Artificial Photosynthesis

6% of total									
Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	**Total**
Points	3	4	3	2	6	6	1	4	**29**
Score									

The field of artificial photosynthesis research aims at storing solar energy in chemical bonds. Photons are absorbed by exciting sensitizers, thereby producing a charge-separated state. The excited electron is transferred to a catalyst (hydrogen evolving catalyst, HER), which is reduced twice and then produces H_2. The photosensitizer or light absorber is often $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine), and the HERs are often cobalt complexes.

Energetics of Water Splitting

3.1 **Calculate** the enthalpy of the reaction $\mathrm{H_2(g) \longrightarrow 2H^+(aq) + 2e^-}$. 3pt

Solvation enthalpy of proton: $\Delta \mathrm{H}_{aq}(\mathrm{H}^+) = -1190\ \mathrm{kJ\ mol^{-1}}$

Ionization energy of hydrogen: $\mathrm{IE}_1 = 13.6\ \mathrm{eV}$

Dissociation enthalpy of $\mathrm{H_2}$: $\Delta \mathrm{H_{diss}(H_2)} = 432\ \mathrm{kJ\ mol^{-1}}$

Ideally, electrochemical water splitting into O_2 and H_2 runs at $1.23\ \mathrm{V}$ at $25\ ^\circ\mathrm{C}$. Since $T\Delta S$ for this process is > 0, heat from the environment is needed. If additional voltage produces the heat required to compensate the decrease in temperature the process is called **thermoneutral**.

The enthalpy of H_2O(l) formation at $25\ ^\circ\mathrm{C}$, $\Delta \mathrm{H}^\circ_{\mathrm{H_2O}}$, is -285 $\mathrm{kJ\ mol^{-1}}$

3.2 **Calculate** (a) the water splitting reaction entropy $\Delta S^\circ_{\mathrm{R}}$ at $25\ ^\circ\mathrm{C}$ of 1 mol of H_2O and (b) the voltage at which water splitting is thermoneutral. 4pt

Catalysts

Cobalt-salen (salcomin) type complexes are potential catalysts for H_2 formation from protons and electrons. The structure of salcomin is given below:

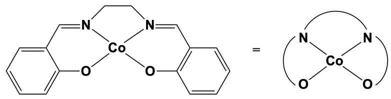

Figure 1. The structure of salcomin.

3.3	• **Determine** the oxidation state of the cobalt atom in salcomin. • **Determine** the geometric structure around the cobalt center of salcomin, choosing from these three possibilities: tetrahedral, square planar or octahedral. **Fill in** the corresponding checkbox on the **answer sheet**.	3pt

In solution, salcomin can bind O_2; that links two salcomin moieties by coordinating to the two Co centres. The oxidation state of both Co centres is then +III.

3.4	**Draw** the resulting structure.	2pt

The H_2 formation takes place exclusively at the cobalt center. The reaction is described by a 4-step catalytic cycle starting with Co^{2+} using 2 H^+ and 2 electrons. During one step a hydride is formed by an intramolecular electron transfer.

3.5 **Write down** two possible variations of the catalytic cycle with charges of the complex and oxidations states of the Co center. The oxidation state on the Co center should not be larger than +III. **Mark** the hydride formation step with an asterisk and **label** H^+ uptake with **C** (chemical reaction), and electron uptake with **E** (electrochemical reaction), see example cycle in **Figure 2** below. $[Co^{II}]$ stands for the Cobalt-salen complex. — 6pt

$$\begin{array}{ccc} [Co^{II}]^0 & \xrightarrow[E]{+ e^-} & [Co^{I}]^- \\ C \uparrow {\scriptstyle +H^+,\ -H_2} & & E \downarrow {\scriptstyle +e^-} \\ [Co^{II}\text{-}H]^- & \xleftarrow[* C]{+ H^+} & [Co^{0}]^{2-} \end{array}$$

Figure 2. An example cycle for **task 3.5**.

Redox Potentials

3.6	• Using the redox potential values of different cobalt complexes given in **Table 1**, **write down** which complex is suitable for **a)** water oxidation at neutral pH **b)** water reduction at neutral pH. • **Write down** the corresponding overall reaction for both processes (only for the complexes, capable of performing it) and **calculate** the cell potentials at neutral pH. • The half-cell potential for the proton reduction at pH = 7, T = 298 K is -0.41 V.	6pt

Co(III/II) redox couple	E° vs normal hydrogen electrode
$[Co(H_2O)_6]^{3+/2+}$	$+1.92$ V
$[Co(C_2O_4)_3]^{3-/4-}$	$+0.55$ V
$[Co(EDTA)]^{1-/2-}$	$+0.38$ V
$[Co(NH_3)_6]^{3+/2+}$	$+0.06$ V
$[Co(en)_3]^{3+/2+}$	-0.18 V
$[Co(CN)_5]^{2-/3-}$	-0.6 V

Table 1. Possible redox couples for **task 3.6**. $[C_2O_4]^{2-}$ = oxalate, en = 1,2-ethylendiamine.

A Glimpse at the Natural Process

The natural storage of biological H_2 equivalents is NADPH, which is produced from $NADP^+$ through the addition of a hydride ion. The structure of NADPH is shown in **Figure 3**.

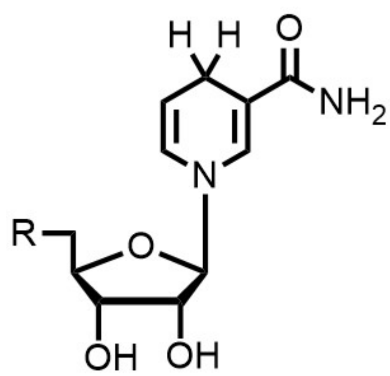

Figure 3. The structure of NADPH.

3.7	**Draw** the structure of $NADP^+$.	1pt

Chlorophyll has an extinction coefficient of about $\varepsilon = 8 \cdot 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at $680\ \mathrm{nm}$.

3.8	Assuming an efficiency (photon to hydrogen H atom) of $\phi = 20\%$ at 680nm and at a photon flux of $100\ \mathrm{nE\ s^{-1}\ cm^{-2}}$ ($1\ \mathrm{E} = 1\ \mathrm{mol\ of\ photons}$), **calculate** a) the number of photons per second and b) the concentration of chlorophyll in a 1x1x1 cm cell needed to get a turnover frequency of $1\ \mathrm{nmol\ H_2\ per\ second}$.	4pt