



PREPARATORY PROBLEMS

AND

WORKED SOLUTIONS

Melbourne, Australia July 5 – 14, 1998

The Royal Australian Chemical Institute

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April 1998

A Note to Mentors

During the 29th International Chemistry Olympiad in Montreal, the International Jury resolved to reduce the number of preparatory theoretical problems from about 50 (that had been common practice in recent years) to 25. We have achieved that aim (almost - we have 26 theory problems but as you will see, Problem 26 is more of a study guide) and have taken pains to ensure that the exercises cover the Level 3 areas that will be represented in the 30th IChO examinations in Melbourne. For your convenience, we have included the list of topics that are generally accepted as the basis for examination questions for the International Chemistry Olympiad - this is the same list of topics that we inherited from Montreal.

More importantly, the problems have been designed to challenge and stimulate the interests of the best pre-university chemistry students in your country! We have also provided detailed worked answers for each problem and hope that your students will learn a considerable amount of chemistry from these worked solutions without your continual assistance.

This year we have 4 detailed preparatory laboratory exercises that cover the skills that your students need to show in Melbourne. We have tried to highlight the procedures in each exercise that need some particular caution, even for students of Olympiad level but our warnings cannot be comprehensive - your students will still need your careful supervision. We have also not included specific details for handling or disposal of the products of these lab exercises, as these will vary greatly from country to country, but we know that you will employ best-practice to responsibly dispose or recycle the materials that your students use and produce. Students should of course also make themselves aware of any hazards associated with the chemicals that they will be using in any exercise and we encourage you to bring these to their attention.

For our junior colleagues who will spend many hours over the coming months thinking about these exercises, we will provide an opportunity to discuss these exercises (and other matters) with their fellow students from all over the world, even before they come together in Melbourne. We have set up a web-based chat forum so that they can get to know one another (after all - isn't that one of the main reasons for the Olympiads?) and we encourage you to bring the chat forum to their attention and indeed, enter into the discussion yourselves.

Finally, despite the valiant proof-reading efforts of my colleagues, it would be surprising if you don't uncover a bug or two still lurking here. Such deficiencies are of course my responsibility, so please don't hesitate to bring them to my attention. Corrections will be regularly sent by email to each delegation and published on the web page whose address is given below. Corrected copies of this document in several formats will also be available for downloading from the web page.

Good luck in your preparations, and we look forward to meeting you in Melbourne.

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The Preparatory Problems page on the WWW is

<http://www.ch.adfa.oz.au/ASO/IChO/30IChO/PrepProblems.html>

Scientific Jury of the 30th International Chemistry Olympiad

Dr Patricia Angus	Australian National University
Dr Alan Arnold (Chair)	University College (UNSW) ADFA
Assoc. Prof. Neil Barnett	Deakin University
Dr Ross Coller	University of Melbourne
Dr Susan Cumming	Royal Australian Chemical Institute
Prof Dainis Dakternieks	Deakin University
Mrs Carolyn Elvins	Presbyterian Ladies College
Dr Greg Klease	Central Queensland University
Dr Simon Petrie	University College (UNSW) ADFA
Prof Colin Raston	Monash University
Prof. Richard Russell	Deakin University
Dr Greg Simpson	CSIRO Molecular Science
Dr Suzanne Smith	ANSTO
Dr Brian Yates	University of Tasmania

Draft Syllabus for the International Chemistry Olympiad

Classification of the chemical topics

Group 1: These topics are included in the overwhelming majority of secondary school chemistry programs.

Group 2: These topics are included in a substantial number of secondary school programs; however, if not covered, it would be expected that the Olympiad level students from every country would have been introduced to these topics.

Group 3: These topics are not included in the majority of secondary school programs.

For a host nation it is no longer necessary to have preparatory problems on Group 1 and Group 2 topics, although, in the latter case, a listing of the specific topics of that Group which might be part of the Olympiad Examination is to be given by the host nation. Any topics in Group 3 which might appear on the Olympiad Examination must be covered in the preparatory problems.

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. Simple molecular structures with central atom	3
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
39	products of reaction of the metals with oxygen	2
40	heavier elements are more reactive	1

- 41 Li 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 reaction with O_2 to form NO_2	1
46	equilibrium between NO_2 and N_2O_4	1
47	products of reaction of NO_2 with water	1
48	HNO_2 and its salts are reductants	1
49	HNO_3 and its salts are oxidants	1
50	N_2H_4 is a liquid and reductant	3
51	there exists acids like $\text{H}_2\text{N}_2\text{O}_2$, HN_3	3
52	to remember, what are products of reduction of nitrates or HNO_3 with different metals and reductors	3
53	reaction of $\text{Na}_2\text{S}_2\text{O}_3$ 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)	2
58	products of reactions of nonmetal oxides with water and stoichiometry of resulting acids	1
59	reactions of halogens with water	2
60	reactivity and oxidizing power of halogens decrease from F_2 to I_2	1
61	differences of chemistry between row 4 and row 3 elements	3

d-BLOCK

62	common oxidation states of the common d-block metals are Cr(III) , Cr(VI) , Mn(II) , Mn(IV) , Mn(VII) , Fe(II) , Fe(III) , Co(II) , Ni(II) , Cu(I) , Cu(II) , Ag(I) , Zn(II) , Hg(I) , Hg(II)	1
63	colors of the listed common ions in aqueous solution	2
64	other oxidation states and chemistry of other d-block elements	3
65	Cr , Mn , Fe , Ni , Co , Zn dissolve in dil HCl ; Cu , Ag , Hg do not dissolve	1
66	products of the dissolution are $(2+)$ cations	2
67	passivation of Cr , Fe (and also Al) Cr(OH)_3 and Zn(OH)_2 are amphoteric, other common hydroxides are not	1
68	MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ are strong oxidants	1

69	products of reduction of MnO_4^- depending on pH	2
70	polyanions other than $\text{Cr}_2\text{O}_7^{2-}$	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 substitution (eg with Cl_2)	1
77	- products	1
78	- free radicals	2
79	- initiation/termination of the chain reaction cycloalkanes	2
80	- names	1
81	- strain in small rings	2
82	- chair/boat conformation	2

ALKENES

83	planarity	1
84	E/Z (cis/trans) isomerism	1
85	addition of Br_2 , HBr - products	1
86	- Markovnikov 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	stabilisation by resonance	1
95	Huckel $(4n+2)$ 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/sec./tert:Lucas reagent	2
117	formula of glycerin	1

CARBONYL COMPOUNDS

118	nomenclature	1
119	keto/enol tautomerism	2
120	preparation - oxidation of alcohols	1
121	- from carbon monoxide	3
122	reactions: - oxidation of aldehydes	1
123	- reduction with Zn metal	2
124	- addition of HCN	2
125	of NaHSO ₃	2
126	of NH ₂ OH	2
127	- aldol condensation	3
128	- Cannizzaro (PhCH ₂ OH disproportionation)	3
129	- Grignard reaction	2
130	- Fehling (Cu ₂ O) and Tollens (Ag mirror)	2

CARBOXYLIC ACIDS

131	inductive effect and strength	2
132	equivalence of oxygen atoms in anions	2
133	preparation: - from esters	2
134	- from nitriles	2
134	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 & preparation of anhydrides	2
143	oxalic acid: name and formula	1
144	multifunctional acids	2

145	optical activity (eg. lactic acid)	2
146	R/S nomenclature	3
147	plant vs animal fats - differences	2

NITROGEN COMPOUNDS

148	amines are basic	1
149	comparing aliphatic vs aromatic	2
150	names: primary, secondary, tertiary, quaternary	2
151	identification of primary/sec/tert/quatern. in lab.	3
	preparation of amines	
152	- from halogen compounds	2
153	- from nitro compounds (PhNH ₂ from PhNO ₂)	3
154	- from amides (Hoffmann)	3
155	mechanism of Hoffmann r. 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	nitrocompounds: aci/nitro tautomerism	3
161	Beckmann (oxime-amide) rearrangements	3

SOME LARGE MOLECULES

162	hydrophilic/hydrophobic groups	2
163	micelle structure	3
164	preparation of soaps	1
	products of polymerization of	
165	- styrene	2
166	- ethene	1
167	- polyamides	3
168	- phenol + aldehydes	3
169	- polyurethanes	3
170	polymers - cross-linking	3
171	- structures (isotactic etc)	3
172	- chain mechanism of formation	2
173	rubber composition	3

BIOCHEMISTRY**AMINO ACIDS AND PEPTIDES**

174	ionic structure of aminoacids	1
175	isoelectric point	2
176	20 aminoacids (classification in groups)	2
177	20 aminoacids (all structures)	3
178	ninhydrin reaction (incl. equation)	3
179	separation by chromatography	3
180	separation by electrophoresis	3

181	peptide linkage	1	217	photosynthesis (products only)	2
PROTEINS			218	light and dark reaction	3
182	primary structure of proteins	1	219	detailed Calvin cycle	3
183	-S-S- bridges	3	KREBS CYCLE AND RESPIRATION CHAIN		
184	sequence analysis	3	220	formation of CO ₂ in the cycle (no details)	3
185	secondary structures	3	221	intermediate compounds in the cycle	3
186	details of alpha-helix structure	3	222	formation of water and ATP (no details)	3
187	tertiary structure	3	223	FMN and cytochromes	3
188	denaturation by change of pH, temp., metals, EtOH	2	224	calculation of ATP amount for 1 mol glucose	3
189	quaternary structure	3	NUCLEIC ACIDS AND PROTEIN SYNTHESSES		
190	separation of proteins (molecule size and solubility)	3	225	pyrimidine, purine	2
191	metabolism of proteins (general)	3	226	nucleosides, nucleotides	3
192	proteolysis	3	227	formulas of all pyrimidine and purine bases	3
193	transamination	3	228	difference between ribose and 2-deoxyribose	3
194	four pathways of catabolism of amino acids	3	229	base combination CG and AT	3
195	decarboxylation of amino acids	3	230	- " (hydrogen bonding structures)	3
196	urea cycle (only results)	3	231	difference between DNA and RNA	3
FATTY ACIDS AND FATS			232	difference between mRNA and tRNA	3
197	IUPAC names from C ₄ to C ₁₈	2	233	hydrolysis of nucleic acids	3
198	trivial names of most important (ca 5) f.acids	2	234	semiconservative replication of DNA	3
199	general metabolism of fats	3	235	DNA-ligase	3
200	beta-oxidation of fatty acids (formulas & ATP balance)	3	236	RNA synthesis (transcription) without details	3
201	fatty acids & fats anabolism	3	237	reverse transcriptase	3
202	phosphoglycerides	3	238	use of genetic code	3
203	membranes	3	239	start and stop codons	3
204	active transport	3	240	translation steps	3
ENZYMES			OTHER BIOCHEMISTRY		
205	general properties, active centres	2	241	hormones, regulation	3
206	nomenclature, kinetics, coenzymes, function of ATP etc	3	242	hormone feedback	3
CARBOHYDRATES			243	insulin, glucagon, adrenaline	3
207	glucose and fructose: chain formulas	2	244	mineral metabolism (no details)	3
208	- Fischer projections	2	245	ions in blood	3
209	- Haworth formulas	3	246	buffers in blood	3
210	osazones	3	247	haemoglobin: function & skeleton	3
211	maltose as reducing sugar	2	248	- diagram of oxygen absorption	3
212	difference between starch & cellulose	2	249	steps of clotting the blood	3
213	difference between alpha- and beta-D glucose	2	250	antigens and antibodies	3
214	metabolism from starch to acetyl-CoA pathway to lactic acid or to ethanol;	3	251	blood groups	3
215	catabolism of glucose	3	252	acetyl choline structure and functions	3
216	ATP balance for these pathways	3			

INSTRUMENTAL METHODS OF DETERMINING STRUCTURE

UV-VIS SPECTROSCOPY

- 253 identification of aromatic compound 3
254 identification of chromophore 3

MASS SPECTRA

- 255 recognition of: - molecular ion 3
256 - fragments with a help of a table 3
257 - typical isotope distribution 3

IR

- 258 interpretation using a table of group frequencies 3
259 recognition of hydrogen bonds 3
260 Raman spectroscopy 3

NMR

- 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 ^{13}C -NMR 3

X-RAYS

- 266 Bragg law 3
267 electron density diagrams 3
268 coordination number 3
269 unit cell 3
structures of:
270 - NaCl 3
271 - CsCl 3
272 - close-packed (2 types) 3
273 determining of the Avogadro constant from X-ray data 3

POLARIMETRY

- 274 calculation of specific rotation angle 3

PHYSICAL CHEMISTRY

CHEMICAL EQUILIBRIA

- 275 dynamical model of chemical equilibrium 1
chemical equilibrium expressed in terms of
276 - relative concentration 1
277 - relative partial pressures 2
278 the relationship between equilibrium constant for

ideal gases expressed in different ways
(concentrations, pressures, mole fractions) 2

- 279 relation of equilibrium constant and standard Gibbs energy 3

IONIC EQUILIBRIA

- 280 Arrhenius theory of acids and bases 1
281 Broensted-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 conjugate acids & 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 $10^{-7} \text{ mol/dm}^3 \text{ HCl}$ 2
290 calculation of pH for multiprotic acids 2
291 definition of activity coefficient 2
292 definition of ionic strength 3
293 Debye-Hueckel formula 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 ΔG 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 (defin.) 2
310 calculation of rate constant for 1st order reactions 2
311 calculation of rate constant for 2, 3 order reactions 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-Herbie cycle for ionic compounds	3
323	lattice energies - approximate calculations (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 $G = H - T S$	2
331	ΔG 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	Temp. 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 nonideal systems	3
341	- use in fractional distillation	3
342	Henry's law	2
343	Raoult's law	2
344	deviations from Raoult's 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 pipette	1
352	using burette	1
353	choice of indicators for acidimetry	1
354	titration curve: pH (strong AND weak acid)	2
355	- EMF (redox titration)	2
356	calculation of pH of simple buffer solution	2
357	identification of: Ag^+ , Ba^{2+} , Cl^- , SO_4^{2-} ions	1
358	- of Al^{3+} , NO_2^- , NO_3^- , Bi^{3+} ions	2
359	- of VO_3^- , ClO_3^- , Ti^{4+} ions	3
360	- using flame test for K, Ca, Sr	1
361	Lambert-Beer-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 c	3
365	calculation of solubility of $AgCl$ in NH_3 (from K_s and β 's)	3
366	<i>cis</i> and <i>trans</i> forms	3

THEORETICAL CHEMISTRY

367	n, l, m quantum numbers	2
368	energy levels of hydrogen atom (formula)	2
369	shape of p-orbitals	2
370	d orbital stereoconfiguration	3
371	molecular orbital diagram: H_2 molecule	3
372	- N_2 or O_2 molecule	3
373	bond orders in O_2 or O_2^+ or O_2^-	3
374	Hueckel 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 Schroedinger equation	3

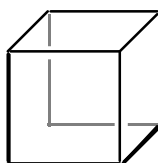
PROBLEM 1.

Hydrocarbons with the empirical formula $(\text{CH})_n$ have a particular fascination for many chemists. Such compounds inevitably feature multiple C-C bonds and/or cyclization in order to achieve valence satisfaction of all atoms. Notable instances of $(\text{CH})_n$ hydrocarbons include:

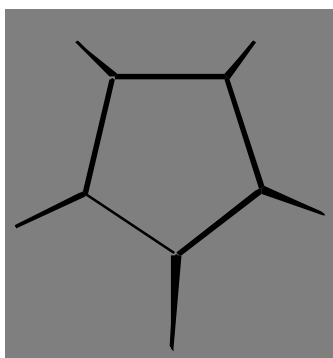
$n = 2$: acetylene (ethyne)

$n = 6$: benzene

$n = 8$: cubane



$n = 20$: dodecahedrane



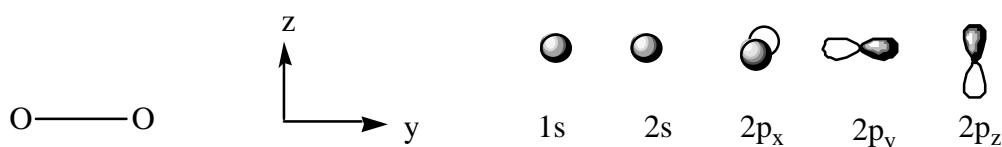
Focussing now on examples with $n = 4$, consider two such compounds: cyclobutadiene and butatriene.

- Draw the structures of these two C_4H_4 isomers.
- The central C=C bond in butatriene is different in length to the other two C=C bonds in this molecule. Why is this? (Hint: consider the hybridization at each atom). Is the central C=C bond shorter, or longer, than the other C=C bonds in butatriene?
- All four carbon atoms in cyclobutadiene are equivalent. There is one other possible valence-satisfied C_4H_4 hydrocarbon for which all four C atoms are equivalent: this compound has not been isolated in the laboratory, despite intense effort by a number of research groups. Draw its structure, and by analogy with some of the other $(\text{CH})_n$ hydrocarbons identified above, suggest a feasible trivial name for this compound.

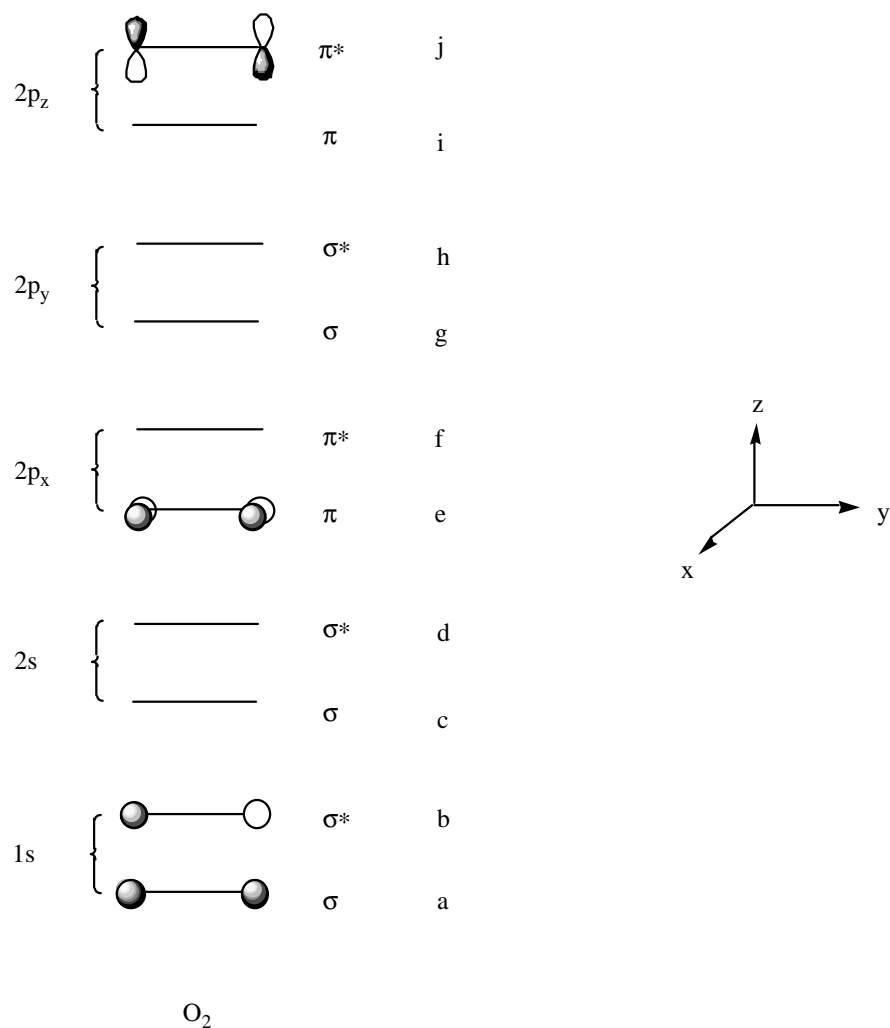
- d). How many different chloro-monosubstituted forms (ie C_4H_3Cl) exist, of
- cyclobutadiene
 - butatriene
 - the compound identified in part c)?
- e). How many different chloro-disubstituted forms (ie $C_4H_2Cl_2$) exist, of
- cyclobutadiene
 - butatriene
 - the compound identified in part c)?
- f). How could the isomers of dichlorobutatriene be distinguished, on the basis of melting points?

PROBLEM 2.

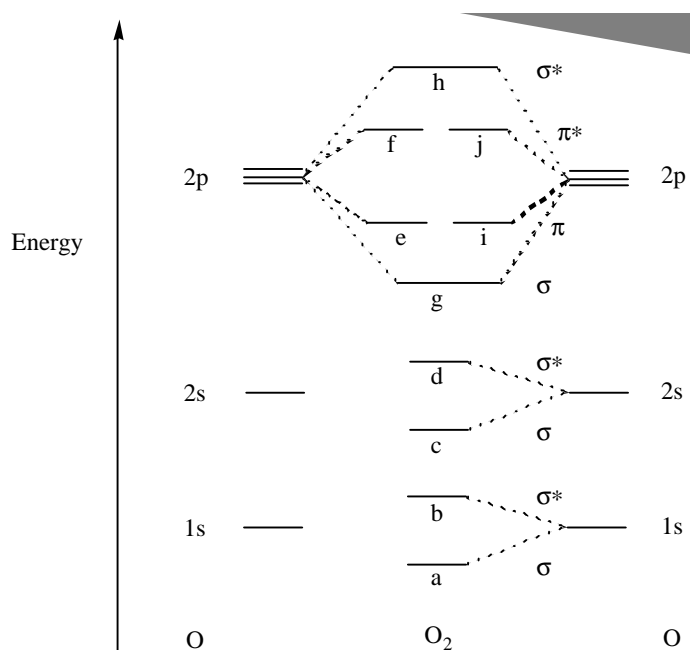
- Draw an energy-level diagram that shows how the 1s atomic orbitals of two hydrogen atoms combine to form the molecular orbitals of H_2 .
- Describe the MOs of H_2 and their relationship to their parent atomic orbitals.
- Why is the higher energy MO in H_2 called an antibonding orbital?
- In a similar way, we may combine the atomic orbitals of more complicated atoms to form molecular orbitals. Consider the oxygen molecule, O_2 . Arrange the oxygen atoms as follows (along the y axis) and assume that there are 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on each atom.



Now, construct the molecular orbitals arising from the interaction of the 2s, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals on two oxygen atoms and fill them in on the diagram below:



- e) We may rearrange these molecular orbitals in order of increasing energy in a molecular orbital diagram:



Why is the energy of orbital g lower than e or i, and similarly, why is the energy of orbital h higher than f or j?

- f) Why do orbitals e and i have the same energy?
- g) If we were to stretch the O₂ molecule (i.e. make the O–O distance bigger) how would the energy of orbital j change? Would this change be more or less than the change in energy of orbital h?

PROBLEM 3.

Molecular orbital theory can be applied to determine the orbital occupancy of CN, NN, and NO.

- a). What is the bond order for each of these molecules?
- b). Which of CN, N₂, and NO has the highest IE (ionization energy)? Which has the lowest IE? $[IE(X) = \Delta H^\circ_f(X^+) - \Delta H^\circ_f(X)]$
- c). Which has the highest electron affinity? (The electron affinity is the energy released upon attachment of an electron to a species, and is positive when electron attachment is exothermic).
- d). Addition or subtraction of electrons from CN or NO produces species which are formally isoelectronic with N₂. Would you expect these isoelectronic analogues to have as high a bond strength as N₂ itself? If so, why? If not, why not?

PROBLEM 4.

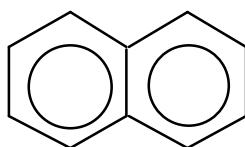
The noble gases were once thought to be completely inert and incapable of chemical bond formation. It is now known that this is not the case, and most general chemistry textbooks now describe some of the krypton- and xenon-containing compounds which have been isolated.

- a). Using valence-bond theory, predict the geometries possible for XeF₂ and XeF₄.
- b). What is the oxidation number of Xe in each of these compounds? Would you expect them to behave as oxidizing or as reducing agents?
- c). Helium is widely known as the most inert of all the elements; yet even helium's 'inertness' is strictly only applicable to its interactions with other neutral atoms and molecules. Compounds of helium, involving formal chemical bonds between helium and other atoms, can exist when the overall entity bears a (generally positive) charge. For example, the helium atom can form observable (though not necessarily long-lived) compounds with H⁺, with He⁺, and with He²⁺. Use MO theory to determine the bond order for each of these cases.

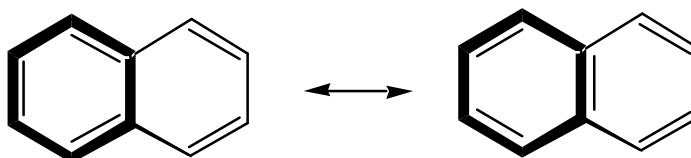
- d). Stable diatomic dications of the formula $X\text{He}^{2+}$ are generally only possible when $\text{IE}(\text{X}^+) < \text{IE}(\text{He})$: that is, when the energy required to further ionize X^+ is less than that needed to ionize He. Without recourse to a table of successive ionization energies, identify which element (called 'Z'), from H to Ar, is most likely to fulfil this criterion.
- e). Which of the immediate neighbours of your identified element Z (ie those elements either 1 left, 1 right, 1 above, or 1 below it in the periodic table) is most likely to also form a stable dication with He? Which of Z's neighbours is least likely to form such a dication?

PROBLEM 5.

Benzene is the prototypical aromatic hydrocarbon. Larger hydrocarbons, consisting of a network of benzenoid rings (somewhat like a small section of a graphitic sheet) can also possess aromatic character and are known as 'polycyclic aromatic hydrocarbons' or PAHs. Many structural features of PAHs can be understood by considering them to be comprised of 6π 'benzenoid' aromatic rings (although larger delocalized systems, such as 10π and 14π systems, should also be considered for completeness). In this question, we shall assume that 6π -delocalized orbitals are sufficient to explain the structural features of PAHs. The simplest PAH is naphthalene, C_{10}H_8 :

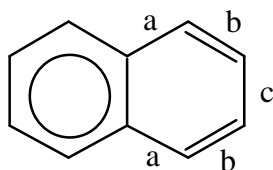


Note that, although naphthalene is generally drawn with both rings fully delocalized, we can expect it to be less aromatic than two separate benzene rings. This is because delocalization in one ring places constraints on the bonding in the other ring:



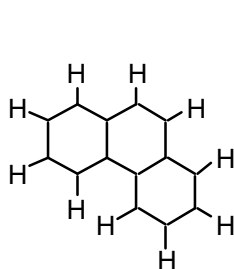
Here, delocalization in the ring shown in bold is only possible if the other ring exhibits a formal alternation of single and double C-C bonds. Obviously in a symmetrical molecule such as naphthalene we should not expect the two rings to exhibit different bonding patterns, and instead we should say that each ring has

some aromatic character (but not as much as a benzene ring) and some tendency to alternation of single and double bonds. If we draw naphthalene like this:

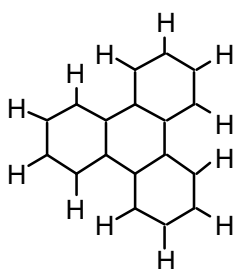


then we can see that bonds 'a' and 'c' have significant single-bond character, while bonds 'b' have substantial double-bond character (and this will also hold true for the analogous bonds on the other ring).

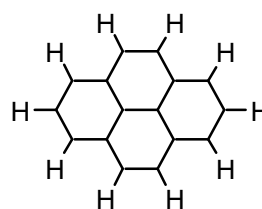
Now consider the carbon skeletons of the following three PAHs:




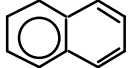
Phenanthrene

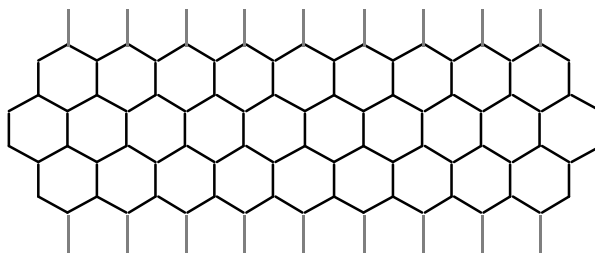


Triphenylene

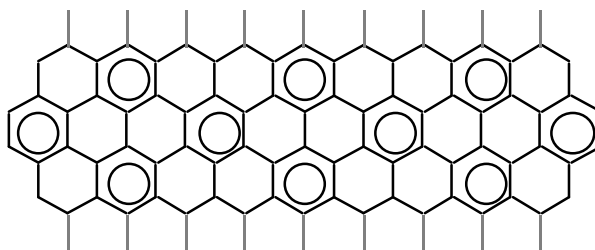


Pyrene

- a). Using  to denote rings having aromatic character, and showing other C-C bonds as formal single or double bonds, show the most aromatic resonance forms possible for each of the above three PAH skeletons. The most aromatic resonance form possible is that having the greatest number of aromatic rings; for naphthalene, this is .
- b). Identify, using the letters 'L' and 'S' respectively, the longest and shortest carbon-carbon bonds in each of phenanthrene, triphenylene, and pyrene. (If a PAH does not feature 'unusually' long or 'unusually' short bonds – i.e. significantly different from the benzene C-C bond length – then do not attempt to label it).
- c). Compare the number of 'fully-aromatic' rings, for the resonance forms obtained in a), to the total number of rings in each PAH. Which is the most aromatic of these PAHs, on this basis? Which is the least aromatic?
- d). Now compare the number of 'fully-aromatic' rings to the number of carbon atoms in each PAH. Which is the most aromatic PAH, and which is the least, on this basis? Is the ordering different from that in c)?
- e). Now consider a sheet of graphite:



- i). What is the average bond order per C-C bond?
- ii). Is each C-C bond longer, or shorter, than in benzene?
- iii). Is graphite more, or less, aromatic (per carbon atom) than benzene?



PROBLEM 6.

A PhD student has received a consignment of all six C_4H_8 isomers (which are gases at room temperature). Unfortunately, during shipping the labels have become detached from the gas cylinders and she cannot correctly identify them. She labels the cylinders as 'A' to 'F' and sets about trying to deduce the contents of each cylinder. She makes the following observations:

- i). A, B, C, and D are seen to decolourise bromine rapidly (even in darkness), while E and F do not.
- ii). The products of the reactions of B and C with Br_2 are found to be stereoisomers of each other.
- iii). A, B, and C all give an identical product when reacted with H_2 over a Pd catalyst.
- iv). E has a higher boiling point than F.
- v). C has a higher boiling point than B.

Identify the contents of the six cylinders.

PROBLEM 7.

One of the most durable general rules in chemistry is that virtually all general rules are violated by some compound or other! For example, O_2 breaks the electron-pairing rule, and PF_5 disobeys the octet rule. Another rule for which

'loopholes' exist is the often-stated requirement for optical isomerism in organic compounds: these compounds must contain an sp^3 hybridized, asymmetric carbon atom which is bonded to four different atoms or groups. It is now known that some of the larger fullerenes, for example some of the C_{76} isomers, are optically active: these are molecules which formally contain only sp^2 hybridized C atoms, and in which each carbon atom is therefore directly bonded to only three other atoms. Here the chirality arises from the fullerene lattice's curvature, and from the asymmetrical pattern of 5- and 6-membered rings which comprise it.

Much simpler organic molecules can also provide unexpected instances of stereoisomerism:

- How many different isomers exist of dichloroethylene? Identify any pairs of stereoisomers. Which category of stereoisomerism is exhibited here?
- How many different dichloropropadiene (dichloroallene) isomers exist? Identify any pairs of stereoisomers. Which category of stereoisomerism is exhibited here?
- For compounds of the general formula $ClHC=(C=)_nCHCl$, formulate a rule which indicates the dependence of isomerism upon n . What is the underlying geometrical basis behind this rule?

PROBLEM 8.

A sample of dichloropropadiene is analyzed in a mass spectrometer. A strong signal is observed in the mass spectrum at a mass-to-charge (m/z) ratio of 75, and another at m/z 77. Under certain operating conditions, these are the only two signals seen in the mass spectrum. Under different conditions, the same sample gives rise to a number of different signals, including m/z 82 (but not 83) and m/z 28 (but not 27). Regardless of the operating conditions, it is found that the signal at m/z 77 is always 60% of the intensity of the peak at m/z 75.

You can assume the following:

- Observed ions are all singly-charged positive ions and arise directly by dissociative ionization of the dichloropropadiene, without any rearrangement occurring during fragmentation.
- The dichloropropadiene has been prepared from elemental carbon, hydrogen, and chlorine in some unspecified fashion: the elemental feedstocks used are known to contain isotopic abundance ratios different from those conventionally observed for hydrogen, carbon, and chlorine, but contain only stable isotopes. Furthermore, no effort has been made to label specific atoms within the molecule with any particular isotope.

- a). What are the chemical formulae of the ions detected at m/z 75 and 77?
- b). What is the isotopic distribution seen in the dichloropropadiene sample? Calculate the percentage of each isotopomer of dichloropropadiene. [Isotopomers are molecules which have identical chemical formulae but which differ in their constituent isotopes.]
- c). What is the molar mass of the sample? Assume, for simplicity, that the atomic mass of each nucleus is exactly equal to its mass number.
- d). Can you identify the isomer of dichloropropadiene studied here?

A recent development of traditional mass spectrometry is Electrospray Mass Spectrometry (ESMS). ESMS differs from conventional mass spectrometry only in the fact that solutions are injected into the mass spectrometer and there is no ionising source. This technique detects only those ions which already pre-exist in solution.

For example, a sample of tetrabutyl ammonium bromide (in an inert solvent) injected into an ESMS gives a peak at $m/z = 242$ as the most intense signal in the positive ion detection mode. There are two major signals, of approximately equal intensity, at $m/z=79$ and $m/z=81$ in the negative ion mode.

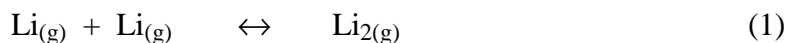
- e). what ion(s) give rise to these three signals?

A sample of isopropanol (propan-2-ol) injected into an ESMS instrument shows a peak at $m/z = 61$ as the most intense signal in the positive ion detection mode. The most intense signal in the negative ion detection mode is at $m/z = 59$.

- f). what ion(s) give rise to these two signals?

PROBLEM 9.

Dilithium, a substance which is crucial to the propulsion system of the Federation starship 'Enterprise', is actually a known species (though it does not exhibit all of the properties which Roddenberry et al.[‡] have ascribed to it!). Dilithium is formed by the adhesion of two lithium atoms in the gas phase:



- a). The enthalpy of formation of dilithium is not easily measurable by direct means. However, the following thermochemical parameters are known:

[‡] For more background information on the starship Enterprise, refer to the WWW sites:
<http://startrek.msn.com/>; <http://startrek.simplenet.com/startrek/>;
<http://www.cs.cityu.edu.hk/~ckmau/engineer.html>; or <http://public.logica.com/~stepneys/sf/filk/dilithim.htm>

$$\Delta H^\circ_f(\text{Li}_{(\text{g})}) = 159.4 \text{ kJ mol}^{-1}$$

$$\text{IE}(\text{Li}_{(\text{g})}) = 5.392 \text{ eV} [1 \text{ eV} = 96.486 \text{ kJ mol}^{-1}]$$

$$D^0(\text{Li}_2^+_{(\text{g})}) = 129.8 \text{ kJ mol}^{-1} [D^0(\text{Li}_2^+_{(\text{g})}) \text{ is the bond strength of } \text{Li}_2^+_{(\text{g})}]$$

$$\text{IE}(\text{Li}_{2(\text{g})}) = 5.113 \text{ eV}$$

Using these values, determine $\Delta H^\circ_f(\text{Li}_{2(\text{g})})$ and $D^0(\text{Li}_{2(\text{g})})$.

- b). The chief warp plasma chemist on the Enterprise is testing the performance of the warp nacelles. He transports 122.045 g of pure lithium into the evacuated reaction chamber within the port warp nacelle. The reaction chamber has a volume of $5.9474 \times 10^5 \text{ m}^3$, and is maintained at an operating temperature of 610.25 K. A highly sensitive pressure monitor indicates that the pressure within the reaction chamber stabilizes at $9.462 \times 10^{-4} \text{ Torr}$ ($1 \text{ Torr} = 0.133322 \text{ kPa}$); a spectrophotojargonometric analysis of the inner surface of the reaction chamber shows that all of the lithium has vaporized. (The reaction chamber, of course, is made from a duranium alloy which has zero vapour pressure at 610.25 K.) What are the concentrations of gaseous lithium and dilithium in the reaction chamber? What is the equilibrium constant, K_c , for reaction (1) at this temperature?

$$[R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}; M_r(\text{Li}) = 6.9410 \text{ g mol}^{-1}]$$

- c). Next, 265.384 g of lithium is transported into an identical, evacuated reaction chamber (also at 610.25 K) within the starboard warp nacelle. The pressure gauge on this chamber stabilizes at $1.0455 \times 10^{-3} \text{ Torr}$. What is the vapour pressure of dilithium at 610.25 K?
- d). Assuming that the reaction $2\text{Li}_{(\text{g})} \rightarrow \text{Li}_{2(\text{g})}$ is the sole source of propulsive energy for the starship Enterprise, calculate the minimum mass of lithium which must be carried as fuel if the Enterprise is to accelerate from rest to a velocity of half lightspeed. The total mass of the Enterprise, which is a large spaceship with a complement of several hundred crew members, is $3.586 \times 10^6 \text{ kg}$ (excluding fuel). To simplify your calculation, you can assume the following:
- relativistic effects can be ignored
 - the reaction chambers can be maintained indefinitely at 610.25 K without any energy cost
 - solid lithium, transported into the reaction chamber, can be vaporized to lithium atoms without any energy cost (conversely, the reverse process does not release any energy)
 - the Li-Li bond enthalpy can be converted with 100% efficiency into the starship's kinetic energy

- the lithium carried as fuel need not be included in the effective mass of the Enterprise.

[Clearly, some of these assumptions are not physically reasonable, but that need not concern us here. We are dealing with science fiction!]

- e). Finally, comment on the apparent suitability (or otherwise) of dilithium formation as a technique for near-light-speed travel. Would formation of diberyllium, $\text{Be}_{2(g)}$, offer a better alternative?

PROBLEM 10.

Elemental analysis of an organic substance, **X**, has indicated its composition as C (40.02% by mass) and H (6.75% by mass). It does not contain detectable quantities of N or S, and it is presumed that the remaining fraction of its composition is oxygen, which cannot be reliably analyzed by direct methods.

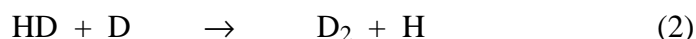
- a). What is the empirical formula of **X**?
- b). **X** is a liquid at room temperature. 10 mL of **X** (density = 1.044 g mL^{-1}) is added to cyclohexane to a total volume of 500 mL. The density of this solution is determined to be 0.777 g mL^{-1} . The solution is found to possess a freezing point of $+2.02^\circ\text{C}$. $T_f(\text{c-C}_6\text{H}_{12}) = 6.60^\circ\text{C}$; $K_f(\text{c-C}_6\text{H}_{12}) = 20.0^\circ\text{C kg mol}^{-1}$. What is the molecular weight and formula of **X**, from the above measurements?
- c). **X** is also readily miscible in water. 50 mL of **X** is added to ultrapure water, again to a total volume of 500 mL. This solution has a density of 1.005 g mL^{-1} , and a freezing point of -3.54°C . $K_f(\text{H}_2\text{O}) = 1.86^\circ\text{C kg mol}^{-1}$. What is the apparent molecular weight of **X** from the above data?
- d). In aqueous solution, **X** is found to react with added base. When 25.00 mL of the aqueous solution of **X**, prepared in c), is titrated against 1.247 mol L^{-1} aqueous NaOH, the endpoint as determined by a pH meter is obtained at 33.60 mL of the hydroxide solution. The titrated system, at endpoint, has a volume of 58.50 mL and a density of 1.003 g mL^{-1} . It is found to freeze at -2.78°C . What is the structure of the product, $(\text{Na}^+)_i\text{Y}^{i-}$, which results from the reaction of **X** with aqueous NaOH?
- e). What is the structure of compound **X**? Comment on any apparent discrepancy in your answers to parts b), c), and d).

PROBLEM 11.

It is often considered that two isotopes will have identical chemical reactivity: however, this is not precisely true. The differing reactivity of different isotopes

arises via the dependence of vibrational energy spacings, in molecules, on the masses of the molecule's constituent atomic nuclei. While the details of this mechanism need not concern us here, it is useful to note that compounds featuring light isotopes (eg. $^1\text{H}^{19}\text{F}$) have slightly lower bond strengths than analogous compounds featuring heavier isotopes (e.g. $^2\text{H}^{19}\text{F}$).

This "isotope effect" is often of little or no importance at room temperature, but it can be crucial in the chemistry of low-temperature regions. One type of widely-studied environment which is characterized by very low temperatures (typically 10 K – 20 K) is that of the dense interstellar clouds, which are the large clouds of gas and dust from which stars ultimately form. Deuterium fractionation in cold interstellar clouds occurs by a variety of processes, including the following mechanism:



Thermochemical parameters relevant to reaction (1) are:

$$\Delta H^\circ_{\text{f}}(\text{H}_{2(\text{g})}) = 0 \text{ kJ mol}^{-1} \quad S^\circ(\text{H}_{2(\text{g})}) = 130.57 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{HD}_{(\text{g})}) = 0.33 \text{ kJ mol}^{-1} \quad S^\circ(\text{HD}_{(\text{g})}) = 143.69 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{H}_{(\text{g})}) = 216.00 \text{ kJ mol}^{-1} \quad S^\circ(\text{H}_{(\text{g})}) = 114.60 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{D}_{(\text{g})}) = 219.76 \text{ kJ mol}^{-1} \quad S^\circ(\text{D}_{(\text{g})}) = 123.24 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Enthalpies of formation are zero Kelvin values (more appropriate to interstellar temperatures than would be 298 K measurements); entropies are 298 K values, but for our purposes can be assumed temperature-independent].

- Determine the free-energy change ΔG° for reaction (1), at $T = 20 \text{ K}$ and at $T = 1000 \text{ K}$. In which direction is this reaction spontaneous, if the initial concentrations of all reactants and products are equal?
- What does the sign of ΔH° (i.e., positive or negative) tell us about the respective bond strengths of H_2 and HD ? What does the sign of ΔS° tell us about reaction (1) in the forward direction, and what is the physical basis for the sign of ΔS° ?
- Now consider reaction (2). What is the sign of ΔH° , and of ΔS° , for reaction in the forward direction? If you assume that the enthalpy and entropy changes are equal in magnitude to those found in a), calculate the free energy change and predict the direction of spontaneous reaction at 20 K, and at 1000 K.
- Molecular hydrogen (in its various isotopic forms) is present in much higher concentrations than atomic hydrogen (and atomic deuterium) in interstellar clouds.

Predict the dominant form of deuterium (ie D, HD or D₂) in interstellar clouds, assuming a temperature of 20 K:

- i). when the cosmic abundance $n(\text{D}) \ll n(\text{H})$ [that is, when the total number of deuterium nuclei, in whatever chemical form, is very much less than the total number of hydrogen nuclei], and
- ii). when $n(\text{D}) = n(\text{H})$. What will be the dominant form of hydrogen under these conditions?

Scenario i) is that which applies in the real universe.

PROBLEM 12.

Helium is the only member of the periodic table to have been detected within an extraterrestrial object (the solar corona) prior to its isolation within the laboratory. We now know much of the physical and chemical properties of helium; but for almost thirty years, from 1868, the solar spectrum was the sole source of information on this novel element.

- a). With our current understanding of quantum theory, this spectrum contains much useful data to analyze. For example, the visible spectrum features a series of absorption lines at wavelengths of 4338, 4540, 4858, 5410 and 6558 Å (1 Å = 10^{-10} m). The spacing of these lines indicates that the absorption is due to excitation of a 'hydrogen-like' atom or ion (i.e., one with an electron configuration equivalent to H). Is this species He, He⁺, or He²⁺?
- b). It can be shown that the energy level common to all of the transitions involved in these absorption lines is the lower energy state $n_i = 4$. To what upper energy states n_f do the respective absorption features lead to? What is the Rydberg-like constant [i.e., the constant analogous to R_H in the atomic hydrogen spectrum] for the absorbing species (Heⁱ⁺) which exhibits these transitions?
- c). The ionization energy (IE) of a species is often measured in electronvolts (eV). What is IE(Heⁱ⁺)?
- d). From atomic spectroscopy, it is now known that $\text{IE}(\text{He}^+) / \text{IE}(\text{He}) = 2.180$. The sum of these two ionization energies gives the appearance energy, AE(He²⁺), for production of He²⁺ from He. The quantity AE(He²⁺) is the minimum quantum of energy which must be deposited into He in order to remove both of its electrons. Calculate the frequency and wavelength of the least energetic photon capable of effecting the double ionization of helium. Is sunlight, at the Earth's surface, an efficient source of such photons?

Useful constants:

$$c = 2.997925 \times 10^8 \text{ m s}^{-1}$$

$$h = 6.62618 \times 10^{-34} \text{ J s}$$

$$1 \text{ eV} = 96.486 \text{ kJ mol}^{-1} = 2.4180 \times 10^{14} \text{ Hz.}$$

PROBLEM 13.

A student (the same unfortunate soul to have featured in Question 6) has received a consignment of alkali halides, but – you guessed it – the labels have come off all but one of the containers: the identified container is potassium bromide. The laboratory in which she works does not have access to any spectroscopic instruments: therefore, in an attempt to identify the unknown alkali halide samples, she uses an ion-exchange column. The ion-exchange resin she selects is a cross-linked polystyrene resin of the strong acid type, containing sulfonic acid groups ($-\text{SO}_3\text{H}$) from which only the protons can be exchanged. She analyzes the six unknown alkali halide samples (and the KBr, as a test of the validity of the method) in the following manner:

She weighs out $0.50 \pm 0.01 \text{ g}$ of each sample, which is dissolved in distilled water in a 100 mL volumetric flask. 40 mL of each solution is passed through the column; the eluant is collected in a 250 mL volumetric flask, and the column is washed through twice with distilled water; the eluant sample is then made up to 250 mL. Before the next sample is run through the column, she recharges the column resin by washing it with sufficient 1M HCl, and then with distilled water. She titrates 50 mL aliquots of each eluant sample, in triplicate, against sodium hydroxide solution (nominal concentration = $3.26 \times 10^{-2} \text{ mol L}^{-1}$) using phenolphthalein as an indicator, obtaining the following results:

Sample	Mean titre volume
A	$21.15 \pm 0.1 \text{ mL}$
B	$29.30 \pm 0.1 \text{ mL}$
C	$7.40 \pm 0.1 \text{ mL}$
D	$21.20 \pm 0.1 \text{ mL}$
E	$10.30 \pm 0.1 \text{ mL}$
F	$29.15 \pm 0.1 \text{ mL}$
KBr	$10.25 \pm 0.1 \text{ mL}$

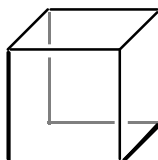
In analyzing these results, you can assume that

- each sample is of $> 99 \%$ purity

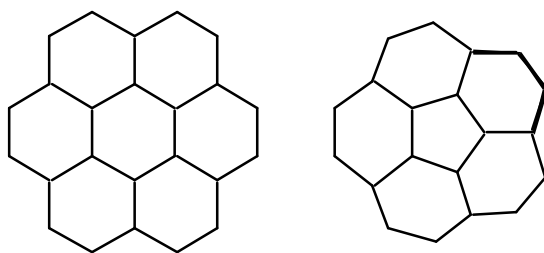
- each container is both water- and air-tight
 - no two containers contain the same alkali halide; the consignment included fluorides, chlorides, bromides and iodides, but no astatine compounds.
- a). What is the reasoning behind the student's use of the above procedure? Write chemical reaction equations for any reactions occurring.
- b). Which of the samples can be positively identified from this analysis? Which of the samples can only be narrowed down to two or three possibilities?
- c). Using available equipment in the lab – including a watchglass, a roll of litmus paper, an acidified solution of sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and a dropper bottle of starch solution – the student was able to identify each of the six unknown samples. Without knowing the results of her tests using these reagents, explain how the above materials would suffice to identify all of the samples not conclusively identified from b).
- d). What property of the alkali halides prevents the unambiguous identification of some of the unknowns by the ion exchange technique used here? Would you expect a similar effect to be as great a problem in, for example, a similar attempt to identify a number of alkaline earth halides MX_2 ?

PROBLEM 14.

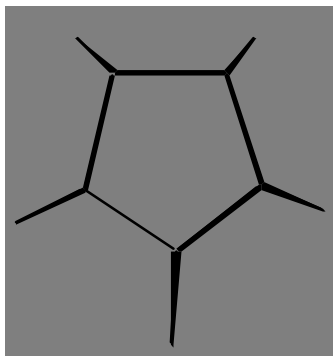
Chemistry can sometimes give rise to 'optical illusions' when three-dimensional structures are considered. For example:



- a). How many C_4 rings does cubane possess?
- b). For a valence-satisfied hydrocarbon C_nH_m , how is **m**, the number of hydrogen atoms, related to **n**, the number of carbon atoms, to **r**, the number of rings and to **d**, the number of double bonds?
- c). According to the answer given in a), what is the formula for cubane? Is this formula correct?
- d). Now for a temporary diversion. Two polycyclic aromatic hydrocarbons (PAHs) are known as coronene and corannulene. They have, respectively, the following carbon skeletons:

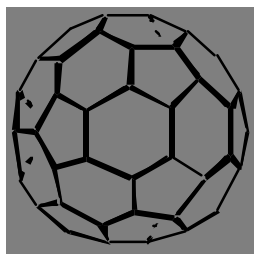


- Both PAHs have fully conjugated carbon-carbon bonding: redraw coronene and corannulene, ensuring that your drawings have as many C=C bonds as is consistent with complete conjugation (including conjugation of each carbon atom on the central polygon). Now, from the number of C atoms, rings, and double bonds, predict the number of hydrogens on each molecule, and draw in the hydrogen atoms to satisfy any valence-unsatisfied C atoms. Does the number of H atoms added tally with the prediction of the formula derived in b)?
- e). The two PAHs drawn above are shown as though they were both flat: in fact, one is flat, while one is not [though it is not very severely distorted from planarity]. Which PAH is not flat, and why?
- f). Now, using your flat drawing of a non-flat PAH as inspiration, draw cubane as though it were flat: do not attempt to introduce any perspective, but preserve the integrity of all C-C and C-H bonds which cubane possesses. The drawing which you produce may well look quite distorted [and so it should - you are drawing a highly 3-dimensional structure as though it occupied only two dimensions!], and it should not feature any instances of bonds crossing other bonds. From your flat drawing of cubane, tally the number of rings present in this molecule. Does this agree with your answer in a)? Does it agree with b)?
- g). A further check: determine the maximum number of C-C bonds which may be broken in each of coronene and corannulene before the molecule must fall into two fragments ie. without fragmenting the carbon skeleton. [Do not make any distinction between double bonds and single bonds in doing this.] Redraw the carbon skeletons of these PAHs, minus these bonds, to ensure that all carbon atoms are still connected. Is there a relationship between the number of bonds which may be broken and the number of rings (and if so, what is the relationship)?
- h). How many bonds in cubane can be broken without fragmenting the carbon skeleton? Does this give a ring number, r , in agreement with a), c), and f)?
- i). Now consider dodecahedrane, $C_{20}H_{20}$:



Draw a flat version of this molecule, by analogy with cubane in f). How many rings does this 12-faceted molecule possess? Is this number in agreement with the formula from b)?

- j). Finally we consider buckminsterfullerene, C_{60} :



For this, you need not attempt a flat drawing [sighs of relief all round], but some calculation is required. Each C atom in C_{60} has three nearest neighbours. How many carbon-carbon bonds are present? [If you have trouble here, refer back to cubane where each C atom also has three nearest neighbour carbons.] How many of these bonds must be double bonds, in order to satisfy valence requirements? From the formula found in b), how many rings does C_{60} possess? A geometrical proof, derived by Euler, indicates that a closed network comprised only of pentagons and hexagons must contain exactly twelve pentagons regardless of the number of hexagons. Can you state unambiguously how many of C_{60} 's rings are pentagons, and how many are hexagons?

PROBLEM 15.

The acidity of a water sample is influenced by gas absorption. The most important gas, in this respect, is generally carbon dioxide.

- a). Give a set of three reaction equations which demonstrate the effect of atmospheric CO_2 upon water acidity.
- b). Arrange the following gas mixtures in order of their tendency for CO_2 (g) to dissolve in aqueous solution (percentages given are mole %):
 - i). 90% Ar, 10% CO_2

- ii). 80% Ar, 10% CO₂, 10% NH₃
- iii). 80% Ar, 10% CO₂, 10% Cl₂

Write equations for any chemical reactions occurring in aqueous solution on exposure to these gas mixtures.

- c). Arrange the following aqueous systems in order of their ability to dissolve CO₂. Assume that, prior to exposure to 10% CO₂ in Ar, they have been allowed to equilibrate with air:
 - i). distilled water
 - ii). 1 M HCl solution
 - iii). 1 M sodium acetate solution
- d). Assuming an atmospheric content of 350 ppm CO₂ (by volume), and assuming that equilibration has been reached between gaseous and aqueous CO₂, calculate the pH of a raindrop at atmospheric pressure. Appropriate constants at 25 °C are: $K_H(\text{CO}_2) = 3.39 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$, $K_b(\text{HCO}_3^-) = 2.24 \times 10^{-8}$, $K_b(\text{CO}_3^{2-}) = 2.14 \times 10^{-4}$.
- e). Calculate the pH of a bottle of carbonated water ($P(\text{CO}_2(\text{g})) = 1 \text{ atm}$).
- f). A 100 mL sample of rainwater is titrated against $1.00 \times 10^{-4} \text{ mol L}^{-1}$ NaOH (in uncarbonated, distilled water) under experimental conditions which prevent further gas exchange. Sketch the pH curve for this titration. Your graph must indicate the expected pH at the start of the titration; at 7.1 mL; and at 21.2 mL of added NaOH solution.

PROBLEM 16.

- a). How many carboxylic acids exist, which satisfy the overall formula C₅H₁₀O₂? Draw and name all such compounds. [Do not name optical isomers, nor draw enantiomers separately, but indicate, with asterisks at chiral carbons, which structures are optically active.]
- b). Rank the above carboxylic acids in decreasing order of their expected K_a values in aqueous solution. Explain your reasoning for this ordering.
- c). How many structural isomers of the formula R-COOH, where R=C₄H₈F, exhibit optical activity? Draw these structural isomers (identifying chiral atoms as in a)), and predict the most acidic and the least acidic species amongst those which you have drawn. Justify your assignments of relative acidity for these species.
- d). What organic product is expected from the reaction of a carboxylic acid with an alcohol under acidic conditions? Write a generalized equation for such a reaction, showing reactants and products.

- e). If ^{18}O -labelled 1-propanol is reacted with acidified, unlabelled ethanoic acid, the isotopic label is found to reside entirely within the organic product. Draw this product, and write a generalized mechanism for the carboxylic acid/alcohol reaction.
- f). If, instead, the reaction employs unlabelled propanol and labelled ethanoic acid ($\text{CH}_3\text{C}(=\text{O})^{18}\text{OH}$), show the products expected:
- for reaction occurring in 1 mol L^{-1} HCl , and
 - for reaction initially in 1 mol L^{-1} NaOH , followed by acidification with 1 mol L^{-1} DCl .

PROBLEM 17.

The noble gases, helium in particular, are not generally thought of in terms of solid-phase chemistry. Nevertheless, several different types of material are known to contain embedded or trapped helium atoms. Molecules which possess the ability to incarcerate noble-gas atoms are known as 'clathrates'. Such compounds are present in meteorites, which are seen to release minute quantities of noble gases upon heating. Comparison of the thermal response of the (currently unidentified) noble-gas-containing phase of meteoritic material, with that of the species He@C_{60} (the '@' indicates that the helium is contained within, but is not chemically bonded to, the fullerene C_{60} cage), has led to the recent suggestion that fullerenes in meteorites may be responsible for the embedded noble gases in these materials.

- The diameter of the C_{60} fullerene cage is 7.0 \AA ($1 \text{ \AA} = 10^{-10} \text{ m}$). Calculate the interior volume of C_{60} ; also determine the 'pressure' within the cage, in the species He@C_{60} , at 298 K.
- In 1994, an analysis was reported of the fullerene content of material from an ancient meteorite impact site (1.85 billion years old), in Sudbury, Ontario. It was hypothesized that the C_{60} found amongst the impact ejecta may have arisen as a result of shock-induced chemistry associated with the impact. In 1996 it was reported that some of the fullerenes extracted from the material contained helium, with the following results being obtained:
 - release of $1.15 \times 10^{-7} \text{ cm}^3$ ^3He (STP) per g C_{60}
 - release of $2.09 \times 10^{-4} \text{ cm}^3$ ^4He (STP) per g C_{60}

What fraction of the C_{60} molecules in the sample contain a ^3He atom? What are the effective mean partial pressures, of ^3He and ^4He respectively, within the C_{60} sample?

- c). The content of ^4He within Earth's atmosphere is currently 5.240 ± 0.004 ppm by volume. If it is assumed that the partial pressure of ^4He within the C_{60} sample reflects the helium partial pressure in the atmosphere in which the fullerene was formed, and if it is also assumed that the terrestrial atmosphere's helium content has remained essentially unchanged over 2 billion years, is the ^4He -release data for the sample consistent with a terrestrial origin of the fullerene cage?
- d). The $^3\text{He}/^4\text{He}$ ratio in the Earth's atmosphere is $1.3 \times 10^{-6}:1$; values for this parameter in material from the Earth's crust are typically lower still. Is the observed $^3\text{He}/^4\text{He}$ ratio in the fullerene sample consistent with a terrestrial origin?
- e). Now for a change of pace. Consider a (purely hypothetical) fullerene with the formula $\text{C}_{5.0 \times 10^9}$, consisting of a single-layer, spherical, carbon shell, and internally pressurized with 120 kPa of helium. Assuming that the carbon-carbon bond distance is 1.42 Å, and that the surface structure is entirely consistent with a single graphitic sheet, calculate:
- the surface area, diameter, and interior volume of this giant fullerene,
 - the density of the helium-filled fullerene, and
 - the density of air at STP (assume $M_r(\text{air}) = 29.0 \text{ g mol}^{-1}$).
 - Comment on the implications of ii) and iii) for the physical properties of the fullerene.

PROBLEM 18.

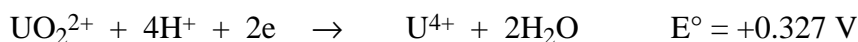
The uses of radioisotopes in nuclear medicine are twofold. Radiotherapy involves targetting of sites of active cell division by radionuclides to induce cell death. Nuclear imaging employs radioisotopes to reveal metabolic details of an organ. One such technique involves determination of a patient's blood volume.

- a). Three radiopharmaceutical compounds contain, respectively, the radioisotopes ^{71}Zn ($t_{1/2} = 2.4$ minutes), ^{67}Ga ($t_{1/2} = 78.25$ hours), and ^{68}Ge ($t_{1/2} = 287$ days), each with activities of 7.0×10^7 Bq per mL. For each of these compounds
- calculate the activity per mL after 30 minutes have elapsed, and
 - calculate the activity per mL after 30 minutes and after dilution of 10 mL of the radiopharmaceutical to 25 L.
- b). Ignoring chemical effects, what advantages does ^{67}Ga have over the other two radioisotopes for determination of a patient's blood volume?
- c). The modes of decay for these three isotopes are β -particle emission (^{71}Zn) and electron capture (^{67}Ga and ^{68}Ge). What are the products of these decay processes?

- d). A pharmacist prepares gallium citrate ($\text{GaC}_6\text{H}_5\text{O}_6 \cdot 3\text{H}_2\text{O}$) from a sample of ^{67}Ga -enriched gallium (5.0×10^{-5} mole % ^{67}Ga ; 10.25 mg Ga in total). The synthesis of gallium citrate is quantitative; following synthesis, the radiopharmaceutical is dissolved in 100 mL of water. Eight hours after the ^{67}Ga is first produced, 1 mL of the solution is administered intravenously to a patient, and one hour later a 1 mL blood sample is taken from the patient.
- Calculate the activity, in Bq, of the 1 mL dose of gallium citrate solution.
 - If the blood sample has an activity of 105.6 Bq, what is the patient's blood volume?

PROBLEM 19.

The following half-reactions relate to the speciation of uranium in aqueous solutions:



- Assign oxidation states to the various uranium-containing species appearing in the above half-reactions.
- By analysis of the above half-reactions, determine the ultimate chemical fate of a small piece of solid uranium placed in contact with a 1 molar solution of a strong, monoprotic acid HX, and in the presence of 1 atm of hydrogen, all at 25°C. Provide balanced reactions and electrode potentials for all reactions. [It can be assumed that the conjugate base X^- does not react perceptibly with uranium or with its compounds].
- What is the most stable uranium-containing species at $\text{pH} = 6$ (and under otherwise standard conditions)?
- Determine the pH range, for acidic or neutral solutions, under which a 1 molar solution of UO_2^+ would be stable:

- i). under otherwise standard conditions (i.e. $P(\text{H}_2) = 1$, concentrations of other uranium-containing species = 1)
- ii). with $P(\text{H}_2) = 1.0 \times 10^{-6}$ atm, and with conditions otherwise standard.

Which set of conditions is more relevant to the speciation of uranium in natural waterways?

PROBLEM 20.

A sealed glass vessel, fitted with two tungsten filaments separated by a 5 mm gap, is filled with clean, dry air at standard temperature and pressure. An electrical discharge is established between the two filaments. Over the next several minutes, the gas within the vessel is seen to take on a distinct brownish tinge.

- a). What species is responsible for the observed coloration? Estimate an upper limit to its concentration within the vessel.
- b). The same brown colour is seen to develop spontaneously when oxygen and nitric oxide are introduced into an evacuated glass bulb. Write an overall equation for the reaction in the bulb.
- c). The following measurements were obtained from several experiments, performed at a temperature of 25°C:

[NO] (mol L ⁻¹)	[O ₂] (mol L ⁻¹)	initial rate (mol L ⁻¹ s ⁻¹)	A _∞ (λ = 400 nm)
1.16 × 10 ⁻⁴	1.21 × 10 ⁻⁴	1.15 × 10 ⁻⁸	0.341
1.15 × 10 ⁻⁴	2.41 × 10 ⁻⁴	2.28 × 10 ⁻⁸	0.331
1.18 × 10 ⁻⁴	6.26 × 10 ⁻⁵	6.24 × 10 ⁻⁹	0.335
2.31 × 10 ⁻⁴	2.42 × 10 ⁻⁴	9.19 × 10 ⁻⁸	0.656
5.75 × 10 ⁻⁵	2.44 × 10 ⁻⁵	5.78 × 10 ⁻⁹	0.166

- i). Determine the reaction order in O₂, in NO, and overall.
- ii). Determine the reaction rate constant at 298 K.
- d). The column on the far right of the above table shows the absorbance at 400 nm (path length = 10 cm) after sufficient time has elapsed for the reaction mixture to have reached equilibrium.
 - i). Does the reaction go essentially to completion, or not?
 - ii). Determine the molar absorption coefficient ε at the stated wavelength.
 - iii). Is the (visible) wavelength of maximum absorbance likely to be closest to 400, 500, or 600 nm?

- e). If the brown gas obtained in this reaction is isolated in an apparatus whose volume can be modified by a piston, the following results are obtained:

V (mL)	P _{tot} (atm)
1000	2.49×10^{-3}
500	4.90×10^{-3}
200	1.18×10^{-2}
100	2.25×10^{-2}
50	4.23×10^{-2}
20	9.60×10^{-2}
10	1.78×10^{-1}

The temperature of the apparatus is maintained at 25 °C for all of the above measurements. Provide a reaction equation which accounts for the dependence of pressure upon volume, and determine the appropriate equilibrium constant.

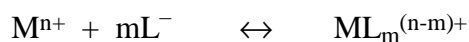
- f). If the system detailed in e) is subjected to yet greater compression, the following data are obtained:

V (mL)	P _{tot} (atm)
10	0.178
5	0.331
2	0.765
1	1.215
0.5	1.215
0.2	1.215

Why does the pressure not continue to increase at volumes of 1 mL and less? Provide equations for any chemical reactions occurring, and calculate the partial pressures of any gas-phase species at V = 1 mL. What is the equilibrium constant for the process responsible for the "pressure cap" of 1.215 atm?

PROBLEM 21.

Investigation of the complexation reactions of transition metal ions



is often complicated by the existence of competing equilibrium processes: for example, very often the ligand L^{-} is the conjugate base of a weak acid, and so its concentration in solution is highly pH dependent. In such circumstances it is common to reframe the transition metal complex's formation constant, β_m :

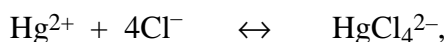
$$\beta_m = \frac{[\text{ML}_m^{(n-m)+}]}{[\text{M}^{n+}] [\text{L}^{-}]^m}$$

by substituting, for $[L^-]$, the parameter $\alpha_{L^-} C_T(L)$, where $C_T(L)$ indicates the total concentration of L in all forms in solution [whether as HL or as L^- or as $ML_i^{(n-i)+}$] and α_{L^-} is that fraction of 'total L' which is in the appropriate form of L^- . Such an approach is often used, for example, in titrimetric analysis involving EDTA, since EDTA (" H_4Y ") is a weak tetraprotic acid which is capable of effective complexation reactions only in its fully deprotonated form, Y^{4-} . It can be shown that $\alpha_{Y^{4-}}$ has the form

$$\alpha_{Y^{4-}} = \frac{K_{a,1} K_{a,2} K_{a,3} K_{a,4}}{[H^+]^4 + K_{a,1}[H^+]^3 + K_{a,1} K_{a,2}[H^+]^2 + K_{a,1} K_{a,2} K_{a,3}[H^+] + K_{a,1} K_{a,2} K_{a,3} K_{a,4}}$$

where $K_{a,i}$ is the i th acid dissociation constant of EDTA (values are, respectively, 1.02×10^{-2} , 2.14×10^{-3} , 6.92×10^{-7} , and 5.50×10^{-11}).

- a). Determine values for the parameter $\alpha_{Y^{4-}}$ at pH's of, respectively, 2, 6, and 10. What is the concentration of the fully deprotonated anion Y^{4-} , in a 500 mL solution containing 3.252 g of EDTA at each of these pH values?
- b). The complex formation constant K_Y , for complexation of M^{n+} with Y^{4-} , has values of 6.3×10^{21} (Hg^{2+}), 2.1×10^{14} (Fe^{2+}), and 5.0×10^{10} (Ca^{2+}). Which of these metal ions will form EDTA complexes at better than 99.9% yield, in a solution containing $5.00 \times 10^{-3} \text{ mol L}^{-1}$ total EDTA buffered to a pH of
 - i). 2
 - ii). 6
 - iii). 10?
- c). The mercuric ion, Hg^{2+} , has a high affinity for chloride:



for which the formation constant is $\beta_{Cl} = 3.98 \times 10^{15}$. For a solution containing 0.5 mol L^{-1} total chloride and $5.00 \times 10^{-3} \text{ mol L}^{-1}$ total EDTA, determine the fraction of Hg existing as the free ion, as the tetrachloride anion, and as the EDTA complex, at a pH of

- i). 2
- ii). 6
- iii). 10

[You should assume that the total metal ion concentration is much less than 0.005 mol L^{-1} .]

- d). An amalgam is known to contain only mercury, sodium, and calcium. 5.218 grams of the sample is treated with an appropriate oxidizing agent, and made up to 500 mL. 25 mL aliquots of this solution, buffered to $\text{pH} = 2.6$, are titrated against a $0.0122 \text{ mol L}^{-1} \text{ MgY}^{2-}$ solution: the mean titre value obtained is 44.19 mol L^{-1} . When 10 mL aliquots are buffered to a pH of 9.5, a titre value of 57.43 mol L^{-1} is obtained. Determine the percentage by mass of the mercury, sodium, and calcium in the amalgam.

PROBLEM 22.

Greenhouse gas emissions are a topic of global environmental concern. The increase in atmospheric concentration of one greenhouse gas, CO_2 , has been well-documented over the past several decades.

- a). Let us approximate the distribution of greenhouse gases in the Earth's atmosphere by assuming that these gases (CO_2 , H_2O vapour etc) are localized within a layer between the altitudes of 10 and 11 km. [Such a description is not accurate, but serves to illustrate some concepts.] What is the effect of such a greenhouse-gas layer upon the temperature of the atmosphere at an altitude of 5 km?
- b). What is the layer's effect on atmospheric temperature at 15 km? Explain, qualitatively, this 'side-effect' of the Greenhouse layer.
- c). How does temperature change in the lower atmosphere influence the equilibria of CO_2 and of H_2O between the gaseous and aqueous phases? Will a shift in the positions of equilibrium for these species have any effect, itself, upon the temperature of the lower atmosphere?
- d). Now we climb above the greenhouse layer to the ozone layer. Ozone is both produced and destroyed photochemically. Devise a mechanism which accounts for ozone production and destruction in a pure-oxygen atmosphere.
- e). The enthalpies of formation of O and O_3 are $\Delta H^\circ_f(\text{O}) = 249 \text{ kJ mol}^{-1}$ and $\Delta H^\circ_f(\text{O}_3) = 143 \text{ kJ mol}^{-1}$. Determine the longest-wavelength photons capable of oxygen and ozone photolysis, respectively.

- f). In polar regions, severe depletion of stratospheric ozone is seen during springtime. It is thought that conditions are 'set up' for this catastrophic depletion (known as the 'ozone hole') by several factors, including the following equilibria:



Here PSC denotes a 'polar stratospheric cloud', resulting from condensation of water vapour and other volatiles at elevated altitudes. PSC formation is common in the Antarctic stratosphere during winter and early spring, but less so in the Arctic where temperatures are not quite so low. It is known that ozone depletion is more severe the further the above equilibria lie to the right hand side. Bearing in mind that bond formation is generally exothermic, how will the above equilibria be affected by temperature?

- g). Ozone hole formation in the Arctic stratosphere is a recently-noted phenomenon: it was originally expected that the Arctic would be 'immune' to ozone hole formation, but this is evidently not the case. Based on information supplied above, suggest which of the following strategies could conceivably account for the development of the Arctic ozone hole:
- Northern hemisphere levels of stratospheric CFC have only very recently risen to levels which the Antarctic stratosphere had already experienced a decade ago; or
 - The continued influx of greenhouse gases into the lower atmosphere is continuing to reduce the temperature of the Arctic stratosphere; or
 - An increase in the concentration of water vapour in the Arctic stratosphere makes PSC formation more favourable than was previously the case; or
 - An increase in the amount of IR radiation reaching the Arctic stratosphere is causing increased photolysis of the Arctic ozone.

PROBLEM 23.

"Queenbee substance" **Q** contains 65.2% carbon and 8.75% hydrogen and no other element except oxygen. **Q** is known to be acidic and titration of 43.7mg of this compound required 23.7mL of 0.0100M aqueous sodium hydroxide to reach the equivalence point. The molecular weight of **Q** was determined to be less than 200.

- a). What is the molecular formula of **Q** and what functional groups might be responsible for the acidity of this compound?

Q reacts with hydrogen in the presence of finely divided platinum metal to afford a new compound **A**. Further reduction of **A** with sodium borohydride in ethanol gives substance **B**. Compound **B** was readily dehydrated upon warming with strong sulfuric acid to afford an alkene **C**. The ^{13}C nmr of **C** revealed amongst other features the presence of a methyl group attached to a double bond.

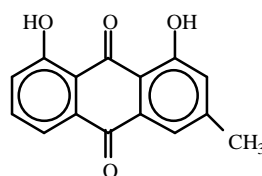
- b). What functional groups are consistent with the above reactions?

Ozonolysis of **C** followed by an oxidative work up gave only two fragments, ethanoic acid and a straight chain dicarboxylic acid **D**. Similar cleavage of **Q** itself yielded oxalic acid (ethanedioic acid) and a substance **E** which contained a carboxylic acid group.

- c). Deduce the structures for **D** and **E** and hence give the possible structures for **Q**.

PROBLEM 24.

Chrysophanic acid is a naturally occurring anthraquinone pigment isolated from the rhubarb root and has the structure shown below. One rather elegant synthesis of this molecule originated in the Research School of Chemistry at the Australian National University.



Chrysophanic acid

3-Methylanisole (3-methyl-methoxybenzene) was reduced with lithium metal in a mixture of liquefied anhydrous ammonia, tetrahydrofuran and t-butanol to afford **B**. ($\text{C}_8\text{H}_{12}\text{O}$). Treatment of **B** with potassium amide in anhydrous liquid ammonia followed by aqueous work up resulted in its isomerisation to **C**.

- a). Draw all three possible structures for **C**.

The ^1H nmr spectrum of **C** revealed amongst other features two olefinic protons which were not adjacent to one another. In addition it revealed two vicinal methylene groups one of which was adjacent to an olefinic proton.

- b). Draw the structures of **C** which fit this information.

Reaction of **C** with 5-hydroxy-naphthalene-1,4-dione afforded the Diels Alder adduct **D** ($\text{C}_{18}\text{H}_{18}\text{O}_4$). The ^1H nmr. spectrum of **D** exhibited amongst other

features a resonance δ 10.5 integrating for 1 proton and indicative of an intramolecularly bonded hydroxyl group.

- c). Suggest three possible structures for compound **D**.

Enolisation of **D** by treatment with potassium carbonate in hot methanol followed by oxidation with the potassium nitrosodisulfonate (Fremy's salt) yielded a yellow orange coloured quinonoid product **E**. ($C_{18}H_{16}O_4$). The ^{13}C nmr. spectrum of **E** contained a total of 9 resonances attributable to quaternary carbons. Pyrolysis of **E** at 180° for 15 minutes resulted in the extrusion of ethene via a retro-Diels Alder reaction resulting in the formation of **F** ($C_{16}H_{12}O_4$). The 1H nmr. spectrum of **F** exhibited amongst other features 3 singlets each integrating for 1 proton (the lowest of these was at δ 11.00) and two 3 proton singlets, one at δ 4.01 and one at δ 2.25 ppm.

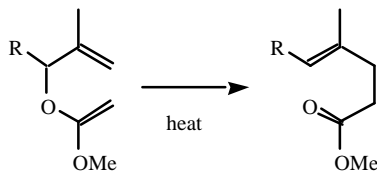
- d). Based on this evidence suggest possible structures for compounds **E** and **F**.

When **F** was treated with boron trichloride in dichloromethane at -10° , it afforded, after work up, an orange coloured solid, the mass spectrum of which gave a molecular ion at m/e 254. This was found to be identical with natural chrysophanic acid.

- e). Using the work you have done above draw a complete set of structures tracing out the total synthesis of chrysophanic acid.

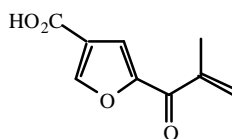
PROBLEM 25.

The so called Claisen type rearrangements provide versatile tools to the synthetic organic chemist. To the student however these reactions are often difficult to recognise and require some thought to understand. A practical example of this reaction is shown below. Study this for a moment and then try the following problem which involves amongst other things an example of this reaction.



In 1977 a sesquiterpene furan (**K**) was isolated from an Australian soft coral *Sinularia gonatodes*. This compound was found to inactivate bee venom and the fact that such a simple compound might act as an anti-inflammatory agent prompted considerable interest from synthetic chemists. One such synthesis is described below.

The acid(**A**) was esterified with 2-(trimethylsilyl)ethanol $[\text{Me}_3\text{Si CH}_2\text{CH}_2\text{OH}]$ and the resulting keto-ester selectively reduced at the ketone carbonyl with $\text{NaBH}_4/\text{CeCl}_3$ to afford a compound **B** ($\text{C}_{14}\text{H}_{22}\text{O}_4\text{Si}$).

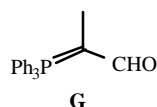


A

Treatment of **B** with 1,1,1-trimethoxyethane in the presence of a trace of anhydrous acid afforded an intermediate compound which underwent a Claisen like rearrangement on heating to afford **C**. Spectroscopic examination of **C** revealed the presence of a trimethylsilylethyl ester and a methyl ester.

- a). Deduce the structures of compounds **B** and **C** and the intermediate which leads to **C**.

Reduction of **C** with lithium borohydride yielded a primary alcohol **D** ($\text{C}_{16}\text{H}_{26}\text{O}_4\text{Si}$) which could be oxidised with pyridinium chlorochromate to yield **F**. Reaction of **F** with the Wittig reagent **G** yielded two isomers **H** and **I**. the major product **H** had the (E)-stereochemistry.



G

- b). Give structures for the compounds **D** - **I**, being careful to show the correct stereochemistry for isomer **H** and **I**.

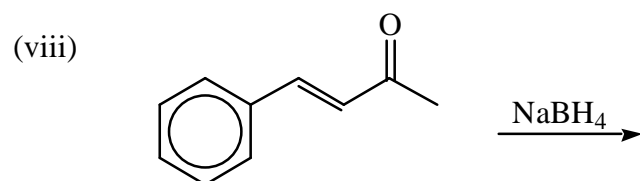
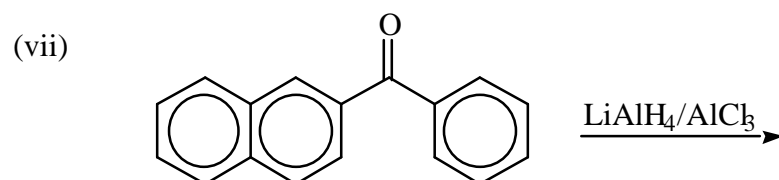
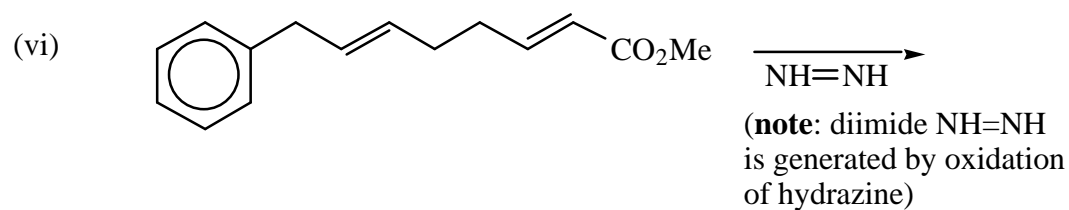
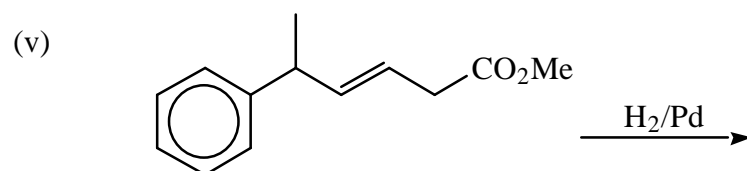
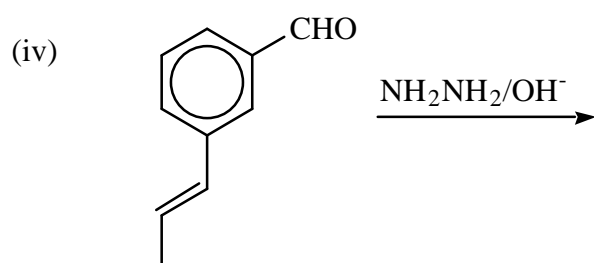
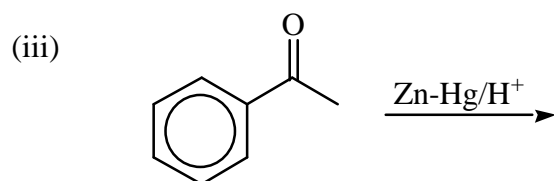
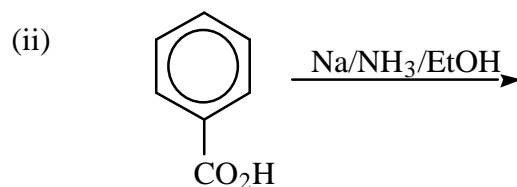
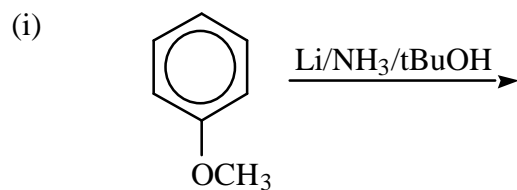
A final Wittig reaction with the ylid derived from methyl triphenylphosphonium iodide afforded **J** which after cleavage of the trimethylsilylethyl ester with tetra-n-butyl ammonium fluoride yielded the desired compound **K**.

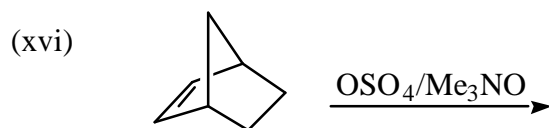
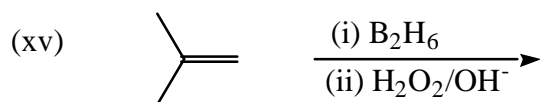
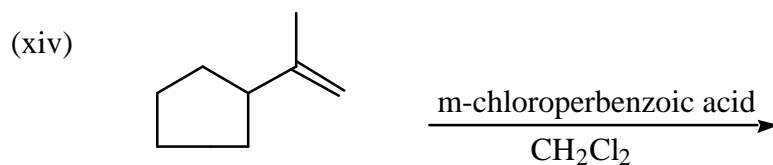
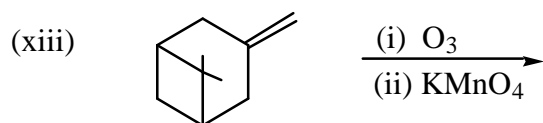
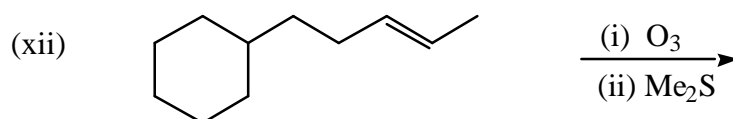
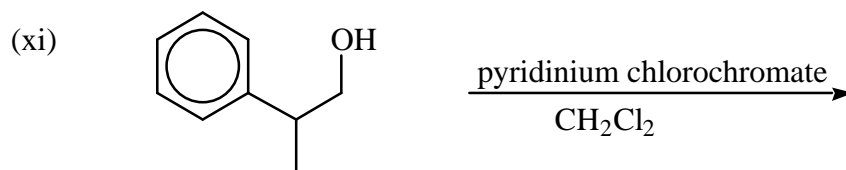
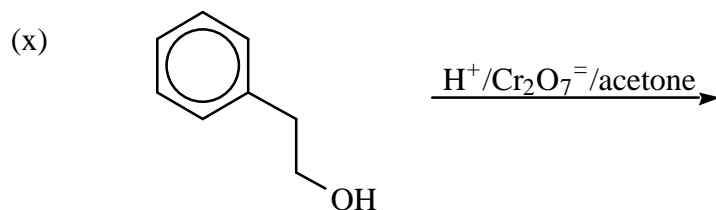
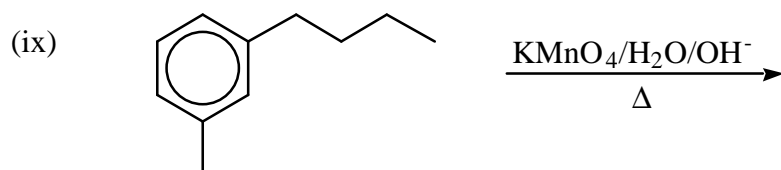
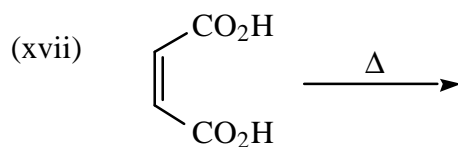
- c). Give structures to complete the synthetic sequence.

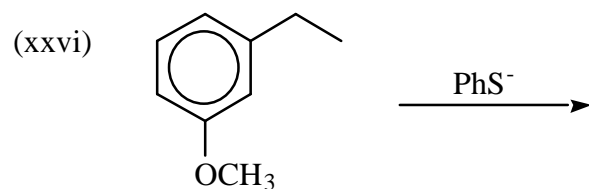
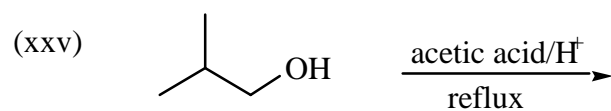
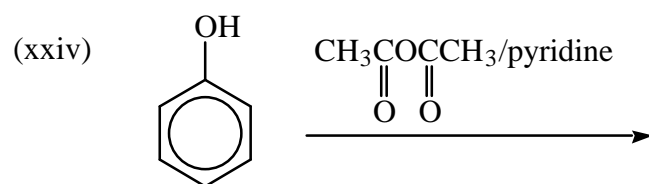
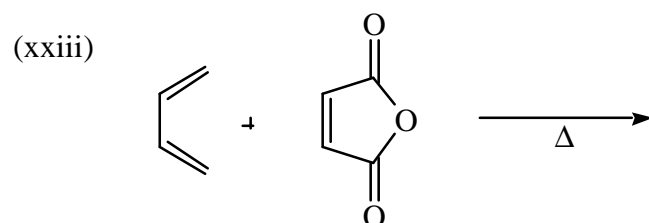
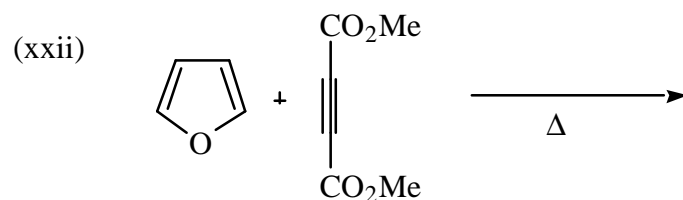
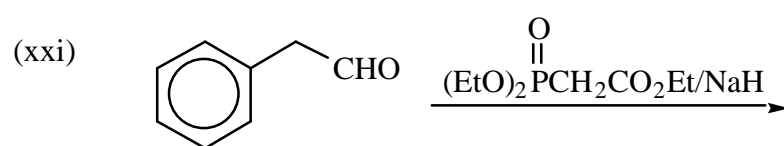
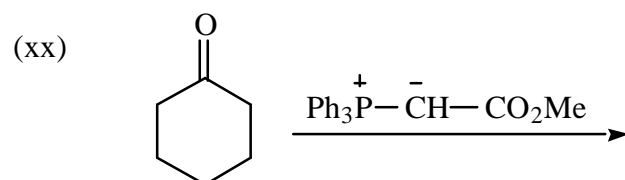
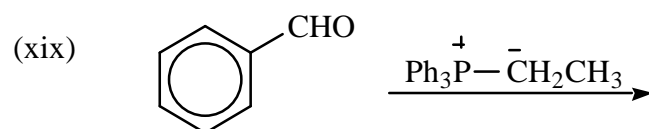
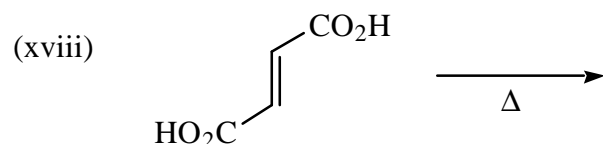
PROBLEM 26.

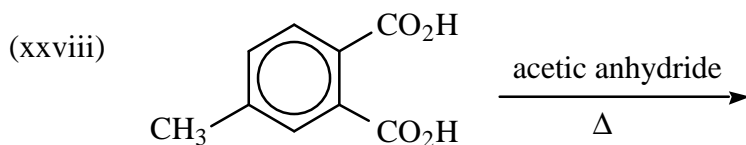
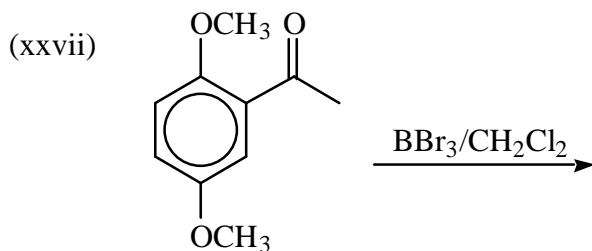
Mentors Note: The following reactions are those which fall outside "normal" high school level chemistry, and may be useful in any of the tasks of the 30th IChO. Whilst an understanding of mechanism may help the student, mechanisms are not considered essential for the tasks. However it is anticipated that students will be aware of stereo and regiochemical outcomes associated with these reactions.

REDUCTIONS (Assume a standard aqueous or pH adjusted work up in each case)



OXIDATIONS**OTHER REACTIONS**





Additional Notes: With the exception of (xiii), (xvi) it is expected that students could derive an IUPAC name for the starting materials. With the exception of (xiv), (xiii), (xx), (xxii), (xxiii), (xvii) a similar expectation would hold true for naming products.

PROBLEM 27 - EXPERIMENTAL

Synthesis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and of the linkage isomers $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$.

a). Preparation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Dissolve 10.0 g of ammonium chloride in 60 mL of concentrated aqueous ammonia (CARE!) in a 500 mL Erlenmeyer flask. While continuously agitating the solution with a magnetic stirrer, add 20 g of finely powdered cobalt chloride 6-hydrate in small portions (CAUTION: avoid exposure to this powder. Grind with care in a fumehood).

With continued stirring of the resultant brown slurry, slowly add 16 mL of 30 % hydrogen peroxide (CARE!) from a dropping funnel. When the effervescence has ceased, slowly add 60 mL of concentrated HCl.

Continue stirring on a hot plate, holding the temperature at about 85°C for 20 min; then cool the mixture to room temperature and filter off the precipitated $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Wash with 40 mL of ice water in several portions, followed by 40 mL of cold 6 M HCl. Dry the product in an oven at 100°C for several hours. The yield is about 18 g of purple product.

This complex can be recrystallised from boiling water to provide small dark purple crystals in high yield, but this is not necessary for the following synthesis.

b). Preparation of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$

Dissolve 10 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in a solution of 15 mL of concentrated aqueous ammonia (CARE!) in 160 mL of water while stirring and heating. Filter off any slight precipitate of cobalt oxide that may form, and cool the filtrate to about 10°C.

Titrate the solution, with continuous cooling, with 2 M HCl until it is just neutral to litmus. The solution will change colour to wine-red.

Dissolve 10.0 g sodium nitrite in the solution, then add 10 mL of 6 M HCl. Allow the solution to stand in an ice bath for an hour or two, and filter off the precipitated pink crystals of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$. Wash with 50 mL of ice water, followed by 50 mL of ethanol, and air dry at room temperature. The yield is about 9 g.

Store cool and in the dark. Upon standing, isomerisation of the nitrito isomer to the nitro isomer slowly occurs.

To prepare a pure sample of the nitro isomer, dissolve 4.0 g of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ in 40 mL of hot water containing a few drops of aqueous ammonia, and then add, while cooling, 40 mL of concentrated HCl. Cool the solution in an ice bath and filter off the orange $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$.

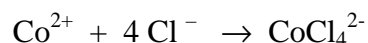
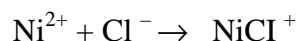
Wash the product with 25 mL of ethanol and air dry at room temperature. The yield is about 3.5 g of orange-yellow product.

PROBLEM 28 - EXPERIMENTAL

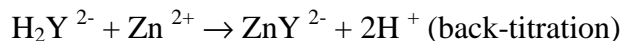
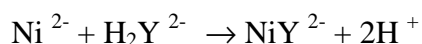
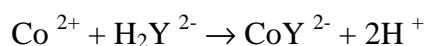
Anion exchange chromatography separation of cobalt and nickel followed by EDTA titration of the metals using back-titration.

Cobalt and nickel are separated on a strong-base anion exchange column (chloride form) by eluting with 9 M HCl and 3 M HCl, respectively. In 9 M HCl, the nickel does not form an anionic chloro complex while the cobalt does; hence, the former will elute. In 3 M HCl, the blue, anionic cobalt chloro complex is dissociated to form the pink aquated cobalt cation, which elutes. Following separation, the metals are titrated indirectly with standard EDTA for quantitation; excess EDTA is added and the unreacted EDTA is back-titrated with a standard zinc solution in slightly acid solution, using xylenol orange indicator.

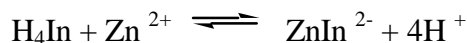
Separation:



Titration:



End point:



yellow-green red-violet

Solutions and Chemicals Required

Miscellaneous. 3M NaOH, 9M HCl, 3M HCl, 0.5% (wt/vol) xylene orange indicator in 10% ethanol (0.5 g dissolved in 10 mL ethanol and diluted to 100 mL with water—must be fresh), zinc granules, 0.2% phenolphthalein in 90% ethanol, hexamine (hexamethylenetetramine), Dowex 1-X8 anion exchange resin (chloride form) or equivalent.

Standard 0.01 M EDTA solution. Prepare from $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ dried at 80°C for 2 hours and cooled in a desiccator by accurately weighing about 1.9 g (to the nearest milligram), dissolving in distilled deionized water, and diluting to 500.0 mL in a volumetric flask. Calculate the molarity.

Standard 0.01 M zinc solution. Accurately weigh approximately 0.33 g pure zinc granules (to the nearest 0.1 mg) and transfer to a 400-mL beaker. Do not use zinc dust. For highest accuracy, the zinc granules should be treated with 2 M HCl to remove any zinc oxide coating. Decant the acid and wash the zinc repeatedly with water. Then, wash several times with ethanol and finally with ether in the fume hood (**FIRE HAZARD**). Dry the granules before weighing. Dissolve with the minimum amount of HCl required. Heat on a steam bath to aid dissolution. Cover with a watch glass during dissolution. After the zinc is in solution, wash the droplets of water on the watch glass with distilled water into the beaker, wash down the sides of the beaker and quantitatively transfer the solution to a 500-mL volumetric flask. Dilute to volume with distilled water. Calculate the molarity of the solution.

Procedure

1. **Preparation of the ion exchange column.** Prepare a column using a 50-mL burette with glass wool in the bottom to hold the resin. Add a slurry of Dowex 1-X8 anion exchange resin (in the chloride form) in 9 M HCl to the burette until

the height of the resin column is about 15-20 cm. Do not allow the liquid level to drop below the resin level. Keep about 2 mL of liquid above the resin.

Wash the column with two 10-mL portions of 9 M HCl using a flow rate of 2 or 3 mL per minute. The column will darken somewhat when treated with HCl, but it will return to normal colour if washed with water. Leave 2–3 cm of HCl above the resin level.

2. **Separation of the unknown mixture.** Obtain an unknown from your instructor in a 50-mL volumetric flask. Dilute to volume with 9 M HCl. The unknown will contain 5 mmol or less each of nickel(II) and cobalt(II) in 9 M HCl.

Add with a pipette 2 mL of the unknown solution onto the column. Elute the nickel with about 75 mL 9 M HCl added in 15-mL portions, using a flow rate of 1-2 mL per minute. Collect in a 250-mL Erlenmeyer flask. The pale yellow-green NiCl^+ complex will flow through the column and may darken the resin. The blue cobalt band (appears green due to yellow resin) will move partway down the column. While the sample is being eluted, it is advisable to perform a practice titration as described below.

After all the nickel is eluted but before the cobalt band reaches the end of the column, stop the flow and replace the collection flask with a clean one. Elute the cobalt with about five 10-mL portions of 3 M HCl, at a flow rate of 1 mL per minute. As the HCl is diluted on the column, the CoCl_4^{2-} complex should dissociate to the pink coloured Co^{2+} . After the cobalt is seen to be eluted, stop the flow and proceed to titrate the separated metals. (Final elution with water may be used to assure complete removal of the cobalt.)

3. **Titration of the nickel and cobalt.** Carefully evaporate the collected samples to near dryness on a hot plate (FUME HOOD). Cool and dilute with 50 mL distilled deionized water. Before titrating your unknown samples, and while they are evaporating, perform a practice titration or two using a prepared cobalt or nickel solution. Titrate the nickel and cobalt solutions indirectly as follows. Neutralize each solution to a phenolphthalein end point with 3M NaOH, avoiding excess NaOH. Add 6M HCl dropwise to just remove the red indicator colour. Add 25.00 mL standard 0.01 M EDTA to the flasks, and add five drops 9 M HCl, 1 g hexamine, and four drops xylenol orange indicator solution. The hexamine buffers the solution at pH 5-6. If the solution is red-violet, warm and add another 10.00 mL EDTA. Back-titrate with standard 0.01 M zinc solution until the indicator changes from yellow-green to red-violet.

Calculations

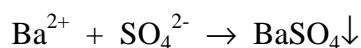
From the millimoles EDTA taken and the number of millimoles excess EDTA found in the back-titration, calculate and report the number of millimoles nickel and cobalt in your unknown.

PROBLEM 29 - EXPERIMENTAL

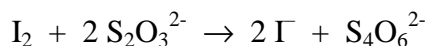
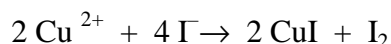
Determination of copper and barium in a mixture of chlorides.

Copper and barium are common components in high temperature superconductors. They are easily separated by removing barium as its insoluble sulfate which is determined gravimetrically. The soluble copper can be determined volumetrically by reaction with excess iodide ion and subsequent estimation of liberated iodine with standardized thiosulfate.

Separation:



Titration:



Solutions and Chemicals Required

Miscellaneous: 10% KI solution, 10% KSCN (or NH_4SCN). Starch indicator, saturated K_2SO_4 .

Standard 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$. This is made by dissolving 25.0 g of AR $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 1 L of "boiled out" distilled water in a volumetric flask. Solutions are best used fresh unless stabilised.

Standardise your sodium thiosulphate against either potassium iodate or potassium bromate as primary standards. This can be found in any text on volumetric or quantitative analysis.

Procedure

1. Accurately weigh approximately 3 g of your "unknown" sample (The "unknown" should contain CuCl_2 and BaCl_2 in a ratio between 3:1 and 8:3). Using a 400 mL beaker, dissolve the solid in 180 mL of water. (Do not use more as your final volume will be 250 mL - see later).

2. **Precipitation.** Heat the solution nearly to boiling and keep the solution just below the boiling point. Add slowly from a Pasteur pipette 10 mL of saturated K_2SO_4 solution; stir vigorously throughout the addition. Let the precipitate settle, then test for complete precipitation by adding a few drops of potassium sulfate without stirring. If additional precipitate forms, add slowly, with stirring, 5 mL more potassium sulfate; let settle, and test again. Repeat this operation until precipitation is complete. Leave the stirring rods in the beakers, cover with watch glasses, and digest on the steam bath until the supernatant liquid is clear. (The initial precipitate is fine particles. During digestion, the particles grow to filterable size.) This will require 30-60 minutes or longer. Add more distilled water if the volume falls below 200 mL.
3. **Filtration and washing of the precipitate.** Prepare an 11-cm No. 42 Whatman hardened, ashless filter paper or equivalent for filtration; the paper should be well fitted to the funnel so that the long stem of the funnel remains filled with distilled water, or the filtration will be very slow. Filter the solutions while hot; be careful not to fill the paper too full, as the barium sulfate has a tendency to "creep" above the edge of the paper. Wash the precipitate into the filter with hot distilled water, clean the adhering precipitate from the stirring rod and beaker with the rubber "policeman" (!), and again rinse the contents of the beaker into the filter. Examine the beaker very carefully for particles of precipitate that may have escaped transfer. Wash the precipitate and the filter paper with hot distilled water until no turbidity appears when a few millilitres of the washings, acidified with a few drops of concentrated nitric acid (CARE!), are tested for chloride with silver nitrate solution. During the washing, rinse the precipitate down into the cone of the filter as much as possible. Examine the filtrate for any precipitate that may have run through the filter. When the precipitate has been thoroughly washed you should test one drop with concentrated ammonia solution (CARE!) on a white tile. The absence of any visible blue colour shows that all the copper has been removed from the precipitate. If a blue colour appears, the washing and testing should be repeated.

Quantitatively transfer the cool filtrate to a 250 mL volumetric flask and make up to volume. Mix thoroughly.

4. **Titration:** Pipette 50.0 mL of this solution into a 250 mL conical flask, add 2 drops of glacial acetic acid (CARE!) followed by 15 mL of 10% KI. Titrate the liberated iodine with standard 0.1 M thiosulfate until the brown iodine colour just fades. Then add 2 mL of starch indicator and continue the titration until the blue colour commences to fade. At this point add ~ 10 mL of 10% potassium (or ammonium) thiocyanate whereupon the blue colour will intensify. Complete the

titration as quickly as possible. When the blue colour has gone, a pale coloured precipitate should remain. A distinct and readily determined endpoint is easily achieved.

Repeat on two further aliquots or until agreement is reached.

You can, if you wish, determine the barium by gravimetric analysis as follows.

- 5 **Ignition and weighing of the precipitate.** Loosen the filter paper in the funnels and allow to drain for a few minutes. Fold each filter into a package enclosing the precipitate, with the triple thickness of paper on top. Place into weighed porcelain crucibles and gently press down into the bottom. Inspect the funnels for traces of precipitate; if any precipitate is found, wipe it off with a small piece of moist ashless filter paper and add to the crucible. Place each crucible on a triangle on a tripod or ring stand, in an inclined position with the cover displaced slightly. Heat gently with a small flame from a gas burner (CARE!) until all the moisture has been driven off and the paper begins to smoke and char. Adjust the burner so that the paper continues to char without catching fire. If the paper inflames, cover the crucible to smother the fire, and lower the burner flame. When the paper has completely carbonised and no smoke is given off, gradually raise the temperature enough to burn off the carbon completely. A red glowing of the carbon as it burns is normal, but there should be no flame. The precipitate should finally be white with no black particles. Allow to cool. Place the crucible in a vertical position in the triangle, and moisten the precipitate with three or four drops of dilute (1:4) sulfuric acid. Heat very gently until the acid has fumed off. (This treatment converts any precipitate that has been reduced to barium sulfide by the hot carbon black to barium sulfate.) Then, cover the crucibles and heat to dull redness in the full flame of the burner for 15 minutes.

Allow the covered crucibles to cool in a desiccator for at least one hour and then weigh them. Heat again to redness for 10-15 minutes, cool in the desiccator, and weigh again. Repeat until two successive weighings agree within 0.3-0.4 mg.

Calculation

Copper. From the volume of standard thiosulfate used, calculate the millimoles of iodine and hence copper present in the 50.0 mL aliquot. Since the sample was taken from a total of 250.0 mL the total copper in millimoles will be 5 times that estimated in the titration.

Barium. The total barium in millimoles follow directly from the mass of barium sulfate.

Report your result as a ratio of Cu:Ba.

PROBLEM 30 - EXPERIMENTAL

Preparation and analysis of potassium trisoxalatoferrate(III) trihydrate, $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$

Introduction

In this experiment, you will prepare the complex trisoxalatoferrate(III) $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ anion and isolate it as its hydrated potassium salt, $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$. This trihydrate is a green crystalline salt, soluble in hot water but rather insoluble when cold. The complex anion is photo-sensitive. This means that upon exposure to light of an appropriate wavelength ($< 450 \text{ nm}$ in this case) the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ undergoes an intramolecular redox reaction in which the Fe(III) atom is reduced to Fe(II) while one of the oxalate groups is oxidised to CO_2 . You will be carrying out such a photo reduction on your sample, as well as applying the photo reaction to make a "blueprint".

Finally, you will also analyse your product for water of crystallisation, oxalate and iron.

WARNING: Oxalate ion is toxic and the analysis procedure for iron uses zinc that has been amalgamated with mercury. Be sure to discard any residues that contain or mercury in a responsible manner!.

Preparation of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$

Weigh approximately 9.0 g of hydrated potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) into a 250 mL beaker; add 30 mL of distilled water and heat to dissolve (do not boil).

In a second small beaker dissolve 4.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the minimum amount of cold water (10-15 mL). Add the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution to the warm oxalate solution and stir with a glass rod. Allow the product to crystallise (away from strong sunlight) by cooling the solution in an ice-water mixture.

Collect the crystalline product by vacuum filtration (discard the filtrate in an appropriate residue bottle). Wash the crystals with about 10 mL acetone and continue suction for a few more minutes until dry.

Recrystallisation: Weigh 5.0 g of your $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ into a small beaker. Add 13 mL of distilled water and warm the mixture on a hot plate until the solid dissolves. Filter the solution quickly by vacuum filtration, wash the filter with no more than 2 mL hot distilled water and immediately transfer the hot filtrate to a clean beaker. Cool the solution in an icebath and when crystallization is complete, filter the crystals and wash twice with 5 mL quantities of ice-cold distilled water.

Dry the crystals by suction. Transfer them to a preweighed container and dry at 50°C for about thirty minutes. Weigh the purified product.

Photochemical Reaction of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$

As mentioned above, light causes an internal electron-transfer reaction to occur in the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ ion, producing CO_2 and Fe^{2+} ions. The Fe^{2+} that is produced can readily be detected by adding a solution of potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ (0.1 M) whereupon a deep blue colour should result, due to the formation of the complex ferrocyanide (Turnbull's blue). For this exercise you will need a bright light source (CAUTION!) such as a 150W spot lamp. Bright sunlight may suffice but the photochemical reactions will be significantly slower.

CAUTION must be exercised in using the ferricyanide solution. Avoid contact with your skin and collect all residues for disposal or recovery. Thoroughly wash your hands following handling.

Dissolve 0.7 g of your complex (it doesn't have to have been recrystallized) in 100 mL of distilled water in a conical flask. Add 3 mL of 2 M H_2SO_4 and swirl the mixture. To each of three labelled test tubes, add 10 mL of this solution.

Keep one tube away from the light source as the control and irradiate the remaining two tubes with the light source for 1 and 5 minutes, respectively.

To all 3 tubes now add 1 mL of the potassium ferricyanide solution ($\text{K}_3\text{Fe}(\text{CN})_6$).

Record and explain your observations. To convince yourself it is Fe^{2+} that is being detected, add a few drops of ferricyanide solution to a test tube containing 5 mL of iron(II) sulfate (FeSO_4) solution.

Blueprinting

Pour about 25 mL of the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ solution you have prepared previously into a petri-dish. Thoroughly soak a 5 cm x 5 cm piece of filter paper in this solution. Using plastic tongs, remove the filter paper and allow to drip dry in a fume cupboard with the light out.

When the treated paper is dry, lay it flat about 75 mm below the lamp and place some small opaque objects (coins, keys, etc.) on the paper.

Irradiate for a few minutes and dip the paper into another petri-dish containing about 25 mL of potassium ferricyanide solution (CAUTION!), using the plastic tongs. Remove the developed "blueprint" and dip in a beaker of distilled water to wash off excess ferricyanide solution.. Explain your observations.

Analysis of the Complex for Oxalate

Preparation of 0.04M KMnO₄ solution: Dissolve 6.3 g A.R. KMnO₄ in 1L of distilled water. If the solution is not to be used immediately, gently boil it for about 1 hour. Cover and let stand overnight. Remove any precipitated MnO₂ by filtration through a fine porosity filtering crucible or sintered glass funnel. The solution should be stored in the dark when not in use.

Standardization of 0.04M KMnO₄ solution: Accurately weigh approx. 3.2 g of finely powdered A.R. sodium oxalate (Na₂C₂O₄) into a 250 mL beaker. Dissolve the sodium oxalate completely in the minimum amount of warm distilled water (about 100 mL). Quantitatively transfer the solution to a 250 mL volumetric flask, and make up to the mark with distilled water.

Pipette 25.0 mL of this solution into a clean 250 mL conical flask and add 25.0 mL of 1M sulfuric acid. Warm the solution to about 60 °C (as a rough guide, 60 °C is the temperature at which the flask is just a little too hot to hold in the hand comfortably (CAUTION!). Titrate the warm solution with the 0.04M KMnO₄ until a faint pink colour persists after 30 seconds.

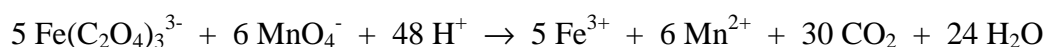
Repeat the determination until triplicate titrations agree to better than 0.1 mL. Average your results and calculate the molarity of the KMnO₄ solution.

Analysis for water: Clean and dry a small Petri dish or watchglass. Place the dish in a microwave oven on high for about one minute. CAUTION: The microwave oven should contain some "ballast" to prevent damage to the oven eg a beaker of sand or silica gel. A conventional oven, set to 110°C will of course do as well - the drying process just takes a little longer. Cool in a desiccator and accurately weigh the dish or watchglass.

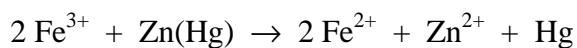
Accurately weigh approximately 1.0 g of recrystallized complex into the dish and heat in the microwave oven on high for 5 minutes. Cool and weigh. Repeat this process until the sample has come to constant weight. The loss of weight is due to removal of lattice water (water of crystallization). Calculate the percentage of lattice water in your sample of complex.

Analysis for oxalate and iron:

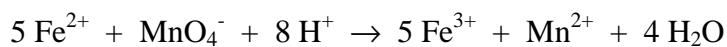
The oxalate ligands in the tris(oxalato)ferrate(III) complex are oxidized by titration with permanganate:



The iron(III) is reduced with an excess of zinc-amalgam (zinc metal coated with metallic mercury) to Fe(II):



The Fe^{2+} that is formed is quantitatively reoxidized to iron(III) by titration with standard permanganate:



Note that any iron(II) impurity in your sample would also be titrated in this step.

In summary, on a weighed sample of your complex:

1. oxalate is firstly determined by permanganate titration,
2. the Fe(III) in the resulting titration solution is reduced to Fe(II) by excess zinc-amalgam, and finally,
3. Fe(II) is determined by permanganate titration.

Procedure

Accurately weigh approximately 0.40 g of recrystallized complex and dissolve the sample in 25 mL of 1 M sulfuric acid in a 100 mL conical flask. Warm the solution to 60°C and determine the amount of oxalate in the solution by titration with standardized 0.04M KMnO_4 as previously. Do not titrate past the endpoint!

Cool the titration solution and quantitatively transfer it into a bottle containing zinc amalgam. Shake the bottle for two minutes and carefully decant the reduced solution into a 250 mL conical flask. Wash the amalgam thoroughly by shaking it with three successive 30 mL portions of a mixture of equal volumes of distilled water and 1 M H_2SO_4 . Add the washings to the conical flask and determine the amount of iron(II) in the solution by titration with standardized KMnO_4 at room temperature.

Calculate the percentages of iron and oxalate in your sample.