September, 2010 – Analytical Chemistry Crib

1. Chemists take advantage of the phenomenon of absorbance for a variety of purposes. Discuss the characteristics of UV/visible absorbance versus IR absorbance with respect to analysis. How are they used? Are there particular advantages of one form of absorbance over the other for particular applications and why?

   (10 points)

   UV/vis is used for quantitative determinations because absorbance lines are broad, which makes absorbance at a single wavelength less prone to wavelength error. UV/vis is generally not very informative as a qualitative analysis tool because the lines are broad and not particularly specific. Lines are much narrower in the IR region and are functional group specific. For this reason, IR is a good qualitative analysis tool. The narrow line shapes associated with IR absorbance, on the other hand, make it more prone to wavelength error.

2. What is a coulometric titration? Describe the principle behind the measurement and a typical way to conduct such a measurement. Compare and contrast a coulometric titration with the more traditional volumetric titration. What are the relative advantages/disadvantages of a coulometric versus volumetric titration?

   (10 points)

   A coulometric titration is one in which the reagent species used to titrate an analyte is generated *in situ* electrochemically. The end-point can be determined by any of a number of means. The number of moles of reagent generated is based on the stoichiometry of the electrochemical reaction and on the number of moles of electrons used to generate the reagent, $Q=It$. Measurement of current x time to reach the end-point provides the necessary information to determine the number of moles of reagent needed to fully react with the analyte (current x time = moles electrons). This is analogous to the measurement of the volume of a reagent solution of known concentration (i.e., volume x concentration = moles reagent). Coulometric titrations are particularly useful for generating highly reactive or unstable reagents that are not amenable to volumetric titrations. The control over the number of electrons can be very precise. The major disadvantage relative to a traditional volumetric titration is that it is more complicated, requiring the appropriate electronics.

3. "Efficiency" is a commonly used term in column chromatography.
   a. What does the term 'efficiency' mean in column chromatography? (5 points)

Efficiency is a term that is related to band broadening in chromatography and is therefore also related to the ability to separate closely eluting components (i.e., resolution).

b. How is efficiency measured? (5 points)

Experimentally, efficiency is usually related by either the number of theoretical plates, N, or the height equivalent of a theoretical plate, H. These two terms are related by $N=L/H$, where L is the length of the column. Experimentally, N is determined by $N=16(t_R/W)^2$, where t_R is the retention time and W is the width of the chromatographic peak at the baseline.

c. What theoretical model is most commonly used to describe the efficiency of a chromatographic column? Provide the relationship and describe the parameters to the extent that you are able. (10 points)

The van Deemter equation is the model most commonly encountered in a discussion of band broadening/efficiency.

$$H = A + B/v + C_s v + C_M v$$

Where A is the eddy diffusion term, B is the longitudinal coefficient, and C_s and C_M are the mass-transfer coefficients in the stationary and mobile phases, respectively.

4. Every measurement is characterized by some degree of random error, as reflected by the standard deviation associated with the measurement method, s_X. The concentration or quantity of an analyte species is often not obtained directly from a measurement. Rather, some relationship is used to convert the measured property to analyte concentration.

a. In general, how does uncertainty in a measurement of a property, s_X, such as voltage, current, absorbance, etc., propagate to uncertainty in concentration, s_C? (5 points)

$$s_C = s_x/\text{sensitivity}$$

where sensitivity is the derivative of response with respect to concentration (d(response)/dC)

b. Depending upon the relationship between the measured quantity and concentration, the concentration error can be concentration dependent. Discuss and compare the concentration dependence of random error for a fluorescence measurement versus an absorbance measurement (remember that an absorbance measurement is really a transmittance measurement). Assume that the standard deviation associated with the measurement is constant with concentration (i.e., standard deviation of fluorescence signal, s_F=constant and standard deviation of transmittance measurement, s_T=constant). (15 points)

Fluorescence case:

$F \approx 2.3\varepsilon bC\kappa P_0$

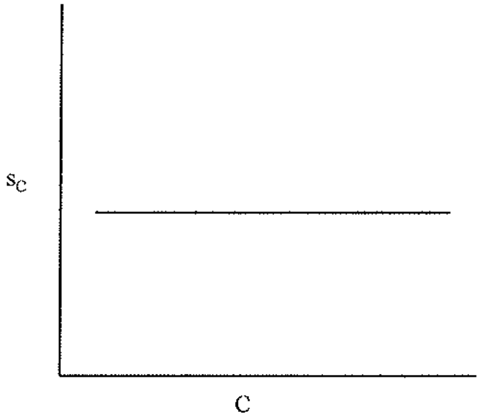
Where ε is molar absorptivity, b is path length, κ is a constant related to quantum efficiency and P_0 is the incident power.

Hence, $C \approx F/(2.3\ \varepsilon b\kappa P_0) = F/\text{constant}$

Sensitivity = $dF/dC = d(2.3\ \varepsilon b\kappa P_0 C)/dC = 2.3\ \varepsilon b\kappa P_0$

Absolute concentration error = $s_C = s_F/\text{sensitivity} = s_F/(2.3\ \varepsilon b\kappa P_0)$

Hence, for a constant s_F, s_C is constant with concentration.



Absorbance/transmittance case:

$T = 10^{-\varepsilon bC} = e^{-2.3\varepsilon bC}$

Sensitivity = $dT/dC = -2.3\varepsilon b e^{-2.3\varepsilon bC}$

Absolute concentration error = $s_C = s_T/\text{sensitivity} = s_T/(2.3\varepsilon b e^{-2.3\varepsilon bC})$

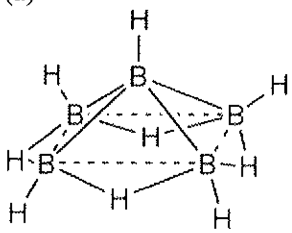
Hence, for constant s_T, s_C increases exponentially

Inorganic Cumulative Exam Solution

September 25, 2010 (All things about boron)

1. Boron hydride compound B_5H_9 was tested as a rocket fuel during the Cold War. Please (**a**, 5 pt) draw its structure; (**b**, 5 pt) determine its point symmetry group; (**c**, 10 pt) describe the types of covalent bonds in this molecule.

(a)

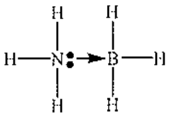


(b) C_{4v}

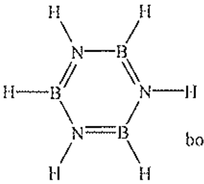
(c) (i) B-B-B three center 2e bonds (between apical and basal boron centers) (ii) terminal B-H bonds (iii) B-H-B three center 2e bonds

2. Ammonia-Borane (NBH_6) has attracted significant interest in recent years as a promising hydrogen storage material. Please (**a**, 5 pt) calculate the mass percentage of H; (**b**, 5 pt) draw its Lewis dot structure. (**c**, 10 pt) Borazine is one of the most stable products formed from the dehydrogenation of ammonia-borane. Draw its structure and determine the mass percentage of H released in the formation of borazine.

(a) 19.6%



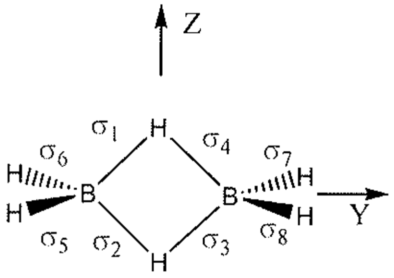
(b)



borazine (c)

(c) 13%

3. (15) Sketch the structure of B_2H_6 and construct the SALCs of σ(B-H) (possibly useful character tables are given below).



D_{2h}	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}	
A_g	1	1	1	1	1	1	1	1	
B_{1g}	1	1	-1	-1	1	1	-1	-1	
B_{2g}	1	-1	1	-1	1	-1	1	-1	
B_{3g}	1	-1	-1	1	1	-1	-1	1	
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	
B_{2u}	1	-1	1	-1	-1	1	-1	1	
B_{3u}	1	-1	-1	1	-1	1	1	-1	
$\Gamma_{\sigma1-\sigma4}$	4	0	0	0	0	0	0	4	$A_g + B_{3g} + B_{1u} + B_{2u}$
σ_1	σ_1	σ_4	σ_2	σ_3	σ_3	σ_2	σ_4	σ_1	
$\Gamma_{\sigma5-\sigma8}$	4	0	0	0	0	4	0	0	$A_g + B_{1g} + B_{2u} + B_{3u}$
σ_5	σ_5	σ_7	σ_6	σ_8	σ_7	σ_5	σ_8	σ_6	

A_g: $(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)/2$ & $(\sigma_5 + \sigma_6 + \sigma_7 + \sigma_8)/2$

B_{1g}: $(\sigma_5 - \sigma_6 + \sigma_7 - \sigma_8)/2$; B_{3g}: $(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2$

B_{1u}: $(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)/2$ B_{2u}: $(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)/2$ & $(\sigma_5 + \sigma_6 - \sigma_7 - \sigma_8)/2$

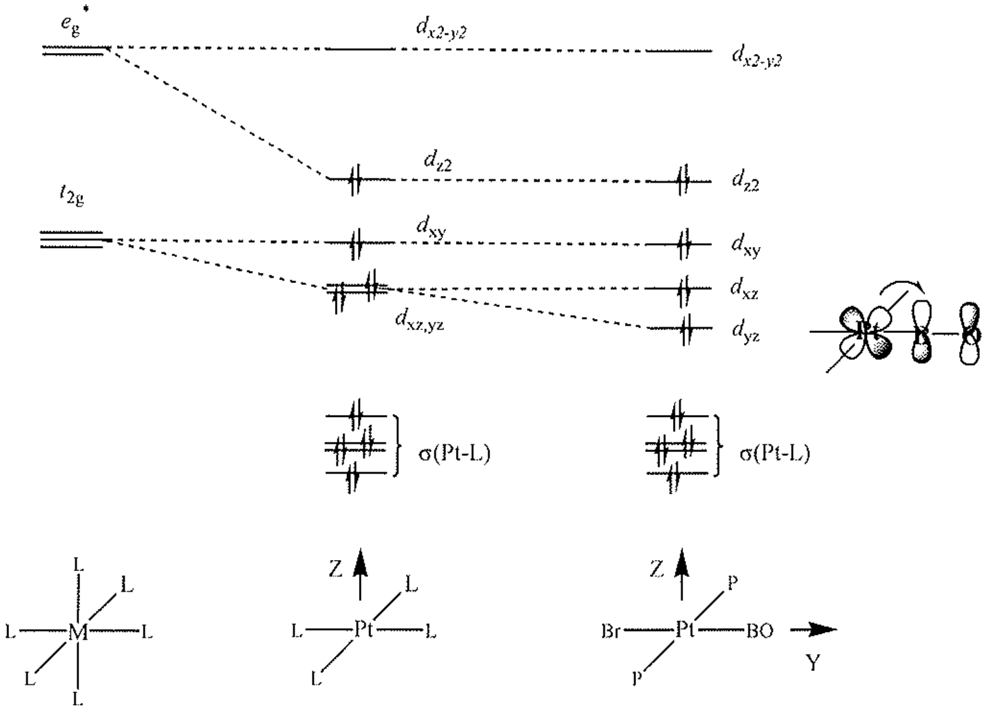
B_{3u}: $(\sigma_5 - \sigma_6 - \sigma_7 + \sigma_8)/2$

4. The first metal oxoboryl complex *trans*-$[(Cy_3P)_2BrPt(BO)]$ (Cy being cyclohexyl) was reported in *Science* this year. Please determine the followings based on your knowledge of basic inorganic chemistry: (**a**, 10) the charge and Lewis dot structure of the "BO" ligand; (**b**, 25) a MO diagram that contains all valence orbitals around the Pt center and comment on the role of "BO"; and (**c**, 10) estimate the "BO" stretch frequency (υ(BO)) assuming its force constant comparable to that of CO ($\upsilon_{CO} \sim 2050$ cm^{-1}).

(a) Four coordinate Pt is +2, and hence "BO" has to be -1.

:O:::B:

(b)



Starting from a *octahedral*

Square planar with σ only

consider π(BO)

(c) reduced mass of "BO": $\mu_1 = 10.8*16/26.8 = 6.45$;
reduced mass of "CO": $\mu_2 = 12*16/28 = 6.86$
$\upsilon_{BO} = 2050\ (\mu_2/\mu_1)^{1/2} \sim 2110\ \mathrm{cm}^{-1}$

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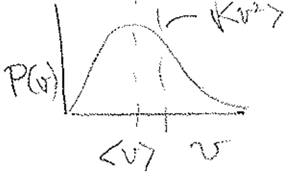
a) $\langle K \rangle = \frac{3}{2} RT \sim 3.7$ kJ/mol at r.t.

b) $\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$ so, $\langle v^2 \rangle = \frac{3 k_B T}{m}$

or in molar units $\langle v^2 \rangle = \sqrt{\frac{3RT}{M}} \approx 500$ m/s

c) 

because P(v) is assymetric one expects $\sqrt{\langle v^2 \rangle} > \langle v \rangle$

d) Two rotational degrees of freedom so, average rotational K.E. is $\frac{2}{2} RT \sim 2.5$ kJ/mol

e) Same as (d)

f) $I = \mu r_0^2 = \left(\frac{\overset{\text{mass of O atom}}{m_O} m_O}{m_O + m_O}\right) r_0^2 \cong 2 \times 10^{-46}$ kg m^2

g) $\omega = 2\pi\nu = \sqrt{\frac{f}{\mu}} \Rightarrow f = \mu\omega^2 = \mu(2\pi c\tilde{\nu})^2$

$= 2\pi c\tilde{\nu}$

h) $\frac{1}{2} h\nu = \frac{1}{2}\hbar\omega$

i) $H = \frac{1}{2}\mu v^2 + \frac{1}{2} f x^2$ two quadratic terms

~~k~~ j) so $\langle H \rangle = \langle K \rangle + \langle V \rangle = \underset{\text{i)}\nearrow}{\frac{1}{2} k_B T} + \underset{\text{j)}\nearrow}{\frac{1}{2} k_B T} = k_B T$

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