I.10 Photochemistry

Civil Services 2016–2026: **24** parts, **230** marks · IFoS 2016–2025: **17** parts, **159** marks

Syllabus. Absorption of light; decay of excited state by different routes; photochemical reactions between hydrogen and halogens and their quantum yields.

Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	15	20	20	15	20	30	20	20	25	25	20
IFoS	20	20	20	8	10	23	10	15	18	15	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2026

CSE 2026 · Q1(i) Colour of a red flower in green light [5 marks]

A flower is red in colour in daylight. What will be its colour in green light at night? Justify your answer.

CSE 2026 · Q3(c) Energy of one einstein of 800 nm radiation; Photodecomposition of HI: rate, quantum yield and order [15 marks]

(i) Calculate the energy of 800 nm electromagnetic radiation per einstein in SI system.

(ii) The photodecomposition of HI(g) takes place following three elementary steps :

$$\mathrm{HI(g)} + h\nu \longrightarrow \mathrm{H(g)} + \mathrm{I(g)}$$

$$\mathrm{H(g)} + \mathrm{HI(g)} \xrightarrow{k_2} \mathrm{H_2(g)} + \mathrm{I(g)}$$

$$\mathrm{I(g)} + \mathrm{I(g)} \xrightarrow{k_3} \mathrm{I_2(g)}$$

Find the expression of $-\dfrac{\mathrm{d[HI(g)]}}{\mathrm{d}t}$, quantum yield ($\phi$) and kinetic order of the reaction.

2025

CSE 2025 · Q5(b) Light absorbed by a dye solution [5 marks]

A dye solution containing 1 g per 100 cc transmitted 60% of the blue light in a cell 1 cm thick.

(i) What percentage of light would be absorbed by a solution containing 2 g per 100 cc in the same cell?

(ii) What should be the cell thickness so that 90% of the light is absorbed by the original solution?

CSE 2025 · Q6(b) Photochemical $H_2 + Br_2$: rate law and quantum yield [20 marks]

Consider the following photochemical reaction:

$$\mathrm{H_2(g)} + \mathrm{Br_2(g)} \xrightarrow{h\nu} 2\,\mathrm{HBr(g)}$$

Give the mechanism of this reaction. Applying steady-state approximations to [Br] and [H], show that the rate of formation of HBr (g) varies with the square root of the intensity (I_a) of the absorbed radiation. What is the quantum yield for this reaction? Why is the value so low?

IFoS 2025 · Q6(a)(ii) Fluorescence and phosphorescence [5 marks]

(ii) Distinguish between fluorescence and phosphorescence. Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light. Why? [5]

IFoS 2025 · Q6(c) Photochemical hydrogen–bromine reaction [10 marks]

The photochemical reaction, $H_2(g) + Br_2(g) \xrightarrow{h\nu} 2\,HBr\,(g)$, follows the following mechanisms:

(i) $Br_2 + h\nu \xrightarrow{k_1} 2\,Br$ (ii) $Br + H_2 \xrightarrow{k_2} HBr + H$ (iii) $H + Br_2 \xrightarrow{k_3} HBr + Br$

(iv) $H + HBr \xrightarrow{k_4} H_2 + Br$ (v) $2\,Br \xrightarrow{k_5} Br_2$

Applying steady-state approximation to [Br] and [H], derive the expression for the rate of formation of HBr. [Given: I_a is the intensity of the absorbed radiation.]

The quantum yield for this reaction is only 0.01. Why is the value so low?

2024

CSE 2024 · Q5(a) Fluorescence and phosphorescence on a Jablonski diagram [10 marks]

Indicating 'Fluorescence' and 'Phosphorescence' processes in Jablonski diagram, distinguish between both processes.

CSE 2024 · Q6(a) Moles of HCl formed per joule absorbed at 480 nm; Molar extinction coefficient from 50 % transmission [15 marks]

(i) Calculate the number of moles of HCl (g) produced by the absorption of one Joule of radiant energy of wavelength 480 nm in the reaction $H_2(g) + Cl_2(g) \longrightarrow 2\,HCl\,(g)$ if the quantum yield of the photochemical reaction is 1.0×10^6. *10*

[Given: $N_A = 6.022 \times 10^{23}$ mol^{-1}, $h = 6.626 \times 10^{-34}$ J s, $c = 2.998 \times 10^8$ m s^{-1}]

(ii) On passing monochromatic light through a 0.04 molar solution kept in a cell of thickness 2 cm, the intensity of the transmitted light was reduced to 50%. Calculate the molar extinction coefficient. *5*

IFoS 2024 · Q1(c) Primary quantum yield [8 marks]

An absorbing substance is exposed to a light of wavelength 400 nm using a 100 mW laser source for 50 minutes. The intensity of the transmitted light is 40% that of incident light. As a result, 0.4 mmol of the absorbing substance is decomposed. Determine the primary quantum yield of this photochemical reaction.

IFoS 2024 · Q3(c) Photostationary dimer concentration [10 marks]

Consider a molecule 'A' in a solution undergoes the following steps when it absorbs UV light of intensity I_{abs}.

(i) $A + h\nu \xrightarrow{I_{abs}} A^*$

(ii) $A^* + A \xrightarrow{k_2} A_2$ (dimerization)

(iii) $A^* \xrightarrow{k_3} A + h\nu'$ (fluorescence)

(iv) $A_2 \xrightarrow{k_4} 2\,A$ (thermal decomposition)

Derive an expression for determining the concentration of A_2 at equilibrium, when the concentration of A is large.

2023

CSE 2023 · Q5(b) Radiative and non-radiative processes; Jablonski diagram [10 marks]

Explain radiative and non-radiative processes by singlet and triplet electronic states of molecule. Also explain it through Jablonski diagram.

CSE 2023 · Q8(c) Light absorbed when the path length is halved [10 marks]

When an incident light of wavelength 300 nm is passed through a solution in a 1 cm cell, it transmits only 10% of the incident light. What percentage of light would be absorbed by the same solution if taken in a 0.5 cm cell?

IFoS 2023 · Q6(b) Threshold wavelength for excitation [15 marks]

In a photochemical reaction, it usually takes 1.5 eV to 2.0 eV to put a molecule into an excited state. What is the maximum wavelength of light capable of exciting the molecule? Which part of electromagnetic spectrum it belongs? Also, calculate the energy per mole (in kJ/mole) associated with photon of that light.

2022

CSE 2022 · Q5(b) Jablonski diagram (A to E); the route to photochemistry [10 marks]

Label each of the following processes with proper explanation in Jablonski diagram:
(A) Allowed absorption (B) Fluorescence (C) Phosphorescence (D) Internal Conversion (IC) (E) Inter System Crossing (ISC)
Discuss the mode of transition which is favourable for a photochemical reaction.

CSE 2022 · Q8(d) Steady-state approximation; photochemical H_2 + Cl_2; quantum yield [10 marks]

What is meant by steady-state approximation? How this approximation helps in deriving the kinetics of following photochemical reaction?

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl\,(g)$$

The quantum yield of this reaction is extremely large. Justify or criticize this statement.

IFoS 2022 · Q6(a) Singlet and triplet excited states [10 marks]

How does singlet excited state differ from triplet excited state? Explain with the help of an energy level diagram.

2021

CSE 2021 · Q5(b) Lambert–Beer law: statement and derivation [10 marks]

State and derive Lambert-Beer law for absorption of light by solutions.

CSE 2021 · Q7(c) Quantum yield for the photodecomposition of oxalic acid [20 marks]

Radiation of wavelength 2500 Å was passed through a cell containing 10 ml of a solution which was 0.05 molar in oxalic acid and 0.01 molar in uranyl sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.
(Given : $N = 6.022 \times 10^{23}$ mol^{-1}, $h = 6.626 \times 10^{-34}$ J s and $c = 3 \times 10^{8}$ m s^{-1})

IFoS 2021 · Q5(b) Stark–Einstein law [8 marks]

State and explain Stark–Einstein law of photochemical equivalence.

IFoS 2021 · Q6(b) Quantum yield and ethylene production [15 marks]

For the photochemical formation of ethylene from di-n-propyl ketone using a wavelength 313 nm, the quantum yield is 0.21. Calculate the number of moles of ethylene formed when the sample is irradiated with 50 watt of this radiation, assuming that all the radiation is absorbed by the same sample.

2020

CSE 2020 · Q5(e) Decay routes of an electronically excited molecule: Jablonski diagram [10 marks]

Discuss all the possible decay routes of an electronically excited molecule with the help of a neat Jablonski diagram.

CSE 2020 · Q8(b) Moles of HI decomposed from the quantum yield [10 marks]

The quantum yield for photo decomposition of HI(g) at wavelength 254 nm is 1.99. If a total of 3070 J of energy is absorbed then how many moles of HI(g) decomposed?

IFoS 2020 · Q7(c) CO formed from propionaldehyde from the quantum yield [10 marks]

When propionaldehyde is irradiated with light λ of 3020 Å, it decomposes to form carbon monoxide. The quantum yield for the reaction is 0·54. The light energy absorbed is 15000 erg mol^{-1} in a given time. Find the amount of carbon monoxide formed in moles in the same time.

2019

CSE 2019 · Q6(a) Quantum yields of the photochemical $H_2 + Cl_2$ and $H_2 + Br_2$ reactions [15 marks]

The quantum yield for the photo-chemical reaction between H_2 and Cl_2 is 10^6 whereas that for H_2–Br_2 reaction is almost unity. Account for the observation.

IFoS 2019 · Q5(d) Photochemical H_2–Cl_2 and H_2–Br_2 reactions: rate laws and quantum efficiency [8 marks]

Write the photochemical reaction between H_2 – Cl_2 and H_2 – Br_2 and also write the rate laws. How do you show that the quantum efficiency of H_2 – Cl_2 is very low, whereas that of H_2 – Br_2 is very high?

2018

CSE 2018 · Q6(b)(i) Fluorescence and phosphorescence [5 marks]

Distinguish fluorescence from phosphorescence.

CSE 2018 · Q6(b)(ii) Quantum yield of the photobromination of cinnamic acid [5 marks]

In the photobromination of cinnamic acid to dibromocinnamic acid using light of wavelength 4358 Å a light intensity of 14,000 ergs sec^{-1} produced, and a decrease of 0.075 millimole of bromine during an exposure for 1105 sec. The solution absorbed 80.1% of the light passing through it. Calculate the quantum yield.

CSE 2018 · Q8(b)(i) Einstein's law of photochemical equivalence [5 marks]

Define and explain Einstein's law of photochemical equivalence.

CSE 2018 · Q8(b)(ii) The photochemical reaction of hydrogen and chlorine [5 marks]

Discuss the photochemical reactions between hydrogen and chlorine.

IFoS 2018 · Q2(c) Number of photons in 1.0 kcal of 350 nm light [10 marks]

Calculate the number of photons in 1·0 kcal of light of wavelength 350 nm.

IFoS 2018 · Q4(b) Why phosphorescence is slower than fluorescence (Jablonski) [10 marks]

Phosphorescence emission rate is slower than fluorescence emission rate. Explain with Jablonski diagram.

2017

CSE 2017 · Q5(b) Intersystem crossing on the Jablonski diagram [10 marks]

What is ISC (Inter System Crossing) for an excited molecule in singlet state? Answer using Jablonski diagram.

CSE 2017 · Q6(b) Concentration from 80 % transmittance (Beer–Lambert law) [10 marks]

Using a particular wavelength of light, a solution of a substance (molar mass 294 g mol^{-1}) transmits 80% of incident light. Determine the concentration of the solution in mol L^{-1}. Given that optical path length of the spectrophotometer tube is 1.0 cm and absorptivity of the substance is 2.0 L g^{-1} cm^{-1}.

IFoS 2017 · Q3(d) Quantum yield from absorbed energy at 3600 Å [10 marks]

For the photochemical reaction

$$A \rightarrow B,$$

it is found that $1{\cdot}00 \times 10^{-5}$ mole of B is formed, as a result of the absorption of $6{\cdot}00 \times 10^{7}$ ergs at 3600 Å. Calculate the quantum yield.

Given : Avogadro number $6{\cdot}02 \times 10^{23}$
Planck's constant $6{\cdot}626 \times 10^{-34}$ J-sec
Velocity of light 3×10^{10} cm/sec

IFoS 2017 · Q8(d) High and low quantum yields [10 marks]

What do you understand by quantum yield? Discuss high and low values of quantum yield by taking suitable examples.

2016

CSE 2016 · Q4(a)(i) Stark–Einstein law; quantum yield and why it is often low [15 marks]

State and explain Einstein law of photochemical equivalence. What is quantum yield? Explain the causes of low quantum yield.

IFoS 2016 · Q4(a)(i) Stark–Einstein law; why the quantum yield is often low [10 marks]

State and explain Einstein law of photochemical equivalence. How is low quantum yield explained?

IFoS 2016 · Q5(a)(i) Fluorescence [5 marks]

Explain the following briefly :
(i) Fluorescence

IFoS 2016 · Q5(a)(ii) Chemiluminescence [5 marks]

Explain the following briefly :
(ii) Chemiluminescence