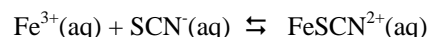


A unanimous chorus of praise
is not an assurance of
survival.--André Gide

Colorimetric Determination of K_c

In order to determine the equilibrium constant for a given reaction system, you must know the concentrations of all species at equilibrium. Different experimental methods have been developed for such investigations, each usually tailored to a particular characteristic of the reaction type. In the case of this experiment that characteristic is color intensity.

The system in this experiment may be represented by this reaction:



In acid solution the first two ions are essentially colorless while the product has a color ranging from pale orange to deep red, depending on concentration. This colored ion may be used to determine the concentration of product with a colorimeter or spectrophotometer. But first known concentrations of the colored ion must be prepared and used to establish a relationship between the measured absorbance and concentration (a calibration curve). Various unknown solutions can then be measured and their concentrations determined from the established relationship.

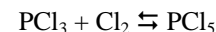
The student should recognize, however, that preparing a solution of the thiocyanatoiron(III) ion (FeSCN^{2+}) by itself is not possible. The ion spontaneously decomposes into the iron(III) and thiocyanate ions (SCN^{-}) in proportions described by the equilibrium constant. How then does one prepare a standard concentration of the FeSCN^{2+} ion? The answer lies in LeChâtelier's Principle. If a mixture of reactants is prepared such that one ion is in great excess compared to the other, then the reaction should be forced far to the right and most of the less concentrated ion should be consumed in the reaction and converted into product. Such a mixture can be used to establish a "two-point" calibration (along with the solvent, water) assuming that the system follows Beer's Law. In this experiment you will be provided with a mixture in which the initial ratio of Fe^{3+} to SCN^{-} is 900:1. It can be assumed that in this mixture all of the SCN^{-} reacts to produce FeSCN^{2+} .

To determine the amount of colored product present in equilibrium mixtures *without* large excesses of either reactant, you will prepare additional solutions and measure their absorbances.

Adapted from: Chemical Equilibrium, *Chemistry, an Experimental Science Lab Manual*, CHEM Study, 1960

Once the equilibrium concentration of the colored product has been determined for each solution (by applying Beer's Law), the equilibrium concentrations of the reactants can be determined by subtraction from the initial amounts. Substituting these values into the correct expression for the equilibrium constant will give the value for K_c at the room temperature. The example below illustrates this approach.

PCl_3 and Cl_2 react to form PCl_5 :



If the initial concentration of PCl_3 in a container is 0.298 M and the initial concentration of Cl_2 is 2.00×10^{-3} M, and the concentration of the PCl_5 formed is 1.79×10^{-3} M, what is the value of K_c for this reaction?

	PCl_3	+	Cl_2	\rightleftharpoons	PCl_5
START	0.298		2.00×10^{-3}		0
EQUIL	$0.298 - x$		$2.00 \times 10^{-3} - x$		x

Since the ratios in this reaction are all unity, the set-up is fairly simple as shown above. Moreover, the value of "x" is known. It is 1.79×10^{-3} M. Thus the EQUIL line simplifies to:

EQUIL	0.296		2.1×10^{-4}		1.79×10^{-3}
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and therefore:

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(1.79 \times 10^{-3})}{(0.296)(2.1 \times 10^{-4})} = 28.8$$

The "position" of equilibrium (i.e., the distribution of products and reactants) at any temperature is related to the balance between the tendency toward minimum energy and maximum energy dispersal. It should not be surprising that there is therefore a mathematical relationship between the equilibrium constant and the free energy change (a measure of spontaneity or the extent to which a reaction proceeds in the forward direction). That relationship may be expressed as:

$$\Delta G^\circ = -RT \ln K_c$$

where **R** is 8.31 J/mol-K, and **T** is the temperature in Kelvin. The free energy calculated from this expression therefore has units of J/mol.

Once you know the equilibrium constant you can determine the free energy using this expression. But just how do the enthalpy change (ΔH) and the entropy change (ΔS) contribute to ΔG in this case?

It is possible to determine ΔH° for many reactions by calorimetry, but this particular system has a fairly small value which is difficult to measure directly. However, you can discover the effect that temperature has on the value of K_c and this will allow you to at least decide on the sign of the enthalpy change (i.e., whether the reaction is exothermic or endothermic) based on LeChâtelier's Principle.

Information about ΔS can be obtained by considering the nature of the reaction and the general relationship

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

Preparing to experiment

You will be provided with the following materials:

1. three 1 mL calibrated beral pipets
2. 0.00200 M $\text{Fe}(\text{NO}_3)_3$ solution in 1 M HNO_3
3. 0.00200 M KSCN solution
4. a colorimeter probe (BLUE light)
5. 2 small test tubes
6. cuvette
7. standard thermometer
8. reaction mixture standard (900:1 ratio)
9. ice
10. very hot water

Measure the % T of the provided reaction mixture in which $\text{Fe}^{3+}:\text{SCN}^- = 900:1$.

Design an experiment around the mixture table on the facing page in order to determine the concentration of FeSCN^{2+} at equilibrium in each mixture.

Design an experiment to determine the sign of the enthalpy change (ΔH°), and entropy change (ΔS°) by finding the equilibrium constant for the system at two additional temperatures ($0^\circ\text{C} < T < 80^\circ\text{C}$) using mixture #4.

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Solution #	0.00200 M $\text{Fe}(\text{NO}_3)_3$ (in 1 M HNO_3)	0.00200 M KSCN	H_2O
1	1.25 mL	0.50 mL	0.75 mL
2	1.25 mL	0.75 mL	0.50 mL
3	1.25 mL	1.00 mL	0.25 mL
4	2.50 mL	2.50 mL	0.00 mL

These solutions (except #4) can be prepared directly in the cuvette but be sure to mix thoroughly (invert several times after capping). Mixture 4 can be prepared in a small beaker, mixed and then divided for the various temperatures.

AS PART OF YOUR PRE-LAB, PREPARE A TABLE OF THE SOLUTIONS IN WHICH YOU HAVE CALCULATED THE INITIAL CONCENTRATIONS OF Fe^{3+} and SCN^- IN EACH MIXTURE. RECALL THAT MIXING SOLUTIONS REDUCES THE CONCENTRATIONS--AND DON'T FORGET THAT THE WATER CONTRIBUTES TO THE TOTAL VOLUME [*hint*: the dilution formula, $V_1M_1 = V_2M_2$ would be useful here]. Leave a column in this table for the % transmittances of the solutions that you will measure in the lab.

The Chemicals

Iron(III) nitrate in hydrated form consists of pale violet to gray deliquescent crystals. Freely soluble in water, it decomposes below 100°C . It is used as a mordant in dyeing, in tanning and as a corrosion inhibitor.

Potassium thiocyanate is colorless and deliquescent. When dissolved in its own weight of water, the temperature drops 30°C . It is used in the manufacture of artificial mustard oil, in printing and dyeing, in photography and in analytical chemistry.

[Analysis section follows on the next page]

Analysis

1. The standard mixture you were given was prepared by mixing 18.0 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3$ with 2.0 mL of 0.00200 M KSCN. Assuming that all of the SCN^- reacted in this mixture, what is the final concentration of FeSCN^{2+} in the mixture?
2. Use the value from #1 and the absorbance of the solution (recall $A = 2 - \log \%T$) to determine the $[\text{FeSCN}^{2+}]$ in the other solutions based on their absorbances (including the ones above and below room temperature). [*hint*: Beer's Law says that absorbance is directly proportional to concentration]
3. Determine, by subtraction (see example in the introduction), the *equilibrium* concentrations of Fe^{3+} and SCN^- in each mixture.
4. Use your results from #2 and #3 to calculate the value of K_c for each mixture. Average the *room temperature* results, rejecting those values which seem to deviate a large amount (justify your rejections!!)
5. Use the average K_c value *at room temperature* to calculate an approximate value for ΔG° .
6. Compare the average value of K_c at room temperature with those determined above and below room temperature. Is the enthalpy change, ΔH° , for this reaction positive or negative? Explain.
7. Based on your answer to #6, what is the likely sign of ΔS° for the forward reaction? (remember, the extent to which a reaction proceeds in the forward direction as written is related to the relative spontaneity). Does this sign make logical sense in light of the nature of the reaction? (look back at the balanced equation)