Experiment 6: Seeing red: determination of an equilibrium constant

Experimental background
Dynamic chemical equilibrium is a state of balance between a forward and a reverse process that each take place at the same rates so that no net change appears occur. However, if we perturb the equilibrium a little bit, the dynamic system responds to produce a new equilibrium state of balance which we might be able to detect. A simple way to see what is happening is to find chemical systems where color changes occur. You have already encountered these in a chemistry lab where an indicator changed colour to show the end point of a titration. You can see the same type of color change in tea when lemon is added; the deeper red brown of the tannins in the tea shifts to a lighter color due to the acid in the lemon.

In this experiment the equilibrium we will study occurs in water between ferric ions (Fe$^{3+}$) and thiocyanate ions (SCN$^-$), both of which are colourless, and a coloured complex ion FeSCN$^{2+}$ which is a brick red colour. The equilibrium can be written as in eqn. 1 and defines the equilibrium constant $K_c$:

$$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$$

$$K_c = \frac{[\text{FeSCN}^{2+}(\text{aq})]}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^-(\text{aq})]}$$

The reaction needs to be studied in aqueous solution containing nitric acid in order to control side reactions of the Fe$^{3+}$. Chemists usually omit the other species present, like the nitrate (NO$_3^-$) and potassium ions needed to balance the charges so that only the key partners in the equilibrium are shown and discussed; see the endnote on this topic for more detail.

To determine the value of $K_c$ from an experiment we need to be able to determine the equilibrium concentration of each of the three species at equilibrium by experiment. Since the FeSCN$^{2+}$ ion is a brick red color we can determine its concentration by visible spectroscopy; the amount of light absorbed by the FeSCN$^{2+}$ is directly proportional the concentration of FeSCN$^{2+}$. We will need to make a calibration curve, and then use the curve to determine the equilibrium concentration of FeSCN$^{2+}$ for a number of different conditions.

How do we determine the equilibrium concentrations of the free Fe$^{3+}$ ion and the free SCN$^-$ ions since they have no absorbance? We know the reaction stoichiometry guarantees that for each mole of FeSCN$^{2+}$ complex produced, one mole each of Fe$^{3+}$ and SCN$^-$ are consumed. If we know the initial amount, we can use this mass balance to find the free concentrations at equilibrium:

$$[\text{Fe}^{3+}(\text{aq})] = [\text{Fe}^{3+}(\text{aq})]_{\text{initial}} - [\text{FeSCN}^{2+}(\text{aq})]$$

$$[\text{SCN}^-(\text{aq})] = [\text{SCN}^-(\text{aq})]_{\text{initial}} - [\text{FeSCN}^{2+}(\text{aq})]$$
Equations 2 and 3 indicate that so long as we know the initial concentrations and can determine the concentration of the FeSCN$^{2+}$ complex then we will know the terms we need to substitute into equation 1 to give a value for $K_c$.

It takes work to make a calibration curve; typically five points are required and that means five separate solutions need to be prepared in volumetric flasks. This experiment uses an alternative approach that is similar to titration. We start with the cuvette for the UV-visible spectrometer that contains a known volume of solution of known concentration ([Fe$^{3+}$(aq)] or [SCN$^-$(aq)]). To this we add a series of small known volumes of a solution (or aliquots) of known concentration ([SCN$^-$(aq)] to titrate Fe$^{3+}$ for example). After each aliquot addition we know the new total volume and the total amount of each species that we have. This allows the calculation of the new concentrations in the cuvette. We need to stir and wait long enough to be sure we have equilibrium, but we can continue to add to the same cuvette and just keep track of the volumes to allow the concentrations to be calculated later. This process is known as an aliquot titration.

The precision of the aliquot titration entirely depends on the precise control of volumes that are added to the cuvette. We need to make sure we get as closely as possible the same volume of solution added in each step. These add up to make the total volume, so any errors at this stage will add up and make the later points progressively less reliable. Fortunately there is a highly repeatable type of pipette called an *autopipettor* that is well suited to doing precise additions on a small scale. You have seen these on CSI (homework – watch an episode and spot the autopipettors). They are reliable but there is technique involved – see [https://www.youtube.com/watch?v=tL0acTneiNY](https://www.youtube.com/watch?v=tL0acTneiNY)

**Experimental procedure**

**Safety notes**
All the solutions in this experiment contain 1M nitric acid. In addition to your lab coat and lab glasses, you need to wear disposable gloves for all manipulations. Put them on before doing anything and do not take them off until after you have cleaned up. If you have a small spill, inform your TA immediately and use the spill kit provided. DO NOT wipe up a nitric acid spill with a paper towel as the nitric acid will react, create heat, and has been known to ignite in the garbage cans. If nitric acid comes in contact with your skin or eyes, inform your TA and immediately start to rinse the affected area with LOTS of water. Quite apart from the chemical burn, nitric acid contact makes very unsightly yellow stains on your skin if left unwashed.

All solutions must be correctly and completely disposed. See the section on waste disposal and cleanup.

**Stock solutions**
The stock Fe(NO$_3$)$_3$ and KSCN solutions in 1.0M HNO$_3$ will be provided in the lab. There are two concentrations of each: concentrated Fe(NO$_3$)$_3$ solution for calibration (about 0.20 M); dilute Fe(NO$_3$)$_3$ solution for $K_c$ determination (about 2.0 mM); a KSCN solution for calibration (about 1.0 mM); a KSCN solution for $K_c$ determination (about 2.0 mM). You need to note the concentrations of all four solutions. Obtain 15 mL of each solution in four clean and labelled beakers and use these as you do the next steps. Caution: do not get the beakers mixed up!
Calibration procedure

1. The spectrometer is a Perkin Elmer Lambda XLS spectrometer. If the instrument is off, press the Power button. The instrument will run a self-diagnostic calibration program that takes about 2 seconds.
2. Select Standard Methods by pressing the number 1 on the number pad. Select Single Wavelength by pressing the number 1 on the number pad. Set the desired wavelength to 468 nm with the number pad and press the OK button.
3. Start with a clean, dry, and empty cuvette. Place a small stir bar into the cuvette and place the cuvette into the spectrometer.
4. Using an autopipettor with a clean tip, rinse the tip and then pipette 2.00 mL of the concentrated Fe$_3^+$ solution into the cuvette. You can accomplish this by using the 1.00 mL autopipettor twice. Start the stirrer and adjust the speed to be fast enough to avoid splashing the contents
5. Change the pipette tip and rinse and pipette 0.10 mL of the SCN$^-$ solution for calibration into cuvette without removing the cuvette from spectrometer. Stir briefly (5-10 s). Record the absorbance at 468 nm on the data table.
6. Now add another 0.10 mL aliquot of the SCN$^-$ solution, stir, and again record the absorbance. There is no need to rinse the tip in this step or in the subsequent steps.
7. Continue until you have made a total of 5 additions or have obtained an absorbance of 1.50, whichever comes first.

Aliquot titration for determination of $K_c$

1. Empty the cuvette, rinse it a number of times with distilled water and dry the cuvette with a Kim wipe. Use a large stir bar to recover the little stir bar so it ba rinsed and dried. Be careful not to lose the stirbar.
2. With a new and rinsed pipette tip, pipette 2.00 mL of the Fe$_3^+$ solution for $K_c$ determination into cuvette and place the cuvette into the spectrometer. Do not forget to start and control the stirring again.
3. With a new and rinsed pipette tip, pipette 0.10 mL of the SCN$^-$ solution for $K_c$ determination into the cuvette, stir the solution and record the absorbance at 468 nm.
4. Continue adding 0.10 mL aliquots of the SCN$^-$ solution for $K_c$ determination into the cuvette and record the absorbance at 468 nm until cuvette is full (no more than five additions in total). This is the SCN titration.
5. Repeat above procedure but this time start with 2.00 mL of the SCN$^-$ solution for $K_c$ determination and add 0.10 mL aliquots of the Fe$_3^+$ solution for $K_c$ determination and record the absorbance at 468 nm until cuvette is full (no more than five additions in total). This is the Fe titration.
**Waste disposal and cleanup**

All solutions contain nitric acid and many will contain iron. They must all be dumped into the appropriate waste containers provided and the cuvettes, pipette tips, and beakers you have used must be well-rinsed with water. It is especially important to rinse the pipette tips before disposal in the landfill waste due to the potential fire hazard as nitric acid reacts with other garbage.

**Data manipulations**

**A) Graph the calibration data to determine the calibration equation**

In 2016 the calibration curve will be provided.

The graph of absorbance as a function of \([\text{FeSCN}^{2+}]\) is an example of the Beer-Lambert law which relates the absorbance \((A; \text{unitless})\) of a solution to the concentration \((c; \text{usually M})\) of a species:

\[
A = \varepsilon bc
\]

In eqn. 5, the \(b\) term (usually cm) is the path length through which the light passes. The coefficient \(\varepsilon\) is the molar absorptivity and has units \(\text{L mol}^{-1}\text{cm}^{-1}\). The molar absorptivity is a property of a species and is a measure of how strongly the species absorbs light at a given wavelength. Usually we are interested in the maximum absorbance which occurs at a specific wavelength \(\lambda_{\text{max}}\) in this experiment \(\lambda_{\text{max}} = 468\ \text{nm}\). If the system obeys the Beer-Lambert law then \(A\) and \(c\) are linearly related with a slope \(\varepsilon b\) determined from the experimental plot.

**B) For each addition in the aliquot titration**

**B1:** Calculate the total volume in the cuvette after the addition

**B2:** Using the stock \(\text{Fe}^{3+}\) solution concentration and the volume added to the cuvette, calculate the molar amount of \(\text{Fe}^{3+}\) initially present. Using the stock SCN\(^-\) solution concentration and the volume added to the cuvette, calculate the molar amount of SCN\(^-\) initially present.

**B3:** Using the observed absorbance reading and the calibration data from part A calculate the equilibrium concentration of \([\text{FeSCN}^{2+}]\) at that point in the titration. Then use the equilibrium concentration with the total volume to calculate the molar amount of \(\text{FeSCN}^{2+}\) present at equilibrium.

**B4:** Using the mass balance equations 2 and 3 and the values you determined in B2 and B3, calculate the equilibrium concentration of \([\text{Fe}^{3+}]\) and \([\text{SCN}^-]\).

**B5:** Using the equilibrium concentrations of \([\text{FeSCN}^{2+}]\), \([\text{Fe}^{3+}]\), and \([\text{SCN}^-]\) calculate the value of \(K_c\) determined at this point in the aliquot titration.

**C) Calculate the average value of \(K_c\) and determine its uncertainty**

Each point in the aliquot titration yields a value of \(K_c\). These independent determinations can be averaged to give a value that represents the overall dataset. The standard deviation of the average is an estimate of the uncertainty in the average value. Both these calculations can be done on the Sharp 510...
calculator (or in Excel). On the calculator select \([2^{nd}]\text{F}[\text{MODE}]\ 1\) to access the data function. Enter the data using \([\text{M+}]\); the display will count the number of points \((n=\#)\). After all your data is entered the average is given with the \(\bar{x}\) key \((\text{[2^{nd}]}\text{F})\text{[]}\) and the standard deviation of the dataset with the \(\sigma\bar{x}\) key \((\text{[2^{nd}]}\text{F})[\div]\).

**Report**

A report form will be given to you in class. The report for this experiment is to be written up during your lab session. All reports must be handed in to your TA at the end of the session. The report will consist of:

- Sample Calculations;
- A Summary Sheet with all your calculated values from the aliquot titration; and
- A discussion of the origin of the uncertainty in \(K_c\). Why is there variation in the derived values of \(K_c\) at each point in the aliquot titration? Hint: it is not related to the skill or technique of the person doing the experiment.

**Pre-lab questions**

1. What is the objective of this experiment?
2. What is the purpose of the calibration curve?
3. The \(\text{Fe}^{3+}\) ion is colorless; how can its equilibrium concentration be determined from a spectroscopic method?
4. Why is an autopipettor used in this experiment? Why not use a regular pipette?
5. Why do the solutions contain nitric acid?
6. How do you clean up a small spill of the nitric acid containing solutions?
7. What are the hazards associated with nitric acid?
Endnote:

You may be a bit bothered by the gaps in the logic and the lack of units for \(K_c\). So are we; let’s sort that out. Our first problem is that under our conditions the aqueous ferric ion is a complex involving six water molecules coordinated to the Fe center. (VSEPR question: what shape is this complex?) The equilibrium process is a substitution of one of the coordinated waters to produce the coloured thiocyanate complex:

\[
\text{(eqn. 2)} \quad \begin{array}{c}
\text{colourless} \\
\text{Fe(H}_2\text{O)}_6^{3+} + \text{SCN}^- \rightarrow \text{Fe(SCN)}^2+ + \text{H}_2\text{O}
\end{array}
\]

The expression for the equilibrium constant \(K'_c\) for the substitution reaction is:

\[
K'_c = \frac{[\text{Fe}^{3+} \text{(aq)}][\text{SCN}^- \text{(aq)}]}{[\text{Fe} - \text{SCN}^2+ \text{(aq)}][\text{H}_2\text{O}]}
\]

The iron and thiocyanate species are present at concentrations well below 1 M so the tiny amount of water that is formally released in the reaction does not alter the concentration of water to any significant extent; \([\text{H}_2\text{O}]\) in pure water is about 55.5M. In these circumstances chemists always assert that the concentration of water term is effectively a constant. We cannot just ignore it, but we can revert to the equilibrium constant \(K_c\) defined by eqn. 1. We do need to specify which equilibrium we mean because \(K_c\) from eqn. 1 and \(K'_c\) are not equal; \(K_c = K'_c \times [\text{H}_2\text{O}]\).

Note as well that this reaction does have the possibility of cancelling the concentration units to make a \(K'_c\) which is unitless, but that is just a lucky accident and does not deal with all cases. The way that this is handled in a fundamental way is to focus on the activity of a species not its concentration. The activity of a species \((a_x)\) is the ratio of its concentration \([X]\) relative to a reference (or standard) state. The standard state in terms of molar concentrations for a species in an ideal solution is 1 M. Thus the \(K_c\) of eqn 1 is:

\[
K_c = \frac{a_{\text{Fe}} a_{\text{SCN}}}{a_{\text{FeSCN}}} = \frac{\{[\text{Fe}^{3+} \text{(aq)}]\}[1\text{M Fe}^{3+} \text{(aq)}]}{[\text{Fe} - \text{SCN}^2+ \text{(aq)}][1\text{M SCN}^- \text{(aq)}]^2}
\]

Since activity is a ratio it must be unitless so any derived constant will also be unitless as shown for \(K_c\) as defined by eqn. 1. Chemists commonly assume that since we are dealing with dilute solutions they are ideal and activity and concentration are numerically equal. This allows us to ignore the units (neat fiddle eh?). The same issues crop up in reactions involving gases (standard state is 1 atm; we usually assume an ideal gas), liquids, and solids (standard state is defined as the pure liquid or solid; we usually assume an ideal liquid).

Bottom line – we know how to do this correctly but we make a couple of good assumptions that allow us to ignore the details under “normal” circumstances of a dilute aqueous solution.