MID-TERM EXAM
150 Points
Time Limit: 75 minutes

Name: [Key]

MULTIPLE CHOICE SECTION: (50 points; 5 points each)

Provide the single best answer to each of the following:

1. Which of the following would not be a good pair of solvents for liquid-liquid extraction?:
   (a) water/acetone
   (b) water/diethyl ether
   (c) water/pentane
   (d) water/toluene
   (e) water/chloroform

2. Which of the following is the least polar solvent?
   (a) dichloromethane
   (b) toluene
   (c) ethyl acetate
   (d) ethanol
   (e) water

3. Decreasing gas pressure on the gas chromatograph would lead to:
   (a) a leaking septum
   (b) a decrease in retention times
   (c) a decrease in peak areas
   (d) an increase in retention times
   (e) an increase in peak areas

4. Which would not lead to loss of unknown organic compound in the Panacetin Experiment:
   (a) Insufficient washing with dichloromethane during starch (sucrose) separation.
   (b) Not shaking long enough during sodium hydroxide extractions.
   (c) Using too much water during hot gravity filtration.
   (d) Not cooling aqueous solution for long enough prior to vacuum filtration of unknown.
5. The blue granules in your desiccator are desiccant with indicator. The white granules are:
(a) Desiccant without indicator.
(b) Calcium carbonate boiling chips.
(c) Sodium hydroxide pellets.
(d) Filler.

6. Which of the following would have the greatest Rf on a silica gel TLC plate using ethyl acetate as solvent?

(a) ![Chemical Structure](image1)
(b) ![Chemical Structure](image2)
(c) ![Chemical Structure](image3)
(d) ![Chemical Structure](image4)

7. Which of the following would give a positive ferric chloride test?

(a) ![Chemical Structure](image5)
(b) ![Chemical Structure](image6)
(c) ![Chemical Structure](image7)
(d) ![Chemical Structure](image8)
8. Which would you expect to have $d = 1.32$?
   (a) a hydrocarbon/ether blend
   (b) ethyl acetate
   (c) dichloromethane
   (d) toluene

9. Which compound would you expect to have the highest melting point?
   (a) [Image of molecule with H₂N-N structure]
   (b) [Image of molecule with H₂N-N and CH₃ structure]
   (c) [Image of molecule with H₂N-N and NO₂ structure]

10. Which is not an advantage of TLC over column chromatography?
    (a) Easier to perform.
    (b) Better separation of components.
    (c) Easier to visualize colorless components.
    (d) Requires less solvent.

11. (10 points) Provide the complete structures of:
    (i.e., explain any abbreviations used)
    ethyl alcohol
    \[ CH_3CH_2OH \]
    acetone
    \[ OCH_3-C\overset{\sim}{\text{C}}H_3 \]

12. (10 points) State how many significant figures there are in each of the following:
    \[ (0.010 + 0.112) \div 2.1 \]
    4
    3.001
    1.099 + 0.112
    4
    1.099/0.11
    2
    400 \times 10^5
    3
13. (10 points) Draw a balanced equation for the reaction of 2-heptanone with 2,4-DNPH. What is the catalyst we used for this reaction?

14. (5 points) Suppose you are sure your derivative is fairly pure since it has a sharp (narrow) melting point range, but on TLC it gives a long smear whereas the standard samples all give single spots. Suggest what you could do to obtain a more desirable result.

Try diluting the spotting solution to avoid overloading plate.

15. (5 points) Sometimes mixtures of liquids are separated by vacuum distillation (distillation at less than one atmosphere pressure). Briefly explain why this might be advantageous in certain cases:

Lower pressures lead to lower boiling points. Distillation of ordinarily high-boiling substances at lower temperatures leads to less decomposition.
16. (15 points) Suppose phthalic anhydride reacts with \( m \)-anisidine at high temperature to afford N-(3-methoxyphenyl)phthalimide according to the equation below.

\[
\begin{align*}
\text{C}_7\text{H}_4\text{NO} & \quad \text{C}_8\text{H}_4\text{O}_2 \\
\text{NH}_2 & \quad \text{OCH}_3 \\
\Delta \rightarrow & \quad \text{OCH}_3 \\
\end{align*}
\]

You are given the following data:

Atomic weights: H = 1.0; C = 12.0; N = 14.0; O = 16.0

Density of \( m \)-anisidine = 1.096

(a) Balance the equation above

(b) Suppose you started with 23.2 g of phthalic anhydride — how many mmol is this? ANSWER: 157 mmol

\[
\frac{23.2 \text{ g}}{148 \text{ g/mol}} \times 10^2 \frac{\text{mmol}}{\text{mol}} = 157
\]

(c) If the 23.2 g of phthalic anhydride above reacts with 15.0 mL of \( m \)-anisidine, what is the limiting reagent? 15.0 mL \times 1.096 g/mL = 16.4 g

\[
\frac{16.4 \text{ g}}{123.5 \text{ g/mol}} \times 10^2 \frac{\text{mmol}}{\text{mol}} = 133 \text{ mmol}
\]

ANSWER: \( m \)-anisidine

(d) What is the theoretical yield of N-(3-methoxyphenyl)phthalimide —

- In mmol? ANSWER: 133 mmol

\[
133 \text{ mmol} \times 10 \frac{\text{g/mol}}{\text{mmol}} \times 253 \frac{\text{g/mol}}{\text{mol}} = 83.6 \text{ g}
\]

- In grams? ANSWER: 33.6 g
17. (15 points) You perform a reaction which converts aniline (bp 184°) to 4-tert-butyl aniline (bp appx. 300°) and monitor it by gas chromatography.

\[
\begin{array}{c}
\text{aniline} \\
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\end{array} \rightarrow \begin{array}{c}
\text{4-tert-butylaniline} \\
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\end{array}
\]

(a) First you run a GC trace of an authentic mixture of benzene (your GC standard, bp 80°), aniline and 4-tert-butyl aniline, 1.000mL each, in diethyl ether solution. Data appears as follows:

\[
\begin{array}{ccc}
\text{Ret. Time} & \text{Area %} & \text{Correction factor} \\
0.35 & 95.932 & 1.000 \text{ (by definition -- the standard)} \\
1.17 \text{ benzene} & 1.011 & \\
3.82 & 1.319 & 0.7664 \text{ benzene} \\
4.97 & 1.738 & 0.5817 \text{ benzene}
\end{array}
\]

Calculate the volume correction factors for aniline and 4-tert-butyl aniline and enter in the spaces above.

(b) You perform the reaction and do a GC of the crude reaction mixture from the 4-tert-butyl aniline synthesis in diethyl ether solution. Data follows:

<table>
<thead>
<tr>
<th>Ret. Time</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.036</td>
<td>95.186</td>
</tr>
<tr>
<td>2.02</td>
<td>0.086</td>
</tr>
<tr>
<td>2.99</td>
<td>0.137</td>
</tr>
<tr>
<td>3.80</td>
<td>0.400</td>
</tr>
<tr>
<td>4.96</td>
<td>3.991</td>
</tr>
<tr>
<td>5.80</td>
<td>0.200</td>
</tr>
</tbody>
</table>

Then you add 1.00mL benzene to the crude reaction mixture and perform another GC analysis as follows:

\[
\begin{array}{ccc}
\text{Ret. Time} & \text{Area %} & \text{benzene} \\
0.35 & 94.872 & \text{benzene} \\
1.18 & 1.775 & \text{benzene} \\
2.03 & 0.060 & \text{benzene} \\
3.00 & 0.095 & \text{benzene} \\
3.80 & 0.279 \times 0.7664 = 0.214 & \text{benzene} \\
4.98 & 2.780 \times 0.5817 = 1.617 & \text{benzene}
\end{array}
\]

\[
\begin{array}{c}
\frac{1.00\text{mL}}{1.775} = \frac{0.214}{x} \\
x = 0.911 \\
\end{array}
\]

How many mL of 4-tert-butyl aniline were produced in this reaction? 0.911 mL

\[
\begin{array}{c}
\frac{1.00\text{mL}}{1.775} = \frac{0.214}{0.121} \\
x = 0.121 \\
\end{array}
\]

(c) From the data in (b) above, how many mL aniline remained unreacted? 0.121 mL
18. (15 points). Suppose acetonilide and phenacetin have the solubilities in water given below and that their solubilities are independent of one another (i.e., how much of either dissolves does not depend in any way on the presence of the other).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sol. 100° Water (g/100mL)</th>
<th>Sol. 0° Water (g/100mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide</td>
<td>5.0</td>
<td>0.54</td>
</tr>
<tr>
<td>Phenacetin</td>
<td>1.22</td>
<td>0.076</td>
</tr>
</tbody>
</table>

Suppose you have 400 mL of a hot (100°) solution (solution means everything fully dissolved - i.e., not a suspension) which, when chilled (0°) yields a mixture of 1.98g phenacetin and 1.21g acetonilide upon vacuum filtration. Answer the following; show your work.

a) How much acetonilide (in g) must the hot solution have contained?

Answer: \( \frac{3.4}{g} \)  
Cold soln has \( \frac{400 \text{ mL} \times 0.54}{100 \text{ mL}} \) = 2.2 g

\[ \frac{2.2}{+} \frac{1.21}{2.4} \]

b) What is the amount of hot (100°) water needed to dissolve the mixture of solids (that is the mixture obtained by filtration above) such that upon chilling (0°) you will obtain the maximum recovery of pure phenacetin?

Answer: \( 2.2 \times 10^2 \text{ mL} \)  
\( \frac{224 \text{ OK}}{} \)

(c) How much pure phenacetin can you hope to recover when the solution of part (b) is chilled?

Answer: \( 1.81 \text{ g} \)  
\[ \text{how much remains in cold H}_2\text{O?} \]

\[ \frac{2.2 \times 10^2 \text{ mL} \times 0.076}{100 \text{ mL}} = 0.175 \]

\[ 1.98 \text{g} - 0.175 \]

\[ \frac{1.81}{1.81} \]
19. (15 points) The compounds shown below are all solids. Illustrate by means of a detailed flow diagram how you would separate a mixture of the three - isolating each component as a solid. Use the format we have employed all along in lab - structures shown in boxes, etc. The pKa data below may be of some help to you in devising your separation scheme.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
<th>Compound</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH₃</td>
<td>41</td>
<td>H₂O</td>
<td>16</td>
</tr>
<tr>
<td>C₆H₅NH₂</td>
<td>27</td>
<td>H₂CO₃</td>
<td>6</td>
</tr>
<tr>
<td>C₆H₅OH</td>
<td>10</td>
<td>HCO₃⁻</td>
<td>10</td>
</tr>
<tr>
<td>C₆H₅NH₃⁺</td>
<td>5</td>
<td>H₃O⁺</td>
<td>-2</td>
</tr>
<tr>
<td>C₆H₅CO₂H</td>
<td>4</td>
<td>HCl</td>
<td>-7</td>
</tr>
</tbody>
</table>

\( \text{(Ac} = \text{COCH₃)} \)

(or other non-water miscible solvent)

1) DISOLVE IN CH₂Cl₂
2) EXTRACT w/ aq. NaHCO₃

\[ \text{Aq.} \]
\[ \text{Org.} \]

\[ \text{NaCl} \]

\[ \text{COOH} \]

\[ \text{NHCOCH₃} \]

\[ \text{NHCOCH₃} \]

\[ \text{Ac} \]

\[ \text{COCH₃} \]

\[ \text{OCH₂CH₃} \]

\[ \text{OH} \]

\[ \text{NaOH} \]

\[ \text{HCl} \]

\[ \text{H₂CO₃} \]

\[ \text{HCO₃⁻} \]

\[ \text{H₃O⁺} \]

\[ \text{HCl} \]

\[ \text{H₂CO₃} \]

\[ \text{HCO₃⁻} \]

\[ \text{H₃O⁺} \]

\[ \text{HCl} \]

\[ \text{NaCl} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]

\[ \text{NHAC} \]