

**29th INTERNATIONAL CHEMISTRY  
OLYMPIAD**

**PREPARATORY PROBLEMS**

**Montréal and Lennoxville, Québec, Canada**

**July 13 - 22, 1997**

*Funding for the printing of this collection of preparatory problems was generously provided by the Department of Chemistry of the University of British Columbia.*

**Authors of the Preparatory Problems of  
the  
29th International Chemistry Olympiad**

André Bandrauk	Université de Sherbrooke
Gordon Bates	University of British Columbia
Suzanne Black	McGill University
David Burns	McGill University
Robert Cook	Bishop's University
Jean-Pierre Farant	McGill University
François Gauvin	Bishop's University
Michael Gresser	Merck-Frosst Canada
John Harrod	McGill University
Gregory Jerkiewicz	Université de Sherbrooke
Normand Voyer	Université Laval
Harold Wilson	John Abbot College

## Preparatory Problem Index

### Physical Chemistry

- Problem 1: Solid state
- Problem 2: Electrochemistry and the solid state
- Problem 3: Electrochemistry
- Problem 4: Electrochemistry
- Problem 5: Electrochemistry

### Biochemistry

- Problem 6: Carbohydrate reactions and conformations
- Problem 7: Carbohydrate structural analysis (unknown determination)
- Problem 8: Carbohydrate structural analysis (unknown determination)
- Problem 9: Carbohydrate reactions and conformations
- Problem 10: Carbohydrate structural analysis (unknown determination)

### Organic Chemistry

- Problem 11: Mechanism (alternate ester formation reactions)
- Problem 12: Mechanism (carbonyl reaction; thermodynamics vs. kinetics)
- Problem 13: Organic synthesis
- Problem 14: Structural analysis (unknown determination)
- Problem 15: Mechanism (nucleophilic acyl substitution; nucleophilic displacement)
- Problem 16: Mechanism (nucleophilic displacement)
- Problem 17: Mechanism (nucleophilic displacement vs. elimination)
- Problem 18: Mechanism (electrophilic aromatic substitution)
- Problem 19: Qualitative analysis (functional group determinations)
- Problem 20: Structural analysis (unknown determination)
- Problem 21: Mechanism (nucleophilic displacement vs. elimination)
- Problem 22: Structural analysis (unknown determination)
- Problem 23: Structural analysis (unknown determination)

### Inorganic Chemistry

- Problem 24: Processes involved in the formation of teeth and bones
- Problem 25: Structural analysis (unknown determination)
- Problem 26: Silicon carbide preparations
- Problem 27: Silicon vs. phosphorus oxides
- Problem 28: High  $T_c$  superconductors
- Problem 29: NO chemistry
- Problem 30: Inorganic complexes

### **Physical/Theoretical**

- Problem 31: Thermodynamic relationships
- Problem 32: Thermodynamics of phase changes
- Problem 33: Thermodynamics of chemical reactions
- Problem 34: Gas phase kinetics
- Problem 35: Solution phase kinetics
- Problem 36: Molecular orbital theory
- Problem 37: Molecular orbital theory

### **Analytical Chemistry**

- Problem 38: Dissolved oxygen by titration
- Problem 39: Phosphate determination by absorbance spectroscopy
- Problem 40: Ligand complexes and  $K_f$  by absorbance spectroscopy
- Problem 41: Lead pollution monitoring (solubility product)
- Problem 42: Redox titration
- Problem 43: Dissolved ammonia by titration

### **Experimental Chemistry**

- Problem 44: Qualitative organic analysis
- Problem 45: Lead concentration by back titration with EDTA
- Problem 46: Qualitative inorganic analysis (electrochemistry)
- Problem 47:  $K_{sp}$  determination by titration
- Problem 48: Organic synthesis (Ritter reaction)
- Problem 49: Organic synthesis ( $\text{NaBH}_4$  reduction)
- Problem 50: Organic synthesis and unknown identification

## 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 $H_2N_2O_2$ , $HN_3$ to remember, what are products of reduction of nitrates	3
52	of $HNO_3$ with different metals and reductants	3
53	reaction of $Na_2S_2O_3$ with iodine	2
54	other thioacids, polyacids, peroxyacids $B(III)$ , $Al(III)$ , $Si(IV)$ , $P(V)$ , $S(IV)$ , $S(VI)$ , $O(II)$ , $F(I)$ , $Cl(I)$ , $Cl(III)$ , $Cl(V)$ and $Cl(VIII)$ are normal oxidation states of 2nd and 3rd row elements in compounds	3
55	with halogens and in oxoanions	1
56	compounds of nonmetals with other oxidation states	3
57	the preferred oxidation states are $Sn(II)$ , $Pb(II)$ , $Bi(III)$ products of reactions of nonmetal oxides with water and stoichiometry	2
58	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		
	common oxidation states of the common d-block metals are $Cr(III)$ , $Cr(VI)$ , $Mn(II)$ , $Mn(IV)$ , $Mn(VII)$ , $Fe(II)$ , $Fe(III)$ , $Co(II)$ , $Ni(II)$ , $Cu(I)$ , $Cu(II)$ ,	
62	$Ag(I)$ , $Zn(II)$ , $Hg(I)$ , $Hg(II)$	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 $Al$ ) $Cr(OH)_3$ and $Zn(OH)_2$ amphoteric, other common hydroxides are not	2
68	$MnO_4^-$ , $CrO_4^{2-}$ , $Cr_2O_7^{2-}$ are strong oxidants	1
69	products of reduction of $MnO_4^-$ depending on pH	2
70	polyanions other than $Cr_2O_7^{2-}$	3
OTHER INORGANIC PROBLEMS		
71	industrial production of $H_2SO_4$ , $NH_3$ , $Na_2CO_3$ , $Na$ , $Cl_2$ , $NaOH$	1
72	chemistry of lanthanides and actinides	3
73	chemistry of noble gases	3

## **ORGANIC CHEMISTRY**

### **ALKANES**

74 isomers of butane

1

75 naming (IUPAC)

1

76	trends in physical properties	1
	substitution (e.g. with Cl <sub>2</sub> )	
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 <sub>2</sub> , 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 <sub>3</sub>	2
126	of NH <sub>2</sub> OH	2
127	- aldol condensation	3
128	- Cannizzaro (PhCH <sub>2</sub> OH disproportionation)	3
129	- Grignard reaction	2
130	- Fehling (Cu <sub>2</sub> O) and Tollens (Ag mirror)	2
<b>CARBOXYLIC ACIDS</b>		
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
<b>NITROGEN COMPOUNDS</b>		
148	amines are basic	1
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	
152	- from halogen compounds	2
153	- from nitro compounds (PhNH <sub>2</sub> from PhNO <sub>2</sub> )	3
154	- from amides (Hoffmann)	3
155	mechanism of Hoffmann rearrangement in acidic/basic medium	3
156	basicity amines vs. amides	2
	diazotation products	
157	- of aliphatic amines	3
158	- of aromatic amines	3
159	dyes: color vs. structure (chromophore groups)	3
160	nitro compounds : aci/nitro tautomerism	3
161	Beckmann (oxime - amide) rearrangements	3
<b>SOME LARGE MOLECULES</b>		
162	hydrophilic/hydrophobic groups	2
163	micelle structure	3
164	preparation of soaps	1

165	products of polymerization of	
	- 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**

### **AMINO ACIDS AND PEPTIDES**

174	ionic structure of aminoacids	1
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

### **PROTEINS**

182	primary structure of proteins	1
183	-S-S- bridges	3
184	sequence analysis	3
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

### **FATTY ACIDS AND FATS**

197	IUPAC names from C <sub>4</sub> to C <sub>18</sub>	2
198	trivial 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**

205	general properties, active centres	2
206	nomenclature, kinetics, coenzymes, function of ATP etc.	3

### **CARBOHYDRATES**

207	glucose and fructose: chain formulas	2
208	- Fischer projections	2

209	- Haworth formulas	3
210	osazones	3
211	maltose as reducing sugar	2

212	difference between starch and cellulose	2
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
219	detailed Calvin cycle	3
<b>KREBS CYCLE AND RESPIRATION CHAIN</b>		
220	formation of CO <sub>2</sub> in the cycle (no details)	3
221	intermediate compounds in the cycle	3
222	formation of water and ATP (no details)	3
223	FMN and cytochromes	3
224	calculation of ATP amount for 1 mol glucose	3
<b>NUCLEIC ACIDS AND PROTEIN SYNTHESSES</b>		
225	pyrimidine, purine	2
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
<b>OTHER BIOCHEMISTRY</b>		
241	hormones, regulation	3
242	hormone feedback	3
243	insulin, glucagon, adrenaline	3
244	mineral metabolism (no details)	3
245	ions in blood	3
246	buffers in blood	3
247	haemoglobin: function & skeleton	3
248	- diagram of oxygen absorption	3
249	steps of clotting the blood	3
250	antigens and antibodies	3
251	blood groups	3
252	acetyl choline structure and functions	3
<b>INSTRUMENTAL METHODS OF DETERMINING STRUCTURE</b>		
<b>UV-VIS SPECTROSCOPY</b>		
253	identification of aromatic compound	3
254	identification of chromophore	3

<b>MASS SPECTRA</b>	
255	recognition of molecular ion 3
256	- fragments with a help of a table 3
257	- typical isotope distribution 3
<b>INFRARED</b>	
258	interpretation using a table of group frequencies 3
259	recognition of hydrogen bonds 3
260	Raman spectroscopy 3
<b>NMR</b>	
261	interpret. of simple spectrum (like ethanol) 3
262	spin-spin coupling 3
263	coupling constants 3
264	identification of o- and p- substituted benzene 3
265	<sup>13</sup> C-NMR 3
<b>X-RAYS</b>	
266	Bragg law 3
267	electron density diagrams 3
268	coordination number 3
269	unit cell 3
270	structures of NaCl 3
271	structures of CsCl 3
272	- close-packed (2 types) 3
273	determining of the Avogadro constant from X-ray data 3
<b>POLARIMETRY</b>	
274	calculation of specific rotation angle 3
<b>PHYSICAL CHEMISTRY</b>	
<b>CHEMICAL EQUILIBRIA</b>	
275	dynamical model of chemical equilibrium 1
	chemical equilibria expressed in terms of
276	- relative concentration 1
277	- relative partial pressures 2
	the relationship between e.c. for ideal gases
278	expressed in different ways (concentration, pressure, mole fraction) 2
279	relation of equilibrium constant and standard Gibbs energy 3
<b>IONIC EQUILIBRIA</b>	
280	Arrhenius theory of acids and bases 1
281	Bronsted-Lowry theory, conjugated acids & bases 1
282	definition of pH 1
283	ionic product of water 1
284	relation between $K_a$ and $K_b$ for conjugated acids and bases 1
285	hydrolysis of salts 1
286	solubility product - definition 1
287	calculation of solubility (in water) from solubility product 1
288	calculation of pH for weak acid from $K_a$ 1
289	calculation of pH for $10^{-7}$ mol/dm <sup>3</sup> HCl 2
290	calculation of pH for multiprotic acids 2
291	definition of activity coefficient 2
292	definition of ionic strength 3



ELECTRODE EQUILIBRIA		
294	electromotive force (definition)	1
295	first kind electrodes	1
296	standard electrode potential	1
297	Nernst equation	2
298	second kind electrodes	2
299	relation between $\Delta G$ and electromotive force	3
KINETICS OF HOMOGENEOUS REACTION		
300	factors influencing reaction rate	1
301	rate equation	1
302	rate constant	1
303	order of reaction	2
304	1st order reactions: time dependence of concentration	2
305	- half life	2
306	- relation between half-life and rate constant	2
307	rate-determining step	2
308	molecularity	2
309	Arrhenius equation, activation energy (definition)	2
310	calculation of rate constant for first order reaction	2
311	calculation of rate constant for second, third order reaction	3
312	calculation of activation energy from experimental data	3
313	basic concepts of collision theory	3
314	basic concepts of transition state theory	3
315	opposing, parallel and consecutive reactions	3
THERMODYNAMICS		
316	system and its surroundings	2
317	energy, heat and work	2
318	relation between enthalpy and energy	2
319	heat capacity - definition	2
320	difference between $C_p$ and $C_v$	3
321	Hess law	2
322	Born-Haber cycle for ionic compounds	3
323	lattice energies - approximate calculation (e.g. Kapustinski equation)	3
324	use of standard formation enthalpies	2
325	heats of solution and solvation	2
326	bond energies - definition and uses	2
SECOND LAW		
327	entropy - definition ( $q/T$ )	2
328	entropy and disorder	2
329	relation $S=k \ln W$	3
330	relation $\Delta G = \Delta H - T \Delta S$	2
331	$\Delta G$ and directionality of changes	2
PHASE SYSTEMS		
332	ideal gas law	1
333	van der Waals gas law	3
334	definition of partial pressure	1
335	temperature dependence of the vapour pressure of liquid	2
336	Clausius-Clapeyron equation	3
337	reading phase diagram: triple point	3

338	- critical temperature	3
339	liquid-vapour system (diagram)	3
340	- ideal and non ideal systems	3

341	- use in fractional distillation	3
342	Henry's law	2
343	Raoult's law	2
344	deviations from Raoult law	3
345	boiling point elevation law	2
346	freezing-point depression, determination of molar mass	2
347	osmotic pressure	2
348	partition coefficient	3
349	solvent extraction	2
350	basic principles of chromatography	2

## OTHER PROBLEMS

### ANALYTICAL CHEMISTRY

351	using pipet	1
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: $\text{Ag}^+$ , $\text{Ba}^{2+}$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ ions	1
358	- of $\text{Al}^{3+}$ , $\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{Bi}^{3+}$ ions	2
359	- of $\text{VO}_3^-$ , $\text{ClO}_3^-$ , $\text{Ti}^{4+}$ ions	3
360	- using flame test for K, Ca, Sr	1
361	Beer-Lambert law	2

### COMPLEXES

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 $\text{AgCl}$ in $\text{NH}_3$ (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: $\text{H}_2$ molecule	3
372	molecular orbital diagram: $\text{N}_2$ or $\text{O}_2$ molecule	3
373	bond orders in $\text{O}_2$ or $\text{O}_2^+$ or $\text{O}_2^-$	3
374	Hückel theory for aromatic compounds	3
375	Lewis acids and bases	2
376	hard and soft Lewis acids	3
377	unpaired electrons and paramagnetism	2
378	square of the wave function and probability	3
379	understanding the simplest Schrodinger equation	3



**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 ( $\theta$ ) of  $10.89^\circ$  it gives a well-defined first-order diffraction pattern. The atomic weight of Au is  $M_{\text{Au}} = 196.97$  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?

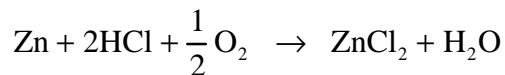
**PROBLEM 2**

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  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_4$ ; the molar concentrations of the salts are  $c_{\text{CuSO}_4} = 0.100$  mM and  $c_{\text{Na}_2\text{SO}_4} = 0.100$  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  $4.077 \times 10^{-8}$  cm.

What is the concentration of  $\text{CuSO}_4$  in the electrolyte after deposition of the Cu epitaxial layer?

**PROBLEM 3**

Pure zinc is in contact with well oxygenated ( $P_{\text{O}_2} = 1.000$  atm) aqueous solution containing HCl and  $\text{ZnCl}_2$ ; the concentrations of HCl and  $\text{ZnCl}_2$  are  $c_{\text{HCl}} = 1.000$  M and  $c_{\text{ZnCl}_2} = 1.000$  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.



- 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 cm<sup>3</sup> of Ni<sup>2+</sup> solution of unknown concentration and Cu is in contact with 100 cm<sup>3</sup> of 0.010 M Cu<sup>2+</sup> solution. The two solutions are connected by a salt bridge and the potential of this cell is measured with the precision of 0.01 mV. The temperature of the system is 25.00 °C. A certain amount of CuCl<sub>2</sub> is added to the solution of Cu<sup>2+</sup> and the potential of the cell increases 9.00 mV upon the addition; the volume change associated with the addition of CuCl<sub>2</sub> can be neglected. The molecular weight of CuCl<sub>2</sub> 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<sub>2</sub> added?

**PROBLEM 5**

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

- What is the concentration of the cations (Cu<sup>2+</sup> and Zn<sup>2+</sup>) in the respective compartments after the discharge?
- 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:

- Cu<sup>2+</sup> (buffer pH >7)
- Br<sub>2</sub>, H<sub>2</sub>O (pH = 6)
- HNO<sub>3</sub>
- CH<sub>3</sub>OH, dry HCl
- product of d) + (CH<sub>3</sub>)<sub>2</sub>SO<sub>2</sub>, NaOH

- f) 1) NaBH<sub>4</sub> 2) H<sub>2</sub>O
- g) 5 HIO<sub>4</sub>
- h) excess acetic anhydride in pyridine
- i) 3 moles of phenylhydrazine, H<sup>+</sup>
- j) 1) Br<sub>2</sub>/H<sub>2</sub>O 2) Fe(III) sulfate, H<sub>2</sub>O<sub>2</sub>
- k) 1) HCN 2) Ba(OH)<sub>2</sub> 3) H<sub>3</sub>O<sup>+</sup> 4) Na-Hg, H<sub>2</sub>O, 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)<sub>2</sub> gives two epimeric aldonic acids **B** and **C**. These aldonic acids are in equilibrium with their respective  $\gamma$ -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<sub>12</sub>H<sub>22</sub>O<sub>12</sub>) gives a negative test with Benedict's solution and does not mutarotate. **A** is hydrolyzed by  $\alpha$ -glucosidases but not by  $\beta$ -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  $\alpha$  and  $\beta$  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.

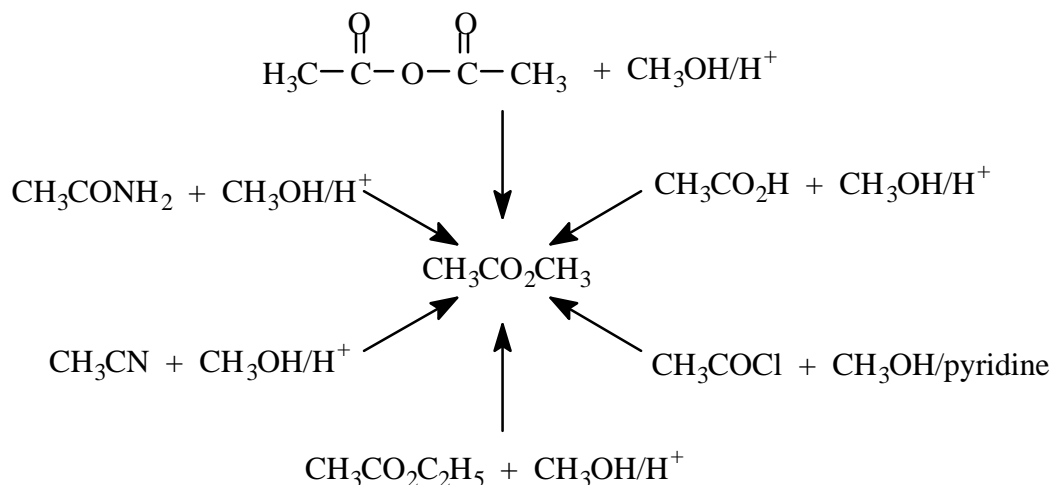
### PROBLEM 10

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  $\alpha$ -galactosidase isolated from almonds.

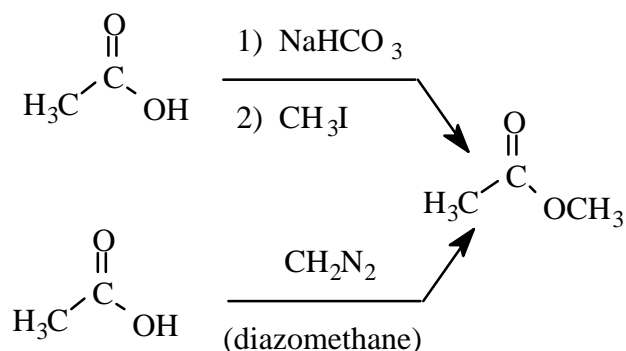
Give structures for **A**, **B**, **C** and **D**.

### 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.

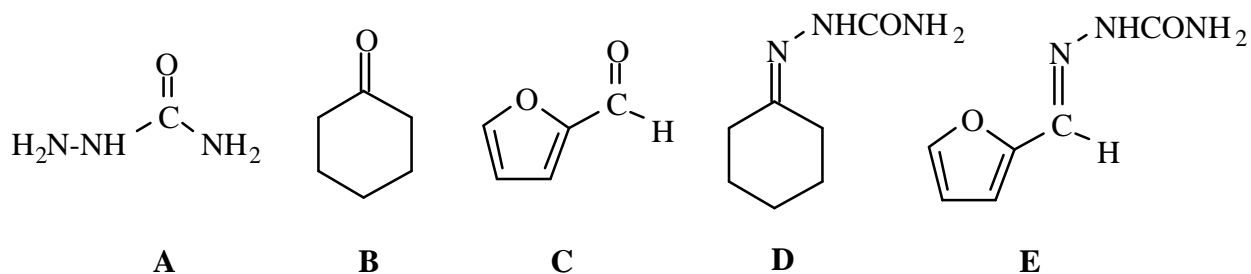


However, other synthetic variations are also known. Two mechanistically closely related reactions are shown below. Outline the mechanisms of these latter two processes.



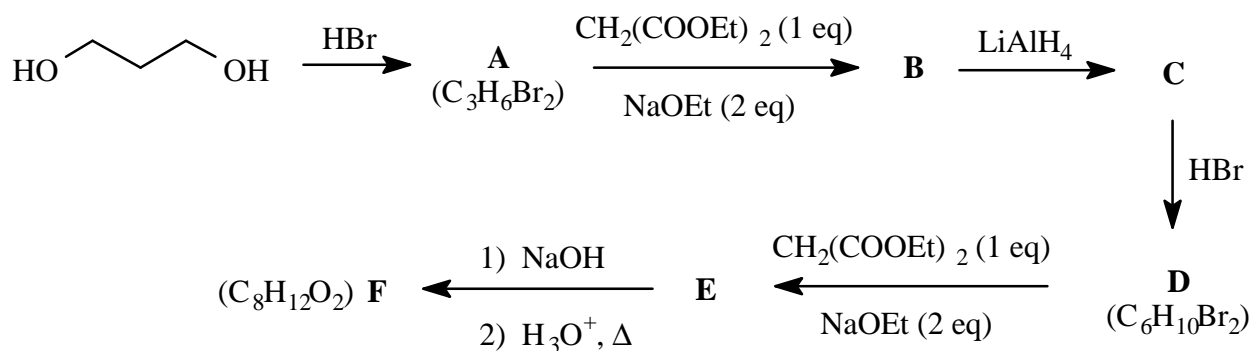
### PROBLEM 12

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.



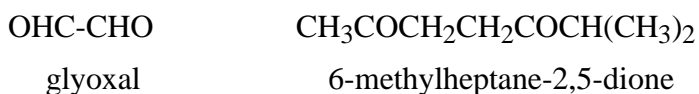
### PROBLEM 13

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



**PROBLEM 14**

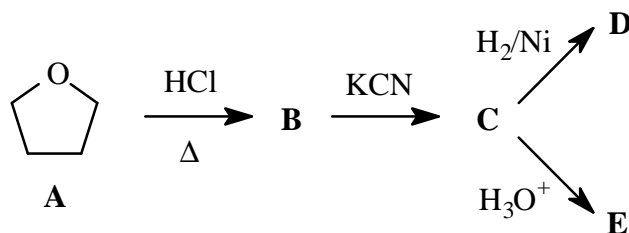
$\alpha$ -Terpinene is a natural oil isolated from turpentine as well as from oil of marjorum and other sources. Its formula is  $C_{10}H_{16}$ . It can be hydrogenated over a palladium catalyst and absorbs two molar equivalents of hydrogen to yield a new hydrocarbon,  $C_{10}H_{20}$ . Upon ozonolysis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



- a) How many degrees of unsaturation does  $\alpha$ -terpinene possess?
- b) How many double bonds does  $\alpha$ -terpinene possess?
- c) How many rings does  $\alpha$ -terpinene possess?
- d) Propose a structure for  $\alpha$ -terpinene consistent with the above information.

**PROBLEM 15**

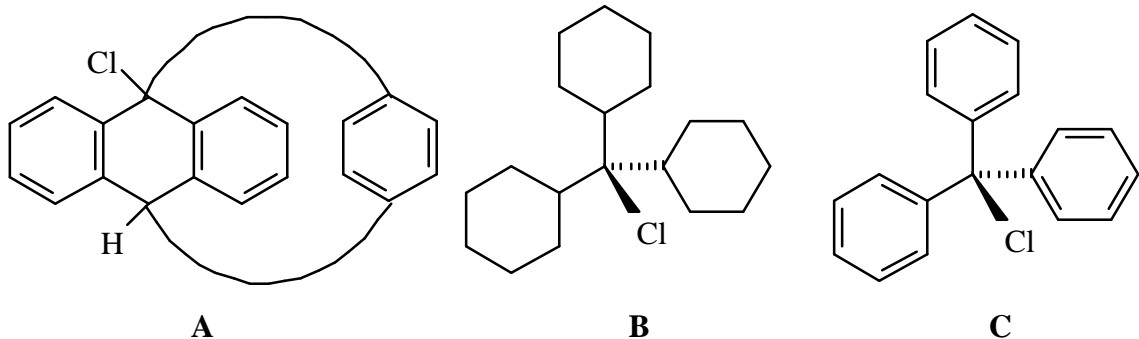
Two useful precursors (**D** and **E**) for the synthesis of a type of Nylon<sup>®</sup> are prepared from tetrahydrofuran (**A**).



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  $\text{AgNO}_3$ . Explain your reasoning.



**PROBLEM 17**

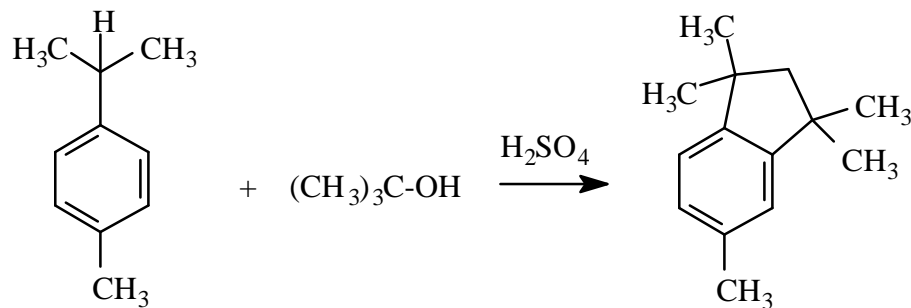
Consider the reactions of 2-bromopropane and 2-methyl-2-bromopropane with sodium ethoxide in ethanol. Which bromide would give the highest yield of alkene? Which bromide would give the highest yield of alkene on solvolysis in 60% aqueous ethanol? Explain your reasoning and write equations for all reactions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

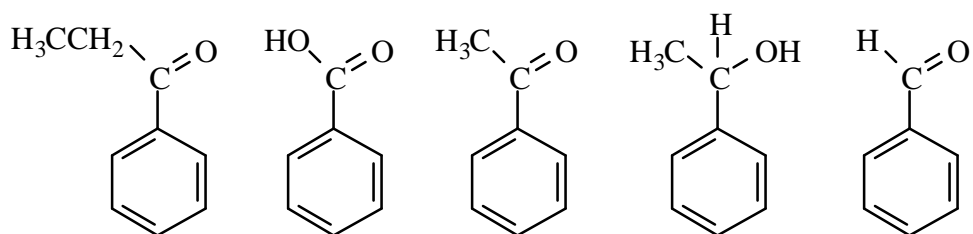
The reaction shown below is interesting from a mechanistic standpoint.

- 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.



- 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.
- When experiment (i) was repeated using 1 drop of 0.2%  $\text{KMnO}_4$  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.

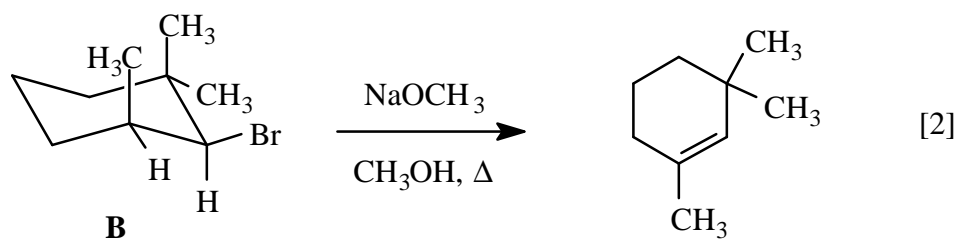
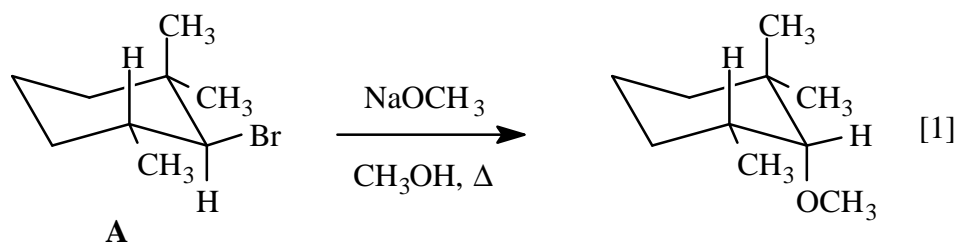
Compound **B** formed a diketone (**E**) which did not contain any chiral carbon atoms.

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  $\text{NaSCH}_3$  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  $\text{LiNH}_2$  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 ( $\text{Br}_2$ , cold, in the dark) yields a racemic product, whereas the reaction with “heavy” hydrogen in the presence of a platinum catalyst (i.e.  $\text{D}_2$  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.



**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  $0\text{ }^\circ\text{C}$  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,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , 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.  
( $K_{\text{sp}}$  of hydroxyapatite =  $6.8 \times 10^{-37}$  and  $K_{\text{sp}}$  of fluoroapatite =  $1.0 \times 10^{-60}$ )
- 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?  
( $K_{\text{w}} = 1.0 \times 10^{-14}$  and  $K_{\text{a}}$  of HF =  $7.2 \times 10^{-4}$ )

### 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  $\text{HgSO}_4$  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  $\text{cm}^{-1}$ , 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  $\text{g/cm}^3$ , 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

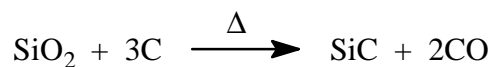
Silicon carbide (SiC) has a high thermal conductivity and a low thermal expansion. These properties make it more resistant to thermal shock than other refractory materials. It is a ceramic material that has many applications in metallurgical, abrasive and refractory industries.

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.

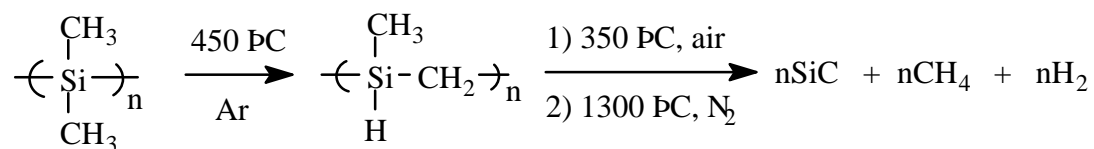
The usual commercial method for the manufacture of SiC, known as the Acheson process, involves high-temperature solid-state reactions of silica (fine grade sand) with graphite or coke in an electrical furnace. Carbon monoxide is also produced during this reaction. The silicon carbide obtained by this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

Acheson Process:



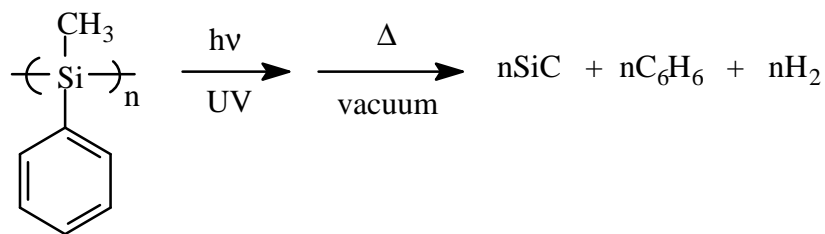
In the mid-1970's, Yajima and coworkers developed a process for the formation of silicon carbide ceramics by the thermal conversion of a low molecular weight poly(dimethylsilane) or  $[(\text{CH}_3)_2\text{Si}]_n$ . The proximity between carbon and silicon atoms in the polymer favours the formation of Si-C bonds and allows the production of silicon carbide in three simple pyrolysis steps as shown below. This process has been adapted for the commercial production of Nikalon® SiC fibers.

Yajima Process:



The poly(dimethylsilane) used by Yajima has a relatively low solubility. The first step of his process was mostly to transform it into a material that is more soluble so that it can be easily processed. A great improvement of his process would be to start with a polymer that is already soluble so that the first pyrolysis step can be avoided. West and coworkers were able to produce such a polymer by substituting a methyl group with a phenyl group to get a poly(methylphenylsilane) or  $[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si}]_n$ . 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.

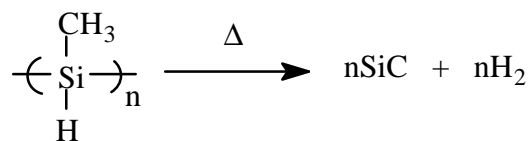
West Process:



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 ( $n = \text{ca. } 170$ ) than those resulting from the Wurtz reactions ( $n > 1000$ ). One of these polymers, poly(methylsilane) or  $[(\text{CH}_3)(\text{H})\text{Si}]_n$ , 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:



- 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  $3.21 \text{ g cm}^{-3}$  and that of diamond is  $3.51 \text{ g cm}^{-3}$ .

- b) Knowing that the shortest possible distance between two neighbouring carbon atoms is  $1.54 \times 10^{-8} \text{ cm}$  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  $1700 \text{ }^\circ\text{C}$ ; phosphorus pentoxide is a colourless solid melting at  $420 \text{ }^\circ\text{C}$ ; sulfur trioxide is a colourless gas which condenses to a liquid at about  $45 \text{ }^\circ\text{C}$  and to a crystalline solid at about  $17 \text{ }^\circ\text{C}$ .
- 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  $850\text{ }^\circ\text{C}$  in air for 12 hours. Then, they were broken, ground, pressed into disks and sintered in a stream of oxygen at  $940\text{ }^\circ\text{C}$  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  $400\text{ }^\circ\text{C}$  it begins to lose oxygen. A 10.00 g sample heated to  $500\text{ }^\circ\text{C}$  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**

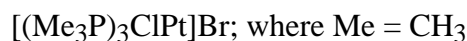
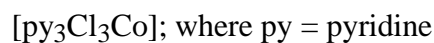
Nitric oxide (NO) is a simple molecule that has been known for a very long time and extensively studied. It recently aroused enormous new interest when it was discovered that this highly reactive, simple molecule plays a key role as a neurotransmitter in a wide range of biochemical systems. As with all 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 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  $\text{Co}^{3+}$  and  $\text{Cr}^{3+}$ . 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:



- 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  $[\text{en}_2\text{Cl}_2\text{Co}]\text{Cl}$  permitted Werner to conclude that  $\text{Co}^{3+}$  complexes have octahedral rather than some other, e.g. trigonal prismatic, coordination geometry? en = ethylenediamine which is a bridging or bidentate ligand.
- d)  $\text{CrCl}_3$  can form a series of compounds with  $\text{NH}_3$  having the general formula  $[(\text{NH}_3)_x\text{Cl}_3\text{Cr}]$  ( $x = 3$  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 ( $\text{NH}_3$  or  $\text{Cl}$ ) attached to  $\text{Cr}$  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  $2 \cdot V$  at a temperature  $T$ .
- d) Calculate the thermodynamic functions  $E$ ,  $S$ ,  $G$  for an irreversible, sudden isothermal expansion from  $V$  to  $2 \cdot V$ .
- e) From the above results, define spontaneity or irreversibility in terms of the sign of  $\Delta S$  and  $\Delta G$ .
- 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  $k = R/N_0$ ,  $W$  is the number of configurations or states available for the molecular system,  $N_0$  is Avogadro's number,  $R$  is the gas constant.

Calculate  $\Delta S$  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  $2 \cdot V$ , there are now two states available, i.e., each of volume  $V$ .

**PROBLEM 32**

- a) One mole of O<sub>2</sub>(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  $\bar{C}_p(\text{g}) = 28.2 \text{ J K}^{-1} \text{ mol}^{-1}$  and is constant over the required temperature range and that O<sub>2</sub>(g) behaves ideally.

Calculate  $q$ ,  $w$ ,  $\Delta H$ ,  $\Delta S_{\text{SYS}}$  and  $\Delta S_{\text{SURR}}$  for this process.

- b) The one mole of O<sub>2</sub>(g), now at 90K and 1 atm pressure, is liquified by application of a pressure infinitesimally greater than 1 atm. The liquid O<sub>2</sub> is then cooled at constant pressure to the normal melting point of 55K, solidified reversibly, and the solid cooled to 10K. Determine  $\Delta H_{\text{SYS}}$  and  $\Delta S_{\text{SYS}}$  for the sum of these events.

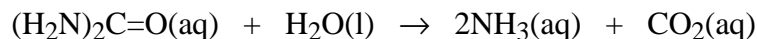
$$\bar{C}_p(\text{l}) = 54 \text{ JK}^{-1} \text{ mol}^{-1}, \bar{C}_p(\text{s}) = 41 \text{ JK}^{-1} \text{ mol}^{-1}, \Delta H^\circ_{\text{vap}} = 6.82 \text{ KJ mol}^{-1}, \Delta H^\circ_{\text{fus}} = 0.42 \text{ KJ mol}^{-1}$$

**PROBLEM 33**

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

	CO <sub>2</sub> (aq)	H <sub>2</sub> O(l)	NH <sub>3</sub> (aq)	(H <sub>2</sub> N) <sub>2</sub> C=O(aq)
$\Delta H^\circ_f$ (kJ mol <sup>-1</sup> )	-412.9	-285.8	-80.8	-317.7
$S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> )	121.0	69.9	110.0	176.0

In aqueous solution, urea ((H<sub>2</sub>N)<sub>2</sub>C=O) is hydrolysed according to the following reaction:



- a) Calculate  $\Delta G^\circ$  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:

$$[(\text{H}_2\text{N})_2\text{C}=\text{O}] = 1.0 \text{ M}; [\text{H}_2\text{O}] = 55.5 \text{ M}; [\text{CO}_2] = 0.1 \text{ M}; [\text{NH}_3] = 0.01 \text{ M}$$

**PROBLEM 34**

The gas phase decomposition of ozone ( $\text{O}_3$ ) in the presence of dioxygen ( $\text{O}_2$ ) at  $80\text{ }^\circ\text{C}$  shows complicated kinetic behaviour that depends on the relative concentrations (or pressures) of  $\text{O}_2$  and  $\text{O}_3$ .

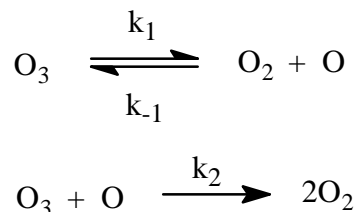
If  $[\text{O}_2] \gg [\text{O}_3]$  the rate law has the form:

$$\frac{-d[\text{O}_3]}{dt} = k_{\text{exp}} [\text{O}_3]^2 [\text{O}_2]^{-1}$$

However, if  $[\text{O}_2] \ll [\text{O}_3]$ , the decomposition follows:

$$\frac{-d[\text{O}_3]}{dt} = k'_{\text{exp}} [\text{O}_3]$$

A proposed mechanism for the reaction is:



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

- On the basis of this mechanism, and using the principle of stationary (steady) state for  $[\text{O}]$ , derive the rate equation for the decomposition of  $\text{O}_3$ . Show that this mechanism is consistent with the observed kinetic behaviour at both high and low values of  $[\text{O}_2]/[\text{O}_3]$ .
- Evaluate  $k_{\text{exp}}$  and  $k'_{\text{exp}}$  in terms of  $k_1$ ,  $k_{-1}$  and  $k_2$  for the proposed mechanism.

**PROBLEM 35**

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

$[X]_0$ (M)	$[Y]_0$ (M)	$[Z]_0$ (M)	Initial Rate $\frac{d[P]}{dt}$ (M h <sup>-1</sup> )
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:

$$[X] = 0.01 \text{ M} \quad [Y] = 1.00 \text{ M} \quad [Z] = 2.00 \text{ M}$$

**PROBLEM 36**

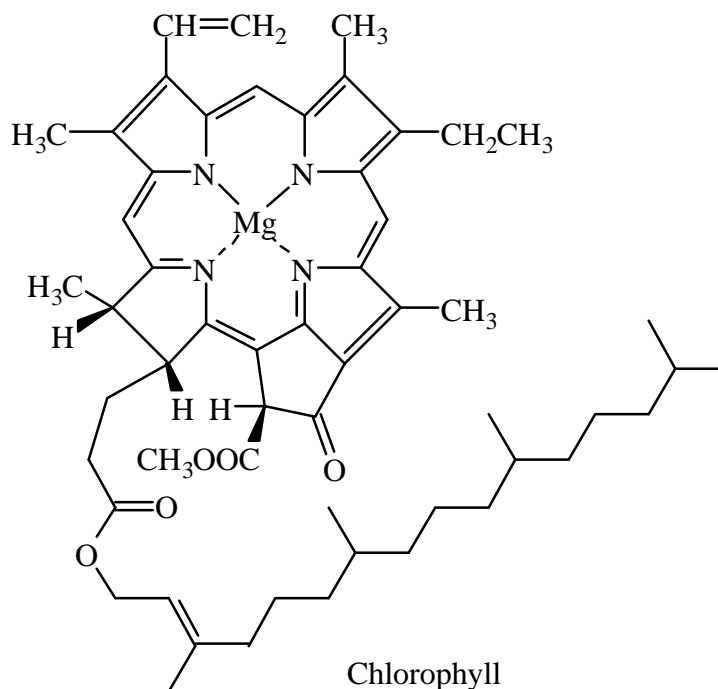
Molecular Orbital (MO) Theory was introduced by Mulliken in the 1940's and 1950's for which he won the 1964 Nobel Prize in Chemistry. It allows for the prediction of bond orders and paramagnetism of simple molecules.

- 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

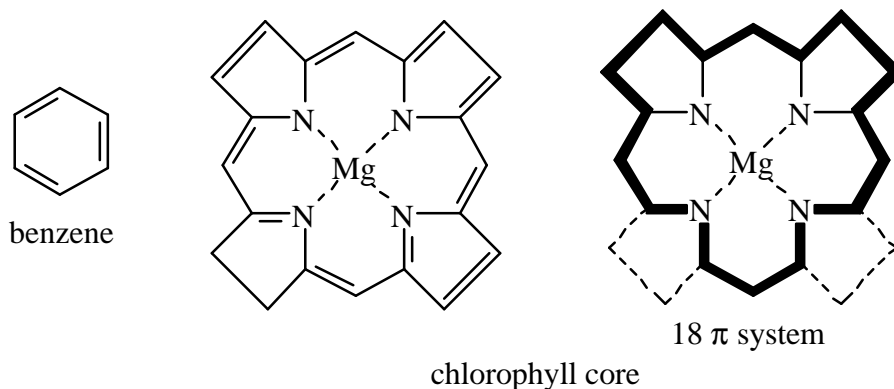
dimeric  $\text{Hg}_2^{++}$  species. Using MO theory, show why the dimeric species  $\text{Hg}_2^{++}$  is more stable than the monomer  $\text{Hg}^+$ .

**PROBLEM 37**

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



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  $\text{sp}^2$  hybridized carbon and two of the nitrogen atoms supply one  $\pi$  electron to the rings in these systems. Thus in benzene there are 6- $\pi$  electrons, whereas in chlorophyll there are 18 (or 22)  $\pi$ -electrons. For the purposes of this question, assume that there are 18 aromatic  $\pi$  electrons in chlorophyll which pass through the aza nitrogens but leave out the pyrrole-type nitrogens of the molecular core. Sigma ( $\sigma$ ) electrons are in the plane of the molecule and  $\pi$ -electrons are perpendicular to the plane of the molecule.



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

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

where  $\hbar = \frac{h}{2\pi}$  ( $h$  = Planck's constant;  $1 \times 10^{-34}$  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  $1.50 \times 10^{-8}$  cm.

- Why does the magnesium not supply  $\pi$ -valence electrons to the chlorophyll ring?
- What is the radius  $r_b$  of the benzene ring and  $r_c$ , that of the chlorophyll ring?
- 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).
- 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.
- Would you expect chlorophyll to be diamagnetic or paramagnetic? Explain in terms of the total spin of the  $\pi$ -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  $MnSO_4 \cdot H_2O$  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  $9.75 \times 10^{-3}$  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  $2.5 \times 10^{-5}$  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  $1.77 \times 10^{-14}$ .

- 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  $3.0 \times 10^{-7}$  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  $\text{NH}_3$  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	test tube rack
dilute $\text{Br}_2/\text{CCl}_4$ (or $\text{Br}_2/\text{H}_2\text{O}$ )	5 small test tubes
Lucas reagent (conc. $\text{HCl} + \text{ZnCl}_2$ )	grease pencil
ceric ammonium nitrate reagent	aluminum foil
0.2% $\text{KMnO}_4$	disposable pipets
acetone	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%  $\text{KMnO}_4$  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  $\text{Mg}^{2+}$  and blue in the absence of available magnesium ions. Lead ions are not bound by Black T. EDTA binds to  $\text{Mg}^{2+}$  and  $\text{Pb}^{2+}$  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  $\text{Mg}^{2+}$ /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  $\text{Pb}^{2+}$ :  
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:  $\text{CuSO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{FeSO}_4$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{MnSO}_4$ , and  $\text{NiSO}_4$ . 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 $K_{\text{sp}}$ of $\text{CaSO}_4$

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  $\text{CaSO}_4$

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<sup>+</sup>. 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<sub>4</sub> 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<sub>4</sub>.

**PROBLEM 48 - EXPERIMENTAL**

**Ritter Reaction**

benzonitrile  
tert-butyl alcohol  
concentrated H<sub>2</sub>SO<sub>4</sub>  
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>B</b> , g	_____
mL NaOH / g <b>B</b>	_____
Molecular weight <b>B</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:

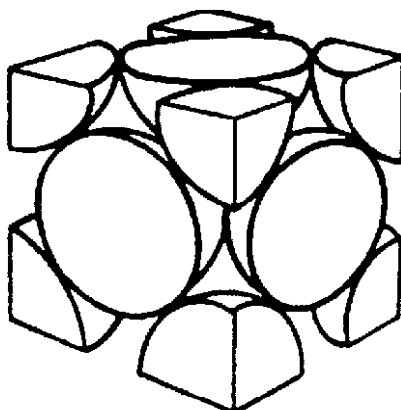
$$V_u = a^3 = (4.077 \times 10^{-10})^3 = 6.777 \times 10^{-29} \text{ m}^3 = 6.777 \times 10^{-23} \text{ cm}^3$$

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  $1.000 \text{ cm}^3$  cube equals:

$$N_{\text{Au}} = N \times n_{\text{u}} = 1.476 \times 10^{22} \times 4 = 5.904 \times 10^{22}$$

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

$$m_{\text{Au}} = \frac{M_{\text{Au}}}{N_{\text{A}}} = \frac{196.97}{6.002214 \times 10^{23}} = 3.271 \times 10^{-22} \text{ g}$$

The mass of the unit cell equals:

$$M_{\text{u}} = n_{\text{u}} m_{\text{Au}} = 4 \times 3.271 \times 10^{-22} = 1.308 \times 10^{-21} \text{ g}$$

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

$$d_{\text{Au}} = N M_{\text{u}} = 1.476 \times 10^{22} \times 1.308 \times 10^{-21} = 19.31 \text{ g cm}^{-3}$$

## SOLUTION 2

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

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

$$A_{\text{u}} = a_{\text{Au}}^2 = (4.077 \times 10^{-8} \text{ cm})^2 = 1.662 \times 10^{-15} \text{ cm}^2$$

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.

$$n_{\text{u}} = 4 \times \frac{1}{4} + 1 = 2$$

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

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

- 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  $1.203 \times 10^{15}$  and the number of Cu atoms within the Cu epitaxial deposit (layer) equals:

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

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

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

- iii) Determination of the number of moles of  $\text{CuSO}_4$  in the electrolyte after deposition of the epitaxial layer.

The number of moles of  $\text{CuSO}_4$  in the electrolyte after the deposition equals the initial number of moles of  $\text{CuSO}_4$  minus the number of moles of Cu deposited on the Au(100) substrate.

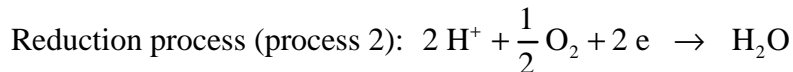
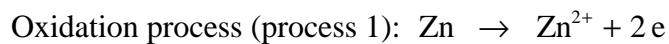
$$n_{\text{Cu}} = 1.000 \times 10^{-4} \times 10.000 \times 10^{-3} - 1.999 \times 10^{-7} = 8.001 \times 10^{-7} \text{ mol}$$

- iv) Determination of the concentration of  $\text{CuSO}_4$  in the electrolyte after deposition of the Cu epitaxial layer

$$c_{\text{CuSO}_4} = \frac{8.001 \times 10^{-7}}{10.000 \times 10^{-3}} = 0.0800 \text{ mM}$$

**SOLUTION 3**

- a) Determination of the spontaneous direction of the reaction.



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

$$E^\circ = E_2^\circ - E_1^\circ = 1.991 \text{ V}.$$

The Gibbs free energy,  $\Delta G^\circ$ , of the process equals:

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

Because  $\Delta G^\circ$  is negative, Zn undergoes spontaneous dissolution.

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

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

$$E = 0.000 \text{ V} \quad \text{when} \quad \frac{R T}{n F} \ln \frac{c_{\text{Zn}^{2+}}}{c_{\text{H}^+}^2} = 1.991 \quad \text{or} \quad \text{when} \quad \ln \frac{c_{\text{Zn}^{2+}}}{c_{\text{H}^+}^2} = 155.0.$$

The latter relation

gives after rearrangement the following ratio:  $\frac{c_{\text{Zn}^{2+}}}{c_{\text{H}^+}^2} = 2.068 \times 10^{67}$ .

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

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

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

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

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

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

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

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

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

$$1 + \Delta c_{\text{Zn}^{2+}} = a (1 - 4 \Delta c_{\text{Zn}^{2+}} + 4 \Delta c_{\text{Zn}^{2+}}^2)$$

or

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

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:

$$4 a \Delta c_{\text{Zn}^{2+}}^2 - 4 a \Delta c_{\text{Zn}^{2+}} + a = 0$$

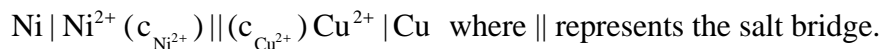
A solution of this quadratic equation leads to the following value of the increase of concentration of  $\text{Zn}^{2+}$ :  $\Delta c_{\text{Zn}^{2+}} = 0.500 \text{ M}$ . The respective concentrations of  $\text{Zn}^{2+}$  and  $\text{H}^+$  when the dissolution of Zn ceases are  $c_{\text{Zn}^{2+}}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



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



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

The cell potential,  $E$ , prior to addition of  $\text{CuCl}_2$  is expressed by the Nernst equation:

$$E = E^{\circ} - \frac{R T}{2 F} \ln \frac{c_{\text{Ni}^{2+}}}{c_{\text{Cu}^{2+}}}$$

After the  $\text{CuCl}_2$  addition, the new potential of the cell,  $E'$ , is expressed by the following formula:

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

where  $c'_{\text{Cu}^{2+}}$  is the new concentration of  $\text{Cu}^{2+}$ . The potential increase,  $\Delta E = E' - E$ , associated with the  $\text{CuCl}_2$  addition may be determined on the basis of the above relations:

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

Thus, it is not necessary to know the  $\text{Ni}^{2+}$  concentration in order to relate the change of the cell potential with the addition of  $\text{CuCl}_2$ .

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

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

The concentration change upon addition of  $\text{CuCl}_2$  equals  $\Delta c_{\text{Cu}^{2+}} = 0.010 \text{ M}$  and the respective number of moles of  $\text{CuCl}_2$  added to the solution is  $1.00 \times 10^{-3} \text{ mol}$ .

Finally, one may evaluate the mass of  $\text{CuCl}_2$  added which is:

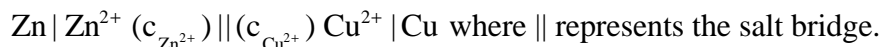
$$m_{\text{CuCl}_2} = n_{\text{CuCl}_2} \times M_{\text{CuCl}_2} = 1.344 \text{ g}.$$

### SOLUTION 5

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



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:



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

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

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

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

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,  $n_{\text{Cu}}$ , and of the dissolved Zn,  $n_{\text{Zn}}$ , equals:

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

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

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

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

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

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

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

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

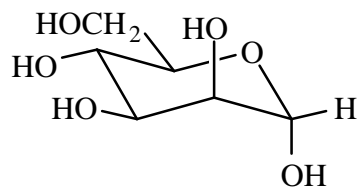
$$E' = E^{\circ} - \frac{R T}{2 F} \ln \frac{c'_{\text{Zn}^{2+}}}{c'_{\text{Cu}^{2+}}} = 1.104 - \frac{R \times 298.15}{2 F} \ln \frac{0.1518}{0.0482} = 1.089 \text{ V}$$

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

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

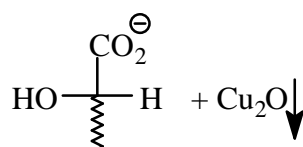
**SOLUTION 6**

The structure of  $\alpha$ -D-(+)-mannopyranose is:

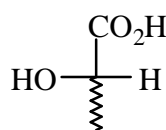


The reaction products are:

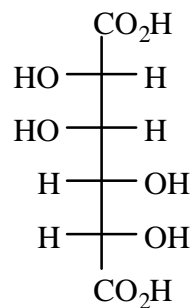
a)



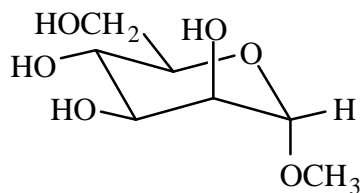
b)



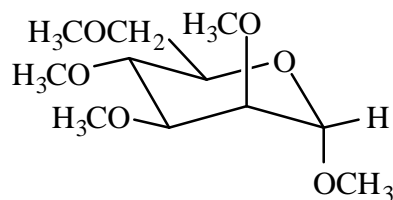
c)



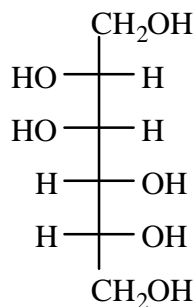
d)



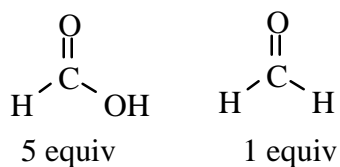
e)



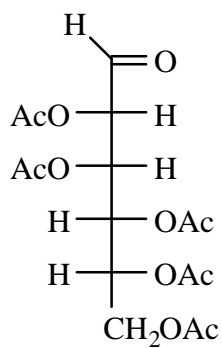
f)



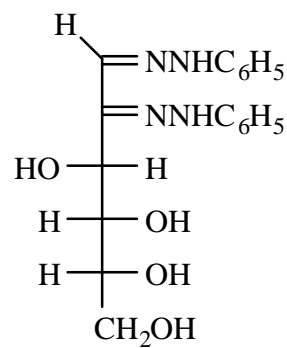
g)



h)

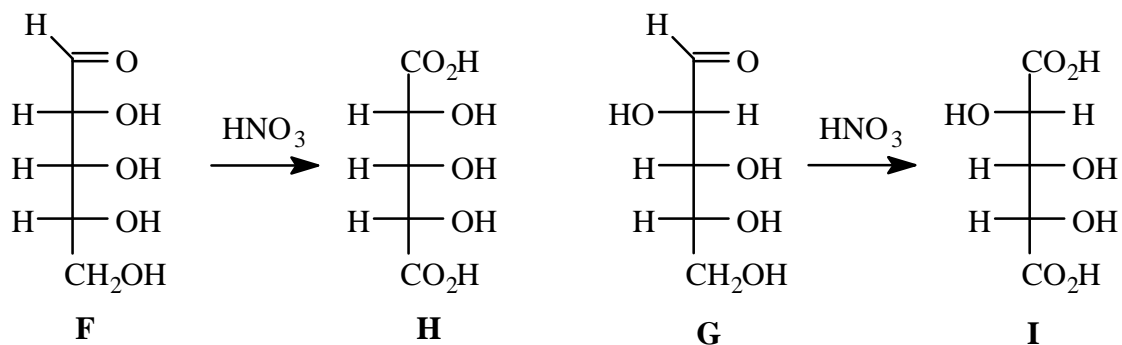


i)



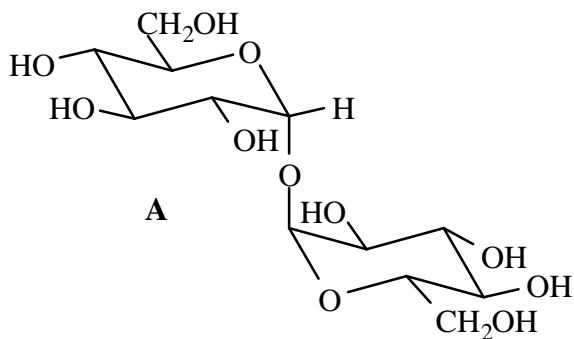


The equilibrium mixture above when treated with Na-Hg and water at pH = 3-5 produces **F** and **G** which when oxidized by nitric acid gives an inactive aldaric acid **H** and an optically active aldaric acid **I**:



### SOLUTION 8

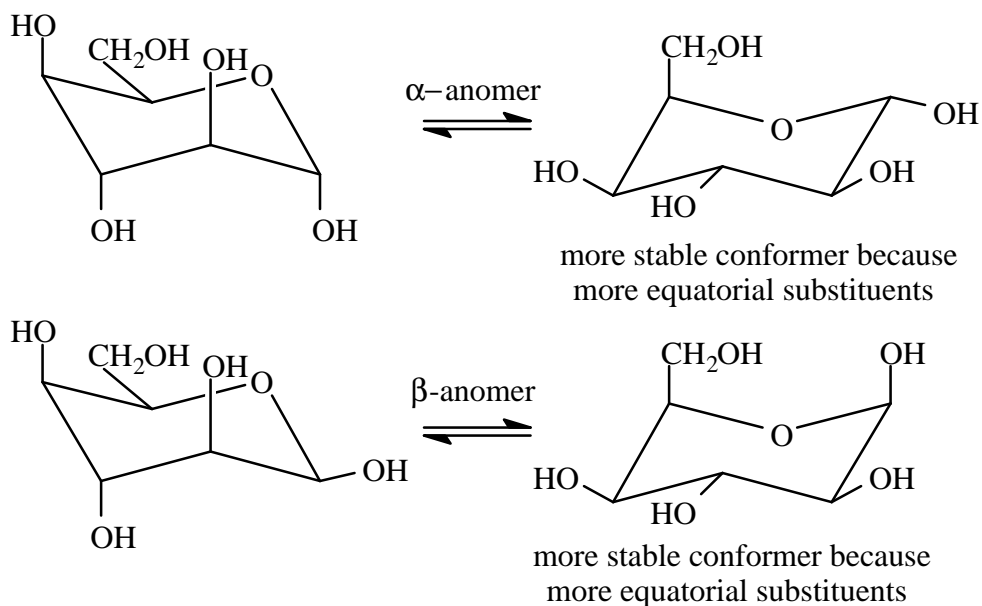
Compound **A** is a non-reducing sugar with an  $\alpha$ -linkage at the anomeric carbon. Since **A** gives only 2,3,4,6 methylated glucoses on hydrolysis the only possible structure for **A** is to have the two glucose molecules dimerize via their respective anomeric carbons:



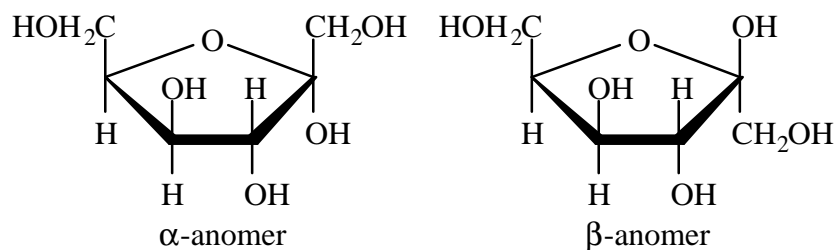
10 moles of HI are needed for the complete cleavage of **A** giving 10 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde).

SOLUTION 9

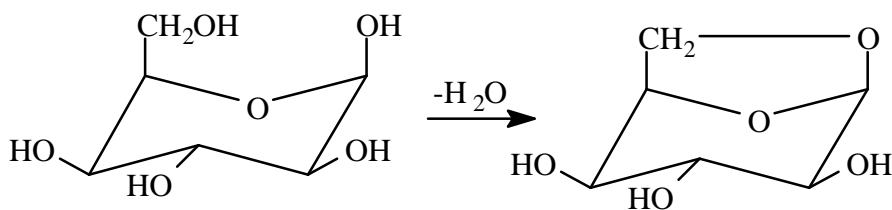
a) Below are the two chair conformations for the two anomers of D-idose:



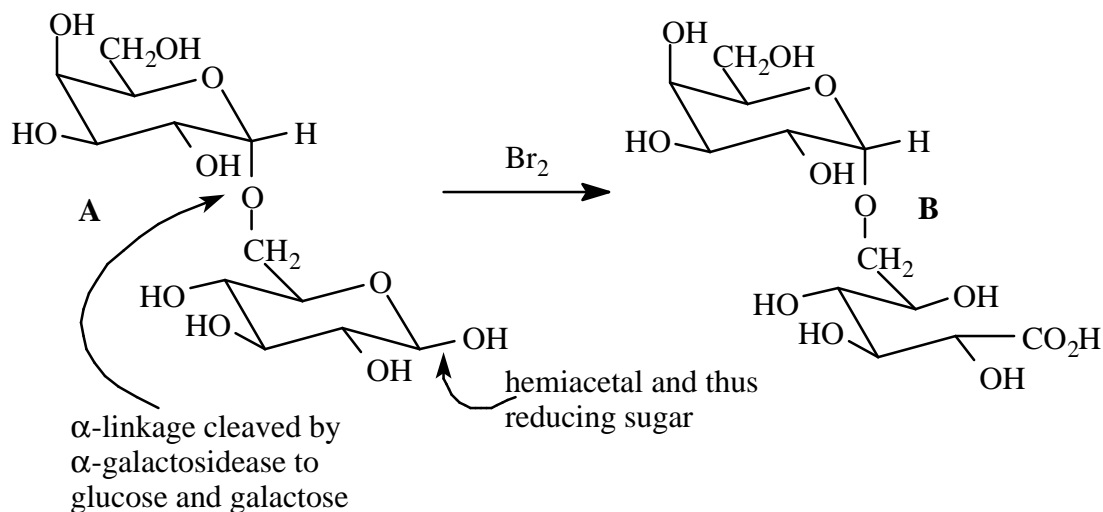
b) The two furanose forms of D-sorbose are shown below.



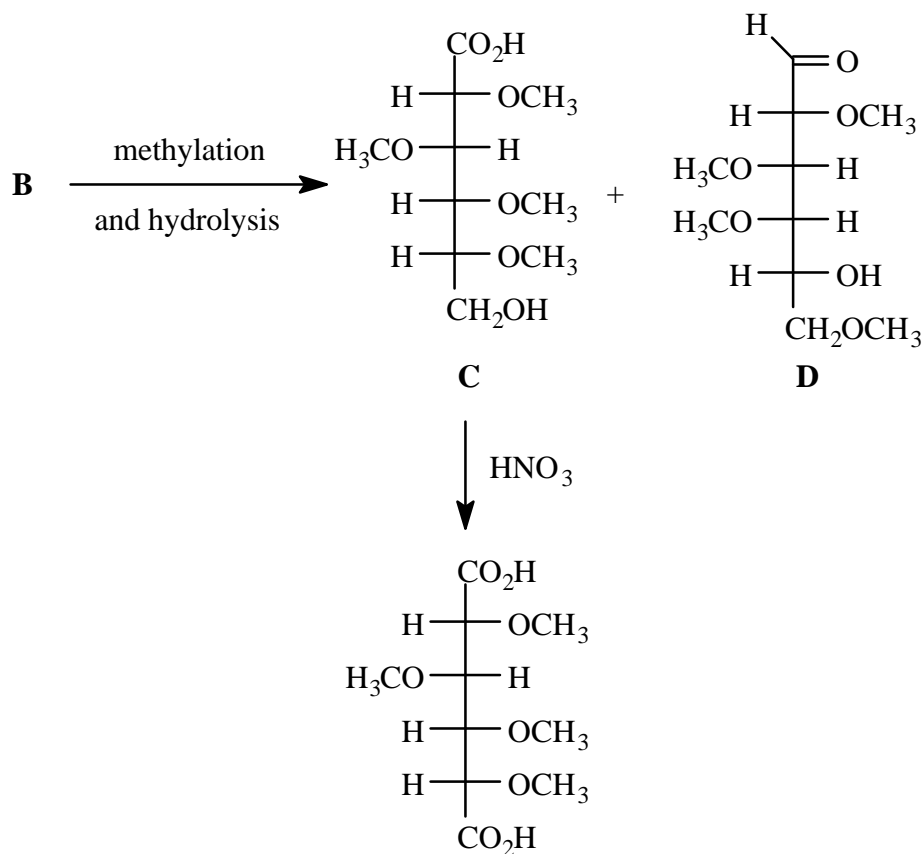
c) The indicated conformer of the  $\beta$ -anomer can cyclize internally to form the anhydro-derivative. Glucose cannot undergo this reaction because it requires the C-6 substituent to be axial, and this conformation is too unstable for the glucose molecule.



SOLUTION 10

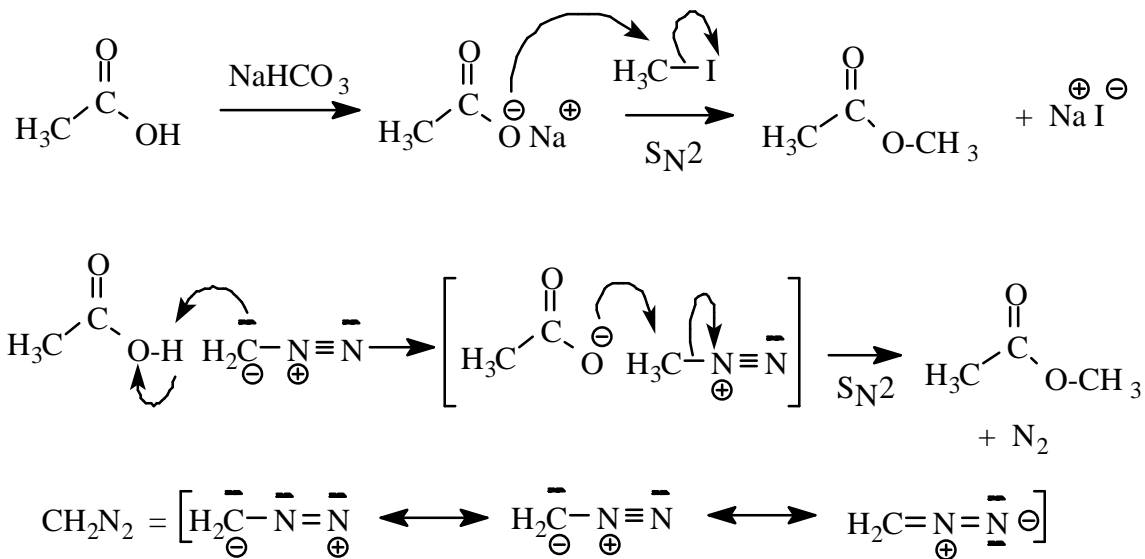


Melibiose A is 6-O-  $\alpha$ -D-galactopyranosyl-D-glucopyranose



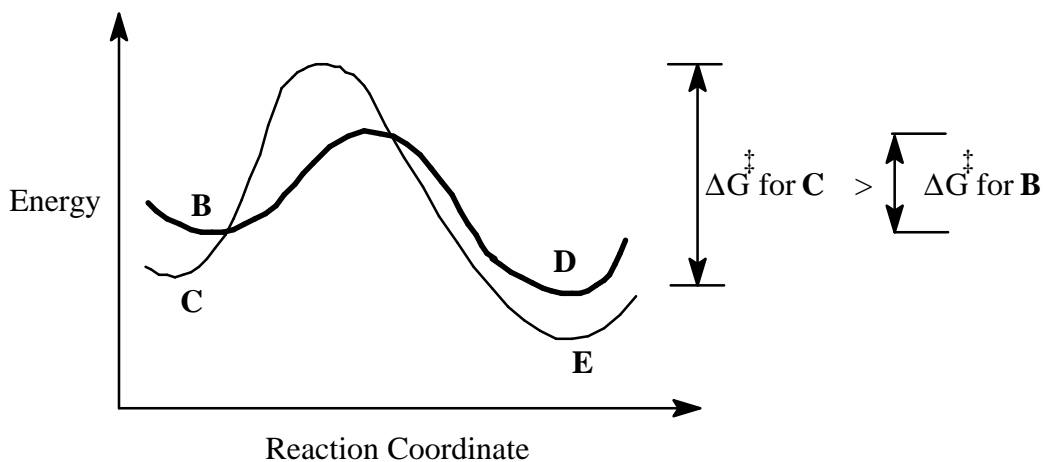
**SOLUTION 11**

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  $N_2$ .

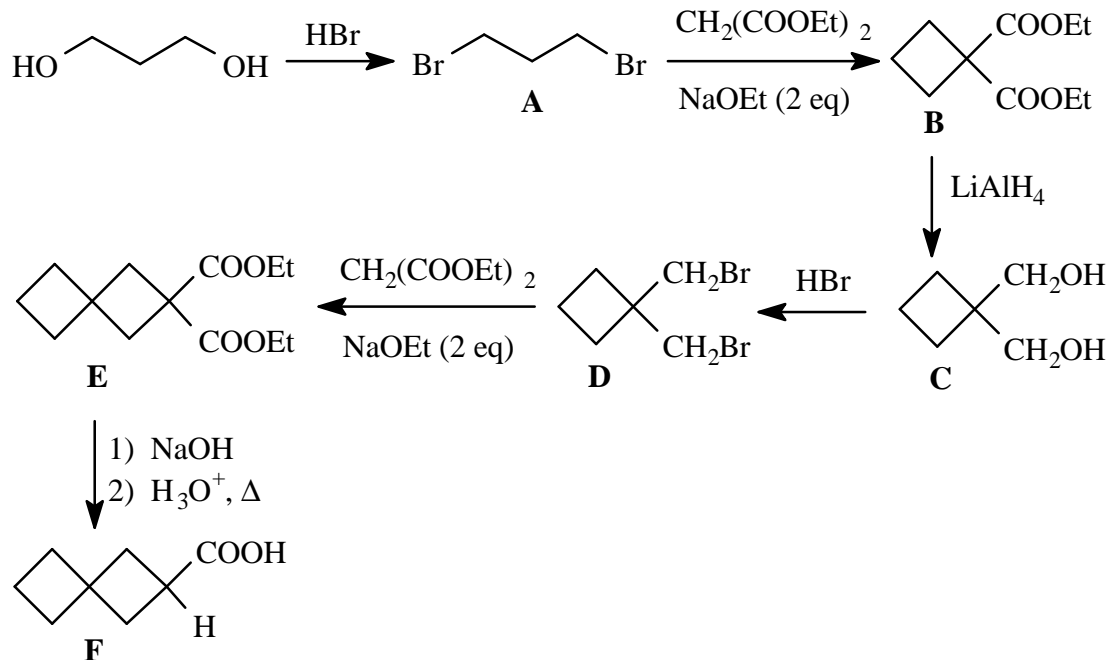


**SOLUTION 12**

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.



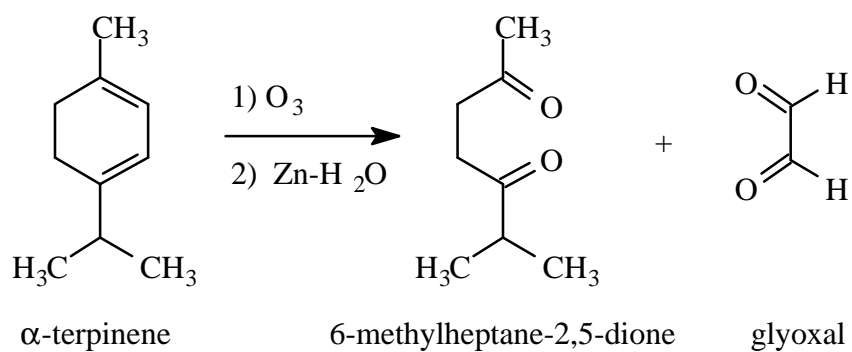
SOLUTION 13



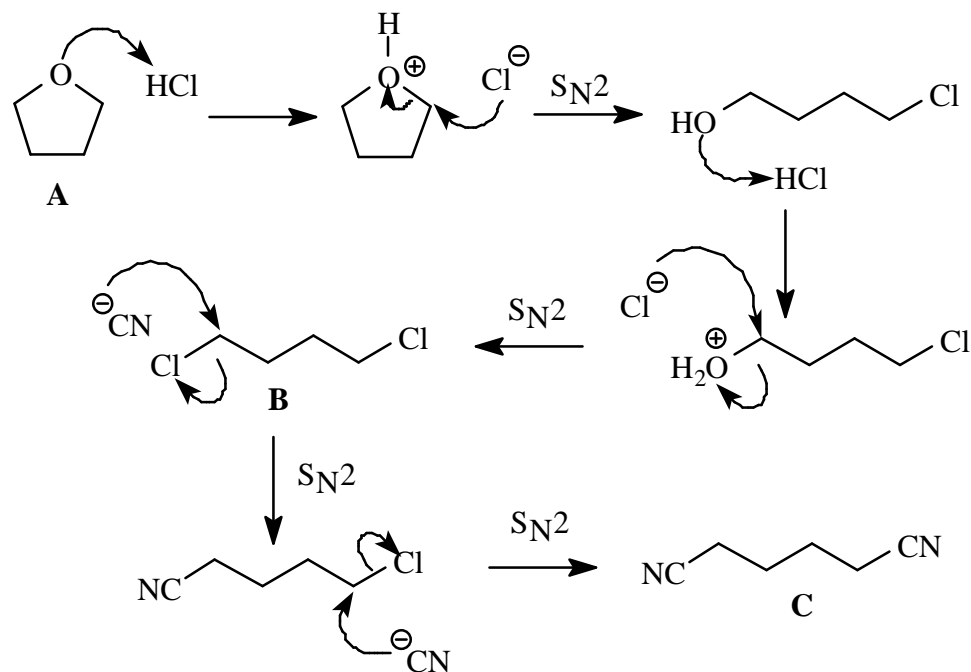
SOLUTION 14

- From the formula, the number of unsaturations can be determined: For a saturated hydrocarbon there should be  $(10 \times 2) + 2 = 22$  hydrogens. Therefore  $(22-16)/2$  H per unsaturation implies that 3 unsaturations are present.
- The hydrogenation product still contains one site of unsaturation and thus there must have been two double bonds present which underwent reduction.
- The hydrogenation product still contains one site of unsaturation and thus there must be one ring present which did not undergo reduction.

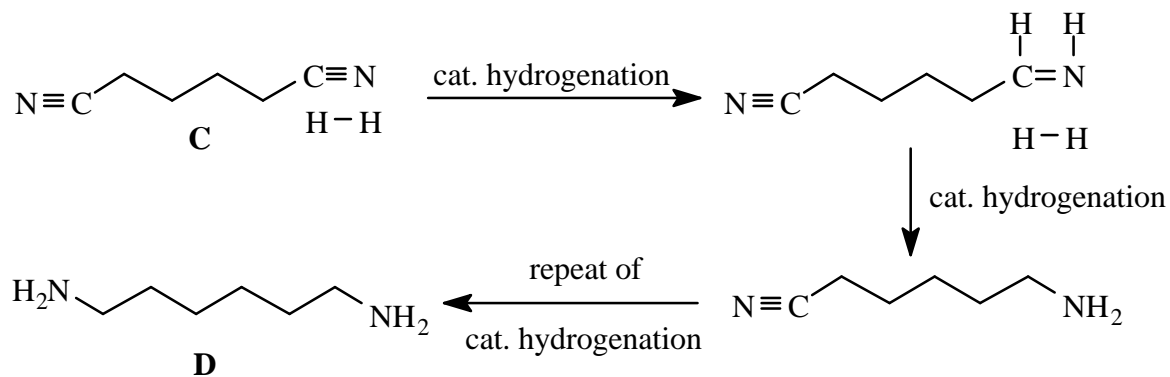
d)



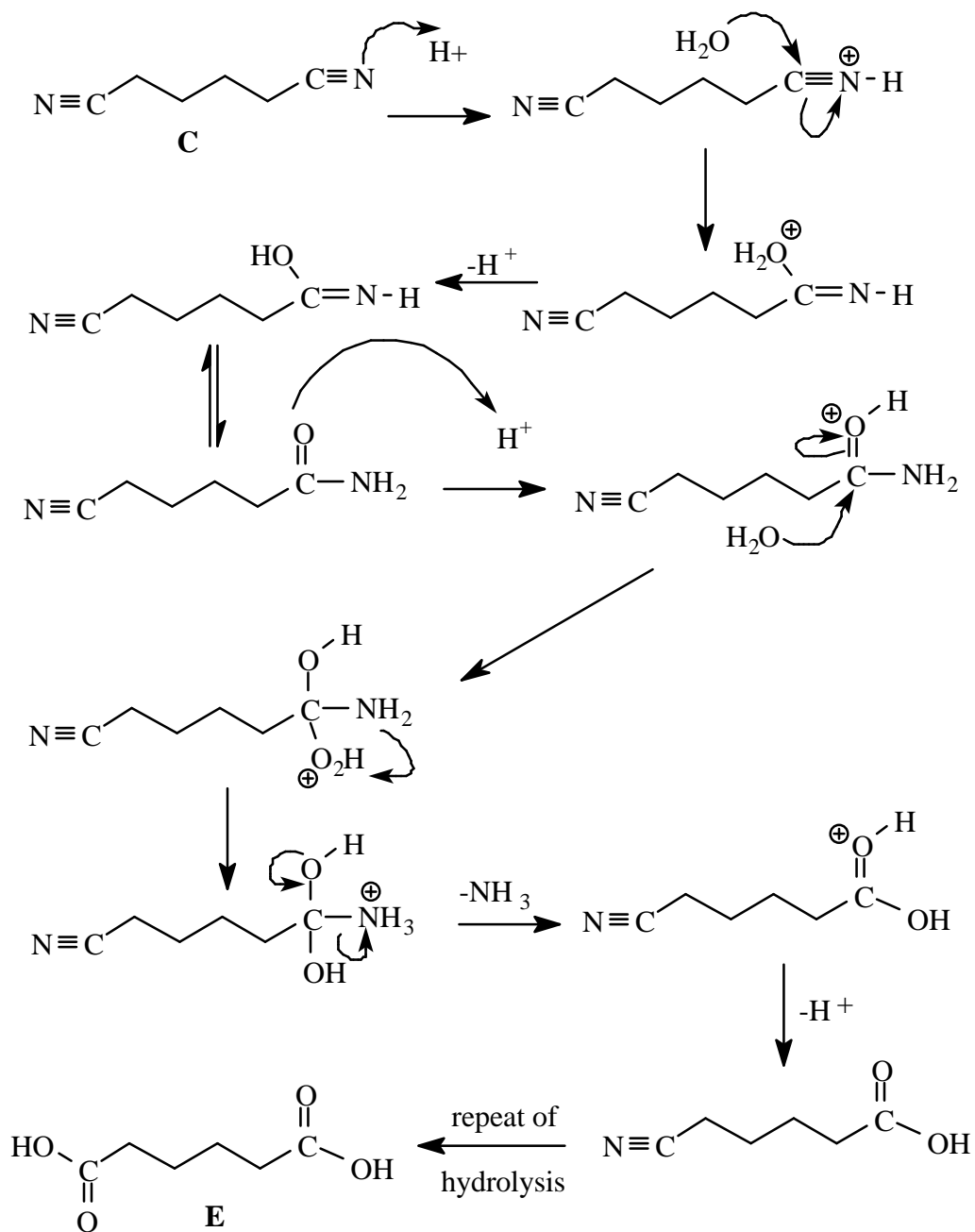
**SOLUTION 15**



Nitrile reduction converts nitrile groups into amino groups:



Nitrile hydrolysis converts nitrile groups into carboxylic acid groups:



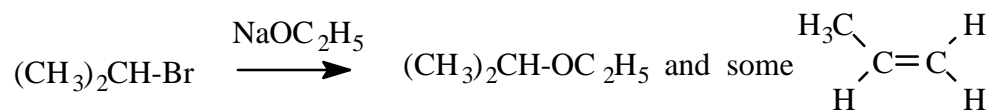
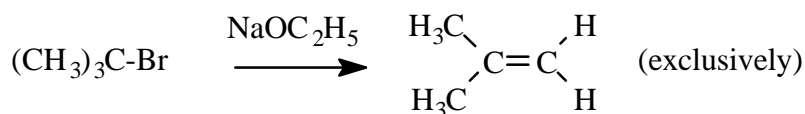
**SOLUTION 16**

The reaction of chlorohydrocarbons with an aqueous solution of  $\text{AgNO}_3$  leads to the corresponding alcohols by means of an  $\text{S}_{\text{N}}1$  mechanism. Since the rate limiting step in  $\text{S}_{\text{N}}1$  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.

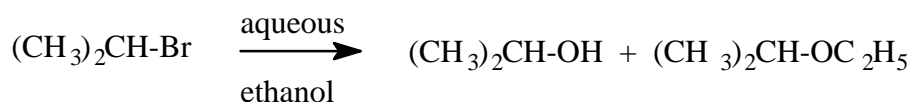
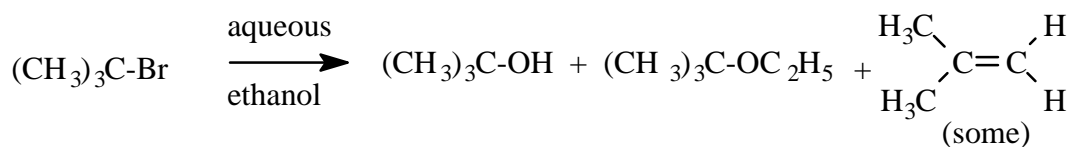
Compound **C** is the most reactive. Its carbocation is tertiary, can adopt a planar structure, and is stabilized by resonance involving the three aromatic substituents. Compound **B** has a reactivity intermediate between those of **A** and **C**.

**SOLUTION 17**

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



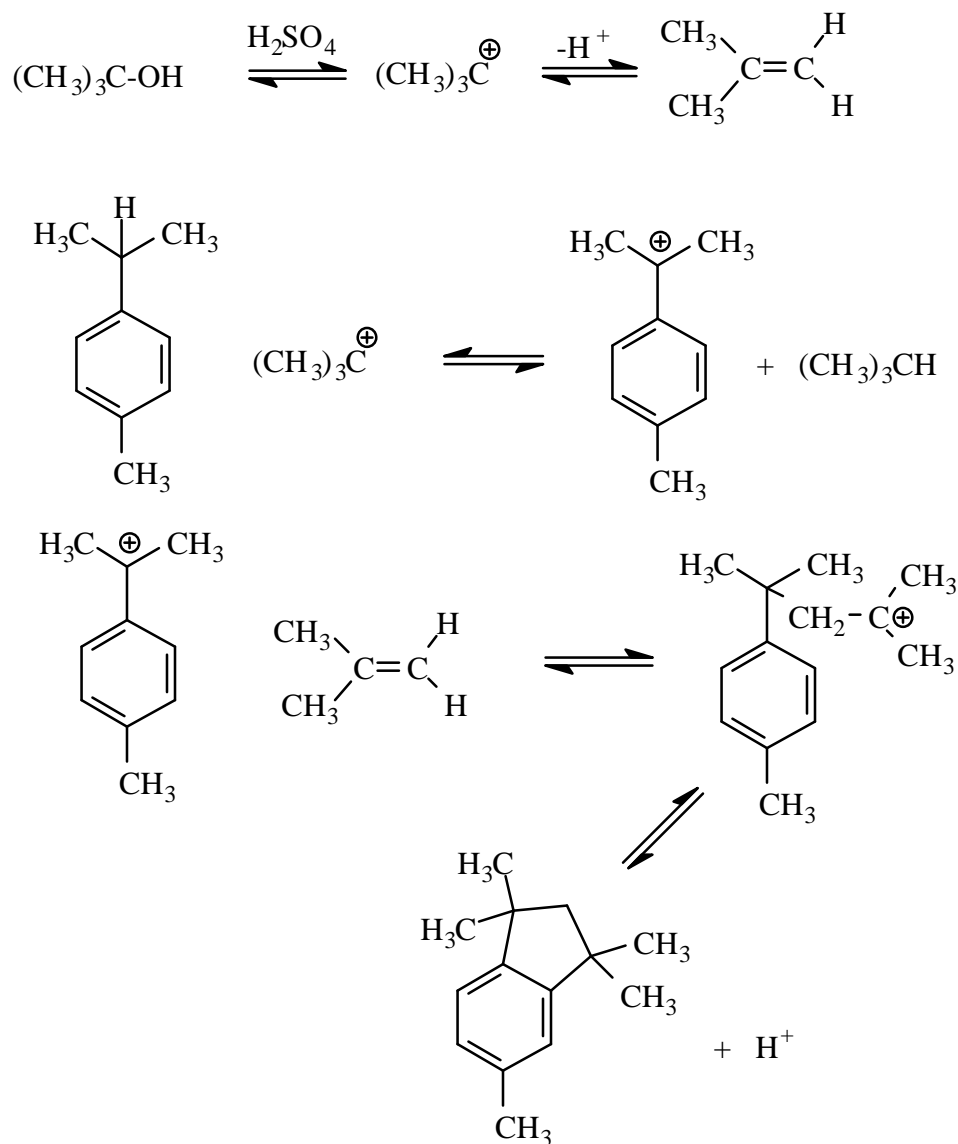
Aqueous 60% ethanol: 2-methyl-2-bromopropane still yields more alkene



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.

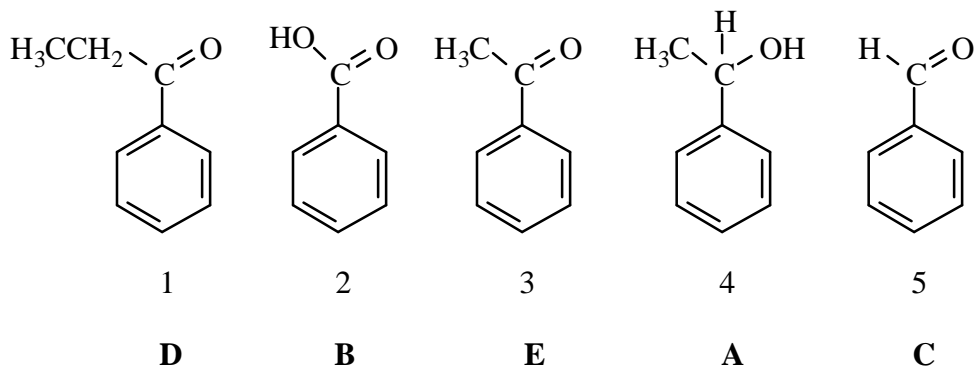
SOLUTION 18

- 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 than 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.



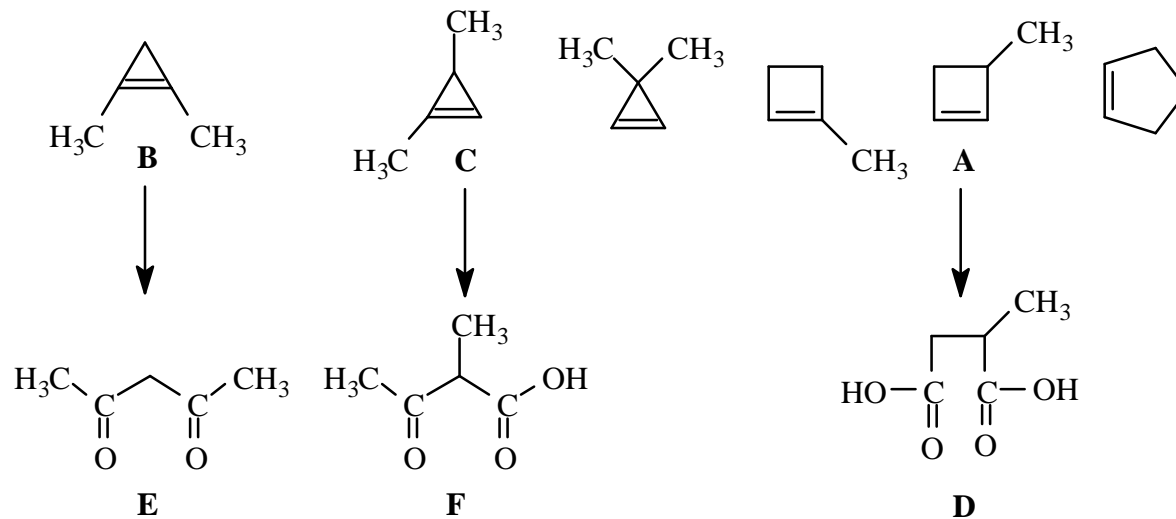
- b) With 1,4-dimethylbenzene, only the 2,5-dimethyl-tert-butylbenzene would be obtained via a normal electrophilic substitution since the abstraction of a hydride ion from a methyl group is unfavourable.

**SOLUTION 19**



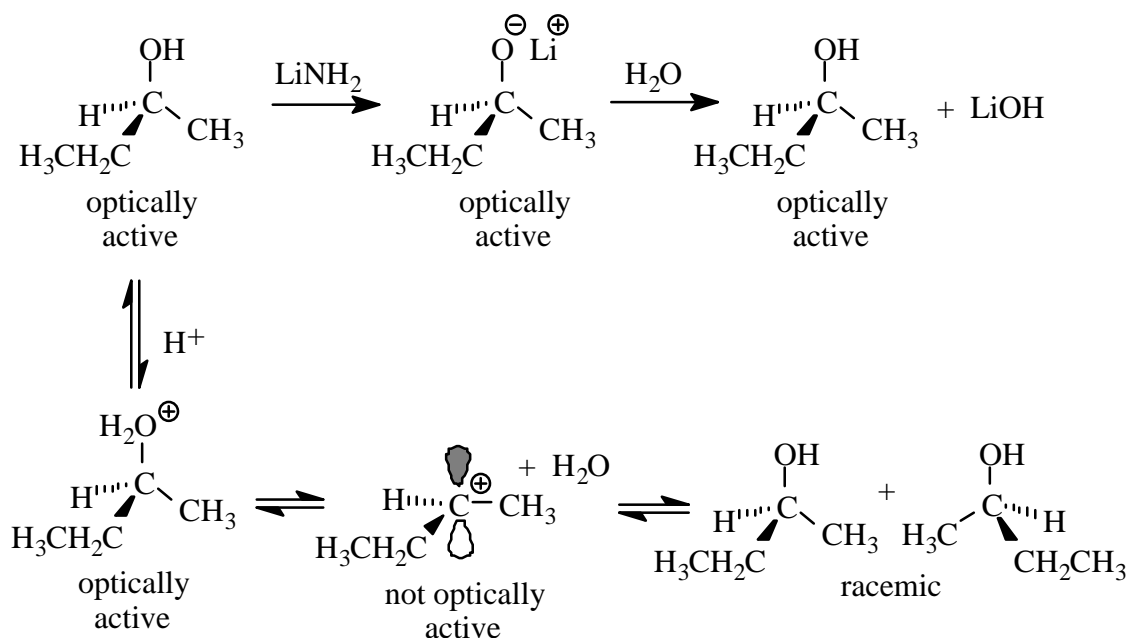
- i) Chromate oxidation will identify readily oxidizable groups such as alcohols and aldehydes and thus 4 and 5 must be **A** and **C** (although which is which cannot be determined yet).
- ii) Permanganate oxidation will also identify readily oxidizable groups such as alcohols and aldehydes in addition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

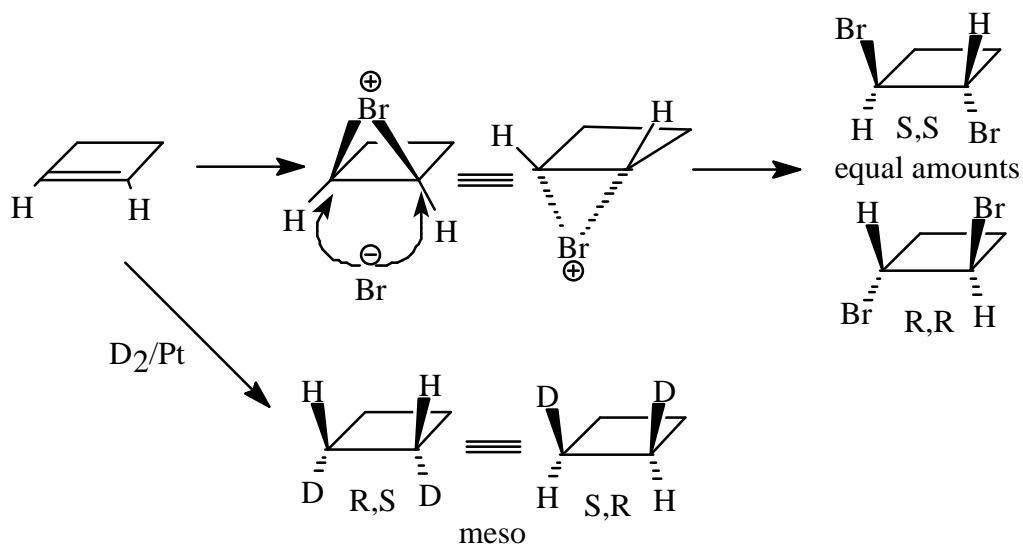


**SOLUTION 21**

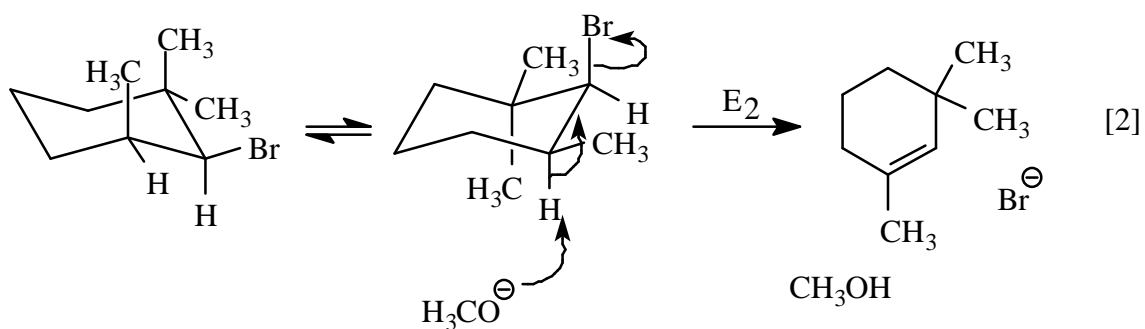
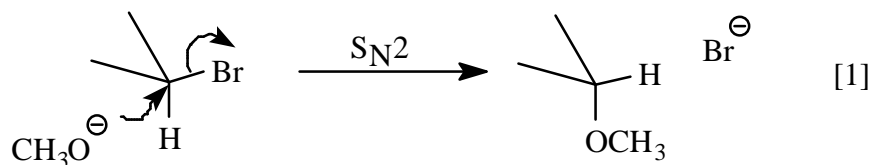
- Both reactions are  $S_N2$  displacements at primary carbon atoms. The  $S_N2$  reaction is primarily controlled by steric interactions. 1-Bromo-2-methylbutane is branched at the  $\beta$ -position which hinders the attack of the thiolate nucleophile, whereas the 1-bromobutane is relatively open to the displacement and thus reacts more rapidly.
- The first reaction involves deprotonation/protonation and affects 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.



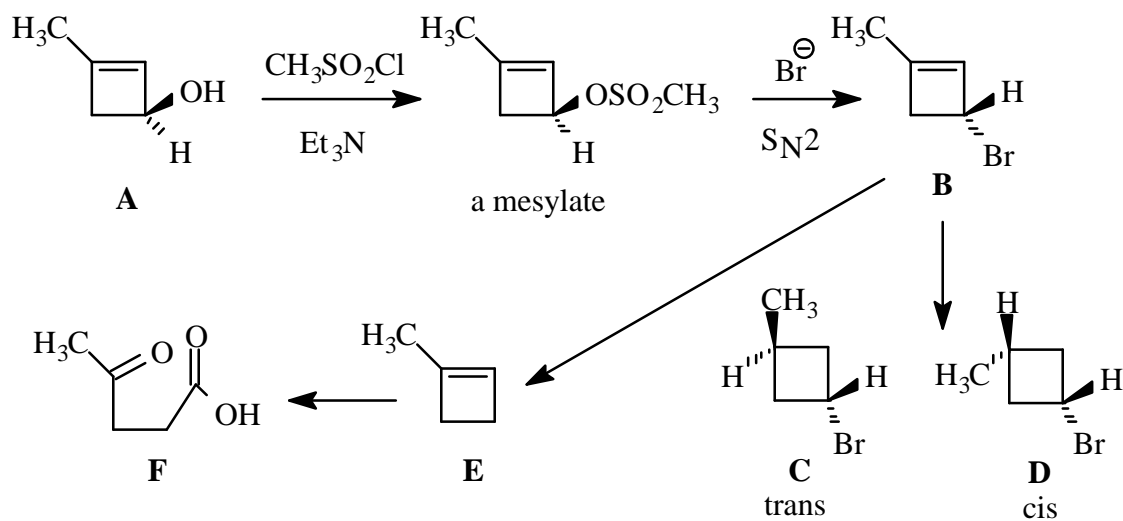
- c) Bromine addition follows an anti process to lead to a trans product. The initial bromonium ion can be formed equally on the top or bottom face of the cyclobutene to form the identical species. Opening of this intermediate at either end of the former double bond by the bromide ion leads to an equal 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.



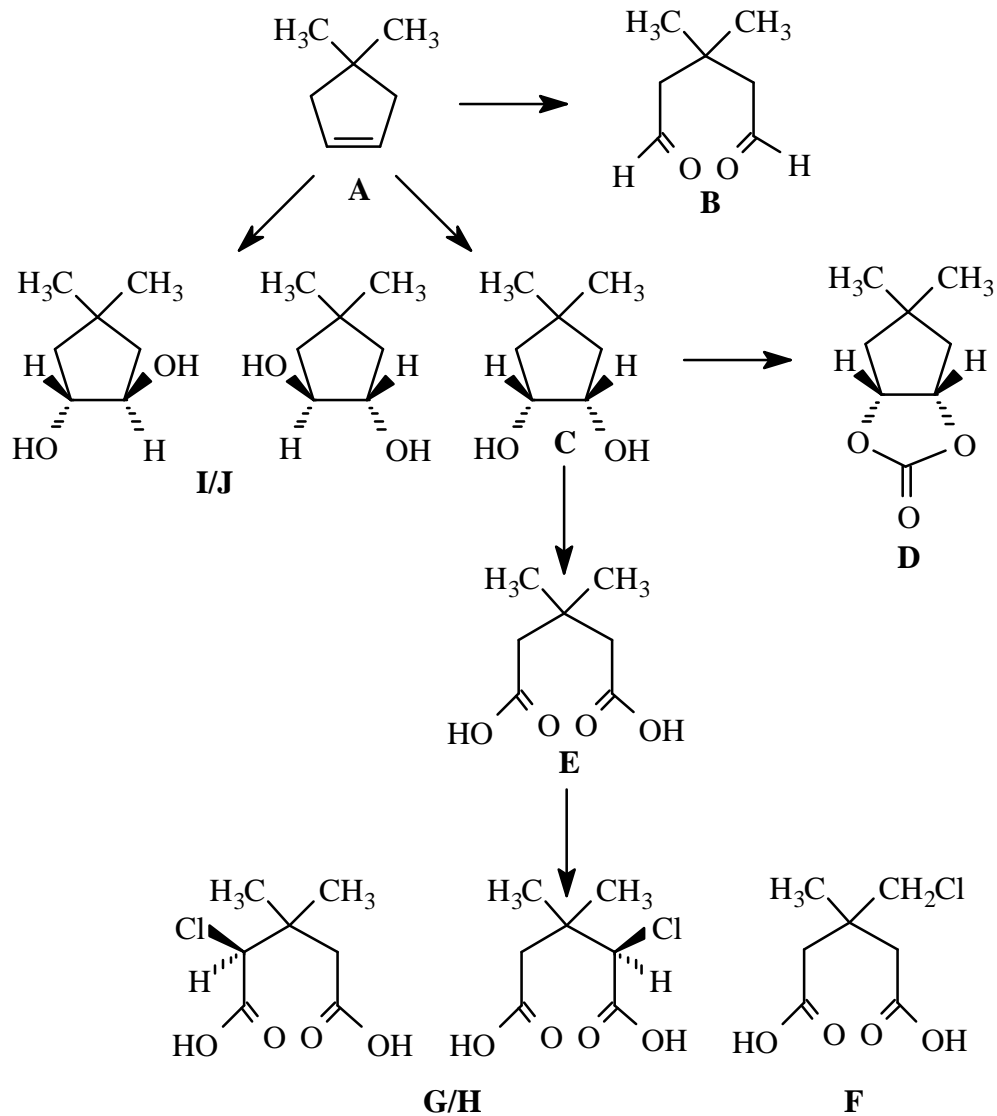
- d) High concentration of the nucleophile ( $\text{HO}^-$ ) favours the  $\text{S}_{\text{N}}2$  reaction which proceeds with 100% inversion of configuration at the displaced centre.
- e) Low concentration of the nucleophile ( $\text{HO}^-$ ) favours the  $\text{S}_{\text{N}}1$  process which proceeds 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  $\text{S}_{\text{N}}1$  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 ( $\text{HO}^-$ ) will have no effect on the rate of the reaction.
- f) Reaction [1] is an  $\text{S}_{\text{N}}2$  reaction in which the nucleophile ( $\text{CH}_3\text{O}^-$ ) 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  $\text{E}_2$  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.



**SOLUTION 22**

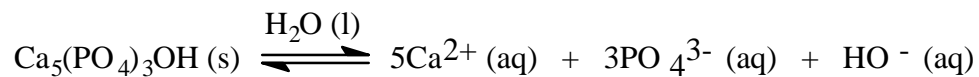


SOLUTION 23

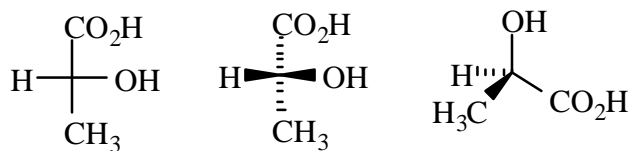


SOLUTION 24

a)



b) other variations also possible



(Fischer)

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

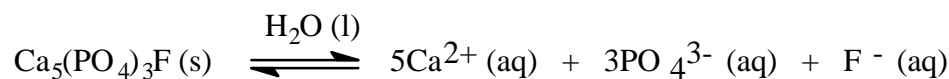
other variations include:

- (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<sup>+</sup> ions can strongly react with two of the three ions produced during demineralization of hydroxyapatite, namely OH<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> ions. The latter are strong bases which will react with H<sup>+</sup> ions to form their respective conjugate acid as shown by the following equations:



d)



The dissolution of  $x$  mol of Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F in 1 L of water will produce  $5x$  mol/L of Ca<sup>2+</sup>,  $3x$  mol/L of PO<sub>4</sub><sup>3-</sup> and  $x$  mol/L of F<sup>-</sup>.

The solubility product,  $K_{\text{sp}}$ , of fluoroapatite is expressed as:

$$K_{\text{sp}} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{F}^-] = 1.0 \times 10^{-60}$$

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

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

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

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

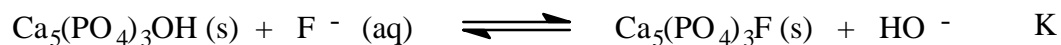
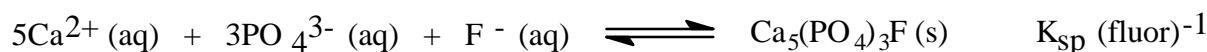
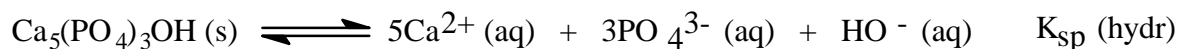
$$K_{sp} = [Ca^{2+}]^5 [PO_4^{3-}]^3 [OH^-] = 6.8 \times 10^{-37}$$

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

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

The solubility of hydroxyapatite in water is  $2.7 \times 10^{-5}$  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:



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

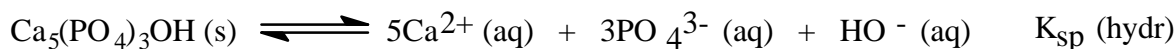
$$K = (6.8 \times 10^{-37}) / (1.0 \times 10^{-60})$$

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

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:

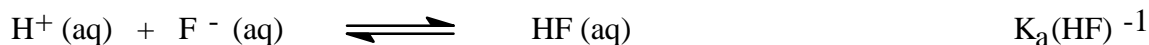
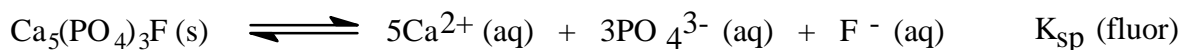


$$\text{where } K_1 = K_{\text{sp}}(\text{hydr.}) / K_{\text{w}}$$

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

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

Reaction with fluoroapatite:



$$\text{where } K_2 = K_{\text{sp}}(\text{fluor.}) / K_{\text{a}}(\text{HF})$$

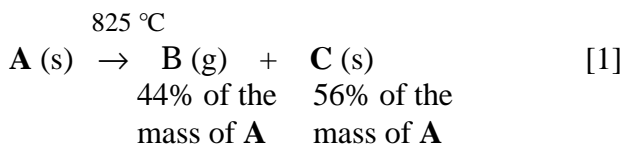
$$K_2 = (1.0 \times 10^{-60}) / (7.2 \times 10^{-4})$$

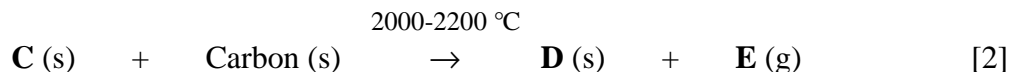
$$K_2 = 1.4 \times 10^{-57}$$

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

### SOLUTION 25

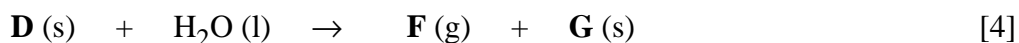
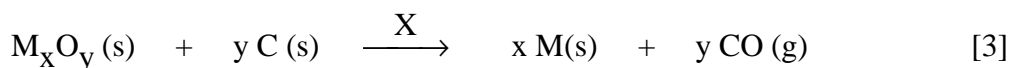
The best way to start this problem is to write the chemical equations including the unknowns in order to represent the different steps with their details.





Gas **E** contains the same elements as gas **B**, but in different proportions. Some possibilities are: NO, NO<sub>2</sub>, N<sub>2</sub>O, NO<sub>3</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>. 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<sub>2</sub> gas evolution (**B**).

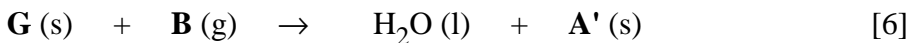
The original purpose of reaction [2] was to isolate the metal in **C** according to reaction [3] below (where **C** would be a metallic oxide), but products **D** and **E** were obtained instead. Gas **E** could be carbon monoxide, CO. In reaction [2], the metal must be in **D** since **E** is a gas.



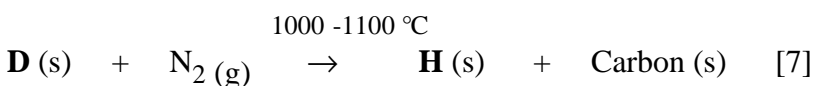
The hydrolysis reaction can be the addition of a water molecule to **D**, an oxidation of **D**, or an acid-base reaction. Since **F** is a gas and **D** contains a metal, then the insoluble compound **G** must contain this metal. A large volume of gas **F** was produced and the latter burns with a brilliant, 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<sub>2</sub>H<sub>4</sub>), ethyne (C<sub>2</sub>H<sub>2</sub>), propene (C<sub>3</sub>H<sub>6</sub>) or propyne (C<sub>3</sub>H<sub>4</sub>). 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<sup>+</sup> ions from H<sub>2</sub>O, and the OH<sup>-</sup> ions are associated with the metal cation. Before hydrolysis, the anion of **D** could be C<sub>2</sub><sup>2-</sup>, HC<sub>2</sub><sup>-</sup>, C<sub>3</sub>H<sub>2</sub><sup>2-</sup> (less probable!) or C<sub>3</sub>H<sub>3</sub><sup>-</sup>. The poorly soluble solid **G** must contain at least one OH<sup>-</sup> ion.



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



The composition of **A'** is exactly the same as that of the mineral substance **A**. If **B** is CO<sub>2</sub> 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<sup>-</sup> ion, can be calcium hydroxide, which has a relatively low solubility.



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**:

$$(15 \text{ g C}) / (12.011 \text{ g/mol}) = 1.25 \text{ mol C}$$

$$(35 \text{ g N}) / (14.007 \text{ g/mol}) = 2.50 \text{ mol N}$$

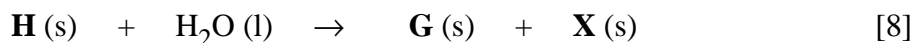
Empirical formula of the anion:  $(\text{CN}_2)_n^{x-}$

If the formula of the anion is CN<sub>2</sub> and that of compound **H** is MCN<sub>2</sub>, 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.

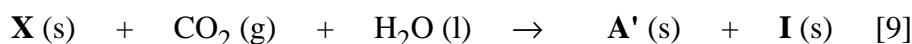
If the formula of the anion is (CN<sub>2</sub>)<sub>2</sub> or C<sub>2</sub>N<sub>4</sub> and that of compound **H** is MC<sub>2</sub>N<sub>4</sub>, then 50 g of the metal is equivalent to 0.625 mol of this metal. The molar mass would be 80 g but there is no metal having such a molar mass.

If the formula of the anion is (CN<sub>2</sub>)<sub>3</sub> or C<sub>3</sub>N<sub>6</sub> and that of compound **H** is MC<sub>3</sub>N<sub>6</sub> 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.

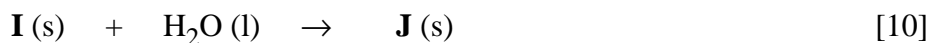
In reaction [1], we noticed a weight loss of 44% between **A** and **C**. So the mass ratio of **C/A** is 56%. Assuming that **B** is  $\text{CO}_2$ , **A** would be calcium carbonate and **C** would be calcium oxide. The mass ratio of  $\text{CaO/CaCO}_3$  is 56%. Gas **E** would be  $\text{CO}$ , which is frequently observed during the reactions of metallic oxides with carbon. So we are dealing with calcium compounds.



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,  $\text{CN}_2^{2-}$ , that is partially hydrogenated into  $\text{HCN}_2^-$  which is an intermediate species in the formation of dihydrogen cyanamide,  $\text{H}_2\text{CN}_2$ .

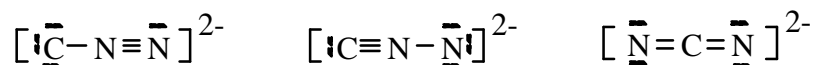


Under these conditions, **X** must be  $\text{Ca}(\text{HCN}_2)_2$  and both protons from the carbonic acid produced by reaction of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  allow the formation of dihydrogen cyanamide,  $\text{H}_2\text{CN}_2$ , i.e. compound **I**.

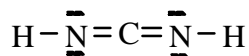


Since only one compound was formed in reaction [10], the hydrolysis must now be an addition of water to **I**. To deduce the structure of compound **J**, one must know that of compound **I**. To deduce the latter, one can refer to that of the cyanamide ion,  $\text{CN}_2^{2-}$ .

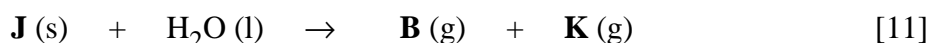
Following are the three possible structures for cyanamide ion of compound **H**:



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.



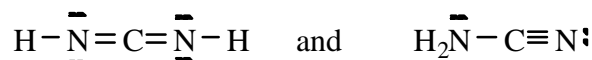
The addition of a water molecule to such a compound produces urea which is frequently used in fertilizers. So compound **J** is urea,  $\text{H}_2\text{N}(\text{CO})\text{NH}_2$ .



Hydrolysis of **J** causes the complete oxidation of carbon into  $\text{CO}_2$  (gas **B**) and into  $\text{NH}_3$  (gas **K**). The latter has a strong, characteristic odour.

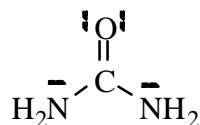
a)	<b>A or A':</b>	CaCO <sub>3</sub> (s)	Calcium carbonate (or calcareous rocks)
	<b>B:</b>	CO <sub>2</sub> (g)	Carbon dioxide
	<b>C:</b>	CaO (s)	Calcium oxide
	<b>D:</b>	CaC <sub>2</sub> (s)	Calcium carbide
	<b>E:</b>	CO (g)	Carbon monoxide
	<b>F:</b>	C <sub>2</sub> H <sub>2</sub> (g)	Ethyne
	<b>G:</b>	Ca(OH) <sub>2</sub> (s)	Calcium hydroxide
	<b>H:</b>	CaCN <sub>2</sub> (s)	Calcium cyanamide
	<b>I:</b>	H <sub>2</sub> CN <sub>2</sub> (s)	Dihydrogen cyanamide
	<b>J:</b>	H <sub>2</sub> N(CO)NH <sub>2</sub> Urea	
	<b>K:</b>	NH <sub>3</sub>	Ammonia
	<b>L:</b>	CH <sub>3</sub> CHO	Ethanal
	<b>M:</b>	CH <sub>3</sub> CO <sub>2</sub> H	Ethanoic acid
	<b>X:</b>	Ca(HCN <sub>2</sub> ) <sub>2</sub>	Calcium hydrogen cyanamide

b) The two possible structures of dihydrogen cyanamide are:

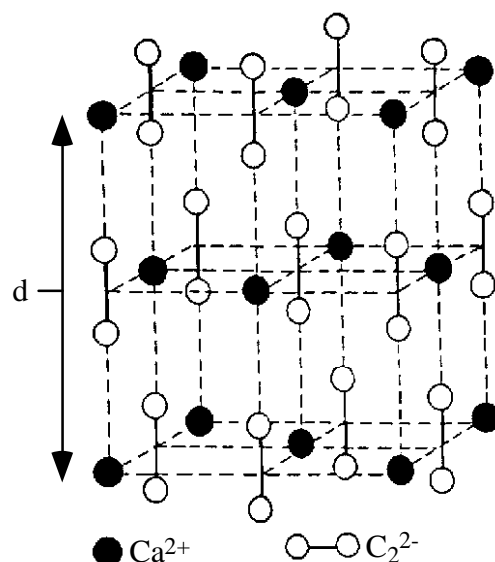


The second structure does not possess any center of symmetry and its  $-\text{C}\equiv\text{N}$  function can absorb between 2260 and 2220  $\text{cm}^{-1}$  in its infrared spectrum. It is thus the major structure.

c) The Lewis structure of urea is:



d) The crystal structure of CaC<sub>2</sub> is shown below. Each unit cell contains 4 Ca<sup>2+</sup> ions and 4 C<sub>2</sub><sup>2-</sup> ions. The distance between two Ca<sup>2+</sup> 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<sub>2</sub> one can calculate the volume of its unit cell.



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

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

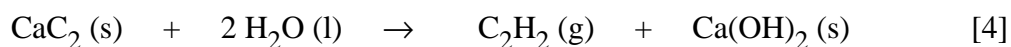
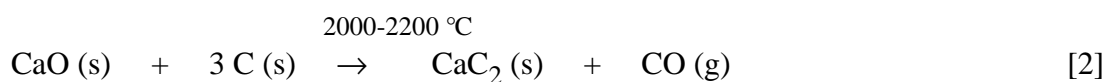
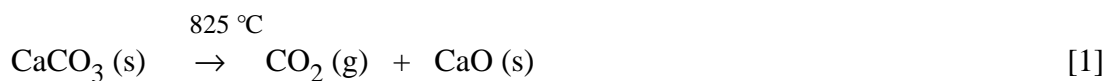
$$V = [(36.1 \text{ cm}^3) / (6.022 \times 10^{23} \text{ CaCN}_2/\text{mol})] \times (4 \text{ CaCN}_2/\text{unit cell})$$

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

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

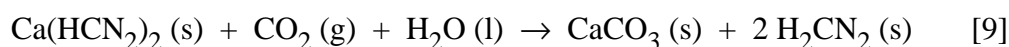
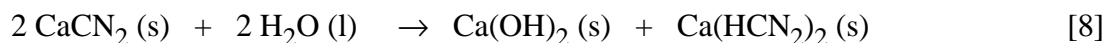
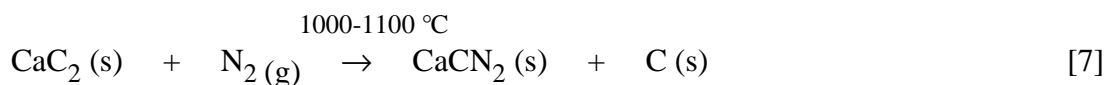
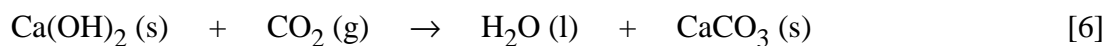
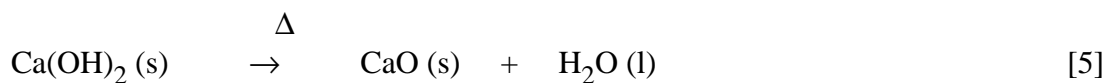
$$d = 6.21 \times 10^{-8} \text{ cm}$$

e)



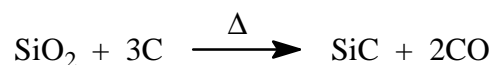
[O], Mn cat.





**SOLUTION 26**

a) Acheson Process:



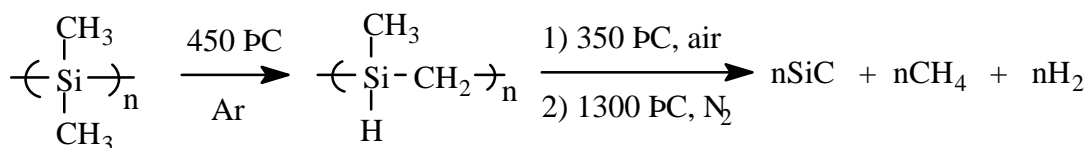
$$\text{Theoretical ceramic yield} = \text{M}[\text{SiC}] / (\text{M}[\text{SiO}_2] + 3 \text{M}[\text{C}])$$

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

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

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:

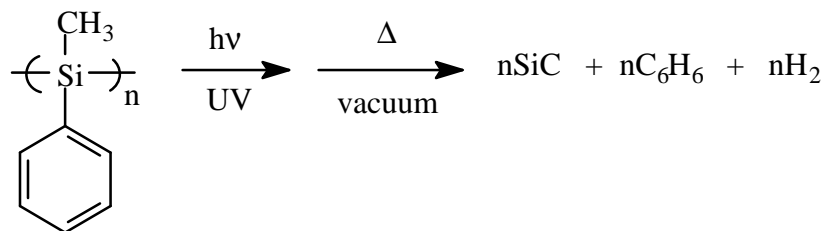


$$\text{Theoretical ceramic yield} = \text{M}[\text{SiC}] / \text{M}[(\text{CH}_3)_2\text{Si}]$$

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

Theoretical ceramic yield = 68.9%

West Process:

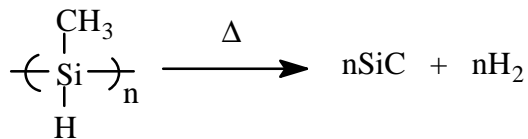


$$\text{Theoretical ceramic yield} = M[\text{SiC}] / M[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si}]$$

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

$$\text{Theoretical ceramic yield} = 33.4\%$$

Harrod Process:

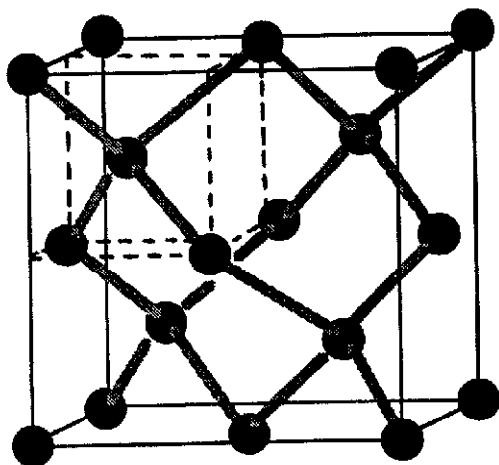


$$\text{Theoretical ceramic yield} = M[\text{SiC}] / M[(\text{CH}_3)(\text{H})\text{Si}]$$

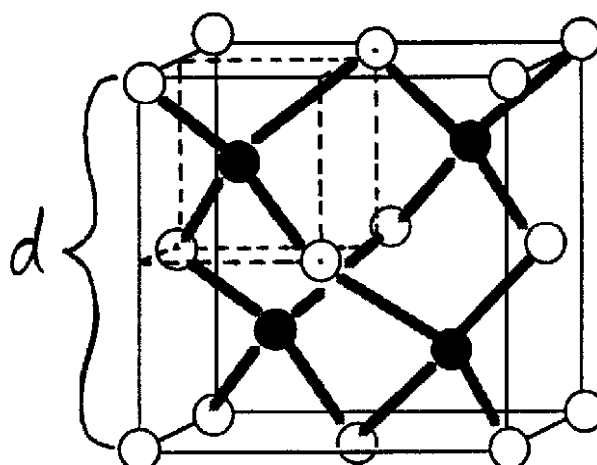
$$\text{Yield} = (40.097 \text{ g mol}^{-1}) / (44.129 \text{ g mol}^{-1})$$

$$\text{Theoretical ceramic yield} = 90.9\%$$

- 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 ( $d_{\text{Si-C}}$ ) then, knowing the atomic radius of carbon, one can calculate the atomic radius of silicon by difference.

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

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

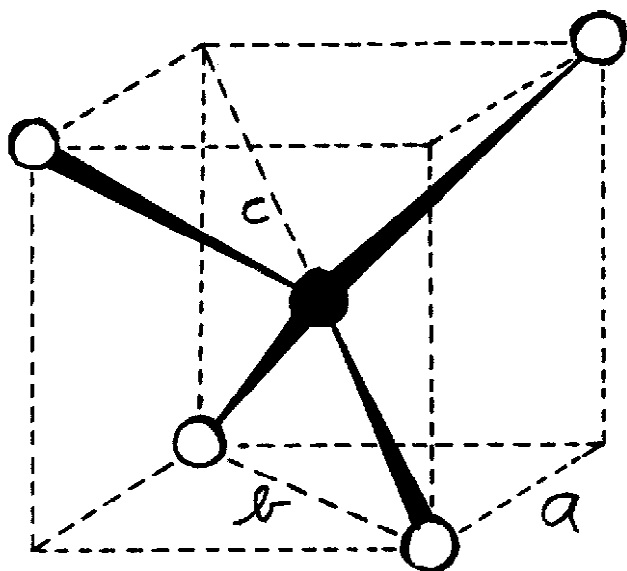
$$V = [(12.5 \text{ cm}^3) / (6.022 \times 10^{23} \text{ SiC/mol})] \times 4 \text{ SiC/unit cell}$$

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

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

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

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,  $d_{\text{Si-C}}$ , is half the length of the diagonal passing through the center of the small cube ( $c/2$ ).



○ : Si

● : C

$$a = \frac{d}{2}$$

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

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

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

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

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

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

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

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

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

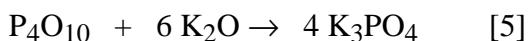
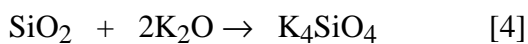
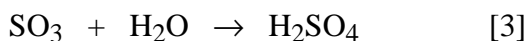
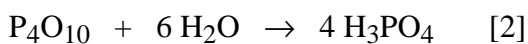
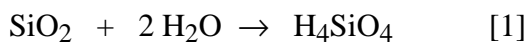
$$\text{Atomic radius of Si} = 1.12 \times 10^{-8} \text{ cm}$$

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

**SOLUTION 27**

- a) Silica,  $\text{SiO}_2$ , 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  $\text{P}_4\text{O}_{10}$  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  $\text{P}=\text{O}$  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  $\text{SiO}_2$ . 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  $\text{P}_4\text{O}_{10}$ , hence its lower melting point.

b)



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  $\text{H}^+$  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  $\text{H}^+$  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)  $2 \text{Y}_2\text{O}_3 + 8 \text{BaCO}_3 + 12 \text{CuO} + \text{O}_2 \rightarrow 4\text{YBa}_2\text{Cu}_3\text{O}_7 + 8\text{CO}_2$
- b)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has 14 negative charges from the 7  $\text{O}^{2-}$ .

The positive charges from the metal ions sum to:

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

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

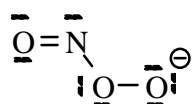
- c) Molecular weight of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is  $666 \text{ g mol}^{-1}$ .  
Observed weight loss is  $9.88/10.00 = 1.2$  per cent.  $1.2$  per cent of  $666 \text{ g} = 7.99 \text{ g}$ .  
If this is all O, then we have lost  $0.5 \text{ g atom}$ . Therefore, the new composition is  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ . 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  $2 \times \text{Cu(II)}$  and a single  $\text{Cu(III)}$ . In the deoxygenated material all three Cu's are  $\text{Cu(II)}$ .

**SOLUTION 29**

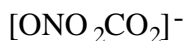
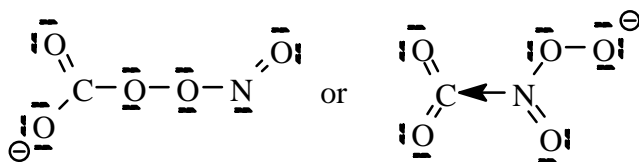
- a) The valence electron counts of the relevant atoms are : H(1), C(4), N(5), O(6).

$O_2^-$ : (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

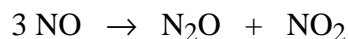
The unpaired electron on the superoxide will pair with the unpaired electron on the N to form a covalent bond. This is a radical combination reaction. Because the N in the product has a lone pair, the molecule will be bent, thus:



$CO_2$  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:



- b) Radical combination and acid/base reactions. See discussion in part (a).
- c)  $Cu^+ + NO_2^- + 2 H^+ \rightarrow Cu^{2+} + NO + H_2O$
- d) Compression of NO to 100 atm at 50 °C leads to a disproportionation according to the equation:



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<sub>2</sub> 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.

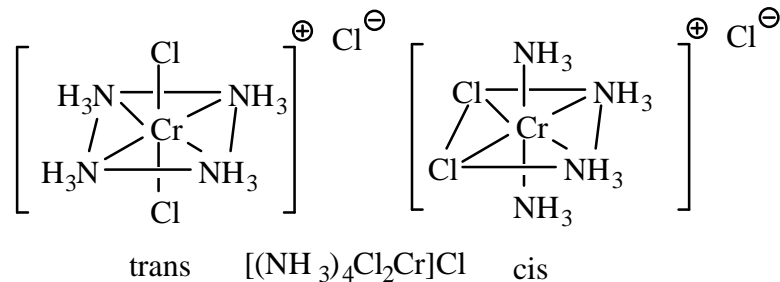
**SOLUTION 30**

a) The Cr<sup>3+</sup> and Co<sup>3+</sup> 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<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>Cr]Cl. This compound has a unipositive complex cation in which a Cr<sup>3+</sup> is surrounded by two Cl's and four NH<sub>3</sub> 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.

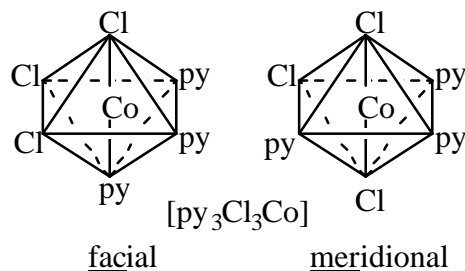
The compounds are: *trans*-tetraamminedichlorochromium(III) chloride  
*cis*-tetraamminedichlorochromium(III) chloride



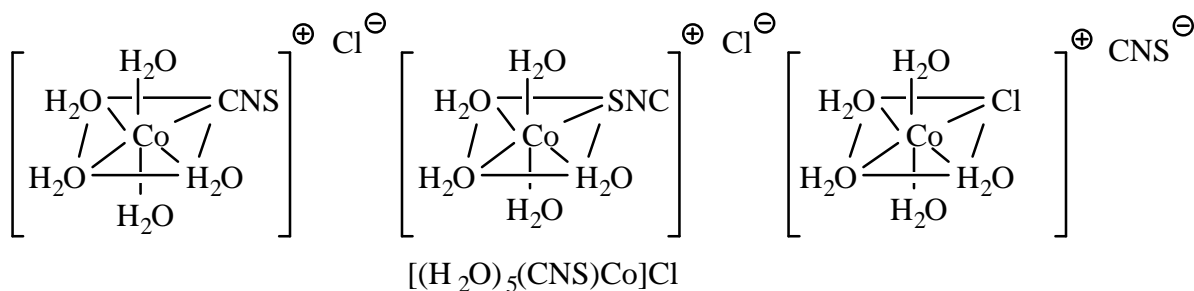
ii) [py<sub>3</sub>Cl<sub>3</sub>Co]. This neutral Co<sup>3+</sup> complex is also octahedral. There are two different ways of arranging the triads of like ligands. The facial isomer is obtained when they are all on the corners of a common triangular face of the octahedron (placing three like ligands 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)



- iii)  $[(\text{H}_2\text{O})_5(\text{CNS})\text{Co}]\text{Cl}$ : 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.



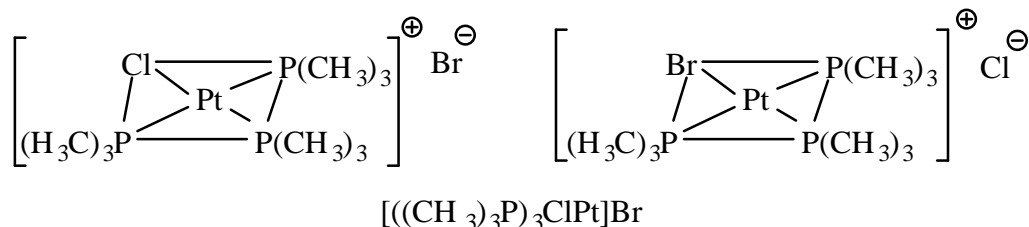
The resulting isomers are known as linkage isomers. Another possible isomer of this compound would result from interchange of the coordinated CNS with the free Cl. This is known as ionization isomerism.

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

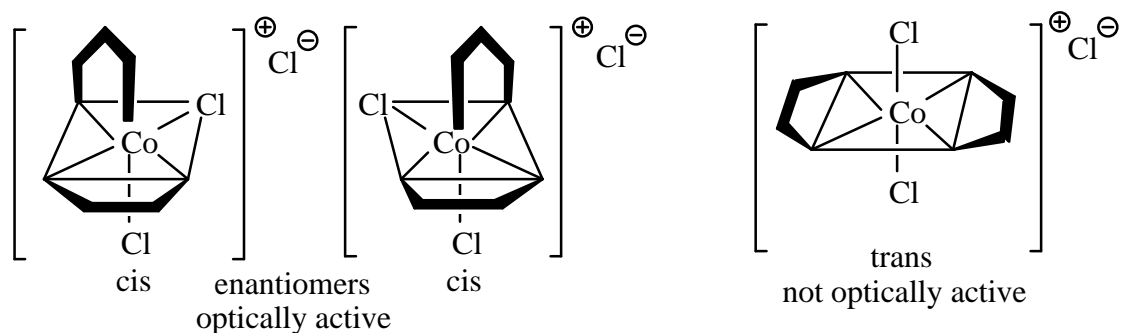
- iv)  $[(\text{Me}_3\text{P})_3\text{ClPt}]\text{Br}$ : The complex ion consists of a  $\text{Pt}^{2+}$  coordinated to three neutral phosphines and a uninegative Cl at the corners of a square. There is

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



- 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  $\text{Co}^{3+}$  complexes have octahedral geometry, he deduced that  $[\text{en}_2\text{Cl}_2\text{Co}]\text{Cl}$  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.



- 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  $[(\text{NH}_3)_x\text{Cl}_3\text{Cr}]$  ( $x=3$  to 6) are:  $[(\text{NH}_3)_3\text{Cl}_3\text{Cr}]$  (neutral);  $[(\text{NH}_3)_4\text{Cl}_2\text{Cr}]\text{Cl}$  (2 ions);  $[(\text{NH}_3)_5\text{ClCr}]\text{Cl}_2$  (3 ions);  $[(\text{NH}_3)_6\text{Cr}]\text{Cl}_3$  (4 ions). From the numbers of ions, it is possible to conclude that the number of ligands coordinated to  $\text{Cr}^{3+}$  remains at 6 throughout the series.

**SOLUTION 31**

- a)  $\Delta E = q + w$  (conservation of energy)
- b)  $\Delta S = \int \frac{dq_{\text{rev}}}{T}$  and can only 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  $dw_{\text{rev}} = -P_{\text{ext}}dV$ , thus

$$dq = -dw = +P_{\text{ext}}dV$$

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

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

Since  $PV = nRT$  we can again substitute to obtain

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

Integrating gives:

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

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

$$\Delta G = -nRT \ln 2 \text{ (which is } < 0 \text{)}$$

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

Therefore:

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

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

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

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

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

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

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

- g) Note that if each particle has two possible states, then with  $N_0$  particles there are  $2^{N_0}$  possible arrangements.

$$\Delta S = S_2 - S_1$$

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

$$= k \ln(2^{N_0}) - k \ln(1^{N_0})$$

$$= k \ln(2^{N_0})$$

$$= N_0 k \ln 2$$

$$= nR \ln 2 \quad (\text{since } k = R/N_0)$$

### SOLUTION 32

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

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

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

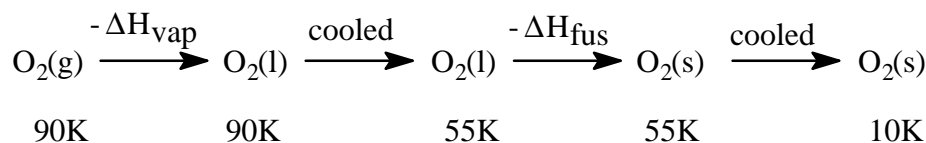
and therefore  $w = +597 \text{ J}$ .

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

$$\begin{aligned}\Delta S_{\text{sys}} &= n\bar{C}_p \ln(T_1/T_2) - nR \ln(P_2/P_1) = n\bar{C}_v \ln(T_2/T_1) + nR \ln(V_2/V_1) \\ &= 28.2 \ln(90/120) - 8.314 \ln(1/4) \\ &= -8.11 + 11.53 \\ &= 3.42 \text{ JK}^{-1} \text{ (which is as it must be = 0)}\end{aligned}$$

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

b) The overall process is:



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

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

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

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

$$\begin{aligned}\Delta S_{\text{sys}} &= -6820/90 + 54 \ln(55/90) - 420/55 + 41 \ln(10/55) \\ &= -75.8 - 26.6 - 7.6 - 69.9 \\ &= -179.9 \text{ JK}^{-1}\end{aligned}$$

### SOLUTION 33

a)  $\Delta H^{\circ}_{\text{rxn}} = \sum \Delta H^{\circ}_{\text{f}}(\text{prod}) - \sum \Delta H^{\circ}_{\text{f}}(\text{reactants})$

$$\begin{aligned}&= \Delta H^{\circ}_{\text{f}}(\text{NH}_3) + \Delta H^{\circ}_{\text{f}}(\text{CO}_2) - \Delta H^{\circ}_{\text{f}}(\text{urea}) - \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}) \\ &= (2(-80.8) + (-412.9)) - ((-317.7) - 285.8)) \\ &= 29.0 \text{ kJ}\end{aligned}$$

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

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

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

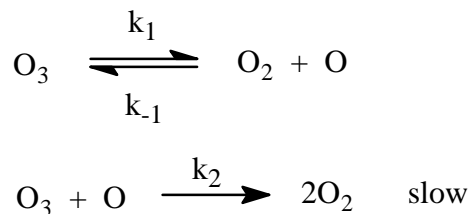
b)  $\Delta G = \Delta G^\circ + RT \ln Q$  and  $Q = \frac{(0.1)(0.01)^2}{(1)(55.5)}$

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)



$$\frac{-d[\text{O}_3]}{dt} = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}_3][\text{O}]$$

The steady state approximation gives  $\frac{d[\text{O}]}{dt} = 0 = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}_3][\text{O}]$

Therefore we have  $[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}$  and substitution of this into the above gives:

$$-\frac{d[\text{O}_3]}{dt} = k_1[\text{O}_3] - \frac{k_1[\text{O}_3]k_{-1}[\text{O}_2]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} + \frac{k_1[\text{O}_3]k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \text{ which simplifies to:}$$

$$-\frac{d[\text{O}_3]}{dt} = k_1[\text{O}_3] \left( \frac{2k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \right) = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}$$

If  $k_{-1}[\text{O}_2] \gg k_2[\text{O}_3]$  then:  $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2]} = \frac{2k_1k_2[\text{O}_3]^2[\text{O}_2]^{-1}}{k_{-1}} = k_{\text{exp}}[\text{O}_3]^2[\text{O}_2]^{-1}$

If  $k_{-1}[\text{O}_2] \ll k_2[\text{O}_3]$  then:  $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_2[\text{O}_3]} = 2k_1[\text{O}_3] = k'_{\text{exp}}[\text{O}_3]$

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

### SOLUTION 35

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

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

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

b) Substituting in data from the first experiment:

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

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

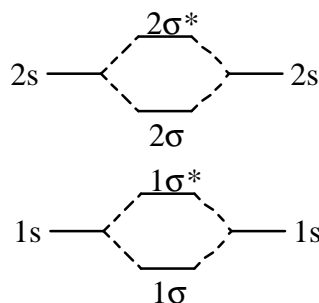
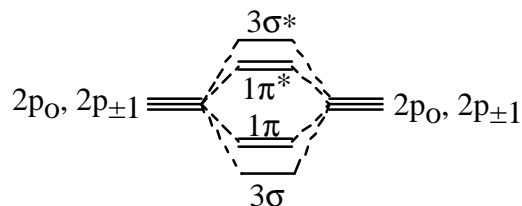
There is a large excess of Y and Z with respect to X and thus the rate equation simplifies and becomes:  $\text{rate} = k'[\text{X}]^2$  where  $k' = k[2.00]^{0.5}$

Pseudo second order kinetics now apply and thus:

$$t_{1/2} = \frac{1}{c_0 k'} = \frac{1}{(0.01)(283\text{M}^{-1}\text{h}^{-1})} = 0.35\text{h} \text{ (21 min)}$$

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  $\sigma_{6s}$  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.

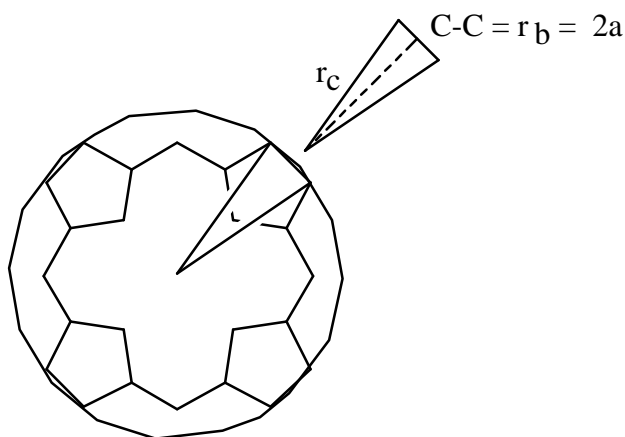
**SOLUTION 37**

- a) Mg has the configuration  $[\text{Ne}](3s^2)$  and does not possess any p orbitals in its valence shell. It thus only has  $\sigma$  electrons available and cannot become involved in the  $\pi$  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

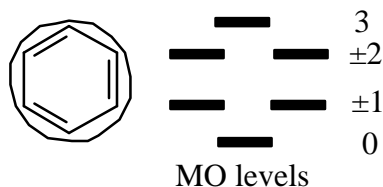


with the internal angle at the centre of each triangle thus being  $360^\circ/12 = 30^\circ$  and a base of one C-C bond length which is equal to  $r_b = 1.50 \times 10^{-8} \text{ cm}$ . Dividing the isosceles triangle in half so that it is made up of two right triangles, we thus have:

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

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

- 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  $\pi$  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  $\pi$  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  $\pi$ -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  $l = \pm 1$ . For chlorophyll, the 18 electrons will fully fill up to and including the orbital having  $l = \pm 4$ .

$$\text{Benzene HOMO } l = \pm 1: \quad E_{\pm 1} = \frac{\hbar^2}{2mr_b^2}$$

$$\text{Chlorophyll HOMO } l = \pm 4: \quad E_{\pm 4} = \frac{\hbar^2 4^2}{2mr_c^2} = \frac{16\hbar^2}{2m(2r_b)^2} = \frac{16\hbar^2}{8mr_b^2} = \frac{2\hbar^2}{mr_b^2}$$

d) Benzene LUMO  $l = \pm 2$ : 
$$E_{\pm 2} = \frac{\hbar^2 2^2}{2mr_b^2} = \frac{4\hbar^2}{2mr_b^2}$$

$$\text{Chlorophyll LUMO } l = \pm 5: \quad E_{\pm 5} = \frac{\hbar^2 5^2}{2mr_c^2} = \frac{25\hbar^2}{2m(2r_b)^2} = \frac{25\hbar^2}{8mr_b^2}$$

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

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

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

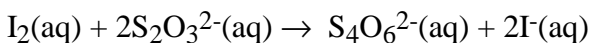
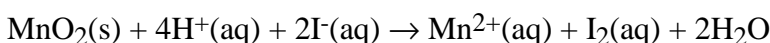
In chlorophyll, the C-C-C path is actually longer than the direct C-C distance determined above. The effective distance is actually about  $\sqrt{2} \times r_c$ . Thus reworking the above relationship gives:

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

Thus  $\Delta E_{\text{abs}}$ (chlorophyll) is again predicted to be less than  $\Delta E_{\text{abs}}$ (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



b)  $n(\text{S}_2\text{O}_3^{2-}) = (9.75 \times 10^{-3} \text{ mol/L}) (0.02753 \text{ L})$   
 $= 2.68 \times 10^{-4} \text{ mol}$   
ratio of  $\text{O}_2 = \text{S}_2\text{O}_3^{2-}$  is 1:4  
moles of  $\text{O}_2 = \frac{2.68 \times 10^{-4}}{4} \text{ mol} = 6.71 \times 10^{-5}$

$\text{O}_2 \text{ g/mol} = 2 \times 15.999 = 31.998 \text{ g/mol}$   
 $\text{O}_2 \text{ mol/L sample} = \frac{6.71 \times 10^{-5} \text{ mol}}{0.25 \text{ L}} = 26.84 \times 10^{-4} \text{ mol}$

$\text{O}_2 \text{ g/L} = 26.84 \times 10^{-5} \text{ mol/L} \times 31.998 \text{ g/mol}$   
 $= 0.008588 \text{ g/L}$   
 $= 8.59 \text{ mg/L}$   
 $= 8.59 \text{ ppm}$

### SOLUTION 39

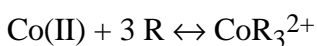
- a) First, correcting for the dilution of the aliquot during the second measurement.  
Corrected absorbance =  $0.517 \times \frac{26.0}{25.0} = 0.538$   
Absorbance due to 0.05 mg of phosphate =  $0.538 - 0.428 = 0.110$
- b) mg phosphate in the aliquot of specimen =  $\frac{0.428}{0.110} \times 0.05 = 0.195 \text{ mg}$
- c) Concentration of phosphate in the patient's urine  
 $= \frac{100}{25.0} \times 0.195 \times \frac{1}{5.00} = 0.156 \text{ mg/mL}$   
 $= 0.156 \text{ mg/mL} \times 1000 \text{ mL/L}$   
 $= 156 \text{ mg/L phosphate}$
- 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  $\text{CoR}_3^{2+}$

b) Formation constant

Stoichiometry where lines intersect indicates the following :



$$\text{formation constant } K_f = \frac{[\text{CoR}_3^{2+}]}{[\text{Co(II)}][\text{R}]^3}$$

$$\text{at } A_1, \text{Co(II)} = \text{CoR}_3^{2+} = 2.5 \times 10^{-5} \text{ mol/L}$$

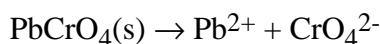
$$\text{R} = 7.5 \times 10^{-5} \text{ mol/L}$$

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

#### SOLUTION 41

a) The solubility product  $K_{sp}$  of lead chromate at 18 °C is  $1.77 \times 10^{-14}$ .

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



Therefore, in pure water, the solubility of lead chromate is equal to the concentration of either the  $\text{Pb}^{2+}$  or the  $\text{CrO}_4^{2-}$  in a saturated salt solution.

Therefore,

$$\text{Pb}^{2+} = \text{CrO}_4^{2-} = S_{\text{PbCrO}_4} = 1.33 \times 10^{-7} \text{ mol/L } (\sqrt{k_{sp}})$$

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,

$$S_{\text{PbCrO}_4} = S_{\text{Pb}^{2+}} = \frac{k_{sp\text{PbCrO}_4}}{[\text{CrO}_4^{2-}]} = \frac{1.77 \times 10^{-14}}{0.1} = 1.77 \times 10^{-13}$$

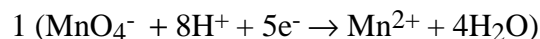
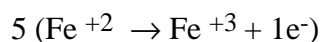
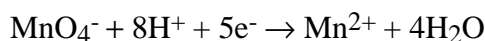
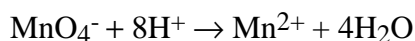
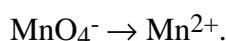
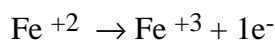
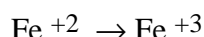
Note: There are two sources of chromate ions in solution.

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

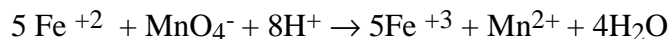
$$\begin{aligned} \text{c) } S_{\text{PbCrO}_4} = [\text{CrO}_4^{2-}] &= \frac{k_{\text{spPbCrO}_4}}{3.00 \times 10^{-7} + [\text{CrO}_4^{2-}]} = \frac{1.77 \times 10^{-14}}{3.00 \times 10^{-7} + [\text{CrO}_4^{2-}]} \\ &= 0.505 \times 10^{-7} \text{ mol/L} \end{aligned}$$

### SOLUTION 42

Balance the reaction:



Overall



Calculate moles of Fe from the titration:

moles of Fe in sample 1:

$$= (0.00749 \text{ L KMnO}_4) (0.0592 \text{ M KMnO}_4) (5 \text{ mol Fe} / 1 \text{ mol KMnO}_4)$$

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

Calculate weight percent Fe<sub>2</sub>O<sub>3</sub> contained in the ore:

$$\begin{aligned} \text{wt Fe}_2\text{O}_3 \text{ sample 1} &= (2.217 \times 10^{-3} \text{ mol Fe}) (1 \text{ mol Fe}_2\text{O}_3 / 2 \text{ mol Fe}) (2(55.847)) \\ &\quad + 3(15.9994) \text{ g Fe}_2\text{O}_3 / \text{mol Fe}_2\text{O}_3 = 0.1770 \text{ g Fe}_2\text{O}_3 \end{aligned}$$

$$\text{wt \% Fe}_2\text{O}_3 \text{ sample 1} = 100 (0.1770 \text{ g Fe}_2\text{O}_3 / 0.500 \text{ g ore}) = 35.4 \% \text{ Fe}_2\text{O}_3$$

**SOLUTION 43**

Calculate grams of cleaner titrated:

$$(10.000 \text{ g} / (10.000 \text{ g} + 90.012 \text{ g})) (5.000 \text{ g}) = 0.4999 \text{ grams solution}$$

Calculate moles of  $\text{NH}_3$  from titration:

$$\text{moles HCl used} = \text{moles NH}_3 \text{ present} = (0.04211 \text{ L}) (0.05042 \text{ M}) = 2.123 \times 10^{-3} \text{ mol}$$

Determine grams of  $\text{NH}_3$  from molecular weight:

$$(2.123 \times 10^{-3} \text{ mol NH}_3) (14.0067 + 3 (1.00797) \text{ g/mol}) = 3.616 \times 10^{-2} \text{ g NH}_3$$

Determine percent  $\text{NH}_3$  in titrated sample:

$$\text{wt \% NH}_3 = 100 (3.616 \times 10^{-2} \text{ g NH}_3 / 0.4999 \text{ g solution}) = 7.233 \%$$

## 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  $\text{Mg}^{2+}$  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  $\text{Pb}^{2+}$  solution and 25.00 mL EDTA solution required 11.00 mL  $\text{Mg}^{2+}$  standard solution:

$$\text{moles EDTA} = \text{moles Mg}^{2+} + \text{moles Pb}^{2+}$$

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

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

$$\text{moles Pb}^{2+} = \text{moles EDTA} - \text{moles Mg}^{2+} = 1.53 \times 10^{-4} \text{ mol Pb}^{2+}$$

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

**PROBLEM 47 - EXPERIMENTAL**

**Determination of the  $K_{sp}$  of  $\text{CaSO}_4$**

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

$$K_{sp}(\text{CaSO}_4) = [\text{Ca}^{2+}] [\text{SO}_4^{2-}]$$

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

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

**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	$1.66054 \times 10^{-27}$ kg	Unité de masse atomique
Avogadro's number	$N$	$6.02214 \times 10^{23}$ mol <sup>-1</sup>	Nombre d'Avogadro
Bohr radius	$a_0$	$5.292 \times 10^{-11}$ m	Rayon de Bohr
Boltzmann constant	$k$	$1.38066 \times 10^{-23}$ J K <sup>-1</sup>	Constante de Boltzmann
Charge of an electron	$e$	$1.60218 \times 10^{-19}$ C	Charge d'un électron
Dissociation constant (H <sub>2</sub> O)	$K_w$	$10^{-14}$ (25 °C)	Constante de dissociation de l'eau (H <sub>2</sub> O)
Faraday's constant	$F$	96,485 C mol <sup>-1</sup>	Constante de Faraday
Gas constant	$R$	$8.31451$ J K <sup>-1</sup> mol <sup>-1</sup> $0.08206$ L atm K <sup>-1</sup> mol <sup>-1</sup>	Constante des gaz
Mass of an electron	$m_e$	$9.10939 \times 10^{-31}$ kg $5.48580 \times 10^{-4}$ amu	Masse d'un électron
Mass of a neutron	$m_n$	$1.67493 \times 10^{-27}$ kg 1.00866 amu	Masse d'un neutron
Mass of a proton	$m_p$	$1.67262 \times 10^{-27}$ kg 1.00728 amu	Masse d'un proton
Planck's constant	$h$	$6.62608 \times 10^{-34}$ J s	Constante de Planck
Speed of light	$c$	$2.997925 \times 10^8$ m s <sup>-1</sup>	Vitesse de la lumière

$$1 \text{ \AA} = 1 \times 10^{-8} \text{ cm}$$

$$1 \text{ eV} = 1.60219 \times 10^{-19} \text{ J}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ atm} = 101.325 \text{ kPa}$$

$$1 \text{ bar} = 1 \times 10^5 \text{ Pa}$$

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.

Gordon Bates  
Department of Chemistry  
University of British Columbia  
Vancouver, B.C.  
Canada  
V6T 1Z1

e-mail: [flip@chem.ubc.ca](mailto:flip@chem.ubc.ca)

NOTES