Chemical Equilibrium: K_{eq} of the $Fe(SCN)_x^{+3}$ Complex

Lab #1, Chem 36

Spring 2009

In many chemical reactions the reactants are not completely converted to the products that are trying to be made. One reason for the incomplete conversion of reactants to products is the observation that reactions can also proceed in the reverse direction. That is, as the products are generated, they react to regenerate the original reactants. Such reactions are said to be <u>reversible</u> and are indicated in an equation by a double arrow ($\rightleftharpoons$). The reaction proceeding to the right is called the <u>forward reaction</u>, and the reaction proceeding to the left, the <u>reverse reaction</u>. Both reactions occur simultaneously.

Every chemical reaction proceeds at a specific rate. The rate of a reaction is variable and depends on the concentrations of the reactants and the conditions under which the reaction is conducted. When the rate of the forward reaction is equal to the rate of the reverse reaction, a condition of <u>chemical equilibrium</u> exists. At equilibrium, the products react to produce the reactants at the same rate that the products are produced. Thus, the concentrations of substances in equilibrium do not change, but both reactions, forward and reverse, are still occurring.

For the general reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

the equilibrium expression is:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where A, B, C, and D are solutes in solution or are gases, and the bracketed expressions are their concentrations in moles per liter at equilibrium. The equilibrium constant, K_c, has a fixed value for the reaction at any given temperature. If A, B, C, and D are mixed arbitrarily in a container, the concentrations of each substance will change until their equilibrium concentrations are reached. It is important to understand that the actual molar concentrations in an equilibrium expression can vary over a wide range and that any combination of concentrations that mathematically give the same equilibrium constant are termed equilibrium concentrations. Thus, depending on the magnitude of K_c and the concentration of each substance when initially mixed together, the reaction will proceed to the right or left until equilibrium is reached. In order to write the correct equilibrium expression for a reaction it is imperative that one know which reaction is taking place.

When dilute solutions of iron (III) cations, Fe^{3+}, and thiocyanate anions, SCN^-, are mixed, several possible reactions can occur. These reactions proceed in a stepwise manner, as shown below. However, while all three of these reactions can occur, in reality only one of them <u>will</u> occur to any appreciable extent under your reaction conditions.

$$Fe^{+3}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{+2}(aq)$$
$$FeSCN^{+2}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)_2^+(aq)$$
$$Fe(SCN)_2^+(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)_3\,(s)$$

The purpose of this experiment is to determine which of these equilibria predominates. This will be accomplished by comparing the values of the equilibrium constants for these reactions. The equilibrium constants will be calculated from experiments in which a series of Fe^{3+} and SCN^- solutions, having known concentrations are mixed.

It is important to remember when performing equilibrium calculations that the overall reaction for both the second step and the third step be used to derive the equilibrium expression. For example the overall reaction for step 2 is:

$$Fe^{3+}(aq) + 2\,SCN^-(aq) \rightleftharpoons Fe(SCN)_2^+(aq)$$

In this experiment, a deep red solution forms as the Fe^{3+} and SCN^- solutions are mixed. The intensity of the red solution is directly proportional to the concentration of the iron-thiocyanate complex formed. Although the human eye is quite sensitive to small changes in color and intensity, more accurate and quantitative data can be obtained using a spectrophotometer. We will use either a Spectronic 20 or Spectronic 21 (see Appendix III) to measure the amount of light absorbed by the red complex formed in the equilibrium mixtures. Measurements will be made at 447 nm, the wavelength at which the complex most strongly absorbs. The absorbance, A, of the complex is proportional to its concentration, c, and can be measured directly on the spectrophotometer. The relationship between absorbance and concentration is given by the Beer-Lambert Law:

$$A = abc$$

In order to determine the iron-thiocyanate concentration in the mixtures being analyzed, a "working curve" from solutions having known concentrations of complex has to first be constructed. The working curve allows one to find the relationship between concentration and absorbance. Note: In all the solutions, a constant concentration of 0.5 M nitric acid will be maintained. Nitric acid (a strong acid - i.e., totally dissociated) serves two purposes here. First, the large amount of H^+ ion will ensure that no Fe^{3+} reacts with base, OH^-, to form brown-colored and insoluble species such as $Fe(OH)_3$. The second, and more important, function of the nitric acid is to maintain a constant ionic strength. Many equilibrium constants, and this one in particular, vary significantly with the number of ions present in solution. However, while this large excess of nitric acid permits the calculation of a uniform equilibrium constant for solutions containing varying concentrations of Fe^{3+} and SCN^-, it also has the effect of decreasing the true value of the equilibrium constant. A qualitative and rather over-simplified explanation of what is happening is that the anions added form a "protective" layer around the Fe^{3+} ions (as do the cations around the SCN^- ions). To an extent, this lessens the prospects for Fe^{3+} and SCN^- ions coming together to form the colored complex, and consequently, decreases the measured value of the equilibrium constant. The equilibrium constant will be calculated without correcting for these interactions.

Procedure

When obtaining solutions in this experiment, be very careful to obtain solutions with the correct concentration. There are two different thiocyanate solutions, and two different iron solutions. If the wrong solution is used, don't expect accurate results.

1. Preparation of a calibration or "working" curve. In order to relate the absorbance observed from the iron-thiocyanate complex formed in the equilibrium mixtures to specific concentrations of iron thiocyanate, solutions containing known concentrations of iron-thiocyanate will have to be examined. To save time in this part, you will work in pairs. Each pair in the laboratory section will prepare one known sample. The TA will assign the volume of KSCN to be used by each pair. Solutions containing known iron-thiocyanate concentrations are prepared by pipetting 5.0 mL of 0.200 M $Fe(NO_3)_3$ in 0.5M HNO_3 into an 18 x 150mm test tube and then pipetting between 0.5 and 5 mL of 4.00 x 10^{-4} M KSCN in 0.5 M HNO_3 into the same test tube. After adding the KSCN solution to the test tube, the final volume is adjusted to 10 mL by adding 0.5 M HNO_3 . The mixture is then mixed thoroughly and its absorbance measured on a Spectronic 20 or 21 at 447 nm. A blank containing 0.200 M $Fe(NO_3)_3$ in 0.5 M HNO_3 should be used to adjust the Spectronic 20 to 100%-T.

The TA will list, on the board, the value of the absorbance obtained for each known concentration of iron-thiocyanate assigned. Be sure to copy these values into your notebook. These data will be used to prepare a "working curve". By plotting absorbance vs. concentration of iron-thiocyanate complex formed, one should obtain a straight line with its intercept at the origin.

2. Preparation of Solutions for Analysis. Label five 18 x 15 test tubes A through E. Pipette 5.0 mL of 4.00 x 10^{-3} M $Fe(NO_3)_3$ in 0.5 M HNO_3 into each test tube. Next, take the test tube labeled A and pipette 1 mL of 2.00 x 10^{-3} M KSCN in 0.5 M HNO_3 into it. Then pipette 2 mL of the KSCN solution into test tube B, 3 mL into test C, and correspondingly 4 and 5 mL into test tubes D and E. A sufficient amount of 0.5 M HNO_3 is then pipetted into test tubes, A-D, to bring the total volume of all the test tubes to 10 mL.

Mix each solution thoroughly by gently shaking the test tubes. Allow the solutions to stand for 10 minutes before measuring their absorbances at 447 nm. This waiting period will ensure that equilibrium has been achieved. Use 4.00 x 10^{-3} M $Fe(NO_3)_3$ in 0.5 M HNO_3 as a blank solution.

Waste

All waste should be placed in the bottles in the hood.

Calculations

1. Write a K_c expression for each of the three reactions under consideration. One of these reactions can be eliminated, why?

2. Using the absorbance values obtained by the class for each of the known concentrations, construct a calibration or "working curve" for each of the two reactions being considered. In the solutions prepared for the calibration curve, the concentrations of the iron-thiocyanate complex formed are assumed to be proportional to the $[SCN^-]$. This is because the $[Fe^{3+}] >>> [SCN^-]$ and it can be concluded, without serious error, that all the SCN^- has been converted to the iron-thiocyanate complex. Thus, the concentration of iron-thiocyanate complex formed in any one trial only depends upon the number of moles of SCN^- used in that trial. The concentration of the iron-thiocyanate complex is determined in the following manner:
   a) Multiply the $[SCN^-]$ by the volume taken for any given trial.
   b) Relate the mole SCN^- to the mole of iron-thiocyanate formed using the appropriate balanced equation.
   c) Divide the mole of iron-thiocyanate by the total volume of sample used.

3. Calculate a K_c for each trial, A though E, assuming the following reaction is occurring, and then calculate an average K_c.

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

4. Calculate a K_c for trials A, C, and E assuming the following reaction is occurring, and then calculate an average K_c. In calculating the $[Fe(SCN)_2^+]$ remember that two mole of SCN^- are used to produce one mole of $Fe(SCN)_2^+$.

$$FeSCN^{+2}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)_2^+(aq)$$

5. Based on the values calculated for K_c select the reaction that is most likely taking place when solutions of Fe^{+3} and SCN^- are mixed at room temperature. Why is it that the set of results that produce the most consistent values of K_c is indicative of the most likely reaction occurring?