Experiment Z6
PHOTOMETRIC STUDY OF EQULIBRIUM

Objectives

To determine the equilibrium constant for a chemical reaction from measurements of the absorption of light by a solution.

Introduction

The equilibrium to be studied is the formation of the monothiocyanatoiron (III) ion, $FeSCN^{2}+$, from iron (III) (ferric) and thiocyanate as follows:

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

(colourless) (deep red)

This is the predominant reaction when an acidic solution of ferric nitrate is added to a dilute ($<10^{-3}$ mol dm^{-3}) solution of potassium thiocyanate. At higher concentrations of thiocyanate or higher pH, significant quantities of other species (higher complexes or $FeOH^{2+}$) may be formed.

Let cf and cs be the total molarities of iron and thiocyanate, respectively, and let c be the equilibrium concentration of the $FeSCN^{2+}$ ion, *i.e.*

$$c = [FeSCN^{2+}]$$

$$c_f = [Fe^{3+}] + [FeSCN^{2+}]$$

$$c_s = [SCN^{-}] + [FeSCN^{2+}]$$

Where [ ] denotes equilibrium concentration.

Thus $[Fe^{3+}] = c_f - c$ and $[SCN\text{-}] = c_s - c$.

The equilibrium constant:

$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}]\,[SCN\text{-}]} = \frac{c}{(c_f - c) \cdot (c_s - c)} \qquad (1)$$

This rearranges to:

$$c_f c_s - c(c_f + c_s + K_c^{-1}) + c^2 = 0 \qquad (2)$$

By definition, $c<c_f$ and $c<c_s$. Hence the numerically smallest term in this equation is c^2, and it is a good approximation to neglect it at sufficiently low concentrations. With this approximation, equation (2) may be rearranged to give:

$$c_f c_s/c = c_f + c_s + K_c^{-1} \qquad (3)$$

In the present experiment, c_f and c_s are equal to the known initial concentrations of iron and thiocyanate, respectively. The $FeSCN^{2+}$ ion is coloured and thus c is determined by measuring the absorbance of the solution in the visible region. The absorbance, A, of a solution is defined as:

$$A = \log (I_o/I)$$

Where I_o and I are light intensities respectively incident on and transmitted by the solution.

According to the Beer-Lambert law, at a particular wave length A is related to the concentrations, c, of the absorbing species by:

$$A = \varepsilon\, c\, l \qquad (4)$$

where:

ε (= α/2.303) is the molar absorption coefficient (extinction coefficient)
l the optical path-length (*i.e.* the thickness of the cell).

Substituting $c = \dfrac{A}{\varepsilon l}$ into the (3) we obtain:

$$\frac{c_f c_s}{A} = \frac{(c_f - c_s)}{\varepsilon\, l} + \frac{1}{K_c\, \varepsilon\, l} \qquad (5)$$

Hence a plot of $c_f c_s/A$ against $(c_f + c_s)$ is linear with a slope of $1/\varepsilon l$ and the y-intercept of $1/K_c\varepsilon l$ Thus K_c = slope/intercept.

Procedure
You are supplied with 0.002 mol dm^{-3} potassium thiocyanate solution, 2.0 mol dm^{-3} nitric acid and 0.1 mol dm^{-3} ferric acid (which contains 0.5 mol dm^{-3} nitric acid).

Prepare a dilute thiocyanate solution by adding 20 ml of the stock potassium thiocyanate solution and 25 ml of the 2.0 mol dm^{-3} nitric to a 100 ml volumetric flask and up to the mark with distilled water. Mix the solution well and transfer carefully to a 250 ml beaker (it will be assumed that the volumetric flask delivers 100 ml).

Using a 1 ml pipette, add successive portions of the stock ferric nitrate solution. After each addition, the solution should be stirred thoroughly and a portion then transferred to the 1 cm path-length optical cell supplied. Measure the absorbance (optical density) with the Cecil 2343 or 272 spectrophotometer at the wave length of the absorption maximum (450 nm) and then return the sample to the beaker before adding the next portion of the ferric nitrate solution. At least six points are to be obtained at ambient temperature (report the temperature with your results).

Treatment of results

Tabulate the values of c_f, c_s (remember to allow for the changing volume of the solution when calculating these concentrations), A, $c_f c_s/A$ and $(c_f + c_s)$. Plot $c_f c_s/A$ against $(c_f + c_s)$ and hence determine K_c as described above. Also report a value for the molar absorption coefficient (ε) of $FeSCN^{2+}$ at 450 nm. Estimate the error limits for your values.

Background information

P W Atkins, Physical Chemistry (4^{th} edition), Section 17.1.