

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. \Rightarrow .

Problem 1 Production of Ammonia

- 1-1 $\eta[\text{H}_2, \textcircled{2}] = 3 \times 1000:2 = 1500 \text{ mol s}^{-1}$
 $\eta[\text{N}_2, \textcircled{6}] = 1000:2 = 500 \text{ mol s}^{-1}$
 $\eta[\text{CH}_4, \textcircled{1}] = 1000:2 = 500 \text{ mol s}^{-1}$
 $\eta[\text{H}_2\text{O}, \textcircled{1}] = 1000:2 = 500 \text{ mol s}^{-1}$
 $\eta[\text{CO}, \textcircled{3}] = 1000:2 = 500 \text{ mol s}^{-1}$
 $\eta[\text{O}_2, \textcircled{4}] = \frac{1}{4} \times 1000:2 = 125 \text{ mol s}^{-1}$
 $\eta[\text{CO}, \textcircled{5}] = \eta[\text{CO}, \textcircled{3}] - 2 \eta[\text{O}_2, \textcircled{4}] = 250 \text{ mol s}^{-1}$
- 1-2 $\eta[\text{N}_2, \textcircled{7}] + \eta[\text{H}_2, \textcircled{7}] = 2 \eta[\text{NH}_3, \textcircled{7}] = 2 \eta[\text{NH}_3, \textcircled{8}]$
 $\eta[\text{N}_2, \textcircled{7}] = 500 \text{ mol s}^{-1} \quad \eta[\text{H}_2, \textcircled{7}] = 1500 \text{ mol s}^{-1}$
- 1-3 $\Delta G_r = 2G(\text{NH}_3) - G(\text{N}_2) - 3 G(\text{H}_2)$
 $\Delta G_r = [2 \times 24.4 + 8.3 + 3 \times 8.3] \times 10^3 = 82 \times 10^3 \text{ J mol}^{-1}$
- 1-4 $\Delta G_r = -RT \ln K_r, \quad K_r = 4.4 \times 10^{-6}$
- 1-5 $p_{\text{N}_2} = (1/4) (1-x) p_{\text{tot}}$
 $p_{\text{H}_2} = (3/4) (1-x) p_{\text{tot}}$
- 1-6 $K_r = \frac{x^2}{(1-x)^4} \left(\frac{4^4}{3^3} \right) \left(\frac{p_0}{p_{\text{tot}}} \right)^2$
- 1-7 $\frac{x^2}{(1-x)^4} = K_r \left(\frac{3^3}{4^4} \right) \left(\frac{p_{\text{tot}}}{p_0} \right)^2 = 0.0418 \rightarrow x = (1-x)^2 \sqrt{0.0418}$
 $-0.204x^2 + 1.408x - 0.204 = 0 \rightarrow x = 0.148$

Problem 2 Myoglobin for Oxygen Storage

- 2-1 Take at the X-axis 100, this corresponds with 0.5 at the Y-axis, thus
 $0.5 = \frac{100}{100 + K_p} \quad 50 + 0.5 K_p = 100 \quad K_p = 100 \text{ Pa}$
- 2-2 Volume of Mb: $V_{\text{Mb}} = 0.5 \times 4.5 \text{ nm} \times 3.5 \text{ nm} \times 2.5 \text{ nm} = 19.6875 \text{ nm}^3 = 19.6875 \times 10^{-27} \text{ m}^3$
Molecular weight of Mb = $V_{\text{Mb}} \times N_A = 19.6875 \times 10^{-27} \times 6.02 \times 10^{23} = 16.6 \text{ kg mol}^{-1}$

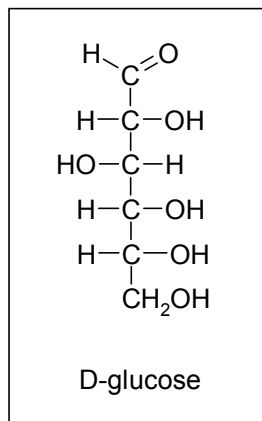
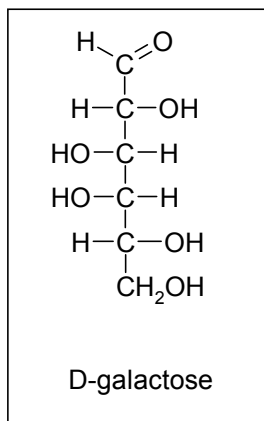
2-3 1 kg Mb is 1/16.6 mol; 20% is $0.2/16.6 = 0,012 \text{ mol kg}^{-1}$

2-4 $400 \text{ kJ mol}^{-1} \rightarrow 400,000 \times 0.012 \text{ J kg}^{-1}$ of muscle tissue. $W = \text{J s}^{-1} \Rightarrow$ per second per kg of muscle tissue 0.5 J. Time = $\frac{400000 \times 0.012}{0.5} = 9,600 \text{ s} = 2 \text{ hours and } 40 \text{ minutes.}$

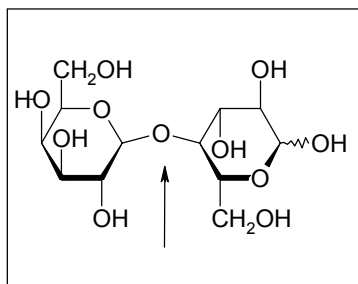
2.5 $(\text{CH}_2)_{3n+6} (\text{CO}_2)_3 \text{H}_2 + (4,5n + 9,5) \text{O}_2 \rightarrow (3n + 9) \text{CO}_2 + (3n + 7) \text{H}_2\text{O}$

Problem 3 Lactose Chemistry

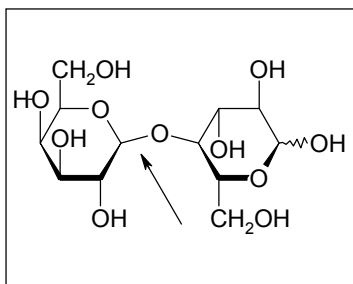
3-1



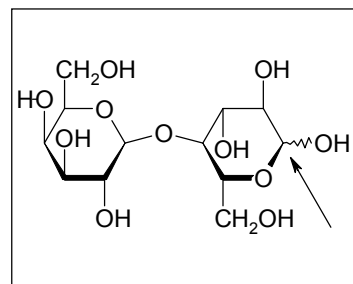
3-2



Answer box a.

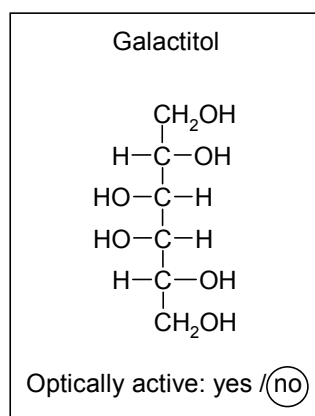
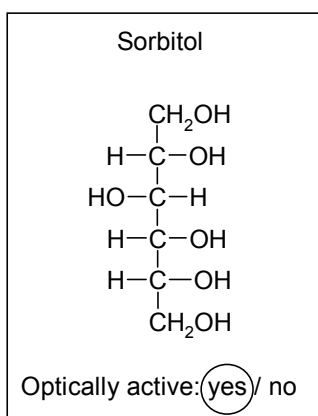


Answer box b.

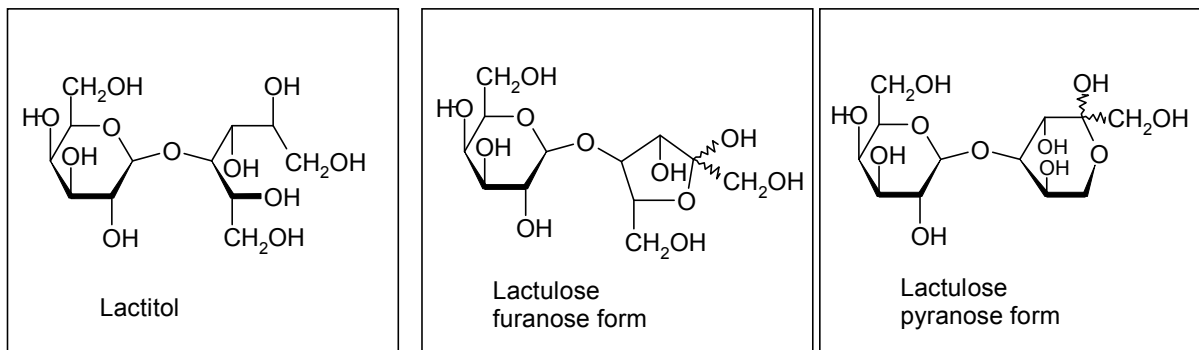


Answer box c

3-3



3-4



Lactulose 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 $a \gg c, d > b$ 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 NH_4HSO_4 = 115

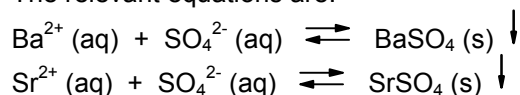
Classical route: Atom utilization = $100/(100+115) = 0.47$ or 47% E -factor = $115/100 = 1.15$
Catalytic route: Atom utilization = $115/115 = 1$ or 100% E -factor = $0/100 = 0$

5-2 Classical chlorohydrin route: Atom utilization = $44/173 = 0.25$ or 25%
Modern petrochemical route: Atom utilization = $44/44 = 1$ or 100%

Classical route: E -factor = $133.4/39.6 = 3.37$
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 = $18.6/37.4 = 0.49$
product : $44 - 15\% = 37.4$
by-products : $2 \text{ CO}_2 + 2 \text{ H}_2\text{O}$ per mole of C_2H_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:

Precipitation of BaSO_4 will start, when

$$[\text{SO}_4^{2-}] = \frac{K_{\text{sp}}(\text{BaSO}_4)}{[\text{Ba}^{2+}]} = \frac{1 \times 10^{-10}}{10^{-2}} = 10^{-8} \text{ M} \quad (1)$$

Precipitation of SrSO_4 will start, when

$$[\text{SO}_4^{2-}] = \frac{K_{\text{sp}}(\text{SrSO}_4)}{[\text{Sr}^{2+}]} = \frac{3 \times 10^{-7}}{10^{-2}} = 3 \times 10^{-5} \text{ M} \quad (2)$$

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:

$$K_{\text{sp}}(\text{BaSO}_4) = 1 \times 10^{-10} = [\text{Ba}^{2+}][3 \times 10^{-5}]$$

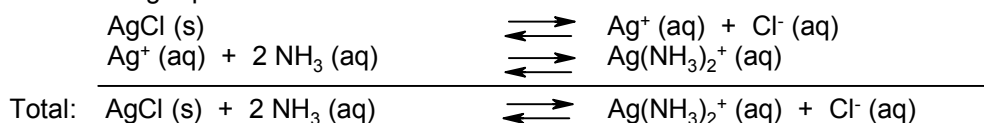
$$[\text{Ba}^{2+}] = \frac{10^{-10}}{3 \times 10^{-5}} = \frac{1}{3} \times 10^{-5} \text{ M}$$

At the starting point the concentration of Ba^{2+} was 10^{-2} M. This means that the loss amounts to

$$\frac{1/3 \times 10^{-5}}{10^{-2}} \times 100\% = 0.033\%$$

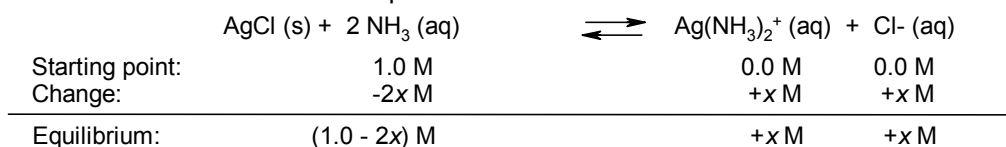
The separation meets the criterion.

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



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

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



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} can be written as:

$$K_{\text{overall}} = \frac{x \cdot x}{(1.0 - 2x)^2} \quad 2.6 \times 10^{-3} = \frac{x^2}{(1.0 - 2x)^2} \quad \text{or} \quad 0.051 = \frac{x}{(1.0 - 2x)}$$

and $x = 0.046 \text{ M}$

This result means that $4.6 \times 10^{-2} \text{ M}$ of AgCl dissolves in 1 L of 1.0 M NH_3 . Thus the formation of the complex ion $\text{Ag(NH}_3)_2^+$ enhances the solubility of AgCl , because in pure water the molar solubility amounts to only $1.3 \times 10^{-5} \text{ M}$.

Problem 7 UV-spectrometry as an Analytical Tool

7-1 2% decrease in light intensity implies: $I/I_0 = 98/100$ and $A = -\log 98/100 = 0.01$
This absorption corresponds with $0.01 = 10500 \times c_{\text{min}} \times l \Rightarrow c_{\text{min}} = 0.95 \times 10^{-6} \text{ mol L}^{-1}$.

7-2 2% light throughput means that: $I/I_0 = 2/100$ and $A = \log 100/2 = 2 - 0.3010 = 1.6990$

For ferriin this absorption at 512 nm corresponds with:

$$1.6990 = 10500 \times c_{\text{max}} \times l \Rightarrow c_{\text{max}} = 1.618 \times 10^{-4} \text{ mol L}^{-1}$$

7-3 Minimum in curve at $x_{\text{M}} = 0.33$: $c_{\text{M}} = 0.33 c_{\text{M}} + 0.33 c_{\text{L}}$ or $0.67 c_{\text{M}} = 0.33 c_{\text{L}}$
The composition of the complex is ML_2

- 7-4** For $x_M = 0$: $c_M / c_M + c_L = 0$, $c_M = 0$ and $c_L = 1$
 For $x_M = 1$: $c_M / c_M + c_L = 1$, $c_M = 1$ and $c_L = 0$
 M and L both absorb and have an absorption of $A_M = 1.0$ and $A_L = 0.5$, respectively.
- 7-5** $x_M = 0$, $c_L = 1$, $A_L = \epsilon_L c_L l$
 $x_M = 1$, $c_M = 1$, $A_M = \epsilon_M c_M l$
 l has the same value in both formulas, just as c_L and c_M , so that
 $\epsilon_L / \epsilon_M = A_L / A_M = 0.5 / 1$, thus $\epsilon_M = 2 \epsilon_L$
- 7-6** For $x_M = 0$ holds $0.5 = -\log I/I_0$, $I/I_0 = 0.32$ thus 32% has been transmitted
 For $x_M = 1$ holds $1 = -\log I/I_0$, $I/I_0 = 0.1$ thus 10% has been transmitted

Problem 8 Reaction Kinetics

- 8-1** Due to the Arrhenius equation: $\log k = \log A - E_a / 2.3RT$
 we can substitute the values of k and T :
- $$\log k_1 = \log A - E_a / 2.3RT_1 \quad \text{and} \quad \log k_2 = \log A - E_a / 2.3RT_2$$

Subtraction gives:

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

$$E_a = 2.3R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \log \frac{k_2}{k_1} = 2,3 \times 8.314 \left(\frac{300 \times 400}{400 - 300} \right) \log \frac{4.9 \cdot 10^{-4}}{2.6 \cdot 10^{-8}}$$

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

- 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: $K = \frac{k_1}{k_{-1}} = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}$

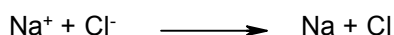
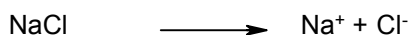
Rewritten this is: $[\text{NO}_3] = K[\text{NO}][\text{O}_2]$

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:

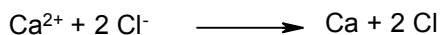
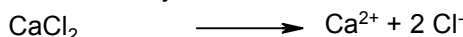


The energy loss in the first step is 464 kJ mol^{-1}

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

Overall loss = dissociation energy = 328 kJ mol^{-1}

- 9-2** Born-Haber cycle for the dissociation of CaCl_2 into $\text{Ca} + 2 \text{Cl}$:



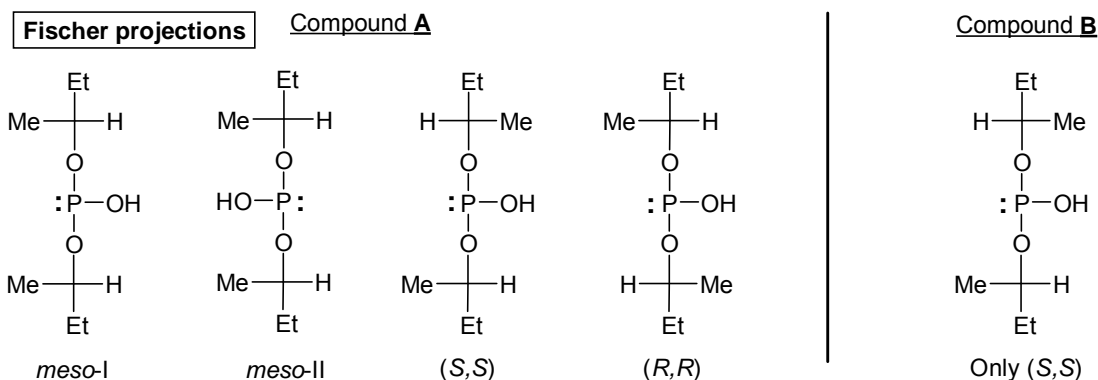
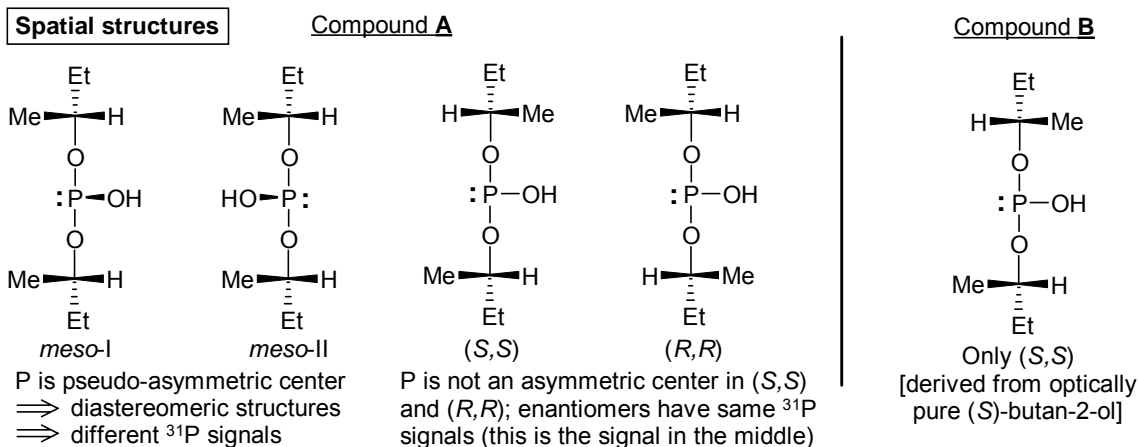
The (ionic) bond energy of $\text{Ca}^{2+}\text{Cl}^- = -429 \times 2 / 0.91 = -943 \text{ kJ mol}^{-1}$

(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 = $-(\text{bond energy of CaCl}_2) = 2 \times 942$ minus the Cl-Cl repulsion. The Cl-Cl repulsion is $(429 / 2) \times (1 / 0.91) = 236 \text{ kJ mol}^{-1}$, so the energy loss in the first step = $+1650 \text{ kJ mol}^{-1}$.
 The energy gain in the second step is $-(2 \times \text{E.A. of Cl} + \text{total I.E. of Ca}) = -1020 \text{ kJ mol}^{-1}$.
 Dissociation energy into atoms = 630 kJ mol^{-1} .

Problem 10 The Nature of Phosphorus

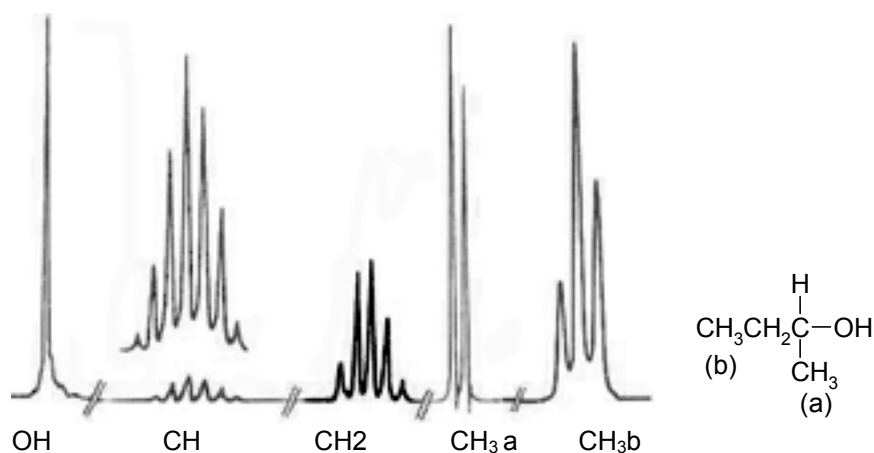
10-1



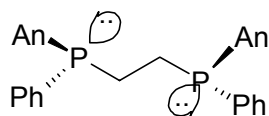
(Hint: You may wish to compare the 2 *meso* structures of 2,3,4-trihydroxypentane)

- 10-2 C: $(\text{CH}_3\text{O})_2\text{P-OH}$ one signal
 D: $[(\text{CH}_3)_2\text{CHO}]_2\text{P-OH}$ one signal
 E: $(\text{Ph}-(\text{CH}_3)\text{CH}_2\text{O})_2\text{P-OH}$ three signals as in 10-1 ratio 1:2:1 (*meso-I* : *RR* + *SS* : *meso-II*)

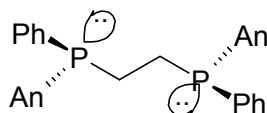
10-3



10-4



meso not chiral
not suitable as catalyst



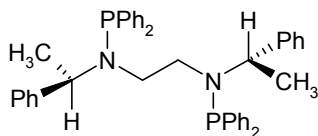
(*R,R*) will give D(+) DOPA
F is (*S,S*) and gives L(-) DOPA

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

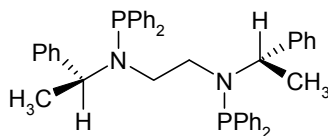
10-5

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

10-6



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 .

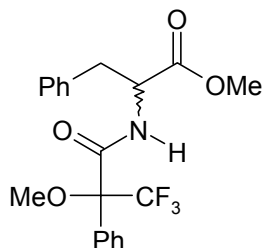
10-8

One signal, substituents have the same chirality (*R*). No splitting.

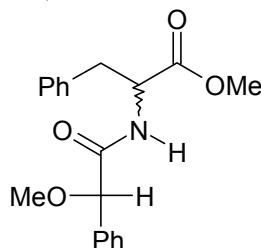
Problem 11 Optical purity

11-1

From P



From Q



11-2

Option 2

11-3



(a) ratio 1:3



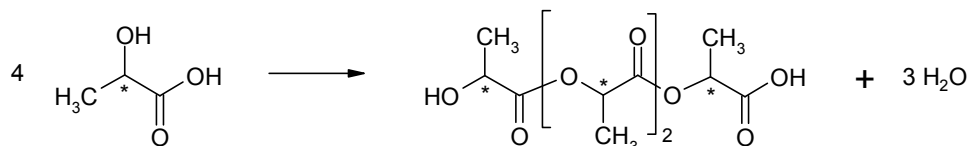
(b) ratio 1:1:3:3 Long range coupling of the CH₃O protons with the CH is very small (close to zero). The essence of the question is to indicate the peak ratio's.

11-4

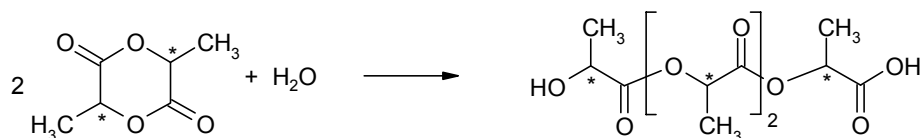


Problem 12 Polylactic Acid

12-1



12-2



12-3

The aim here is working with reactive groups.

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

12-4

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

$$\left. \begin{aligned} K = 4 &= \frac{[\text{Ester}][\text{Water}]}{[-\text{OH}][-\text{COOH}]} = \frac{p^2 U W}{(1-p)^2 U^2} \\ U = 10 \text{ and } P = 100 &= \frac{1}{1-p} \Rightarrow p = 0.99 \end{aligned} \right\} \Rightarrow W = 0.0040404 \text{ mol}$$

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

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

Problem 13 A Chemical Puzzle

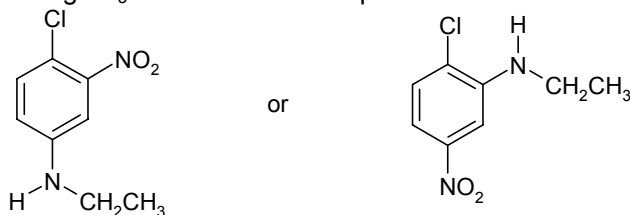
13-1 Nitrogen atom

13-2 $-\text{NH}_2$ or $-\text{NHR}$

13-3 $-\text{CH}_2\text{CH}_3$

13-4 $-\text{NO}_2$

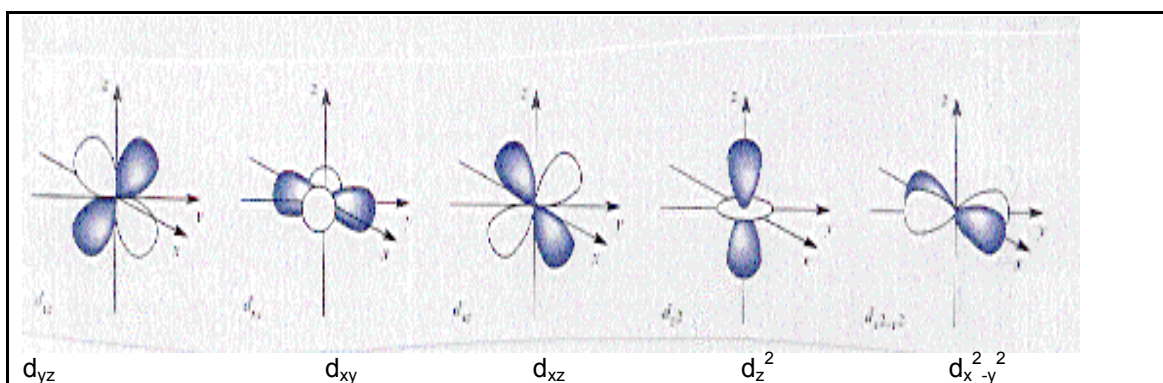
13-5 No AgNO_3 reaction \longrightarrow no aliphatic chlorine substituent



Problem 14 Delft Blue and Vitamin B 12

14-1 $\boxed{\text{Electron configuration of } \text{Co}^{2+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7}$

14-2



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

$$\boxed{A = -\log I/I_0 \quad A = \epsilon \cdot c \cdot l \Rightarrow -\log 0.1 = 20 \cdot c \cdot 0.1 \Rightarrow c = 1/(20 \cdot 0.1) = 0.5 \text{ M}}$$

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

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.

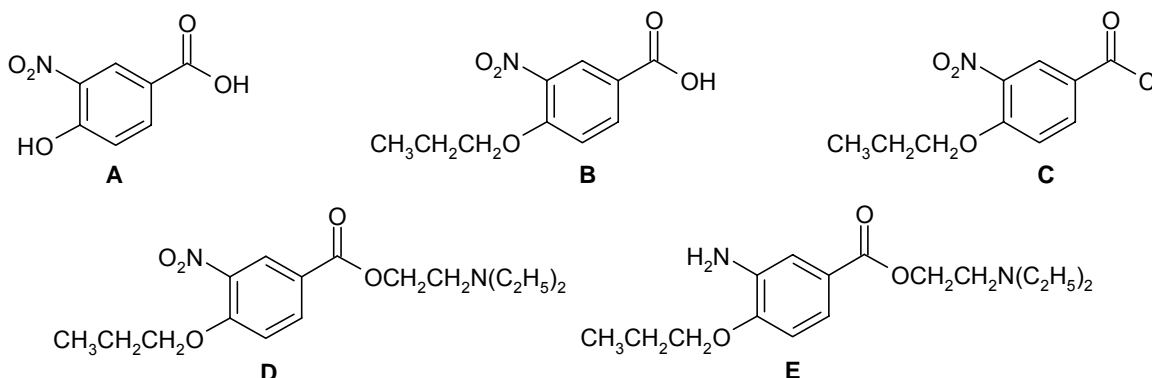
Co^+	yes / \neq
Co^{2+}	yes / \neq
Co^{3+}	yes / \neq

14-6 $\boxed{(3 \cdot 10^{-6}) / (58.93 \cdot 1.67 \cdot 10^{-27}) = 3 \cdot 10^{19} \text{ Co ions.}}$

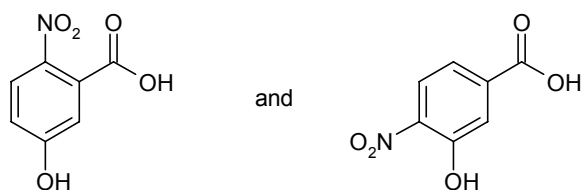
14-7 $\boxed{1 \ 2 \ 3 \ 4 \ 5 \ ⑥ \ 7 \ 8}$

Problem 15 Synthesis of a local anaesthetic

15-1



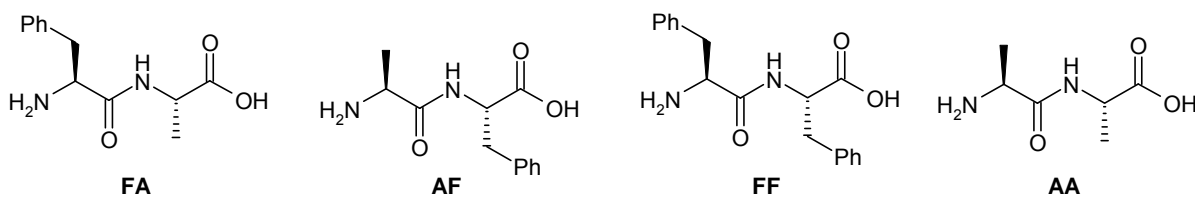
15-2



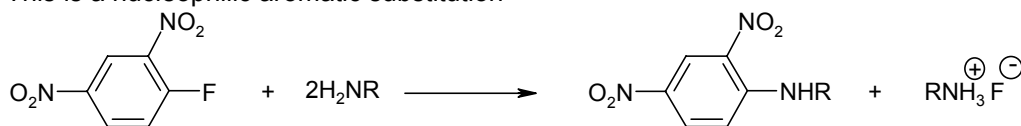
15-3 Decomposition of the *tert*-C₄H₉Cl.

Problem 16 Structure of peptides

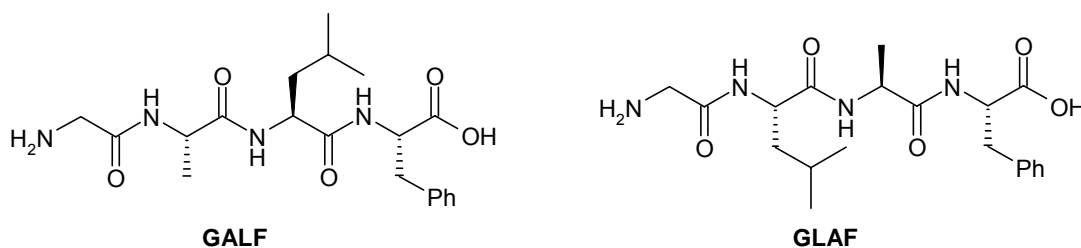
16-1



16-2 This is a nucleophilic aromatic substitution



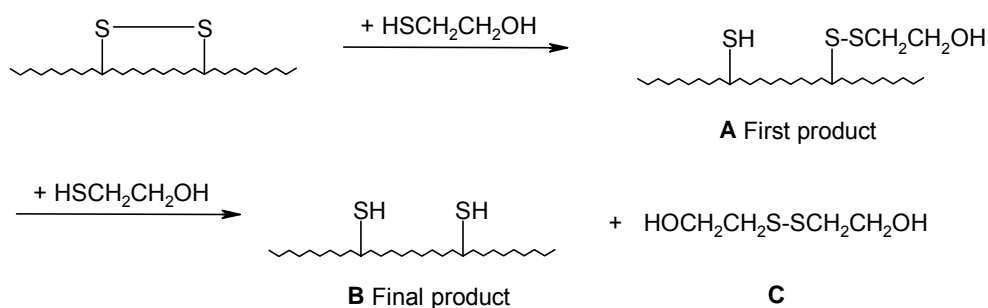
16-3



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

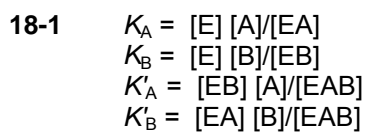
17-1



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: $1/7 \times 1/5 \times 1/3 \times 1/1 = 1/105$.

Problem 18 Enzyme Kinetics



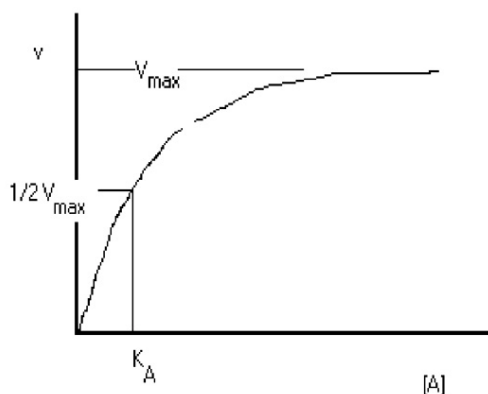
18-2
$$v = \frac{V_{\max}}{1 + K_A/[A]}$$

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

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

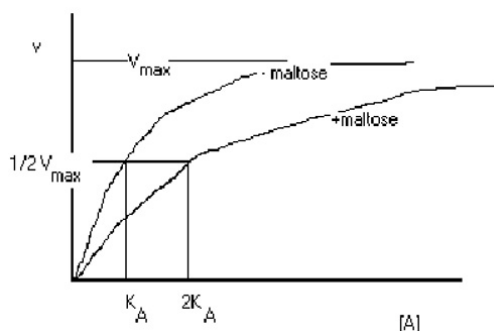
18-5 A high affinity corresponds with a small K_A .
 $v = 1/2 V_{\max}$ when $[A] = K_A$.

18-6

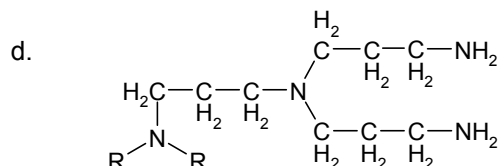
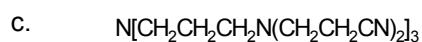
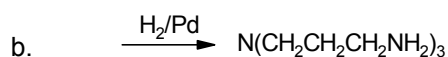


18-7 Maltose functions as a competitive inhibitor

18-8



Problem 19 Dendrimers: Tree-like Macromolecules

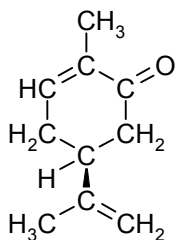


R = Same chains at these positions

- 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 = $50/2 = 25 \text{ \AA}$. Volume: $4/3 \pi r^3$.

Problem 20 Carvone

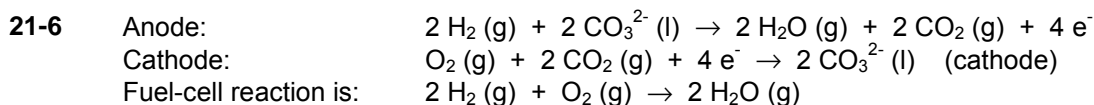
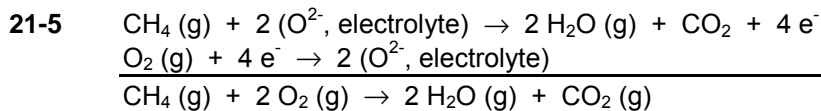
- 20-1** Number of C-atoms: $n_C = (M_r \times \%_C)/12 = (150 \times 0.8)/12 = 10$
 Number of H-atoms: $n_H = (M_r \times \%_H)/1 = (150 \times 0.0933)/1 = 14$
 Number of O-atoms: $n_O = (M_r \times \%_O)/16 = (150 \times 0.1067)/16 = 1$
- 20-2** A fully saturated hydrocarbon with 10 carbon atoms has 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 (-CO₂H 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 ¹H-NMR are two -CH₃ groups with no vicinal coupling.
 The multiplet from 1.9-2.2 ppm consists of a -CH and a -CH₂- group (from the question)
 The multiplet from 2.2-2.5 ppm is most likely a -CH₂- 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 =CH₂ 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 -CH₂- group.
 Combining all this information with the given 1,2,4 substitution pattern gives the structure below as the most likely structure of carvone.



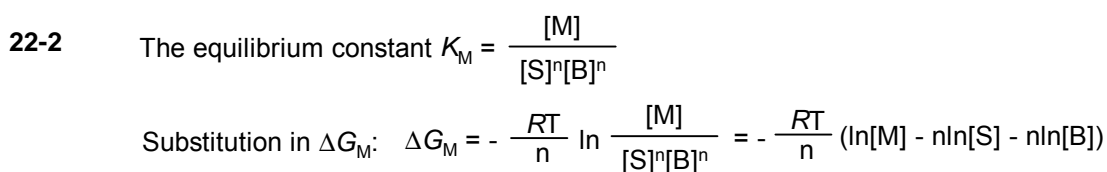
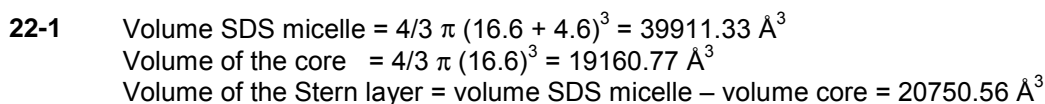
Problem 21 Experiment

- 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: $4 H^+ + 4 e^- + O_2 (g) \rightarrow 2 H_2O (g)$
 Fuel cell reaction: $2 H_2 (g) + O_2 (g) \rightarrow 2 H_2O (g)$
- 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

$$\Delta G_0 = -nFE = -4 \times 96487 \text{ C} \times (1.23 \text{ V} - 0 \text{ V}) = -474,716 \text{ J}$$



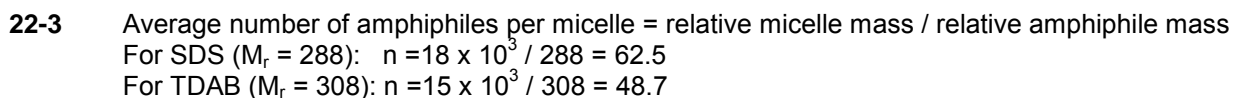
Problem 22 Experiment



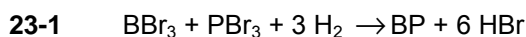
At the CMC there are no micelles: $[M] = 0$ and $[S] \approx [B]$ thus: $\Delta G_M = 2RT \ln[S]$

For SDS: $\Delta G_M = -23.86 \text{ kJ mol}^{-1}$

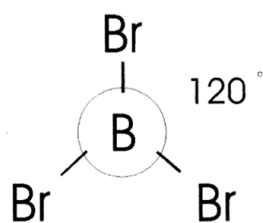
For TDAB: $\Delta G_M = -21.01 \text{ kJ mol}^{-1}$



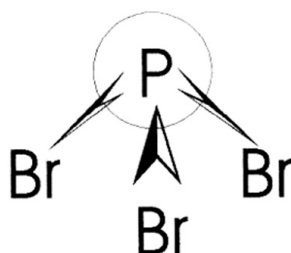
Problem 23 Experiment



23-2

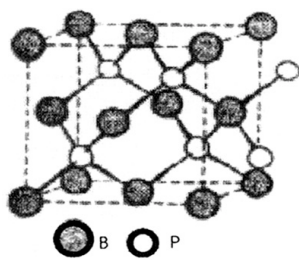


planar and trigonal



trigonal pyramidal

23-3



Zinc blende structure

23-4 A FCC-structure of the B-atoms and that gives:
 Angular points: $8 \times 1/8 = 1$
 Planes: $6 \times 1/2 = 3$
 Total = 4
 In each cell 4 phosphorus atoms are present which are tetrahedrally surrounded by boron.

23-5 Atom masses of boron and phosphorus are 11 and 31, respectively.

$$R = \frac{m}{V} = \frac{(n M_{bp})}{N a^3} = \frac{4 \times 42}{(6.022 \cdot 10^{26} (4.78 \cdot 10^{-10}))^3} = 2554 \text{ kg/m}^3$$

23-6 Distance B-P is $1/2 \times 3^{1/2} \times 1/3 \times a = 2.069 \text{ \AA}$

23-7 Lattice energy of BP:

$$= - \frac{1390 \times 3 \times 3 \times 1.638 Z_+ Z_- Ae^2}{2.069} \frac{6}{7} = 8489 \text{ kJ/mol}$$

23-8 The order of the reaction is 2

$$r = k [\text{BBr}_3][\text{PBr}_3]$$

23-9 $k_{800} = r_{800} / [\text{BBr}_3][\text{PBr}_3] = 4.60 \cdot 10^{-8} / 2.25 \cdot 10^{-6} \times 9 \cdot 10^{-6} \frac{\text{mol s}^{-1}}{\text{mol}^2 \text{L}^{-2}} = 2272 \text{ L}^2 \text{ mol}^{-1} \text{ s}^{-1}$

$$k_{880} = r_{880} / [\text{BBr}_3][\text{PBr}_3] = 19.60 \cdot 10^{-8} / 2.25 \cdot 10^{-6} \times 9 \cdot 10^{-6} \frac{\text{mol s}^{-1}}{\text{mol}^2 \text{L}^{-2}} = 9679 \text{ L}^2 \text{ mol}^{-1} \text{ s}^{-1}$$

23-10 $\Delta H = -R \ln (k_2/k_1) \times (1/T_2 - 1/T_1)^{-1}$

$$T_1 = 880 + 273 = 1073 \text{ K and } T_2 = 800 + 273 = 1073 \text{ K}$$

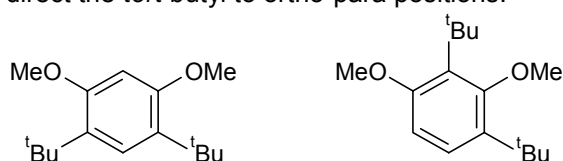
$$\Delta H = -R \ln (9679 / 2272) \times (1/1073 - 1/1073)^{-1} = 186 \text{ kJ mol}^{-1}$$

Problem 24 Experiment

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

24-1 *tert*-butyl cation: $(\text{CH}_3)_3\text{C}^+$

24-2 Methoxy group is strongly activating in electrophilic aromatic substitution reactions and will direct the *tert*-butyl to ortho-para positions.



much less likely due to steric hindrance

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.

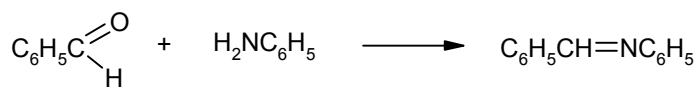
25-1 a: pKa phenolphthalein $pK_a > 6.1$
 b: pKa methylorange $pK_a > 1.8$

25-2 Explanation according to option a

Problem 26 Experiment

- the yield will be ca 360 mg, m.p. = 125° C

26-1

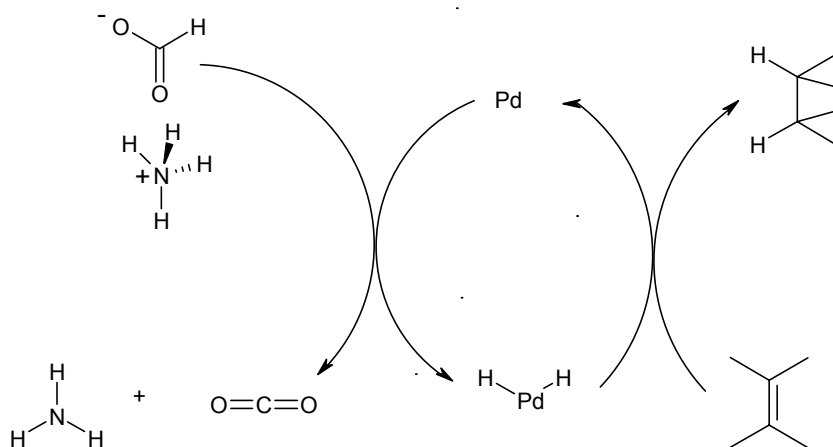
**Problem 27 Experiment**

- 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.