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
	simple molecular structures with central atom	
19	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

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

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
HALOGEN COMPOUNDS		
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

CARBOXYLIC ACIDS

131	inductive effect and strength	2
132	equivalence of oxygen atoms in anions	2
133	preparation: from esters	2
134	- from nitriles	2
135	products of reaction with alcohols (esters)	1
136	mechanism of esterification	2
137	isotopes in mechanism elucidation	3
138	nomenclature : acid halides	2
139	preparation of acid chlorides	2
140	amides from acid chlorides	2
141	nitriles from acid chlorides	3
142	properties and preparation of anhydrides	2
143	oxalic acid: name and formula	1
144	multifunctional acids	2
145	optical activity (e.g. lactic acid)	2
146	R/S nomenclature	3
147	plant vs. animal fats - differences	2

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149	comparing aliphatic vs. aromatic	2
150	names: primary, secondary, tertiary, quaternary	2
151	identification of primary/secondary/tertiary/quaternary amines in laboratory	3
	preparation of amines	
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153	- from nitro compounds ($PhNH_2$ from $PhNO_2$)	3
154	- from amides (Hoffmann)	3
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156	basicity amines vs. amides	2
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157	- of aliphatic amines	3
158	- of aromatic amines	3
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160	nitro compounds : aci/nitro tautomerism	3
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163	micelle structure	3
164	preparation of soaps	1
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165	- styrene	2
166	- ethene	1

167	- polyamides	3
168	- phenol + aldehydes	3
169	- polyurethanes	3
170	polymers - cross-linking	3
171	- structures (isotactic etc.)	3
172	- chain mechanism of formation	2
173	rubber composition	3

BIOCHEMISTRY

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175	isoelectric point	2
176	20 amino acids (classification in groups)	2
177	20 amino acids (all structures)	3
178	ninhydrin reaction (including equation)	3
179	separation by chromatography	3
180	separation by electrophoresis	3
181	peptide linkage	1

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183	-S-S- bridges	3
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185	secondary structures	3
186	details of alpha-helix structure	3
187	tertiary structure	3
188	denaturation by change of pH, temperature, metals, ethanol	2
189	quaternary structure	3
190	separation of proteins (molecule size and solubility)	3
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

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198	trival names of most important (ca. 5) fatty acids	2
199	general metabolism of fats	3
200	beta-oxidation of fatty acids (formulas & ATP balance)	3
201	fatty acids and fats anabolism	3
202	phosphoglycerides	3
203	membranes	3
204	active transport	3

ENZYMES

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CARBOHYDRATES

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208	- Fischer projections	2
209	- Haworth formulas	3

210	osazones	3
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213	difference between alpha- and beta-D glucose	2
214	metabolism from starch to acetyl-CoA	3
215	pathway to lactic acid or to ethanol; catabolism of glucose	3
216	ATP balance for this pathways	3
217	photosynthesis (products only)	2
218	light and dark reaction	3
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221	intermediate compounds in the cycle	3
222	formation of water and ATP (no details)	3
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226	nucleosides, nucleotides	3
227	formulas of all pyrimidine and purine bases	3
228	difference between ribose and 2-deoxyribose	3
229	base combination CG and AT	3
230	- CG and AT - (hydrogen bonding structures)	3
231	difference between DNA and RNA	3
232	difference between mRNA and tRNA	3
233	hydrolysis of nucleic acids	3
234	semiconservative replication of DNA	3
235	DNA-ligase	3
236	RNA synthesis (transcription) without details	3
237	reverse transcriptase	3
238	use of genetic code	3
239	start and stop codons	3
240	translation steps	3

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242	hormone feedback	3
243	insulin, glucagon, adrenaline	3
244	mineral metabolism (no details)	3
245	ions in blood	3
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247	haemoglobin: function & skeleton	3
248	- diagram of oxygen absorption	3
249	steps of clotting the blood	3
250	antigens and antibodies	3
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254	identification of chromophore	3

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256	- fragments with a help of a table	3
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258	interpretation using a table of group frequencies	3
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260	Raman spectroscopy	3
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261	interpret. of simple spectrum (like ethanol)	3
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265	^{13}C-NMR	3
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271	structures of CsCl	3
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276	- relative concentration	1
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281	Bronsted-Lowry theory, conjugated acids & bases	1
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283	ionic product of water	1
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285	hydrolysis of salts	1
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288	calculation of pH for weak acid from K_a	1
289	calculation of pH for 10^{-7} mol/dm^3 HCl	2
290	calculation of pH for multiprotic acids	2
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292	definition of ionic strength	3
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296	standard electrode potential	1
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300	factors influencing reaction rate	1
301	rate equation	1
302	rate constant	1
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305	- half life	2
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307	rate-determining step	2
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311	calculation of rate constant for second, third order reaction	3
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319	heat capacity - definition	2
320	difference between C_p and C_v	3
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328	entropy and disorder	2
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332	ideal gas law	1
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335	temperature dependence of the vapour pressure of liquid	2
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350	basic principles of chromatography	2

OTHER PROBLEMS

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352	using buret	1
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
359	- of VO_3^-, ClO_3^-, Ti^{4+} ions	3
360	- using flame test for K, Ca, Sr	1
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362	writing down complexation reactions	1
363	complex formation constants (definition)	2
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
366	cis and trans forms	3

THEORETICAL CHEMISTRY

367	n, l, m quantum numbers	2
368	energy levels of hydrogen atom (formula)	2
369	shape of p-orbitals	2
370	d orbital stereoconfiguration	3
371	molecular orbital diagram: H_2 molecule	3
372	molecular orbital diagram: N_2 or O_2 molecule	3
373	bond orders in O_2 or O_2^+ or O_2^-	3
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377	unpaired electrons and paramagnetism	2
378	square of the wave function and probability	3
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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° it gives a well-defined first-order diffraction pattern. The atomic weight of Au is $M_{Au} = 196.97$ 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 $c_{CuSO_4} = 0.100$ mM and $c_{Na_2SO_4} = 0.100$ 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 $0.010\text{ M }\text{Cu}^{2+}$ 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 $M_{\text{CuCl}_2} = 134.45\text{ g mol}^{-1}$. 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 $0.100\text{ M }\text{Cu}^{2+}$ solution and a Zn plate immersed in $100\,\text{cm}^3$ of $0.100\text{ M }\text{Zn}^{2+}$ 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) + $(\text{CH}_3)_2\text{SO}_2$, 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.

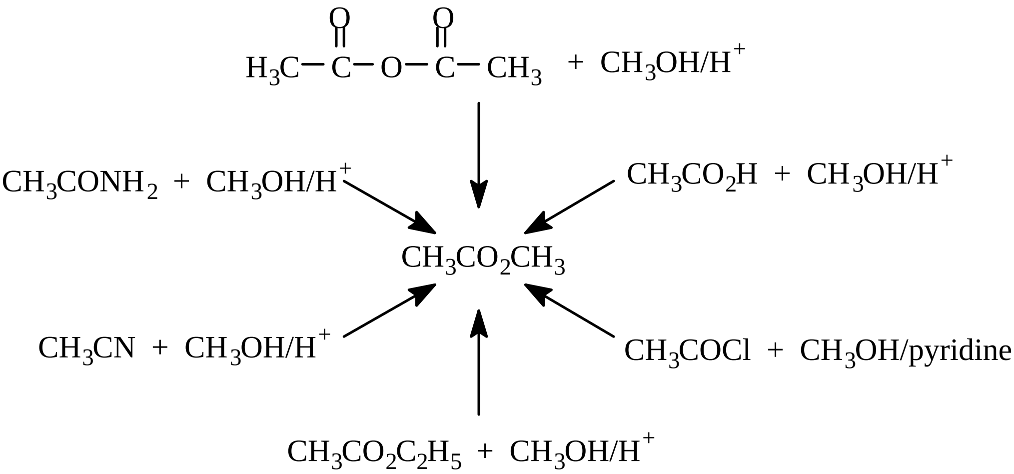
PROBLEM 10

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.

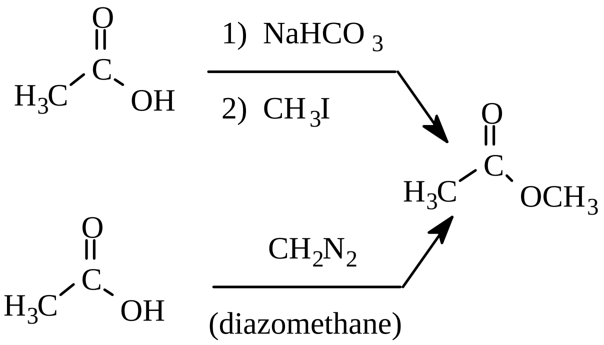
Give structures for **A, B, C** and **D**.

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.

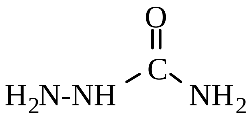


However, other synthetic variations are also known. Two mechanistically closely related reactions are shown below. Outline the mechanisms of these latter two processes.

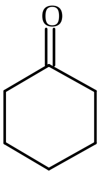


PROBLEM 12

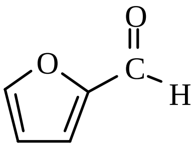
When 1 mol of semicarbazide (**A**) is added to 1 mol of cyclohexanone (**B**) and 1 mol of furfural (**C**) in ethanol with a trace of acid, a mixture of semicarbazones (**D** and **E**) is obtained. If the reaction is stopped after 5 minutes, the mixture contains mainly the semicarbazone **D**. However, 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.



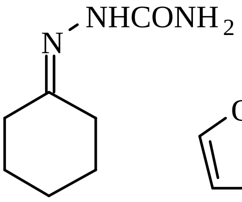
A



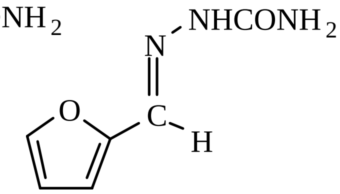
B



C



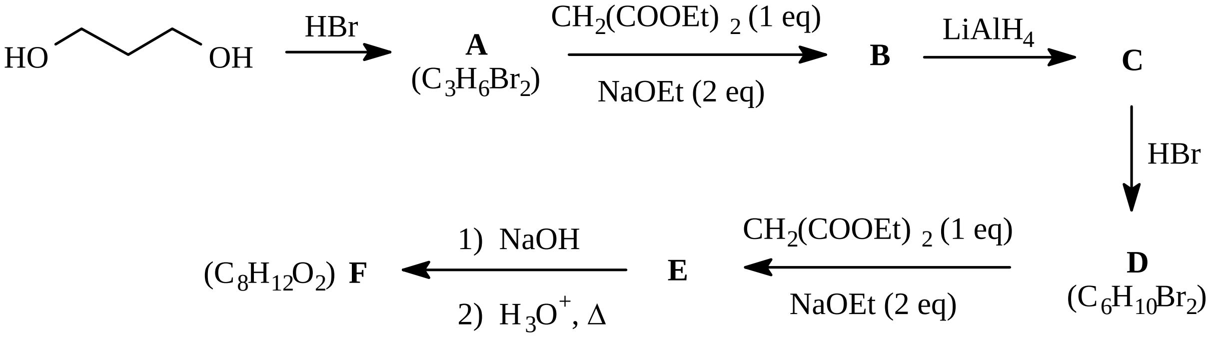
D



E

PROBLEM 13

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



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?

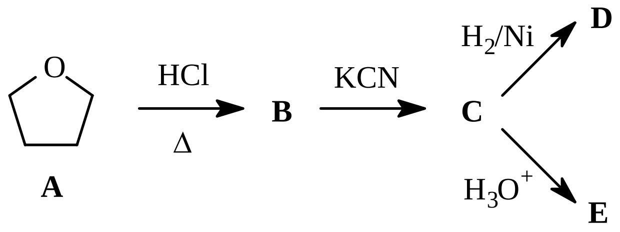
b) How many double bonds does α-terpinene possess?

c) How many rings does α-terpinene possess?

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

PROBLEM 15

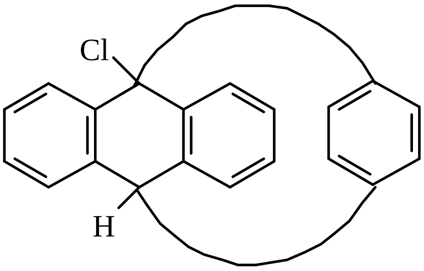
Two useful precursors (**D** and **E**) for the synthesis of a type of Nylon® are prepared from tetrahydrofuran (**A**).



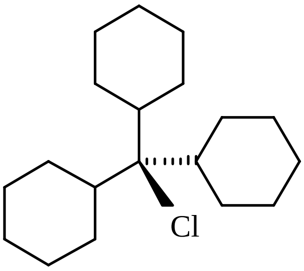
Give the reaction mechanisms for this synthetic sequence and the structure of the compounds **B - E**.

PROBLEM 16

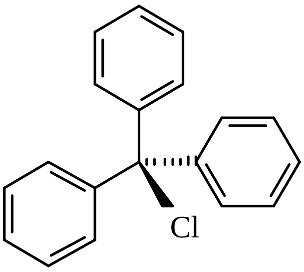
Arrange the following compounds in order of increasing reactivity towards aqueous $AgNO_3$. Explain your reasoning.



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.

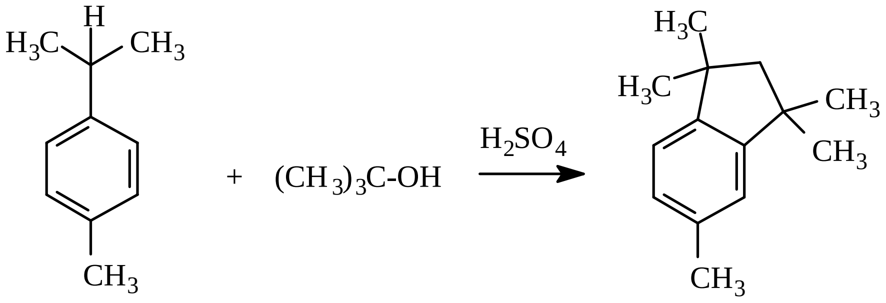
Which of the two systems, sodium ethoxide or 60% aqueous ethanol, would give the higher yield of alkene?

PROBLEM 18

The reaction shown below is interesting from a mechanistic standpoint.

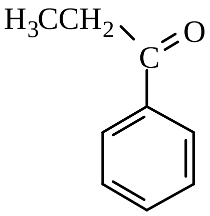
a) Suggest how this reaction takes place by writing the sequence of steps involved.

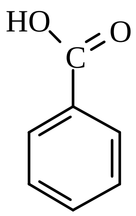
b) What products would you expect if you replaced the starting material with 1,4-dimethylbenzene?

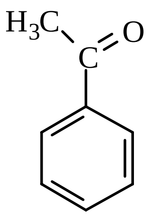


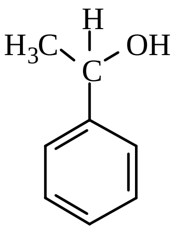
PROBLEM 19

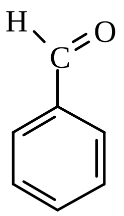
The compounds shown below were in five unlabelled bottles. A set of simple qualitative functional group tests were carried out on the contents of five bottles. Based on the following experimental observations, assign the correct letters to the structures shown.











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 milliliters 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.

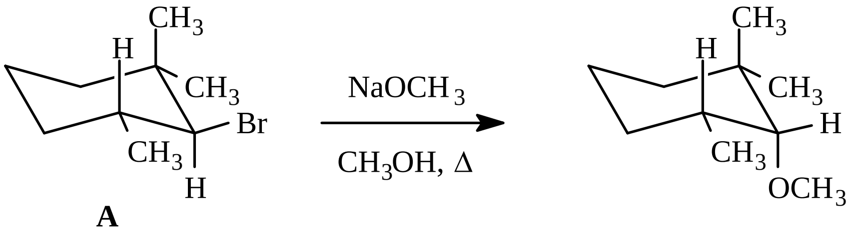
b) When enantiomerically pure (S)-2-butanol is treated with a strong base such as $LiNH_2$ and then recovered, it retains its optical activity. However, when (S)-2-butanol is treated with warm water in the presence of a small amount of sulfuric acid, it is found that the recovered alcohol has lost its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

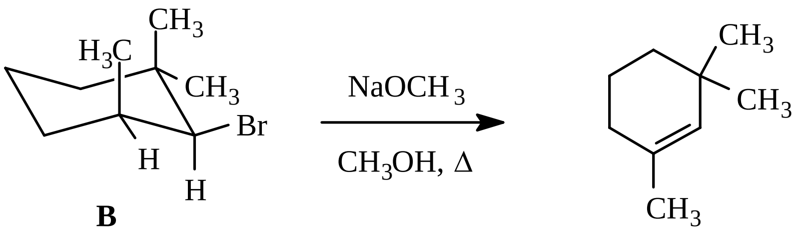
d) (S)-2-Butanol was produced when (R)-2-bromobutane was refluxed in a concentrated NaOH solution of aqueous ethanol.

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.



[1]



[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.

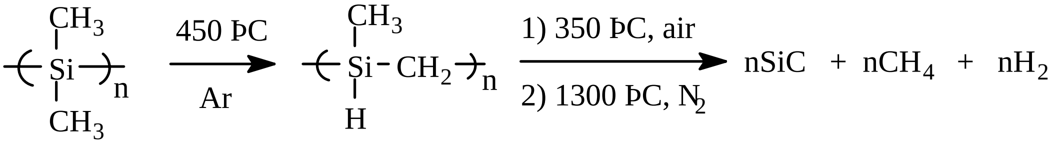
The usual commercial method for the manufacture of SiC, known as the Acheson process, involves high-temperature solid-state reactions of silica (fine grade sand) with graphite or coke in an electrical furnace. Carbon monoxide is also produced during this reaction. The silicon carbide obtained by this 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.

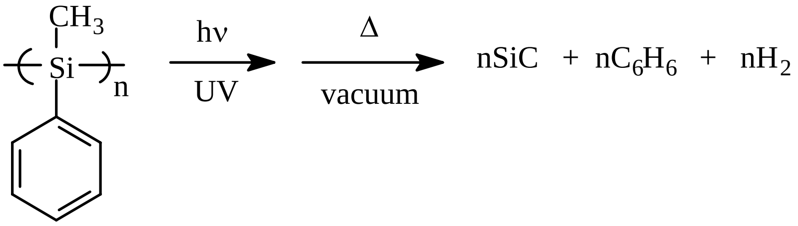
Yajima Process:



$$-\!\!\left(\overset{CH_3}{\underset{CH_3}{Si}}\right)\!\!-_n \xrightarrow[\text{Ar}]{450\ °C} -\!\!\left(\overset{CH_3}{\underset{H}{Si}}-CH_2\right)\!\!-_n \xrightarrow[\text{2) 1300 °C, } N_2]{\text{1) 350 °C, air}} nSiC + nCH_4 + nH_2$$

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.

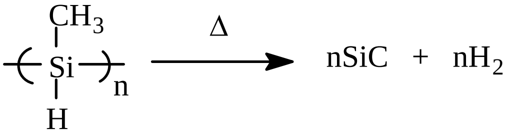
West Process:



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:



$$\left(\overset{CH_3}{\underset{H}{Si}}\right)_n \xrightarrow{\Delta} nSiC + nH_2$$

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 cm^{-3} and that of diamond is 3.51 g 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:

$$[(NH_3)_4Cl_2Cr]Cl$$

$$[py_3Cl_3Co]; \text{ where py = pyridine}$$

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

$$[(Me_3P)_3ClPt]Br; \text{ where Me} = CH_3$$

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 $[O_2]>>[O_3]$ the rate law has the form:

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

However, if $[O_2] << [O_3]$, 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 → 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^-.

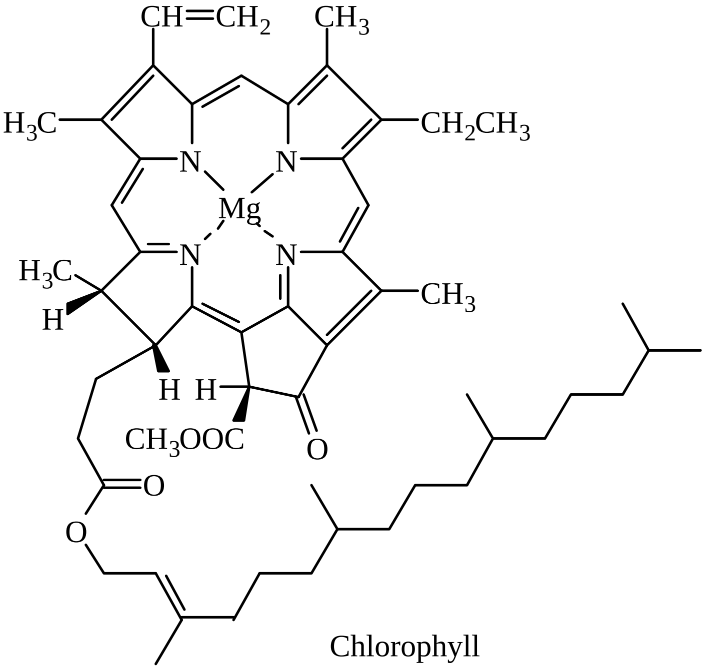
c) Which species in (b) are expected to have the same stability?

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^+.

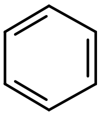
PROBLEM 37

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

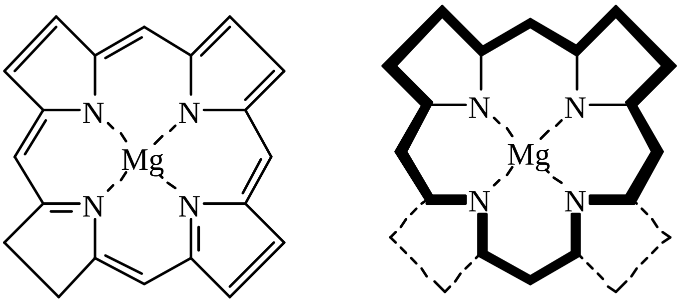


Chlorophyll

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



chlorophyll core

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

$$E_n = \frac{\hbar^2 l^2}{2mr^2} \qquad l = 0, \pm 1, \pm 2, \pm 3\ldots$$

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 2.5×10^{-5} mol/L in solutions with different concentrations of R. The absorbance data (1 cm cell) were obtained as follows:

Conc. R (mol/L) $\times 10^{-5}$	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 x 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 x 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**:

SOLUTION 1

a) Bragg law, $n\,\lambda = 2\,a\,\sin\theta$, allows one to determine the lattice constant of Au according to the following:

$$a = \frac{n\,\lambda}{2\sin\theta} = \frac{1 \times 154.05 \times 10^{-12}}{2\sin(10.89^{\circ})}$$

$$a = 4.077 \times 10^{-10}\ \text{m} = 4.077 \times 10^{-8}\ \text{cm}$$

The volume of the crystallographic unit (unit cell) of Au equals:

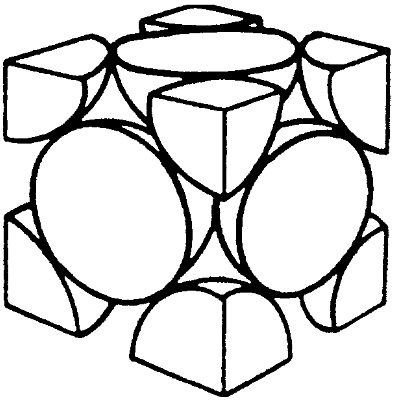
$$V_u = a^3 = \left(4.077 \times 10^{-10}\right)^3 = 6.777 \times 10^{-29}\ \text{m}^3 = 6.777 \times 10^{-23}\ \text{cm}^3$$

The number of crystallographic units of Au within $1.000\ \text{cm}^3$ equals:

$$N = \frac{1.000}{6.777 \times 10^{-23}} = 1.476 \times 10^{22}$$

Each crystallographic cell has four atoms, $n_u = 4$. The corner atoms belong to eight unit cells, thus $1/8$ of each corner atom belongs to the cell; the face atoms belong to two unit cells, thus $1/2$ of each face atom belongs to the cell.

$$n_u = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$



Face-centered cubic crystal structure

The number of Au atoms in the $1.000\,\mathrm{cm}^3$ cube equals:

$$N_{Au} = N \times n_u = 1.476 \times 10^{22} \times 4 = 5.904 \times 10^{22}$$

b) The weight of one Au atom (m_{Au}) equals:

$$m_{Au} = \frac{M_{Au}}{N_A} = \frac{196.97}{6.002214 \times 10^{23}} = 3.271 \times 10^{-22}\ \mathrm{g}$$

The mass of the unit cell equals:

$$M_u = n_u\, m_{Au} = 4 \times 3.271 \times 10^{-22} = 1.308 \times 10^{-21}\ \mathrm{g}$$

c) The density of Au, thus the weight of the $1.000\,\mathrm{cm}^3$ cube, equals the number of unit cells within $1.000\,\mathrm{cm}^3$ times the mass of the cell:

$$d_{Au} = N\, M_u = 1.476 \times 10^{22} \times 1.308 \times 10^{-21} = 19.31\ \mathrm{g\,cm^{-3}}$$

SOLUTION 2

i) Determination of the number of Au atoms within the $1.000\,\mathrm{cm}$ long square having the (100) surface structure.

The area of the Au(100) surface unit equals:

$$A_u = a_{Au}^2 = \left(4.077 \times 10^{-8}\ \mathrm{cm}\right)^2 = 1.662 \times 10^{-15}\ \mathrm{cm}^2$$

There are two Au atoms per surface unit cell; the atoms in the corners belong to four unit cells, thus $1/4$ of each corner atom belongs to the (100) surface unit cell, and the atom in the middle of the cell belongs to the cell.

$$n_u = 4 \times \frac{1}{4} + 1 = 2$$

The number of Au atoms (the surface atom concentration) within $1.000\,\mathrm{cm}^2$ of the Au(100) surface equals:

$$\sigma_{\mathrm{Au(100)}} = \frac{n_u}{A_u} = \frac{2}{1.662 \times 10^{-15}} = 1.203 \times 10^{15}\ \mathrm{cm}^{-2}$$

ii) Determination of the number of Cu atoms in the epitaxial layer.

In the case of the epitaxial deposition (growth), the Au(100) substrate acts as a template and the Cu layer has the same structure as the substrate. Thus the number of Cu atoms within one monolayer equals 1.203×10^{15} and the number of Cu atoms within the Cu epitaxial deposit (layer) equals:

$$N_{\mathrm{Cu}} = 100 \times 1.203 \times 10^{15} = 1.203 \times 10^{17}$$

The number of moles of Cu within the epitaxial layer equals:

$$n_{\mathrm{Cu}} = \frac{N_{\mathrm{Cu}}}{N_A} = \frac{1.203 \times 10^{17}}{6.02214 \times 10^{23}} = 1.999 \times 10^{-7}\ \mathrm{mol}$$

iii) Determination of the number of moles of $CuSO_4$ in the electrolyte after deposition of the epitaxial layer.

The number of moles of $CuSO_4$ in the electrolyte after the deposition equals the initial number of moles of $CuSO_4$ minus the number of moles of Cu deposited on the Au(100) substrate.

$$n_{\mathrm{Cu}} = 1.000 \times 10^{-4} \times 10.000 \times 10^{-3} - 1.999 \times 10^{-7} = 8.001 \times 10^{-7}\ \mathrm{mol}$$

iv) Determination of the concentration of $CuSO_4$ in the electrolyte after deposition of the Cu epitaxial layer

$$c_{\mathrm{CuSO_4}} = \frac{8.001 \times 10^{-7}}{10.000 \times 10^{-3}} = 0.0800\ \mathrm{mM}$$

SOLUTION 3

a) Determination of the spontaneous direction of the reaction.

Oxidation process (process 1): $Zn \rightarrow Zn^{2+} + 2\,e$

Reduction process (process 2): $2\,H^+ + \frac{1}{2}O_2 + 2\,e \rightarrow H_2O$

The reduction potentials for the two above processes are: $E_1^o = -0.762\ V$ and $E_2^o = 1.229\ V$. The standard potential of the overall process (the concentrations of Zn^{2+} and H^+ equal unity) is:

$$E^o = E_2^o - E_1^o = 1.991\ V.$$

The Gibbs free energy, ΔG^o, of the process equals:

$$\Delta G^o = -\,n\,F\,E^o = -\,3.842 \times 10^5\ J\ mol^{-1}$$

Because ΔG^o is negative, Zn undergoes spontaneous dissolution.

b) During the dissolution of Zn the concentration of Zn^{2+} increases and that of H^+ decreases. The process ceases when the concentrations of Zn^{2+} and H^+ reach such values that the newly established potential of the process, E, as established through the Nernst equation, equals zero.

$$E = E^o - \frac{R\,T}{n\,F}\ln\frac{c_{Zn^{2+}}}{c_{H^+}^2}$$

$E = 0.000\ V$ when $\frac{R\,T}{n\,F}\ln\frac{c_{Zn^{2+}}}{c_{H^+}^2} = 1.991$ or when $\ln\frac{c_{Zn^{2+}}}{c_{H^+}^2} = 155.0$. The latter relation gives after rearrangement the following ratio: $\frac{c_{Zn^{2+}}}{c_{H^+}^2} = 2.068 \times 10^{67}$.

Based upon the above ratio, one may evaluate the concentrations of Zn^{2+} and H^+ when the process ceases. The concentration of H^+ decreases twice as fast as the concentration of Zn^{2+} increases. Thus the new concentration of Zn^{2+} and H^+ can be described through the following equations:

$$c_{Zn^{2+}} = 1.000 + \Delta c_{Zn^{2+}}$$

$$c_{H^+} = 1.000 - \Delta c_{H^+}$$

where $\Delta c_{Zn^{2+}}$ is the increase of the concentration of Zn^{2+} caused by Zn dissolution and Δc_{H^+} is the decrease of the concentration of H^+. Bearing in mind that $\Delta c_{Zn^{2+}} = 2\Delta c_{H^+}$, one may rewrite the above equations as follows:

$$c_{Zn^{2+}} = 1.000 + \Delta c_{Zn^{2+}}$$

$$c_{H^+} = 1.000 - 2\ \Delta c_{Zn^{2+}}$$

Substituting these two formulae into $\frac{c_{Zn^{2+}}}{c^2_{H^+}} = 2.068 \times 10^{67}$, one gets the following relation:

$$\frac{1 + \Delta c_{Zn^{2+}}}{\left(1 - 2\ \Delta c_{Zn^{2+}}\right)^2} = 2.068 \times 10^{67}$$

which leads to the following quadratic equation (for simplicity we introduce the following coefficient $a = 2.068 \times 10^{67}$):

$$1 + \Delta c_{Zn^{2+}} = a\left(1 - 4\ \Delta c_{Zn^{2+}} + 4\ \Delta c^2_{Zn^{2+}}\right)$$

or

$$4\ a\ \Delta c^2_{Zn^{2+}} - (4\ a + 1)\,\Delta c_{Zn^{2+}} + a - 1 = 0$$

Bearing in mind the very large value of a ($a = 2.068 \times 10^{67}$), thus remembering that $4\,a + 1 \cong 4\,a$ and that $a - 1 \cong a$, one may rewrite the above equation as follows:

$$4\,a\ \Delta c^2_{Zn^{2+}} - 4\ a\ \Delta c_{Zn^{2+}} + a = 0$$

A solution of this quadratic equation leads to the following value of the increase of concentration of Zn^{2+}: $\Delta c_{Zn^{2+}} = 0.500\ \text{M}$. The respective concentrations of Zn^{2+} and H^+ when the dissolution of Zn ceases are $c_{Zn^{2+}} = 1.500\ \text{M}$ and $c_{H^+} = 0.000\ \text{M}$. Thus the dissolution of Zn ceases when all HCl is consumed in the process.

SOLUTION 4

The respective half-reactions and corresponding reduction potentials are:

$$\mathrm{Ni^{2+} + 2\,e \rightarrow Ni} \qquad E^{o}_{\mathrm{Ni^{2+}/Ni}} = -\,0.257\ \mathrm{V}$$

$$\mathrm{Cu^{2+} + 2\,e \rightarrow Cu} \qquad E^{o}_{\mathrm{Cu^{2+}/Cu}} = 0.342\ \mathrm{V}$$

Thus the above cell may be represented by the following scheme:

$\mathrm{Ni\,|\,Ni^{2+}\,(c_{Ni^{2+}})\,||\,(c_{Cu^{2+}})\,Cu^{2+}\,|\,Cu}$ where || represents the salt bridge.

The standard potential of the cells is $E^{o} = 0.599\ \mathrm{V}$.

The cell potential, E, prior to addition of $\mathrm{CuCl_2}$ is expressed by the Nernst equation:

$$E = E^{o} - \frac{R\,T}{2\,F}\ln\frac{c_{\mathrm{Ni^{2+}}}}{c_{\mathrm{Cu^{2+}}}}$$

After the $\mathrm{CuCl_2}$ addition, the new potential of the cell, E', is expressed by the following formula:

$$E' = E^{o} - \frac{R\,T}{2\,F}\ln\frac{c_{\mathrm{Ni^{2+}}}}{c'_{\mathrm{Cu^{2+}}}}$$

where $c'_{\mathrm{Cu^{2+}}}$ is the new concentration of $\mathrm{Cu^{2+}}$. The potential increase, $\Delta E = E' - E$, associated with the $\mathrm{CuCl_2}$ addition may be determined on the basis of the above relations:

$$\Delta E = E' - E = \frac{R\,T}{2\,F}\ln\frac{c'_{\mathrm{Cu^{2+}}}}{c_{\mathrm{Cu^{2+}}}}$$

Thus, it is not necessary to know the $\mathrm{Ni^{2+}}$ concentration in order to relate the change of the cell potential with the addition of $\mathrm{CuCl_2}$.

The above relation allows one to determine the new concentration of $\mathrm{Cu^{2+}}$:

$$c'_{Cu^{2+}} = c_{Cu^{2+}} \exp\left(\frac{2\,\Delta E\,F}{R\,T}\right) = 0.020\ M$$

The concentration change upon addition of $CuCl_2$ equals $\Delta c_{Cu^{2+}} = 0.010\ M$ and the respective number of moles of $CuCl_2$ added to the solution is $1.00 \times 10^{-3}\ mol$.

Finally, one may evaluate the mass of $CuCl_2$ added which is:

$$m_{CuCl_2} = n_{CuCl_2} \times M_{CuCl_2} = 1.344\ g\,.$$

SOLUTION 5

a) The respective half-reactions and corresponding reduction potentials are:

$$Zn^{2+} + 2\,e \;\rightarrow\; Zn \qquad E^{o}_{Zn^{2+}/Zn} = -\,0.762\ V$$
$$Cu^{2+} + 2\,e \;\rightarrow\; Cu \qquad E^{o}_{Cu^{2+}/Cu} = 0.342\ V$$

Cu has a higher value of the reduction potential than Zn, thus Zn is the anode whereas Cu is the cathode. The above cell may be represented by the following scheme:

$Zn\,|\,Zn^{2+}\ (c_{Zn^{2+}})\,||\,(c_{Cu^{2+}})\ Cu^{2+}\,|\,Cu$ where || represents the salt bridge.

The standard potential of the cell is $E^{o} = 1.104\ V$.

The cell potential, E, prior to the galvanostatic discharge is expressed by the Nernst equation:

$$E = E^{o} - \frac{R\,T}{2\,F} \ln \frac{c_{Zn^{2+}}}{c_{Cu^{2+}}}$$

Because the concentrations of the cations are the same in both compartments, the cell potential equals the standard one, thus $E = 1.104\ V$.

Galvanostatic discharge of the cell results in cathodic deposition of Cu and in anodic dissolution of Zn causing the concentrations of the cations in the respective compartments to change. The total charge of the galvanostatic discharge of the cell equals:

$$Q = I \times t = 1.00 \times 10^{-2} \times 10^{5} = 1000 \text{ C}$$

The amount of the deposited Cu and that of the dissolved Zn are determined on the basis of the Faraday law or on the basis of the reasoning presented below. The number of moles of the deposited Cu, n_{Cu}, and of the dissolved Zn, n_{Zn}, equals:

$$n_{Cu} = n_{Zn} = \frac{Q}{2\text{ e } N_A} = \frac{1000}{2\text{ e } N_A} = 5.18 \times 10^{-3} \text{ mol}$$

The numbers of moles of Cu^{2+} and Zn^{2+} in the respective compartments after the galvanostatic discharge are:

$$n'_{Cu^{2+}} = 1.00 \times 10^{-2} - 5.18 \times 10^{-3} = 4.82 \times 10^{-3} \text{ mol}$$

$$n'_{Zn^{2+}} = 1.00 \times 10^{-2} + 5.18 \times 10^{-3} = 1.518 \times 10^{-2} \text{ mol}$$

The molar concentrations of Cu^{2+} and Zn^{2+} in the respective compartments of the cell after the discharge are:

$$c'_{Cu^{2+}} = 4.82 \times 10^{-2} \text{ M}$$

$$c'_{Zn^{2+}} = 1.518 \times 10^{-1} \text{ M}$$

b) The cell potential, E', after the galvanostatic discharge is expressed by the formula:

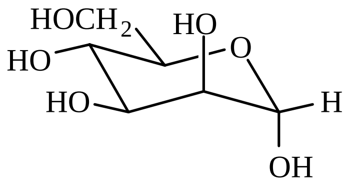
$$E' = E^{o} - \frac{R\,T}{2\,F} \ln \frac{c'_{Zn^{2+}}}{c'_{Cu^{2+}}} = 1.104 - \frac{R \times 298.15}{2\,F} \ln \frac{0.1518}{0.0482} = 1.089 \text{ V}$$

Finally, the potential change cased by the discharge of the cell equals:

$$\Delta E = E' - E = -0.015 \text{ V}$$

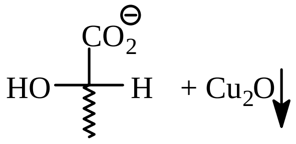
SOLUTION 6

The structure of α-D-(+)-mannopyranose is:

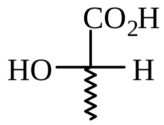


The reaction products are:

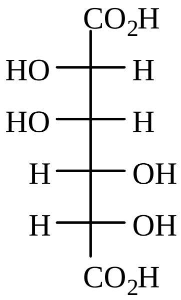
a)



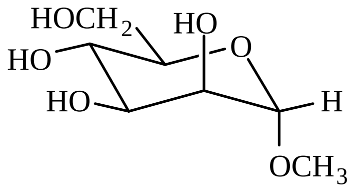
b)



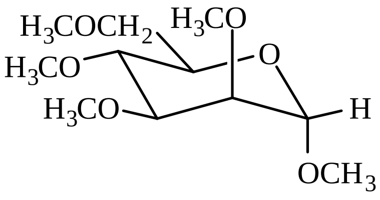
c)



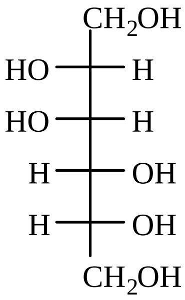
d)



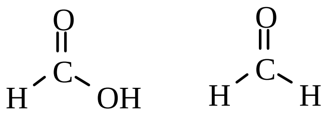
e)



f)

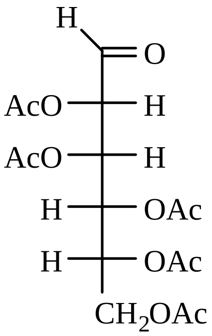


g)

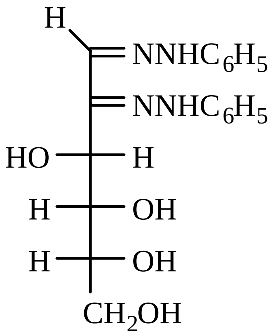


5 equiv 1 equiv

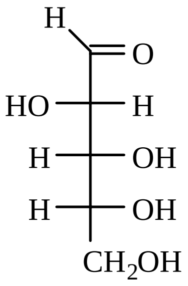
h)



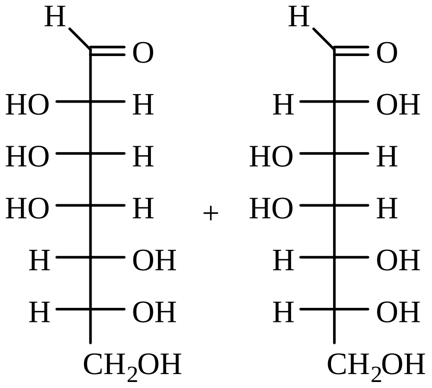
i)



j)

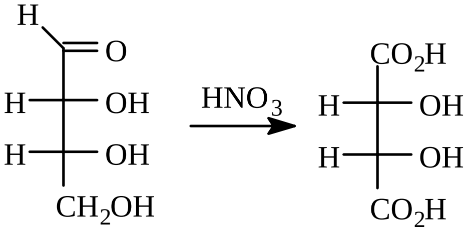


k)



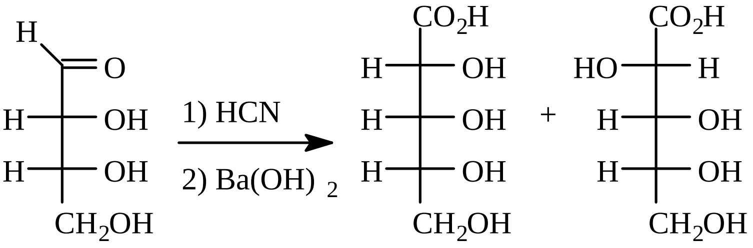
SOLUTION 7

The only D-aldotetrose which will give an inactive product when oxidized with nitric acid is:



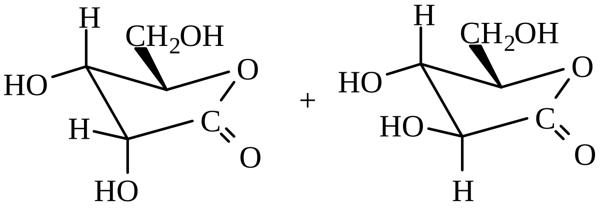
A

A gives **B** and **C** when treated with HCN followed by aqueous Ba(OH)$_2$



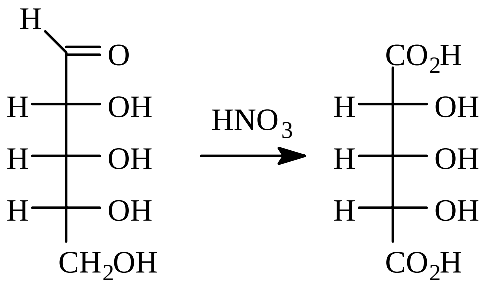
A **B** **C**

Their respective γ-aldonolactones **D** and **E** are:

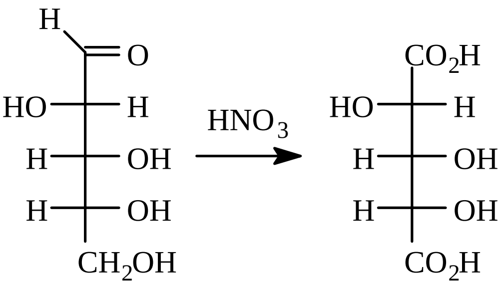


D **E**

The equilibrium mixture above when treated with Na-Hg and water at pH = 3-5 produces **F** and **G** which when oxidized by nitric acid gives an inactive aldaric acid **H** and an optically active aldaric acid **I**:



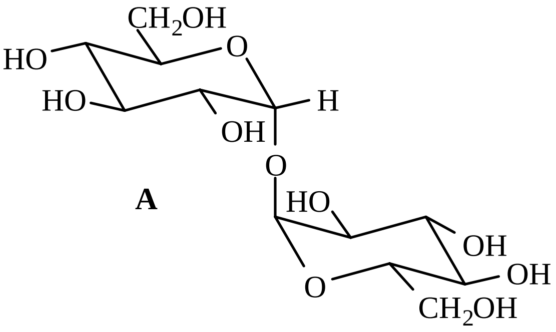
F **H**



G **I**

SOLUTION 8

Compound **A** is a non-reducing sugar with an α-linkage at the anomeric carbon. Since **A** gives only 2,3,4,6 methylated glucoses on hydrolysis the only possible structure for **A** is to have the two glucose molecules dimerize via their respective anomeric carbons:

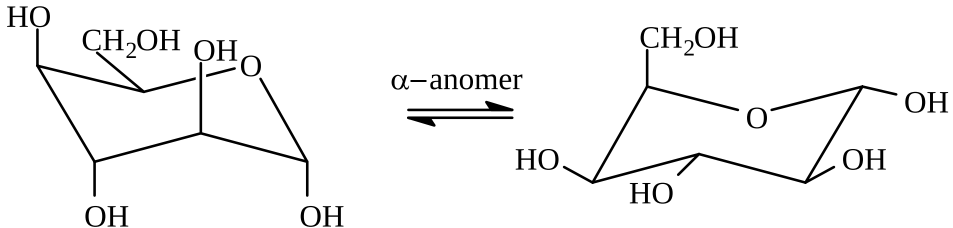


A

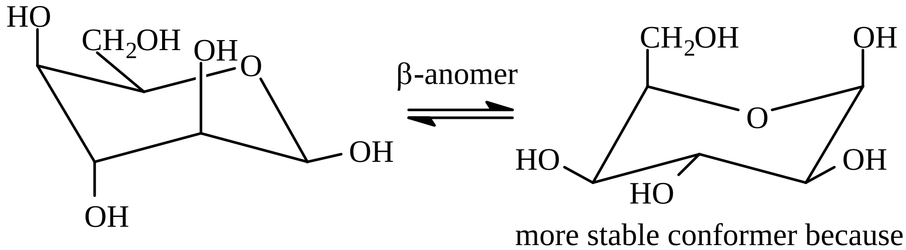
10 moles of HI are needed for the complete cleavage of **A** giving 10 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde).

SOLUTION 9

a) Below are the two chair conformations for the two anomers of D-idose:

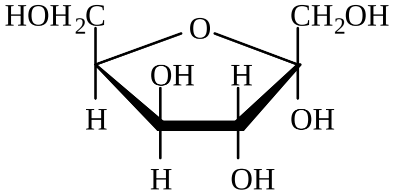


more stable conformer because more equatorial substituents

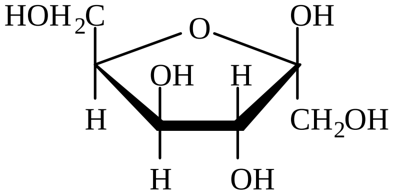


more stable conformer because more equatorial substituents

b) The two furanose forms of D-sorbose are shown below.

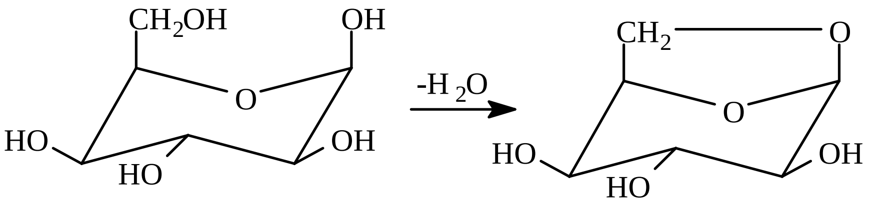


α-anomer

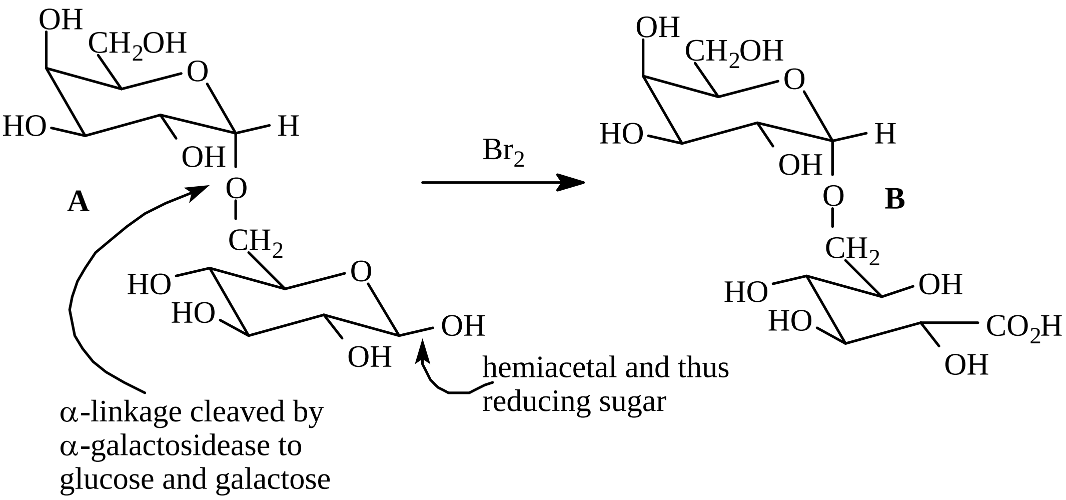


β-anomer

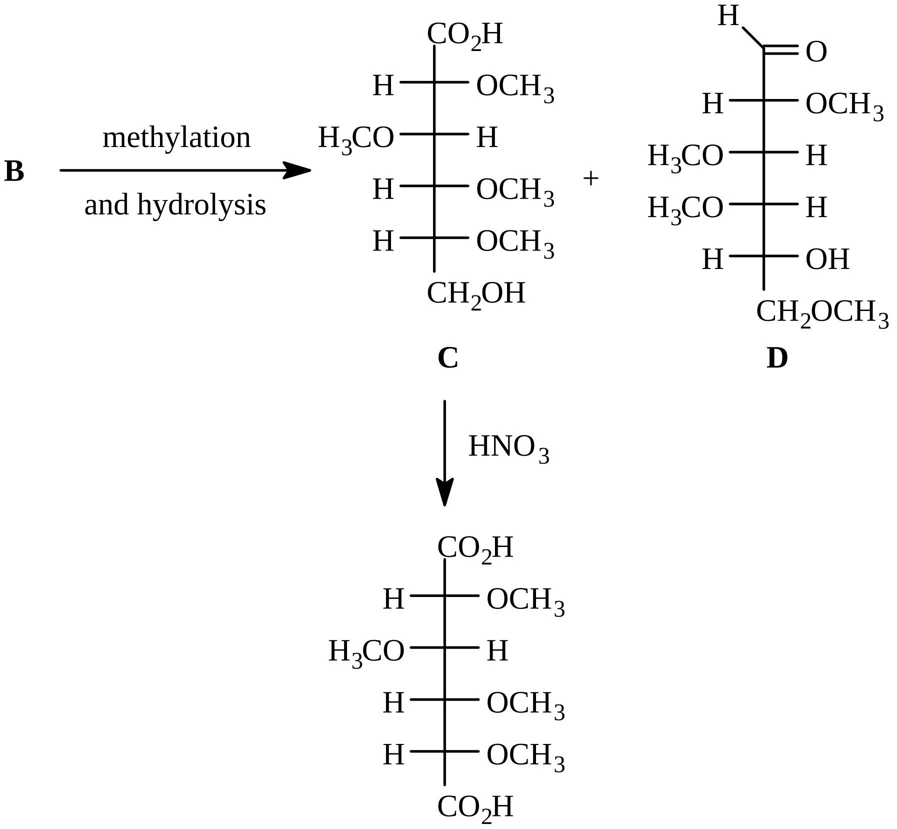
c) The indicated conformer of the β-anomer can cyclize internally to form the anhydro-derivative. Glucose cannot undergo this reaction because it requires the C-6 substituent to be axial, and this conformation is too unstable for the glucose molecule.



SOLUTION 10

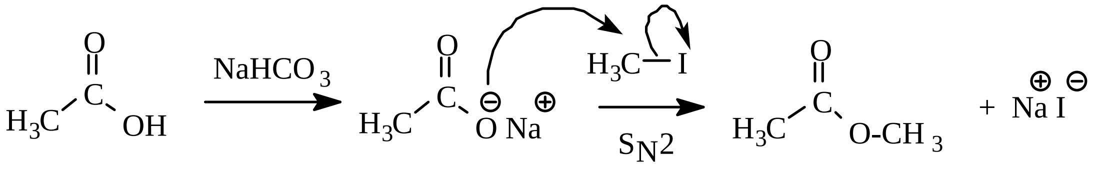


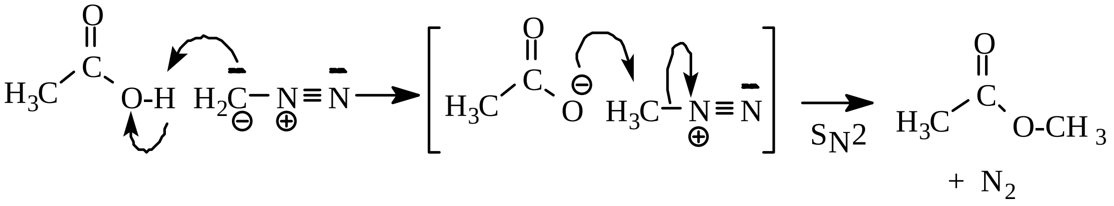
Melibiose **A** is 6-O- α-D-galactopyranosyl-D-glucopyranose

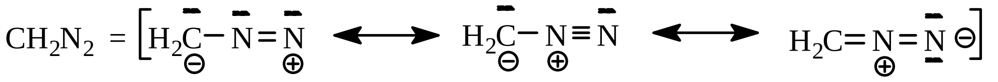


SOLUTION 11

Both reactions involve converting the carboxylic acid into the more nucleophilic carboxylate salt which then reacts in an S_N2 displacement reaction to form the ester. In the former case, iodide anion is the leaving group and in the latter example the carboxylate (formed by initial proton transfer to diazomethane) displaces N_2.

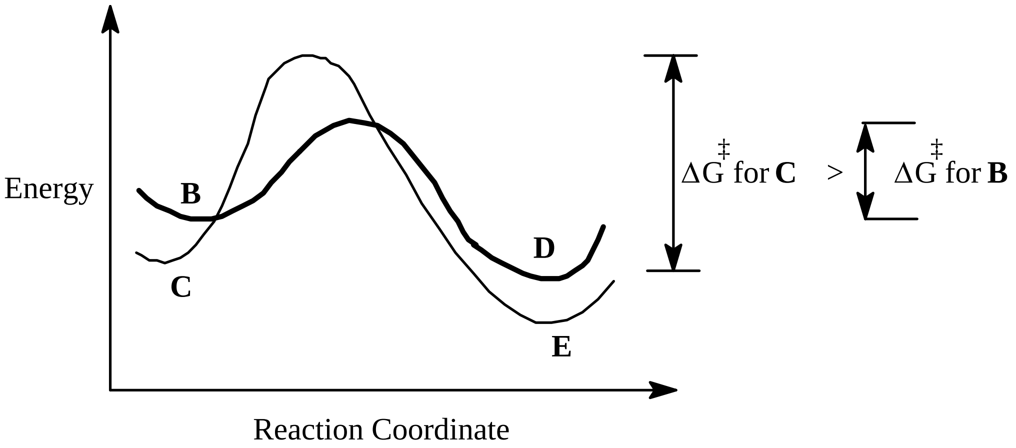




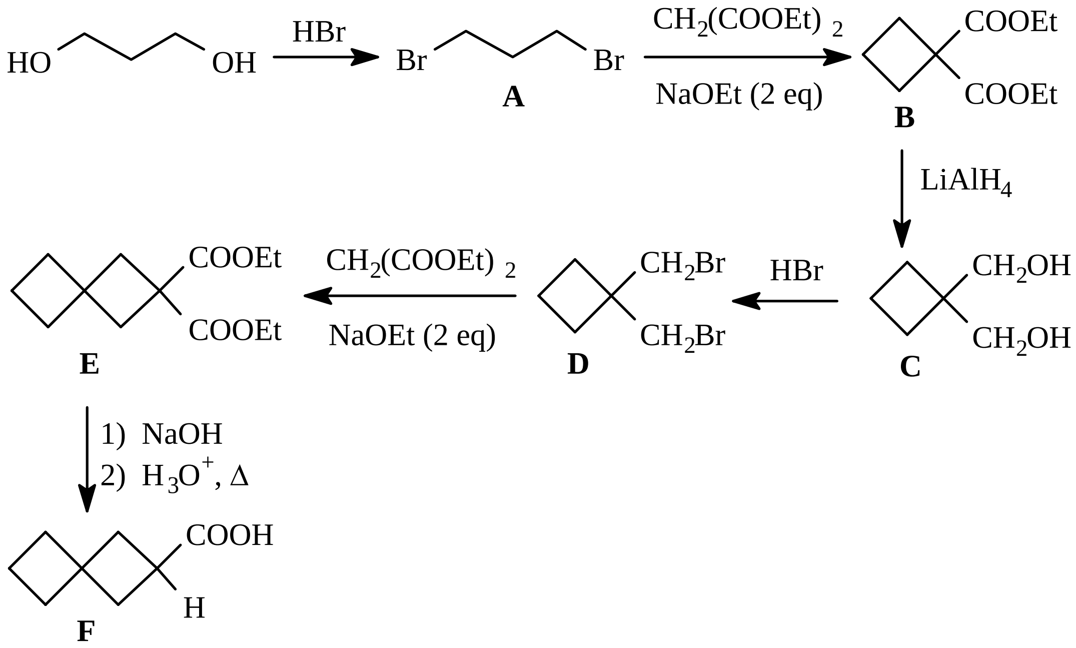


SOLUTION 12

The carbonyl group of cyclohexanone is more reactive (electrophilic) than the one of furfural since the latter is stabilized by conjugation with the aromatic ring. Therefore, if the reaction is quenched after a short period of time, the major product obtained is the one formed the most rapidly, i.e. the kinetic controlled product **D**. However, the reaction is in equilibrium and after enough time, the major compound formed is the most thermodynamically stable product, the semicarbazone **E**. The situation is illustrated by the following energy diagram.



SOLUTION 13



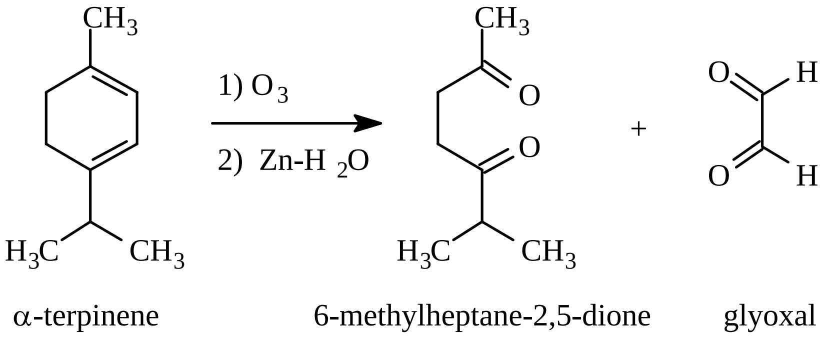
SOLUTION 14

a) From the formula, the number of unsaturations can be determined: For a saturated hydrocarbon there should be (10 x 2) + 2 = 22 hydrogens. Therefore (22-16)/2 H per unsaturation implies that 3 unsaturations are present.

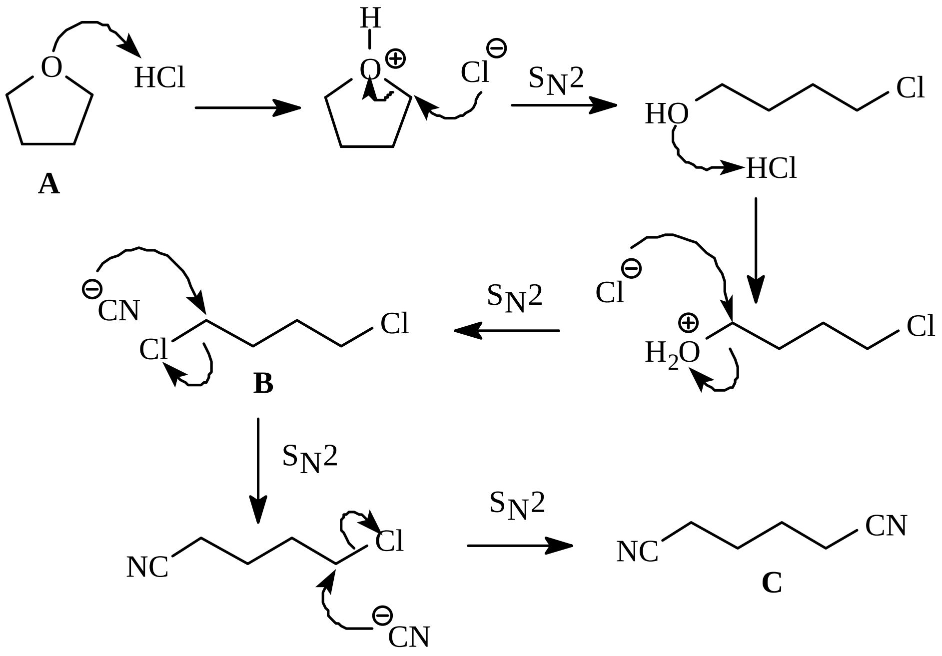
b) The hydrogenation product still contains one site of unsaturation and thus there must have been two double bonds present which underwent reduction.

c) The hydrogenation product still contains one site of unsaturation and thus there must be one ring present which did not undergo reduction.

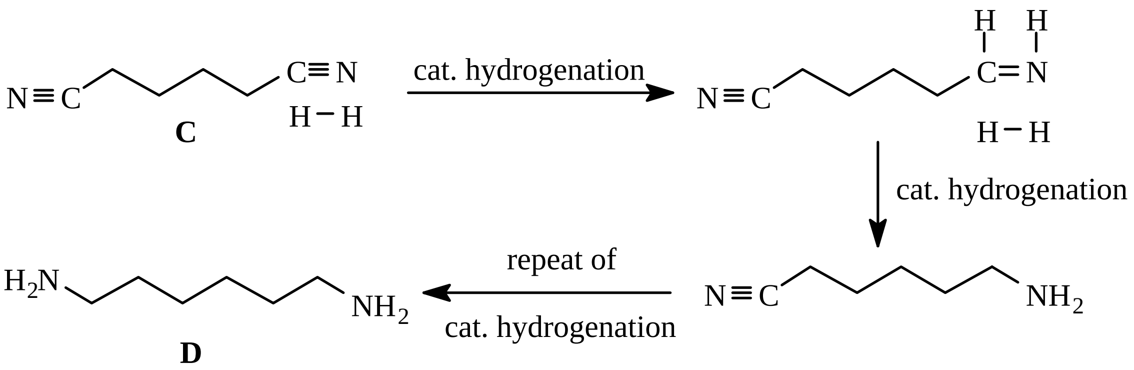
d)



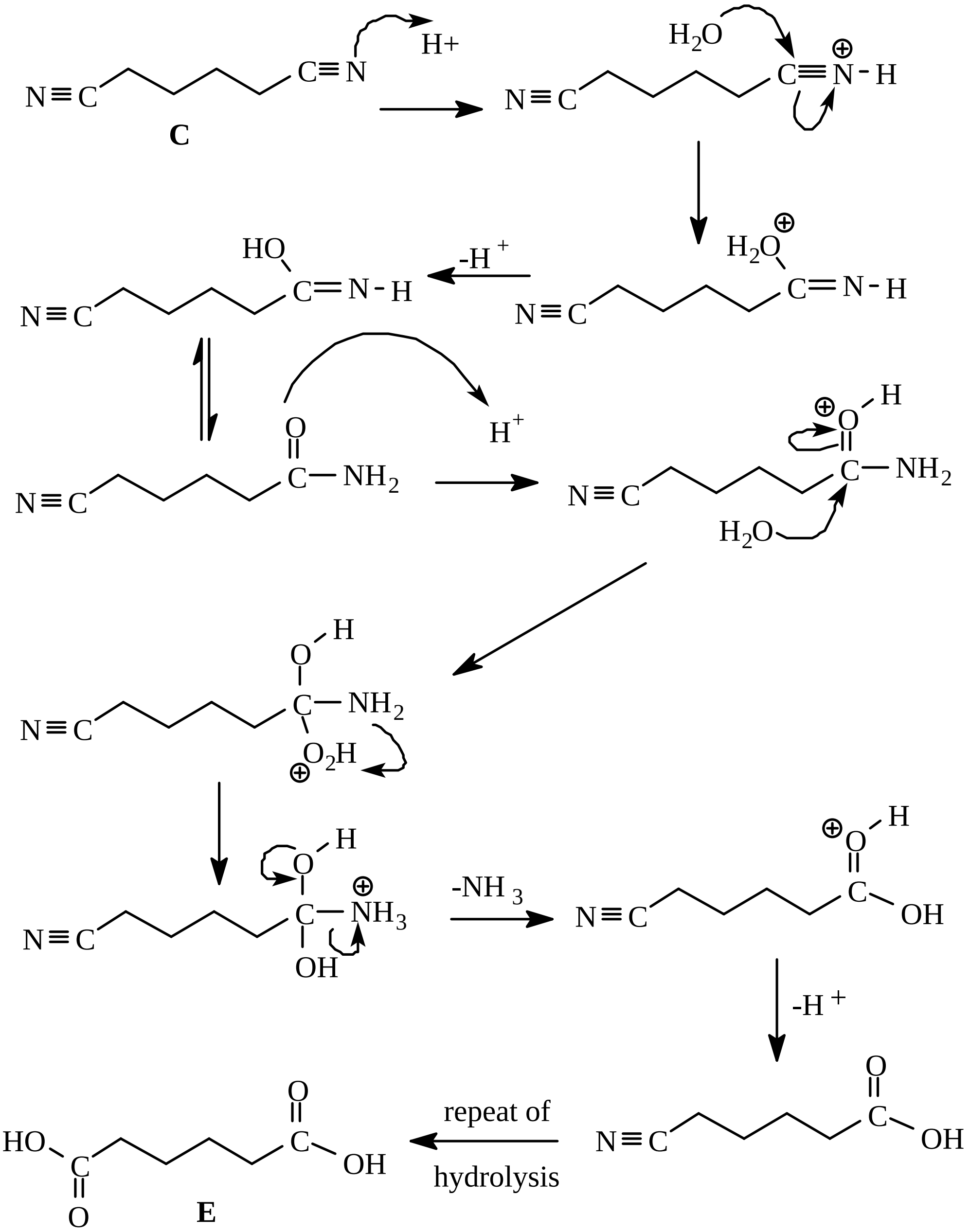
SOLUTION 15



Nitrile reduction converts nitrile groups into amino groups:



Nitrile hydrolysis converts nitrile groups into carboxylic acid groups:



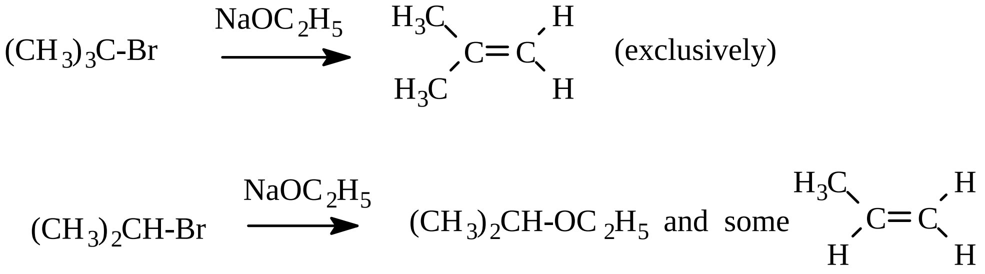
SOLUTION 16

The reaction of chlorohydrocarbons with an aqueous solution of $AgNO_3$ leads to the corresponding alcohols by means of an S_N1 mechanism. Since the rate limiting step in S_N1 reactions is the formation of the carbocation, the compound that generates the most stable cation will react more rapidly. Compound **A** is the least reactive since the carbocation cannot be planar due to its bridge nature. Also the carbocation cannot be stabilized by resonance because delocalization introduces too much strain into the system.

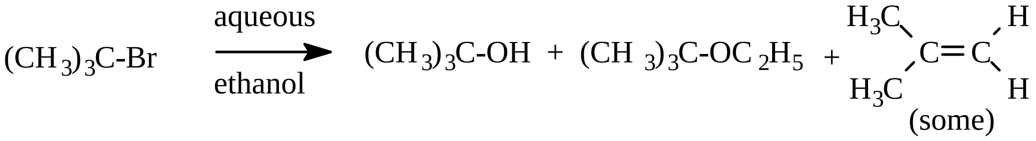
Compound **C** is the most reactive. Its carbocation is tertiary, can adopt a planar structure, and is stabilized by resonance involving the three aromatic substituents. Compound **B** has a reactivity intermediate between those of **A** and **C**.

SOLUTION 17

Sodium ethoxide: 2-methyl-2-bromopropane yields more alkene



Aqueous 60% ethanol: 2-methyl-2-bromopropane still yields more alkene

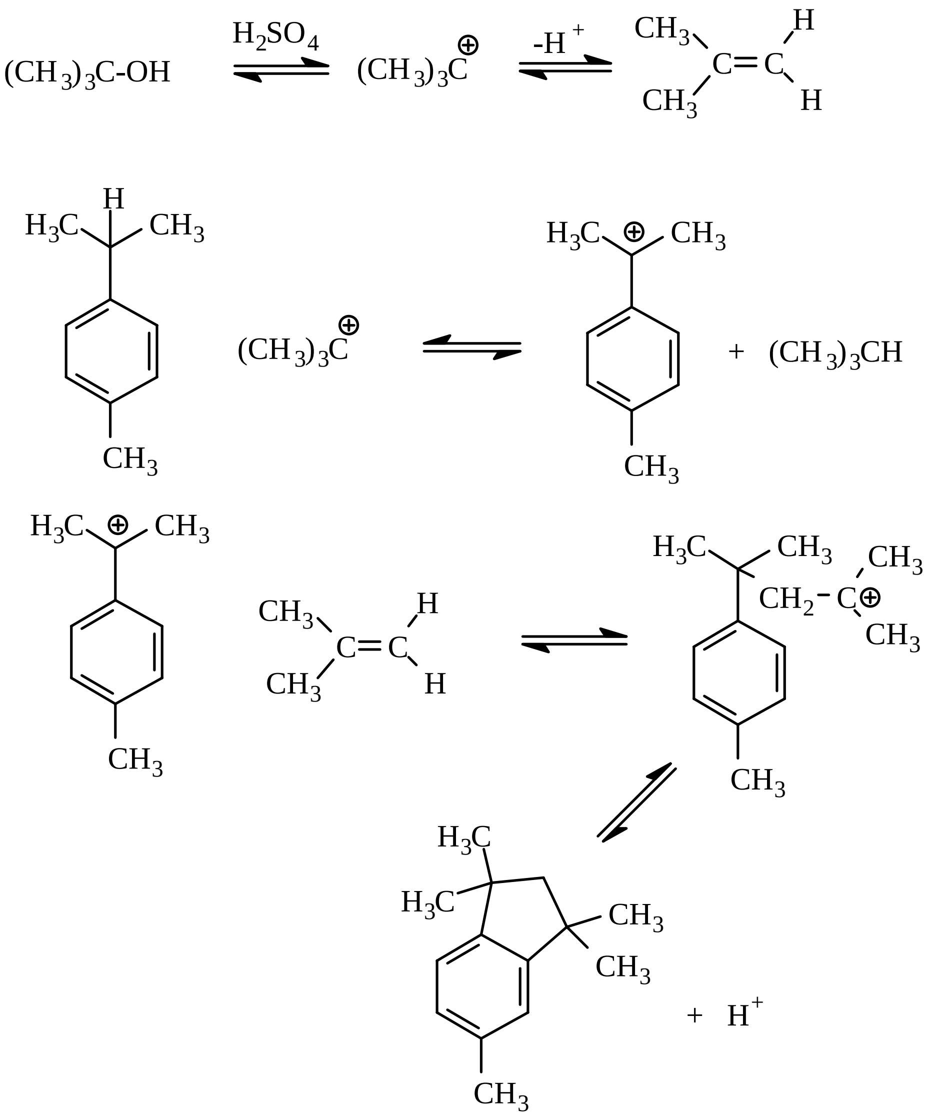


$$(CH_3)_2CH\text{-}Br \xrightarrow[\text{ethanol}]{\text{aqueous}} (CH_3)_2CH\text{-}OH + (CH_3)_2CH\text{-}OC_2H_5$$

The stronger the base, the higher the percentage of elimination and thus more elimination occurs in sodium ethoxide. Elimination is also favoured over substitution on tertiary halides since the double bond formed is more stable and the substitution site is more sterically hindered than in secondary halides. In the case of aqueous ethanol, a mixture of alcohol and ether are obtained since both water and ethanol can compete as nucleophiles.

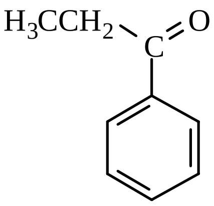
SOLUTION 18

a) In the first step, the tert-butyl alcohol is converted to the corresponding carbocation. The latter can lose a proton to yield 2-methylpropene or can abstract a hydride ion from the isopropyl group of the starting material. This reaction is feasible because the new carbocation generated is more stable that the tert-butylcarbocation since it is also tertiary and furthermore is stabilized by resonance with the aromatic ring. The new carbocation can react with the electron-rich 2-methylpropene to yield yet another carbocationic intermediate which can perform an intramolecular electrophilic substitution on the aromatic ring to give the final product.



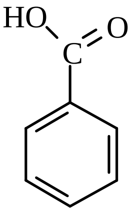
b) With 1,4-dimethylbenzene, only the 2,5-dimethyl-tert-butylbenzene would be obtained via a normal electrophilic substitution since the abstraction of a hydride ion from a methyl group is unfavourable.

SOLUTION 19



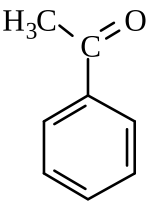
1

D



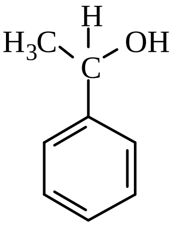
2

B



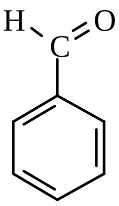
3

E



4

A



5

C

i) Chromate oxidation will identify readily oxidizable groups such as alcohols and aldehydes and thus 4 and 5 must be **A** and **C** (although which is which cannot be determined yet).

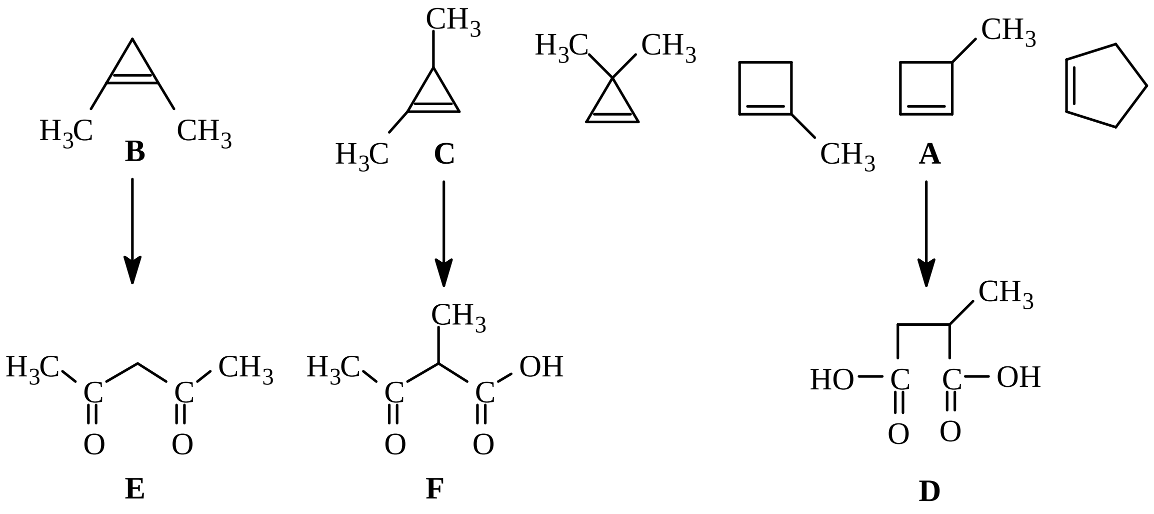
ii) Permanganate oxidation will also identify readily oxidizable groups such as alcohols and aldehydes in addition to alkenes (absent in this case). This test merely confirms the tentative assignment of part (i).

iii) Solubility in base and a positive litmus test implies an acidic group. The only acidic system is the carboxylic acid 2 and thus this must be **B**.

iv) The iodoform test will be positive for methyl ketones and for secondary methyl alcohols (which are oxidized to methyl ketones by the reagent) and thus 3 and 4 must be **A** and **E**. Since from (i) and (ii) above we know that 4 and 5 must be **A** and **C**, it follows that 5 is **C**, 4 is **A** and thus 3 must be **E**. At this point only 1 is unassigned and thus must be **D**.

v) The 2,4-dinitrophenylhydrazine is a test for aldehydes and ketones. Only 1, 3 and 5 will react which serves to confirm the above carbonyl group assignments.

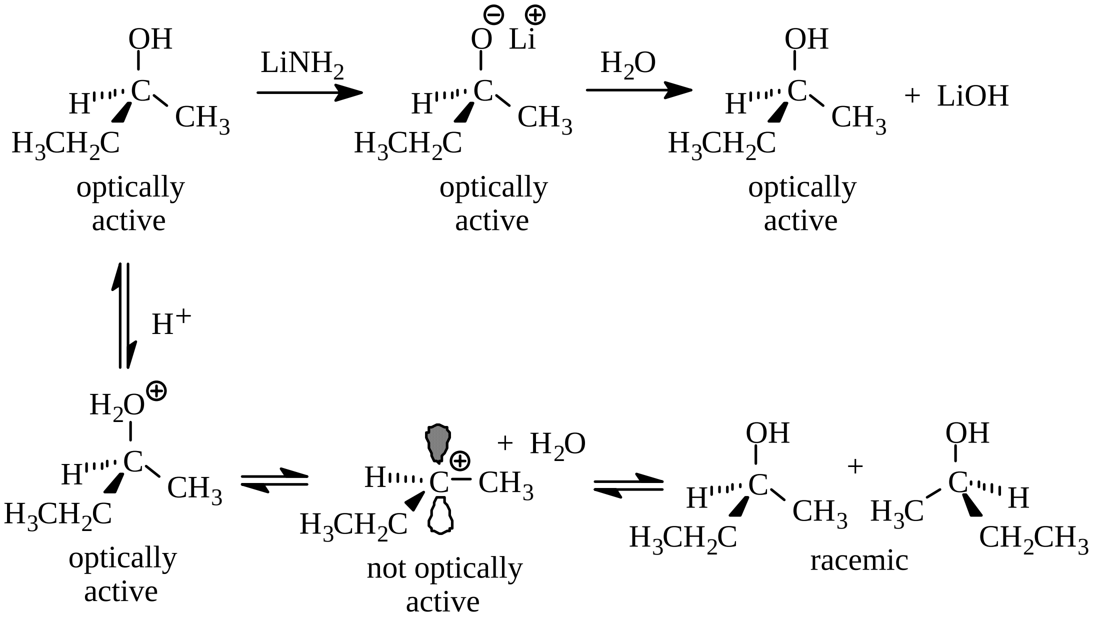
SOLUTION 20



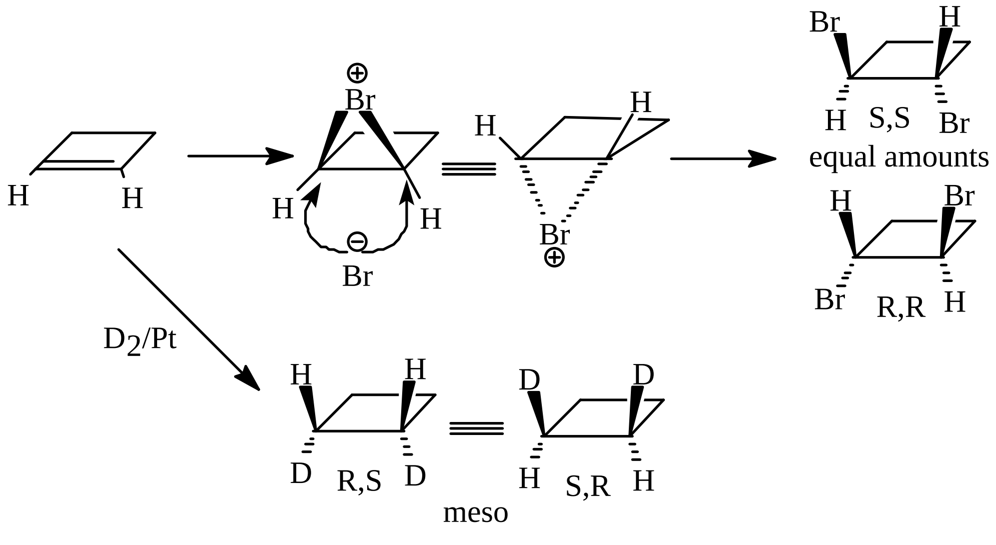
SOLUTION 21

a) Both reactions are S_N2 displacements at primary carbon atoms. The S_N2 reaction is primarily controlled by steric interactions. 1-Bromo-2-methylbutane is branched at the β-position which hinders the attack of the thiolate nucleophile, whereas the 1-bromobutane is relatively open to the displacement and thus reacts more rapidly.

b) The first reaction involves deprotonation/protonation and effects only the O-H bond and not the configuration of the chiral centre. Thus there is no loss of optical activity. The second reaction involves the C-O bond of the chiral centre and proceeds via the formation of a carbocation which is a planar species. Addition of water to the carbocation may occur equally from either side leading to formation of racemic recovered alcohol and thus loss of optical activity.



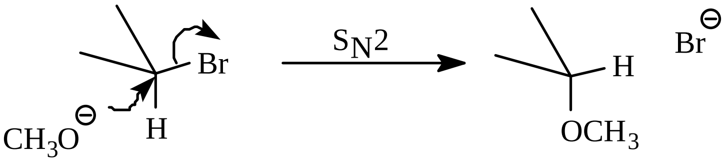
c) Bromine addition follows an anti process to lead to a trans product. The initial bromonium ion can be formed equally on the top or bottom face of the cyclobutene to form the identical species. Opening of this intermediate at either end of the former double bond by the bromide ion leads an equal mixture of the (R,R)- and (S,S)- products, i.e. a racemate, which is optically inactive. Hydrogen addition (involving any of the isotopes) follows a syn process to lead to a cis product. The addition may again take place with equal ease from the top or the bottom face of the cyclobutene but this time both products are the identical meso compound. The product is also optically inactive.



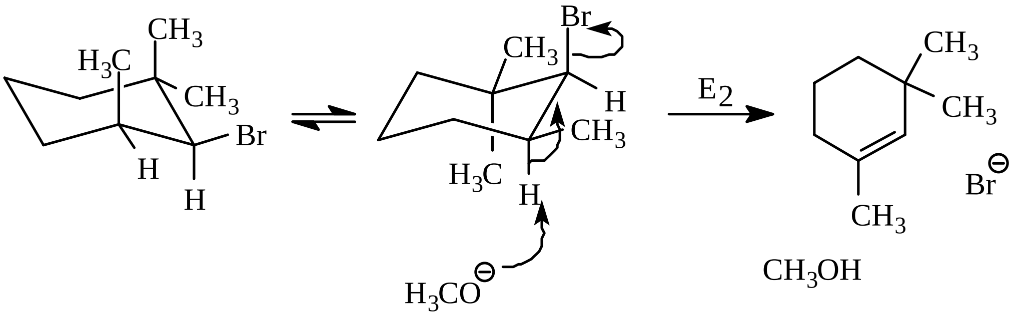
d) High concentration of the nucleophile (HO^-) favours the S_N2 reaction which proceeds with 100% inversion of configuration at the displaced centre.

e) Low concentration of the nucleophile (HO^-) favours the S_N1 process which proceeds via a carbocation. This planar intermediate can be trapped by the solvent or the nucleophile from either side leading to racemization. Under a given set of conditions, the rate of an S_N1 reaction is directly dependent only on the concentration of the alkyl halide. Thus doubling the alkyl halide concentration will double the rate of formation of the alcohol. Doubling the concentration of the nucleophile (HO^-) will have no effect on the rate of the reaction.

f) Reaction [1] is an S_N2 reaction in which the nucleophile (CH_3O^-) displaces the bromide anion with inversion of configuration. Elimination is not possible because the bromine and the lone hydrogen on the adjacent carbon atom cannot assume the necessary anti-periplanar conformation; i.e. both cannot be axial.
Reaction [2] is an E_2 elimination process which occurs readily because a “ring flip” of the conformer shown will produce the anti-periplanar arrangement of the hydrogen and the bromine.

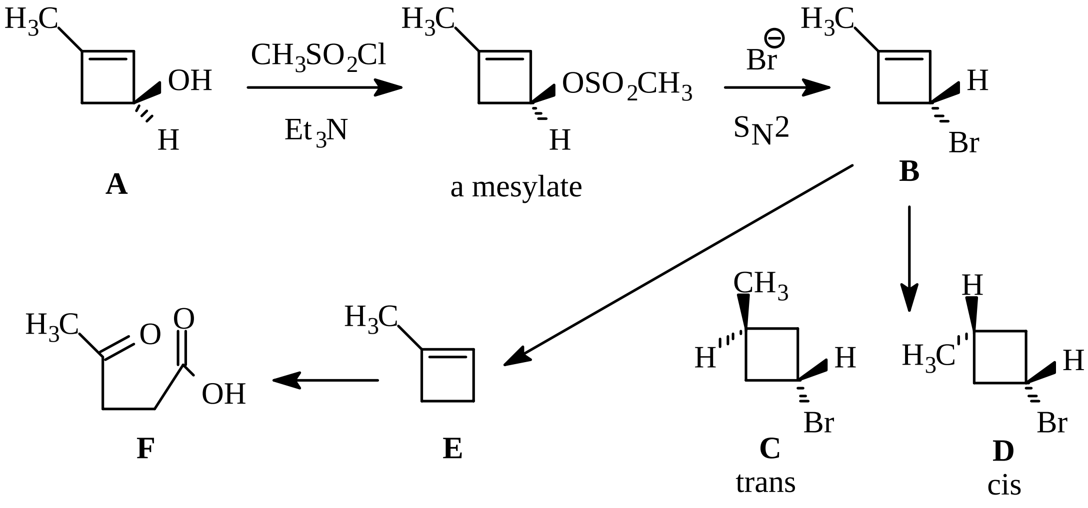


[1]

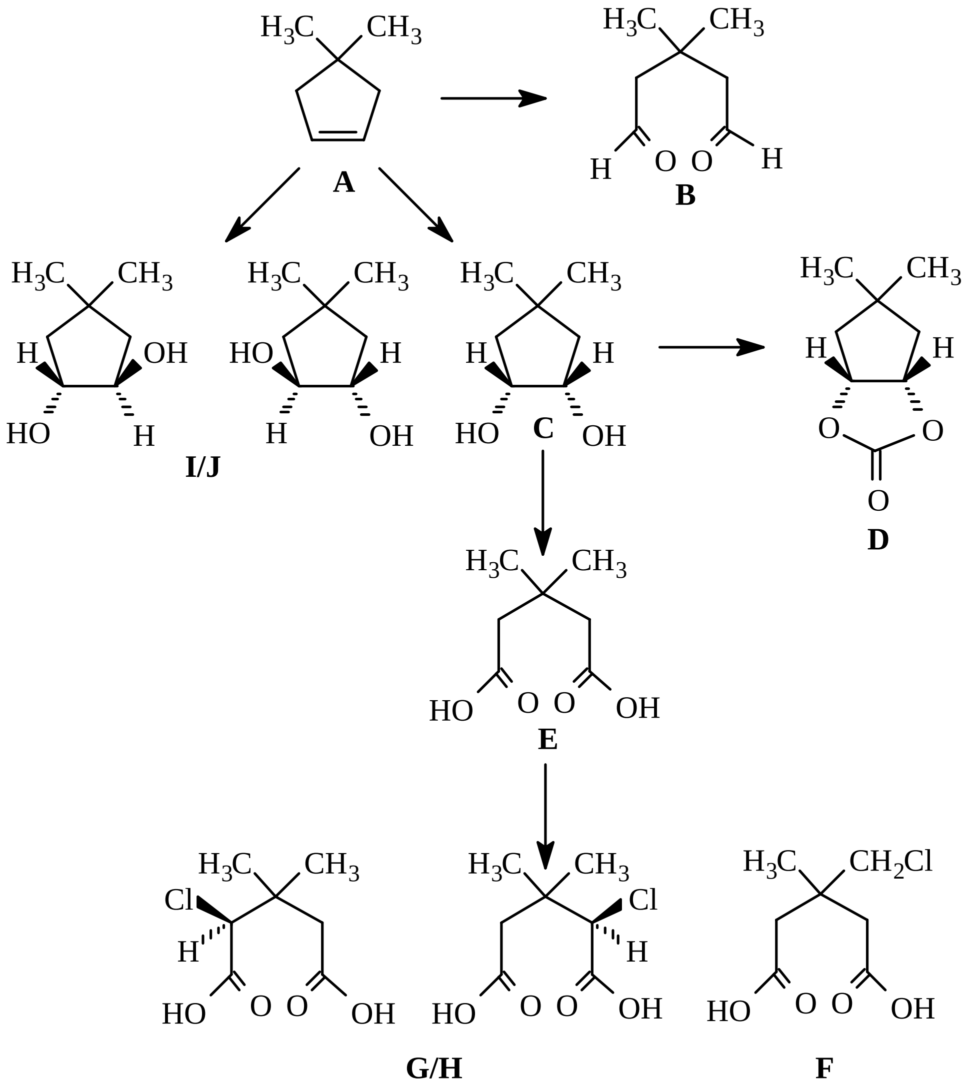


[2]

SOLUTION 22



SOLUTION 23

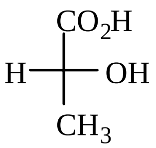


SOLUTION 24

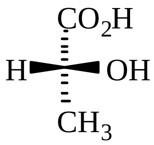
a)

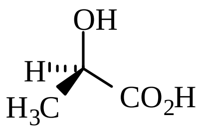
$$Ca_5(PO_4)_3OH\ (s) \xrightleftharpoons{H_2O\ (l)} 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + HO^{-}\ (aq)$$

b) other variations also possible



(Fischer)





IUPAC name: (2*R*)-(-)-2-hydroxypropanoic acid

other variations include:
(2*R*)-(*l*)-2-hydroxypropanoic acid
(*R*)-(-)-2-hydroxypropanoic acid
(*R*)-(*l*)-2-hydroxypropanoic acid
(2*R*)-(-)-lactic acid
(2*R*)-(*l*)-lactic acid
(*R*)-(-)-lactic acid
(*R*)-(*l*)-lactic acid

c) Tooth decalcification is related to the reaction of demineralization of hydroxyapatite, or to the shift of its equilibrium through the formation of the ions in solution. So, the influence of an acidic medium should shift the equilibrium to the right. Since the quantity of solid hydroxyapatite has no effects, one has to look at the species that can react with acids. In an acidic medium, the H^+ ions can strongly react with two of the three ions produced during demineralization of hydroxyapatite, namely OH^- and PO_4^{3-} ions. The latter are strong bases which will react with H^+ ions to form their respective conjugate acid as shown by the following equations:

$$HO^- \text{ (aq)} + H^+ \text{ (aq)} \rightleftharpoons H_2O \text{ (l)} \qquad K_w^{-1}$$

$$PO_4^{3-} \text{ (aq)} + H^+ \rightleftharpoons HPO_4^{2-} \text{ (aq)} \qquad K_{a3}^{-1}$$

d)

$$Ca_5(PO_4)_3F \text{ (s)} \overset{H_2O \text{ (l)}}{\rightleftharpoons} 5Ca^{2+} \text{ (aq)} + 3PO_4^{3-} \text{ (aq)} + F^- \text{ (aq)}$$

The dissolution of x mol of $Ca_5(PO_4)_3F$ in 1 L of water will produce 5x mol/L of Ca^{2+}, 3x mol/L of PO_4^{3-} and x mol/L of F^-.
The solubility product, K_{sp}, of fluoroapatite is expressed as:

$$K_{sp} = [Ca^{2+}]^5 [PO_4^{3-}]^3 [F^-] = 1.0 \times 10^{-60}$$

$$1.0 \times 10^{-60} = (5x)^5 (3x)^3 (x) = (3125x^5) (27x^3) (x) = 84375x^9$$

$$x = [(1.0 \times 10^{-60})/84375]^{1/9} = 6.1 \times 10^{-8} \text{ mol/L}$$

The solubility of fluoroapatite in water is 6.1×10^{-8} mol/L.

Similarly, and according to the equation of part a), one can calculate the solubility of hydroxyapatite in water.

$$K_{sp} = [Ca^{2+}]^5\ [PO_4^{3-}]^3\ [OH^-] = 6.8 \times 10^{-37}$$

$$6.8 \times 10^{-37} = (5x)^5\ (3x)^3\ (x) = (3125x^5)\ (27x^3)\ (x) = 84375x^9$$

$$x = [(6.8 \times 10^{-37})/84375]^{1/9} = 2.7 \times 10^{-5} \text{ mol/L}$$

The solubility of hydroxyapatite in water is 2.7×10^{-5} mol/L

e) In order to show how the remineralization process is preferred in presence of F^- ions, one must evaluate the equilibrium constant of the reaction of hydroxyapatite with F^-. This reaction can be described as the sum of the following reactions:

$$Ca_5(PO_4)_3OH\ (s) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + HO^-\ (aq) \qquad K_{sp}\ (hydr)$$

$$5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + F^-\ (aq) \rightleftharpoons Ca_5(PO_4)_3F\ (s) \qquad K_{sp}\ (fluor)^{-1}$$

$$Ca_5(PO_4)_3OH\ (s) + F^-\ (aq) \rightleftharpoons Ca_5(PO_4)_3F\ (s) + HO^- \qquad K$$

$$\text{where } K = K_{sp}(hydr.) / K_{sp}(fluor.)$$

$$K = (6.8 \times 10^{-37}) / (1.0 \times 10^{-60})$$

$$K = 6.8 \times 10^{23}$$

Since the value of K is very large, this reaction will always be complete, so that the remineralization process is preferred when hydroxyapatite is in the presence of F^- ions.

f) Here again, we have to calculate the equilibrium constants of the reactions of hydroxyapatite (or fluoroapatite) with the H^+ ions of the acidic medium.

Reaction with hydroxyapatite:

$$Ca_5(PO_4)_3OH\ (s) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + HO^-\ (aq) \qquad K_{sp}\ (hydr)$$

$$H^+\ (aq) + HO^-\ (aq) \rightleftharpoons H_2O\ (l) \qquad K_w^{-1}$$

$$Ca_5(PO_4)_3OH\ (s) + H^+\ (aq) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + H_2O\ (l) \quad K_1$$

where $K_1 = K_{sp}(hydr.) / K_w$

$$K_1 = (6.8 \times 10^{-37}) / (1.0 \times 10^{-14})$$

$$K_1 = 6.8 \times 10^{-23}$$

Reaction with fluoroapatite:

$$Ca_5(PO_4)_3F\ (s) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + F^-\ (aq) \qquad K_{sp}\ (fluor)$$

$$H^+\ (aq) + F^-\ (aq) \rightleftharpoons HF\ (aq) \qquad K_a(HF)^{-1}$$

$$Ca_5(PO_4)_3F\ (s) + H^+\ (aq) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + HF\ (aq) \quad K_2$$

where $K_2 = K_{sp}(fluor.) / K_a(HF)$

$$K_2 = (1.0 \times 10^{-60}) / (7.2 \times 10^{-4})$$

$$K_2 = 1.4 \times 10^{-57}$$

Since the equilibrium constant K_2 is smaller, the reaction of hydroxyapatite with H^+ ions is preferred relative to the reaction of fluoroapatite with H^+ ions.

SOLUTION 25

The best way to start this problem is to write the chemical equations including the unknowns in order to represent the different steps with their details.

$$\mathbf{A}\ (s) \xrightarrow{825\ ^\circ C} \underset{\text{44\% of the mass of }\mathbf{A}}{\mathbf{B}\ (g)} + \underset{\text{56\% of the mass of }\mathbf{A}}{\mathbf{C}\ (s)} \qquad [1]$$

$$\mathbf{C}\,(s) + \text{Carbon}\,(s) \xrightarrow{2000\text{-}2200\ ^\circ C} \mathbf{D}\,(s) + \mathbf{E}\,(g) \qquad [2]$$

Gas **E** contains the same elements as gas **B**, but in different proportions. Some possibilities are: NO, NO_2, N_2O, NO_3, CO, CO_2, SO_2, and SO_3. It can not be a pure gaseous element since gases **B** and **E** contains the same elements. Hydrogen halides (HX) must also be excluded since no other gases with H and X can be formed with other proportions. Large evolutions of nitrogen- or sulfur-based gases are rarely observed during the pyrolysis of minerals. Moreover, the temperature of reaction [1] can correspond to that of a calcification with CO_2 gas evolution (**B**).

The original purpose of reaction [2] was to isolate the metal in **C** according to reaction [3] below (where **C** would be a metallic oxide), but products **D** and **E** were obtained instead. Gas **E** could be carbon monoxide, CO. In reaction [2], the metal must be in **D** since **E** is a gas.

$$M_xO_y\,(s) + y\,C\,(s) \xrightarrow{X} x\,M(s) + y\,CO\,(g) \qquad [3]$$

$$\mathbf{D}\,(s) + H_2O\,(l) \rightarrow \mathbf{F}\,(g) + \mathbf{G}\,(s) \qquad [4]$$

The hydrolysis reaction can be the addition of a water molecule to **D**, an oxidation of **D**, or an acid-base reaction. Since **F** is a gas and **D** contains a metal, then the insoluble compound **G** must contain this metal. A large volume of gas **F** was produced and the latter burns with a brilliant, sooty flame. The major constituents of **F** form a large proportion of **D** and it must contain carbon. If **F** reacts with water to form an aldehyde **L**, it does not initially contain an oxygen atom. Its reactivity with water indicates that **F** can be ethene (C_2H_4), ethyne (C_2H_2), propene (C_3H_6) or propyne (C_3H_4). The heavier alkenes or alkynes are not gases. Nevertheless, ethyne and propyne are more probable since the formation of aldehyde **L** would be difficult with only one unsaturation in the molecule. Reaction [4] would then be an acid-base reaction. The anionic part of **D** acts as a base and removes the H^+ ions from H_2O, and the OH^- ions are associated with the metal cation. Before hydrolysis, the anion of **D** could be C_2^{2-}, HC_2^-, $C_3H_2^{2-}$ (less probable!) or $C_3H_3^-$. The poorly soluble solid **G** must contain at least one OH^- ion.

$$\mathbf{G}\,(s) \xrightarrow{\Delta} \mathbf{C}\,(s) + H_2O\,(l) \qquad [5]$$

Pyrolysis of **G** produces water and compound **C**. There must be another source of H in **G**. If other OH^- ions are present in **G**, then compound **C** is an oxide. This reinforces the hypothesis stated from the results of reaction [2].

$\mathbf{G}\,(s) + \mathbf{B}\,(g) \rightarrow H_2O\,(l) + \mathbf{A'}\,(s)$ [6]

The composition of **A'** is exactly the same as that of the mineral substance **A**. If **B** is CO_2 then **A** (or **A'**) must be a carbonate, which is possible for a mineral substance. Compound **A'** could be calcium carbonate which is the most common natural carbonate. Compound **G**, containing at least one OH^- ion, can be calcium hydroxide, which has a relatively low solubility.

$\mathbf{D}\,(s) + N_{2\,(g)} \xrightarrow{1000\text{ -}1100\ ^\circ C} \mathbf{H}\,(s) + \text{Carbon}\,(s)$ [7]

Compound **H** is ionic and very reactive. It contains 15%C and 35%N, the remaining material being the metal. So, the anionic part is made of carbon and nitrogen.

Assume 100 g of compound **H**: (15 g C) / (12.011 g/mol) = $1.2\underline{5}$ mol C
(35 g N) / (14.007 g/mol) = $2.5\underline{0}$ mol N

Empirical formula of the anion: $(CN_2)_n^{x-}$

If the formula of the anion is CN_2 and that of compound **H** is MCN_2, then 50 g of the metal is equivalent to 1.25 mol of this metal. The molar mass of the latter would then be 40 g and it would be calcium. This is highly probable taking into account the information deduced already.

If the formula of the anion is $(CN_2)_2$ or C_2N_4 and that of compound **H** is MC_2N_4, then 50 g of the metal is equivalent to 0.625 mol of this metal. The molar mass would be 80 g but there is no metal having such a molar mass.

If the formula of the anion is $(CN_2)_3$ or C_3N_6 and that of compound **H** is MC_6N_6 then 50 g of the metal is equivalent to 0.417 mol of this metal. The molar mass of the latter would be of 120 g which could be a heavy metal like tin or lead. However, these metals are not present as carbonates in nature.

In reaction [1], we noticed a weight loss of 44% between **A** and **C**. So the mass ratio of **C**/**A** is 56%. Assuming that **B** is CO_2, **A** would be calcium carbonate and **C** would be calcium oxide. The mass ratio of $CaO/CaCO_3$ is 56%. Gas **E** would be CO, which is frequently observed during the reactions of metallic oxides with carbon. So we are dealing with calcium compounds.

H (s) + H_2O (l) → **G** (s) + **X** (s) [8]

Since **H**, **G**, and **X** are ionic, and they are formed from the same metal, the anionic part containing C and N is in compound **X**. As in reaction [4], it is a hydrolysis where an acid reacts with a base. The base is the cyanamide ion, CN_2^{2-}, that is partially hydrogenated into HCN_2^- which is an intermediate species in the formation of dihydrogen cyanamide, H_2CN_2.

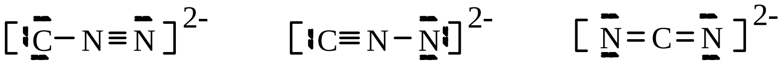
X (s) + CO_2 (g) + H_2O (l) → **A'** (s) + **I** (s) [9]

Under these conditions, **X** must be $Ca(HCN_2)_2$ and both protons from the carbonic acid produced by reaction of CO_2 and H_2O allow the formation of dihydrogen cyanamide, H_2CN_2, i.e. compound **I**.

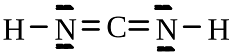
I (s) + H_2O (l) → **J** (s) [10]

Since only one compound was formed in reaction [10], the hydrolysis must now be an addition of water to **I**. To deduce the structure of compound **J**, one must know that of compound **I**. To deduce the latter, one can refer to that of the cyanamide ion, CN_2^{2-}.

Following are the three possible structures for cyanamide ion of compound **H**:



The first two must be excluded because of the heavy negative charge (2-) on their respective carbon and nitrogen atoms. In the third structure, the two negative charges are evenly distributed on the two terminal nitrogen atoms. Adding two protons to this structure, one obtains a possible structure of compound **I** which is a symmetrical molecule.



The addition of a water molecule to such a compound produces urea which is frequently used in fertilizers. So compound **J** is urea, $H_2N(CO)NH_2$.

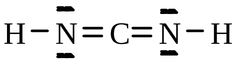
J (s) + H_2O (l) → **B** (g) + **K** (g) [11]

Hydrolysis of **J** causes the complete oxidation of carbon into CO_2 (gas **B**) and into NH_3 (gas **K**). The latter has a strong, characteristic odour.

a)

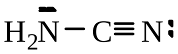
A or A':	$CaCO_3$ (s)	Calcium carbonate (or calcareous rocks)
B:	CO_2 (g)	Carbon dioxide
C:	CaO (s)	Calcium oxide
D:	CaC_2 (s)	Calcium carbide
E:	CO (g)	Carbon monoxide
F:	C_2H_2 (g)	Ethyne
G:	$Ca(OH)_2$ (s)	Calcium hydroxide
H:	$CaCN_2$ (s)	Calcium cyanamide
I:	H_2CN_2 (s)	Dihydrogen cyanamide
J:	$H_2N(CO)NH_2$	Urea
K:	NH_3	Ammonia
L:	CH_3CHO	Ethanal
M:	CH_3CO_2H	Ethanoic acid
X:	$Ca(HCN_2)_2$	Calcium hydrogen cyanamide

b) The two possible structures of dihydrogen cyanamide are:



$H-N=C=N-H$

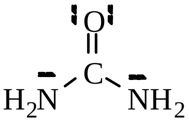
and



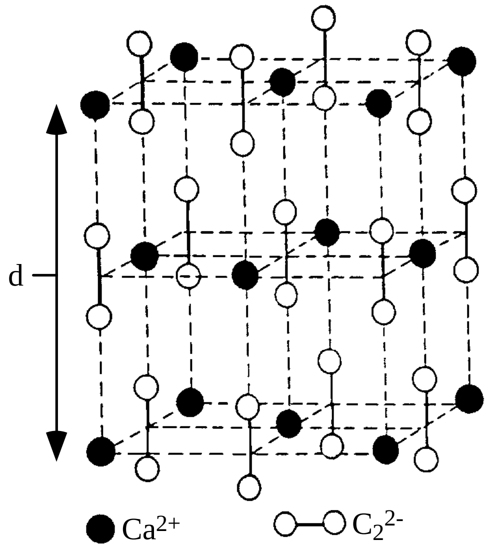
$H_2N-C\equiv N$

The second structure does not possess any center of symmetry and its $-C \equiv N$ function can absorb between 2260 and 2220 cm^{-1} in its infrared spectrum. It is thus the major structure.

c) The Lewis structure of urea is:



d) The crystal structure of CaC_2 is shown below. Each unit cell contains 4 Ca^{2+} ions and 4 C_2^{2-} ions. The distance between two Ca^{2+} cations on the edge of the cell is equal to the thickness "d" of this cell. This distance is the cubic root of volume "V" of the cell. From the density of CaC_2 one can calculate the volume of its unit cell.



$$d = (V)^{1/3}; \quad \rho = 2.22\ g/cm^3; \quad M = 80.105\ g/mol$$

$$\text{volume of 1 mol} = M/\rho = (80.105\ g/mol) / (2.22\ g/cm^3) = 36.1\ cm^3$$

$$V = [(36.1\ cm^3) / (6.022 \times 10^{23}\ CaCN_2/mol)] \times (4\ CaCN_2/\text{unit cell})$$

$$V = 2.40 \times 10^{-22}\ cm^3$$

$$d = (2.40 \times 10^{-22}\ cm^3)^{1/3}$$

$$d = 6.21 \times 10^{-8}\ cm$$

e)

$CaCO_3\ (s) \xrightarrow{825\ ^\circ C} CO_2\ (g) + CaO\ (s)$ [1]

$CaO\ (s) + 3\ C\ (s) \xrightarrow{2000\text{-}2200\ ^\circ C} CaC_2\ (s) + CO\ (g)$ [2]

$CaC_2\ (s) + 2\ H_2O\ (l) \rightarrow C_2H_2\ (g) + Ca(OH)_2\ (s)$ [4]

$C_2H_2 + H_2O\ (l) \xrightarrow{HgSO_4} CH_3CHO$ [4']

[O], Mn cat.

CH_3CHO → CH_3CO_2H [4"]

$Ca(OH)_2\ (s) \xrightarrow{\Delta} CaO\ (s) + H_2O\ (l)$ [5]

$Ca(OH)_2\ (s) + CO_2\ (g) \rightarrow H_2O\ (l) + CaCO_3\ (s)$ [6]

$CaC_2\ (s) + N_{2\ (g)} \xrightarrow{1000\text{-}1100\ ^\circ C} CaCN_2\ (s) + C\ (s)$ [7]

$2\ CaCN_2\ (s) + 2\ H_2O\ (l) \rightarrow Ca(OH)_2\ (s) + Ca(HCN_2)_2\ (s)$ [8]

$Ca(HCN_2)_2\ (s) + CO_2\ (g) + H_2O\ (l) \rightarrow CaCO_3\ (s) + 2\ H_2CN_2\ (s)$ [9]

$H_2CN_2\ (s) + H_2O\ (l) \rightarrow H_2N(CO)NH_2\ (s)$ [10]

$H_2N(CO)NH_2\ (s) + H_2O\ (l) \rightarrow CO_2\ (g) + 2\ NH_3\ (g)$ [11]

SOLUTION 26

a) Acheson Process:

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

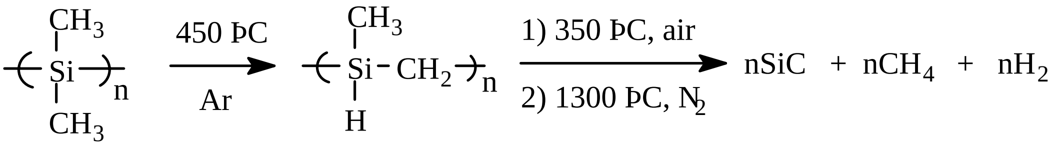
$$\text{Theoretical ceramic yield} = M[SiC] / (M[SiO_2] + 3\ M[C])$$

$$\text{Yield} = (40.097\ g\ mol^{-1}) / [(60.086\ g\ mol^{-1}) + 3 \times (12.011\ g\ mol^{-1})]$$

$$\text{Theoretical ceramic yield} = 41.7\%$$

Since all other processes refer to thermal treatment of polymers, one can take only the mass of their monomers to do the calculations.

Yajima Process:

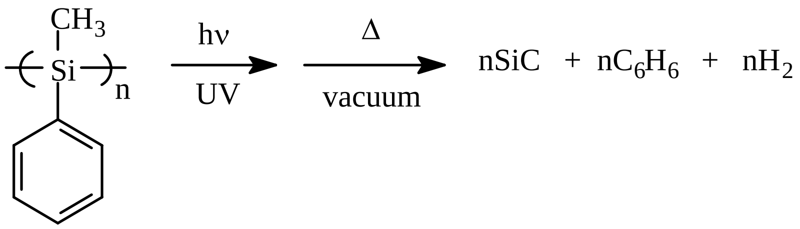


$$\text{Theoretical ceramic yield} = M[SiC] / M[(CH_3)_2Si]$$

Yield = (40.097 g mol^{-1}) / (58.156 g mol^{-1})]

Theoretical ceramic yield = 68.9%

West Process:

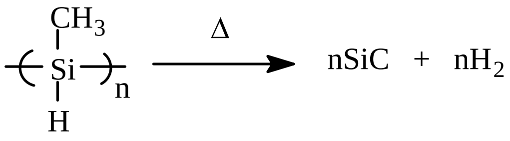


$$\text{Theoretical ceramic yield} = M[\mathrm{SiC}] / M[(\mathrm{CH_3})(\mathrm{C_6H_5})\mathrm{Si}]$$

$$\text{Yield} = (40.097\ \mathrm{g\ mol^{-1}}) / (120.227\ \mathrm{g\ mol^{-1}})]$$

Theoretical ceramic yield = 33.4%

Harrod Process:



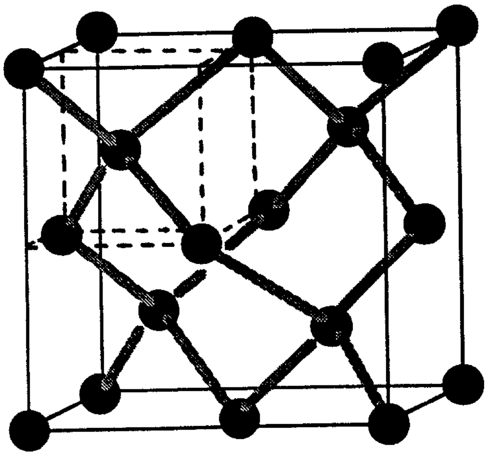
$$-\!\!\left(\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{Si}}}\right)\!\!-_{n} \xrightarrow{\Delta} n\mathrm{SiC} + n\mathrm{H_2}$$

$$\text{Theoretical ceramic yield} = M[\mathrm{SiC}] / M[(\mathrm{CH_3})(\mathrm{H})\mathrm{Si}]$$

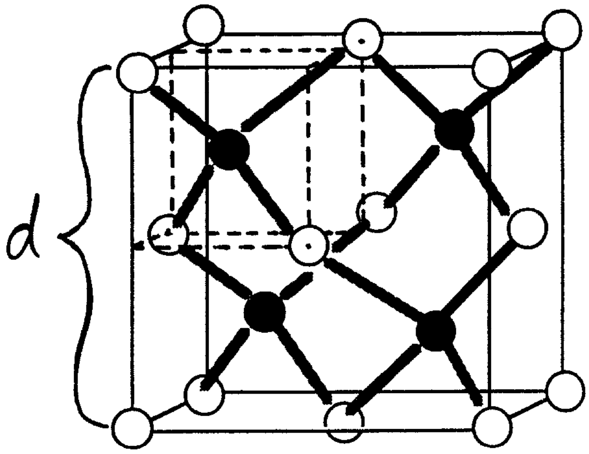
$$\text{Yield} = (40.097\ \mathrm{g\ mol^{-1}}) / (44.129\ \mathrm{g\ mol^{-1}})]$$

Theoretical ceramic yield = 90.9%

b) The cubic structures of diamond and silicon carbide are shown below. That of SiC corresponds to the structure of zinc blende (ZnS).



Diamond



SiC

According to these structures, each unit cell of diamond contains 8 carbon atoms, and each unit cell of silicon carbide contains 4 carbon atoms and 4 silicon atoms.

In diamond, each carbon atom bonds to 4 other carbon atoms forming a tetrahedron. The unit cell of diamond contains 4 of these tetrahedrons, and each one occupies the volume of a small cube having half the edge length of the unit cell.

In silicon carbide, we have a lattice of silicon atoms having a face-centered cubic structure, and 4 carbon atoms that occupy half of the tetrahedral holes available in the cell. The edge of the small cube containing each tetrahedron corresponds to half the edge "d" of the SiC unit cell. From the density of SiC, one can evaluate the volume "V" of the unit cell, the value of "d", then that of the edge of the small cube. Simple trigonometry allows us to calculate the Si-C distance ($d_{Si\text{-}C}$) then, knowing the atomic radius of carbon, one can calculate the atomic radius of silicon by difference.

$$\text{Volume of 1 mole of SiC} = M[\text{SiC}] / \rho(\text{SiC}) = (40.097 \text{ g mol}^{-1}) / (3.21 \text{ g cm}^{-3})$$

$$\text{Volume of 1 mole of SiC} = 12.5 \text{ cm}^3$$

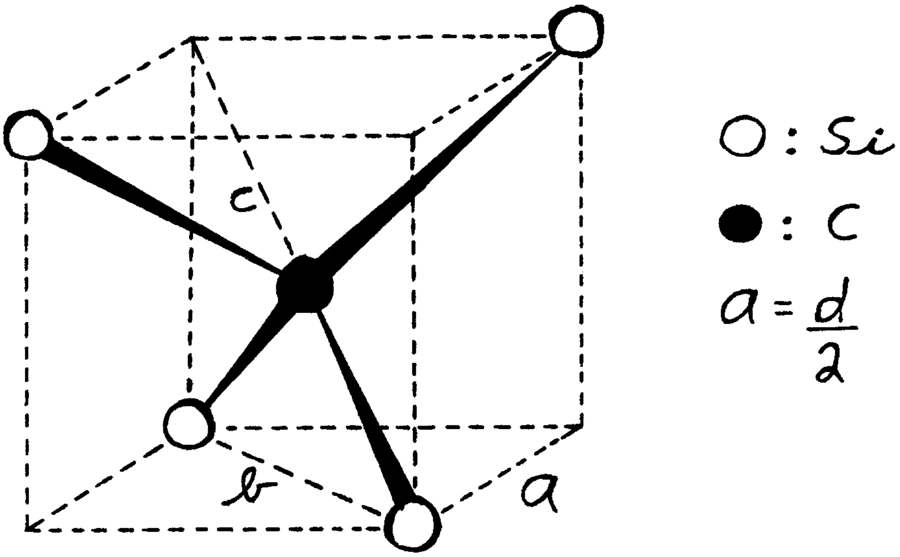
$$V = [(12.5 \text{ cm}^3) / (6.022 \text{ x } 10^{23} \text{ SiC/mol})] \text{ x } 4 \text{ SiC/unit cell}$$

$$V = 8.30 \text{ x } 10^{-23} \text{ cm}^3 = d^3$$

$$d = (V)^{1/3} = (8.30 \text{ x } 10^{-23} \text{ cm}^3)^{1/3}$$

$$d = 4.36 \text{ x } 10^{-8} \text{ cm}$$

Each carbon atom is in the center of a small cube in which is the silicon atoms tetrahedron. The length of the edge of the small cube is d/2. The Si-C distance, $d_{Si\text{-}C}$, is half the length of the diagonal passing through the center of the small cube (c/2).



$a = d/2; \qquad b^2 = 2a^2; \qquad c^2 = a^2 + b^2 = 3a^2$

$c = (3a^2)^{1/2} = [3(d/2)^2]^{1/2}$

$c = [3 \times ((4.36 \times 10^{-8}\ \text{cm})/2)^2]^{1/2}$

$c = 3.78 \times 10^{-8}$ cm

$d_{\text{Si-C}} = c/2 = (3.78 \times 10^{-8}\ \text{cm})/2$

$d_{\text{Si-C}} = 1.89 \times 10^{-8}$ cm

Atomic radius of Si = $d_{\text{Si-C}}$ - Atomic radius of C

where atomic radius of C = $(1.54 \times 10^{-8}$ cm$)/2 = 0.77 \times 10^{-8}$ cm

Atomic radius of Si = $(1.89 \times 10^{-8}$ cm$)$ - $(0.77 \times 10^{-8}$ cm$)$

Atomic radius of Si = 1.12×10^{-8} cm

(literature value = 1.17×10^{-8} cm; Butler & Harrod, 1988, p. 48)

SOLUTION 27

a) Silica, SiO_2, is a covalent lattice compound in which each Si is surrounded by a tetrahedron of O and each O bridges between two Si atoms. To melt this lattice requires rupture of very strong chemical bonds and hence the compound has a very high melting point. Phosphorus pentoxide is actually P_4O_{10} in the solid state. The P is surrounded by a tetrahedron of O, three of which are bonding to other P's and the fourth, a P=O is terminal. The solid consists of a lattice of these molecules, with relatively weak secondary bonding forces holding the lattice together. Hence the relatively low melting point compared to SiO_2. Sulfur trioxide is also a simple molecular compound and in the solid the intermolecular forces are weak. It is monomeric and of substantially lower molecular weight than P_4O_{10}, hence its lower melting point.

b)

$SiO_2 + 2\,H_2O \rightarrow H_4SiO_4$ [1]

$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4$ [2]

$SO_3 + H_2O \rightarrow H_2SO_4$ [3]

$SiO_2 + 2K_2O \rightarrow K_4SiO_4$ [4]

$P_4O_{10} + 6\,K_2O \rightarrow 4\,K_3PO_4$ [5]

$SO_3 + K_2O \rightarrow K_2SO_4$ [6]

Energetics:

[1] is an endothermic reaction. A large amount of energy is required to break strong Si-O-Si bonds; the resulting acid is weak due to the low electronegativity of Si and hence not much H^+ solvation energy is available to compensate (the hydration of a proton in water liberates a large amount of energy). The higher electronegativities of P(V) and S(VI) result in strong acids in [2] and [3]; the ionization of H^+ is essentially complete, liberating a huge amount of hydration energy. In [4], [5] and [6], the oxide ion is a powerful base, which has no difficulty in attacking the electron deficient Si, P or S to produce additional strong X-O- bonds. The formation of highly charged ions in these reactions also gives rise to very large, favourable electrostatic attraction energies, known as lattice energies in the solid compounds.

c) The Si-O-Si bond is not appropriate as an energy storage bond because its hydrolysis is not exothermic under physiological conditions. In addition it reacts only very slowly with mild reagents (witness the geological time-scale for the erosion of silicate rocks!). The S-O-S bond (pyrosulfate) hydrolyses exothermically, but the hydrolysis occurs too easily (rapidly) for pyrosulfate to be used as a storage device. The pyrophosphate link hydrolyses exothermically, but only does it very slowly under physiological conditions. Thus the bond energy can be stored and only released in the presence of a suitable catalyst. Living systems are rich in natural catalysts (enzymes) with the special function of catalyzing the reaction of pyrophosphate linkages to take advantage of the stored energy.

SOLUTION 28

a) $2\ Y_2O_3 + 8\ BaCO_3 + 12\ CuO + O_2 \rightarrow 4YBa_2Cu_3O_7 + 8CO_2$

b) $YBa_2Cu_3O_7$ has 14 negative charges from the 7 O^{2-}.

The positive charges from the metal ions sum to:

$$Y(3^+) + Ba(2 \times 2^+) + Cu(3 \times n^+) = 14.$$

Therefore, the average n= $\frac{7}{3}$ is the oxidation state of Cu in this material.

c) Molecular weight of $YBa_2Cu_3O_7$ is 666 g mol^{-1}.

Observed weight loss is 9.88/10.00 = 1.2 per cent. 1.2 per cent of 666 g = 7.99 g.

If this is all O, then we have lost 0.5 g atom. Therefore, the new composition is $YBa_2Cu_3O_{6.5}$. There are now only 13 negative charges, which requires 6 positive charges from the Cu so the average oxidation state of the Cu is now 2.

d) The common oxidation states of Cu are I, II and (rarely) III. For three Cu ions to have an average oxidation state of $\frac{7}{3}$, there are 2 x Cu(II) and a single Cu(III). In the deoxygenated material all three Cu's are Cu(II).

SOLUTION 29

a) The valence electron counts of the relevant atoms are : H(1), C(4), N(5), O(6).

O_2^-: (2 x 6) electrons from O + one for the charge = 13 *

NO: 5 electrons from N + 6 electrons from O = 11*

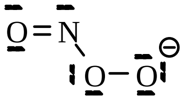
$[ONO_2]^-$: 5 electrons from N + (3 x 6) electrons from O + one for the charge = 24

CO_2: 4 electrons from C + (2 x 6) electrons from O = 16

$[HCO_3]^-$: 1 electron from H + 4 electrons from C + (3 x 6) electrons from O + one for the charge = 24

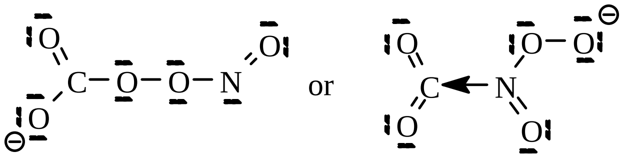
$[ONO_2CO_2]^-$: 4 electrons from C + 5 electrons from N + (5 x 6) electrons from O + one for the charge = 40

The unpaired electron on the superoxide will pair with the unpaired electron on the N to form a covalent bond. This is a radical combination reaction. Because the N in the product has a lone pair, the molecule will be bent, thus:



$[ONO_2]^-$

CO_2 is a weak Lewis acid and the peroxonitrite is a weak Lewis base. We will get an acid/base reaction. It is hard to predict whether the peroxonitrite will bond through the lone pair on the N or through the O. Two structures are possible:



$[ONO_2CO_2]^-$

b) Radical combination and acid/base reactions. See discussion in part (a).

c) $Cu^+ + NO_2^- + 2H^+ \rightarrow Cu^{2+} + NO + H_2O$

d) Compression of NO to 100 atm at 50 ˚C leads to a disproportionation according to the equation:

$$3NO \rightarrow N_2O + NO_2$$

Because the number of molecules drops to 2/3 of the initial amount, the pressure at constant volume will drop to 2/3 its original value. Because NO_2 can dimerize (it is an odd electron count molecule with an unpaired electron on the N), the pressure will drop even more, i.e. to less than 2/3 the original value.

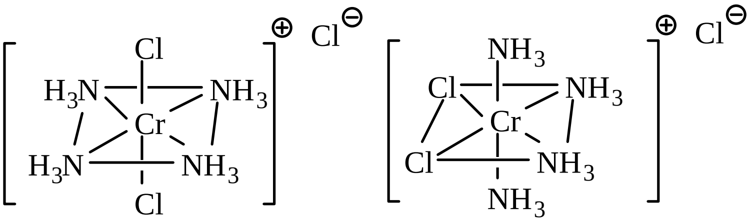
SOLUTION 30

a) The Cr^{3+} and Co^{3+} belong to a class of ions we now call "substitution inert". Unlike most transition ions in aqueous solution, the equilibration between the ligands initially attached to the metal and the large excess of water solvent is very slow with these particular ions. This allows their synthesis, isolation, recrystallization etc. without loss of ligands by water substitution, or without rapid equilibration of isomers.

b)

i) $[(NH_3)_4Cl_2Cr]Cl$. This compound has a unipositive complex cation in which a Cr^{3+} is surrounded by two Cl's and four NH_3 molecules at the corners of an octahedron. There are two distinct ways of placing the Cl ligands, either on adjacent corners, or on diagonally opposite corners. These are known as the cis and trans isomers respectively and this is a case of geometric isomerism.

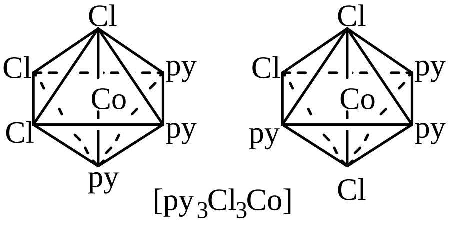
The compounds are: *trans*-tetraamminedichlorochromium(III) chloride
cis-tetraamminedichlorochromium(III) chloride



trans $[(NH_3)_4Cl_2Cr]Cl$ cis

ii) $[py_3Cl_3Co]$. This neutral Co^{3+} complex is also octahedral. There are two different ways of arranging the triads of like ligands. The facial isomer is obtained when they are all on the corners of a common triangular face of the octahedron (placing three like ligands on a common face forces the other three to occupy the diagonally opposite triangular face of the octahedron). The meridional isomer results from placing three like ligands at three corners of an equatorial square of the octahedron (the other three are then forced to occupy three corners of another equatorial square perpendicular to the first). This type of isomerism is also geometric.

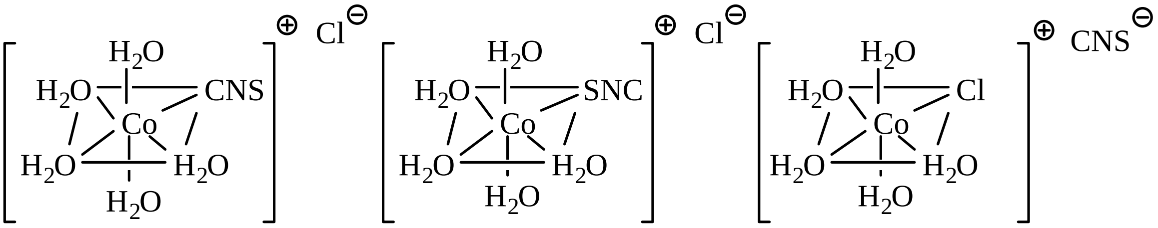
The compounds are: *fac*-trichlorotris(pyridine)cobalt(III)
mer-trichlorotris(pyridine)cobalt(III)



$[py_3Cl_3Co]$

facial meridional

iii) $[(H_2O)_5(CNS)Co]Cl$: There is only one geometric arrangement of the five water and one CNS ligands. However, the CNS may be attached either by the C atom, or by the S atom.



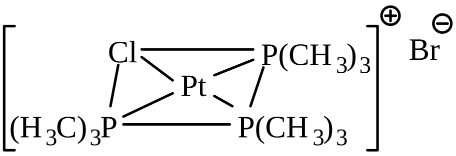
$[(H_2O)_5(CNS)Co]Cl$

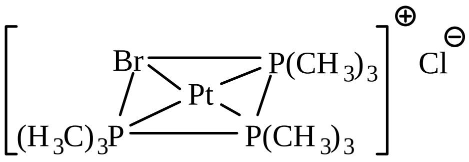
The resulting isomers are known as linkage isomers. Another possible isomer of this compound would result from interchange of the coordinated CNS with the free Cl. This is known as ionization isomerism.

The compounds are: pentaaquathiocyanato-C-cobalt(II) chloride.
pentaaquathiocyanato-S-cobalt(II) chloride
pentaaquachlorocobalt(II) thiocyanate

iv) $[(Me_3P)_3ClPt]Br$: The complex ion consists of a Pt^{2+} coordinated to three neutral phosphines and a uninegative Cl at the corners of a square. There is only one possible geometric arrangement, but interchange of the Cl and the Br gives rise to ionization isomers.

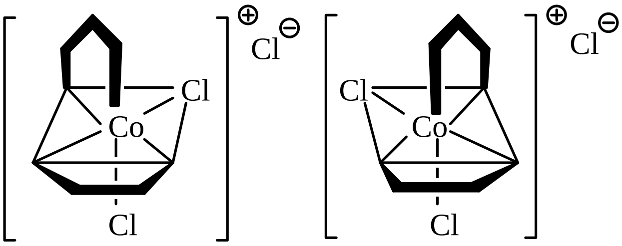
The compounds are: chlorotris(trimethylphosphine)platinum(II) bromide
bromotris(trimethylphosphine)platinum(II) chloride



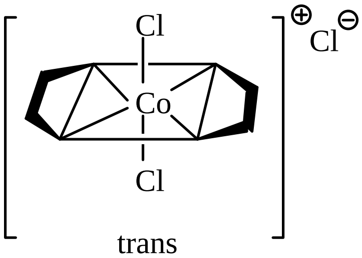


$[((CH_3)_3P)_3ClPt]Br$

c) The relevant concept was the recognition that compounds possessing the property of not being superimposable on their mirror image (we now call this property chirality) cause a rotation in the plane of polarization of plane-polarized light. Werner therefore set out to prepare a coordination compound with this property. On the assumption that Co^{3+} complexes have octahedral geometry, he deduced that $[en_2Cl_2Co]Cl$ should have two non-superimposable structures that differ only in that they are mirror images of each other. This was indeed found to be the case, establishing that the geometry of the complex is rigid and octahedral.



cis enantiomers cis
optically active



trans
not optically active

d) The new theory was the theory of ionic conductivity. The new theory allowed the determination of the number of ions in an ionic compound from conductivity measurements. The series of compounds $[(NH_3)_xCl_3Cr]$ (x=3 to 6) are : $[(NH_3)_3Cl_3Cr]$ (neutral); $[(NH_3)_4Cl_2Cr]Cl$ (2 ions); $[(NH_3)_5ClCr]Cl_2$ (3 ions); $[(NH_3)_6Cr]Cl_3$ (4 ions). From the numbers of ions, it is possible to conclude that the number of ligands coordinated to Cr^{3+} remains at 6 throughout the series.

SOLUTION 31

a) $\Delta E = q + w$ (conservation of energy)

b) $\Delta S = \int \frac{dq_{rev}}{T}$ and can <u>only</u> be calculated for a reversible process

c) Since $E = \frac{3}{2}(nRT)$, it is thus independent of volume.

Thus $\Delta E = 0$ in this process which is isothermal.

Since $\Delta E = 0$, thus $q = -w$ and therefore $dq = -dw$.
The only work performed is PV work and since $dw_{rev} = -P_{ext}dV$, thus
$dq = -dw = +P_{ext}dV$

From b) $\Delta S = \int \frac{dq_{rev}}{T}$ and thus $dS = \frac{dq_{rev}}{T}$; substituting $dw_{rev} = -P_{ext}dV$ we obtain

$$dS = \frac{-dw_{rev}}{T} = \frac{P_{ext}dV}{T}$$

Since PV = nRT we can again substitute to obtain

$$dS = \frac{-dw_{rev}}{T} = \frac{P_{ext}dV}{T} = \frac{nRTdV}{VT} = nR\frac{dV}{V}$$

Integrating gives:

$$\Delta S = \int dS = \int_V^{2V} nR\frac{dV}{V}$$
$$= nR\ln 2V - nR\ln V$$
$$= nR\ln\frac{2V}{V} = nR\ln 2$$

Thus $\Delta S = nR\ln 2$ (which is > 0)

Since $G = H - TS$ it follows that $G = (U + PV) - TS$ and that $\Delta G = \Delta U + \Delta(PV) - T\Delta S$
But $\Delta E = 0$ and $PV = nRT$ which is a constant and thus $\Delta(PV) = 0$.
Therefore $\Delta G = -T\Delta S$ and from above $\Delta S = nR\ln 2$ which upon substitution gives
$\Delta G = -nRT\ln 2$ (which is < 0)

d) Each of E, S and G are state functions and are thus independent of the pathway. Therefore:

$\Delta E_{rev} = \Delta E_{irrev} = 0$

$\Delta S_{rev} = \Delta S_{irrev} = nR\ln 2$

$\Delta G_{rev} = \Delta G_{irrev} = -nRT\ln 2$

e) For spontaneity and irreversibility: $\Delta S > 0$ and $\Delta G < 0$.

f) From the Second Law of Thermodynamics, $\Delta S_{total} = 0$ or $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0$

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = nR\ln 2$$

$$\Delta S_{surr} = -\int \frac{dq_{rev}}{T} = -nR\ln 2$$

g) Note that if each particle has two possible states, then with N_o particles there are 2^{N_o} possible arrangements.

$\Delta S = S_2 - S_1$

$= k\ln W_2 - k\ln W_1$

$= k\ln(2^{N_o}) - k\ln(1^{N_o})$

$= k\ln(2^{N_o})$

$= N_o k\ln 2$

$= nR\ln 2$ (since $k = R/N_o$)

SOLUTION 32

a) The process is adiabatic and thus q = 0 and thus

$\Delta E = -w = n\overline{C}_v\Delta T = 1(\overline{C}_p - R)\Delta T = 1(28.2 - 8.314)(-30) = -597$ J

(also $\Delta E = \Delta H - \Delta(PV) = \Delta H - nR\Delta T = -846 - 8.314(-30) = -597$ J)

and therefore w = +597 J.

$\Delta H = n\overline{C}_p\Delta T = 28.2(-30) = -846$ J

$\Delta S_{sys} = n\,\overline{C}_p \ln(T_1/T_2) - nR\ln(P_2/P_1) = n\,\overline{C}_v \ln(T_2/T_1) + nR\ln(V_2/V_1)$

$= 28.2\ln(90/120) - 8.314\ln(1/4)$

$= -8.11 + 11.53$

$= 3.42\ JK^{-1}$ (which is as it must be ≥ 0)

$\Delta S_{surr} = \int -\frac{q_{rev}}{T} = 0$ since the process is adiabatic

b) The overall process is:

$$\underset{90K}{O_2(g)} \xrightarrow{-\Delta H_{vap}} \underset{90K}{O_2(l)} \xrightarrow{\text{cooled}} \underset{55K}{O_2(l)} \xrightarrow{-\Delta H_{fus}} \underset{55K}{O_2(s)} \xrightarrow{\text{cooled}} \underset{10K}{O_2(s)}$$

The entire process of cooling is at constant pressure and thus $\Delta H = q_p$.

$$\Delta H_{sys} = -\Delta H^o_{vap} + \int_{90}^{55} n\overline{C}_p(l)dT - \Delta H^o_{fus} + \int_{55}^{10} n\overline{C}_p(s)dT$$

$\Delta H_{sys} = -6820 + 54(55-90) - 420 + 41(10-55) = -10975\ J = -10.97\ kJ$

$$\Delta S_{sys} = -\frac{\Delta H^o_{vap}}{T_{bp}} + \int_{90}^{55} \frac{n\overline{C}_p(l)dT}{T} - \frac{\Delta H^o_{fus}}{T_{mp}} + \int_{55}^{10} \frac{n\overline{C}_p(s)dT}{T}$$

$\Delta S_{sys} = -6820/90 + 54\ln(55/90) - 420/55 + 41\ln(10/55)$

$= -75.8 - 26.6 - 7.6 - 69.9$

$= -179.9\ JK^{-1}$

SOLUTION 33

a) $\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_f(\text{prod}) - \Sigma\Delta H^\circ_f(\text{reactants})$

$= \Delta H^\circ_f(NH_3) + \Delta H^\circ_f(CO_2) - \Delta H^\circ_f(\text{urea}) - \Delta H^\circ_f(H_2O)$

$= (2(-80.8) + (-412.9)) - ((-317.7 - 285.8))$

$= 29.0\ kJ$

$$\Delta S^\circ_{rxn} = \Sigma\Delta S^\circ(\text{prod}) - \Sigma\Delta S^\circ(\text{reactants})$$
$$= 2(110) + 121 - 176 - 69.9 = 95.1\ \text{JK}^{-1}$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$
$$= 29000 - 298(95.1)$$
$$= 660\ \text{J}$$

Since $\Delta G^\circ = -RT\ln K$, thus $K = e^{\frac{-\Delta G^\circ}{RT}} = e^{-0.266} = 0.766$

b) $\Delta G = \Delta G^\circ + RT\ln Q$ and $Q = \dfrac{(0.1)(0.01)^2}{(1)(55.5)}$

Thus $\Delta G = 660 + 8.314(298)(-15.53) = -37.8\ \text{kJ}$

Since $\Delta G < 0$ the hydrolysis of urea would proceed forward under the given reaction conditions.

SOLUTION 34

a)

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

$$O_3 + O \xrightarrow{k_2} 2O_2 \qquad \text{slow}$$

$$\frac{-d[O_3]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + k_2[O_3][O]$$

The steady state approximation gives $\dfrac{d[O]}{dt} = 0 = k_1[O_3] - k_{-1}[O_2][O] - k_2[O_3][O]$

Therefore we have $[O] = \dfrac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$ and substitution of this into the above gives:

$$-\frac{d[O_3]}{dt} = k_1[O_3] - \frac{k_1[O_3]k_{-1}[O_2]}{k_{-1}[O_2] + k_2[O_3]} + \frac{k_1[O_3]k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$ which simplifies to:

$$-\frac{d[O_3]}{dt} = k_1[O_3]\left(\frac{2k_2[O_3]}{k_{-1}[O_2]+k_2[O_3]}\right) = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]+k_2[O_3]}$$

If $k_{-1}[O_2] >> k_2[O_3]$ then: $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]} = \frac{2k_1k_2[O_3]^2[O_2]^{-1}}{k_{-1}} = k_{exp}[O_3]^2[O_2]^{-1}$

If $k_{-1}[O_2] << k_2[O_3]$ then: $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_2[O_3]} = 2k_2[O_3]^2 = k'_{exp}[O_3]^2$

Thus $k_{exp} = \frac{2k_1k_2}{k_{-1}}$ and $k'_{exp} = 2k_1$

SOLUTION 35

a) Assuming that the rate law has the form: $\frac{d[P]}{dt} = k[X]^x[Y]^y[Z]^z$

Then by inspection x = 2, y = 0, and z = 1/2

Thus $\frac{d[P]}{dt} = k[X]^2[Z]^{\frac{1}{2}}$

b) Substituting in data from the first experiment:

$0.002\ M\ h^{-1} = \frac{d[P]}{dt} = k[0.01M]^2[0.01M]^{\frac{1}{2}}$

which provides $k = 200\ M^{\frac{3}{2}}h^{-1}$

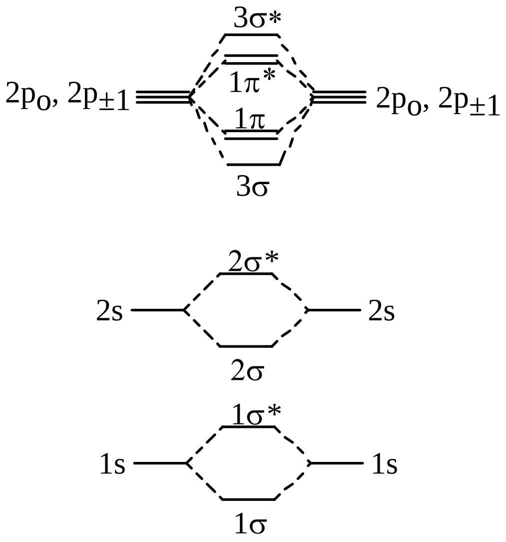
There is a large excess of Y and Z with respect to X and thus the rate equation simplifies and becomes: rate = $k'[X]^2$ where $k' = k[2.00]^{0.5}$

Pseudo second order kinetics now apply and thus:

$$t_{\frac{1}{2}} = \frac{1}{c_0k'} = \frac{1}{(0.01)(283M^{-1}h^{-1})} = 0.35h\ (21\,min)$$

SOLUTION 36

a)



b)

H_2:	$1\sigma^2$	Bond order 1
H_2^-:	$1\sigma^2 1\sigma^{*1}$	Bond order 0.5
He_2:	$1\sigma^2 1\sigma^{*2}$	Bond order 0
He_2^-:	$1\sigma^2 1\sigma^{*2} 2\sigma^1$	Bond order 0.5

c) From the bond orders in (b) it is apparent that H_2^- and He_2^- have the same stability.

d) O_2 has 16 electrons and an MO description of: $1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*2}$

The $1\pi^*$ orbital is doubly degenerate and thus from Hund's Rule $1\pi^*_+(\uparrow)$ $1\pi^*_-(\uparrow)$ giving two unpaired electrons and thus a biradical, paramagnetic species.

e) The electronic configuration of Hg is $[Xe]5d^{10}6s^2$ and therefore Hg^+ will have a configuration of $[Xe]5d^{10}6s^1$. All electrons are paired up except for the valence 6s electron. In the monomeric species there is a single unpaired electron and no bond. On the other hand in the dimeric species the inner electrons can all still be paired and the new σ_{6s} MO ($6s_a + 6s_b$ combination) will gain one electron from each of the Hg^+ ions to provide stability with the net formation of a single bond. Thus the dimer is more stable than the monomer.

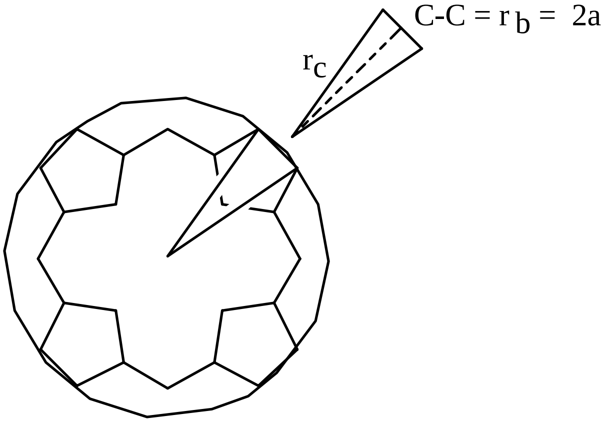
SOLUTION 37

a) Mg has the configuration [Ne]($3s^2$) and does not possess any p orbitals in its valence shell. It thus only has σ electrons available and cannot become involved in the π bonding.

b) The hexagon of benzene can be regarded as being made up of 6 equilateral triangles and thus the radius of the ring is equal to the length along one edge.

$$r_b = 1.50 \times 10^{-8}\ \text{cm}$$

For the chlorophyll core which is being approximated by a dodecagon, the ring can be regarded as being made up of 12 isosceles triangles

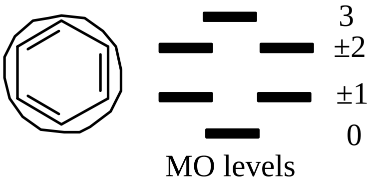


with the internal angle at the centre of each triangle thus being 360 °/12 = 30 ° and a base of one C-C bond length which is equal to $r_b = 1.50 \times 10^{-8}$ cm. Dividing the isosceles triangle in half so that it is made up of two right triangles, we thus have:

$$\sin(30^\circ/2) = \frac{a}{r_c}$$

$$\therefore r_c = \frac{\frac{1}{2} r_b}{\sin(15^\circ)} \approx \frac{\frac{1}{2} r_b}{0.25} = 2r_b = 3.00 \times 10^{-8}\ \text{cm}$$

c) Recall that each atomic orbital will be transformed into a molecular orbital. Thus from the six atomic centres donating an electron each to the π system of benzene we will generate six molecular orbitals. From the 18 atomic centres involved in the chlorophyll core we will similarly generate 18 molecular orbitals. To obtain a crude estimate of where the molecular orbitals are with respect to each other, the following scheme works quite well. Inscribe a circle around the atomic framework which involves the π system being sure that a single vertex is at the lowest point of the circle. Each vertex of the system will map onto a molecular orbital, some of which will be at the same level (i.e. will be degenerate). Thus for benzene we obtain 6 orbitals, two sets of which are degenerate. The lower three are the bonding molecular orbitals and the upper three are anti-bonding orbitals. The π-electrons are placed into the orbitals according to Hund's rule to arrive at the ground-state configuration of the molecule. A similar operation with the chlorophyll core will lead to nine bonding (one lowest level and four degenerate pairs) and nine anti-bonding orbitals (four degenerate pairs and one at the highest level).



For benzene the 6 electrons will be placed in the lowest three MO's and thus the HOMO will be that involving *l* = ±1. For chlorophyll, the 18 electrons will fully fill up to and including the orbital having *l* = ±4.

Benzene HOMO *l* = ±1: $E_{\pm1} = \dfrac{\hbar^2}{2mr_b^{\,2}}$

Chlorophyll HOMO *l* = ±4: $E_{\pm4} = \dfrac{\hbar^2 4^2}{2mr_c^{\,2}} = \dfrac{16\hbar^2}{2m(2r_b)^2} = \dfrac{16\hbar^2}{8mr_b^{\,2}} = \dfrac{2\hbar^2}{mr_b^{\,2}}$

d) Benzene LUMO *l* = ±2: $E_{\pm2} = \dfrac{\hbar^2 2^2}{2mr_b^{\,2}} = \dfrac{4\hbar^2}{2mr_b^{\,2}}$

Chlorophyll LUMO *l* = ±5: $E_{\pm5} = \dfrac{\hbar^2 5^2}{2mr_c^{\,2}} = \dfrac{25\hbar^2}{2m(2r_b)^2} = \dfrac{25\hbar^2}{8mr_b^{\,2}}$

e) Benzene: $\Delta E_{abs} = E_2 - E_1 = \dfrac{4\hbar^2}{2mr_b^{\ 2}} - \dfrac{\hbar^2}{2mr_b^{\ 2}} = \dfrac{3\hbar^2}{2mr_b^{\ 2}} = \dfrac{12\hbar^2}{8mr_b^{\ 2}}$

Chlorophyll: $\Delta E_{abs} = E_5 - E_4 = \dfrac{25\hbar^2}{2mr_c^{\ 2}} - \dfrac{16\hbar^2}{2mr_c^{\ 2}} = \dfrac{9\hbar^2}{2mr_c^{\ 2}} = \dfrac{9\hbar^2}{8mr_b^{\ 2}}$

Thus ΔE_{abs} (chlorophyll) is predicted to be less than ΔE_{abs} (benzene) by a factor of 12:9 whereas the observed ratio is 2:1 (or 12:6).

In chlorophyll, the C-C-C path is actually longer than the direct C-C distance determined above. The effective distance is actually about $\sqrt{2}$ x r_c. Thus reworking the above relationship gives:

$$\Delta E_{abs} = E_5 - E_4 = \frac{25\hbar^2}{2m(\sqrt{2}r_c)^2} - \frac{16\hbar^2}{2m(\sqrt{2}r_c)^2} = \frac{9\hbar^2}{2m(\sqrt{2}r_c)^2} = \frac{9\hbar^2}{4m(r_c)^2} = \frac{9\hbar^2}{16mr_b^{\ 2}}$$

Thus ΔE_{abs}(chlorophyll) is again predicted to be less than ΔE_{abs}(benzene) but now by a factor of about 12:4.5 which agrees much better with the experimental value of 12:6. (Closer agreement is obtained with a more detailed analysis of the two systems — the assumptions made in this question are very crude.)

f) From Hund’s rule the electrons will go into the orbitals in an unpaired manner until required to form pairs. The $l_{\pm 4}$ orbital is degenerate but will be completely filled with the last of the 18 electrons. The resulting species will have S = 0 and will be diamagnetic.

SOLUTION 38

a) $2\ Mn^{2+}(aq) + O_2(aq) + 4OH^-(aq) \rightarrow 2\ MnO_2(s) + 2H_2O$

$MnO_2(s) + 4H^+(aq) + 2I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O$

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

b) $n(S_2O_3^{2-}) = (9.75 \times 10^{-3}$ mol/L) (0.02753 L)

$= 2.68 \times 10^{-4}$ mol

ratio of $O_2 = S_2O_3^{2-}$ is 1:4

moles of $O_2 = \dfrac{2.68 \times 10^{-4}}{4}$ mol $= 6.71 \times 10^{-5}$

O_2 g/mol = 2 x 15.999 = 31.998 g/mol

O_2mol/L sample = $\dfrac{6.71 \times 10^{-5}}{0.25\text{L}}$ mol = 26.84×10^{-4} mol

O_2 g/L = 2.684×10^{-5} mol/L x 31.998 g/mol

= 0.008588 g/L

= 8.59 mg/L

= 8.59 ppm

SOLUTION 39

a) First, correcting for the dilution of the aliquot during the second measurement.

Corrected absorbance = $0.517 \times \dfrac{26.0}{25.0} = 0.538$

Absorbance due to 0.05 mg of phosphate = 0.538 - 0.428 = 0.110

b) mg phosphate in the aliquot of specimen = $\dfrac{0.428}{0.110} \times 0.05 = 0.195$ mg

c) Concentration of phosphate in the patient’s urine

$= \dfrac{100}{25.0} \times 0.195 \times \dfrac{1}{5.00} = 0.156$ mg/mL

= 0.156 mg/mL x 1000 mL/L

= 156 mg/L phosphate

d) No matrix effect; greater accuracy and precision; rapid.

SOLUTION 40

a) Ligand to cation ratio

From the graph of absorbance versus R concentration obtain a mole ratio of 3.0 and therefore the complex is CoR_3^{2+}

b) Formation constant

Stoichiometry where lines intersect indicates the following :

$Co(II) + 3\ R \leftrightarrow CoR_3^{2+}$

formation constant $K_f = \dfrac{[CoR_3^{2+}]}{[Co(II)][R]^3}$

at A_1, $Co(II) = CoR_3^{2+} = 2.5 \times 10^{-5}$ mol/L

$R = 7.5 \times 10^{-5}$ mol/L

therefore $K_f = \dfrac{2.5 \times 10^{-5}}{(2.5 \times 10^{-5})(7.5 \times 10^{-5})^3} = 2.37 \times 10^{-12}$

SOLUTION 41

a) The solubility product K_{sp} of lead chromate at 18 ˚C is 1.77×10^{-14}.

The dissolution of lead chromate is represented by the following equation:

$$PbCrO_4(s) \rightarrow Pb^{2+} + CrO_4^{2-}$$

Therefore, in pure water, the solubility of lead chromate is equal to the concentration of either the Pb^{2+} or the CrO_4^{2-} in a saturated salt solution.

Therefore,

$Pb^{2+} = CrO_4^{2-} = S_{PbCrO_4} = 1.33 \times 10^{-7}$ mol/L ($\sqrt{k_{sp}}$)

b) In such a solution, the solubility of lead chromate is no longer equal to the concentration of chromate ions since a large part of these ions are provided by potassium chromate. However, its solubility is equal to the concentration of lead ions all provided by lead chromate.

Therefore,

$S_{PbCrO_4} = S_{Pb^{2+}} = \dfrac{k_{spPbCrO_4}}{[CrO_4^{2-}]} = \dfrac{1.77 \times 10^{-14}}{0.1} = 1.77 \times 10^{-13}$

Note: There are two sources of chromate ions in solution.

Therefore, some of the lead chromate will precipitate from solution.

c) $$S_{PbCrO_4} = CrO_4^{2-} = \frac{k_{spPbCrO_4}}{3.00 \text{ x } 10^{-7} + [CrO_4^{2-}]} = \frac{1.77 \text{ x } 10^{-14}}{3.00 \text{ x } 10^{-7} + [CrO_4^{2-}]}$$

$= 0.505 \text{ x } 10^{-7}$ mol/L

SOLUTION 42

Balance the reaction:

$Fe^{+2} \rightarrow Fe^{+3}$	$MnO_4^- \rightarrow Mn^{2+}$.
$Fe^{+2} \rightarrow Fe^{+3} + 1e^-$	$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$5\,(Fe^{+2} \rightarrow Fe^{+3} + 1e^-)$

$1\,(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$

Overall

$5\,Fe^{+2} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+3} + Mn^{2+} + 4H_2O$

Calculate moles of Fe from the titration:

moles of Fe in sample 1:

= (0.00749 L $KMnO_4$) (0.0592 M $KMnO_4$) (5 mol Fe / 1 mol $KMnO_4$)

= $2.217 \text{ x } 10^{-3}$ mol Fe

Calculate weight percent Fe_2O_3 contained in the ore:

wt Fe_2O_3 sample 1 = ($2.217 \text{ x } 10^{-3}$ mol Fe) (1 mol Fe_2O_3 / 2 mol Fe) (2(55.847))

+ 3(15.9994) g Fe_2O_3 / mol Fe_2O_3) = 0.1770 g Fe_2O_3

wt % Fe_2O_3 sample 1 = 100 (0.1770 g Fe_2O_3 / 0.500 g ore) = 35.4 % Fe_2O_3

SOLUTION 43

Calculate grams of cleaner titrated:

(10.000 g / (10.000 g +90.012 g)) (5.000 g) = 0.4999 grams solution

Calculate moles of NH_3 from titration:

moles HCl used = moles NH_3 present = (0.04211 L) (0.05042 M) = 2.123×10^{-3} mol

Determine grams of NH_3 from molecular weight:

(2.123×10^{-3} mol NH_3) (14.0067 + 3 (1.00797) g /mol) = 3.616×10^{-2} g NH_3

Determine percent NH_3 in titrated sample:

wt % NH_3 = 100 (3.616×10^{-2} g NH_3 / 0.4999 g solution) = 7.233 %

SOME SPECIFIC COMMENTS ON THE EXPERIMENTAL PROBLEMS

PROBLEM 45 - EXPERIMENTAL

Determination of Lead Ions by Back Titration with EDTA

1) The pH 10 buffer must be an ammonium buffer.
2) Sufficient buffer must be added to ensure that the pH does not fall during the titration.

Sample Calculations:

i) 10.00 mL Mg^{2+} standard solution required 17.00 mL EDTA solution:

$$\frac{1.00\text{ mg Mg}^{2+}}{1.00\text{ mL Mg}^{2+}} \times \frac{10.00\text{ mL Mg}^{2+}}{17.00\text{ mL EDTA}} \times \frac{1000\text{ mL EDTA}}{1\text{ L EDTA}} \times \frac{1\text{ mole Mg}^{2+}}{24.31 \times 10^{3}\text{ mg Mg}^{2+}} \times \frac{1\text{ mole EDTA}}{1\text{ mole Mg}^{2+}}$$
$$= 2.42 \times 10^{-2}\text{ M EDTA}$$

ii) 10.00 mL Pb^{2+} solution and 25.00 mL EDTA solution required 11.00 mL Mg^{2+} standard solution:

moles EDTA = moles Mg^{2+} + moles Pb^{2+}

$$25.00\text{ mL EDTA} \times \frac{2.42 \times 10^{-2}\text{ mol EDTA}}{1000\text{ mL}} = 6.05 \times 10^{-4}\text{ mol EDTA}$$

$$11.00\text{ mL Mg}^{2+} \times \frac{1.00\text{ mg Mg}^{2+}}{1.00\text{ mL Mg}^{2+}} \times \frac{\text{mol Mg}^{2+}}{24.31 \times 10^{3}\text{ mg Mg}^{2+}} = 4.52 \times 10^{-4}\text{ mol Mg}^{2+}$$

moles Pb^{2+} = moles EDTA - moles Mg^{2+} = 1.53×10^{-4} mol Pb^{2+}

$$\frac{1.53 \times 10^{-4}\text{ mol Pb}^{2+}}{0.010\text{ L Pb}^{2+}\text{ sol'n}} = 1.53 \times 10^{-2}\text{ M Pb}^{2+}$$

PROBLEM 47 - EXPERIMENTAL

Determination of the K_{sp} of $CaSO_4$

Note that each Ca^{2+} displaces two H^+ from the column:

$$K_{sp}\ (CaSO_4) = [Ca^{2+}]\,[SO_4^{2-}]$$

$$[Ca^{2+}] = \frac{\text{moles } Ca^{2+}}{0.0010\ \text{L solution}}$$

$$\text{moles } Ca^{2+} = 0.5\ \text{moles } H^+ \text{ from titration}$$

PROBLEM 48 - EXPERIMENTAL

Ritter Reaction

The product is N-tert-butyl benzamide. See *Journal of Chemical Education*, Vol 71, 1994, pages A200-202.

PROBLEM 50 - EXPERIMENTAL

Synthesis and Identification of an Organic Compound

Compound **A**: 2,5-furandione (maleic anhydride)
Compound **B**: butanedioic acid (succinic acid)

Data Sheet/Fiche de données

	Symbol Symbole	Value Quantité numérique	
Atomic mass unit	amu	1.66054×10^{-27} kg	Unité de masse atomique
Avogadro's number	N	6.02214×10^{23} mol^{-1}	Nombre d'Avogadro
Bohr radius	a_0	5.292×10^{-11} m	Rayon de Bohr
Boltzmann constant	k	1.38066×10^{-23} J K^{-1}	Constante de Boltzmann
Charge of an electron	e	1.60218×10^{-19} C	Charge d'un électron
Dissociation constant (H_2O)	K_w	10^{-14} (25 ˚C)	Constante de dissociation de l'eau (H_2O)
Faraday's constant	F	96,485 C mol^{-1}	Constante de Faraday
Gas constant	R	8.31451 J K^{-1} mol^{-1} 0.08206 L atm K^{-1} mol^{-1}	Constante des gaz
Mass of an electron	m_e	9.10939×10^{-31} kg 5.48580×10^{-4} amu	Masse d'un électron
Mass of a neutron	m_n	1.67493×10^{-27} kg 1.00866 amu	Masse d'un neutron
Mass of a proton	m_p	1.67262×10^{-27} kg 1.00728 amu	Masse d'un proton
Planck's constant	h	6.62608×10^{-34} J s	Constante de Planck
Speed of light	c	2.997925×10^{8} m s^{-1}	Vitesse de la lumière

1 Å = 1×10^{-8} cm

1 eV = 1.60219×10^{-19} J

1 cal = 4.184 J

1 atm = 101.325 kPa

1 bar = 1×10^{5} Pa

This set of preparatory problems was prepared using a Macintosh Centris 610 with Word (version 5.1a from Microsoft) and ChemIntosh (version 3.4.4 from SoftShell International). The fonts used are Times and Symbol (both from Adobe).

An electronic version of these preparatory problems is available by sending a disk to the address below. The file will be provided as a self-extracting StuffIt archive in a Macintosh format. The compressed file is approximately 400 K. The expanded file is approximately 1.8 Meg. Electronic mail transfer of the file is also possible. If this route is chosen, it is strongly recommended that the recipient use Eudora or another mail programme which is capable of receiving and decoding attached files which have been Binhexed.

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