AUSTRALIAN
SCIENCE
OLYMPIADS

CHEMISTRY

2000 NATIONAL QUALIFYING EXAMINATION

Time Allowed
Reading Time: 15 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.

  Section A: Answer **ALL** questions — spend no more than 30 minutes on this section.

  Section B: Apportion your time equally on the questions in this section.
  Question 16 is **compulsory**
  Answer **any two** of Questions 17, 18 or 19

- All answers must be written in the space provided in the answer book.
- Use **blue** or **black** pen to write your answers, pencil is **not** acceptable.
- Rough working must be done only in the indicated areas of the answer book.
- You are not permitted to refer to books, periodic tables or written notes.
- The only permitted aid is a non-programmable electronic calculator.
- Relevant data that may be required for a question will be found on page 2.

DATA

Avogadro constant (N)
6.02 x 10^{23} mol^{-1}

1 faraday 96,486 coulombs

1 coulomb 1 A s

Universal gas constant (R)
8.314 J K^{-1} mol^{-1}
8.206 x 10^{-2} L atm K^{-1} mol^{-1}

Planck's constant (h)
6.626 x 10^{-34} J s

Standard temperature and pressure (STP)
273 K and 101.3 kPa
0˚C and 101.3 kPa
0˚C and 1 atm
0˚C and 760 mm Hg

Molar volume of ideal gas at STP
22.4 L

Velocity of light (c)
2.998x 10^{8} m s^{-1}

Density of water
1000 kg m^{-3}

Acceleration due to gravity
9.8 m s^{-2}

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES[*]

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	9	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.07	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98)[†]	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

[*] The relative values given here are to four significant figures.

[†] A value given in parentheses denotes the mass of the longest-lived isotope.

SECTION A

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake **correct it clearly** so that the examiners can read your answer.

Q1 The most active metals on the periodic table have

A large radii and high electronegativities.

B large radii and low ionisation energies.

C small radii and low electronegativities.

D small radii and low ionisation energies.

E small radii and high electronegativity.

Q2 What is the oxidising agent in the unbalanced equation?

$$HAsO_2(aq) + Sn^{2+}(aq) + H^+(aq) \longrightarrow As(s) + Sn^{4+}(aq) + H_2O(l)$$

A $HAsO_2(aq)$

B $Sn^{2+}(aq)$

C $H^+(aq)$

D $Sn^{4+}(aq)$

E $H_2O(l)$

Q3 When ionic hydrides react with water, the products are

A acidic solutions and hydrogen gas.

B acidic solutions and oxygen gas.

C basic solutions and hydrogen gas.

D basic solutions and oxygen gas.

E both hydrogen and oxygen gases.

Q4 A sample contains 3.01×10^{20} molecules of SF_n and its mass is 54 mg. What is the value of n?

A 1

B 2

C 4

D 6

E 8

Q5 A colourless aqueous solution contains a single ionic compound. Use the following experimental information to deduce the identity of the compound.

- When a small amount of dilute NaOH solution is added to the solution, a precipitate forms. This precipitate dissolves when excess NaOH is added.
- Addition of $AgC_2H_3O_2$ (silver acetate) to the solution gives a white precipitate.

A $PbSO_4$

B $Ba(NO_3)_2$

C $CuSO_4$

D $AlCl_3$

E FeI_2

Q6 HCN is a weak acid ($K_a = 6.2 \text{ x } 10^{-10}$). NH_3 is a weak base ($K_b = 1.8 \text{ x } 10^{-5}$). A 1.0 M solution of NH_4CN would be

A strongly acidic

B weakly acidic

C neutral

D weakly basic

E strongly basic

Q7 A 20.00 mL sample of a $Ba(OH)_2$ solution is titrated with 0.245 M HCl. If 27.15 mL of HCl is required, what is the molarity of the $Ba(OH)_2$ solution?

A 0.166 M

B 0.180 M

C 0.333 M

D 0.666 M

E 1.136 M

Q8 The molar mass of a gas with a density of 5.8 g L^{-1} at 25 °C and 740 mm Hg is closest to

A 190 g mol^{-1}

B 150 g mol^{-1}

C 20 g mol^{-1}

D 10 g mol^{-1}

E 5 g mol^{-1}

Q9 When the aluminium oxide is electrolysed in the industrial process for the production of aluminium metal, aluminium is produced at one electrode and oxygen gas is produced at the other. For a given quantity of electricity, what is the ratio of moles of aluminium to moles of oxygen gas?

A 1:1

B 2:1

C 2:3

D 3:2

E 4:3

Q10 What is the coefficient for $H^+(aq)$ when the following equation is balanced with whole number coefficients?

$$\_Mn^{2+}(aq) + \_BiO_3^-(aq) + \_H^+(aq) \longrightarrow \_Bi^{3+}(aq) + \_MnO_4^-(aq) + \_H_2O(l)$$

A 21

B 14

C 7

D 4

E 3

Q11 The ion-product constant for water, K_W, at 45 °C is 4.0×10^{-14}. What is the pH of pure water at this temperature?

A 6.7

B 7.0

C 7.3

D 8.5

E 13.4

Q12 When the isoelectronic species, K^+, Ca^{2+}, and Cl^-, are arranged in order of increasing radius, what is the correct order?

A K^+, Ca^{2+}, Cl^-

B Cl^-, K^+, Ca^{2+}

C Cl^-, Ca^{2+}, K^+

D Ca^{2+}, K^+, Cl^-

E K^+, Cl^-, Ca^{2+}

Q13 Consider the following table containing solubility products for four metal sulphates:

	Salt	**K_{sp}**
1	$CaSO_4$	9×10^{-6}
2	$SrSO_4$	3×10^{-7}
3	$PbSO_4$	2×10^{-8}
4	$BaSO_4$	1×10^{-10}

In which cases would a precipitate be expected to form when equal volumes of a 0.0001 M solution of sodium sulfate is mixed with a 0.0001 M solution containing the appropriate cation?

A 1, 2 and 3 only

B 1 and 2 only

C 1 and 3 only

D 2 and 4 only

E 4 only

Q14 Which of the following groups of molecules and ions does **not** contain an example with a planar geometry?

A ClF_3, SO_4^{2-}, PCl_3

B SF_4, CO_3^{2-}, BF_3

C NH_3, H_2O_2, N_2H_4

D O_3, PH_3, CO_2

E H_2O, H_2S, H_2Se

Q15 To which of the following solutions would the addition of an equal volume of 0.5 M NaOH cause a decrease in the pH?

1 H_2O

2 0.25 M Na_2CO_3

3 0.5 M HCl

4 0.6 M KOH

A 1, 2 and 3 only

B 1 and 2 only

C 1 and 3 only

D 2 and 4 only

E 4 only

SECTION B

Candidates are advised that the correct use of significant figures will be taken into consideration when marking answers to these problems. Candidates are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Question 16 is compulsory. You have a choice of answering any two questions of the remaining three questions.

Compulsory question

Candidates should note that for calculations they are required to give answers both as expressions and as computed results. Failure to provide either of these will result in marks being deducted.

Q16 Lead is produced naturally from its most common ore, galena. Galena consists mainly of lead(II) sulfide, but is often contaminated by other metals, including some elemental lead. It is often necessary to determine the purity of a galena sample, and the composition; that is, the ratio of lead present as elemental lead to total lead present.

The production of lead from galena begins by roasting the galena in a limited supply of air to give lead(II) oxide, and liberating sulfur dioxide gas.

(a) Write a balanced equation for the oxidation of PbS to give PbO and SO_2.

(b) Why is it important to limit the supply of air in this reaction?

(c) What do you think happens to the elemental lead present in the sample under these conditions? (Write balanced equations for any reactions you mention)

(d) Give a mathematical expression for the number of moles of lead present as PbS in a galena sample in terms of the volume of SO_2 gas evolved (if the volume is measured once the gases have returned to 298 K and 101.3 kPa).

The lead(II) oxide formed by the above process is then reduced with more galena in a blast furnace to produce liquid lead and again liberates sulfur dioxide gas.

(e) Write a balanced equation for the reduction of PbO by PbS to give Pb and SO_2.

(f) What species is acting as an oxidising agent in this process?

Use your answers to parts (a) - (e) above to answer the following questions:

A 1.045 g sample of lead-rich galena is to be analysed for purity and composition. Two-thirds of the sample is roasted in a limited air supply to give lead oxide. 66.2 mL of sulfur dioxide gas was liberated from the oxidation (when measured at 298 K and 101.3 kPa).

(g) Calculate the number of moles of lead sulfide present in the original sample of galena.

(h) Calculate the purity of the galena (mass of lead sulfide per gram of galena).

(i) What mass of lead oxide was produced by the oxidation?

The lead oxide was then reduced with the remaining third of the galena sample in a blast furnace, and the liquid lead produced was cooled into an ingot weighing just 0.8663 g.

(j) What percent of the lead in the original galena sample was present as elemental lead?

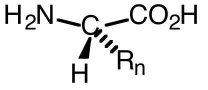
A 100.0 mL solution of lead(II) nitrate was prepared with exactly the same number of moles of lead present as in the galena sample mentioned above. To this solution, 0.200 M sodium hydroxide solution was added. During the addition, $Pb(OH)_2$ was precipitated, and once excess

Question continues on the next page.

NaOH had been added, eventually redissolved. After 83.3 mL of sodium hydroxide solution had been added, all of the precipitate had just redissolved.

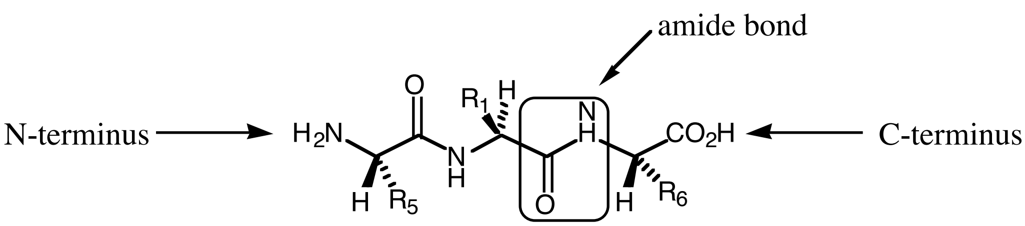
(k) Based on the data given, in what form might you expect the lead to be present in the final solution?

Q17 Proteins and peptides represent classes of molecules which are essential to life. They are built up from amino acids which have the general structure,



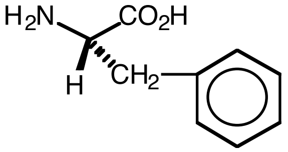
where R_n is simply a side chain. There are 26 common amino acids which differ only in the nature of R_n.

A typical tripeptide (one made up of three amino acids) might be represented

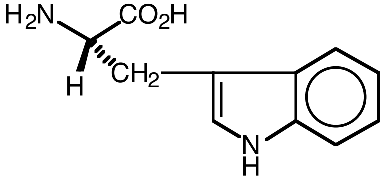


where the amino acids are joined with amide bonds. Like most peptides this molecule has an amine (NH_2) at one end, the so-called N-terminus and a carboxylic acid (CO_2H) at the other, the so-called C-terminus. The order in which the amino acids are joined from the N-terminus to the C-terminus is referred to as the **primary structure** of the molecule.

In order to save space when drawing large molecules amino acids are abbreviated by a three letter code



phenylalanine (**Phe**)



tryptophan (**Trp**)

These three letter codes are always read N→C, so that the tetrapeptide Phe-Gly-Gly-Trp has Phe as its N-terminus amino acid and Trp as its C-terminus amino acid.

Determining the primary structure of proteins and large peptides is similar to doing a “jig-saw” puzzle. Large molecules are broken up into smaller peptides since the primary structure of these can be determined more easily. The “cutting-up” of large peptides is often achieved by using **enzymes** which cleave the molecule at very specific points. Two key enzymes are **chymotrypsin** and **trypsin**.

Chymotrypsin cuts amide bonds of the type: Phe-Xyz ⟶ Phe + Xyz
Tyr-Xyz ⟶ Tyr + Xyz
Trp-Xyz ⟶ Trp + Xyz

Similarly, trypsin cleaves amide bonds of the type: Lys-Xyz and Arg-Xyz

(Xyz being any of the common amino acids)

Given this information try to solve the following problem.

The peptide viscotoxin A_2 is a large peptide containing 46 amino acids. Both the C and N terminal amino acids are lysine (Lys). Viscotoxin A_2 is cleaved both by trypsin and chymotrypsin and some of the primary structures of these reactions are shown below. Note that not all of the identified peptides from the cleavage reactions are shown.

Peptides from trypsin cleavage:

1 Asn-Ile-Tyr-Asn-Thr-Cys-Arg

2 Lys-Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg

3 Ile-Ile-Ser-Ala-Ser-Thr-Cys-Pro-Ser-Tyr-Pro-Asp-Lys

4 Phe-Gly-Gly-Gly-Ser-Arg

5 Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg

Peptides from chymotrypsin cleavage:

6 Asn-Thr-Cys-Arg-Phe

7 Gly-Gly-Gly-Ser-Arg-Glu-Val-Cys-Ala-Ser-Leu

8 Lys-Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg-Asn-Ile-Tyr

9 Ser-Gly-Cys-Lys-Ile-Ile-Ser-Ala-Ser-Thr-Cys-Pro-Ser-Tyr-Pro-Asp-Lys

Using the three letter code answer the following questions:

(a) What is the structure of the largest peptide fragment which contains the C-terminus amino acid?

(b) What is the structure of the shortest peptide fragment which contains the N-terminus amino acid?

(c) Which two peptide fragments from the chymotrypsin reaction contain **neither** the N-terminus **nor** C-terminus?

(d) Underline in your answer book the sequences of amino acids, which contain **neither** the C-terminus **nor** N-terminus, that are common to the fragments produced from trypsin and chymotrypsin cleavage.

(e) If you look at the fragments produced in the chymotrypsin cleavage you will see one fragment which ends with an anomalous amino acid. Which fragment is this and explain why it appears to be anomalous?

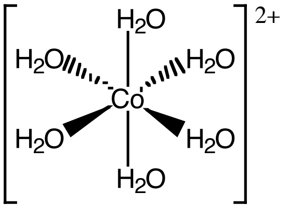
(f) Assuming, as did the original workers, that the peptide viscotoxin A_2 consists of only one strand of amino acids, what is the most likely primary structure of viscotoxin A_2?

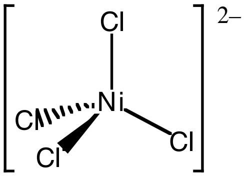
Q18 **Ligands** are neutral molecules or ions that donate one or more pairs of electrons to a transition metal ion to form covalent metal-ligand bonds, known as **co-ordinate covalent bonds**. **Unidentate** ligands have one donor atom (the atom of the ligand that is directly bound to the metal ion) and typically donate one pair of electrons to the metal ion. Some examples are shown below:

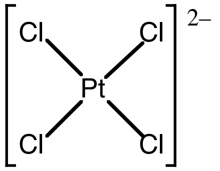
neutral molecules: H_2O, NH_3, CH_3NH_2

ionic: Cl^-, Br^-, F^-, I^-, SCN^-, NO_2^-, CN^-, OH^-

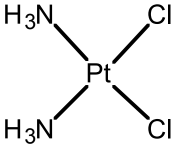
The resulting species are known as complexes or complex ions e.g. $[Co(H_2O)_6]^{2+}$, $[NiCl_4]^{2-}$and $[PtCl_4]^{2-}$. [Note that square brackets are placed around the complex ion]. The number of donor atoms bound to the metal ion is referred to as the **co-ordination number** of the metal ion. The most common co-ordination number is six (octahedral geometry), closely followed by 4 (tetrahedral or square planar geometry). The geometries of the three above mentioned complex ions are shown below:



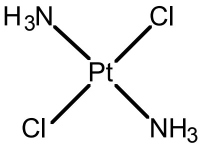




Two arrangements are possible for the related square planar complex $[PtCl_2(NH_3)_2]$ (known as geometrical isomers):



cis



trans

(a) How many geometrical isomers are possible for each of the following species? Sketch them.

(i) square planar $[PtBrCl(NH_3)_2]$ (ii) $[CoCl_2(NH_3)_4]^+$

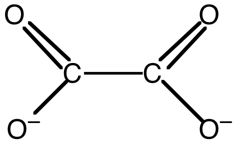
(iii) square planar $[PtBrCl(NH_3)(CH_3NH_2)]$ (iv) $[Co(NCS)_3(NH_3)_3]$.

The unidentate ligand NO_2^- can bind to a metal ion either *via* the N or an O atom. Isomers in which the point of attachment of a ligand is different are known as linkage isomers e.g. $[Co(NO_2)(NH_3)_5]^{2+}$ and $[Co(ONO)(NH_3)_5]^{2+}$ are linkage isomers. [Note that the atom directly attached to the metal is listed first i.e. ONO indicates the ligand is O-bound]. Similarly SCN^- is an example of an ambidentate ligand as it can bind to a metal ion either *via* the S or N atom.

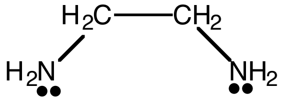
(b) Sketch all of the possible linkage and geometrical isomers for each of the following species.

(i) cis-$[CoCl(NO_2)(NH_3)_4]^+$ (ii) trans-$[Pd(SCN)_2(NH_3)_2]$.

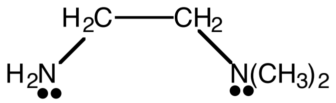
Bidentate ligands have two donor atoms and typically donate two pairs of electrons to metal ions. Three examples are shown below :



oxalate (**ox**) ion

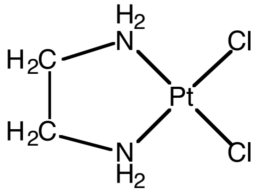


ethylenediamine (**en**)



N,N-dimethylethylene-
diamine (**dmen**)

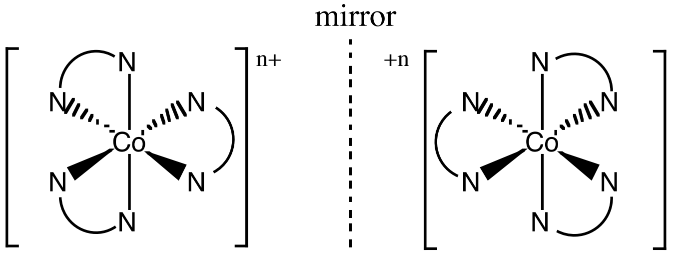
All three bidentate ligands form a five-membered ring on complexation to a metal ion as exemplified below for [PtCl$_2$(en)]:



(c) Sketch all of the possible linkage and geometrical isomers for each of the following species.

(i) square planar [Pt(SCN)$_2$(dmen)] (ii) cis-[Co(ONO)$_2$(NH$_3$)$_2$(en)]$^+$.

Octahedral complexes containing two or three bidentate ligands can exhibit a third type of isomerism. For example, the complex ion [Co(en)$_3$]$^{3+}$ exhibits optical isomerism; it exists as a pair of non-superimposable, mirror image isomers termed <u>optical</u> isomers:



(where N⌒N is **en** and n = 3)

Λ Δ

(d) Do any of the species mentioned in parts (a) – (c) exhibit optical isomerism? Explain.

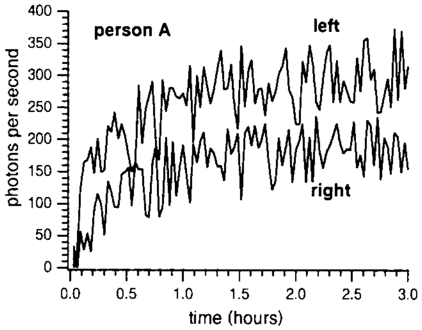
Optical and geometrical isomers are often referred to as <u>stereoisomers</u>; they only differ in the spatial arrangement of the atoms.

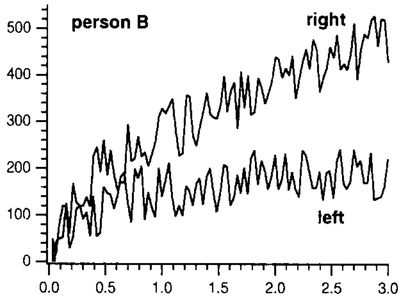
(e) How many stereoisomers are possible for each of the following species? Sketch them.

(i) [Al(C$_2$O$_4$)$_3$]$^{3-}$ (ii) [CoCl$_2$(en)$_2$]$^+$

(iii) square planar [Pt(dmen)$_2$]$^{2+}$ (iv) tetrahedral [Zn(dmen)$_2$]$^{2+}$.

Q19 A cancer researcher and a biophysicist sat down together in the university café one lunch time and started chatting about their work. The cancer researcher explained that he studied the treatment of eye tumours and was always looking for better ways of determining the growth rate of the tumours. Generally, he would inject the patient with a small quantity of radioactive phosphorus isotope (phosphorus-32) as a sodium phosphate solution ($Na_3{}^{32}PO_4$), this would be consumed more highly in cancerous cells than normal cells, and if the cancer was growing so would the rate of phosphorus consumption. By placing a Geiger counter next to the affected eye he could get an idea of the tumour activity by the increase of radioactivity in the eye. The problem was that little radiation got through the tissue around the eye to the Geiger counter, and the results were difficult to interpret. The biophysicist became excited, she asked if he had heard of Cherenkov light. She explained that in water, light travels around 25% slower than it does in a vacuum. When a charged particle is emitted during radioactive decay it is possible for this energetic particle to travel faster than light can in water. The charged particle produces a shock wave that is the equivalent of a sonic boom made by a jet travelling faster than the speed of sound in air, and emits a blue light called Cherenkov light. She finished by proposing that looking at the blue glow in the vitreous humour of eyes might be a better way of monitoring tumour activity. The two set about designing an experiment, and called for two volunteers. Each person had one eye tumour of similar size, one was growing, the other one dormant. The biophysicist was not told which eye was affected. She placed very sensitive light detectors in front of each of the persons' eyes, who were then injected with a radioactive phosphate solution of 3.7×10^6 Bq. The number of blue photons per second was recorded from each eye for 3 hours. [Note: 1 Becquerel = 1 Bq = 1 disintegration per second]





(a) By examining the graphs determine for each eye whether there was a tumour or not, and if so if it were growing. For the growing tumour estimate the rate of increase of radioactivity, knowing that one beta particle from ^{32}P gives about 30 Cherenkov photons. After the duration of the experiment what proportion of the original injected ^{32}P has ended up in the growing tumour?

(b) When ^{32}P decays emitting a beta particle what does it become?

(c) The rate of radioactive decay is constant for a particular isotope and is independent of the amount of material. That is, in a given period of time the same *fraction* of material will decay irrespective of how much was there to begin with ; this is the nature of exponential decay processes. The *Half life* of an isotope is defined as the time needed for half the initial number of radioactive nuclei to disintegrate. Hence, if the half life and the amount of radioactivity are known then the activity some period in the future can be estimated by the number of half lives spent. The half-life of ^{32}P is 2 weeks. For a solution of sodium phosphate with a radioactivity of 3.7×10^6 Bq what is the radioactivity after 20 days?