2F52: Instrumental Analytical Chemistry

Important Formula Sheet

Topic 1: Principles

Error in Sampling

$$\sigma_{total} = \sqrt{\sigma_{sampling}^2 + \sigma_{method}^2}$$

Single Standard (External)

$$Concentation_{Unknown} = \frac{Response_{Unknown}}{Response_{Known}} x\ Concentration_{Known}$$

Internal Standard

$$\frac{concentration\ ratio\ \left(\frac{X}{S}\right) in\ unknown}{concentration\ ratio\ in\ standard\ mixture} = \frac{signal\ ratio\ \left(\frac{X}{S}\right) in\ unknown}{signal\ ratio\ in\ standard\ solution}$$

Shot Noise

$$I_{shot}(rms) = \sqrt{2eI\Delta f}$$

Thermal Noise

$$V_{thermal}(rms) = \sqrt{4kTR\Delta f}$$

Flicker Noise

$$V_{flicker}(rms) = \sqrt{\frac{KI^2}{f}}$$

Noise Reduction

$$\frac{\left(\frac{S}{N}\right)_{T1}}{\left(\frac{S}{N}\right)_{T2}} = \sqrt{\frac{T2}{T1}}$$

Signal to Noise Ratio

$$\frac{S}{N} = \frac{average\ signal\ amplitude}{average\ noise\ amplitude}$$

When noise has a sign

$$\frac{S}{N} = \frac{average\ signal\ amplitude}{root\ mean\ square\ (rms)\ noise\ amplitude}$$

Topic 2: Absorption & Fluorescence

Beer-Lambert Law

$$A = \ log_{10}\left(\frac{I_0}{I}\right) = \varepsilon cl$$

Linear Reciprocal Dispersion

$$D^{-1} = \frac{d\lambda}{dx}$$

Dispersion

$$D = f\left(\frac{d\theta}{d\lambda}\right)$$

Resolution

$$R = \ \frac{\bar{\lambda}}{d\lambda}$$

$$R \propto w^{-1}\left(\frac{d\theta}{d\lambda}\right)$$

F/number

$$f/number = \frac{f_c}{d_c}$$

Fluorescence

$$I_f = \Phi_f I_0 \ x \ 2.303\varepsilon cl$$

Fluorescence Lifetimes

$$I_t = I_0 e^{-\left(\frac{t}{\tau_f}\right)}$$

Topic 3: Electroanalytical Chemistry

Nernst Equation

$$E_{ISE} = Cell_{constant} + \frac{2.303RT}{jF}\log[X]_{sample}$$

$$E_{ISE} = Cell_{constant} + \frac{0.059}{j}\log[X]_{sample}$$ at 25'C

Amperometrics

$$E = E^0 + \frac{RT}{nF} ln\left(\frac{[O]}{[R]}\right)$$

$$[R] = \frac{100}{\left(1 + e^{\left(\frac{nF}{RT}(E-E^0)\right)}\right)}$$

Step Voltammetry

$$concentration\ gradient = \frac{C^{bulk} - C^{at\ electrode\ surface}}{distance}$$

Cottrell Equation

$$|i(t)| = \frac{nFAC_O^{bulk}D_O^{1/2}}{\pi^{1/2}t^{1/2}}$$

$$|i| = nFAk_{het}(E)C_{analyte}^{at\ electrode\ surface}$$

Cyclic Voltammetry

Reversibility

$$\frac{i_p^a}{i_p^c} = 1$$

Reduction Potential

$$E^0 = \frac{E_p^a + E_p^c}{2}$$

Electron Stochiometry

$$n = \frac{0.06\ V}{E_p^a - E_p^c}\ at\ 25'C$$

Diffusion Coefficients

$$i_p^c = -(2.69x10^5)n^{3/2}AD_0^{1/2}v^{1/2}C_O^{bulk}$$

Topic 4: Chromatography

Plate Theory

Partition Coefficient (K)

$$K = \frac{[solute]_{stationary\,phase}}{[solute]_{mobile\,phase}}$$

Retention factor (k')

$$k' = \frac{t_r - t_0}{t_0}$$

$$k' = \frac{KV_s}{V_m}$$

Separation Factor (α)

$$\alpha = \frac{K_b}{K_a} = \frac{k'_b}{k'_a} = \frac{t_{rb} - t_0}{t_{ra} - t_0}$$

$$\alpha \geq 1$$

Plate Number (N)

$$N = 16\left(\frac{t_r}{w}\right)^2 = 5.54\left(\frac{t_r}{w_{0.5}}\right)^2$$

Height equivalent to a theoretical plate HETP (H)

$$H = \left(\frac{L}{N}\right)$$

Resolution (R_s)

$$R_s = 2\left(\frac{t_{r2} - t_{r1}}{w_1 + w_2}\right) = 1.176\left(\frac{t_{r2} - t_{r1}}{w_{0.5,1} + w_{0.5,2}}\right)$$

Van Deemter Equation

$$H = A + \frac{B}{u} + (C_s + C_m)u$$

Topic 5: Atomic Spectroscopy

Intensity

$$I = I_0 e^{-k_v lc}$$

Atomic Absorption Transmission

$$T = \frac{I}{I_0} = e^{-k_v lc}$$

Absorbance

$$A = \varepsilon cl$$

Characteristic Concentration

$$Concentration_{Characteristic} = 0.0044\ x\ \frac{concentration of standard}{measured\ absorbance}$$

Log(1/0.99) = 0.0044