Reaction Kinetics V.: Photochemistry

P129. The molar absorbance of a solute dissolved in hexane is 855 $dm^3\ mol^{-1}\ cm^{-1}$ at 270 nm. Calculate how much the intensity of the light decreases if it passes through a solution of 3.25 mmol dm^{-3} concentration. The path length of the cuvette is 2.5 mm. (79.8%)

P130. A certain laser can generate radiation in pulses, each of which delivers an energy of 0.10 mJ, with peak power of 5.0 MW and average power of 7.0 kW. What is the pulse duration and the repetition frequency? (t = 20 ps, ν = 70 MHz)

P131. In an experiment to measure the quantum efficiency of a photoreaction, the absorbing species was exposed to 490 nm light from a 100 W lamp for 45 min. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of illumination, 0.344 mol the absorbing species decomposed. Calculate the quantum efficiency. (0.52)

P132. Consider the quenching of an organic fluorescent species with τ_0 = 3.5 ns by a *d*-metal ion with $k_Q = 2.5\cdot10^9\ dm^3\ mol^{-1}\ s^{-1}$. Predict the concentration of quencher required to decrease the fluorescence intensity of the organic species to 75 per cent of the unquenched value. (c_Q = 0.038 mol dm^{-3})

P133. An electrically excited state of Hg can be quenched by N_2 molecules as follows:

$$Hg^*\ (g) + N_2\ (g, v = 0) \rightarrow Hg\ (g) + N_2\ (g, v = 1)$$

In the reaction, energy transfer from Hg* excites N_2 vibrationally. Fluorescence lifetimes were measured with and without N_2. The data are summarized in the table at T = 300 K:

p_{N2} = 0.0 atm

Relative fluorescence intensity	1.000	0.606	0.360	0.220	0.135
t/µs	0.0	5.0	10.0	15.0	20.0

$p_{N2} = 9.74\cdot10^{-4}$ atm

Relative fluorescence intensity	1.000	0.585	0.342	0.200	0.117
t/µs	0.0	3.0	6.0	9.0	12.0

Determine the rate constant for the energy transfer process. You may assume that all gases are perfect. ($k = 2.0\cdot10^9\ dm^3\ mol^{-1}\ s^{-1}$)

P134. Ultraviolet radiation photolyses O_3 to O_2 and O. Determine the rate at which ozone is consumed by 305 nm radiation in a layer of the stratosphere of 1.0 km thickness. The quantum yield is 0.94 at 220 K, the ozone concentration is about $8\cdot10^{-9}$ mol dm^{-3}, the molar absorption coefficient is 260 $dm^3\ mol^{-1}\ cm^{-1}$, and the flux of 305 nm radiation is about $1\cdot10^{14}$ photon $cm^{-2}\ s^{-1}$. ($v = 5.95\cdot10^{-13}\ mol\ dm^{-3}\ s^{-1}$)