

46th International Chemistry Olympiad

July 25, 2014

Hanoi, Vietnam

THEORETICAL EXAMINATION



46th IChO
HANOI, VIETNAM 2014

Country:	
Name as in passport:	
Student Code:	
Language:	

This booklet contains 24982 characters

Chemistry: The flavor of life

GENERAL INTRODUCTION

- You have **additional 15 minutes** to read the whole set.
- This booklet is composed of 9 problems. You have **5 hours to fulfill the problems**. Failure to stop after the STOP command may result in zero points for the current task.
- Write down answers and calculations within the designated boxes. Give your work where required.
- Use only the pen and calculator provided.
- The draft papers are provided. If you need more draft paper, use the back side of the paper. Answers on the back side and the draft papers will NOT be marked.
- There are **48 pages** in the booklet including the answer boxes, Cover Sheet and Periodic Table.
- The official English version is available on demand for clarification only.
- Need to go to the restroom – raise your hand. You will be guided there.
- **After the STOP signal** put your booklet in the envelope (do not seal), leave at your table. Do not leave the room without permission.

Good luck !



46th IChO
HANOI, VIETNAM 2014

Chemistry: The flavor of life

Student name**Student code****Physical Constants, Units, Formulas and Equations**

Avogadro's constant	$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant	$R = 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Speed of light	$c = 2.9979 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Planck's constant	$h = 6.6261 \times 10^{-34} \text{ J}\cdot\text{s}$
Standard pressure	$p^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$
Atmospheric pressure	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg}$
Zero of the Celsius scale	273.15 K
Mass of electron	$m_e = 9.1094 \times 10^{-31} \text{ kg}$

1 nanometer (nm) = 10^{-9} m ; 1 angstrom (Å) = 10^{-10} m

1 electron volt (eV) = 1.6022×10^{-19} J = $96485 \text{ J}\cdot\text{mol}^{-1}$

Energy of a light quantum with wavelength λ	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$
van't Hoff equation in integral form	$\ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Relationship between internal energy, heat and work	$\Delta U = q + w$
Molar heat capacity at constant volume	$C_{v,m} = \left(\frac{dU}{dT}\right)_v$
Change in internal energy from T_1 to T_2 assuming constant $C_{v,m}$	$U(T_2) = U(T_1) + nC_{v,m}(T_2 - T_1)$,
Spin only formula relating number of unpaired electrons to effective magnetic moment	$\mu_{eff} = \sqrt{n(n+2)} \text{ B.M.}$

Student name

Student code

Theoretical Problem 1 5.0 % of the total	Code:		Question	1	2	3	4	5	Total
	Examiner		Mark	3	7	6	4	7	27
			Grade						

Problem 1. Particles in a box: polyenes

In quantum mechanics, the movement of π electrons along a neutral chain of conjugated carbon atoms may be modeled using the ‘particle in a box’ method. The energy of the π electrons is given by the following equation:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where n is the quantum number ($n = 1, 2, 3, \dots$), h is Planck’s constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2) \times 1.40 \text{ \AA}$ (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ , to the number of double bonds k and constant B is as follows:

$$\lambda \text{ (nm)} = B \times \frac{(k + 2)^2}{(2k + 1)} \quad \text{Equation 1}$$

1. Using this semi-empirical formula with $B = 65.01 \text{ nm}$ **calculate** the value of the wavelength λ (nm) for octatetraene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$).

Student name

Student code

2. **Derive** Equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants, and hence **calculate** theoretical value of the constant $B_{\text{calc.}}$.

3. We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, **determine** the number of conjugated double bonds (k) in this polyene and **give** its structure. [*If you did not solve Part 2, use the semi-empirical Equation 1 with $B = 65.01$ nm to complete Part 3.*]

Student name

Student code

4. For the polyene molecule found in Part 3, **calculate** the difference in energy between the HOMO and the LUMO, ΔE , ($\text{kJ}\cdot\text{mol}^{-1}$).

In case Part 3 was not solved, take $k = 5$ to solve this problem.

5. The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x , L_y , and L_z , yielding the following expression for the allowed energy levels:

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

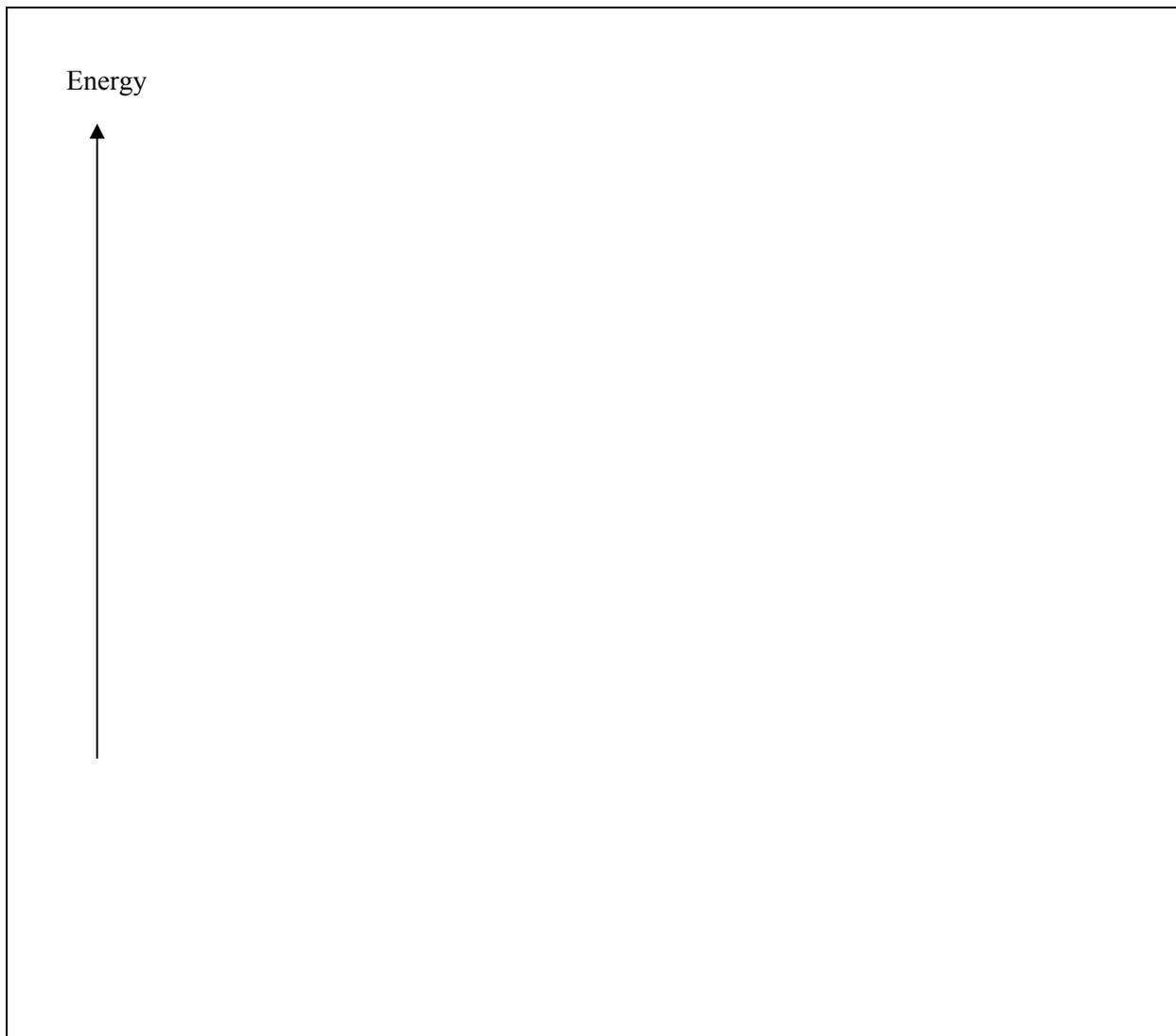
The three quantum numbers n_x , n_y , and n_z must be integer values and are independent of each other.

5.1 Give the expressions for the three **different** lowest energies, assuming that the box is cubic with a length of L .

Student name

Student code

5.2 Levels with the same energy are said to be degenerate. **Draw** a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.



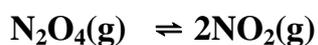
Student name

Student code

Theoretical	Code:		Question	1a	1b	2	3	Total
Problem 2	Examiner		Mark	12	8	3	10	33
5.0 % of the total			Grade					

Problem 2. Dissociating Gas Cycle

Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:



1.00 mole of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3 . The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

1a. Calculate ΔG^0 of the reaction at 298K, assuming the gases are ideal.

1b. Calculate ΔH^0 and ΔS^0 of the reaction, assuming that they do not change significantly with temperature.

Student name

Student code

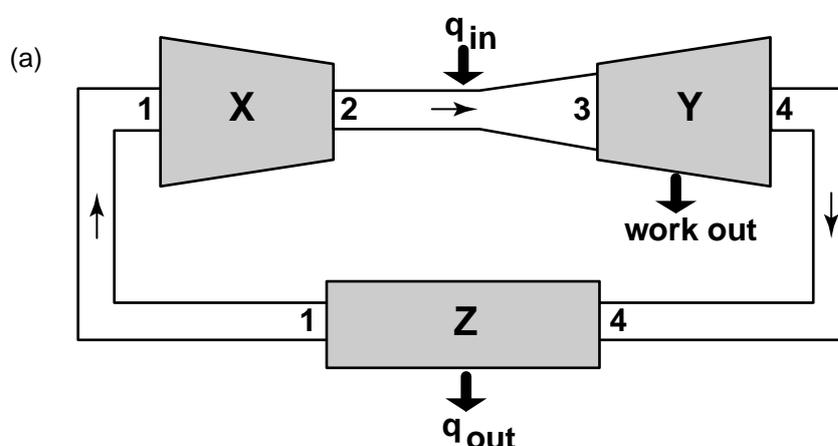
$$\Delta G^0 (298 \text{ K}) = \underline{\hspace{15em}}$$

$$\Delta H^0 = \underline{\hspace{15em}}$$

$$\Delta S^0 = \underline{\hspace{15em}}$$

If you cannot calculate ΔH^0 , use $\Delta H^0 = 30.0 \text{ kJ}\cdot\text{mol}^{-1}$ for further calculations.

The tendency of N_2O_4 to dissociate reversibly into NO_2 enables its potential use in advanced power generation systems. A simplified scheme for one such system is shown below in Figure (a). Initially, "cool" N_2O_4 is compressed ($1 \rightarrow 2$) in a compressor (**X**), and heated ($2 \rightarrow 3$). Some N_2O_4 dissociates into NO_2 . The hot mixture is expanded ($3 \rightarrow 4$) through a turbine (**Y**), resulting in a decrease in both temperature and pressure. The mixture is then cooled further ($4 \rightarrow 1$) in a heat sink (**Z**), to promote the reformation of N_2O_4 . This recombination reduces the pressure, thus facilitates the compression of N_2O_4 to start a new cycle. All these processes are assumed to take place reversibly.



To understand the benefits of using reversible dissociating gases such as N_2O_4 , we will focus on step $3 \rightarrow 4$ and consider an ideal gas turbine working with 1 mol of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, **no heat is exchanged**.

2. **Give the equation** to calculate the work done by the system $w(\text{air})$ during the **reversible adiabatic** expansion for 1 mol of air during stage $3 \rightarrow 4$. Assume that $C_{v,m}(\text{air})$ (the isochoric molar heat capacity of air) is constant, and the temperature changes from T_3 to T_4 .

Student name

Student code

3. Estimate the ratio $w_{(\text{N}_2\text{O}_4)}/w_{(\text{air})}$, in which $w_{(\text{N}_2\text{O}_4)}$ is the work done by the gas during the reversible adiabatic expansion process $3 \rightarrow 4$ with the cycle working with 1 mol of N_2O_4 . T_3 and T_4 are the same as in Part 2. Take the conditions at stage 3 to be $T_3 = 440$ K and $P_3 = 12.156$ bar and assume that:

(i) the gas is at its equilibrium composition at stage 3;

(ii) $C_{v,m}$ for the gas is the same as for air;

(iii) the adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture ($\text{N}_2\text{O}_4 + \text{NO}_2$) is unchanged until the expansion is completed.

Student name

Student code

--

Student name

Student code

Theoretical	Code:		Question	1	2	3	4	Total
Problem 3	Examiner		Marks	8	14	2	12	36
9.0 % of the total			Grade					

Problem 3. High-valent Silver Compounds

Silver chemistry is dominated by Ag (I) compounds. Compounds of silver in higher oxidation state (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electro-chemical oxidations or in chemical oxidations using powerful oxidizing agents.

1. In some peroxydisulfate ($S_2O_8^{2-}$) oxidations catalyzed by Ag^+ , black solid (**A**) with the composition AgO can be isolated.

1a. **Choose** the appropriate magnetic behaviour of **A** if it exists as $Ag^{II}O$.

<input type="checkbox"/> Diamagnetic	<input type="checkbox"/> Paramagnetic
---	--

Single crystal X - ray studies reveal that the lattice of **A** contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, **A** should be assigned as $Ag^I Ag^{III} O_2$ rather than $Ag^{II} O$.

1b. **Assign** the oxidation number of Ag1 and Ag2.

Oxidation number of Ag1 :
Oxidation number of Ag2 :

1c. **What** is the coordination number of O atoms in the lattice of **A**?

The coordination number of O atoms =.....

Student name

Student code

1d. **How many** Ag^{I} and Ag^{III} bond to one O atom in the lattice of **A**?

Number of Ag^{I} =

Number of Ag^{III} =

1e. **Predict** the magnetic behaviour of **A**. **Check** the appropriate box below.

Diamagnetic

Paramagnetic

1f. The compound **A** can also be formed on warming a solution of Ag^+ with peroxydisulfate. **Write down** the equation for the formation of **A**.

2. Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound **A** is not a $\text{Ag}^{\text{II}}\text{O}$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

Atom	Standard enthalpy of formation ($\text{kJ}\cdot\text{mol}^{-1}$)	1 st ionization ($\text{kJ}\cdot\text{mol}^{-1}$)	2 nd ionization ($\text{kJ}\cdot\text{mol}^{-1}$)	3 rd ionization ($\text{kJ}\cdot\text{mol}^{-1}$)	1 st electron affinity ($\text{kJ}\cdot\text{mol}^{-1}$)	2 nd electron affinity ($\text{kJ}\cdot\text{mol}^{-1}$)
Cu(g)	337.4	751.7	1964.1	3560.2		
Ag(g)	284.9	737.2	2080.2	3367.2		
O(g)	249.0				-141.0	844.0

Compounds	$\Delta H^{\circ}_{\text{f}}$ ($\text{kJ}\cdot\text{mol}^{-1}$)
$\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_{2(\text{s})}$	-24.3
$\text{Cu}^{\text{II}}\text{O}_{(\text{s})}$	-157.3

The relationship between the **lattice dissociation energy** (U_{lat}) and the **lattice dissociation enthalpy** (ΔH_{lat}) for monoatomic ion lattices is: $\Delta H_{\text{lat}} = U_{\text{lat}} + nRT$, where n is the number of ions in the formula unit.

Student name

Student code

2a. **Calculate** U_{lat} at 298 K of $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$ and $\text{Cu}^{\text{II}}\text{O}$. Assume that they are ionic compounds.

U_{lat} of $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$

U_{lat} ($\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$)

U_{lat} ($\text{Cu}^{\text{II}}\text{O}$)

If you can not calculate the U_{lat} of $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$ and $\text{Cu}^{\text{II}}\text{O}$, use following values for further calculations: U_{lat} of $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2 = 8310.0 \text{ kJ}\cdot\text{mol}^{-1}$; U_{lat} of $\text{Cu}^{\text{II}}\text{O} = 3600.0 \text{ kJ}\cdot\text{mol}^{-1}$.

Student name

Student code

The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

$$U_{lat} = C \times \left(\frac{1}{V_m} \right)^{\frac{1}{3}}$$

Where: V_m (nm^3) is the volume of the formula unit and C ($\text{kJ}\cdot\text{nm}\cdot\text{mol}^{-1}$) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

Oxides	V_m (nm^3)
$\text{Cu}^{\text{II}}\text{O}$	0.02030
$\text{Ag}^{\text{III}}_2\text{O}_3$	0.06182
$\text{Ag}^{\text{II}}\text{Ag}^{\text{III}}_2\text{O}_4$	0.08985

2b. Calculate U_{lat} for the hypothetical compound $\text{Ag}^{\text{II}}\text{O}$. Assume that $\text{Ag}^{\text{II}}\text{O}$ and $\text{Cu}^{\text{II}}\text{O}$ have the same type of lattice, and that $V_m(\text{Ag}^{\text{II}}\text{O}) = V_m(\text{Ag}^{\text{II}}\text{Ag}^{\text{III}}_2\text{O}_4) - V_m(\text{Ag}^{\text{III}}_2\text{O}_3)$.

$U_{lat}(\text{Ag}^{\text{II}}\text{O})$

2c. By constructing an appropriate thermodynamic cycle or otherwise, **estimate** the enthalpy change for the solid-state transformation from $\text{Ag}^{\text{II}}\text{O}$ to 1 mole of $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$.

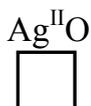
(Use $U_{lat} \text{Ag}^{\text{II}}\text{O} = 3180.0 \text{ kJ}\cdot\text{mol}^{-1}$ and $U_{lat} \text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2 = 8310.0 \text{ kJ}\cdot\text{mol}^{-1}$ if you cannot calculate $U_{lat} \text{Ag}^{\text{II}}\text{O}$ in Part 2b).

Student name

Student code

$\Delta H_{\text{rxn}} =$

2d. **Indicate** which compound is thermodynamically more stable by checking the appropriate box below.



3. When $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$ is dissolved in aqueous HClO_4 solution, a paramagnetic compound (**B**) is first formed then slowly decomposes to form a diamagnetic compound (**C**). Given that **B** and **C** are the only compounds containing silver formed in these reactions, **write down** the equations for the formation of **B** and **C**.

For **B**:

For **C**:

Student name

Student code

4. Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex **Z** is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of AgNO_3 and 2 mL of pyridine ($d = 0.982 \text{ g/mL}$) is added to a stirred, ice-cold aqueous solution of 5.000 g of $\text{K}_2\text{S}_2\text{O}_8$. The reaction mixture becomes yellow, then an orange solid (**Z**) is formed which has a mass of 1.719 g when dried.

Elemental analysis of **Z** shows the mass percentages of C, H, N elements are 38.96%, 3.28%, 9.09%, respectively.

A 0.6164 g **Z** is added to aqueous NH_3 . The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (**D**). The filtrate is collected and treated with excess BaCl_2 solution to obtain 0.4668 g (when dry) of white precipitate (**E**).

4a. **Determine** the empirical formula of **Z** and calculate the percentage yield in the preparation.

Student name

Student code

4b. Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in **Z**, the effective magnetic moment (μ_{eff}) of **Z** was determined and found to be 1.78 BM. Use the spin only formula to **determine** the number of unpaired electrons in **Z** and the molecular formula of **Z**. (**Z** contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)

4c. Write down all chemical equations for the preparation of **Z**, and its analysis.

Formation of **Z**:

Destruction of **Z** with NH_3 :

Formation of **D**:

Formation of **E**:

Student name

Student code

Theoretical Problem 4 4.0 % of the total	Code:		Question	1a	1b	2	3a	3b	3c	Total
	Examiner		Mark	4	1	10	2	6	4	27
			Grade							

Problem 4. Zeise's Salt

1. Zeise's salt, $\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4]$, was one of the first organometallic compounds to be reported. W. C. Zeise, a professor at the University of Copenhagen, prepared this compound in 1827 by reacting PtCl_4 with boiling ethanol and then adding potassium chloride (Method 1). This compound may also be prepared by refluxing a mixture of $\text{K}_2[\text{PtCl}_6]$ and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from $\text{K}_2[\text{PtCl}_4]$ and ethylene (Method 3).

1a. **Write** balanced equations for each of the above mentioned preparations of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise's salt consumes 2 moles of ethanol.

Student name

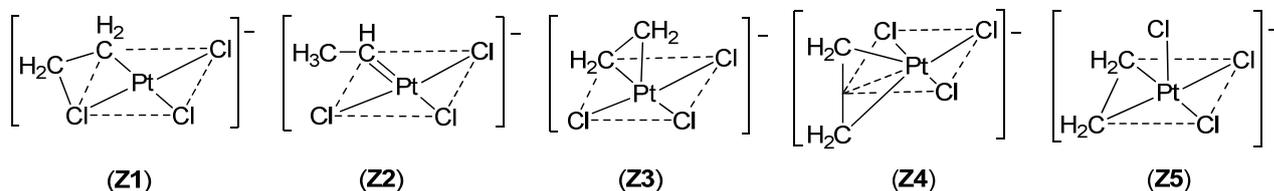
Student code

1b. Mass spectrometry of the anion $[\text{PtCl}_3\text{C}_2\text{H}_4]^-$ shows one set of peaks with mass numbers 325-337 and various intensities.

Calculate the mass number of the anion which consists of the largest natural abundance isotopes (using given below data).

Isotope	$^{192}_{78}\text{Pt}$	$^{194}_{78}\text{Pt}$	$^{195}_{78}\text{Pt}$	$^{196}_{78}\text{Pt}$	$^{198}_{78}\text{Pt}$	$^{35}_{17}\text{Cl}$	$^{37}_{17}\text{Cl}$	$^{12}_6\text{C}$	$^{13}_6\text{C}$	^1_1H
Natural abundance, %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

2. Some early structures proposed for Zeise's salt anion were:



In structure **Z1**, **Z2**, and **Z5** both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

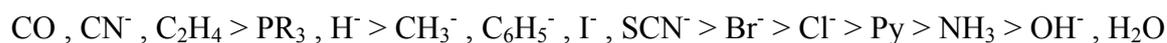
Student name

Student code

2a. NMR spectroscopy allowed the structure for Zeise's salt to be determined as structure **Z4**. For each structure **Z1-Z5**, **indicate** in the table below how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are.

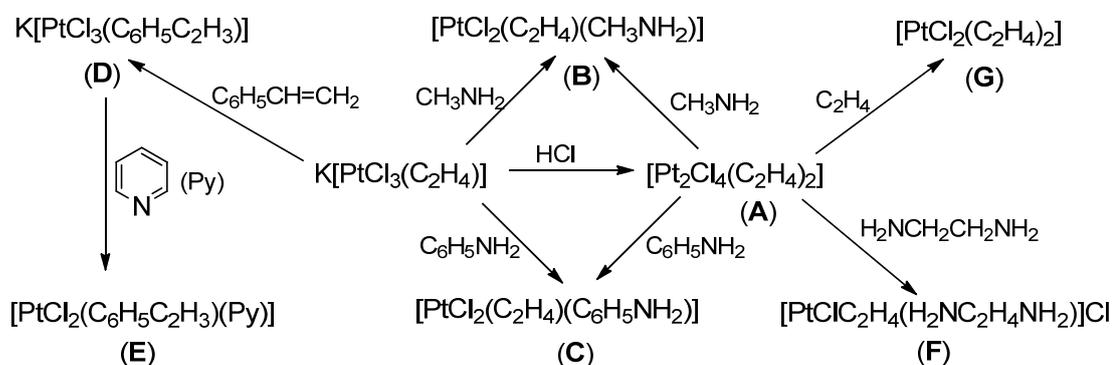
Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1		
Z2		
Z3		
Z4		
Z5		

3. For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position *trans* to themselves (*the trans effect*). The ordering of ligands is:



In above series a left ligand has stronger *trans effect* than a right ligand.

Some reactions of Zeise's salt and the complex $[\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2]$ are given below.



Student name

Student code

3a. **Draw the structure of A**, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.

A

3b. **Draw** the structures of **B**, **C**, **D**, **E**, **F** and **G**.

B	C	D
E	F	G

3c. **Suggest** the driving force(s) for the formation of **D** and **F** by choosing one or more of the following statements (for example, i and ii):

- i) Formation of gas
- ii) Formation of liquid
- iii) Trans effect
- iv) Chelate effect

Structure	D	F
Driving force(s)		

Student name

Student code

Theoretical	Code:		Question	1	2	3	4	Total
Problem 5	Examiner		Mark	6	4	4	6	20
6.5 % of the total			Grade					

Problem 5. Acid-base Equilibria in Water

A solution (**X**) contains two weak monoprotic acids (those having *one* acidic proton); HA with the acid dissociation constant of $K_{HA} = 1.74 \times 10^{-7}$, and HB with the acid dissociation constant of $K_{HB} = 1.34 \times 10^{-7}$. The solution **X** has a pH of 3.75.

1. Titration of 100 mL solution **X** requires 100 mL of 0.220 M NaOH solution for completion.

Calculate the initial (total) concentration ($\text{mol}\cdot\text{L}^{-1}$) of each acid in the solution **X**.

Use reasonable approximations where appropriate. [$K_W = 1.00 \times 10^{-14}$ at 298 K.]

Student name

Student code

A large empty rectangular box with a black border, intended for the student to write their name and code.

Student name

Student code

2. **Calculate** the pH of the solution **Y** which initially contains 6.00×10^{-2} M of NaA and 4.00×10^{-2} M of NaB.

Student name

Student code

3. Adding large amounts of distilled water to solution **X** gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero. **Calculate** the percentage of dissociation of each acid in this dilute solution.

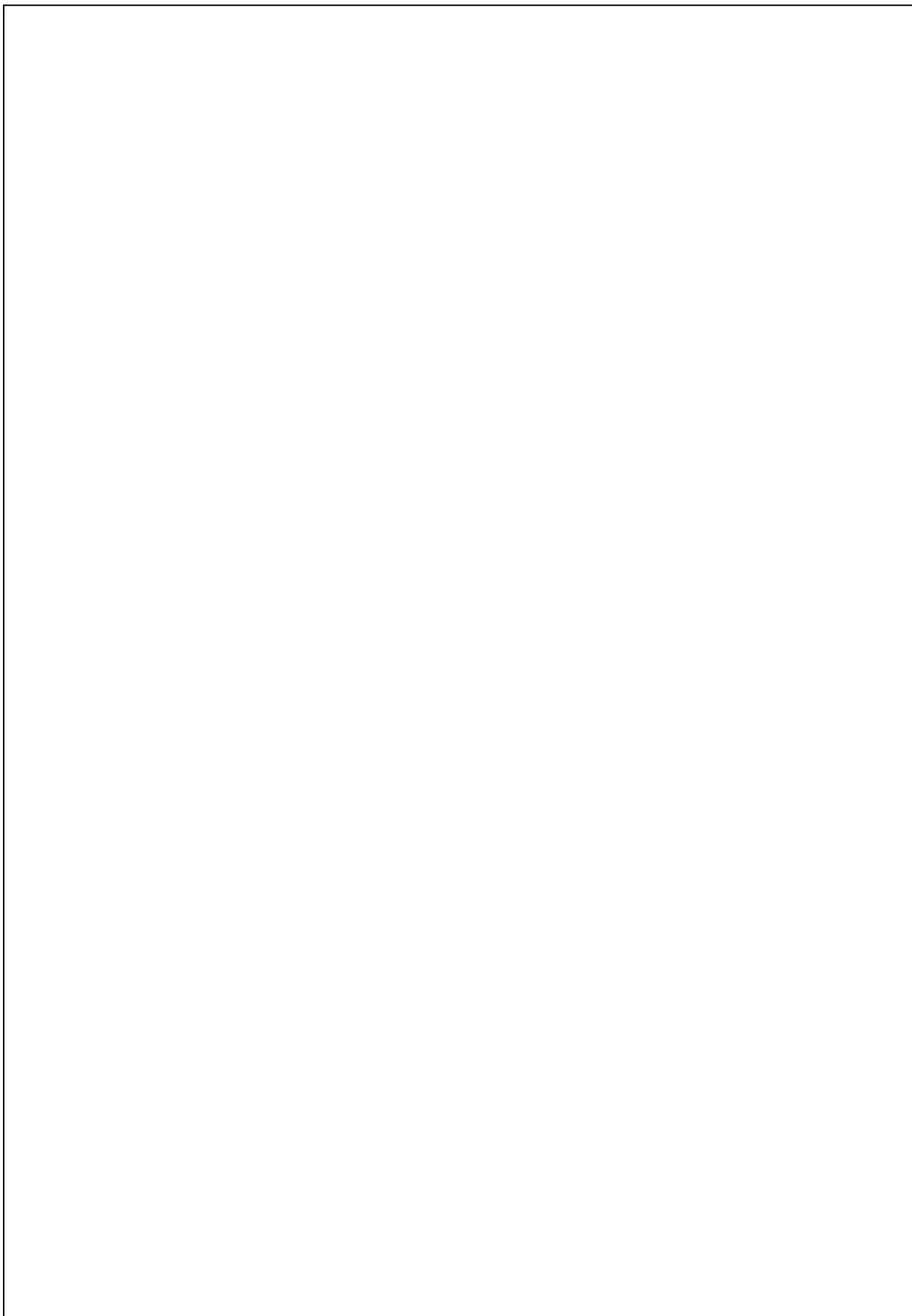
4. A buffer solution is added to solution **Y** to maintain a pH of 10.0. Assume no change in volume of the resulting solution **Z**.

Calculate the solubility (in mol·L⁻¹) of a substance M(OH)₂ in **Z**, given that the anions A⁻ and B⁻ can form complexes with M²⁺:



Student name

Student code



Theoretical Problem 6 7.0 % of the total	Code:		Question	6a	6b	6c	6d	6e	Total
	Examiner		Marks	6	8	4	12	2	32
			Grade						

Problem 6. Chemical Kinetics

The transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to synthesize arylamines. The overall reaction for the nickel-catalyzed amination of aryl chloride in basic conditions is:



in which NiLL' is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

6a. To determine the reaction order with respect to each reactant, the dependence of the initial rate of the reaction on the concentrations of each reagent was carried out with all other reagents present in large excess. Some kinetic data at 298 K are shown in the tables below. **(Use the grids if you like)**

[ArCl] (M)	Initial rate (M s ⁻¹)
0.1	1.88 × 10 ⁻⁵
0.2	4.13 × 10 ⁻⁵
0.4	9.42 × 10 ⁻⁵
0.6	1.50 × 10 ⁻⁴

Student name

Student code

[NiLL'] (M)	Initial rate (M s ⁻¹)
6×10^{-3}	4.12×10^{-5}
9×10^{-3}	6.01×10^{-5}
1.2×10^{-2}	7.80×10^{-5}
1.5×10^{-2}	1.10×10^{-4}

[L'] (M)	Initial rate (M s ⁻¹)
0.06	5.8×10^{-5}
0.09	4.3×10^{-5}
0.12	3.4×10^{-5}
0.15	2.8×10^{-5}

Determine the order with respect to the reagents assuming they are integers.

- Order with respect to $[\text{ArCl}] =$
- Order with respect to $[\text{NiLL}'] =$
- Order with respect to $[\text{L}'] =$

6b. To study the mechanism for this reaction, ^1H , ^{31}P , ^{19}F , and ^{13}C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, $\text{NiL}(\text{Ar})\text{Cl}$, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL' (step 1) at $50\text{ }^\circ\text{C}$, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

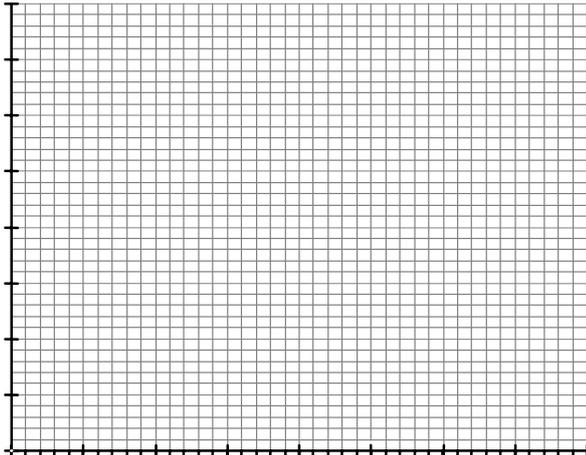


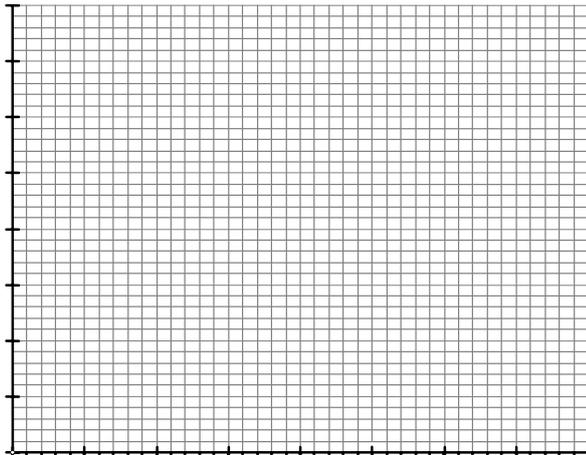
Using the steady state approximation, **derive** an expression for the rate equation for the formation of $[\text{NiL}(\text{Ar})\text{Cl}]$.

Student name

Student code

The next steps in the overall reaction involve the amine (RNH_2) and ${}^t\text{BuONa}$. To determine the order with respect to RNH_2 and ${}^t\text{BuONa}$, the dependence of the initial rates of the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

$[\text{NaO}^t\text{Bu}]$, (M)	Initial rate ($\text{M}\cdot\text{s}^{-1}$)	
0.2	4.16×10^{-5}	
0.6	4.12×10^{-5}	
0.9	4.24×10^{-5}	
1.2	4.20×10^{-5}	

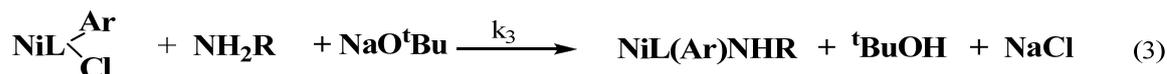
$[\text{RNH}_2]$ (M)	Initial rate (M s^{-1})	
0.3	4.12×10^{-5}	
0.6	4.26×10^{-5}	
0.9	4.21×10^{-5}	
1.2	4.23×10^{-5}	

6c. **Determine** the order with respect to each of these reagents, assuming each is an integer. (Use the grids if you like.)

- Order with respect to $[\text{NaO}^t\text{Bu}] =$
- Order with respect to $[\text{RNH}_2] =$

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining.

A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:



6d. **Use** the steady-state approximation and material balance equation to **derive** the rate law for $d[\text{ArNHR}]/dt$ for the above mechanism in terms of the initial concentration of the catalyst $[\text{NiLL}']_0$ and concentrations of $[\text{ArCl}]$, $[\text{NH}_2\text{R}]$, $[\text{NaO}^t\text{Bu}]$, and $[\text{L}']$.

Student name

Student code

A large empty rectangular box with a black border, intended for the student to write their name and code.

Student name

Student code

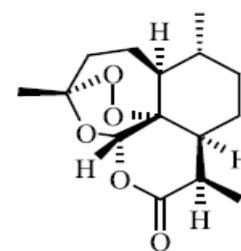
6e. Give the simplified form of the rate equation in **6d** assuming that k_1 is very small.

$$d[\text{ArNHR}]/dt = - d[\text{ArCl}]/dt =$$

Theoretical Problem 7 8.0 % of the total	Code:		Question	7a	7b	7c	7d	7e	7f	Total
	Examiner		Mark	12	8	8	12	12	12	64
			Grade							

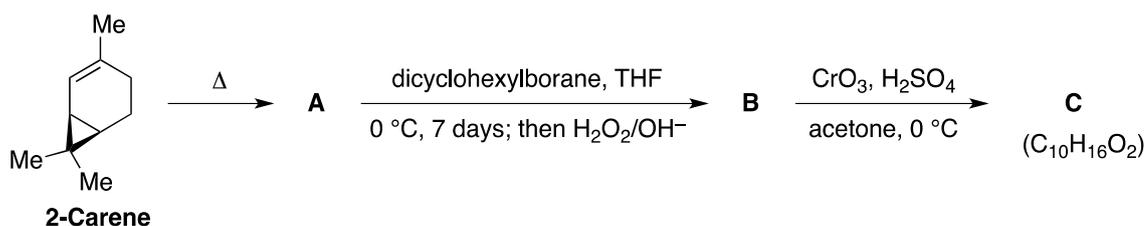
Problem 7. Synthesis of Artemisinin

(+)-Artemisinin, isolated from *Artemisia annua* L. (Qinghao, *Compositae*) is a potent antimalarial effective against resistant strains of *Plasmodium*. A simple route for the synthesis of Artemisinin is outlined below.



(+)-Artemisinin

First, pyrolysis of (+)-2-Carene broke the cyclopropane ring forming, among other products, (1*R*)-(+)-*trans*-isolimonene **A** (C₁₀H₁₆), which then was subjected to regioselective hydroboration using dicyclohexylborane to give the required alcohol **B** in 82% yield as a mixture of diastereoisomers. In the next step, **B** was converted to the corresponding γ,δ -unsaturated acid **C** in 80% yield by Jones' oxidation.



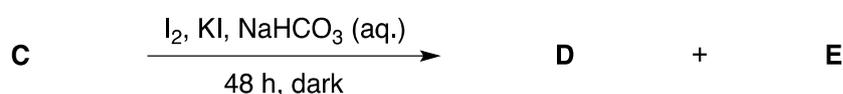
7a. Draw the structures (with stereochemistry) of the compounds **A-C**.

A	B	C
----------	----------	----------

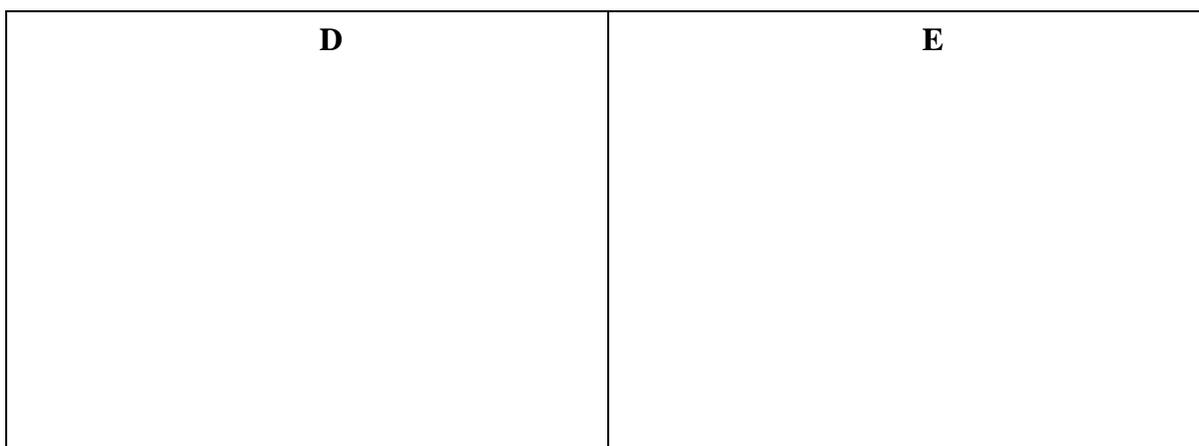
Student name

Student code

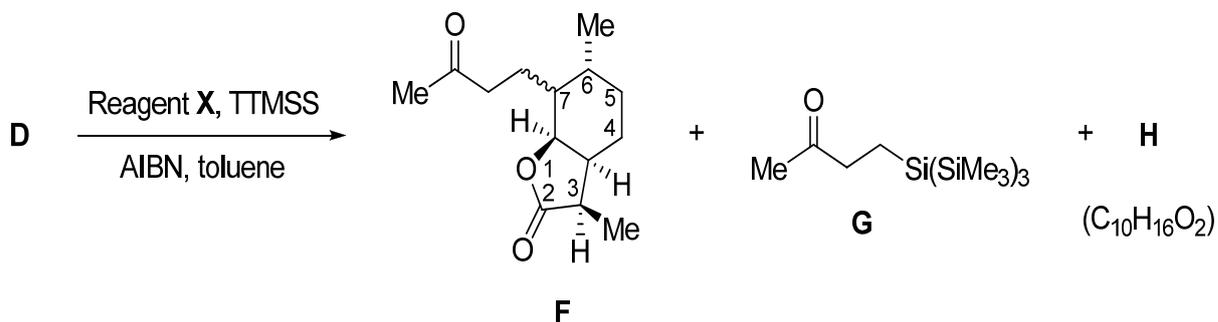
The acid **C** was subjected to iodolactonization using KI, I₂ in aqueous NaHCO₃ solution to afford diastereomeric iodolactones **D** and **E** (which differ in stereochemistry only at C₃) in 70% yield.



7b. **Draw** the structures (with stereochemistry) of the compounds **D** and **E**.



The iodolactone **D** was subjected to an intermolecular radical reaction with ketone **X** using tris(trimethylsilyl)silane (TTMSS) and AIBN (azobisisobutyronitrile) in a catalytic amount, refluxing in toluene to yield the corresponding alkylated lactone **F** in 72% yield as a mixture of diastereoisomers which differ only in stereochemistry at C₇ along with compound **G** (~10%) and the reduced product **H**, C₁₀H₁₆O₂ (<5%).



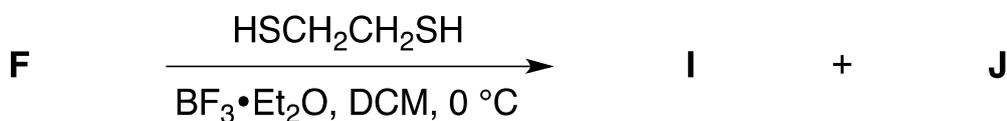
Student name

Student code

7c. **Draw** the structures (with stereochemistry) of compound **H** and the reagent **X**.

X	H
----------	----------

The keto group of **F** reacted with ethanedithiol and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in dichloromethane (DCM) at 0 °C to afford two diastereomers: thioketal lactones **I** and **J** in nearly quantitative yield (98%). The thioketalization facilitated the separation of the major isomer **J** in which the thioketal group is on the opposite face of the ring to the adjacent methyl group.



7d. **Draw** the structures (with stereochemistry) of the compounds **I** and **J**.

I	J
----------	----------

The isomer **J** was further subjected to alkaline hydrolysis followed by esterification with diazomethane providing hydroxy methyl ester **K** in 50% yield. The hydroxy methyl ester **K** was transformed into the keto ester **L** using **PCC** (Pyridium ChloroChromate) as the oxidizing agent in dichloromethane (DCM).

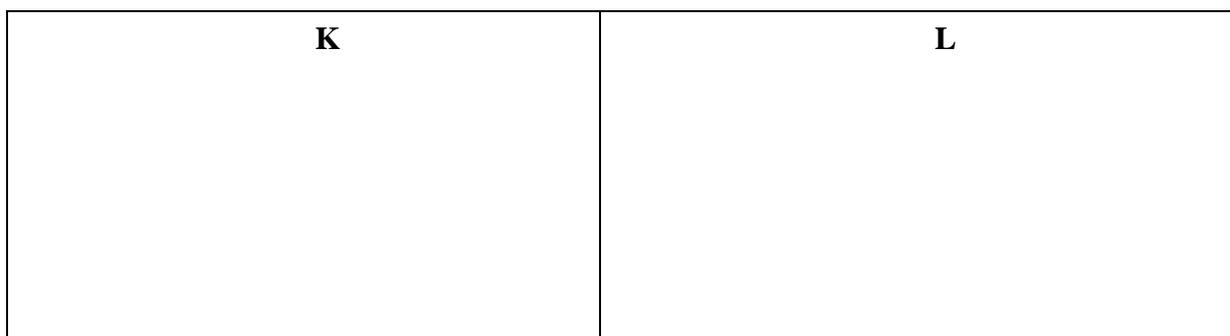
Student name

Student code

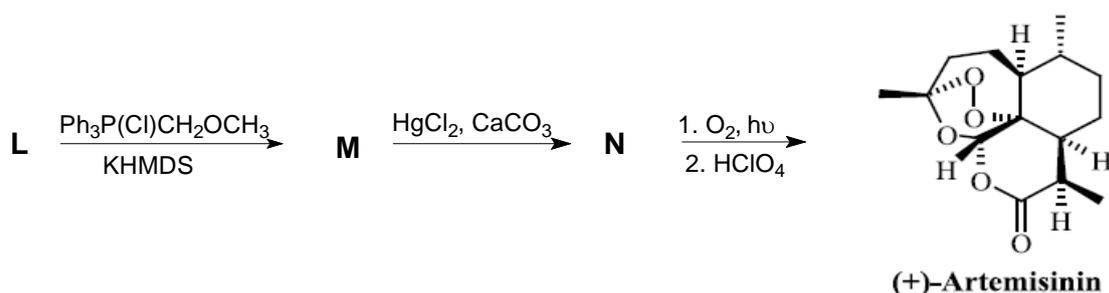
A two-dimensional NMR study of the compound **L** revealed that the two protons adjacent to the newly-formed carbonyl group are *cis* to each other and confirmed the structure of **L**.



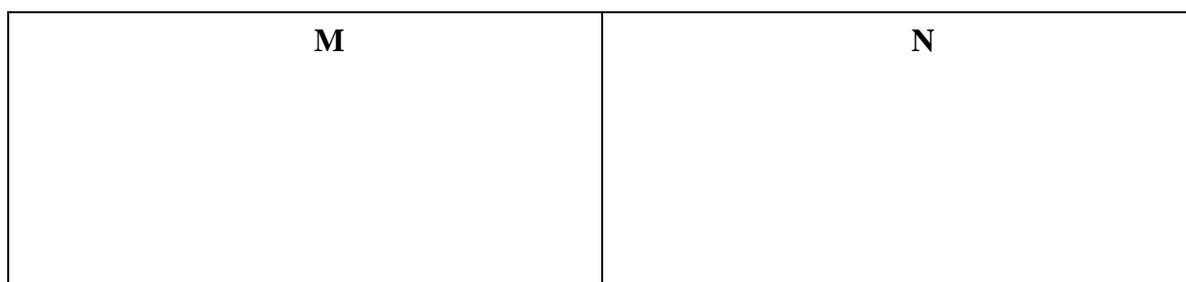
7e. **Draw** the structures (with stereochemistry) of the compounds **K** and **L**.



The ketone **L** was subjected to a Wittig reaction with methoxymethyl triphenylphosphonium chloride and KHMDS (Potassium HexaMethylDiSilazid - a strong, non-nucleophilic base) to furnish the required methyl vinyl ether **M** in 45% yield. Deprotection of thioketal using HgCl_2 , CaCO_3 resulted in the key intermediate **N** (80%). Finally, the compound **N** was transformed into the target molecule Artemisinin by photo-oxidation followed by acid hydrolysis with 70% HClO_4 .



7f. **Draw** the structures (with stereochemistry) of the compounds **M** and **N**.

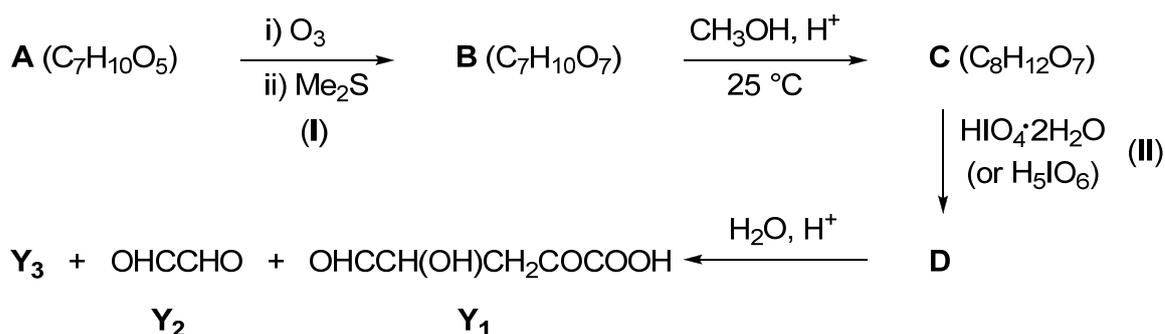


Theoretical Problem 8 8.0% of the total	Code:		Question	8a	8b	8c	8d	Total
	Examiner		Marks	15	2	12	10	39
			Grade					

Problem 8. Star Anise

Illicium verum, commonly called *Star anise*, is a small native evergreen tree grown in northeast Vietnam. *Star anise* fruit is used in traditional Vietnamese medicine. It is also a major ingredient in the making the flavour of 'phở', a Vietnamese favourite soup.

Acid **A** is isolated from the *star anise* fruit. The constitutional formula of **A** has been deduced from the following sequence of reactions:



(I): this overall process results in alkene cleavage at the C=C bond, with each carbon of this becoming doubly bonded to an oxygen atom.

(II): this oxidative cleavage process of 1,2-diols breaks C(OH)–C(OH) bond and produces corresponding carbonyl compounds.

8a. **Draw** the structures for the compounds **Y**₁ and **Y**₂ and hence **deduce** the structure of **Y**₃ and **A**, **B**, **C**, **D**, given that in **A** there is only one ethylenic hydrogen atom.

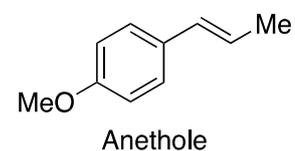
Y ₁	Y ₂	Y ₃
-----------------------	-----------------------	-----------------------

Student name

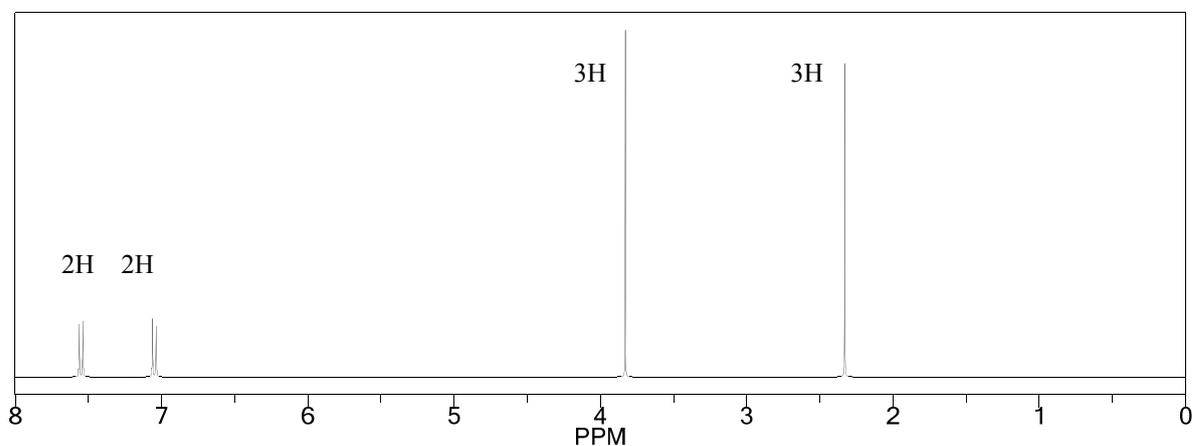
Student code

A	B
C	D

Anethole, a main component of star anise oil, is an inexpensive chemical precursor for the production of many pharmaceutical drugs.



Treating anethole with sodium nitrite in acetic acid gives a crystalline solid **E** ($C_{10}H_{10}N_2O_3$). The IR spectrum of **E** shows there is no non-aromatic C=C double bond. The 1H NMR spectrum of **E** is given below.



Student name

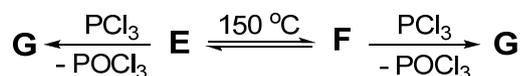
Student code

8b. **What differences** in the structure between **E** and anethole can be obtained from the ^1H NMR data?

- i) **E** contains a *cis*-C=C ethylenic bond while that of anethole is *trans*.
- ii) **E** cannot contain a non-aromatic C=C bond.
- iii) **E** is the adduct of anethole and N_2O_2 .
- iv) **E** is the adduct of anethole and N_2O_3 .
- v) **E** does not contain two *trans* ethylenic protons as anethole.

	Pick one of the above statements
From ^1H NMR data	

On heating at $150\text{ }^\circ\text{C}$ for several hours, **E** is partially isomerized into **F**. Under the same conditions, **F** gives the identical equilibrium mixture to that obtained from **E**. On heating with phosphorus trichloride, both **E** and **F** lose one oxygen atom giving compound **G**. Compounds **E** and **F** have the same functional groups.



The chemical shifts of methyl protons in **E**, **F** and **G** are given below.

	E	F	G
$\text{CH}_3\text{-O}$	3.8 ppm	3.8 ppm	3.8 ppm
$\text{CH}_3\text{-C}$	2.3 ppm	2.6 ppm	2.6 ppm

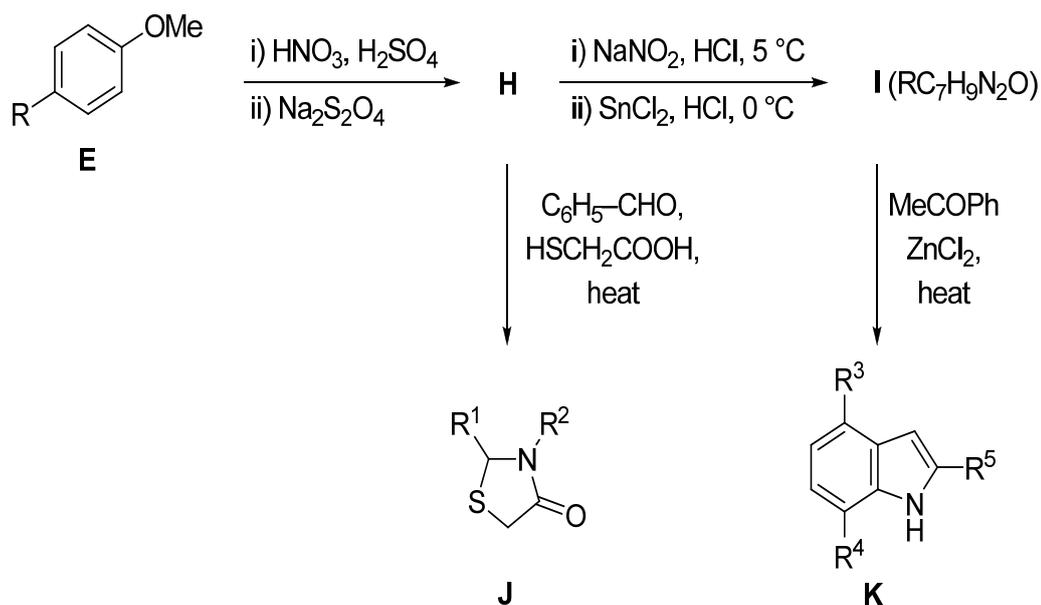
8c. **Suggest** structures for **E**, **F** and **G**, assuming that they do NOT contain three-membered rings.

E	F	G

Student name

Student code

A simplified structure for compound **E** is shown below; the R group does not change throughout the rest of this question. Compound **E** is nitrated and subsequently reduced with sodium dithionite to **H**. Treatment of **H** with sodium nitrite and hydrochloric acid at 0–5 °C and subsequently reduced with stannous chloride to provide **I** ($R-C_7H_9N_2O$). One-pot reaction (three component reaction) of **H**, benzaldehyde and thioglycolic acid ($HSCH_2CO_2H$) leads to the formation of **J**. Reaction of **I** and methyl phenyl ketone in the presence of $ZnCl_2$ affords **K**.



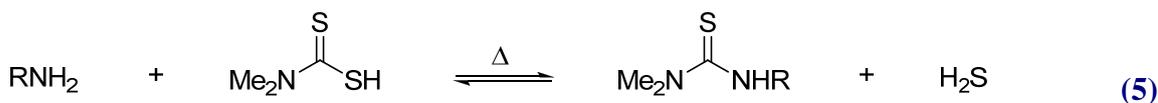
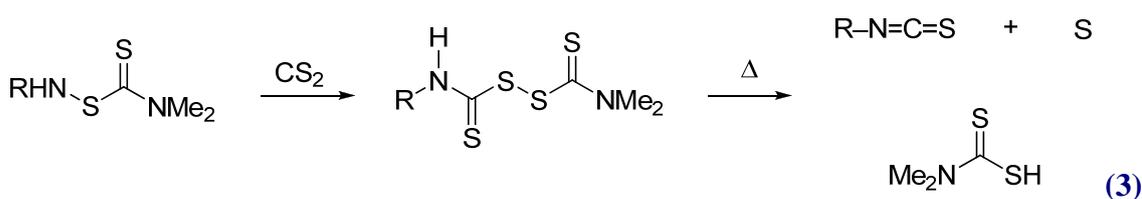
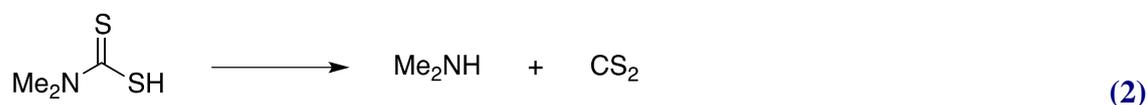
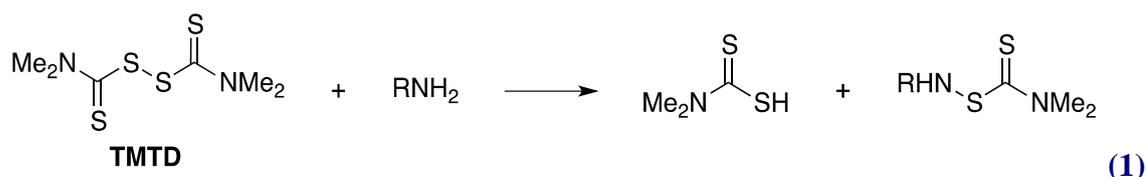
8d. Give the structures for **H**, **I**, **J** and **K**.

H	I
J	K

Theoretical Problem 9 7.5 % of the total	Code:		Question	9a	9b	9c	9d	9e	9f	Total
	Examiner		Marks	8	4	6	4	2	9	33
			Grade							

Problem 9. Heterocycle Preparation

Tetramethylthiurame disulfide (**TMTD**) is emerging as a useful reagent to prepare many sulfur-nitrogen functional groups and heterocycles in organic chemistry. The reactions of **TMTD** with primary amines, as well some corresponding post-transformations of the resulting product(s) are presented in the following schemes:

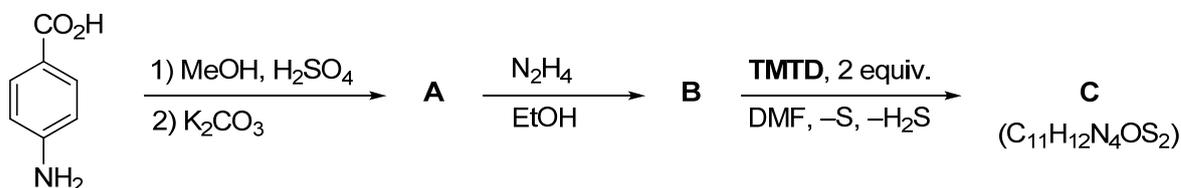


Similar transformations of benzohydrazides (containing nucleophilic NH_2 group) and **TMTD** have been observed.

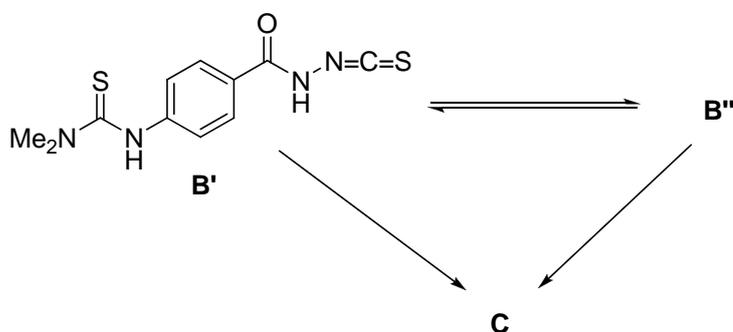
Student name

Student code

In the synthetic scheme below, the thiocarbamoylation reaction of an aroyl hydrazine with **TMTD** produces compound **C** containing a heterocyclic moiety from *p*-aminobenzoic acid.



During the formation of **C** from **B**, an intermediate **B'** was observed. This intermediate tautomerizes to **B''**. **C** can be formed from **B'** or **B''**.



9a. **Give** the structures of **A**, **B**, and **C**.

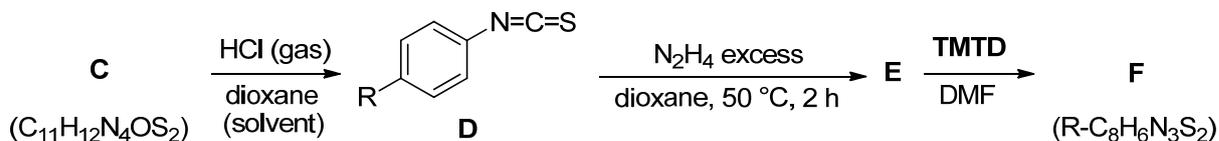
A	B	C

9b. **Suggest** a structure for the tautomer **B''** and **give a curly-arrow mechanism** for the formation of **C**.

Student name

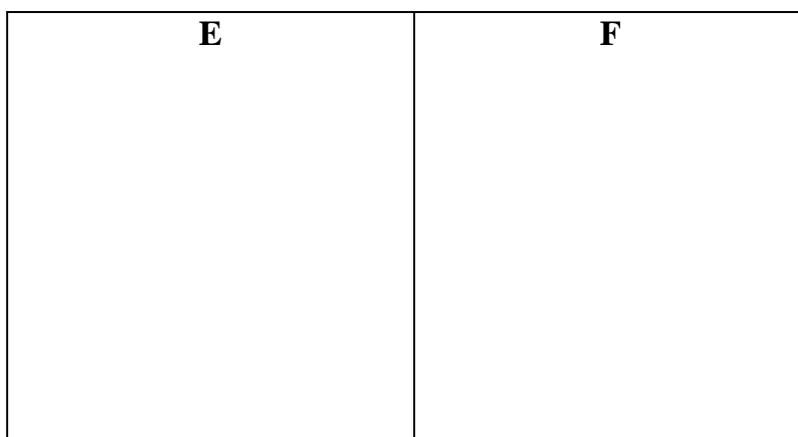
Student code

Compound **C** was then converted to **F** by the following pathway:



[The group R remains exactly the same throughout the rest of the question.]

9c. Draw the structures of **E**, and **F**. (You do not need to draw the structure for the R group from this point)



E was only obtained when **D** was slowly added to the solution of excess N_2H_4 in dioxane. If N_2H_4 was added to the solution of **D** in dioxane instead, a major side product **D'** ($\text{R}_2\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}_2$) was formed.

9d. Give the structure of **D'**.



Slightly heating **D** with ethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$) in dioxane for 2 hours yielded **G** ($\text{R}-\text{C}_9\text{H}_{11}\text{N}_2\text{OS}$).

Student name

Student code

9e. **Draw** the structural formula of **G**.

G

9f. Heating **G** in the presence of *p*-toluenesulfonic acid as the catalyst could form a number of different five-membered heterocyclic products.

i) **Draw** 2 structures that have different molecular formulae.

--	--

ii) **Draw** 2 structures that are constitutional isomers.

--	--

iii) **Draw** 2 structures that are stereoisomers.

--	--

Periodic Table of the Elements

	1																	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012	Transition Elements										5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.98	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	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 65.41	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.9)	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
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	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 (209.0)	85 At (210.0)	86 Rn (222.0)
7	87 Fr (223.0)	88 Ra (226.0)	89 Ac (227.0)	104 Rf (261.1)	105 Db (262.1)	106 Sg (263.1)	107 Bh (262.1)	108 Hs (265)	109 Mt (266)	110 Ds (271)	111 Rg (272)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (292)	117 Uus (294)	118 Uuo (294)

6	Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (144.9)	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 174.0
7	Actinides	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237.1)	94 Pu (244.1)	95 Am (243.1)	96 Cm (247.1)	97 Bk (247.1)	98 Cf (251.1)	99 Es (252.1)	100 Fm (257.1)	101 Md (258.1)	102 No (259.1)	103 Lr (260.1)