PREPARATORY PROBLEMS
SOLUTIONS

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MINISTÈRE
DE L'ÉDUCATION
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DE L'ENSEIGNEMENT SUPÉRIEUR,
DE LA RECHERCHE
ET DE L'INNOVATION

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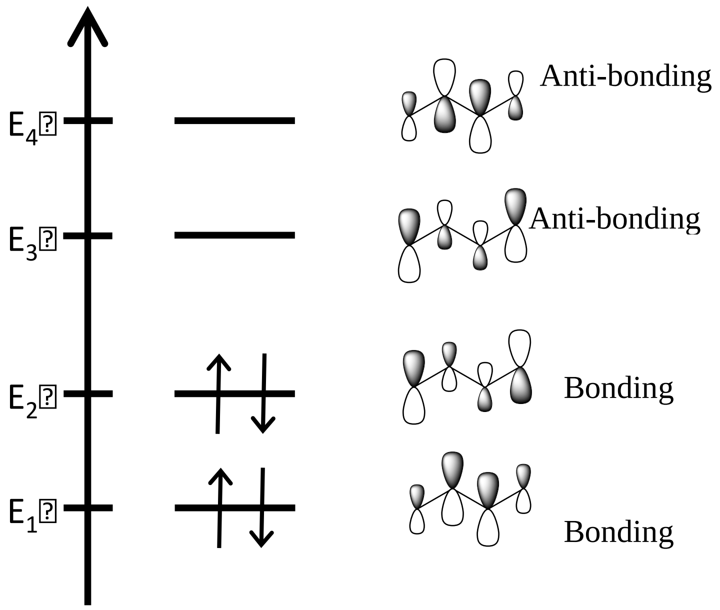
Theoretical problems

Problem 1. Butadiene π-electron system

1. Butadiene possesses 4 π-electrons.

2.



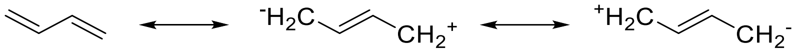
3. $\Delta E_f = 2E_1 + 2E_2 - 4\alpha = 4.48\,\beta$

4. $\Delta E_c = 2E_1 + 2E_2 - 2 \times 2(\alpha + \beta) = 0.48\,\beta < 0$
   Correct statement: Butadiene

5. $q_1 = q_2 = 0$; $q_3 = q_2 = 0$ et $q_1 = q_4 = 0$

6. $I_{12} = 0.8943$
   $I_{23} = 0.4473$
   $I_{34} = 0.8943$
   Strongest double-bond character: bonds C_1C_2 and C_3C_4.

7.



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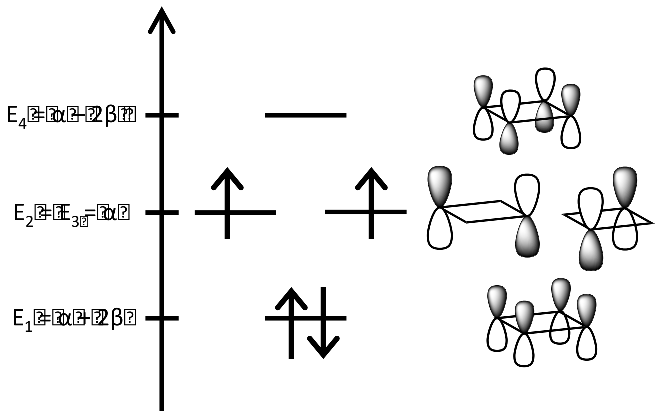


9. $c_{12} = c_{13} = c_{14} = 0.5$
   $c_{22} = c_{24} = 0$; $c_{23} = -0.707$
   $c_{31} = c_{33} = 0$; $c_{34} = -0.707$
   $c_{42} = c_{44} = -0.5$; $c_{43} = 0.5$

10. $\Delta E_f' = 2E_1 + 2E_2 - 4\alpha = 4\beta$
    $\Delta E_c' = 2E_1 + 2E_2 - 2 \times 2(\alpha + \beta) = 0$
    Correct answer: Both are equally stable

11. ΔE_f (butadiene) < $\Delta E_f'$(cyclobutadiene)
    Correct statement: Butadiene

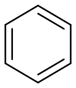
12. Correct statements:
    This deformation stabilizes C=C double bonds. (shortening of the double bonds, stronger overlap of the $2p_z$ orbitals)
    This deformation does not affect the stability due to electronic conjugation. ($\Delta E_c' = 0$ so there was no stabilization due to delocalization in the square geometry. Hence, localizing the double bonds does not affect the electronic conjugation)

13. Correct statement:
    More stable than the square cyclobutadiene.

Problem 2. Localization and delocalization in benzene

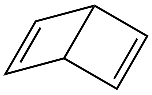
1. $3\ C_2H_2 = C_6H_6$

2.



(K1)

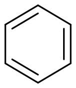
3.



4. $E_\pi = 2t$

5. $E_{K1} = 3 \times 2t = 6t$

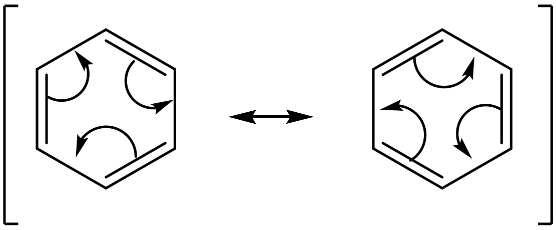
6.



(K2)

7. $E_{K2} = E_{K1} = 6t$

8.



9. Using $c_1^2 + c_2^2 = 1$,

$$c_2 = \sqrt{1 - c_1^2}$$

Hence $E_K = E_{K2} + (E_{K1} - E_{K2})c_1^2 + 2c_1\sqrt{1 - c_1^2}H_{12}$

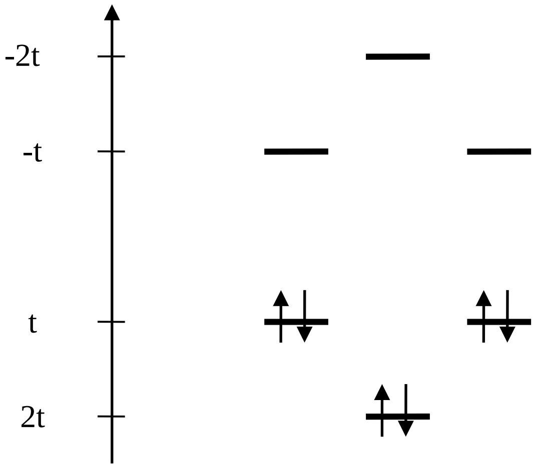
10. $E_K(H_{12} = 0) = (1 - c_1^2)\,E_{K2} + c_1^2\,E_{K1}$

$\Delta E_1 = 7t - 6t = t$

11. t < 0, so $\Delta E_1 < 0$: electronic delocalization contributes to stabilize the benzene molecule.

12. See answer 13.

13.



14. $E_{MO} = 2 \times 2t + 4t = 8t$ and $\Delta E_2 = (2 \times 2t + 4t) - 6t = 2t$

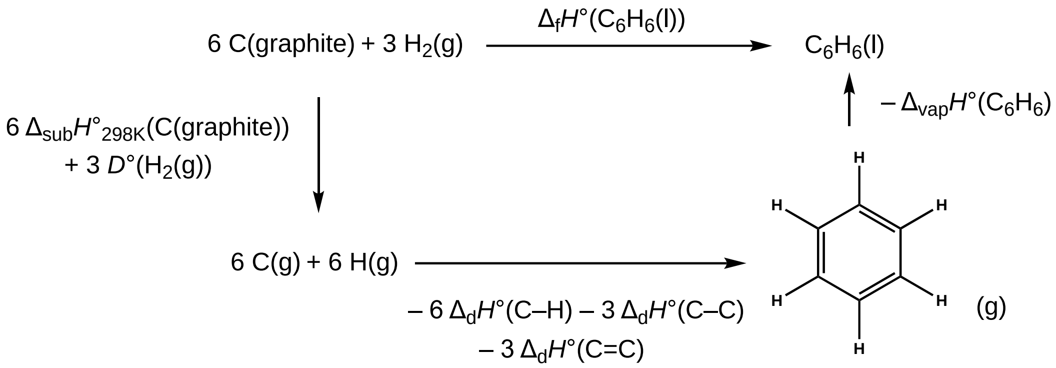
15. Since $t < 0$, $\Delta E_2 = 2t < t = \Delta E_1$

16. <u>Correct answer</u>: $|\Delta_r H_b°| < 3\,|\Delta_r H_c°|$

Problem 3. Study of liquid benzene hydrogenation

1. 6 C(graphite) + 3 H_2(g) = C_6H_6(l)

2.



$\Delta_f H°(C_6H_6(l)) = 6\Delta_{sub}H°(C(graphite)) + 3D°(H_2(g)) - 6\Delta_d H°(C\text{-}H) - 3\Delta_d H°(C\text{-}C) - 3\Delta_d H°(C{=}C) - \Delta_{vap}H°(C_6H_6(l))$
$\Delta_f H°(C_6H_6(l)) = 6 \times 716.7 + 3 \times 436.0 - 6 \times 414.8 - 3 \times 346.9 - 3 \times 614.5 - 33.9$
$\Delta_f H°(C_6H_6(l)) = 201.3$ kJ mol^{-1}

3. $\Delta_f H°(C_6H_6(l)) = 6\Delta_{comb}H°(C(graphite)) - 3\Delta_{comb}H°(H_2(g)) - \Delta_{comb}H°(C_6H_6(l))$
$\Delta_f H°(C_6H_6(l)) = -6 \times 393.5 - 3 \times 285.6 + 3268.0$
$\Delta_f H°(C_6H_6(l)) = 50.2$ kJ mol^{-1}

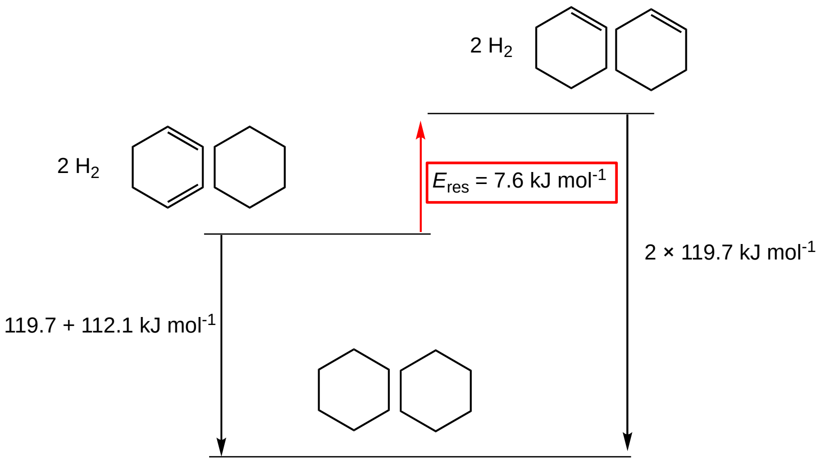
4. $E_{resonance} = 50.2 - 201.3 = -151.1$ kJ mol^{-1}
Correct statement:
The method used at question 2 does not take into account the nature of bonds in benzene.

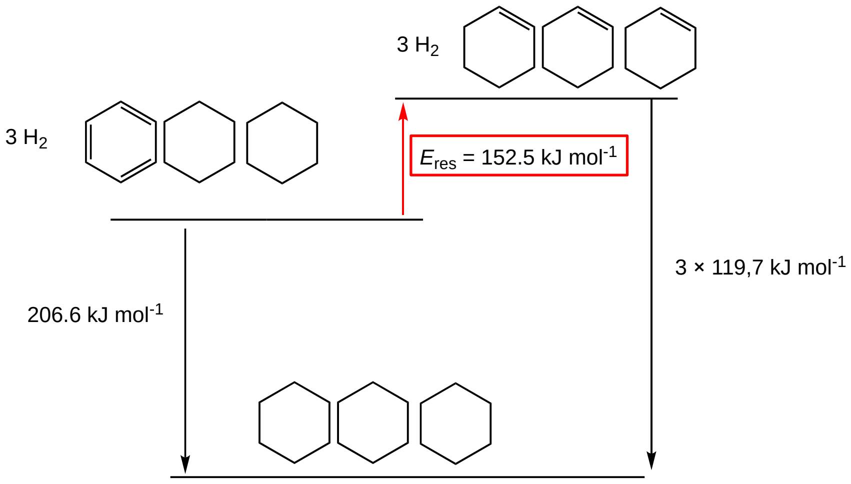
5. $C_6H_6(l) + 3H_2(g) = C_6H_{12}(l)$
$\Delta_r H°(\text{hydrogenation}) = -\Delta_f H°(C_6H_6(l)) - 3\Delta_f H°(H_2(g)) + \Delta_f H°(C_6H_{12}(l))$
$\Delta_r H° = -50.2 - 3 \times 0.0 - 156.4 = -206.6$ kJ mol^{-1}

6. $\Delta_r H°(\text{hydrogenation}) = x - 112.1 - 119.7 = -206.6$
$x = 25.2$ kJ mol^{-1}

7. Correct statement:
The breaking of benzene aromaticity.

8.





Problem 4. Use of dihydrogen: fuel cells

1. At the anode: $H_2(g) = 2\ H^+(aq) + 2\ e^-$
   At the cathode: $1/2\ O_2(g) + 2\ H^+(aq) + 2\ e^- = H_2O(l)$
   Global reaction: $H_2(g) + 1/2\ O_2(g) = H_2O(l)$

2. $U = E°(O_2(g)/H_2O(l)) - E°(H^+(aq)/H_2(g)) = 1.23$ V

3. The temperature and the pressure of the system are fixed. Hence, the maximum energy that can be recovered from a system is computed from Gibbs free energy.
   $\Delta_{comb}G°_{298K}(H_2(g)) = -n\ F\ U = -2 \times 96485 \times 1.23 = -237\ \text{kJ mol}^{-1}$

4. E being the energy to be produced:
   $n(H_2(g)) = \dfrac{E}{\Delta_{comb}G°_{298K}(H_2(g))} = 3.0 \cdot 10^2$ mol
   $V = \dfrac{n_{H2(g)}RT}{P} = \dfrac{3.0 \cdot 10^2 \times 8.31 \times 298}{1.0 \cdot 10^5} = 7.5\ \text{m}^3$

5.

$$\begin{tikzcd}
H_2(g)\ (298\ K) + 1/2\ O_2(g)\ (298\ K) \arrow[rr, "\Delta_{comb}H°_{298K}(H_2(g))"] \arrow[d, "\Delta_f H°_{298K}(H_2O(g))"'] & & H_2O_{(l)}\ (298\ K) \\
H_2O_{(g)}\ (298\ K) \arrow[r, "C°_p(H_2O(g)) \times (373 - 298)"'] & H_2O_{(g)}\ (373\ K) \arrow[r, "-\Delta_{vap}H°_{373K}(H_2O)"'] & H_2O_{(l)}\ (373\ K) \arrow[u, "C°_p(H_2O(l)) \times (298 - 373)"']
\end{tikzcd}$$

$\Delta_{comb}H°_{298K}(H_2(g)) = \Delta_f H°_{298K}(H_2O(g)) + C°_p{}^{H2O(g)}\ (373 - 298) - \Delta_{vap}H°_{373K}(H_2O) + C°_p{}^{H2O(l)}\ (298 - 373)$
$\Delta_{comb}H°_{298K}(H_2(g)) = -241.8 + 33.6 \cdot 10^{-3} \times (373 - 298) - 40.66 + 75.3 \cdot 10^{-3} \times (298 - 373)$
$\Delta_{comb}H°_{298K}(H_2(g)) = -286\ \text{kJ mol}^{-1}$

Thus, the thermodynamic efficiency of the dihydrogen fuel cell is:
$\gamma_{thermo} = \dfrac{\Delta_{comb}G°_{298K}(H_2(g))}{\Delta_{comb}H°_{298K}(H_2(g))} = \dfrac{-237}{-287} = 0.83$

6. $\Delta_{\text{comb}}G°_{298\text{K}}(\text{H}_2\text{(g)}) = \Delta_{\text{comb}}H°_{298\text{K}}(\text{H}_2\text{(g)}) - T\Delta_{\text{comb}}S°_{298\text{K}}(\text{H}_2\text{(g)})$ with $T = 298$ K
   $\Delta_{\text{comb}}S°_{298\text{K}}(\text{H}_2\text{(g)}) = \frac{\Delta_{\text{comb}}H°_{298\text{K}}(\text{H}_2\text{(g)}) - \Delta_{\text{comb}}G°_{298\text{K}}(\text{H}_2\text{(g)})}{T} = \frac{-286+237}{298}$
   $\Delta_{\text{comb}}S°_{298\text{K}}(\text{H}_2\text{(g)}) = -164 \text{ J mol}^{-1}\text{ K}^{-1}$

7. The difference between the stoichiometric coefficients of the gaseous compounds in the balanced chemical equation for the reaction is:
   $0 - (1 + 1/2) = -3/2 < 0$
   This is consistent with a decrease of the disorder.

8. in methanol: OS(C) = –II
   in CO_2: OS(C) = +IV

9. At the anode: $\text{CH}_3\text{OH(l)} + \text{H}_2\text{O(l)} = \text{CO}_2\text{(g)} + 6\text{ H}^+\text{(aq)} + 6\text{ e}^-$
   At the cathode: $3/2\text{ O}_2\text{(g)} + 6\text{ H}^+\text{(aq)} + 6\text{ e}^- = 3\text{ H}_2\text{O(l)}$
   Global reaction: $\text{CH}_3\text{OH(l)} + 3/2\text{ O}_2\text{(g)} = \text{CO}_2\text{(g)} + 2\text{ H}_2\text{O(l)}$

10. $\Delta_{\text{comb}}G°_{298\text{K}}(\text{CH}_3\text{OH(l)}) = -nF\,[E°(\text{O}_2\text{(g)}/\text{H}_2\text{O(l)}) - E°(\text{CH}_3\text{OH(l)}/\text{CO}_2\text{(g)})]$
    $\Delta_{\text{comb}}G°_{298\text{K}}(\text{CH}_3\text{OH(l)}) = -6 \times 96485 \times (1.23 - 0.03)$
    $\Delta_{\text{comb}}G°_{298\text{K}}(\text{CH}_3\text{OH(l)}) = -695 \text{ kJ mol}^{-1}$

    $\Delta_{\text{comb}}H°_{298\text{K}}(\text{CH}_3\text{OH(l)}) = -\Delta_{\text{f}}H°_{298\text{K}}(\text{CH}_3\text{OH(l)}) + \Delta_{\text{f}}H°_{298\text{K}}(\text{CO}_2\text{(g)}) + 2\Delta_{\text{f}}H°_{298\text{K}}(\text{H}_2\text{O(l)})$
    $\Delta_{\text{f}}H°_{298\text{K}}(\text{H}_2\text{O(l)}) = \Delta_{\text{comb}}H°_{298\text{K}}(\text{H}_2\text{(g)}) = -286 \text{ kJ mol}^{-1}$ (question 5). Hence:
    $\Delta_{\text{comb}}H°_{298\text{K}}(\text{CH}_3\text{OH(l)}) = -(-239) + (-394) + 2 \times (-286)$
    $\Delta_{\text{comb}}H°_{298\text{K}}(\text{CH}_3\text{OH(l)}) = -727 \text{ kJ mol}^{-1}$
    $\gamma_{\text{thermo}} = \frac{-695}{-727} = 0.96$

11. $n_{\text{CH}_3\text{OH(l)}} = \frac{E}{\Delta_{\text{comb}}G°_{298\text{K}}(\text{CH}_3\text{OH(l)})} = \frac{-20 \times 3600}{-695} = 1.04{\cdot}10^2 \text{ mol}$
    $V = \frac{n_{\text{CH}_3\text{OH(l)}} \times M}{\mu_{\text{CH}_3\text{OH(l)}}} = \frac{104 \times 32}{0.79} = 4.2{\cdot}10^3 \text{ mL} < V(\text{gaseous dihydrogen})$

12. E being the energy to be produced:
    $n_{\text{H}_2\text{(g)}} = \frac{E}{\Delta_{\text{comb}}G°_{298\text{K}}(\text{H}_2\text{(g)})} = \frac{-20 \times 3600}{-237} = 3.04{\cdot}10^2 \text{ mol}$
    $P = \frac{n_{\text{H}_2\text{(g)}}RT}{V} = \frac{3.04{\cdot}10^2 \times 8.31 \times 298}{4.2{\cdot}10^{-3}} = 1.8{\cdot}10^8 \text{ Pa}$

Problem 5. Hydrogen storage

1. $PV = nRT \Leftrightarrow \frac{P}{RT} = \frac{\rho}{M}$
   $\rho = \frac{MP}{RT} = \frac{2.0{\cdot}10^{-3} \times 500{\cdot}10^5}{8.314 \times 293} = 41.1 \text{ kg m}^{-3}$

2. Correct statements:
   16 K, 25 K

3. Using the Clausius-Clapeyron relation and the boiling point under a pressure of 1 atm:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{\text{vap}}H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \text{ so: } P_{27.15\text{K}} = P_{\text{atm}}\exp\left[\frac{\Delta_{\text{vap}}H°}{R}\left(\frac{1}{T_v} - \frac{1}{T_{27.15K}}\right)\right]$$

$$\Delta_{vap}H°_m = 448.69\ \text{kJ kg}^{-1}\text{, so that } \Delta_{vap}H° = 897.38\ \text{J mol}^{-1}$$

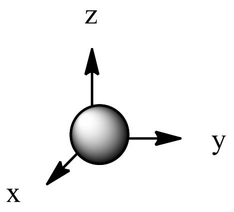
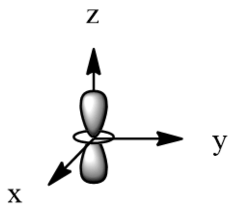
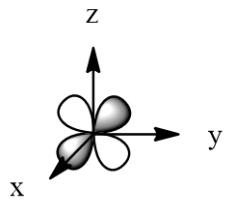
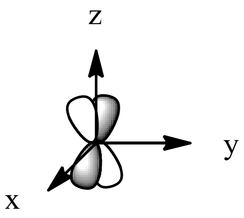
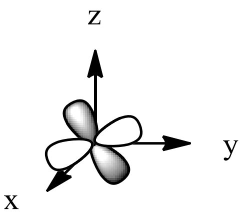
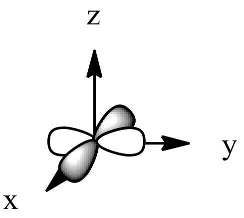
$$P_{27.15K} = 1.0 \cdot 10^5 \exp\left[\frac{897.38}{8.314}\left(\frac{1}{20.37} - \frac{1}{27.15}\right)\right] = 0.380\ \text{MPa} = 3.75\ \text{atm}$$

4. Dehydrogenated complex: $W(CO)_3(P(iPr)_3)_2 = WC_{21}O_3P_2H_{42}$ $M = 588.4$ g mol^{-1}
   Each complex can store one molecule of dihydrogen. In 1 kg of dihydrogen, there are 500 mol of dihydrogen. Hence, $m = 294.2$ kg of dehydrogenated complex are needed to store 1 kg of dihydrogen.
   Once bound to 1 kg of H_2, the complex thus weighs $m_{Kubas} = 295.2$ kg

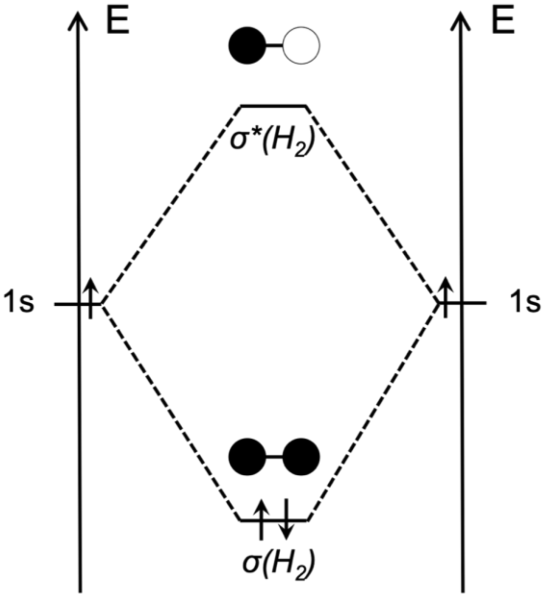
$$\rho_H = \frac{m_H \rho_{Kubas}}{m_{Kubas}} \quad \text{hence} \quad \rho_H = 6.6 \cdot 10^{-6}\ \text{kg(H}_2\text{) m}^{-3}$$

5. [Xe] $(6s)^2(4f)^{14}(5d)^4$ so 6 valence electrons (4f layer is full)

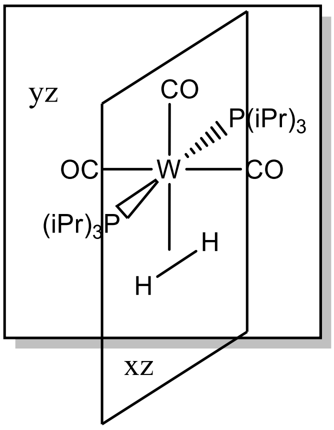
6.

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

7.



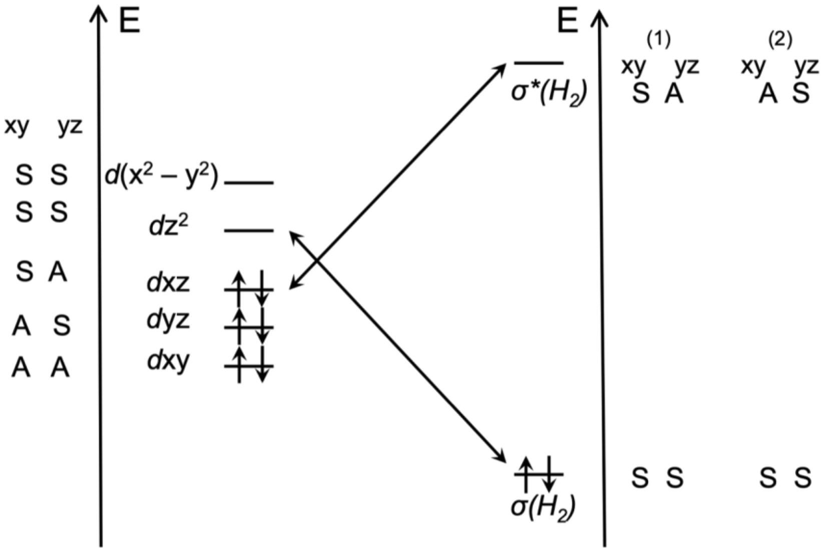
8. xz and yz planes



9. An orbital is symmetric with respect to a symmetry element if it remains the same when the symmetry operation is applied. An orbital is antisymmetric with respect to a symmetry element if it changes to its opposite when the symmetry operation is applied. The results are gathered in the diagram below.

10. As a general rule, interactions between two orbitals implying two electrons with the same symmetry lead to a stabilization inversely proportional to the difference of energy between the two orbitals. On the contrary, an interaction between two orbitals implying four electrons destabilizes the complex. Two orbitals have the same symmetry if all the symmetry elements are the same for each of the fragments. Moreover, all valence electrons have to be considered for tungsten to fill the d orbitals. Thus, 6 electrons for the metallic core and 2 electrons for hydrogen molecules are considered. One has to use Aufbau and Pauli principles. The result is depicted on the diagram below.

11. For all conformations, d_{z^2} and $d_{x^2-y^2}$ interacts with σH_2.
For conformation (1), only d_{xz} interacts with $\sigma{*}H_2$.
For conformation (2), only d_{yz} interacts with $\sigma{*}H_2$.



In conformation (1), σ* is SA (symmetric for xz plane and antisymmetric for yz plane) and in conformation (2), σ* is AS. So in conformation (1), σ* interacts with d_{xz} (same symmetry

SA), while in conformation (2) it interacts with d_{yz}. In conformation (1), the energies of the two interacting parts are the closest, thus leading to an enhanced stabilization.

12. $\rho_H = \frac{m_H}{V} = \frac{n_H M_H}{V} = \frac{2n_{HCOOH} M_H}{V} = \frac{2m_{HCOOH} M_H}{M_{HCOOH} V} = \frac{2\rho_{HCOOH} M_H}{M_{HCOOH}}$

$\rho_H = \frac{2 \times 1.22.10^3}{(2+12+32)} = 53.0 \text{ kg m}^{-3}$

The hydrogen density is higher in formic acid than for high pressure (500 bars) dihydrogen (31 kg m^{-3}) but lower than for cryogenic liquid hydrogen (70.85 kg m^{-3}). If one can extract efficiently H_2 molecule from formic acid, it constitutes a good alternative to pure H_2 storage.

13.

$$\Delta_r H^\circ = \sum_{i=1}^{N} \nu_i \Delta_f H_i^\circ$$

$\Delta_r H^\circ = -(-425.09) + (-393.51) + 0 = 31.58 \text{ kJ mol}^{-1}$

$$\Delta_r S^\circ = \sum_{i=1}^{N} \nu_i S_{i,m}^\circ$$

$\Delta_r S^\circ = -(131.84) + 213.79 + 130.68 = 212.63 \text{ J mol}^{-1} \text{ K}^{-1}$

14. $\Delta_r G^\circ(T) = \Delta_r H^\circ - T \cdot \Delta_r S^\circ$

$\Delta_r G^\circ(T) = 31.58 - 0.213 \times 293 = -30.8 \text{ kJ mol}^{-1}$

$K^\circ = e^{-\frac{\Delta_r G^\circ}{RT}}$

So: $K^\circ = 3.1 \cdot 10^5$

15. $n_{N_2} = n_{N_2,0} = \frac{PV}{RT}$

$n_{N_2} = \frac{1.013.10^5 \times 1.0.10^{-3}}{8.314 \times 298.15} = 0.04 \text{ mol}$

	HCOOH(l)	CO_2(g)	H_2(g)
Initial	n_{HCOOH}	$n_{CO_{2,0}}$	$n_{H_{2,0}}$
Intermediate	$n_{HCOOH} - \xi$	$n_{CO_{2,0}} + \xi$	$n_{H_{2,0}} + \xi$
Final	0	$n_{CO_{2,0}} + n_{HCOOH}$	$n_{H_{2,0}} + n_{HCOOH}$

$n_{HCOOH} = \frac{m_{HCOOH}}{M_{HCOOH}}$

$n_{HCOOH,0} = n_0 = \frac{2.3}{46.0} = 0.05 \text{ mol}$

Due to its high equilibrium constant, the reaction can be considered as total, and $n_{CO_2,0} = n_{H_2,0} = 0$ mol, so at equilibrium: $n_{CO_2} = n_{H_2} = n_{HCOOH,0}$

16. $LaNi_5H_6$: $\rho_H = 118 \text{ kg m}^{-3}$

Mg_2NiH_4: $\rho_H = 95 \text{ kg m}^{-3}$

17. $\ln\left(\frac{P}{P_0}\right) = \frac{Q_{ads}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$

From the slope of the curves

$\ln\left(\frac{P}{P_0}\right) = f\left(\frac{1}{T}\right)$

We find:
$LaNi_5H_6$: $Q_{ads} = –31.9$ kJ mol$^{–1}$
Mg_2NiH_4: $Q_{ads} = –83.0$ kJ mol$^{–1}$

Problem 6. Deacidification and desulfurization of natural gas

1. $C_nH_{2n+2} + n\ H_2O = n\ CO + (2n+1)\ H_2$

2. $\Delta_rH° = 205.9$ kJ mol$^{–1}$; $\Delta_rS° = 214.7$ J K$^{–1}$ mol$^{–1}$; $\Delta_rG° = –46$ kJ mol$^{–1}$ $= –RT \ln(K°)$ then $K° = 102$

3. pH > 7: $HCO_3^–$ and $CO_3^{2–}$ can be encountered in solution
   (i) with amine:
   $A + CO_2 + H_2O = AH^+ + HCO_3^–$ $10^{2.9}$
   $A + H_2S = HS^– + AH^+$ $10^{2.5}$

   (ii) with NaOH:
   if, for kinetic reasons, CO_2 and/or H_2S do not react with the amine:
   $CO_2 + 2\ HO^– = CO_3^{2–} + H_2O$ ($HO^–$ in excess) $10^{11.3}$
   $H_2S + 2\ HO^– = S^{2–} + H_2O$ (idem) $10^{8.0}$
   in all cases:
   $CH_3SH + HO^– = CH_3S^– + H_2O$ $10^{3.7}$

4. With MEA, case (i) of question 5:
   $HCO_3^–$: n_1; $HS^–$: n_2; MEA: $n_0 – (n_1 + n_2)$; $MEAH^+$: $n_1 + n_2$

5. CH_3SH

6. A1F1, titration by H^+ first:
   $V_{eq} = 24$ mL hence 24 mmol $= n_0 – (n_1 + n_2)$
   so: $n_1 + n_2 = 26$ mmol

   A1F2:
   between V_1 and V_2 (4 mL): titration of $CH_3S^–$ (n_3) → $n_3 = 4$ mmol

7. A2F1, titration by H^+ first:
   $V_{eq} = 36$ mL so 36 mmol $= n_0 – n_i$ ($i = 1$ or $i = 2$)
   so: $n_i = 14$ mmol

8. Two possibilities:
   - at half-equivalence of last step of A2F2, pH = 6.4. Hence gas 2 contains CO_2, so H_2S has reacted.
     $n_1 = 12$ mmol et $n_2 = 14$ mmol
   - more complete, considering both hypotheses:

$CO_2 - H_2S - CH_3S$	Gas 1	$CO_2 - H_2S - CH_3S$
CO_2 has reacted with MDEA	**hypothesis**	**H_2S has reacted with MDEA**
$MDEA - MDEAH^+ - HCO_3^-$	F1	$MDEA - MDEAH^+ - HS^-$
CH_3SH (4 mmol) – H_2S (12 mmol)	Gas 2	CH_3SH (4 mmol) – CO_2 (12 mmol)
HO^- (22 mmol) – CH_3S^- (4 mmol) S^{2-} (12 mmol)	F2	HO^- (22 mmol) – CH_3S^- (4 mmol) CO_3^{2-} (12 mmol)
pK_a = 14.0; 13.0; 10.3; 7.0 so V_{eq} should be 34 – 38 – 50 mL	V_{eq}	pK_a = 14.0; 10.3; 10.3; 6.4 so V_{eq} should be 22 – 38 – 50 mL
22 mL is lacking → false	**validity of the hypothesis**	**22 mL is present → true**

Problem 7. Lavoisier's experiment

1. Correct statement: $100\ J\ K^{-1}\ mol^{-1}$
   Since Hg_2O is a solid, its $S_m°$ should be smaller than that of gases like O_2 ($200\ J\ K^{-1}\ mol^{-1}$). In addition, the standard molar entropy of a compound can be $0\ J\ K^{-1}\ mol^{-1}$ only in a perfect crystalline state at 0 K, which is not the case here (298 K).

2. HgO formation: $Hg(l) + 1/2\ O_2(g) = HgO(s)$
   Hg_2O formation: $2\ Hg(l) + 1/2\ O_2(g) = Hg_2O(s)$

3. a) HgO (red)
   Calculation:
   $\Delta_r H° = \Delta_f H°(HgO(s)) = -90\ kJ\ mol^{-1}$ (because $\Delta_f H°(Hg(l)) = 0\ kJ\ mol^{-1}$)
   $\Delta_r S° = S°_m(HgO(s)) - S°_m(Hg(l)) - 1/2\ S°_m(O_2(g)) = -105\ J\ K^{-1}\ mol^{-1}$
   $\Delta_r G° = \Delta_r H° - 298 \times \Delta_r S° = -58.7 \cdot 10^3\ J\ mol^{-1}$
   $K° = \exp(-\Delta_r G°/RT) = 1.95 \cdot 10^{10}$

   b) HgO (yellow)
   Calculation:
   $\Delta_r H° = \Delta_f H°(HgO(s)) = -87\ kJ\ mol^{-1}$
   $\Delta_r S° = S°_m(HgO(s)) - S°_m(Hg(l)) - 1/2\ S°_m(O_2(g)) = -105\ J\ K^{-1}\ mol^{-1}$
   $\Delta_r G° = \Delta_r H° - 298 \times \Delta_r S° = -55.7 \cdot 10^3\ J\ mol^{-1}$
   $K° = 5.83 \cdot 10^9$

   c) Hg_2O
   Calculation:
   $\Delta_r H° = \Delta_f H°(Hg_2O(s)) = -90\ kJ\ mol^{-1}$
   $\Delta_r S° = S°_m(Hg_2O(s)) - 2 \times S°_m(Hg(l)) - 1/2\ S°_m(O_2(g)) = -150\ J\ K^{-1}\ mol^{-1}$
   $\Delta_r G° = \Delta_r H° - 298 \times \Delta_r S° = -45.3 \cdot 10^3\ J\ mol^{-1}$
   $K° = 8.72 \cdot 10^7$

4. HgO (red): $Hg(NO_3)_2(s) = HgO(s) + 2\ NO_2(g) + O_2(g)$
   HgO (yellow): $Hg^{2+}(aq) + 2\ HO^-(aq) = HgO(s) + H_2O(l)$

5. $n(Hg,i) = 122 / 200.6 = 6.08 \cdot 10^{-1}\ mol$
   At 25 °C, $V_m = 24\ L\ mol^{-1}$ so 0.80 L of air corresponds to 0.0333 mol of gas molecules.
   O_2 constitutes 20% of air, so:

$n(O_2) = 0.0333 \times 0.20 = 6.7 \cdot 10^{-3}$ mol
The reaction is quantitative and O_2 is the limiting reagent therefore $\xi_{max} = 6.7 \cdot 10^{-3}$ mol.
$n(Hg) = n(Hg,i) - 2\,\xi_{max} = 6.08 \cdot 10^{-1} - (2 \times 6.7 \cdot 10^{-3}) = 5.95 \cdot 10^{-1}$ mol
$n(O_2) = 0$ mol (limiting)
$n(HgO) = 2\,\xi_{max} = 1.3 \cdot 10^{-2}$ mol

6. $M(HgO) = 200.6 + 16.0 = 216.6$ g mol^{-1}
   $m(HgO) = n(HgO) \times M(HgO) = 2.8$ g

7. Correct statement: The yield is not maximum.
   Relative difference: (2.8 – 2.3) / 2.8 = 18%, which is a rather high discrepancy: Lavoisier did not reach the maximum yield (maybe for kinetic reasons?).
   The other statements are not satisfactory as they would explain an apparent yield higher than expected.

Problem 8. Which wine is it? Blind tasting challenge

1. Half-reactions:
   $C_6H_{12}O_6(s) + 12\ H^+(aq) + 12\ e^- = 3\ C_2H_6O(l) + 3\ H_2O\ (l)$
   $C_2H_6O(l) + 3\ H_2O(l) = 2\ CO_2(g) + 12\ H^+(aq) + 12\ e^-$
   Hence:
   $C_6H_{12}O_6(s) = 2\ C_2H_6O(l) + 2\ CO_2(g)$
   No, this reaction does not require the presence of dioxygen.

2. $\Delta_r H°(298\ K) = 2\ \Delta_f H°(C_2H_6O(l)) + 2\ \Delta_f H°(CO_2(g)) - \Delta_f H°(C_6H_{12}O_6(s))$
   $= -67.0$ kJ mol^{-1}
   $\Delta_r S°(298\ K) = 2\ S°_m(C_2H_6O(l)) + 2\ S°_m\ (CO_2(g)) - S°_m\ (C_6H_{12}O_6(s))$
   $= 536.5$ J mol^{-1} K^{-1}
   $\Delta_r G°(298\ K) = \Delta_r H°(298\ K) - T\ \Delta_r S°(298\ K) = -226.9$ kJ mol^{-1}
   Yes, this reaction generates heat because $\Delta_r H° < 0$.

3. $C_6H_{12}O_6(s) + 6\ O_2(g) = 6\ CO_2(g) + 6\ H_2O(l)$
   Yes, this reaction requires the presence of dioxygen.

4. Half-reactions:
   (1) $C_2H_6O(l) + H_2O\ (l) = C_2H_4O_2(l) + 4\ H^+(aq) + 4\ e^-$
   (2) $Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- = 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
   Hence:
   2×(2) + 3×(1):
   $2\ Cr_2O_7^{2-}(aq) + 3\ C_2H_6O(l) + 16\ H^+(aq) = 4\ Cr^{3+}(aq) + 3\ C_2H_4O_2(l) + 11\ H_2O(l)$

5. $\Delta_r G°(Cr_2O_7^{2-}/Cr^{3+}) = -6FE°(Cr_2O_7^{2-}/Cr^{3+})$
   $\Delta_r G°(C_2H_4O_2/C_2H_6O) = -4FE°(C_2H_4O_2/C_2H_6O)$
   Hence $\Delta_r G° = 12F(E°(C_2H_4O_2/C_2H_6O) - E°(Cr_2O_7^{2-}/Cr^{3+})) = -RT\ln K°$
   And $K° = 10^{231}$
   $K° >> 1$, so the reaction can be used to determine the concentration of alcohol in wine.

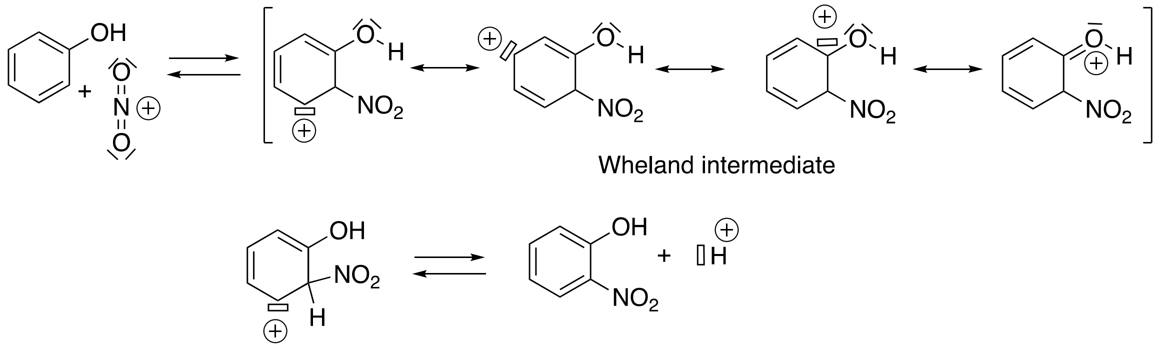
6. $pH = -\log[H_3O^+] = -\log(c(H_2SO_4)) = 1$

7. At the equivalence point, $n(H_3O^+) = n_0(H_3O^+) - 8V_0 \times [Cr_2O_7^{2-}] = 1\cdot10^{-2} - 8 \times 1.00\cdot10^{-1} \times 5\cdot10^{-3} = 6\cdot10^{-3}$ mol.
   Hence, $pH = -\log[H_3O^+] = 1.3$ taking into account the dilution.
   No, because the pH does not change significantly along the reaction course.

8. At the equivalence point, $\frac{n(C_2H_6O)}{3} = \frac{n(Cr_2O_7^{2-})}{2}$, *i.e.* $\frac{c(C_2H_6O)V_e}{3} = \frac{c(Cr_2O_7^{2-})V(Cr_2O_7^{2-})}{2}$,
   Where $c(C_2H_6O)$ is the concentration of alcohol in the diluted wine.
   $c(C_2H_6O) = 0.05$ mol L^{-1} so the concentration of ethanol in the non-diluted wine is 2.5 mol L^{-1}.
   In terms of mass concentration: $c_m(C_2H_6O) = c(C_2H_6O) \times M(C_2H_6O) = 115$ g L^{-1}.
   The percentage of alcohol per volume of this wine is thus:
   $\frac{c_m(C_2H_6O)}{\rho(\text{ethanol})} \times 100 = \frac{115}{0.79\cdot10^3} \times 100 = 14.6\%$
   Wine X is thus a Châteauneuf du Pape.

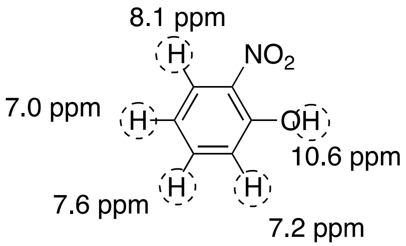
Problem 9. Nitrophenols: synthesis and physical properties

1.

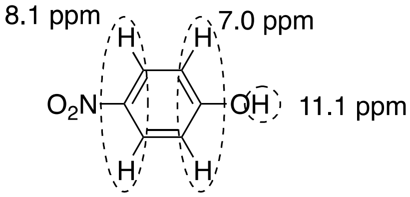


2. 2,6-dinitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol are possible products due to polynitration. 3-nitrophenol is also a possible side-product but it is not favored because the corresponding Wheland intermediate is less stable.

3. **A**: 2-nitrophenol, **B**: 4-nitrophenol
   The easiest assignment is for the 4-nitrophenol **B**. Indeed, due to the symmetry of the molecule, it presents two doublets with an integration of 2 protons. To assign the shifts, we have to keep in mind that the OH group is an electro-donating group and increases the density in ortho position, which explains a lower shift. On the contrary, NO_2 is an electron-withdrawing group, which explains a higher shift.
   For **A**, the hydrogens will all have a different shift. The two singlets correspond to hydrogens in ortho position of OH and NO_2 groups. The assignment can be explained using the same argument as before. Other protons are also assigned using the electronic effects too. In para position of the OH (NO_2) group, the density is more (less) important, which decreases (increases) the NMR displacement of the corresponding proton.



A



B

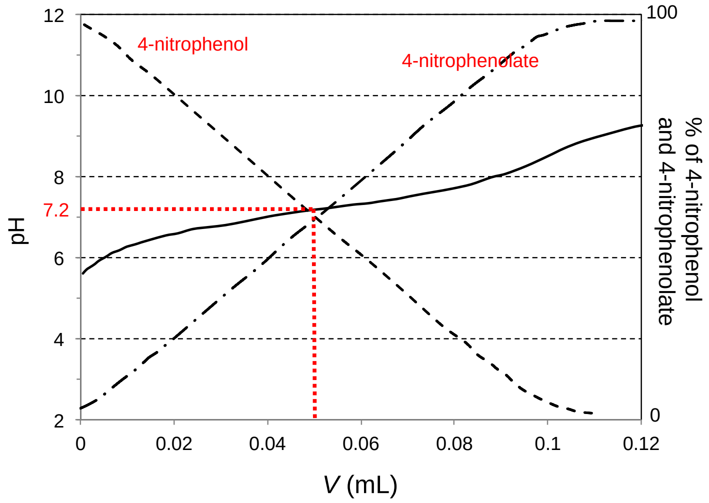
4. Correct answer:
   Intermolecular hydrogen bonds
   B can develop hydrogen bonds with water molecules, which increases its solubility, while **A** develops more intramolecular hydrogen bonds.

5. Correct statements:
   A has a higher retardation factor (R_f) than **B** on the TLC because:
   A develops an intramolecular hydrogen bond.
   B develops intermolecular hydrogen bonds with the silica.
   Due to its intramolecular hydrogen bond, the 2-nitrophenol exhibits a higher migration because fewer interactions are developed with the silica. On the contrary, **B** develops hydrogen bonds with the silica and is retained.

6. Correct answer:
   Yellow
   At pH = 7, the absorbance in the visible light is important around 390 nm, which corresponds to purple. The complementary color is yellow.

7. Correct answer:
   4-nitrophenol has a shorter absorption wavelength than its conjugated base because its conjugation is less important.

8. Assignment of spectra on figure:



9. pH = pK_a when [acid] = [basis]. Using the figure above, we find pK_a = 7.2.

10. Correct answers:
    UV-Visible spectroscopy, NMR, conductometry.

Problem 10. French stone flower

1. To determine the stoichiometry of crystallized water y, the molar mass of laumontite needs first to be calculated:
   $\rho = \frac{m}{V} = \frac{m}{abc \times sin\beta}$ and $n = \frac{m}{M} = \frac{Z}{N_A}$ i.e. $m = \frac{MZ}{N_A}$ then:
   $$M = \frac{\rho \times N_A \times abc \times sin\beta}{Z} = 470 \text{ g mol}^{-1}$$
   In dry air the crystallized water is removed: we can then deduce it corresponds to 15.3% of the total mass as a further heat treatment does not make the mass of the sample vary.
   15.3% corresponds to 72 g mol^{-1} and then $y = 72/18 = 4$.
   According to the laumontite formula, this number corresponds also to the stoichiometry of the oxide **A**.

2. The mass of the residue can be calculated as the difference of masses of the crucible before and after the calcination. A mass of 0.255 g is obtained: it corresponds to a molar mass for the binary compound of 470 × 0.255 / 0.500 = 240 g mol^{-1}.
   This binary compound is either the oxide **A** or **B**.
   Knowing that $y = 4$ we obtain $M_A = 60$ g mol^{-1} which is univocally SiO_2 (ScO and CO_3 are not relevant): the addition of HCl yielded a $SiO_2{\cdot}nH_2O$ precipitate which lost its water molecules during calcination.
   The hypothesis that precipitate is **B** with possible values of $z = 1, 2, 3, 5$, etc. does not lead to satisfying results.
   The unknown part $(CaO)_x(\mathbf{B})_z$ still needs to be elucidated. Its molar mass can be calculated as: $M_{(CaO)x(\mathbf{B})z} = (470 - 72 - 240) = 158$ g mol^{-1}. It can then be deduced that the value of x cannot exceed 2. If $x = 2$, $\mathbf{B}_z$ has a molar mass M = 46 g mol^{-1}, which is not possible, since there is no oxide with this molar mass. So, $x = 1$ and the molar mass of $\mathbf{B_z}$ is 102 g mol^{-1}.
   For $z = 1$, we find $\mathbf{B} = Al_2O_3$.

3. From the qualitative data (formation of a $FeSCN^{2+}$ red complex) we can deduce that **E** is Fe (Fe^{3+} when oxidized and Fe^{2+} in the crystal).

4. $Fe^{3+}(aq) + SCN^{-}(aq) = Fe(SCN)^{2+}(aq)$
   $Fe^{3+}(aq) + 3\ NH_3(aq) + 3\ H_2O(l) = Fe(OH)_3(s) + 3\ NH_4^+(aq)$
   $2\ Fe(OH)_3(s) + 6\ H^+(aq) + Zn(s) = 2\ Fe^{2+}(aq) + Zn^{2+}(aq) + 6\ H_2O(l)$
   $Fe^{2+}(aq) + Ce^{4+}(aq) = Ce^{3+}(aq) + Fe^{3+}(aq)$
   (several answers and notations are acceptable)

5. Using the titration reaction $Fe^{2+}(aq) + Ce^{4+}(aq) = Ce^{3+}(aq) + Fe^{3+}(aq)$ we find that:
   $n(Fe^{3+}) = 5.15{\cdot}10^{-3} \times 2.00{\cdot}10^{-3} = 1.03{\cdot}10^{-5}$ mol in the titrated solution and thus:
   $n(Fe^{3+}) = 1.03{\cdot}10^{-5} \times 100.0/20.0 = 5.15{\cdot}10^{-5}$ mol in the initial solution which corresponds to $n(Fe^{2+}) = 5.15{\cdot}10^{-5}$ mol in 0.500 g of the solid. In 0.500 g of the pure crystal, $n(Ca^{2+}) = 0.500 / 471 = 1.06{\cdot}10^{-3}$ mol, so the molar percentage of the impurity compared to calcium is $5.15{\cdot}10^{-5} / 1.06{\cdot}10^{-3} = 4.86\%$.

6. The titration reaction is: $Fe^{2+}(aq) + Ce^{4+}(aq) = Ce^{3+}(aq) + Fe^{3+}(aq)$. Then, at the equivalence point, Fe^{2+} and Ce^{4+} have been introduced in equivalent quantities. When the reaction occurs, equal quantities of Fe^{2+} and Ce^{4+} are consumed and equal quantities of Fe^{3+} and Ce^{3+} are produced. Thus, at equilibrium, the following relationships can be written: $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$.

At equilibrium, the potential $E_{\text{e.p.}}$ of the solution can be expressed as a function of each of the redox couples:

$$E_{\text{e.p.}} = E°(\text{Fe}^{3+}/\text{Fe}^{2+}) - \frac{RT}{F}\ln\left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}\right) = E°(\text{Ce}^{4+}/\text{Ce}^{3+}) - \frac{RT}{F}\ln\left(\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}\right)$$

The combination of these two expressions leads to:

$$E_{\text{e.p.}} = \frac{1}{2}\left(E°(\text{Fe}^{3+}/\text{Fe}^{2+}) - \frac{RT}{F}\ln\left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}\right) + E°(\text{Ce}^{4+}/\text{Ce}^{3+}) - \frac{RT}{F}\ln\left(\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}\right)\right)$$

$$E_{\text{e.p.}} = \frac{E°(\text{Fe}^{3+}/\text{Fe}^{2+}) + E°(\text{Ce}^{4+}/\text{Ce}^{3+})}{2} - \frac{1}{2}\frac{RT}{F}\ln\left(\frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]}\right)$$

$$= \frac{E°(\text{Fe}^{3+}/\text{Fe}^{2+}) + E°(\text{Ce}^{4+}/\text{Ce}^{3+})}{2}$$

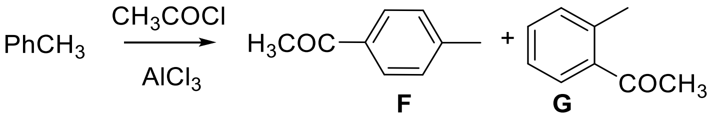
then:

$$E_{\text{e.p.}} = \frac{0.53 + 1.09}{2} = 0.81\ V\ /SCE$$

Note: such a formula WILL NOT be expected to be known by heart for the competition exam but the simple use of Nernst equation as it is demonstrated here could be required.

7. According to the value of the potential at the equivalence point (0.81 V /SCE), we can use the following indicators that exhibit the standard potential the closest to this value: 5,6-dimethy-l,10-phenanthroline and 4-ethoxychrysoidine hydrochloride.

8.



9. According to the values of the diameters given in the text of the problem, the product **F** seems to be smaller than **G**: **F** is then the main one that can be synthesized in laumontite.

Problem 11. The mineral of winners

1. To determine the formula of pyromorphite, its molar mass needs first to be calculated:

$\rho = \frac{m}{V} = \frac{m}{abc \times sin\beta}$ and $n = \frac{m}{M} = \frac{Z}{N_\text{A}}$ *i.e.* $m = \frac{MZ}{N_\text{A}}$ then:

$$M = \frac{\rho \times N_\text{A} \times abc \times sin\beta}{Z} = 1356 \text{ g mol}^{-1}$$

The cation **A** can be identified from the reaction with potassium iodide. Using the problem data and the molar mass of the mineral, the number of moles of the mineral in solution can be calculated: in 1.000 g of solid, there is 1 / 1356 = $7.375 \cdot 10^{-4}$ mol of pyromorphite. 1.224 g of KI, that is 1.224 /1 66 = $7.37 \cdot 10^{-3}$ mol. Hence, the ratio between both reagents is $7.37 \cdot 10^{-4} \times 5 / 7.375 \cdot 10^{-3} = 0.500$ and the reaction between both reads:

$$\mathbf{A}^{2+} + 2\ \text{I}^- = \mathbf{A}\text{I}_2$$

The molar mass of the precipitate is then 1.700 / $3.688 \cdot 10^{-3}$ mol = 461 g mol^{-1} and we can finally calculate the molar mass of **A**: M(**A**) = 461 – (2 × M(I)) = 207 g mol^{-1}. We can deduce: **A** = Pb.

To determine **B**: $M(\mathbf{B}) = 1356 - 5 \times 207 - 3 \times 95 = 36$ g mol^{-1}. Therefore, **B** = Cl and the formula of pyromorphite is $\mathbf{Pb}_5(PO_4)_3\mathbf{Cl}$.

2. $PbI_2(s) + 2I^-(aq) = PbI_4^{2-}(aq)$

3. $M(\mathbf{C}) = 207 / 3.98 = 52$ g mol^{-1}. Therefore, **C** = Cr.

   $Pb^{2+}(aq) + SO_4^{2-}(aq) = PbSO_4\ (s)$
   $Cr^{3+}(aq) + 3\ NH_3(aq) + 3\ H_2O(l) = Cr(OH)_3(s) + 3\ NH_4^+(aq)$
   $Cr(OH)_3(s) + 3\ H^+(aq) = Cr^{3+}(aq) + 3\ H_2O(l)$
   $2\ Cr^{3+}(aq) + 3\ S_2O_8^{2-}(aq) + 7\ H_2O(l) = Cr_2O_7^{2-}(aq) + 6\ SO_4^{2-}(aq) + 14\ H^+(aq)$
   $Cr_2O_7^{2-}(aq) + 6\ Fe^{2+}(aq) + 14\ H^+(aq) = 2\ Cr^{3+}(aq) + 6\ Fe^{3+}(aq) + 7\ H_2O(l)$
   $5\ Fe^{2+}(aq) + MnO_4^-\ (aq) + 8\ H^+(aq) = Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$
   (several notations are acceptable)

4. The method described here is a back titration. Indeed, after the following reaction:
   $Cr_2O_7^{2-}(aq) + 6\ Fe^{2+}(aq) + 14\ H^+(aq) = 2\ Cr^{3+}(aq) + 6\ Fe^{3+}(aq) + 7\ H_2O(l)$
   the excess iron (II) is titrated by a solution of potassium permanganate:
   $5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) = Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$
   According to the last reaction, the amount of iron titrated by potassium permanganate: $n_{excess}(Fe^{2+}) = 5 \times c(MnO_4^-) \times V(MnO_4^-) = 7.08 \cdot 10^{-4}$ mol
   We can then deduce that, in the 10.0 mL aliquot, $10.0 \cdot 10^{-3} \times 0.100 - 7.08 \cdot 10^{-4} = 2.92 \cdot 10^{-4}$ mol of Fe^{2+} reacted with $Cr_2O_7^{2-}$. In the aliquot:
   $m_{al}(Cr) = (2.92 \cdot 10^{-4} \times 2 \times M(Cr)) / 6 = 5.1$ mg
   For 1.00 g of the mineral, we find then: $m(Cr) = m_{al}(Cr) \times V_{vol.fl.} / V_{al.} = 51$ mg
   Hence, the weight content of chromium in the mineral is equal to: 0.051 / 1.00 = 5.1 w.%

5. $5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) = Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$
   $\Delta_r G° = -5 \times FE°(MnO_4^-/Mn^{2+}) - 5 \times (-FE°(Fe^{3+}/Fe^{2+}))$
   $K° = \exp(-\Delta_r G° / RT) = \exp(-5F(E°(Fe^{3+}/Fe^{2+}) - E°(MnO_4^-/Mn^{2+})) / RT)) = 3.8 \cdot 10^{62}$

6. $2\ Mn^{2+}(aq) + 5\ S_2O_8^{2-}(aq) + 8\ H_2O(l) = 2\ \underline{\mathbf{MnO_4}}^-(aq) + 10\ SO_4^{2-}(aq) + 16\ H^+(aq)$
   Mn^{2+} is oxidized only after the complete oxidation of Cr^{3+} ($E°(MnO_4^-/Mn^{2+}) > E°(\mathbf{C}(+m)/\mathbf{C}(+n))$).
   The solution will then turn pink.

7. Correct answer:
   $FeSO_4$ is not stable and get quickly oxidized by the oxygen in the air.
   $4\ Fe^{2+}(aq) + O_2(aq) + 4H^+(aq) = 4\ Fe^{3+}(aq) + 2\ H_2O(l)$

Problem 12. Reaction progress kinetics

1. $r = k_2[2][5]$

2. $[4]_{tot} = [4] + [5]$

3. Steady state approximation for **5**: $k_{-1}[5] + k_2[2][5] = k_1[1][4]$

$$[5] = \frac{k_1[4][1]}{k_{-1} + k_2\,[2]}$$

   With result from question 3, one obtains

$$[5] = \frac{k_1[4]_{\text{tot}}[1]}{k_{-1} + k_2[2]} - \frac{k_1[5][1]}{k_{-1} + k_2[2]}$$

This allows writing

$$[5]\frac{k_1[1] + k_{-1} + k_2[2]}{k_{-1} + k_2[2]} = \frac{k_1[4]_{\text{tot}}[1]}{k_{-1} + k_2[2]}$$

Finally using result from question 2 one obtains:

$$r = \frac{k_1k_2[1][2][4]_{\text{tot}}}{k_{-1} + k_1[1] + k_2[2]}$$

4. Replace [2] in the above equation by [1] + [“excess”] and the relation is found.

$$r = \frac{k_1k_2[1]([1] + [\text{"excess"}])}{k_{-1} + k_1[1] + k_2[1] + k_2[\text{"excess"}]}[4]_{\text{tot}}$$

It is easy to show that

$$\frac{a}{1 + b[1]} = \frac{k_1k_2}{k_{-1} + k_1[1] + k_2[1] + k_2[\text{"excess"}]}$$

5. The rate of the reaction is expressed as $r = 1 / V \times (\mathrm{d}n / \mathrm{d}t)$ where dn is the amount of matter that has been transformed in the reaction with molar heat $\Delta_\mathrm{r}H$ during the time dt. Consequently, the heat flow during time dt is $\mathrm{d}q = \mathrm{d}n\Delta_\mathrm{r}H = \Delta_\mathrm{r}H\, V\, r\, \mathrm{d}t$.

6. Correct answer: Experiment A because the initial concentration in reactant was higher.

7. Correct answer: Experiment A because if more product has been formed, it implies that more catalyst turnovers have been achieved.

8. Correct answer: True because in the case of product inhibition, the formation of the product would hamper the reaction and thus the more product the less efficient the reaction.

9. Correct answer: True because catalyst deactivation is occurring with time and therefore the more turnovers have been achieved the more likely catalyst deactivation is to happen. Moreover, catalyst deactivation implies that less catalyst is present and thus the rate decreases.

10. Correct answer: True because the rates of the two reactions with same excess but different initial concentration do overlap.

11. Correct answer: True; in that case, the reaction of Experiment C with the same excess but larger initial concentration has a rate lower rate than that of Experiment D. Therefore, either catalyst deactivation or product inhibition is taking place. If product inhibition is the reason for the observed behavior, then setting an experiment for Experiment D where more product is present right from the start would create a situation similar to that observed in Experiment C and thus the curves should overlap. If the curve obtained remains similar to that observed for Experiment D then product inhibition is not the investigated factor and catalyst deactivation is.

Problem 13. Nylon 6

1. The initial initiator concentration is equal to the sum of the concentrations of the remaining initiator in solution and of the initiator in the ionic or neutral polymer chain:

$$[\mathrm{I}]_0 = [\mathrm{I}] + \sum_{i=1}^{n} [\mathrm{P_i}] + \sum_{i=1}^{n} [\mathrm{A_i}]$$

2. If we apply the steady state approximation to all the A_i we obtain:

$$k_1[\mathrm{I}][\mathrm{M}^-] = k_2[\mathrm{A_1}] + k_3[\mathrm{MH}][\mathrm{A_1}]$$
$$k_1[\mathrm{P_1}][\mathrm{M}^-] = k_2[\mathrm{A_2}] + k_3[\mathrm{MH}][\mathrm{A_2}]$$
$$\cdots$$
$$k_1[\mathrm{P_{n-1}}][\mathrm{M}^-] = k_2[\mathrm{A_n}] + k_3[\mathrm{MH}][\mathrm{A_n}]$$

3. The rate of disappearance of the monomer **MH** is:

$$-\frac{\mathrm{d[MH]}}{\mathrm{d}t} = k_3[\mathrm{MH}]\sum_{i=1}^{n}[\mathrm{A_i}]$$

From the previous question, we have:

$$(k_2 + k_3[\mathrm{MH}])\left(\sum_{i=1}^{n}[\mathrm{A}_i]\right) = k_1[\mathrm{M}^-]\left([\mathrm{I}] + \sum_{i=1}^{n}[\mathrm{P}_i]\right)$$

hence, from the relation obtained at question 1:

$$\sum_{i=1}^{n}[\mathrm{A}_i] = \frac{k_1[\mathrm{M}^-][\mathrm{I}]_0}{k_1[\mathrm{M}^-] + k_2 + k_3[\mathrm{MH}]}$$

The concentration of $[\mathrm{M}^-]$ is related to the ion pair [MNa] via the equilibrium constant $K° = \frac{[\mathrm{Na}^+][\mathrm{M}^-]}{[\mathrm{MNa}]}$. If we neglect the concentration of the intermediates $\mathbf{A}_i$, the electroneutrality condition imposes $[\mathrm{Na}^+] = [\mathrm{M}^-]$. Hence:

$$[\mathrm{M}^-] = \sqrt{K°[\mathrm{MNa}]}$$

Finally, the disappearance rate of monomer **MH** is:

$$-\frac{\mathrm{d[MH]}}{\mathrm{d}t} = \frac{k_1 k_3[\mathrm{MH}]\sqrt{K°[\mathrm{MNa}]}[\mathrm{I}]_0}{k_1\sqrt{K°[\mathrm{MNa}]} + k_2 + k_3[\mathrm{MH}]}$$

4. If we assume that the acid base reaction between $\mathbf{A_1}$ and **MH** is the rate determining step, then $k_2 >> k_3[\mathrm{MH}]$ and $k_1\sqrt{K°[\mathrm{MNa}]} \gg k_3[\mathrm{MH}]$, so the rate expression can be simplified as:

$$-\frac{\mathrm{d[MH]}}{\mathrm{d}t} = \frac{k_1 k_3\sqrt{K°[\mathrm{MNa}]}}{k_1\sqrt{K°[\mathrm{MNa}]} + k_2}[\mathrm{I}]_0[\mathrm{MH}]$$

In this case, the monomer reaction order is equal to 1 and the conversion rate of the monomer is:

$$\tau = \frac{[\mathrm{MH}]_0 - [\mathrm{MH}]}{[\mathrm{MH}]_0} = 1 - \exp\left(-\frac{k_1 k_3\sqrt{K°[\mathrm{MNa}]}}{k_1\sqrt{K°[\mathrm{MNa}]} + k_2}[\mathrm{I}]_0 t\right)$$

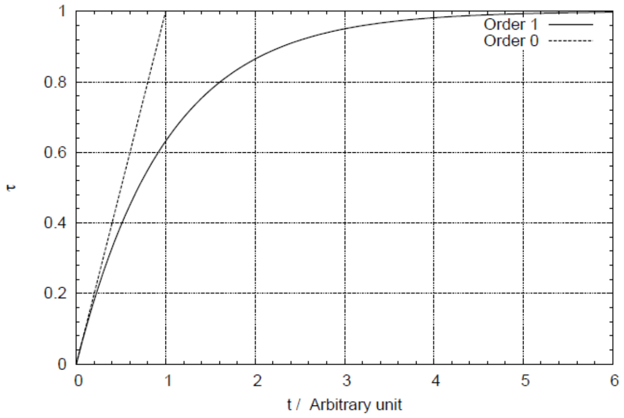
On the contrary, if we assume that $k_2 << k_3[\mathrm{MH}]$ and $k_1\sqrt{K°[\mathrm{MNa}]} \ll k_3[\mathrm{MH}]$, the rate can be rewritten as:

$$-\frac{\mathrm{d}[\mathrm{MH}]}{\mathrm{d}t} = k_1\sqrt{K^\circ[\mathrm{MNa}]}[\mathrm{I}]_0$$

The monomer reaction order is then equal to 0 and the conversion rate of the monomer is:

$$\tau = \frac{[MH]_0 - [MH]}{[MH]_0} = \frac{k_1\sqrt{K^\circ[\mathrm{MNa}]}}{[\mathrm{MH}]_0}[\mathrm{I}]_0 t$$

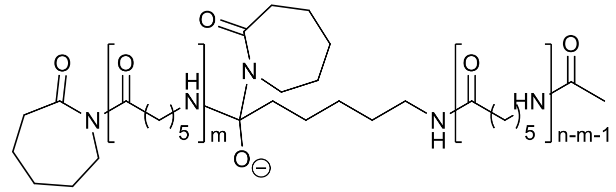
5. The conversion of monomer versus time of the two limiting cases is thus:



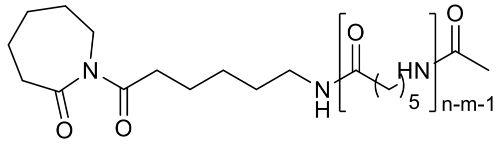
6. <u>Correct answers:</u> An autocatalytic process, A catalyzed reaction
   The sigmoid curve stresses out that the polymerization reaction is an autocatalytic process.

7. The structures of the intermediates are the following:

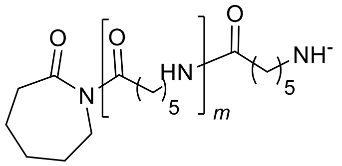
$B^{\ominus}$



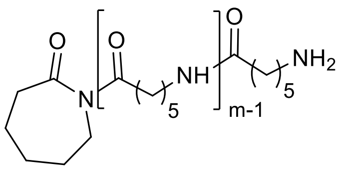
C



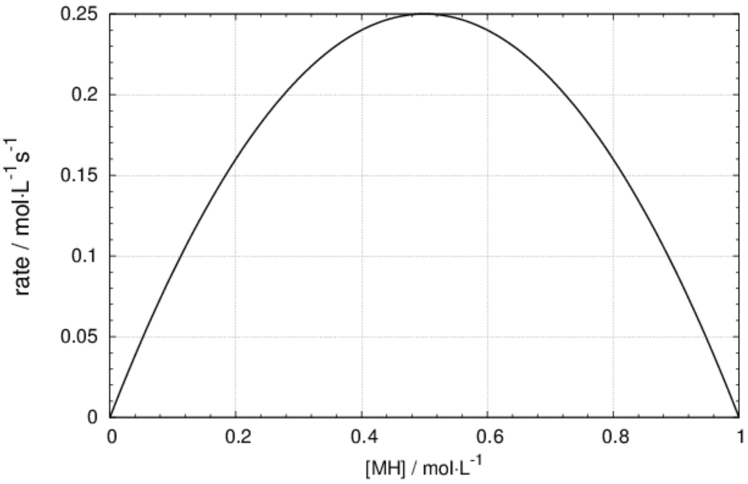
$D^{\ominus}$



E



8. $-\frac{\mathrm{d[MH]}}{\mathrm{d}t} \sim [\mathrm{MH}]([\mathrm{MH}]_0 - [\mathrm{MH}])$

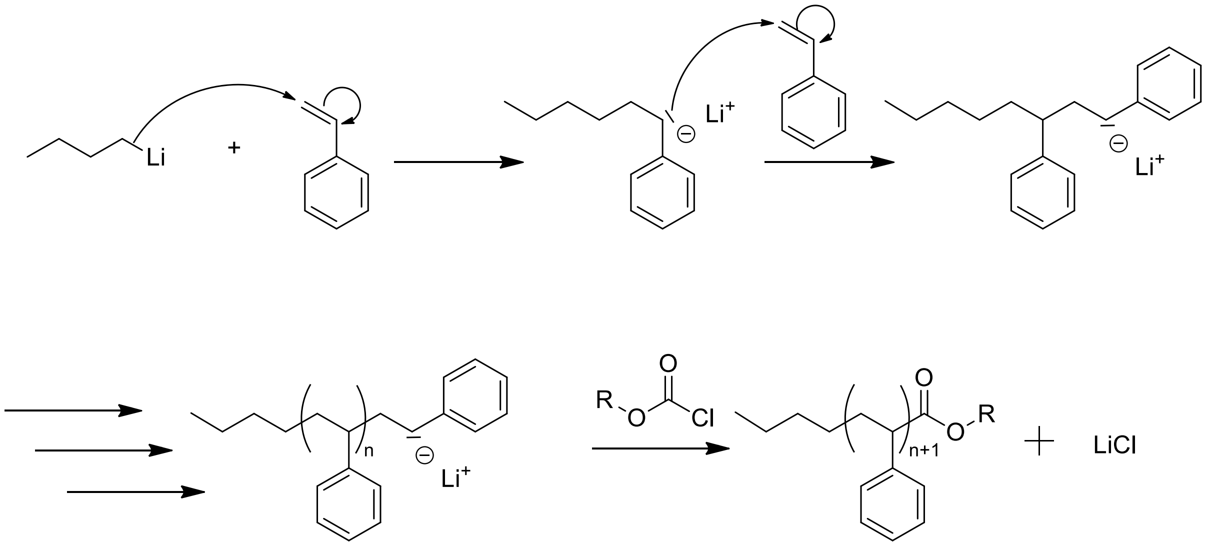


The disappearance rate of the monomer **MH** increases until the monomer concentration reaches $[\mathrm{MH}]_0 / 2$ and then decreases. The rate is then the highest for $[\mathrm{MH}] = [\mathrm{MH}]_0 / 2$. It means that the conversion versus time curve of the monomer slowly increases (induction time), then the conversion changes rapidly and then slowly increases. This degradation mechanism can explain the sigmoid curve observed by Macosco.

Problem 14. Synthesis of block copolymers followed by size-exclusion chromatography

1. Correct answer: *n*-Butyllithium (*n*-BuLi)

2.



3. $k_a >> k_p$

4. The rate of disappearance of the monomer corresponds to –d[M]/d*t*, and M is consumed at each polymerization step *i*. Therefore:

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_\mathrm{p} \sum_i [\mathrm{AM}_i^-][\mathrm{M}]$$

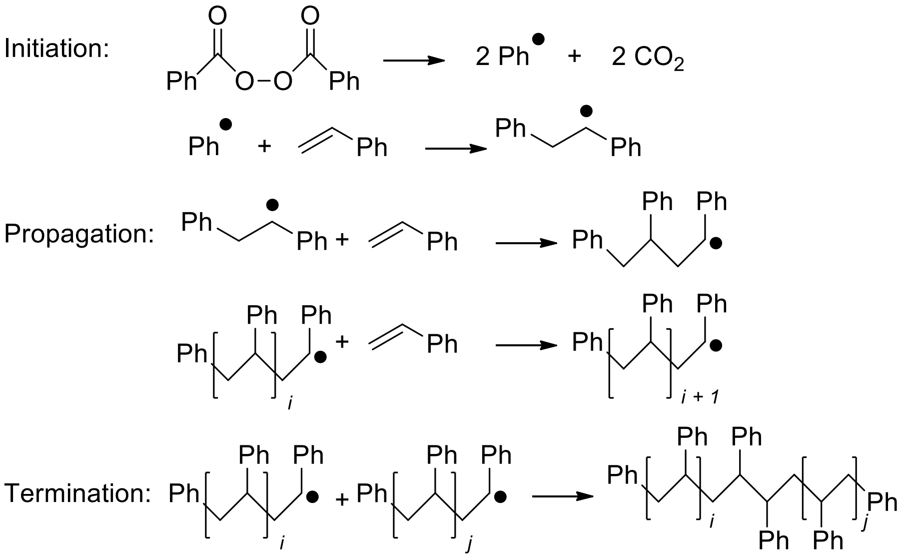
5. The active species concentration is constant and equal to C, so

$$\sum_i [\mathrm{AM}_i^-] = C$$

Therefore, $-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}]C$.

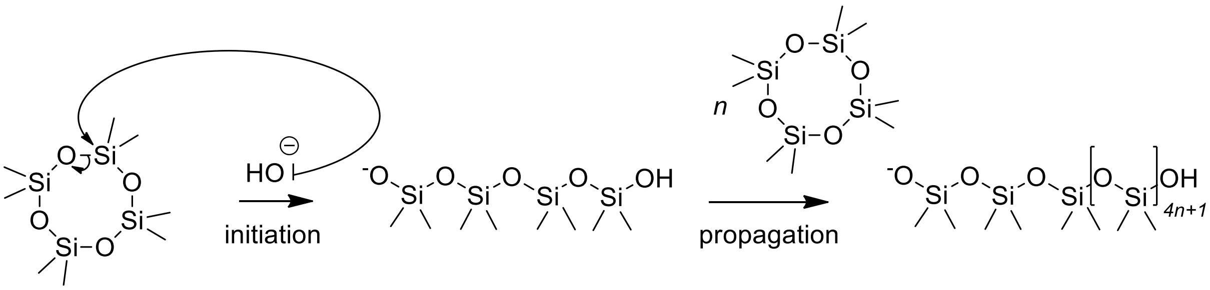
6. $[\mathrm{M}](t) = [\mathrm{M}](t=0)\mathrm{e}^{-\frac{t}{k_\mathrm{p}C}}$
   The half-time is thus $t_{1/2} = \ln(2)/(k_\mathrm{p}C)$

7.

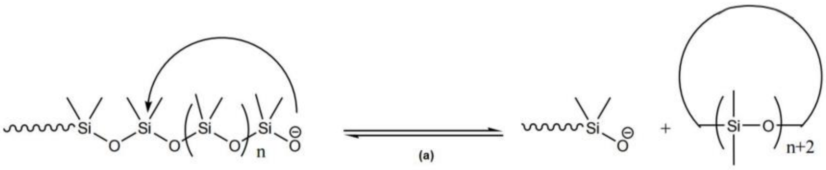


8. Correct answer: Yes, because of the preferential formation of one product over another (the reaction selectively generates one constitutional isomer over the other). Radicals add to the terminal carbon atom of styrene to form a benzyl-type radical.

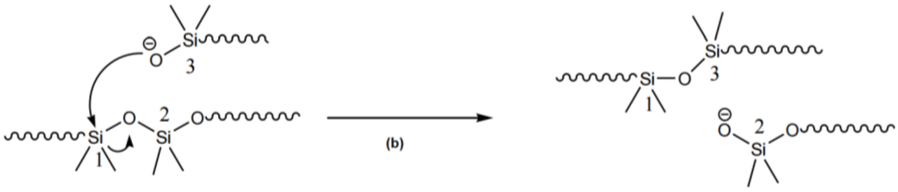
9.



10.



11.



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12. M_n is more sensitive to molecules of **low** molecular mass while M_w is more sensitive to molecules of **high** molecular mass. Therefore, the more the polymer chains approach uniform chain length, the more I_p is close to 1.

13. Curve (b) (the shorter the polymer, the higher the elution volume).

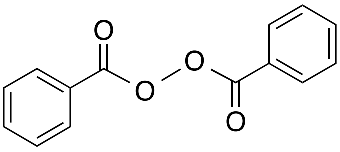
14. The full width half maximum of the SEC signal is related to the I_p value: the closer to 1 the I_p, the thinner the SEC curve. Curves (a) and (b) correspond then to similar I_p values, whereas curves (c) corresponds to a larger one. Since sample (II) was prepared at a low temperature, starting from (I), are likely to display similar polydispersities and then we can state: (I) → (a), (II) → (b) and (III) → (c).

15. PS-PDMS-$O(CH_3)_2SiCH_2CH_2Si$-$(CH_3)_2$-O-PDMS-PS or in a more condensed form PS-PDMS-PS (as the linkage is chemically close to PDMS).

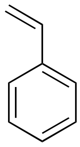
16. **PS → 3** (because it is the shortest molecule of the list)
 PS-PDMS precursor → 2 (because it is a molecule that is bigger than PS, but smaller than the final product)
 unfractionated product → 1 (because we observe that there are two SEC curves that reach the lowest elution volume, therefore they could be the final product. But as we suggest an unfractionated product, it should correspond to the curve with 2 signals i.e. 2 products with the desired and the unwanted product)
 fractionated product → 4

Problem 15. Radical polymerization

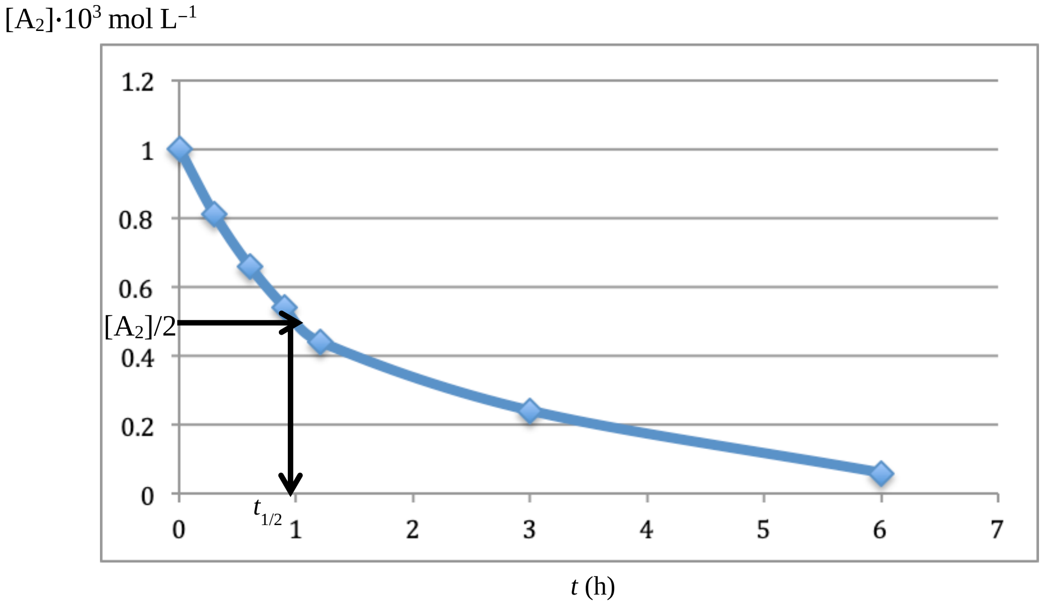
1. The initiator is benzoyl peroxide.



The monomer used is styrene.



2. The half-life is the time required to consume 50% of the reactants.



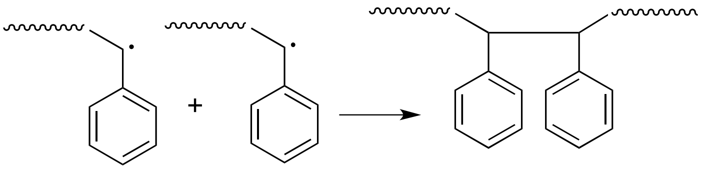
We can graphically determine $t_{½}$ as roughly 1 h.

3. $\mathbf{A_2}$ is a unimolecular initiator, and its decomposition follows a first order kinetic. In this case the half-life is:

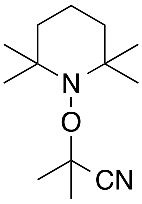
$$k_\mathrm{d} = \frac{\ln 2}{t_{½}}$$

Given the half-life estimate from question 2: $k_\mathrm{d} = 1.9\cdot10^{-4}$ s^{-1}

4. Self-combination



5. **ALK1**:



6. By substituting the provided data in the following equation:

$$M_{\mathrm{n}} = conv \times \frac{m}{f \times n}$$

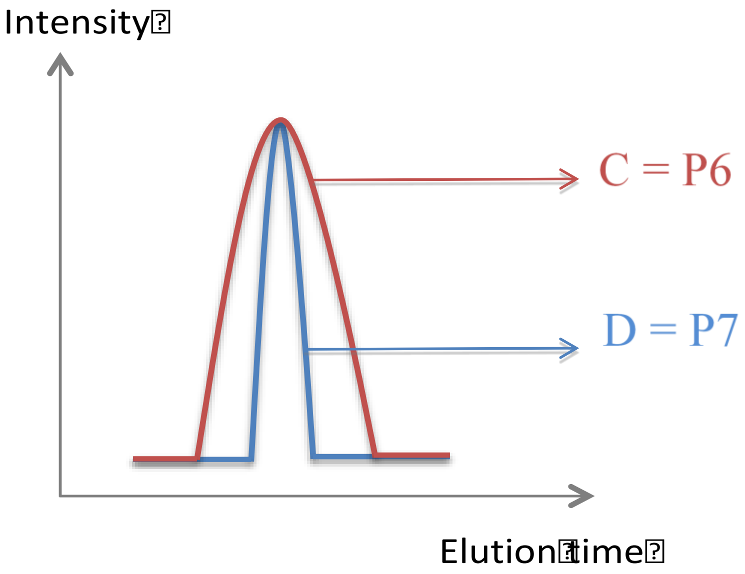
we obtain:

$$n = 5 \cdot 10^{-4}\ \mathrm{mol}$$
$$m(\mathrm{ALK1}) = n \times M(\mathrm{ALK1}) = 0.112\ \mathrm{g}$$

7. When the pyridine is protonated, the block copolymer is fully soluble in water so **A** = **P5**. When the pyridine is not protonated the block copolymer is amphiphilic. In water, the block copolymer thus self-organizes as a micelle. The core is composed of the hydrophobic block (P4VP). The outside of the micelle is composed of the hydrophilic PHEA block. Hence **B** = **P4**.

8. 2 signals (triplet) for the two non-equivalent CH_2 groups, 1 signal (singlet) for OH.

9. Contrary to a conventional radical polymerization, RDRP techniques limit the occurrence of irreversible termination reactions of the propagating radical chains. Ideally, all the chains are created and grow at the same time. Narrow molecular weight distributions are obtained, hence the following answer.



Problem 16. Biodegradable polyesters

1. Correct answer:
   A polymer transformable by microorganisms into less polluting molecules.

2. The ester function can be easily degraded (hydrolyzed) by enzymatic processes.

3. $X_{\mathrm{n}} = (M_{\mathrm{n}} - M_{\mathrm{end\ chain}})/M_0$ with M_0 the molecular weight of the monomer (= average number of monomer unit), M_{n} its number averaged molecular weight, and $M_{\mathrm{end\ chain}}$ the molar mass of the chain end.

4. Peaks from benzyl (j) and methyl (a) groups were chosen because these peaks are isolated and well defined. The first one *corresponds* to 5 protons, the second one to 3. If the polymerization degree was equal to 1 then the ratio $(I_j/5)/(I_a/3)$ should be also equal to 1, with I_j and I_a the integration value of *j* and *a* peaks.
   Therefore : $X_{n,NMR} = (I_j/5)/(I_a/3) = 29$

5. $M_{n,NMR} = X_{n,NMR} \times M_0 + M_{end\ chain} = 29 \times 278 + 88 = 8150\ g\ mol^{-1}$

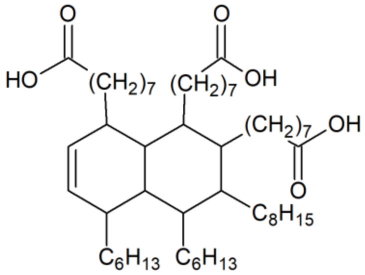
6. Determining M_n thanks to NMR spectroscopy requires to measure accurately integration value of peaks related to the end group and to the monomer. When the size of the polymer increases, the relative intensity of the peak from the end group decreases. In addition, peaks are broadened due to relaxation issues. Therefore, the correct statements are:
   The peaks at the ends of the chains are not sufficiently resolved compared to the peaks of the main chain.
   The integration of the different peaks observed may be distorted due to the observed peak broadening for high mass polymers.

7. Here $M_{n,SEC}$ (8950 g mol^{-1}) is larger than $M_{n,NMR}$ (8150 g mol^{-1}) so the value of M_n is overestimated by SEC therefore the polystyrene used for calibration has not the same hydrodynamic radius than polyBED. More precisely, it means that a polystyrene of 8650 g mol^{-1} has the same hydrodynamic radius as a polyBED of 8150 g mol^{-1}. Therefore, the correct statement is:
   Polystyrene has a smaller hydrodynamic volume than that of polyBED.

8. Mass average molecular weight M_w or dispersity which is the ratio M_w / M_n.

Problem 17. Vitrimers

1. **Q** is an acid:



   (Other acceptable answers possible, *e.g.* **Q** can be an ester)

2. Each epoxy group in **A** reacts with two reactive groups from **B**, thus forming two esters. Since there are 2 epoxy groups, there can be at most 4 esters formed by a molecule of **A**. If the conversion is ζ, it follows that $n_{EA} = 4\zeta$.

3. Each reactive group in **B** can form one ester. Since there are three reactive groups per **B** molecule, a **B** molecule can form three ester bonds at most. Therefore, $n_{EB} = 3\zeta$.

4. Every **A** molecule forms on average n_{EA} ester bonds, every **B** molecule forms on average n_{EB} ester bonds. Since these bonds are shared, we find for the total number of formed esters:

$$N_E = \frac{1}{2}\ N_A n_{EA} + \frac{1}{2} N_B n_{EB}$$

5. The number of attached ester groups counts every ester bond twice (once per attachment). Consequently, we have:

$$\bar{n} = \frac{2N_\mathrm{E}}{N} = \frac{N_\mathrm{A}}{N} n_\mathrm{EA} + \frac{N_\mathrm{B}}{N} n_\mathrm{EB}$$

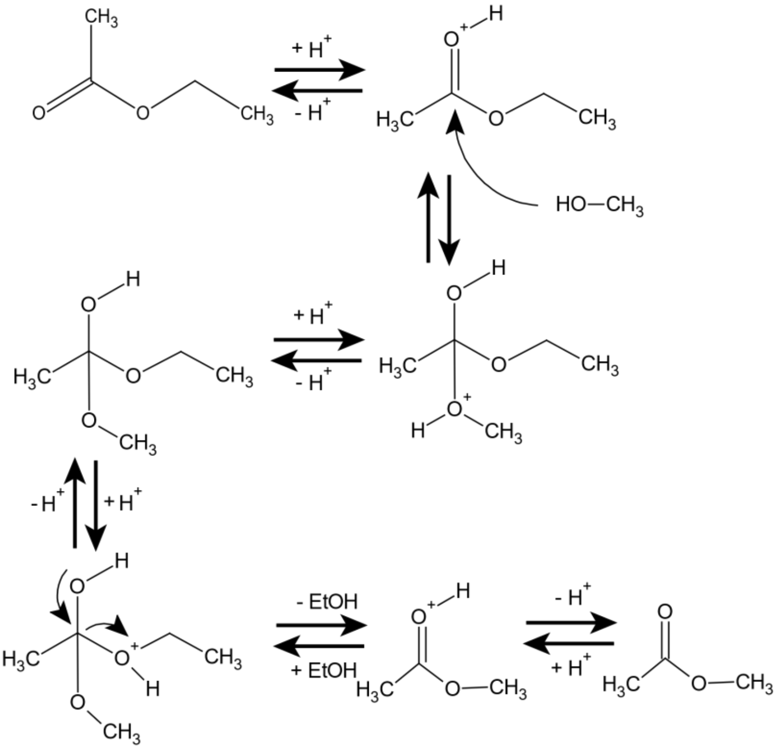
   A and **B** are mixed in a 3:4 ratio. So 3 out of 7 molecules are an **A** molecule ($\frac{N_\mathrm{A}}{N} = \frac{3}{7}$) and 4 out of 7 molecules are a **B** molecule ($\frac{N_\mathrm{B}}{N} = \frac{4}{7}$).

   Therefore, per molecule, the number of formed ester bonds can be expressed as:

   $\bar{n} = \frac{3}{7}\, 4\, \zeta + \frac{4}{7}\, 3\, \zeta = \frac{24}{7}\, \zeta.$

6. To obtain a crosslinked network, a molecule should on average have more than two links to a neighbor. Then, $\bar{n} > 2$, which means $\zeta > \frac{7}{12}$.

7.



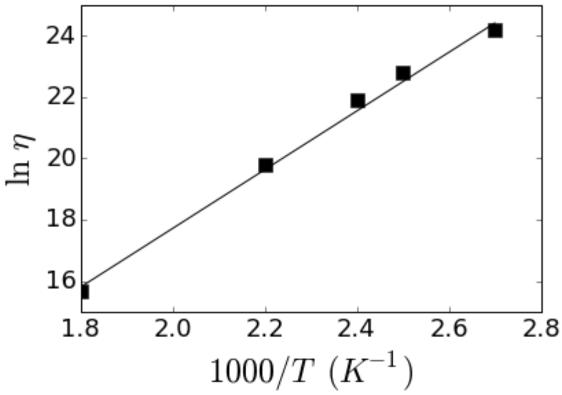
   U, W are protonated intermediates, given in above figure

   V = methanol (HOCH$_3$), **X = H$^+$** see also the above figure.

8. $\eta(T) \propto \frac{1}{k} = \frac{1}{A} \exp\left(\frac{E_\mathrm{A}}{RT}\right)$ hence

   $\ln(\eta) = \frac{E_\mathrm{A}}{R} \times \frac{1}{T} + C$ where C is a constant.

Then, a linear regression of the plot gives:



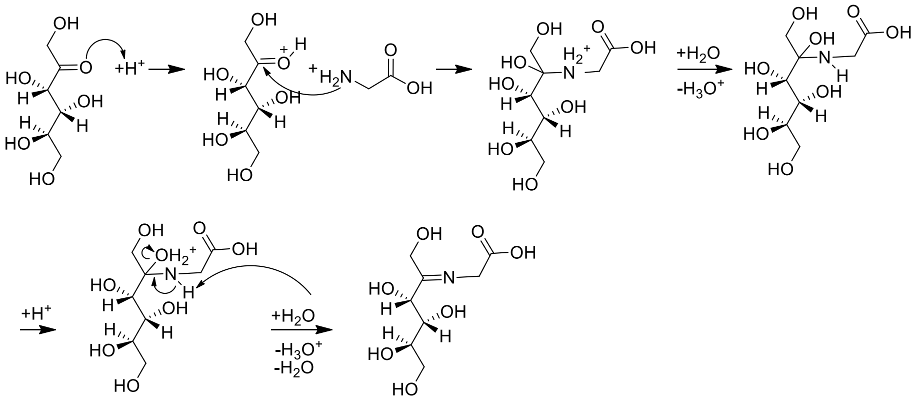
y = 9.65 x – 1.54
$r^2 = 0.994$

From which we estimate $E_A = R \times 1000 \times 9.65 = 80.2$ kJ mol^{-1}.

9. Correct answers: Anything that makes k increase, makes also η decrease, so:
   I) η **decreases** (Transesterification catalyst increases k)
   II) η **increases** (Lower temperature decreases k, see Arrhenius)
   III) η **decreases** (Transesterification can be base-catalyzed or acid-catalyzed)

Problem 18. A kinetic study of the Maillard reaction

1.



(only the intermediates are required)

2. The rate equations can be written:

$$-\frac{\mathrm{d[Fru]}}{\mathrm{d}t} = k_1[\mathrm{Fru}]^{\alpha}$$

$$-\frac{\mathrm{d[I]}}{\mathrm{d}t} = -k_1[\mathrm{Fru}]^{\alpha} + k_3[\mathrm{I}]$$

3. Correct answers:
   Equilibrium constants can depend on temperature.
   Rate constants can depend on pH.
   Rate constants can depend on temperature.

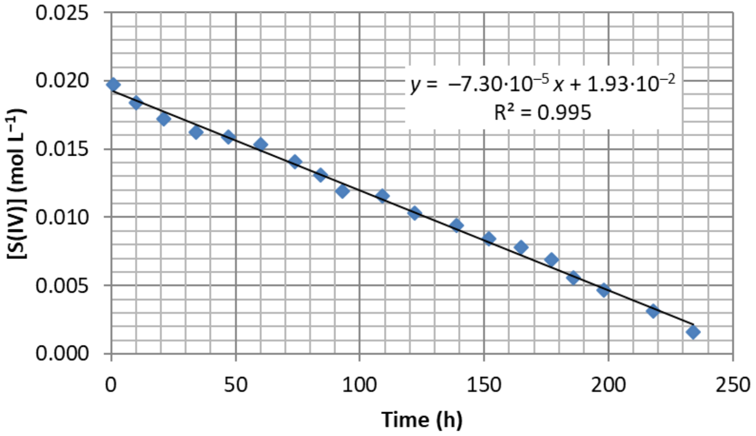
4. **S**(IV) is known to react with Ellmann's reagent to form a colored compound with an absorbance maximum at 412 nm. Hence, 412 nm is an appropriate wavelength to work at

as **S**(IV) reacts completely and quickly with the intermediate **I**. Thus, no melanoidin is likely to be formed.

5. Reaction (2) is hindered by the faster reaction (3) between **I** and **S**(IV), thus, reaction (1) gives: [I] = $[\text{Fru}]_0 - [\text{Fru}]$.
   Reaction (3) between **I** and **S**(IV) is fast and complete. Knowing what remains of **S**(IV) in the presence of Ellman's reagent, the concentration of **I** at a time t can be deduced: $[\text{I}] = [\text{S(IV)}]_0 - [\text{S(IV)}]$.
   It can thus be shown that: $[\text{Fru}] = [\text{Fru}]_0 - [\text{S(IV)}]_0 + [\text{S(IV)}]$.

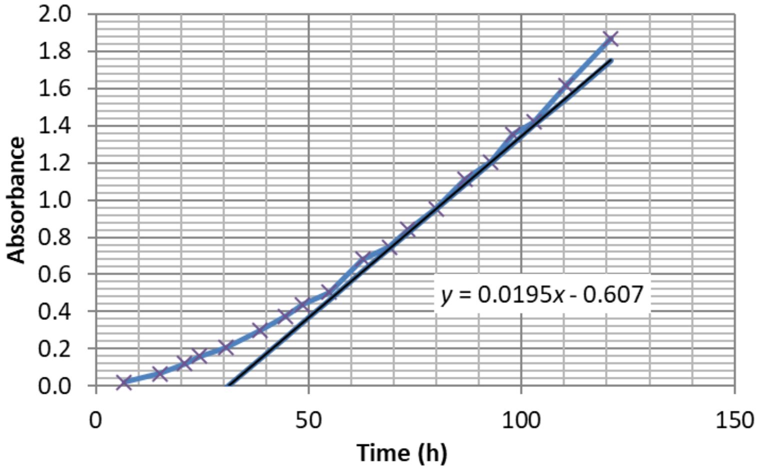
6. According to question 2: $-\frac{\mathrm{d}[\text{Fru}]}{\mathrm{d}t} = k_1[\text{Fru}]^\alpha$
   As no **M** is produced, the reaction can be followed by a kinetic order analysis.
   Case $\alpha = 0$: $[\text{Fru}] = [\text{Fru}]_0 - k_1t$
   Case $\alpha = 1$: $\ln[\text{Fru}] = \ln[\text{Fru}]_0 - k_1t$
   Case $\alpha = 2$: $\frac{1}{[\text{Fru}]} = \frac{1}{[\text{Fru}]_0} + k_1t$
   The following plot is a straight line: the assumption $\alpha = 0$ is the correct one.

7. By graphical calculation of the slope:



   $k_1 = 7.3 \cdot 10^{-5}$ mol L^{-1} h^{-1}

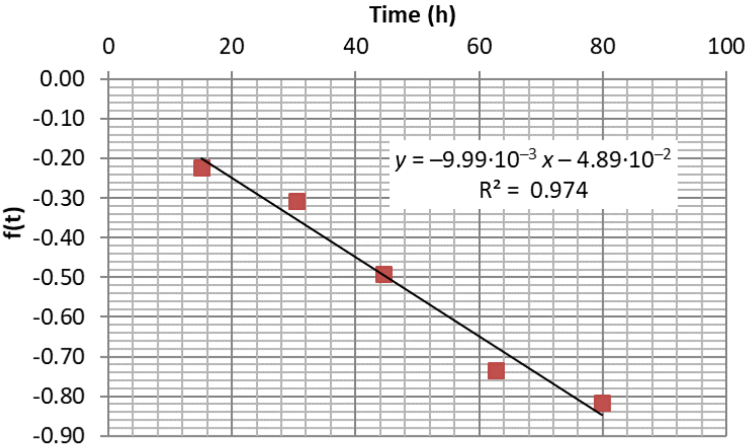
8. By graphical measurement of the slope:



   $${}^{\mathrm{d}A_{470}}\!/_{\mathrm{d}t}\Big|_{t=80\mathrm{h}} = 0.019\ \mathrm{h}^{-1}$$

9. The following function can be plotted versus time:

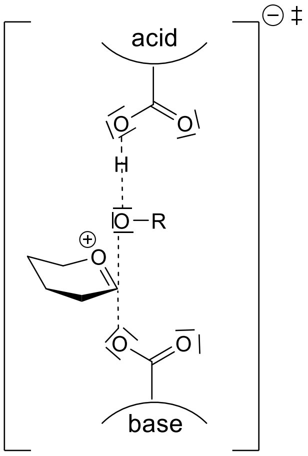
$$\ln\left[1-\frac{1}{\varepsilon_M l k_1}\frac{\mathrm{d}A_{470}}{\mathrm{d}t}\right]=f(t)$$



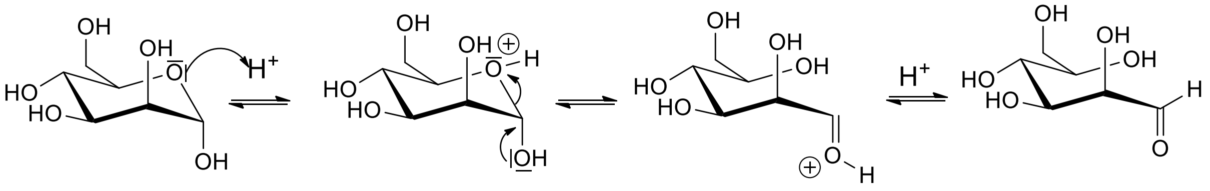
$k_2 = 9.99\cdot10^{-3}\ \mathrm{h}^{-1}$

Problem 19. Glycosidases and inhibitors

1. Structure of the transition state of the first step of the mechanism with retention of configuration:

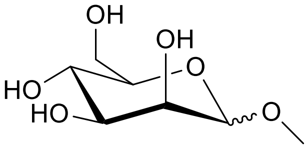


2. Carbon 1



(only the tautomeric forms are required)

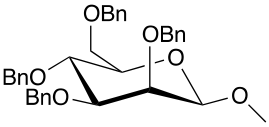
3. Compound **2:**



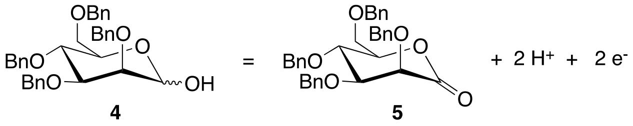
4. <u>Correct statement</u>: base.

5. <u>Correct statement</u>: nucleophilic substitution.

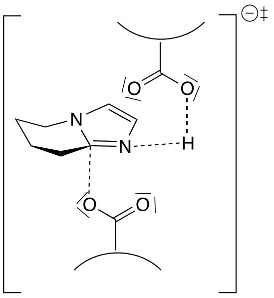
6. Compound **3**:



7. Half-reaction between **4** and **5**:



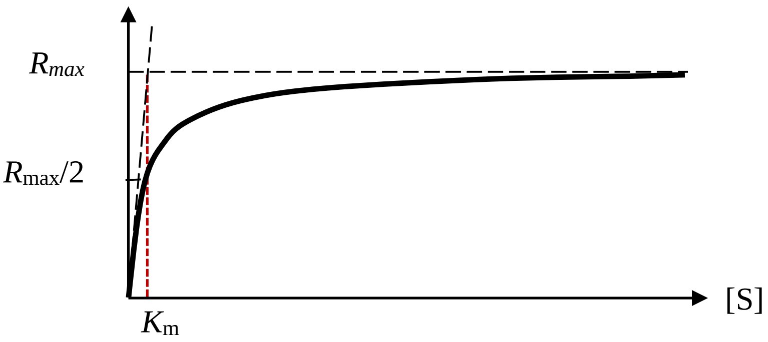
8. Mode of action for the mimic **7**:



9. The first equilibrium is fast, then:
$\frac{\mathrm{d[ES]}}{\mathrm{d}t} = k_+[\mathrm{E}][\mathrm{S}] - k_-[\mathrm{ES}] - k_{\mathrm{cat}}[\mathrm{ES}] = 0$ and $r = k_{\mathrm{cat}}[\mathrm{ES}]$
Conservation of matter:
$[\mathrm{E}]_{\mathrm{tot}} = [\mathrm{E}] + [\mathrm{ES}]$ thus $[\mathrm{E}] = [\mathrm{E}]_{\mathrm{tot}} - [\mathrm{ES}]$
If we replace [E] in the first expression, we get:
$k_+([\mathrm{E}]_{\mathrm{tot}} - [\mathrm{ES}])[\mathrm{S}] - k_-[\mathrm{ES}] - k_{\mathrm{cat}}[\mathrm{ES}] = 0$
so $[\mathrm{ES}](k_+[\mathrm{S}] + k_- + k_{\mathrm{cat}}) = k_+[\mathrm{S}][\mathrm{E}]_{\mathrm{tot}}$
$\Leftrightarrow [\mathrm{ES}] = \frac{k_+[\mathrm{E}]_{\mathrm{tot}}[\mathrm{S}]}{k_+[\mathrm{S}] + k_- + k_{\mathrm{cat}}}$
As $r = k_{\mathrm{cat}}[\mathrm{ES}]$ we deduce the expression:

$$r = \frac{k_{\mathrm{cat}}[\mathrm{E}]_{\mathrm{tot}}[\mathrm{S}]}{[\mathrm{S}] + \frac{k_- + k_{\mathrm{cat}}}{k_+}}$$

10. 1st case: $[\mathrm{S}] \gg K_{\mathrm{m}}$: $r = R_{\mathrm{max}} = k_{\mathrm{cat}}\,[\mathrm{E}]_{\mathrm{tot}}$
2nd case: $[\mathrm{S}] \ll K_{\mathrm{m}}$: $r = \frac{R_{max}[\mathrm{S}]}{K_{\mathrm{m}}}$



[S] << K_m [S] >> K_m

11. If $k_- >> k_{cat}$, $K_m = \frac{k_-}{k_+}$. It is the dissociation constant (affinity between enzyme and substrate).

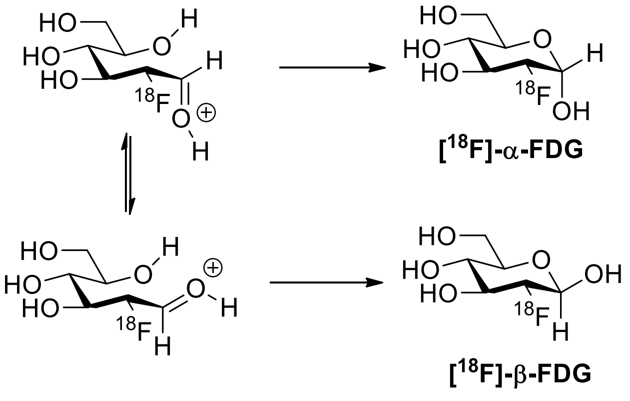
12.

	K_m low	K_m high
High affinity	×	
Low affinity		×

13. At the equilibrium: $K_i = ([E][I])/([EI])$ and for $[I] = c_i$, $[EI] = [E]$, so $c_i = K_i$.
The mimic that seems to be the best is the one that displays the smallest dissociation constant K_i, that is the smallest value of c_i. It is thus 10a.

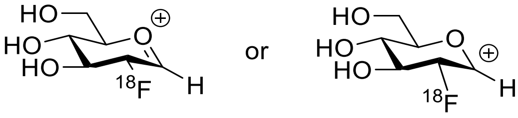
Problem 20. Fluoro-deoxyglucose and PET imaging

1.



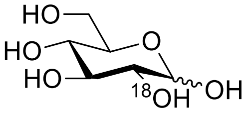
2. Correct statements:
$[^{18}F]$-α-FDG and $[^{18}F]$-β-FDG are epimers.
$[^{18}F]$-α-FDG and $[^{18}F]$-β-FDG are diastereoisomers.

3.

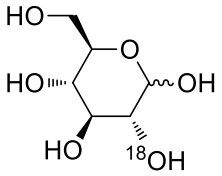


4. $^{18}_{9}F \rightarrow {}^{18}_{8}O + {}^{0}_{1}\beta^{+}$

5.



or

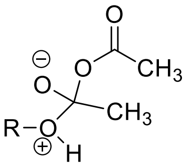


6. $N(t) = N(0)\times e^{-\lambda t}$, hence $\lambda = \ln(2) / t_{1/2} = 0.0063\ \text{min}^{-1}$

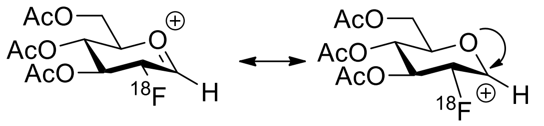
7. (i) One hour (60 min) is required between injection and imaging, and $N(0) = 370$ MBq so the remaining activity at the time of imaging is $N(60) = N(0)\times\exp(-0.0063 \times 60) = 254$ MBq
(ii) Similarly after 4 h (240 min), $N(240) = 370\times\exp(-0.0063 \times 240) = 81.5$ MBq

8. <u>Correct answer</u>: second-order nucleophilic substitution

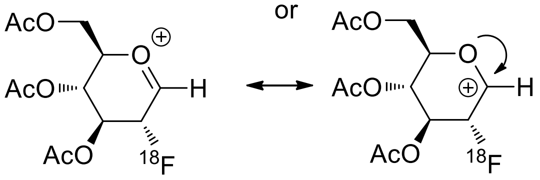
9.



10.



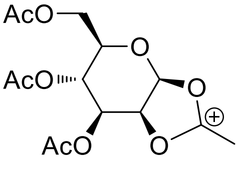
or



11. <u>Correct answer</u>: nucleophile

12. <u>Correct answer</u>: base

13. Mesomeric structures featuring the positive charge on both oxygens are also acceptable.

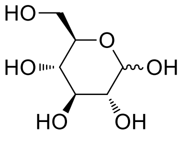


14. <u>Correct answer</u>: **F**

15. <u>Correct answer</u>: Crypt-222 provides a chelation of potassium ion enhancing the fluoride nucleophilicity.

16. <u>Correct answer</u>: Crypt-222 is eluted in first place, then [^{18}F]-FDG.

17.



D-Glucose

Glucose is not a toxic compound and can be injected together with FDG.

18. $370 \cdot 10^6$ Bq are required for one injection, the transformation and process from **E** to **J** take 30 min.

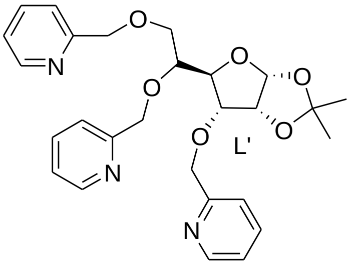
So $N(0) = N(\mathrm{t}) \cdot e^{\lambda t}$ with $t = 30$ min and $\lambda = 0.0063$ min^{-1} (according to question 6), thus $N(0) = 447 \cdot 10^6$ Bq.

Chemical yield of 75%: $n = N(0) / 0.75 = 447 \cdot 10^6 / 0.75 = 596 \cdot 10^6$ Bq are initially required.

The determination of the amount of $^{18}F^-$ is obtained by considering the specific activity of ^{18}F, SA = $6.336 \cdot 10^{19}$ Bq mol^{-1}: $\frac{596 \times 10^6}{6.336 \times 10^{19}} = 9.41 \cdot 10^{-12}$ mol (9.41 pmol)

Problem 21. Catalysis and stereoselective synthesis of cobalt glycocomplexes

1.



2. Molecular formula of **L**: $C_{27}H_{31}N_3O_6$ and $M = 493.548$ g mol^{-1}

Molecular formula of **P**: $C_xH_yN_zO_aCo_bP_cF_d$

$12x + y + 14z + 16a + 58.9b + 31c + 19d = M$

Hypothesis:

- 1 ligand for 1 Co then $x = 27$, $y = 31$, $z = 3$, $a = 6$
- Co(II) or (III) then 2 PF_6^- or 3 PF_6^- then $c = 2$, $d = 12$ or $c = 3$, $d = 18$

Test with Co(II): 493.548 + 58.93 + 2×30.98 + 12×19.00 = M = 842.438 g mol^{-1}

%C: 27×12.01 / 842.438 = 38.49%

%H: 31×1.008 / 842.438 = 3.71%

%N: 3×14.01 / 842.438 = 4.99%

%Co: 1×58.93 / 842.438 = 7.00%

%P: 2×30.98 / 842.438 = 7.35%

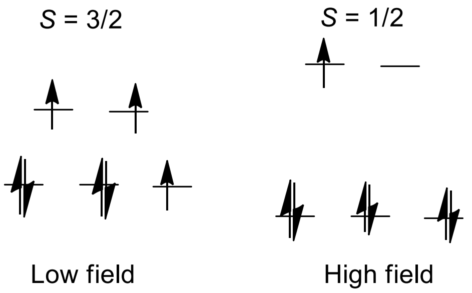
%F: 12×19.00 / 842.438 = 27.06%

The result is consistent with the experimental data, so:

Co(II): Z = 27 $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^0(3d)^7$

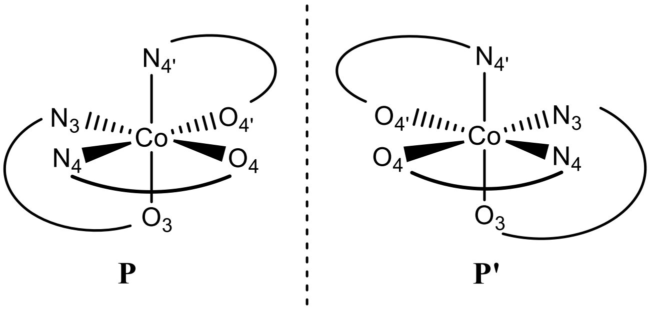
3. $\lambda_{max} = 515$ nm ($\varepsilon = 50$ L mol^{-1} cm^{-1}) => d-d band

4. Two hypotheses:

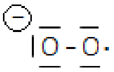


If the ligand is associated with a “Low field”, the resulting complex is “High spin”, while if the ligand is associated with a “High field”, the resulting complex is “Low spin”.
By comparison with the experimental data, a “High spin” complex is evidenced. Therefore, **L** is a “**Low field**” ligand.

5. **P’** is a quasi-enantiomer that is formed simultaneously.

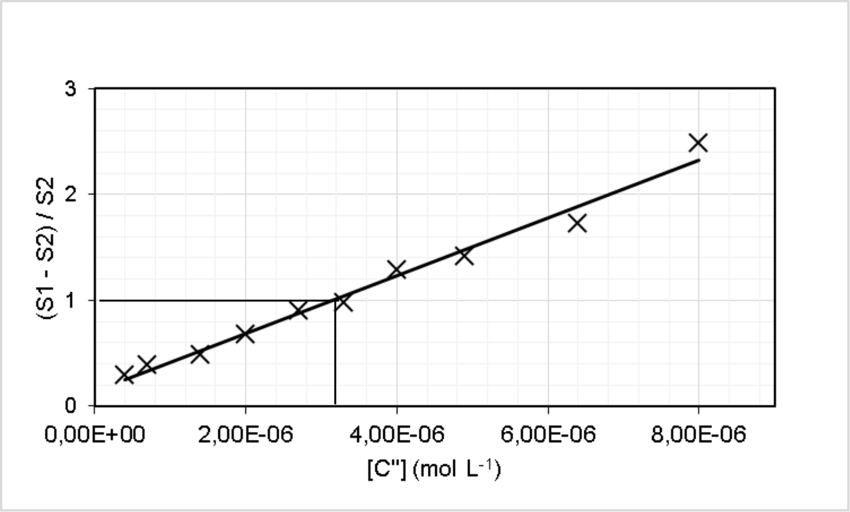


6.



7. $2\,O_2^{\bullet-} + 2\,H^+ = O_2 + H_2O_2$

8. *IC*50 is obtained when $S2 = S1 / 2$
i.e. $(S1 - S2) / S2 = 1$
*IC*50 = 3.2 µmol L^{-1} (accepted values 3.1-3.3 µmol L^{-1})



Problem 22. Structural study of copper (II) complexes

1. The complex responsible for the color of the solution is the hexaaquacopper (II) complex $Cu(H_2O)_6^{2+}$. This compound absorbs light mainly in the orange region, which is the complementary color of blue, *i.e.* $\lambda_1 = 620$ nm.

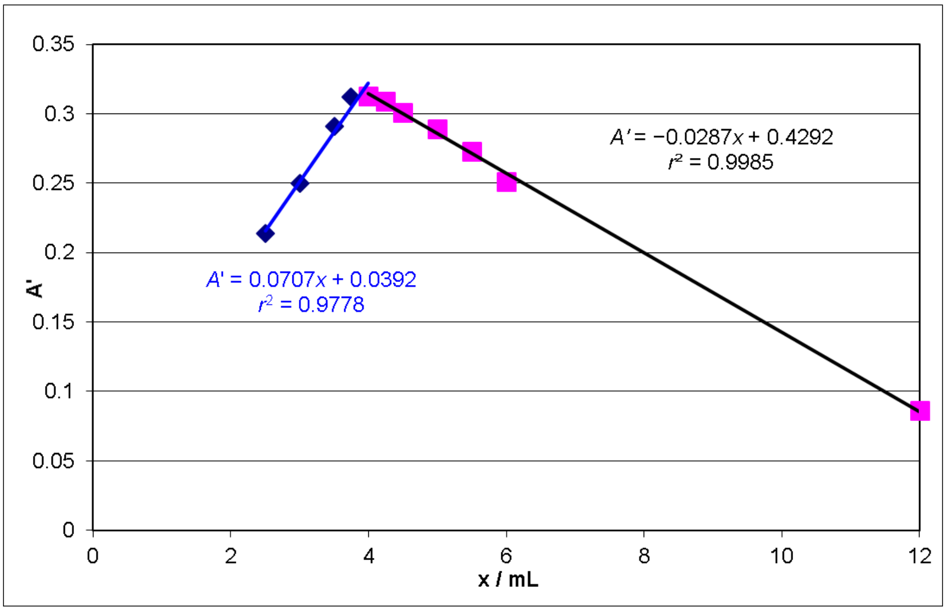
2. Using the Beer Lambert law:
   $A = l\,(\varepsilon_Z\,[Z] + \varepsilon_{Cu}\,[Cu^{2+}])$

   The conservation of copper in the solution leads to:
   $(x/20)[Cu^{2+}]_0 = [Z] + [Cu^{2+}]$
   Hence:
   $A = l\,(\varepsilon_Z\,[Z] + \varepsilon_{Cu}\,[Cu^{2+}])$
   $A = l\,(\varepsilon_Z\,[Z] + \varepsilon_{Cu}\,((x/20)[Cu^{2+}]_0 - [Z])))$
   $A = l\,\varepsilon_{Cu}\,((x/20)[Cu^{2+}]_0 + l\,(\varepsilon_Z - \varepsilon_{Cu})[Z]$
   As $A_{12} = l\,\varepsilon_{Cu}\,[Cu^{2+}]_0$
   $A - x/20\,A_{12} = l\,(\varepsilon_Z - \varepsilon_{Cu})[Z]$

3. The corrected absorbances for each solution are:

	x /mL	$(20\text{–}x)$ /mL	A	A'
1	2.50	17.50	0.224	0.214
2	3.00	17.00	0.262	0.250
3	3.50	16.50	0.305	0.291
4	3.75	16.25	0.327	0.312
5	4.00	16.00	0.329	0.313
6	4.25	15.75	0.326	0.309
7	4.50	15.50	0.319	0.301
8	5.00	15.00	0.309	0.289
9	5.50	14.50	0.295	0.273
10	6.00	14.00	0.275	0.251
11	12.00	8.00	0.134	0.086
12	20.00	0.00	0.080	0.000

And the graph of the corrected absorbance with respect to the volume of copper solution added is:



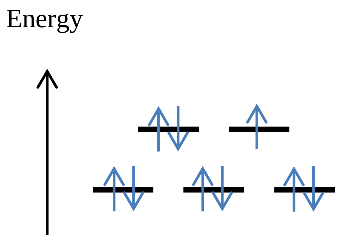
4. If the copper ion is the limiting reagent, the concentration of the complex is equal to $(x/20)[Cu^{2+}]_0$ so the corrected absorbance increases with x:
   $A' = l\,(\varepsilon_Z - \varepsilon_{Cu})\,(x/20)[Cu^{2+}]_0$

5. If the ligand is the limiting reagent, the complex concentration is equal to $(20 - x/(20n))[Cu^{2+}]_0$ so the corrected absorbance decreases with x:
   $A' = l\,(\varepsilon_Z - \varepsilon_{Cu})\,[Cu^{2+}]_0/n - l\,(\varepsilon_Z - \varepsilon_{Cu})\,x\,[Cu^{2+}]_0/(20n)$

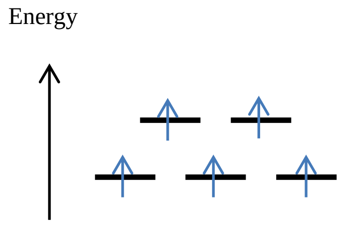
6. The two lines intersect when $A'_{\text{question 4}} = A'_{\text{question 5}}$
   so $x_{max} = 20/(1 + n)$.

7. The two curves plotted in question 3 intersect at $x_{max} = 3.92$ which gives $n = 4.10 \approx 4$
   The molecular formula of the complex is then: $Cu(H_2O)_2(NH_3)_4^{2+}$

8. Cu^{II} possesses 9 d electrons and water is a low-field ligand so the filled diagram in a hypothetical regular octahedral field would be:

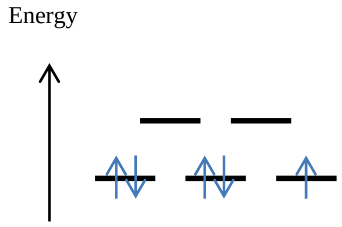


9. Mn^{II} possesses 5 d electrons, and water is still a low-field ligand so the filled diagram in an octahedral field is:

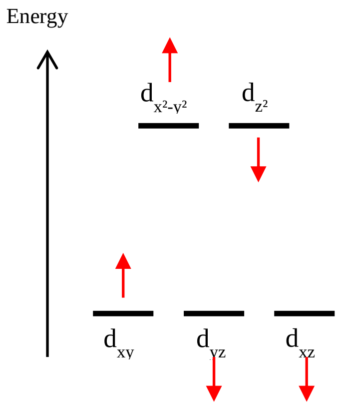


   The maximum value for the spin in this configuration is thus 5/2.

10. The cyano ligand is a high-field ligand so the electrons are located on the low-energy levels. The maximum value for the spin in this configuration is thus 1/2.



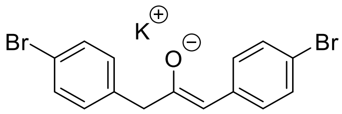
11. Let us assume that the NH_3 ligands are located in the *xy* plane. A stronger crystal field is applied to the orbitals by these ligands than by H_2O (located along the *z* axis). Thus, the splitting will be enforced for the orbitals lying in the *xy* plane. The result is depicted on the scheme below.



The potential crossing of the d_{xy} and d_{z^2} levels is beyond the scope of this problem.

Problem 23. Synthesis and study of a molecular motor

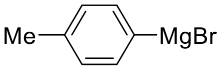
1.



or any of the resonance structures of this enolate species

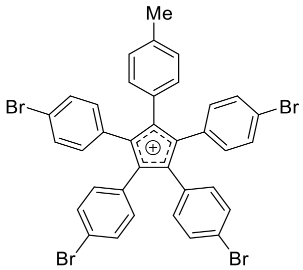
2. Correct answer: Yes: the base is regenerated after each aldol condensation sequence. However, an excess of KOH is usually used in such reactions.

3. Addition of an organolithium reagent or a Grignard reagent, such as:

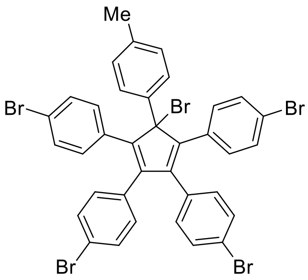


4. Correct statement: Unimolecular nucleophilic substitution S_N1.

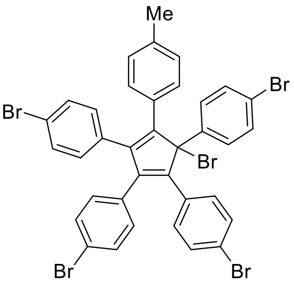
5.



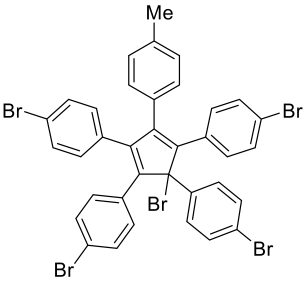
6.



F



F'



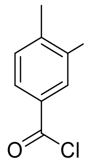
F''

7. Ru^0

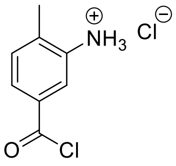
8. Ru^{2+}: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}(4p)^6(5s)^0(4d)^6$ ie $[Kr](5s)^0(4d)^6$

9. 3 **F** + $Ru_3(CO)_{12}$ → 3 **G** + 6 CO

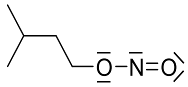
10.



can be accepted but formally the actual intermediate is

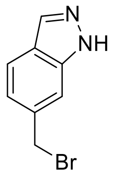


11.

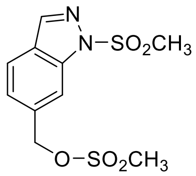


12. Correct statement: $LiAlH_4$ in diethyl ether

13. In the fourth step (**M** → **N**), the hydroxy group is converted into a better leaving group in view of the nucleophilic substitution step (**N** → **P**). Alcohol **M** is thus treated with HBr in acetic acid.



14.



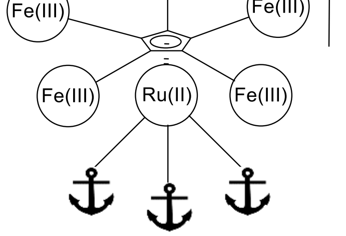
15. Correct statement: Brønsted base

16. 3 **P** + KBH_4 → **Q** + 3 H_2

17. Fe^{II}

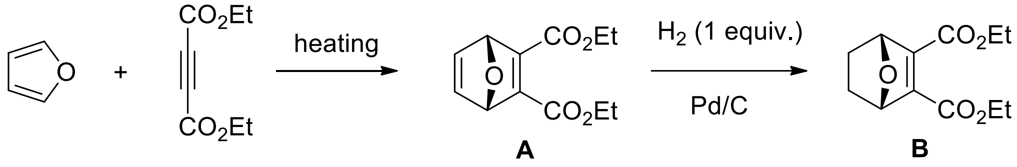
18. $E°(Fe^{3+}/Fe^{2+}) < E°(Ox/Red) < E°(Ru^{3+}/Ru^{2+})$

19.



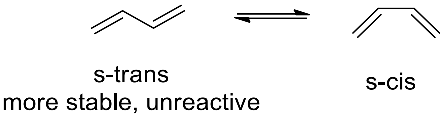
Problem 24. Some steps of a synthesis of cantharidin

1.

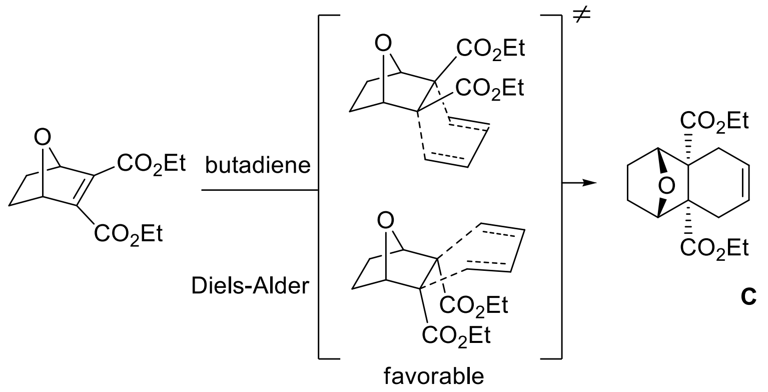


2. Correct answer: no.

3.

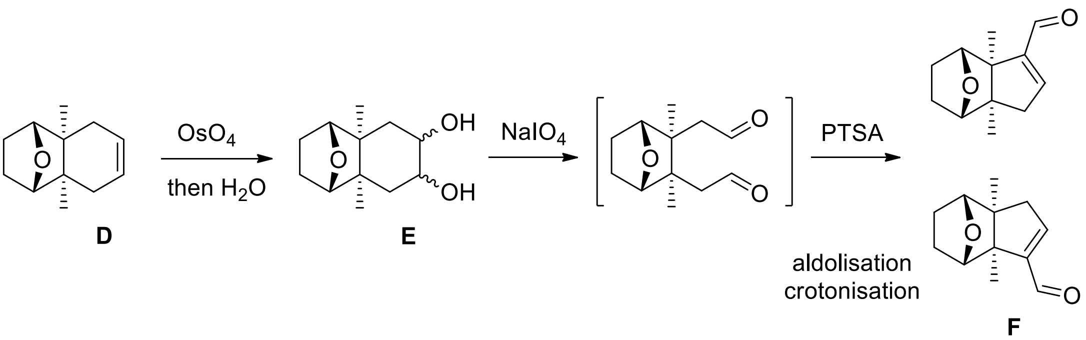


4.



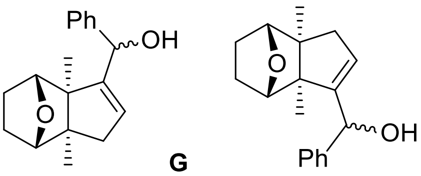
5. See question 4.

6.



7. Correct answers: by heating, by using anhydrous magnesium sulfate

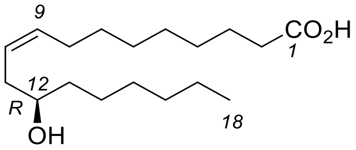
8.



Problem 25. Study of ricinoleic acid

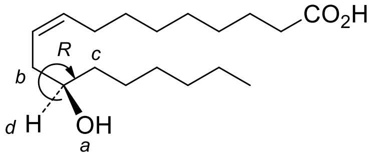
1. $H_3C–[CH_2]_n–COOH$ or $C_nH_{2n}O_2$

2. The trans configuration of the double bond is obtained from the NMR data.



3. Ricinoleic acid has one stereogenic carbon and one double bond so $2^2 = 4$ stereoisomers.

4. Using usual rules, the priority of the groups is a > b > c > d, leading to a *R* configuration.



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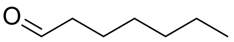
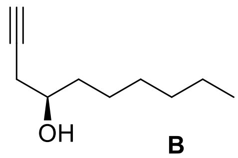


A

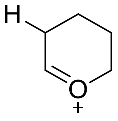


B

6. <u>Correct answers</u>: the mixture obtained while forming **B** is not optically active, **B** contains one stereogenic carbon, **B** is obtained as a 50/50 *R*/*S* mixture.

7. <u>Correct answers</u>: benzyl bromide $PhCH_2Br$, trimethylsilyl chloride Me_3SiCl.

8.



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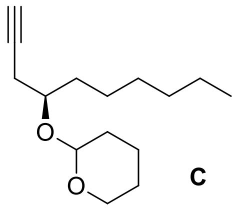
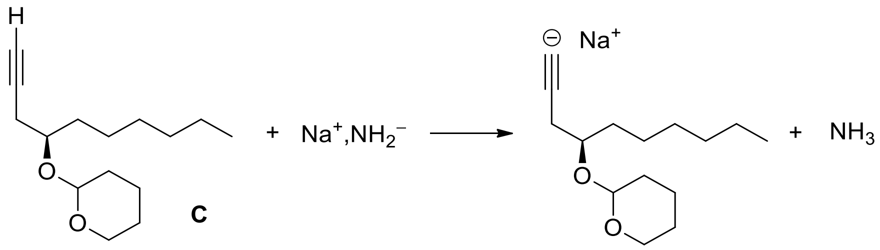


C

10.



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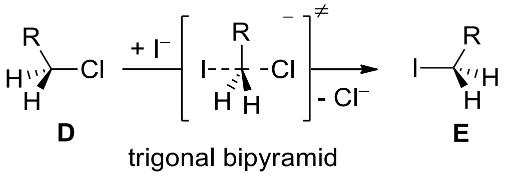

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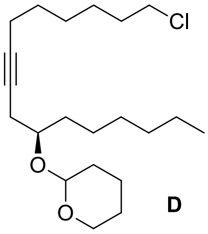
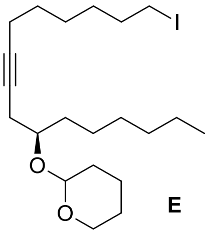
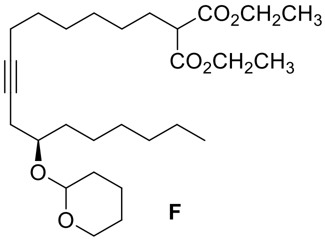


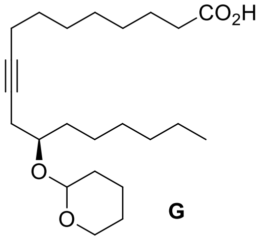
D



E

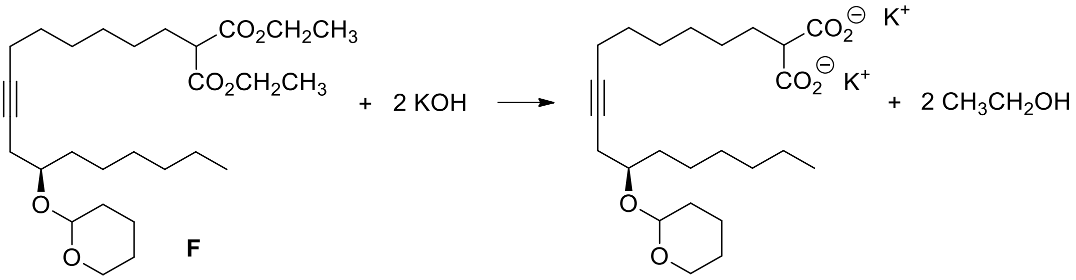


F



G

13.



The preparation of **G** from **E** corresponds to the first stages of a malonic synthesis, a set of reactions for synthesizing carboxylic acids from diethyl malonate. During the step **F** → **G**, the compound **F** ($C_{28}H_{48}O_6$), which possesses two ester functions, is transformed into compound **G** ($C_{18}H_{32}O_3$) with one carboxylic acid function. The gas that is produced latter in the synthesis is **carbon dioxide (CO_2)**.

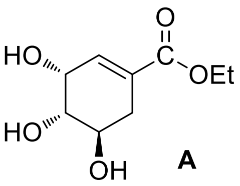
14. Correct answers: Stereoselective, diastereoselective.

Problem 26. Synthesis of oseltamivir

1. Three independent stereogenic centers (no particular symmetry) so $2^3 = 8$ stereoisomers.

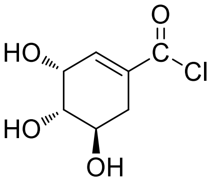
2. Correct statements:
   It is the sign of the specific rotatory power of shikimic acid.
   Shikimic acid is levorotatory.
   Shikimic acid rotates the polarization plane to the left when the observer faces the source.

3.



A

4.



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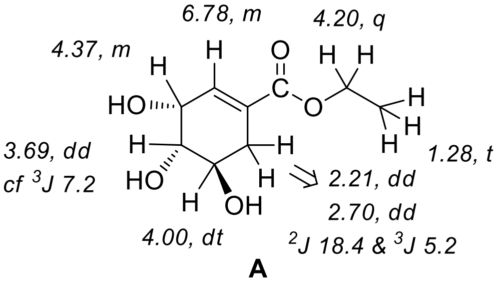
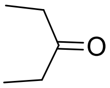
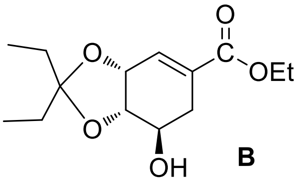


A

6.

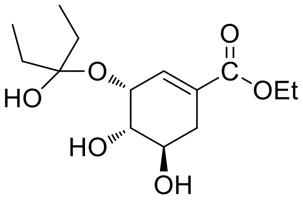


X

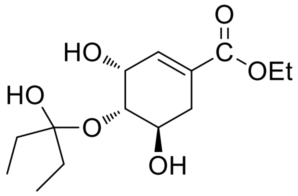


B

7.



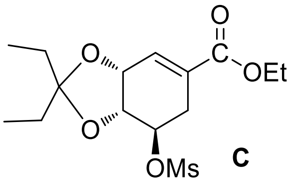
or



.

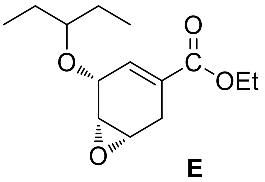
8. Correct statements:
Protect the C3 and C4 hydroxy groups
Prepare the derivatization of the C3 hydroxy group
Differentiate chemically the 3 hydroxy groups

9.



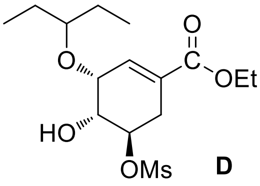
C

10.

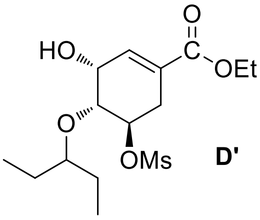


E

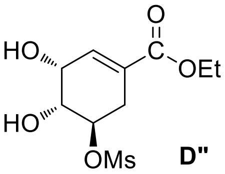
11.



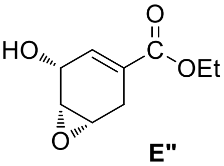
D



D'

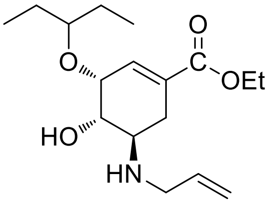


D"



E"

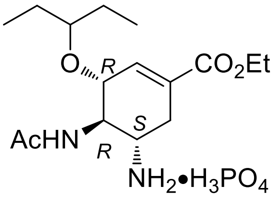
12.



F

cf ring-opening of the epoxide by an SN_2 mechanism

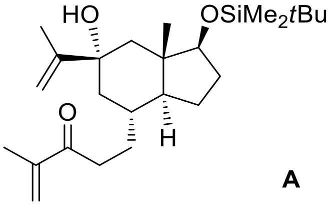
13.



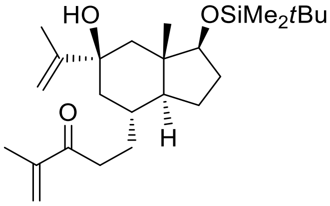
oseltamivir

Problem 27. Formal synthesis of testosterone

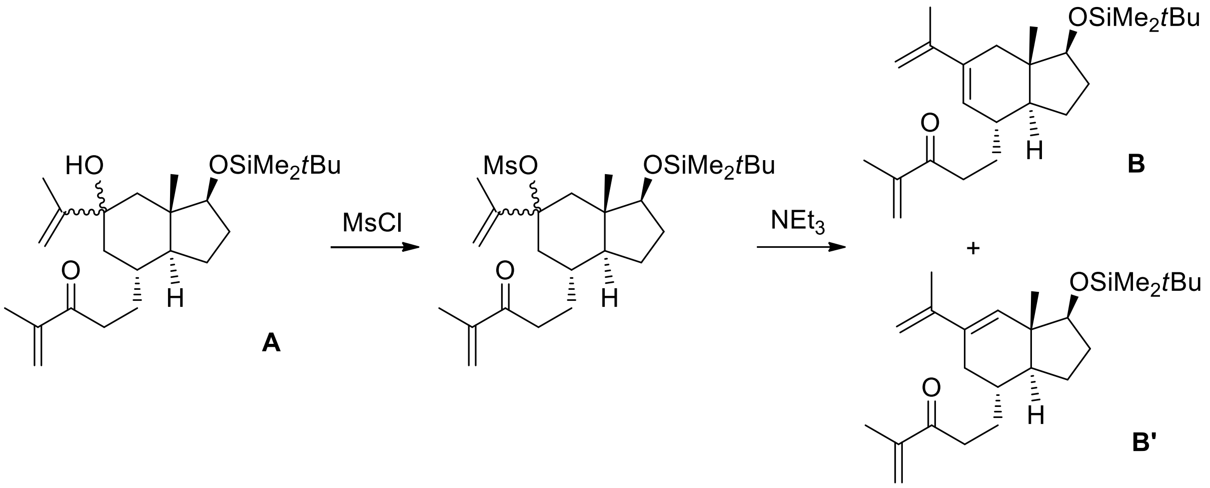
1. Correct answer: Yes.
2. After quenching of the reaction:



A

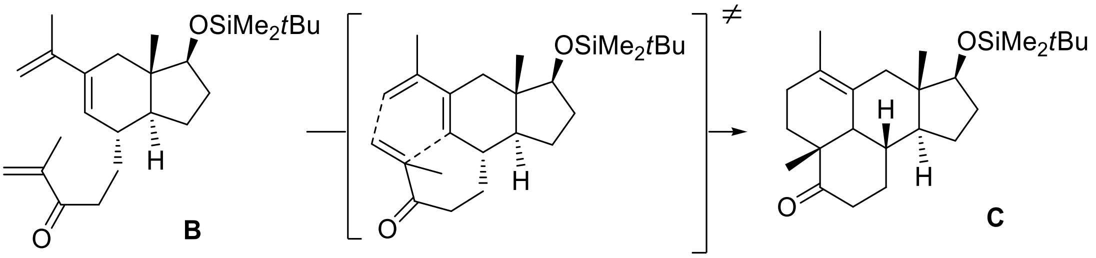


3.

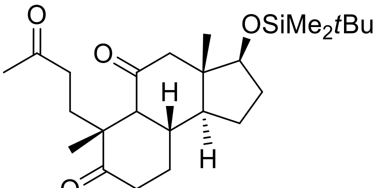


4. See question 3.

5. **B** reacts because the reaction involving **B'** would lead to a too stretched transition state for the reaction to occur.

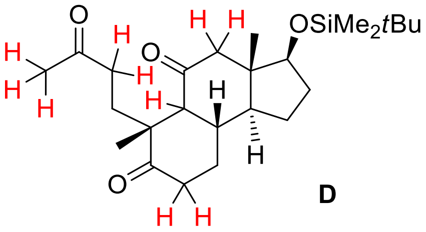


6.

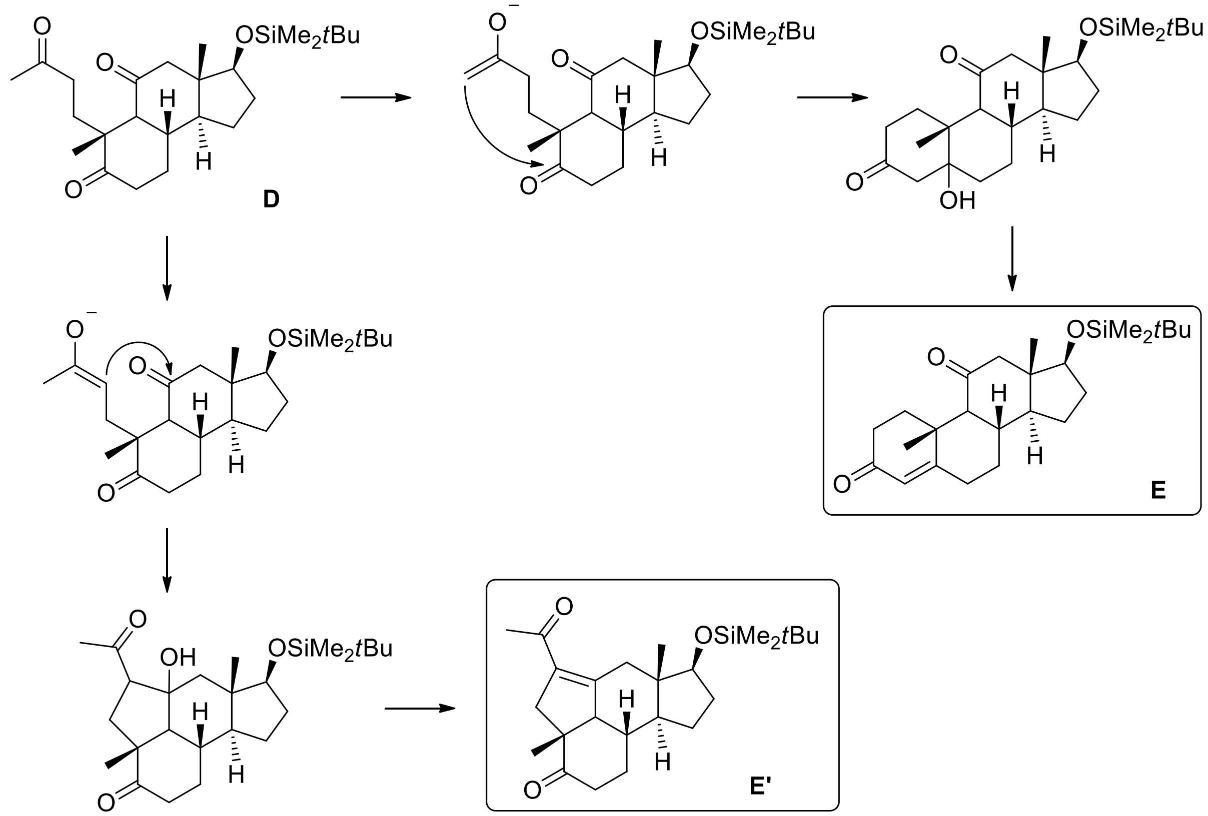


D

7. The protons in α position from a C=O double bond are more acidic than the others.



8.



Back to 1990: Aqueous solutions of copper salts

1. The acidity measured through the pH can be explained by the following reaction:
   Simplified equation: $Cu^{2+}(aq) + H_2O(l) = CuOH^{+}(aq) + H^{+}(aq)$
   Full equation: $Cu(H_2O)_4^{2+}(aq) + H_2O(l) = [Cu(OH)(H_2O)_3]^{+}(aq) + H_3O^{+}(aq)$

2. $pH = ½\ pK_a – ½ \log c$ thus $pK_a = 2\ pH + \log c = 9.30 – 2.00 = 7.30$

3. $K_{sp} = [Cu^{2+}][OH^–]^2 = 10^{–20}$
   At the beginning of the precipitation, $[Cu^{2+}] = 1.00·10^{–2}$ mol L$^{–1}$ thus $[OH^–]^2 = 10^{–18}$, and pH = 5.
   pH << pK_a and $[CuOH^+]$ is negligible.

4. Disproportionation: redox reaction of a chemical species with itself.
   $2\ Cu^{+}(aq) = Cu^{2+}(aq) + Cu(s) \qquad K° = \frac{[Cu^{2+}]}{[Cu^{+}]^2}$
   $E_{Cu2+/Cu} – E_{Cu+/Cu} = 0.52 – 0.16 = 0.36 = 0.06 \log K°$, so $K° = 10^6$

5. Two equivalents of Cu^+ yield one equivalent of Cu^{2+} and one equivalent of Cu. Then:
   $[Cu^+] + 2[Cu^{2+}] = 10^{-2}$ mol L$^{–1}$
   And at equilibrium: $K° = 10^6 = [Cu^{2+}]/[Cu^{2+}]^2$, so: $[Cu^+] + 2·10^6\ [Cu^+]^2 = 10^{–2}$ mol L$^{–1}$
   $[Cu^+] = \frac{\sqrt{2}}{2} \times 10^{-4} = 7.07 \cdot 10^{-5}$ mol L$^{–1}$
   $[Cu^{2+}] = \frac{993}{2} \times 10^{-5} = 4.96 \cdot 10^{-3}$ mol L$^{–1}$

6. H_2O_2 and dihalogens X_2 disproportionate.
   In the case of $H_2O_2 = 2\ H_2O + O_2$, catalytic conditions are required.
   In the case of dihalogens: $2\ X_2 + 2\ OH^- = 2\ HX + 2\ XO^-$, basic conditions are required.

7. $Cu_2O(s) + 2\ H^+(aq) + 2\ e^- = 2\ Cu(s) + H_2O(l)$

$$E_1 = E_1° + 0.06 \log[\mathrm{Cu}^+] = 0.52 + 0.06 \log \frac{10^{-15}}{[\mathrm{OH}^-]} = 0.46 + 0.06\ \mathrm{pH}$$

   $2\ Cu^{2+}(aq) + H_2O(l) + 2\ e^- = Cu_2O(s) + 2\ H^+(aq)$

$$E_2 = E_2° + 0.06 \log \frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Cu}^+]} = 0.16 + 0.06 \log \frac{1.00 \cdot 10^{-2}}{10^{-15}} [\mathrm{OH}^-] = 0.10 + 0.06\ \mathrm{pH}$$

   Cu_2O is stable if $E_2 > E_1$ *i.e.* pH > 3

8. Cu_2O can be obtained by the reduction of Cu^{2+} or of copper (II) complexes in slightly acidic or basic media, *e.g.* Fehling's solution or reducing sugars.

9. $[Cu(NH_3)_2]^+$: $pK_{D1} = 11$
   At the equilibrium, the following relationships can be written:
   $E_3 = E_3° + 0.06 \log \frac{[[\mathrm{Cu(NH_3)_2}]^+]}{[\mathrm{NH_3}]^2}$
   and $E_1° + 0.06 \log[\mathrm{Cu}^+] = E_1° + 0.06 \log \frac{[[\mathrm{Cu(NH_3)_2}]^+]}{[\mathrm{NH_3}]^2} \times \frac{1}{K_{D1}}$
   Since the electrode potential of a solution is unique, $E_1 = E_3$ and then:
   $E_3° = 0.52 – 0.06\ pK_{D1} = –0.14$ V

10. Standard electrode potential of Cu^{2+}/Cu: (0.52 + 0.16) / 2 = 0.34 V
    $[Cu(NH_3)_4]^{2+}$ / Cu: $E_4° = 0.34 – 0.03\ pK_{D2} = –0.02$ V so $pK_{D2} = 12$

11. $[Cu(NH_3)_4]^{2+}$ / $[Cu(NH_3)_2]^+$: $E_5° = 0.16 – 0.06\ (pK_{D2} – pK_{D1}) = 0.10$ V

12. Conclusion: No, since $E_5° > E_4°$, the $[Cu(NH_3)_2]^+$ ion does not disproportionate in standard conditions.

Practical problems

Problem P1: Synthesis of dibenzylideneacetone

12. Reactant quantities:

$$n_{\text{acetone}} = \frac{m_{\text{acetone}}}{M_{\text{acetone}}} = \frac{2.2\ \text{g}}{58.1\ \text{g mol}^{-1}} = 38\ \text{mmol}$$

$$n_{\text{benzaldehyde}} = \frac{m_{\text{benzaldehyde}}}{M_{\text{benzaldehyde}}} = \frac{7.9\ \text{g}}{106.1\ \text{g mol}^{-1}} = 74\ \text{mmol}$$

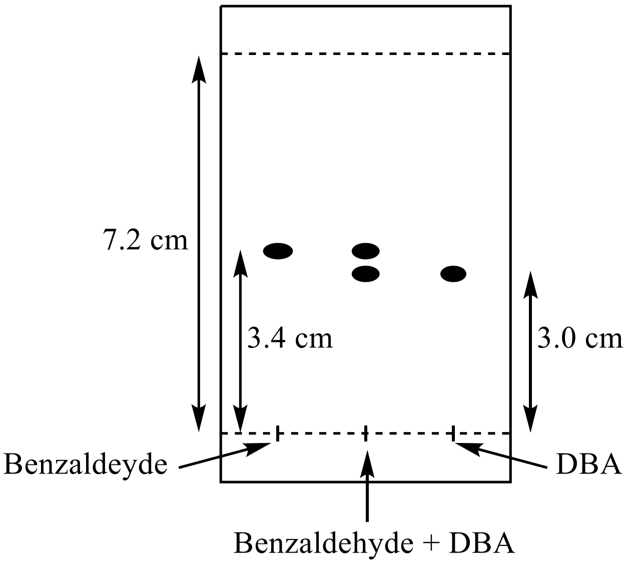
Given that 2 benzaldehyde molecules react with 1 acetone molecule, the maximum quantity expected for DBA is: $n_{\text{max}} = 37$ mmol.
Expected mass (if 100% yield):

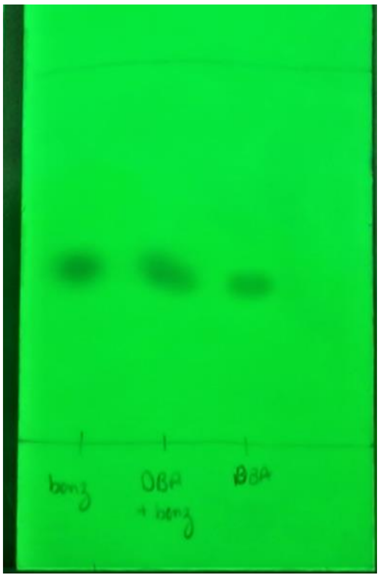
$$m_{\text{max,DBA}} = M_{\text{DBA}} \times n_{\text{max}} = 234.3\ \text{g mol}^{-1} \times 37\ \text{mmol} = 8.7\ \text{g}$$

The yield is:

$$y(\%) = 100 \times \frac{m}{m_{max,\text{DBA}}}$$

13. TLC obtained:





R_f calculations:

- Benzaldehyde: $R_f = \frac{3.4\ \text{cm}}{7.2\ \text{cm}} = 0.47$
- DBA: $R_f = \frac{3.0\ \text{cm}}{7.2\ \text{cm}} = 0.42$

Problem P2: Oxidation of (–)-borneol to (–)-camphor

8. Reactant quantities:

$$n_{\text{borneol}} = \frac{m_{borneol}}{M_{\text{borneol}}} = \frac{2.0\ \text{g}}{154.2\ \text{g mol}^{-1}} = 13\ \text{mmol}$$

$$n_{\text{Oxone}} = \frac{m_{\text{Oxone}}}{M_{\text{Oxone}}} = \frac{4.8\ \text{g}}{614.8\ \text{g mol}^{-1}} = 7.8\ \text{mmol}$$

with Oxone$^{\text{TM}}$ as the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$.

Given that each Oxone formula gives 2 HSO_5^- ions, the limiting reactant is (as expected) borneol: n_{max} = 13 mmol.

Expected mass (if 100% yield):

$$m_{\text{max,camphor}} = M_{\text{camphor}} \times n_{\text{max}} = 152.2\ \text{g mol}^{-1} \times 13\ \text{mmol} = 2.0\ \text{g}$$

The yield is:

$$y(\%) = 100 \times \frac{m}{m_{\text{max,camphor}}}$$

Problem P3: Aspirin® tablet

8. Let us take V_1 = 19.80 mL as a typical value for V_1.

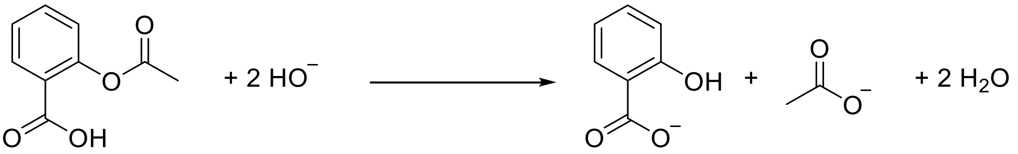
The reaction equation for the standardization of the sodium hydroxide solution is:

$$HO^-(aq) + H_3O^+(aq) = 2\ H_2O(l)$$

At the equivalence point:

$$n_{HO^-} = n_{H_3O^+}$$
$$c_{HO^-} \times V_{HO^-} = c_{H_3O^+} \times V_1$$
$$c_{HO^-} = \frac{V_1 \times c_{H_3O^+}}{V_{HO^-}}$$
$$c_{HO^-} = \frac{19.80\ \text{mL} \times 0.200\ \text{M}}{10.00\ \text{mL}}$$
$$c_{HO^-} = 0.396\ \text{M}$$

9. During step 2., 2 equivalents of hydroxide ions react with acetylsalicylic acid (1 equivalent for the saponification and 1 equivalent for the reaction with the carboxylic acid).



With phenolphthalein as indicator, salicylate and acetate ions are not titrated.

Let us take V_2 = 11.75 mL as a typical value for V_2.

In the titration flask:

$$n_{\text{remaining HO}^-} = c_{H_3O^+} \times V_2$$
$$n_{\text{remaining HO}^-} = 0.200\ \text{M} \times 11.75\ \text{mL}$$
$$n_{\text{remaining HO}^-} = 2.35\ \text{mmol}$$

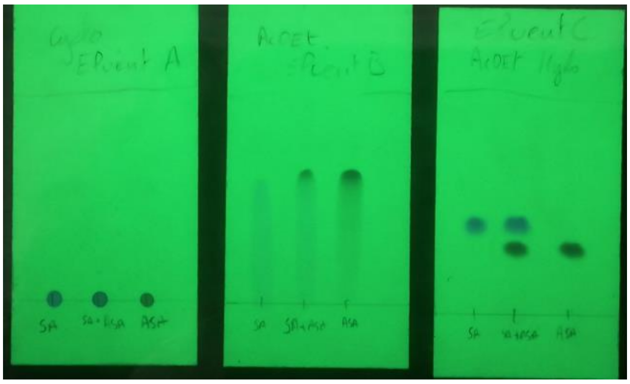
Therefore:

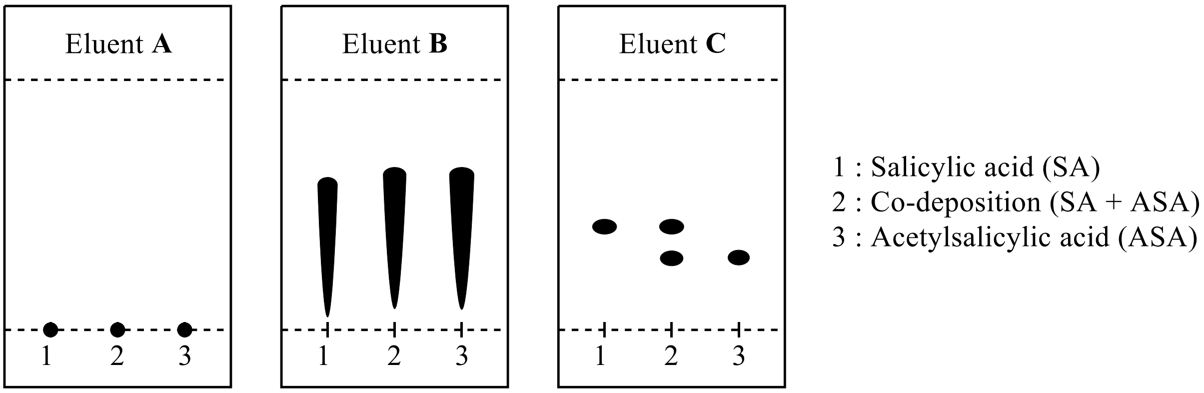
$$n_{\text{remaining HO}^-} = n_{\text{added HO}^-} - 2n_{\text{acetylsalicylic acid}}$$
$$n_{\text{acetylsalicylic acid}} = \frac{n_{\text{added HO}^-} - n_{\text{remaining HO}^-}}{2}$$
$$n_{\text{acetylsalicylic acid}} = \frac{20.00\ \text{mL} \times 0.396\ \text{M} - 2.35\ \text{mmol}}{2}$$
$$n_{\text{acetylsalicylic acid}} = 2.79\ \text{mmol}$$

The mass amount is derived directly:

$$m_{\text{acetylsalicylic acid}} = M_{\text{acetylsalicylic acid}} \times n_{\text{acetylsalicylic acid}}$$
$$m_{\text{acetylsalicylic acid}} = 180.2\ \text{g mol}^{-1} \times 2.79\ \text{mmol}$$
$$m_{\text{acetylsalicylic acid}} = 503\ \text{mg}$$

15. TLC obtained:





1 : Salicylic acid (SA)
2 : Co-deposition (SA + ASA)
3 : Acetylsalicylic acid (ASA)

With eluent **A**, all spots are on the start line.
With eluent **B**, the spots are in the middle of the TLC sheet, but they are tailing a lot and the separation between salicylic acid and acetylsalicylic acid is poor.
With eluent **C**, the separation of salicylic acid and the acetylsalicylic acid is clear, and the spots are well defined.
Eluent **C** is the best to monitor the reaction.

Problem P4: Illuminated Europe

2. The reaction is performed with stoichiometric amounts of reactants.

$$n_{2,6-\text{pyridinedicarboxylic acid}} = \frac{m}{M} = \frac{0.70\ g}{167.1\ \text{g}} = 4.2\ \text{mmol}$$

   Given that 3 equivalents of 2,6-pyridinedicarboxylic acid react with 1 equivalent of lanthanide salt:

$$n_{max,\text{complex}} = \frac{4.2\ \text{mmol}}{3} = 1.4\ \text{mmol}$$

   Required mass for the different lanthanide salts:
   - $EuCl_3,6H_2O$: $m = 1.4\ \text{mmol} \times 366.4\ \text{g mol}^{-1} = 0.51\ \text{g}$
   - $LuCl_3,6H_2O$: $m = 1.4\ \text{mmol} \times 389.4\ \text{g mol}^{-1} = 0.55\ \text{g}$
   - $TbCl_3,6H_2O$: $m = 1.4\ \text{mmol} \times 373.4\ \text{g mol}^{-1} = 0.52\ \text{g}$

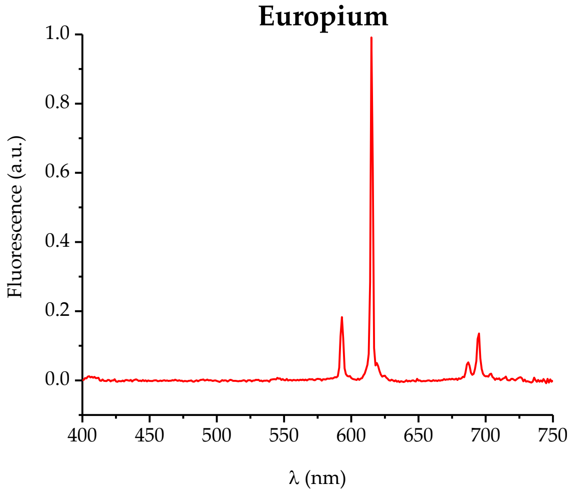
5. Expected mass (if 100% yield):

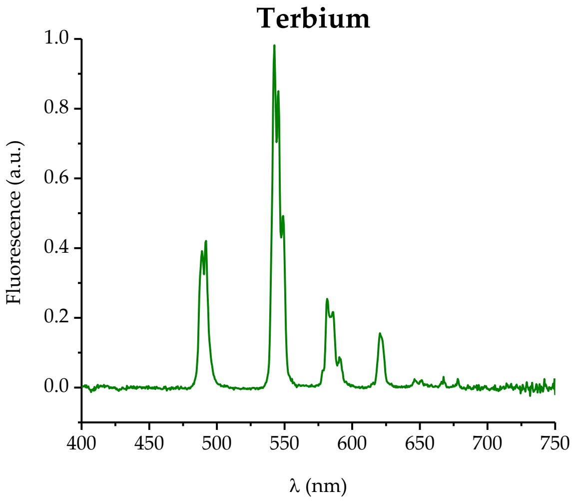
$$m_{max,\text{Eu complex}} = M_{\text{Eu complex}} \times n_{max,\text{complex}} = 827.5\ \text{g mol}^{-1} \times 1.4\ \text{mmol} = 1.16\ \text{g}$$
$$m_{max,\text{Lu complex}} = M_{\text{Lu complex}} \times n_{max,\text{complex}} = 850.5\ \text{g mol}^{-1} \times 1.4\ \text{mmol} = 1.19\ \text{g}$$
$$m_{max,\text{Tb complex}} = M_{\text{Tb complex}} \times n_{max,\text{complex}} = 834.5\ \text{g mol}^{-1} \times 1.4\ \text{mmol} = 1.17\ \text{g}$$

   The yield is:

$$y(\%) = 100 \times \frac{m}{m_{max,\text{complex}}}$$

6. Europium complex: red fluorescence (see the fluorescence spectrum below)
   Lutetium complex: no fluorescence
   Terbium complex: green fluorescence (see the fluorescence spectrum below)
   Mixture of europium and terbium complex: yellow fluorescence





7. Red dots, red stars and red door: Europium complex
   Green stars, green background and green flag: Terbium complex
   Yellow stars on the little flag: mixture of Europium and Terbium complexes

Problem P5: Protecting the vineyard

A fake Bordeaux mixture can be prepared by mixing the same mass of anhydrous copper sulfate $CuSO_4$ and calcium hydroxide $Ca(OH)_2$. The weight percentage of copper in this solid mixture is around 20%.

8. Standardization of sodium thiosulfate:

$$\mathrm{IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O}$$
$$\mathrm{I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}}$$

or

$$\mathrm{IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O}$$
$$\mathrm{I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}}$$

Further calculations will be performed considering I_2.

9. Iodate $\mathrm{IO_3^-}$ is the limiting reactant in the comproportionation leading to iodine.

$$n_{\mathrm{I_2}} = 3n_{\mathrm{IO_3^-}}$$
$$n_{\mathrm{I_2}} = 3c_{\mathrm{IO_3^-}} \times V_{\mathrm{IO_3^-}}$$
$$n_{\mathrm{I_2}} = 3 \times 0.001600\ \mathrm{M} \times 20.00\ \mathrm{mL}$$
$$n_{\mathrm{I_2}} = \ 0.09600\ \mathrm{mmol}$$

Let us take V_1 = 9.80 mL as a typical value for V_1.
At the equivalence point:

$$n_{\mathrm{S_2O_3^{2-}}} = 2n_{\mathrm{I_2}}$$
$$c_{\mathrm{S_2O_3^-}} \times V_1 = 2n_{\mathrm{I_2}}$$
$$c_{\mathrm{S_2O_3^{2-}}} = \frac{2n_{I_2}}{V_1}$$
$$c_{\mathrm{S_2O_3^{2-}}} = \frac{2 \times 0.09600\ \mathrm{mmol}}{9.80\ \mathrm{mL}}$$
$$c_{\mathrm{S_2O_3^{2-}}} = 0.0196\ \mathrm{mol\ L^{-1}}$$

10. Iodometric titration of copper in **SBM**.

$$\mathrm{2Cu^{2+} + 4I^- = I_2 + 2CuI\ (s)}$$
$$\mathrm{I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}}$$

or

$$\mathrm{2Cu^{2+} + 5I^- = I_3^- + 2CuI\ (s)}$$
$$\mathrm{I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}}$$

or

$$\mathrm{2Cu^{2+} + 6I^- = I_2 + 2CuI_2^-}$$
$$\mathrm{I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}}$$

or

$$\mathrm{2Cu^{2+} + 7I^- = I_3^- + 2CuI_2^-}$$
$$\mathrm{I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}}$$

With high iodide concentration copper(I) iodide CuI is dissolved as $\mathrm{CuI_2^-}$.
Further calculations will be performed considering I_2.

11. The reduction of copper(II) is quantitative:

$$n_{Cu^{2+}} = 2n_{I_2}$$

Let us take V_2 = 12.45 mL as a typical value for V_2.
At the equivalence point:

$$2n_{\mathrm{I_2}} = n_{\mathrm{S_2O_3^{2-}}}$$
$$n_{\mathrm{Cu^{2+}}} = n_{\mathrm{S_2O_3^{2-}}}$$
$$c_{\mathrm{Cu^{2+}}} \times V_{\mathrm{Cu^{2+}}} = c_{\mathrm{S_2O_3^-}} \times V_2$$
$$c_{\mathrm{Cu^{2+}}} = \frac{c_{\mathrm{S_2O_3^-}} \times V_2}{V_{\mathrm{Cu^{2+}}}}$$
$$c_{\mathrm{Cu^{2+}}} = \frac{0.0196\ \mathrm{M} \times 12.45\ \mathrm{mL}}{20.00\ \mathrm{mL}}$$
$$c_{\mathrm{Cu^{2+}}} = 0.0122\ \mathrm{M}$$

12. The mass m_{Cu} of copper in the 250 mL of $\mathbf{S_{BM}}$ solution is:

$$m_{\mathrm{Cu}} = c_{\mathrm{Cu^{2+}}} \times M_{\mathrm{Cu}} \times V_{\mathbf{S_{BM}}}$$
$$m_{\mathrm{Cu}} = 0.0122\ \mathrm{M} \times 63.55\ \mathrm{g\ mol^{-1}} \times 250\ \mathrm{mL}$$
$$m_{\mathrm{Cu}} = 194\ \mathrm{mg}$$

Assuming that m_{BM} = 1.000 g of Bordeaux Mixture was weighed in step 1., the weight percentage %Cu is:

$$\%\mathrm{Cu} = 100 \times \frac{m_{\mathrm{Cu}}}{m_{\mathrm{BM}}}$$
$$\%\mathrm{Cu} = 100 \times \frac{194\ \mathrm{mg}}{1.000\ \mathrm{g}}$$
$$\%\mathrm{Cu} = 19.4$$

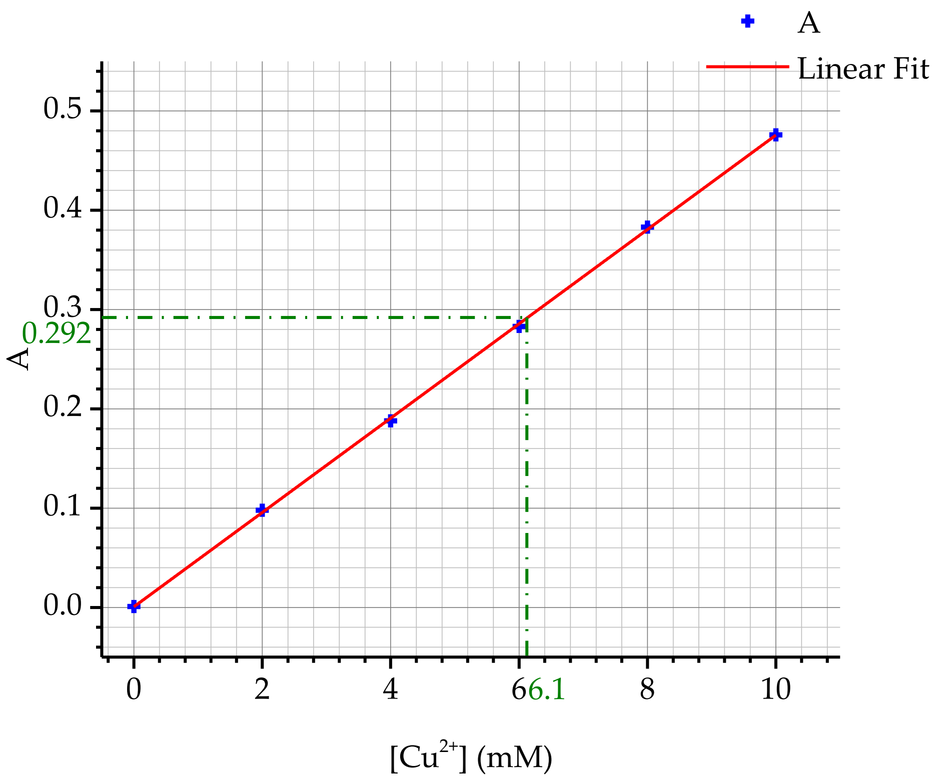
13. Copper concentration in $\mathbf{S_{BM}}$ was found to be $c_{\mathrm{Cu^{2+}}}$ = 0.0122 M. A 0.0200 M standardized copper(II) solution is provided. In order to have absorbance values around the one of "Bordeaux" test tube, the following volumes may be used:

Tube #	**0**	**1**	**2**	**3**	**4**	**5**	**Bordeaux**
0.0200 M copper sulfate solution	0 mL	1.0 mL	2.0 mL	3.0 mL	4.0 mL	5.0 mL	0 mL
1 M ammonia solution	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL
Deionized water	5.0 mL	4.0 mL	3.0 mL	2.0 mL	1.0 mL	0 mL	0 mL
Solution $\mathbf{S_{BM}}$	0 mL	0 mL	0 mL	0 mL	0 mL	0 mL	5.0 mL
Copper(II) concentration in the tube	0 mM	2.0 mM	4.0 mM	6.0 mM	8.0 mM	10.0 mM	6.1 mM (estimated)
Absorbance (at 610 nm)	0.001	0.098	0.188	0.283	0.383	0.476	0.292

17. The plot $A = f([\mathrm{Cu^{2+}}])$ is shown hereafter.

The plot $A = f([\mathrm{Cu^{2+}}])$ is linear. The determination of $[\mathrm{Cu^{2+}}]$ concentration in the tube **Bordeaux** is performed by reporting the absorbance value of 0.292 on the linear fit.
We found $[\mathrm{Cu^{2+}}] = 6.1$ mM in the tube **Bordeaux.**
Given that the tube is obtained by dilution with a factor of 2 from the $\mathbf{S_{BM}}$ solution, we find that:

$$[\mathrm{Cu^{2+}}]_{\mathbf{S_{BM}}}^{\mathrm{spectro}} = 0.0122\ \mathrm{M}$$



18. Using the calculation as in question 12., we found:

$$m_{\mathrm{Cu}}^{\mathrm{spectro}} = c_{\mathrm{Cu}^{2+}} \times M_{\mathrm{Cu}} \times V_{\mathbf{S_{BM}}}$$
$$m_{\mathrm{Cu}}^{\mathrm{spectro}} = 0.0122\ \mathrm{M} \times 63.55\ \mathrm{g\ mol^{-1}} \times 250\ \mathrm{mL}$$
$$m_{\mathrm{Cu}}^{\mathrm{spectro}} = 194\ \mathrm{mg}$$

Assuming that m_{BM} = 1.000 g of Bordeaux Mixture was weighed in step 1., the weight percentage $\%\mathrm{Cu}^{\mathrm{spectro}}$ is:

$$\%\mathrm{Cu}^{\mathrm{spectro}} = 100 \times \frac{m_{\mathrm{Cu}}}{m_{\mathrm{BM}}}$$
$$\%\mathrm{Cu}^{\mathrm{spectro}} = 100 \times \frac{194\ \mathrm{mg}}{1.000\ \mathrm{g}}$$
$$\%\mathrm{Cu}^{\mathrm{spectro}} = 19.4$$

Problem P6: Equilibrium constant determination

7. Solutions **S$_{A,BPB}$** and **S$_{B,BPB}$** are both prepared by the same dilution of **S$_{0,BPB}$** (dilution factor of 50). Therefore, the analytical concentration of BPB in **S$_{A,BPB}$** and in **S$_{B,BPB}$** are the same. Each tube is prepared by mixing only **S$_{A,BPB}$** and **S$_{B,BPB}$**. Therefore, the analytical concentration of BPB in each tube is the same as its value in **S$_{A,BPB}$** and **S$_{B,BPB}$**: c_{BPB}.

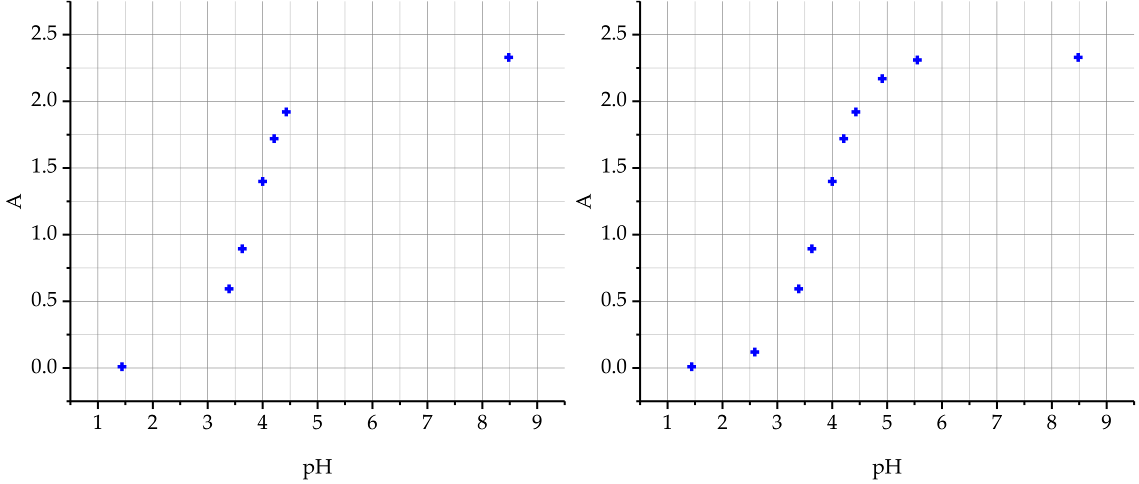
8. The results are presented in the following table.

Tube #	**1**	**2**	**3**	**4**	**5**	**6**	**7**
S$_{A,BPB}$	0.0 mL	5.0 mL	6.0 mL	7.0 mL	8.0 mL	8.5 mL	10.0 mL
S$_{B,BPB}$	10.0 mL	5.0 mL	4.0 mL	3.0 mL	2.0 mL	1.5 mL	0.0 mL
pH	8.48	4.43	4.21	4.00	3.63	3.39	1.44
Absorbance A (at 590 nm)	2.33	1.92	1.72	1.40	0.89	0.59	0.01

The data are presented in the following graphs.

9. In tube 1, the mixture is basic enough to exhibit only the absorption of Ind$^-$:
$[\mathrm{Ind}^-] \approx c_{\mathrm{BPB}}$ and [HInd] is negligible.
Therefore: $A_1 \approx \varepsilon_{\mathrm{Ind}^-}\, l\, c_{\mathrm{BPB}}$.
In tube 7, the mixture is acidic enough to exhibit only the absorption of HInd:
$[\mathrm{HInd}] \approx c_{\mathrm{BPB}}$ and $[\mathrm{Ind}^-]$ is negligible.
Therefore: $A_7 \approx \varepsilon_{\mathrm{HInd}}\, l\, c_{\mathrm{BPB}}$.

At the end of the problem, one should compare the pK_a value to the pH value in tube 1 and tube 7 to check these hypotheses.



Left: Data obtained from tube 1 to 7. Right: with extra points using different ratio of **S$_{A,BPB}$** *and* **S$_{B,BPB}$**

10. At any pH:

$$A = \varepsilon_{\mathrm{HInd}}\, l\, [\mathrm{HInd}] + \varepsilon_{\mathrm{Ind}^-}\, l\, [\mathrm{Ind}^-]$$

$$A = \varepsilon_{\mathrm{HInd}}\, l\, c_{\mathrm{BPB}} \times \frac{[\mathrm{HInd}]}{c_{\mathrm{BPB}}} + \varepsilon_{\mathrm{Ind}^-}\, l\, c_{\mathrm{BPB}} \times \frac{[\mathrm{Ind}^-]}{c_{\mathrm{BPB}}}$$

$$A = A_7 \times \frac{[\mathrm{HInd}]}{c_{\mathrm{BPB}}} + A_1 \times \frac{[\mathrm{Ind}^-]}{c_{\mathrm{BPB}}}$$

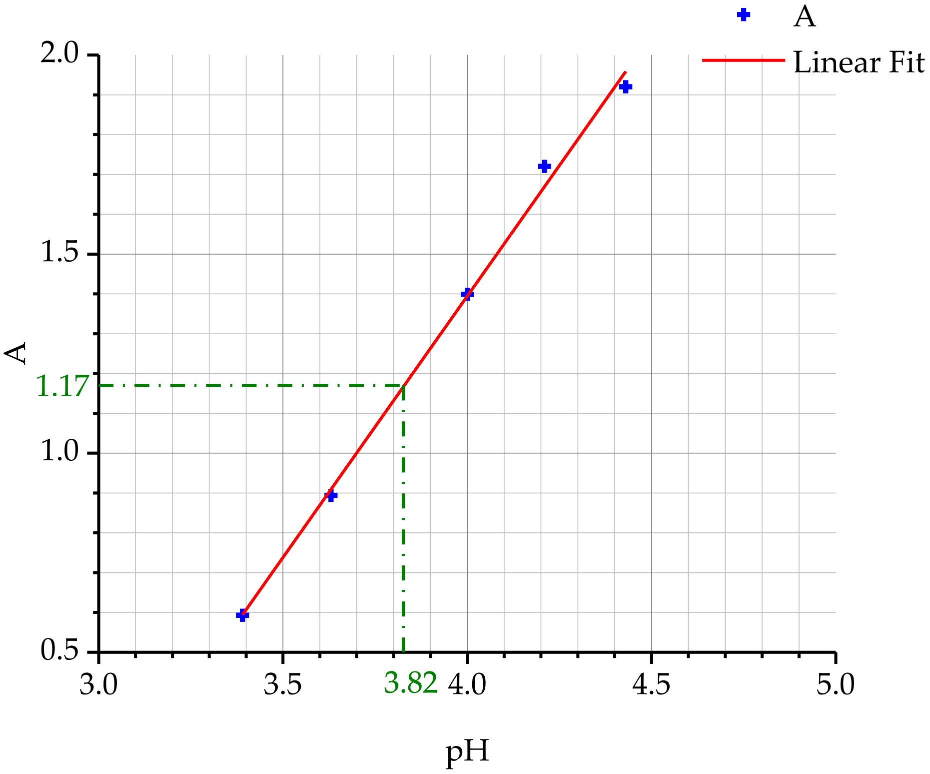
11. The Henderson-Hasselbalch equation is:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{Ind}^-]}{[\mathrm{HInd}]}$$

At pH = pK_a: $[\mathrm{Ind}^-] = [\mathrm{HInd}] = \frac{c_{BPB}}{2}$

Therefore: $A_{\mathrm{pH}=\mathrm{p}K_\mathrm{a}} = \frac{A_1+A_7}{2} = \frac{0.01+2.33}{2} = 1.17$

12. To get a better graphical determination, the following graph shows a close-up in the central values.



The graphical determination leads to a pK_a value of 3.82. The literature data report a value around 3.85 at 25 °C.

Given that the pH in tube 1 and 7 is at least two units far from the pK_a, the hypotheses in question 9 are valid.