AUSTRALIAN SCIENCE INNOVATIONS

Australian Science Olympiads

2021 AUSTRALIAN SCIENCE OLYMPIAD EXAM

CHEMISTRY

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS.

Student Name: ……………………………………………………………………………….

Home Address: ……………………………………………………………………………..

……………………………………………………………………… **Post Code:** …………

Telephone: (……….) …………………………… **Mobile:** ……………………

E-Mail: ………………………………………………… **Date of Birth:** ……/……/……

☐ **Male** ☐ **Female** ☐ **Unspecified** **Year 10** ☐ **Year 11** ☐ **Other:** …….

Name of School: ……………………………………………………… **State:** ……...

Examiners Use Only:

2021 AUSTRALIAN SCIENCE OLYMPIAD EXAM

CHEMISTRY

Time Allowed

Reading Time: 10 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- *Attempt all questions in ALL sections of this paper.*
- Permitted materials: non-programmable, non-graphical calculator, pens, pencils, erasers and a ruler.
- Marks will not be deducted for incorrect answers.

MARKS

▪ SECTION A	15 multiple choice questions	30 marks
▪ SECTION B	3 short answer questions	30 marks each
	Total marks for the paper	120 marks

Integrity of Competition

If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.

DATA

Avogadro constant (N) = 6.022×10^{23} mol^{-1}	Velocity of light (c) = 2.998×10^{8} m s^{-1}
1 faraday = 96 485 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}
Molar volume of ideal gas • at 0 °C and 100 kPa = 22.71 L • at 25 °C and 100 kPa = 24.79 L • at 0 °C and 101.3 kPa = 22.41 L • at 25 °C and 101.3 kPa = 24.47 L	pH = $-\log_{10}[H^+]$ pH + pOH = 14.00 at 25°C $K_a = \{[H^+]\,[A^-]\} / [HA]$ pH = pK_a + $\log_{10}\{[A^-] / [HA]\}$ PV = nRT E = hν
Surface area of sphere A = $4\pi r^2$	c = νλ

Periodic Table of Elements

Key: atomic number / Symbol / atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. Which of the following lists species in order of increasing ionic radius?

   A. Cs^+, Rb^+, Na^+

   B. S^{2-}, Cl^-, K^+

   C. O^{2-}, Na^+, Ba^{2+}

   D. I^-, Cl^-, Br^-

   E. Sr^{2+}, Rb^+, Br^-

2. Which of the following pairs of compounds will form a precipitate when 0.1 mol L^{-1} solutions of each are mixed?

   A. $AgNO_3$ and $Ba(NO_3)_2$

   B. K_2SO_4 and $Cu(NO_3)_2$

   C. $Ca(NO_3)_2$ and KBr

   D. NaOH and $CuCl_2$

   E. $CuCl_2$ and NH_4NO_3

3. A component of diesel fuel is the hydrocarbon $C_{12}H_{24}$, with density 0.790 g mL^{-1}. What volume of CO_2 (measured at 25 °C and 100 kPa) is produced from the complete combustion of 2.00 L of $C_{12}H_{24}$ in excess oxygen?

   A. 2.79 L

   B. 3.53 L

   C. 1400 L

   D. 2790 L

   E. 3530 L

4. Which of the following compounds has a trigonal pyramidal geometry?

   A. NCl_3

   B. CH_2Cl_2

   C. $COCl_2$

   D. CH_4

   E. BCl_3

5. When the given amounts of each reagent are mixed together, which of the following will release the **largest** mass of CO_2?

   A. 0.3 mol $CuCO_3$ and 0.1 mol H_2SO_4

   B. 0.2 mol $CuCO_3$ and 0.3 mol HCl

   C. 0.2 mol $CuCO_3$ and 0.2 mol H_2SO_4

   D. 0.3 mol $CuCO_3$ and 0.3 mol HCl

   E. 0.1 mol $CuCO_3$ and 0.3 mol H_2SO_4

   F. 0.1 mol $CuCO_3$ and 0.2 mol HCl

6. Biological tissue samples are often stained with dyes, which are coloured organic salts.
   - Basic dyes consist of a coloured cation and a colourless anion.
   - Acidic dyes consist of a coloured anion and a colourless cation.

   Which of the following dyes are acidic? Select all that apply.

   A. $C_{21}H_{22}N_3Cl$

   B. $C_{25}H_{33}N_2O_2Cl$

   C. $C_{16}H_{17}N_2ClS$

   D. $C_{19}H_{17}N_2NaO_5S$

   E. $C_{33}H_{43}N_3Na_2O_8S_2$

7. What is the total number of valence electrons in the PO_2^{3-} ion?

A. 15

B. 17

C. 20

D. 30

E. 34

8. Which of the following molecules contains 29.67% sulfur by mass?

A. SF_4

B. SO_2Cl_2

C. $SOCl_2$

D. SF_6

E. S_2F_{10}

9. Which of the following lists substances in order of increasing boiling point?

A. CO_2, PCl_3, CaO

B. PCl_3, CaO, CO_2

C. CaO, CO_2, PCl_3

D. CaO, PCl_3, CO_2

E. CO_2, CaO, PCl_3

F. PCl_3, CO_2, CaO

10. First ionisation energy is defined as the energy required to remove one mole of electrons from one mole of gaseous ions. Which of the following lists elements in order of increasing first ionisation energy?

A. C, F, N, Li

B. C, N, Li, F

C. Li, C, N, F

D. Li, N, F, C

E. F, N, C, Li

F. F, Li, N, C

11. How many atoms are present in a 1.0 kg sample of C_2H_4O?

A. 1.4×10^{22}

B. 9.6×10^{22}

C. 1.4×10^{25}

D. 9.6×10^{25}

E. 9.6×10^{28}

12. Acrylonitrile (C_3H_3N) can be synthesised industrially according to the following chemical equation:

$$2\ C_3H_6(g) + 2\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ C_3H_3N(g) + 6\ H_2O(g)$$

When 100 kg of C_3H_6, 50 kg of NH_3 and 125 kg of O_2 are mixed, which of these reactants is present in excess? **Select all that apply.**

A. C_3H_6

B. NH_3

C. O_2

13. Which of the following is both an empirical formula and a molecular formula?

A. C_3F_6

B. C_3F_8

C. C_4F_6

D. C_4F_8

E. C_4F_{10}

14. A 1.620 g of **X**F_6 can be produced from 1.000 g of element **X**.

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

A. W

B. Se

C. Mo

D. Rh

E. U

15. Of the following elements, which has the highest **third** ionisation energy?

A. Ar

B. Si

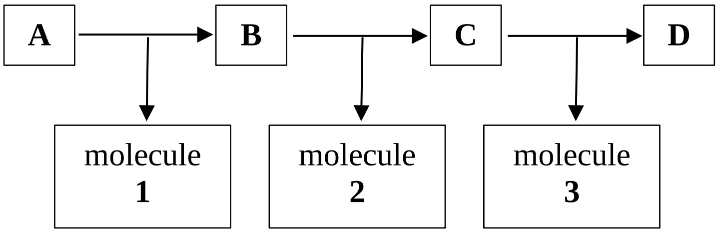
C. Mg

D. Al

E. Cl

Question 16

Thermogravimetric analysis involves measuring the mass of a sample as it is heated. Compound **A** decomposes with increasing temperature to give a sequence of compounds **B**, **C** and **D**, all of which contain calcium. At each stage, a small molecule is also given off (denoted molecules 1, 2 and 3 respectively), which results in the mass of each successive compound being smaller.



The mass of each compound, expressed as a percentage of the original mass of **A**, is recorded in the table below.

Compound	Percentage of original mass of **A** remaining
A	100.0
B	87.67
C	68.50
D	38.38

It is known that compound **B** is calcium oxalate, CaC_2O_4.

(a) Calculate the molar mass of compound **A**.

MM(compound A) = 100/87.67 × 128.1 = 146.1 g mol^{-1}

(b) Calculate the molar mass of molecule **1**.

18.0 g mol^{-1}

(c) Identify the formula of molecule **2**.

MM(molecule 2) = 28.0 g mol^{-1}, so molecule 2 = CO.

(d) Identify the formula of Compound **C**.

$CaCO_3$

(e) Identify the formula of Compound **D**.

CaO

A solution is prepared by dissolving 1.946 g of oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$, molar mass 126.068 g mol^{-1}) in water and making the solution up to 250.0 mL in a volumetric flask.

(f) Calculate the concentration of the oxalic acid solution (in mol L^{-1}).

n($H_2C_2O_4{\cdot}2H_2O$) = 1.946 g / 126.068 g mol^{-1} = 0.01544 mol
[$H_2C_2O_4$] = 0.01544 mol / 0.2500 L = 0.06174 mol L^{-1}

Oxalic acid reacts with sodium hydroxide to produce sodium oxalate and water, according to the following chemical equation:

$H_2C_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$

20.00 mL of the oxalic acid solution above requires 18.57 mL of a sodium hydroxide solution for complete reaction.

(g) Calculate the concentration of the sodium hydroxide solution (in mol L^{-1}).

n($H_2C_2O_4$) = 0.06174 mol L^{-1} × 20.00 mL = 1.235 mmol
n(NaOH) = 2 × 1.235 mmol = 2.470 mmol
[NaOH] = 2.470 mmol / 18.57 mL = 0.1330 mol L^{-1}

The ammonium ion content of a salt can be determined using the following procedure. A 1.988 g sample of an ammonium salt is placed in a flask and heated with 50.00 mL of 0.5493 mol L^{-1} potassium hydroxide solution (a known excess). The ammonium and hydroxide ions react to produce water and ammonia, which is expelled from the flask by evaporation:

$NH_4^+(aq) + OH^-(aq) \rightarrow H_2O(l) + NH_3(g)$

The potassium hydroxide remaining in the flask after all of the ammonia is expelled is determined with 0.1032 mol L^{-1} hydrochloric acid, 23.89 mL of which is required for complete reaction.

(h) Calculate the amount (in mol or mmol) of hydrochloric acid added.

n(HCl) = 0.1032 mol L^{-1} × 23.89 mL = 2.465 mmol (= 0.002465 mol)

(i) Calculate the amount (in mol or mmol) of potassium hydroxide added in the original 50.00 mL sample.

n(KOH) = 0.5493 mol L^{-1} × 50.00 mL = 27.47 mmol (= 0.02747 mol)

(j) Calculate the amount (in mol or mmol) of ammonium ions in the 1.988 g ammonium salt sample.

n(NH_4^+) = 27.47 mmol – 2.465 mmol = 25.00 mmol (= 0.02500 mol)

(k) Calculate the percentage by mass of ammonium ions in the 1.988 g ammonium salt sample.

$m(NH_4^+)$ = 0.02500 mol × 18.042 g mol^{-1} = 0.4510 g
%(NH_4^+) = 0.4510 g / 1.988 g ×100 = 22.69%

In the absence of volumetric glassware, it is possible to use only mass measurements to determine the composition of solutions.

KHP ($KC_8H_5O_4$) is an acid commonly used in such determinations.

(l) Calculate the molar mass of KHP (in g mol^{-1})

204.22 g mol^{-1}

20.58 g of KHP ($KC_8H_5O_4$) is dissolved in water, giving a solution with a mass of 118.48 g.

(m) Calculate the mass of water (in g) that must have been added to the KHP to make the 118.48 g solution.

$m(H_2O)$ = 118.48 – 20.58 = 97.90 g

A solution of sodium hydroxide is also prepared. 4.471 g of this sodium hydroxide solution reacts completely with 5.979 g of the KHP solution above. Sodium hydroxide reacts in a 1:1 mole ratio with KHP.

In a similar reaction, 4.359 g of the sodium hydroxide solution reacts completely with a 5.925 g sample of vinegar (containing acetic acid, CH_3COOH). Sodium hydroxide reacts in a 1:1 mole ratio with acetic acid.

(n) Calculate the mass (in g) of the KHP solution required to react completely with 4.359 g of the sodium hydroxide solution

m(KHP solution) = 4.359 g / 4.471 g × 5.979 g = 5.829 g

(o) Calculate the amount of pure KHP (in mol or mmol) required to react completely with 4.359 g of the sodium hydroxide solution.

m(pure KHP) = 5.829 g × 20.58 g / 118.48 g = 1.013 g
n(KHP) = 1.013 g / 204.22 g mol^{-1} = 0.004958 mol (= 4.958 mmol)

(p) Calculate the percentage by mass of acetic acid present in the vinegar sample.

m(acetic acid) = 0.004958 mol × 60.052 g mol^{-1} = 0.2977 g
%(acetic acid) = 0.2977 g / 5.925 g × 100 = 5.025%

(q) If the density of the sodium hydroxide solution is 1.045 g mL^{-1}, calculate the concentration of the sodium hydroxide solution (in mol L^{-1}).

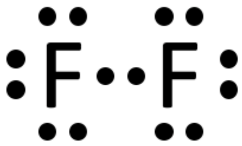
m(pure KHP) = 5.979 g × 20.58 g / 118.48 g = 1.039 g
n(KHP) = 1.039 g / 204.22 g mol^{-1} = 0.005085 mol (= 5.085 mmol)
n(NaOH) = 0.005085 mol (= 5.085 mmol)
V(NaOH) = 4.471 g / 1.045 g mL^{-1} = 4.278 mL
[NaOH] = 5.085 mmol / 4.278 mL = 1.189 mol L^{-1}

Question 17

The following question will explore the role symmetry has to play in chemistry, and how it affects the physical and chemical properties of molecules.

We start by revising the basics of Lewis structures.

(a) Draw a correct Lewis structure for F_2.

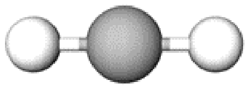
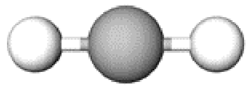
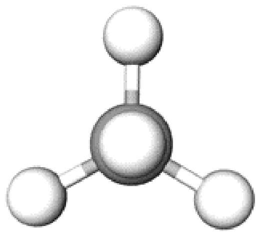
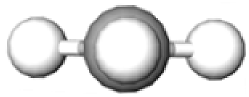
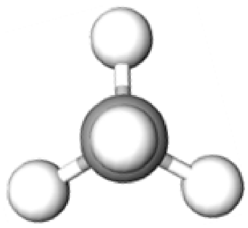
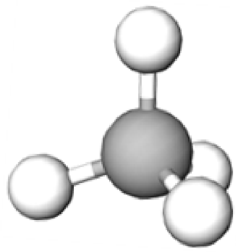
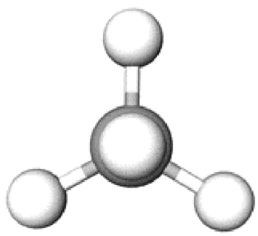
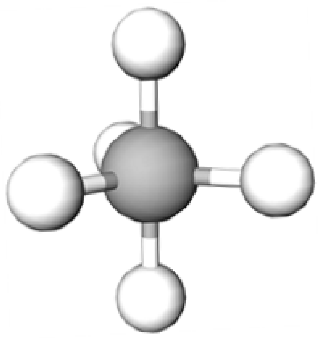
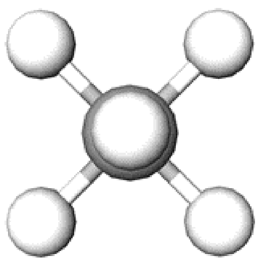
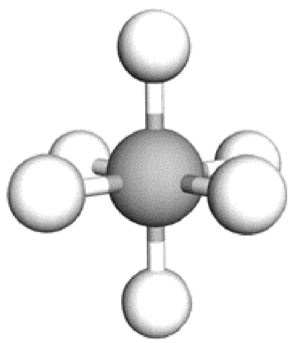


(b) Draw a correct Lewis structure for H_2S.

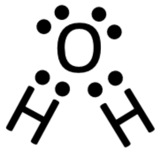
(c) Draw a correct Lewis structure for HCN.

(d) Draw a correct Lewis structure for NO_2^+.

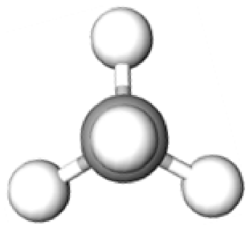
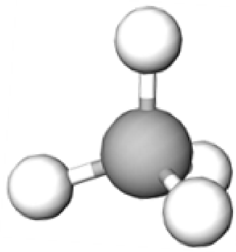
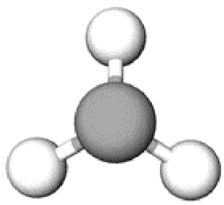
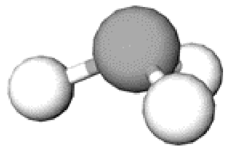
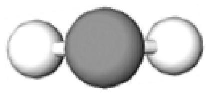
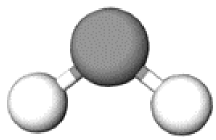
Recall that the electron geometry of a molecule is determined by the number of *domains* (i.e. lone pairs or atoms) around the central atom, as given in the table below.

Number of domains	**Electron Geometry**	**Top View**	**Side View**
2	Linear		
3	Trigonal Planar		
4	Tetrahedral		
5	Trigonal Bipyramidal		
6	Octahedral		

For example, the central oxygen in water (drawn below) is bonded to two hydrogen atoms and contains two electron lone pairs. As such, there are four domains around the central oxygen and its electron geometry is tetrahedral.



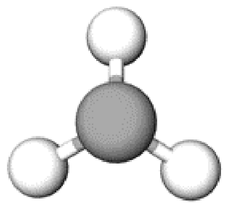
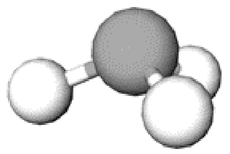
To determine the molecular geometry of a molecule, we only look at the geometry of the atoms surrounding a particular molecule (not including lone pairs). As an example, the possible configurations for 4 domains are shown in the table below.

Number of Domains	**Number of Lone Pairs**	**Molecular Geometry**	**Top View**	**Side View**
4	0	Tetrahedral		
4	1	Trigonal Pyramidal		
4	2	Bent		

For example, since water has two lone pairs and four domains around the central oxygen, it has a bent molecular geometry.

(e) Identify the number of domains and lone pairs bonded to the central atom in each of the following molecular geometries.

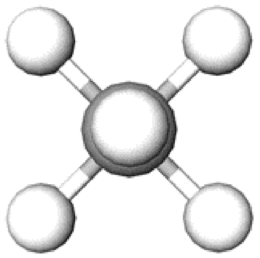
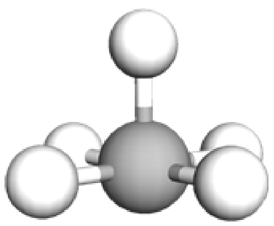
(i)

Top View	**Side View**
	

Domains: **4**

Lone pairs: **1**

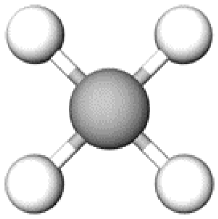
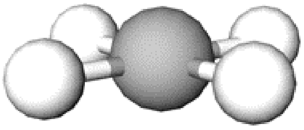
(ii)

Top View	**Side View**
	

Domains: **6**

Lone pairs: **1**

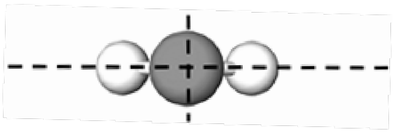
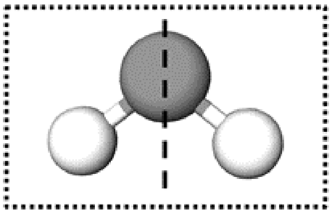
(iii)

Top View	Side View
	

Domains: **6**

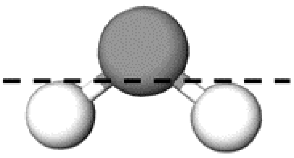
Lone pairs: **2**

Now that we have revised molecular geometries, we can consider the symmetries that molecules may have. The first type of symmetry we will consider is reflectional symmetry. To be precise, a molecule has a mirror plane of symmetry if reflecting the molecule through that plane leaves the molecule exactly the same. For example, water has two planes of symmetry, shown below.

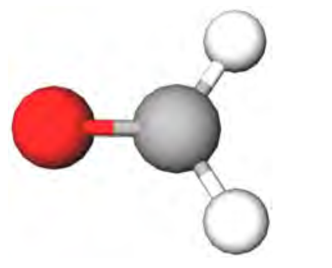
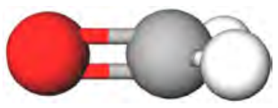
Top View	**Side View**
	

The dotted rectangle indicates a plane of symmetry in the plane of the page.

However, the following is **not** a plane of symmetry of water, since it does not leave the configuration of the atoms the same:

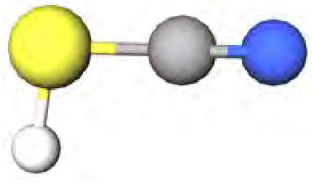
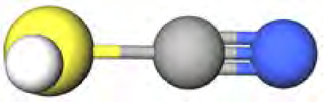


(f) How many planes of symmetry does a CH_2O molecule have?

Top View	Side View
	

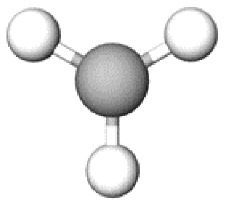
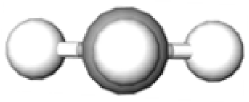
2

(g) How many planes of symmetry does a HSCN molecule have?

Top View	Side View
	

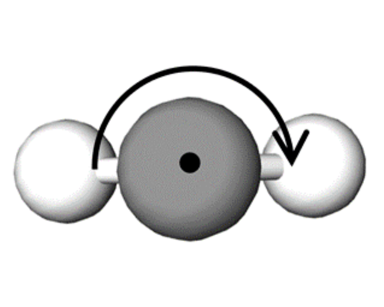
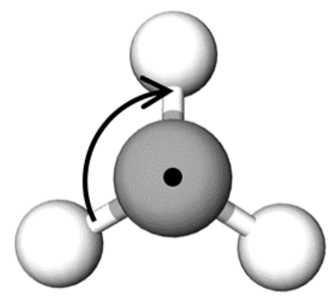
1

(h) How many planes of symmetry does a BF_3 molecule have?

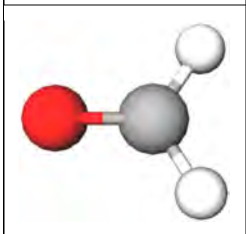
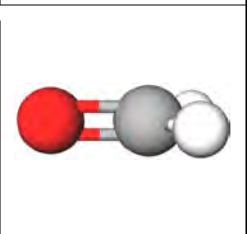
Top View	Side View
	

4

The second type of symmetry we consider is **rotational symmetry**. A molecule has an *n*-fold rotational symmetry about an axis (where $n \geq 2$), if rotating around that axis by an angle $\frac{360°}{n}$ leaves the molecule the same. For example, water has a 2-fold (180°) rotational symmetry about the vertical axis while ammonia (NH_3) has a 3-fold (120°) rotational symmetry about the vertical axis:

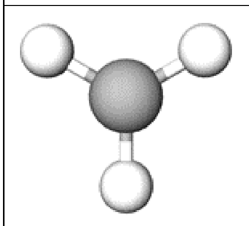
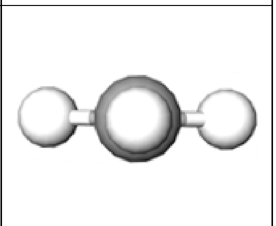
Water (top view)	**Ammonia (top view)**
	

(i) How many axes of symmetry does a CH_2O molecule have?

Top View	**Side View**
	

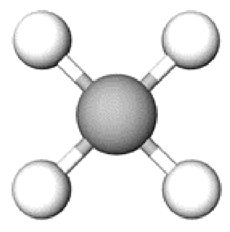
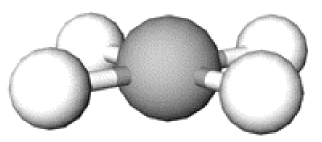
1

(j) How many axes of symmetry does a $AlCl_3$ molecule have?

Top View	**Side View**
	

4

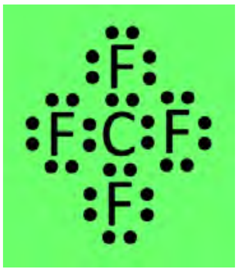
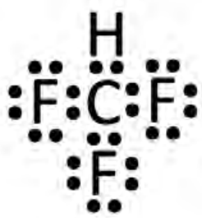
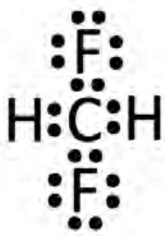
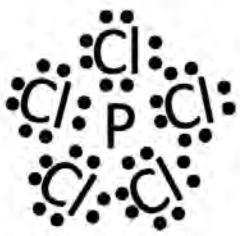
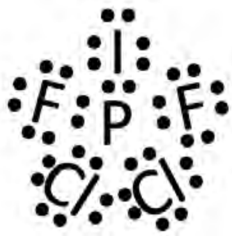
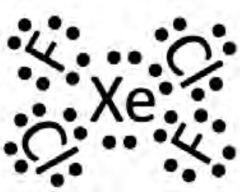
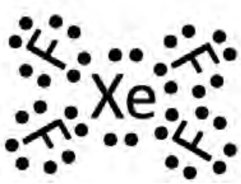
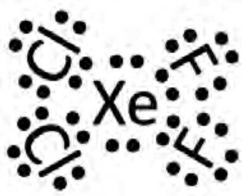
The following XeF_4 molecule has five axes of symmetry.

Top View	**Side View**
	

(k) How many axes of symmetry of each degree, *n*, does XeF_4 have?

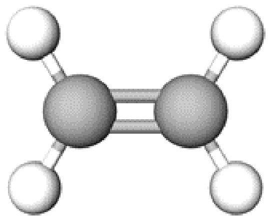
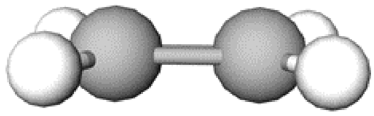
One four-fold axis and four two-fold axes.

(l) Which of the following molecules has four 3-fold axes of symmetry and three 2-fold axes of symmetry?

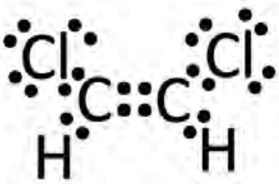
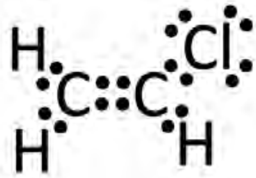
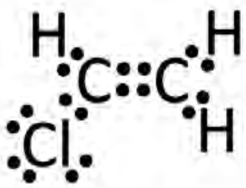
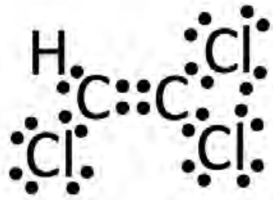
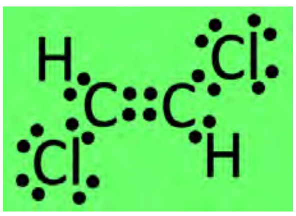
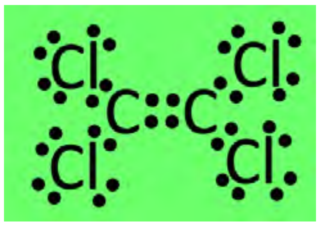
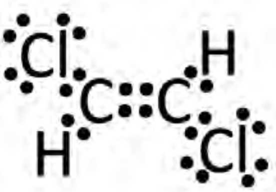
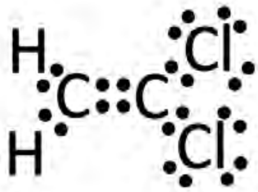
We can now discuss the first application of symmetry to the properties of molecules - dipole moments. A molecule is *non-polar* if it contains two or more different rotational axes of symmetry, *or* if it contains a mirror plane of symmetry perpendicular to a rotation axis. Otherwise, the molecule is *polar*.

First consider ethene, whose molecular geometry is given below. Note that the hydrogen atoms on each side of the double bond cannot rotate relative to each other.

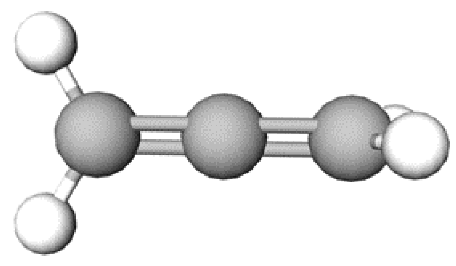
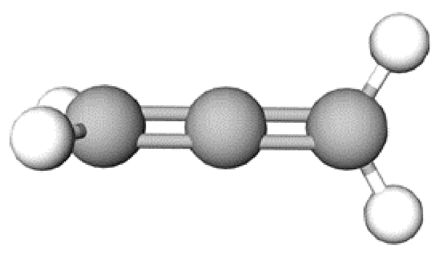
Top View	**Side View**
	

Now consider the following molecules, which have been formed by replacing some of the hydrogen atoms in ethene with chlorine atoms.

Select all of the molecules that are **non**-polar.

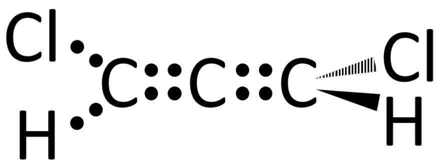
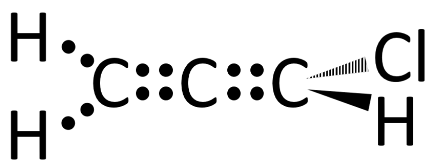
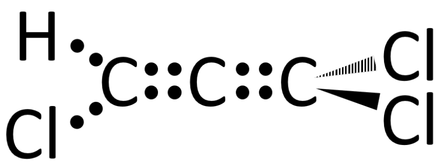
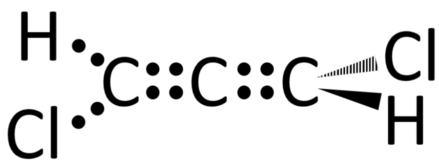
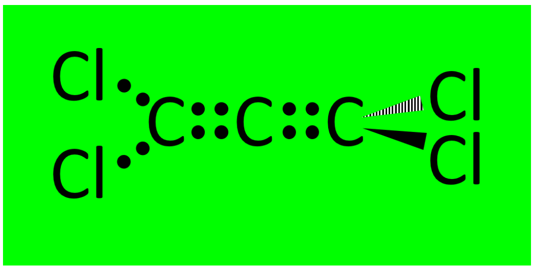
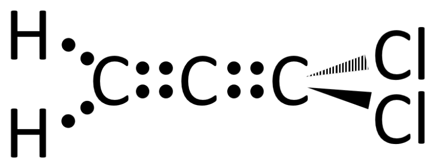
	
	
	
	

Next, consider allene, whose molecular geometry is given below. Note that the hydrogen atoms on each side of the double bond cannot rotate relative to each other.

Top View	**Side View**
	

Now consider the following molecules, which have been formed by replacing some of the hydrogen atoms in allene with chlorine atoms. *Note that in the diagrams below, the wedged line refers to the atoms coming out of the page in the side view, while the dashed line refers to the atoms going into the page.*

Select all of the molecules that are non-polar.

(m) Consider a water molecule. Which of the following factors would turn water into a more polar species?

A. Replacing both H atoms with Cl atoms.

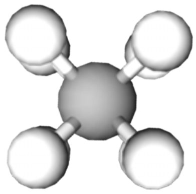
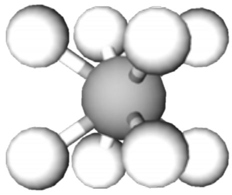
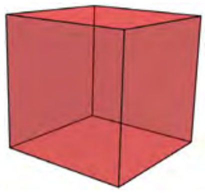
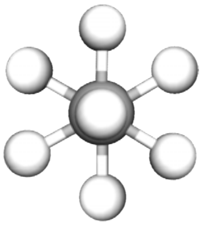
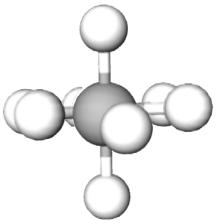
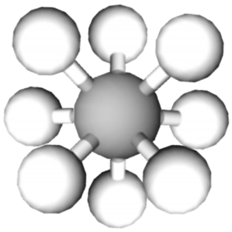
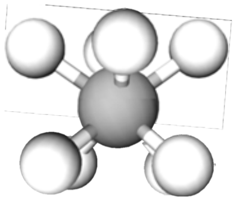
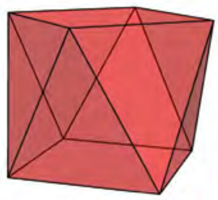
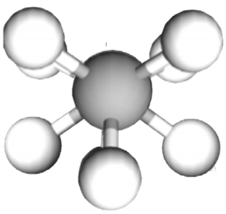
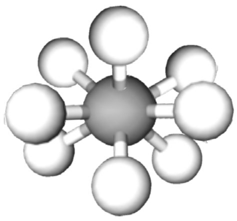
B. Removing one of the H atoms (making OH^-)

C. Replacing the oxygen with a sulfur atom.

D. Decreasing the H-O-H bond angle

At the start of the question, we considered the electron and molecular geometry of molecules consisting of a central atom connected to up to six electron domains. In the next part of the question, we use the symmetry elements discussed above to determine the molecular geometry of XeI_8^{2-}, an ion with eight electron domains around the central xenon atom. Its Lewis structure is provided below:

We consider four possible molecular geometries for XeI_8^{2-}: cubic, hexagonal bipyramidal, square antiprismatic, and bicapped trigonal prismatic, each pictured below.

Molecular Geometry	**Top View**	**Side View**	**Polyhedron**
Cubic			
Hexagonal Bipyramidal			
Square Antiprismatic			
Bicapped Trigonal Prismatic			

Replacing one iodine atom in XeI_8^{2-} with chlorine gives a number of different molecules. How many different molecules would this result in for each of the possible geometries?

Molecular Geometry	**Number of molecules formed**
Cubic	**1**
Hexagonal Bipyramidal	**2**
Square Antiprismatic	**1**
Bicapped Trigonal Prismatic	**4**

4 marks

The following information is given about the structure of XeI_8^{2-}:

- When one of the iodine atoms is replaced with chlorine, giving $XeClI_7^{2-}$, only one molecule is produced.
- When two of the iodine atoms are replaced with chlorine atoms, giving $XeCl_2I_6^{2-}$, none of the molecules are non-polar.

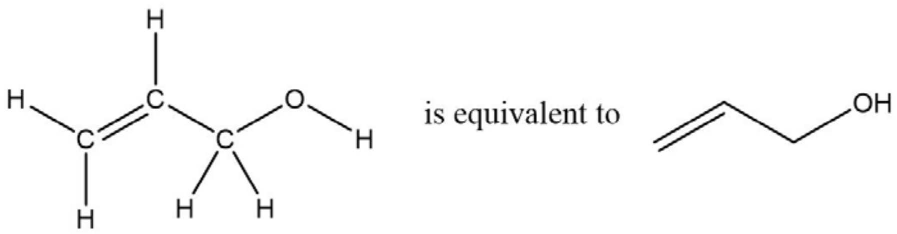
(n) What is the structure of XeI_8^{2-}?

Square Antiprismatic

Question 18

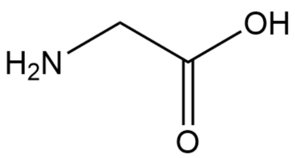
When representing organic compounds, skeletal formula notation is often used for simplicity. In this notation, bonds are still represented by lines, but the symbol for carbon atoms is not used. Hence, the end of a line segment or the meeting point of line segments indicate carbon atoms.

Hydrogen atoms connected to carbon atoms are implied rather than explicitly shown. Any other elements are shown.



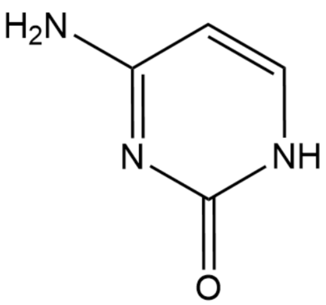
(b) How many hydrogen atoms are present in the following organic compounds?

(i)



5

(ii)

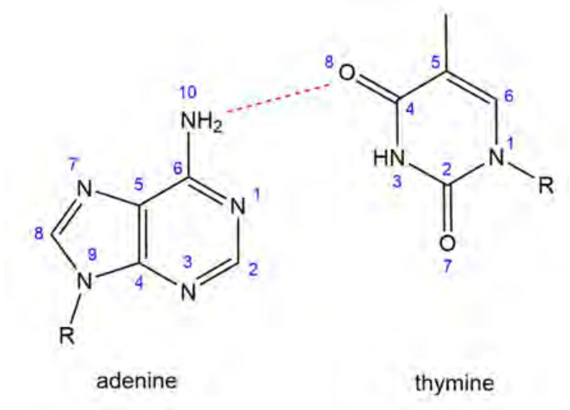


5

Nucleotides are the building blocks of nucleic acid macromolecules such as DNA and other forms of genetic material. Nucleotides have three main components; a five-membered sugar, a phosphate group, and a nucleobase. There are different types of nucleobases which produce different nucleotides.

Adenine and thymine are examples of nucleobases, and their structure is shown below. (The 'R' group is shorthand notation for the rest of nucleotide chain that the base is attached to, which has no relevance to this question.)

One example of an intermolecular interaction between these two nucleobases has been shown with a dashed line:



When identifying hydrogen bond interactions, **a group that can be either a hydrogen bond donor or acceptor, will first and foremost, be a hydrogen bond donor.**

(c) Identify the type of intermolecular force interactions that can occur at the following positions:

Adenine N-1

(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

Adenine C-2

(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

Adenine N-10

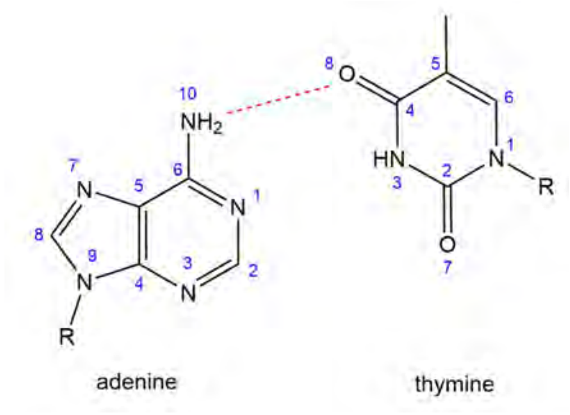
(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

The intermolecular interaction depicted in the previous question (and below) is known as base pairing, and is responsible for holding nucleotide strands together in DNA.

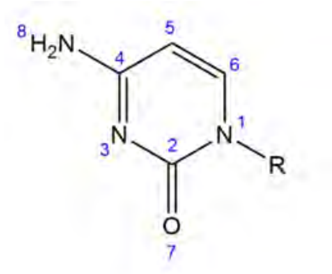


Base pairing is only possible if there are feasible intermolecular interactions between the nucleobases. This depends on their type of intermolecular interactions possible, and whether the groups are close enough to interact. In the diagram, there is a base pairing interaction between adenine N-10 and thymine O-8.

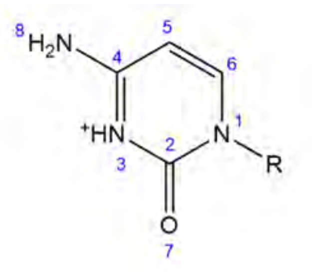
(d) Identify another feasible base pairing interaction between adenine and thymine.

Adenine N-1 — Thymine N-3

Cytosine is another nucleobase, two different forms of which have been shown below, denoted structure **1** and structure **2**.



1



2

Recall that when identifying hydrogen bond interactions, **a group that can be either a hydrogen bond donor or acceptor, will first and foremost, be a hydrogen bond donor**.

(e) Identify the type of intermolecular force interactions that can occur at the following positions:

Structure 1 N-3

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

Structure 2 N-3

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

Structure 1 O-7

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

Structure 1 N-8

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

The two forms of cytosine shown in the previous question differ in their protonation state. Protonation refers to the addition of a proton (H^+) to a molecule.

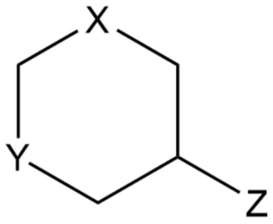
A proton acceptor, A, can exist in one of two different protonation states:

- A
- AH^+

Each protonated species has an associated acid dissociation constant (pK_a), which describes how the pH of its environment will affect its protonation state.

- When pH is equal to pK_a, the two forms will be present in equal concentrations.
- When pH is less than pK_a, the predominant species will be AH^+.
- When pH is greater than pK_a, the predominant species will be A.

Consider the generic organic compound, and its associated pK_a data.



Group	**pK_a**
X	6.5
Y	11.0
Z	3.0

(f) Predict the protonation state that each group will be in at pH 10.

(i) **X:**

☐ X

☐ XH^+

(ii) **Y:**

☐ Y

☐ YH^+

(iii) **Z:**

☐ Y

☐ YH^+

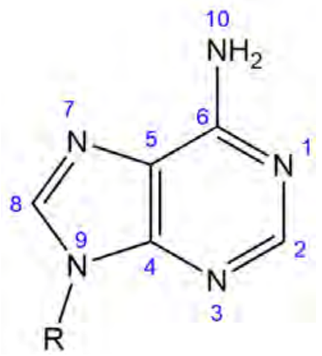
The table below shows pK_a data for N-1 and N-10 positions of the nucleobase, adenine.

Group	**pK_a**
N-1	4.15
N-10	9.80

Multiple forms of adenine are shown below.

(g) Choose the most abundant form of adenine at pH 4.

(i)



(ii)

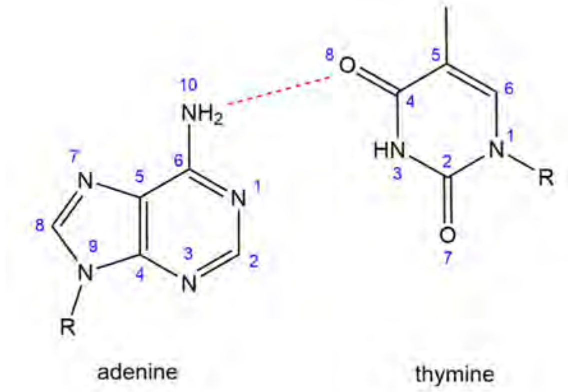
(iii)

(iv)

Adenine regularly base pairs with thymine, by interacting with both:

1. ideal base pairing interactions
2. appropriate protonation states

One example of a correct combination has been provided below:

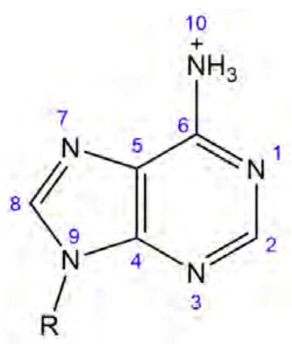


The table below shows pK_a data for N-1 and N-10 positions of adenine.

Group	**pK_a**
N-1	4.15
N-10	9.80

(h) Choose the form or forms of adenine that can interact with thymine and have both:

1. ideal base pairing interactions
2. appropriate protonation states

(i)		(ii)		(iii)	

The table below shows pK_a data for N-1 and N-10 positions of adenine.

Group	**pK_a**
N-1	4.15
N-10	9.80

(i) Select the option that best describes the pH range where both adenine and thymine can form feasible base pairing interactions.

(i) The pH must be less than 4.15.

(ii) The pH must be greater than 4.15 and less than 9.8.

(iii) The pH must be greater than 4.15, with no upper limit.

(iv) The pH must be less than 9.8, with no lower limit.

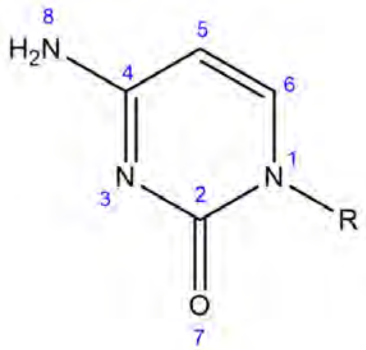
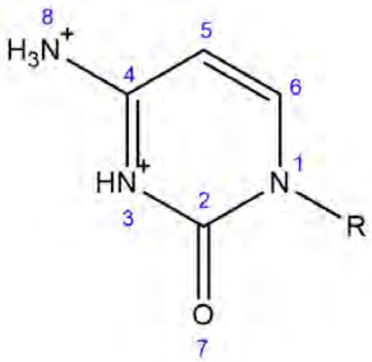
(v) The pH must be greater than 9.8.

The table below shows pK_a data for N-3 and N-8 positions of the nucleobase, cytosine.

Group	**pK_a**
N-1	4.6
N-10	12.2

Multiple forms of cytosine are shown below.

(j) Choose the most abundant form of cytosine at pH 4.

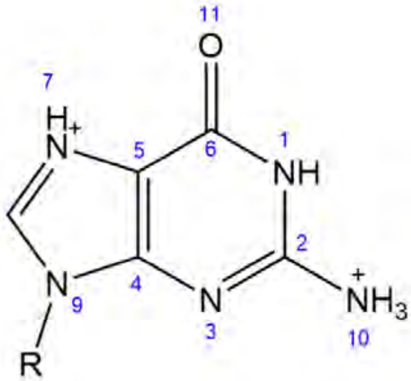
(i)		(ii)	
(iii)		(iv)	

The table below shows pK_a data for N-1, N-7 and N-10 positions of the nucleobase, guanine.

Group	**pK_a**
N-1	3.3
N-7	9.4
N-10	12.6

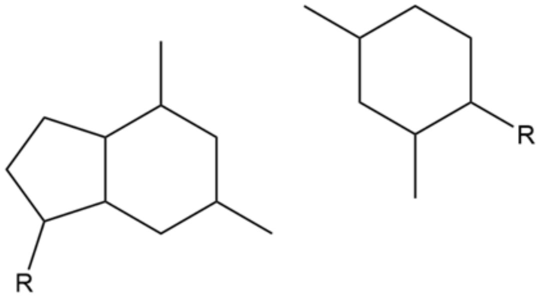
Multiple forms of guanine are shown below.

(k) Choose the most abundant form of guanine at pH 4.

(i) 	(ii) 
(iii) 	(iv) 
(v) 	(vi) 

Cytosine regularly base pairs with guanine.

The template below has been provided to indicate the orientation of the nucleobases when they undergo base pairing (guanine on the left, cytosine on the right). The actual structures of these nucleobases are shown in the question options.

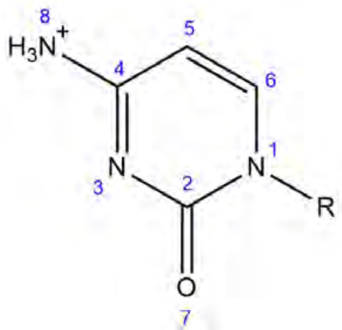
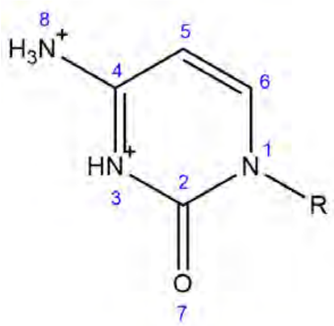
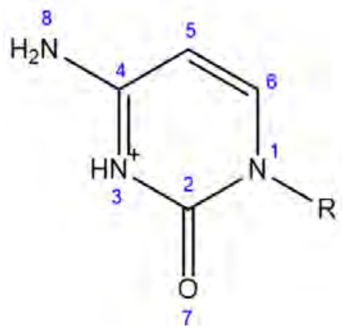


The table below shows pK_a data for N-3 and N-8 positions of cytosine.

Group	**pK_a**
N-3	4.6
N-8	12.2

(l) Choose the form or forms of cytosine that can interact with guanine and have both:

1. ideal base pairing interactions
2. appropriate protonation states

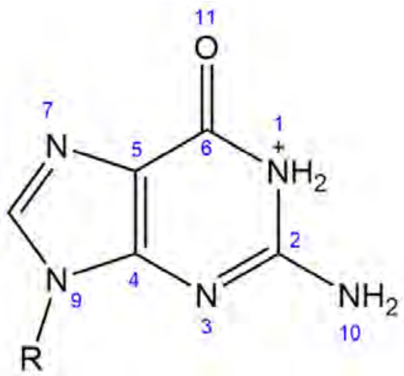
(i)		(ii)	
(iii)		(iv)	

The table below shows pK_a data for N-1, N-7 and N-10 positions of the nucleobase, guanine.

Group	**pK_a**
N-1	3.3
N-7	9.4
N-10	12.6

(m) Choose the form or forms of cytosine that can interact with guanine and have both:

1. ideal base pairing interactions
2. appropriate protonation states

(i)		(ii)	
(iii)		(iv)	
(v)		(vi)	

Complete the following sentence with the appropriate choice.

(n) For cytosine and guanine to form feasible base pairing interactions, the pH must be **greater than**:

(i) No lower limit

(ii) 3.3

(iii) 4.6

(iv) 9.4

(v) 12.2

(vi) 12.6

AND less than:

(i) No upper limit

(ii) 3.3

(iii) 4.6

(iv) 9.4

(v) 12.2

(vi) 12.6

END OF EXAM