SEMI-FINAL: Problems

Dear students,

We congratulate you on your participation in the Chemistry Olympiad and wish you lots of success in this second round, as well as in your studies and in all your future endeavours. We also congratulate you on your success in the first round, which allows you to tackle the 'Problems' test today. **Before starting this test, please read the following carefully.**

Attached you will find 4 problems. The subjects covered by these questions are: general chemistry, stoichiometry, acids and bases, redox equations and organic chemistry.

You have **two hours** (120 minutes) to complete the test. You may use a non-programmable calculator, but you must not carry any personal documents.

Write your name and school name at the beginning of **each** question. Answer each problem on the sheet of paper (front and back, if necessary) of the corresponding question. **Clearly indicate your reasoning and calculations**. **Justify your answers and indicate the units for the final answers.** The last sheet is a draft sheet and will not be taken into account for the final assessment.

Following the assessment of this second round, the 12 best students will be invited to take part in a **training day**, which will take place on **Saturday, April 5th, 2025,** at the laboratories of the University of Luxembourg (Limpertsberg), from 9 am to 5 pm. More information will be sent to the finalists in due course. **The final (practical) test will** then take place on **Saturday, April 26th, 2025,** at the same laboratories of the University of Luxembourg (Limpertsberg). This final test will select the four winners of the National Chemistry Olympiad, who will at the same time constitute the Luxembourg team for the 57th IChO, which will be organised by the United Arab Emirates, from July 5th to July 14th, 2025, in Dubai. For more information, visit https://chimie.olympiades.lu/.

The results of this second round will be taken into account for the ranking of the four finalists!

Best wishes and good luck,

The organisers of the Chemistry Olympiad

Useful Constants

Periodic Table

I	II											III	IV	V	VI	VII	VIII	
1,0 H 1																	4,0 He 2	1
6,9 Li 3	9,0 Be 4											10,8 B 5	12,0 C 6	14,0 N 7	16,0 O 8	19,0 F 9	20,2 Ne 10	2
23,0 Na 11	24,3 Mg 12											27,0 Al 13	28,1 Si 14	31,0 P 15	32,1 S 16	35,5 Cl 17	39,9 Ar 18	3
39,1 K 19	40,1 Ca 20	45,0 Sc 21	47,9 Ti 22	50,9 V 23	52,0 Cr 24	54,9 Mn 25	55,8 Fe 26	58,9 Co 27	58,7 Ni 28	63,5 Cu 29	65,4 Zn 30	69,7 Ga 31	72,6 Ge 32	74,9 As 33	79,0 Se 34	79,9 Br 35	83,8 Kr 36	4
85,5 Rb 37	87,6 Sr 38	88,9 Y 39	91,2 Zr 40	92,9 Nb 41	95,9 Mo 42	(97) Tc 43	101,1 Ru 44	102,9 Rh 45	106,5 Pd 46	107,9 Ag 47	112,4 Cd 48	114,8 In 49	118,7 Sn 50	121,8 Sb 51	127,6 Te 52	126,9 I 53	131,3 Xe 54	5
132,9 Cs 55	137,3 Ba 56	57-71	178,5 Hf 72	180,9 Ta 73	183,8 W 74	186,2 Re 75	190,2 Os 76	192,2 Ir 77	195,1 Pt 78	197,0 Au 79	200,6 Hg 80	204,4 Tl 81	207,2 Pb 82	209,0 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86	6
223 Fr 87	226 Ra 88	89-103	(267) Rf 104	(268) Db 105	(269) Sg 106	(270) Bh 107	(269) Hs 108	(278) Mt 109	(281) Ds 110	(282) Rg 111	(285) Cn 112	(286) Nh 113	(289) Fl 114	(290) Mc 115	(293) Lv 116	(294) Ts 117	(294) Og 118	7
		Lanthanides	138,9 La 57	140,1 Ce 58	140,9 Pr 59	144,2 Nd 60	(145) Pm 61	150,4 Sm 62	152,0 Eu 63	157,3 Gd 64	158,9 Tb 65	162,5 Dy 66	164,9 Ho 67	167,3 Er 68	168,9 Tm 69	173,0 Yb 70	175,0 Lu 71	
		Actinides	(227) Ac 89	232,0 Th 90	231,0 Pa 91	238,0 U 92	(237) Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(266) Lr 103	

Constants:

$R = 8{,}31\ J \cdot mol^{-1} \cdot K^{-1}$	$1\ F = 9{,}65 \cdot 10^{4}\ C \cdot mol^{-1}$
$R = 8{,}21 \cdot 10^{-2}\ L \cdot atm \cdot mol^{-1} \cdot K^{-1}$	$N_A = 6{,}022 \cdot 10^{23}\ mol^{-1}$
Volume of one mole of an ideal gas at 273 K and 101325 Pa: 22,4 $dm^3 \cdot mol^{-1}$ ($L \cdot mol^{-1}$).	
One year corresponds to 365 days.	

Simplified pH formulas:

Strong acid	Weak acid	Strong base	Weak base
$pH = -\log c_{acid}$	$pH = \frac{1}{2}(pK_a - \log c_{acid})$	$pH = 14 + \log c_{base}$	$pH = 14 - \frac{1}{2}(pK_B - \log c_{base})$

Buffer mixture: $pH = pK_a + \log \frac{c_{base}}{c_{acid}}$ at 25 °C : $K_w = K_{H_2O} = [H_3O^+] \cdot [OH^-] = 1{,}0 \cdot 10^{-14}$

For a weak acid HA: $HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad | \quad K_a = \frac{[A^-] \cdot [H_3O^+]}{[HA]}$

with the dissociation degree $\alpha = \frac{[A^-]}{c_0} : K_a = \frac{\alpha \cdot [H_3O^+]}{1-\alpha}$.

General chemistry:

The activity (A) in Becquerels (Bq) of a radioactive source is related to the number of nuclei (N) that decay and the half-life ($T_{1/2}$) of the radioisotope:

$$A = \frac{\ln 2}{T_{1/2}} \cdot N$$

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Problem I: Iodate salts

1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	Total Problem I
1	2	1	2	2	2	5	6	1	2	24

Most iodine-containing minerals contain iodate ions, IO_3^-. One of these minerals is called salesite.

a) Give the oxidation number of iodine in the iodate ion.

b) Draw the Lewis structure of the iodate ion.

c) What is the most likely O-I-O bond angle in the iodate ion? Mark the correct answer.

i. < 109,5°	ii. 109,5°	iii. > 109,5°

Nuclear disasters can release radioactive iodine isotopes that bind to the thyroid gland. A daily dose of iodine equivalent to 130 mg of potassium iodide can prevent the absorption of such radioactive isotopes. Since potassium iodide degrades easily, the government has a stock of the more stable potassium iodate as an iodine source.

d) Calculate the mass of potassium iodate that contains the same amount of iodine as 130 mg of potassium iodide.

Iodate ions react with iodide ions in an acidic medium to produce iodine.

e) Write an ionic equation (without counter ions) for the reaction between iodate ions and iodide ions in an acidic medium.

This reaction is used to determine the quantity of iodate ions in a sample. The iodine formed after reaction with an excess of potassium iodide in an acidic medium is titrated with a solution of thiosulphate ions ($S_2O_3^{2-}$). During the titration, the thiosulphate reacts with the iodine to give iodide ions and tetrathionate ions ($S_4O_6^{2-}$).

f) Write an ionic equation for the reaction between thiosulphate ions and iodine.

Salesite is a mineral with the molecular formula $M(IO_3)Z$, containing iodate, a metal ion M and an anion Z in a ratio of 1:1:1. The molar mass of this mineral is 255,46 $g \cdot mol^{-1}$.

1,000 g of the mineral was dissolved in 30 mL of 2M HNO_3. The resulting solution was filled up to 100,0 mL with distilled water, forming a stock solution.

10,00 mL of this stock solution react with an excess of potassium iodide. The iodine formed is titrated with a 0,10 $mol \cdot L^{-1}$ sodium thiosulphate solution.

g) Calculate the volume of sodium thiosulphate solution added during the titration, assuming that the reaction of iodate ions with iodide ions is complete.

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However, the metal ion M^{n+} in this mineral also reacts with iodide ions to form additional iodine. As a result, the actual volume of sodium thiosulphate solution required for the titration turned out to be 27,40 mL.

h) Calculate the number of moles of iodine produced by the reaction of one mole of a metal ion M^{n+} with an excess of iodide ions.

If you were unable to obtain a value in question g), assume that the answer was 15,67 mL.

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i) The oxidation state of the metal ion M^{n+} in the mineral can be written as +n. Give the oxidation state of the metal ion after reaction with iodide ions. Mark the correct answer.

i. +(n+2)	ii. +(n+1)	iii. +(n)	iv. +(n-1)	v. +(n-2)

When the mineral is dissolved in nitric acid, no reaction is observed.

j) Considering all the information given in the problem, choose (circle) the metal ion M^{n+} and the anion Z^{m-} from the list of ions below.

M^{n+}	Sc^{3+}	Fe^{2+}	Fe^{3+}	Cu^{+}	Cu^{2+}	Mg^{2+}	Ga^{2+}	Zn^{2+}
Z^{m-}	F^{-}	Cl^{-}	Br^{-}	H^{-}	O^{2-}	OH^{-}	PO_4^{3-}	SO_3^{2-}

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Problem II: Uranium

2a	2b	2c	2d	2e	2f	Total Problem II
1	5	9	4	4	2	25



Uranium is a radioelement best known for its use in nuclear power plants. Natural uranium is made up of 2 main isotopes in the following proportions: ^{238}U 99.3% and ^{235}U 0.7%. Their half-lives, i.e. the time required for half the nuclei initially present to decay, are 4.5 billion years for ^{238}U and 704 million years for ^{235}U.

Pitchblende is a uranium ore containing an average of 1% triuranium octaoxide$(U_3O_8)_{(s)}$. It is the main source of natural uranium. To extract the radioactive element, the ore is dissolved in nitric acid to form uranyl nitrate $(UO_2(NO_3)_2)_{(aq)}$. During the dissolution reaction, nitrogen dioxide is released.

a) What type of reaction is this? Tick the right answer.

i. redox	ii. acid-base	iii. radioactive	iv. radical

b) Give the weighted equation for the dissolution of triuranium octaoxide by nitric acid.

c) Calculate the activity of the uranyl nitrate solution after dissolving one gram of pitchblende.

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Uranium can be re-precipitated in the form of autunite $(Ca(UO_2)_2(PO_4)_2)_{(s)}$ by adding hydroxyapatite $(Ca_5(PO_4)_3OH)_{(s)}$ to the acid solution containing uranyl nitrate.

d) Give the weighted reaction for the precipitation of autunite in an acidic medium.

e) Assuming a complete reaction, what is the mass of autunite that will be recovered?

When ^{235}U radioactive nuclei decay, they emit alpha particles $(^4_2\alpha)$.

f) Write down the equation for the transmutation of ^{235}U.

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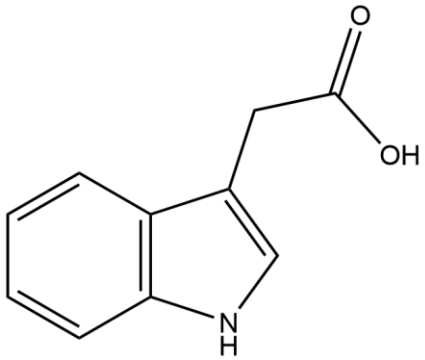
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Problem III: Indole

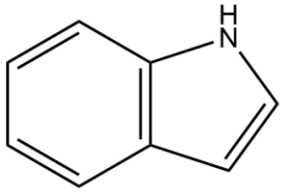
3a	3b	3c	3d	3e	3f	3g	Total Problem III
2	1	4	10	2	2	6	27

Theoretical introduction

Auxin or indole-3-acetic acid is one of the most important phytohormones. This chemical messenger is responsible for the elongation of plant cells and is involved in phototropism.



Auxin



Indole

The molecular structure of auxin is shown above. It is an indole derivative.

Indole, or 2,3-benzopyrrole, is composed of two fused unsaturated rings. Hückel's rule can be used to predict the behaviour of such rings. It postulates that the presence of 4n+2 π electrons allows the delocalisation of these electrons and increases the stability of the molecules in question. The ring is said to be aromatic. On the other hand, rings with only 4n π electrons are not very stable and are known as antiaromatic.

a) Indicate the number of π electrons in the indole (*Note*: in the case of rings containing heteroatoms (N or O for example), the free doublet electrons can contribute to aromaticity if they are oriented towards the inside of the ring).

b) Indole-3-acetic acid is:

i.	aromatic
ii.	antiaromatic
iii.	non-aromatic

Auxin is transported unidirectionally in plant cells by a mechanism involving an acid-base reaction. This is known as polarised auxin transport. In the following we will use the notation HA/A- to designate indole-3-acetic acid ($pK_a = 4{,}75$) and its deprotonated form.

c) Calculate the degree of dissociation α of auxin at $pH = 7$ and at $pH = 5$.

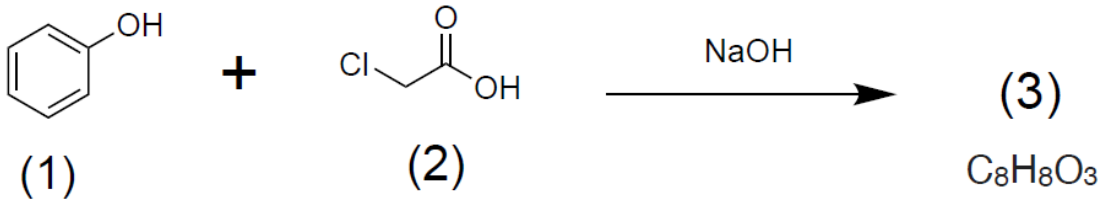
In order to analyse the acid-base properties of indole-3-acetic acid, a chemist prepares a buffer solution by adding 1.362 g of solid sodium methanoate to 200 mL of a methanoic acid solution($pK_a = 3{,}75$) of concentration $c = 0{,}1$ M . He adds a small amount of indole-3-acetic acid and determines the degree of dissociation α.

d) What volume of HCl or NaOH ($c = 0{,}1$ M) should be added to the buffer mixture so that only 10% of the indole-3-acetic acid is present in the deprotonated form?

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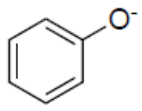
2,4-D is a pesticide that acts on plant cells in a similar way to auxin. This molecule can be synthesised in two stages from phenol.

In a first step 1.9 mL of phenol (1), 95% by mass, ρ = 1.053 g/mL, reacts with 3 g chloroacetic acid (2) in a basic medium, according to the following scheme.



(1) + (2) → (3) $C_8H_8O_3$

Sodium hydroxide deprotonates the alcohol group to form the phenolate anion.



phenolate

e) Which statement(s) is/are correct?

- ☐ Water is formed as a by-product.
- ☐ The phenolate anion is an excellent electrophilic reagent.
- ☐ The oxygen atom of the phenolate anion carries three free electron doublets.
- ☐ The Na^+ cation acts as a Brønsted-Lowry acid.

f) Draw the structure of the intermediate product (3).

g) The yield of this reaction is 55%. Calculate the mole fraction of chloroacetic acid that reacted.

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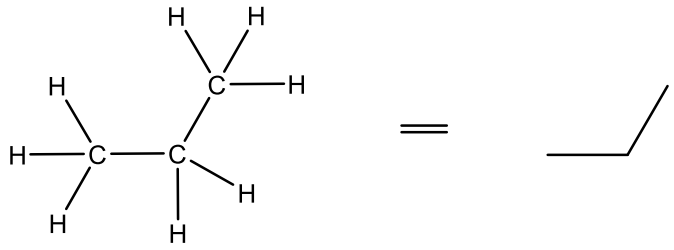
Problem IV: Palladium coupling

4a	4b	4d	4e	4f	Total Problem IV
1	10	7	3	3	24

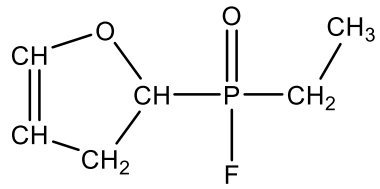
In organic chemistry, the synthesis of molecules of therapeutic interest is a key issue. Despite the complexity of certain target molecules, impressive synthesis strategies have been put in place to produce increasingly complex compounds.

A very important tool in organic chemistry is *palladium coupling*, which is used to form carbon-carbon bonds that are often difficult to create. Palladium coupling is a catalytic process, where palladium *complexes* are used to catalyse otherwise unthinkable reactions.

In skeletal (topological) form, all the hydrogen atoms are omitted and the bonds between the carbon atoms are represented by lines such as:



a) Represent the molecule below in skeletal form:



N.B.: The letter **R** in a structure can represent any group.

Transition metals form very complicated arrangements known as *complexes*. These are often represented in simplified form [M], omitting the molecular surroundings that are not relevant to the reaction under consideration.

The metal centre has an oxidation number written in Roman numerals next to the metal in question:

$[Pd^{II}]$ | oxidation number: 2

Consider the following elementary reactions:

Transmetallation:

$[M_1^Y] - R + [M_2^Y] \rightarrow [M_1^Y] + [M_2^Y] - R$

Oxidative addition:

$R - X + [M^Y] \rightarrow R - [M^{Y+2}] - X$

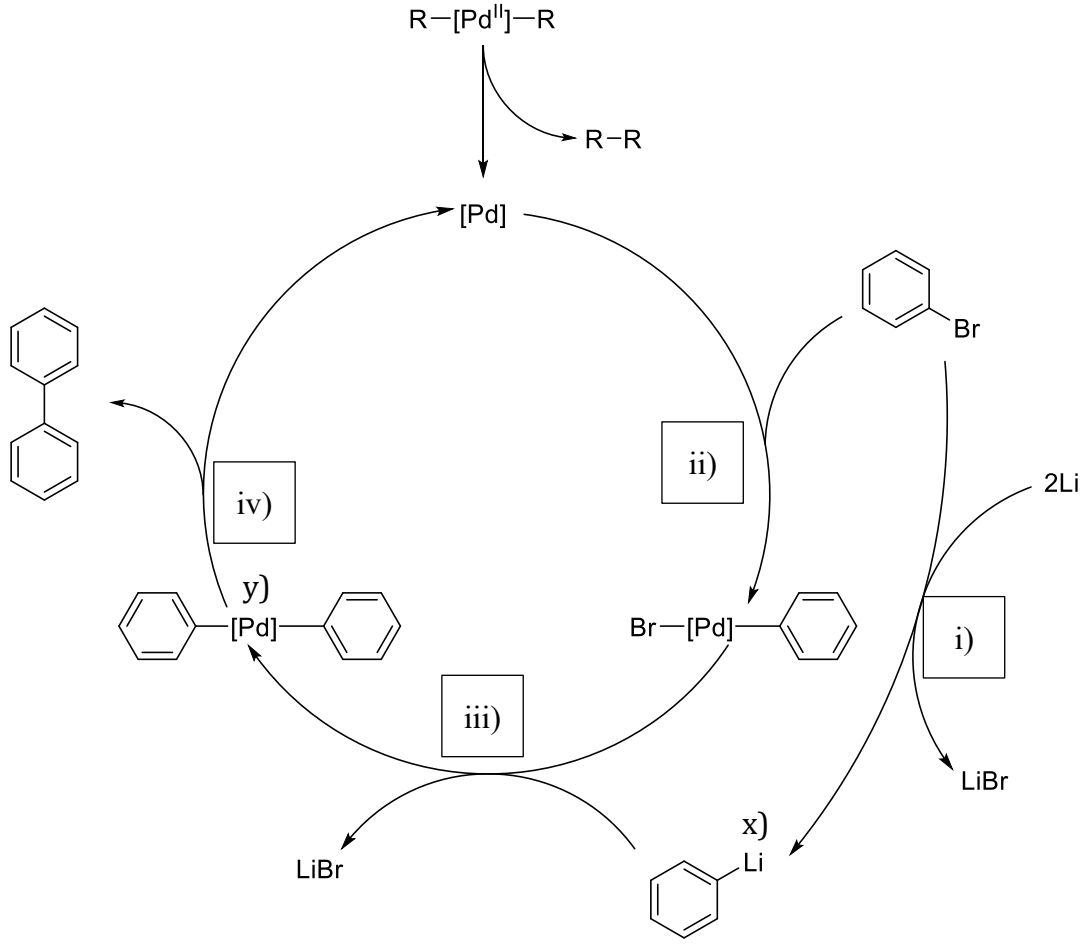
Halogen (X) - metal (M) exchange:

$R - X + 2M \rightarrow R - M + MX$

Reductive elimination:

$R - [M^{Y+2}] - X \rightarrow R - X + [M^Y]$

b) For the following catalytic cycle, name the elementary steps i) to iv) and give the oxidation numbers of the metals marked x) and y).



i)	
ii)	
iii)	
iv)	

x)	
y)	

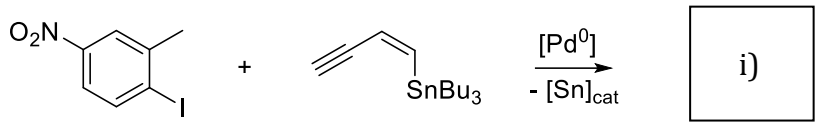
Several versions of palladium coupling have been developed over the years. One of the most important ones is the Stille coupling, whose general diagram is shown below:

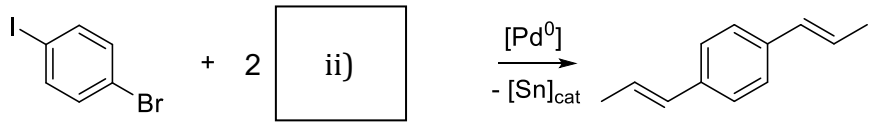
$$R_1{-}SnR'_3 \quad + \quad R_2{-}X \xrightarrow{[Pd^0]} R_1{-}R_2 \quad + \quad XSnR'_3$$

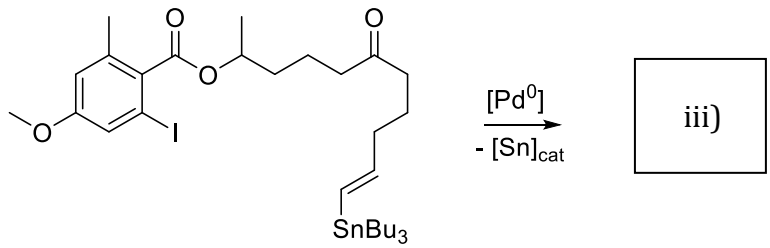
where: R_1 and R_2 = unsaturated substituents, R' = alkyl chains and X = halogen.

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c) Consider the reactions below and give a possible missing structure in the form of skeletal formulas.







i)	
ii)	
iii)	

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In the complexes used, palladium can be present in different oxidation states, which can vary according to their electronic configurations.

In most cases, it is energetically more favourable for an element or ion to have a completely or half-filled d orbital, rather than a single electron or even two electrons in an s orbital. This is due to the electronic stabilisation that results from the symmetry of electronic configurations and interactions between electrons.

Examples:

- For silver, the expected electronic configuration would be $[Kr]5s^2 4d^9$, but silver adopts $[Kr]5s^1 4d^{10}$ instead. Here, having a filled 4d orbital (more stable) is favoured over a configuration where the d orbital would be incomplete.
- For molybdenum, the expected configuration would be $[Kr]5s^2 4d^4$, but Mo prefers to adopt $[Kr]5s^1 4d^5$. Here, filling half of the 4d orbital is stabilising because it reduces electron repulsions.

d) Considering the explanations above, give the electronic configurations of the following atoms or ions.

i)	Pd^0	
ii)	Pd^{2+}	
iii)	Pd^{4+}	

The element palladium is made up of six stable isotopes, with a natural occurrence of:

- ^{102}Pd: 1.02 %
- ^{104}Pd: 11.14 %
- ^{106}Pd: 27.33 %
- ^{108}Pd: 26.46 %
- ^{110}Pd: 11.72 %

e) Identify the sixth stable isotope of palladium.

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