NATIONAL

QUALIFYING EXAMINATION

CHEMISTRY 1998

(1) This paper is in **two** sections and you must answer each section according to the instructions.
ie. Section A: Answer **ALL** questions
Section B: Question 16 is **compulsory**
Answer **any two** of Questions 17, 18 or 19

(2) All answers must be written in the space provided in the answer book.

(3) **Use blue or black pen to write your answers**, pencil is not acceptable.

(4) Rough working must be done only in the indicated areas of the answer book.

(5) You are not permitted to refer to books, periodic tables or written notes and the only permitted aid is a non-programmable electronic calculator.

(6) You are permitted **15 minutes** to read the paper and supply the requested information on the front cover and page 2 of the answer book, followed by **120 minutes** to work the questions.

(7) Relevant data that may be required for a question will be found on page 2.

Avogadro constant (N)	6.02×10^{23} mol^{-1}
1 faraday	96,486 coulombs
1 coulomb	1 amp sec
Universal gas constant (R)	8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}
Planck's constant (h)	6.626×10^{-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)	2.998×10^{8} ms^{-1}

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	89	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	32.06	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 What happens to the mass number and the atomic number of an element when it undergoes beta decay?

A neither the mass number nor the atomic number change

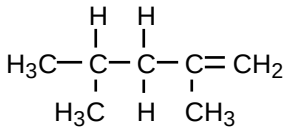
B the mass number does not change and the atomic number increases by 1

C the mass number does not change and the atomic number decreases by 2

D the mass number decreases by 4 and the atomic number decreases by 2

E the mass number increases by 2 and the atomic number increases by 1

Q2 What is the IUPAC (systematic) name for the following compound?



A 2,4-methylbutene

B 2,5-dimethylpentane

C 2,4-ethylbutene

D 2,4-dimethyl -1-pentene

E 2,4-dimethyl-4-pentene

Q3 Which species would be a free radical?

A N_2O

B NO_2^-

C NO_2^+

D NO

E N_2O_4

Q4 In the reaction between the hydrogen sulfate ion and water,

$$HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{2-}$$

the water acts as

A an acid

B a base

C a salt

D an inert medium

E a catalyst

Q5 For the $_{25}Mn$ atom, which subshell is partially filled?

A 3*s*

B 4*s*

C 4*p*

D 3*d*

E 4*d*

Q6 Which end of the bonds Si–Cl, At–Br, and Hg–P are positively charged?

A Si, At, P

B Cl, At, Hg

C Cl, Br, P

D Cl, Br, Hg

E Si, At, Hg

Q7 The Mond process produces pure nickel metal via the thermal decomposition of nickel tetracarbonyl as shown in the equation.

$$Ni(CO)_4\ (l) \longrightarrow Ni\ (s) + 4CO\ (g)$$

How may litres of CO would be formed from 444 g of $Ni(CO)_4$ at 752 mm Hg and 22°C?

A 0.356

B 63.7

C 255

D 20.2

E 11.0

Q8 What is the molarity of HCl in a solution prepared by dissolving 5.5 g of HCl gas in 200 g of ethanol if the density of the solution is 0.79 g mL^{-1}?

A 21 M

B 0.93 M

C 6.0×10^{-4} M

D 1.7 M

E 0.58 M

Q9 The energy in joules of a photon of radiation of wavelength 1.23×10^{-5} m is

A $(6.63 \times 10^{-34})(3.00 \times 10^{8}) / (1.23 \times 10^{-5})$

B $(6.63 \times 10^{-34})(1.23 \times 10^{-5})$

C $(3.00 \times 10^{8}) / (1.23 \times 10^{-5})$

D $(1.23 \times 10^{-5}) / (6.63 \times 10^{-34})$

E $(6.63 \times 10^{-34})(1.23 \times 10^{-5}) / (3.00 \times 10^{8})$

Q10 Some physical properties of four elements, **L**, **M**, **Q** and **R**, are given in the table below.

Physical property	L	M	Q	R
MP (°C)	–7	63	–189	1083
BP (°C)	58	766	–186	2582
Colour at STP	dark red	silvery	colourless	browny-red
Density at STP (g cm^{-3})	3.1	0.86	1.7×10^{-3}	8.9

These elements, in the order **L**, **M**, **Q** and **R**, are from the following groups in the periodic table:

	L	M	Q	R
A	group I	transition elements	group VII	group VIII
B	group VII	group I	group VIII	transition elements
C	group VII	transition elements	group VIII	group I
D	transition elements	group I	group VII	group VIII
E	transition elements	group VIII	group I	group VII

Q11 The balanced equation for the reduction of the nitrate anion by the Fe(II) ion in an acidic solution is

A $3Fe^{2+}(aq) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$

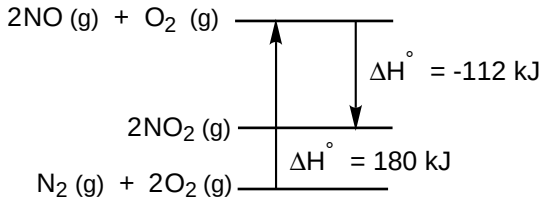
B $Fe^{2+}(aq) + NO_3^-(aq) + 8H^+(aq) \longrightarrow Fe^{3+}(aq) + NO(g) + 4H_2O(l)$

C $2Fe^{2+}(aq) + 2NO_3^-(aq) + 4H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2NO(g) + 4H_2O(l)$

D $3Fe^{3+}(aq) + NO(g) + 2H_2O(l) \longrightarrow 3Fe^{3+}(aq) + NO_3^-(aq) + 4H^+(aq)$

E $Fe^{2+}(aq) + 3NO_3^-(aq) + 12H^+(aq) \longrightarrow Fe^{3+}(aq) + 3NO(g) + 6H_2O(l)$

Q12 The diagram below shows the reaction heat for the chemical reactions between N_2, O_2, NO, and NO_2.



Which of the following statements pertaining to the formation of NO and NO_2 are correct?

1. The standard heat of formation of NO_2 is 68 kJ mol^{-1}.
2. NO_2 is formed faster than NO at higher temperature.
3. The oxidation reaction of nitrogen to NO_2 is endothermic.
4. These two reactions often take place in the troposphere and cause greenhouse effect.
5. These two reactions are both responsible for the city smog.

A 1 and 2
B 1 and 3
C 1 and 4
D 3 and 4
E 3 and 5

Q13 Analysis of a quantity of a compound shows that it contains 0.110 mol of C, 0.055 mol of N, and 0.165 mol of O. Its molecular weight is about 270. How many atoms of carbon are there in the empirical formula for the compound and how many in the molecular formula?

A Empirical, 1; molecular, 3

B Empirical, 2; molecular, 2

C Empirical, 2; molecular, 6

D Empirical, 3; molecular, 2

E Empirical, 2; molecular, 3

Q14 Given the following standard half reactions and their corresponding electrode potentials:

$Cd^{2+} + 2e^- \longrightarrow Cd \qquad E^\circ = -0.40\ V$

$Ag^+ + e^- \longrightarrow Ag \qquad E^\circ = +0.80\ V$

The balanced spontaneous reaction involving silver and cadmium species would be

A $2Ag^\circ(s) + Cd^\circ(aq) \longrightarrow 2Ag^+(aq) + Cd^{2+}(aq)$

B $2Ag^\circ(s) + Cd^{2+}(aq) \longrightarrow 2Ag^+(ag) + Cd^\circ(s)$

C $Cd^\circ(s) + 2Ag^+(aq) \longrightarrow Cd^{2+}(aq) + 2Ag^\circ(s)$

D $Cd^\circ(s) + Ag^+(aq) \longrightarrow Cd^{2+}(aq) + Ag^\circ(s)$

E $2Cd^\circ(s) + Ag^+(aq) \longrightarrow 2Cd^{2+}(aq) + Ag^\circ(s)$

Q15 If each of the following salts has a K_{sp} value of 1.00×10^{-9}, which is the least soluble in pure water?

A XY

B XY_2

C X_3Y

D X_2Y_3

E XY_4

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 Potassium permanganate and potassium chromate are both able to oxidise the iodide ion to iodine in acidic solution. These reactions respectively reduce permanganate ion (MnO_4^-) to Mn^{2+} and chromate ion (CrO_4^{2-}) to Cr^{3+}.

(a) Write balanced half equations for

(i) the reduction of MnO_4^- in acidic solution

(ii) the reduction of CrO_4^{2-} in acidic solution

(iii) the oxidation of I^-

Iodine reacts with the thiosulfate ion, ($S_2O_3^{2-}$), to afford iodide ion and the tetrathionate anion, ($S_4O_6^{2-}$), a reaction frequently used in the volumetric determination of iodine.

(b) Write a balanced ionic equation for the reaction of iodine with the thiosulfate anion.

Given the above information solve the following problem.

(c) A 0.2400 g sample of a mixture of $KMnO_4$ and K_2CrO_4 is reacted with an excess of acidic KI solution to liberate iodine. Titration of this iodine with 0.1000 M $Na_2S_2O_3$ required a total of 60.00 mL to achieve the end point.

Calculate the percentage (by mass) of Mn and Cr in the mixture, and give the answer to three significant figures.

Q17 The answers to parts (a)-(i) refer to the following list of oxides, oxyacids and oxyanions of the elements C, N and S:

- HCO_3^- , $C_2O_4^{2-}$, CO, H_2CO_3, CO_2, CO_3^{2-}
- N_2O, NO_2^- , HNO_3, NO, HNO_2, NO_3^- , NO_2
- SO_4^{2-} , SO_3, H_2SO_4, HSO_3^- , SO_3^{2-} , HSO_4^- , H_2SO_3, $S_2O_3^{2-}$, SO_2

(a) One of the oxides of C is acidic, ie. it reacts with water to form an acid. Identify the oxide and write a balanced equation for the reaction of the oxide with water.

(b) The acid in (a) is a weak acid. What species are present in an aqueous solution of the acid?

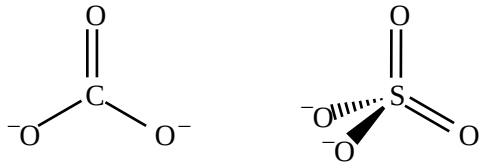
(c) Nitric acid is a strong acid and a powerful oxidising agent. Which of the oxides of N reacts with water to form nitric acid? Write a balanced equation for the reaction. [Note: the oxide **disproportionates** in water, ie. it is both oxidised to nitric acid and reduced to a second oxide of N. Known as a **disproportionation reaction**.]

(d) Both of the oxides of S are acidic. One of the oxides forms a weak acid in water whereas the other forms a strong acid. Write a balanced equation for each of these two reactions.

(e) What species are present in an aqueous solution of the weak acid in (d)?

(f) What species are present in an aqueous solution of the strong acid in (d)?

(g) The CO_3^{2-} ion has a trigonal planar geometry and the SO_4^{2-} ion a tetrahedral shape:



Predict and sketch the shapes of the following species:

NO_3^- , SO_3, NO_2^- , HCO_3^- , $C_2O_4^{2-}$, $S_2O_3^{2-}$.

(h) Molecules **A**, **B**, **C** and **D** are all triatomic species that exist as gases under normal conditions. **A** and **B** have a linear geometry whereas **C** and **D** are bent molecules. **B** and **C** contain the same elements. **B** does not react with water while **A**, **C** and **D** are acidic oxides: **A** and **D** react with water to form weak diprotic acids and **C** readily disproportionates in water to give a strong acid and a diatomic species **E**. Each of the species **A** to **D** can be prepared by one of the following preparative routes:

$$NH_4NO_3(s) \xrightarrow{250\ ^oC}$$

$$CaCO_3(s) \xrightarrow{\text{heat}}$$

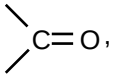
$$S_8(s) + O_2(g) \xrightarrow{\text{heat}}$$

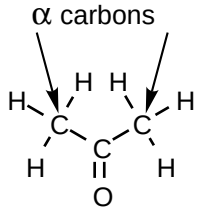
$$\mathbf{E}(g) + O_2(g) \longrightarrow$$

Using chemical formulae identify molecules **A** - **E** and complete the above equations. Sketch the molecular shapes of the three acids.

(i) When equimolar quantities of **C** and **E** [from (h)] are passed through a solution of aqueous sodium hydroxide a salt **F** is formed. Treatment of **F** with sulfuric acid produces a weak acid **G** and sodium sulfate. **G** readily decomposes to give a strong acid, water and **E**. Using chemical formulae identify **F** and **G** and write a balanced equation for the decomposition of **G**. What type of reaction is this?

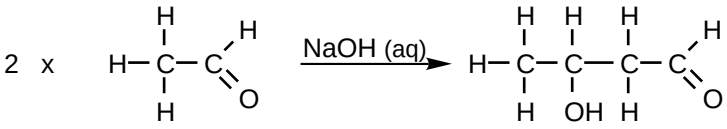
Q18 **Note:** Further information concerning some of the following structures is available at the end of the question.

The carbonyl group,  , forms part of a number of key functional groups in organic chemistry including aldehydes, ketones, esters, carboxylic acids and amides. Acetone (propanone) contains a carbonyl group and its structure is illustrated below. In certain cases the presence of a carbonyl group in a molecule gives rise to increased acidity of the protons on the carbon α (next door or adjacent) to the functionality. This in turn gives rise to a variety of base catalysed reactions.



Acetone (propanone)

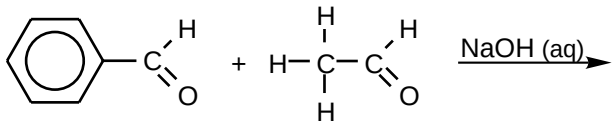
For example ethanal (acetaldehyde) will react in the presence of sodium hydroxide as follows

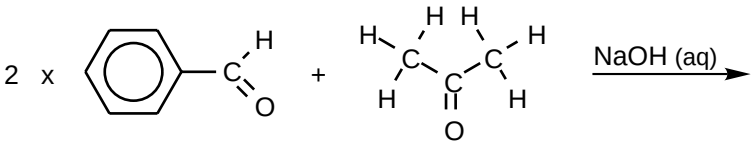


Based on this information alone

(a) What would be the structure of the product formed by reacting 2 molecules of propanone (acetone).

(b) What would be the product(s) formed by the following reactions noting that the carbonyl group of an aldehyde is more reactive than that of a ketone.

(i) 

(ii) 

In practice the answers to question (b) aren't the alcohols you might have predicted, the product actually isolated in question b(i) is a compound with the molecular formula C_9H_8O.

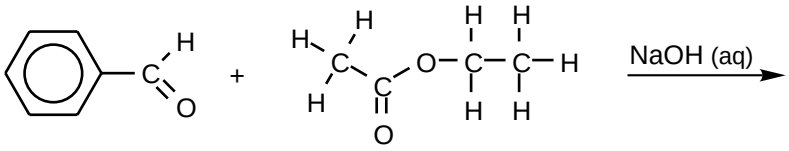
(c) (i) The process involved in the formation of this new compound, C_9H_8O, is

1	reduction	4	oxidation
2	hydration	5	cyclisation
3	dehydration	6	aromatisation

(ii) What would be a reasonable structure to write for the compound formed that has the molecular formula C_9H_8O.

(Q18 is continued on the next page)

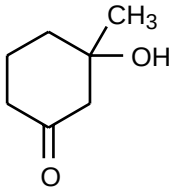
(d) If you consider a related reaction, namely the reaction of benzaldehyde and ethyl acetate (ethyl ethanoate)



it is possible to form a new ester with the molecular formula $C_{11}H_{12}O_2$.

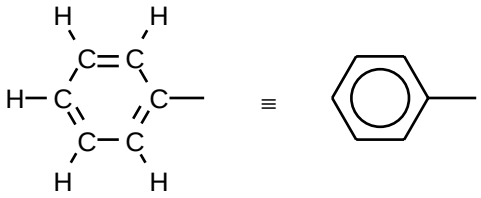
Suggest a structure for this compound.

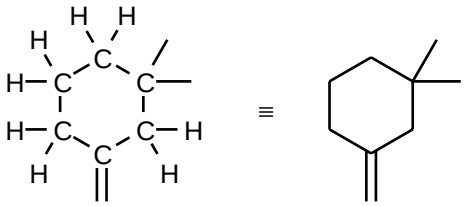
(e) If you have mastered all of the above questions you can try your hand at designing a synthesis. The molecule below can be prepared by the base catalysed reaction of a symmetrical diketone. Suggest the structure of this starting ketone.



Further information.

For clarity, accepted shorthand convention with ring structures has been used. H and C atoms forming the ring structures have not been shown. The following illustrations should assist you.





Q19 A chemist, a physicist and a molecular biologist were brainstorming over recent advances in the synthesis of artificial muscles and were discussing the possibility of collaborating on this multi-disciplinary subject. In living organisms muscle activity is a complex system of chemical changes, one change being the controlled release of small ions such as K^+ and Ca^{2+}. Over lunch the following conversation developed.

*Biologist - **B**, Chemist - **C** , Physicist - **P***

***B**:* Which ion is the smaller, K^+ or Ca^{2+}?

***C**:* Well on the periodic table potassium has a lower atomic number than calcium so K^+ should be the smaller of the two. Potassium is the 19th element, calcium the 20th, I seem to remember.

***P**:* Rubbish! Ca^{2+} is the smallest, it must be. It's lost two electrons so the remaining electrons must be pulled in towards the nucleus even more strongly than those electrons left around the K^+ nucleus, which has only lost one of its electrons.

***C**:* Yeah, it's all very well to say that but don't forget we're not dealing with ions floating around in the vacuum of space. We're considering ions in the aqueous environment of a living cell! The water molecules will make a shell around the ions and it really isn't clear to me how thick the shell might be. This will dictate how big an ion really is.

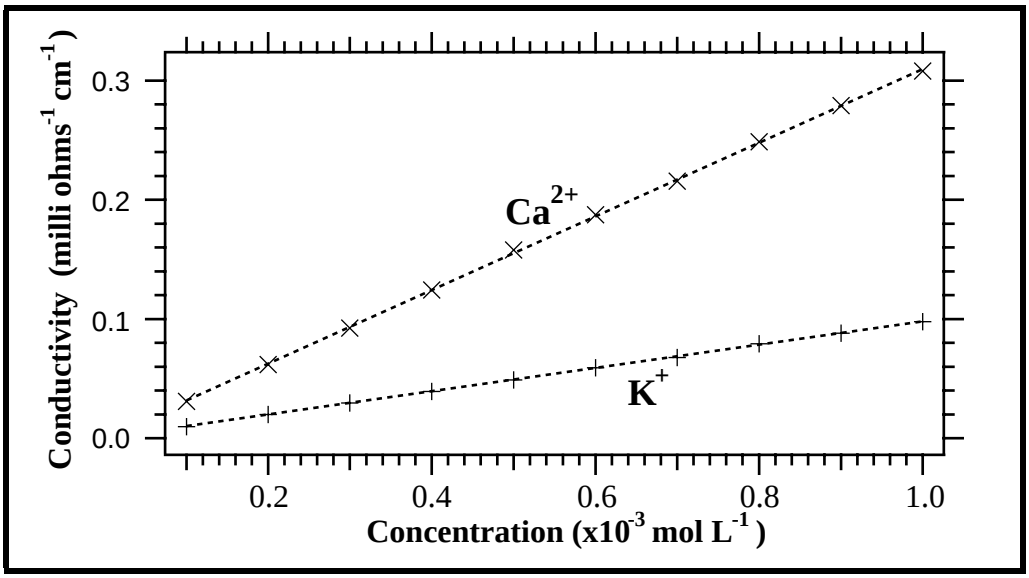
***B**:* Ok, settle down, I'm sure we can work this out. Let's go back to basics. What do we know, and what type of experiment can we do? When an ion is placed between two electrodes with a voltage across them the ion will move towards the electrode of the opposite sign to the ion. So electrical conductivity is a measure of how charged and how big an ion is, right?

***C**:* Yep that's right, and the conductivity of a solution will be *inversely proportional* to the radius of the ion. The bigger the ion, the slower it moves. Let's say that ions are spherical, it's easier that way.

***P**:* Ok, but don't forget that the conductivity also will be *proportional* to charge on the ion *squared*. We'll have to take this into consideration before we can compare the relative size of the two ions.

B And the *higher the concentration* the *higher* the *solution conductivity*. Great! This gives us the framework, but we can't work out everything, we'll have to do an experiment.

1 day later - The three are sitting down at lunch again looking over the following conductivity data for the two ions.



***B**:* Ok, now we're cooking with gas! Firstly, we can work out which ion is the larger of the two.

***C**:* Yep, and secondly we can work out the ratio of size of the Ca^{2+}: K^+ .

P: Can we eat our lunch first?

Follow through and determine what the Biologist and the Chemist claim is possible from their data.