06
CHEMICAL EQUILIBRIUM

EFFECT OF INITIAL CONCENTRATIONS: FE(III)-THIOCYANATE

CHEMISTRY 136L // FALL 2019

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GIBBS FREE ENERGY

Chemical Equilibrium

A spontaneous process is one that takes place without (continuous) input of energy.

ΔG – change in Gibbs free energy

The maximum amount of energy (in the form of work) that can be extracted from a reaction/system.

REACTION OF INTEREST

The Fe(III)-thiocyanate equilibrium

Our focus today is the following equilibrium:

$$Fe^{3+}\,(aq) + x\,SCN^{-}\,(aq) \rightleftharpoons [Fe(SCN)_x]^{3-x}\,(aq)$$

where x is a small integer.

Main Purposes

Stoichiometry of Fe(III)-thiocyanate complex

Molar absorptivity (ε) of complex

Constancy of the value of K (independent of initial concentrations)

PART 1: STOICHIOMETRY OF COMPLEX

General idea

Use Job's method to determine the value of x

$$Fe^{3+}\,(aq) + x\,SCN^{-}\,(aq) \rightleftharpoons [Fe(SCN)_x]^{3-x}\,(aq)$$

If the product is a 1:1 complex (x = 1), maximum amount of product is formed in solution with mole fraction of SCN^- = 1/2.

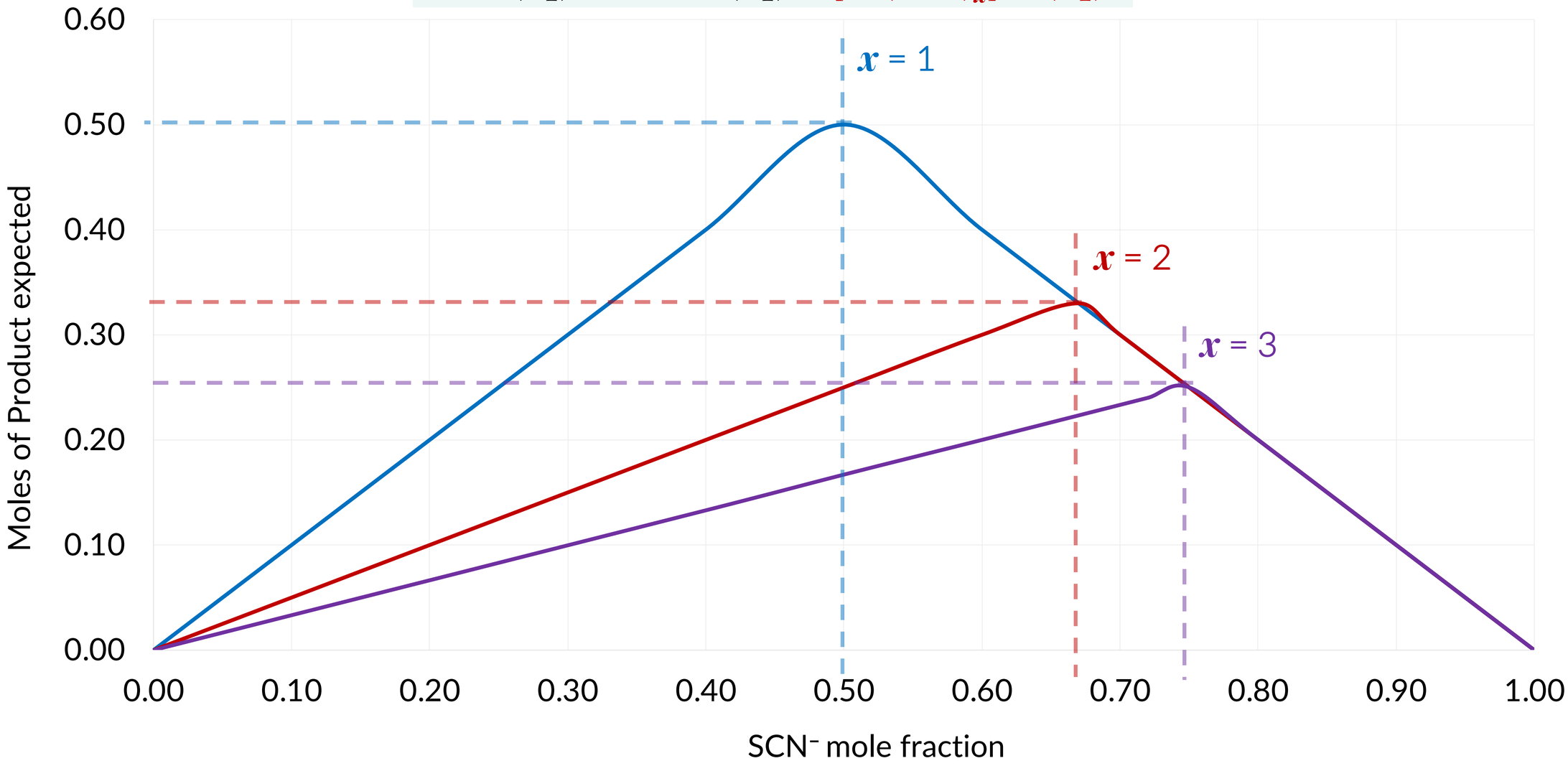
If the product is a 1:2 complex (x = 2), maximum amount of product is formed in solution with mole fraction of SCN^- = 2/3.

If the product is a 1:3 complex (x = 3), maximum amount of product is formed in solution with mole fraction of SCN^- = 3/4.

This prediction always holds true.

EXPECTED RESULTS

$$Fe^{3+}\,(aq) + x\,SCN^{-}\,(aq) \rightleftharpoons [Fe(SCN)_x]^{3-x}\,(aq)$$



PART 2: DETERMINATION OF ε

Molar absorptivity

Use spectrophotometry to determine $[\{Fe(SCN)_x\}^{3-x}]$

Beer-Lambert Law: $A = \varepsilon cl$

General Procedure

Prepare three calibrating solutions with known $[\{Fe(SCN)_x\}^{3-x}]$

↓

Measure their absorbances at a chosen wavelength

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Plot absorbance vs. $[\{Fe(SCN)_x\}^{3-x}]$

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Determine ε from the slope

PART 3: CONSTANCY OF K

Independent of initial concentrations

$$Fe^{3+}\,(aq) + x\,SCN^{-}\,(aq) \rightleftharpoons [Fe(SCN)_x]^{3-x}\,(aq)$$

What is the equilibrium constant (K) expression?

How do we determine the three concentrations needed?

Determine $[Fe(SCN)^{2+}]_{eq}$ experimentally using Beer-Lambert Law

Apply atom conservation (material balance) to calculate:

$[Fe^{3+}]_{eq}$ and $[SCN^{-}]_{eq}$

$$[Fe^{3+}]_{eq} = [Fe^{3+}]_o - [Fe^{3+}]_{consumed} = [Fe^{3+}]_o - [Fe(SCN)^{2+}]_{eq}$$

Notes

Make solutions first, then take spectra:

Part 1:	nine solutions	label A–I	(E is max)
Part 2:	three solutions	label 1–3	
Part 3:	five solutions	label J–M	

Part 2: Beer-Lambert plot (accuracy grade, $R^2 > 0.98$)

- Pipet and syringe with care
- Label everything
- Avoid contamination (rest equipment on Kimwipes)