1) Compound $A$ has a molar absorbtivity of $10000 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}$ at $\lambda 475 \mathrm{~nm}$. Compound $B$ has a molar absorbtivity of $500 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1} \lambda 475 \mathrm{~nm}$. Using the same spectrometer set at $\lambda 475 \mathrm{~nm}$ and identical cuvettes, you obtain identical absorbance readings. Which sample has the greater concentration?
$A=\varepsilon b c$. Since absorbance is identical for both readings $A_{A}=A_{B}$. Setting both equations equal to each other and canceling " $b$ " from both sides gives:

$$
\begin{aligned}
& (10,000 \mathrm{~L} / \mathrm{mol} \cdot \mathrm{~cm})\left(\mathrm{c}_{\mathrm{A}}\right)=(500 \mathrm{~L} / \mathrm{mol} \cdot \mathrm{~cm})\left(\mathrm{c}_{\mathrm{B}}\right) \\
& \mathrm{c}_{\mathrm{B}} / \mathrm{c}_{\mathrm{A}}=10,000 / 500=20
\end{aligned}
$$

To have the same absorbance reading, the concentration of B is 20 times greater than the concentration of A.
2) A blue dye is used in a blue raspberry flavored drink. You have been asked to find out the concentration of this blue dye in the prepared beverage. You have 1.0 g of the dye (MW =369 $\mathrm{g} / \mathrm{mol}$ ) available to you and need to prepare the solutions in Table 1.
a) Describe (in detail) how you would prepare 100 mL of sample 2 .

One could take two different approaches.

1) To make a 100 mL of 0.002 M dye solution one could weigh out solid dye, place it in the 100 mL volumetric, and add water. Using this approach we calculate the amount of dye needed to add to the flask.

| 100 mL | 0.002 mol | 369 g | 0.074 g |
| :---: | :---: | :---: | :---: |
|  | 1000 mL | mol |  |

Note that our lab balances are accurate to $\sim 0.001$ grams. Thus, weighing error will introduced about $1.4 \%$ uncertainty into our concentration.
2) One could make a stock solution and then dilute to obtain the final concentration.

| 1.000 g | 1000 mL | mol | 0.00542 M |
| :---: | :---: | :---: | :---: |
| 500.0 mL | 1 L | 369 g |  |

We need to add 0.0002 mol to 100 mL flask to generate 0.002 M solution

| 0.0002 mol | 1000 mL | 36.9 mL |
| :---: | :---: | :---: |
|  | 0.00542 mol |  |

Using this method, the weighing error is $\sim 0.1 \%$ ( 14 x less). The error from the buret is $\sim 0.1 \%$. This method is also convenient since you only have to weigh once and then all solutions can be generated from the buret. Method 2 is superior.
b) Why would you choose 686 nm as the wavelength that you measure?

The dye appears blue because "blue" photons are not absorbed by the dye. A blue dye is likely to absorb in the yellow to red (that is why it doesn't appear green to purple) and thus 686 nm is a good guess for its absorbance maximum.

After preparing the solutions and a sample of the drink mix, you obtain the absorbance data in Table 1.

| Table 1: Data for Problem 2 |  |  |
| :---: | :---: | :---: |
| Sample |  |  |
| Name | Conc (M) | Absorbance <br> $(686 n m)$ |
| Blank | 0 | 0.001 |
| 1 | 0.001 | 0.19 |
| 2 | 0.002 | 0.415 |
| 3 | 0.004 | 0.876 |
| 4 | 0.005 | 1.2 |
| drink |  | 0.235 |

c) What is the molar absorptivity of the dye (assume you used a 1 cm wide cuvette)?

The data from Table 1 is plotted below.


The molar absorptivity of the dye is the slope $(A=\varepsilon b c$ or $y=m x)$ since $b=1$. Thus, molar absorptivity $=\varepsilon=248 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}$. If we really only have one significant figure for our solution molarity than we must report $\varepsilon=200 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}$.
d) What is the concentration of the dye in the drink mix?

This can be found by reading off the graph or by employing the equation for the linear fit to the data.
$\mathrm{y}=248.1 \mathrm{x}-0.0745$
$0.235=248.1 x-0.0745$
$\mathrm{x}=0.00125$
Once again, significant figures in our initial molarity limits our conclusions and we report the concentration of the dye in the drink as 0.001 M .

3a) Based on the Well Wishes case study, is there enough $\mathrm{O}_{2}$ in the drainfield to oxidize all the carbon, nitrogen and sulfur species under unsaturated soil conditions?
$\mathrm{NH}_{4}^{+}+2 \mathrm{O}_{2} \rightarrow \mathrm{NO}_{3}{ }^{-}+2 \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{CH}_{2} \mathrm{O}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{H}_{2} \mathrm{~S}+2 \mathrm{O}_{2} \rightarrow \mathrm{SO}_{4}{ }^{2-}+2 \mathrm{H}^{+}$
From the case study, we learn that the oxygen uptake is $236 \mathrm{~g} / \mathrm{day} \cdot \mathrm{m}^{2}$. We need to convert this oxygen uptake into a concentration we can use to compare to the $\mathrm{NH}_{4}{ }^{+}, \mathrm{CH}_{2} \mathrm{O}$, and $\mathrm{H}_{2} \mathrm{~S}$ concentrations.

The drain field is $80 \mathrm{~m}^{2}$
The moles of $\mathrm{O}_{2}$ available in a day is:

| 236 g | $80 \mathrm{~m}^{2}$ | mol | $590 \mathrm{~mol} \mathrm{O}_{2}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{~m}^{2}$ |  | 32 g |  |

The moles of $\mathrm{NH}_{4}{ }^{+}$placed in drainfield per day:

| 91.2 mg | 238 L | mol | $1.20 \mathrm{~mol} \mathrm{NH}_{4}{ }^{+}$ |
| :--- | :--- | :--- | :--- |
| Liter |  | 18000 mg |  |

The moles of $\mathrm{CH}_{2} \mathrm{O}$ placed in drainfield per day:

| 531 mg | 238 L | mol | $4.21 \mathrm{~mol} \mathrm{CH}_{2} \mathrm{O}$ |
| :--- | :--- | :--- | :--- |
| Liter |  | 30000 mg |  |

The moles of $\mathrm{H}_{2} \mathrm{~S}$ placed in drainfield per day:

| 12.5 mg | 238 L | mol | $0.088 \mathrm{~mol} \mathrm{H}_{2} \mathrm{~S}$ |
| :--- | :--- | :--- | :--- |
| Liter |  | 34000 mg |  |

The number of moles of $\mathrm{O}_{2}$ required to oxidize all species is:
$\left(2 *\right.$ mols $\left.\mathrm{NH}_{4}{ }^{+}\right)+\left(\right.$mols $\left.\mathrm{CH}_{2} \mathrm{O}\right)+\left(2 *\right.$ mols $\left.\mathrm{H}_{2} \mathrm{~S}\right)=6.8$ moles. This far less than the 590 mol present under unsaturated conditions.
b) Under saturated soil conditions?

From the case study, we learn that the oxygen uptake is $6.7 \times 10^{-4} \mathrm{~g} / \mathrm{day} \cdot \mathrm{m}^{2}$.
Concentration of $\mathrm{O}_{2}$ available in a day is:

| $6.7 \times 10^{-4} \mathrm{~g}$ | $80 \mathrm{~m}^{2}$ | mol | $1.7 \times 10^{-3} \mathrm{~mol} \mathrm{O}_{2}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{~m}^{2}$ |  | 32 g |  |

This is far less than athe 6.8 moles needed to oxidize all species.
4) How would you prepare 500 mL of a $2.00 \times 10^{-6} \mathrm{M} \mathrm{KCl}$ (molar mass $=74.4 \mathrm{~g}$ ) solution by using a balance that can measure mass only to 0.01 g .

In the blue dye case, it was possible to simply weigh the dye and place it in the 100 mL flask although it was not the most accurate way to prepare the solution. In this case, if we try to measure the KCl and added the required mass into the 500 mL volumetric

| 500.0 mL | $2.00 \times 10^{-6} \mathrm{~mol}$ | 74.4 g | 0.000074 g |
| :--- | :--- | :--- | :--- |
|  | 1000 mL |  |  |

It is physically impossible to weigh this amount of sample on the balance. In order to make this solution, we will need to use a technique called "serial dilution." We will first make one solution and then dilute it to generate our desired solution.
To keep the weighing error under $1 \%$, lets weigh out 2.000 g of KCl , place it in a 1000 mL volumetric, and dilute to the mark. This gives a solution that is:

| 2.000 g | 1 mol | 0.02688 M |
| :--- | :--- | :--- |
| 1.000 L | 74.4 g |  |

Using the first two columns of the first calculation, we can determine that we need to place 1.00 x 10-6 mol KCl into the 500 mL volumetric flask. Using our stock solution, the means we would add:

| $1.00 \times 10^{-6} \mathrm{~mol}$ | 1000 mL | 0.037 mL |
| :--- | :--- | :--- |
|  | 0.02688 mol |  |

We can't do that using our buret! Remember, it has 0.1 mL marks. So, we'll use the stock solution we prepared to make another more dilute solution. Let's just add 10.0 mL to a 1 L volumetric flask. That will deliver:

| 0.02688 mol | 10.0 mL | $2.69 \times 10^{-4} \mathrm{~mol}$ |
| :--- | :--- | :--- |
| $1000 . \mathrm{mL}$ |  |  |

And leave us with a $2.69 \times 10^{-4} \mathrm{M}$ solution. Trying again to make the desired solution:

| $1.00 \times 10^{-6} \mathrm{~mol}$ | 1000 mL | 3.7 mL |
| :--- | :--- | :--- |
|  | $2.69 \times 10^{-4} \mathrm{~mol}$ |  |

So we need to add 3.7 mL and dilute to the mark in a 1.000 L volumetric flask to make our desired $2.00 \times 10^{-6} \mathrm{M} \mathrm{KCl}$ solution.

Moore, Stanitski, and Jurs: Chapter 5: 13, 19, 24, 30, 59, 63, 67, 71, 77, 103, 108, 118
13) Solubility of ions
a) $\mathrm{K}_{2} \mathrm{HPO}_{4}$-water soluble $-\mathrm{K}^{+}{ }_{(\mathrm{aq})}$ and $\left(\mathrm{HPO}_{4}\right)^{2-}{ }_{(\mathrm{aq})}$
b) $\mathrm{Na}(\mathrm{ClO})-$ water soluble $-\mathrm{Na}^{+}{ }_{(\text {aq })}$ and $(\mathrm{ClO})^{-}{ }_{\text {(aq) }}$
c) $\mathrm{MgCl}_{2}$ - water soluble $-\mathrm{Mg}^{2+}{ }_{(\mathrm{aq})}$ and $\mathrm{Cl}^{-}{ }_{\text {(aq) }}$
d) $\mathrm{Ca}(\mathrm{OH})_{2}$ - slightly soluble - those few ions that dissolve are $\mathrm{Ca}^{2+}{ }_{(\text {aq })}$ and $(\mathrm{OH})^{-}{ }_{(\text {aq })}^{-}$
e) $\mathrm{AlBr}_{3}-$ soluble $-\mathrm{Al}^{+3}{ }_{(\mathrm{aq})}$ and $\mathrm{B}^{\mathrm{r}-}{ }_{(\mathrm{aq})}$
19) $\mathrm{K}_{2} \mathrm{CO}_{3}+\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \rightarrow \mathrm{Cu}\left(\mathrm{CO}_{3}\right)+2 \mathrm{~K}\left(\mathrm{NO}_{3}\right)$

The reactants described in the problem are on the left hand side of the equation listed above.
This will put the following ions into solution as indicated by the complete equation given below.
$2 \mathrm{~K}_{(\mathrm{aq})}^{+}+\left(\mathrm{CO}_{3}\right)^{2-}{ }_{(\text {aq })}+\mathrm{Cu}^{+2}{ }_{(\text {aq })}+2\left(\mathrm{NO}_{3}\right)^{-}{ }_{(\text {aq })} \rightarrow \mathrm{Cu}\left(\mathrm{CO}_{3}\right)_{(\mathrm{s})}+2 \mathrm{~K}_{(\mathrm{aq})}^{+}+2\left(\mathrm{NO}_{3}\right)^{-}{ }_{(\text {aq })}^{-}$
For the net equation, we remove the ions that are present on both sides.
$\left(\mathrm{CO}_{3}\right)^{2-}{ }_{(\mathrm{aq})}+\mathrm{Cu}^{+2}{ }_{(\mathrm{aq})} \rightarrow \mathrm{Cu}\left(\mathrm{CO}_{3}\right)_{(\mathrm{s})}$
The product is copper(II) carbonate
24) Balance and write complete and net equations.
a) complete: $\mathrm{Zn}^{+2}{ }_{(\mathrm{aq})}+2 \mathrm{Cl}_{(\mathrm{aq})}^{-}+2 \mathrm{~K}_{(\mathrm{aq})}^{+}+2(\mathrm{OH})_{(\mathrm{aq})}^{-} \rightarrow \mathrm{Zn}(\mathrm{OH})_{2(\mathrm{~s})}+2 \mathrm{Cl}_{(\mathrm{aq})}^{-}+2 \mathrm{~K}_{(\mathrm{aq})}^{+}$ net: $\mathrm{Zn}^{+2}{ }_{(\mathrm{aq})}+2(\mathrm{OH})_{(\text {(aq) }}^{-} \rightarrow \mathrm{Zn}(\mathrm{OH})_{2(\mathrm{~s})}$
b) complete: $\mathrm{Ag}_{(\text {(aq) }}^{+}+\left(\mathrm{NO}_{3}\right)^{-}{ }_{(\text {aq })}+\mathrm{K}_{(\text {aq })}^{+}+\mathrm{I}_{(\text {aq })}^{-} \rightarrow \mathrm{AgI}_{(\mathrm{s})}+\left(\mathrm{NO}_{3}\right)^{-}{ }_{(\text {aq })}+\mathrm{K}_{(\text {aq })}^{+}$
net: $\mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{I}_{(\mathrm{aq})}^{-} \rightarrow \mathrm{AgI}_{(\mathrm{s})}$
c) complete: $\mathrm{Fe}^{+2}{ }_{(\text {aq) }}+2 \mathrm{Cl}^{-}{ }_{(\mathrm{aq})}+2 \mathrm{Na}^{+}{ }_{(\mathrm{aq})}+2(\mathrm{OH})_{(\mathrm{aq})}^{-} \rightarrow \mathrm{Fe}(\mathrm{OH})_{2(\mathrm{~s})}+2 \mathrm{Cl}^{-}{ }_{(\text {aq) }}+2 \mathrm{Na}^{+}{ }_{(\text {aq) }}$ net: $\mathrm{Fe}^{+2}{ }_{(\text {aq })}+2(\mathrm{OH})^{-}{ }_{(\text {aq) }} \rightarrow \mathrm{Fe}(\mathrm{OH})_{2(\mathrm{~s})}$
30) $\mathrm{Na}_{2} \mathrm{CO}_{3}+\quad \mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \rightarrow \quad \mathrm{Cu}\left(\mathrm{CO}_{3}\right)+\quad 2 \mathrm{Na}\left(\mathrm{NO}_{3}\right)$ sodium carbonate copper(II) nitrate copper(II) carbonate sodium nitrate

This will put the following ions into solution as indicated by the complete equation given below.
$2 \mathrm{Na}^{+}{ }_{\text {(aq) }}+\left(\mathrm{CO}_{3}\right)^{2-}{ }_{(\text {aq })}+\mathrm{Cu}^{+2}{ }_{(\text {aq })}+2\left(\mathrm{NO}_{3}\right)^{-}{ }_{(\text {aq })} \rightarrow \mathrm{Cu}\left(\mathrm{CO}_{3}\right)_{(\text {s })}+2 \mathrm{Na}^{+}{ }_{\text {(aq) }}+2\left(\mathrm{NO}_{3}\right)^{-}{ }_{(\text {aq })}^{-}$
For the net equation, we remove the ions that are present on both sides.
$\left(\mathrm{CO}_{3}\right)^{2-}{ }_{(\mathrm{aq})}+\mathrm{Cu}^{+2}{ }_{(\mathrm{aq})} \rightarrow \mathrm{Cu}\left(\mathrm{CO}_{3}\right)_{(\mathrm{s})}$
59) A solution of $0.25 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ contains $\mathrm{NH}_{4}{ }^{+}$(aq) and $\left(\mathrm{SO}_{4}\right)^{-2}$ (aq) ions. It contains 0.25 M $\left(\mathrm{SO}_{4}\right)^{-2}{ }_{(\mathrm{aq})}$ ions and $0.50 \mathrm{M} \mathrm{NH}_{4}{ }^{+}$(aq) ions.
63) $100 . \mathrm{mL}$ of a $1.023 \times 10^{-3} \mathrm{M}$ solution of $\mathrm{Na}_{3} \mathrm{PO}_{4}$ has the following mass of solute.

| $100 . \mathrm{mL}$ | $1.023 \times 10^{-3} \mathrm{~mol}$ | 163.94 g | $0.0168 \mathrm{~g} \mathrm{Na}_{3} \mathrm{PO}_{4}$ |
| :--- | :--- | :--- | :--- |
|  | 1000 mL | mol |  |

67) If 25.0 mL of 1.5 M HCl is diluted to $500 . \mathrm{mL}$ the concentration of the solution is:

| 25.0 mL | 1.5 mol | 0.0375 mol | 0.0375 mol | 0.075 M HCl |
| :--- | :--- | :--- | :--- | :--- |
|  | 1000 mL |  | 0.500 L |  |

71) Mass of hydrazine $=$

| $250 . \mathrm{mL}$ | 0.225 mol | $2 \mathrm{~mol} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 32.04 g | 3.60 g |
| :--- | :--- | :--- | :--- | :--- |
|  | 1000 mL | $1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{SO}_{4}$ | $1 \mathrm{~mol} \mathrm{~N}_{2} \mathrm{H}_{4}$ |  |

77) $\mathrm{FeCl}_{3}+3 \mathrm{NaOH} \rightarrow \mathrm{Fe}(\mathrm{OH})_{3}+3 \mathrm{NaCl}$

| 25.0 mL | 0.234 mol | $0.00585 \mathrm{~mol} \mathrm{FeCl}_{3}$ |
| :--- | :--- | :--- |
|  | 1000 mL |  |


| 42.5 mL | 0.453 mol | 0.0192 mol NaOH |
| :--- | :--- | :--- |
|  | 1000 mL |  |

The limiting reagent is the $\mathrm{FeCl}_{3}$ since a complete reaction only require 0.0176 mol NaOH .
a) The moles of $\mathrm{FeCl}_{3}=$ moles $\mathrm{Fe}(\mathrm{OH})_{3} . \quad 0.00585 \mathrm{~mol} \times 106.84 \mathrm{~g} / \mathrm{mol}=0.625 \mathrm{~g} \mathrm{Fe}(\mathrm{OH})_{3}$.
b) NaOH
c) $0.0192-(3 \times 0.00585)=0.0016 \mathrm{~mol}$ of NaOH left. The total volume of solution is $25.0+42$. $5=67.5 \mathrm{~mL} . \quad 0.0016 \mathrm{~mol} / 0.0675 \mathrm{~L}=0.024 \mathrm{M} \mathrm{NaOH}$.
103)
a) A
b) C
c) $B \& E$
d) D
e) $6 / 750=2 / 250$ or $4 / 500$. None of the solutions have these concentrations
f) A
g) $B$
108)
a)

Group A: $\mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{Cl}_{(\text {(aq) }}^{-} \rightarrow \mathrm{AgCl}_{(\mathrm{s})}$
Group B: $\mathrm{Ag}^{+}{ }_{(\text {aq })}+\mathrm{Cl}^{-}{ }_{\text {(aq) }} \rightarrow \mathrm{AgCl}_{(\mathrm{s})}$
Group C: $\mathrm{Ag}^{+}{ }_{(\text {aq })}+\mathrm{Br}^{-}($aq $) \rightarrow \operatorname{AgBr}_{(\mathrm{s})}$
Group D: $\mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{Br}_{(\mathrm{aq})}^{-} \rightarrow \mathrm{AgBr}_{(\mathrm{s})}$
b) $\mathrm{A} \& \mathrm{~B}$ lie on the same line because the product is the same $\mathrm{AgCl} . \mathrm{C} \& \mathrm{D}$ lie on the same line, but different line from $\mathrm{A} \& \mathrm{~B}$, because this time the product is AgBr .
c) Since the salts were all used at the same molarity, equal amounts of $\mathrm{Cl}^{-}$or $\mathrm{Br}^{-}$are available in each flask. They level of at the same point because all of the $\mathrm{Cl}^{-}$or $\mathrm{Br}-$ has been consumed. The offset in product mass results from the difference in weight between $\mathrm{Cl}^{-}$or $\mathrm{Br}^{-}$.
118) The molarity of water in pure water is determined by know the mass of water in one liter. Water is $1 \mathrm{~g} / \mathrm{mL}$ or 1000 g per Liter.

| 1000 g | mol | 55.5 M |  |  |
| :--- | :--- | :--- | :--- | :--- |
| 1 L | 18 g |  |  |  |

