29th INTERNATIONAL CHEMISTRY OLYMPIAD

PREPARATORY PROBLEMS

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Preface

During the 28th International Chemistry Olympiad held in Moscow in July 1996, many of the mentors informally expressed concerns regarding the increasing level of difficulty of the sets of preparatory problems prepared by hosting nations. A general concensus became apparent: some of the topics were felt to greatly exceed the knowledge base which a high school student, albeit even some of the best high school students in the world, could be reasonably expected to have without being exposed to rigorous and extensive additional study. It was strongly felt by some delegates that such high-level material would challenge even university students specializing in chemistry and that this situation was leading to overtraining by some competitors.

In the collection of problems presented herein, we have attempted to address this concern. It is hoped that you will find in this material a blend of the interesting and difficult along with some more modest questions which are also felt to be of significant challenge to the large majority of the student competitors in the upcoming 29th International Chemistry Olympiad to be held in Montréal, Canada in July 1997. There are some areas of emphasis which certainly go beyond the routine material studied in most high schools around the world. But this is how it should be since the competitors involved are among the best that our countries have to offer. However, it is felt that even these topics and the level of expertise expected can be mastered by our students without significant additional tutoring. For example, the biochemistry section concentrates on the organic chemical aspects of one important class of biomolecules (carbohydrates) but deliberately does not examine the related metabolic pathways of these compounds. The coverage of the carbohydrates is at the level found in many introductory textbooks on organic chemistry, rather than that found in a senior university course specializing in the study of biochemistry, an entire subject in its own right.

The rules for eligibility of the competitors is summarized below for the benefit of our newer friends who have recently become involved in the International Chemistry Olympiad.

1) The competitors must be students of secondary schools which are not specilized in chemistry and, moreover, must be under the age of 20 on July 1 of the year of the competition.
2) The competitors must be passport holders of the country they represent or they have taken part in the secondary school educational system of the country for more than one academic year.
3) Training or any other special instruction, that is to be carried out for a selected group of 50 or fewer students, containing the IChO team, must be no longer than two weeks.

Draft Syllabus for Topics for the International Chemistry Olympiad

The following information was provided by Witold Mizerski who has been a member of the Steering Committee of the International Chemistry Olympiad. It consists of the draft list of topics which are generally regarded as suitable as the basis for examination questions for the International Chemistry Olympiad and appears in the order provided. This information has been included here for the benefit of those delegations who may not have had access to this material previously.

For ease of referral and for future discussions, the topics have been numbered.

The topics had been assigned a tentative difficulty ranking which is indicated to the right of each entry.

Level One questions should be able to be done by all competent high school students. Material from Level One topics may appear on our examinations and does not require preparatory questions.

Level Two questions are on topics likely to be covered in only some high school curricula and thus require preparatory questions.

Level Three questions are on topics which are not likely to be covered in virtually any high school curricula and thus require preparatory questions.

INORGANIC CHEMISTRY

ELECTRONIC CONFIGURATION

1	main groups	1
2	transition metals	2
3	lanthanide and actinide metals	3
4	Pauli exclusion principle	1
5	Hund’s rule	1

TRENDS IN THE PERIODIC TABLE (MAIN GROUPS)

6	electronegativity	1
7	electron affinity	2
8	first ionization energy	2
9	atomic size	1
10	ionic size	2
11	highest oxidation number	1

TRENDS IN PHYSICAL PROPERTIES (MAIN GROUPS)

12	melting point	1
13	boiling point	1
14	metal character	1
15	magnetic properties	2
16	thermal properties	3

STRUCTURES

17	metal structures	3
18	ionic crystal structures	3
19	simple molecular structures with central atom exceeding the octet rule	3
20	stereochemistry	3

NOMENCLATURE

21	main group compounds	1
22	transition metal compounds	1
23	simple metal complexes	2
24	multicenter metal complexes	3
25	coordination number	1

STOICHIOMETRY

26	balancing equations	1
27	mass and volume relationships	1
28	empirical formula	1
29	Avogadro’s number	1
30	concentration calculations	1

ISOTOPES

31	counting of nucleons	1
32	radioactive decay	1
33	nuclear reaction (alpha, beta, gamma, neutrino)	2

NATURAL CYCLES

34	nitrogen	2
35	oxygen	2
36	carbon	2

s-BLOCK

products of reaction of group I and II metals

37	with water, basicity of the products	1
38	products of reaction of the metals with halogens	1

39 products of reaction of the metals with oxygen 2

40	heavier elements are more reactive	1
41	lithium combine with H_2 and N_2, forming LiH and Li_3N	2
p-BLOCK		
42	stoichiometry of simplest nonmetal hydrides	1
43	properties of metal hydrides	3
44	acid-base properties of CH_4, NH_3, H_2S, H_2O, HX	1
45	NO react with O_2 to form NO_2	1
46	there is equilibrium between NO_2 and N_2O_4	1
47	products of reaction of NO_2 with water	1
48	HNO_2 and it's salts are reductants	1
49	HNO_3 and it's salts are oxidants	1
50	N_2H_4 is a liquid and reductant	3
51	there exist acids like $H_2N_2O_2$, HN_3	3
52	to remember, what are products of reduction of nitrates of HNO_3 with different metals and reductants	3
53	reaction of $Na_2S_2O_3$ with iodine	2
54	other thioacids, polyacids, peroxoacids	3
55	B(III), Al(III), Si(IV), P(V), S(IV), S(VI), O(II), F(I), Cl(I), Cl(III), Cl(V) and Cl(VIII) are normal oxidation states of 2nd and 3rd row elements in compounds with halogens and in oxoanions	1
56	compounds of nonmetals with other oxidation states	3
57	the preferred oxidation states are Sn(II), Pb(II), Bi(III)	2
58	products of reactions of nonmetal oxides with water and stoichiometry of resulting acids	1
59	reactions of halogens with water	2
60	reactivity and oxidizing power of halogens decrease from F_2 to I_2	1
61	differences of chemistry between row 4 and row 3 elements	3
d-BLOCK		
62	common oxidation states of the common d-block metals are Cr(III), Cr(VI), Mn(II), Mn(IV), Mn(VII), Fe(II), Fe(III), Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Hg(I), Hg(II)	1
63	colors of the listed common ions in aqueous solution	2
64	other oxidation states and chemistry of other d-block elements	3
65	Cr, Mn, Fe, Ni, Co, Zn dissolve in dilute HCl; Cu, Ag, Hg do not dissolve	5
66	products of the dissolution are (2+) cations	2
67	passivation of Cr, Fe (and also Al)	2
	$Cr(OH)_3$ and $Zn(OH)_2$ amphoteric, other common hydroxides are not	1
68	MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$ are strong oxidants	1
69	products of reduction of MnO_4^- depending on pH	2
70	polyanions other than $Cr_2O_7^{2-}$	3
OTHER INORGANIC PROBLEMS		
71	industrial production of H_2SO_4, NH_3, Na_2CO_3, Na, Cl_2, NaOH	1
72	chemistry of lanthanides and actinides	3
73	chemistry of noble gases	3

ORGANIC CHEMISTRY

ALKANES

74 isomers of butane 1
75 naming (IUPAC) 1

76	trends in physical properties	1
	substitution (e.g. with Cl_2)	
77	- products	1
78	- free radicals	2
79	- initiat./termin. of the chain reaction	2
80	cycloalkanes - names	1
81	- strain in small rings	2
82	- chair/boat conformation	2
ALKENES		
83	planarity	1
84	E/Z (cis/trans) isomerism	1
85	addition of Br_2, HBr - products	1
86	- Markovnikoff's rule	2
87	- carbonium ions in addition reaction	3
88	- relative stability of carbonium ions	3
89	- 1,4-addition to alkadiene	3
ALKYNES		
90	linear geometry	1
91	acidity	2
ARENES		
92	formula of benzene	1
93	delocalization of electrons	1
94	stabilization by resonance	1
95	Hückel (4n+2) rule	3
96	aromaticity of heterocycles	3
97	nomenclature (IUPAC) of heterocycles	3
98	polycyclic aromatic compounds	3
99	effect of first substituent: - on reactivity	2
100	- on direction of substitution	2
101	explanation of substituent effects	2
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102	hydrolysis reactions	2
103	exchange of halogens	3
104	reactivity (primary vs. secondary vs. tertiary)	2
105	ionic mechanism	2
106	side products (elimination)	2
107	reactivity (aliphatic vs. aromatic)	2
108	Wurtz (RX + Na) reaction	3
109	halogen derivatives & pollution	3
ALCOHOLS, PHENOLS		
110	hydrogen bonding - alcohols vs. ethers	1
111	acidity of alcohols vs. phenols	2
112	dehydration to alkenes	1
113	dehydration to ethers	2
114	esters with inorganic acids	2
115	iodoform reaction	2
116	reactions of primary/secondary/tertiary: Lucas reagent	2
117	formula of glycerin	1
CARBONYL COMPOUNDS		
118	nomenclature	1

119	keto/enol tautomerism	2
120	preparation - oxidation of alcohols	1

121	- from carbon monoxide	3
122	reactions: - oxidation of aldehydes	1
123	- reduction with Zn metal	2
124	- addition of HCN	2
125	of $NaHSO_3$	2
126	of NH_2OH	2
127	- aldol condensation	3
128	- Cannizzaro ($PhCH_2OH$ disproportionation)	3
129	- Grignard reaction	2
130	- Fehling (Cu_2O) and Tollens (Ag mirror)	2
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131	inductive effect and strength	2
132	equivalence of oxygen atoms in anions	2
133	preparation: from esters	2
134	- from nitriles	2
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146	R/S nomenclature	3
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163	micelle structure	3
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166	- ethene	1

167	- polyamides	3
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172	- chain mechanism of formation	2
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180	separation by electrophoresis	3
181	peptide linkage	1

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185	secondary structures	3
186	details of alpha-helix structure	3
187	tertiary structure	3
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189	quaternary structure	3
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191	metabolism of proteins (general)	3
192	proteolysis	3
193	transamination	3
194	four pathways of catabolism of amino acids	3
195	decarboxylation of amino acids	3
196	urea cycle (only results)	3

FATTY ACIDS AND FATS

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198	trival names of most important (ca. 5) fatty acids	2
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200	beta-oxidation of fatty acids (formulas & ATP balance)	3
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203	membranes	3
204	active transport	3

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206	nomenclature, kinetics, coenzymes, function of ATP etc.	3

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229	base combination CG and AT	3
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232	difference between mRNA and tRNA	3
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235	DNA-ligase	3
236	RNA synthesis (transcription) without details	3
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284	relation between K_a and K_b for conjugated acids and bases	1
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351	using pipet	1
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353	choice of indicators for acidimetry	1
354	titration curve: pH (strong and weak acid)	2
355	- EMF (redox titration)	2
356	calculation of pH of simple buffer solution	2
357	identification of: Ag^+, Ba^{2+}, Cl^-, SO_4^{2-} ions	1
358	- of Al^{3+} , NO_2^-, NO_3^-, Bi^{3+} ions	2
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360	- using flame test for K, Ca, Sr	1
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364	E_g and T_{2g} terms: high and low spin octahedral complexes	3
365	calculation of solubility of AgCl in NH_3 (from K_s and betas)	3
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THEORETICAL CHEMISTRY

367	n, l, m quantum numbers	2
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PROBLEM 1

A gold single crystal has a cubic shape and the dimension of the cube is $a = 1.000$ cm. When irradiated with Cu $K_{\alpha 1}$ X-rays ($\lambda = 154.05$ pm) at the angle (θ) of 10.89^{o} it gives a well-defined first-order diffraction pattern. The atomic weight of Au is $M_{Au} = 196.97 \text{ g mol}^{-1}$.

a) How many gold atoms are in the cube?

b) What is the mass of the unit cell of gold?

c) What is the density of gold?

PROBLEM 2

A gold thin film is deposited on a square piece of mica having the dimension of $a = 1.000$ cm. The gold film forms an ideal (100) surface structure. Such prepared gold layer and a gold wire are immersed in 10.000 cm^3 of aqueous electrolyte containing $CuSO_4$ and Na_2SO_4; the molar concentrations of the salts are $c_{CuSO_4} = 0.100 \text{ mM}$ and $c_{Na_2SO_4} = 0.100 \text{ M}$, respectively. A constant potential is applied between the two electrodes; the gold (100) layer acts as a cathode and the gold wire as an anode. An epitaxial layer of Cu having 100 atomic monolayers is deposited on the Au(100) substrate. Gold has the face centered cubic (fcc) crystallographic structure and its lattice constant equals 4.077×10^{-8} cm.

What is the concentration of $CuSO_4$ in the electrolyte after deposition of the Cu epitaxial layer?

PROBLEM 3

Pure zinc is in contact with well oxygenated ($P_{O_2} = 1.000$ atm) aqueous solution containing HCl and $ZnCl_2$; the concentrations of HCl and $ZnCl_2$ are $c_{HCl} = 1.000$ M and $c_{ZnCl_2} = 1.000$ M, respectively, and the temperature of the electrolyte is 25.00 °C. The dissolution of Zn in this solution is represented by the equation given below. A table of standard reduction potentials will be required for this question.

$$Zn + 2HCl + \frac{1}{2}O_2 \rightarrow ZnCl_2 + H_2O$$

a) Does Zn dissolve in this solution or not?

b) If Zn does dissolve in this solution, when will the process cease in a spontaneous manner?

PROBLEM 4

Ni is in contact with $100\,\text{cm}^3$ of Ni^{2+} solution of unknown concentration and Cu is in contact with $100\,\text{cm}^3$ of $0.010\ \text{M}\ Cu^{2+}$ solution. The two solutions are connected by a salt bridge and the potential of this cell is measured with the precision of $0.01\,\text{mV}$. The temperature of the system is 25.00 ˚C. A certain amount of $CuCl_2$ is added to the solution of Cu^{2+} and the potential of the cell increases 9.00 mV upon the addition; the volume change associated with the addition of $CuCl_2$ can be neglected. The molecular weight of $CuCl_2$ is $M_{CuCl_2} = 134.45\,\text{g mol}^{-1}$. A table of standard reduction potentials will be required for this question.

What is the mass of the $CuCl_2$ added?

PROBLEM 5

An electrochemical cell (battery) consists of a Cu plate immersed in $100\,\text{cm}^3$ of $0.100\ \text{M}\ Cu^{2+}$ solution and a Zn plate immersed in $100\,\text{cm}^3$ of $0.100\ \text{M}\ Zn^{2+}$ solution; the two compartments are connected by a salt bridge and the cell is maintained at $25.00\ ^\circ\text{C}$. The cell is discharged by passing a 10.00 mA current for 10^5 seconds. A table of standard reduction potentials will be required for this question.

a) What is the concentration of the cations (Cu^{2+} and Zn^{2+}) in the respective compartments after the discharge?

b) What is the change of the potential (voltage) of the cell caused by the discharge?

PROBLEM 6

α-D-(+)-Mannopyranose is an epimer of α-D-(+)-glucopyranose.

Draw its structure in its most stable chair conformation.

Give the products of the reaction of α-D-(+)-mannopyranose with the following reagents:

a) Cu^{2+} (buffer pH >7)
b) Br_2, H_2O (pH = 6)
c) HNO_3
d) CH_3OH, dry HCl
e) product of d) + $(CH_3)_2SO_2$, NaOH

f) 1) $NaBH_4$ 2) H_2O

g) 5 HIO_4

h) excess acetic anhydride in pyridine

i) 3 moles of phenylhydrazine, H^+

j) 1) Br_2/H_2O 2) Fe(III) sulfate, H_2O_2

k) 1) HCN 2) $Ba(OH)_2$ 3) H_3O^+ 4) Na-Hg, H_2O, pH 3-5

PROBLEM 7

D-Aldotetrose **A** when reacted with nitric acid gives an optically inactive compound. This same aldotetrose when treated with HCN followed by aqueous $Ba(OH)_2$ gives two epimeric aldonic acids **B** and **C.** These aldonic acids are in equilibrium with their respective γ-aldonolactones **D** and **E.** Treatment of this mixture with Na-Hg and water at pH 3-5 gives **F** and **G**, respectively. Nitric acid oxidation of **F** gives an optically inactive aldaric acid **H** while the same reaction with **E** gives an optically active aldaric acid **I**.

Give structures for compounds **A**-**I**.

PROBLEM 8

A disaccharide **A** ($C_{12}H_{22}O_{12}$) gives a negative test with Benedict's solution and does not mutarotate. **A** is hydrolyzed by α-glucosidases but not by β-glucosidases. Methylation of **A** followed by hydrolysis yields two molar equivalents of 2,3,4,6-tetra-*O*-methyl-D-glucose.

a) Give the structure of **A**.

b) How many moles of periodic acid will react with **A**?

c) How many moles of methanal (formaldehyde) and how many moles of methanoic (formic) acid are formed in the reaction of **A** with periodic acid?

PROBLEM 9

D-Idose has the opposite configuration of D-glucose at C-2, C-3, and C-4.
D-idose, at equilibrium, exists in both pyranose (75%) and furanose forms (25%).

a) Draw both cyclohexane conformations for the α and β anomers of D-idopyranose. Which of the two anomers do you believe to be the most stable? Why?

b) D-Idose can isomerize, via the Lobry de Bruyn — Alberda van Ekenstein transformation, to a 2-ketose (D-sorbose). Draw a furanose form of D-sorbose.

c) When heated D-idose undergoes a reversible loss of water and exists primarily as 1,6-anhydro-D-idopyranose. For which anomer will this reaction be favored? Draw this compound. Explain why this reaction will not occur with glucose.

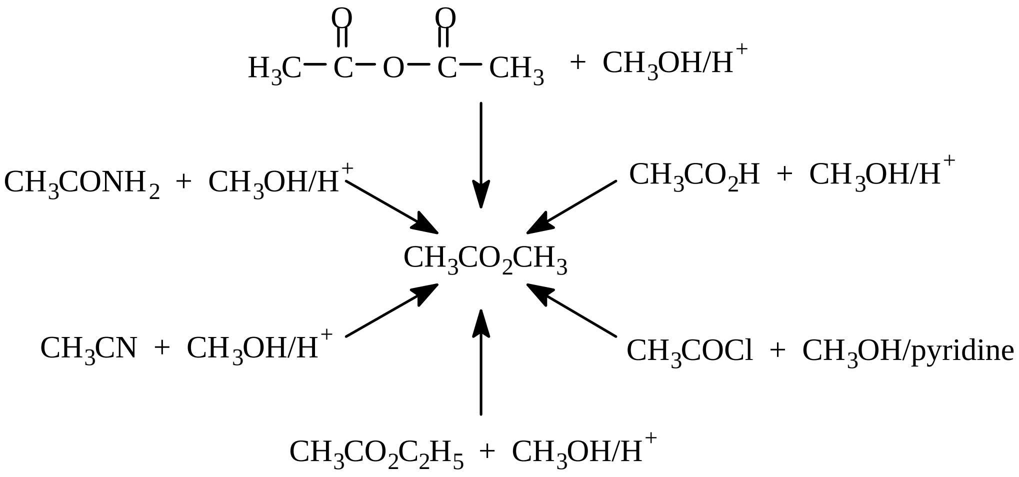
PROBLEM 10

Disaccharide **A** is hydrolyzed by dilute acid to a mixture of D-glucose and D-galactose. Compound **A** is a reducing sugar and is oxidized by bromine water to an acid, **B,** which is methylated by sodium hydroxide and dimethylsulfate to yield an octa-*O*-methylated compound. Hydrolysis of the latter gives a tetra-*O*-methylgluconic acid **C,** and a tetra-*O*-methylgalactose **D**. Compound **C** is oxidized by nitric acid to tetra-*O*-methylglucaric acid. Compound **C** is also obtained by the acidic hydrolysis of methyl 2,3,4,6-tetra-*O*-methylgalactopyranoside. Compound **A** is hydrolyzed by an α-galactosidase isolated from almonds.

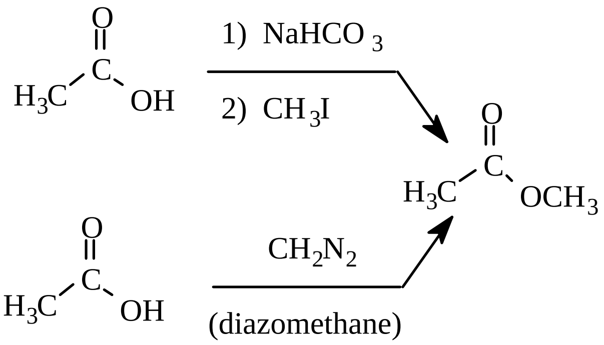
Give structures for **A, B, C** and **D**.

PROBLEM 11

The ester functionality is very commonly found in organic compounds. Chemists have devised a number of methods to prepare this important functional group. Several of these (shown below) are mechanistically related and all involve nucleophilic acyl substitutions.

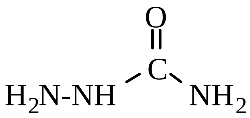

$H_3C-C(=O)-O-C(=O)-CH_3$ + CH_3OH/H^+
CH_3CONH_2 + CH_3OH/H^+
CH_3CO_2H + CH_3OH/H^+
$CH_3CO_2CH_3$
CH_3CN + CH_3OH/H^+
CH_3COCl + CH_3OH/pyridine
$CH_3CO_2C_2H_5$ + CH_3OH/H^+

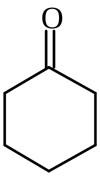
However, other synthetic variations are also known. Two mechanistically closely related reactions are shown below. Outline the mechanisms of these latter two processes.

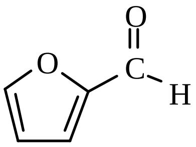

1) NaHCO 3
2) CH3I
CH2N2
(diazomethane)
H3C
OH
OCH3

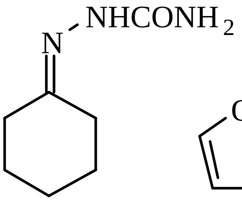
PROBLEM 12

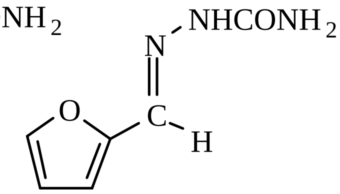
When 1 mol of semicarbazide (**A**) is added to 1 mol of cyclohexanone (**B**) and 1 mol of furfural (**C**) in ethanol with a trace of acid, a mixture of semicarbazones (**D** and **E**) is obtained. If the reaction is stopped after 5 minutes, the mixture contains mainly the semicarbazone **D**. However, when the reaction is run overnight, the product obtained is almost quantitatively the semicarbazone **E**. Explain these results and use energy diagrams to support your answer.


A


B

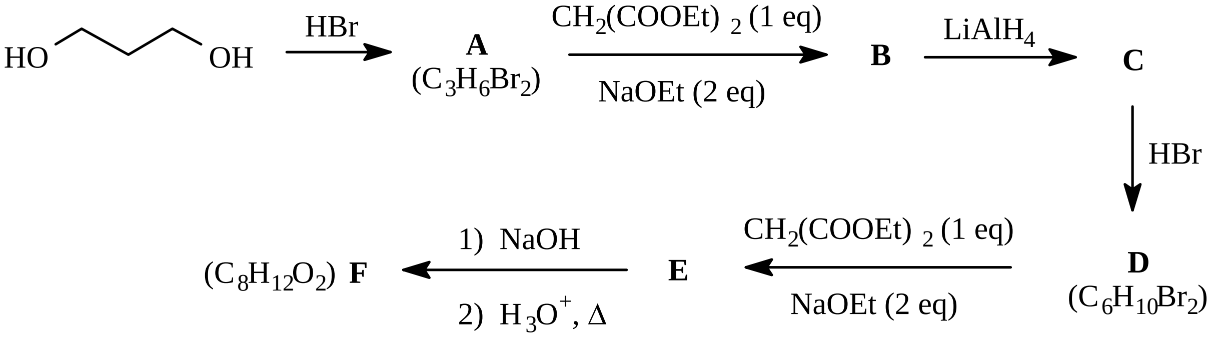

C


D


E

PROBLEM 13

Give the structures for the compounds **A - E** formed in the following synthetic sequence.


HO
OH
HBr
A
(C3H6Br2)
CH2(COOEt) 2 (1 eq)
NaOEt (2 eq)
B
LiAlH4
C
HBr
D
(C6H10Br2)
CH2(COOEt) 2 (1 eq)
NaOEt (2 eq)
E
1) NaOH
2) H3O+, Δ
(C8H12O2) F

PROBLEM 14

α-Terpinene is a natural oil isolated from turpentine as well as from oil of marjorum and other sources. Its formula is $C_{10}H_{16}$. It can be hydrogenated over a palladium catalyst and absorbs two molar equivalents of hydrogen to yield a new hydrocarbon, $C_{10}H_{20}$. Upon ozonolysis followed by a reductive workup (Zn-H_2O), α-terpinene yields the two carbonyl compounds shown below.

OHC-CHO	$CH_3COCH_2CH_2COCH(CH_3)_2$
glyoxal	6-methylheptane-2,5-dione

a) How many degrees of unsaturation does α-terpinene possess?

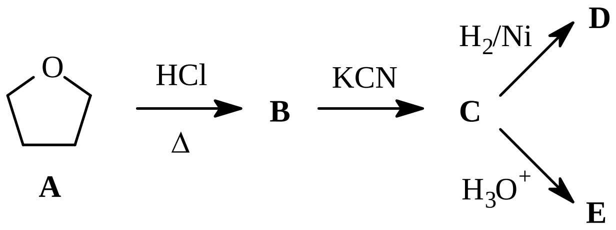
b) How many double bonds does α-terpinene possess?

c) How many rings does α-terpinene possess?

d) Propose a structure for α-terpinene consistent with the above information.

PROBLEM 15

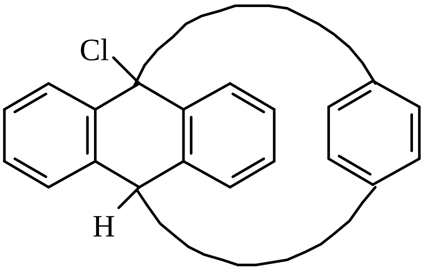
Two useful precursors (**D** and **E**) for the synthesis of a type of Nylon® are prepared from tetrahydrofuran (**A**).



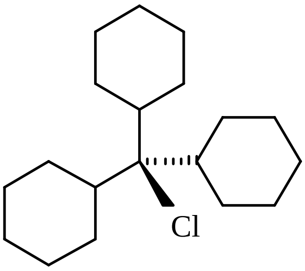
Give the reaction mechanisms for this synthetic sequence and the structure of the compounds **B - E**.

PROBLEM 16

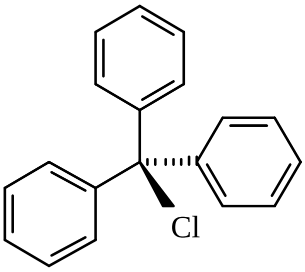
Arrange the following compounds in order of increasing reactivity towards aqueous $AgNO_3$. Explain your reasoning.



A



B



C

PROBLEM 17

Consider the reactions of 2-bromopropane and 2-methyl-2-bromopropane with sodium ethoxide in ethanol. Which bromide would give the highest yield of alkene? Which bromide would give the highest yield of alkene on solvolysis in 60% aqueous ethanol? Explain your reasoning and write equations for all reactions involved clearly showing the possible reaction products.

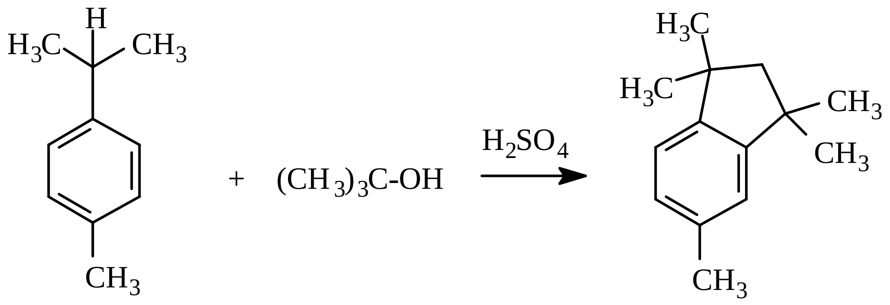
Which of the two systems, sodium ethoxide or 60% aqueous ethanol, would give the higher yield of alkene?

PROBLEM 18

The reaction shown below is interesting from a mechanistic standpoint.

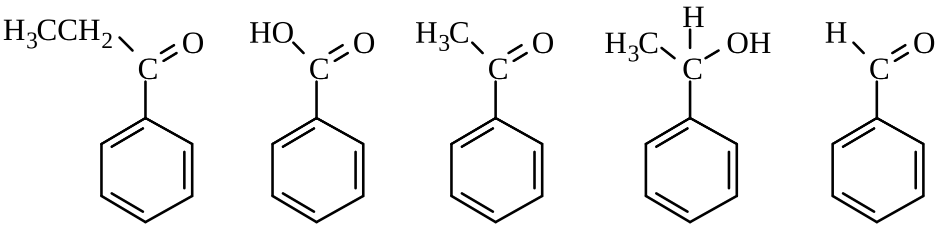
a) Suggest how this reaction takes place by writing the sequence of steps involved.

b) What products would you expect if you replaced the starting material with 1,4-dimethylbenzene?



PROBLEM 19

The compounds shown below were in five unlabelled bottles. A set of simple qualitative functional group tests were carried out on the contents of five bottles. Based on the following experimental observations, assign the correct letters to the structures shown.



i) One millilitre of acetone was placed into a series of small test tubes. Approximately 10-20 mg of each of the compounds to be tested was added to each tube and then one drop of a chromic-sulfuric acid reagent was added and the tube gently shaken to mix the contents. After a few minutes, samples containing **A** and **C** reacted with the orange dichromate solution to turn the solution blue-green and a precipitate was visible. To confirm the blue-green colour of the precipitate, the supernatant was carefully decanted and a few millilitres of water was added to the test tube. The precipitate was rinsed twice in this manner until the colour of the precipitate was apparent.

ii) When experiment (i) was repeated using 1 drop of 0.2% $KMnO_4$ solution instead of the chromic-sulfuric acid reagent, again a colour change occurred and a precipitate was observed to form for only compounds **A** and **C**.

iii) Only compound **B** dissolved when a 10-20 mg sample of each of the unknown compounds was added to a few millilitres of dilute aqueous sodium hydroxide and the test tubes gently shaken to mix the contents. It was also the only compound to yield a positive test when a solution of each was tested with litmus paper.

iv) Only compounds **A** and **E** produced a bright yellow precipitate when added to a solution of sodium hypoiodite prepared by dissolving iodine in aqueous sodium hydroxide.

v) Compounds **C**, **D** and **E** produced red-orange precipitates when a small amount of each was added to a similar volume of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent.

PROBLEM 20

There are six constitutional isomers of C_5H_8 which are cyclic alkenes which do not contain an ethyl group.

a) Give the structures of the six compounds

b) You are now given samples of three of the above compounds in bottles labeled **A**, **B**, and **C**, but you do not know which compound is in which bottle. Based on the results of the following reactions with $KMnO_4$, give the structures of compounds **A** - **F**.

Compound **A** formed a dicarboxylic acid (**D**) which contained a chiral carbon atom.

Compound **B** formed a diketone (**E**) which did not contain any chiral carbon atoms.

Compound **C** formed **F** which contained both a carboxylic acid and a ketone functional group and also had a chiral carbon atom.

PROBLEM 21

Provide a brief rationale for each of the following observations:

a) Under identical conditions, the reaction of $NaSCH_3$ with 1-bromo-2-methylbutane is significantly slower than the corresponding reaction involving 1-bromobutane.

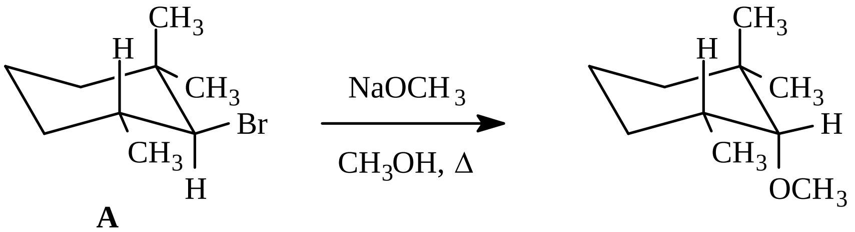
b) When enantiomerically pure (S)-2-butanol is treated with a strong base such as $LiNH_2$ and then recovered, it retains its optical activity. However, when (S)-2-butanol is treated with warm water in the presence of a small amount of sulfuric acid, it is found that the recovered alcohol has lost its optical activity.

c) Reaction of cyclobutene with bromine (Br_2, cold, in the dark) yields a racemic product, whereas the reaction with "heavy" hydrogen in the presence of a platinum catalyst (i.e. D_2 with Pt) yields a meso compound.

d) (S)-2-Butanol was produced when (R)-2-bromobutane was refluxed in a concentrated NaOH solution of aqueous ethanol.

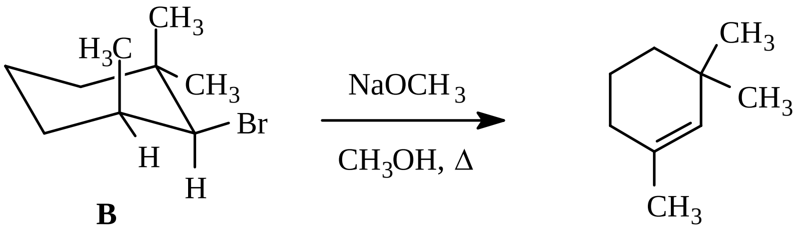
e) Racemic 2-butanol was produced when (R)-2-bromobutane was refluxed in a dilute NaOH solution of aqueous ethanol. What will happen to the rate of the alcohol formation if the alkyl bromide concentration is doubled? If the NaOH concentration is doubled?

f) Reaction of the diastereoisomers **A** and **B** under identical conditions leads to dramatically different reaction products. Hint: Consider the three-dimensional stereochemical aspects of the problem.



A

[1]



B

[2]

PROBLEM 22

Compound **A** (C_5H_8O) was found to be optically pure (S-enantiomer), and could be converted into compound **B** (C_5H_7Br) which was also found to be optically pure (R-enantiomer) using a two-step sequence of i) CH_3SO_2Cl, triethylamine ii) LiBr. Compound **B** was converted into the achiral molecules **C** and **D** (both C_5H_9Br) upon reaction with hydrogen gas in the presence of a metal catalyst. When **B** was converted into the corresponding Grignard reagent, and then hydrolyzed with water, the achiral compound **E** (C_5H_8) was produced. Treatment of **E** with an acidic solution of $KMnO_4$ led to the formation of **F** ($C_5H_8O_3$). The infrared spectrum of **F** indicated the presence of two different carbonyl groups as well as the presence of a hydroxy group. Give stereochemical structures for compounds **A**-**F**.

PROBLEM 23

Compound **A**, which contains a five-membered ring and has the molecular formula C_7H_{12}, when treated with ozone followed by a reductive workup (Zn/H_2O) gives a dialdehyde **B** of formula $C_7H_{12}O_2$. Compound **A** also reacts with alkaline $KMnO_4$ at 0 ˚C to produce compound **C**, $C_7H_{14}O_2$, which is achiral and reacts readily with one equivalent of phosgene (Cl_2CO) in the presence of pyridine to yield a bicyclic compound **D** ($C_8H_{12}O_3$). Treatment of **C** with hot aqueous $KMnO_4$ generates a diacid **E**, $C_7H_{12}O_4$. Chlorination of the diacid **E** gives rise to three isomers **F**, **G**, and **H**, which are monochloro compounds of formula $C_7H_{11}O_4Cl$. Compound **F** is achiral and compounds **G** and **H** are enantiomers. Treatment of **A** with a peroxyacid followed by acid hydrolysis generates **I** and **J** (both are $C_7H_{14}O_2$) which are enantiomeric. Compounds **I** and **J** are diastereoisomers of compound **C**.

Give stereochemical structures for compounds **A**-**I**.

PROBLEM 24

At the dentist, the inorganic chemist is mostly interested by the composition of the visible part of the teeth, namely the dental crown. Dental crown is made of two constituents: the enamel and the dentine. The enamel is the hard, white substance that covers the crown. This part is made of 97 to 99% hydroxyapatite, $Ca_5(PO_4)_3OH$. The crystals of this mineral are rather thin and long over the whole thickness of the enamel, which is about 2 mm. The dentine (or the ivory of the teeth) is the inside part of the crown and the roots. It is made of 20% organic matter, 10% water and 70% hydroxyapatite. The crystals of the latter are shorter than those contained in the enamel. They have the form of needles, or plates, that are attached to each other in the organic matrix.

In the mouth, mineral substances such as calcium and phosphate ions that are present in saliva, contribute to the formation and the decomposition of hydroxyapatite. These two processes can occur simultaneously until an equilibrium is reached. The formation process is called mineralization or remineralization of the enamel, whereas the decomposition process is called demineralization.

a) Write the balanced equation describing the mineralization and demineralization of tooth enamel in water.

Dental cavities, or the direct attack of dentine by organic acids and bacteria, is initiated by the demineralization process. The major cause of this process is the presence of dental plaque. The latter is a gelatinous mass of closely-packed microorganisms and polysaccharides attached to the tooth surface and maintained by the food particles that remain in the mouth. Improper dental hygiene will make the dental plaque thicker and it will become a good medium in which bacteria may grow. Under the plaque, near the enamel, anaerobic bacteria will decompose carbohydrates into organic acids such as acetic and lactic acids.

b) The natural lactic acid is levorotatory and possesses an R-configuration according to the Cahn-Ingold-Prelog rules. Draw a three-dimensional structure of lactic acid and give a systematic name of this acid.

The pH of the dental plaque can be significantly reduced by presence of acetic and lactic acids. If it goes below the critical value of pH 5.6 for a long period of time, an important demineralization process can occur and dental cavities will appear.

c) The influence of an acidic medium on the demineralization of teeth can be described by two different processes which depend on the ions produced by this reaction. Write the equations that correspond to each of these processes and explain their specific influence in the demineralization process.

It is known that fluoride ions ensure a better protection for teeth. Two mechanisms are proposed to explain this phenomenon. First of all, fluoride ions can inhibit the action of some enzymes such as those involved in the fermentation of the carbohydrates that produce the harmful organic acids. However, the major effect of the fluoride ions against the demineralization process is believed to occur during this process itself. Because their sizes are similar, the hydroxide ions of hydroxyapatite can be substituted by fluoride ions during the remineralization process to form a fluoroapatite, $Ca_5(PO_4)_3F$, which has a lower solubility.

d) Write the balanced equation for the reaction describing the decomposition and recomposition of fluoroapatite in water. Calculate the solubilities of hydroxyapatite and fluoroapatite in water.
(K_{sp} of hydroxyapatite = 6.8×10^{-37} and K_{sp} of fluoroapatite = 1.0×10^{-60})

e) Show, from the proper chemical and mathematical equations, how the remineralization process is favoured when hydroxyapatite is in the presence of fluoride ions.

Actually, all the hydroxide ions of the enamel are not substituted by fluoride ions. To ensure sufficient protection, the substitution does not need to be complete. Studies have demonstrated that a 30% ratio of substitution is enough to make the tooth enamel stable against acid attack. It is then important to keep a constant concentration of fluoride ions in the mouth to favour the formation of fluoridated hydroxyapatite.

f) Show, from the proper chemical and mathematical equations, how fluoroapatite can be more stable than hydroxyapatite in acidic medium?
($K_w = 1.0 \times 10^{-14}$ and K_a of HF = 7.2×10^{-4})

PROBLEM 25

Some natural substances are very important for industry. From them we can often do a series of simple reactions that will produce many new compounds that will each have many applications. In the present problem, we will follow the transformation of one of these substances that had a place of choice in Canada’s economy, especially that of the Shawinigan area of Québec, at the beginning of the 20th century.

A mineral substance **A** is pyrolyzed at 825 ˚C in an electrical furnace. A gas **B** evolves until the mass of the remaining residue becomes equal to 56% of the initial mass. The reaction of **C** with coal, coke or coal tar at 2000-2200 ˚C forms compound **D** and a gas **E**. The latter contains the same element as gas **B**, but in a different proportion. Initially, the purpose of this reaction was to isolate the metal contained in **C**, but instead compound **D** was obtained. This material is of major importance in industrial organic and mineral chemistry. Impure, it looks like a dark-coloured mass containing about 80% of **D**. Purified, it is a colourless ionic solid having the same crystal structure as NaCl, but it is slightly distorted at room temperature.

Hydrolysis of **D** produces a large volume of gas **F** that burns in air giving a brilliant and sooty flame. A good example of the industrial applications of gas **F** comes from its reaction with water, in presence of a $HgSO_4$ catalyst, to form an aldehyde **L** that can be oxidized in air into an acid **M** with a manganese catalyst.

A reactive and poorly soluble solid, **G**, was also formed by the hydrolysis of **D**. Reaction of **G** with gas **B** produces water and a compound **A'** having the same formula as the mineral substance **A**. Moreover, pyrolysis of **G** leads to the formation of **C** and water.

Gaseous nitrogen is passed through a bed of **D** at 1000 - 1100 ˚C in order to start its transformation into a highly reactive ionic solid **H** and a carbon residue (the heat source is then removed as the reaction continues because of its strong exothermic character). Elemental analysis reveals that **H** contains 15%C and 35%N. Hydrolysis of **H** gives **G** and an ionic intermediate **X** which then reacts with carbon dioxide in water to form **A'** and **I**. Compound **I** is a molecular solid that can be represented by two different Lewis structures that are tautomeric with each other. However, only one of these structures is actually observed for this substance.

Compound **I** is mostly used in the production of chemical fertilizers. Its hydrolysis produces another molecular solid **J** that can be directly used in fertilizers. On the other hand, hydrolysis of **J** forms two gases, **B** and **K**, one of which has a strong, characteristic odour.

a) What compounds are represented by the letters **A - M** and **X**?

b) Draw the two possible Lewis structures for compound **I** and specify the one that is actually observed knowing that its infrared spectrum shows an absorption band between 2260 and 2220 cm^{-1}, and that it does not possess a center of symmetry.

c) Draw the Lewis structure of compound **J**.

d) The crystal structure of **D** is formed by a lattice of cations in which the anions are inserted. Assuming that all the sides of the unit cell are of same dimension and knowing that the density of **D** is 2.22 g/cm^3, calculate the distance between two cations on one edge of the unit cell.

e) Write the balanced chemical equations of all the reactions described in this problem.

PROBLEM 26

Silicon carbide (SiC) has a high thermal conductivity and a low thermal expansion. These properties make it more resistant to thermal shock than other refractory materials. It is a ceramic material that has many applications in metallurgical, abrasive and refractory industries.

However, the useful properties (hardness, high melting point, and chemical inertness) of this material present enormous problems in fabrication. In fact, these types of ceramics were traditionally manufactured as powders, and objects were made by cementing and sintering these powders into the required forms. These processes are costly because they necessitate many technical steps and consume much energy. Moreover, the desired physical and chemical properties of the final products are severely limited by the presence of gaps and other defects in their structures.

A great deal of effort is now being directed to the development of new methods for the preparation of ceramics of this type. One of these methods is the use of inorganic and organometallic polymers as pre-ceramic materials. In this problem, we will examine the specific case of the preparation of silicon carbide by such processes.

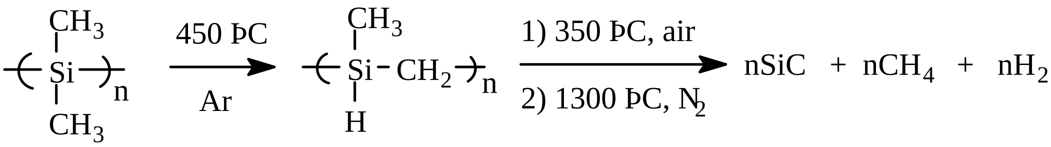
The usual commercial method for the manufacture of SiC, known as the Acheson process, involves high-temperature solid-state reactions of silica (fine grade sand) with graphite or coke in an electrical furnace. Carbon monoxide is also produced during this reaction. The silicon carbide obtained by this method is infusible, intractable, and not useful for the preparation of fibers or films.

Acheson Process:

$$SiO_2 + 3C \xrightarrow{\Delta} SiC + 2CO$$

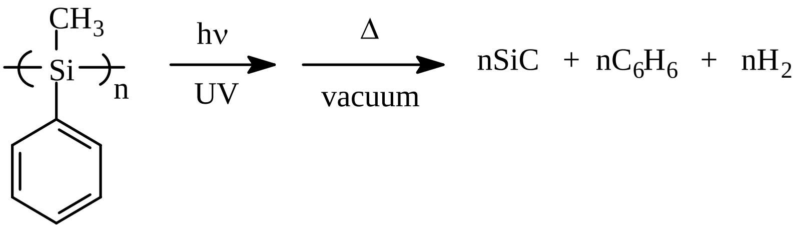
In the mid-1970’s, Yajima and coworkers developed a process for the formation of silicon carbide ceramics by the thermal conversion of a low molecular weight poly(dimethylsilane) or $[(CH_3)_2Si]_n$. The proximity between carbon and silicon atoms in the polymer favours the formation of Si-C bonds and allows the production of silicon carbide in three simple pyrolysis steps as shown below. This process has been adapted for the commercial production of Nikalon® SiC fibers.

Yajima Process:



The poly(dimethylsilane) used by Yajima has a relatively low solubility. The first step of his process was mostly to transform it into a material that is more soluble so that it can be easily processed. A great improvement of his process would be to start with a polymer that is already soluble so that the first pyrolysis step can be avoided. West and coworkers were able to produce such a polymer by substituting a methyl group with a phenyl group to get a poly(methylphenylsilane) or $[(CH_3)(C_6H_5)Si]_n$. From this material, silicon carbide was obtained after an ultraviolet treatment to cross-link the polymer, then a pyrolysis under vacuum at temperatures above 800 ˚C.

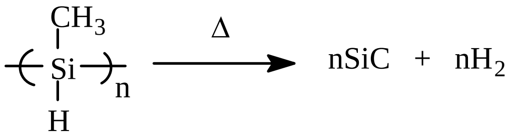
West Process:



The polymers used by Yajima and West are produced by Wurtz coupling reactions where the starting dichlorosilanes react with an active metal such as sodium in refluxing, inert solvents like toluene or xylene. These drastic experimental conditions allow the formation of a range of polymers having relatively high molecular weights.

A new catalytic process has been developed by Harrod and coworkers, then adapted by other teams around the world. The molecular weight of the polysilanes obtained were generally lower (n = ca. 170) than those resulting from the Wurtz reactions (n > 1000). One of these polymers, poly(methylsilane) or $[(CH_3)(H)Si]_n$, possesses only one carbon atom bound to each silicon atom in the chain. The formation of SiC by the pyrolysis of poly(methylsilane) is shown below.

Harrod Process:



$$-\!\!\left(\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_n \xrightarrow{\Delta} n\mathrm{SiC} + n\mathrm{H_2}$$

a) Evaluate the theoretical ceramic yield (i.e. the mass percentage of SiC formed as a function of the initial mass of reagents) for each of the processes described above.

Both silicon carbide and diamond can crystallize in a cubic structure (the other possibility being a hexagonal structure). In silicon carbide, the carbon atoms occupy the points of a face-centered cubic lattice (fcc) and the silicon atoms occupy half of the tetrahedral holes available. In diamond, the same tetrahedral holes are occupied by other carbon atoms. Because of the sizes of carbon and silicon atoms, these two structures are not close-packed. The density of silicon carbide is 3.21 g $\mathrm{cm^{-3}}$ and that of diamond is 3.51 g $\mathrm{cm^{-3}}$.

b) Knowing that the shortest possible distance between two neighbouring carbon atoms is 1.54×10^{-8} cm in diamond, calculate the atomic radius of silicon in SiC.

PROBLEM 27

The following are some facts about a set of important p-group oxides.

i) Silica is a colourless solid which melts around 1700 °C; phosphorus pentoxide is a colourless solid melting at 420 °C; sulfur trioxide is a colourless gas which condenses to a liquid at about 45 °C and to a crystalline solid at about 17 °C.

ii) At room temperature, silica is essentially insoluble in neutral water. However, both phosphorus pentoxide and sulfur trioxide dissolve violently and exothermically in neutral water.

iii) Silica can be fused with potassium oxide to give potassium silicate, but the reaction is not violent. Both phosphorus pentoxide and sulfur trioxide react violently and exothermically with molten potassium oxide.

iv) Living systems use the pyrophosphate linkage (P-O-P) for energy storage in the form of adenosine triphosphate (ATP), but the pyrosilicate (Si-O-Si) and pyrosulfate (S-O-S) linkages have not been encountered in living systems.

a) Suggest an explanation for (i) in terms of the structures of the oxides.

b) Write equations for all of the reactions mentioned in (ii) and (iii) and comment on the energetics of each reaction.

c) Suggest an explanation for (iv) in terms of your answers to question (b).

PROBLEM 28

The following is a description of the synthesis of a high T_c superconductor: “The samples were prepared from mixtures of high purity Y_2O_3, $BaCO_3$ and CuO powders. After grinding and pressing into a disc, materials were pre-fired at 850 ˚C in air for 12 hours. Then, they were broken, ground, pressed into disks and sintered in a stream of oxygen at 940 ˚C for 12 hours. The samples were then allowed to cool slowly to room temperature under oxygen.” The final product of this reaction has an idealized formula $YBa_2Cu_3O_7$.

a) Write an equation for the above reaction.

b) Given that neither Y nor Ba can change their oxidation state in this reaction, what is the average oxidation state of the Cu in the product?

When $YBa_2Cu_3O_7$ is heated above 400 ˚C it begins to lose oxygen. A 10.00 g sample heated to 500 ˚C under a stream of inert gas for 24 hours was found to weigh 9.88 g.

c) What is the molecular formula for the product and what is the average oxidation state of the Cu?

d) Explain the numbers you get for the Cu oxidation states in $YBa_2Cu_3O_7$ and in its thermal decomposition product?

PROBLEM 29

Nitric oxide (NO) is a simple molecule that has been known for a very long time and extensively studied. It recently aroused enormous new interest when it was discovered that this highly reactive, simple molecule plays a key role as a neurotransmitter in a wide range of biochemical systems. As with all biologically active chemical species a number of important questions immediately arise: How is the molecule made? Is it stored or made on demand?

How is it stored? What are its targets? How is it removed when no longer required? The inorganic chemist makes important contributions to answering these questions by designing simple model systems which mimic the chemistry occurring in the more complex living systems. Some observations on the chemistry of NO of relevance to understanding its participation in biochemical processes are the following:

i) Superoxide ion, O_2^-, reacts rapidly with NO in water under physiological conditions to give the peroxonitrite ion, $[ONO_2]^-$.

ii) The peroxonitrite ion reacts rapidly with aqueous CO_2, or HCO_3^-, to a give a species believed to be $[ONO_2CO_2]^-$.

iii) Enzymes, called nitrite reductases and which contain Cu^+ ions in the active site, effect the reduction of NO_2^- to NO.

iv) A sample of NO gas at 50 ˚C after rapid compression to 100 atmospheres shows a rapid drop in pressure at constant volume due to a chemical reaction. By the time the temperature has re-equilibrated to 50 ˚C, the pressure has dropped to less than 66 atmospheres.

a) Identify those chemical species mentioned in (i) and (ii) which possess an odd number of valence electrons. Suggest structures for $[ONO_2]^-$ and $[ONO_2CO_2]^-$, indicating the geometry about the N and C atoms.

b) To what classes of reaction do the reactions described in (i) and (ii) belong?

c) Write a balanced equation for the reduction of NO_2^- with Cu^+ in aqueous acid solution.

d) If one of the products in (iv) is N_2O, what is the other product? How does the formation of these two products explain the experimental observations? To what class of reaction does this reaction belong?

PROBLEM 30

a) Much of our understanding of the chemistry of the transition elements is still based on the coordination theory of Alfred Werner, formulated at the end of the 19th century. A very large proportion of the experiments used by Werner to prove his coordination theory involved complexes of Co^{3+} and Cr^{3+}. Why was this so?

b) Werner was able to deduce many things about the geometry of coordination compounds from the existence, or non-existence of isomers. Name, draw the structures of, and discuss the isomerism of the following coordination compounds:

$[(NH_3)_4Cl_2Cr]Cl$

$[py_3Cl_3Co]$; where py = pyridine

$[(H_2O)_5(CNS)Co]Cl$

$[(Me_3P)_3ClPt]Br$; where Me = CH_3

c) New concepts concerning the structure of organic compounds, largely developed by Pasteur and by van’t Hoff and LeBel, were immediately seized upon by Werner to answer some outstanding questions arising from the coordination theory. What special features of the complex $[en_2Cl_2Co]Cl$ permitted Werner to conclude that Co^{3+} complexes have octahedral rather than some other, e.g. trigonal prismatic, coordination geometry? en = ethylenediamine which is a bridging or bidentate ligand.

d) $CrCl_3$ can form a series of compounds with NH_3 having the general formula $[(NH_3)_xCl_3Cr]$ (x= 3 to 6). How did Werner use a new theory that explained the electrical conductivity of salts in water to show that in all of these compounds the number of groups (NH_3 or Cl) attached to Cr is always 6?

PROBLEM 31

a) State the First Law of Thermodynamics in terms of changes of the internal energy E, and the heat q and the work w.

b) Define thermodynamically the entropy S and state what kind of process is necessary to calculate it.

c) For a perfect gas, $E=\frac{3}{2}(nRT)$ and $PV=nRT$. Use this information to calculate the change in the thermodynamic functions, E, S, G for a reversible isothermal expansion from an initial volume V to a final volume 2•V at a temperature T.

d) Calculate the thermodynamic functions E, S, G for an irreversible, sudden isothermal expansion from V to 2•V.

e) From the above results, define spontaneity or irreversibility in terms of the sign of ΔS and ΔG.

f) What is the change of entropy of the surroundings in the reversible expansion mentioned above?

g) Another definition of S is statistical (Boltzmann):

$$S = k\ln W$$

where $k=R/N_o$, W is the number of configurations or states available for the molecular system, N_o is Avogadro’s number, R is the gas constant.

Calculate ΔS from this statistical definition by assuming that when a molecule is in the initial volume V, this corresponds to one state, whereas when the volume is expanded to 2•V, there are now two states available, i.e., each of volume V.

PROBLEM 32

a) One mole of O_2(g), initially at a temperature of 120K and under a pressure of 4 atm, is expanded adiabatically to 1 atm in such a way that the temperature of the gas falls to infinitesimally above the normal boiling point of the liquid (90K). You may assume $\overline{C}_p$(g) = 28.2 J K^{-1} mol^{-1} and is constant over the required temperature range and that O_2(g) behaves ideally.

Calculate q, w, ΔH, ΔS_{sys} and ΔS_{surr} for this process.

b) The one mole of O_2(g), now at 90K and 1 atm pressure, is liquified by application of a pressure infinitesimally greater than 1 atm. The liquid O_2 is then cooled at constant pressure to the normal melting point of 55K, solidified reversibly, and the solid cooled to 10K. Determine ΔH_{sys} and ΔS_{sys} for the sum of these events.

$\overline{C}_p$(l) = 54 JK^{-1} mol^{-1}, $\overline{C}_p$(s) = 41 JK^{-1} mol^{-1}, ΔH°_{vap} = 6.82 KJ mol^{-1}, ΔH°_{fus} = 0.42 KJ mol^{-1}

PROBLEM 33

Some standard enthalpies of formation and standard third law entropies (all at 298K) are:

	CO_2 (aq)	H_2O(l)	NH_3(aq)	$(H_2N)_2C{=}O$(aq)
ΔH°_f (kJ mol^{-1})	-412.9	-285.8	-80.8	-317.7
S° (JK^{-1} mol^{-1})	121.0	69.9	110.0	176.0

In aqueous solution, urea ($(H_2N)_2C{=}O$) is hydrolysed according to the following reaction:

$$(H_2N)_2C{=}O(aq) + H_2O(l) \rightarrow 2NH_3(aq) + CO_2(aq)$$

a) Calculate ΔG° and the equilibrium constant for this reaction at 298K.

b) Determine whether or not the hydrolysis of urea will proceed spontaneously at 298K under the following conditions:

$$[(H_2N)_2C{=}O] = 1.0\text{ M};\ [H_2O] = 55.5\text{ M};\ [CO_2] = 0.1\text{ M};\ [NH_3] = 0.01\text{ M}$$

PROBLEM 34

The gas phase decomposition of ozone (O_3) in the presence of dioxygen (O_2) at 80 ˚C shows complicated kinetic behaviour that depends on the relative concentrations (or pressures) of O_2 and O_3.

If $[O_2] \gg [O_3]$ the rate law has the form:

$$\frac{-d[O_3]}{dt} = k_{exp}[O_3]^2[O_2]^{-1}$$

However, if $[O_2] \ll [O_3]$, the decomposition follows:

$$\frac{-d[O_3]}{dt} = k'_{exp}[O_3]$$

A proposed mechanism for the reaction is:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

where the second step is assumed to be much slower than the first (equilibrium) step.

a) On the basis of this mechanism, and using the principle of stationary (steady) state for [O], derive the rate equation for the decomposition of O_3. Show that this mechanism is consistent with the observed kinetic behaviour at both high and low values of $[O_2]/[O_3]$.

b) Evaluate k_{exp} and k'_{exp} in terms of k_1, k_{-1} and k_2 for the proposed mechanism.

PROBLEM 35

The reaction X + Y + Z $\rightarrow$ P + Q was studied using the method of initial rates and the following data were obtained:

$[X]_0$ (M)	$[Y]_0$ (M)	$[Z]_0$ (M)	Initial Rate $\frac{d[P]}{dt}$ (M h^{-1})
0.01	0.01	0.01	0.002
0.02	0.02	0.01	0.008
0.02	0.02	0.04	0.016
0.02	0.01	0.04	0.016

a) What are the orders of the reaction with respect to X, Y, and Z?

b) Determine the rate constant and the time it will take for one half of X to be consumed in a reaction mixture that has the initial concentrations:

[X] = 0.01 M [Y] = 1.00 M [Z] = 2.00 M

PROBLEM 36

Molecular Orbital (MO) Theory was introduced by Mulliken in the 1940’s and 1950’s for which he won the 1964 Nobel Prize in Chemistry. It allows for the prediction of bond orders and paramagnetism of simple molecules.

a) Give a relative energy diagram for the MO’s of diatomic molecules which possess only 1s, 2s and 2p electrons.

b) Give the MO configurations and bond orders of H_2, H_2^-, He_2, and He_2^-.

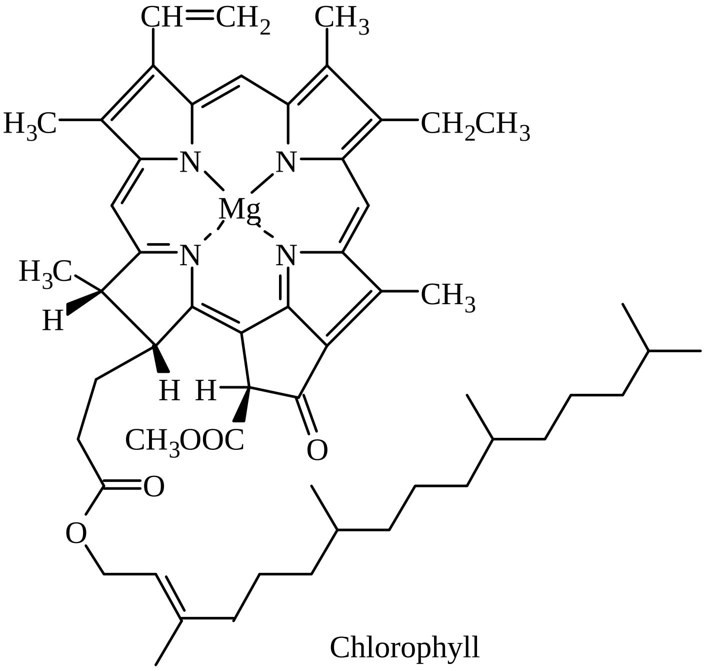
c) Which species in (b) are expected to have the same stability?

d) Show that dioxygen, O_2, is a biradical species.

e) In analytical chemistry the Hg^{2+} ion is identified by reduction to Hg^+. However, the actual structure of the latter as determined from X-ray analysis is found to be the dimeric Hg_2^{++} species. Using MO theory, show why the dimeric species Hg_2^{++} is more stable than the monomer Hg^+.

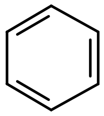
PROBLEM 37

Benzene is an aromatic ring system in that in follows Hückel's rule of being a closed, cyclic, coplanar system with (4n + 2; n = 0, 1, 2, 3…) π electrons. Chlorophyll is also aromatic. There is some controversy over how to count the number of π electrons, however

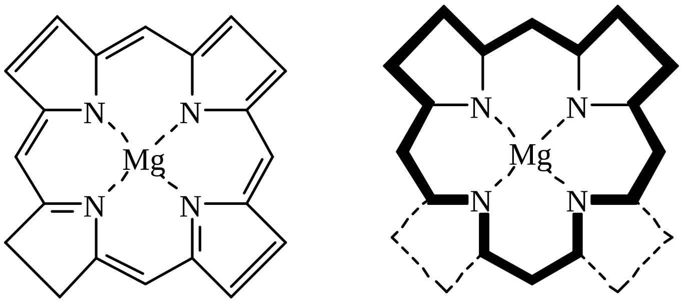


Chlorophyll

the total number are generally agreed to be either 18 or 22; either of which make the system aromatic. Benzene and the core segment of chlorophyll are two planar species which approximate a circular ring structure: a hexagon (6) for benzene and a dodecagon (12) for chlorophyll. Each sp^2 hybridized carbon and two of the nitrogen atoms supply one π electron to the rings in these systems. Thus in benzene there are 6-π electrons, whereas in chlorophyll there are 18 (or 22) π-electrons. For the purposes of this question, assume that there are 18 aromatic π electrons in chlorophyll which pass through the aza nitrogens but leave out the pyrrole-type nitrogens of the molecular core. Sigma (σ) electrons are in the plane of the molecule and π-electrons are perpendicular to the plane of the molecule.



benzene



18 π system

chlorophyll core

The energy of the molecular orbitals (MO's) of an electron confined to a ring of radius r is given by:

$$E_n = \frac{\hbar^2 l^2}{2mr^2} \qquad l = 0, \pm1, \pm2, \pm3\ldots$$

where $\hbar = \frac{h}{2\pi}$ (h = Planck's constant; 1 x 10^{-34} joules sec), m is the mass of the electron, and l is the rotational quantum number of the electron (the equivalent of m_l in an atom). As an approximation, the C-C bond distance can be assumed to be 1.50 x 10^{-8} cm.

a) Why does the magnesium not supply π-valence electrons to the chlorophyll ring?

b) What is the radius r_b of the benzene ring and r_c, that of the chlorophyll ring?

c) Find an expression for the energy of the highest occupied molecular orbital (HOMO) of each ring in terms of $\hbar$, m, and r_b. Similarly, find the expression for the energy of the lowest unoccupied molecular orbital (LUMO).

d) Find an expression for the lowest (i.e. first) absorption band of each ring. The experimental absorptions occur at 300 nm for benzene and for 600 nm for chlorophyll. Suggest an improvement of the ring model which will bring the theoretical and experimental data more into agreement.

e) Would you expect chlorophyll to be diamagnetic or paramagnetic? Explain in terms of the total spin of the π-system.

PROBLEM 38

The concentration of dissolved O_2 is essential to the survival of aquatic animals. For instance, most fish species require 5-6 ppm of dissolved O_2. Thermal pollution and the presence of oxidizable substances in water are, in part, responsible for O_2 depletion. The concentration of dissolved O_2 is normally measured with an "oxygen meter." Assume that no such instrument is available and that you are required to determine the dissolved O_2 in an important salmon stream using the modified Winkler method and chemicals available in your laboratory. With this method, Mn^{2+}(aq) is stoichiometrically oxidized to MnO_2(s) by dissolved O_2 and the MnO_2 is then titrated iodometrically.

According to this method, 1 mL $MnSO_4 \bullet H_2O$ solution is added to a water sample (250 mL) in an Erlenmeyer flask. This is followed by 2 mL of a sodium hydroxide-sodium iodide-sodium azide solution. The flask is capped tightly and the solutions thoroughly mixed by inverting the flask repeatedly. The solution is allowed to stand until the precipitate has settled. Then 1 mL of concentrated H_2SO_4 is added and the solution titrated with 9.75×10^{-3} mol/L sodium thiosulfate until a pale yellow colour is reached. Starch indicator (10-15 drops) is added and titration continued until the blue-black colour just disappears: 27.53 mL of this solution is used.

a) Give the chemical equations for the reaction involved in this determination.

b) Determine the amount of dissolved oxygen and report your results in ppm.

PROBLEM 39

For any analysis to achieve the desired level of accuracy, a calibration curve is usually prepared using concentrations of the standard which covers a reasonable range of analyte concentrations in a solution whose overall composition approximates that of the test solution. In real life, this is very near impossible and most analysts tend to rely on a procedure called "standard addition" in which a known quantity of the analyte is added to an aliquot of the sample.

This procedure was applied to the determination of the concentration of phosphate in a patient's urine. A 5.0 mL urine sample was diluted to 100 mL. The absorbance of a 25 mL aliquot of the solution was measured spectrophotometrically and found to be 0.428. A 1.0 mL sample of a solution containing 0.050 mg of phosphate was added to a second 25.0 mL aliquot and its absorbance determined to be 0.517.

a) What is the absorbance due to the added phosphate?

b) What is the concentration of phosphate in the aliquot of the specimen?

c) What is the concentration of phosphate in the patient's urine? (In mg/L of urine)

d) Give other advantages of using this procedure.

PROBLEM 40

The complex between Co(II) and the ligand R was investigated spectrophotometrically. A green filter at 550 nm was used for the measurements, the wavelength of absorbance maximum for the complex. The cation concentration was maintained at 2.5 x 10^{-5} mol/L in solutions with different concentrations of R. The absorbance data (1 cm cell) were obtained as follows:

Conc. R (mol/L) x 10^{-5}	Absorbance (A)
1.50	0.106
3.25	0.232
4.75	0.339
6.25	0.441
7.75	0.500
9.50	0.523
11.5	0.529
12.5	0.531
16.5	0.529
20.0	0.530

a) Determine the ligand to cation ratio for the complex .

b) Calculate the value of the formation constant K_f for the complex using the stoichiometry where the lines intersect.

PROBLEM 41

A certain quantity of lead chromate was accidentally spilled into a reservoir, and the city engineers would like to know to what extent drinking water was contaminated. The solubility product K_{sp} of lead chromate at 18 ˚C is 1.77×10^{-14}.

a) What is the solubility of lead chromate in pure water?

b) Some engineers believe that the lead in the water could be removed by treating it with potassium chromate (K_2CrO_4). What is the solubility of lead chromate in 0.1 mol/L of potassium chromate?

c) It was also believed that chromate ions could be removed from potable water by treating it with lead nitrate. What is the solubility of lead chromate in a 3.0×10^{-7} mol/L solution of lead nitrate?

PROBLEM 42

A redox titration was made from a sample of steel ore to determine the amount of Fe_2O_3. The titration used 0.500 g of ore in 100 mL of 0.5 M HCl to produce Fe^{2+}. The solution was titrated with 0.0592 M $KMnO_4$ which converted the Fe^{2+} to Fe^{3+} while MnO_4^- goes to Mn^{2+}. The sample of steel ore required 7.49 mL of titrant.

Report the percent of Fe_2O_3 contained in the ore sample.

PROBLEM 43

The most common ingredient in window cleaner is ammonia, often in high concentrations. For dilute ammonia samples, the amount of ammonia in a given window cleaner can be determined using a titration of the ammonia weak base with a strong acid. Suppose you have a 10.000 g sample of window cleaner containing ammonia which you first dilute with 90.012 g of water. You then take 5.000 g of solution and titrate it with 42.11 mL of 0.05042 M HCl to reach a bromocresol green end point.

Find the weight percent of NH_3 in the cleaner.

PROBLEM 44 - EXPERIMENTAL

Organic Qualitative Analysis

You are given five bottles containing five different organic compounds. Identify the class of each compound (saturated hydrocarbon, unsaturated hydrocarbon, 1° alcohol, 2° alcohol, 3° alcohol) using the tests listed below. You are not required to perform each test on each bottle.

Many of these compounds have distinctive odours. To prevent the lab from becoming too odorous, you must keep each bottle tightly capped and dispose of the waste materials in a safe manner.

One set of five unknowns
dilute Br_2/CCl_4 (or Br_2/H_2O)
Lucas reagent (conc. HCl + $ZnCl_2$)
ceric ammonium nitrate reagent
0.2% $KMnO_4$
acetone

test tube rack
5 small test tubes
grease pencil
aluminum foil
disposable pipets
hotplate
100 mL beaker

Standard Reagent Tests and Procedures

i) Ceric Ammonium Nitrate Test:
Place two drops of the ceric ammonium nitrate reagent into a small test tube. Add five drops of the compound to be tested. Observe and record any colour change. Dispose of the resulting solution in a waste bottle. Rinse the test tube once with acetone into the waste bottle.

ii) Potassium Permanganate Test:

Place 1 mL of acetone into a small test tube. Add one drop of the compound to be tested. Then add one drop of 0.2% $KMnO_4$ solution and shake the tube gently. Observe for two minutes and record any colour change. Dispose of resulting solution in a waste bottle. Rinse the test tube once with acetone into the waste bottle.

iii) Bromine Test:

Screen a test tube from light by using a piece of aluminum foil. Into it place a drop of the compound to be tested, add two drops of the bromine test solution and gently shake the test tube. Note any colour changes which occur within one minute.

iv) Lucas Test:

Prepare a hot water bath using the 100 mL beaker and your hotplate before starting this test. Place 25-30 drops of the Lucas reagent in a small test tube and add five drops of the compound to be tested. Do not shake the test tube. Look for turbidity at the interface between the two liquids which is an indication of a reaction. If there is no turbidity, shake the test tube and place it in the hot water bath. Record any changes which you observe within three minutes. (Note: Do not overheat; this can result in false observations.)

PROBLEM 45 - EXPERIMENTAL

Determination of Lead Ions by Back Titration with EDTA

In a solution buffered at pH 10, Eriochrome Black T (Black T) is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Lead ions are not bound by Black T. EDTA binds to Mg^{2+} and Pb^{2+} even in the presence of Black T. The stoichiometry of both EDTA-metal interactions is 1:1.

100 mL sample of lead solution
buffer solution, pH 10
Eriochrome Black T, indicator (Black T)
standard magnesium solution, (1.00 mg Mg^{2+}/mL solution)
ethylenediaminetetraacetic acid (EDTA) solution

i) Standardization of the EDTA solution:

Standardize the EDTA solution against a solution made of 10.00 mL of the standard magnesium solution, 40 mL of distilled water, 10 mL of buffer solution pH 10, and three drops of Black T indicator.

ii) Back Titration of Pb^{2+}:

Quantitatively transfer 10.00 mL of the lead ion solution to a 125 mL Erlenmeyer flask. Add 25.00 mL of the standardized EDTA solution, 15 mL of distilled water, 10 mL of buffer solution pH 10, and three drops of Black T indicator to the same flask. Titrate the excess EDTA with the standard magnesium solution.

Calculate the concentration of the EDTA solution in moles/liter.
Calculate the concentration of the lead ion solution in moles/liter.

PROBLEM 46 - EXPERIMENTAL

Electrochemistry

Six bottles numbered from 1 to 6 contain 1.0 M solutions of the following compounds: $CuSO_4$, $Zn(NO_3)_2$, $FeSO_4$, $Pb(C_2H_3O_2)_2$, $MnSO_4$, and $NiSO_4$. Six vials numbered from 11 to 16 contain small pieces of the following metals: Cu, Zn, Fe, Pb, Mn, and Ni. Using the contents of the bottles and vials and a table of standard reduction potentials, identify the contents of each bottle and vial. Write equations for all reactions.

PROBLEM 47 - EXPERIMENTAL

Determination of the K_{sp} of $CaSO_4$

ion exchange resin
glass wool
litmus paper
aluminum foil
disposable pipets
10 mL graduated cylinder
spatula
1.00 mL pipet

10 mL buret
2 x 50 mL Erlenmeyer flasks
phenolphthalein
saturated solution of $CaSO_4$
1 M HCl
standardized NaOH (ca. 0.01M)

Preparation

i) Assemble an ion-exchange column in one of the disposable pipets by placing a small plug of glass wool in the bottom of the pipet and packing the column with the provided resin.

ii) Charge the column by passing 5 mL of HCl through the column to load it with H^+. Remove the excess acid by rinsing with distilled water until the wash is neutral to litmus. Do not allow the liquid level to fall below the surface of the resin.

Procedure

i) Pipet 1 mL of saturated $CaSO_4$ solution directly onto the column. Collect the eluent off the column into an Erlenmeyer flask. Elute the column with five aliquots of distilled water into the Erlenmeyer flask. Check the pH of a drop of the eluent. If acidic, elute the column with another aliquot of water and test again. Repeat until the eluent is neutral.

ii) Titrate the contents of the flask with the standardized NaOH using phenolphthalein as the indicator.

Calculate the K_{sp} of $CaSO_4$.

PROBLEM 48 - EXPERIMENTAL

Ritter Reaction

benzonitrile
tert-butyl alcohol
concentrated H_2SO_4
ice

In a 5 mL Erlenmeyer flask, 0.50 mL of benzonitrile and 0.50 mL of tert-butyl alcohol are mixed thoroughly by swirling. The mixture is cooled in an ice-water bath to 0 ˚C and 0.50 mL of concentrated sulfuric acid is added carefully dropwise with swirling of the flask to ensure complete mixing. The reaction is removed from the cold bath and warmed at 40-50 ˚C for 30 minutes. At the end of this time the cloudy viscous mixture is transferred into a 25 mL beaker containing chipped ice and water. The white solid product that forms is isolated by vacuum filtration. The crude product is recrystallized from ethanol/water and isolated by vacuum filtration.

Write the equation for the reaction that occurred.
Report the mass of your product and its melting point.

PROBLEM 49 - EXPERIMENTAL

Sodium Borohydride Reduction

benzophenone
sodium borohydride
ethanol
hexane
ice
concentrated hydrochloric acid

Dissolve 0.9 g benzophenone in 10 mL of ethanol in a 50 mL Erlenmeyer flask. In a second 50 mL Erlenmeyer flask dissolve 0.2 g of sodium borohydride in 3 mL of cold water (hydrogen gas is given off from this solution). Add the aqueous solution of sodium borohydride to the benzophenone solution one drop at a time using a disposable pipet. Swirl the reaction mixture between each drop. After all of the sodium borohydride solution has been added, continue to stir the reaction mixture for 15 minutes or until the benzhydrol product begins to precipitate.

Decompose the excess sodium borohydride by adding the crystalline slurry slowly and with stirring to a mixture of 20 g crushed ice and about 2 mL of concentrated hydrochloric acid in a 100 mL beaker. Isolate the benzhydrol by vacuum filtration and wash it with two 10 mL portions of water. Recrystallize the product from hexane.

PROBLEM 50 - EXPERIMENTAL

Synthesis and Identification of an Organic Compound

An unknown compound **A** has the empirical formula $C_4H_2O_3$. It is possible to convert it into an acid, **B**, with the empirical formula $C_2H_3O_2$ using the procedure below. Synthesize **B**, determine its molar mass, and identify **A** and **B**.

standardized solution of NaOH (ca. 0.5 M)
phenolphthalein
zinc
concentrated HCl
unknown compound **A**

Add 3.0 g of 20 or 40 mesh zinc to a 125 mL flask and cover the zinc with 25 mL of deionized water. Heat the water to boiling. Remove the flask from the heat and carefully add a total of 5.0 g of **A** over a 5-10 minute period. Stir occasionally during the addition. Allow the flask to stand for five minutes, stir occasionally. In a hood and with constant stirring, slowly add 10 mL of concentrated HCl over a 10 minute period.

When all of the zinc has dissolved heat the solution until it is clear and then allow it to cool in an ice bath to produce white crystals.

Suction filter the cold solution to obtain product **B** which can be recrystallized from water. Dry and weigh the crystals.

Titrate product **B** with the standardized sodium hydroxide provided.

Complete the following table:

Yield **B**, g ______
mL NaOH / g **B** ______
Molecular weight **B** ______

Structure of **B**:

Structure of **A**: