

CHEMISTRY. OLYMPIAD.CH CHEMIE-OLYMPIADE

OLYMPIADES DE CHIMIE OLIMPIADI DELLA CHIMICA

SwissChO 2023 - Central Exam

INSTRUCTIONS

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem.
- Write all necessary calculations legibly.
- Put your pages into the provided envelope at the end of the exam. Do not seal the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only answers written on the answer sheets can be considered.
- This exam has 20 pages.

Viel Erfolg! Bonne chance! Buona fortuna! Good luck!

CONSTANTS AND FORMULAE

Avogadro constant	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Ideal gas law	pV = nRT
Universal gas constant	$R = 8.314 \mathrm{J} \mathrm{mol}^{-1} \mathrm{K}^{-1} \qquad \text{Gibbs energy}$		G = H - TS
Faraday constant	$F = 96485 \mathrm{C} \mathrm{mol}^{-1}$	$\Delta_r G^0 = -RT \cdot \ln(K$	$\tilde{T}) = -nFE_{\text{Zelle}}^0$
Planck constant	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation	$E = E^{0} + \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{c_{\text{ox}}}{c_{\text{red}}}\right)$
Speed of light	$c = 2.998 \cdot 10^8 \text{ m s}^{-1}$	Energy of a photon	$E = \frac{h \cdot c}{\lambda}$
Temperature	$0 ^{\circ}\text{C} = 273.15 \text{K}$	Lambert-Beer law	$A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot c \cdot L$

For the calculation of equilibrium constants all concentrations, refer to the standard concentration $1 \mod dm^{-3} = 1 \mod L^{-1}$. If not stated otherwise in a task, consider all gases ideal throughout this test.

2 He 4.003	10	Ne	0.18	18	Ar	9.95	36	Kr	3.80	54	Xe	1.29	86	Rn	212]	118	Og	294]							
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																			71		ГЛ	74.97	103	Lr	[266]
						32.06				-												_			[259]
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SCORE SHEET

NOT TO BE FILLED IN BY PARTICIPANTS

Name of participant: _____

Task	Title	Maximum Points	Achieved Points
1	Periodic trends	12.0	
2	Chemical Bonding	10.0	
3	Stoichiometry	10.0	
4	Gases	10.0	
5	Chemical equilibrium	10.0	
6	Thermochemistry	10.0	
7	Chemical kinetics	10.0	
8	Acid base	10.0	
9	Redox	10.0	
10	Electrochemistry	10.0	
11	Solubility	10.0	
12	Organic chemistry	10.0	
Total		122.0	

PROBLEM 1 - PERIODIC TRENDS

The periodic table is often considered to be the "best friend" of chemists and chemistry students alike. It includes information about atomic masses and element symbols, but it can also be used to make predictions about atomic size, electronegativity, ionisation energies, bonding, solubility and reactivity.

1.1 Consider the data in Model 1 on the next page:

- a) Each element has three numbers listed under it. Which value out of the 1^{st} , 2^{nd} or 3^{rd} from the top represents the atomic radius?
- b) What are the units for the atomic radius?
- c) Write a complete sentence to convey your understanding of atomic radius. Note: you may not use the word "radius" in your definition.

1.2 In general, what is the trend in atomic radius as you go down a group in Model 1? Support your answer using an example from a group.

1.3 Using your knowledge of Coulombic attraction and the structure of the atom, explain the trend in atomic radius that you identified in question 1.2. Hint: you should discuss either a change in distance between the nucleus and outer shell of electrons or a change in the number of protons in the nucleus.

1.4 In general, what is the trend in atomic radius as you go across a period (left to right) in Model 1? Support your answer using an example.

1.5 Using your knowledge of Coulombic attraction and the structure of the atom, explain the trend in atomic radius that you identified in question 1.4.

1 H							2 He ©
37							31
1312							2372
2.1							N/A
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
\odot	٢	۲	۲	۲	۲	۲	٢
152	112	83	77	71	66	71	70
520	900	801	1086	1402	1314	1681	2081
1.0	1.5	2.0	2.5	3.0	3.5	4.0	N/A
11 Na	12 Mg	13 A1	14 Si	15 P	16 \$	17 C1	18 Ar
\bigcirc	\odot	0	0	0	0		0
186	160	143	117	115	104	99	98
496	738	578	786	1011	1000	1251	1521
0.9	1.2	1.5	1.8	2.1	2.5	3.0	N/A
19 K	20 Ca	31 Ga	32 Ge	33 A s	34 Se	35 Br	36 Kr
							0
227	197	122	123	125	117	114	112
404	550	558	709	834	869	1008	1170
0.8	1.0	1.7	1.8	1.9	2.1	2.5	N/A

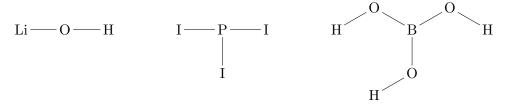
Model 1 - Main Group Elements

Atomic Number Element Symbol Electron Shell Diagram Atomic Radius (pm) 1st lonization Energy (kJ/mol) Electronegativity Note: The transition elements and f-block elements have been removed from the periodic table here to ease the analysis of the trends.

10 POINTS

PROBLEM 2 - CHEMICAL BONDING

2.1 Here is a series of developed formulas:



- a) Correct the false bonds representations on the molecules or salts above (you do not have to take into account steric mistakes).
- b) If applicable, draw the missing electron pairs.
- c) Name all the bond types and justify your answer
- d) Indicate all the charges and if necessary, modify the formalism of the bonds

2.2 Fill in the table below appropriately.

Formula	Lewis structure	VSEPR (3D molecule)	Dipolar moment vectors	Main intermolec- ular force
CH ₃ Cl				
H ₂ O				
SO ₃				

Example for Dipolar moment vectors:

$$H \xrightarrow{\delta^+} F$$

PROBLEM 3 - STOICHIOMETRY

Calcium chloride can be produced by calcic attack using hydrochloric acid with a mass percentage of 36.0% and a density of 1.18 g/mL.

Consider a limestone sample in which the mass percentage of calcium carbonate ($CaCO_3$) is equal to 98.0%.

3.1 Calculate, in kilograms, the mass of limestone and, in litres, the volume of hydrochloric acid required to produce 400.0 L of calcium chloride solution of mass percent 35.0% (ρ = 1.338 g/mL at 20°C) assuming the reaction is complete under stoichiometric conditions.

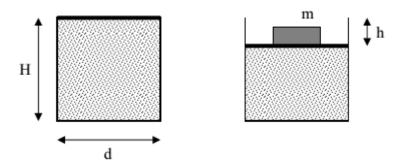
3.2 What volume of carbon dioxide will be released at a temperature of 20°C and a pressure of 1.00 bar?

PROBLEM 4 - GASES

10 POINTS

A **cylinder** of diameter d = 25 cm and height H = 35 cm is closed, at its upper end, by a piston of negligible mass and thickness. Inside the cylinder, is an ideal gas.

An object is delicately placed on the piston which then sinks down by h = 5 cm.



4.1 Assuming that the temperature of the system ($T = 27^{\circ}C$) remains unchanged and that the atmospheric pressure is the normal pressure, calculate the mass m of the object.

4.2 Without removing the object, we want to return the piston to its initial position. To do this, the gas in the cylinder is heated. To what temperature (in °C) must it be brought?

PROBLEM 5 - CHEMICAL EQUILIBRIUM

 NO_2 gas is an atmospheric pollutant. Depending on the conditions, it can exist in the air in equilibrium with its dimer N_2O_4 according to the equation below:

$$2 \operatorname{NO}_2(g) \rightleftharpoons \operatorname{N}_2\operatorname{O}_4(g)$$

At the beginning under normal temperature and pressure conditions, $3.35 \text{ mol of } N_2O_4$ are introduced into a 50.00 L container. Once the equilibrium is reached (with NO₂), a N₂O₄ concentration of 0.0643 M is measured.

5.1 What is the K_c for the above equilibrium (direct reaction)?

5.2 What are all the possible ways to shift this equilibrium towards N_2O_4 ? Each proposal must be justified to be validated.

5.3 What is the K_c for the equilibrium below (indirect reaction)?

$$2 \operatorname{NO}_2(g) \rightleftharpoons \operatorname{N}_2\operatorname{O}_4(g)$$

10 POINTS

10 POINTS

PROBLEM 6 - THERMOCHEMISTRY

When aluminium is added to iron (III) oxide, metallic iron and aluminium oxide are formed.

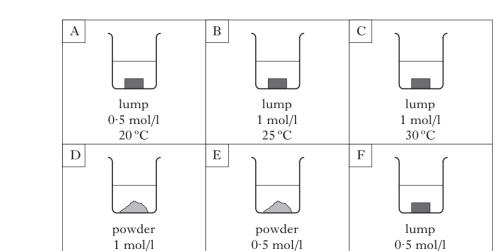
- **6.1** Write the reaction equation and balance it.
- **6.2** Is this reaction exo- or endothermic? Sketch its reaction profile.
- **6.3** Is this reaction spontaneous at 25°C? Justify your answer with a calculation.
- 6.4 At what temperature does this reaction become spontaneous?
- 6.5 What is the name of this mixture of aluminium and iron oxide seen in the series "Breaking Bad"?

6.6 For which "everyday life" operation do we use this reaction?

	Thermochemical tables						
Substance	Δ Hf° (kJ/mol)	Δ Gf° (kJ/mol)	S° (J/mol K)				
Al(s)	0.0	0.0	28.3				
Al(g)	330.0	289.4	164.6				
AlCl ₃ (s)	-704.2	-628.8	109.3				
$Al_2O_3(s)$	-1675.7	-1582.3	50.9				
Fe(s)	0.0	0.0	27.3				
Fe(g)	416.3	370.7	180.5				
Fe ²⁺ (aq)	-89.1	-78.9	-137.7				
Fe ³⁺ (aq)	-48.5	-4.7	-315.9				
FeCl ₂ (s)	-341.8	-302.3	118.0				
FeCl ₃ (s)	-399.5	-334.0	142.3				
FeO(s)	-272.0	-251.4	60.7				
$Fe_2O_3(s)$	-824.2	-742.2	87.4				
$Fe_3O_4(s)$	-1118.4	-1015.4	146.4				
FeS ₂ (s)	-178.2	-166.9	52.9				
FeCO ₃ (s)	-740.6	-666.7	92.9				
$NO_2(g)$	33.05	51.84	239.74				
$N_2O_4(g)$	9.67	98.28	304.30				

PROBLEM 7 - CHEMICAL KINETICS

10 POINTS



7.1 A student is analysing the reaction rate of dissolving chalk in hydrochloric acid.

a) Identify three experiments, among the 6 above, that can be compared to show the effect of concentration on the reaction rate. Justify.

 $25 \,^{\circ}\mathrm{C}$

 $25 \,^{\circ}\mathrm{C}$

b) Identify the experiment that will have the greatest reaction rate and explain why.

7.2 The kinetics of the reaction CCl_3COOH (aq) $\longrightarrow CO_2 + CHCl_3$ at 70°C is followed. We then measure the following concentrations of the reagent as a function of time:

t/h	$[CCl_3COOH] / mol L^{-1}$
0.00	0.1000
1.00	0.09403
2.00	0.08842
3.00	0.08314
4.00	0.07817
5.00	0.07351

What is the order of the reaction and the value of the rate constant k?

 $30\,^{\rm o}{\rm C}$

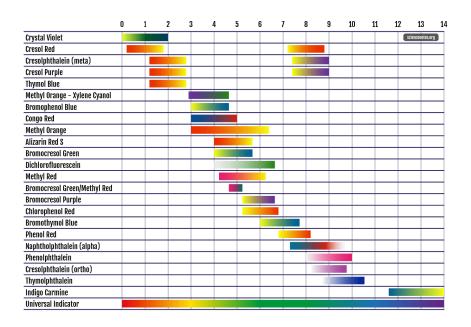
PROBLEM 8 - ACID BASE

10 POINTS

You find an unlabelled vial in the acid cabinet of your laboratory. You decide to determine what type of acid it is by performing a titration. You take 0.82 g of the unknown acid and dissolve it in 50 mL of deionized water. You then titrate your solution with 0.4 M NaOH and you obtain the following curve:



- a) Determine which acid it is.
- b) Write down the first two hydrolysis reaction equations.
- c) If you did not have access to a pH-meter, what mixture of coloured indicators could you use to determine the two equivalence points? What colours will the solution be during all of the titration when using this mixture?



Acid	HA	A ⁻	Ка	рКа
Iodic	HIO ₃	IO ₃ ⁻	$1.6 \ge 10^{-1}$	0.80
Oxalic (1)	$H_2C_2O_4$	HC ₂ O ₄ ⁻	$5.9 \ge 10^{-2}$	1.23
Sulfurous (1)	H_2SO_3	HSO ₃ -	$1.54 \text{ x } 10^{-2}$	1.81
Sulfuric (2)	HSO ₄ -	SO4 ²⁻	$1.2 \ge 10^{-2}$	1.92
Chlorous	HClO ₂	ClO ₂ -	$1.1 \ge 10^{-2}$	1.96
Phosphoric (1)	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.52 x 10 ⁻³	2.12
Arsenic (1)	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	$5.0 \ge 10^{-3}$	2.30
Chloroacetic	CH ₂ ClCOOH	CH ₂ ClCOO ⁻	1.4 x 10 ⁻³	2.85
Citric (1)	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	8.4 x 10 ⁻⁴	3.08
Hydrofluoric	HF	F ⁻	$7.2 \ge 10^{-4}$	3.14
Nitrous	HNO ₂	NO ₂ ⁻	$4.0 \ge 10^{-4}$	3.39
Formic	НСООН	HCOO ⁻	$1.77 \text{ x } 10^{-4}$	3.75
Lactic	HCH ₃ H ₅ O ₃	CH ₃ H ₅ O ₃ ⁻	$1.38 \ge 10^{-4}$	3.86
Ascorbic (1)	$H_2C_6H_6O_6$	HC ₆ H ₆ O ₆ ⁻	7.9 x 10 ⁻⁵	4.10
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	6.46 x 10 ⁻⁵	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4 x 10 ⁻⁵	4.19
Hydrazoic	HN ₃	N3 ⁻	$1.9 \ge 10^{-5}$	4.72
Citric (2)	$H_2C_6H_5O_7^-$	$HC_{6}H_{5}O_{7}^{2-}$	$1.8 \ge 10^{-5}$	4.74
Acetic	CH₃COOH	CH ₃ COO ⁻	$1.76 \ge 10^{-5}$	4.75
Propionic	CH ₃ CH ₂ COOH	CH ₃ CH ₂ COO ⁻	$1.34 \ge 10^{-5}$	4.87
Pyridinium ion	C ₅ H ₄ NH ⁺	C ₅ H ₄ N	5.6 x 10 ⁻⁶	5.25
Citric (3)	$HC_{6}H_{5}O_{7}^{2-}$	$C_6H_5O_7^{3-}$	4.0 x 10 ⁻⁶	5.40
Carbonic (1)	H_2CO_3	HCO ₃ ⁻	$4.3 \ge 10^{-7}$	6.37
Sulfurous (2)	HSO ₄ -	SO4 ²⁻	$1.02 \ge 10^{-7}$	6.91
Arsenic (2)	H ₂ AsO ₄ ⁻	HAsO4 ²⁻	8/9.3 x 10 ⁻⁸	7.10/7.03
Hydrosulfuric	H ₂ S	HS ⁻	$1.0 \ge 10^{-7} / 9.1 \ge 10^{-8}$	7/7.04
Phosphoric (2)	H ₂ PO ₄ ⁻	HPO4 ²⁻	6.23 x 10 ⁻⁸	7.21
Hypochlorous	HClO	ClO-	3.5/3.0 x 10 ⁻⁸	7.46/7.53
Hypobromous	HBrO	BrO ⁻	2.0 x 10 ⁻⁹	8.70
Hydrocyanic	HCN	CN ⁻	$6.17 \ge 10^{-10}$	9.21
Boric (1)	H ₃ BO ₃	H ₂ BO ₃ ⁻	5.8 x 10 ⁻¹⁰	9.23
Ammonium ion	NH4 ⁺	NH ₃	5.6 x 10 ⁻¹⁰	9.25
Phenol	C ₆ H ₅ OH	C ₆ H ₅ O ⁻	$1.6 \ge 10^{-10}$	9.80
Carbonic (2)	HCO ₃ -	CO ₃ ²⁻	$4.8 \ge 10^{-11}$	10.32
Hypoiodous	HIO	IO ⁻	$2.0 \ge 10^{-11}$	10.70
Arsenic (3)	HAsO4 ²⁻	AsO4 ³⁻	$6.0 \ge 10^{-10} / 3.0 \ge 10^{-12}$	9.22/11.53
Hydrogen peroxide	H ₂ O ₂	HO ₂ -	2.4 x 10 ⁻¹²	11.62
Ascorbic (2)	HC ₆ H ₆ O ₆ -	C ₆ H ₆ O ₆ ²⁻	1.6 x 10 ⁻¹²	11.80
Phosphoric (3)	HPO4 ²⁻	PO4 ³⁻	$4.8/2.2 \ge 10^{-13}$	12.32/12.66

PROBLEM 9 - REDOX

10 POINTS

To determine the iron in solution in the form of ferrous ions (Fe²⁺ (aq)), it is possible to titrate them in acid medium (containing H^+) by reacting them with an acidic permanganate solution (MnO₄⁻ (aq)) of known concentration.

9.1 Determine the oxidation half-equation.

9.2 Determine the reduction half-equation.

9.3 Write and balance the global redox equation.

Workaround: If you have not found the global equilibrium equation, you can use the equation of the titration in neutral medium for the rest of the exercise:

 $10 \text{ FeSO}_4 + 2 \text{ KMnO}_4 + 8 \text{ H}_2\text{O} \longrightarrow 2 \text{ MnSO}_4 + 5 \text{ Fe}_2(\text{SO}_4)_3 + 16 \text{ KOH}$

The iron II sulphate content of a sample must be determined. For this purpose, 1.00 g of FeSO4 is dissolved in water and the solution is acidified.

The obtained solution is titrated by adding drop by drop a permanganate solution. Dropwise a 0.025 M until a persistent purple colour appears after addition of 24.5 mL (because of the excess of MnO_4^- (aq)).

9.4 Calculate in grams the mass of FeSO₄ contained in this sample.

9.5 Calculate the mass content of FeSO₄ (in %) in this sample.

PROBLEM 10 - ELECTROCHEMISTRY

10 POINTS

Jetsetter that you are, you leave for a weekend on your private yacht to make a small cruise in the Mediterranean. Unfortunately, your boat hits some rocks during a storm and you run aground on an unknown and empty beach. When you wake up, you look around to see if you have anything that could help you get out of this situation. You find your cell phone and its power cable, but unfortunately, its battery is empty. You look around on the beach and realize that you have access to the following materials:

- Aluminium cans
- Charcoal
- Oxygen from the air and water
- Sea water
- Material from your clothes

Assuming you need approximately 12 V to turn on your phone and make a call for help, explain how you will do this. Make diagrams to help you. To make life easier, consider that we are working under standard, non-acidic conditions!

10.1 Draw a labelled diagram of a device allowing the production of the 12 V according to the electrochemistry standards.

In your diagram, the following information must appear:

- The negative and positive poles
- The anode and the cathode
- The direction of the half reactions
- The directions of the ions in the salt bridge
- The direction of the electron movement and of the electrical current

10.2 Give both half reactions and the overall reaction.

10.3 Calculate the standard potential difference of the device drawn.

	Reduction Half-Reaction		(V)	page 775
Change	F₂(g) + 2 e⁻	> 2 F"(aq)	2.87	
Stronger ddizing agent	H ₂ O ₂ (aq) + 2 H*(aq) + 2 €	$\longrightarrow 2 H_2O(l)$	1.78	Weaker reducing age
a agon	Mn O₄⁻(aq) + 8 H*(aq) + 5 e	$\rightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	reducing age
	Cl ₂ (g) + 2 e ⁻	> 2 Cl ⁻ (aq)	1.36	
ТГ	Cr ₂ O ₇ ²⁻ (aq) + 14 H*(aq) + 6	€> 2 Cr ³ *(aq) + 7 H ₂ O(/)	1.33	
	O ₂ (g) + 4 H⁺(aq) + 4 €	—→ 2 H ₂ O(I)	1.23	
	Br ₂ (<i>I</i>) + 2 e ⁻	> 2 Br(aq)	1.09	
	Ag*(aq)+ e⁻	$\longrightarrow Ag(s)$	0.80	
	Fe ³⁺ (aq) + e ⁻	$\longrightarrow Fe^{2*}(aq)$	0.77	
	O ₂ (g) + 2 H*(aq) + 2 € [−]	\longrightarrow H ₂ O ₂ (aq)	0.70	
	l ₂ (s) + 2 e	> 2 ⊢(aq)	0.54	
	O ₂ (g) + 2 H ₂ O(l) + 4 e	\longrightarrow 4 OH ⁻ (ag)	0.40	
	Cu ² *(aq) + 2 e ⁻	$\longrightarrow Cu(s)$	0.34	
	Sn ⁴ *(<i>aq</i>)+ 2 €	\longrightarrow Sn ²⁺ (aq)	0.15	
	2 H*(aq)+ 2 e	$\longrightarrow H_2(g)$	0	
	Pb2+(aq) + 2e-	> Pb(s)	-0.13	
	Ni ² *(<i>aq</i>) + 2 e ⁻	> Ni(<i>s</i>)	-0.26	
	Cd ²⁺ (aq) + 2 €	$\longrightarrow Cd(s)$	-0.40	
	Fe ²⁺ (aq) + 2 e ⁻	> Fe(s)	-0.45	
	Zn ² *(<i>aq</i>) + 2 €	\longrightarrow Zn(s)	-0.76	
	2 H ₂ O(<i>l</i>) + 2 σ	\longrightarrow H ₂ (g) + 2 OH ⁻ (aq)	-0.83	
	Al ³⁺ (aq) + 3 €	$\longrightarrow AI(s)$	-1.66	
Weaker	Mg ²⁺ (aq) + 2 e ⁻	$\longrightarrow Mg(s)$	-2.37	▼
dizing agent	Na*(aq)+ e ⁻	$\longrightarrow Na(s)$	-2.71	Stronger reducing age
arenig agont	Li+(aq) + e-	$\longrightarrow Li(s)$	-3.04	reducing age

PROBLEM 11 - SOLUBILITY

10 POINTS

Urinary (or renal) lithiasis is a condition characterized by the formation of small crystalline accretions called "kidney stones".

These "stones" are made up mainly of calcium oxalate (CaC₂O₄) crystals.

Knowing that the K_s value of this salt is $2.3 \cdot 10^{-9} M^2$:

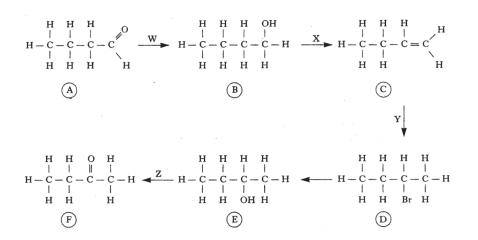
11.1 Write the expression of the ionic product of the species in solution.

11.2 Determine the minimum volume of aqueous solution required to solubilize a pure CaC_2O_4 kidney stone weighing 768 mg.

11.3 In the urine sample of a patient, a concentration of $2.5 \cdot 10^{-6}M$ oxalate ions (C₂O₄²⁻) and $5.0 \cdot 10^{-4}M$ of calcium ions is measured in the urine sample of a patient. Is there a risk of precipitation of a kidney stone in this patient? The answer must be justified with all necessary calculations.

PROBLEM 12 - ORGANIC CHEMISTRY

A student designed the following reaction sequence:



- **12.1** Suggest a suitable reagent to carry out:
 - a) Step W
 - b) Step Y
- 12.2 What type of reaction occurs at:
 - a) Step X
 - b) Step Z
- 12.3 Name the other product which is likely to be formed in step Y.
- 12.4 Name a reagent which could be used to distinguish between A and F.
- 12.5 Why does C not have geometric isomers despite the presence of a carbon-carbon double bond?
- 12.6 Which of the compounds A-F have optical isomers?
- **12.7** Give the IUPAC name of compound B.

10 POINTS