AUSTRALIAN
SCIENCE
OLYMPIADS

CHEMISTRY

2007 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. [This section is worth 30 marks.]
Section B:	Apportion your time equally on the questions in this section. Answer **ANY THREE (3)** of Questions 16, 17, 18 or 19 [This section is worth 90 marks.]

- All answers to Section A must be answered, using a 2B pencil, on the Multiple Choice answer sheet.
- All answers to Section B must be written in the spaces provided in the booklet.

- Use **blue** or **black** pen to write your answers; pencil is **NOT** acceptable.

- Rough working must be done only on pages 30 and 31 of this booklet.

- 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)	6.02×10^{23} mol^{-1}	Velocity of light (c)	2.998×10^{8} m s^{-1}
1 Faraday	96,486 coulombs	Density of water at 25°C	0.9971 g cm^{-3}
1 Coulomb	1 A s^{-1}	Acceleration due to gravity	9.81 m s^{-2}
Universal gas constant (R) 8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}		1 Newton (N)	1 kg m s^{-2}
Planck's constant (h)	6.626×10^{-34} J s	1 Pascal (Pa)	1 N m^{-2}
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		$\text{pH} = -\log_{10}[\text{H}^+]$ pH + pOH = 14.00 at 25°C $K_a = [\text{H}^+]\,[\text{A}^-] / [\text{HA}]$ $PV = nRT$ $E = h\nu$ $c = \nu\lambda$ Surface area of sphere $A = 4\pi r^2$	
Molar volume of ideal gas at STP	22.4 L		
1 atm = 101.3 kPa			

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	32.07	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 on the multiple choice answer sheet, using a 2B pencil. Only one choice is allowed per question. If you make a mistake **make sure that your incorrect answer is completely erased.**

Please note the following:

- **It is recommended that you first record your answer on this question paper by circling ONE of the letters A, B, C, D or E.**
- **Then transfer these answers on to the computer sheet which will be computer marked for assessment.**

Q1 A fuel/oxidant system consisting of *N*,*N*-dimethylhydrazine, $(CH_3)_2NNH_2$, and dinitrogen tetraoxide, N_2O_4, (both liquids) is commonly used in space vehicle propulsion. The components are mixed stoichiometrically so that N_2, CO_2 and H_2O, all gases under the reaction conditions, are the only products. How many moles of gas are produced from 1 mol of $(CH_3)_2NNH_2$?

A 8

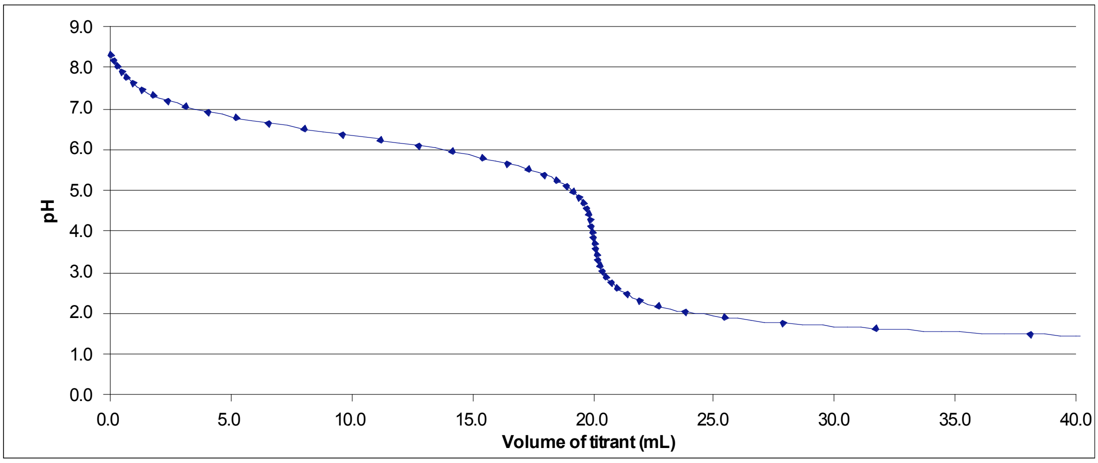
B 9

C 10

D 11

E 12

Q2 20 mL of solution **X** was pipetted into a conical flask and titrated with solution **Y** from a burette. The pH was monitored with a pH meter throughout the experiment, and was plotted against the volume of solution **Y** added to give the graph below.



Which one of the following alternatives is most likely the identity of solutions **X** and **Y**?

	X	Y
A	KOH	CH_3COOH
B	$NaHCO_3$	HBr
C	CH_3COOH	$NaHCO_3$
D	KOH	HBr
E	HBr	$NaHCO_3$

Q3 The density of liquid nitrogen is 0.807 g mL^{-1}. If a person accidentally swallowed a 0.025 mL drop of liquid nitrogen, what volume of nitrogen gas would be evolved in their body at 100.0 kPa and 37 °C?

A 0.018 mL

B 0.025 mL

C 19 mL

D 23 mL

E 37 mL

Q4 By referring to the standard reduction potentials below, which of the species listed is the best oxidising agent?

$Cu^{2+}\,(aq) + 2e^- \rightleftharpoons Cu\,(s)$ $E^0 = +0.34$ V

$Ni^{2+}\,(aq) + 2e^- \rightleftharpoons Ni\,(s)$ $E^0 = -0.23$ V

$Cd^{2+}\,(aq) + 2e^- \rightleftharpoons Cd\,(s)$ $E^0 = -0.40$ V

$Fe^{2+}\,(aq) + 2e^- \rightleftharpoons Fe\,(s)$ $E^0 = -0.44$ V

$Zn^{2+}\,(aq) + 2e^- \rightleftharpoons Zn\,(s)$ $E^0 = -0.76$ V

A Cd *(s)*

B Zn^{2+} *(aq)*

C Ni *(s)*

D Cu^{2+} *(aq)*

E Fe *(s)*

Q5 Which one of the following species does **not** have eight valence electrons surrounding the central atom?

A $CC\ell_4$ molecule

B NH_3 molecule

C NH_4^+ ion

D OF_2 molecule

E $BC\ell_3$ molecule

Q6 Which one of the following series is arranged in order of increasing ionic radius?

A $Mg^{2+} < S^{2-} < C\ell^- < K^+ < Ca^{2+}$

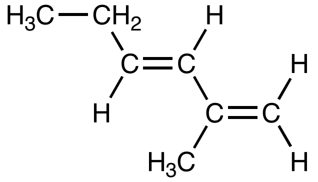
B $Mg^{2+} < Ca^{2+} < K^+ < C\ell^- < S^{2-}$

C $S^{2-} < C\ell^- < K^+ < Mg^{2+} < Ca^{2+}$

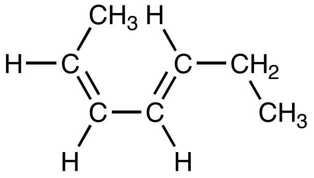
D $S^{2-} < Mg^{2+} < Ca^{2+} < C\ell^- < K^+$

E $Ca^{2+} < C\ell^- < K^+ < Mg^{2+} < S^{2-}$

Q7 Which one of the following is **not** an isomer of the molecule depicted below?



A



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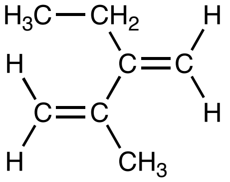
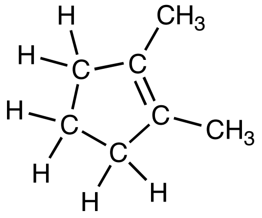


C



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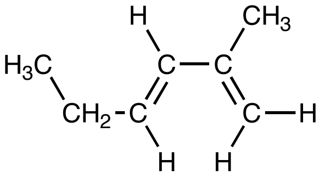
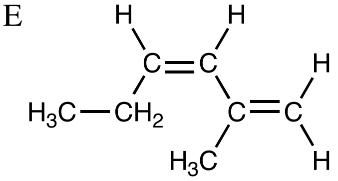


E



Q8 Which of the following compounds could not be obtained by oxidising phosphorus trifluoride, PF_3?

A $Na_4P_2O_7.10H_2O$

B $H_4P_2O_6$

C KPF_6

D $(NH_4)_2HPO_3.H_2O$

E $Ca_5(PO_4)_3F$

Q9 Elements **Q** and **R** form both oxides and chlorides. Under laboratory conditions, $\mathbf{Q}C\ell_2$ is a cherry-red liquid while $\mathbf{R}C\ell_2$ is a white solid. Which one of the following statements is most likely to describe the oxides of these elements?

A **Q** forms a basic oxide **Q**O while **R** forms an acidic oxide **R**O.

B **Q** forms a basic oxide $\mathbf{Q}O_2$ while **R** forms two acidic oxides **R**O and $\mathbf{R}O_2$.

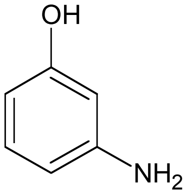
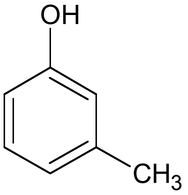
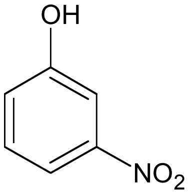
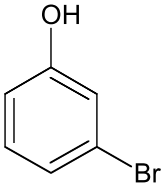
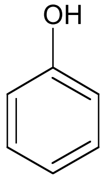
C **Q** forms two acidic oxides $\mathbf{Q}O_2$ and $\mathbf{Q}O_3$ while **R** forms a basic oxide **R**O.

D **Q** forms an acidic oxide **Q**O while **R** forms a basic oxide **R**O.

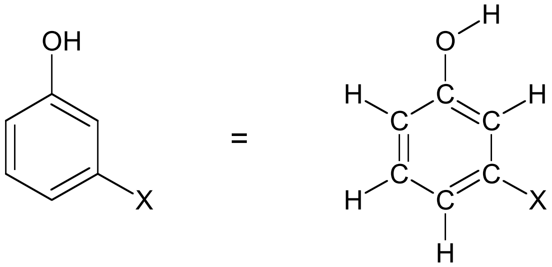
E **Q** forms two acidic oxides **Q**O and $\mathbf{Q}O_2$ while **R** forms a basic oxide $\mathbf{R}O_2$.

Q10 Ethanoic acid was heated with an unknown compound **X** and a catalytic amount of concentrated sulfuric acid. The reaction mixture was shown by mass spectrometry to contain a compound of molar mass 193 g mol^{-1}.

Which of the following could be compound **X**?

				
A	**B**	**C**	**D**	**E**

Note that a shorthand notation has been used to draw these structures:



Q11 What is the enthalpy change for the complete combustion of one mole of liquid isopropanol (molecular formula C_3H_8O)?

$$3C\,(s) + 4H_2\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow C_3H_8O\,(l) \qquad \Delta_fH = -318 \text{ kJ mol}^{-1}$$

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) \qquad \Delta_fH = -394 \text{ kJ mol}^{-1}$$

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l) \qquad \Delta_fH = -286 \text{ kJ mol}^{-1}$$

A -362 kJ

B -998 kJ

C -2008 kJ

D -2116 kJ

E -4016 kJ

Q12 Equal masses of each of the following compunds were treated with excess hydrochloric acid. Which produced the greatest volume of carbon dioxide gas?

A sodium carbonate

B magnesium carbonate

C potassium carbonate

D calcium carbonate

E rubidium carbonate

Q13 Sodium metal is produced industrially by the electrolysis of molten NaCℓ, while steel is produced by CO reduction of ores containing Fe(III) in a blast furnace. Tantalum is another useful metal, often used surgically to repair bone because of its high resistance to corrosion. Which of the following methods could be used industrially to produce tantalum from naturally occurring Ta(V)?

$Na^+ (aq) + e^- \rightleftharpoons Na (s)$ $E^0 =$ –2.71 V

$Fe^{3+} (aq) + 3e^- \rightleftharpoons Fe (s)$ $E^0 =$ +0.82 V

$Ta_2O_5 (s) + 10H^+ (aq) + 10e^- \rightleftharpoons 2Ta (s) + 5H_2O (l)$ $E^0 =$ –0.75 V

$CO_2 (g) + 2H^+ (aq) + 2e^- \rightleftharpoons CO (g) + H_2O (l)$ $E^0 =$ –0.10 V

A Either reduction with sodium metal or reduction in a blast furnace.

B Either electrolysis or reduction with sodium metal.

C Electrolysis only.

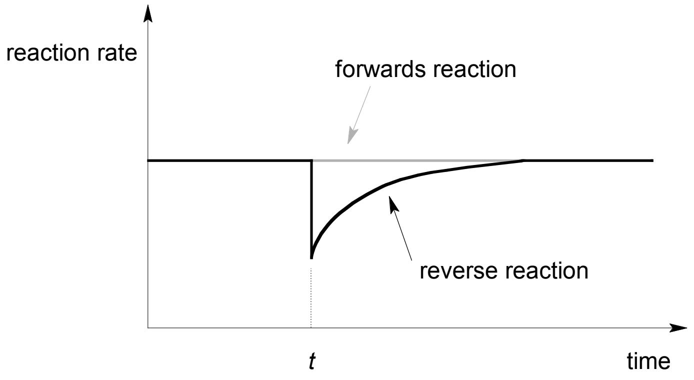
D Reduction in a blast furnace only.

E Reduction with sodium metal only.

Q14 A small amount of solid lead iodide was added to a beaker of water, which was stirred. Most of the solid settled on the bottom of the beaker, but a little dissolved, establishing the equilibrium

$$PbI_2 (s) \rightleftharpoons Pb^{2+} (aq) + 2I^- (aq).$$

The rates of the forward and reverse reactions were monitored over time, producing the graph shown below:



What happened at time *t*?

A The beaker was cooled in an ice-bath.

B A small amount of solid $Pb(NO_3)_2$ was added to the beaker.

C A small amount of solid KI was added to the beaker.

D A small amount of solid PbI_2 was removed from the beaker.

E A small amount of water was added to the beaker.

Q15 The dichromate ion $Cr_2O_7^{2-}$ is orange in aqueous solution whereas Cr^{3+} is green. An acidified solution of potassium dichromate is thus a useful reagent for identifying many chemical species.

The following five aqueous solutions were prepared, and a few drops of acidified potassium dichromate solution were added to each one. Three of them turned green; one turned a murky brown colour, and one remained orange.

Which solution remained orange?

A $SnC\ell_2$

B KI

C CH_3CH_2OH

D $NaNO_2$

E $A\ell_2(SO_4)_3$

SECTION B

Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.
Answer any three of the four questions in this section.

Q16

Transition metal ions are often brightly coloured and can exist in a wide range of oxidation states. Vanadium is particularly diverse: an oft-used chemistry demonstration involves swirling a vanadium(V) solution with zinc in a flask, which causes the solution to change colour from yellow to blue to green and finally, pale violet.

(a) Complete the following table.

Species	**Colour**	**Oxidation State**
V *(s)*		0
V^{2+} *(aq)*	pale violet	+2
V^{3+} *(aq)*	green	
VO^{2+} *(aq)*	deep blue	
VO_3^- *(aq)*	yellow	

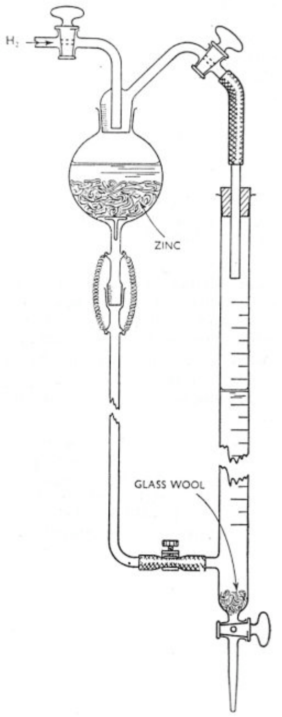
The vanadous ion (V^{2+}) is used in a redox titration to determine the concentration of an unknown solution containing the Fe^{3+} ion. Iron(III) is reduced to iron(II), and the solution is acidic throughout the determination.

(b) What are the two half equations and the balanced full equation for this reaction? The first one has been done for you.

$$V^{2+} \longrightarrow V^{3+} + e^-$$

Fiona, an earnest young analytical chemist, decided to make some 0.500 mol L^{-1} vanadous sulfate (VSO_4) solution. She had a bottle of vanadyl sulfate ($VOSO_4.2H_2O$), which she stirred with an excess of zinc metal (amalgamated with a small amount of mercury(II) catalyst). Since it was getting late, Fiona decided to filter the solution and leave it out on the bench, with the intention to perform the titration the next day. Disaster struck! Fiona returned to find her perfectly prepared pale violet solution had a slight green tinge.

(c) Write a possible equation for the reaction of the V^{2+} ion with air.



Fiona did a little background reading and found the apparatus shown in the diagram at the right was used for the titration. The setup allows the V^{2+} ion to be conveniently produced and stored *in situ*. The whole apparatus is filled with hydrogen gas to prevent reaction with air.

Fiona also learnt that even a small amount of *dissolved* oxygen could affect the titration. To her unknown iron(III) solution, she added saturated sodium carbonate solution, forming a rusty yellow precipitate, followed by dilute hydrochloric acid solution, forming bubbles of colourless gas. The effervescence completely removes any dissolved oxygen in the solution.

(d) What is the chemical formula of the rusty yellow precipitate and the colourless gas?

Precipitate
Gas

25.00 mL aliquots of an iron(III) solution of unknown concentration were titrated against the standard 0.500 mol L^{-1} V^{2+} solution. The average titre, i.e. the average volume of the solution containing the V^{2+} ions needed to completely react with the solution containing the Fe^{3+} ions, was 22.14 mL.

(e) Calculate the mass of $VOSO_4.2H_2O$ required to make 250 mL of the standard solution.

(f) Calculate the concentration of the iron(III) solution.

The indicator used in the titration is potassium thiocyanate, KSCN. The thiocyanate ions, SCN^-, form an intense blood red complex ion with Fe^{3+} in solution.

(g) What colour change occurs at the end point of the titration?

Q16 continues on the next page.

Fiona also discovered the possibility of the following reaction between the vanadous ions and hydrogen ions in solution:

$$2V^{2+}\,(aq) + 2H^{+}\,(aq) \longrightarrow 2V^{3+}\,(aq) + H_2\,(g)$$

Fortunately this reaction is very slow under normal conditions. Fiona remembered that solution-phase reactions usually occur in two steps: the reactants first associate, or come together, and then react to form products.

$$(1)\qquad A + B \rightleftharpoons A.B$$

$$(2)\qquad A.B \longrightarrow C$$

(h) Explain why the reaction might be slow?

To improve the accuracy of the titration, the solution of V^{2+} ions was standardised against potassium permanganate solution ($KMnO_4$). In the reaction with permanganate ion, V^{2+} is converted into VO_3^{-}, and MnO_4^{-} is converted into Mn^{2+}.

(i) Give the equation for the reaction between V^{2+} ion and the MnO_4^{-} ion.

(j) 25.00 mL aliquots of the solution containing V^{2+} ions required an average of 25.34 mL of a 0.283 mol L^{-1} $KMnO_4$ solution. Calculate the true concentration of the V^{2+} ion in the solution.

(k) Using the answer obtained in (j), what is the true concentration of the Fe^{3+} ion in the solution?

Q17

Mass spectrometry is an important tool in the determination of the structures of organic compounds.

The process begins with the ionisation of the sample to form a positively charged ion, the *molecular ion*. At this stage, the molecular ion commonly fragments to form additional cations. These cations are passed through a magnetic field where they are observed to follow a curved path. The radius of curvature of the path is dependent upon the mass to charge ratio (m/z) of individual ions. Measurement of the radius of curvature thus gives an accurate measure of the m/z ratio for each ion. The abundance of ions detected for each m/z is plotted as a graph of the mass spectrum.

Since ions with a multiple positive charge are much less abundant than those with a single positive charge, the detected m/z ratio is effectively equal to the mass of the ion, m.

(a) The empirical formula of a compound may be calculated from percentage composition data. An unknown compound consisting of carbon, hydrogen and oxygen only was analysed to contain 54.5% carbon and 9.15% hydrogen.

(i) Calculate the empirical formula of the unknown compound.

(ii) Deduce the molecular formula of the unknown compound given it has a molecular mass of 88 g mol^{-1}.

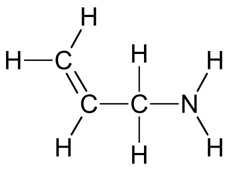
The molecular mass of a compound is readily obtained from mass spectrometry. However, compounds with different molecular formulae may have molecular masses that are identical to the nearest unit value. *High resolution mass spectrometry* overcomes this issue by providing molecular mass measurements with great precision (often to several decimal places).

Q17 continues on the next page.

(b) The *m*/*z* of a molecular ion containing only carbon, hydrogen and oxygen was determined to be 58.0417 units by high resolution mass spectrometry.

(i) In the following structures, circle those with a molecular mass of 58 g mol^{-1}.

A



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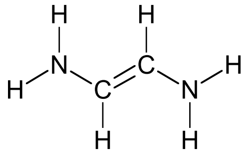
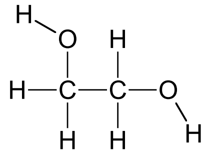
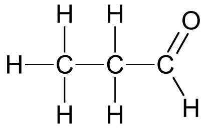


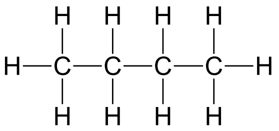
C



D



E

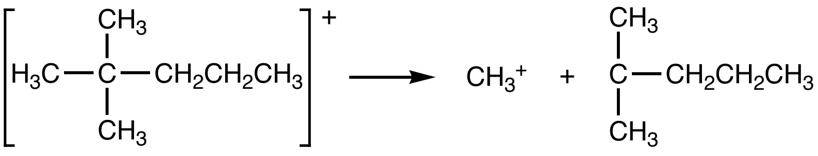


(ii) By considering the following table of atomic masses, identify the structure in part (i) which could give rise to a molecular ion peak of 58.0417 units.

Atom	Relative atomic mass (amu)
^{12}C	12.0000
^{16}O	15.9949
^{1}H	1.0078
^{14}N	14.0031

Fragmentation of a molecular ion often occurs according to predictable patterns. In general, fragmentation involves the breaking of weak bonds and formation of stable fragment ions. The location where bonds are commonly broken include:

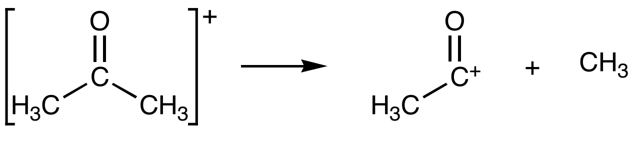
- At branch points, for example:



- Adjacent to heteroatoms (atoms other than carbon and hydrogen), for example:

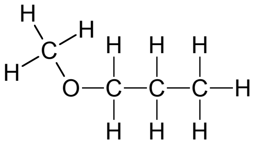
$$\left[H_3CCH_2-O-CH_2CH_3\right]^+ \longrightarrow H_3CCH_2^+ + O-CH_2CH_3$$

- Adjacent to carbonyl groups (C=O), for example:

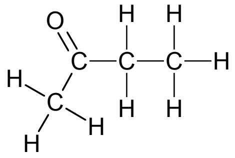


(c) Indicate on each of these molecules the two bonds most liable to break upon fragmentation of the molecular ion.

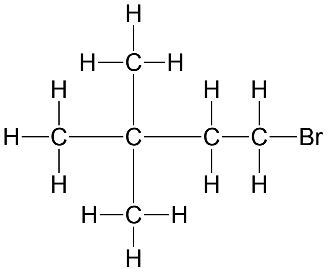
(i)



(ii)

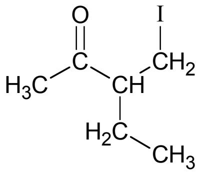


(iii)



The fragmentation of a molecular ion into lower molecular mass fragments may result in the observation of peaks corresponding to lower *m*/*z*.

(d) The following compound was analysed by mass spectrometry. Propose structures for each fragment corresponding to observed *m*/*z* peaks in the obtained spectrum.



(i) $m/z = 15$	(ii) $m/z = 29$	(iii) $m/z = 43$	(iv) $m/z = 127$

(e) A four-carbon compound containing only carbon, hydrogen and oxygen displayed a molecular ion peak at *m*/*z* 74.0729 when subjected to high resolution mass spectrometry. Significant fragment peaks were also observed at *m*/*z* 15, 17 and 57.

(i) Provide the molecular formula for this compound.

(ii) Provide a possible structure for the fragments corresponding to each of the peaks.

m/*z* = 15	*m*/*z* = 17	*m*/*z* = 57

(iii) Propose a possible structure for the compound, based on your answers from (ii).

Q17 continues on the next page.

Some elements exist in nature as a mixture of more than one isotope of high natural abundance. Bromine appears as two abundant isotopes: ^{79}Br (49.3% abundance) and ^{81}Br (50.7% abundance). A compound containing one bromine atom will give rise to two molecular peaks depending on which isotope it contains. One peak will result from molecular ions containing ^{79}Br, and the other will result from molecular ions containing ^{81}Br. The two peaks differ by two *m/z* units. The relative intensities of these two peaks correspond to the natural abundance of the isotopes (49.3 : 50.7).

Chlorine and sulfur likewise exist as several isotopes. This is shown in the following table:

Isotope	**Natural Abundance (%)**
$^{35}C\ell$	75.8
$^{37}C\ell$	24.2
^{32}S	95.0
^{33}S	0.75
^{34}S	4.2

(f) For each of the following compounds, provide the expected *m/z* values corresponding to the peaks for the **molecular** ion, and state the relative intensity of the peaks in each case.

(i) $CH_3CH_2CH_2—SH$

m/z	**Relative Intensity**

(ii) $C\ell — CH_2CH_2\ CH_2CH_2— C\ell$

m/z	**Relative Intensity**

(iii) $Br — CH_2CH_2— C\ell$

m/z	**Relative Intensity**

Q18

Whether a pure substance exists as a solid, liquid or gas depends not only on the *temperature* of the system, but also on the *pressure* of the system. To illustrate this concept, we will investigate a physical property called the **vapour pressure**.

The **vapour pressure** of a pure substance is defined as the pressure of the vapour (of this substance) in equilibrium with its non-vapour phases (i.e. solid and liquid phases). The vapour pressure of a pure substance is **temperature dependent** (i.e. it has different values at different temperatures).

For example, liquid water in equilibrium with water vapour, as represented by the equation:

$$H_2O\,(l) \rightleftharpoons H_2O\,(g)$$

has a vapour pressure of 3.17 kPa at 298 K. This means that the forward and reverse rates of this process are equal when the pressure of water vapour is 3.17 kPa.

An important implication is that, when the vapour pressure of a substance exceeds the pressure of the system (which, for open beakers of liquid, is the pressure of the surrounding air), the equilibrium between gaseous and non-gaseous phases is no longer achievable, and molecules rapidly become gaseous in bulk (i.e. the substance boils or sublimes).

The boiling point of water is 373.15 K.

(a) What is the vapour pressure of water at 373.15 K and standard atmospheric pressure? *(Give a numerical answer.)*

(b) Butane has a vapour pressure of 47.156 kPa at 253 K, and 149.03 kPa at 283 K. **Circle** whether butane is gaseous or non-gaseous under the following conditions:

	Pressure	
Temperature	1 atm	2 atm
253 K	Gaseous / Non-gaseous	Gaseous / Non-gaseous
283 K	Gaseous / Non-gaseous	Gaseous / Non-gaseous

In mixtures of two or more pure substances, each substance establishes its own equilibrium with its gaseous phase and thus has its own vapour pressure (called the **partial vapour pressure**). The **total vapour pressure** of a mixture is the sum of the partial vapour pressures of every component in the mixture.

We can use Raoult's law to calculate partial vapour pressures of each pure substance in a mixture. Naming any particular substance in the mixture as A, **Raoult's law** states that:

$$p_A = \chi_A p_A^*$$

where p_A^* is the partial vapour pressure of A **in its pure form**, p_A is the partial vapour pressure of A **in the mixture**, and χ_A is the **mole fraction** of A (i.e. the number of moles of A expressed as a fraction of the total number of moles of the mixture).

Q18 continues on the next page.

For example, since pure water has a vapour pressure of 3.17 kPa at 298 K, then in a mixture containing 0.50 moles of water and 1.5 moles of ethanol, at 298 K, the **partial vapour pressure** of water will be

$$p_{H_2O} = \frac{0.50}{0.50 + 1.5} \times 3.17\ \text{kPa} = 0.79\ \text{kPa}.$$

At a temperature of 323 K, benzene has a vapour pressure of 36.60 kPa and toluene a vapour pressure of 12.28 kPa

(c) A liquid mixture contains 0.530 mol benzene and 1.12 mol toluene at 323 K. Calculate the following (show all working):

(i) Partial vapour pressure of benzene

(ii) Partial vapour pressure of toluene

(iii) Total vapour pressure of mixture

(d) What is the **mole fraction** of benzene in the **vapour** above the mixture described above?

As mentioned earlier, vapour pressure is temperature-dependent. For small changes in temperature, a crude estimation of the change in vapour pressure can be made. With a known vapour pressure p_b at temperature T_b, the **vapour pressure** p at a **different temperature** T (in Kelvin) is given by the equation:

$$1 - \frac{p_b}{p} = \frac{\Delta_{vap}H}{R(T_b)^2}(T - T_b)$$

where $\Delta_{vap}H$ is the molar enthalpy of vaporisation in joules per mole, and R is the gas constant in joules per Kelvin per mole (see data page on page 2 of this paper).

At atmospheric pressure, the boiling point (T_b) of bromine is 332.4 K, and its molar enthalpy of vaporisation is $\Delta_{vap}H = 29960 \text{ J mol}^{-1}$ (or $\Delta_{vap}H = 29.96 \text{ kJ mol}^{-1}$).

(e) Using the formula given above, calculate (showing all working) the vapour pressure of bromine at:

(i) T = 320 K

(ii) T = 340 K

(f) Using the formula given above, calculate the temperature at which bromine boils if the pressure of the system is raised to twice atmospheric pressure (2.000 atm). Show all working.

Raoult's law and the **dependence of vapour pressure on temperature** can be used to explain why solutes raise the boiling point of the solvent in which they are dissolved. This phenomenon is known as **boiling point elevation**.

For simplicity, we make the sound assumption that solutes mentioned in these problems are not volatile (i.e. the vapour pressure of solutes is always zero).

(g) Calculate the mole fraction of **solute particles** in the two mixtures below. Show all working.

(i) 160.0 g glucose ($C_6H_{12}O_6$) dissolved in 500.0 g of water

(ii) 50.0 g sodium chloride dissolved in 500.0 g of water

(h) Using Raoult's law and the equation that relates vapour pressure to temperature, which of the following solutes (when dissolved in 1 kg of water) would you expect to have a higher boiling point elevation (or do they have the same amount of boiling point elevation)? Give reasons to justify your answer.

(i) 50 g sodium chloride or 50 g sodium bromide

(ii) 1 mole calcium chloride or 1 mole calcium carbonate.

Q18 continues on the next page.

(iii) 0.5 mole acetic acid (CH_3COOH) or 0.75 mole glucose ($C_6H_{12}O_6$).

(j) Raoult's law states that the vapour pressure of the solvent above a solution is proportional to the mole fraction of the solvent. Propose an explanation, at the **molecular level**, why this is so. You may find it helpful to draw a diagram to illustrate your answer.

(k) The equation:

$$1 - \frac{p_b}{p} = \frac{\Delta_{vap}H}{R(T_b)^2}(T - T_b)$$

and Raoult's law can be used to derive an equation for the boiling point elevation, of the form $T - T_b = K\chi$, where χ is the mole fraction of **solute particles** in the solution, T_b is the boiling point of **pure solvent**, and T the boiling point of the **solution**. Perform this derivation below, expressing K in terms of physical constants relevant to the equation.

(l) Hence or otherwise, given that the molar enthalpy of evaporation of water is $\Delta_{vap}H = 40.65 \text{ kJ mol}^{-1}$, estimate the **boiling point** of **EACH** of the **TWO** solutions in question (g). Show all working.

Q19

Ionic compounds, such as $NaC\ell$, dissolve in water to give hydrated Na^+ and $C\ell^-$ ions.

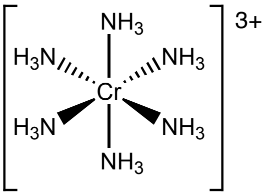
$$NaC\ell\ (s) \xrightarrow{H_2O} Na^+\ (aq) + C\ell^-\ (aq)$$

The compound $[Ag(NH_3)_2]C\ell$ similarly dissolves in water to give a cation $[Ag(NH_3)_2]^+$ (known as a **complex ion**) and the $C\ell^-$ ion.

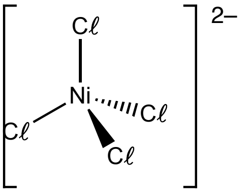
$$[Ag(NH_3)_2]C\ell\ (s) \xrightarrow{H_2O} [Ag(NH_3)_2]^+\ (aq) + C\ell^-\ (aq)$$

A complex ion is a transition metal ion surrounded by **ligands**. Ligands are neutral molecules or ions which behave as Lewis bases, donating an unshared pair of electrons to the metal ion (Lewis acid) to form a covalent metal-ligand bond. The resulting complexes are known as coordination compounds. A square bracket is placed around the formula of the complex ion.

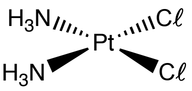
The charge of a complex ion is the sum of the charges on the central metal and on its surrounding ligands. In $[Ag(NH_3)_2]^+$ the charge on the complex ion is +1. The charge on the complex ion can now be used to determine the oxidation state of silver. Because the NH_3 ligands are neutral molecules, the oxidation state of silver must be +1.



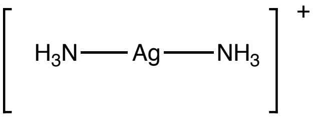
Octahedral



Tetrahedral



Square planar



Linear

The number of atoms directly bonded to the metal atom in a complex ion is called the **coordination number**. The atom of the ligand bound directly to the metal is called the **donor atom**. Nitrogen, for example is the donor atom in the $[Ag(NH_3)_2]^+$ complex ion. The silver ion in $[Ag(NH_3)_2]^+$ has a coordination number of 2. The most common coordination number is six (octahedral geometry), closely followed by 4 (tetrahedral or square planar geometry) then 2 (linear geometry).

(a) What is the oxidation state and coordination number of the central metal in each of the following compounds?

(i) $[Rh(NH_3)_5C\ell](NO_3)_2$

Oxidation state: ______________________________

Coordination number:

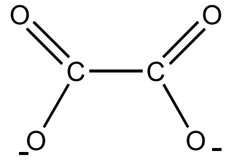
(ii) $Cs_2[NiC\ell_4]$

Oxidation state: ______________________________

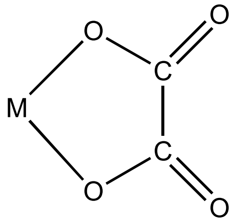
Coordination number:

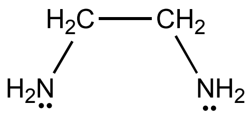
NH_3 is an example of a **unidentate** ligand and has one donor atom which donates one pair of electrons to the metal ion. Other examples of unidentate ligands are the halide ions and CN^-, NO_2^-, OH^-, CO, SCN^- and H_2O.

Bidentate ligands have two donor atoms each of which typically donates one pair of electrons to metal ions. If both donor atoms are bound to the same metal ion the complex is also known as a **chelate**. Three examples are shown on the next page:

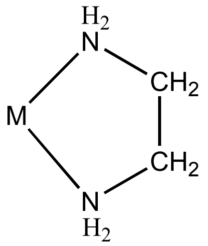


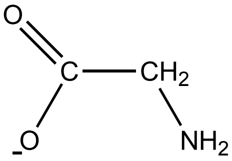
oxalate (**ox**) ion



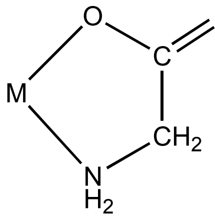


ethylenediamine (**en**)





glycinate (**gly**) ion



When complexes were first discovered and few were known, they were named after the chemist who originally prepared them. A few of these names still persist; for example, the dark red substance $NH_4[Cr(NH_3)_2(NCS)_4]$ is still known as Reinecke's salt. Once the structures of complexes were more fully understood, it was possible to name them more systematically. For example:

$[Co(NH_3)_5C\ell]C\ell_2$ $\overbrace{\text{pentaamminechlorocobalt(III)}}^{\textbf{cation}}\ \overbrace{\text{chloride}}^{\textbf{anion}}$

5 NH_3 ligands

cobalt in +3 oxidation state

$C\ell^-$ ligand

The rules for naming coordination compounds are:

(i) The cation is named before the anion.

(ii) When naming the complex ion, the ligands are named **as prefixes** (i.e. before the metal ion).

(iii) When naming anionic ligands ($C\ell^-$) an **o** is added to the root name of the anion. For example the anionic ligand, $C\ell^-$, would be named as chloro. Neutral ligands retain the name of the molecule, except for the following: H_2O is aqua, NH_3 is ammine and CO is carbonyl.

(iv) The prefixes mono-, di-, tri-, tetra-, penta-, hexa-, etc, are used to denote the number of simple (typically unidentate) ligands; bis-, tris-, tetrakis-, etc for more complicated (bidentate) ligands or ones that already contain di-, tri, etc.

(v) Ligands are named in alphabetical order. Prefixes do not affect the order.

(vi) The oxidation state of the metal ion is designated by a Roman numeral in parentheses after the name of the metal ion.

Q19 continues on the next page.

(vii) Negatively charged complex ions have the suffix **–ate** added to the name of the metal – usually that from which the atomic symbol is derived. For example: nickel becomes nickelate, iron becomes ferrate and copper becomes cuprate.

(b) Give the formula for each of the following compounds.

(i) aquacyanobis(ethylenediamine)cobalt(III) chloride

(ii) sodium diaquadioxalatoruthenate(III)

(c) Give the name of each of the following coordination compounds.

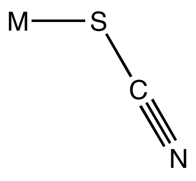
(i) $[Cr(H_2O)_4C\ell_2]C\ell$

(ii) $K_2[Ni(CN)_4]$

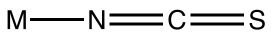
(iii) $[Co(en)_3]C\ell_3$

Structural isomerism

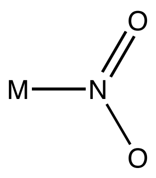
Many different types of structural isomerism are known in coordination chemistry. **Linkage isomerism** is an interesting type that arises when a particular ligand is capable of coordinating to a metal in two different ways. Ligands of this type are called **ambidentate** ligands. The nitrite ion, NO_2^-, for example, can coordinate through either a nitrogen or oxygen atom. When it coordinates through the nitrogen atom, the NO_2^- ligand is called *nitro*; when it coordinates through the oxygen atom, it is called *nitrito*. Another ligand capable of coordinating through either of two donor atoms is the thiocyanate ion, SCN^-, whose potential donor atoms are N (*isothiocyanato*) and S (*thiocyanato*). When writing chemical formula of coordination compounds containing ligands of this type, the symbol for donor atom of the ambidentate ligand is written first. For example, $[Co(NH_3)_5(NO_2)]C\ell$, for N-bound NO_2^- and $[Co(NH_3)_5(ONO)]C\ell$ for O-bound NO_2^-.



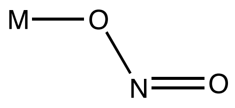
thiocyanato



isothiocyanato



nitro



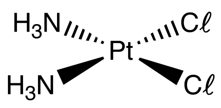
nitrito

Stereoisomerism

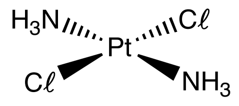
Stereoisomers have the same chemical bonds but different spatial arrangements. The term covers geometric isomers and optical isomers.

Geometric isomerism

In the square planar complex $[Pt(NH_3)_2C\ell_2]$, for example, the chloro ligands can be either adjacent or opposite to each other as shown on the next page.



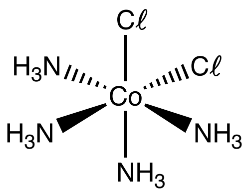
cis



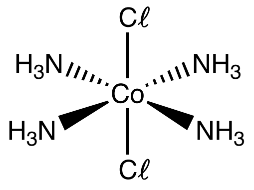
trans

Geometric isomers have different properties, such as colour, solubility and melting points. They may also have very different chemical reactivities. For example, *cis*-[Pt(NH$_3$)$_2$Cℓ_2], also called *cisplatin*, is effective in the treatment of certain cancers, whereas the trans isomer is ineffective.

Geometric isomerism is also possible in octahedral complexes when two or more different ligands are present. For example, the cis and trans isomers of the tetraamminedichlorocobalt(III) ion are shown below.



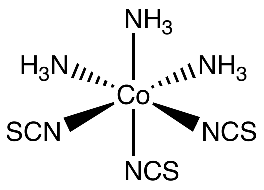
cis



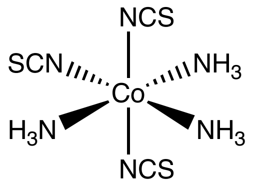
trans

A similar type of isomerism occurs for octahedral complexes when there are two sets of three identical ligands since each trio of donor atoms can occupy either adjacent positions at the corners of an octahedral face (**fac**ial) or positions around the meridian of the octahedron (**mer**idional).

For example, *fac*- and *mer*-[Co(NCS)$_3$(NH$_3$)$_3$]:



fac



mer

(d) Consider the following coordination compound: [Pd(NCS)$_2${P(CH$_3$)$_3$}$_2$] where P(CH$_3$)$_3$ is a neutral, unidentate ligand called trimethylphosphine.

(i) Name the above compound.

(ii) Indicate how many geometric isomers are possible and sketch the structure of each of them.

More space available on the next page.

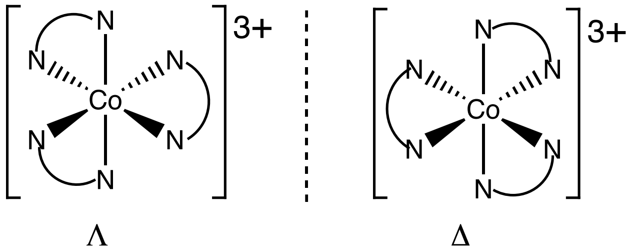
(iii) Would you expect the above compound to exhibit linkage isomerism? If so, name the linkage isomer and sketch **one** of its stereoisomers.

Optical isomerism

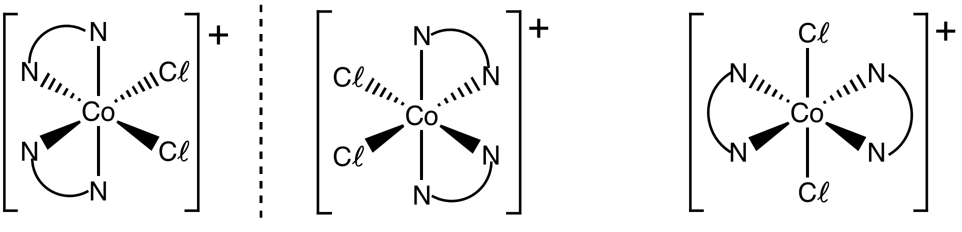
Optical isomers, called **enantiomers**, are mirror images that cannot be superimposed on each other – like a left and a right hand.

Enantiomers are said to be optically active because when plane polarised light is passed through a solution containing one of them the plane is rotated. The **dextrorotatory** [or dextro] isomer causes the plane to rotate to the right (clockwise). That is, it has a positive rotation (+α^o) while the **levorotatory** [or levo] isomer causes the plane to rotate in the opposite direction but having the sae magnitude (–α^o). Enantiomers have the same physical and chemical properties except in the presence of plane polarised light or other optically active compounds. This is an important method of identification.

Enantiomers are called **chiral.** The most common types of chiral transition metal complexes are six-coordinate complexes of the type ML_3 and MX_2L_2 (where L is a bidentate ligand). For example, the complex ion $[Co(en)_3]^{3+}$ has two enantiomeric forms whereas $[CoC\ell_2(en)_2]^+$ has three stereoisomeric forms.



Λ Δ



cis-Λ cis-Δ trans

The enantiomeric species are assigned Λ (lambda) and Δ (delta) configurations on the basis of the helicity of the complexes. A Λ configuration refers to a left-handed helicity. That is, the optical isomer can be viewed as having a left-handed (or anticlockwise) screw into the plane of the page. The Δ configuration has a right-handed helicity.

Non-mirror image stereoisomers are referred to as **diastereoisomers** and, in contrast to enantiomers, do have different physical and chemical properties. Thus, in the case of the complex ion, $[CoC\ell_2(en)_2]^+$, the *cis*-Λ (or *cis*-Δ) isomer and the trans isomer are diastereoisomers.

(e) Draw and name all of the possible isomers of the following complex ion: $[CoBr(NCS)(en)_2]^+$.

(f) What type of structural isomerism could be exhibited by the complex ion in (e) above?

(g) What type of isomerism, if any, could be exhibited by a **four-coordinate** complex of the type $[M(H_2NCH_2CO_2)_2]$? Sketch the isomers.

More space available on the next page.

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Integrity of the Competition

To ensure the integrity of the competition and to identify outstanding students the competition organisers reserve the right to re-examine or disqualify any student or group of students before determining a mark or award where there is evidence of collusion or other academic dishonesty.