Answers to the Problems

Important notice:
In accordance with the decision of the International Jury of the Chemistry Olympiad only partial answers will be published on the website. Worked solutions to the problems are included in the booklet that has been sent to all Olympiad organizations of participating countries. The worked solutions will also be published on the web in due time. For any questions you can contact us by e-mail (Icho34@chem.rug.nl or Ich034@sci.kun.nl).

Problem 1 Production of Ammonia

1-1 $n[H_2,②] = 1500 \text{ mol s}^{-1}$
$n[N_2,⑥] = 500 \text{ mol s}^{-1}$
$n[CH_4,①] = 500 \text{ mol s}^{-1}$
$n[H_2O,①] = 500 \text{ mol s}^{-1}$
$n[CO,③] = 500 \text{ mol s}^{-1}$
$n[O_2,④] = 125 \text{ mol s}^{-1}$
$n[CO,⑤] = 250 \text{ mol s}^{-1}$

1-2 $n[N_2,⑦] = 500 \text{ mol s}^{-1}$ $n[H_2,⑦] =1500 \text{ mol s}^{-1}$

1-3 $\Delta G_r = 82 \times 10^3 \text{ J mol}^{-1}$

1-4 $K_r = 4.4\times10^{-6} \text{ J mol}^{-1}$

1-5 $p_{N2} = (1/4)\,(1 - x)\,p_{tot}$
$p_{H2} = (3/4)\,(1 - x)\,p_{tot}$

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

1-7
$$\frac{x^2}{(1-x)^4} = 0.0418$$
x = 0.148

Problem 2 Myoglobin for Oxygen Storage

2-1 $K_p = 100$ Pa

2-2 Volume of Mb: $19.6875 \times 10^{-27}\ m^3$
Molecular weight of Mb = 16.6 kg mol^{-1}

2-3 $0.012 \text{ mol kg}^{-1}$

2-4 2 hours and 40 minutes.

2.5 $(CH_2)_{3n+6} (CO_2)_3 H_2 + (4,5n + 9,5) O_2 \rightarrow$

Problem 3 Lactose Chemistry

3-1

Formula

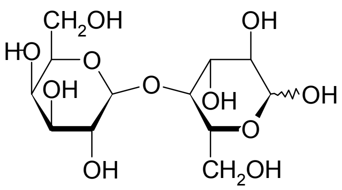
D-galactose

Formula

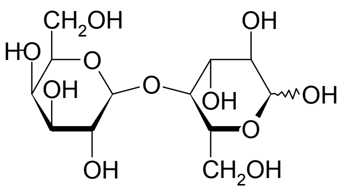
D-glucose

Answers in textbook

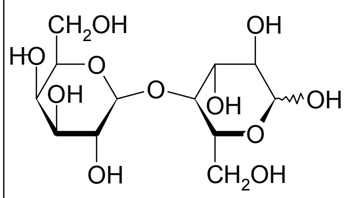
3-2



Answer box a.



Answer box b.



Answer box c

3-3

Sorbitol

Formula

Optically active: yes / no

Galactitol

Formula

Optically active: yes / no

Answers in textbook

3-4 Find answer in textbook

formula	formula	formula
Lactitol	Lactulose furanose form	Lactulose pyranose form

Lactulose is a mixture of the furanose and pyranose form in the ration 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 Classical route: Atom utilization =0.47 or 47% *E*-factor = 1.15
Catalytic route: Atom utilization = 1 or 100% *E*-factor = 0

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

Classical route: *E*-factor = 3.37
Modern route: *E*-factor = 0.49

Problem 6 Selective Solubility

6-1 The relevant equations are:

$$Ba^{2+}\ (aq) + SO_4^{2-}\ (aq) \rightleftharpoons BaSO_4\ (s) \downarrow$$
$$Sr^{2+}\ (aq) + SO_4^{2-}\ (aq) \rightleftharpoons SrSO_4\ (s) \downarrow$$

$[SO_4^{2-}] = 3 \times 10^{-5}$ M

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

At the starting point the concentration of Ba^{2+} was 10^{-2} M. This means that the loss amounts to 0.033%

The separation meets the criterion.

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

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$
$$Ag^+\ (aq) + 2\ NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^+\ (aq)$$

Total: $AgCl\ (s) + 2\ NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^+\ (aq) + Cl^-\ (aq)$

$K_{overall} = K_{sp}\, K_f = 2.6 \times 10^{-3}$

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

	AgCl (s) + 2 NH_3 (aq)	⇄	$Ag(NH_3)_2^+$ (aq)	+ Cl- (aq)
Starting point:	1.0 M		0.0 M	0.0 M
Change:	-2x M		+x M	+x M
Equilibrium:	(1.0 - 2x) M		+x M	+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 $[Ag^+] = [Cl^-]$
Complex formation leads to: $[Ag(NH_3)_2^+] = [Cl^-]$

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

x = 0.046 M

This result means that 4.6 x 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 x 10^{-5} M.

Problem 7 UV-spectrometry as an Analytical Tool

7-1 c_{max} = 1.618 x 10^{-4} mol L^{-1}.

7-2 c_{min} = 0.95 x 10^{-6} mol L^{-1}

7-3 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 $\varepsilon_M = 2\,\varepsilon_L$

7-6 For $x_M = 0$ 32% has been transmitted
For $x_M = 1$ 0% has been transmitted

Problem 8 Reaction Kinetics

8-1 Arrhenius equation: $\log k = \log A - E_a / 2.3RT$
we can substitute the values of k and T:

E_a = 98.225 kJ mol^{-1}

8-2 The expression for s is: $\frac{d[NO_2]}{dt} = k_2\,[NO_3]\,[NO]$
s = $k_2\,K\,[NO]^2\,[O_2]$

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:

$NaCl \longrightarrow Na^{+} + Cl^{-}$

$Na^{+} + Cl^{-} \longrightarrow Na + Cl$

Dissociation energy = 328 kJ mol^{-1}

9-2 Born-Haber cycle for the dissociation of $CaCl_2$ into Ca + 2 Cl:

$CaCl_2 \longrightarrow Ca^{2+} + 2\ Cl^{-}$

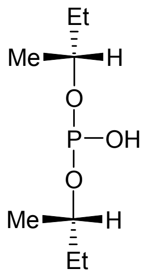
$Ca^{2+} + 2\ Cl^{-} \longrightarrow Ca + 2\ Cl$

Dissociation energy into atoms = 630 kJ mol^{-1}.

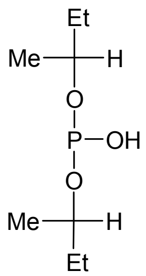
Problem 10 The Nature of Phosphorus

10-1

Spatial structures

	Compound **A**			Compound **B**
	formula	formula	formula	formula
meso-I	*meso*-II	(*S*,*S*)	(*R*,*R*)	Only (*S*,*S*) [derived from optically pure (*S*)-butan-2-ol]

Fisher projections

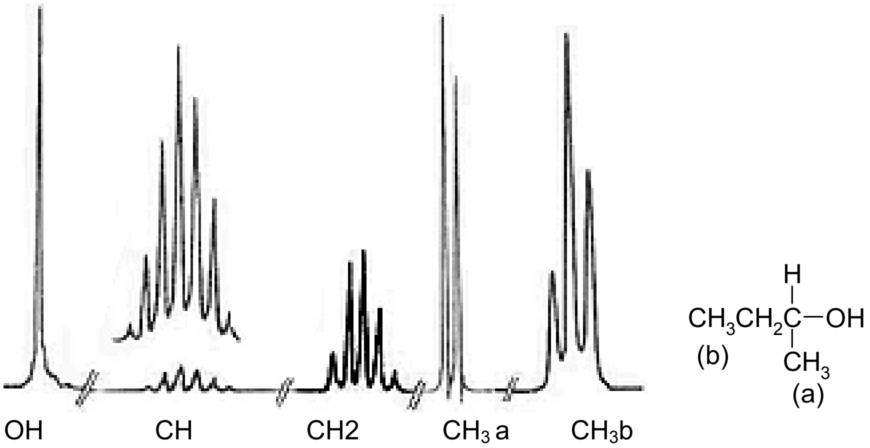
	Compound **A**			Compound **B**
	formula	formula	formula	formula
meso-I	*meso*-II	(*S*,*S*)	(*R*,*R*)	Only (*S*,*S*)

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

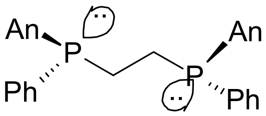
10-2

C: $(CH_3O)_2P\text{-}OH$ one signal
D: $[(CH_3)_2CHO]\text{-}P\text{-}OH$ one signal
E: $(Ph\text{-}(CH_3)CH_2O)_2P\text{-}OH$ three signals as in **10-1** ratio 1:2:1 (*meso*-**I** : *RR* + *SS* : *meso*-**II**)

10-3



10-4



formula

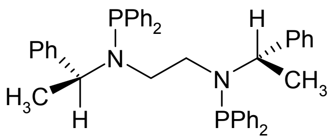
meso not chiral
not suitable as catalyst

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

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

formula



meso compound
not suitable as
chiral catalyst

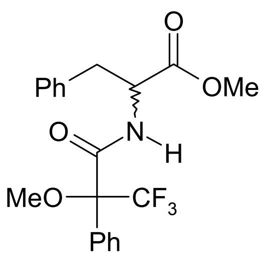
(S,S) will give D(+) DOPA
G is (R,R) and gives L(-) DOPA

10-7 Option … and option ….

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

Problem 11 Optical purity

11-1 From **P** From **Q**

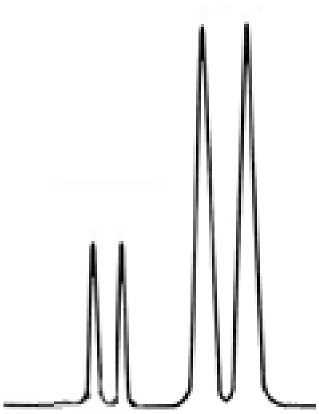


formula

11-2 Option …

11-3

Spectrum



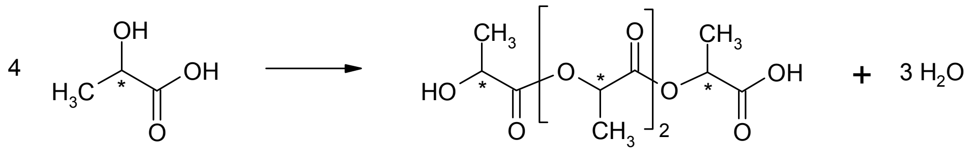
(a) ratio 1:3 (b) ratio 1:1:3:3 Small splitting due to coupling with CH

11-4 Spectrum

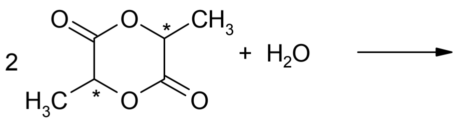
ratio 1:3

Problem 12 Polylactic Acid

12-1



12-2



12-3

$$P = \frac{1}{1-p} = 3$$

12-4 First the remaining amount of water at a chain length of 100 units is calculated:

$$K = 4 = \frac{[\text{Ester}][\text{Water}]}{[\text{-OH}][\text{-COOH}]}$$

$\text{U} = 10$ and $P = 100$

Water formed: $p\text{U}$

Water removed $= 178$ g of H_2O

Problem 13 A Chemical Puzzle

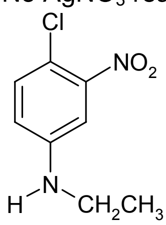
13-1 …

13-2 …

13-3 …

13-4 …

13-5 No $AgNO_3$ reaction → no aliphatic chlorine substituent

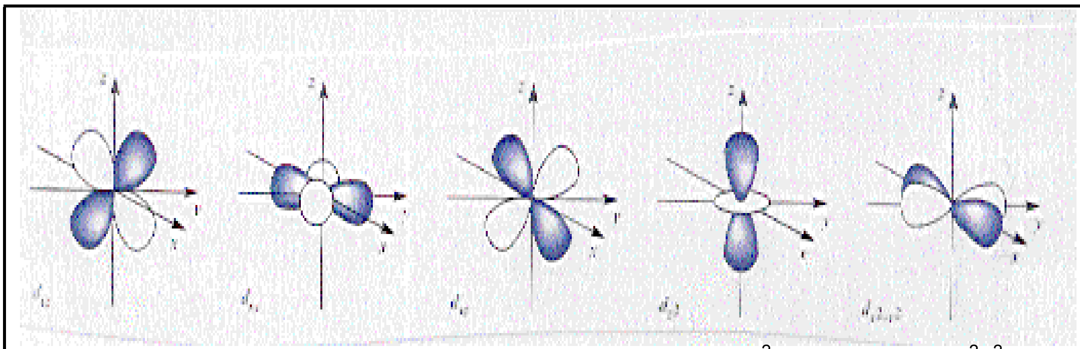


or formula

Problem 14 Delft Blue and Vitamin B 12

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

14-2



d_{yz} d_{xy} d_{xz} d_{z^2} $d_{x^2-y^2}$

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

$A = -\log I/I_0$ $A = \varepsilon * c * l$ c = 0.5 M

14-4

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 ~~/ no~~
Co^{2+}	yes ~~/ no~~
Co^{3+}	yes ~~/ no~~

14-6 $3 * 10^{19}$ Co ions.

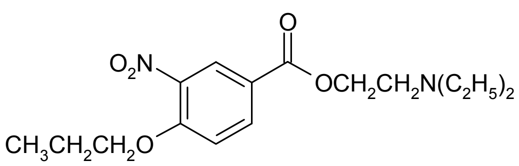
14-7 1 2 3 4 5 ⑥ 7 8

Problem 15 Synthesis of a local anaesthetic

15-1

formula formula formula

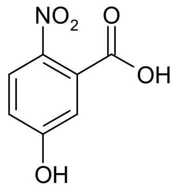
A **B** **C**



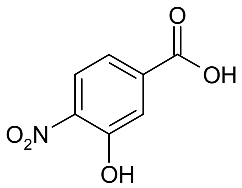
formula

D **E**

15-2



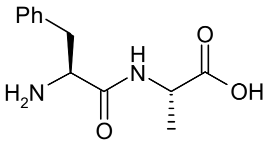
and



15-3 Decomposition of the *tert*-C_4H_9Cl.

Problem 16 Structure of peptides

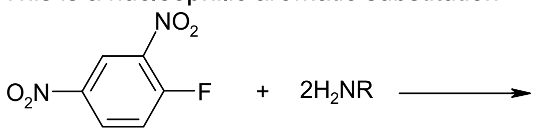
16-1



formula formula formula

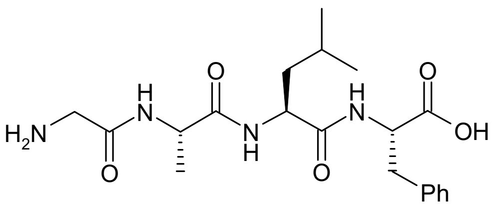
FA **AF** **FF** **AA**

16-2 This is a nucleophilic aromatic substitution



formula + formula

16-3



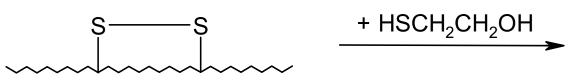
formula

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.

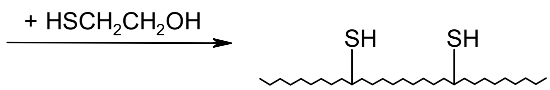
Problem 17 Ribonuclease

17-1



formula

A First product



B Final product

formula

C

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.) The fraction of active molecules is: 1/105.

Problem 18 Enzyme Kinetics

18-1 K_A =
K_B =
K'_A =
K'_B =

18-2

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

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

18-4 If $[A] \longrightarrow \infty$ $v = V_{max}$. This corresponds with zero order kinetics.

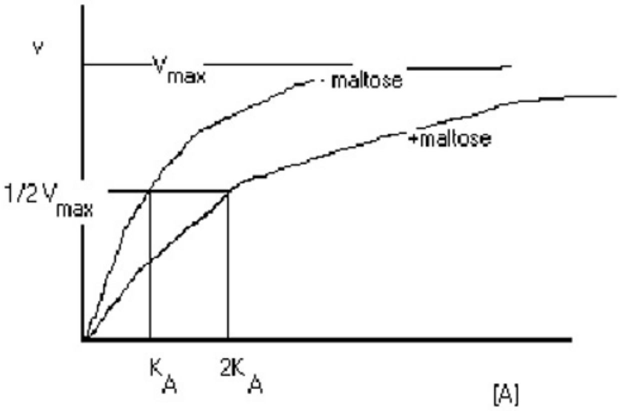
18-5 A high affinity corresponds with a small K_A.
$v = ½ V_{max}$ when $[A] = K_A$.

18-6

figure

18-7 Maltose functions as a competitive inhibitor

18-8



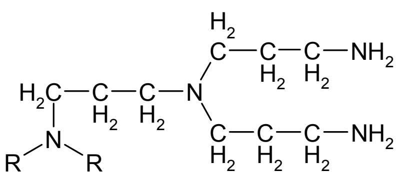
Problem 19 Dendrimers: Tree-like Macromolecules

19-1 a. NH_3 + $H_2C{=}CHCN$ $\longrightarrow$

b. $\xrightarrow{H_2/Pd}$ structure

c. structure

d.



R = Same chains at these positions

19-2 After the first cycle there are 3 amine groups. After 5 full cycles, the total number of amine end-groups is 48.

19-3 a. After 5 full cycles 93 moles of H_2 have been used.
b. Idem for acrylonitrile (93 moles).
c. Radius is 25 Å. Volume: $4/3\ \pi\ r^3$.

Problem 20 Carvone

20-1 Number of C-atoms: $n_C = 10$
Number of H-atoms: $n_H = 14$
Number of O-atoms: $n_O = 1$

20-2 Carvone has the formula $C_{10}H_{14}O$ and 4 unsaturated sites.

20-3 C=O group

20-4 -OH (-CO_2H is not a correct answer! Carvone only has one oxygen atom)

20-5 Look up structure in a textbook or encyclopedia, then interpret the spectrum

Problem 21

21-1 At the cathode, half-reaction (1)

21-2 At the anode, reaction (2).

21-3 Anode:
Cathode:
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
$\Delta G_o = -\ n\ F\ E = -474{,}716$ J

21-5 $CH_4\ (g) + 2\ (O^{2-}, \text{electrolyte}) \rightarrow 2\ H_2O\ (g) + CO_2 + 4\ e^-$
$O_2\ (g) + 4\ e^- \rightarrow 2\ (O^{2-}, \text{electrolyte})$

……………………………………………………………………..

21-6 Anode:
Cathode:
Fuel-cell reaction is: $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g)$

Problem 22

22-1 Volume SDS micelle = 39911.33 Å^3
Volume of the core = 19160.77 Å^3
Volume of the Stern layer = 20750.56 Å^3

22-2 The equilibrium constant K_M = ...

Substitution in ΔG_M: ....

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

22-3 Average number of amphiphiles per micelle
For SDS (M_r = 288) = 62.5
For TDAB (M_r = 308) = 48.7

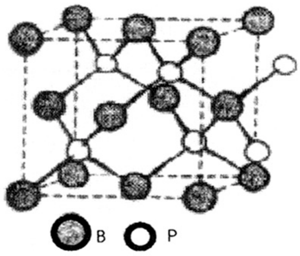
Problem 23

23-1 $BBr_3 + PBr_3 + 3 H_2 \rightarrow BP + 6 HBr$

23-2 figure figure

BBr_3 planar and trigonal PBr_3 trigonal pyramidal

23-3



Zinc blende structure

23-4 A FCC-structure of the B-atoms and that gives:
Angular points: =1
Planes: =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 = 2554 kg m^{-3}

23-6 Distance B-P is 2.069 Å

23-7 Lattice energy of BP:
= 8489 kJ mol^{-1}

23-8 The order of the reaction is 2
$r = k [BBr_3][PBr_3]$

]23-9 k_{800}= 2272 L^2 mol^{-1} s^{-1}

k_{800}= 9679 L^2 mol^{-1} s^{-1}

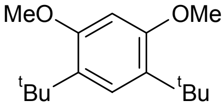
23-10 $\Delta H = -R \ln (k_2/k_1) \times (1/T_2-1/T_1)^{-1}$
ΔH = 186 kJ mol^{-1}

Problem 24

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

24-1 *tert*-butyl cation

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



formula

much less likely due
to steric hindrance

Problem 25

- 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.

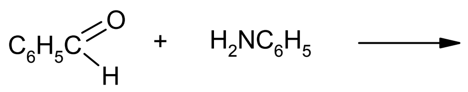
25-1 a: p*K*a phenolphthalein $pK_a > 6.1$
b: p*K*a methylorange $pK_a > 1.8$

25-2 Explanation according to option a

Problem26

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

26-1



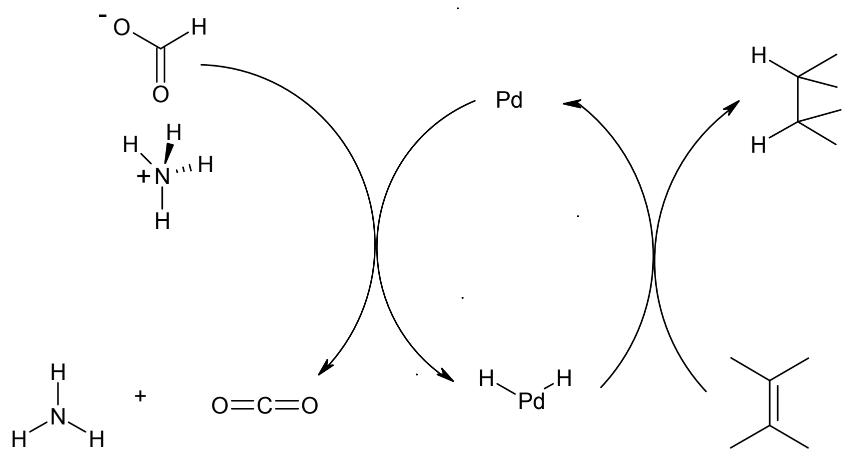
Problem 27

- 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

29-1 Yes

29-2 optically enriched

29-3 optically pure

29-4 When the enzyme is highly selective: no
When the enzyme is <u>not</u> highly selective: yes. In this case the preferred enantiomer will be hydrolyzed very fast and the other enantiomer will be converted more slowly.

VNCI

gemeente Groningen

KNCV
Koninklijke Nederlandse Chemische Vereniging

CW

tyco
Specialty Products

Mallinckrodt Baker

DSM

DUPONT
The miracles of science

AVEBE

Ministerie van Economische Zaken

RuG

Shell

OCenW
Ministerie van Onderwijs Cultuur en Wetenschappen

AKZO NOBEL

ROHM AND HAAS

34th International Chemistry Olympiad | Nijenborgh 4 | 9747 AG Groningen | The Netherlands
telephone +31 50 363 46 15 | fax +31 50 363 45 00 | e-mail: icho34@chem.rug.nl | www.chem.rug.nl/icho34

ISBN 90 806903 1 7