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SwissChO 2023 - Theoretical Final Exam

SOLUTION KEY

Cool High-Temperature Superconductors (15.0 points)

Note that most of the points should be awarded for the calculations and not for their numerical results. Also watch out for consequential errors stemming from miscalculations in earlier exercises.

1.1 **Determine** the chemical formulae of compounds **A** – **C**. 1.5pt

A: $BaSO_4$, **B:** Y_2O_3, **C:** $CuSO_4 \cdot 5\,H_2O$

1.5pts total. 0.5pts per correct compound.

1.2 **Calculate** $\alpha - \delta$, assuming them to be integers. 5.0pt

$M_{BaSO_4} = 233.39$ g mol^{-1}, $M_{Y_2O_3} = 225.82$ g mol^{-1}, $M_{CuSO_4 \cdot 5\,H_2O} = 249.61$ g mol^{-1}

$n = \frac{m}{M}$
$\rightarrow n_{BaSO_4} = 3.02$ mmol $\rightarrow 3.02$ mmol Ba
$\rightarrow n_{Y_2O_3} = 0.75$ mmol $\rightarrow 1.51$ mmol Y
$\rightarrow n_{CuSO_4 \cdot 5\,H_2O} = 4.53$ mmol $\rightarrow 4.53$ mmol Cu

$1\,\text{g} - m_{tot.metal} = 0.163\,\text{g} \rightarrow 10.20$ mmol O

From the respective n, we can deduce, that Y:Ba:Cu = 1:2:3. As for O, we obtain 6.75. However, we know that $\epsilon = 0.25$, therefore we round up to 7.

$\alpha = 1, \beta = 2, \gamma = 3, \delta = 7$

5.0 pts total. 0.5 pts for each correct coefficient. 3.0 pts for the calculations.

1.3 **Note** the number of each atom type per unit cell. **Assign** the colours to each of the elements (Y, Ba, Cu, O). 2.5pt

There are 1 Y, 2 Ba, 3 Cu and 7 O per unit cell.
Y is blue. Ba is pink. Cu is orange. O is yellow.

2.5 pts total. 0.5pts for the correct amount of atoms per unit cell. 0.5pts for each correct assignment.

1.4 **Calculate** the density of the YBCO crystal in g cm^{-3}, assuming $\epsilon = 0.25$. 4.0pt

$V_{cell} = 3.82\,\text{Å} \cdot 3.89\,\text{Å} \cdot 11.68\,\text{Å} = 173.6\,\text{Å}^3 = 1.736 \times 10^{-22}\,\text{cm}^3$
$M_{cell} = N_A \cdot (M_Y \cdot \alpha + M_{Ba} \cdot \beta + M_{Cu} \cdot \gamma + M_O \cdot (\delta - \epsilon)) = 662.20\,\text{g mol}^{-1}$
$m_{cell} = M_{cell}/N_A = 1.10 \times 10^{-21}\,\text{g}$
$\rho = \frac{m_{cell}}{V_{cell}} = \frac{1.10 \times 10^{-21}\,\text{g}}{1.736 \times 10^{-22}\,\text{cm}^3} = 6.336\,\text{g cm}^{-3}$

4.0pts total. 1.0pt for each calculation.

1.5 **Write** a balanced chemical equation for this reaction ($\epsilon = 0.25$). 1.0pt

$4\,Y_2(CO_3)_3 + 16\,BaCO_3 + 24\,CuCO_3 + O_2 \longrightarrow 8\,YBa_2Cu_3O_{6.75} + 52\,CO_2$

1.0pt total.

1.6 **Assign** each metallic ion in solution a colour and **propose** a reason as to why some of them lack colour. 1.0pt

Y^{3+}: colourless, Ba^{2+}: colourless, $[Cu^{2+}(OH_2)_6]$: blue

Y^{3+} and Ba^{2+} both lack colour as they do not have any possible electronic transitions.

1.0pt total. 0.5pts for all colours and all reasons each.

Equilibria of Lime Scale Formation in Hard Water (15.0 points)

Students will have to make assumptions throughout this problem. If they are sensible, mark accordingly.

2.1 **Determine** if such a concentration of $Ca(OH)_2$ is theoretically possible under standard conditions. Also **calculate** the initial pH and pOH of this solution. 2.5pt

Assumption: Autoprotonation of water can be neglected in such high concentrations.

At $20\,°C$ the solubility product K_{sp} of $Ca(OH)_2$ is $5.02 \times 10^{-6}\,mol^3\,L^{-3} = [Ca^{2+}] \cdot [OH^-]^2 = [Ca^{2+}] \cdot (2[Ca^{2+}])^2$.

Solving for $[Ca^{2+}]$, we get that $[Ca^{2+}] = \sqrt[3]{\frac{K_s}{4}} = 0.1079\,mol\,L^{-1} > 0.01\,mol\,L^{-1}$. Therefore, our solution of calcium hydroxide contains less calcium than is maximally possible, and it will not precipitate.

OR

Starting from $[Ca^{2+}] \cdot (2[Ca^{2+}])^2$, if we plug in $0.01\,mol\,L^{-1}$, we get $4.0 \times 10^{-6}\,mol^3\,L^{-3} < 5.02 \times 10^{-6}\,mol^3\,L^{-3}$. Therefore, such a concentration is feasible.

$pOH = -\log([OH^-]) = -\log(0.02) = 1.70$, meaning $pH = 12.30$.

2.5pts total. 2.0pts for the calculation of solubility. 0.5pts for the calculation of pOH and pH.

2.2 **Formulate** a balanced chemical equation for the reaction of lime with carbonic acid - as it can occur during the decomposition of lime-containing rock. **Give** an explanation why the product is easily dissolved away. 1.0pt

$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2$

Because of the lower charge on HCO_3^-, the Coulomb interactions between cation and anion(s) are weaker, therefore leading to a more soluble salt.

1.0pt total. 0.5pts for the equation. 0.5pts for the explanation.

2.3 **Calculate** the molar amount of CO_2 that would theoretically have to be introduced into 0.5 L of our solution for maximum precipitation of lime. **Argue** why the $CO_2 - H_2CO_3$ equilibrium is irrelevant in this reaction. 1.5pt

Assumptions: Protonation of OH^- is irreversible in water. $CO_3{}^{2-}$ is only protonated by H_2CO_3 and any protonation from water can be neglected.

0.5 L of a 0.01 mol L^{-1} solutions means that there are 0.005 mol of $Ca(OH)_2$ in solution.
$2\,OH^- + H_2CO_3 \longrightarrow 2\,H_2O + CO_3{}^{2-}$. As there are 0.01 mol OH^-, and carbonic acid is diprotic, exactly 0.005 mol H_2CO_3 are needed.

The hydration equilibrium can be neglected, as the protonation of OH^- can be seen as irreversible, meaning the equilibrium will eventually shift to the right side no matter what.
Also, this is the maximum precipitation as the introduction of any more CO_2, would once again start creating $HCO_3{}^-$.

1.5pts total. 1.0pt for the calculation. 0.5pts for the correct reasoning.

2.4 **Calculate** both the maximum concentration of CO_2 at $20\,°C$ and the pH of such a solution (applying the Erlenmeyer rule). 1.5pt

Assumption: Hydrogen carbonate is such a weak acid, its deprotonation can be neglected.
Solubility of CO_2 is 1.7 g L^{-1}, meaning that a saturated solution has a concentration of $\frac{1.7\,\text{g L}^{-1}}{44\,\text{g mol}^{-1}} = 0.0386$ mol L^{-1}.
Applying the Erlenmeyer rule, 1% of that (i.e. 3.86×10^{-4} mol L^{-1}) is the concentration of H_2CO_3.
Applying the formula for pH values of weak acids, we get that pH = $\frac{6.46 - \log(3.86 \cdot 10^{-4})}{2} = 4.94$.

1.5pts total. 1.0pt for the calculation of concentration. 0.5pts for the correct pH.

2.5 **Calculate** the pH of the remaining solution. 2.5pt

Assumptions: $CO_3{}^{2-}$ is only protonated by H_2CO_3 and any protonation from water can be neglected. Only carbonate is formed. Hydrogen carbonate is such a weak acid, its deprotonation can be neglected.

Assuming that only $CO_3{}^{2-}$ is formed, we get that $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$. We also neglect any water formed in the reaction in the new volume of water.
$n_{CO_2 new} = n_{CO_2 old} - n_{Ca(OH)_2} = 7.73$ mmol $- 5$ mmol $= 2.72$ mmol of CO_2 are now in solution.
Applying Erlenmeyer's rule, we get a $\frac{2.72\,\text{mmol} \cdot 0.01}{0.7\,\text{L}} = 3.90 \times 10^{-5}$ mol L^{-1} H_2CO_3-solution.
pH $= \frac{6.46 - \log(3.90 \cdot 10^{-5})}{2} = 5.43$

2.5pts total. 1.5pts for the new concentration of CO_2. 0.5pts for the new concentration of H_2CO_3. 0.5pts for the pH of the solution.

2.6 **Determine** the mass of lime precipitated in the reaction. 3.0pt

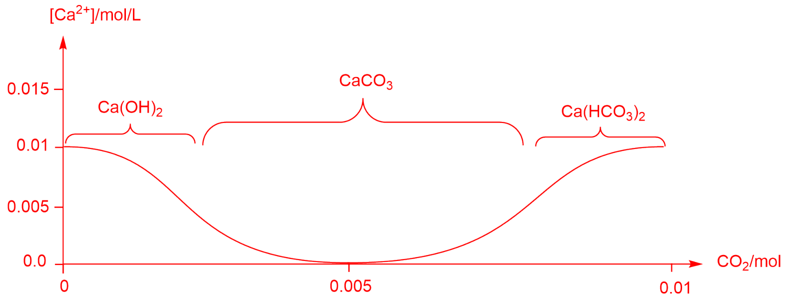
Assumptions: Water does not play a role as base/acid. ΔpK_a between carbonate and carbonic acid is great enough to see the formation of hydrogen carbonate as taking place fully. Lime is insoluble in water. $Ca(HCO_3)_2$ is fully soluble in water.

Starting from the previous solution, we have 2.72 mmol CO_2 in 0.7 L of water as well as 0.005 mol of preciptated lime. The CO_2 will now react fully with any lime to form soluble $Ca(HCO_3)_2$.

$$n_{lime.new} = n_{lime.old} - n_{CO_2 remaining} = 0.005\,\text{mol} - 0.002\,72\,\text{mol} = 0.002\,27\,\text{mol}$$
$$m = n \cdot M = 0.002\,27\,\text{mol} \cdot 100.09\,\text{g mol}^{-1} = 0.227\,\text{g}$$

3.0pts total. 1.5pts for the calculation of remaining lime. 1.5pts for the correct mass precipitated.

2.7 **Draw** the $[Ca^{2+}]$ concentration of our initial solution as a function added CO_2, **labelling** all major Ca^{2+} salts (dissolved or precipitated) at their respective intervals of occurrence. 3.0pt



3.0pts total. 1.5pts for the curve. 1.5pts for the major species.

Thermodynamics in a Car Engine (15.0 points)

3.1 **Write** the reaction equation for the formation of the simplest nitrogen oxide, **drawing** the complete Lewis formula of the product. 1.0pt

1.0pt total. 0.5pts for correct stoichiometry. 0.5pts for correct Lewis structure (radical on O also accepted).

3.2 **Elaborate** on why NO_2 is more likely to dimerise than NO. 0.5pt

N_2O_4 is resonance-stabilised while this would not be the case for N_2O_2.

0.5pts total.

3.3 **Calculate** the enthalpy change $\Delta_r H^0$ of the reaction described in **3.1** at $25\,°\text{C}$ and **suggest** how you need to change the temperature to decrease the yield of the product. 1.0pt

$2H_{\text{NO}} - (H_{O_2} + H_{N_2}) = 2 \cdot 90\,\text{kJ mol}^{-1} - (0\,\text{kJ mol}^{-1} + 0\,\text{kJ mol}^{-1}) = 180\,\text{kJ mol}^{-1}$.

As this is an endothermic reaction, we can use Le Châtelier's principle and increase the temperature, shifting the equilibrium to the product side.

1.0pt total. 0.5pts for the enthalpy change. 0.5pts for the correct reasoning.

3.4 **Calculate** the entropy change ΔS^0 for the reaction taking place under **3.1**. 0.5pt

$2 \cdot S_{\text{NO}} - (S_{O_2} + S_{N_2}) = 2 \cdot 211\,\text{J mol}^{-1}\,\text{K}^{-1} - (192\,\text{J mol}^{-1}\,\text{K}^{-1} + 205\,\text{J mol}^{-1}\,\text{K}^{-1}) = 25\,\text{J mol}^{-1}\,\text{K}^{-1}$.

0.5pts total.

3.5 **Determine** the equilibrium constant K_p of the formation of NO at $25\,°\text{C}$. 2.0pt

$\Delta G = \Delta H - T \cdot \Delta S = 172.55\,\text{kJ mol}^{-1}$ at $T = 298.15\,\text{K}$.

$\Delta G = -RT \ln(K_p)$, therefore $K_p = e^{-\frac{\Delta G}{RT}} = 5.88 \cdot 10^{-31}$.

2.0pts total. 1.0pt for ΔG. 1.0pt for K_p.

3.6 **Calculate** both the new enthalpy change $\Delta_r H$ and the new K_p under these conditions. 3.0pt

Kirchhoff's law states that $\Delta H_{T_1} = \Delta H_{T_2} + \Delta C_p \cdot \Delta T$, if C_p is independent of T.
$\Delta C_p = 2C_p(\mathrm{NO}) - (C_p(\mathrm{O_2}) + C_p(\mathrm{N_2})) = 1.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$.
Therefore: $\Delta H_{2173} = \Delta H_{298} + \Delta C_p \cdot \Delta T = 180\,\mathrm{kJ\,mol^{-1}} + 1.2\,\mathrm{J\,K^{-1}\,mol^{-1}} \cdot 1875\,\mathrm{K} = 182.25\,\mathrm{kJ\,mol^{-1}}$

$\Delta G_{2173} = \Delta H_{2173} - T \cdot \Delta_S = 127.92\,\mathrm{kJ\,mol^{-1}}$.
$K_p(2173) = 8.41 \cdot 10^{-4}$.

3.0pts total. 2.0pts for ΔH_{2173}. 1.0pt for ΔG and K.

3.7 **Calculate** the partial pressures $p_c()$ of nitrogen and oxygen in the cylinder after combustion, but before any nitrogen oxide is formed. 2.0pt

Initally, there the container was filled with $450\,\mathrm{mL}$ of atomospheric air. $V_0(\mathrm{N_2}) = 0.8 \cdot 450\,\mathrm{mL} = 360\,\mathrm{mL}$, $V_0(\mathrm{O_2}) = 0.2 \cdot 450\,\mathrm{mL} = 90\,\mathrm{mL}$.
Applying $n = \frac{pV}{RT} = \frac{1\times10^5\,\mathrm{Pa}V_{gas}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}298.15\,\mathrm{K}}$
$\rightarrow n_{\mathrm{N_2}} = 0.0145\,\mathrm{mol}$

$\rightarrow n_{\mathrm{O_2}} = 0.0036\,\mathrm{mol}$
Applying $p = \frac{nRT}{V} = \frac{n8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}2137.15\,\mathrm{K}}{0.5\times10^{-3}\,\mathrm{m^3}}$. **Note** that the volume is now $500\,\mathrm{mL}$, as the liquid has turned into a gas as well. Also, half of all oxygen was consumed in the combustion.
$\rightarrow p_c(\mathrm{N_2}) = 5.2481 \times 10^5\,\mathrm{Pa}$

$\rightarrow p_c(\mathrm{O_2}) = 6.560 \times 10^4\,\mathrm{Pa}$

2.0pts total. 0.5pts for each calculation. 0.5pts for each correct result.

3..8 **Calculate** the mass of nitrogen oxide that can be expected to be produced per combustion. **Note**: If you could not determine K_p in **3.6**, you may use the approximation $K_p' = 1.0 \times 10^{-3}$. 5.0pt

We know that $K_p = \frac{p(\mathrm{NO})^2}{p(\mathrm{N_2})p(\mathrm{O_2})} = 8.41 \times 10^{-4}$.
And because $\mathrm{N_2} + \mathrm{O_2} \rightleftharpoons 2\,\mathrm{NO}$, it follows that:
$K_p = \frac{(2x)^2}{(p_c(\mathrm{N_2})-x)(p_c(\mathrm{O_2})-x)}$, where x is the amount of oxygen (or nitrogen) consumed.

Algebraic manipulation leads to

$$(4-K)x^2 + xK(p_c(\mathrm{O_2}) + p_c(\mathrm{N_2})) - Kp_c(\mathrm{N_2})p_c(\mathrm{O_2}) = 0$$

Let $a = (4-K), b = K(p_c(\mathrm{O_2}) + p_c(\mathrm{N_2}))$ and $c = -Kp_c(\mathrm{N_2})p_c(\mathrm{O_2})$, then

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = 2629.28\,\mathrm{Pa}$$

$p(\mathrm{NO}) = 2x = 5258.56\,\mathrm{Pa}$
Applying the ideal gas law, we get
$n_{\mathrm{NO}} = 1.455 \times 10^{-4}$ mol, which corresponds to 4.37 mg.

IF K_p' WAS USED
$x = 2861.16$ Pa and $n_{\mathrm{NO}} = 1.584$ mol and $m_{\mathrm{NO}} = 4.75$ mg

5.0pts total. 1.0pt for the expression of K with x. 1.0pt for the quadratic. 1.5pts for solving the quadratic. 1.0pt for the correct n_{NO}. 0.5pts for the correct mass.

Electrochemistry of Chromium (14.0 points)

4.1 **Calculate** the missing potentials **a-d**. 2.0pt

a $= 0.56\,\text{V}$, b $= 1.34\,\text{V}$, c $= 1.33\,\text{V}$, d $= -0.74\,\text{V}$

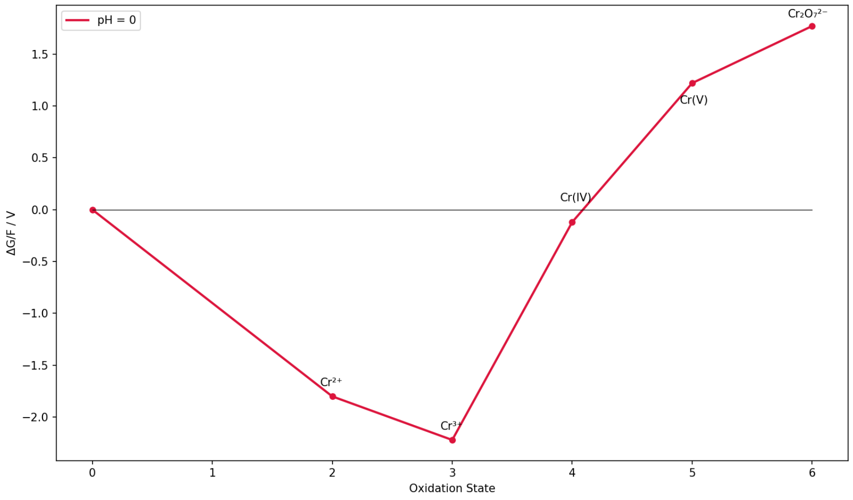
2.0pts total. 0.5pts for each correct value.

4.2 **Determine,** for the calculated potentials, whether the corresponding reductions are exergonic or endergonic. 1.0pt

All positive potentials are exergonic and vice versa, meaning all of them are exergonic - except for d.

1.0pt total.

4.3 **Draw** a complete Frost diagram of Cr in acidic solution, **adding** the missing point Cr(IV). 1.5pt



1.5pts total. 1.0pt for the correct point in the diagram. 0.5pt for labelling all axes and points correctly.

4.4 **Elaborate** on the thermodynamic stability of Cr(II) and Cr(VI) and **provide** whether these oxidation states can be produced as a result of a disproportionation. 3.0pt

In acidc solution:
Neither of the two oxidation states are stable, as the lowest point is Cr^{3+}. Cr(II) cannot be produced in a disproportionation. Cr(VI) is produced in the disproportion of Cr(V).

In basic solution:
Cr(VI) is thermodynamically stable. It cannot be produced in a disproportionation reaction.
3.0pts total. 0.5pts for each assessment of stability. 0.5pts for each correct assignment of (im)possibility of being produced in a disproportionation.

4.5 **Calculate** the standard cell potential of the comproportionation of Cr^{3+} and another Cr-species to form Cr(II). 1.5pt

$\mathrm{Cr} + 2\,\mathrm{Cr}^{3+} \rightleftharpoons 3\,\mathrm{Cr}^{2+}$
$\Delta E_{cell} = E_{red} - E_{ox} = -0.42\,\mathrm{V} - -0.9\,\mathrm{V} = 0.48\,\mathrm{V}$.

1.5pts total. 0.5pts for the correct chemical equation. 1.0pt for the correct cell potential.

4.6 **Give** a balanced half-reaction equation for the reduction of $Cr_2O_7{}^{2-}$ to Cr^{3+} in aqueous acidic solution. 1.0pt

$\mathrm{Cr_2O_7{}^{2-}} + 14\,\mathrm{H^+} + 6\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O}$

1.0pt total.

4.7 **Give** an equation for the non-standard reduction potential of $Cr_2O_7{}^{2-}$ to Cr^{3+}, which is linearly dependent on pH at 25 °C. 4.0pt

The Nernst equation is utilised here.
At 25 °C, the Nernst equation can be written in with a decadic logarithm as follows

$$E = E^0 - \frac{0.059\,\mathrm{V}}{n} \cdot \log(Q) = 1.33\,\mathrm{V} - \frac{0.059\,\mathrm{V}}{6} \cdot \log\left(\frac{[\mathrm{Cr}^{3+}]^2}{[\mathrm{Cr_2O_7}^{2-}][\mathrm{H}^+]^{14}}\right)$$

With $[\mathrm{H}^+]^{14} = 10^{-14pH}$, this gives $\log(Q) = \log\left(\frac{[\mathrm{Cr}^{3+}]^2}{[\mathrm{Cr_2O_7}^{2-}]\cdot 10^{-14pH}}\right) = \log\left(\frac{[\mathrm{Cr}^{3+}]^2}{[\mathrm{Cr_2O_7}^{2-}]}\right) + \log\left(10^{14pH}\right)$
Which gives

$$E = 1.33\,\mathrm{V} - \frac{0.059\,\mathrm{V}}{6}\left(\log\left(\frac{[\mathrm{Cr}^{3+}]^2}{[\mathrm{Cr_2O_7}^{2-}]}\right) + 14pH\right)$$

4.0pts total. 1.0pt for the nernst equation of the half equation. 1.0pt for the substution of $[\mathrm{H}^+]^{14}$*. 1.0pt for "splitting" the log in two. 1.0pt for the final formula.*

Enzyme Kinetics (14.5 points)

5.1 **State** which parameter of a reaction is changed by the enzyme. In keywords, **note** what the change is. 1.0pt

The activation energy is lowered.

(0.5pt for activation energy, 0.5pt for decreased)

5.2 **Write** the differential rate laws for the following three concentrations: [S], [ES] and [P]. 3.0pt

$\frac{\mathrm{d[S]}}{\mathrm{d}t} = -k_1[\mathrm{E}][\mathrm{S}] + k_{-1}[\mathrm{ES}]$

$\frac{\mathrm{d[ES]}}{\mathrm{d}t} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$

$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_2[\mathrm{ES}]$

1.0pt for each

5.3 **Explain** what change you expect for [ES], if the substrate concentration is increased. 1.0pt

[ES] increases for higher [S] (shifts equilibrium to side of [ES])

5.4 Applying the steady-state assumption for the enzyme-substrate complex, **write** the expression for [ES] based on the correct rate law that you found in task **5.2**. E_0 and ES should be the only enzyme-containing species in your final equation. 3.0pt

$\frac{\mathrm{d[ES]}}{\mathrm{d}t} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}] = 0$

$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}]$

$k_1[\mathrm{E}][\mathrm{S}] = (k_{-1} + k_2)[\mathrm{ES}]$

$k_1([\mathrm{E}]_0 + [\mathrm{ES}])[\mathrm{S}] = (k_{-1} + k_2)[\mathrm{ES}]$

$k_1[\mathrm{E}]_0[\mathrm{S}] = (k_{-1} + k_2 + k_1[\mathrm{S}])[\mathrm{ES}]$

$[\mathrm{ES}] = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_{-1}+k_2+k_1[\mathrm{S}]} = \frac{[\mathrm{E}]_0[\mathrm{S}]}{\frac{k_{-1}+k_2}{k_1}+[\mathrm{S}]}$

(0.5pt for correct implementation of steady state, 0.5pts for $[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}]$, 1.0pt for correct rearrangement, 0.5pt for correct simplification at end)

5.5 **Rearrange** the equation that you obtained in **5.4** so that you have an expression for v that does no longer depend on [ES]. 1.0pt

$\frac{v}{v_{\mathrm{max}}} = \frac{[\mathrm{ES}]}{[\mathrm{E}]_0} = \frac{[\mathrm{S}]}{\frac{k_{-1}+k_2}{k_1}+[\mathrm{S}]}$

$v = \frac{v_{\mathrm{max}}[\mathrm{S}]}{\frac{k_{-1}+k_2}{k_1}+[\mathrm{S}]}$

(0.5pt for correct insertion into equation, 0.5pt for correct rearrangement)

5.6 **Develop** a simplified expression for K_M that only contains rate constants. Show your working. 2.0pt

$$v = \frac{v_\mathrm{max}[\mathrm{S}]}{\frac{k_{-1}+k_2}{k_1}+[\mathrm{S}]}$$

$$\frac{v_\mathrm{max}}{2} = \frac{v_\mathrm{max}K_\mathrm{M}}{\frac{k_{-1}+k_2}{k_1}+K_\mathrm{M}}$$

$$\frac{k_{-1}+k_2}{k_1} + K_\mathrm{M} = 2K_\mathrm{M}$$

$$K_\mathrm{M} = \frac{k_{-1}+k_2}{k_1}$$

(0.5pt for correct insertion into equation, 1.0pt for correct rearrangement)

5.7 **Simplify** the expression for v for the following three cases: 2.0pt

(i) [S] $\gg K_\mathrm{M}$
(ii) [S] $= K_\mathrm{M}$
(iii) [S] $\ll K_\mathrm{M}$

(i) $v = \frac{[\mathrm{S}]v_\mathrm{max}}{K_\mathrm{M}+[\mathrm{S}]} \approx \frac{[\mathrm{S}]v_\mathrm{max}}{[\mathrm{S}]} = v_\mathrm{max}$

(ii) $v = \frac{[\mathrm{S}]v_\mathrm{max}}{K_\mathrm{M}+[\mathrm{S}]} = \frac{[\mathrm{S}]v_\mathrm{max}}{2[\mathrm{S}]} = \frac{v_\mathrm{max}}{2}$

(iii) $v = \frac{[\mathrm{S}]v_\mathrm{max}}{K_\mathrm{M}+[\mathrm{S}]} \approx \frac{[\mathrm{S}]v_\mathrm{max}}{K_\mathrm{M}}$

0.5pt for correct insertion of K_M into equation for v, 0.5pt for each result of (i) - (iii)

5.8 For cases (i) and (ii) in task **5.7**: **Write** the expression for the concentration of the enzyme-substrate complex as a function of the total enzyme concentration. 1.5pt

(i) $[\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{K_\mathrm{M}+[\mathrm{S}]} \approx [\mathrm{E}]_0$

(ii) $[\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{K_\mathrm{M}+[\mathrm{S}]} = \frac{[\mathrm{E}]_0[\mathrm{S}]}{2[\mathrm{S}]} = \frac{[\mathrm{E}]_0}{2}$

0.5pt for use of correct equation, 0.5pt for each result of (i) - (ii)

The Diversity of Nickel (14.0 points)

6.1 **Write** down the forward reaction described above. **Assign** oxidation numbers to all atoms in the product. 2.5pt

$\text{Ni} + 4\,\text{CO} \longrightarrow [\text{Ni(CO)}_4]$

Ni^{0}, $\text{C}^{+\text{II}}$, $\text{O}^{-\text{II}}$,

2.5pts total. 1.0pt for the equation. 0.5pts for each oxidation state.

6.2 **Elaborate** on the thermodynamic driving force of the decomposition of complex **C** at higher temperatures. 1.0pt

Entropy is the driving force. As T increases, the entropy term in $\Delta G = \Delta H - T\Delta S$ increases, driving the system to favour more particles.

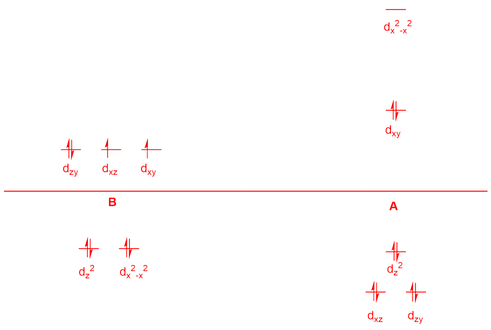
1.0pt total.

6.3 **Determine** the number of d-electrons in these complexes. 1.0pt

As both are $\text{Ni}^{+\text{II}}$-complexes, they have a d^8-system.

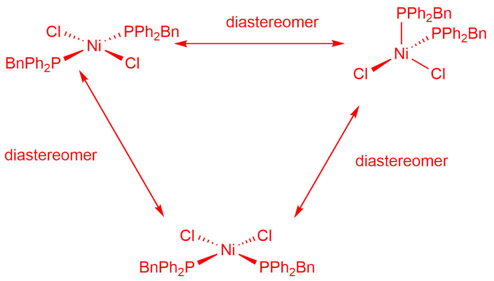
1.0pt total.

6.4 **Draw** the orbital diagrams with all d-electrons of the metal centre of compounds **A** and **B** on your answer sheet, **labelling** all orbitals and **using** the same energy axis for both of the compounds. 3.0pt



3.0pts total. 1.5pts for the correct assignment of the compounds. 1.0pt for the correct "positions" of the electrons and orbital labels. 0.5pts for the qualitatively correct energy differences.

6.5 **Draw** all possible structures of **A** as well as **B**. **Establish** all relations between the isomers (constitutional isomer, enantiomer, diastereomer…). 3.0pt



3.0pts total. 0.5pts for each correct structure. 0.5pts for each correct relationship.

6.6 **Elaborate** on whether you would assume the colour of **B** to be closer to blue or red, compared to **A**. 1.5pt

The colour of **B** is closer to blue, as the transition in a tetrahedral complex requires less energy, compared to a square-planar complex. This results in the absorption of red light, leading to a blue colouration.

1.5pts total. 0.5pts for the correct colour. 1.0pt for the correct reasoning.

6.7 **Give** a reason for why $[Ni(PPh_2Bn)_2(CN)_2]$ only exists in a single isomer. 1.0pt

Strong-splitting ligands favour square-planar complexes. When Cl^- was weak and PPh_2Bn was somewhat strong, it was on the verge, and thus both forms exist. Now that CN^- is very strong and PPh_2Bn still somewhat strong, it's strong splitting and thus squre-planar.

1.0pt total.

6.8 Judging on the colour of **A**, **make** an educated guess about the colour of $[Ni(PPh_2Bn)_2(CN)_2]$. 1.0pt

A is red, which means it absorbs "green" photons. By increasing the field splitting, even higher-energy photons will be required for the electronic transitions. These are either fall out of the visible spectrum, making the new complex colourless (absorbent in UV) or they absorb just in the blue spectrum, making the new complex orange.

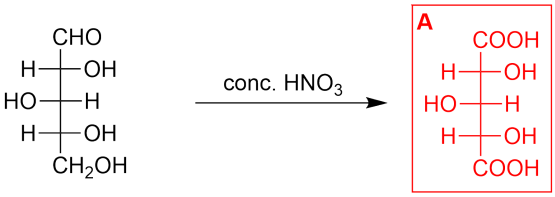
1.0pt total.

Biomolecules - Carbohydrates and Peptides (14.0 points)

7.1 **Calculate** how many stereoisomers of aldohexoses exist? 1.0pt

4 stereocentres -> $2^4 = 16$ stereoisomers

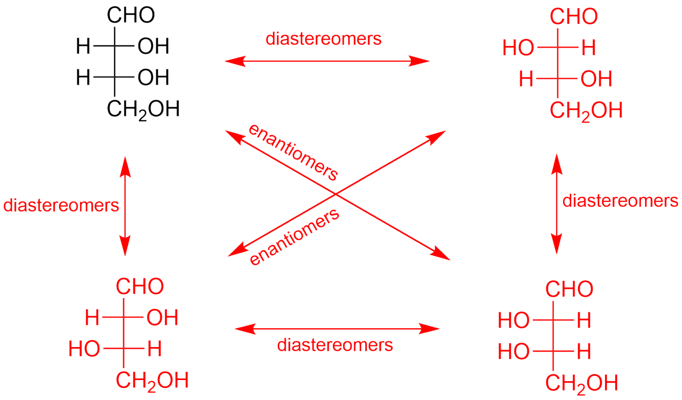
7.2 **Draw** the product **A** of the reaction shown below. 1.0pt



7.3 **Explain** the optical activity of xylaric acid. **State** how such a compound is called. 1.5pt

The compound has an internal reflection plane and is thus symmetrical. A symmetrical structure is optically inactive.
Such a compound is said to be meso.
(1.0pt for correct explanation, 0.5pts for correct term)

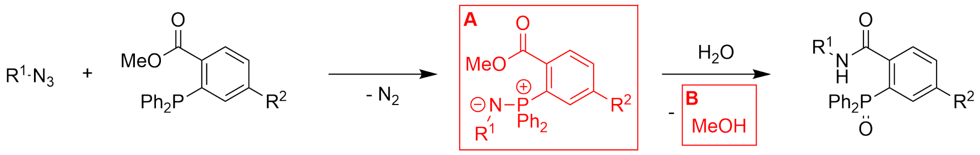
7.4 Below, you can see the structure of D-erythrose. **Copy** the structure on your answer sheet and **draw** all stereoisomers. **Note** the relationships (enantiomer, diastereomer) between all combinations of two structures. 3.5pt



(1.5pts total for stereoisomers:
0.5pts per correct isomer (no points for copying the first from task), -0.5pts per wrong additional isomer, not lower than 0pts for stereoisomers;

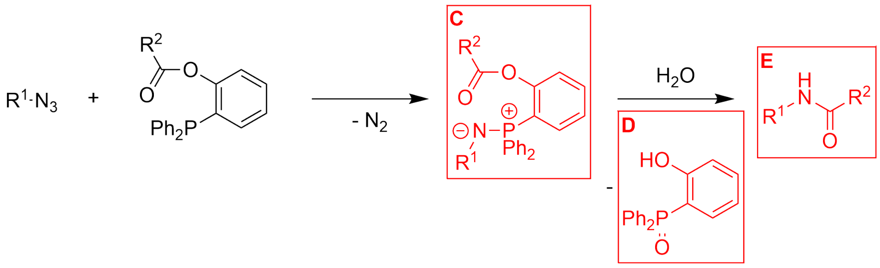
2.0pts total for relationships:
0.5pts per correct relationship (up to a max. of 2.0pts), -0.5pts per wrongly assigned relationship, no deduction for wrong isomers that have already gotten a penalty, not lower than 0pts for relationships)

7.5 **Draw** the intermediate **A** and compound **B** for the Staudinger ligation. 1.5pt



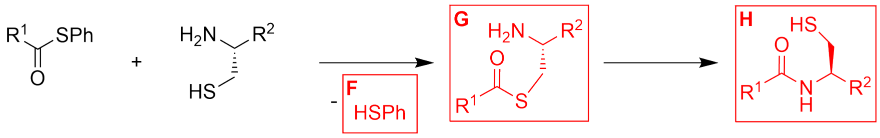
(1.0pt for **A**, 0.5pts for **B**)

7.6 **Draw** intermediate **C**, compound **D** and product **E** of the traceless Staudinger ligation. 3.0pt



1.0pt for each **C**, **D**, **E**

7.7 **Draw** compound **F**, intermediate **G** and product **H** of the native chemical ligation. 2.5pt



(0.5pts for **F**, 1.0pt for **G**, 1.0pt for **H**)

Analysis of an Unknown Compound (15.5 points)

8.1 Of the two U-tubes, one contains sodium hydroxide solution and the other contains dry calcium chloride. **Explain** the use of each of the two tubes and **state** (if necessary) the correct order of the tubes. 1.5pt

$NaOH$ solution: absorbs carbon dioxide
$CaCl_2$: absorbs water
1 is $CaCl_2$, 2 is $NaOH$, since second tube contains aqueous solution, water cannot be determined after that
(0.5pts for use of each tube, 0.5pts for explanation of order)

8.2 You now have ammonia in an alkaline aqueous solution, however you do not know the exact amounts of sulfuric acid or sodium hydroxide solution that you have used in your experiment. **Describe** a procedure to quantify the ammonia. 1.5pt

Distill ammonia into an acidic solution of known concentration. Titrate the remaining acid with a base.
(OR)
Distill ammonia into water. Titrate ammonia with an acid.
(OR)
other individual solution?

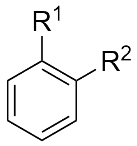
8.3 **Calculate** the number of double bond equivalents. 1.5pt

9 C, 11 H, 1 N
$DBE = \mathrm{C} - \frac{\mathrm{H}}{2} + \frac{\mathrm{N}}{2} = 9 - \frac{11}{2} + \frac{1}{2} = 4$

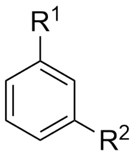
8.4 **Note** what causes this vibration. 0.5pt

$C{=}O$ stretching vibration

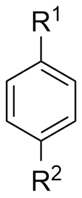
8.5 What is the substitution pattern on the aromatic ring? **Choose** one of the five patterns below. **Explain** your choice. 1.5pt



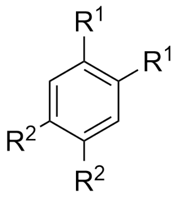
A



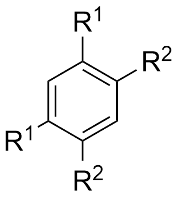
B



C



D



E

C (or *para*).
- signal from four protons
- each proton couples to one other proton (OR) two doublets -> must be symmetrical structure

(0.5pts for correct choice, 1.0pt for correct explanation)

8.6 Considering peak D: This signal comes from one or more protons bound to a single atom. **Give** the element of this atom. **Comment** on the peak width. 1.0pt

Nitrogen

The peak is broadened because the protons are exchangeable.

(0.5pts for correct choice of atom, 0.5pts for correct explanation)

8.7 Considering peak E: **Give** the letter of the other peak to which this/ these proton(s) couple to? **Explain** your answer. 1.0pt

E couples to C.

E is a triplet and thus couples to 2 protons. C is a quartet and thus couples to 3 protons.

(0.5pts for correct choice of peak, 0.5pts for correct explanation)

8.8 In which of the following forms is the nitrogen atom present? **Choose** one of the following: amide, amine or nitro group. **Explain** your choice. 1.5pt

Amine. We have identified before that signal D is from two protons on a nitrogen atom, we can therefore exclude a nitro group. The shift (<5 ppm) tells us that it is an amine.

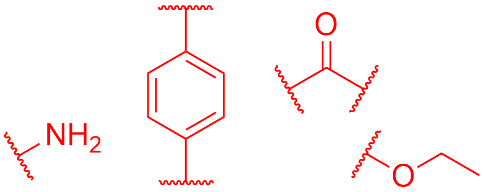
(0.5pts for correct functional group, 1.0pt for correct explanation)

8.9 From the chemical shift of peak C, you see that the carbon atom carrying this/ these proton(s) is connected to a heteroatom. **Explain** what influence you expect on the proton chemical shift due to a heteroatom in this position. **Decide** what element the heteroatom is. 1.5pt

A heteroatom next to the carbon carrying the protons will increase the chemical shift of these protons. Heteroatom is oxygen.

(1.0pt for correct explanation, 0.5pts for correct choice of heteroatom)

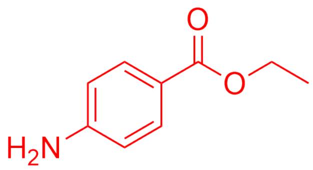
8.10 **Draw** all fragments that you could identify so far. If there are remaining atoms, list them too. 2.0pt



If the amine is already connected to the benzene ring -> also fine

(0.5pts per fragment)

8.11 **Draw** the final compound based on the fragments that you listed in **8.10** and using all the information you got from solving tasks **8.3** to **8.9**. 1.0pt



As can been found out from 8.6 and 8.8, the nitrogen must be connected to one carbon and not be an amide → N must be bound to aromatic ring. Only one way to connect the remaining fragments. (NO explanation necessary for full points)

8.12 **Note** what causes the peak at 7.26 ppm. 0.5pt

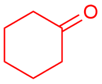
$CHCl_3$
(OR)
remaining undeuterated solvent

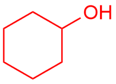
8.13 **Note** what causes the peak at 0.00 ppm. 0.5pt

TMS
(OR)
reference

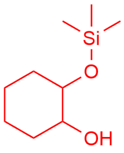
Playing with Cyclohexenone (14.0 points)

9.1 **Draw** the structure of all products **A-I** and **G**. **Draw** the major product if there are multiple. 8.0pt

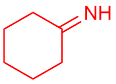

A


B

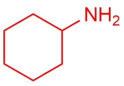

C



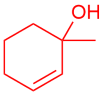
D



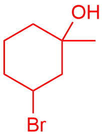
E



F



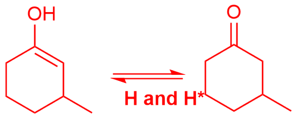
G



I

8.0pts total. 1.0pts for each correct structure.

9.2 **Draw** the structure of **H** and its tautomer **H***. 1.0pt



1.0pt total. 0.5pts for the each structure.

9.3 Suggest suitable reagents for transformations $1-4$, that give the desired products. 2.0pt

1) H_2SO_4
2) H_2O
3) $H^+ (cat.)$
4) 1. O_3, (DCM, -78°C) 2. H_2O_2

2.0pts total. 0.5pts for each correct reaction condition.

9.4 **Draw** the structure of **X** and correctly **name** the reaction taking place. 1.5pt

X

Aldol condensation.

1.5pts total. 1.0pt for the correct structure. 0.5pts for the name of the reaction.

9.5 **Give** the IUPAC-name of one of these compounds and **suggest** a path to convert it to **X**. 1.5pt

There are three possible solutions to this problem.

a) Hexanedioic acid

1) $LiAlH_4$ or $NaBH_4$ or any suitable reducing agent. 2) PCC, Swern oxidation, or other oxidation going selectively to aldehyde.

No full marks if oxidation is done too harshly, i.e. $KMnO_4$.

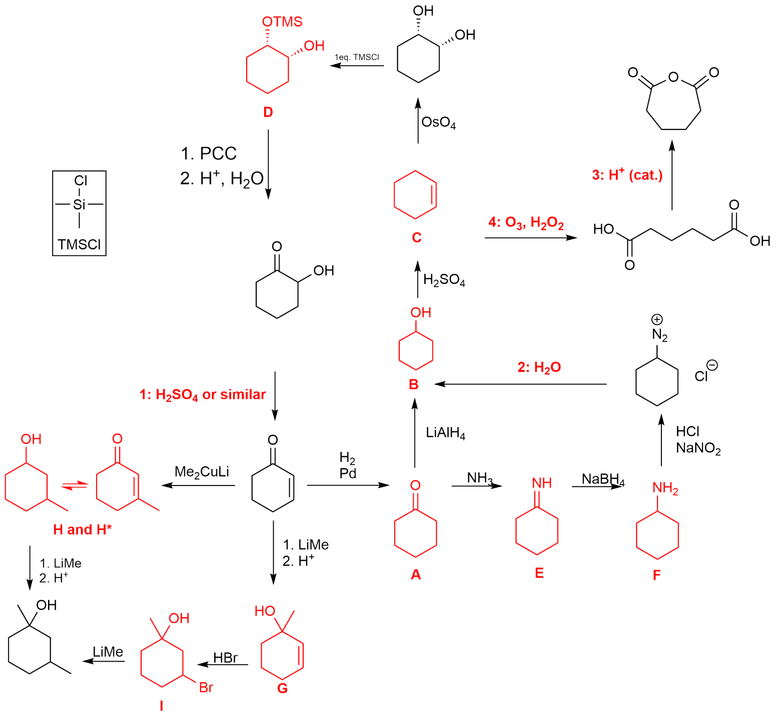
b) Cyclohexene

1) O_3 (DCM, -78 °C) 2) Me_2S

c) Cyclohexane-1,2-diol

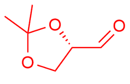
1) $NaIO_4$

1.5pts total. 0.5pts for the name. 1.0pt for the reaction conditions. No further points if multiple pathways are suggested.

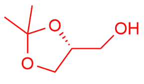


Total Synthesis of Cidofovir (16.0 points)

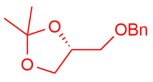
10.1 **Draw** all structures **A**-**C** with all necessary stereochemical information given. **Note**: One equivalent of **3** will yield two equivalents of **A**. 3.0pt



A



B



C

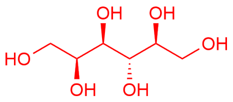
3.0pts total. 1.0pt for each correct structure.

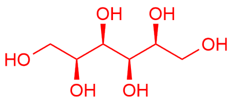
10.2 **Propose** conditions for the transformation under **a**. 1.5pt

Acetone, H^+

1.5pts total. -0.5pts if base is suggested instead of acid, as this will only form the hemiketal.

10.3 **Draw** all stereoisomers of **2** that could also be used to reach product **4**. 2.0pt





2.0pts total.

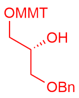
10.4 **Name** two reasons for why the steps from **B** to **C** and **C** to **4** must be performed in that order. 2.0pt

1) Non-selective benzylation of the alcohol.

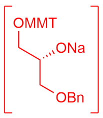
2) It would give the racemate.

2.0pts total.

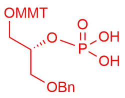
10.5 **Draw** the structures of compounds **D**, **F**, **G** as well as intermediate **E** with correct stereochemistry. 4.0pt



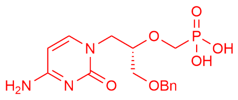
D



E



F



G

4.0pts total. 1.0pt for each correct structure.

10.6 **Propose** conditions for reaction **b**. 1.5pt

MsCl (CH_3SO_2Cl) + weak base (NEt_3 or pyridine)

1.5pts total. 1.0pt for the MsCl*. 0.5pts for the base.*

10.7 **Give** the name of the reaction occurring between **G** and **1**. What purpose did the fragment lost in this reaction serve? 2.0pt

Hydrogenation (deprotection).
The Bn was a protecting group.

2.0pts total. 1.0pt for the reaction name (0.5 if only "deprotection"). 1.0pt for the purpose.