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Spectrophotometric Determination of an Equilibrium Constant
--Manuscript Draft--

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Corresponding Author:	Michael Evans UNITED STATES
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Michael Evans
First Author Secondary Information:	
Order of Authors:	Michael Evans
Order of Authors Secondary Information:	

PI: Michael Evans

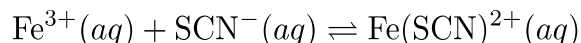
Chemistry Science Education Title: Spectrophotometric Determination of an Equilibrium Constant

Overview

The equilibrium constant K for a chemical system is the ratio of product concentrations to reactant concentrations at equilibrium, each raised to the power of their respective stoichiometric coefficients. Measurement of K involves determination of these concentrations for systems in chemical equilibrium.

Reaction systems containing a single colored component can be studied spectrophotometrically. The relation between absorbance and concentration for the colored component is measured and used to determine its concentration in the reaction system of interest. Concentrations of the colorless components can be calculated indirectly using the balanced chemical equation and the measured concentration of the colored component.

In this video, the Beer's law curve for $\text{Fe}(\text{SCN})^{2+}$ are determined empirically and applied to the measurement of K for the following reaction:



Four reaction systems with different initial concentrations of reactants are investigated to illustrate that K remains constant irrespective of initial concentrations.

Principles

Every chemical reaction is associated with an equilibrium constant K , which reflects the ratio of product concentrations to reactant concentrations at chemical equilibrium. For the generic reaction $a \text{A} + b \text{B} \rightleftharpoons c \text{C} + d \text{D}$, the equilibrium constant is defined as

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

where the concentrations on the right-hand side of the equation are molarities at equilibrium. This equation is known as the equilibrium expression for the reaction. In chemical systems that are not in equilibrium, the forward and reverse reactions occur at different rates until the concentrations of reactants and products satisfy the equilibrium expression.

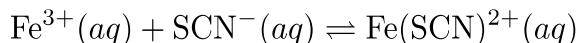
To measure the value of K for a system in chemical equilibrium, it is necessary to determine the concentrations of reactants and products either directly or indirectly. Spectrophotometric methods for the determination of K involve direct measurement of the concentration of one colored component and indirect measurement of the others. Visible spectroscopy of the colored component at known concentrations reveals the relation between absorbance and concentration for this component. According to Beer's law, this relation has the form

$$A = \epsilon lc$$

where ε is the molar absorptivity of the component in L/mol-cm, l is the path length of light through the sample in cm, c is the molarity of the component in mol/L, and A is the absorbance.

The Beer's law curve for the colored component can be applied to a reaction system in equilibrium to determine the concentration of this component from absorbance measurements. Concentrations of the remaining reactants and products can then be calculated by adjusting initial concentrations based on the measured molarity of the colored species.

The system studied here is the reaction of iron (III) cation with thiocyanate anion to form an iron (III) thiocyanate complex.



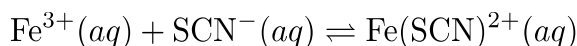
The equilibrium expression for this reaction system is

$$K = \frac{[\text{Fe}(\text{SCN})^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^{-}]_{eq}}$$

where the *eq* subscript denotes equilibrium concentrations. The iron (III) thiocyanate product is orange, but both reactants are colorless in aqueous solution. Hence, $[\text{Fe}(\text{SCN})^{2+}]_{eq}$ can be determined directly from absorbance measurements.

$$[\text{Fe}(\text{SCN})^{2+}]_{eq} = \frac{A}{\epsilon l}$$

Equilibrium concentrations of the reactants can be calculated by subtracting the equilibrium concentration of the product from the initial concentrations of the reactants. An Initial-Change-Equilibrium (ICE) table illustrates how initial and equilibrium concentrations are related (**Table 1**).



Repeated trials of this experiment involving different initial concentrations of reactants should yield the same value of K , as the value of K is independent of concentration.

Procedure

1. Determining the Beer's Law Curve for $\text{Fe}(\text{SCN})^{2+}$

- 1.1. Calibrate a visible spectrophotometer using distilled water.
- 1.2. Add 1.0 mL of 1.0×10^{-4} M $\text{Fe}(\text{NO}_3)_3$ solution to a medium test tube.
- 1.3. To the same test tube, add 5.0 mL of 0.50 M KSCN solution.
- 1.4. To the same test tube, add 4.0 mL of 0.10 M HNO_3 solution, and mix the solution well.

- 1.5. Use a Pasteur pipette to transfer a small quantity of the solution to a cuvette. Ensure that the liquid level is above the path of the light beam in the spectrophotometer.
 - 1.6. Place the cuvette in the spectrophotometer, so the light passes through the smooth sides.
 - 1.7. Acquire a spectrum and record the λ_{max} value and the absorbance at λ_{max} .
 - 1.8. Repeat steps 1.2 – 1.7 using the volumes of $\text{Fe}(\text{NO}_3)_3$, KSCN, and HNO_3 solutions in **Table 2**.
 - 1.9. Plot the measured absorbance versus the concentration of $\text{Fe}(\text{SCN})^{2+}$ in each test tube and determine the line of best fit for the data. The slope of this line is the molar absorptivity ϵ and the path length is 1 cm.
2. Measuring K for the Iron (III) Thiocyanate System.
- 2.1. Prepare four medium test tubes containing the indicated volumes of 0.0025 M $\text{Fe}(\text{NO}_3)_3$, 0.0025 M KSCN, and 0.10 M HNO_3 solutions in **Table 3**.
 - 2.2. Mix each solution well and allow them to stand for at least 10 min. This resting period ensures that the solutions are at chemical equilibrium.
 - 2.3. Use a Pasteur pipette to transfer a small quantity of solution 6 to a cuvette. Ensure that the liquid level is above the path of the light beam in the spectrophotometer.
 - 2.4. Acquire a spectrum and record the λ_{max} value and the absorbance at λ_{max} .
 - 2.5. Repeat steps 2.3 and 2.4 for solutions 7 – 9.

Representative Results

Table 4 lists the absorbance and λ_{max} data for solutions 1 – 5. Concentrations of $\text{Fe}(\text{SCN})^{2+}$ were determined from initial concentrations of Fe^{3+} under the assumption that all of the Fe^{3+} is converted to $\text{Fe}(\text{SCN})^{2+}$. A large excess of SCN^- was used in tubes 1 – 5 to ensure that this assumption holds true.

The molarity $[\text{Fe}(\text{SCN})^{2+}]$ and absorbance are plotted in **Figure 2**. The measured absorbance agrees well with Beer's law.

Table 5 lists measured absorbance and calculated K values for tubes 6 – 9. Equilibrium concentrations of Fe^{3+} and SCN^- were calculated by subtracting the measured concentration of $\text{Fe}(\text{SCN})^{2+}$ from the initial concentrations of Fe^{3+} and SCN^- .

The mean K value was 147 ± 11 , illustrating that K is roughly constant over the range of concentrations studied.

Applications

The equilibrium constant provides useful information about the extent to which a reaction will proceed to form products over time. Reactions with a large value of K , much larger than 1, will form products nearly complete given enough time (**Figure 3**). Reactions with a value of K less than 1 will not proceed forward to a significant degree. The equilibrium constant thus serves as a measure of the feasibility of a chemical reaction.

The equilibrium constant also provides useful thermodynamic information about the changes in free energy, enthalpy, and entropy in the course of a chemical reaction. The equilibrium constant is related to the free energy change of reaction:

$$\Delta G = -RT \ln K$$

The free energy change of reaction is in turn related to the enthalpy and entropy changes of reaction:

$$\Delta G = \Delta H - T\Delta S$$

Measurements of the temperature dependence of K can reveal the enthalpy change ΔH and the entropy change ΔS for a reaction. In addition to providing chemists with insight into patterns in molecular behavior, tables of thermodynamic data can be used to identify reactions with favorable thermodynamic properties. For example, redox reactions that release large amounts of energy (associated with negative ΔG values) are attractive candidates for batteries (**Figure 4**).

Legend

Figure 1: Beer's law curve for iron (III) thiocyanate.

Figure 2: Line graph of Absorbance versus Concentration for $\text{Fe}(\text{SCN})_2^+$.

Figure 3: The equilibrium constant of this reaction is greater than 1. A significant amount of colored product forms in each case, even though the initial concentrations of reactants differ.

Figure 4: The redox reaction of copper (II) cations in aqueous solution with aluminum metal is a strongly exergonic reaction with a large value of K .

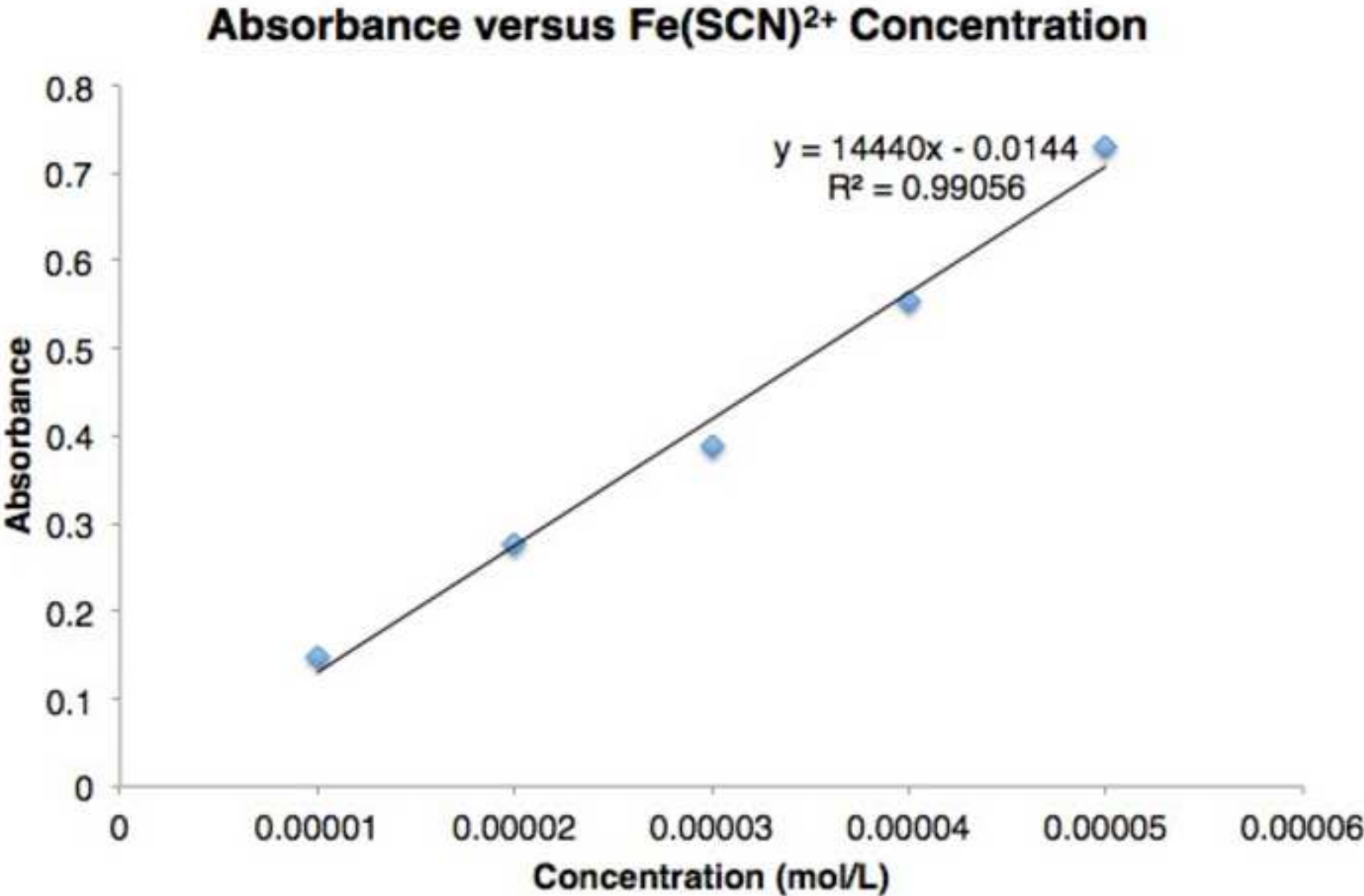
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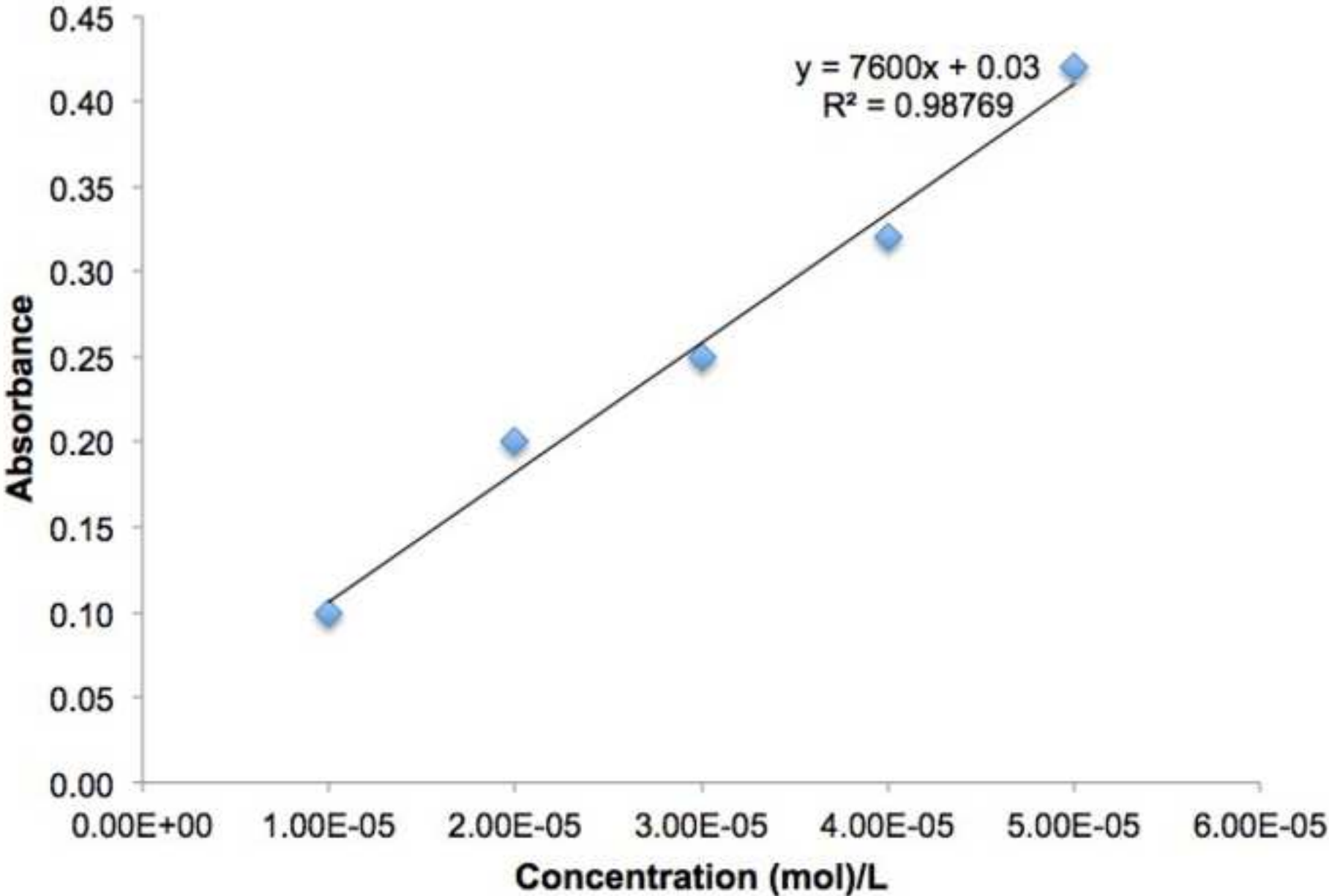
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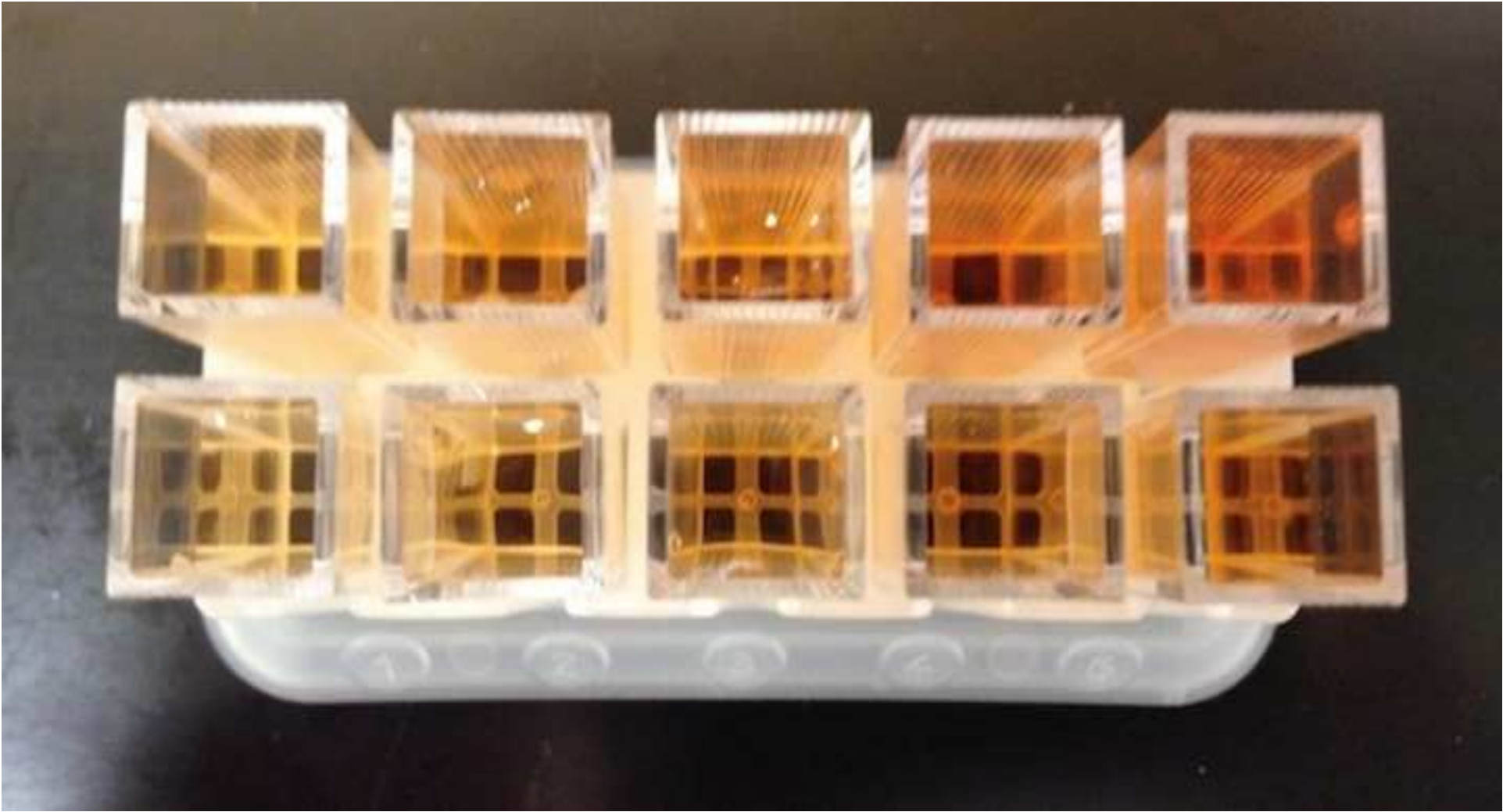
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Table 5: Measured absorbance values and calculated K for the reaction of iron (III) with thiocyanate.









	Fe^{3+}	SCN^-	$\text{Fe}(\text{SCN})^{2+}$
Initial	$[\text{Fe}^{3+}]_i$	$[\text{SCN}^-]_i$	0
Change	$-[\text{Fe}(\text{SCN})^{2+}]_{eq}$	$-[\text{Fe}(\text{SCN})^{2+}]_{eq}$	$+\text{[Fe(SCN)}^{2+}]_{eq}$
Equilibrium	$[\text{Fe}^{3+}]_i - [\text{Fe}(\text{SCN})^{2+}]_{eq}$	$[\text{SCN}^-]_i - [\text{Fe}(\text{SCN})^{2+}]_{eq}$	$[\text{Fe}(\text{SCN})^{2+}]_{eq}$

Tube Number	Volume 1.0×10^{-4} M $\text{Fe}(\text{NO}_3)_3$ (mL)	Volume 0.50 M KSCN (mL)	Volume 0.10 M HNO_3 (mL)
2	2.0	5.0	3.0
3	3.0	5.0	2.0
4	4.0	5.0	1.0
5	5.0	5.0	0.0

Tube Number	Volume 0.0025 M Fe(NO ₃) ₃ (mL)	Volume 0.0025 M KSCN (mL)	Volume 0.10 M HNO ₃ (mL)
6	1.0	1.0	5.0
7	1.0	2.0	4.0
8	2.0	2.0	3.0
9	2.0	3.0	2.0

Tube	$[\text{Fe}(\text{SCN})^{2+}]$ (mol/L)	Absorbance
1	1.00×10^{-5}	0.10
2	2.00×10^{-5}	0.20
3	3.00×10^{-5}	0.25
4	4.00×10^{-5}	0.32
5	5.00×10^{-5}	0.42

Tube	Absorbance	<i>K</i>
6	0.120	136
7	0.268	161
8	0.461	142
9	0.695	150

PI: Michael Evans

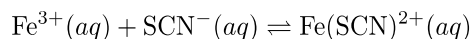
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Four reaction systems with different initial concentrations of reactants are investigated to illustrate that K remains constant irrespective of initial concentrations.

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Every chemical reaction is associated with an equilibrium constant K , which reflects the ratio of product concentrations to reactant concentrations at chemical equilibrium. For the generic reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, the equilibrium constant is defined as

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

where the concentrations on the right-hand side of the equation are molarities at equilibrium. This equation is known as the equilibrium expression for the reaction. In chemical systems that are not in equilibrium, the forward and reverse reactions occur at different rates until the concentrations of reactants and products satisfy the equilibrium expression.

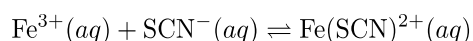
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$$A = \epsilon lc$$

where ϵ is the molar absorptivity of the component in L/mol-cm, l is the path length of light through the sample in cm, c is the molarity of the component in mol/L, and A is the absorbance.

The Beer's law curve for the colored component can be applied to a reaction system in equilibrium to determine the concentration of this component from absorbance measurements (**Figure 1**). Concentrations of the remaining reactants and products can then be calculated by adjusting initial concentrations based on the measured molarity of the colored species.

The system studied here is the reaction of iron (III) cation with thiocyanate anion to form an iron (III) thiocyanate complex.



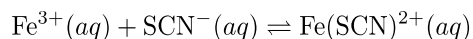
The equilibrium expression for this reaction system is

$$K = \frac{[\text{Fe}(\text{SCN})^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^{-}]_{eq}}$$

where the eq subscript denotes equilibrium concentrations. The iron (III) thiocyanate product is orange, but both reactants are colorless in aqueous solution. Hence, $[\text{Fe}(\text{SCN})^{2+}]_{eq}$ can be determined directly from absorbance measurements.

$$[\text{Fe}(\text{SCN})^{2+}]_{eq} = \frac{A}{\epsilon l}$$

Equilibrium concentrations of the reactants can be calculated by subtracting the equilibrium concentration of the product from the initial concentrations of the reactants. An Initial-Change-Equilibrium (ICE) table illustrates how initial and equilibrium concentrations are related (**Table 1**).



Repeated trials of this experiment involving different initial concentrations of reactants should yield the same value of K , as the value of K is independent of concentration.

Procedure

1. Determining the Beer's Law Curve for $\text{Fe}(\text{SCN})^{2+}$

- 1.1. Calibrate a visible spectrophotometer using distilled water as a blank.
- 1.2. Add 1.0 mL of 1.0×10^{-4} M $\text{Fe}(\text{NO}_3)_3$ solution to a ~~medium~~ test tube.
- 1.3. To the same test tube, add 5.0 mL of 0.50 M KSCN solution.

1.4. To the same test tube, add 4.0 mL of 0.10 M HNO₃ solution, ~~and~~ Cover the tube with a finger and gently shake to mix, mix the solution well.

Comment [A1]: Vortex? Shake by hand? Cover with Parafilm and invert?

1.5. Use a Pasteur pipette to transfer a small quantity of the solution to a cuvette. Ensure that the liquid level is above the path of the light beam in the spectrophotometer.

1.6. Place the cuvette in the spectrophotometer, so the light passes through the ~~smooth~~ transparent sides.

1.7. Acquire a spectrum and record the λ_{max} value and the absorbance at λ_{max} .

1.8. In order to construct a Beer's law curve, additional solutions with known concentrations of Fe(SCN)²⁺ must be prepared and measured. Repeat steps 1.2 – 1.7 using the volumes of Fe(NO₃)₃, KSCN, and HNO₃ solutions in **Table 2**.

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Comment [A2]: This reads more like a lab exercise than a demonstration. Is there any reason these values were chosen? What was the logic behind it?

1.9. Plot the measured absorbance versus the concentration of Fe(SCN)²⁺ in each test tube and determine the line of best fit for the data. The slope of this line is the molar absorptivity ϵ and the path length is 1 cm.

2. Measuring K for the Iron (III) Thiocyanate System-

2.1. Prepare four medium test tubes containing the indicated volumes of 0.0025 M Fe(NO₃)₃, 0.0025 M KSCN, and 0.10 M HNO₃ solutions in **Table 3**.

Comment [A3]: Same question as 1.8

2.2. Cover each tube with a finger and gently shake to mix. Mix each solution well, and allow them to stand for at least 10 min. This resting period ensures that the solutions are at chemical equilibrium.

2.3. Use a Pasteur pipette to transfer a small quantity of solution 6 to a cuvette. Ensure that the liquid level is above the path of the light beam in the spectrophotometer.

2.4. Acquire a spectrum and record the λ_{max} value and the absorbance at λ_{max} .

2.5. Multiple reactions with different initial concentrations of reactants can be studied to illustrate that K does not depend on concentration. To determine K for different initial conditions, repeat Repeat steps 2.3 and 2.4 for solutions 7 – 9.

Representative Results

Table 4 lists the absorbance and concentration ~~λ_{max}~~ data for solutions 1 – 5. Concentrations of Fe(SCN)²⁺ were determined from initial concentrations of Fe³⁺ under the assumption that all of the Fe³⁺ is converted to Fe(SCN)²⁺. A large excess of SCN⁻ was used in tubes 1 – 5 to ensure that this assumption holds true.

Comment [A4]: Not in the table.

The molarity $[\text{Fe}(\text{SCN})^{2+}]$ and absorbance are plotted in **Figure 2**. The measured absorbances agrees well with Beer's law.

Table 5 lists measured absorbances and calculated K values for tubes 6 – 9. *Equilibrium concentrations of Fe^{3+} and SCN^- were calculated by subtracting the measured concentration of $\text{Fe}(\text{SCN})^{2+}$ from the initial concentrations of Fe^{3+} and SCN^- . K values were determined using the ICE table method. Initial reactant concentrations were based on the known molarities of Fe^{3+} and SCN^- in the reactant solutions and the total volume of the reaction (10 ml). The equilibrium concentration of $\text{Fe}(\text{SCN})^{2+}$ was determined by dividing measured absorbance by the molar absorptivity of $\text{Fe}(\text{SCN})^{2+}$. Because all of the product was formed from the 1:1 reaction of Fe^{3+} and SCN^- , the equilibrium concentration of $\text{Fe}(\text{SCN})^{2+}$ corresponds to the decreases in concentration of the reactants. **Table 6** shows the process for test tube 6.*

The equilibrium constant is calculated from the concentrations in the equilibrium row. For test tube 6,

$$K_6 = \frac{1.58 \times 10^{-4}}{(3.41 \times 10^{-4})^2} = 136$$

The mean K value was 147 ± 11 , illustrating that K is roughly constant over the range of concentrations studied.

Applications

The equilibrium constant provides useful information about the extent to which a reaction will proceed to form products over time. Reactions with a large value of K , much larger than 1, will form products nearly complete given enough time (**Figure 3**). Reactions with a value of K less than 1 will not proceed forward to a significant degree. The equilibrium constant thus serves as a measure of the feasibility of a chemical reaction.

The equilibrium constant also provides useful thermodynamic information about the changes in free energy, enthalpy, and entropy in the course of a chemical reaction. The equilibrium constant is related to the free energy change of reaction:

$$\Delta G = -RT \ln K$$

The free energy change of reaction is in turn related to the enthalpy and entropy changes of reaction:

$$\Delta G = \Delta H - T\Delta S$$

Measurements of the temperature dependence of K can reveal the enthalpy change ΔH and the entropy change ΔS for a reaction. In addition to providing chemists with insight into patterns in molecular behavior, tables of thermodynamic data can be used to identify reactions with

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Comment [A5]: You introduce the concept of ICE tables, but never demonstrated their use. Provide an example on it's implantation.

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Comment [A6]: What can you demonstrate in the lab and provide data/media for?

favorable thermodynamic properties. For example, redox reactions that release large amounts of energy (associated with negative ΔG values) are attractive candidates for batteries (**Figure 4**).

Values of K for acid dissociation reactions (K_a values) are useful for predicting the outcomes of acid-base reactions, which are thermodynamically controlled. Strong acids are associated with large K_a values and weak acids with small K_a values. pH indicators are weak acids with differently colored acidic and basic forms, and the pK_a (the negative base-10 logarithm of K_a) of an indicator represents the pH at which a color change occurs as an acid or base is added to a solution of the indicator.

Similarly, K_a values are used in the preparation of buffer solutions to achieve a target pH value. The pK_a of a weak acid represents the pH at which the acid and its conjugate base are present in the solution in equal concentrations. When equal amounts of a weak acid and its conjugate base are dissolved in a solution, the pH of the solution equals the pK_a of the weak acid.

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Legend

Figure 1: Beer's law curve for iron (III) thiocyanate.

Figure 2: Line graph of Absorbance versus Concentration for $\text{Fe}(\text{SCN})^{2+}$.

Figure 3: The equilibrium constant of this reaction is greater than 1. A significant amount of colored product forms in each case, even though the initial concentrations of reactants differ.

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Table 1: An Initial-Change-Equilibrium (ICE) table that illustrates how initial and equilibrium concentrations are related.

Table 2: Appropriate volumes of $\text{Fe}(\text{NO}_3)_3$, KSCN , and HNO_3 solutions to be placed in tubes 2 – 5.

Table 3: Appropriate volumes of 0.0025 M $\text{Fe}(\text{NO}_3)_3$, 0.0025 M KSCN , and 0.10 M HNO_3 solutions.

Table 4: Absorbance versus Concentration Data for $\text{Fe}(\text{SCN})^{2+}$.

Table 5: Measured absorbance values and calculated K for the reaction of iron (III) with thiocyanate.

Table 6: The ICE table that illustrates the process used for test tube 6.

Comment [A7]: What is the difference between these two?

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Comment [JR8]: Hi Andrew, here's a note from Mike about these figures: "Regarding Figures 1 and 2, Figure 1 is just meant to be an example for the Principles section. Figure 2 is the actual curve based on the data in Table 1. The measured molar absorptivities may throw up some red flags, as they look wildly different...but I know from running this lab in our general chemistry labs that this value can vary widely (it's probably instrument error, as the measured K 's tend to be much more consistent). If the different molar absorptivities look bad, it might be best to remove Figure 1."

We discussed removing Figure 1 and ultimately decided we'd leave this decision up to you. If you want us to remove it, just let us know and it can be easily done. Thanks!

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	[Fe ³⁺] (mol/L)	[SCN ⁻] (mol/L)	[Fe(SCN) ²⁺] (mol/L)
Initial	3.57×10 ⁻⁴	3.57×10 ⁻⁴	0
Change	-1.58×10 ⁻⁵	-1.58×10 ⁻⁵	+1.58×10 ⁻⁵
Equilibrium	3.41×10 ⁻⁴	3.41×10 ⁻⁴	1.58×10 ⁻⁵