Montogue

QUIZ CH110
Photochemistry
Lucas Montogue

▶▶ PROBLEMS

▶ Problem 1

A 5.0×10^{-4} M solution of aniline in H_2O has absorbance $A = 0.474$ at 290 nm, when measured in a 1.00-cm cell. Find the transmittance of a 3.0×10^{-3} M solution of aniline in water when measured at the same wavelength but in a 0.6-cm cell.

A) $T = 0.415$
B) $T = 0.520$
C) $T = 0.605$
D) $T = 0.710$

▶ Problem 2 (Modified from Harris, 2016, w/ permission)

Vapor at a pressure of 30.3 μbar from the solid compound pyrazine had a transmittance of 24.4% at a wavelength of 266 nm in a 3.0-cm cell at 298 K.

Part 1: Convert transmittance to absorbance.

A) $A = 0.487$
B) $A = 0.535$
C) $A = 0.613$
D) $A = 0.727$

Part 2: Convert pressure to concentration (mol/L) using the ideal gas law.

A) $C = 1.22 \times 10^{-6}$ mol/L
B) $C = 3.19 \times 10^{-6}$ mol/L
C) $C = 4.81 \times 10^{-6}$ mol/L
D) $C = 6.25 \times 10^{-6}$ mol/L

Part 3: Determine the molar absorptivity.

A) $\varepsilon = 54,900$ $M^{-1} \cdot cm^{-1}$
B) $\varepsilon = 78,400$ $M^{-1} \cdot cm^{-1}$
C) $\varepsilon = 118,000$ $M^{-1} \cdot cm^{-1}$
D) $\varepsilon = 167,000$ $M^{-1} \cdot cm^{-1}$

▶ Problem 3

1.0 mmol of X in 1.0 L of water has absorbance equal to 0.222 at 500 nm when measured in a 1.0 cm cell. In water, X undergoes the reaction X → 2Y. At 500 nm, the molar absorptivities of X and Y are $\varepsilon_x = 500$ and $\varepsilon_y = 12$ $L \cdot mol^{-1} \cdot cm^{-1}$, respectively. Find the equilibrium constant for X → 2Y.

A) $K = 8.11 \times 10^{-4}$
B) $K = 1.02 \times 10^{-3}$
C) $K = 3.29 \times 10^{-3}$
D) $K = 6.58 \times 10^{-3}$

▶ Problem 4

The absorbances of three solutions of methyl orange, each at the same (unknown) formal concentration C but at different pH values, were measured in a 1.0-cm cell at 512 nm; the data are summarized below. What is the value of K_a for methyl orange?

pH	Strongly acidic	4.6	Strongly basic
A	0.467	0.180	0.132

A) $K_a = 1.5 \times 10^{-4}$
B) $K_a = 3.0 \times 10^{-4}$
C) $K_a = 6.0 \times 10^{-4}$
D) $K_a = 1.2 \times 10^{-3}$

1

▶ Problem 5

Titanium and vanadium form colored peroxide complexes, and their concentrations can be measured spectrophotometrically. Absorption data for these two species, measured in a 1.0-cm cell, are listed below.

Complex	Metal concentration, µg/mL	Absorbance	
		400 nm	480 nm
Ti	35.0	0.588	0.396
V	105.0	0.402	0.586

The absorbance of a solution containing both titanium and vanadium peroxides was determined using a 1.0-cm cell and found to be 0.822 at 400 nm and 0.705 at 480 nm. Determine the Ti and V contents of the solution.

A) C_{Ti} = 19.5 µg/mL and C_V = 50.6 µg/mL
B) C_{Ti} = 19.5 µg/mL and C_V = 75.6 µg/mL
C) C_{Ti} = 37.4 µg/mL and C_V = 50.6 µg/mL
D) C_{Ti} = 37.4 µg/mL and C_V = 75.6 µg/mL

→ Problem 6.1 (Modified from Harris, 2016, w/ permission)

The following graph shows the molar absorptivity spectrum of ozone. As can be seen, ozone reaches a maximum absorption level at a wavelength close to 260 nm. Also shown is the variation of *absorption cross section* σ, which is related to transmittance T by the equation

$$T = e^{-n\sigma b}$$

where n is the number of absorbing molecules per cubic centimeter and b is the pathlength. The total ozone in the atmosphere amounts to approximately 8×10^{18} molecules above each square centimeter of Earth's surface (from the surface up to the top of the atmosphere). If this were compressed into a 1-cm thick layer, the concentration would be 8×10^{18} molecules/cm^3. Using the ozone spectrum given, estimate the absorbance of this 1-cm^3 sample at 325 and 300 nm.
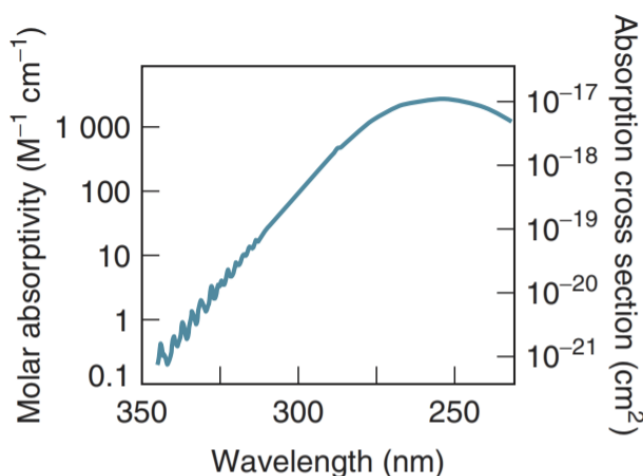
A) $A_{300} \in (0.4, 1.2)$, $A_{325} \in (0.01, 0.08)$
B) $A_{300} \in (0.4, 1.2)$, $A_{325} \in (0.08, 0.4)$
C) $A_{300} \in (1.2, 2.5)$, $A_{325} \in (0.01, 0.08)$
D) $A_{300} \in (1.2, 2.5)$, $A_{325} \in (0.08, 0.4)$

→ Problem 6.2

Sunburns are caused by radiation in the 295- to 310-nm region. At the center of this region, the transmittance of atmospheric ozone is 0.14. Calculate the absorption cross-section for $T = 0.14$, $n = 8 \times 10^{18}$ molec./cm^3, and $b = 1$ cm. By what percentage does the transmittance increase if the ozone concentration decreases by 5% to 7.6×10^{18} molec./cm^3?

A) $\sigma = 2.01 \times 10^{-19}$ cm^2 and the decrease in concentration will cause the transmittance to rise by 10%.
B) $\sigma = 2.01 \times 10^{-19}$ cm^2 and the decrease in concentration will cause the transmittance to rise by 15%.
C) $\sigma = 2.46 \times 10^{-19}$ cm^2 and the decrease in concentration will cause the transmittance to rise by 10%.
D) $\sigma = 2.46 \times 10^{-19}$ cm^2 and the decrease in concentration will cause the transmittance to rise by 15%.

2

→ Problem 6.3

Atmospheric ozone is measured in *Dobson units* (1 unit = 2.69×10^{16} molecules O_3 above each cm^2 of Earth's surface). [Dobson unit = thickness (in hundredths of a millimeter) that the O_3 column would occupy if it were compressed to 1 atm at 0°C]. The graph shows variations in O_3 concentration as a function of latitude and season. Using an absorption cross-section of 2.5×10^{-19} cm^2, calculate the transmittance in the winter and in the summer at 30°-50° N latitude, at which O_3 varies from 290 to 350 Dobson units. By what percentage is the ultraviolet transmittance greater in winter than in summer?
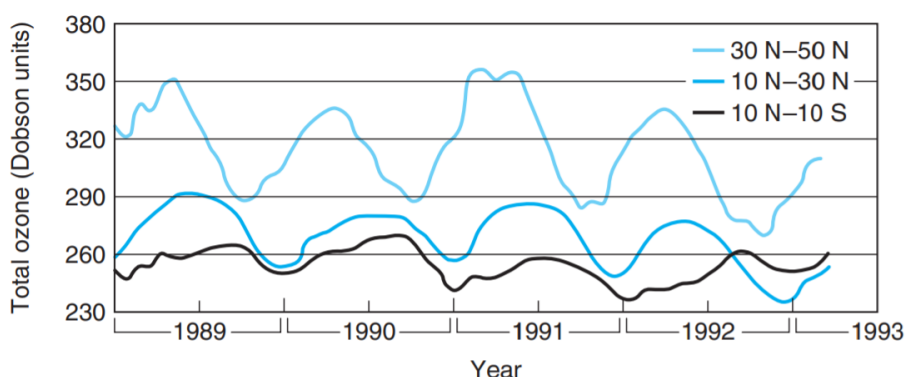
Variation in atmospheric ozone at different latitudes.

A) The transmittance in winter is about 33% greater than the transmittance in summer.

B) The transmittance in winter is about 49% greater than the transmittance in summer.

C) The transmittance in winter is about 65% greater than the transmittance in summer.

D) The transmittance in winter is about 81% greater than the transmittance in summer.

▶ Problem 7

Phosphorus in urine can be determined by treating with molybdenum(VI) and then reducing the phosphomolybdate with aminonaphtholsulfonic acid to give the characteristic molybdenum blue color. This absorbs at 690 nm. A patient excreted 1270 mL urine in 24 h, and the pH of urine was 6.5. A 1.00-mL aliquot of the urine was treated with molybdate reagent and aminonaphthosulfonic acid and was diluted to a volume of 50.0 mL. A series of phosphate standards was similarly treated. The absorbance of the solutions at 690 nm, measured against a blank, were as follows:

Solution	Absorbance
1.00 ppm P	0.205
2.00 ppm P	0.410
3.00 ppm P	0.615
4.00 ppm P	0.820
Urine sample	0.625

Part 1: Calculate the number of grams of phosphorus excreted per day.
A) m_P = 0.194 g P
B) m_P = 0.334 g P
C) m_P = 0.541 g P
D) m_P = 0.769 g P

Part 2: Calculate the phosphate concentration in the urine as millimoles per liter.
A) $[PO_4^{3-}]$ = 0.444 mmol/L urine
B) $[PO_4^{3-}]$ = 1.94 mmol/L urine
C) $[PO_4^{3-}]$ = 3.44 mmol/L urine
D) $[PO_4^{3-}]$ = 4.94 mmol/L urine

Part 3: Calculate the ratio of HPO_4^{2-} to $H_2PO_4^-$ concentrations in the sample, given ionization constants K_1 = 1.1×10^{-2}, K_2 = 7.5×10^{-8}, and K_3 = 4.8×10^{-13}.
A) $[HPO_4^{2-}]/[H_2PO_4^-]$ = 0.0972
B) $[HPO_4^{2-}]/[H_2PO_4^-]$ = 0.237
C) $[HPO_4^{2-}]/[H_2PO_4^-]$ = 0.325
D) $[HPO_4^{2-}]/[H_2PO_4^-]$ = 0.414

3

▶ Problem 8

Write the basic law relating fluorescence to concentration and show that, at low concentrations, fluorescence and molar concentration are linearly related.

▶ Problem 9

In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from an 87.5-W source for 28.0 min. The intensity of the transmitted radiation was 0.257 that of the incident radiation. As a result of irradiation, 0.324 mol of the absorbing substance decomposed. Evaluate the quantum yield.

A) $\phi = 1.02$
B) $\phi = 1.11$
C) $\phi = 1.32$
D) $\phi = 1.60$

▶ Problem 10 (Modified from Atkins *et al.*, 2018, w/ permission)

The quenching of tryptophan fluorescence by dissolved O_2 gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process from the following data:

$[O_2]$ (10^{-2} mol dm^{-3})	0	2.3	5.5	8	10.8
τ (ns)	2.6	1.5	0.92	0.71	0.57

A) $k_Q = 8.14 \times 10^8$ dm^3·mol^{-1}·s^{-1}
B) $k_Q = 4.31 \times 10^9$ dm^3·mol^{-1}·s^{-1}
C) $k_Q = 8.14 \times 10^9$ dm^3·mol^{-1}·s^{-1}
D) $k_Q = 1.27 \times 10^{10}$ dm^3·mol^{-1}·s^{-1}

▶ Problem 11 (Modified from Atkins *et al.*, 2018, w/ permission)

Consider the quenching of an organic fluorescent species with fluorescent lifetime $\tau_0 = 6.0$ ns by a d-metal ion with quenching constant $k_Q = 3.0 \times 10^8$ dm^3·mol^{-1}·s^{-1}. Predict the concentration of quencher required to decrease the fluorescence intensity of the organic species to 50 percent of the unquenched value.

A) $[Q] = 0.132$ mol·dm^{-3}
B) $[Q] = 0.345$ mol·dm^{-3}
C) $[Q] = 0.556$ mol·dm^{-3}
D) $[Q] = 0.738$ mol·dm^{-3}

→ Problem 12.1 (Modified from Atkins *et al.*, 2018, w/ permission)

Dansyl chloride, which absorbs maximally at 330 nm and fluoresces maximally at 510 nm, can be used to label amino acids in fluorescence microscopy and FRET studies. Tabulated below is the variation of the fluorescence intensity of an aqueous solution of dansyl chloride with time after excitation by a short laser pulse (with I_0 the initial fluorescence intensity). The ratio of intensities is equal to the ratio of the rates of photon emission. Calculate the observed fluorescence lifetime of dansyl chloride in water.

t (ns)	5.0	10.0	15.0	20.0
I_f/I_0	0.45	0.21	0.11	0.05

A) $\tau_0 = 3.14$ ns
B) $\tau_0 = 6.67$ ns
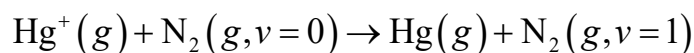**C)** $\tau_0 = 9.25$ ns
D) $\tau_0 = 12.1$ ns

→ Problem 12.2

The fluorescence quantum yield of dansyl chloride in water is 0.70. What is the fluorescence rate constant?

A) $k_f = 0.105$ ns^{-1}
B) $k_f = 0.348$ ns^{-1}
C) $k_f = 0.671$ ns^{-1}
D) $k_f = 0.981$ ns^{-1}

▶ Problem 13 (Modified from Atkins *et al.*, 2018, w/ permission)

An electronically excited state of Hg can be quenched by N_2 according to

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

in which energy transfer from Hg^* excites N_2 vibrationally. The data below give the measured time dependence of the intensity of fluorescence for samples of Hg with and without N_2 present; the temperature is $T = 300$ K in both cases. Evaluate the rate constant for the energy transfer process. You may assume that all gases are perfect.

→ *Data for* $P_{N_2} = 0$

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

→ *Data for* $P_{N_2} = 0.8$ 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

A) $k_Q = 1.05 \times 10^6$ dm³·mol⁻¹·s⁻¹
B) $k_Q = 2.40 \times 10^6$ dm³·mol⁻¹·s⁻¹
C) $k_Q = 4.12 \times 10^6$ dm³·mol⁻¹·s⁻¹
D) $k_Q = 6.71 \times 10^6$ dm³·mol⁻¹·s⁻¹

▶▶ SOLUTIONS

P.1 ▶ Solution

With $A = 0.474$, $b = 1.0$ cm and $c = 5.0 \times 10^{-4}$ M, the Beer-Lambert law gives the molar absorptivity ε,

$$A = \varepsilon bc \rightarrow \varepsilon = \frac{A}{bc}$$

$$\therefore \varepsilon = \frac{0.474}{1.0 \times (3.0 \times 10^{-3})} = 158 \, \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$$

For the second solution, the Beer-Lambert law yields

$$-\log T = \varepsilon bc = 158 \times 0.6 \times (3.0 \times 10^{-3}) = 0.284$$

so that $T = 10^{-0.284} = 0.520$.

◆ The correct answer is **B**.

P.2 ▶ Solution

Part 1: Absorbance is the antilog of transmittance,

$$A = -\log_{10} T$$

with $T = 24.4\% = 0.244$, we obtain

$$A = -\log_{10} 0.244 = \boxed{0.613}$$

◆ The correct answer is **C**.

Part 2: Note that, from the ideal gas law, $PV = nRT$, or

$$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT}$$

Noting that $R = 0.0821$ atm·L/mol·K and $P = 30.3$ μbar $= 2.99 \times 10^{-5}$ atm, the concentration is calculated to be

$$C = \frac{P}{RT} = \frac{2.99 \times 10^{-5}}{0.0821 \times 298} = \boxed{1.22 \times 10^{-6} \, \text{mol/L}}$$

◆ The correct answer is **A**.

5

Part 3: Substituting into the Beer-Lambert law the absorbance found in part A, the concentration found in part B, and b = 3.0 cm, molar absorptivity ε is calculated to be

$$A = \varepsilon bc \rightarrow 0.613 = \varepsilon \times 3.0 \times \left(1.22 \times 10^{-6}\right)$$

$$\therefore \varepsilon = \frac{0.613}{3.0 \times \left(1.22 \times 10^{-6}\right)} = \boxed{167,000 \ \text{M}^{-1}\text{cm}^{-1}}$$

♦ The correct answer is **D**.

P.3 ➡ Solution

If x mol/L of X reacts, then at equilibrium the concentrations are $[X]$ = $10^{-3} - x$ and $[Y]$ = $2x$. Then, applying the Beer-Lambert law to the system, we obtain

$$0.222 = 500 \times 1.0 \times \left(10^{-3} - x\right) + 12 \times 1.0 \times 2x$$

$$\therefore x = 5.84 \times 10^{-4} \ \text{M}$$

It follows that $[X]$ = $10^{-3} - x$ = 4.16×10^{-4} M and $[Y]$ = $2x$ = 1.17×10^{-3} M. It remains to determine equilibrium constant K,

$$K = \frac{[Y]^2}{[X]} = \frac{\left(1.17 \times 10^{-3}\right)^2}{4.16 \times 10^{-4}} = \boxed{3.29 \times 10^{-3}}$$

♦ The correct answer is **C**.

P.4 ➡ Solution

In the strongly acidic solution, most of the indicator should be in the form of HIn. It follows that the Beer-Lambert law can be written for methyl orange as

$$A = \varepsilon bc \rightarrow 0.467 = \varepsilon_{\text{HIn}} \times 1.0 \times C$$

In the strongly basic solution, most of the indicator should be dissociated as In⁻. Accordingly,

$$A = \varepsilon bc \rightarrow 0.132 = \varepsilon_{\text{In}^-} \times 1.0 \times C$$

At a pH of 4.6, $[H^+]$ = $10^{-4.6}$ = 2.51×10^{-5} M, and

$$0.180 = \varepsilon_{\text{HIn}} \times 1.0 \times \left(1 - f\right)C + \varepsilon_{\text{In}^-} \times 1.0 \times fC$$

where f is the fraction of methyl orange in dissociated form. Substituting from the two previous results and solving for f, we obtain

$$0.180 = \underbrace{\varepsilon_{\text{HIn}}C}_{=0.467}\left(1 - f\right) + \underbrace{\varepsilon_{\text{In}^-}C}_{=0.132}f \rightarrow 0.180 = 0.467\left(1 - f\right) + 0.132f$$

$$\therefore 0.180 = 0.467 - 0.467f + 0.132f$$

$$\therefore -0.287 = -0.335f$$

$$\therefore f = 0.857$$

It remains to estimate K_a,

$$K_a = \frac{[H^+][In^-]}{[HIn]} = \frac{\left(2.51 \times 10^{-5}\right) \times 0.857C}{\left(1 - 0.857\right)C} = \boxed{1.50 \times 10^{-4}}$$

♦ The correct answer is **A**.

P.5 ➡ Solution

From the Beer-Lambert law, we have, at 400 nm, ε_{Ti} = 0.588/35.0 = 0.0168 and ε_V = 0.402/105.0 = 0.00383; at 480 nm, ε_{Ti} = 0.396/35.0 = 0.0113 and ε_V = 0.586/105 = 0.00558; all values are in mL· μg⁻¹·cm⁻¹. Let α and β denote the content of titanium and vanadium in the solution, respectively, in μg/mL. Appealing to the Beer-Lambert law, we have

$$A_{400} = 0.822 = 0.0168 \times 1.0\alpha + 0.00383 \times 1.0\beta$$

6

$$A_{480} = 0.705 = 0.0113 \times 1.0\alpha + 0.00558 \times 1.0\beta$$

This system of linear equations can be easily solved with the Mathematica code

```
In[1759]:= Solve[{0.822 == 0.0168 * a + 0.00383 * b, 0.705 == 0.0113 * a + 0.00558 * b}, {a, b}]

Out[1759]= {{a → 37.3845, b → 50.6371}}
```

That is, α = 37.4 µg/mL and β = 50.6 µg/mL.

♦ The correct answer is **C**.

P.6 ➡ Solution

Part 1: The absorbances can be estimated from the transmittances, and the transmittances can be readily estimated from the equation we were given. To use this equation, we need estimates of absorption cross section σ, which can be read from the graph and equal $\sigma_{300} \approx 6\times10^{-19}$ cm² (blue lines below) and $\sigma_{325} \approx 1.2\times10^{-20}$ cm² (red lines). Substituting these values, along with b = 1 cm and n = 8×10¹⁸ molec./cm³, yields

$$T_{300} = e^{-\left(8\times10^{18}\right)\times\left(6\times10^{-19}\right)\times1.0} = 0.00823$$

$$T_{325} = e^{-\left(8\times10^{18}\right)\times\left(1.2\times10^{-20}\right)\times1.0} = 0.908$$
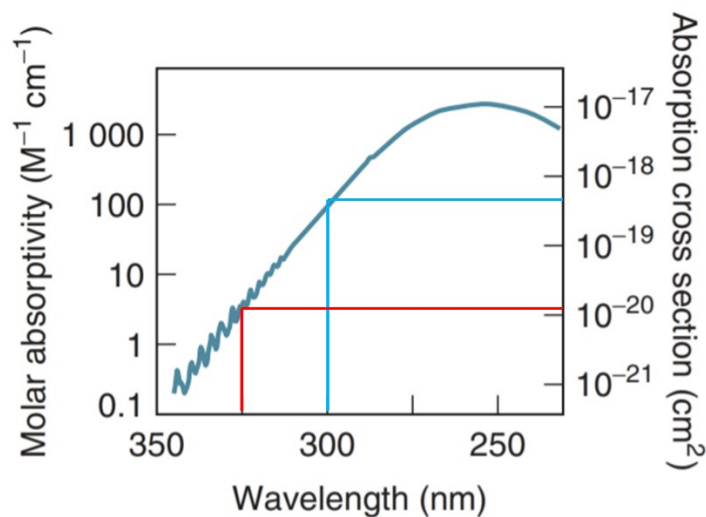
Lastly, absorbance is the antilogarithm of transmittance,

$$A_{300} = -\log_{10} T_{300} = -\log_{10} 0.00823 = \boxed{2.08}$$

$$A_{325} = -\log_{10} 0.908 = \boxed{0.0419}$$

♦ The correct answer is **C**.

Part 2: We first use the equation given to estimate the absorption cross section σ,

$$T = e^{-n\sigma b} \rightarrow \sigma = -\frac{\ln T}{nb}$$

$$\therefore \sigma = -\frac{\ln 0.14}{\left(8\times10^{18}\right)\times1.0} = \boxed{2.46\times10^{-19} \text{ cm}^2}$$

The transmittance at n = 7.6×10¹⁸ molec./cm³ is then

$$T' = e^{-\left(7.6\times10^{18}\right)\times\left(2.46\times10^{-19}\right)\times1.0} = 0.154$$

which represents a 10% increase in transmittance relatively to the initial concentration.

♦ The correct answer is **C**.

Part 3: At the latitude range in question, O_3 level in winter equals 290 Dobson units. Noting that 1 D = 2.69×10¹⁶ molec. O_3/cm³ and σ = 2.5×10⁻¹⁹ cm², we write

$$T_{winter} = e^{-n\sigma b} = \exp\left\{-\left[290\times\left(2.69\times10^{16}\right)\right]\times\left(2.5\times10^{-19}\right)\times1.0\right\} = 0.142$$

7

In summer, the O_3 level is 350 Dobson units and corresponds to a transmittance such that

$$T_{summer} = e^{-n\sigma b} = \exp\left\{-\left[350\times\left(2.69\times10^{16}\right)\right]\times\left(2.5\times10^{-19}\right)\times1.0\right\} = 0.0950$$
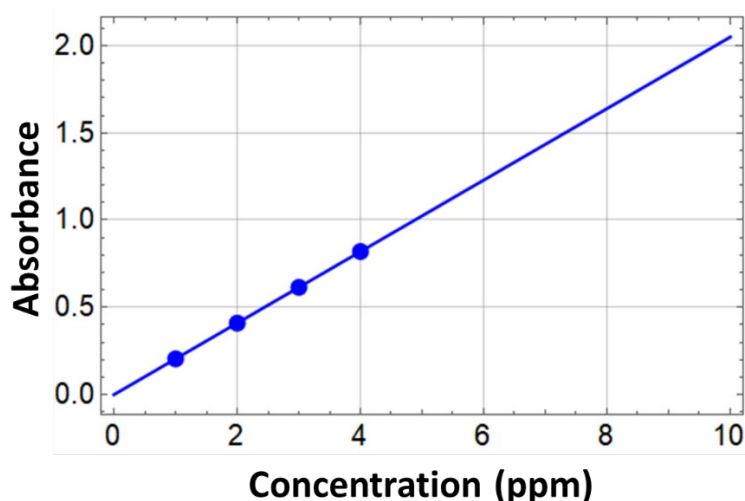
The difference in values amounts to

$$\Delta = \frac{0.142-0.095}{0.095} = \boxed{49.5\%}$$

◆ The correct answer is **B**.

P.7 ➡ Solution

Part 1: Absorbance is plotted as a function of phosphorus concentration, and a linear fit to the data is provided.

The linear fit found has the form $y = 0.205x + 0$. The urine sample has a phosphorus concentration of 0.625 ppm, which corresponds to an absorbance $x = 0.625/0.205 = 3.05$ ppm. The dilution factor is 50, hence the concentration of phosphorus in the urine is $50 \times 3.05 = 153$ ppm, or 0.153 g P/L. If the patient releases 1270 mL of urine in one day, the mass of phosphorus released is calculated to be $0.153 \times 1.27 = 0.194$ g.

◆ The correct answer is **A**.

Part 2: If 1270 mL of urine contains 0.194 g of phosphorus, then 1 L of urine contains 0.153 g of this element. Further, 31 g of phosphorus is present in 95 g of phosphate, or

$$\frac{31\,g\,P}{95\,g\,PO_4^{3-}} = \frac{0.153\,g\,P}{M} \rightarrow M = 0.469\,g\,PO_4^{3-}$$

$$\therefore \left[PO_4^{3-}\right] = \frac{\dfrac{0.469\,g\,PO_4^{3-}}{1\,L\,urine}}{\dfrac{95\,g\,PO_4^{3-}}{1\,mol\,PO_4^{3-}}} = \boxed{\frac{4.94\,mmol\,PO_4^{3-}}{1\,L\,urine}}$$

◆ The correct answer is **D**.

Part 3: Consider the second dissociation of phosphoric acid,

$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)$$

Here,

$$K_2 = \frac{\left[HPO_4^{2-}\right]\left[H^+\right]}{\left[H_2PO_4^-\right]} = 7.5\times10^{-8}$$

Here, $[H^+] = 10^{-6.5} = 3.16\times10^{-7}$ M (the pH of the urine is 6.5), so that

$$K_2 = \frac{\left[HPO_4^{2-}\right]\times\left(3.16\times10^{-7}\right)}{\left[H_2PO_4^-\right]} = 7.5\times10^{-8} \rightarrow \frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = \frac{7.5\times10^{-8}}{3.16\times10^{-7}}$$

8

$$\therefore \frac{\left[\text{HPO}_4^{2-} \right]}{\left[\text{H}_2\text{PO}_4^- \right]} = 0.237$$

♦ The correct answer is **B**.

P.8 ➡ *Solution*

Fluorescence *F* is related to concentration *c* by an expression of the form

$$F = \phi I_0 \left(1 - e^{-\varepsilon bc} \right)$$

where ϕ is quantum efficiency, I_0 is the incident radiant power, ε is the molar absorptivity, b is the path length of the cell, and c is the molar concentration. At low concentrations, the exponential on the right-hand side can be expanded to give

$$e^{-\varepsilon bc} \approx 1 - \varepsilon bc + \frac{1}{2} b^2 \varepsilon^2 c^2 - \left(... \right)$$

so that, retaining the first two terms only, we have

$$F \approx \phi I_0 \left[1 - \left(1 - \varepsilon bc \right) \right] \rightarrow \boxed{F = \phi I_0 \varepsilon bc}$$

Thus, in very dilute solutions ($\varepsilon bc \leq 0.05$ or so), a plot of fluorescence versus concentration should be linear. The equation also indicates which other quantities affect the fluorescence-concentration relationship; importantly, we can verify the influence of three main parameters:

1. *Quantum efficiency*, ϕ: The quantum efficiency ϕ denotes the ratio of the total energy emitted by a molecule per quantum of energy absorbed. Needless to say, the greater the value of ϕ, the greater the fluorescence. A nonfluorescent molecule is a molecule whose quantum efficiency is zero, or so close to zero that it is not measurable (i.e., all energy absorbed by the molecule is rapidly lost through collisional deactivation).

2. *Intensity of incident radiation*, I_0: Theoretically, a more intense source will yield greater fluorescence. In practice, however, an exceedingly intense source may lead to photodecomposition of the sample. A compromise between light intensity and sample photostability must be pursued.

3. *Molar absorptivity of the compound*, ε: In order to emit radiation, a molecule must first absorb radiation. Hence, the higher the molar absorptivity, the better will be the fluorescence stability of the compound. It is for this reason that saturated nonaromatic compounds, for example, are nonfluorescent.

P.9 ➡ *Solution*

The energy contained in one 320-nm photon is $E = hc/\lambda = 6.22 \times 10^{-19}$ J. If the substance was irradiated at 87.5 W continuously for 28 min, an amount of energy equal to $28 \times 87.5 \times 60 = 147{,}000$ J was involved in the process. The number n of photons involved in the procedure is then

$$n = \frac{147{,}000 \, \text{J}}{6.22 \times 10^{-19} \, \text{J/photon}} = 2.36 \times 10^{23} \, \text{photons}$$

Converting to einsteins,

$$Q = \frac{2.36 \times 10^{23} \, \text{photons}}{\dfrac{6.02 \times 10^{23} \, \text{photons}}{\text{mol}}} = 0.392 \, \text{mol}$$

If the intensity of the transmitted light is 0.257 times the intensity of the incident light, the number of photons absorbed should equal $(1 - 0.257) \times 0.392 = 0.291$ mol. It remains to compute the quantum yield,

9

$$\phi = \frac{\text{No. of moles decomposed}}{\text{No. of einsteins absorbed}} = \frac{0.324\,\text{mol}}{0.291\,\text{mol}} = \boxed{1.11}$$

♦ The correct answer is **B**.

P.10 ➡ Solution

The Stern-Volmer equation is given by

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_Q[Q]$$

Because the axes of plots should be labelled with pure numbers, it is necessary to introduce and handle units before using this equation for the analysis of the data. To bring the expression into a form suitable for plotting, it needs to be expressed in terms of $\tau/(10^{-9}\,\text{s})$ and $[Q]/(10^{-2}\,\text{mol}\cdot\text{dm}^{-3})$ to match the data, and therefore (with these dimensionless terms in blue) to write it as

$$\frac{1}{\left(10^{-9}\,\text{s}\right)\tau / \left(10^{-9}\,\text{s}\right)} = \frac{1}{\tau_0} + k_Q\left\{[Q]/\left(10^{-2}\,\text{mol}\cdot\text{dm}^{-3}\right)\right\}\times\left(10^{-2}\,\text{mol}\cdot\text{dm}^{-3}\right)$$

Now multiply through by 10^{-9} s to obtain

$$\frac{1}{\tau / \left(10^{-9}\,\text{s}\right)} = \frac{10^{-9}\,\text{s}}{\tau_0} + k_Q\left\{[Q]/\left(10^{-2}\,\text{mol}\cdot\text{dm}^{-3}\right)\right\}\times\left(10^{-2}\,\text{mol}\cdot\text{dm}^{-3}\right)\times 10^{-9}\,\text{s}$$

and collect terms,

$$\frac{1}{\tau / \left(10^{-9}\,\text{s}\right)} = \frac{1}{\tau_0 / \left(10^{-9}\,\text{s}\right)} + k_Q\left(10^{-11}\,\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}\right)\left\{[Q]/\left(10^{-2}\,\text{mol}\cdot\text{dm}^{-3}\right)\right\}$$

Note that because $slope = k_Q \times 10^{-11}$ mol·dm^{-3}·s, then $k_Q = slope \times 10^{11}$ dm^3·mol^{-1}·s^{-1}. Draw up the following table.

$[O_2]$ (10^{-2} mol dm^{-3})	0	2.3	5.5	8	10.8
$1/\tau$ (ns)	0.385	0.667	1.09	1.41	1.75

The data are plotted below.
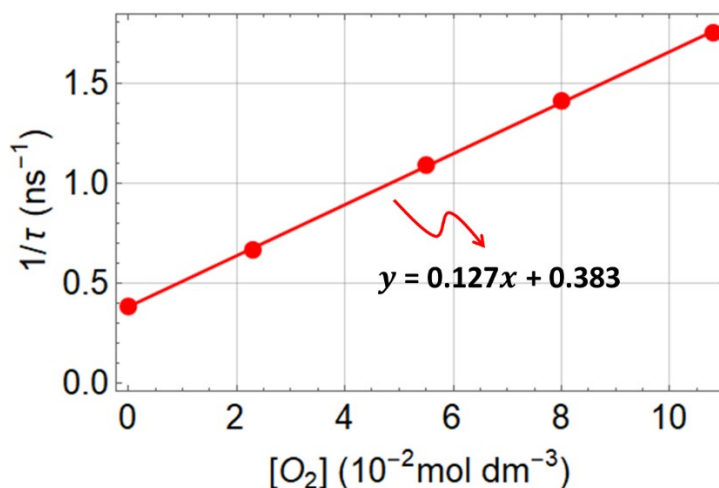
As can be seen, the linear fit to the data has the form $y = 0.127x + 0.383$. Given the slope = 0.127, constant k_Q is calculated to be

$$k_Q = slope \times 10^{11}\,\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1} = \boxed{1.27\times 10^{10}\,\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}}$$

♦ The correct answer is **D**.

P.11 ➡ Solution

Appealing to the Stern-Volmer equation, we write

$$\frac{\phi_{f,0}}{\phi_f} = 1 + \tau_0 k_Q[Q]$$

Here, $\phi_{f,0}$ is the fluorescence quantum yield without quencher Q, ϕ_f is the quantum yield in the presence of Q, τ_0 is the observed fluorescence lifetime, k_Q is the quenching constant, and $[Q]$ is the concentration of

10

quencher. Substituting $\phi_f = 0.5\phi_{f,0}$ and other data, we can solve for $[Q]$ and obtain

$$\frac{\phi_{f,0}}{\phi_f} = 1 + \tau_0 k_Q [Q] \rightarrow \frac{\phi_{f,0}}{0.5\phi_{f,0}} = 1 + \left(6.0 \times 10^{-9}\right) \times \left(3.0 \times 10^8\right)[Q]$$

$$\therefore 2 = 1 + 1.8[Q]$$

$$\therefore [Q] = \frac{2-1}{1.8} = \boxed{0.556 \, \text{mol} \cdot \text{dm}^{-3}}$$

◆ The correct answer is **C**.

P.12 ➡ *Solution*

Part 1: The observed fluorescence intensity I_f is related to time t by an expression of the form

$$I_f = I_0 \exp\left(-\frac{t}{\tau_0}\right)$$

where I_0 is the initial fluorescence intensity and τ_0 is the observed fluorescence lifetime. The equation can be adjusted to yield

$$I_f = I_0 \exp\left(-\frac{t}{\tau_0}\right) \rightarrow \frac{I_f}{I_0} = \exp\left(-\frac{t}{\tau_0}\right)$$
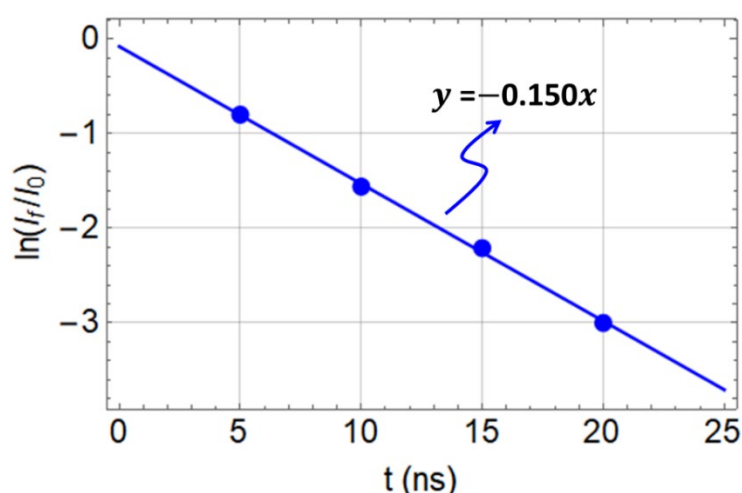
$$\therefore \ln\left(\frac{I_f}{I_0}\right) = \ln\left[\exp\left(-\frac{t}{\tau_0}\right)\right]$$

$$\therefore \ln\left(\frac{I_f}{I_0}\right) = -\frac{1}{\tau_0}t$$

Thus, a plot of $ln(I_f/I_0)$ versus time should yield a straight line with slope $-1/\tau_0$. The data are processed below.

t (ns)	I_f/I_0	$\ln(I_f/I_0)$
5	0.45	-0.80
10	0.21	-1.56
15	0.11	-2.21
20	0.05	-3.00

We proceed to plot $ln(I_f/I_0)$ (red column) versus time (blue column) and fit the data to a linear model with y-intercept equal to zero ($y = ax + 0$).

The line of best fit has slope -0.150, and the observed fluorescence lifetime is calculated to be

$$-0.150 = -\frac{1}{\tau_0} \rightarrow \boxed{\tau_0 = 6.67 \text{ ns}}$$

◆ The correct answer is **B**.

11

Part 2: Quantum yield, fluorescence lifetime and fluorescence rate constant are related by the simple expression

$$k_f = \frac{\phi_f}{\tau_0} = \frac{0.70}{6.67} = \boxed{0.105\,\text{ns}^{-1}}$$

◆ The correct answer is **A**.

P.13 ➡ *Solution*

We need to determine the fluorescence lifetime for the system with and without quencher (N_2); in both cases, the process is identical to the one adopted in Problem 12. The data for $P_{N_2} = 0$ are processed below.

t (microsec)	I_f/I_0	$\ln(I_f/I_0)$
0	1	0.00
5	0.606	-0.50
10	0.36	-1.02
15	0.22	-1.51
20	0.135	-2.00

Then, the data in the red column are plotted against the data in the blue column, as shown.
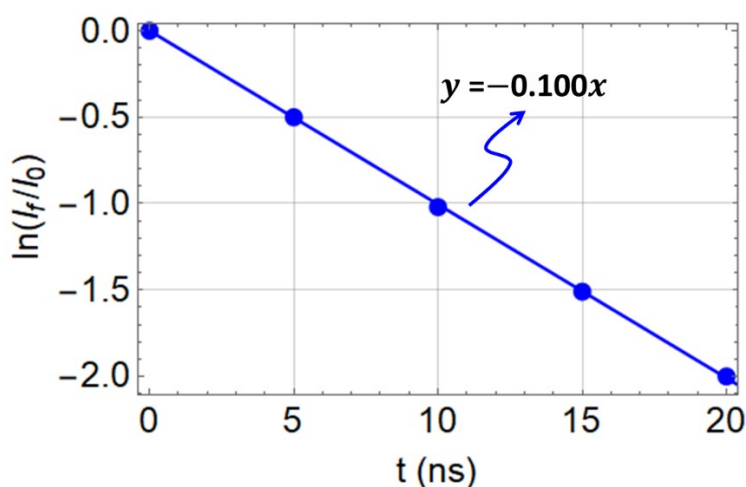
Using the slope of the linear fit, we can determine the fluorescence lifetime τ_0 with no quencher present,

$$-\frac{1}{\tau_0} = -0.100 \rightarrow \tau_0 = 10 \; \mu s$$

The data for the system *with* quencher (N_2) present is processed next.

t (microsec)	I_f/I_0	$\ln(I_f/I_0)$
0	1	0.00
3	0.585	-0.54
6	0.342	-1.07
9	0.2	-1.61
12	0.117	-2.15

Fitting the data pairs to a line should yield an expression of the form $y = -0.179x$. We proceed to compute the fluorescence lifetime τ in the presence of a quencher,

$$-\frac{1}{\tau} = -0.179 \rightarrow \tau = 5.59 \; \mu s$$

Now, the rate constant k is related to the quantities determined up to this point by the equation

$$\frac{1}{\tau} - \frac{1}{\tau_0} = k_Q[Q]$$

Noting that N_2 is the quencher and solving for k, we have

12

$$\frac{1}{\tau} - \frac{1}{\tau_0} = k_Q[Q] \rightarrow k_Q = \frac{\tau^{-1} - \tau_0^{-1}}{[N_2]} \text{ (I)}$$

We don't have the concentration of N_2, but we can express it in terms of available quantities with the ideal gas law,

$$PV = nRT \rightarrow P = \frac{n}{V}RT$$

$$\therefore P = [N_2]RT$$

$$\therefore [N_2] = \frac{P}{RT}$$

so that, substituting in (I),

$$k_Q = \frac{\tau^{-1} - \tau_0^{-1}}{[N_2]} \rightarrow k_Q = \frac{RT(\tau^{-1} - \tau_0^{-1})}{P_{N_2}}$$

$$\therefore k_Q = \frac{0.0821 \times 300 \times \left[(0.179 - 0.100) \times 10^6\right]}{0.8} = \boxed{2.40 \times 10^6 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}$$

♦ The correct answer is **B**.

ANSWER SUMMARY

Problem 1		B
Problem 2	2.1	C
	2.2	A
	2.3	D
Problem 3		C
Problem 4		A
Problem 5		C
Problem 6	6.1	C
	6.2	C
	6.3	B
Problem 7	7.1	A
	7.2	D
	7.3	B
Problem 8		Open-ended
Problem 9		B
Problem 10		D
Problem 11		C
Problem 12	12.1	B
	12.2	A
Problem 13		B

REFERENCES

- ATKINS, P., DE PAULA, J. and KEELER, J. (2018). *Atkins' Physical Chemistry*. 11th edition. Oxford: Oxford University Press.
- GORDUS, A. (1985). *Schaum's Outlines: Analytical Chemistry*. New York: McGraw-Hill.
- GUILBAULT, P. (1990). *Practical Fluorescence*. 2nd edition. London: Taylor and Francis.
- HARRIS, D. (2016). *Quantitative Chemical Analysis*. 9th edition. New York: W.H. Freeman and Company.

? Got any questions related to this quiz? We can help!
Send a message to contact@montogue.com and we'll
answer your question as soon as possible.