Chem 1B Midterm Review

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1 Spectroscopy

Spectroscopy takes advantage of compounds' distinct absorbance properties to detect concentration. Recall that

$$\Delta E = hv = \frac{hc}{\lambda} \tag{1}$$

This DeltaE is the difference in energy between two levels (E2 - E1) **for one photon**, meaning one must multiply by Avagadro's number for one mole of photons.

There are two key processes:

- **Absorbance** - going from a lower energy state to a higher state
- **Emission** - going from a higher energy state to a lower energy state

With absorbance spectroscopy, we can ID an unknown.

1.1 UV/Vis Electronic Transitions

The pi (bonding) to pi* (antibonding) promotion deltaE is in the UV wavelength, and **occurs with double and triple bonds**. When you have more double blonds (a larger box), the pi electrons in the molecular orbitals are confined to a larger area which ersults in a smaller deltaE and a higher lambda max. DeltaE is smaller because it's inversely related to lambda.

1.1.1 Uses of UV/Vis Spectroscopy

To ID Compounds

- Match lambdaMax
- be careful of matrix effects (example: solvent) and other species that absorb at the same lambdaMax

1.2 Partile in a 1D Box

There is an equation relating deltaE with respect to frequency and wavelength to the length of a box: The 'box' is from one end of the delocalization (chain of double bonds) to the other end. With pi bonds, the electron is bouncing in between the two atoms on either end of hte bond, and this delocalization occurs with the chain of double bonds. The more double bonds, the **larger** the box.

1.3 Beer's Law: Quantification of UV/Vis Data

Beer's Law relates absorbance to concentration linearly.

$$A = log(\frac{L_0}{L}) = -log(\frac{L}{L_0}) = \epsilon cl \tag{2}$$

- ϵ = molar absorption coefficient
- c = concentration (M)
- l = path length **(cm)**
- A = absorbance (unitless)

2 Chromatography

2.1 Chromatography Standards

In order of decreasing accuracy.

2.1.1 Internal Standards

Internal standards are nice because we don't have to assume the matrix. With internal standards, we first run a test with known concentrations of the analyte compound and another compound and find the response factor (ratio of machine response relative to concentration in the *sample*) between these two compounds. We then:

1. Find a linear regression equation that represents Analyte Peak Area/Other Compound Peak Area vs. Known Analyte Concentration/Other Compound Concentration.
2. Add the other compound to the matrix and analyze it.
3. Plug in the relative peak areas (Analyte Peak Area/Other Compound Peak Area) for the added other compound and the analyte in question as x into the linear regression equation, and we get y, which is the two compounds' **relative concentrations** in the **diluted** sample.
4. Multiply the ratio of concentration by the **concentration** of the other compound that we added in the **diluted** solution.
5. *Alternatively, solve for the response factor with the standard sample where all concentrations and areas are known, and then plug the known concentration of standard and the responses of standard and analyte in the diluted unknown into the response factor equation and solve for the **diluted** concentration of the unknown*
6. Do M1V1 = M2V2, where M1 and V1 are the concentration of the analyte in the diluted solution and the volume of the diluted solution, respectively, and V2 is the volume of the original sample before we added any other compounds and diluted it.

2.1.2 Standard Addition

Slightly less accurate than internal standards, though it **amplifies weak signal**, standard addition is a process where we add known amounts of the analyte in question to the sample and dilute, which, obviously, contains an *unknown* concentration of the analyte.

1. Run the test with different amounts of the analyte compound added to the sample (diluted to the same volume each time)
2. Linearly regress an equation that represents Concentration of Added Standard in the **Diluted** Solution vs. Response.
3. Find the x intercept (the thing that makes y = 0) for this equation, which should be negative. The negative value is the concentration of the sample **once it is diluted**.
4. Do M1V1 = M2V2, where M1 and V1 are the concentration of the analyte in the diluted solution and the volume of the diluted solution, respectively, to find the concentration in the original, undiluted volume of the sample.

2.2 Gas Chromatograpy

With gas chromatography, the mobile phase is a gas, and we only consider polarity of stationary phase. The stationary phase is the column itself, and can be polar or nonpolar. Things that stick to the stationary phase (due to attraction with 'like dissolves like') take **longer** to come out. With a **nonpolar** column, interactions with the compounds and the columns are generally **weak** because all they have are LDFs, which are, by definition, weak.

2.2.1 Things Affecting Retention Time/Separation

- Less time spent in column means **more** separation between compounds
- In a **non-polar** column, the boiling points of the compounds dominates.
- All the compounds are retained longer on a polar column, since polar columns have greater IMFs than nonpolar columns.
- A **lower** boiling point means that the compound in question is more likely to leave the column sooner due to high vapor pressure
- Temperature programming and higher temperature helps elute larger compounds and maintain good resolution If you make temperature high enough, you can 'overcome' the aforementioned attractions and get the analyte to elute out

2.3 High Performance Liquid Chromatography

HPLC is a type of chromatography where the mobile phase is a liquid, the stationary phase is a soid or liquid interior of a column, and the analyte is a liquid. With HPLC, we consider polarity of both stationary and mobile phases and the effect of pH on mobile phase.

- Normal Phase - Polar stationary phase and non-polar mobile phase
- Reverse Phase - Non-polar stationary phase and polar mobile phase

2.3.1 Things Affecting Retention Time/Separation

- **Polarity of the mobile phase** can affect retention time. If the polarity of the mobile phase becomes more similar to the stationary phase, retention times will **decrease** and peaks will become less separated as competition occurs between mobile phase and stationary phase and between the increasingly polar/non-polar mobile phase itself and analytes for the spots on the stationary phase
- **PH of the mobile phase** affects retention time significantly when dealing with acids and bases. With acids, as pH increases, H+ ions dissociate and the compound becomes more charged **and therefore more likely to cling to a polar mobile phase and elute faster**, especially once pH exceeds pKa. The converse is true for bases (lower pH leads to more charge).

2.4 Plate Model

More plates (N) and smaller plate height (H) yields better separation of compounds because the chromatographic process occurs within each plate. It's not real, it's theoretical.

2.5 What are desirable qualities in a chromatogram?

With a longer column, separation (resolution) goes up, peak height goes down, peak width goes up, and peak area should be equal.

3 Titrations

- **Equivalence Point** - The point on the curve where the number of **moles** of acid is equal to the number of moles of base added.
- **Buffer Zone** - The part of the curve before equivilence point where, during titration from an acid to a base, for each time you add any OH to swallow up an H+ ion, an H+ ion is released by the acid in question to keep pH low (though it goes up a little due to the conjugate base). This stops once the moles of OH- added is equal to the number of moles of the acid.
- When 1/2 of the moles of added base needed to equal moles of acid have been added, pH = pKa.
- Ka = [H+][Conjugate Base]/[Acid]

3.1 Redox

Think about oxidation before reduction: The thing being oxidized is **losing** an electron so the thing being reduced gain gain it. Remember that redox reactions/titrations don't always involve 1:1 ratios. Remember that oxidizing agents and reduction **agents** is like the opposite of oxidation reaction and reduction reaction – an oxidizing agent gets reduced and a reduction agent gets oxidized.

4 Polarity and IMFs

How to determine if a molecule is polar:

1. Look at it's Lewis Dot Structure
2. Look at its VSEPR structure
3. Look at the dipole moment of each indiidual bond and sum them up. If they don't equal zero, it's polar.

4.1 IMFs

In order of decreasing strength.

1. Is there a bond between N, O, F, and hydrogen present? If yes, hydrogen bonds are present.
2. Is the molecule polar? If yes, dipole-dipole bonds are present.
3. Otherwise, LDFs are present.

5 Partition Coefficient

K = [A1]/[A2] = Concentration of Solute A in Solvent 1/Concentration of Solute A (same solute) in Solvent 2