ANALYTICAL CRIB
2-3-07

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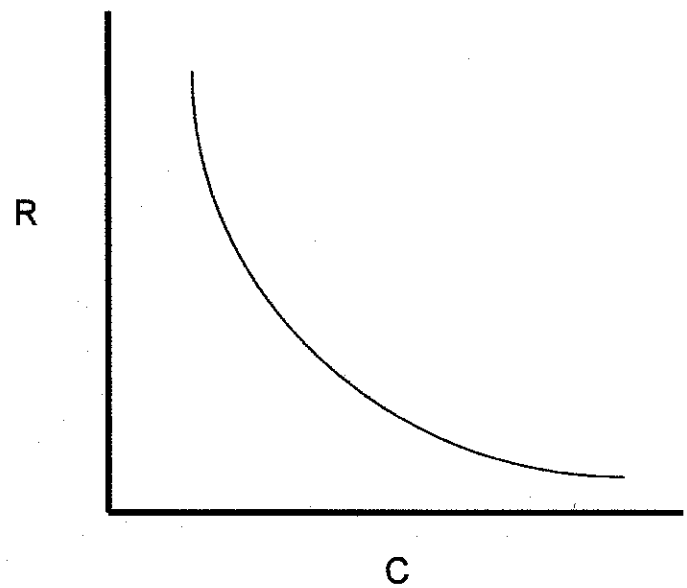
1. The relationship between instrument response, R, and analyte concentration, C, for a particular method is:

$$R = e^{-(\alpha+\beta C)}$$

a) Sketch the shape of the response versus concentration curve. **[5 pts]**



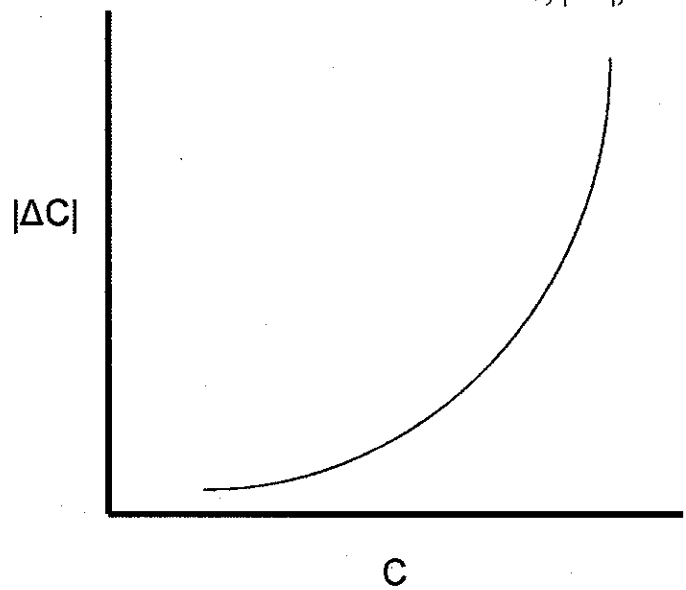
b) What is the sensitivity of this method? **[10 pts]**

$$sensitivity = \frac{dR}{dC} = -\beta e^{-(\alpha+\beta C)}$$

c) What is the relationship between the error in R, ΔR, and the resulting error in C, ΔC? **[10 pts]**

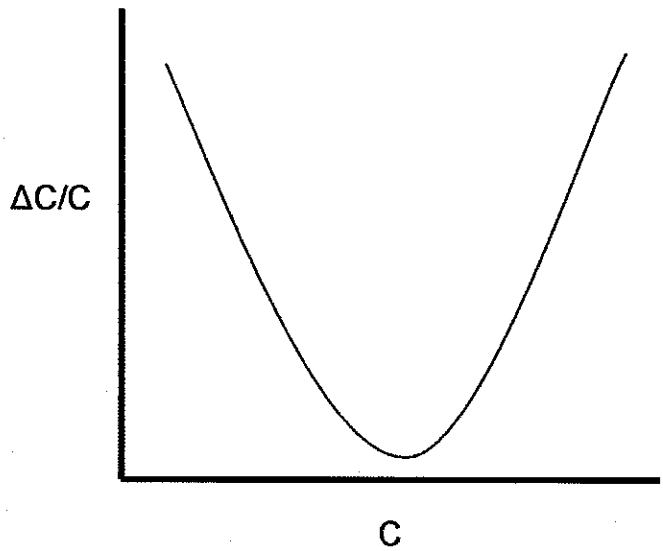
$$\Delta C = -\frac{\Delta R}{\beta e^{-(\alpha+\beta C)}} = \frac{\Delta R \cdot e^{-(\alpha+\beta C)}}{\beta}$$

d) For a constant error in response (fixed ΔR), sketch the shape of the plot of the absolute value of error in concentration, $|\Delta C|$, versus concentration. **[5 pts]**



e) To minimize the relative random error ($\Delta C/C$) associated with measuring concentration with this method, are measurements best taken at high concentration, intermediate concentration, low concentration, or is relative random error independent of concentration? Justify your answer. **[10 pts]**

Intermediate concentration. The $\Delta C/C$ versus C curve looks roughly like:



f) Indicate a quantitative analytical method for which the response versus concentration relationship is of the form indicated above. **[5 pts]**

Transmittance (the basis for absorbance).

2. Discuss the physical/chemical bases for the selectivities of the following approaches:

   a) Chemical ionization mass spectrometry **[5 pts]**

   i) ion/molecule reaction kinetics/thermodynamics – i.e. proton affinities, gas phase acidities, ionization energies, electron affinities

   ii) m/z measurement

   b) Electrogravimetry **[5 pts]**

   reduction potential

   c) Laser-induced fluorescence **[5 pts]**

   absorption wavelength
   emission wavelength
   fluorescence lifetime

   d) A Kjeldahl determination **[5 pts]**

   Digestion of organic N and conversion to NH_3 for subsequent titration.

3. Some analytical methods are based on the establishment of equilibrium (i.e., equilibrium methods) and some are based on the measurement of rates of reactions (i.e., kinetic methods).

   a) List two advantages of kinetic methods over equilibrium methods. **[5 pts]**

i) kinetic methods are often faster than equilibrium methods
ii) useful when equilibrium is slow to achieve
iii) can take advantage of selective catalysts, e.g. enzymes

   b) List two disadvantages of kinetic methods relative to equilibrium methods. **[5 pts]**

i) sensitivity is usually poorer
ii) usually lest robust than equilibrium methods

   c) Glucose is the most widely determined biomarker in the world. Many of the approaches used for glucose determination are kinetic methods. Why is this so? **[5 pts]**

kinetic methods can take advantage of selective enzymes, i.e. glucose oxidase

4. Species A reacts with species B with 1:1 stoichiometry, an equilibrium constant of 10^{40}, and a rate constant of $1.80x10^{-2}$ $M^{-1}s^{-1}$. After rapid mixing of solutions containing A and B, 50.0% of A was converted to products after 30.0 s. If the concentration of B was significantly higher than that of A such that the concentration of B was essentially constant over 30s, what was the concentration of B? **[10 pts]**

$$\frac{A_{t=30}}{A_{t=0}} = e^{-k[B]t}$$

$$[B] = \frac{-\ln \frac{A_{t=30}}{A_{t=0}}}{kt} = \frac{-\ln 0.5}{(1.8x10^{-2})(30)} = 1.28M$$

5. The concentration of a species of interest can be computed from the several measured values as follows:

$$C = 3.4x10^{-3}(\pm 2x10^{-4})M + \frac{2.6x10^{-3}(\pm 1x10^{-4})M \times 1.2x10^{-3}(\pm 3x10^{-4})M}{1.8x10^{-3}(\pm 2x10^{-4})M}$$

What is the uncertainty of the computed value of C? **[10 pts]**

An error propagation problem:

Approach is to determine error of the product/quotient and then the sum.

$$\frac{s_y}{1.7x10^{-3}} = \sqrt{\left(\frac{10^{-4}}{2.6x10^{-3}}\right)^2 + \left(\frac{3x10^{-4}}{1.2x10^{-3}}\right)^2 + \left(\frac{2x10^{-4}}{1.8x10^{-3}}\right)}$$

$$s_y = 4.7x10^{-4}$$

$$C = 3.4x10^{-3}(\pm 2x10^{-4})M + 1.7x10^{-3}(\pm 4.7x10^{-4})$$

$$s_C = \sqrt{(2x10^{-4})^2 + (4.7x10^{-4})^2} = 5.1x10^{-4}M$$

Useful relationships:

$$\frac{de^u}{dx} = e^u \frac{du}{dx} \qquad \frac{d \ln u}{dx} = \frac{1}{u}\frac{du}{dx}$$

No Biochemistry crib available
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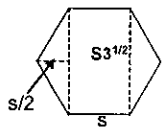
Written by Professor Shah

Inorganic Cume Answers 2-3-07

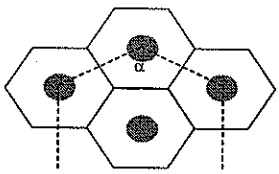
1A. Each vertex shared 6 ways. Therefore 2 B/cell.

B. If s is the edge length, the area (A) of the hexagon is $1.5(3)^{1/2}s^2$ and one can solve for the interplanar spacing b by equating the density to MW/(NAb) where N is Avagadro's number, and MW is the molecular weight. $b = 3.419 \times 10^{-8}$ cm.

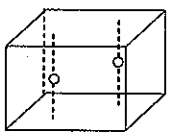


C. CN = 6.

D. The angle α is 120° because it is the interior angle of another hexagon, and the other angle is 60° because the sum of the interior angles is 360°. The edge length is $s3^{1/2}$.



E. The Hf atoms at the corners not shown.



2.

$Hf(BH_4)_4(g)$ →	$HfB_2(s)$ +	$B_2H_6(g)$ +	$5\ H_2(g)$
Hf(IV)B(III)H(-I)	Hf(II)B(-I)	B(III)H(-I)	H(0)

B. Hf(II) is d^2, and the electrons should be in non-bonding d(xy) and $d(x^2-y^2)$.

C. With a half-filled d band, expect the material to be an electronic conductor.

No Organic crib available
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Written by Professor Ghosh

No Physical crib available
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Written by Professor Naumann
317-271-5222