Determination of the Equilibrium Constant

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1 Purpose

The purpose of this experiment is to determine the equilibrium constant for the reaction $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ and to see if the constant is indeed the same under different conditions.

2 Procedure

First, reference solutions are made by mixing an excess of Fe^{3+} ions with known amounts of SCN^- ions. We then assume that the reactions are driven to completion due to Le Chtelier's Principle, so they contain a known concentration of $FeSCN^{2+}$ ions. Second, test solutions are made by mixing a constant amount of Fe^{3+} ions with varying amounts of SCN^- ions, which contain an unknown concentration of $FeSCN^{2+}$ ions.

Then, the absorbance of the solutions are measured with a spectrophotometer. With the reference solution's absorbances, a calibration curve is made to then determine the concentrations of the test solutions. Then, with the calculated concentrations, the equilibrium constant can be calculated.

3 Data

The following data were collected:

3.1 Reference Solutions

Sample	$[FeSCN^{2+}]$	Absorbance
Reference #1	4.0×10^{-5}	0.233
Reference #2	6.0×10^{-5}	0.299
Reference #3	8.0×10^{-5}	0.409
Reference #4	1.0×10^{-4}	0.524
Reference #5	1.2×10^{-4}	0.600

3.2 Test Solutions

Sample	$[Fe^{3+}]$	$[SCN^-]$	Absorbance
Test #6	1.0×10^{-3}	2.0×10^{-4}	0.233
Test #7	1.0×10^{-3}	4.0×10^{-4}	0.412
Test #8	1.0×10^{-3}	6.0×10^{-4}	0.568
Test #9	1.0×10^{-3}	8.0×10^{-4}	0.792
Test #10	1.0×10^{-3}	1.0×10^{-3}	0.985

4 Calculations

Using the method of least squares with the absorbance of the reference solutions, we can find that

$$A = 5010 \cdot [FeSCN^{2+}] + 0.011 \tag{1}$$

Where A is the absorbance for each $[FeSCN^{2+}]$. This curve can also be written for the concentration.

$$[FeSCN^{2+}] = \frac{A - 0.011}{5010} \tag{2}$$

Using this equation on each test solution absorbance, we can find the unknown $[FeSCN^{2+}]_{eq}$ concentrations. For example, with the absorbance of 0.233, the $[FeSCN^{2+}]_{eq} = \frac{0.233 - 0.011}{5010} = 4.4 \times 10^{-5}$

Since each compound in the reaction is used or made in a 1:1 ratio, they will decrease or increase (respectively) by the same amount. So, let $[FeSCN^{2+}]$ increase by x, then $[Fe^{3+}]$ will decrease by x. Then, since $[FeSCN^{2+}]$ is starting at 0 for the experiment, the x is the final concentration at equilibrium. For example, if $[FeSCN^{2+}]$ gets to be 4.4×10^{-5}, $[Fe^{3+}]$ will be $1.0 \times 10^{-3} - 4.4 \times 10^{-5} = 9.6 \times 10^{-4}$

With the same logic, we can find $[SCN^-]_{eq}$ which is the initial concentration of SCN^- less the change in $[FeSCN^{2+}]$. This is, for example, $2.0 \times 10^{-4} - 4.4 \times 10^{-5} = 1.6 \times 10^{-4}$

According to known rules, the equilibrium constant for this reaction is

$$K_p = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} \tag{3}$$

Then, using calculations from the results table, we can find the K_{eq} values for each test solution. For example, for test solution #6, the $K_{eq} = \frac{4.4 \times 10^{-5}}{(9.6 \times 10^{-4})(1.6 \times 10^{-4})} = 290$

The mean of the K_{eq} values is $\frac{\sum K_{eq}}{5} = 280$

The average deviation of the K_{eq} is $\frac{\sum |K_{eq} - 280|}{5} = 16$

4.1 Results

Sample	$[\text{FeSCN}^{2+}]_{eq}$	$[\text{Fe}^{3+}]_{eq}$	$[\text{SCN}^-]_{eq}$	K_{eq}
Test #6	4.4×10^{-5}	9.6×10^{-4}	1.6×10^{-4}	290
Test #7	8.0×10^{-5}	9.2×10^{-4}	3.2×10^{-4}	270
Test #8	1.1×10^{-4}	8.9×10^{-4}	4.9×10^{-4}	250
Test #9	1.6×10^{-4}	8.4×10^{-4}	6.4×10^{-4}	300
Test #10	1.9×10^{-4}	8.1×10^{-4}	8.1×10^{-4}	290

Mean: 280
Average Deviation: 16

5 Discussion

1. The equilibrium constant is a quantity which characterizes an equilibrium in a reaction and is based on the final concentrations of involved compounds. The value was constant for all of the experiments (within a good margin of error). It should be consistent because this constant is defined to be the relation between all concentrations of involved compounds at chemical equilibrium.

2. The calculated value of the equilibrium constant indicates that there are mostly products since it is $280 > 1$. Also, since 280 is quite large (compared to the Haber process which has a K of about 30), it should prefer the products.

3. A spectrophotometer is a device that measures the amount of light that can pass through a given substance. In this experiment, we used it to determine the percent absorbance for each solution. The reference solutions were obtained by mixing a known amount of SCN^- in an excess of Fe^{3+} so that we could assume that the reaction went to completion and we would have a known amount of FeSCN^{2+}. We can then find the absorbances of the

reference solutions to create a function that relates concentration to absorbance which can then be applied to the unknown concentrations with the measured absorbances to calculate the unknown concentration.

4. The spectrophotometer should not be set to the same color as that of the solution because the visible color is that which is transmitted which mean none is absorbed. Another color's absorbance, such as the complement of the solution's color, such as cyan (since the complex ion is a red), or the components of cyan (green and blue), would probably change with different concentrations because it is a color that must be absorbed to only allow red through. In this experiment, 450nm light was used, which corresponds to blue. Since the complex ion is red, this blue light will be absorbed and can then be measured.

5. The precision indicates that the equilibrium constant is indeed constant for the experiment because it is such a small percentage of the mean K_{eq}. It is only $\frac{16}{280} = 5.7\%$ of the mean constant. This means that the calculated K_{eq} for each solution is very close to each other and that, for allowing for experimental error, they really are equal (noting that they seem to be randomly larger or smaller than the mean without any correlation to any of the concentrations that could otherwise explain this behavior).