**CHEMISTRY 203**

# CHEMICAL EQUILIBRIUM
## Determination of an  Equilibrium Constant

# I. Purpose:

1. To review the concepts and principles of chemical equilibrium.
2. To study the effects of temperature and concentration changes on the position of equilibrium of a reversible reaction.
3. To learn the principles  and use of a spectrophotometer.
4. To apply the principles of chemical analysis by spectrophotometric means.
5. To determine, spectrophotometrically, the equilibrium constant Kc for the reaction between iron (III) ion and thiocyanate ion ($SCN^-$) at a given  temperature.

# II. Theory:
## A. Spectrophotometry

- A *spectrophotometric method* of analysis involves the interaction of *electromagnetic radiation* (EM) with matter.
- The most common regions of EM spectrum used for analysis are the ultraviolet UV, **visible**, and the infrared IR regions.
- When a substance is colored it absorbs light in the visible region.
- **Visible region** has a wavelength ranging from **400-700 nm**.



THE ELECTROMAGNETIC SPECTRUM
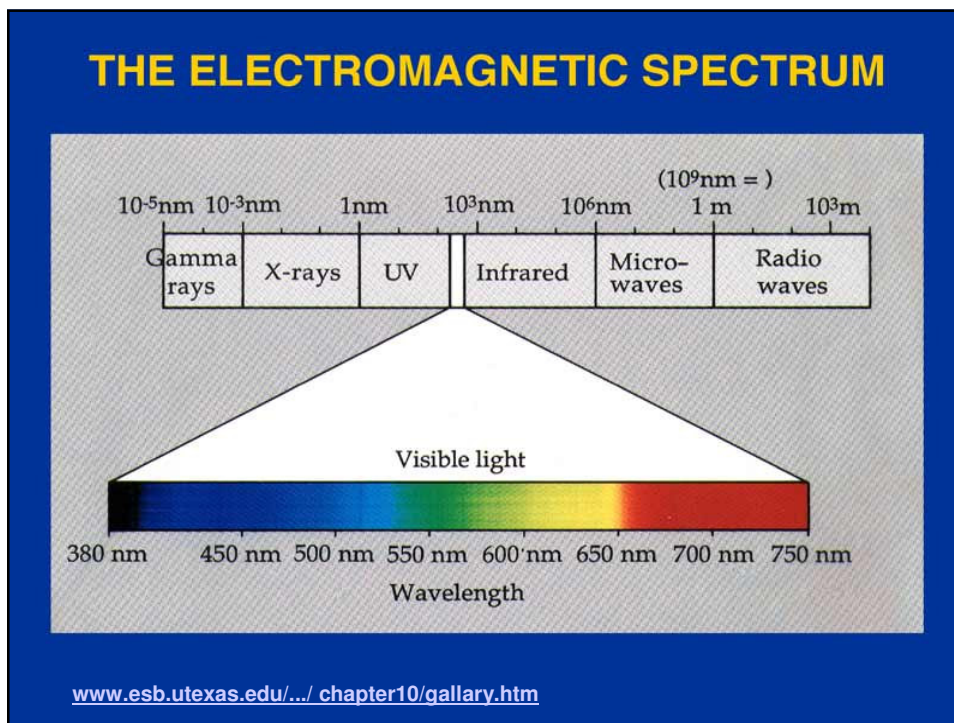
## a. What do we see?

- When continuous electromagnetic radiation (light) passes through a substance, a portion of the light may be absorbed. The remaining light exits the sample and when passed through a prism will yield a spectrum with gaps in it, this is called the *absorption spectrum*.
- The color the eye sees is due to the wavelengths of light the sample did not absorb, that is we see the transmitted color.

## b. Colors and wavelengths in the visible region of the electromagnetic spectrum:

| Color absorbed | Wavelength (nm) | Color transmitted |
|---|---|---|
| Red | 750-610 | Green-blue |
| Orange | 610-595 | Blue-green |
| Yellow | 595-580 | Violet |
| Green | 580-500 | Red-violet |
| Blue | 500-435 | Orange yellow |
| Violet | 435-380 | yellow |

**c. Relationship between energy, frequency and wavelength:**

$$E = h\nu \qquad\qquad \nu = c / \lambda$$

**h** = Planck's constant = 6.626 x $10^{-34}$ Js
**C** = speed of light = 3.00 x $10^{8}$ m $s^{-1}$
**λ** = wavelength in m,    1 nm = $10^{-9}$ m
**ν** = frequency $s^{-1}$ or hz

**E decreases ↓ as λ increases ↑**

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d. Absorption Spectrum of a Chemical Substance and Spectrophotometer

**Absorption spectrum:** A plot of absorbance **A** versus wavelength **λ**

- The wavelength (**λ $_{max}$**) at which the **maximum** absorption of the (EM) radiation by the absorbing substance occurs is **determined** and **set** on the **spectrophotometer**.
- *Spectrophotometer*: A laboratory instrument that measures the amount of light transmitted through a sample.
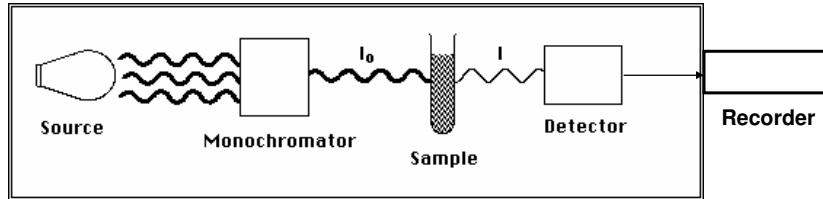
# e. Spectrophotometer Components



Figure I

- **Source of light**, stable source of radiant energy
- **Wavelength selector** or **monochromator**, that isolates a limited region of the spectrum for measurement
- **Sample container**.
- **Radiation detector**, which converts radiant energy to a measurable electrical signal.
- **Recorder**, signal processing and read out unit.

# f. Transmittance and Absorbance

The **transmitted** light $I_t < I_o$ **incident** light

**Transmittance**:   $T = \dfrac{I_t}{I_o} < 1$

$$\% \, T = \frac{I_t}{I_o} \times 100$$

**Absorbance**:   $A = - \log T$

$$A = - \log \frac{\%T}{100}$$

# g. Beer-Lambert's Law:

- The wavelength with which the compound interacts with light is an experimental parameter.
- Several factors control the amount EM radiation (light energy) that a sample absorbs.

   1. Concentration of the absorbing substance.

   2. Thickness of the sample containing the absorbing substance (determined by the width of the cuvet).

   3. Probability of light absorption by the absorbing substance (called the **molar absorptivity coefficient** or the **extinction coefficient**).

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- A spectrophotometer measures the amount of light absorbed by a colored substance. **Beer-Lambert's Law** relates quantitatively the extent of absorption to the concentration of the absorbing species according to the following relationship:

$$A = \varepsilon \cdot b \cdot c$$

   A: optical activity or absorbance at specific wavelength $\lambda_{max}$

   $\varepsilon$: extinction coefficient or molar absorptivity $(M^{-1}cm^{-1})$, f $(\lambda$, temp. solvent)

   b: width of cuvet (cell), light path length, or depth(cm)

   c: Molar concentration (M)

 Beer-Lambert's law applies best near maximum absorption regions, and for dilute solutions.

A plot of absorbance versus concentration data is linear; it provides a **calibration curve**. The calculated slope and the absorbance data of an absorbing species can be used to determine the molar concentration of this species in an unknown solution.    slope = $\varepsilon \cdot b \ (M^{-1})$
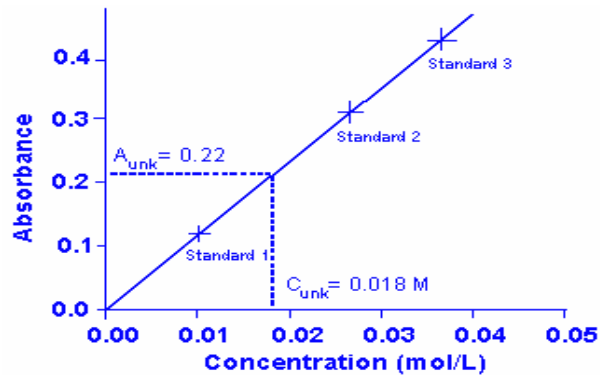
# II. Theory (continued):
## B. Chemical Equilibrium

- Few chemical reactions proceed in only one direction. Most are *reversible*.
- A reversible chemical reaction leads to an equilibrium state which is characterized by constant composition.
- Although the reaction has not stopped at equilibrium, the *rate of disappearance of the reactants is equal to the rate of formation of reactants from the products*.
- Chemical equilibrium is a *dynamic* process.
- Chemical equilibrium represents a balance between forward and reverse reactions.
- Thus, the concentrations of reactants and products remain constant.

•*Homogeneous* equilibrium applies to reactions in which all reacting species are in the *same phase.*

•In general, for a reversible reaction at a specific temperature,
$$aA + bB \leftrightarrows cC + dD$$

•The molar concentrations (mol/L) of reactants and products at equilibrium are related by the equilibrium constant expression Kc:

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

Note: The equilibrium mixtures can vary, but *the value for K at a specific temperature is constant.*

# Le Chatelier's Principle

**Le Chatelier's principle** summarizes the effect of stressing a chemical system at equilibrium as follows:

When a *stress* is applied to a system at equilibrium the system will *shift* in such a direction to *relieve* the stress and establish a *new* state of equilibrium.

Factors that affect chemical equilibrium:
➢ Change in concentration
➢ Change in temperature
➢ Change in volume and pressure

## Formation of FeSCN $^{2+}$ complex ion:

$Fe^{3+}_{(aq)}$  +  $SCN^-_{(aq)}$  ⇄  $FeSCN^{2+}_{(aq)}$
*(pale yellow)*  *(colorless)*  *(Deep red)*
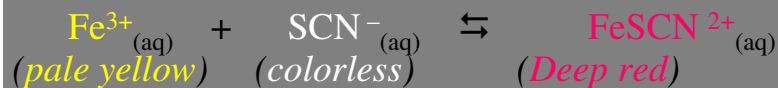
The equilibrium constant is defined as:

$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

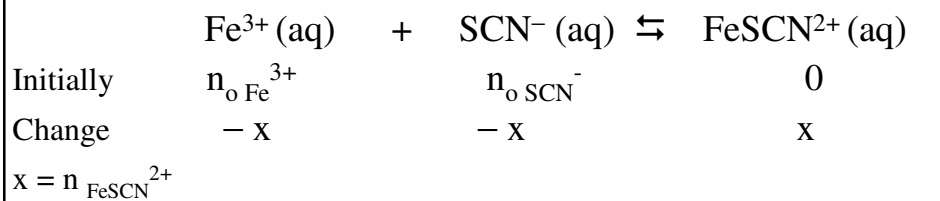$FeSCN^{2+}$ complex ion has a deep blood red color and absorbs light in the visible region at $\lambda_{max}$ = 447 nm

In this experiment the concentration of $FeSCN^{2+}$ will be determined spectrophotometrically, using Beer-Lambert's law.

$$A = \varepsilon \, b \, c$$

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- **Part One.** A set of standard solutions will be prepared, their absorbance measured, and the absorbance for each solution is plotted vs. the molar concentrations of $FeSCN^{2+}$ to establish the calibration curve.
- In preparing the standard solution, the $Fe^{3+}$ concentration will far exceed the $SCN^-$ concentration.
- This huge excess of $Fe^{3+}$ pushes the equilibrium far to the right consuming all the $SCN^-$ placed in the system .
- As a result, the $FeSCN^{2+}$ concentration at equilibrium approximates the original $SCN^-$ concentration.
- We assume that the position of the equilibrium is driven so far to the right that all the $SCN^-$ is complexed forming $FeSCN^{2+.}$

- **Part Two.** The chemical system is prepared by mixing known molar concentrations of $Fe^{3+}$ and $SCN^-$, so by knowing the initial concentrations and measuring the equilibrium concentration of $FeSCN^{2+}$ spectrophotometrically, the equilibrium concentrations of $Fe^{3+}$ and $SCN^-$ are calculated.

# III. Calculations:

$$Fe^{3+}(aq) \quad + \quad SCN^-(aq) \leftrightarrows \quad FeSCN^{2+}(aq)$$

| | $Fe^{3+}(aq)$ | $SCN^-(aq)$ | $FeSCN^{2+}(aq)$ |
|---|---|---|---|
| Initially | $n_{o\,Fe}^{3+}$ | $n_{o\,SCN}^-$ | $0$ |
| Change | $-x$ | $-x$ | $x$ |

$x = n_{FeSCN}^{2+}$

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At equil. $(n_{o\,Fe}^{3+} - n_{FeSCN}^{2+}) \quad (n_{o\,SCN}^- - n_{FeSCN}^{2+}) \quad n_{FeSCN}^{2+}$

Where: $n_{o\,Fe}^{3+} = (M_{o\,Fe}^{3+})(V_{o\,Fe}^{3+})$

$n_{o\,SCN}^- = (M_{o\,SCN}^-)(V_{o\,SCN}^-)$

$n_{FeSCN}^{2+} = x = [FeSCN^{2+}]_{eq} V_{tot} = (A/\epsilon b) V_{tot}$

A is the measured absorbance for that particular solution.

$\varepsilon b$ = slope of calibration curve

$$n_{eq\ Fe}{}^{3+} = n_{o\ Fe}{}^{3+} - n_{FeSCN}{}^{2+}$$

$$n_{eq\ SCN}{}^{-} = n_{o\ SCN}{}^{-} - n_{FeSCN}{}^{2+}$$

$$[\ Fe^{3+}]_{eq} = n_{eq\ Fe}{}^{3+} / V_{tot}$$

$$[SCN^{-}]_{eq} = n_{eq\ SCN}{}^{-} / V_{tot}$$

$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$$