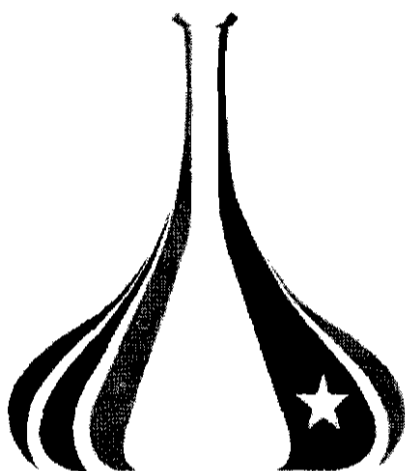Official version
(Answers)

46th International Chemistry Olympiad

July 25, 2014

Hanoi, Vietnam

THEORETICAL EXAMINATION

WITH ANSWER SHEETS GRADING

46th IChO
HANOI, VIETNAM 2014

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

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 <u>and calculations</u> 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. <u>Answers on the back side and the draft papers will NOT be marked.</u>

- There are <u>**53 pages**</u> 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

Physical Constants, Units, Formulas and Equations

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

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

1 electron volt (eV) $= 1.6022 \times 10^{-19}$ J $= 96485$ J·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	$K = \exp\left(-\dfrac{\Delta G°}{RT}\right)$
van't Hoff equation in integral form	$\ln\dfrac{K_2}{K_1} = \dfrac{\Delta H°}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$
Relationship between internal energy, heat and work	$\Delta U = q + w$
Molar heat capacity at constant volume	$C_{v,m} = \left(\dfrac{dU}{dT}\right)_v$
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	$\mu_{eff} = \sqrt{n(n+2)}$ B.M.

Theoretical	Code:		Question	1	2	3	4	5	Total
Problem 1 5.0 % of the 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 ($n = 1, 2, 3, ...$), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2) \times 1.40$ Å (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:

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

1. Using this semi-empirical formula with $B = 65.01$ nm **calculate** the value of the wavelength λ (nm) for octatetraene ($CH_2 = CH - CH = CH - CH = CH - CH = CH_2$).

1. From the given semi-empirical formula, the wavelength λ (nm) is calculated as follows: $$\lambda \ (nm) = 65.01 \times \frac{(k+2)^2}{(2k+1)}$$ For octatetraene molecule, with k = 4; $\lambda = \textbf{260.0 nm}$	3 points

The 46th IChO – Theoretical Examination. Official English Version

4

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 $B_{calc.}$.
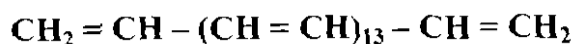
2. The formula: $E = \dfrac{n^2 h^2}{8mL^2}$ (1) ΔE is calculated as: $\Delta E = E_{LUMO} - E_{HOMO} = h\nu = \dfrac{hc}{\lambda}$ (2) In which, λ and ν are wavelength and frequency for the corresponding photon respectively. k is the quantum number for the HOMO, which is equal to the number of double bonds. So, we have: $\Delta E = \dfrac{h^2}{8mL^2}[(k+1)^2 - k^2] = \dfrac{hc}{\lambda} = \dfrac{h^2}{8mL^2}[2k+1]]$ (3) Replace $L = (k+2) \times 1.40$ Å into (3): $\dfrac{hc}{\lambda} = \dfrac{h^2(2k+1)}{8m[(k+2)\times 1.40\times 10^{-10}]^2} \Rightarrow \lambda = \dfrac{8mc[(k+2)\times 1.40\times 10^{-10}]^2}{h(2k+1)}$ $\Rightarrow \lambda = \dfrac{8\times 9.1094\times 10^{-31}\times 2.9979\times 10^8 \times (1.40\times 10^{-10})^2}{6.6261\times 10^{-34}} \times \dfrac{(k+2)^2}{(2k+1)}$	 5 points
$\Rightarrow \lambda\,(m) = 6.462\times 10^{-8} \times \dfrac{(k+2)^2}{(2k+1)};$ $\Rightarrow \lambda\,(nm) = 64.62 \times \dfrac{(k+2)^2}{(2k+1)}$ (4) $B_{calc.} = 64.6$ nm	2 points

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.*]

3. With $\lambda = 600$ nm, we have $\dfrac{600}{64.62} = \dfrac{(k+2)^2}{(2k+1)} = 9.285 \Rightarrow k^2 - 14.57k - 5.285 = 0$ Solve the equation to obtain: $k_1 = \mathbf{14.92}$, $k_2 = -0.355$ (Eliminated).	4 points

Thus, $k = 15$. So, the formula of polyene is: $$CH_2 = CH - (CH = CH)_{13} - CH = CH_2$$	2 points

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

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

$$\Delta E = E_{LUMO} - E_{HOMO} = \frac{h^2}{8mL^2}\left[(k+1)^2 - k^2\right]$$ $$\Delta E = \frac{(6.6261\times10^{-34})^2 \times 10^{-3} \times 6.022\times10^{23}}{8\times9.1094\times10^{-31}\times(1.40\times10^{-10})^2} \times \left[\frac{2k+1}{(k+2)^2}\right] \text{ (kJ·mol}^{-1})$$ $$\Delta E = 1851 \times \left[\frac{2k+1}{(k+2)^2}\right] \text{ (kJ/mol)}$$ For polyene **with** $k = 15$: $\Delta E = 199$ kJ·mol^{-1}. Taking the value of $k = 5$; $\Delta E = 415$ kJ·mol^{-1}	4 points

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.

$$L_x = L_y = L_z; E_{xyz} = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2}$$	1 point
$$E_{111} = \frac{h^2(1^2 + 1^2 + 1^2)}{8mL^2} = \frac{3h^2}{8mL^2}$$	1 point

The 46th IChO – Theoretical Examination. Official English Version

6

$$E_{112} = \frac{h^2(1^2 + 1^2 + 2^2)}{8mL^2} = \frac{6h^2}{8mL^2} = E_{121} = E_{211}$$

1 point

$$E_{122} = \frac{h^2(1^2 + 2^2 + 2^2)}{8mL^2} = \frac{9h^2}{8mL^2} = E_{212} = E_{221}$$

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.
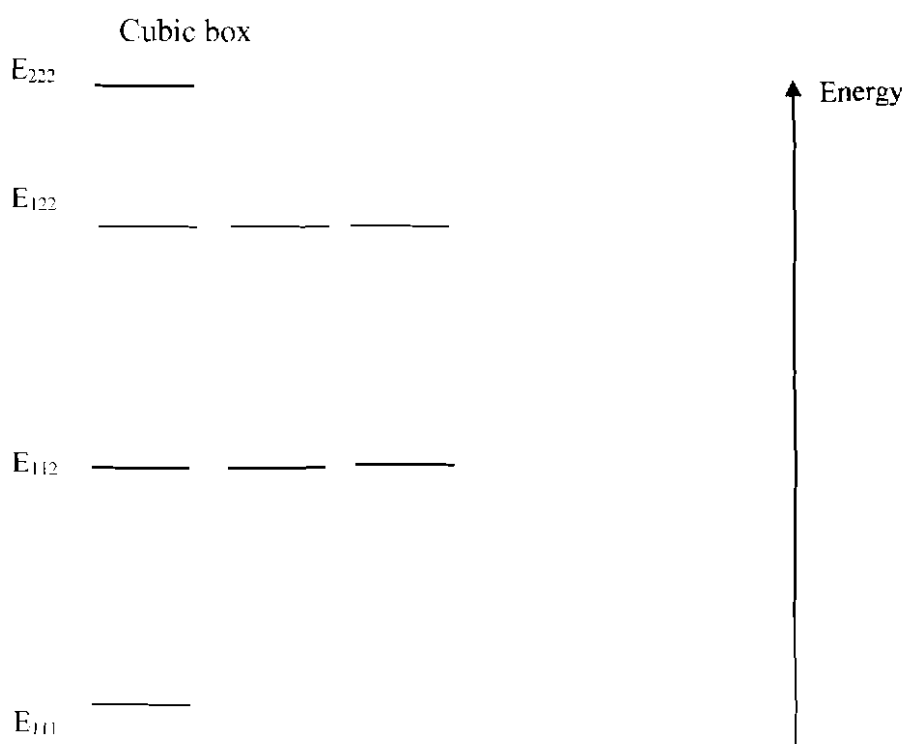
E_{111}: only a single state.

E_{112}: triple degenerate, either n_x, n_y or n_z can equal to 2.

E_{122}: triple degenerate, either n_x, n_y or n_z can equal to 1.

E_{222}: single state.

Energy diagram:

Cubic box

E_{222} _____

E_{122} _____ _____ _____

E_{112} _____ _____ _____

E_{111} _____

↑ Energy

4 pts

Theoretical	Code:		Question	1a	1b	2	3	Total
Problem 2	**Examiner**		Mark	12	8	3	10	**33**
5.0 % of the total			Grade	^{i}2	4	3	/6	

Problem 2. Dissociating Gas Cycle

Dininitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
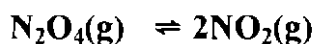
1.00 mole of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

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.

1a.	$N_2O_4 \rightleftharpoons 2 NO_2$	

Initial molar number   1   0

At equilibrium   1 - x   2x

$n_{total.equi.} = 1 - x + 2x = 1 + x$ (mol)

$P_{total.equi} = P_{ini}(1 + x)$

(P_{ini} - initial pressure; $n_{total.equi.}$ - total molar number of gases at equilibrium; $P_{total.equi}$ - total pressure of gases at equilibrium; x - number of moles N_2O_4 dissociated).

$$n_{total\,.equi} = \frac{PV}{RT} = \frac{(1.190\,\text{bar})\left(\dfrac{10^5\,\text{Pa}}{1\,\text{bar}}\right)(24.44\,\text{dm}^3)\left(\dfrac{1\,\text{m}^3}{1000\,\text{dm}^3}\right)}{(8.3145\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\,\text{K})} = 1.174\,(\text{mol})$$

$1.174 = 1 + x$

4pts

The 46th IChO – Theoretical Examination. Official English Version

8

x = 0.174 (mol)

ΔG^0 at 298 K

At equilibrium:

$$P_{N_2O_4} = \frac{1-x}{1+x} \times P_{total} = \frac{1-0.174}{1+0.174} \times (1.190\,\text{bar}) = 0.837\,\text{bar}$$

$$P_{NO_2} = \frac{2x}{1+x} \times P_{total} = \frac{2\times0.174}{1+0.174} \times (1.190\,\text{bar}) = 0.353\,\text{bar}$$

$$K_{298} = \frac{\left(\dfrac{P_{NO_2}}{P^0}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\dfrac{0.353}{1}\right)^2}{\left(\dfrac{0.837}{1}\right)} = 0.1489$$

At 298 K,

$$\Delta G^0 = -RT\ln K_{298} = -8.3145 \times 298 \times \ln(0.1489) = 4719\,(J \cdot mol^{-1}) = 4.72\,(kJ \cdot mol^{-1})$$ 4pts

1b. ΔG^0 at 348 K

$$n_{total,equi} = \frac{PV}{RT} = \frac{(1.886\,\text{bar})\left(\dfrac{10^5\,\text{Pa}}{1\,\text{bar}}\right)(24.44\,\text{dm}^3)\left(\dfrac{1\,\text{m}^3}{1000\,\text{dm}^3}\right)}{(8.3145\,J \cdot K^{-1} \cdot mol^{-1})(348\,K)} = 1.593\,(\text{mol})$$

1.593 = 1 + x

x = 0.593 (mol)

At equilibrium:

$$P_{N_2O_4} = \frac{1-x}{1+x} \times P_{total} = \frac{1-0.593}{1+0.593} \times (1.886\,\text{bar}) = 0.482\,\text{bar}$$

$$P_{NO_2} = \frac{2x}{1+x} \times P_{total} = \frac{2\times0.593}{1+0.593} \times (1.886\,\text{bar}) = 1.404\,\text{bar}$$

$$\Rightarrow K_{348} = \frac{\left(\dfrac{P_{NO_2}}{P^0}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\dfrac{1.404}{1}\right)^2}{\left(\dfrac{0.482}{1}\right)} = 4.0897$$

At 348 K.

$$\Delta G^0 = -RT\ln K_{348} = -8.3145 \times 348 \times \ln(4.0897) = -4075\,(J \cdot mol^{-1}) = -4.07\,(kJ \cdot mol^{-1})$$

4pts

The 46th IChO – Theoretical Examination. Official English Version

9

|	
ΔS^0 $\Delta G^0_{348} = -4.07\ kJ = \Delta H - 348\Delta S$ (1) $\Delta G^0_{298} = 4.72\ kJ = \Delta H - 298\Delta S$ (2) (2) - (1) → $\Delta S = 0.176\ kJ \cdot mol^{-1} \cdot K^{-1}$	4pts
ΔH^0 $\Delta H^0 = 4.720 + 298 \times 0.176 = 57.2\ (kJ \cdot mol^{-1})$	4pts

If you cannot calculate ΔH^0, use $\Delta H^0 = 30.0\ kJ \cdot mol^{-1}$ 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→2) in a compressor (**X**), and heated (2→3). Some N_2O_4 dissociates into NO_2. The hot mixture is expanded (3→4) through a turbine (**Y**), resulting in a decrease in both temperature and pressure. The mixture is then cooled further (4→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.
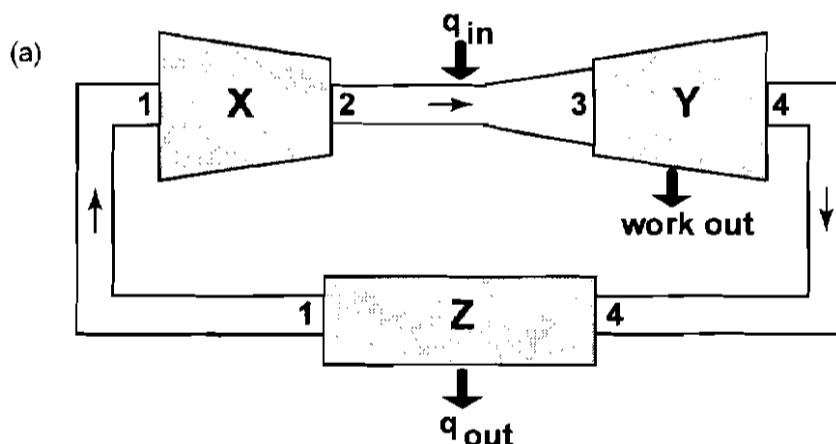
To understand the benefits of using reversible dissociating gases such as N_2O_4, we will focus on step 3 → 4 and consider an ideal gas turbine working with 1 mol of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, **no heat is exchanged.**

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

$\Delta U = q + w$: work done by turbine w(air)$=-w$	1 pt
$q = 0$, thus w(air) $= \Delta U = C_{v,m}$(air)$[T_3\text{-}T_4]$	2 pts

3. Estimate the ratio $w_{(N2O4)}/w_{(air)}$, in which $w_{(N2O4)}$ 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 (N_2O_4 + NO_2) is unchanged until the expansion is completed.

$$\ln\frac{K_{440}}{K_{348}} = \frac{\Delta H^0}{R}\left(\frac{1}{348} - \frac{1}{440}\right) = \frac{57200}{8.3145}\left(\frac{1}{348} - \frac{1}{440}\right)$$ $$\ln K_{440} = \ln K_{348} + \frac{57200}{8.3145}\times\left(\frac{1}{348} - \frac{1}{440}\right) = \ln 4.0897 + \frac{57200}{8.314}\times\left(\frac{1}{348} - \frac{1}{440}\right) = 5.542$$ $\rightarrow K_{440} = 255.2$ N_2O_4 $\rightleftharpoons$ $2\,NO_2$ (1) Initial molar number 1 0 At equilibrium 1 - x 2x $n_{total} = 1 - x + 2x = 1 + x$ (mol); $P_{total} = 12.156$ bar At equilibrium: $P_{N_2O_4} = \dfrac{1-x}{1+x}\times 12.156$ (bar); $P_{NO_2} = \dfrac{2x}{1+x}\times 12.156$ (bar)	3 pts

$$\Rightarrow K_{440} = \frac{\left(\dfrac{P_{NO_2}}{P^0}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\dfrac{\dfrac{2x}{1+x} \times 12.156}{1}\right)^2}{\left(\dfrac{\dfrac{1-x}{1+x} \times 12.156}{1}\right)} = 255.2$$

$$(P^0 = 1 \text{ bar}) \quad \rightarrow \quad \frac{\left(\dfrac{2x}{1+x}\right)^2}{\left(\dfrac{1-x}{1+x}\right)} = 20.99 \Rightarrow \frac{4x^2}{1-x^2} = 20.99 \Rightarrow \quad 4x^2 = 20.99 - 20.99\, x^2$$

$$\rightarrow 24.99\, x^2 = 20.99 \quad \rightarrow \quad x = 0.92; \quad n_{total} = 1 + x = 1.92$$

3pt

$$\rightarrow \quad w_{N_2O_4} = 1.92 \times C_{v,air} \times (T_3 - T_4); \quad \rightarrow \quad \frac{w_{N_2O_4}}{w_{air}} = 1.92$$

4 pt

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 $Ag^{II}O$.

☐	☐
Diamagnetic	Paramagnetic
	x 1 point

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 : ....+1
Oxidation number of Ag2 : .... +3   2 points

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

The coordination number of O atoms = ... 3	1 point

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

Number of Ag^I = ... 1 Number of Ag^{III} = ... 2	2 points

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

☐ Diamagnetic   ☐ Paramagnetic

x   1 point

The Ag^I is d^{10} hence diamagnetic; the Ag^{III} is square planar d^8 also diamagnetic

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**.

$$S_2O_8^{2-}{}_{(aq)} + 2Ag^+{}_{(aq)} + 2H_2O_{(l)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + Ag^IAg^{III}O_2{}_{(s)} + 4H^+{}_{(aq)}$$
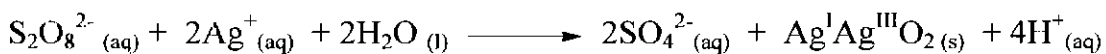
1 point

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

Atom	Standard enthalpy of formation (kJ·mol⁻¹)	1ˢᵗ ionization (kJ·mol⁻¹)	2ⁿᵈ ionization (kJ·mol⁻¹)	3ʳᵈ ionization (kJ·mol⁻¹)	1ˢᵗ electron affinity (kJ·mol⁻¹)	2ⁿᵈ electron affinity (kJ·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	ΔH°_{f} (kJ·mol⁻¹)
$Ag^{I}Ag^{III}O_{2\,(s)}$	–24.3
$Cu^{II}O_{(s)}$	–157.3

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

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

U_{lat} of $Ag^{I}Ag^{III}O_{2}$

Calculations:

$\Delta H_{lat}(Ag^{I}Ag^{III}O_{2})$ $= 2\,\Delta H^{\circ}_{f}(O^{2-}) + \Delta H^{\circ}_{f}(Ag^{+}) + \Delta H^{\circ}_{f}(Ag^{3+}) - \Delta H^{\circ}_{f}(Ag^{I}Ag^{III}O_{2})$

$= (2\times249 - 2\times141 + 2\times844) + (284.9 + 737.2) + (284.9 + 737.2 + 2080.2 + 3367.2) - (-24.3)$

$= +9419.9\ (kJ\cdot mol^{-1})$

$U_{lat}(Ag^{I}Ag^{III}O_{2})$ $= \Delta H_{lat}(Ag^{I}Ag^{III}O_{2}) - 4RT$

$= +9419.9 - 10.0 = +\mathbf{9409.9}\ (kJ\cdot mol^{-1})$ 3 points

(no penalty if negative sign)

U_{lat} of $Cu^{II}O$

Calculations for: **U_{lat} of $Cu^{II}O$**

$\Delta H_{lat}(Cu^{II}O) = \Delta H^{\circ}_{f}(O^{2-}) + \Delta H^{\circ}_{f}(Cu^{2+}) - \Delta H^{\circ}_{f}(Cu^{II}O)$

$= (249 - 141 + 844) + (337.4 + 751.7 + 1964.1) - (-157.3)$

$= 4162.5\ (kJ\cdot mol^{-1})$

$U_{lat}(Cu^{II}O) = \Delta H_{lat}(Cu^{II}O) - 2RT = 4162.5 - 5.0 = \mathbf{4157.5}\ (kJ\cdot mol^{-1})$

3 points

(no penalty if negative sign)

---

*If you can not calculate the U_{lat} of $Ag^{I}Ag^{III}O_{2}$ and $Cu^{II}O$, use following values for further calculations: U_{lat} of $Ag^{I}Ag^{III}O_{2}$ = **8310.0** kJ·mol⁻¹; U_{lat} of $Cu^{II}O$ = **3600.0** kJ·mol⁻¹.*

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 (kJ·nm·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)
Cu^{II}O	0.02030
Ag$^{III}_2$O$_3$	0.06182
Ag^{II}Ag$^{III}_2$O$_4$	0.08985

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

Calculations:

$V_m(\text{Ag}^{II}\text{O})$ = $V_m(\text{Ag}^{II}\text{Ag}^{III}_2\text{O}_4)$ - $V_m(\text{Ag}^{III}_2\text{O}_3)$ = 0.08985 − 0.06182 = **0.02803 nm^3**

From the relationship $U_{lat} = C \times (V_m)^{-1/3}$ we have

$$\frac{U_{lat}(\text{Ag oxide})}{U_{lat}(\text{Cu oxide})} \approx \left[\frac{V_m(\text{Cu oxide})}{V_m(\text{Ag oxide})} \right]^{\frac{1}{3}}$$

$$U_{lat}(\text{Ag}^{II}\text{O}) = 4157.5 \times \sqrt[3]{\frac{0.02030}{0.02803}} = \textbf{3733.6} \ (\text{kJ·mol}^{-1}) \qquad \text{3 points}$$

Answer: **3733.6**   (kJ.mol^{-1}) [or 3232.9 kJ·mol^{-1} if using U_{lat} Cu^{II}O = 3600 kJ·mol^{-1}]

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

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

$$2Ag^{II}O_{(s)} \xrightarrow{\Delta H_{rxn}} Ag^{I}Ag^{III}O_{2\,(s)}$$

$$\downarrow 2U_{lat}(AgO) + 4RT \qquad\qquad \uparrow -U_{lat}(Ag^{I}Ag^{III}O) - 4RT$$

$$2Ag^{2+}{}_{(g)} + 2O^{2-}{}_{(g)} \xrightarrow{IE_3(Ag) - IE_2(Ag)} Ag^{+}{}_{(g)} + Ag^{3+}{}_{(g)} + 2O^{2-}{}_{(g)}$$

Calculations:

$$\Delta H_{rxn} = 2U_{lat}(Ag^{II}O) + 4RT + IE_3 - IE_2 - U_{lat}(Ag^{I}Ag^{III}O_2) - 4RT$$

$$= 2 \times 3733.6 + 3367.2 - 2080.2 - 9409.9$$

$$= -655.7 \text{ (kJ/mol) or } -663.0 \text{ kJ/mol using given } U_{lat} \text{ values} \quad 4 \text{ pts}$$
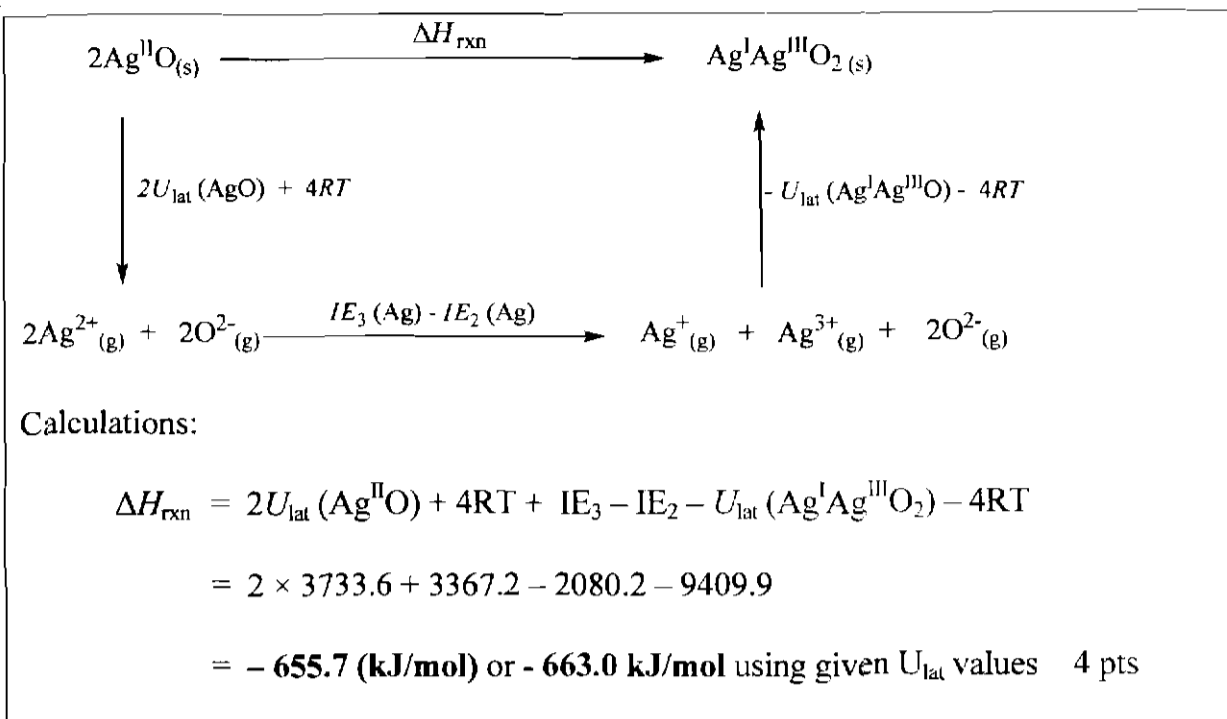
2d. Indicate which compound is thermodynamically more stable by checking the appropriate box below.

$Ag^{II}O$	$Ag^{I}Ag^{III}O_2$
☐	☐
	x 1 point

3. When $Ag^{I}Ag^{III}O_2$ 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**:
$$Ag^{I}Ag^{III}O_{2\,(s)} + 4\,HClO_{4\,(aq)} \longrightarrow 2Ag(ClO_4)_{2\,(aq)} + 2\,H_2O_{(l)} \qquad 1 \text{ point}$$

For **C**: $4Ag(ClO_4)_{2\,(aq)} + 2\,H_2O_{(l)} \longrightarrow 4\,AgClO_{4\,(aq)} + 4\,HClO_{4\,(aq)} + O_{2\,(g)}$
$$1 \text{ point}$$
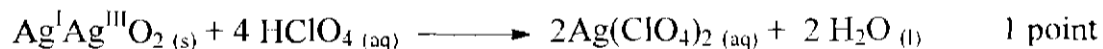
4. Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex **Z** is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of $AgNO_3$ and 2 mL of pyridine (d = 0.982 g/mL) is added to a stirred, ice-cold aqueous solution of 5.000 g of $K_2S_2O_8$. 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.

Calculations:

Calculations:

- Mole Ag in 0.6164 g of **Z** = mole of AgCl = 0.001 mole

- Mole SO_4^{2-} from 0.6160 g of **Z** = mole $BaSO_4$ = 0.002 mol

- Mass percentage of Ag = $0.001 \times 107.87/0.6164 = 17.50\%$

- Mass percentage of $SO_4^{2-} = 0.002 \times 96.06/0.6164 = 31.17\%$

- From EA:

Ratio $Ag^{2+} : SO_4^{2-} : C : H : N = \dfrac{17.50}{107.87} : \dfrac{31.17}{192.12} : \dfrac{38.96}{12.01} : \dfrac{3.28}{1.01} : \dfrac{9.09}{14.01} = 1 : 2 : 20 : 20 : 4$

The empirical formula of **Z** is: $C_{20}H_{20}AgN_4O_8S_2$ **2 points**

$\text{Yield} = \dfrac{1.719}{\dfrac{0.500}{169.87} \times 616.4} \times 100\% = 94.7\%$ **1 point**

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.)

-    $\sqrt{n(n+2)} = 1.78$ (n is number of unpaired electron of Ag)
-    $n = 1$, corresponds to Ag^{II} (d^9)
-    Most rational molecular formula of **Z** is $[Ag^{II}(Py)_4](S_2O_8)$ **3 point**

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

Formation of **Z**:

$2Ag^+_{(aq)} + 8Py_{(l)} + 3S_2O_8^{2-}_{(aq)} \longrightarrow 2[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 2SO_4^{2-}_{(aq)}$ 2 pts
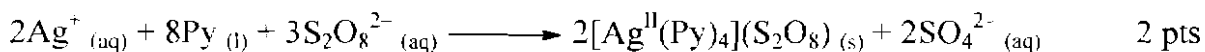
Destruction of **Z** with NH_3:

$[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 6NH_{3(l)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + \frac{1}{2}N_{2(g)} + 2SO_4^{2-}_{(aq)} + 3NH_4^-_{(aq)} + 4Py_{(l)}$ 2 pts
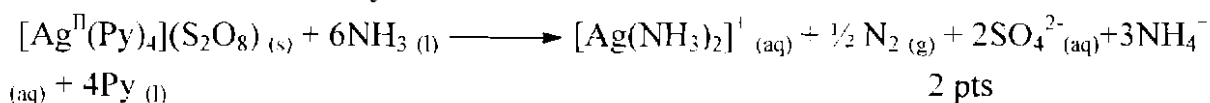
(All reasonable N –containing products and O_2 are acceptable)

Formation of **D**:

$[Ag(NH_3)_2]^+_{(aq)} + 2H^-_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)} + 2NH_4^+_{(aq)}$ 1 pt

Formation of **E**:

$Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow BaSO_{4(s)}$ 1pt

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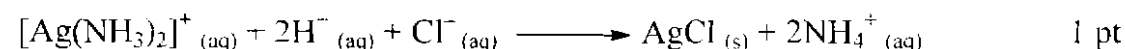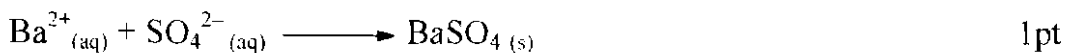
Theoretical	**Code:**		Question	1a	1b	2a	3a	3b	3c	Total
Problem 4	**Examiner**		Mark	4	1	10	2	6	4	27
4.0 % of the total			Grade							

Problem 4. Zeise's Salt

1. Zeise's salt, $K[PtCl_3C_2H_4]$, 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 $K_2[PtCl_6]$ and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from $K_2[PtCl_4]$ 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.

$PtCl_4 + 2\ C_2H_5OH \rightarrow H[PtCl_3C_2H_4] + CH_3CH=O + HCl + H_2O$

$H[PtCl_3C_2H_4] + KCl \rightarrow K[PtCl_3C_2H_4] + HCl$

$K_2[PtCl_6] + 2\ C_2H_5OH \rightarrow K[PtCl_3C_2H_4] + CH_3CH=O + KCl + 2\ HCl + H_2O$

$K_2[PtCl_4] + C_2H_4 \rightarrow K[PtCl_3C_2H_4] + KCl$
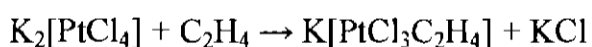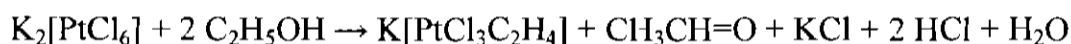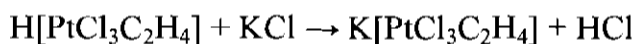
1pt for each (2 pts if the first two reactions combined). total of 4 pts

---

1b. Mass spectrometry of the anion $[PtCl_3C_2H_4]^-$ shows one set of peaks with mass numbers 325-337 au and various intensities.

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

Isotope	$^{192}_{78}Pt$	$^{194}_{78}Pt$	$^{195}_{78}Pt$	$^{196}_{78}Pt$	$^{198}_{78}Pt$	$^{35}_{17}Cl$	$^{37}_{17}Cl$	$^{12}_{6}C$	$^{13}_{6}C$	$^{1}_{1}H$
Natural abundance, %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

Calculations:

$195 + 3 \times 35 + 2 \times 12 + 4 \times 1 = 328$ 1 pt

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

(Z1)   (Z2)   (Z3)   (Z4)   (Z5)
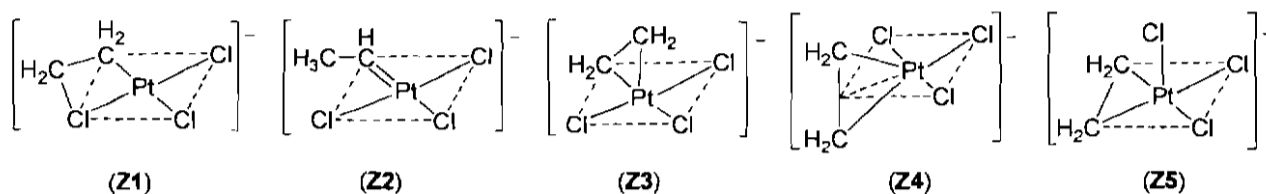
In structure **Z1**, **Z2**, and **Z5** both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

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 hydrogen atoms are in different environments, and 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	2 1pt	2 1 pt
Z2	2 1pt	2 1 pt
Z3	2 1pt	2 1 pt
Z4	1 1pt	1 1 pt
Z5	2 1pt	1 1 pt

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:

$$CO, CN^-, C_2H_4 > PR_3, H^- > CH_3^-, C_6H_5^-, I^-, SCN^- > Br^- > Cl^- > Py > NH_3 > OH^-, H_2O$$
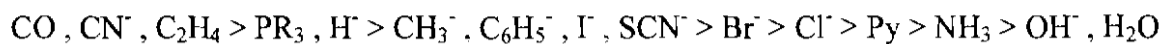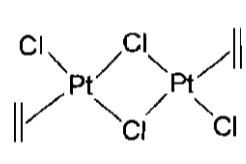
In above series a left ligand has stronger *trans effect* than a right ligand.
Some reactions of Zeise's salt and the complex $[Pt_2Cl_4(C_2H_4)_2]$ are given below.
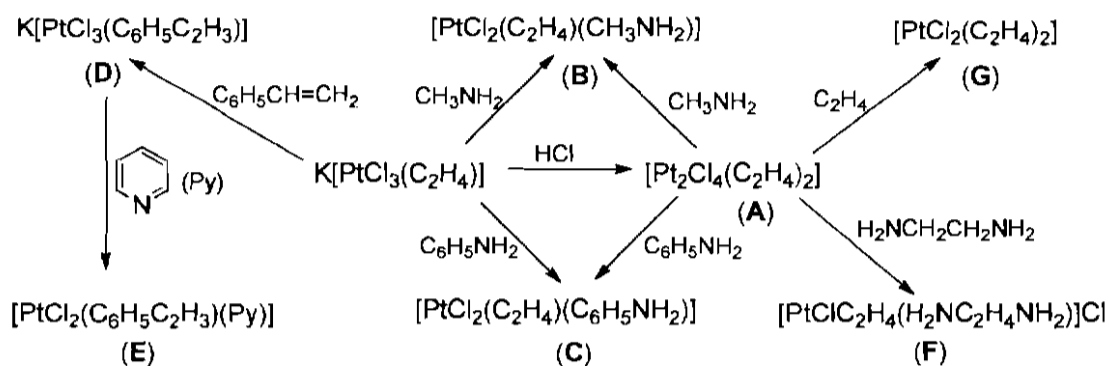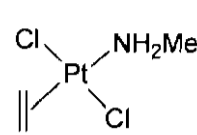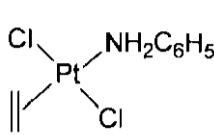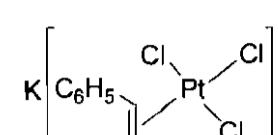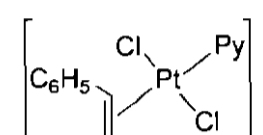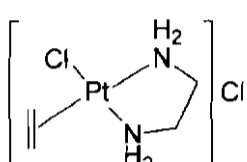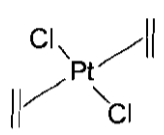
3a. <u>**Draw the structure of A**</u>, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.

Structure of A		2 pt

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

B	C	D
Cl⟍ Pt ⟋NH₂Me, ‖, Cl	Cl⟍ Pt ⟋NH₂C₆H₅, ‖, Cl	K [C₆H₅‖ Pt with Cl, Cl, Cl]
1 pt	1 pt	1 pt

E	F	G
[C₆H₅‖ Cl Pt Py, Cl]	[Cl‖ Pt N H₂, N H₂] Cl	Cl⟍ Pt ‖, Cl
1 pt	1 pt	1 pt

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)	i	iii and iv
	2 pts	2 pts

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.]

Solution: In solution **X**, H^+ was produced from the reactions :

$$HA \rightleftharpoons H^+ + A^- \quad \text{and} \quad HB \rightleftharpoons H^+ + B^- \quad \text{and} \quad H_2O \rightleftharpoons H^+ + OH^-$$

The positive and negative charges in an aqueous solution must balance. Thus the charge balance expression is:

$$[OH^-] + [A^-] + [B^-] = [H^+] \qquad (\text{Eq.1})$$

In the acidic solution (pH = 3.75), $[OH^-]$ can be neglected, so:

$$[A^-] + [B^-] = [H^+] \qquad (\text{Eq. 2})$$

From equilibrium expression: $\dfrac{[H^+] \times [A^-]}{[HA]} = K_{HA}$

and $[HA] = [HA]_i - [A^-]$ *(where [HA]$_i$ is the initial concentration)*

So: $[H^+] \times [A^-] = K_{HA} \times [HA] = K_{HA}([HA]_i - [A^-])$

Thus, the equilibrium concentration of $[A^-]$ can be presented as:

$$[A^-] = \frac{K_{HA} \times [HA]_i}{K_{HA} + [H^+]}$$

Similarly, the equilibrium concentration of $[B^-]$ can be presented as:

$$[B^-] = \frac{K_{HB} \times [HB]_i}{K_{HB} + [H^+]}$$

Substitute equilibrium concentrations of [A⁻] and [B⁻] into Eq.2:

$$\frac{K_{HA} \times [HA]_i}{K_{HA} + [H^+]} + \frac{K_{HB} \times [HB]_i}{K_{HB} + [H^+]} = [H^+]$$

2 pts

Since K_{HA}, K_{HB} are much smaller than [H⁺], thus:

$$\frac{K_{HA} \times [HA]_i}{[H^+]} + \frac{K_{HB} \times [HB]_i}{[H^+]} = [H^+]$$

or $1.74 \times 10^{-7} \times [HA]_i + 1.34 \times 10^{-7} \times [HB]_i = [H^+]^2 = (10^{-3.75})^2$

$1.74 \times [HA]_i + 1.34 \times [HB]_i = 0.316$ (Eq. 3)

Neutralization reactions show:

$$HA + NaOH \longrightarrow NaA + H_2O$$

$$HB + NaOH \longrightarrow NaB + H_2O$$
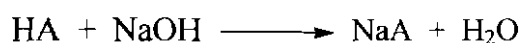
$n_{HA} + n_{HB} = n_{NaOH}$

or $([HA]_i + [HB]_i) \times 0.1\ L = 0.220\ M \times 0.1\ L$ 2 pts

$[HA]_i + [HB]_i = 0.220\ M$ (Eq. 4)

Solving Eq.3 and Eq.4 gives: $[HA]_i = 0.053\ M$ and $[HB]_i = 0.167\ M$

Concentration of HA =   0.053 M

Concentration of HB =   0.167 M   **2 pts**

---

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.

Solution:

Solution Y contains NaA 0.06 M and NaB 0.04 M. The solution is basic, OH⁻ was produced from the reactions:

$NaA + H_2O \rightleftharpoons HA + OH^-$ $K_{b,A} = K_w/K_{HA} = 5.75 \times 10^{-8}$

$NaB + H_2O \rightleftharpoons HB + OH^-$ $K_{b,B} = K_w/K_{HB} = 7.46 \times 10^{-8}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00\ 10^{-14}$

and we have:

$[H^+] + [HA] + [HB] = [OH^-]$ (Eq. 5)

In the basic solution, $[H^+]$ can be neglected, so:

$[HA] + [HB] = [OH^-]$ (Eq. 6)

From equilibrium expression: $\dfrac{[OH^-] \times [HA]}{[A^-]} = K_{b,A}$

and $[A^-] = 0.06 - [HA]$ 1 pt

Thus, the equilibrium concentration of HA can be presented as: $[HA] = \dfrac{K_{b,A} \times 0.06}{K_{b,A} + [OH^-]}$

Similarly, the equilibrium concentration of HB can be presented as: $[HB] = \dfrac{K_{b,B} \times 0.04}{K_{b,B} + [OH^-]}$

Substitute equilibrium concentrations of HA and HB into Eq. 6:

$\dfrac{K_{b,A} \times 0.06}{K_{b,A} + [OH^-]} + \dfrac{K_{b,B} \times 0.04}{K_{b,B} + [OH^-]} = [OH^-]$ 2 points

Assume that $K_{b,A}$ and $K_{b,B}$ are much smaller than $[OH^-]$ (*), thus:

$[OH^-]^2 = 5.75 \times 10^{-8} \times 0.06 + 7.46 \times 10^{-8} \times 0.04$

$[OH^-] = 8.02 \times 10^{-5}$ (the assumption (*) is justified)

So   pOH = 4.10 and **pH = 9.90**   **1 point**

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.

Solution: HA in the dilute solution:

$[A^-] = \alpha \times [HA]_i$

$[HA] = (1 - \alpha) \times [HA]_i$

$[H^+] = 10^{-7}$

Substitute these equilibrium concentrations into K_{HA} expression:

$\dfrac{10^{-7} \times \alpha \times [HA]_i}{(1-\alpha) \times [HA]_i} = K_{HA}$ or $\dfrac{10^{-7} \times \alpha}{(1-\alpha)} = 1.74 \times 10^{-7}$ 2 pts

Solving the equation gives: $\alpha = 0.635$

Similarly, for HB: $\dfrac{10^{-7} \times \alpha}{(1-\alpha)} = 1.34 \times 10^{-7}$

Solving the equation gives: $\alpha = 0.573$

- The percentage of dissociation of HA = **65.5 %** $6\,7,5\,°/,$

- The percentage of dissociation of HB = **57.3 %**   **2 points**

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 $mol\cdot L^{-1}$) of a subtancce $M(OH)_2$ in **Z**, given that the anions A^- and B^- can form complexes with M^{2+}:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.1 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.0 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^-$ $K'_1 = 6.2 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.3 \times 10^2$

Solution:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00 \times 10^{-14}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.10 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.00 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.20 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.30 \times 10^2$
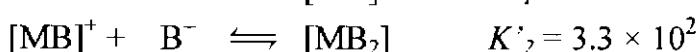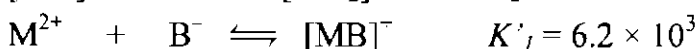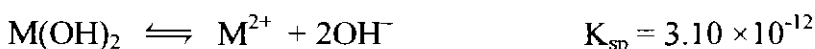
Solubility of $M(OH)_2 = s = [M^{2+}] + [MA^+] + [MA_2] + [MB^+] + [MB_2]$

pH of **Z** = 10.0

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{3.10 \times 10^{-12}}{(10^{-4})^2} = 3.10 \times 10^{-4} \text{ M}$$ Eq.1

At pH = 10.0

$$[A^-]_{total} = \frac{K_{HA} \times 0.06}{(K_{HA} + 10^{-10})} = 0.06$$

$[MA^+] = K_1[M^{2+}][A^-] = 2.1 \times 10^3 \times 3.10 \times 10^{-4} \times [A^-] = 0.651 \times [A^-]$ Eq. 3

$[MA_2] = K_1K_2[M^{2+}][A^-]^2 = 325.5 \times [A^-]^2$ Eq. 4

$[A^-]_{total} = [A^-] + [MA^+] + 2 \times [MA_2] = 0.06$ M   Eq. 5

Substitute Eq. 3 and Eq. 4 into Eq. 5:

$[A^-] + 0.651 \times [A^-] + 2 \times 325.5 \times [A^-]^2 = 0.06$ **2 pts**

Solve this equation: $[A^-] = 8.42 \times 10^{-3}$ M

Substitute this value into Eq. 3 and Eq. 4:

$[MA^+] = 0.651 \times [A^-] = 5.48 \times 10^{-3}$ M

$[MA_2] = 325.5 \times [A^-]^2 = 2.31 \times 10^{-2}$ M

Similarly,

$[B^-]_{total} = 0.04$ M

$[MB^+] = K_1'[M^{2+}][B^-] = 6.2 \times 10^3 \times 3.10 \times 10^{-4} \times [B^-] = 1.92 \times [B^-]$ Eq. 6

$[MB_2] = K_1'K_2'[M^{2+}][B^-]^2 = 634.3 \times [B^-]^2$ Eq.7

$[B^-]_{total} = [B^-] + [MB^+] + 2 \times [MB_2] = 0.04$ M   Eq. 8   2pts

Substitute Eq. 6 and Eq. 7 into Eq. 8:

$[B^-] + 1.92 \times [B^-] + 2 \times 634.3 \times [B^-]^2 = 0.04$

Solve this equation: $[B^-] = 4.58 \times 10^{-3}$ M

Substitute this value into Eq. 6 and Eq. 7:

$[MB^+] = 1.92 \times [B^-] = 8.79 \times 10^{-3}$ M

$[MB_2] = 634.3 \times [B^-]^2 = 1.33 \times 10^{-2}$ M

Thus, solubility of $M(OH)_2$ in **Z** is **s'**

s' $= 3.10 \times 10^{-4} + 5.48 \times 10^{-3} + 2.31 \times 10^{-2} + 8.79 \times 10^{-3} + 1.33 \times 10^{-2} = 5.10 \times 10^{-2}$ M

Answer: Solubility of $M(OH)_2$ in Z = 5.10×10^{-2} M.   **2 points**

Theoretical	Code:		Question	6a	6b	6c	6d	6e	Total
Problem 6 7.0 % of the 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:

$$\textbf{ArCl} \ + \textbf{RNH}_2 \ \xrightarrow[\text{NaO}^t\text{Bu, } Solvent]{\text{NiLL'}} \ \textbf{Ar-NHR} \ + \ \textbf{HCl}$$
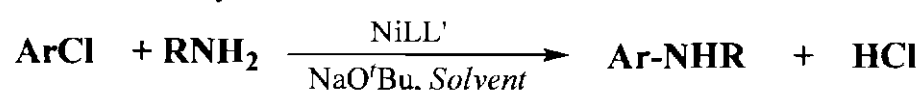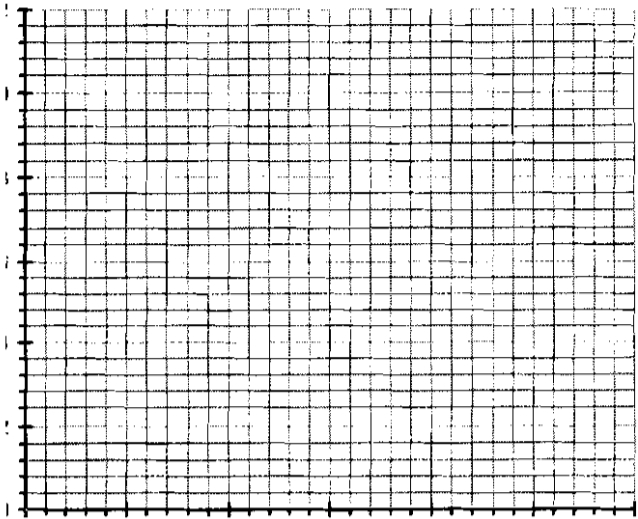
in which NiLL' is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

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)**
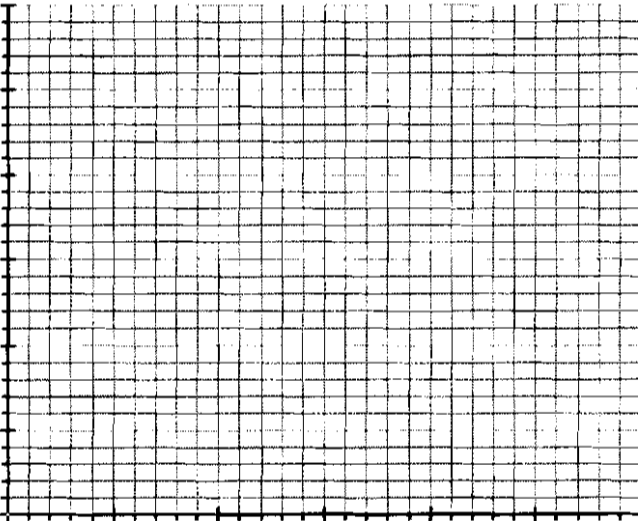
[ArCl] (M)	Initial rate (M s^{-1})	
0.1	1.88×10^{-5}	
0.2	4.13×10^{-5}	
0.4	9.42×10^{-5}	
0.6	1.50×10^{-4}	

The 46th IChO – Theoretical Examination. Official English Version

29

[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 **[ArCl]** = = 1
- Order with respect to **[NiLL']** = = 1
- Order with respect to **[L']** =   = -1   6 pts

6b. To study the mechanism for this reaction, ^{1}H, ^{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, NiL(Ar)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 °C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

$$\text{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NiL} + \text{L'} \qquad (1)$$

$$\text{NiL} + \text{ArCl} \xrightarrow{k_2} \text{NiL(Ar)Cl} \qquad (2)$$

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

The rate law expression for the formation of NiLAr(Cl) $$\text{rate} = \frac{k_1 k_2 [NiLL']\,[ArCl]}{k_{-1}[L'] + k_2[ArCl]} = \frac{k_1(k_2/k_{-1})[NiLL']\,[ArCl]}{[L'] + (k_2/k_{-1})[ArCl]}$$ **(4pts for [NiL] calculation)** **(4 pts for rate calculation)**	**8 pts**
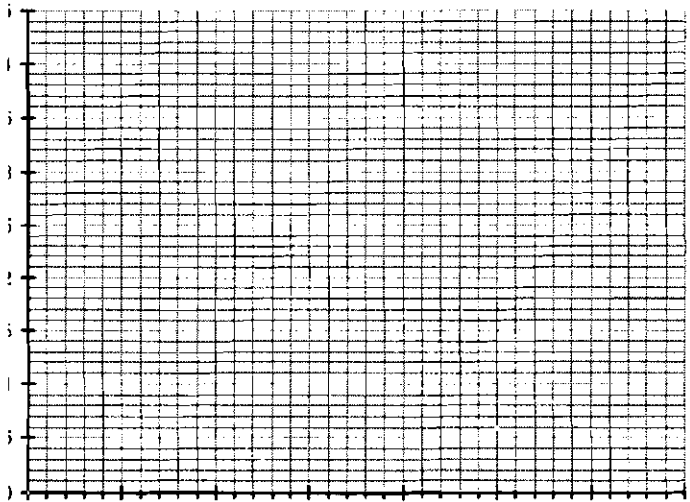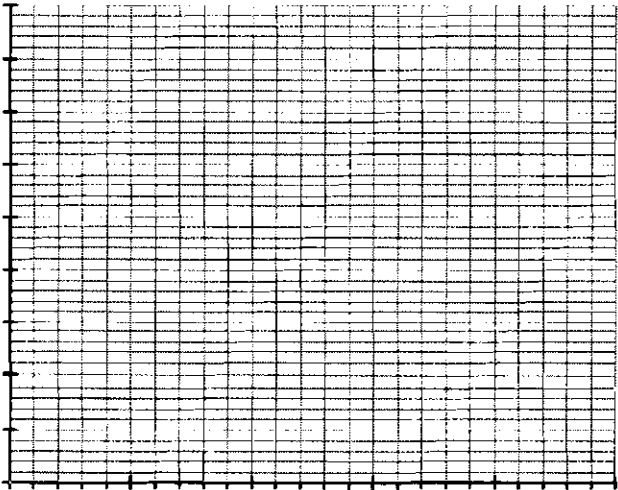
The 46th IChO – Theoretical Examination. Official English Version

31

The next steps in the overall reaction involve the amine (RNH$_2$) and ^{t}BuONa. To determine the order with respect to RNH$_2$ and ^{t}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.

[NaO^{t}Bu], (M)	Initial rate (M·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}

[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 each of these reagents, assuming each is an interger.
(Use the grids if you like)

- Order with respect to [NaO^{t}Bu] =	0	2 pts
- Order with respect to [RNH$_2$] =	0	2 pts

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:

$$NiLL' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL + L' \tag{1}$$

$$NiL + ArCl \xrightarrow{k_2} NiL\overset{Ar}{\underset{Cl}{<}} \tag{2}$$

$$NiL\overset{Ar}{\underset{Cl}{<}} + NH_2R + NaO^tBu \xrightarrow{k_3} NiL(Ar)NHR + {}^tBuOH + NaCl \tag{3}$$

$$NiL(Ar)NHR \xrightarrow{k_4} ArNHR + NiL \tag{4}$$
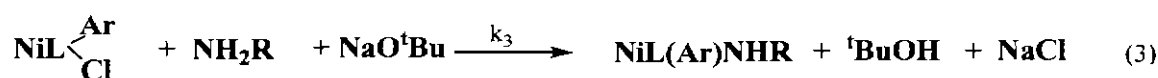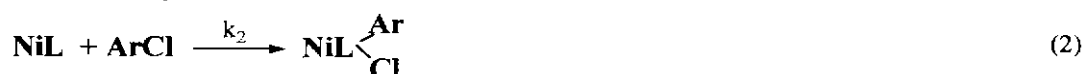
6d. Use the steady-state approximation and material balance equation to **derive** the rate law for d[ArNHR]/dt for the above mechanism in terms of the initial concentration of the catalyst [NiLL']$_0$ and concentrations of [ArCl], [NH$_2$R], [NaO^{t}Bu], and [L'].

Using the mechanism depicted by Reaction (1) through (4), the rate equation:

$$\frac{d[NiLL']}{dt} = -k_1[NiLL'] + k_{-1}[NiL][L']$$

$$\frac{d[NiL]}{dt} = k_1[NiLL'] - k_{-1}[NiL][L'] - k_2[NiL][ArCl] + k_4[NiL(Ar)NHR]$$

Apply the steady-state approximation to the concentrations for the intermediates:

$$\frac{d[NiL]}{dt} = 0$$

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)HNR] \quad \text{(Equation 1)} \quad 1pt$$

$$\frac{d[NiL(Ar)Cl]}{dt} = k_2[NiL][ArCl] - k_3[RNH_2][NaOBu][NiL(Ar)Cl] = 0$$

$$[NiL(Ar)Cl] = \frac{k_2}{k_3} \frac{[ArCl][NiL]}{[NH_2R][NaOBu]} \quad \text{(Equation 2)} \quad 1pt$$

$$\frac{d[NiL(Ar)NHR]}{dt} = k_3[NiL(Ar)Cl][NH_2R][NaOBu] - k_4[NiL(Ar)NHR] = 0$$

$$[NiL(Ar)NHR] = \frac{k_3}{k_4}\frac{[NiL(Ar)Cl][NH_2R][NaOBu]}{}$$ (Equation 3)

Substitute Equation 2 into Equation 3:

$$[NiL(Ar)NHR] = \frac{k_3}{k_4}\frac{[NH_2R][NaOBu]}{} \times \frac{k_2}{k_3}\frac{[ArCl][NiL]}{[NH_2R][NaOBu]} = \frac{k_2}{k_4}[ArCl][NiL]$$ (Eq. 4) 1pt

Substitute Equation 4 into Equation 1:

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)NHR]$$

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4 \times \frac{k_2}{k_4}[ArCl][NiL] = k_{-1}[NiL][L']$$ (Eq.5)

The material balance equation with respect to the catalyst is

$[NiLL']_0 = [NiLL'] + [NiL] + [NiLAr(Cl)] + [NiLAr(Cl)NHR]$ 2 pts

$$[NiLL']_0 = \frac{k_{-1}}{k_1}[NiL][L'] + [NiL] + \frac{k_2}{k_3}\frac{[NiL][ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[NiL][ArCl]$$

$$[NiLL']_0 = [NiL]\left[\frac{k_{-1}}{k_1}[L'] + 1 + \frac{k_2}{k_3}\frac{[ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[ArCl]\right]$$ 3 pts

$$[NiL] = [NiLL']_0 \times \frac{k_1k_3k_4[NH_2R][NaOBu]}{k_{-1}k_3k_4[L'][NH_2R][NaOBu] + k_1k_3k_4[NH_2R][NaOBu] + k_1k_2k_4[ArCl] + k_1k_2k_3[ArCl][NH_2R][NaOBu]}$$

<div align="right">Equation 6</div>

Substituting Equation 6 into the differential rate for [ArCl]:

$$-\frac{d[ArCl]}{dt} = k_2[ArCl][NiL],$$ results in the following predicted rate law expression for

the reaction mechanism:

d[ArNHR]/dt = - d[ArCl]/dt =

$k_2[ArCl] [NiL] = k_1k_2k_3k_4 [ArCl][NiLL']_0[NaO^tBu][NH_2R]$

$/\{k_{-1}k_3k_4[NH_2R][NaOBu][L'] + k_1k_3k_4[NaOBu][NH_2R] + k_1k_2k_4[ArCl] + k_1k_2k_3$

$[ArCl][NH_2R][NaOBu]\}$ 4 pts

6e. <u>Give</u> the simplified form of the rate equation in 6d assuming that k_1 is very small.

$d[ArNHR]/dt = - d[ArCl]/dt = $ $k_2[ArCl]\ [NiL] = k_1k_2\ [ArCl][NiLL^\cdot]_0\ /\ k_{-1}[L^\cdot]$ (i.e. consistent with all the orders of reaction as found in the beginning)   2 pts

Theoretical	Code:		Question	7a	7b	7c	7d	7e	7f	Total
Problem 7	Examiner		Mark	12	8	8	12	12	12	64
8.0 % of the total			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.
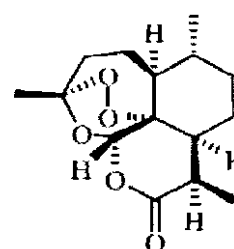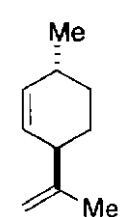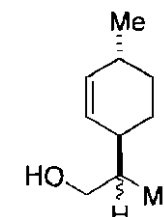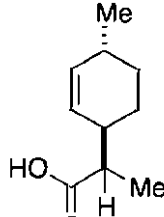
(+)-Artemisinin

First, pyrolysis of (+)-2-Carene broke the cyclopropane ring forming, among other products, (1R)-(+)-*trans*-isolimonene **A** ($C_{10}H_{16}$), 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.
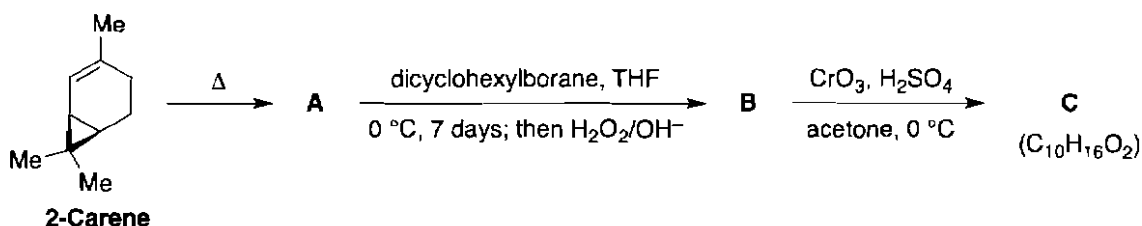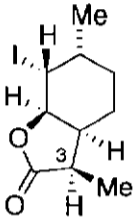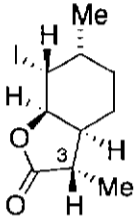
7a. Draw the structures (with stereochemistry) of the compounds **A-C**.

A	B	C
4 pts (2 pts if wrong stereochemistry)	4 pts	4 pts

The 46th IChO – Theoretical Examination. Official English Version

36

The acid **C** was subjected to iodolactonization using KI, I_2 in aqueous. $NaHCO_3$ solution to afford diastereomeric iodolactones **D** and **E** (which differ in stereochemistry only at C_3) in 70% yield.

$$\text{C} \xrightarrow[\text{48 h, dark}]{\text{I}_2,\ \text{KI, NaHCO}_3\ (\text{aq.})} \text{D} + \text{E}$$
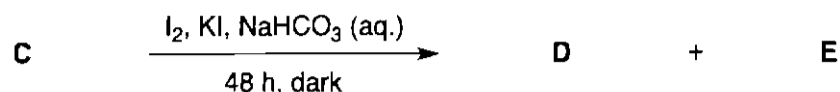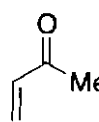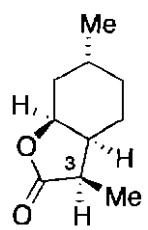
7b. <u>Draw</u> the structures (with stereochemistry) of the compounds **D** and **E**.

The acid **C** was converted to diastereomeric iodolactones **D** and **E** (epimeric at the chiral center C_3). Look at the number-indicated in the structure **F** in the next step.	
D	**E**
4 pts	4pts

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 C_7 along with compound **G** (~10%) and the reduced product **H**. $C_{10}H_{16}O_2$ (<5%).
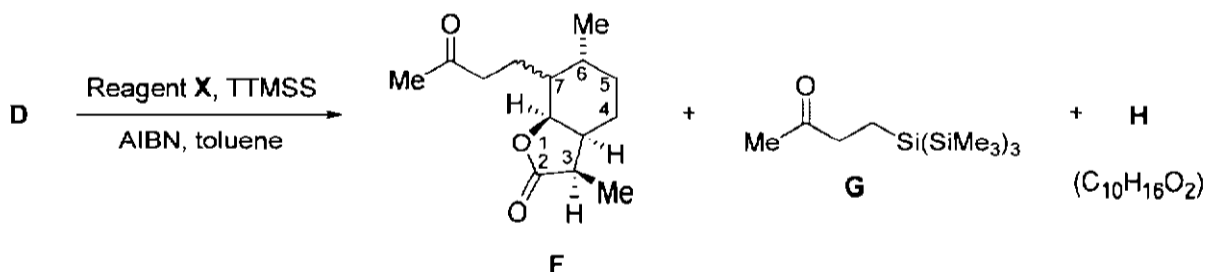
7c. Draw the structures (with stereochemistry) of compound **H** and the reagent **X**.
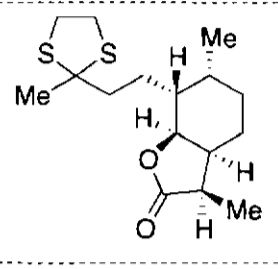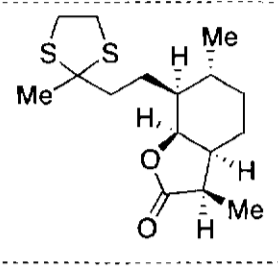
Because alkylated lactone **F** is known, we can deduce the reagent **X** as methyl vinyl ketone. **H** is the reduced product of **D**.

X	H
methyl vinyl ketone	
2 pts	6 pts

The keto group of **F** reacted with ethanedithiol and $BF_3 \cdot Et_2O$ 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.

$$\mathbf{F} \quad \xrightarrow[\text{BF}_3 \cdot \text{Et}_2\text{O, DCM, 0 °C}]{\text{HSCH}_2\text{CH}_2\text{SH}} \quad \mathbf{I} \quad + \quad \mathbf{J}$$
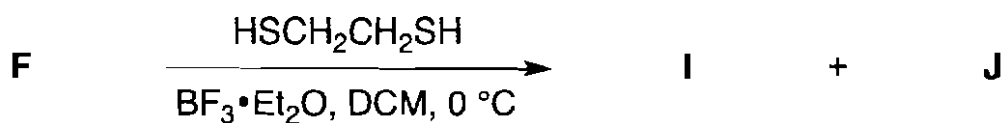
7d. <u>Draw</u> the structures (with stereochemistry) of the compounds **I** and **J**.

The keto group of lactone **F** reacted with ethanedithiol and $BF_3 \cdot Et_2O$ in dichloromethane to afford thioketal lactones. **I** and the major isomer **J**.

I	J
6 pts (3 pts if **I** and **J** are swapped)	6 pts (3 pts if **I** and **J** are swapped)

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).

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**.

$$
\textbf{J} \quad \xrightarrow[\text{3) } CH_2N_2/Et_2O]{\substack{\text{1) 10\% NaOH} \\ \text{2) 1\% HCl}}} \quad \textbf{K} \quad \xrightarrow{\text{PCC, 0 °C}} \quad \textbf{L}
$$
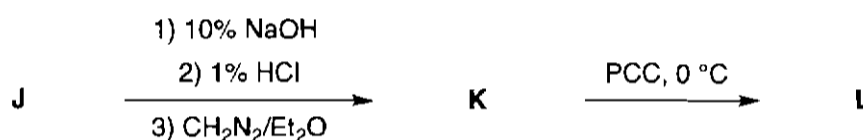
7e. Draw the structures (with stereochemistry) of the compounds K and L.

Hydrolysis followed by esterification of **J** provided hydroxy ester **K**.
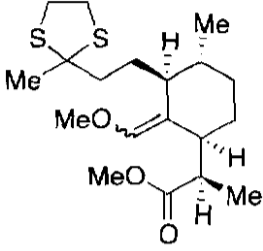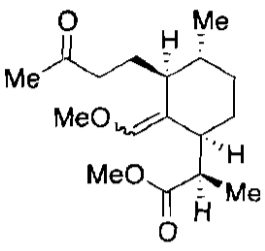
Oxidation of the hydroxy group in **K** by PCC resulted in the keto ester **L** in which two protons adjacent to the carbonyl group are cis-oriented.

K	L
6 pts	6 pts
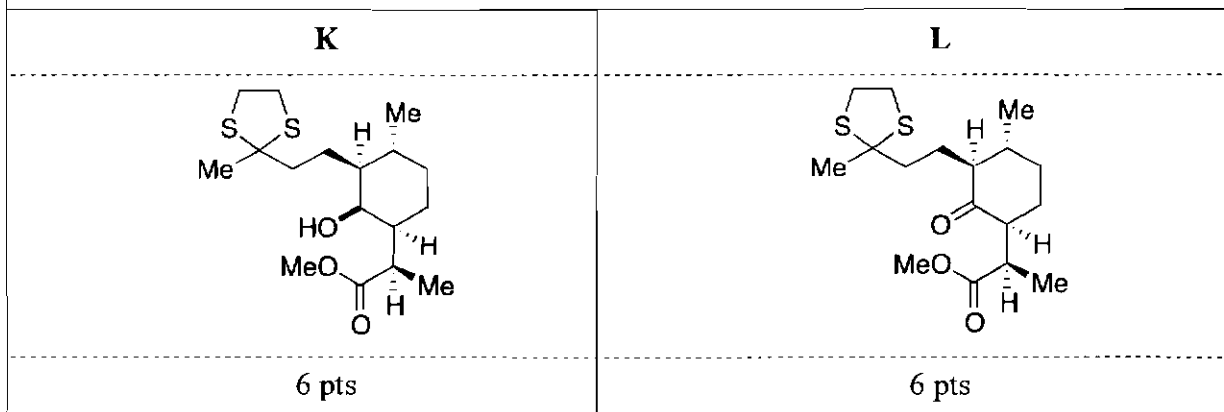
The ketone **L** was subjected to a Wittig reaction with methoxymethyl triphenylphosphonium chloride and KHMDS (Potassium HexaMethylDiSilazid - a strong, non-nucleophilic base) to furnish the required methyl vinyl ether **M** in 45% yield. Deprotection of thioketal using $HgCl_2$, $CaCO_3$ resulted in 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% $HClO_4$.

L $\xrightarrow[\text{KHMDS}]{\text{Ph}_3\text{P(Cl)CH}_2\text{OCH}_3}$ **M** $\xrightarrow{\text{HgCl}_2, \text{CaCO}_3}$ **N** $\xrightarrow[\text{2. HClO}_4]{\text{1. O}_2, \text{h}\nu}$

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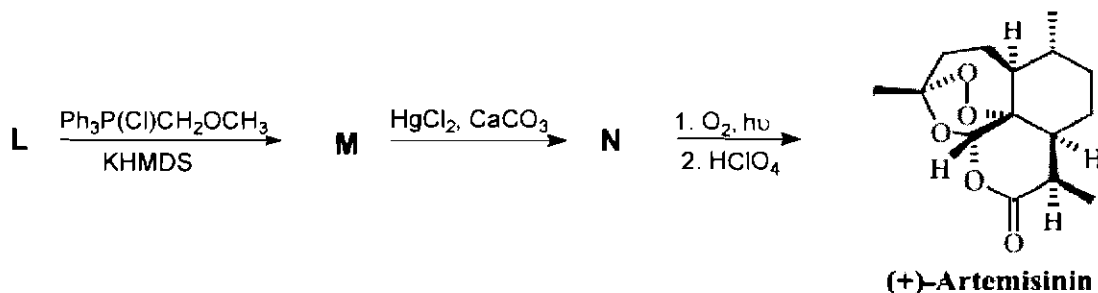
7f. Draw the structures (with stereochemistry) of the compounds **M** and **N**.

The Wittig reaction of the ketone **L** resulted in the formation of methyl vinyl ether **M**. Deprotection of the thioketal group forms the intermediate **N**.	
M	**N**
6 pts	6 pts

Theoretical	Code:		Question	8a	8b	8c	8d	Total
Problem 8	**Examiner**		Marks	15	2	12	10	**39**
8.0% of the total			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.
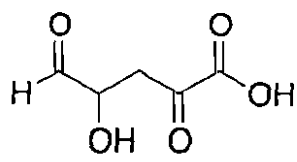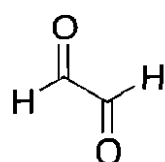
Acid **A** is isolated from the *star anise* fruit. The constitutional formula of **A** has been deduced from the following sequence of reactions:

$$A\ (C_7H_{10}O_5) \xrightarrow[\text{ii) Me}_2\text{S}]{\text{i) O}_3} B\ (C_7H_{10}O_7) \xrightarrow[25\ °C]{CH_3OH,\ H^+} C\ (C_8H_{12}O_7)$$

(I)

$$C \xrightarrow[(or\ H_5IO_6)]{HIO_4\cdot2H_2O} D \quad (II)$$

$$Y_3 + OHCCHO + OHCCH(OH)CH_2COCOOH \xleftarrow{H_2O,\ H^+} D$$
$$\quad\quad\quad Y_2 \quad\quad\quad\quad\quad Y_1$$
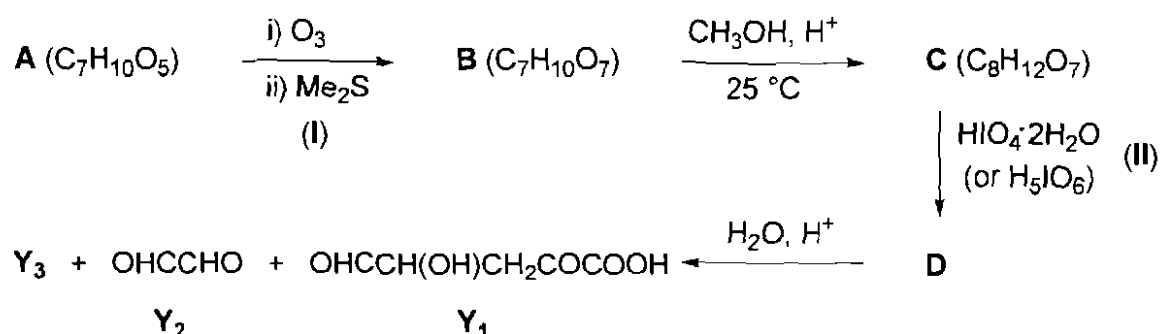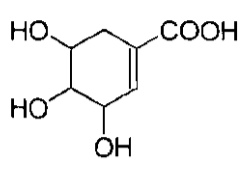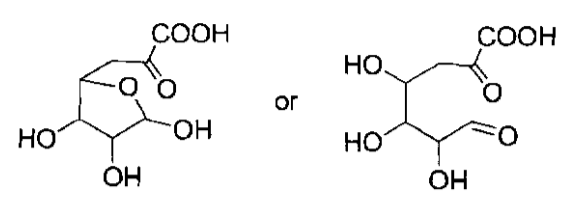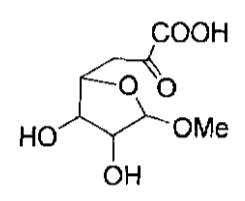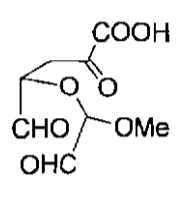
(I): this overall process results in alkene cleavage at the C=C bond, with each carbon of this becoming doubly bonded to an oxygen atom.

(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
(structure: OHC–CH(OH)–CH₂–C(=O)–COOH)	(structure: OHC–CHO)	CH₃OH
1pt	1 pt	2 pts

A	B
2 pts	2 pts

C	D
3 pts	4 pts

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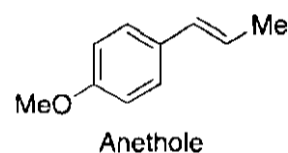
Anethole

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 ^{1}H NMR spectrum of **E** is given below.

The 46th IChO – Theoretical Examination. Official English Version

43
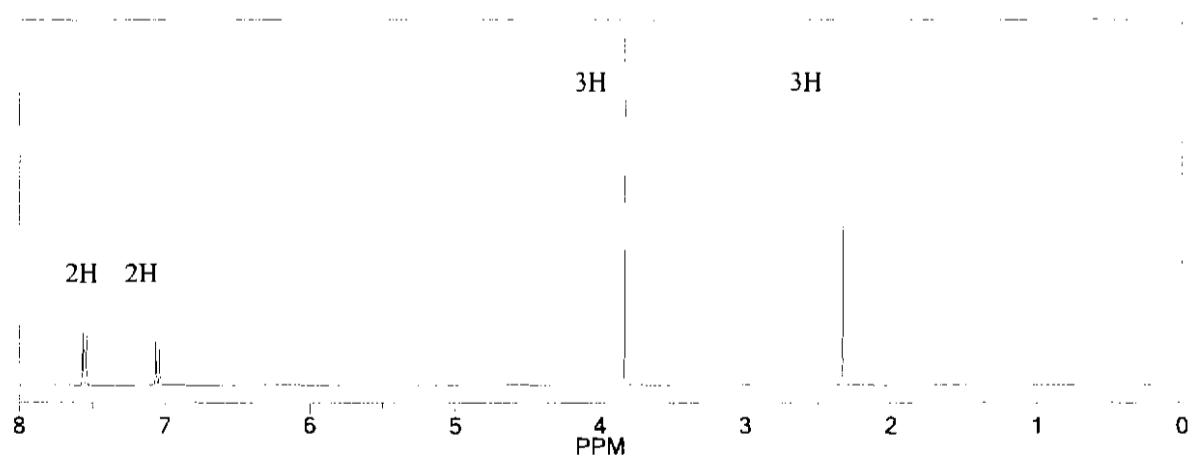
8b. What differences in the structure between **E** and anethole can be obtained from the ^{1}H NMR data?

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 ^{1}H NMR data	*v* [only]	2 pts
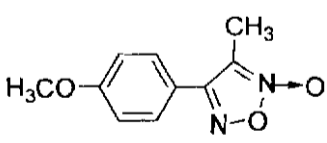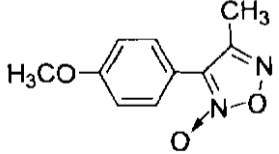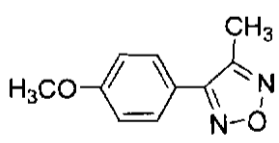
On heating at 150 °C for several hours, **E** is partially isomerized into **F**. Under the same conditions, **F** gives the identical equilibrium mixture to that obtained from **E**. On heating with phosphorus trichloride, both **E** and **F** lose one oxygen atom giving compound **G**. Compounds **E** and **F** have the same functional groups.
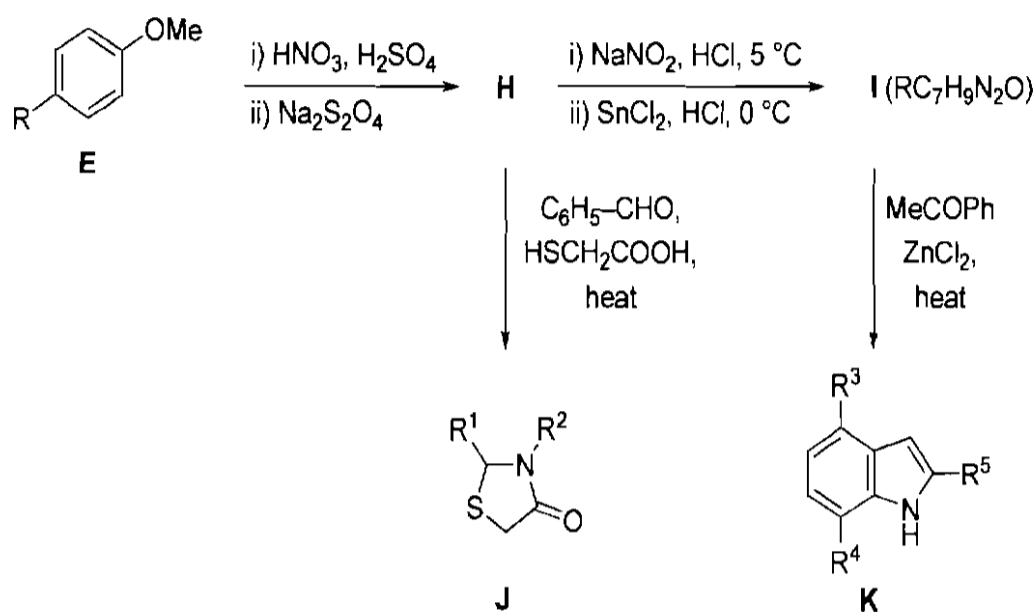
$$G \xleftarrow[- \text{POCl}_3]{\text{PCl}_3} E \xrightleftharpoons{150\ ^{\circ}C} F \xrightarrow[- \text{POCl}_3]{\text{PCl}_3} G$$
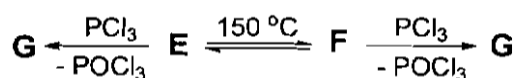
The chemical shifts of methyl protons in **E**, **F** and **G** are given below.

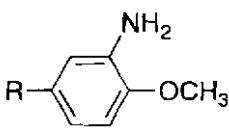|	**E**	**F**	**G**
CH_3-O	3.8 ppm	3.8 ppm	3.8 ppm
CH_3-C	2.3 ppm	2.6 ppm	2.6 ppm
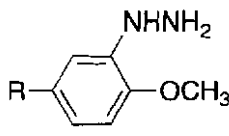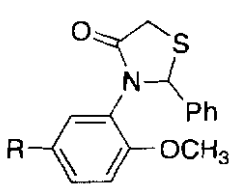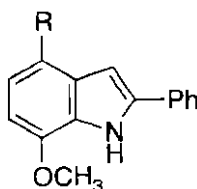
8c. Suggest structures for **E**, **F** and **G**, assuming that they do NOT contain three-membered rings.

E	**F**	**G**
4 pts	4 pts	4 pts

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$_2$CO$_2$H) leads to the formation of **J**. Reaction of **I** and methyl phenyl ketone in the presence of ZnCl$_2$ affords **K**.

The 46th IChO – Theoretical Examination. Official English Version

45

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

H	I
2 pts	2 pts
J	**K**
3 pts	3 pts

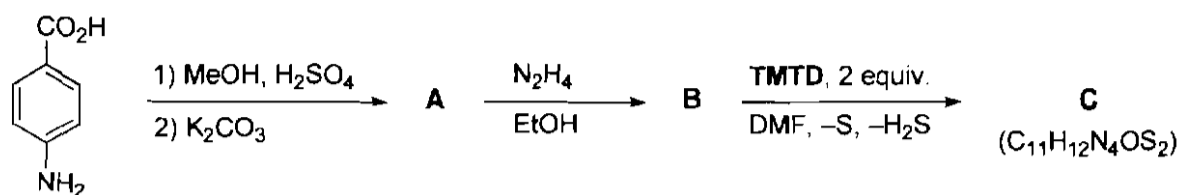The 46th IChO – Theoretical Examination. Official English Version

46

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:
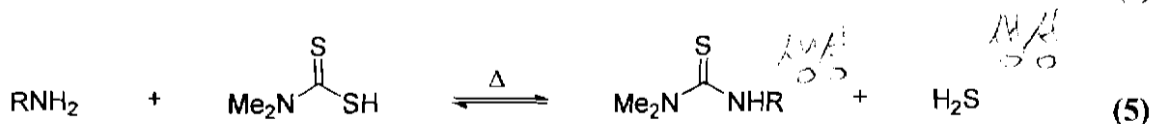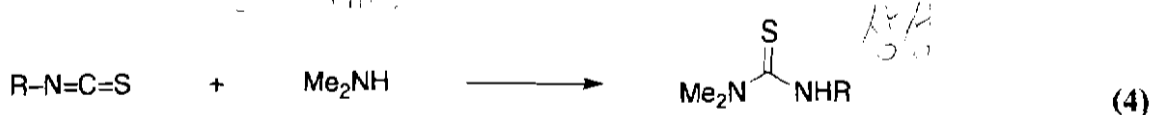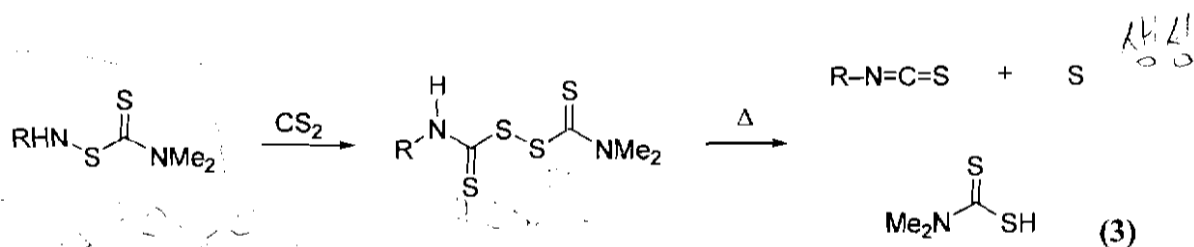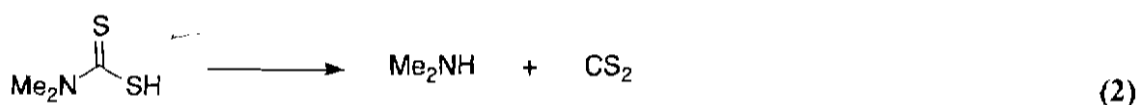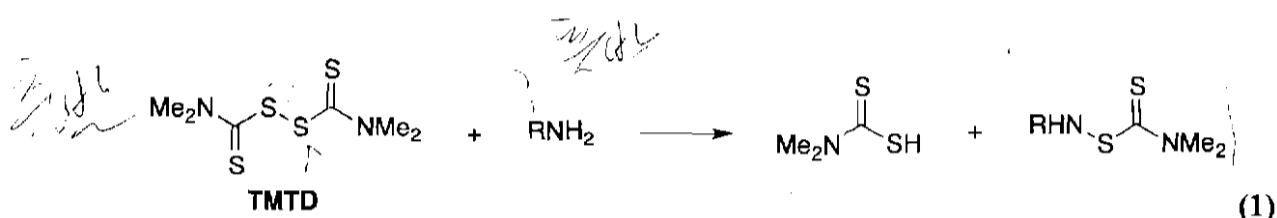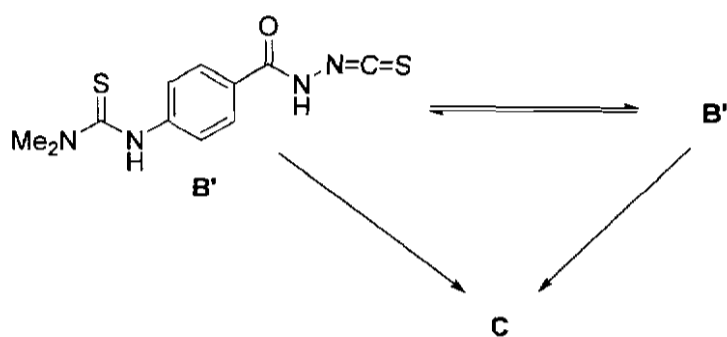

Similar transformations of benzohydrazides (containing nucleophilic NH_2 group) and **TMTD** have been observed.

The 46th IChO – Theoretical Examination. Official English Version
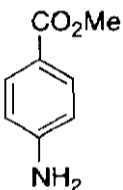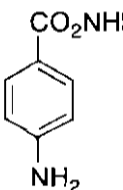
47
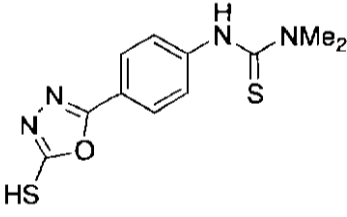
In the synthetic scheme below, the thiocarbamoylation reaction of an aroyl hydrazine with **TMTD** produces compound **C** containing a heterocyclic moiety from *p*-aminobenzoic acid.

$$CO_2H$$

1) MeOH, H$_2$SO$_4$
——————————→ **A**
2) K$_2$CO$_3$

N$_2$H$_4$
————→ **B**
EtOH

TMTD, 2 equiv.
————————→ **C**
DMF, −S, −H$_2$S
($C_{11}H_{12}N_4OS_2$)

NH$_2$

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
CO$_2$Me NH$_2$	CO$_2$NHNH$_2$ NH$_2$	 C: $C_{11}H_{12}N_4OS_2$
2 pts	2 pts	4 pts

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

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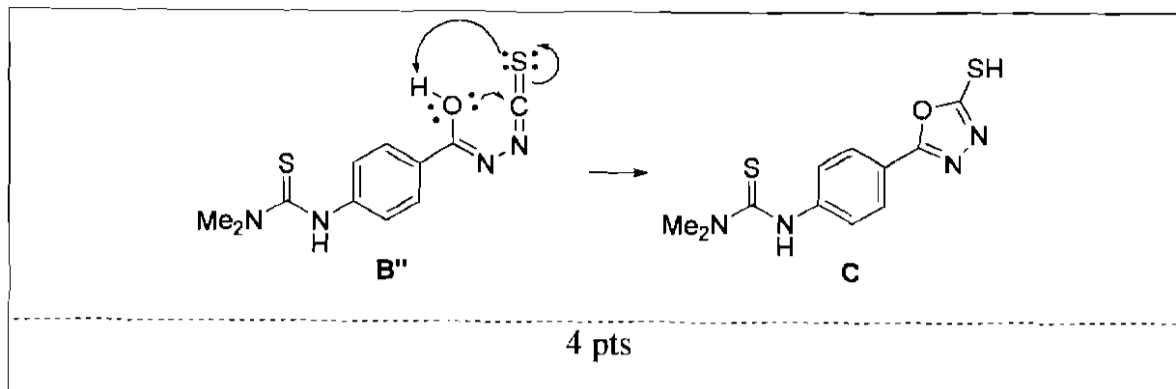
Compound **C** was then converted to **F** by the following pathway:

C
(C$_{11}$H$_{12}$N$_4$OS$_2$)

$\xrightarrow[\substack{\text{dioxane} \\ \text{(solvent)}}]{\text{HCl (gas)}}$

D

$\xrightarrow[\text{dioxane, 50 °C, 2 h}]{\text{N}_2\text{H}_4 \text{ excess}}$ **E** $\xrightarrow[\text{DMF}]{\text{TMTD}}$ **F**

(R-C$_8$H$_6$N$_3$S$_2$)
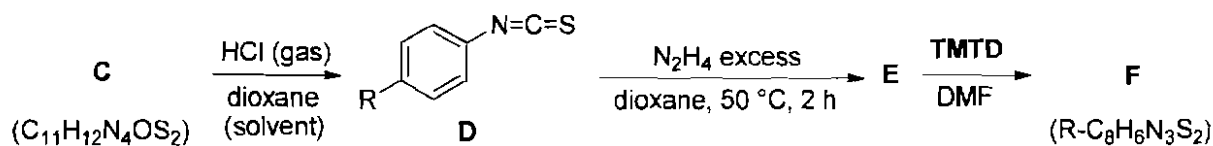
[The group R remains exactly the same throughout the rest of the question.]

9c. Draw the structures of **E**, and **F**. (You do not need to draw the structure for the R group from this point)
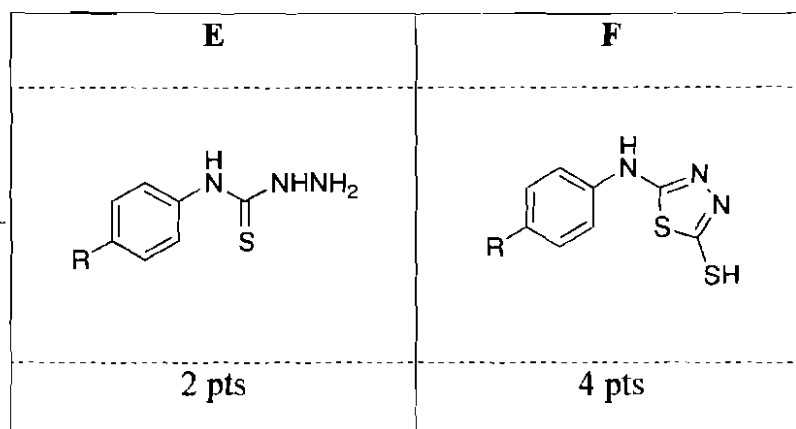
E	F
2 pts	4 pts
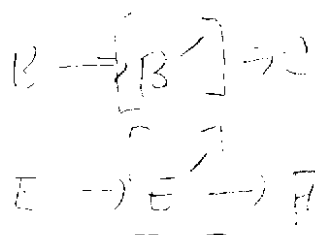
E was only obtained when **D** was slowly added to the solution of excess N$_2$H$_4$ in dioxane. If N$_2$H$_4$ was added to the solution of **D** in dioxane instead, a major side product **D'** (R$_2$C$_{14}$H$_{12}$N$_4$S$_2$) was formed.

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

D': R$_2$C$_{14}$H$_{12}$N$_4$S$_2$

4 pts
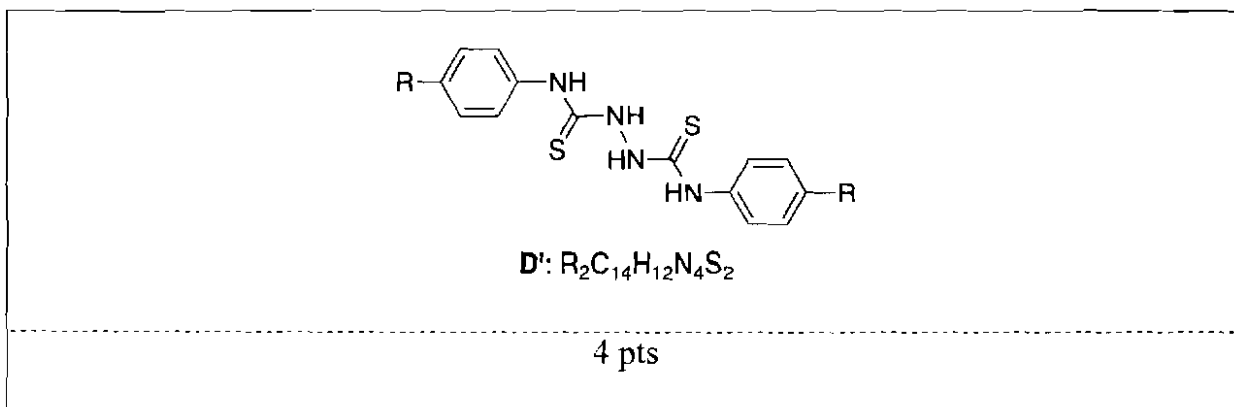
Slightly heating **D** with ethanolamine ($HOCH_2CH_2NH_2$) in dioxane for 2 hours yielded **G** ($R-C_9H_{11}N_2OS$).

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

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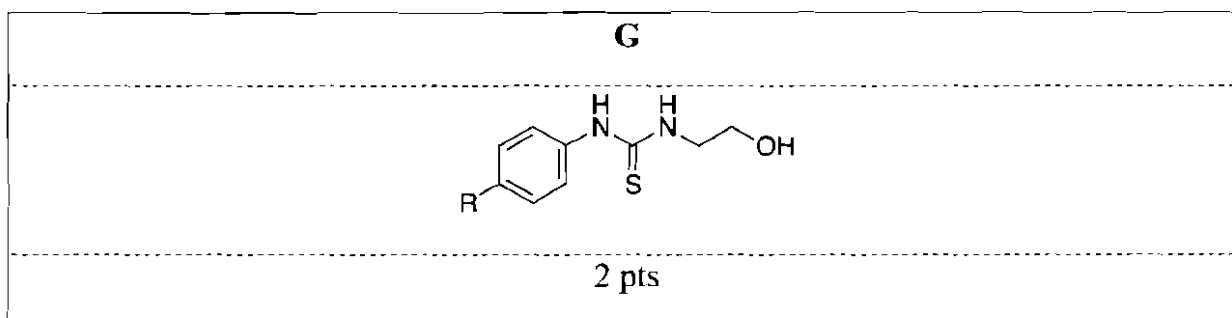
9f. Heating **G** in the presence of p-toluenesulfonic acid as the catalyst could form a number of different five-membered heterocyclic products.

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

Eg H1	H3
(3 pts)	
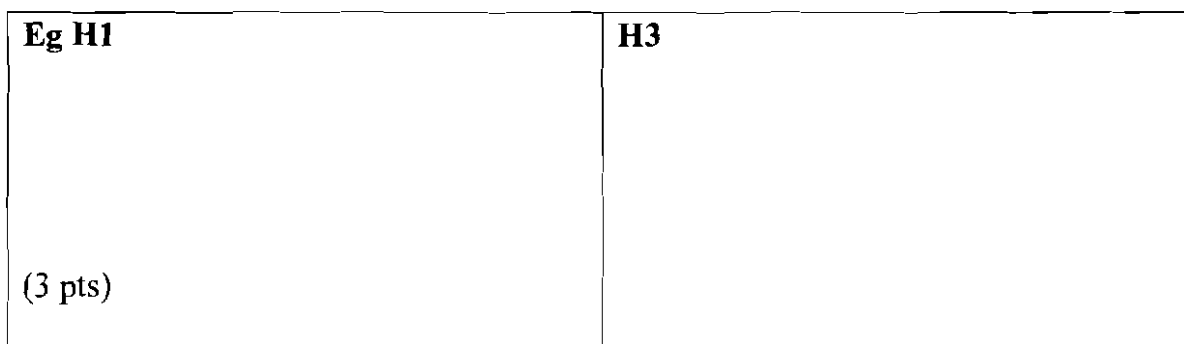
ii) **Draw** 2 structures that are constitutional isomers. (3 pts)

E.g H1	H5
(3 pts)	
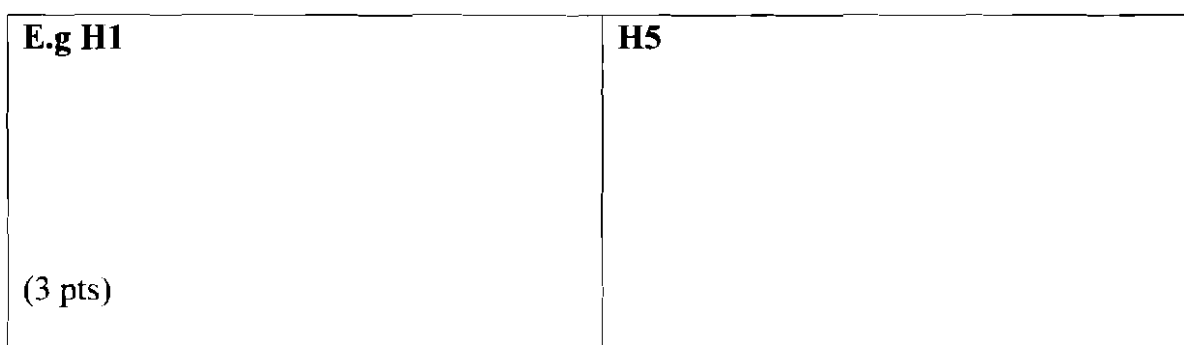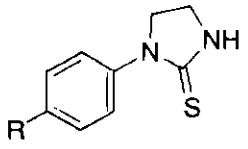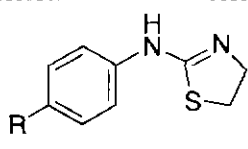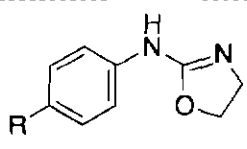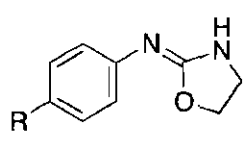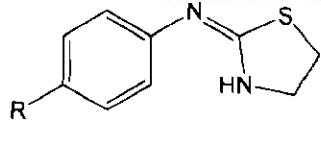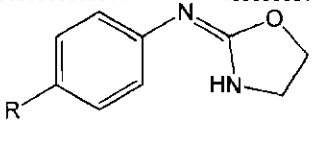
iii) **Draw** 2 structures that are stereoisomers. (3 pts)

E.g H5	H7
(3 pts)	

H_1	H_2	H_3
2 pts	2 pts	2 pts
H_4	H_5	H_6
2 pts	2 pts	2 pts
	H_7	H_8
	2 pts	2 pts

Periodic Table of the Elements

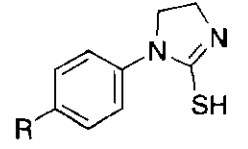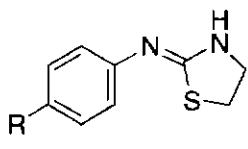| 1																	18
1 **H** 1.008	2				Transition Elements							13	14	15	16	17	**He** 4.003
3 **Li** 6.941	**4** **Be** 9.012											**5** **B** 10.81	**6** **C** 12.01	**7** **N** 14.01	**8** **O** 16.00	**9** **F** 19.00	**10** **Ne** 20.18
11 **Na** 22.99	**12** **Mg** 24.31	3	4	5	6	7	8	9	10	11	12	**13** **Al** 26.98	**14** **Si** 28.09	**15** **P** 30.98	**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** 65.41	**31** **Ga** 69.72	**32** **Ge** 72.61	**33** **As** 74.92	**34** **Se** 78.96	**35** **Br** 79.90	**36** **Kr** 83.80
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
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)
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)

The 46th IChO – Theoretical Examination. Official English Version

53