Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

G-1

English (Official)

General Instructions

- This exam has 8 problems.
- You may begin working when the **START** signal is given. You have 5 hours to complete the exam.
- All results must be written **in the appropriate answer boxes** with pen on the answer sheets.
- Use the back of the question sheets if you need scrap paper. Remember that **answers written outside the answer boxes will not be graded**. If you run out of space raise your card.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers **only when your work is shown**.
- For questions requiring you to tick the correct box(es), to change your initial answer, shade the check box completely and draw a new box next to it. Tick the box corresponding to your intended answer.
- **Use only the pen and calculator provided.**
- The official English version is available upon request for clarification.
- The supervisors will announce a **30-minute warning** before the **STOP** signal.
- You must **stop your work immediately when the STOP signal is announced**. Failure to stop writing can lead to nullification of your exam.
- You are not allowed to leave your working place without permission. If you need any assistance, raise the corresponding card.
- After the supervisor tells you to do so, put all sheets back into the envelope. Do not seal the envelope.

1																		
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 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Physical constants

Avogadro constant	$N_A = 6.022 \times 10^{23}$ mol^{-1}
Universal gas constant	$R = 8.314$ J K^{-1} mol^{-1}
Faraday constant	$F = 96485$ C mol^{-1}
Planck constant	$h = 6.626 \times 10^{-34}$ J s
speed of light in vacuum	$c = 2.998 \times 10^{8}$ m s^{-1}
mass of electron	$m_e = 9.109 \times 10^{-31}$ kg
charge of electron	$e = 1.602 \times 10^{-19}$ C
standard pressure	$p^0 = 1$ bar $= 10^5$ Pa
atmospheric pressure	$p_{atm} = 101325$ Pa
ionic product of water at 298 K	$K_w = 1 \times 10^{-14}$
Zero of the Celsius scale	0 °C = 273.15 K
Electronvolt	1 eV $= 1.602 \times 10^{-19}$ J
Watt	1 W = 1 J s^{-1}
Coulomb	1 C = 1 A s
Nanometre	1 nm $= 1 \times 10^{-9}$ m
Ångstrom	1 Å $= 1 \times 10^{-10}$ m
metric ton	1 ton = 1000 kg
litre	1 L = 1 dm^3

Consider all gases ideal.

In equilibrium constant calculations, all concentrations are referenced to the concentration of 1 mol dm^{-3}.

Ideal gas law	$PV = nRT$
Energy of a photon	$E = h\nu = \dfrac{hc}{\lambda}$
Gibbs energy and equilibrium constant	$\Delta_r G^\circ = -RT \ln K$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_a + \log_{10} \dfrac{[\mathrm{A}^-]}{[\mathrm{HA}]}$
Average reaction rate	$r = \dfrac{\Delta c}{\Delta t}$
Bragg's Law	$n\lambda = 2d \sin\theta$
Interplanar Spacing Formula	$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$ where h, k, l are integer numbers

Volume of a sphere of radius r	$V = \frac{4}{3}\pi r^3$
Surface area of a sphere of radius r	$S = 4\pi r^2$

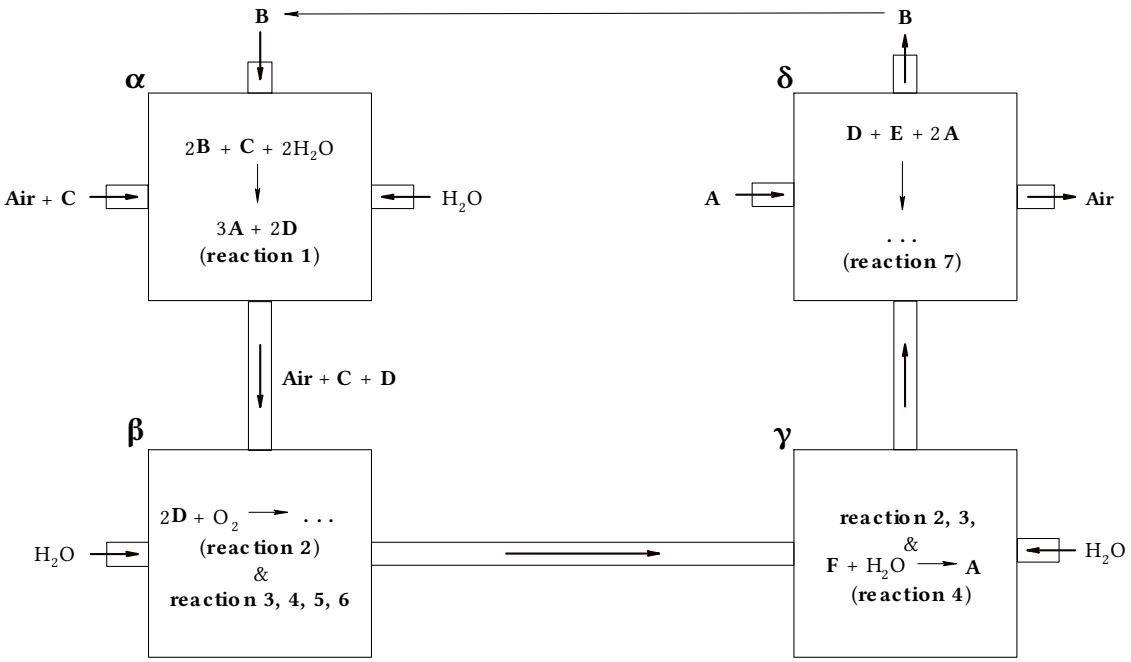
The clouds of Venus

7.5%						
1.1	1.2	1.3	1.4	1.5	1.6	∑
2	2	8	1	3	7	23



In 1983, scientists proposed an elegant model to explain the formation of Venusian clouds involving substance **A**. They compared the formation of substance **A** in the clouds of Venus with its industrial production process.

The scheme for the industrial production of **A** is shown below:



Overall reaction: $2\mathbf{C} + 2H_2O + O_2 \longrightarrow 2\mathbf{A}$

Additional information:

- The four reactors are labelled **α**-**δ**, and the gas flow is shown by arrows on the lines connecting the reactors.
- **A** is produced in reactions **1, 4**, and **6**.
- Crystals of substance **B** decompose in reaction **6**.
- Liquid **A** and a small amount of water remain at the bottom of each reactor.
- **Air** is a mixture of N_2 and O_2 and it is always present in a large excess throughout the process.
- In reactors **β** and **γ**, almost the same processes occur, with the difference that in one of the reactors, white crystals of substance **B** are formed.

Q1.1 (2 points)

In which reaction(s) is substance **B** formed? **Tick** the correct answer(s).

Four of the substances **A–F** are binary compounds.

Q1.2 (2 points)

Tick which of the substances **A–F** are NOT binary compounds.

The following relationship between the molar masses is known:

$M(\mathbf{C}) + M(\mathbf{E}) = M(\mathbf{D}) + M(\mathbf{F})$

B is an acid with a molar mass of 127 g/mol. The mass fraction of oxygen in one of the substances is 53.3%.

Q1.3 (8 points)

Identify the formulae of compounds **A-F**.

However, Venus's atmosphere contains almost no diatomic oxygen. Therefore, one difference between the industrial production process and the corresponding process in the atmosphere of Venus is that atomic oxygen is produced by the irradiation of CO_2 with UV photons:

$CO_2 + h\nu \longrightarrow CO + O$

The experimentally observed wavelength of the UV radiation causing the photodissociation of CO_2 is 167 nm, while a simple calculation based on the C–O bond dissociation energy predicts a threshold wavelength of 227 nm.

Q1.4 (1 point)

Explain why the experimentally observed wavelength differs from the calculated value. **Tick** the correct option(s).

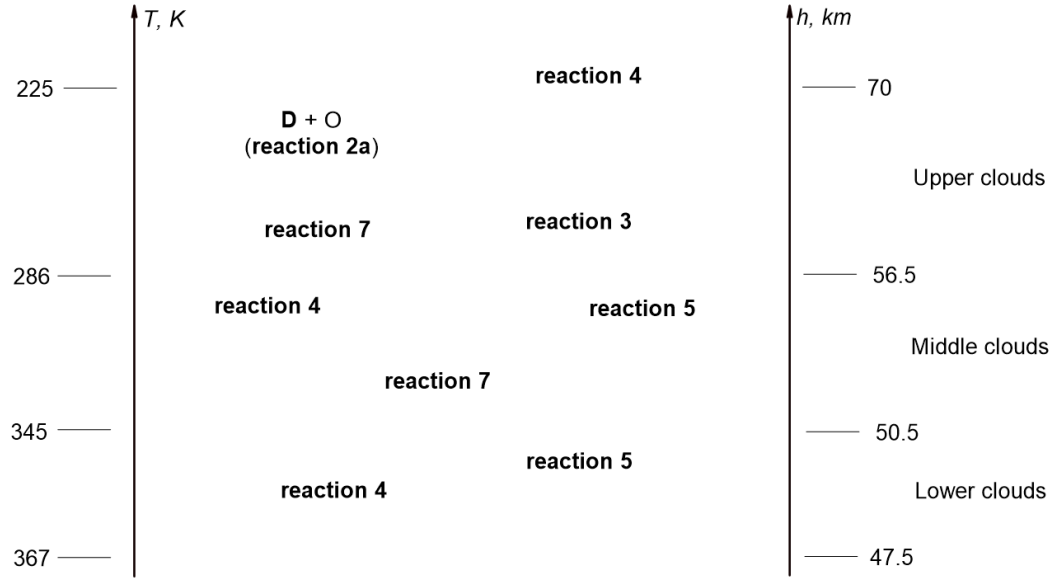
a) Light directed towards the atmosphere of Venus does not contain photons with a wavelength longer than 167 nm.

b) The calculation considers only bond breaking, while photodissociation involves electronic excitation.

c) Nitrogen absorbs part of the UV radiation before it reaches CO_2.

d) The average C–O bond energy is different in gaseous CO_2 than in an isolated bond.

The proposed mechanism for the formation of **A** in the clouds of Venus is shown below. The axes represent atmospheric temperature (T, in K) and altitude (h, in km) respectively:



Compound	A	B	C	D	E	F
T_{melt} / K	283	347	198	110	264	290

The melting points, T_{melt}, do not differ significantly from that under terrestrial conditions. The atmospheric temperature, T (in K) varies linearly with altitude, h (in km) according to the following equation:

$$T = 658 - 6.28h$$

Atmospheric samples from Venus revealed three types of particles present in the clouds: the first type consists of aerosols, the second of liquid droplets of **A**, and the third of solid crystals of various shapes found below an altitude of 60 km.

Q1.5 (3 points)

Tick which of the substances **A-F** could theoretically be components of the solid crystals?

Q1.6 (7 points)

Write equations for reactions **1–7**.

Theoretical examination

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A1-1

English (Official)

The clouds of Venus

7.5%						
1.1	1.2	1.3	1.4	1.5	1.6	∑
2	2	8	1	3	7	23

1.1 (2pt)

☐ Reaction 1 ☐ Reaction 2 ☐ Reaction 3 ☐ Reaction 4 ☐ Reaction 5

☐ Reaction 6 ☐ Reaction 7 ☐ Reaction 8

1.2 (2pt)

☐ A ☐ B ☐ C ☐ D ☐ E

☐ F

1.3 (8pt)

A: _____ B: _____

C: _____ D: _____

E: _____ F: _____

1.4 (1pt)

☐ a)

☐ b)

☐ c)

☐ d)

1.5 (3pt)

☐ A ☐ B ☐ C ☐ D ☐ E

☐ F ☐ G

1.6 (7pt)

1) _____

2) _____

3) _____

4) _____

5) _____

6) _____

7) _____

Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

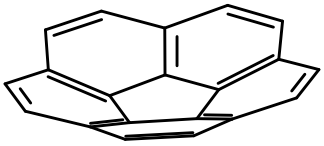
Q2-1

English (Official)

Corannulene

7.5%						
2.1	2.2	2.3	2.4	2.5	2.6	∑
6	32	3	9	12	6	68





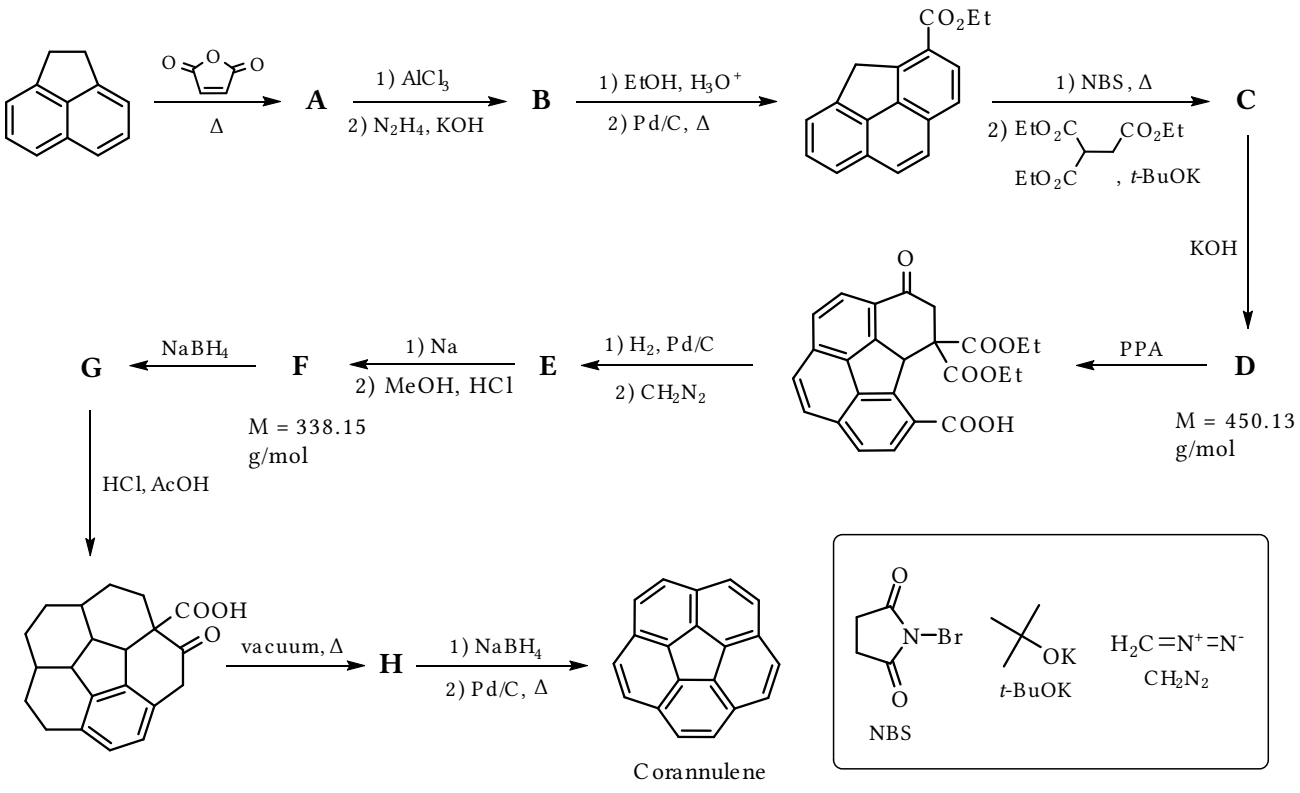
Corannulene is a beautiful, symmetrical organic molecule with a convex shape resembling an Uzbek pilaf dish. Corannulene can be considered a fragment of C_{60} buckminsterfullerene.

Q2.1 (6 points)

Complete the table in the answer sheet with the number (n) of each type of symmetry element possessed by corannulene.

Type	C_2 axis	C_3 axis	C_4 axis	C_5 axis	C_6 axis	Mirror plane (σ)	Inversion centre (i)

The synthesis of corannulene is shown below.



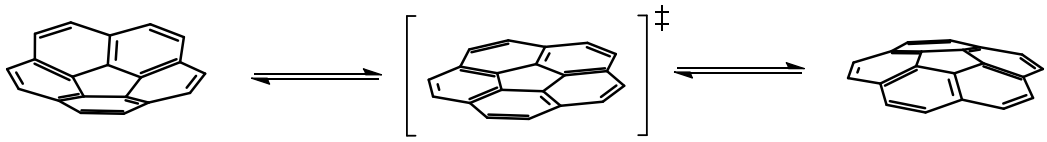
Additional information:

- PPA – Polyphosphoric acid.
- **A** has a naphthalene-like aromatic system and has two stereocentres.
- There is only one singlet in the ^{1}H NMR spectrum of **E** (of 3H intensity); all other signals are multiplets.

Q2.2 (32 points)

Draw the structures of the compounds **A-H**. Stereochemistry is not required.

Corannulene undergoes a bowl-to-bowl inversion as shown below:



Q2.3 (3 points)

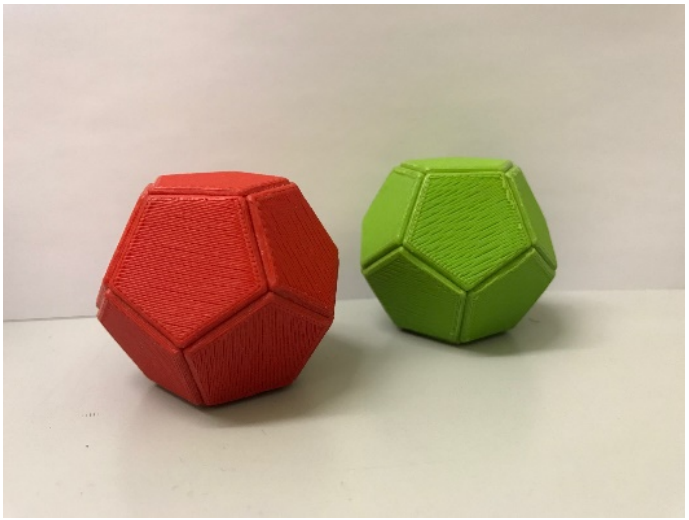
Tick the sign of the ΔG° of the bowl-to-bowl inversion process.

Q2.4 (9 points)

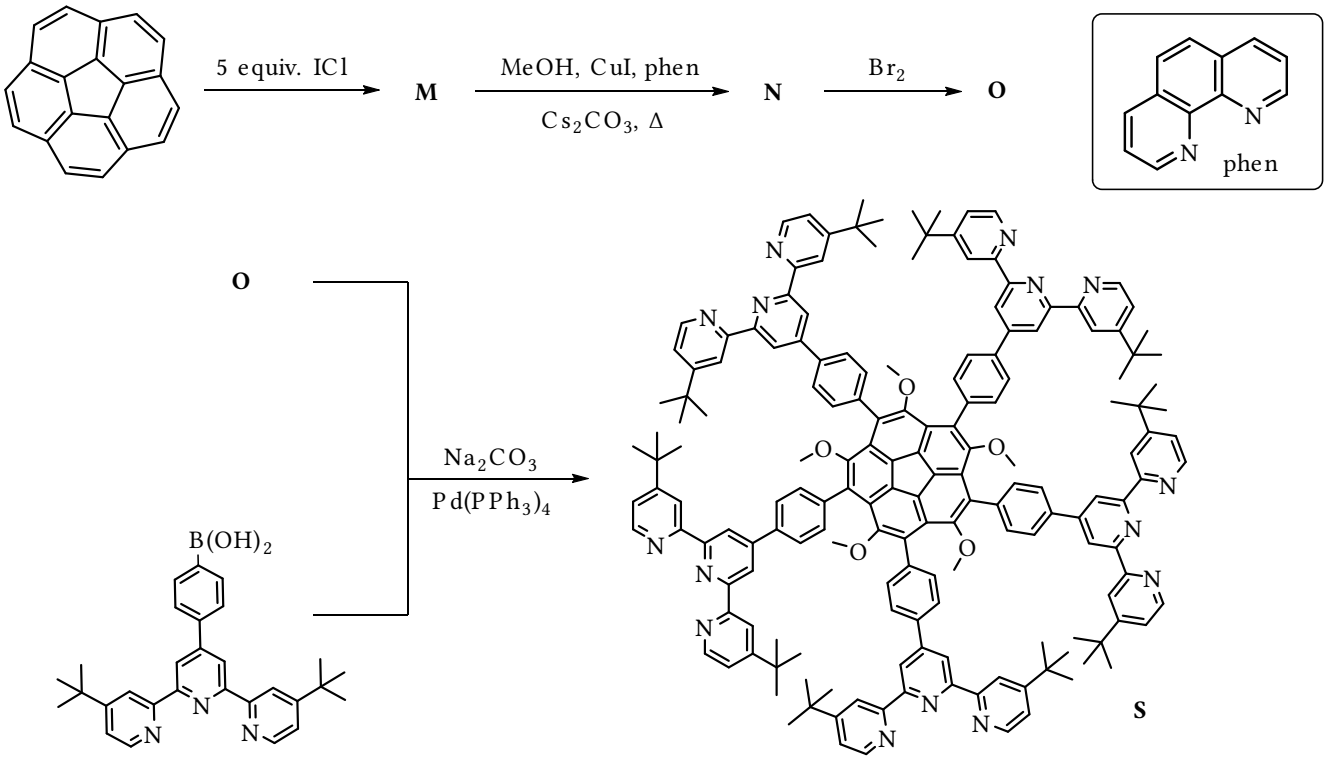
Complete the table in the answer sheet with the number (n) of each type of symmetry element possessed by the transition state structure.

Type	C_2 axis	C_3 axis	C_4 axis	C_5 axis	C_6 axis	Mirror plane (σ)	Inversion centre (i)

A self-assembling capsid with dodecahedral symmetry can be synthesised from corannulene. Models of these are shown below.



Each of the twelve pentagonal faces (tectons) of the capsid is made from one molecule of compound **S**, the synthesis of which is shown below.

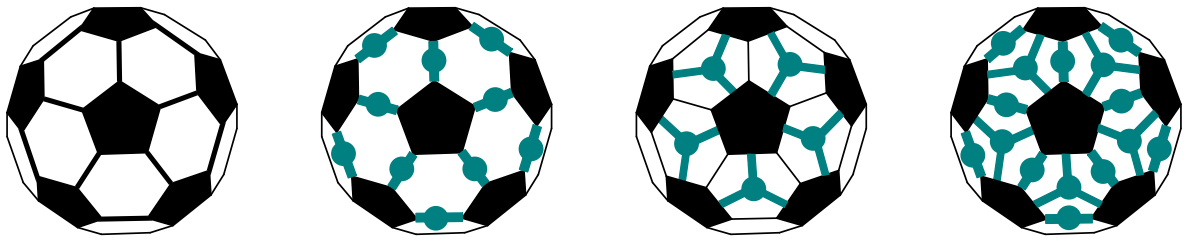


The mass fraction of carbon in **M** is 56.85%.

Q2.5 (12 points)

Draw the structures of compounds **M**-**O**.

Upon addition of Cd^{2+} to **S**, the capsid $[Cd_x\mathbf{S}_{12}]^{Z+}$ is formed. The cadmium ions are six-coordinate within $[Cd_x\mathbf{S}_{12}]^{Z+}$. The structure of the capsid can be schematically compared to a football: the black objects represent the tectons, while the green objects represent the linkers.



a **b** **c** **d**

Q2.6 (6 points)

Determine x and tick which type (**a-d**) the $[Cd_x\mathbf{S}_{12}]^{Z+}$ capsid belongs to.

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A2-1

English (Official)

Corannulene

7.5%						
2.1	2.2	2.3	2.4	2.5	2.6	∑
6	32	3	9	12	6	68

2.1 (6pt)

Type	C_2	C_3	C_4	C_5	C_6	σ	i
n							

2.2 (32pt)

A	**B**
C	**D**
E	**F**
G	**H**

2.3 (3pt)

☐ $\Delta G^\circ > 0$ ☐ $\Delta G^\circ < 0$ ☐ $\Delta G^\circ = 0$

2.4 (9pt)

Type	C_2	C_3	C_4	C_5	C_6	σ	i
n							

2.5 (12pt)

M	**N**
O	

2.6 (6pt)

x = _____

☐ a ☐ b ☐ c ☐ d

Chust at the elementary level

7.5%					
3.1	3.2	3.3	3.4	3.5	∑
5	6	7	7	15	40



Chust knives are the premier Uzbek handmade knives, carefully crafted from high-quality materials. One such material is an alloy containing iron.

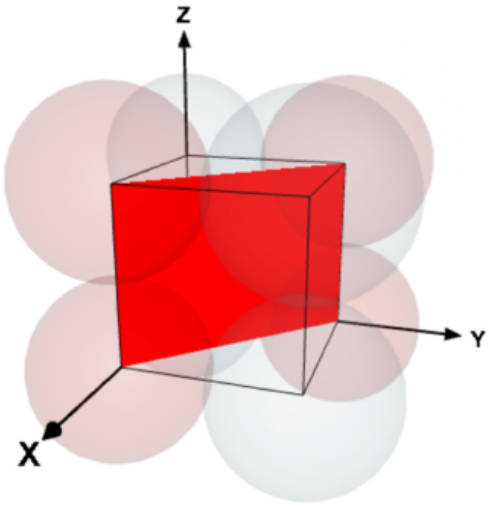
X-ray structural analysis of iron (Cu α-K = 1.5406 Å) shows a peak at 2θ = 44.85°. This corresponds to the body-centred cubic (BCC) lattice plane (110).

Q3.1 (5 points)

Calculate the density of iron.

To understand why chust knives are the best, we need to examine the mechanism of the plastic deformation and hardness.

Miller indices, which can be any integers, are used to designate planes in crystals. To find the section of the axis where it intersects the plane designated by the indices, divide 1 by the numbers in the index, as shown below for a primitive cubic cell:



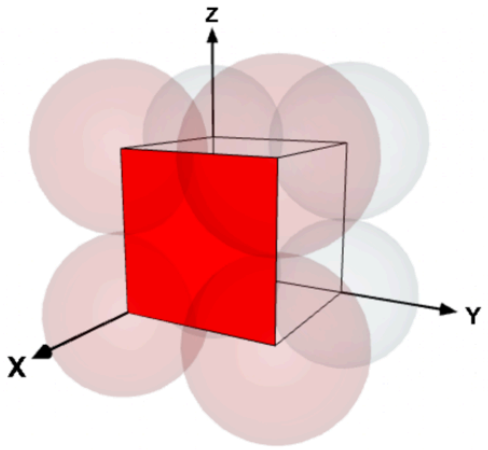
Axes	x	y	z
Miller indices	1	1	0
Reciprocal	1/1 a	1/1 b	∞ c

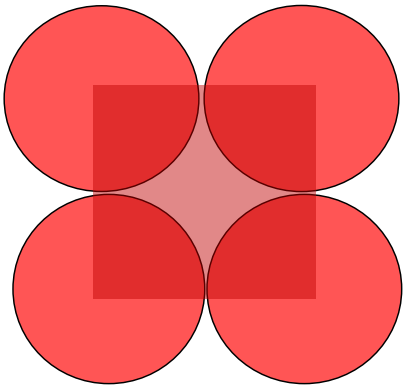
Q3.2 (6 points)

Draw the (021) and (222) planes on a primitive cubic cell.

Plastic deformation is caused by movement within the crystal lattice, known as slip, which generally favours densely packed directions and planes and determines the material's mechanical properties. Slip only occurs in certain planes and directions in crystal lattices.

Consider the calculation of the planar packing density (PPD), the number of atoms per unit of plane area, in a primitive cubic cell with a lattice parameter, a = 1 Å, and for the (100) plane.





$$\mathrm{PPD} = \frac{4 \cdot 1/4}{a^2} = 1\text{Å}^{-2} \tag{1}$$

In this case, the planar density (PPD) is 1 Å^{-2}.

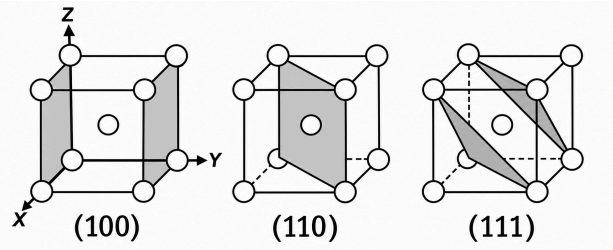


Figure 1. Planes (100), (110), and (111) in a BCC lattice

Q3.3 (7 points)

Calculate the PPD for the planes (100), (110), and (111) (Figure 1) of the BCC lattice of iron at room temperature; and **determine** the plane along which the crystal lattice will slip during deformation, i.e., the densest plane (PPD_{max}).

The hardness of Chust knives is achieved by the hammering shown in the picture. Hammering moves the line vectors, initiating slip across the densest plane. The slip trajectory is determined by the slip vector, which follows the densest line, determined by the linear packing density (LPD). This is also the 1D analogue to the PPD.

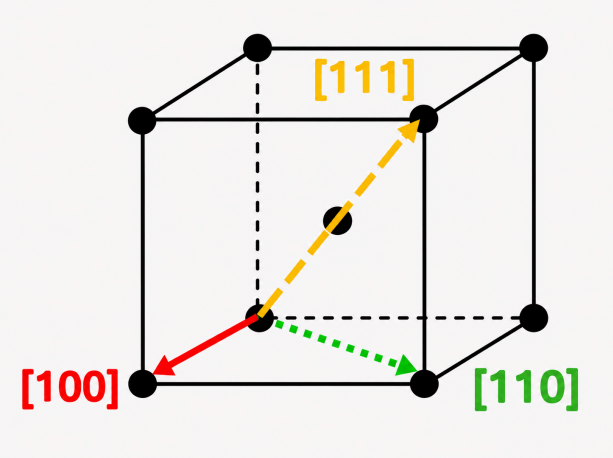


Figure 2. Vectors in the BCC lattice

Q3.4 (7 points)

Calculate the LPD of vectors: [100] – red, [110] – green, and [111] – yellow (Figure 2) of the BCC lattice of iron. **Arrange** the vectors in ascending order of LPD.

Linear dislocations can interact with each other and annihilate the plastic deformation. These interactions can be recorded as chemical reactions. Consider, for example, the reaction:

$$\frac{a}{4}[111] \rightarrow \frac{a}{4}[101] + \frac{a}{4}[010]$$

This dissociation reaction is analogous to chemical dissociation reaction. The criteria for dislocation reactions in crystal lattices, analogous to the laws of mass conservation and thermodynamically favourable energy change, are as follows:

Material balance in each axis: $x: \frac{a}{4}1 = \frac{a}{4}1 + \frac{a}{4}0,\ y: \frac{a}{4}1 = \frac{a}{4}0 + \frac{a}{4}1,\ z: \frac{a}{4}1 = \frac{a}{4}1 + \frac{a}{4}0.$

Frank's energy criterion: ($\sum_{\text{reagents}} b^2_{i,\text{ reagents}} > \sum_{\text{products}} b^2_{j,\text{ products}}$) must be satisfied for the reaction to be energetically favourable:

$$\left(\frac{a}{4}\sqrt{1^2+1^2+1^2}\right)^2 = \left(\frac{a}{4}\sqrt{1^2+0^2+1^2}\right)^2 + \left(\frac{a}{4}\sqrt{0^2+1^2+0^2}\right)^2$$

In this reaction, there is no change in energy, and the reaction does not occur without external force or kinetic activation.

Q3.5 (15 points)

For the reactions below, **complete** the blank boxes and **choose** if the reaction is possible (✓) or not (✗). (Note: $\overline{1}$ means in the negative 1 direction of the corresponding axis).

$\frac{1}{2}[110] \rightarrow \frac{1}{6}[...11] + ...\left[1...\overline{1}\right]$

$\frac{a}{2}[0...1] + \frac{a}{2}\left[10\overline{1}\right] \rightarrow \frac{a}{6}[1...0] + ...\left[...1\overline{2}\right] + \frac{a}{6}[112]$

$\frac{1}{2}[111] + \frac{1}{2}[.....] \rightarrow [100]$

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A3-1

English (Official)

Chust at the elementary level

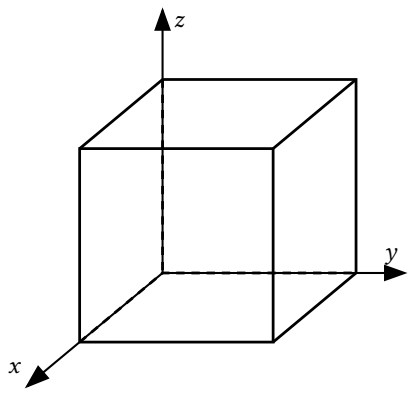
7.5%					
3.1	3.2	3.3	3.4	3.5	∑
5	6	7	7	15	40

3.1 (5pt)

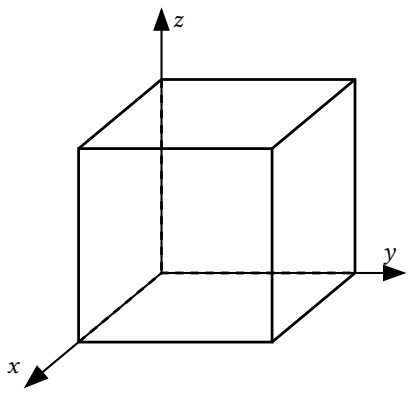
ρ = _____ g/cm³

3.2 (6pt)

(021)



(222)



3.3 (7pt)

PPD(100) = _____ $Å^{-2}$

PPD(110) = _____ $Å^{-2}$

PPD(111) = _____ $Å^{-2}$

PPD(max)= _____ $Å^{-2}$

3.4 (7pt)

LPD[100] = _____ Å^{-1}

LPD[110] = _____ Å^{-1}

LPD[111] = _____ Å^{-1}

_____ < _____ < _____

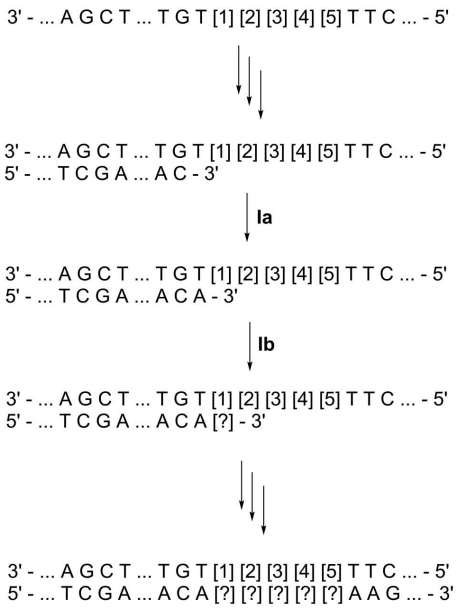
3.5 (15pt)

a/4 [111] → a/4 [101]+a/4 [010]	(✗)
	☐
	☐
	☐

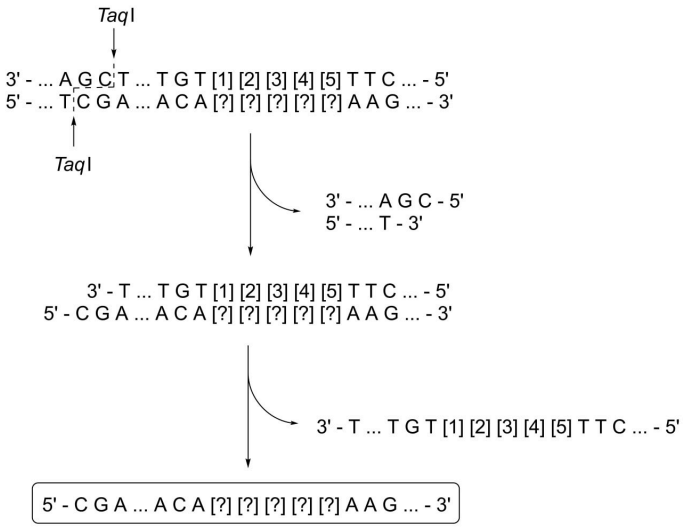
DNA sequencing

7.5%						
4.1	4.2	4.3	4.4	4.5	4.6	∑
5	5	5	6	4	10	35

The ΦX174 bacteriophage was the first DNA-based genome sequenced by Frederick Sanger and his team in 1977. He used the original single-stranded DNA of the bacteriophage as a template, DNA polymerase, and deoxynucleotide triphosphates (dNTPs) for template-directed synthesis. Some steps of this synthesis are given below:



Then he divided the obtained double-stranded DNA into fragments using endonuclease *Taq*I. After denaturation of the double-stranded DNA fragments, the single-stranded daughter DNA molecules were obtained and separated from each other by gel electrophoresis (one of the daughter DNA molecules is shown in the solid line box below):



Q4.1 (5 points)

In the Answer sheet, complete the template of the reaction equation for step Ia. Use abbreviations for the nitrogenous bases and draw the structure of the byproduct formed.

If hypothetically, step Ib is blocked, the oligonucleotide 5'-CGA...ACA-3' with the molecular weight of X g mol^{-1} can be separated as a product by gel electrophoresis. Sanger reduced the concentration of dTTP and added some amount of ddTTP to the reaction mixture. As a result, he obtained the daughter oligonucleotide with a molecular weight of (X + 288.21) g mol^{-1} (in addition to other daughter molecules) as detected by gel electrophoresis (experiment #1).

Q4.2 (5 points)

Identify the composition of this oligonucleotide and decipher nucleotide [1] in the original DNA of the ΦX174.

Hint: Molar masses in this problem ignore the dissociation of acidic or protonation of basic groups. Molar masses of the following molecules (in g mol^{-1}) are: 491.20 for dATP, 507.20 for dGTP, 467.18 for dCTP, and 482.19 for dTTP.

In experiment #1 gel electrophoresis revealed an additional, longer oligonucleotide with a molecular weight of (X + 592.42) g mol^{-1}. In each of experiments #2-4 Sanger reduced concentrations of one of dATP, dGTP, or dCTP and added some amounts of ddATP, ddGTP, and ddCTP, respectively, in the template-directed synthesis. The following daughter oligonucleotides with the molecular weights of (X + 1194.84), (X + 1524.06), (X + 881.62) g mol^{-1}, respectively, were found.

Q4.3 (5 points)

Identify the composition of these oligonucleotides and decipher nucleotides [2]-[5] in the original DNA of the ΦX174.

Other template-directed syntheses were carried out based on the original DNA strand. In all cases, the reaction mixtures contained DNA polymerase, whereas the syntheses were always followed by treatment with endonuclease and denaturation of the obtained duplexes. The composition of the initial reaction mixtures is given below.

Q4.4 (6 points)

Tick those mixtures in which the same pattern of daughter oligonucleotides as considered in Q4.3 could be obtained. The pattern is considered the same when the number of bases is the same and they are in the same sequence. The structure of phosphodiester backbone is ignored.

(a)	Equimolar mixture of dATP, dGTP, dCTP, and dTTP.
(b)	Equimolar mixture of 3 of 4 (dATP, dGTP, dCTP, dTTP) deoxytriphosphates. 4 experiments with 1 different deoxytriphosphate missing in each case performed.
(c)	Equimolar mixture of 3 of 4 (dATP, dGTP, dCTP, dTTP) deoxytriphosphates and the other deoxytriphosphate with a lower concentration. 4 experiments with 1 different deoxytriphosphate at a lower concentration in each case performed.
(d)	Equimolar mixture of 3 of 4 (dATP, dGTP, dCTP, dTTP) deoxytriphosphates also containing ddNTP (contains nitrogenous base other than the 3 triphosphates). 4 experiments with different ddNTP molecules (ddATP, ddGTP, ddCTP, ddTTP) in each case performed.
(e)	Mixture of 4 deoxytriphosphates (dATP, dGTP, dCTP, dTTP) also containing NTP. The concentration of the corresponding dNTP was decreased relative to other deoxytriphosphates. 4 experiments with different NTP molecules (ATP, GTP, CTP, TTP) in each case performed. Note: in this series of experiments, denaturation was followed by alkaline hydrolysis of the phosphodiester bond at the NTP residue.

To improve visualisation of the obtained oligonucleotides on gel electrophoresis ^{32}P labelled dNTP can be used as reagent. One of such reagents, R, with concentration of 0.54 μg/mL demonstrates 10 mCi/mL relative activity. 1 Ci = 3.7 × 10^{10} decays per second; $t_{1/2}$ (^{32}P) = 14.3 days.

Q4.5 (4 points)

Determine the reagent R and show at which position(s) (α, β, γ, or their combination) ^{32}P is located.

Some parts of the ΦX174 DNA encode proteins ‘very densely’. One such fragment with 17 coding nucleotides is shown below:

5’-...	?	?	?	?	?	G	?	?	?	?	A	?	?	?	T	C	T	...-3’

This fragment encodes the C-termini of two different proteins (**D** and **E**) and the N-terminus of protein **J**. The corresponding sequences are:

Encoded protein	**Amino acid sequence**
C-end of **D**	...GlyValMet
C-end of **E**	...Glu
N-end of **J**	MetSer...

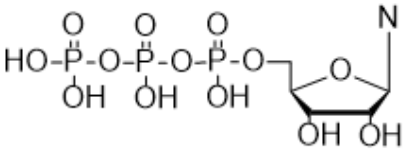
Q4.6 (10 points)

Determine the nucleotide sequence of the above ΦX174 DNA fragment.

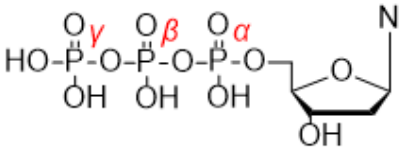
Hint: The amino acid sequence from N- to C-terminal groups corresponds to the DNA direction from 5'- to 3'-ends.

Genetic code

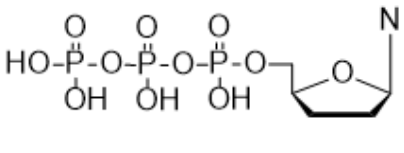
TTT Phe	TCT Ser	TAT Tyr	TGT Cys
TTC Phe	TCC Ser	TAC Tyr	TGC Cys
TTA Leu	TCA Ser	**TAA (STOP)**	**TGA (STOP)**
TTG Leu	TCG Ser	**TAG (STOP)**	TGG Trp
CTT Leu	CCT Pro	CAT His	CGT Arg
CTC Leu	CCC Pro	CAC His	CGC Arg
CTA Leu	CCA Pro	CAA Gln	CGA Arg
CTG Leu	CCG Pro	CAG Gln	CGG Arg
ATT Ile	ACT Thr	AAT Asn	AGT Ser
ATC Ile	ACC Thr	AAC Asn	AGC Ser
ATA Ile	ACA Thr	AAA Lys	AGA Arg
ATG Met (START)	ACG Thr	AAG Lys	AGG Arg
GTT Val	GCT Ala	GAT Asp	GGT Gly
GTC Val	GCC Ala	GAC Asp	GGC Gly
GTA Val	GCA Ala	GAA Glu	GGA Gly
GTG Val	GCG Ala	GAG Glu	GGG Gly



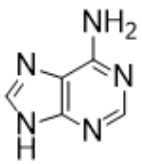
NTP



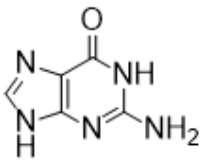
dNTP



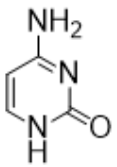
ddNTP



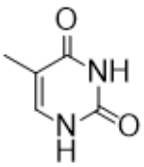
A



G



C



T

N – Nitrogenous base (A, G, C, T)

NTP – Nucleotide triphosphate

dNTP – Deoxynucleotide triphosphate

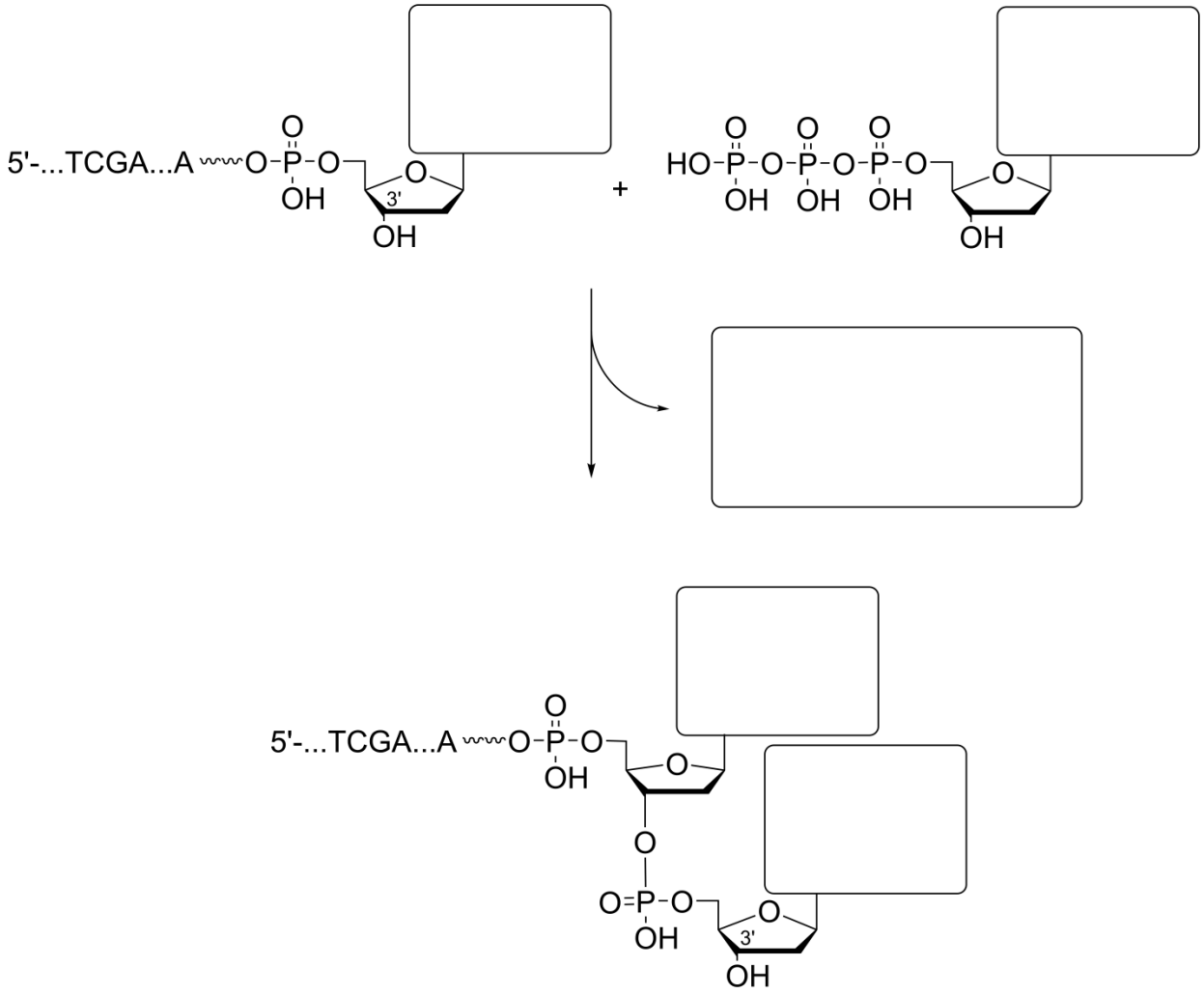
ddNTP – Dideoxynucleotide triphosphate

DNA sequencing

7.5%						
4.1	4.2	4.3	4.4	4.5	4.6	∑
5	5	5	6	4	10	35

4.1 (5pt)

Step Ia:



4.2 (5pt)

Composition: _____

[1] is _____

4.3 (5pt)

(X + 592.42): _____

(X + 1194.84): _____

(X + 1524.06): _____

(X + 881.62): _____

[2] is _____ [3] is _____ [4] is _____ [5] is _____

4.4 (6pt)

☐ (a) ☐ (b) ☐ (c) ☐ (d) ☐ (e)

4.5 (4pt)

R is _____

Position(s) of ^{32}P: _____

4.6 (10pt)

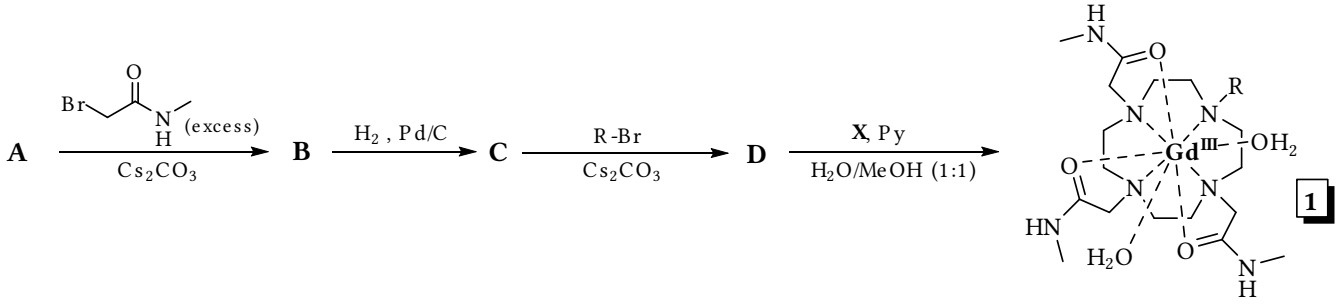
5'-…						G					A				T	C	T	…-3'

CO_2 detection with a gadolinium complex

7.5%							
5.1	5.2	5.3	5.4	5.5	5.6	5.7	∑
6	8	3	6	9	3	1	36

Recently, the determination of CO_2 content in seawater has become an important task in environmental monitoring and oceanography. In seawater, CO_2 exists mainly as bicarbonate ions, HCO_3^-.

Gd^{3+} complex cation **1** can be used to determine bicarbonate content. Its synthesis is shown below, where M(**A**) = 262.40 g/mol:



Q5.1 (6 points)

Draw the structures of **A-D**.

When hydrated halide **X** is heated in a crucible in an atmosphere of its own water vapour, it decomposes in two stages. Upon heating in the range 65-275 °C, **X**, aside from other products, gives an equimolar mixture of anhydrous salt **Y,** and a compound **Z**, which together have 63.55% of the initial mass of **X**. **Y** is a binary compound.

On further heating at 300-370 °C, the residual **Y** in this mixture converts into **Z.** The overall mass of **Z** has 56.16% of the initial mass of **X**. The oxidation states of all elements remain unchanged throughout the thermal decomposition. M(Gd) = 157.3 g/mol.

Q5.2 (8 points)

Determine the formulae of **X**, **Y**, and **Z**. **Write** chemical equations for the reactions occurring. **Show** your calculations.

Complex **1** is also used as an MRI contrast-agent-type probe whose relaxivity responds to bicarbonate. For simplicity, the following notation can be used:

$$\mathrm{GdL} + \mathrm{D} \rightleftharpoons \mathrm{GdLD} \qquad K_a = \frac{[\mathrm{GdLD}]}{[\mathrm{GdL}][\mathrm{D}]}$$

where GdL is the gadolinium-based complex, K_a is the association constant, and D is HCO_3^-.

The binding of bicarbonate changes the coordination environment of Gd^{3+} and the relaxivity, R, of the solution. Relaxivity is the ability of Gd^{3+} to accelerate the relaxation of water proton spins in a magnetic field so they return to equilibrium after excitation.

Q5.3 (3 points)

Determine the electronic configuration of the Gd^{3+} ion, the number of unpaired electrons (*N*), and establish whether it is paramagnetic (**p**) or diamagnetic (**d**).

When a solution of GdL is titrated with bicarbonate and *R* is measured after each addition, K_a can be obtained from the titration curve. *R* can be expressed as follows when the total complex concentration is kept constant:

$$R = \alpha_{\mathrm{GdL}} R_{\mathrm{GdL}} + \alpha_{\mathrm{GdLD}} R_{\mathrm{GdLD}}$$

where R_{GdL} and R_{GdLD} are the relaxivities of the solution when the complex is entirely free and entirely bound respectively. α_{GdL} and α_{GdLD} are the mole fractions of each form of the complex in the solution.

Q5.4 (6 points)

Derive the expressions for R at very low $([D]_{\mathrm{low}})$ and very high concentrations $\left([D]_{\mathrm{high}}\right)$ of $[D]_0$.

A titration of a solution of the complex with anion D was carried out. The total complex concentration $[\mathrm{GdL}]_0$ was kept constant at 500 μM. The results of the titration are shown in the table:

№	1	2	3	4	5	6	7	8	9
$[\mathrm{D}]_0$ / mM	0.000	0.050	0.100	0.300	0.500	0.550	3.00	5.00	10.0
R / $\mathrm{mM^{-1}\ s^{-1}}$	6.392	6.099	5.811	4.740	3.966	3.843	3.283	3.264	3.240

Q5.5 (9 points)

Determine the numerical values of R_{GdL}, R_{GdLD}, and K_a. **Show** your calculations.

If you did not answer **Q5.5**, use the values below for the rest of the problem:

$R_{\mathrm{GdL}} = 6.01\mathrm{mM^{-1}s^{-1}}$; $R_{\mathrm{GdLD}} = 2.74\mathrm{mM^{-1}s^{-1}}$; $K_a = 3.0 \times 10^5\mathrm{M^{-1}}$

Experimental studies have shown that the river water in the city of Nukus has a relaxivity value R = 3.500 $\mathrm{mM^{-1}\ s^{-1}}$ at $[\mathrm{GdL}]_0$ = 500 μM.

Q5.6 (3 points)

Calculate the concentration of HCO_3^- in this river.

Q5.7 (1 point)

Why is the individual contribution from the free anionic guest D not considered when determining the relaxivity R? **Choose** the correct option(s).

a) It does not bind directly to Gd^{3+}, and therefore does not affect relaxivity

b) The anion D does not create a local magnetic field to accelerate relaxation

c) Its concentration is higher than that of Gd^{3+}, so its contribution is neglected

d) D is a small molecule, and relaxivity can only be enhanced by large molecules

e) D irreversibly reacts with the solvent, losing its influence on relaxation

Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

A5-1

English (Official)

CO_2 detection with a gadolinium complex

7.5%							
5.1	5.2	5.3	5.4	5.5	5.6	5.7	∑
6	8	3	6	9	3	1	36

5.1 (6pt)

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

5.2 (8pt)

X: _____ Y: _____ Z: _____

5.3 (3pt)

Gd(3+): _____

N = _____

☐ p ☐ d

5.4 (6pt)

$([D]_{low})$ _____

$([D]_{high})$ _____

5.5 (9pt)

R(GdL) = _____ $mM^{-1}\ s^{-1}$

R(GdLD) = _____ $mM^{-1}\ s^{-1}$

K_a = _____ M^{-1}

5.6 (3pt)

$[HCO_3^-]$ = _____

5.7 (1pt)

☐ a ☐ b ☐ c ☐ d ☐ e

Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

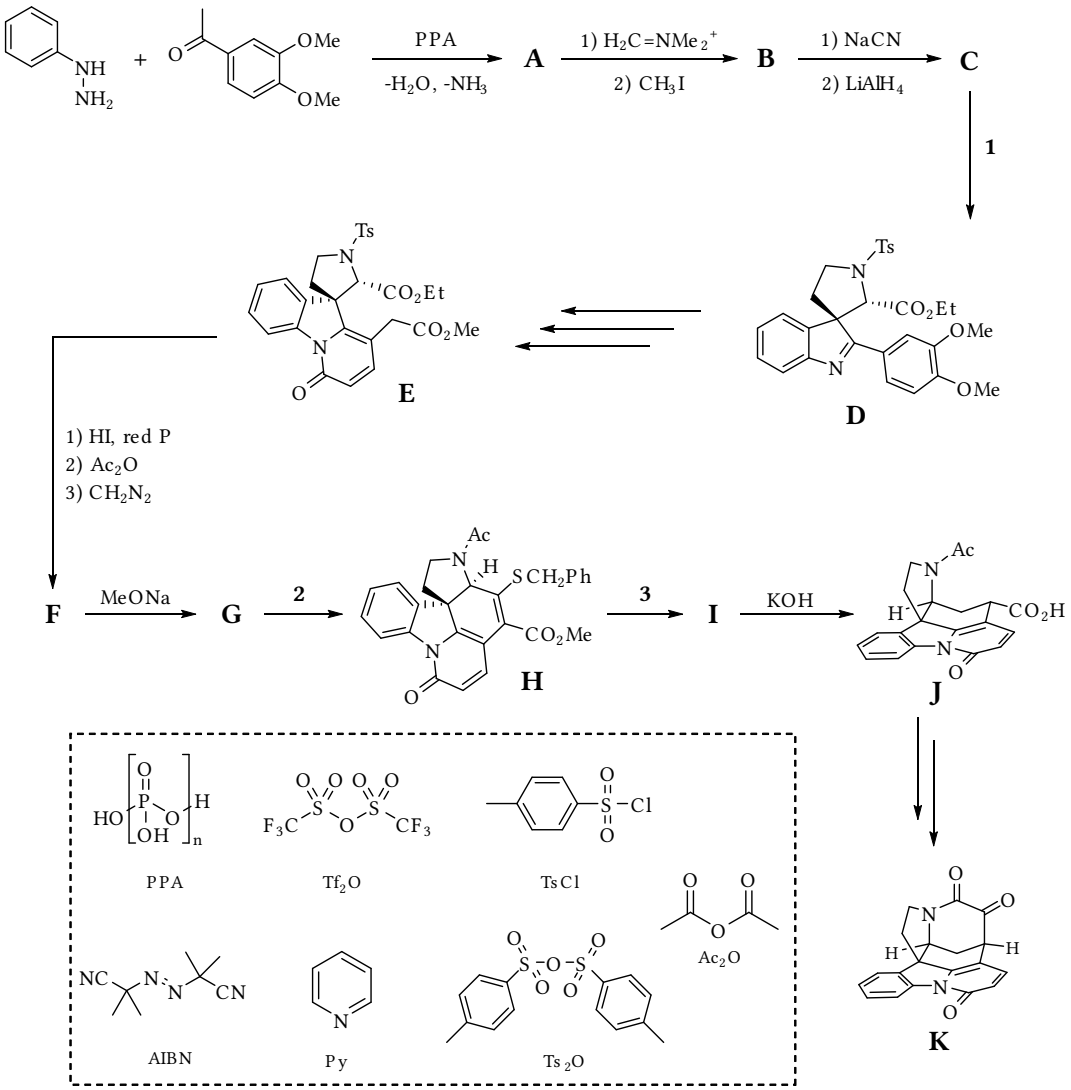
Q6-1

English (Official)

Strychnine

7.5%					
6.1	6.2	6.3	6.4	6.5	∑
24	6	6	30	7	73

In 1898, Walter Horsford was executed in England for murdering his cousin Annie Holmes by strychnine poisoning – one of the first cases in which the poison's distinctive convulsive symptoms led investigators directly to the killer. The first part of strychnine's total synthesis, performed by R. B. Woodward in 1954, is shown below.



In the ^{1}H NMR spectrum of compound **C**, among other signals, there are two singlets with integrals of 3H each.

Q6.1 (24 points)

Draw the structures of **A**, **B**, **C**, **F**, **G**, and **I**. Stereochemistry is not required.

Q6.2 (6 points)

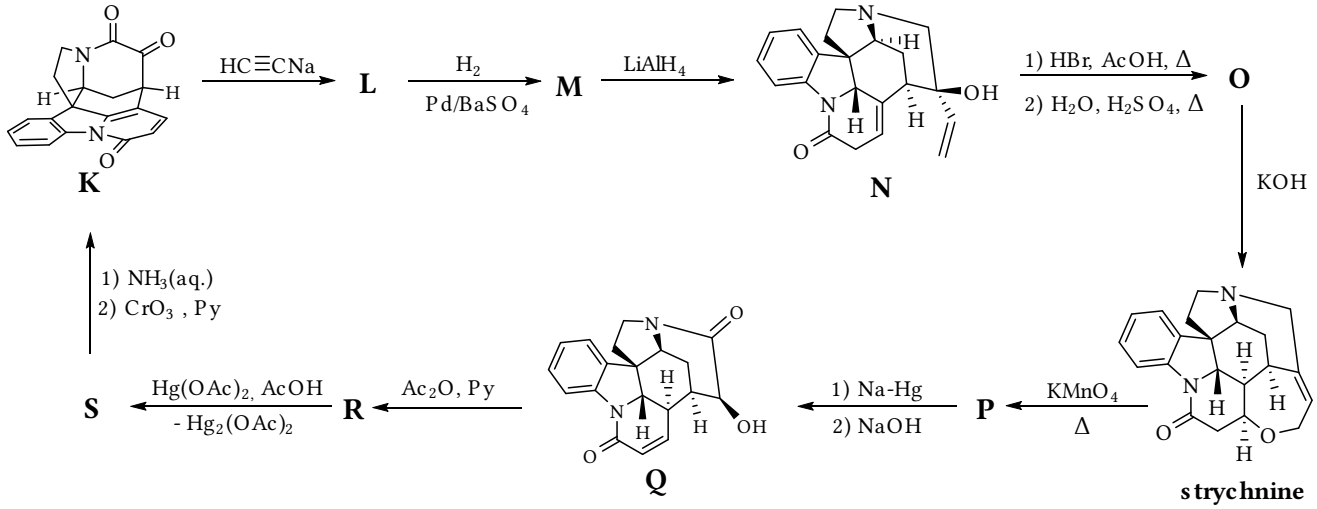
Select the appropriate reagent for each of the reactions marked with numbers **1–3**.

a) I) Tf_2O; Py II) PhSNa	e) I) H_2; Raney-Ni II) H_2, Pd/C
b) I) OHC–CO_2Et; II) *p*-TsCl, Py	f) I) CH_3–C(=O)–CO_2Et; II) Ts_2O
c) I) $POCl_3$, Py; II) KCN	g) I) TsCl; Py II) $PhCH_2SNa$
d) H_2, Pd/C	h) Bu_3SnH, AIBN

Q6.3 (6 points)

Indicate the configurations (*R* or *S*) of all chiral carbon atoms in **J**.

In 1948, Woodward had previously obtained **J** and **K** by breaking down natural strychnine. These degradation products helped to establish the structure of strychnine, and since **K** could be converted back into strychnine by known reactions, its synthesis completed the total synthesis of the alkaloid.



Q6.4 (30 points)

Draw the structures of **L**, **M**, **O**, **P**, **R**, and **S**. **Show** stereochemistry.

Q6.5 (7 points)

Circle all the stereocenters in strychnine on the Answer Sheet.

Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

A6-1

English (Official)

Strychnine

7.5%					
6.1	6.2	6.3	6.4	6.5	$\sum$
24	6	6	30	7	73

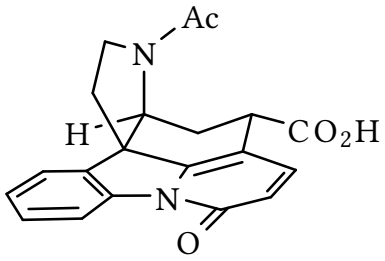
6.1 (24pt)

A (4 pts)	**B (4 pts)**
C (4 pts)	**F (4 pts)**
G (4 pts)	**I (4 pts)**

6.2 (6pt)

1	2	3

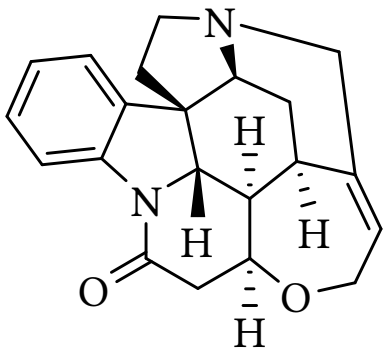
6.3 (6pt)



6.4 (30pt)

L (4 pts)	**M (4 pts)**
O (6 pts)	**P (6 pts)**
R (6 pts)	**S (4 pts)**

6.5 (7pt)



Pb means Problem

7.5%							
7.1	7.2	7.3	7.4	7.5	7.6	7.7	$\sum$
2	5	2	2	1	4	4	20

Lead ions in water pose a significant health and environmental concern due to their toxicity. They enter water primarily through the corrosion of lead pipes and other plumbing materials, as well as industrial and agricultural runoff. The quantitative measure to control the concentration of lead ions is solubility. Assume only the following equilibria occur in wastewater :

$Pb^{2+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons PbOH^+_{(aq)}$	$\log \beta_1 = 7.5$
$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Pb(OH)_{2\ (aq)}$	$\log \beta_2 = 10.5$
$Pb^{2+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons Pb(OH)^-_{3\ (aq)}$	$\log \beta_3 = 14$
$Pb(OH)_{2\ (s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2OH^-_{(aq)}$	$K_s = 5.5 \times 10^{-16}$
$H_2O \rightleftharpoons H^+ + OH^-$	$K_w = 1.0 \times 10^{-14}$

Q7.1 (2 points)

Calculate the equilibrium constant, K_1, for the process $Pb(OH)_{2\ (s)} \rightleftharpoons Pb(OH)_{2\ (aq)}$.

The solubility of $Pb(OH)_2$ represents the sum of the concentrations of all forms of Pb^{2+} ions in water.

Q7.2 (5 points)

(a) **Express** concentrations for all forms of Pb^{2+} in equilibrium, using equilibrium constants and $[H^+]$.

(b) **Derive** the expression for solubility of $Pb(OH)_{2\ (s)}$, s_{Pb}, as a function of $[H^+]$ and equilibrium constants only, using expressions obtained in **Q7.2(a).**

If you were not able to derive the equation in Q7.2(b), use the following equation in subsequent questions.

$$s = \frac{K_s[H^+]^2}{K_w^2} + \frac{K_s\beta_1[H^+]}{K_w} + \frac{K_s}{[H^+]}$$

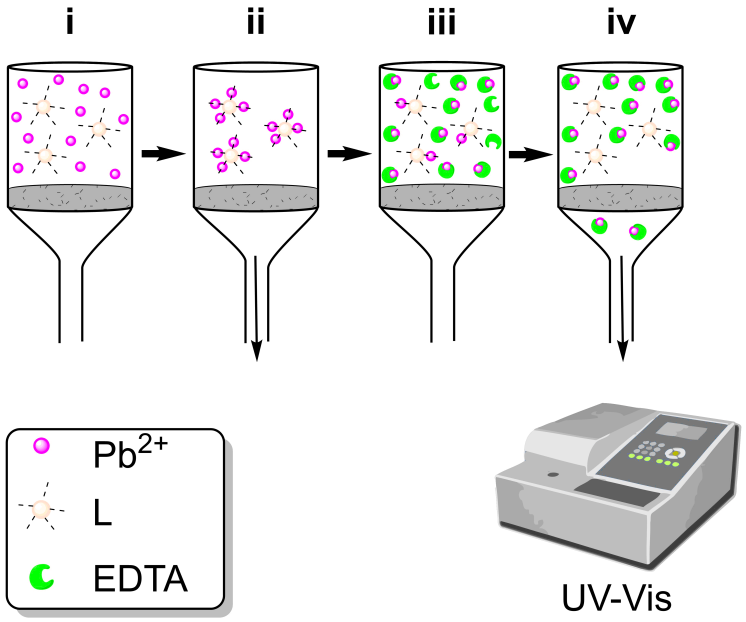
The average pH of wastewater is around 6.5-8.5.

Q7.3 (2 points)

Calculate the solubility of $Pb(OH)_{2\ (s)}$ (s_{Pb}) in the saturated equilibrium solution at: (a) pH = 6.5; and (b) pH = 8.5.

Peptide-immobilised beads (L) and EDTA were used to analyse lead in wastewater samples. The experiment is shown schematically below: (i) Beads are added to wastewater containing lead ions; (ii) the lead ions bind to the beads and then the wastewater is filtered off; (iii) EDTA solution is added to the beads and the lead ions bind to the EDTA; (iv) the beads are filtered off and the solution containing the Pb-EDTA complex is analysed by UV-Vis spectroscopy.

The pH of the solution is maintained using a pH = 6 buffer, and EDTA is present in very large excess. The acid dissociation constants for EDTA are: $K_{a1} = 1.02 \times 10^{-2}$, $K_{a2} = 2.14 \times 10^{-3}$, $K_{a3} = 6.92 \times 10^{-7}$, $K_{a4} = 5.50 \times 10^{-11}$.



For questions 7.4, 7.5, and 7.6, assume that lead ions form a 1:1 complex with L. Assume L is a neutral molecule and EDTA is a tetraprotic acid H_4Y.

Q7.4 (2 points)

Write equilibrium reaction equations for processes occurring: (a) lead ions binding to the beads; and (b) lead ions moving from the beads to the EDTA.

Q7.5 (1 point)

Analysing the scheme provided, **compare** the dissociation constants, K_d, of the PbL and Pb-EDTA (PbY^{2-}) complexes. **Choose** one of the options given in the answer sheets.

Q7.6 (4 points)

Calculate the dissociation constant ($K_d(PbL)$) of the PbL complex, if $\Delta G°_{298}$(ii-iii) $= 50.77$ kJ/mol and the dissociation constant of the Pb-EDTA complex is $K_d(PbY^{2-}) = 1 \times 10^{-18}$.

Initial Concentration of Pb^{2+} / μM	Normalised Absorbance / a.u.
0	0.004
1.12	0.017
4.47	0.041
11.17	0.109
71.51	0.679

Initial Concentration of Pb^{2+} / μM	Normalised Absorbance / a.u.
90.50	0.849
140.78	0.941
250.28	0.942
500.56	0.959
1000	0.997

To determine the Pb:L ratio in the complex, experiments were performed with an initial concentration of beads of 100 μM in each experiment.

Q7.7 (4 points)

(a) **Determine** the Pb:L ratio in the complex.

(b) **Calculate** the saturation concentration, c_{sat}, (the point where L are saturated with lead ions) to 2 decimal places.

Hint: You are advised to draw the graph for better visualisation. The graph will not be graded.

Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

A7-1

English (Official)

Pb means Problem

7.5%							
7.1	7.2	7.3	7.4	7.5	7.6	7.7	∑
2	5	2	2	1	4	4	20

7.1 (2pt)

K_1 = _____

7.2 (5pt)

(a)

$[PbOH^+]$ = _____

$[Pb(OH)_2(aq)]$ = _____

$[Pb(OH)_3^-]$ = _____

$[Pb^{2+}]$ = _____

(b)

s(Pb) = _____

7.3 (2pt)

(a) pH = 6.5: s(Pb) = _____

(b) pH = 8.5: s(Pb) = _____

7.4 (2pt)

(a) _____

(b) _____

7.5 (1pt)

☐ $K_d(\text{Pb-L}) < K_d(\text{PbY}^{2-})$

☐ $K_d(\text{Pb-L}) > K_d(\text{PbY}^{2-})$

☐ $K_d(\text{Pb-L}) = K_d(\text{PbY}^{2-})$

7.6 (4pt)

Kd (PbL) = _____

7.7 (4pt)

Pb : L = _____

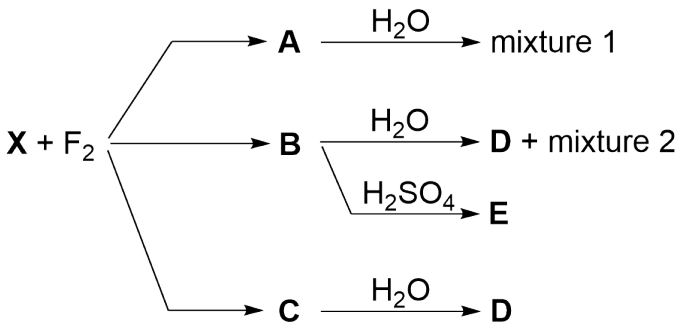
eXotic

7.5%			
8.1	8.2	8.3	∑
7	4	8	19

Element **X** forms compounds that seem impossible to synthesise at first glance. In this problem, you will explore the different types of compounds that **X** can form.

Binary compounds

Depending on the temperature and pressure, the reaction of **X** with fluorine (F_2) yields only **A**, **B**, or **C**. When **A** reacts with water (t < 20 °C), it produces **gas mixture 1** along with other product(s). In the reaction of **B** with water (t < 20 °C) compound **E** was expected; but in practice, compound **D** and **gas mixture 2** were observed. The conversion of compound **B** to **E** can be achieved through treatment with concentrated sulfuric acid. **C** does not produce any gases upon reaction with water, yielding **D** as the only **X**-containing compound.



Hints:

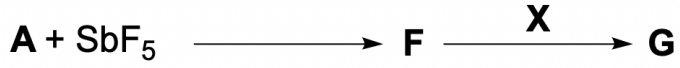
- Compounds **A**, **B**, **C**, **D**, and **E** are binary compounds.
- **Mixture 1** has the same qualitative composition as **mixture 2** and consists of elementary gases, with average molar masses of **mixtures 1** and **2** being 98.20 g/mol and 88.74 g/mol respectively.
- Compounds **D** and **E** have the same qualitative composition and explosively decompose upon heating.

Q8.1 (7 points)

Identify element **X** and compounds **A-E**. **Show** your calculations.

Compounds with an X–X bond

Reaction of **A** with 2 equivalents of SbF_5 produces compound **F**, which then reacts with **X** in a HF-SbF_5 mixture at −30 °C to give compound **G** with an **X–X** bond.



Hints:

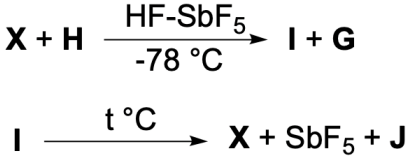
- Both the cation and the anion in **F** contain fluorine atoms.
- Compound **G** contains 22.86% **X** and 34.74% fluorine by mass.

Q8.2 (4 points)

Identify unknown compounds **F** and **G**. **Show** your calculations where necessary. **Write** the equations of the reactions described on the reaction scheme.

Compounds with X–d-metal bonds

Reaction of the binary compound **H** dissolved in a HF-SbF_5 mixture with **X** at −78 °C in a molar ratio of 1:6 yields dark red compound **I**, containing **X**–d-metal bonds. A slight increase in temperature causes **I** to decompose into **X**, SbF_5, and salt **J**.



Hints:

- **I** and **G** are formed in equimolar amounts.
- The anion in **I** is the same as that in compound **F**.
- The solid phase loses 32.28% of its mass during the conversion of **I** to **J**.
- The formal oxidation state of the d-metal in **H** is one higher than in **I** and **J**.
- The crystal structure of **H** consists of square planar repeating units, where each central atom has two bridging ligands.

Q8.3 (8 points)

Identify unknown compounds **H, I**, and **J**. **Show** your calculations where necessary. **Write** the equations of the reactions described on the reaction scheme.

Theoretical examination

3rd ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

A8-1

English (Official)

eXotic

7.5%			
8.1	8.2	8.3	$\sum$
7	4	8	19

8.1 (7pt)

X: _____ A: _____

B: _____ C: _____

D: _____ E: _____

8.2 (4pt)

F _____

G _____

Reactions:

_____

_____

8.3 (8pt)

H: _____

I: _____

J: _____

Reactions:

_____

_____