T8. Recycling of Carbon Dioxide

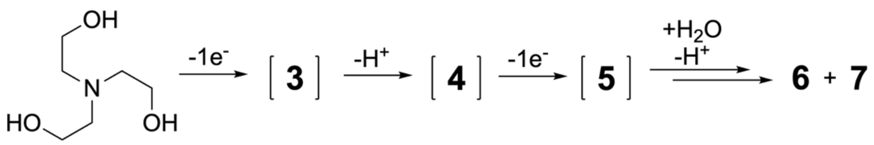
7%										
8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10	Σ
2	16	2	29	5	10	2	4	12	2	84

Removing CO_2 gas from the atmosphere is key to combat climate change. One promising solution is the photocatalytic reduction of CO_2 to CO using molecular catalyst **1**.

$$CO_2 \xrightarrow{\mathbf{1}} CO$$

8.1	**Write** the half equation for the reduction of CO_2 to CO in an acidic medium.	2.0 pt

The conjugate oxidation reaction occurs with sacrificial reductant **2** in aqueous solution with the following mechanism:

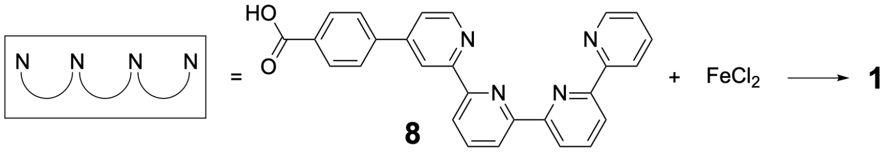


2

Species **3**, **4**, and **5** are short-lived ionic and/or radical intermediates. **7** yields a silver mirror with the $[Ag(NH_3)_2]OH$ test.

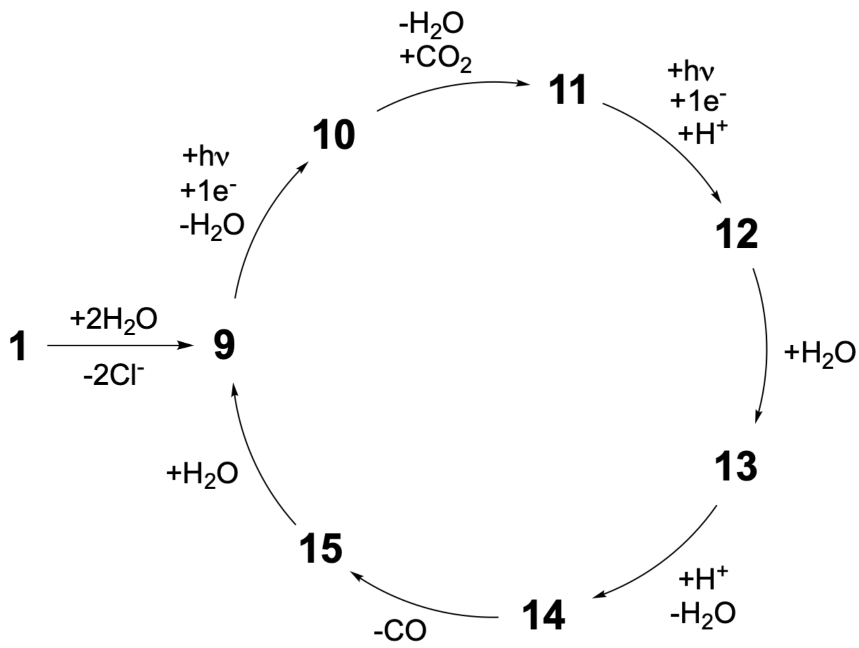
8.2	**Draw** the structures of **3-7**.	16.0 pt

Catalyst **1** can be synthesised with the following reaction.



8.3	**Tick** the correct geometry for the structure of **1**.	2.0 pt

When **1** is loaded on crystalline carbon nitride (C_3N_4) support material, it can reduce CO_2 via the following mechanism.



8.4	**Draw** the structures of **9-15**. Use the cartoon structure for ligand **8** shown above. For **9-15**, **specify** the oxidation state, OS, coordination number, CN, and number of valence electrons, VE, of Fe, along with the total charge of corresponding complex structures, Z. Note: Some information is provided on the answer sheet.	29.0 pt

8.5	**Calculate** the number of catalytic molecules per nm^2, N_{cat}, of C_3N_4 loaded with **1**, when the mass fraction of catalyst, ω_{cat}= 3.8%, if the specific surface area of C_3N_4 is 17.8 m^2 g^{-1}. M_{cat} = 557.21 g mol^{-1}.	5.0 pt

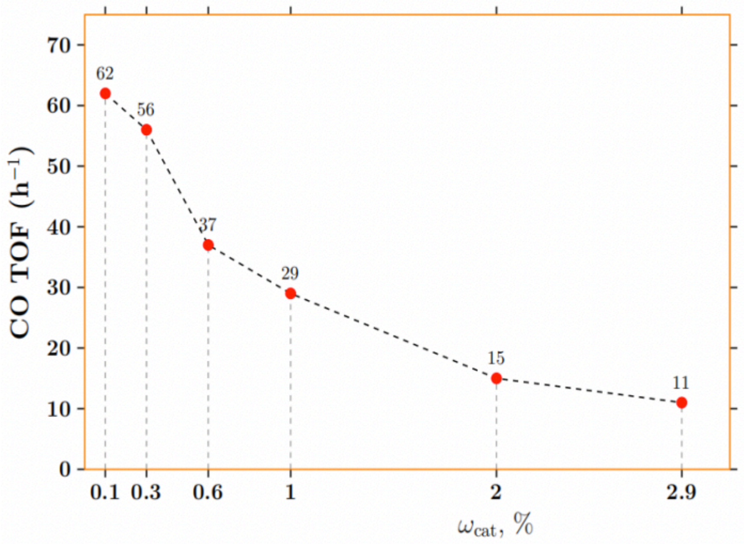
The Turnover Frequency of a catalyst (TOF) is the number of product molecules formed per active catalyst molecule per hour. Under LED illumination (λ = 390 nm) with power of 50 mW, there was a TOF of 8 h^{-1} for 10 mg of C_3N_4, loaded with **1** with ω_{cat} = 3.8%

The formula for calculating the quantum yield is given below:

$$\varphi = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \cdot 100\%$$

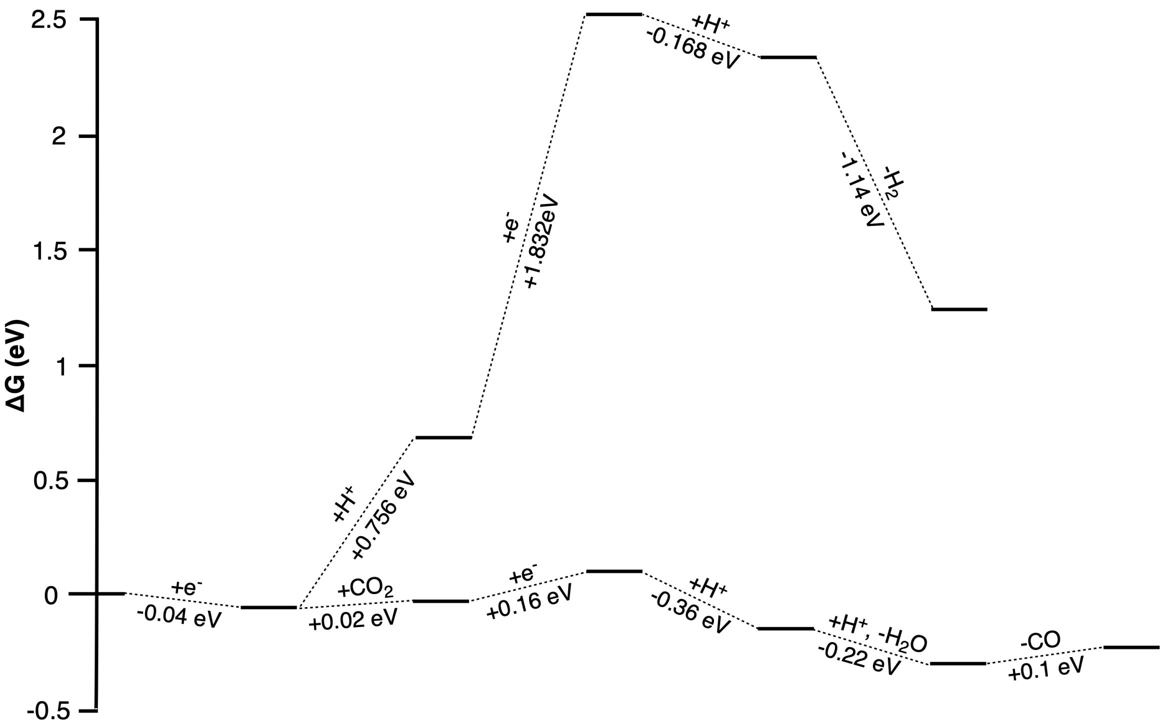
8.6	**Calculate** the quantum yield, $\varphi(\%)$, for CO formation.	10.0 pt

The diagram below shows the change in the TOF of CO as ω_{cat} is varied.

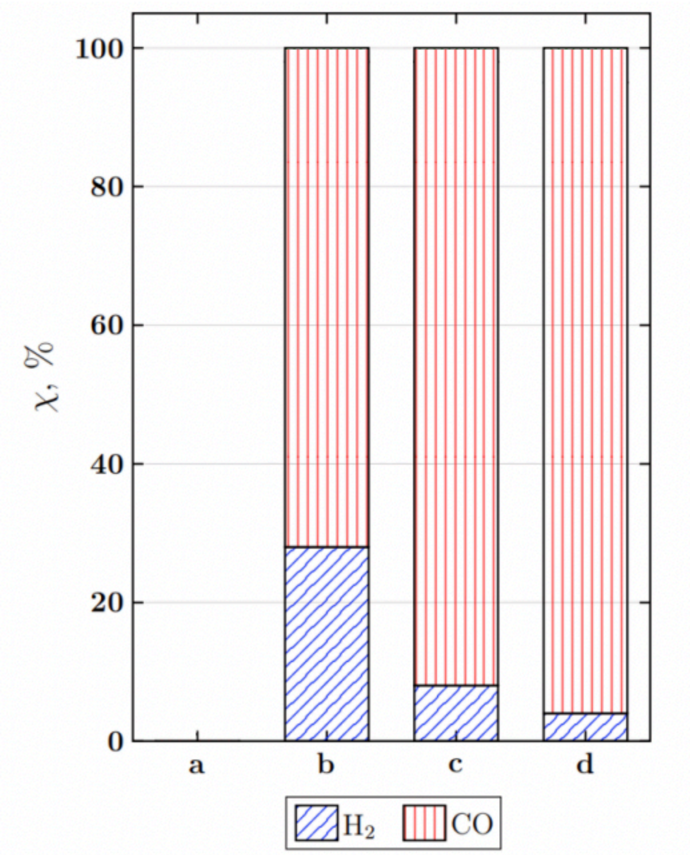


8.7	**<u>How does</u>** the overall rate of CO formation per gram of C_3N_4 loaded with **1** change with increasing ω_{cat}, within the range $0.1 \leq \omega_{cat} \leq 2.9$? **<u>Tick</u>** the correct box. *a) increases* *b) decreases* *c) doesn't change*	2.0 pt

The reduction of CO_2 can be accompanied by the reduction of additional protons. The changes in Gibbs energy during these two reactions are shown in the diagram.



The system was irradiated using different LEDs. The diagram below shows the mole percentages, χ, of H_2 and CO produced during the reduction of CO_2 under four different conditions: no irradiation (N) and irradiation with red (R), green (G), and blue (B) light.



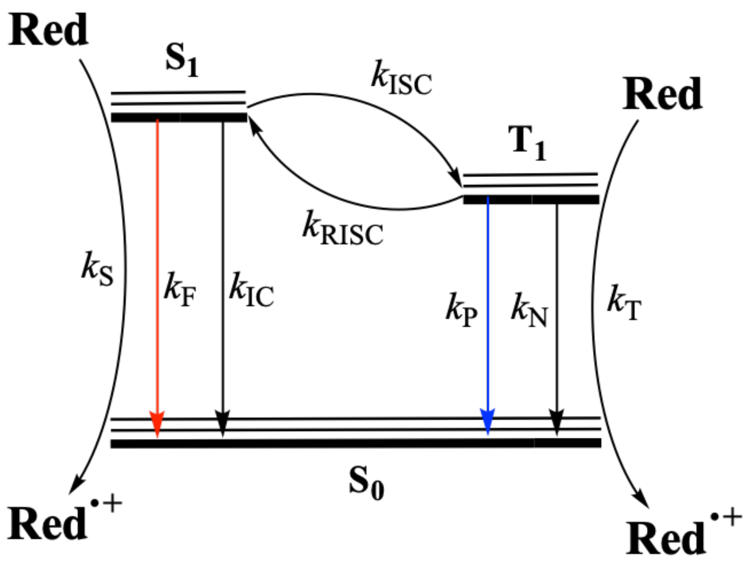
8.8	**Tick** which of the four conditions, mentioned above, corresponds to **a**, **b**, **c** and **d** in the diagram.	4.0 pt

Photosensitisers (PS) offer some advantages over C_3N_4 for the reduction of CO_2. Mn(I)-containing complexes combined with PS can achieve ~23% quantum yield. In this system, reductive quenching of the *singlet* (**S_1**) and *triplet* (**T_1**) excited states of a PS by reductant (Red) forms $\mathrm{PS}^{\bullet -}$, which donates electrons to CO_2 through the Mn(I)-containing complex.

$$\mathrm{PS}_{(\mathrm{S_1})} + \mathrm{Red} \xrightarrow{k_S} \mathrm{PS}^{\bullet -} + \mathrm{Red}^{\bullet +} \quad k_S = 2.7 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

$$\mathrm{PS}_{(\mathrm{T_1})} + \mathrm{Red} \xrightarrow{k_T} \mathrm{PS}^{\bullet -} + \mathrm{Red}^{\bullet +} \quad k_T = 1.5 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

The following Jablonski diagram describes the processes occurring in the PS:



$\tau_0(\mathbf{S_1}) = 2.9$ ns and $\tau_0(\mathbf{T_1}) = 84$ μs, where τ_0 is the emission lifetime in the absence of the quencher.

8.9	**Calculate** the percentage of quenching, η_q, (in %) of **S_1** and **T_1** states, when [Red] = 0.1 M. Note: here the values of k_{ISC} and k_{RISC} are negligible.	12.0 pt

8.10	**How** do the emission lifetimes of **S_1** and **T_1** states change when [Red] increases? **Tick** the correct box. *a) increases* *b) decreases* *c) doesn't change*	2.0 pt