EXPERIMENT

12

Determination of a Chemical Formula by Job's Method

INTRODUCTION

Beer's Law, $A = \varepsilon lc$, states that the light absorbed by a chemical species in solution depends directly on the concentration of that species. In this experiment, Beer's Law is used as a means of determining the stoichiometry of a reaction.

When solutions of Fe^{3+} and SCN^-, both colorless ions, are mixed together, a reaction occurs that results in a red solution. This reaction corresponds to the formation of a new substance composed of iron and thiocyanate. An equation for the reaction is

$$m\ Fe^{3+} + n\ SCN^- \rightarrow Fe_m(SCN)_n^{(3m-n)}$$

where m and n are respectively the moles of $Fe^{3+}$and SCN^- that react. If the number of thiocyanate ions that react with each iron ion can be determined, the correct formula of the product and the stoichiometry of the reaction can be deduced. Since only the product is colored, spectrophotometric methods are suggested as a way of determining the amount of product in solution.

Solutions of both reactants of known concentrations can be easily prepared. If the absolute concentration of the product formed by the reaction of these solutions could be measured spectrophotometrically the stoichiometry of the reaction could be determined directly. However, there is no means of determining the absolute value of the concentration of product since the value of εl for the product is unknown. *Relative* amounts of $Fe_m(SCN)_n^{(3m-n)}$ present in solution, however, can be measured. <u>If several solutions of varying concentrations of Fe^{3+} and SCN^- are prepared, the solution exhibiting a maximum absorbance corresponds to the solution having the maximum concentration of product.</u>

Suppose solutions are prepared such that the sum of the concentrations of Fe" and SCN^- in solution is constant. The maximum absorbance readings will be obtained for the solution in which Fe" and SCN - are present in <u>exact stoichiometric ratios.</u> From the relative concentrations of Fe^{3+} and SCN^- at which maximum absorbance is observed the stoichiometry of the reaction can be determined.

To illustrate these principles consider the following examples. ***<u>Be sure you read these before lab and digest and understand them thoroughly.</u>*** Suppose the stoichiometry of the reaction is such that one Fe^{3+} combines with one SCN^- to form product.

$$Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$$

Assume 1 mmole Fe^{3+} (1 millimole = 10^{-3} mole) is mixed with 9 mmoles SCN^- in l0 mL solution. If the reaction goes to completion, l mmole $Fe(SCN)^{2+}$ is formed, and 8 mmoles SCN^- remain in solution. Since only the complex is colored, one relative absorbance unit of $FeSCN^{2+}$ is observed.Then, if 2 mmoles Fe^{3+} and 8 mmoles SCN^- are mixed, (remember the total number of moles must be kept constant), 2 mmoles of product are formed and 6 mmoles of SCN^- remain in solution. This results in a relative absorbance of two units corresponding to twice as much $FeSCN^{2+}$. The table on the following page considers these and other mixtures of Fe^{3+} and SCN^-.

At 6 mmoles of Fe^{3+} and 4 mmoles of SCN^-, the SCN^- becomes the limiting reagent. Only 4 mmoles of product are formed and 2 mmoles of Fe^{3+} remain in solution. As predicted, maximum absorbance is observed where the Fe^{3+} and SCN^- are present in the correct stoichiometric ratios.

mmoles Fe^{3+} in 10mL Soln.	mmoles SCN^- in l0 mL Soln.	mmoles $FeSCN^{2+}$ Formed	Relative A Observed
1	9	1	1
2	8	2	2
3	7	3	3
4	6	4	4
5	5	5	5
6	4	4	4
7	3	3	3
8	2	2	2
9	l	1	1

Now suppose the stoichiometric ratio of Fe^{3+} to SCN^- were 1 to 2. This corresponds to the reaction

$$1\ Fe^{3+} + 2\ SCN^- \rightarrow Fe(SCN)_2^+$$

If 1 mmole Fe^{3+} and 9 mmoles SCN^- are mixed in l0 mL solution, 1 mmole $Fe(SCN)_2^+$ forms and 7 mmoles SCN^- remain. One mmole of product corresponds to one relative absorbance unit. The following table considers other mixtures. Maximum absorbance is observed between 3 and 4 mmoles Fe^{3+}added.

mmoles Fe^{3+} in 10 mL Soln.	mmoles SCN^- in 10 mL Soln.	mmoles $Fe(SCN)_2^+$ Formed	Relative A Observed
1	9	1	1
2	8	2	2
3	7	3	3
4	6	3	3
5	5	21/2	21/2
6	4	2	2
7	4	1 1/2	1 1/2
8	2	1	1
9	1	1/2	1/2

If you understand this chart, then you will be able to complete this lab. If you do not understand this chart, you *must* study it until you understand it.

A convenient way of expressing the amount of Fe^{3+} added to the solution in relation to the total number of moles of Fe^{3+} and SCN^- added is the mole fraction.

$$\text{Mole fraction } Fe^{3+} = X_{Fe3+} = \frac{\text{moles } Fe^{3+}}{\text{moles } Fe^{3+} \;\; \text{moles SCN}}$$

In the example illustrating the formation of $Fe(SCN)_2^+$ a plot of mole fraction Fe^{3+} versus A would show the maximum absorbance at $X_{Fe}{}^{3+} = 0.33$. The composition of the complex is thus 33% Fe^{3+} and 67% SCN^- which corresponds to $Fe(SCN)_2^+$ as postulated. A plot of mole fraction versus absorbance is called a Job's Plot.

In this experiment the stoichiometry of the reaction of Fe^{3+} and SCN^- is determined by preparing a Job's Plot.

PROCEDURE

1. Fill two clean burets obtained from the stockroom, with the two standard solutions. (5×10^{-3} M Fe^{3+} and 5×10^{-1}M SCN^-)
2. Set the wavelength on the Spectronic 20 to 447 nm. Blank the instrument at zero absorbance using distilled water as the blank solution. Check the standardization of the instrument before each measurement.
3. Measure the absorbances of pure iron (III) and thiocyanate solutions and record these absorbance values.
4. Mix 0.5mL of iron (III) and 9.5mL of thiocyanate in a clean, dry beaker and stir them together. Pour some of this solution into the spectrophotometer tube. Measure and record its absorbance.
5. Repeat this procedure for 1.0 mL of iron (III) and 9.0 mL of thiocyanate, then 1.5mL of iron (III) and 8.5mL of thiocyanate and so on, until the absorbance of a solution of 9.5mL of iron (III) and 0.5mL of thiocyanate solution has been measured. Record the data on the data sheet.
6. Construct a Job's Plot from the data on the graph paper provided. Make sure the best straight lines are drawn using the experimentally determined values of absorbance. The lines should fit the data as closely as possible but need not pass through each experimental point.

DETERMINATION OF A CHEMICAL FORMULA BY JOB'S METHOD

Name________________________

Section________________________

DATA

mL Fe^{3+}	**mL SCN^{-}**	**Mole Fraction Fe^{3+}**	A
0.0	10.0		
0.5	9.5		
1.0	9.0		
1.5	8.5		
2.0	8.0		
2.5	7.5		
3.0	7.0		
3.5	6.5		
4.0	6.0		
4.5	5.5		
5.0	5.0		
5.5	4.5		
6.0	4.0		
6.5	3.5		
7.0	3.0		
7.5	2.5		
8.0	2.0		
8.5	1.5		
9.0	1.0		
9.5	0.5		
10.0	0.0		

RESULTS

Write the balanced chemical equation for the reaction as deduced from your data, including the correct formula for the complex formed.

QUESTION

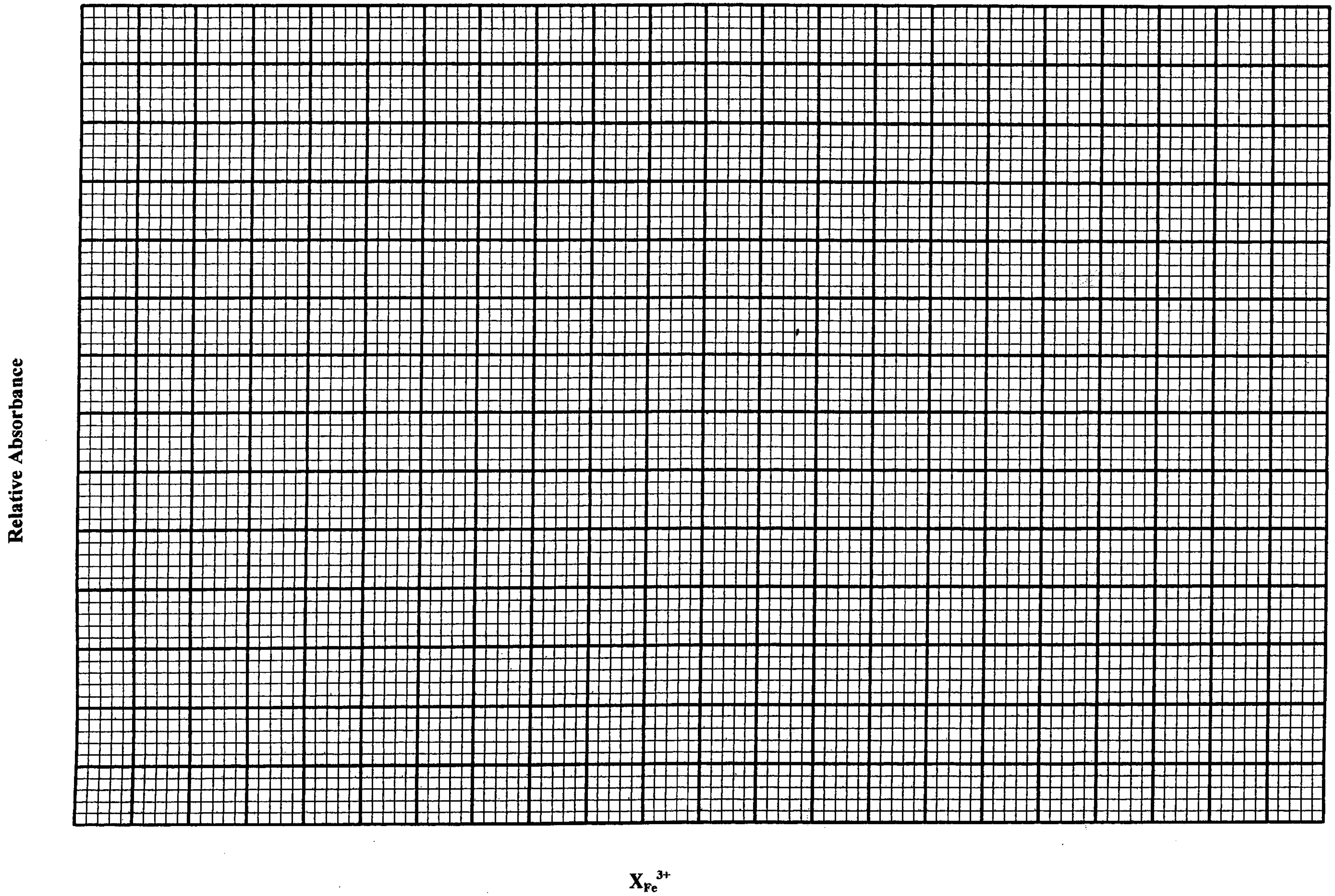
Assume or pretend that the reaction of Fe' with SCN^- obeyed the following stoichiometry. This may or may not be the same as the stoichiometry that you observe experimentally.

$$1\ Fe^{3+} + 3\ SCN^- \rightarrow Fe(SCN)_3$$

Complete the following table and construct the appropriate Job's Plot for this reaction.

0.1 M Fe^{3+} (ML)	**0.1M SCN^- (ML)**	**mmoles Fe^{3+}**	**mmoles SCN^-**	**mmoles $Fe(SCN)_3$ Formed**	$X_{Fe^{3+}}$	**Relative A Observed**
1	9					
2	8					
3	7					
4	6					
5	5					
6	4					
7	3					
8	2					
9	1					

Title:



Relative Absorbance

Title:

$X_{Fe^{3+}}$