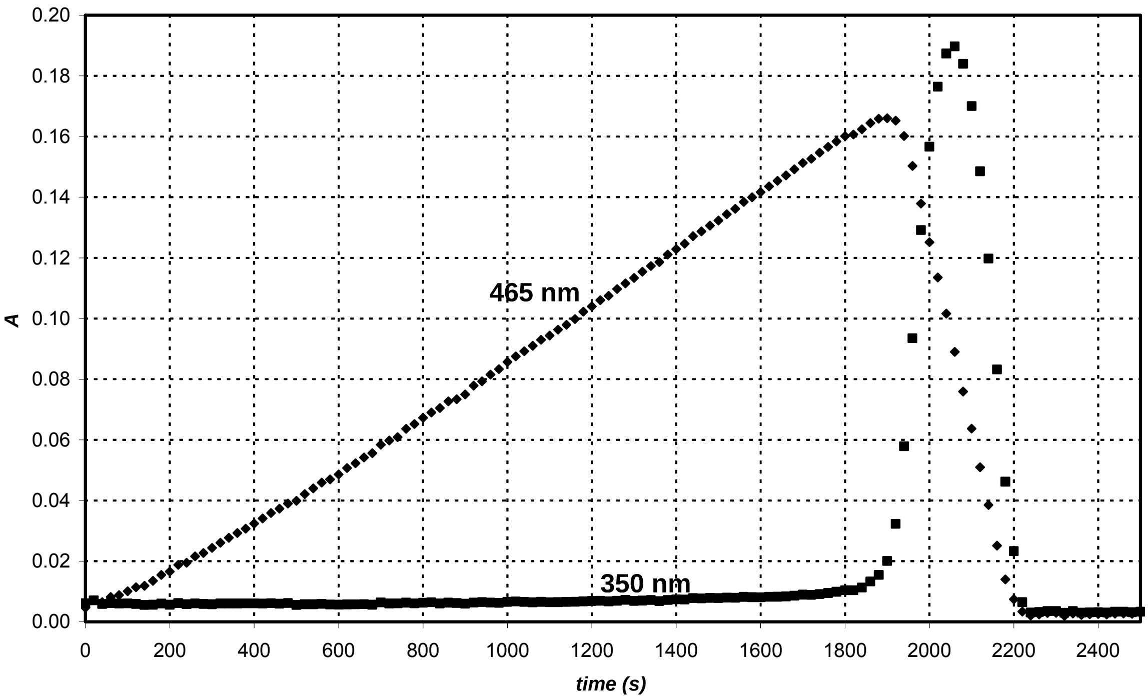
Problem 7



i) Estimate the equilibrium constant for the formation of I_3^- ion from the two curves.

At about 2050 s: A_{465nm} = 0.090, A_{350nm} = 0.190.

$A_{465nm} = 0.090 \Rightarrow [I_2] = 0.090 / 740\ M^{-1}cm^{-1} / 0.874\ cm = 1.4\cdot10^{-4}\ M$

$A_{350nm} = 0.190 \Rightarrow [I_3^-] = 0.190 / 10500\ M^{-1}cm^{-1} / 0.874\ cm = 2.07\cdot10^{-5}\ M$

$[I^-] = [H_4IO_6^-]_0 - 2[I_2] - 3[I_3^-] = 5.3\cdot10^{-4}\ M - 2\cdot1.4\cdot10^{-4}\ M - 3\cdot2.07\cdot10^{-5}\ M$

$= 1.9\cdot10^{-4}\ M$

$K = [I_3^-]/([I^-]\cdot[I_2]) = 7.8\cdot10^{2}\ M^{-1}$

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Problem 0 (reserve)

0a	0b	0c	0d	0e	Task 0
4	3	8	8	2	25

The difference in the chemical behaviour of various isotopes is usually negligible, unless the relative change in the molecular mass is considerable.

a) What would be the highest percentage change in the molecular mass of a neutral molecule upon substitution of a single atom with its isotope?

100%, $H_2 \rightarrow HT$

The following reaction continuously takes place in liquid bromine:

$$^{79}Br_2 + {}^{81}Br_2 \rightleftharpoons 2\ {}^{79}Br\text{-}{}^{81}Br$$

b) What are the mole fractions of these species in bromine at natural abundance (50 % ^{79}Br, 50 % ^{81}Br)?

Let us suppose that 1 mol bromine contains p and $(1–p)$ mole of the two isotopes.
The mole fraction of the various molecules is: p^2, $(1 – p)^2$, $2\,p(1 – p)$.
At natural abundance the mole fractions are 0.25, 0.25 and 0.5.

$x(^{79}Br_2)$ $x(^{81}Br_2)$ $x(^{79}Br\text{-}^{81}Br)$

c) Give the equilibrium constant of the process in mole fractions.

$$K = \frac{[^{79}Br\,^{81}Br]^2}{[^{79}Br_2][^{81}Br_2]} = 4$$

K:

d) What is the standard molar entropy change associated with this reaction, supposing that the chemical behaviour of the molecules involved is identical?

The chemical identity of the molecules means that $\Delta_r H^o$ for this reaction is zero.
$\Delta_r G^o = – RT \ln K = \Delta_r H^o – T\,\Delta_r S^o$
$\Delta_r S^o = R \ln 4 = 11.52\ J\ K^{–1}\ mol^{–1}$

$\Delta_r S^o$:

In 1913 Hevesy and Paneth carried out the following experiment that began the use of isotopes as tracers and eventually lead to a Nobel Prize for Hevesy for his isotope tracer studies.
They collected in a closed tube a strongly radioactive, completely unreactive gas emitted from radium (at that time known as Curie emanation). It has a relative atomic mass of 222.

e) What is this gas known as today? Give its formula.

^{222}Rn

This gas was known to go through a succession of radioactive decay processes, forming products called radium A, B, C, D, E , F, G one after the other. The following was already known about this decay chain:

If the gas was left to equilibrate for a few days over water, a solution containing mainly radium D was obtained. After a few weeks, the intensity of the α radiation from Radium F was seen to increase, and slowly reached a steady value, but the quantity of Radium D did not decrease significantly during this time.

f) Which could be the slowest step in the successive transformations?

Radium ☐ A→B ☐ B→C ☐ C→D ☐ D→E ☐ E→F ☐ F→G

Hevesy had earlier worked with Radium D and he was unable to separate it from the inactive lead it was mixed with. The inactive Radium G (atomic mass 206) had shown exactly the same chemical behaviour.

The formation of Radium A, B and G from its precursor was found to be an α-decay, while the formation of Radium C, E and F was a β-decay.

g) How could Radium D form from Radium C? Use α and β in your answer.

The starting material is ^{222}Rn, the product is ^{206}Pb. There are 3 alpha and 3 beta decays in the sequence. The only missing step must cause a decrease of 4 in the nuclear mass and a decrease of 1 in the nuclear charge.
α + β

In his experiment, Hevesy mixed some aqueous lead-chloride solution (containing 9.69 mg $PbCl_2$) to the radium D solution he obtained. They measured the β-activity of 1.00 cm^3 of the 120.0 cm^3 mixture to be 16.90 in arbitrary units.

At the same time, with the same equipment they measured the activity of a sample prepared in the following way: Potassium chromate was added to of the lead solution to quantitatively precipitate lead chromate. The precipitate was filtered and was left to stand with approximately 100 cm^3 distilled water for a day at 25 C. The water from this experiment was carefully filtered off. The first part of the filtrate was discarded and 70.0 cm^3 was separated and concentrated by evaporation. Its activity was found to be 0.15 relative units.

h) Give an estimate of the solubility product of lead chromate based on these results.

The activity of all the Radium D in the 120 ml was 2030 units. This activity was mixed with 9.69 mg lead-chloride – that is equivalent to 11.35 mg lead chromate.
The activity in the 70 ml solution is thus equivalent to $0.15/2030 \cdot 11.35 = 8.39 \cdot 10^{-4}$ mg lead chromate.
$K_{sp} = 1.4 \cdot 10^{-15}$

K_{sp}