13-1 The definition relating absorbance and transmittance is

\[ A = -\log_{10} T \]

This equation inverted gives

\[ T = 10^{-A} \]

For these three examples, we have

(a) \( T = 10^{-0.0510} = 0.889 = 88.9\% \)
(b) \( T = 10^{-0.918} = 0.121 = 12.1\% \)
(c) \( T = 10^{-0.379} = 0.418 = 41.8\% \)

13-2 This is just the reverse of the above equation. The only trick is to make sure that you take the percent transmittance data and divide by 100 to get transmittance. Remember that transmittance must be a number between 0 and 1.

(a) \( A = -\log_{10} (0.0358) = 1.45 \)
(b) \( A = -\log_{10} (0.085) = 1.07 \)
(c) \( A = -\log_{10} (0.538) = 0.269 \)

13-5 First convert concentration from ppm in M or mol/L.

\[
4.48 \text{ ppm} = 4.48 \frac{\text{mg}}{\text{L}} \quad M(\text{KMnO}_4) = 158.03 \text{ g}
\]

\[
c = 4.48 \frac{\text{mg}}{\text{L}} \times \frac{10^{-3} \text{ g}}{\text{mg}} \times \frac{1 \text{ mol}}{158.03 \text{ g}} = 2.835 \times 10^{-5} \text{ M}
\]

Now convert the transmittance into an absorbance value, since it is absorbance which is linearly related to concentration, as shown in Beer’s Law. Then rewrite Beer’s Law to solve for absorptivity.

\[
A = -\log(T) = -\log(0.309) = 0.5100 = \varepsilon bc
\]

\[
\varepsilon = \frac{0.5100}{bc} = \frac{0.5100}{(1.00 \text{ cm})(2.835 \times 10^{-5} \text{ M})} = 1.80 \times 10^{4} \text{ cm}^{-1} \text{ M}^{-1}
\]

13.7 (a) Directly apply Beer’s Law to find the absorbance.

\[
A = \varepsilon bc = (9.32 \times 10^{-3} \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(6.24 \times 10^{-5} \text{ M}) = 0.582
\]

(b) Apply relation between A and %T. Don’t forget the question asked for %T and not just T.

\[
%T = 100 \times 10^{-A} = 100 \times 10^{-0.582} = 26.2\%
\]
(c) New rewrite Beer’s Law to solve for concentration but with the new cell path length.

\[
c = \frac{A}{\varepsilon b} = \frac{0.582}{9.32 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1} (5.00 \text{ cm})} = 1.25 \times 10^{-5} \text{ M}
\]

13-11 (a) Write out the equilibrium expression and derive the solutions for the concentrations of the two photoactive components. We will assume that the dissociation of the indicator is extensive enough to produce enough hydronium ion so that the autodissociation of water can be ignored. Let \( c_{\text{HIn}} \) be the formal concentration of the indicator. We find

\[
K = \frac{[\text{In}^-][\text{H}_3\text{O}^+]}{[\text{HIn}]} = 8.00 \times 10^{-5}
\]

if \([\text{H}_3\text{O}^+] >> 10^{-7} \text{ M}\) then \([\text{H}_3\text{O}^+] = [\text{In}^-]
\]

also \([\text{HIn}] = c_{\text{HIn}} - [\text{In}^-]
\]

\[
K = \frac{[\text{In}^-]^2}{c_{\text{HIn}} - [\text{In}^-]}
\]

For each formal concentration, we can solve the equilibrium expression for the two concentrations.

\[
\frac{[\text{In}^-]^2}{3.00 \times 10^{-4} - [\text{In}^-]} = 8.00 \times 10^{-5}
\]

\[
[\text{In}^-]^2 + 8.00 \times 10^{-5} [\text{In}^-] - 2.4 \times 10^{-8} = 0
\]

\[
[\text{In}^-] = \frac{-8.00 \times 10^{-5} \pm \sqrt{(8.00 \times 10^{-5})^2 - 4(1)(-2.4 \times 10^{-8})}}{2} = 1.2 \times 10^{-4} \text{ M}
\]

\[
[\text{HIn}] = 3.00 \times 10^{-4} - 1.2 \times 10^{-4} = 1.8 \times 10^{-4} \text{ M}
\]

Then, with the given molar absorptivities, we can find the absorbance at the two wavelengths of interest.

\[
A_{430} = (1.20 \times 10^{-4}) \times (0.775 \times 10^3) + (1.80 \times 10^{-4}) \times (8.04 \times 10^3) = 1.54
\]

\[
A_{600} = (1.20 \times 10^{-4}) \times (6.96 \times 10^3) + (1.80 \times 10^{-4}) \times (1.23 \times 10^3) = 1.06
\]

The calculation is the same, with just a different formal concentration. The complete results are in this table.
<table>
<thead>
<tr>
<th>cHIn (M)</th>
<th>[In⁻]</th>
<th>[HIn]</th>
<th>A430</th>
<th>A600</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00 x 10⁻⁴ M</td>
<td>1.20 x 10⁻⁴ M</td>
<td>1.80 x 10⁻⁴ M</td>
<td>1.54</td>
<td>1.06</td>
</tr>
<tr>
<td>2.00 x 10⁻⁴ M</td>
<td>9.27 x 10⁻⁵ M</td>
<td>1.07 x 10⁻⁴ M</td>
<td>0.935</td>
<td>0.777</td>
</tr>
<tr>
<td>1.00 x 10⁻⁴ M</td>
<td>5.80 x 10⁻⁵ M</td>
<td>4.20 x 10⁻⁵ M</td>
<td>0.383</td>
<td>0.455</td>
</tr>
<tr>
<td>0.50 x 10⁻⁴ M</td>
<td>3.48 x 10⁻⁵ M</td>
<td>1.52 x 10⁻⁵ M</td>
<td>0.149</td>
<td>0.261</td>
</tr>
<tr>
<td>0.25 x 10⁻⁴ M</td>
<td>2.00 x 10⁻⁵ M</td>
<td>5.00 x 10⁻⁶ M</td>
<td>0.056</td>
<td>0.145</td>
</tr>
</tbody>
</table>

And here is the graph of the two absorbance functions. Note the non-linearity due to the concentration shifts arising from the equilibrium reaction.
13-14 (a) We measure transmittance as a ratio of power with absorber over power without absorber. Since the same device is used, the light power is proportional to the measured current and hence the ratio is the same.

\[
T = \frac{P}{P_0} = \frac{24.9 \, \mu A}{73.6 \, \mu A} = 0.338 = 33.8\%
\]

(b) Just use the definition of absorbance.

\[
A = \varepsilon b c \quad \varepsilon b \left(\frac{c}{3}\right) = \frac{1}{3} A
\]

\[
A_2 = \frac{1}{3} A_1 = \frac{1}{3} (0.471) = 0.157
\]

\[
T = 10^{-A} = 10^{-0.157} = 0.697 = 69.7\%
\]

(d) Same thing but for twice the absorbance.

\[
A_2 = 2A_1 = 2(0.471) = 0.942
\]

\[
T = 10^{-A} = 10^{-0.942} = 0.114 = 11.4\%
\]

13-30. Qualitative analysis requires narrow slits so that any fine structure in the spectrum can be observed. One tries to provide the most concentrated solution that is appropriate for the job to do qualitative work. On the other hand, quantitative analysis needs to be able to detect weak concentration solutions and as such it opens the slits as wide as possible, without introducing errors so as to increase the signal level. Usually one tunes the spectrometer to the spectral peak where slope is 0 and spectral power is changing slowly with wavelength. One also chooses a wavelength that avoids interfering spectral features.