-edge}}$ be described by the following equation:

$$P_{pc\text{-edge}} = B\,t^{\beta}$$

Determine best-fit values of B and β. The latter is the diffusion scaling coefficient for the purple cloud edge. Carefully plot this function on the same graph constructed in (3).

(5) Make a high-quality, full-scale sketch of the test-tube. Identify the winner and loser regions of the precipitation process.

(6) Please answer the following questions:

(a) Simple diffusive motion in one dimension requires that α and β both equal 1/2. Was this the case in the solubility / precipitation experiment? In other words, is simple diffusion entailed during the nucleation and growth stages? Or is the motion more complicated due to the chemical reactions taking place?

(b) What factors determine the positions of the winner regions? The loser regions?

(c) What can be done to reduce the number of loser nuclei?

V. Ye Olde Data Sheet

Please turn in a well-labeled graph showing the turbidity edge position versus time in minutes. In applying the equation in Part 2 of Section IV, what are reasonable values for A and α?

VI. Ye Olde Lab Report

Please write a lab report according to the following outline.

I. Introduction: As always, this should address briefly the purpose and significance of the experiment.

II. Equipment and Procedure: This should describe the materials and steps required of the experiment.

III. Results: This section should contain the results of the experiments in concise table and graph form. Careful attention should be given to units and the labeling of axes. Commentary should be included in this section to assist the reader.

IV. Discussion: Please use this section to identify best-fit values of A,α and B,β. Please address the questions posed at the end of Section IV.

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Pre-Lab Exercises

(1) $K_{sp} = 6 \times 10^{-12}$ for magnesium hydroxide at temperature 298 K. What is the minimum number of moles of magnesium sulfate must a chemist add to 1.00 liter of 0.20 molar ammonium hydroxide at 298 K in order to initiate the formation of solid magnesium hydroxide? (Answer: 1.50×10^{-10} moles)

(2) A chemist records the edge position P_{edge} of diffusing material in solution as a function of time t. The data are plotted on the next page.

Let the behavior of P_{edge} be described by the following equation:

$$P_{edge} = C\, t^{\beta}$$

Determine best-fit values of C and β. (Answer: 2.5 and 0.65)

Ye Olde Precipitation Pre-Lab Kinetics Data