Worked Solutions to the Problems

Important general remark:
For the sake of clarity, most answers are more elaborate than strictly necessary. In many cases the explaining text can be replaced by arrows, e.g. ⇒.

Problem 1 Production of Ammonia

1-1  \( n[H_2, \bigodot] = 3 \times 1000:2 = 1500 \text{ mol s}^{-1} \)
\( n[N_2, \bigotimes] = 1000:2 = 500 \text{ mol s}^{-1} \)
\( n[CH_4, \S] = 1000:2 = 500 \text{ mol s}^{-1} \)
\( n[H_2O, \$] = 1000:2 = 500 \text{ mol s}^{-1} \)
\( n[CO, \%] = 1000:2 = 500 \text{ mol s}^{-1} \)
\( n[O_2, &] = \frac{1}{4} \times 1000:2 = 125 \text{ mol s}^{-1} \)
\( n[CO, '] = n[CO, \%] - 2 \times n[O_2, &] = 250 \text{ mol s}^{-1} \)

1-2  \( n[N_2, \bigotimes] + n[H_2, \bigodot] = 2 \times n[NH_3, \bigodot] = 2 \times n[NH_3, \S] \)
\( n[N_2, \bigotimes] = 500 \text{ mol s}^{-1} \quad n[H_2, \bigodot] = 1500 \text{ mol s}^{-1} \)

1-3  \( \Delta G_r = 2G(NH_3) - G(NH_2) - 3 \times G(H_2) = [2 \times 24.4 + 8.3 + 3 \times 8.3] \times 10^3 = 82 \times 10^3 \text{ J mol}^{-1} \)

1-4  \( \Delta G_r = -RT \ln K_r, \quad K_r = 4.4 \times 10^{-6} \)

1-5  \( p_{N_2} = (\frac{1}{4}) \times (1-x) \times p_{tot} \)
\( p_{H_2} = (\frac{3}{4}) \times (1-x) \times p_{tot} \)

1-6  \( K_r = \frac{x^2}{(1-x)^2} \left( \frac{4^4}{3^4} \right) \left( \frac{p_0}{p_{tot}} \right)^2 \)

1-7  \( \frac{x^2}{(1-x)^2} = K_r \left( \frac{3^3}{4^4} \right) \left( \frac{p_{tot}}{p_0} \right)^2 = 0.0418 \quad \rightarrow \quad x = (1-x) \sqrt{0.0418} \)
\( -0.204x^2 + 1.408x - 0.204 = 0 \quad \rightarrow \quad x = 0.148 \)

Problem 2 Myoglobin for Oxygen Storage

2-1  Take at the X-axis 100, this corresponds with 0.5 at the Y-axis, thus
\( 0.5 = \frac{100}{100 + K_p} \quad 50 + 0.5 \times K_p = 100 \quad K_p = 100 \text{ Pa} \)

2-2  Volume of Mb: \( V_{Mb} = 0.5 \times 4.5 \text{ nm} \times 3.5 \text{ nm} \times 2.5 \text{ nm} = 19.6875 \text{ nm}^3 = 19.6875 \times 10^{-27} \text{ m}^3 \)
Molecular weight of Mb = \( V_{Mb} \times N_A = 19.6875 \times 10^{-27} \times 6.02 \times 10^{23} = 16.6 \text{ kg mol}^{-1} \)
2-3 1 kg Mb is $1/16.6$ mol; 20% is $0.2/16.6 = 0.012$ mol kg$^{-1}$

2-4 $400$ kJ mol$^{-1}$ → $400,000 \times 0.012$ J kg$^{-1}$ of muscle tissue. $W = J \text{ s}^{-1} \Rightarrow$ per second per kg of muscle tissue $0.5$ J. Time $= \frac{400,000 \times 0.012}{0.5} = 9,600$ s = 2 hours and 40 minutes.

2.5 $(\text{CH}_2)_n (\text{CO}_2)_3 \text{ H}_2 + (4.5n + 9.5) \text{ O}_2 \rightarrow (3n + 9) \text{ CO}_2 + (3n + 7) \text{ H}_2\text{O}$

**Problem 3  Lactose Chemistry**

3-1

\[
\begin{align*}
\text{D-galactose} & \\
\text{D-glucose}
\end{align*}
\]

3-2

Answer box a.  
Answer box b.  
Answer box c

3-3

\[
\begin{align*}
\text{Sorbitol} & \\
\text{Galactitol} & \quad \text{Optically active: yes / no}
\end{align*}
\]
Lactitol is a mixture of the furanose and pyranose form in the ratio 4 : 6. When a student gives either the furanose or the pyranose form, he/she will receive full marks.

Problem 4 Atom Mobility (Dynamics) in Organic Compounds

4-1 \( a >> c, \ d > b \)

4-2 \( y > x \)

4-3 No

Problem 5 Towards Green Chemistry: The E-factor

5-1 The molecular weight of methyl methacrylate = 100
The molecular weight of NH₄HSO₄ = 115

Classical route: Atom utilization = \( \frac{100}{100+115} = 0.47 \) or 47% \( E \)-factor = \( \frac{115}{100} = 1.15 \)
Catalytic route: Atom utilization = \( \frac{115}{115} = 1 \) or 100% \( E \)-factor = \( \frac{0}{100} = 0 \)

5-2 Classical chlorohydrin route: Atom utilization = \( \frac{44}{173} = 0.25 \) or 25%
Modern petrochemical route: Atom utilization = \( \frac{44}{44} = 1 \) or 100%

Classical route: \( E \)-factor = \( \frac{133.4}{39.6} = 3.37 \)
product : \( 44 - 10\% = 39.6 \)
by-products : \( 111 + (10\% \text{ of } 62) + (18 - 10\%) = 111 + 6.2 + 16.2 = 133.4 \)
Modern route: \( E \)-factor = \( \frac{18.6}{37.4} = 0.49 \)
product : \( 44 - 15\% = 37.4 \)
by-products : \( 2 \text{ CO}_2 + 2 \text{ H}_2\text{O} \) per mole of \( \text{C}_2\text{H}_4 \) (15%) \( \Rightarrow 2 \times 15\% \text{ of } 44 + 2 \times 15\% \text{ of } 18 = 18.6 \)

Problem 6 Selective Solubility

6-1 The relevant equations are:
\[
\begin{align*}
\text{Ba}^{2+} \text{(aq)} + \text{SO}_4^{2-} \text{(aq)} & \rightleftharpoons \text{BaSO}_4 \text{(s)} \\
\text{Sr}^{2+} \text{(aq)} + \text{SO}_4^{2-} \text{(aq)} & \rightleftharpoons \text{SrSO}_4 \text{(s)}
\end{align*}
\]

Precipitation of \( \text{BaSO}_4 \) will start, when
\[
[\text{SO}_4^{2-}] = \frac{K_{sp}(\text{BaSO}_4)}{[\text{Ba}^{2+}]} = \frac{1 \times 10^{-10}}{10^{-2}} = 10^{-8} \text{ M} \quad (1)
\]

Precipitation of \( \text{SrSO}_4 \) will start, when
\[ [\text{SO}_4^{2-}] = \frac{K_{sp}(\text{SrSO}_4)}{[\text{Sr}^{2+}]} = \frac{3 \times 10^{-7}}{10^{-2}} = 3 \times 10^{-6} \text{M} \] (2)

If there are no kinetic complications (for example when the formation of BaSO\(_4\) would be very slow) first BaSO\(_4\) will be formed. This results in a decrease of the concentration of Ba\(^{2+}\) ions. If the concentration SO\(_4^{2-}\) satisfies equation (2), the concentration of Ba\(^{2+}\) can be calculated from the formula:

\[ K_{sp}(\text{BaSO}_4) = 1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \]

At the starting point the concentration of Ba\(^{2+}\) was \(10^{-2}\) M. This means that the loss amounts to \(\frac{1}{3} \times 10^{-5} \times 100\% = 0.033\%\)

*The separation meets the criterion.*

6-2 The following equilibrium reactions have to be considered:

\[
\begin{align*}
\text{AgCl (s)} & \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \\
\text{Ag}^+ (\text{aq}) + 2 \text{NH}_3 (\text{aq}) & \rightleftharpoons \text{Ag(NH}_3)_2^+ (\text{aq})
\end{align*}
\]

Total: \(\text{AgCl (s)} + 2 \text{NH}_3 (\text{aq}) \rightleftharpoons \text{Ag(NH}_3)_2^+ (\text{aq}) + \text{Cl}^- (\text{aq})\)

\[ K_{overall} = K_{sp} K_f = \frac{[\text{Ag(NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = 1.7 \times 10^{-10} \times 1.5 \times 10^{-7} = 2.6 \times 10^{-3} \]

If \(x\) is the molar solubility of AgCl (mol L\(^{-1}\)) then the changes in concentration of AgCl as the result of the formation of the complex ion are

\[
\text{AgCl (s)} + 2 \text{NH}_3 (\text{aq}) \rightleftharpoons \text{Ag(NH}_3)_2^+ (\text{aq}) + \text{Cl}^- (\text{aq})
\]

Starting point: \(1.0\ M\) \hspace{2cm} \(0.0\ M\) \hspace{2cm} \(0.0\ M\)

Change: \(-2x\ M\) \hspace{2cm} \(+x\ M\) \hspace{2cm} \(+x\ M\)

Equilibrium: \((1.0 - 2x)\ M\) \hspace{2cm} \(+x\ M\) \hspace{2cm} \(+x\ M\)

\(K_f\) is quite large, so most of the Ag\(^{+}\) ions exist in the complexed form.

In absence of NH\(_3\) at equilibrium holds \([\text{Ag}^+] = [\text{Cl}^-]\)

Complex formation leads to: \([\text{Ag(NH}_3)_2^+] = [\text{Cl}^-]\)

\[ K_{overall} \text{ can be written as:} \]

\[ K_{overall} = \frac{x \cdot x}{(1.0 - 2x)^2} \]

\[ 2.6 \times 10^{-3} = \frac{x^2}{(1.0 - 2x)^2} \]

or \(0.051 = \frac{x}{(1.0 - 2x)}\)

and \(x = 0.046\ M\)

*This result means that 4.6 \times 10^{-2} M of AgCl dissolves in 1 L of 1.0 M NH\(_3\). Thus the formation of the complex ion Ag(NH\(_3\))\(_2^+\) enhances the solubility of AgCl, because in pure water the molar solubility amounts to only 1.3 \times 10^{-5} M.*

**Problem 7** UV-spectrometry as an Analytical Tool

7-1 2% decrease in light intensity implies: \(\text{I}_0/\text{I} = 98/100\) and \(A = -10\log 98/100 = 0.01\)

This absorption corresponds with \(0.01 = 10500 \times c_{\text{min}} \times 1 \Rightarrow c_{\text{min}} = 0.95 \times 10^{-6} \text{mol L}^{-1}\).

7-2 2% light throughput means that: \(\text{I}_0/\text{I} = 2/100\) and \(A = -10\log 100/2 = 2 - 0.3010 = 1.6990\)

For ferroin this absorption at 512 nm corresponds with:

\(1.6990 = 10500 \times c_{\text{max}} \times 1 \Rightarrow c_{\text{max}} = 1.618 \times 10^{-4} \text{mol L}^{-1}\).

7-3 Minimum in curve at \(x_M = 0.33\): \(c_M = 0.33 c_M + 0.33 c_L\) or \(0.67 c_M = 0.33 c_L\)

The composition of the complex is ML\(_2\)
Problem 8  Reaction Kinetics

8-1  Due to the Arrhenius equation: \( \log k = \log A - \frac{E_a}{2.3RT} \)
we can substitute the values of \( k \) and \( T \):

\[
\log k_1 = \log A - \frac{E_a}{2.3R T_1} \quad \text{and} \quad \log k_2 = \log A - \frac{E_a}{2.3R T_2}
\]

Subtraction gives:

\[
\log k_1 - \log k_2 = -\frac{E_a}{2.3R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\[
E_a = 2.3R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \log \left( \frac{k_2}{k_1} \right) = 2.3 \times 8.314 \left( \frac{300 \times 400}{400 - 300} \right) \log \frac{4.9 \times 10^{-4}}{2.6 \times 10^{-3}}
\]

\[
E_a = 98.225 \text{ kJ mol}^{-1}
\]

8-2  The slow step is rate determining; this is the second reaction.

The expression for \( s \) is:

\[
\frac{d[\text{NO}_2]}{dt} = k_2 [\text{NO}_3][\text{NO}]
\]

The equilibrium gives:

\[
K = k_1 k_2 = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}
\]

Rewritten this is: \([\text{NO}_3] = K[\text{NO}][\text{O}_2] \]

Substitution gives for \( s \): \( s = k_2 K[\text{NO}]^2[\text{O}_2] \)

8-3  b. The mechanism is correct.

Problem 9  Bonding and Bond Energies

9-1  Born-Haber cycle for the dissociation of NaCl into Na + Cl:

\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-
\]

\[
\text{Na}^+ + \text{Cl}^- \rightarrow \text{Na} + \text{Cl}
\]

The energy loss in the first step is 464 kJ mol\(^{-1}\).

The energy gain in the second step is -(I.E. of Na + E.A. of Cl) = -136 kJ mol\(^{-1}\).

Overall loss = dissociation energy = 328 kJ mol\(^{-1}\).

9-2  Born-Haber cycle for the dissociation of CaCl\(_2\) into Ca + 2 Cl:

\[
\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2 \text{Cl}^-
\]

\[
\text{Ca}^{2+} + 2 \text{Cl}^- \rightarrow \text{Ca} + 2 \text{Cl}
\]

The (ionic) bond energy of Ca\(^{2+}\)Cl\(^-\) = -429 x 2 / 0.91 = -943 kJ mol\(^{-1}\).

(The measured value for CaCl is -429, but the charge of Ca is now +2 and the bond length has decreased by a factor of 0.91).
The energy loss in the first step = -(bond energy of CaCl2) = 2 x 942 minus the Cl-Cl repulsion. 
The Cl-Cl repulsion is (429 / 2) x (1 / 0.91) = 236 kJ mol⁻¹, so the energy loss in the first step = 
+1650 kJ mol⁻¹. 
The energy gain in the second step is –(2 x E.A. of Cl + total I.E. of Ca) = -1020 kJ mol⁻¹. 
Dissociation energy into atoms = 630 kJ mol⁻¹.

Problem 10  The Nature of Phosphorus

10-1

**Spatial structures**  
<table>
<thead>
<tr>
<th>Compound A</th>
<th>Compound B</th>
</tr>
</thead>
</table>
| ![Structure A](structure_a.png)  
| ![Structure B](structure_b.png) |

P is pseudo-asymmetric center  
\[ \Rightarrow \] diastereomeric structures  
\[ \Rightarrow \] different ³¹P signals  

P is not an asymmetric center in (S,S) and (R,R); enantiomers have same ³¹P signals (this is the signal in the middle)

**Fischer projections**

<table>
<thead>
<tr>
<th>Compound A</th>
<th>Compound B</th>
</tr>
</thead>
</table>
| ![Fischer A](fischer_a.png)  
| ![Fischer B](fischer_b.png) |

(Hint: You may wish to compare the 2 meso structures of 2,3,4-trihydroxypentane)

10-2

C: (CH₃O)₂P-OH  
D: [(CH₃)₂CHO]-P-OH  
E: (Ph-(CH₃)CH₂O)₂P-OH

one signal  
one signal  
three signals as in 10-1 ratio 1:2:1 (meso-I : RR + SS : meso-II)

10-3

![NMR spectra](nmr_spectra.png)

CH₃CH₂CH₃

(b) CH₃

(a)
10-4

![Chemical structures]

*meso* not chiral
not suitable as catalyst

(R,R) will give D(+) DOPA
F is (S,S) and gives L(-) DOPA

It should be noted that this is extra information, which was not part of the question.
The essence is that the nonchiral *meso* isomer is recognized

10-5
Option 1 and option 3; P is the asymmetric center.
Phosphorus compounds are pyramidal and they are configurationally very stable (no inversion).

10-6

![Chemical structures]

*meso* compound
not suitable as chiral catalyst

(S,S) will give D(+) DOPA
G is (R,R) and gives L(-) DOPA

10-7
Option 2.

10-8
One signal, substituents have the same chirality (R). No splitting.

**Problem 11 Optical purity**

11-1 From P

![Chemical structures]

11-2 Option 2

11-3

![NMR spectra]

(a) ratio 1:3
(b) ratio 1:1:3:3

Long range coupling of the CH$_3$O protons with the CH is very small (close to zero). The essence of the question is to indicate the peak ratio's.
Problem 12  Polylactic Acid

12-1

\[ 4 \text{H}_2\text{C} \cdot \text{CH}_2 \cdot \text{COOH} \rightarrow \text{HO} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} + 3 \text{H}_2\text{O} \]

12-2

\[ 2 \text{H}_2\text{C} \cdot \text{O} \cdot \text{O} \cdot \text{O} + \text{H}_2\text{O} \rightarrow \text{HO} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \]

12-3

The aim here is working with reactive groups.

\[ K = \frac{[\text{Ester}][\text{Water}]}{[\text{OH}][\text{COOH}]} = \frac{p^2U^2}{(1-p)^2U^2} = 4 \Rightarrow \frac{p}{1-p} = 2 \Rightarrow p = \frac{2}{3} \Rightarrow P = \frac{1}{1-p} = 3 \]

12-4

First the remaining amount of water at a chain length of 100 units is calculated:

\[ K = 4 = \frac{[\text{Ester}][\text{Water}]}{[\text{OH}][\text{COOH}]} = \frac{p^2UW}{(1-p)^2U^2} \Rightarrow W = 0.0040404 \text{ mol} \]

\[ U = 10 \text{ and } P = 100 = \frac{1}{1-p} \Rightarrow p = 0.99 \]

Water formed: \( pU = 0.99 \times 10 = 9.9 \text{ mol} \)

Water removed: \( 9.9 - 0.0040404 = 9.896 \text{ mol} = 178 \text{ g of } \text{H}_2\text{O} \)

Problem 13  A Chemical Puzzle

13-1  Nitrogen atom

13-2  -NH₂ or -NHR

13-3  -CH₂CH₃

13-4  -NO₂
13-5  No AgNO₃ reaction \( \rightarrow \) no aliphatic chlorine substituent

\[
\begin{align*}
\text{Cl} & \quad \text{NO}_2 \\
\text{H} & \quad \text{N} - \text{CH}_2\text{CH}_3
\end{align*}
\]

\[\text{or}\]

\[
\begin{align*}
\text{Cl} & \quad \text{N} - \text{CH}_2\text{CH}_3 \\
\text{H} & \quad \text{NO}_2
\end{align*}
\]

**Problem 14  Delft Blue and Vitamin B 12**

14-1  Electron configuration of Co^{2+}: 1s²2s²2p⁶3s²3p⁶3d⁷

14-2

14-3  If 90% of the light is absorbed, the transmission T is 0.1 (10% transmitted). Fill out:

\[
A = -\log \frac{I}{I_0} \quad A = -\log 0.1 = 20 \quad \Rightarrow \quad c = 1 / (20 \times 0.1) = 0.5 \text{ M}
\]

14-4  \( r(\text{Co}^{3+}) < r(\text{Co}^{2+}) < r(\text{Co}^+) \).

14-5  All three oxidation states have unpaired d-electrons (\( d^6 \), \( d^7 \) and \( d^8 \)) in the high spin configuration and thus for all three oxidation states an EPR spectrum can be measured.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>EPR Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co⁺</td>
<td>yes ( \notin )</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>yes ( \notin )</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>yes ( \notin )</td>
</tr>
</tbody>
</table>

14-6  \[ (3 \times 10^{16}) / (58.93 \times 1.67 \times 10^{-27}) = 3 \times 10^{19} \text{ Co ions} \]

14-7  1 2 3 4 5 6 7 8

**Problem 15  Synthesis of a local anaesthetic**

15-1
Problem 16  Structure of peptides

16-1

\[
\begin{align*}
FA & : \text{H}_2\text{N} & \text{N} & \text{C} & \text{O} & \text{H} \\
AF & : \text{H}_2\text{N} & \text{N} & \text{C} & \text{O} & \text{H} & \text{Ph}
\end{align*}
\]

FF

AA

16-2  This is a nucleophilic aromatic substitution

\[ \text{NO}_2\text{C}_6\text{H}_4\text{F} + 2\text{H}_2\text{NR} \rightarrow \text{NO}_2\text{C}_6\text{H}_4\text{NHR} + \text{RNH}_3\text{F} \]

16-3

GALF

GLAF

Only the positions of G and F are determined, the other two are in the middle, but no information is provided if this is AL or LA.

Problem 17  Ribonuclease

17-1

\[
\begin{align*}
\text{S-S} & \quad + \text{HSCH}_2\text{CH}_2\text{OH} \\
\text{A First product} & \quad \text{S-SCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

\[ + \text{HSCH}_2\text{CH}_2\text{OH} \quad \text{B Final product} \quad + \text{HOCH}_2\text{CH}_2\text{S-SCH}_2\text{CH}_2\text{OH}
\]

17-2  Electrostatic forces, hydrogen bonds and van der Waals forces.

17-3  There are 8 Cys residues. The probability that any residue is coupled to its correct partner is 1:7. Next there remain 6 residues to consider. The chance that any of those is coupled to its correct partner is 1:5, etc. Therefore the fraction of active molecules is: 1/7 x 1/5 x 1/3 x 1/1 = 1/105.
Problem 18  Enzyme Kinetics

18-1  \( K_A = [E][A]/[EA] \)
\( K_B = [E][B]/[EB] \)
\( K'_A = [EB][A]/[EAB] \)
\( K'_B = [EA][B]/[EAB] \)

18-2  \( v = \frac{V_{\text{max}}}{1 + K_A/[A]} \)

18-3  If \( [A] \rightarrow 0 \) then \( K_A/[A] >> 1 \) and \( v = V_{\text{max}} [A]/K_A \). This corresponds with first order kinetics.

18-4  If \( [A] \rightarrow \infty \) then \( K_A/[A] << 1 \) and \( v = V_{\text{max}} \). This corresponds with zero order kinetics.

18-5  A high affinity corresponds with a small \( K_A \).
\( v = \frac{1}{2} V_{\text{max}} \) when \( [A] = K_A \).

Problem 19  Dendrimers: Tree-like Macromolecules

19-1  a.  \( \text{NH}_3 + \text{H}_2\text{C}=\text{CHCN} \rightarrow \text{N(CH}_2\text{CH}_3\text{C}=\text{N)}_3 \)

b.  \( \text{H}_2/\text{Pd} \rightarrow \text{N(CH}_2\text{CH}_3\text{CH}_2\text{NH}_2)_3 \)

c.  \( \text{N(CH}_2\text{CH}_3\text{CH}_2\text{N(CH}_2\text{CH}_3\text{N)}_3 \)

d.  \( \text{R} = \text{Same chains at these positions} \)
19-2 After the first cycle there are 3 amine groups (see answer). Then, the number of amine groups is doubled after each cycle (see answer 19-1c and d). Thus, after 5 full cycles, the total number of amine end-groups is 48.

19-3 a. After 5 full cycles $3 + (3 \times 2) + (6 \times 2) + (12 \times 2) + (24 \times 2) = 93$ moles of H$_2$ have been used.
b. Idem for acrylonitrile (93 moles).
c. Radius is diameter/2 = 50/2 = 25 Å. Volume: $4/3 \pi r^3$.

Problem 20 Carvone

20-1 Number of C-atoms: $n_C = (M_r \times \%C)/12 = (150 \times 0.8)/12 = 10$

Number of H-atoms: $n_H = (M_r \times \%H)/1 = (150 \times 0.0933)/1 = 14$

Number of O-atoms: $n_O = (M_r \times \%O)/16 = (150 \times 0.1067)/16 = 1$

20-2 A fully saturated hydrocarbon with 10 carbon atoms has the formula C$_{10}$H$_{22}$
Carvone has the formula C$_{10}$H$_{14}$O, for calculation of the unsaturation, the O is not relevant. Subtraction gives a shortage of 8H for carvone, this is equivalent to 4 unsaturated sites (either double bonds or rings).

20-3 C=O group

20-4 -OH (-CO$_2$H is not a correct answer! Carvone only has one oxygen atom). There is no relevant strong absorption above 3000 cm$^{-1}$. That means no -OH group present.

20-5 Carvone is a 6-membered ring, this leaves three more unsaturated sites.
The IR show the presence of a C=O group, this leaves 2 more unsaturated sites, these must be C=C bonds.
The strong UV-absorption suggests a conjugated system, most likely C=C-C=O.
The singlets at 1.63 and 1.68 ppm in the $^1$H-NMR are two –CH$_3$ groups with no vicinal coupling.
The multiplet from 1.9-2.2 ppm consists of a –CH and a –CH$_2$- group (from the question)
The multiplet from 2.2-2.5 ppm is most likely a –CH$_2$- group with many neighboring H-atoms.
The doublets at 4.75 and 4.93 ppm are indicative of two =CH- groups, it might even be =CH$_2$ given the small and identical coupling constants (see the enlarged area).
The triplet at 6.73 ppm is indicative of a =CH- group which is situated next to a –CH$_2$- group.
Combining all this information with the given 1,2,4 substitution pattern gives the structure below as the most likely structure of carvone.

\[
\begin{align*}
\text{CH}3 & \\
\text{HC} & \text{C} \\
\text{H}2 & \text{C} \\
\text{H} & \text{C} \\
\text{H}3 & \text{C} \\
\text{HC} & \text{C} \\
\text{H}2 & \text{C} \\
\text{H} & \text{C} \\
\text{H}2 & \text{C} \\
\end{align*}
\]

Problem 21 Experiment

21-1 At the cathode oxygen is reduced to hydroxide, i.e., half-reaction (1)

21-2 At the anode hydrogen is oxidized to water, i.e. reaction (2).

21-3 Anode: $2$ H$_2$ (g) $\rightarrow$ $4$ e$^-$ + $4$ H$^+$
Cathode: $4$ H$^+$ + $4$ e$^-$ + O$_2$ (g) $\rightarrow$ $2$ H$_2$O (g)
Fuel cell reaction: $2$ H$_2$ (g) + O$_2$ (g) $\rightarrow$ $2$ H$_2$O (g)

21-4 The standard electrode potential of the reaction at the anode = 0 V
The standard electrode potential of the reaction at the cathode = + 1.23 V
The total number of electrons transferred in the reaction = 4
\[ \Delta G_o = -n \cdot F \cdot E = -4 \times 96487 \cdot C \times (1.23 \text{ V} - 0 \text{ V}) = -474,716 \text{ J} \]

21-5 \[ \begin{align*} &\text{CH}_4 (g) + 2 (\text{O}^{2-}, \text{electrolyte}) \rightarrow 2 \text{H}_2\text{O} (g) + \text{CO}_2 (g) + 4 \text{e}^- \\ &\text{O}_2 (g) + 4 \text{e}^- \rightarrow 2 (\text{O}^{2-}, \text{electrolyte}) \\ &\text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (g) + \text{CO}_2 (g) \end{align*} \]

21-6 Anode: \[ 2 \text{H}_2 (g) + 2 \text{CO}_3^{2-} (l) \rightarrow 2 \text{H}_2\text{O} (g) + 2 \text{CO}_2 (g) + 4 \text{e}^- \]
Cathode: \[ \text{O}_2 (g) + 2 \text{CO}_2 (g) + 4 \text{e}^- \rightarrow 2 \text{CO}_3^{2-} (l) \]
Fuel-cell reaction is: \[ 2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (g) \]

### Problem 22 Experiment

22-1 Volume SDS micelle = \( \frac{4}{3} \pi (16.6 + 4.6)^3 = 39911.33 \text{ Å}^3 \)
Volume of the core = \( \frac{4}{3} \pi (16.6)^3 = 19160.77 \text{ Å}^3 \)
Volume of the Stern layer = volume SDS micelle – volume core = 20750.56 Å³

22-2 The equilibrium constant \( K_M = \frac{[M]}{[S]^n[B]^n} \)

Substitution in \( \Delta G_M \):

\[ \Delta G_M = -\frac{RT}{n} \ln \frac{[M]}{[S]^n[B]^n} = -\frac{RT}{n} \ln([M] \cdot n\ln[S] \cdot n\ln[B]) \]

At the CMC there are no micelles: \([M] = 0\) and \([S] = [B]\) thus: \( \Delta G_M = 2 RT \ln[S] \)
For SDS: \( \Delta G_M = -23.86 \text{ kJ mol}^{-1} \)
For TDAB: \( \Delta G_M = -21.01 \text{ kJ mol}^{-1} \)

22-3 Average number of amphiphiles per micelle = relative micelle mass / relative amphiphile mass
For SDS (\( M_r = 288 \)): \( n = 18 \times 10^3 / 288 = 62.5 \)
For TDAB (\( M_r = 308 \)): \( n = 15 \times 10^3 / 308 = 48.7 \)

### Problem 23 Experiment

23-1 \( \text{BBr}_3 + \text{PBr}_3 + 3 \text{H}_2 \rightarrow \text{BP} + 6 \text{HBr} \)

23-2

\[ \text{Br} \quad 120^\circ \]
\[ \text{Br} \quad \text{Br} \]

planar and trigonal

\[ \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \]

trigonal pyramidal

23-3

Zinc blende structure
A FCC-structure of the B-atoms and that gives:
Angular points: $8 \times \frac{1}{8} = 1$
Planes: $6 \times \frac{1}{2} = 3$
Total = 4
In each cell 4 phosphorus atoms are present which are tetrahedrally surrounded by boron.

Atom masses of boron and phosphorus are 11 and 31, respectively.

$$R = \frac{m}{V} = \frac{n M_m}{N \cdot a^3} = \frac{4 \times 42}{6.022 \cdot 10^{23} \left(4.78 \cdot 10^{-10}\right)} = 2554 \text{ kg/m}^3$$

Distance B-P is $\frac{1}{2} \times 3^{1/2} \times \frac{1}{3} \times a = 2.069 \text{ Å}$

Lattice energy of BP:
$$\frac{1390 \times 3 \times 3 \times 1.638Z}{2.069} \frac{Z \cdot e^2}{6} = 848 \text{kJ/mol}$$

The order of the reaction is 2
$$r = k [\text{BBR}_3][\text{PBr}_3]$$

$$k_{880} = \frac{r_{880}}{[\text{BBR}_3][\text{PBr}_3]} = 16.9 \times 10^8 \text{ / mol}^{-1} \text{L}^2 \text{mol}^{-1} \text{s}^{-1}$$

$$k_{880} = \frac{r_{880}}{[\text{BBR}_3][\text{PBr}_3]} = 9.679 \times 10^7 \text{ / mol}^{-1} \text{L}^2 \text{mol}^{-1} \text{s}^{-1}$$

$$\Delta H = -R \ln \left(\frac{k_2}{k_1}\right) \times (\frac{1}{T_2} - \frac{1}{T_1})^{-1}$$

$$T_1 = 880 + 273 = 1073 \text{ K} \text{ and } T_2 = 880 + 273 = 1153 \text{ K}$$

$$\Delta H = -R \ln \left(\frac{9679}{2272}\right) \times (\frac{1}{1153} - \frac{1}{1073})^{-1} = 186 \text{kJ mol}^{-1}$$

- the yield will be ca. 75%, mp =104-105°C

**Problem 24** Experiment

- **tert-butyl cation:** $(\text{CH}_3)_3\text{C}^+$

**Problem 25** Experiment

- 2.5 mmole of diacid, ca 5 mL of 1.0 M NaOH is needed in procedure 1; ca 2.5 mL in procedure 2.
- color changes: colorless to violet in procedure 1, red to yellow in procedure 2.

**Problem 25** Experiment

- 2.5 mmole of diacid, ca 5 mL of 1.0 M NaOH is needed in procedure 1; ca 2.5 mL in procedure 2.
- color changes: colorless to violet in procedure 1, red to yellow in procedure 2.

25-1 **a:** $pK_a$ phenolphthalein $pK_a > 6.1$

25-1 **b:** $pK_a$ methylorange $pK_a > 1.8$

25-2 Explanation according to option a
Problem 26 Experiment
- the yield will be ca 360 mg, m.p. = 125°C

\[
\text{C}_6\text{H}_5\text{C}=\text{O} + \text{H}_2\text{NC}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH}\equiv\text{NC}_6\text{H}_5
\]

Problem 27 Experiment
- The yield will be ca. 64%, m.p. = 103.5-104.5°C

27-1 From the experiment
27-2 From the experiment
27-3 Catalytic cycle

Problem 29 Experiment
29-1 Yes
29-2 optically enriched
29-3 optically pure
29-4 When the enzyme is highly selective: no
When the enzyme is not highly selective: yes. In this case the preferred enantiomer will be hydrolyzed very fast and the other enantiomer will be converted more slowly.