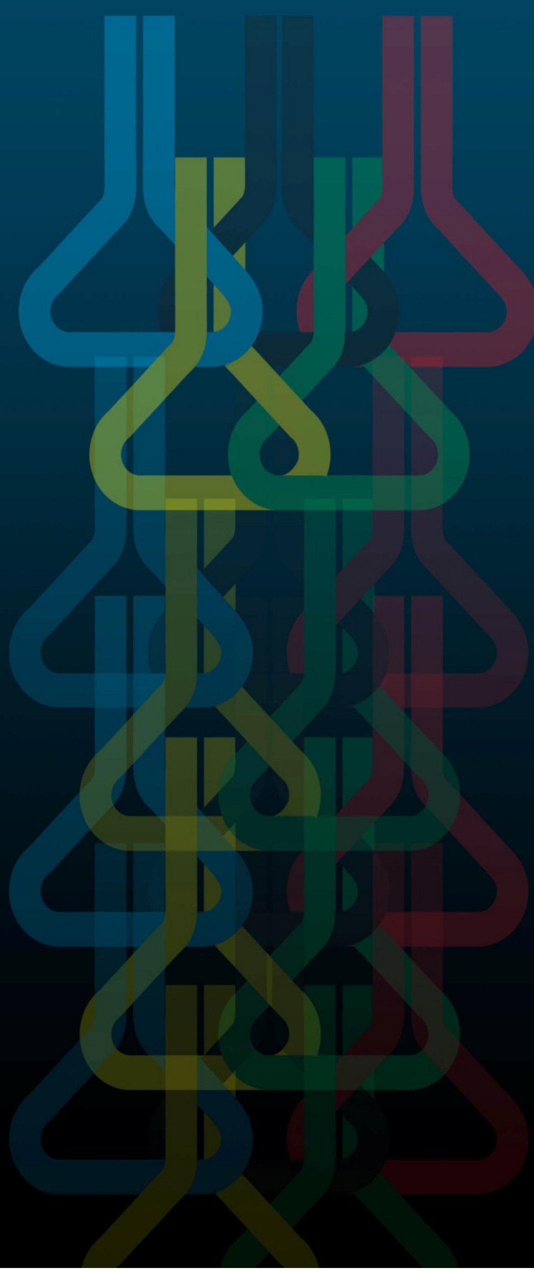
43rd International Chemistry Olympiad
2011 Ankara, Turkey

the Preparatory Problems



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43rd International Chemistry Olympiad

Preparatory Problems

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Editor: Saim Özkar

Department of Chemistry,

Middle East Technical University

Tel +90 312 210 3203, Fax +90 312 210 3200

e-mail icho2011@metu.edu.tr

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Problem Authors

O. Yavuz Ataman

Sezer Aygün

Metin Balcı

Özdemir Doğan

Jale Hacaloğlu

Hüseyin İşçi

Ahmet M. Önal

İlker Özkan

Saim Özkar

Cihangir Tanyeli

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey.

Preface

We have provided this set of problems with the intention of making the preparation for the 43rd International Chemistry Olympiad easier for both students and mentors. We restricted ourselves to the inclusion of only a few topics that are not usually covered in secondary schools. There are six such advanced topics in theoretical part that we expect the participants to be familiar with. These fields are listed explicitly and their application is demonstrated in the problems. In our experience each of these topics can be introduced to well-prepared students in 2-3 hours. Solutions will be sent to the head mentor of each country by e-mail on 1st of February 2011. We welcome any comments, corrections or questions about the problems via e-mail to icho2011@metu.edu.tr. Preparatory Problems with Solutions will be on the web in July 2011.

We have enjoyed preparing the problems and we hope that you will also enjoy solving them. We look forward to seeing you in Ankara.

Acknowledgement

I thank all the authors for their time, dedication, and effort. All the authors are Professors in various fields of chemistry at Middle East Technical University. I also thank Dr. Murat Sümbül, Dr. Salih Özçubukçu and Yunus Emre Türkmen for their ideas and valuable contributions regarding the preparatory problems for 43rd IChO. In both preparation and testing of practical problems, we are most grateful to Professor Şahinde Demirci and the laboratory team members, our assistants, Pınar Akay, Seylan Ayan, Derya Çelik, Melek Dinç, Çağatay Dengiz, Zeynep İnci Günler, Tuğba Orhan, Suriye Özlem, Burak Ural, and Emrah Yıldırım.

Ankara, 26 January 2011

Editor

Prof. Dr. Saim Özkar

Contents

Physical constants, symbols, and conversion factors

Avogadro's constant, $N_A = 6.0221 \times 10^{23}$ mol^{-1}

Boltzmann constant, $k_B = 1.3807 \times 10^{-23}$ J·K^{-1}

Gas constant, $R = 8.3145$ J·K^{-1}·mol^{-1} **=** 0.08205 atm·L·K^{-1}·mol^{-1}

Faraday constant, $F = 96485$ C·mol^{-1}

Speed of light, $c = 2.9979 \times 10^{8}$ m·s^{-1}

Planck's constant, $h = 6.6261 \times 10^{-34}$ J·s

Standard pressure, $P° = 1$ bar $= 10^{5}$ Pa

Atmospheric pressure, $P_{atm} = 1.01325 \times 10^{5}$ Pa

Zero of the Celsius scale, 273.15 K

Mass of electron, $m_e = 9.10938215 \times 10^{-31}$ kg

1 nanometer (*nm*) = 10^{-9} m

1 micrometer (*μm*) = 10^{-6} m

1 electronvolt (*eV*) = 1.602×10^{-19} J

Periodic Table of Elements with Relative Atomic Masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac (227)	104 Rf (261)	105 Ha (262)													

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (257)

Fields of Advanced Difficulty

Theoretical

Kinetics: Integrated first order rate equation; analysis of complex reaction mechanisms using the steady state approximation; determination of reaction order and activation energy.

Thermodynamics: Relationship between equilibrium constant, electromotive force and standard Gibbs free energy; the variation of equilibrium constant with temperature.

Quantum Mechanics: Energetics of rotational, vibrational, and electronic transitions using simple model theories.

Molecular Structure and Bonding Theories: The use of Lewis theory, VSEPR theory and hybridization for molecules with coordination number greater than four.

Inorganic Chemistry: Stereochemistry and isomerism in coordination compounds.

Spectroscopy: Interpretation of relatively simple ^{13}C- and ^{1}H-NMR spectra; chemical shifts, multiplicities, coupling constants and integrals.

Practical

Column chromatograpy.

Thin layer chromatography.

Theoretical problems

Problem 1 Superacids

The acids which are stronger than pure sulfuric acid are called superacids. Superacids are very strong proton donors being capable of protonating even weak Lewis acids such as Xe, H_2, Cl_2, Br_2, and CO_2. Cations, which never exist in other media, have been observed in superacid solutions. George Olah received the Nobel Prize in Chemistry in 1994 for the discovery of carbocation generation by using superacids. The enhanced acidity is due to the formation of a solvated proton. One of the most common superacids can be obtained by mixing SbF_5 and HF. When liquid SbF_5 is dissolved in liquid HF (in molar ratio of SbF_5/HF greater than 0.5) the SbF_6^- and $Sb_2F_{11}^-$ anions are formed, and the proton released is solvated by HF.

a) Write balanced chemical equations to show the species formed when HF and SbF_5 are mixed.

b) Draw the structures of SbF_6^- and $Sb_2F_{11}^-$ (in both ions the coordination number of antimony is 6 and in $Sb_2F_{11}^-$ there is a bridging fluorine atom).

c) Write the chemical equations for the protonation of H_2 and CO_2 in HF/SbF_5 superacid solution.

d) Draw the Lewis structure of HCO_2^+ including the resonance forms and estimate the H–O–C bond angle in each resonance form.

Problem 2 Stabilization of high-valent transition metal ions

Relatively few high-valent transition metal oxide fluoride cations are known. OsO_3F^+, $OsO_2F_3^+$ and μ-F$(OsO_2F_3)_2^+$ are some of these, where μ-F indicates the F^- ion bridging the two Os units. In a recent study (*Inorg. Chem*. **2010**, *49*, 271) the $[OsO_2F_3][Sb_2F_{11}]$ salt has been synthesized by dissolving solid *cis*-OsO_2F_4 in liquid SbF_5, which is a strong Lewis acid, at 25 °C, followed by removal of excess SbF_5 under vacuum at 0 °C. The crystal structure of $[OsO_2F_3][Sb_2F_{11}]$ determined by XRD reveals the existence of $OsO_2F_3^+$ cation and fluoride bridged $Sb_2F_{11}^-$ anion. Under dynamic vacuum at 0 °C, the orange, crystalline $[OsO_2F_3][Sb_2F_{11}]$ loses SbF_5, yielding [μ-F$(OsO_2F_3)_2$]$[Sb_2F_{11}]$ salt. In both salts osmium is sixcoordinate in solid state, but in liquid SbF_5 solution, both ^{19}F-NMR and Raman data are consistent with the presence of five-coordinate osmium in the trigonal bipyramidal $OsO_2F_3^+$ cation.

a) Write balanced chemical equations for the formation of $[OsO_2F_3][Sb_2F_{11}]$ and $[\mu\text{-}F(OsO_2F_3)_2]$ $[Sb_2F_{11}]$.

b) Draw all the possible geometrical isomers of trigonal bipyramidal $OsO_2F_3^+$ cation.

c) What is the oxidation number of Os in the $OsO_2F_3^+$ and $\mu\text{-}F(OsO_2F_3)_2^+$ cations?

d) When we assume a free rotation around Os-F(bridging) bond, $\mu\text{-}F(OsO_2F_3)_2^+$ cation complex can be represented as a mononuclear octahedral complex of osmium, $[OsO_2F_3X]^+$, where X = F-OsO_2F_3. Assuming that X is a monodentate ligand, draw all possible geometrical isomers of $[OsO_2F_3X]^+$ complex ion. Is there any optical isomer of $[OsO_2F_3X]^+$?

Problem 3 Colemanite mineral as boron source

Boron is an important element in the world from both strategic and industrial points of view. Although the element is not directly used, its compounds have a wide range of applications almost in all manufacturing areas, except food. Boron is oxophilic and, therefore, occurs primarily as oxide (borates) in nature. Borate minerals occur in a few locations in the world. The largest reserves of boron minerals are in the western part of Turkey. One of the most important borate minerals is colemanite with the formula $2CaO \cdot 3B_2O_3 \cdot 5H_2O$. Boric acid ($H_3BO_3$) is produced in Turkey and Europe mainly from the reaction of colemanite with sulfuric acid.

The reaction is carried out at temperatures above 80 °C. Calcium sulfate dihydrate (Gypsum, $CaSO_4 \cdot 2H_2O$) crystallizes from the reaction solution and the crystals are filtered out from the hot solution. Subsequently, boric acid crystallizes from the solution when it is cooled down to room temperature. Filtration of gypsum crystals from the reaction solution is a crucial process in the boric acid production for achieving high purity and high efficiency, as the subsequent crystallization of boric acid from the supernatant solution is substantially affected by contaminations. The reaction of sulfuric acid with colemanite takes place in two steps: In the first step colemanite is dissolved in sulfuric acid forming the calcium(II) ion and boric acid. In the second step, calcium sulfate, formed from Ca^{2+} and SO_4^{2-} ions, precipitates as gypsum crystals. In an experiment, 184.6 g colemanite containing 37.71% wt. B_2O_3 and 20.79% wt. CaO is dissolved in aqueous sulfuric acid yielding initially 1.554 M boric acid at 80 ºC. The reaction is carried out in a closed system so that the volume of the solution remains essentially constant. The saturation concentration of calcium ion in this solution is $[Ca^{2+}]_{sat}$ = 0.0310 M at 80 °C.

a) Write a balanced equation for the dissolution of colemanite in sulfuric acid.

b) Calculate the amount of gypsum obtained from the crystallization.

c) Calculate the mass of calcium ion remained in the solution.

d) Calculate the theoretical amount of boric acid that can be obtained in this experiment.

e) After hot filtration of gypsum crystals, boric acid is obtained by crystallization when the solution is cooled down to room temperature. The boric acid obtained is still contaminated by sulfate ions. The sulfur contamination is not desired in industrial use of boric acid, such as production of borosilicate glasses. Can recrystallization of boric acid in water remove the sulfate contamination of the product?

Problem 4 Magnesium compounds

Magnesium is one of the important elements in human body. Hundreds of biochemical reactions that drive energy metabolism and DNA repair are fueled by magnesium. Over 300 different enzymes rely on magnesium to facilitate their catalytic action. Magnesium maintains blood pressure and relaxes blood vessels and arteries. Magnesium deficiency leads to physiological decline in cells setting the stage for cancer. Among the numerous available magnesium dietary supplements, magnesium citrate has been reported as more bioavailable than the most commonly used magnesium oxide. Magnesium is a highly flammable metal. Once ignited, it is difficult to extinguish as it is capable of burning in water, carbon dioxide, and nitrogen.

a) Write a balanced equation for the formation of magnesium oxide by reaction of magnesium with

i. oxygen, O_2

ii. carbon dioxide, CO_2

b) Magnesium hydroxide is formed by reaction of Mg or MgO with H_2O. Write a balanced equation for the formation of magnesium hydroxide from the reaction of H_2O with

i. Mg

ii. MgO

c) When magnesium metal is heated in N_2 atmosphere the white-yellow compound **A** is formed. Hydrolysis of **A** yields the colorless gas **B** which has basic character when dissolved in water. The reaction of **B** with aqueous solution of hypochlorite ion generates chloride ion, water, and the molecular compound **C** which is soluble in water. The reaction of **B** with hydrogen peroxide also produces the compound **C** and water. When the colorless gas **B** is heated with sodium metal, a solid compound **D** and hydrogen gas are produced. The reaction of compound **D** with nitrous oxide produces gaseous ammonia, solid sodium hydroxide, and a solid compound **E**. When the solid **E** is heated it decomposes to sodium metal and nitrogen gas. Write balanced equations for the formation of each compound **A**, **B**, **C**, **D**, and **E**.

d) Draw the Lewis structure of the anion present in compound **E**. Choose the most stable resonance structure.

e) Compound **C** was first used as rocket fuel during World War II. Today, it is used as a low-power propellant in spacecrafts. In the presence of certain catalysts such as carbon nanofibers or molybdenum nitride supported on alumina, one of the decomposition reactions of **C** involves production of ammonia and nitrogen gas. Write a balanced equation for the decomposition reaction of compound **C** generating ammonia and nitrogen gas.

f) Estimate the energy associated with the decomposition of compound **C** into ammonia and nitrogen gas and standard enthalpy of formation of NH_3 at 298 K. Standard enthalpy of formation of liquid and gaseous **C** are 50.6 and 95.4 $kJ \cdot mol^{-1}$, respectively, at 298 K. Average bond energies of N≡N, N=N, N-N and N-H are 946, 418, 163, and 389 $kJ \cdot mol^{-1}$, respectively, at 298 K.

g) In an experiment, 2.00 mL of **C** is placed in a 1.00 L evacuated reaction vessel containing a suitable catalyst at 298 K. After decomposition, the reaction vessel is cooled down to 298 K. Calculate the final pressure inside the vessel (density of liquid **C** is 1.0045 $g \cdot cm^{-3}$).

h) Calculate the work done if isothermal expansion of the reaction vessel discussed in part (g) occurs against the atmospheric pressure of 1 atm.

Problem 5 Nitrogen oxides and oxoanions

Nitrogen occurs mainly in the atmosphere. Its abundance in Earth`s Crust is only 0.002% by mass. The only important nitrogen containing minerals are sodium nitrate (Chile saltpeter) and potassium nitrate (saltpeter). Sodium nitrate, $NaNO_3$, and its close relative sodium nitrite, $NaNO_2$, are two food preservatives with very similar chemical formulae, but different chemical properties. Sodium nitrate helps to prevent bacterial colonization of food. Sodium nitrite is a strong oxidizing agent used as a meat preservative. As in the case of almost any food additive or preservative, sodium nitrate is linked to several adverse reactions in susceptible people. Consuming too much sodium nitrate can cause allergies. Excessive ingestion of the preservative can also cause headaches.

a) Draw the Lewis structures for the anions of these two salts including all possible resonance forms. Which one of these two anions has shorter N-O bond distance?

b) Zn reduces NO_3^- ions to NH_3 in basic solution forming tetrahydroxozincate(II) ion. Write a balanced equation for the reaction between zinc and ammonia in basic solution.

c) When a strong base is gradually added to a solution containing Zn^{2+} ions a white precipitate of $Zn(OH)_2$ first forms (K_{sp} = 1.2×10^{-17} for $Zn(OH)_2$). To a 1.0 L solution of 5.0×10^{-2} mol Zn^{2+} ions, 0.10 mol OH^- is added. Calculate the pH of this solution.

d) When more base is added to the solution, the white precipitate of $Zn(OH)_2$ dissolves forming the complex ion $Zn(OH)_4^{2-}$. The formation constant for the complex ion is 4.6×10^{17}. Calculate the pH of the solution in part (c) when 0.10 mol OH^- ion is added (assuming the total volume does not change).

e) A mixture containing only NaCl and $NaNO_3$ is to be analyzed for its $NaNO_3$ content. In an experiment, 5.00 g of this mixture is dissolved in water and solution is completed to 100 mL by addition of water; then a 10 mL aliquot of the resulting solution is treated with Zn under basic conditions. Ammonia produced during the reaction is passed into 50.0 mL of 0.150 M HCl solution. The excess HCl requires 32.10 mL of 0.100 M NaOH solution for its titration. Find the mass % of $NaNO_3$ in the solid sample.

f) Both NaCl and $NaNO_3$ are strong electrolytes. Their presence in solution lowers the vapor pressure of the solvent and as a result freezing point is depressed. The freezing point depression depends not only on the number of the solute particles but also on the solvent itself. The freezing point depression constant for water is K_f = 1.86 °C/molal. Calculate the freezing point of the solution prepared by dissolving 1.50 g of the mixture described in (d) consisting of NaCl and $NaNO_3$ in 100.0 mL water. Density of this solution is d = 0.985 g·cm^{-3}.

g) N_2H_4 is one of the nitrogen compounds which can be used as a fuel in hydrazine fuel cell. Calculate the standard free energy change for the fuel cell reaction given below.

$N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$

The standard potentials are given below:

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ E° = 1.23 V

$N_2(g) + 4H_2O(l) + 4e^- \rightarrow N_2H_4(g) + 4OH^-(aq)$ E° = - 0.33 V

h) The free energy change is related to the maximum amount of work that can be obtained from a system during a change at constant temperature and pressure. The relation is given as $-\Delta G = w_{max}$. Calculate the maximum amount of work that can be obtained from the fuel cell which consumes 0.32 g $N_2H_4(g)$ under standard conditions.

Problem 6 Ferrochrome

Chromium is one of the most abundant elements in Earth's Crust and it is mined as chromite mineral, $FeCr_2O_4$. South Africa, Kazakhstan, India, Russia, and Turkey are substantial producers. For the production of pure chromium, the iron has to be separated from the mineral in a two step roasting and leaching process.

$4\ FeCr_2O_4(s) + 8\ Na_2CO_3(s) + 7\ O_2(g) \rightarrow 8\ Na_2CrO_4(s) + 2\ Fe_2O_3(s) + 8\ CO_2(g)$

$2\ Na_2CrO_4(s) + H_2SO_4(aq) \rightarrow Na_2Cr_2O_7(s) + Na_2SO_4(aq) + H_2O(l)$

Dichromate is converted to chromium(III) oxide by reduction with carbon and then reduced in an aluminothermic reaction to chromium.

$Na_2Cr_2O_7(s) + 2\ C(s) \rightarrow Cr_2O_3(s) + Na_2CO_3(s) + CO(g)$

$Cr_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Cr(s)$

a) Calculate the mass of Cr that can be theoretically obtained from 2.1 tons of ore which contains 72.0% $FeCr_2O_4$ mineral.

b) Chromium, due to its strong corrosion resistance, is an important alloying material for steel. A sample of certain steel is to be analyzed for its Mn and Cr content. Mn and Cr in a 5.00 g steel sample are oxidized to MnO_4^- and $Cr_2O_7^{2-}$, respectively, via a suitable treatment to yield 100.0 mL solution. A 50.0 mL portion of this solution is added to $BaCl_2$

and by adjusting pH, chromium is completely precipitated as 5.82 g $BaCrO_4$. A second 50.0 mL portion of the solution requires exactly 43.5 mL of 1.60 M Fe^{2+} for its titration in acidic solution. The unbalanced equations for the titration reactions are given below.

$MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$

$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$

Balance the equations for the titration reactions.

c) Calculate the % Mn and % Cr in the steel sample.

Problem 7 Xenon compounds

Xenon, although present in the earth atmosphere in trace level, has several applications. It is used in the field of illumination and optics in flash and arc lamps. Xenon is employed as a propellant for ion thrusters in spacecraft. In addition, it has several medical applications. Some of xenon isotopes are used in imaging the soft tissues such as heart, lung, and brain. It is used as a general anesthetic and recently its considerable potential in treating brain injuries, including stroke has been demonstrated.

Xenon being a member of noble gases has extremely low reactivity. Yet, several xenon compounds with highly electronegative atoms such as fluorine and oxygen are known. Xenon reacts with fluorine to form three different xenon fluorides, XeF_2, XeF_4 and XeF_6. All these fluorides readily react with water, releasing pure Xe gas, hydrogen fluoride and molecular oxygen. The oxide and oxofluorides of xenon are obtained by partial or complete hydrolysis of xenon fluorides. Xenon trioxide can be obtained by the hydrolysis of XeF_4 or XeF_6. The hydrolysis of XeF_4 yields XeO_3, Xe, HF, and F_2. However, hydrolysis of XeF_6 produces only XeO_3 and HF. When partially hydrolyzed, XeF_4 and XeF_6 yield $XeOF_2$ and $XeOF_4$, respectively, in addition to HF.

a) Write balanced equations for the generation of

i. XeO_3 by hydrolysis of XeF_4

ii. XeO_3 by hydrolysis of XeF_6

iii. $XeOF_2$ by partial hydrolysis of XeF_4

iv. $XeOF_4$ by partial hydrolysis of XeF_6

b) Draw the Lewis structures and give the hybridization at the central atom of

i. XeF_2

ii. XeF_4

iii. XeO_3

iv. $XeOF_2$

v. $XeOF_4$

Problem 8 Structure of phosphorus compounds

Phosphorus is very reactive and, therefore, never found in the native elemental form in the Earth's Crust. Phosphorus is an essential element for all living organisms. It is the major structural component of bone in the form of calcium phosphate and cell membranes in the form of phospholipids. Furthermore, it is also a component of DNA, RNA, and ATP. All energy production and storage, activation of some enzymes, hormones and cell signaling molecules are dependent on phosphorylated compounds and phosphorylation. Compounds of phosphorus act as a buffer to maintain pH of blood and bind to hemoglobin in red blood cells and affect oxygen delivery.

Phosphorus has five valence electrons as nitrogen, but being an element of the third period, it has empty d orbitals available to form compounds up to six coordination number. One allotrope of phosphorus is the white phosphorus which is a waxy solid consisting of tetrahedral P_4 molecules. White phosphorus is very reactive and bursts into flame in air to yield the phosphorus(V) oxide P_4O_{10}. Its partial oxidation in less oxygen yields the phosphorus(III) oxide P_4O_6. Disproportionation of white phosphorus in basic solution yields the gaseous phosphine, PH_3 and hypophosphite ion, $H_2PO_2^-$. Phosphorous acid, H_3PO_3 and phosphoric acid, H_3PO_4 can be produced by the reaction of P_4O_6 or P_4O_{10} with water, respectively. White phosphorus reacts with halogens to yield halides with general formulae PX_3 and PX_5. Oxidation of PCl_3 forms phosphoryl trichloride, $POCl_3$. Reaction of PCl_5 with LiF yields $LiPF_6$ which is used as an electrolyte in lithium-ion batteries.

a) Write balanced equations for the preparation of

i. PH_3

ii. PCl_3

iii. PCl_5

iv. P_4O_6

v. P_4O_{10}

vi. H_3PO_3

vii. H_3PO_4

viii. $POCl_3$

ix. $LiPF_6$

b) Draw the Lewis structures of the following molecules or ions, including the resonance forms if any.

i. PCl_3

ii. PCl_5

iii. PO_4^{-3}

iv. $POCl_3$

v. PF_6^-

c) Draw the structures of the phosphorus oxides P_4O_6 and P_4O_{10}, starting with tetrahedral P_4 skeleton. Each of six oxygen atom will be bridging two phosphorus atoms on an edge. An additional oxygen atom will be bonded to each phosphorus atom as terminal oxo-group in the case of P_4O_{10}.

d) Using the Valence Shell Electron Pair Repulsion model determine the geometry of the following molecules or ions.

i. PCl_3

ii. $POCl_3$

iii. PCl_5

iv. PF_6^-

e) What is the hybridization at phosphorus atom in the following molecules or ions?

i. PCl_3

ii. $POCl_3$

iii. PCl_5

iv. PF_6^-

Problem 9 Arsenic in water

Arsenic is known as a pollutant in environment and a toxic element. However, in December 2010 researchers of the National Aeronautics and Space Administration (NASA) of USA reported a species of bacterium in Mono Lake, California, that can use arsenic instead of phosphorus in biological molecule structures. It seems that monitoring concentration and identities of arsenic species in water will become even more important in near future.

In natural waters, arsenic is present in the form of oxoacids: Arsenous or arsenic acid with oxidation states of +3 and +5, respectively. The source of arsenic in natural waters is often of geological origin. Arsenous acid and arsenic acid have the following dissociation constants.

H_3AsO_3 $K_{a1} = 5.1\times10^{-10}$

H_3AsO_4 $K_{a1} = 5.8\times10^{-3}$ $K_{a2} = 1.1\times10^{-7}$ $K_{a3} = 3.2\times10^{-12}$

In aqueous systems, oxidation state of arsenic is dependent on the presence of oxidants and reductants, dissolved oxygen plays an important role. World Health Organization (WHO) has established a maximum total arsenic concentration of 10 µg/L in drinking water; this value has been adapted by many countries.

In a water sample obtained from a river as a potential source of drinking water, pH value is found to be 6.50. Using atomic absorption spectrometry, speciation analysis is also performed and arsenic(III) and arsenic(V) concentrations are found to be 10.8 µg/L and 4.3 µg/L, respectively.

a) Calculate the total molar concentration for arsenic(III) and arsenic(V) inorganic species in the system, assuming that these are the only arsenic species present.

b) What will be the predominant molecular or ionic species for arsenic(III) at pH = 6.50? Write the formula(s).

c) What will be the predominant molecular or ionic species for arsenic(V) at pH = 6.50? Write the formula(s).

d) Calculate the molar concentration(s) of arsenic(III) species suggested in (b).

e) Calculate the molar concentration(s) of predominant arsenic(V) species suggested in (c).

f) arsenic(III) is known to be significantly more toxic to human as compared to arsenic(V). Is it advantageous or disadvantageous to have oxidizing agents such as dissolved oxygen in water?

Problem 10 Amphoteric lead oxide

In aqueous media, Pb^{2+} ions form a precipitate, PbO, which is an amphoteric oxide. In acidic medium, only Pb^{2+} species is present; with increasing pH, PbO and $Pb(OH)_3^-$ are formed in appreciable quantities. The important equilibria for lead species in aqueous medium are given below:

Reaction 1 $PbO(s) + H_2O(l) \rightleftharpoons Pb^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = 8.0\times10^{-16}$

Reaction 2 $PbO(s) + 2H_2O(l) \rightleftharpoons Pb(OH)_3^-(aq) + H_3O^+(aq)$ $K_a = 1.0\times10^{-15}$

a) The amphoteric PbO completely dissolves when pH is sufficiently low. When initial concentration of Pb^{2+} is 1.00×10^{-2} mol·L^{-1}, what is the pH at which PbO starts to precipitate?

b) Starting from the value in (b), when pH is increased to a certain value, precipitate is redissolved. At what pH value does the precipitate dissolve completely?

c) Write a general expression for molar solubility, s, of PbO.

d) Theoretically, the minimum solubility is achieved when pH is 9.40. Calculate the molar concentration of all the species and the molar solubility at this pH.

e) Calculate the pH range where the solubility is 1.0×10^{-3} mol·L^{-1} or lower.

Problem 11 Analyzing a mixture of calcium salts

When a 5.000 g mixture of $CaCO_3$, $Ca(HCO_3)_2$, $CaCl_2$ and $Ca(ClO_3)_2$ is heated at elevated temperature gaseous CO_2, H_2O, and O_2 are evolved. The gases evolved exert a pressure of 1.312 atm in an evacuated 1.000 L cylinder at 400.0 K. When the temperature inside the cylinder is decreased to 300.0 K, the pressure drops to 0.897 atm. The vapor pressure of water at this temperature is 27.0 torr. The gas in the cylinder is used to combust an unknown amount of acetylene C_2H_2. The enthalpy change during the combustion process is determined as -7.796 kJ with the use of a calorimeter.

$\Delta_f H°(C_2H_2(g)) = 226.8$ kJ.mol^{-1}; $\Delta_f H°(CO_2(g)) = -393.5$ kJ.mol^{-1};

$\Delta_f H°(H_2O(g)) = -241.8$ kJ.mol^{-1}; $\Delta_{vap}H°_{298K}(H_2O(l)) = 44.0$ kJ.mol^{-1}

a) Write balanced equations for the possible decomposition reactions generating gases.

b) Write a balanced equation for the combustion of C_2H_2.

c) Calculate the total number of moles of gases produced in the cylinder.

d) Calculate the number of moles of O_2 that was present in the cyclinder.

e) Calculate number of moles of CO_2 and H_2O produced.

f) Calculate the weight percentage of $CaCO_3$ and $CaCl_2$ in the original mixture.

Problem 12 Breath analysis

Ethanol is dissolved in blood and distributed to organs in the body. As a volatile compound, ethanol can be vaporized quite easily. In lungs, ethanol can change its phase from liquid to gaseous and, hence, it can be exhaled with air. Since the concentration of alcohol vapor in lungs is directly related to its concentration in blood, blood alcohol concentration can be measured using a device called a breathalyzer. In one of the older versions of breathalyzer, a suspect breathes into the device and exhaled air is allowed to pass through a solution of potassium dichromate which oxidizes ethanol to acetic acid. This oxidation is accompanied by a color change from orange to green and a detector records the change in intensity, hence, the change in color, which is used to calculate the percentage of alcohol in breath. When the oxidation of alcohol by potassium dichromate is carried out in an electrochemical cell, either the electrical current generated by this reaction or the change in the electromotive force can be measured and used for the estimation of alcohol content of blood.

a) Write a balanced equation for the oxidation of ethanol by the dichromate ion in acidic solution.

b) If the standard potential for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+} is 1.330 V and reduction of acetic acid to ethanol is 0.058 V, calculate the standard electromotive force E° for the overall reaction and show that overall reaction is spontaneous at 25 °C and 1.0 bar.

c) In a breathalyzer which uses oxidation of ethanol, the volume of solution is 10.0 mL. When a suspect breathes into the device, 0.10 A of current flow is recorded for 60 s. Calculate the mass of alcohol per volume of exhaled breath.

d) In calculating the alcohol content of blood from the amount of alcohol in a breath, the "2100:1 partition ratio" needs to be considered. The ratio states that 2100 mL of expired air (breath) contains the same amount of ethanol as 1 mL of blood. Alternatively, each milliliter of blood has 2100 times the amount of ethanol as each milliliter of expired air. If the volume of expired air described in part (c) is 60.0 mL, calculate the amount of alcohol per mL of blood.

e) Cr^{3+} precipitates in basic solution as $Cr(OH)_3$. The solubility product of chromium(III) hydroxide is 6.3×10^{-31} at 25 °C. Calculate the standard potential for the reduction of $Cr(OH)_3$ to Cr. Standard potential for the reduction of Cr^{3+} to Cr is -0.74 V.

Problem 13 Decomposition kinetics of sulfuryl dichloride

Sulfuryl dichloride (SO_2Cl_2) is a compound of industrial, environmental and scientific interest and widely used as chlorinating/sulfonating agent or as component of the catholyte system in batteries. At room temperature, SO_2Cl_2 is a colorless liquid with a pungent odor; its boiling point is 70 °C. It decomposes to SO_2 and Cl_2 when heated to or above 100 °C.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

An empty container is filled with SO_2Cl_2. Its decomposition to SO_2 and Cl_2 is followed by monitoring the change in total pressure at 375 K. The following data are obtained.

Time (s)	0	2500	5000	7500	10000
P_{total} (atm)	1.000	1.053	1.105	1.152	1.197

a) By graphical approach, show that the decomposition is a first order reaction and calculate the rate constant at 375 K.

b) When the same decomposition reaction is carried out at 385 K, the total pressure is found to be 1.55 atm after 1 h. Calculate the activation energy for the decomposition reaction.

c) There will be a negligible amount of $SO_2Cl_2(g)$ in the reaction vessel after a long period of time. Therefore, the content of the vessel might be considered to be a mixture of SO_2 and Cl_2 gases. $SO_2(g)$ is separated from $Cl_2(g)$ as H_2SO_4 and $Cl_2(g)$ is used to construct a Cl_2/Cl^- electrode. This electrode is combined with a Cu^{2+}/Cu electrode to make a Galvanic cell. Which electrode is the cathode? $E°(Cu^{2+}/Cu) = +0.36$ V and $E°(Pt/Cl_2, Cl^-) = +1.36$ V

d) Calculate the $\Delta G°$ for the cell reaction given in (c).

e) A possible way for separating SO_2 and Cl_2 from each other is to pass the mixture over solid CaO which will convert all SO_2 to $CaSO_3$, a strong electrolyte. Calculate the pH of a 0.020 M $CaSO_3$ solution. For H_2SO_3 $K_{a1} = 1.7\times10^{-2}$ and $K_{a2} = 6.4\times10^{-8}$.

Problem 14 Clock reaction

The iodine clock reaction is a classical chemical clock demonstration experiment to display chemical kinetics in action. In this reaction two clear solutions are mixed and after a short time delay, the colorless liquid suddenly turns to a shade of dark blue. The iodine clock reaction has several variations. One of them involves the reaction between peroxydisulfate(VI) and iodide ions:

Reaction **A**: $S_2O_8^{2-}(aq) + 3\ I^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_3^-(aq)$

The I_3^- ion formed in Reaction **A** reacts immediately with ascorbic acid ($C_6H_8O_6$) present originally in the solution to form I^- ion (Reaction **B**).

Reaction **B**: $C_6H_8O_6(aq) + I_3^-(aq) \rightarrow C_6H_6O_6(aq) + 3\ I^-(aq) + 2\ H^+(aq)$

When all the ascorbic acid present in the solution is consumed, the I_3^- ion generated in Reaction **A** forms a blue colored complex with starch present in solution (Reaction **C**).

Reaction **C**: $I_3^-(aq)$ + starch $\rightarrow$ Blue-complex.

Thus, the time *t* elapsed between mixing the reactants and the appearance of the blue color depends on the amount of I_3^- ion formed. Therefore 1/*t* can be used as a measure of reaction rate.

At 25 °C, 25.0 mL $(NH_4)_2S_2O_8$, 25.0 mL KI, 5.0 mL 0.020 M $C_6H_8O_6$, and 5.0 mL starch solutions are mixed with different initial concentrations of $(NH_4)_2S_2O_8$ and KI, and the elapsed time *t* for the appearance of blue color is measured. All the data are tabulated below.

Experiment No	$[(NH_4)_2S_2O_8]_o$ (mol/L)	$[KI]_o$ (mol/L)	t (s)
1	0.200	0.200	20.5
2	0.100	0.200	41.0
3	0.050	0.200	82.0
4	0.200	0.100	41.0

a) Find the rate law for Reaction **A** using the data given in Table.

b) Using the data for the experiment 1, find the initial rate of Reaction **A** in mol·L^{-1}·s^{-1}.

c) Calculate the rate constant for Reaction **A** at 25 °C.

d) The following mechanism is proposed for Reaction **A**:

$$I^-(aq) + S_2O_8^{2-}(aq) \xrightarrow{k_1} IS_2O_8^{3-}(aq)$$

$$IS_2O_8^{3-}(aq) \xrightarrow{k_2} 2\ SO_4^{2-}(aq) + I^+(aq)$$

$$I^+(aq) + I^-(aq) \xrightarrow{k_3} I_2(aq)$$

$I_2(aq) + I^-(aq) \xrightarrow{k_4} I_3^-(aq)$

Derive an equation for the rate of formation of I_3^-(aq) assuming that the steady-state approximation can be applied to all intermediates. Is the given mechanism consistent with the rate law found in part (a)?

e) Ascorbic acid is a weak diprotic acid. In order to find its first acid dissociation constant, K_{a1}, 50.0 mL of 0.100 M ascorbic acid solution is titrated with 0.200 M NaOH solution. The pH of solution is measured as 2.86 after addition of 1.00 mL NaOH solution. Calculate acid dissociation constant K_{a1} for ascorbic acid.

f) Give the predominant species present at pH = 7.82 if K_{a2} for ascorbic acid is 2.5×10^{-12}.

Problem 15 Mixing ideal gases

Two rigid containers in thermal equilibrium at 298 K connected by a valve are isolated from the surroundings. In one of the containers, 1.00 mol of He(g) and 0.50 mol of A(g) are present at 1.00 atm. In the other container, 2.00 mol of Ar(g) and 0.50 mol of B_2(g) are present at 1.00 atm.

a) Predict whether the entropy will increase or decrease when the valve separating the two containers is opened assuming that no chemical reaction takes place.

b) Predict whether the entropy will increase or decrease, stating all factors that will have contribution, if a chemical reaction takes place according to the following equation when the valve separating the two containers is opened.

$A(g) + \frac{1}{2}B_2(g) \rightarrow BA(g) \qquad \Delta H^\circ_{298} = -\ 99.0$ kJ

c) Assuming that all the gases present are ideal, calculate the final pressure at the end of the reaction. The total heat capacity of two containers is 547.0 J/°C.

Problem 16 Kinetics in gas phase

The gas phase reaction

$A_2(g) + 2\ B(g) \rightarrow 2\ AB(g)$

is accelerated by catalyst C. The overall rate constant is found to increase linearly with the catalyst concentration. Following measurements are done at 400 K with [C] = 0.050 mol·L^{-1}:

Experiment No	$[A_2]$ (mol·L^{-1})	[B] (mol·L^{-1})	Initial rate (mol·L^{-1}·s^{-1})
1	0.010	0.10	1.600×10^{-10}
2	0.010	0.20	3.200×10^{-10}
3	0.100	0.20	1.012×10^{-9}

a) What is the rate law of this reaction?

b) Calculate the numerical value of $k_{overall}$ at 400 K.

c) For this hypothetical reaction following mechanism was proposed.

$A_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,A(g)$ fast equilibrium

$A(g) + B(g) + C(g) \xrightarrow{k_2} ABC(g)$ slow step

$ABC(g) \xrightarrow{k_3} AB(g) + C(g)$

Check that the suggested mechanism gives the equation for the overall reaction.

d) Show that the suggested mechanism is consistent with the rate law determined experimentally.

e) Calculate the dissociation enthalpy of A_2 bond using the following information:

- At 400 K, when $[A_2]$ is 1.0×10^{-1} mol·L^{-1}, [A] is 4.0×10^{-3} mol·L^{-1}.
- When the first experiment is repeated at 425 K, the initial reaction rate increases to a three-fold value.
- Activation energy of the slowest step is 45.0 kJ.

Problem 17 Chemical Equilibrium

Iodine is an essential trace element for life and is the heaviest element commonly needed by living organisms. At high temperatures an equilibrium between $I_2(g)$ and $I(g)$ takes place.

The following table summarizes the initial pressure of $I_2(g)$ and the total pressure when the equilibrium is reached at the given temperatures.

T (K)	1073	1173
$P(I_2)$ (atm)	0.0631	0.0684
P_{total} (atm)	0.0750	0.0918

a) Calculate $\Delta H°$, $\Delta G°$ and $\Delta S°$ at 1100 K. (Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature in the temperature range given.)

b) Calculate the mole fraction of I(*g*) in the equilibrium mixture when the numerical value of K_p is the half of the total pressure.

c) Assuming ideal gas behavior for I_2(*g*) and I(*g*), calculate the bond energy of I_2 at 298 K.

d) Calculate the wavelength of radiation that must be used to dissociate I_2(*g*) at 298 K.

e) In an experiment, when a sample of I_2(*g*) is irradiated by a laser beam of $\lambda = 825.8$ nm, at a rate of 20.0 $J \cdot s^{-1}$ for 10.0 s, 1.0×10^{-3} mol of I(*g*) is produced. Calculate the quantum yield for the dissociation process (*i.e.*, the number of moles of I_2 dissociated per mole of photons absorbed by the system).

Problem 18 Iodine equilibrium

Drinking water may contain small amount of some contaminants that are harmful to living organisms. Iodine is used as a disinfectant for drinking water for the International Space Station Alpha. Aqueous I_2 forms a number of inorganic derivatives, such as hypoiodous acid, HOI; iodate, IO_3^-; iodide, I^- and triiodide, I_3^-. An equilibrium reaction takes place involving I_2, I^- and I_3^- in water according to the following equation;

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

When dichloromethane, CH_2Cl_2 is added to aqueous solution of iodine, I_2 is distributed in water and CH_2Cl_2 phases according to the following equilibrium process. The equilibrium constant for the distribution is 150.

$$I_2\,(aq) \rightleftharpoons I_2\,(CH_2Cl_2)$$

a) For the homogenous equilibrium reaction which species acts as a Lewis acid?

b) One method for determining the concentration of I_2 and I_3^- in a solution is the titration with a standard solution of $S_2O_3^{2-}$. An oxidation-reduction reaction takes place when I_2 or I_3^- interacts with $S_2O_3^{2-}$ yielding I^- and $S_4O_6^{2-}$. Write the balanced equations for chemical reactions that take place during the titration of I_2 and I_3^- with $S_2O_3^{2-}$. Indicate the oxidant and the reductant in each reaction? Give the oxidation state of S in $Na_2S_2O_3$.

c) In order to determine the equilibrium constant of the reaction involving I_2, I^- and I_3^- in water the following experiments are performed at 298 K. When 50.0 mL of 0.010 M KI aqueous solution is added to 25.0 mL solution of I_2 in CH_2Cl_2, two separate phases, aqueous and organic, are formed. Assume that there is no volume change upon mixing.

In order to determine concentrations of I_2 distributed in CH_2Cl_2 and aqueous phases, a 5.00 mL aliquot of the CH_2Cl_2 phase is diluted to 100.0 mL by addition of the solvent, CH_2Cl_2. The visible spectrum of I_2 in the diluted solution, recorded in a 1.00 cm-cell, had a band with a maximum absorbance of 0.516 at 510.0 nm. The molar absorption coefficient, ε of I_2 in CH_2Cl_2 at 510 nm is 858 $L\cdot mol^{-1}\cdot cm^{-1}$. Calculate equilibrium concentrations of I_2 in CH_2Cl_2 and aqueous phases.

d) In order to determine the equilibrium concentrations of I^- and I_3^-, a 25.0 mL aliquot is taken from the aqueous phase. To this solution, an excess amount of KI, namely 10.0 mL of 0.100 M KI solution, is added to avoid evaporation of I_2. Then, the final solution is titrated with a 0.0100 M solution of $Na_2S_2O_3$. The end point is reached upon addition of 3.10 mL of $Na_2S_2O_3$ solution. Calculate the equilibrium concentrations of I^-, and I_3^- in the aqueous phase and the equilibrium constant at 298 K.

e) Calculate $\Delta_f G°[I_2(CH_2Cl_2)]$, if $\Delta_f G°[I_2(aq)]$ is 16.4 $kJ\cdot mol^{-1}$.

Problem 19 Molecular weight determination by osmometry

Measurement of osmotic pressure is one of the techniques used to determine the molecular weight of large molecules, like polymers. The device, osmometer, used to measure the osmotic pressure, consists of a semipermeable membrane that separates pure solvent from a solution. The flow of solvent from pure solvent side to solution side, due to concentration gradient, across the semipermeable membrane is called osmosis.

Polyvinylchloride, PVC, is one of the most widely used plastics and can be prepared *via* chain polymerization. In chain polymerization monomers are added to a growing polymer chain. A typical chain polymerization involves three main steps named as initiation, propagation, and termination. In termination reaction two growing chains combine to form either one dead polymer chain (termination by combination) or two dead polymer chains (termination by disproportionation). In an attempt to determine the molecular weight of PVC via osmotic pressure measurement, a PVC solution is prepared by dissolving 7.0 g of PVC in cyclohexanone ($C_6H_{10}O$) to make a 1.0 L solution at 295 K. One arm of the osmometer is filled with this solution of density 0.980 $g\cdot cm^{-3}$ and the other arm is filled with pure solvent cyclohexanone to the same level. After a certain time, the height of liquid in the solution side arm increases and at equilibrium a 5.10 cm level difference between two arms is recorded.

a) Calculate the osmotic pressure and average molecular weight of PVC. (density of Hg = 13.6 $g \cdot cm^{-3}$, g = 9.81 $m \cdot s^{-2}$).

b) The kinetic chain length ν is the ratio of the number of monomer units consumed per activated center produced in the initiation step and used to estimate the mode of termination. In the chain polymerization of vinyl chloride to produce PVC, the concentration of active centers produced in the initiation step and the change in the concentration of monomer is found to be 1.00×10^{-8} mol/L and 2.85×10^{-6} mol/L, respectively. Calculate the kinetic chain length,ν.

c) Predict whether the termination is by combination or by disproportionation.

d) The vapor pressure of pure solvent cyclohexanone is 4.33 torr at 25 °C. Calculate the vapor pressure of the PVC solution.

e) For pure solvent cyclohexanone, normal freezing point is -31.000 ^{o}C. If the freezing point of the PVC solution is -31.003 ^{o}C, find the molal freezing point depression constant of cyclohexanone.

Problem 20 Allowed energy levels and requirements for absorption of light

It is a well-established experimental fact that the internal energies of a given atom or a molecule M are confined to discrete values, so called "quantized energies". "Internal" energy is the total energy of M excluding its translational energy. Translational energy of M is equal to the kinetic energy of a free particle that has the mass of M, which is moving along a straight line with a constant speed. It is not quantized, and it does not play a role in absorption of light by M. Internal energy of an atom is the energy associated with the motion of its electrons around the nucleus. In molecules, there are additional contributions from rotational and vibrational motions. The "allowed" internal energies of M can be numbered as E_1, E_2, E_3, ... in increasing order of energy. These are called the "energy levels" of M. The lowest energy level, E_1, is called the "ground" level, and when M has this lowest possible energy, M is said to be in its ground state. All the other, higher energy levels are referred to as "excited" levels of M, and if M is in a state with one of these higher energies it is said to be in an excited state. There is one and only one ground level whereas there are infinitely many excited states of M. Each atom or molecule has its own characteristic set of energy levels.

When a sample of M molecules is exposed to a beam of monochromatic light with wavelength λ there may be an energy exchange between the light and the M molecules. In its interaction with M, the monochromatic light beam is considered to consist of identical "photons", with all photons moving in parallel and along the direction of the beam with the speed of light. Each photon carries an energy given by $E_{photon} = h\nu$, where h is Planck's constant and ν is the frequency of the light, related to its wavelength by: $\nu = c/\lambda$. Since c is a constant, a given monochromatic light may be characterized by stating either λ or ν.

A molecule M may take energy from an external source such as light, thereby changing its initial energy level $E_{initial}$ to a final level E_{final}. For example, consider a case, where M is initially in its ground state with the lowest energy E_1. Its final energy (E_{final}) can only be one of E_2, E_3, E_4, ... As a consequence, the amount of energy that M can accept from the external source is restricted to the values: $\Delta E = E_n - E_1$, where n=2, 3, ... Conservation of total energy requires that if M gains energy equal to one of these allowed ΔE values, the external source must provide precisely the same amount of energy.

When light is used as the energy source, a photon from the light beam may or may not be absorbed by an M molecule in the sample, depending on the frequency ν of light used. Only when the photon energy is exactly equal to one of the allowed ΔE values of M, the energy of the photon may be accepted by M. The fundamental condition for absorption of light by M is expressed as $h\nu = \Delta E$. This is a minimum requirement for absorption of light. Depending on whether M is an atom or molecule, and the nature of the energy levels involved in the transition, additional conditions called "selection rules" may have to be concurrently satisfied.

A closed test tube containing gaseous H atoms is irradiated by monochromatic light. Six experiments are done, differing from each other only by the wavelength, λ, of light employed.

Experiment No.	1	2	3	4	5	6
λ (nm)	129.6	121.6	101.6	97.25	94.97	94.11

Find out the experiments in which light will be absorbed by the H atoms in the sample, and describe the transitions involved.

Additional Data:

The allowed energy levels for the electron in a hydrogen atom are given (in SI units) by

$$E_n = -\frac{R_H}{n^2}, \qquad n = 1, 2, 3, \ldots$$

where R_H = 2.1787×10^{-18} J is a constant; *i.e.* R_H is same for all values of the "n" quantum number. Assume that initially all of the hydrogen atoms in the sample are in their ground electronic states. Conservation of total energy is the only requirement for absorption of a photon by a H atom; *i.e.* there are no extra selection rules regarding the "n" quantum number.

Problem 21 Rotational and vibrational energy levels of a diatomic molecule

Part A: Rotational Energies

Within the rigid-rotor approximation, the list of allowed rotational energies of a diatomic molecule, AB(g) in the gas phase, are given by:

$E_{rotation} = B\,J(J+1)$, $\qquad$ J = 0, 1, 2, …

where $B = \dfrac{h^2}{8\pi^2 I}$ is a characteristic property of the molecule called the "rotational constant" of the molecule. The expression for *B* is in SI units; *h* is Planck's constant, and *I* is the moment of inertia of the molecule defined by: $I = \mu R^2$, where R is the bond length, and μ is called the "reduced mass" of the diatomic molecule. The latter quantity is defined in terms of the masses, m_A and m_B, of the atoms in the diatomic molecule AB.

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Theory indicates that the bond length, R, does not change when either A or B is replaced by other isotopes of the atoms A or B.

When a sample of gaseous molecules is exposed to microwave radiation, a molecule in the sample that is initially in a rotational energy level with $J = J_i$ may absorb a photon, ending up in a higher energy level with $J=J_f$. It may be shown that only those rotational transitions in which $J_f = J_i+1$ can occur in absorption of light that changes the rotational state.

The rotational constant of the $^{12}C^{16}O$ molecule has been experimentally determined as *B* = 23.115 J·mol^{-1}. The isotopic masses of the two atoms in this molecule are known: mass of ^{12}C = 12 amu by definition, and that of ^{16}O = 15.994915 amu. The longest wavelength of electromagnetic radiation that causes a transition between the rotational levels of $^{12}C^{16}O$ molecule in a sample has been observed to be λ = 0.25876 cm.

a) What are the values of J_i and J_f for a molecule that absorbs a photon with a wavelength of 0.25876 cm?

b) Calculate the moment of inertia and the bond length of the carbon monoxide molecule.

c) Predict the values of the rotational constants, B, for each of the following three molecules: $^{12}C^{18}O$, $^{13}C^{18}O$, and $^{13}C^{16}O$. (Additional data: masses of ^{18}O=17.999159 and ^{13}C=13.003355 amu.)

d) Calculate the longest wavelengths of microwave radiation that may be absorbed by each of $^{12}C^{18}O$, $^{13}C^{18}O$, and $^{13}C^{16}O$ molecules.

Part B: Rotational plus Vibrational Energies

Within the harmonic oscillator approximation, the list of allowed vibrational energies of a diatomic molecule, AB(g) in the gas phase, are given by:

$$E_{\text{vibration}} = (v + \frac{1}{2})\varepsilon, \qquad v = 0, 1, 2, \ldots$$

where ε is a characteristic vibrational property of the molecule defined by

$$\varepsilon = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

In this expression *h* is Planck's constant, *k* is called the "force constant "of the molecule, and μ is the reduced mass of the diatomic molecule. In SI units, ε is in joules, *k* in $N{\cdot}m^{-1}$, and μ in kg. Theory shows that the force constant *k* is independent of isotopic substitution in the molecule. When a sample of gas molecules is exposed to infrared (IR) radiation, a molecule in the sample that is initially in a vibrational energy level with $v = v_i$ may absorb a photon, ending up in a higher energy vibrational level with $v = v_f$. It may be shown that only those transitions in which $v_f = v_i+1$ can occur in absorption of light that changes the vibrational state.

Absorption of light in the IR region changes not only the vibrational state, but also the rotational state; *i.e.*, a simultaneous change in v and J is involved now. This is because the allowed vibrational plus rotational energies of a molecule are given by

$E_{rot.+vib.} = E_{rotation} + E_{vibration}$

a) The force constant of the carbon monoxide molecule is 1901.9 N·m^{-1}. Find ε in kJ·mol^{-1} (to 4 significant figures) for each of the following isotopically related CO molecules:

   i. $^{12}C^{16}O$

   ii. $^{12}C^{18}O$

   iii. $^{13}C^{18}O$

   iv. $^{13}C^{16}O$

b) Find the wavelengths (to 4 significant figures) of IR radiation that may be absorbed by a molecule in making a transition from an initial state with (v,J) = (0,0) to a final state with (v,J) = (1,1) for each of the following isotopically related CO molecules:

   i. $^{12}C^{16}O$

   ii. $^{12}C^{18}O$

   iii. $^{13}C^{18}O$

   iv. $^{13}C^{16}O$

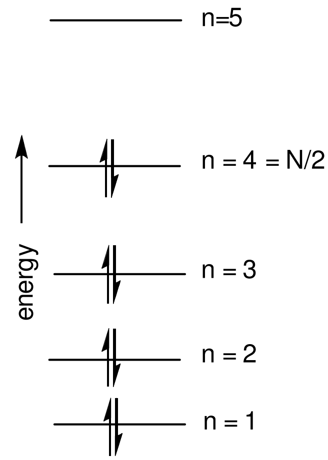
Problem 22 Particle in a box: Cyanine dyes and polyenes

In quantum mechanics, particle in a one dimensional box model describes a particle moving between two impenetrable walls separated by a distance L. The allowed energies for a particle in one dimensional box are

$$E_n = \frac{n^2h^2}{8mL^2} \qquad \text{for } n = 1, 2, 3, ...$$

where h is Plank's constant, m is the mass of the particle, and L is the box length.

The electronic absorption spectra of conjugated linear molecules can be simulated by the one dimensional particle in a box model. The delocalized π electrons are treated as free electrons and they are distributed into the allowed energy levels obeying the Pauli Exclusion Principle. If the molecule contains N delocalized π electrons, then the levels from n = 1 to n = N/2 are occupied in the ground state. Figure given below exhibits the energy levels for a conjugated molecule with N = 8.

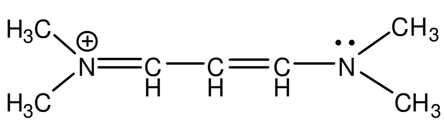


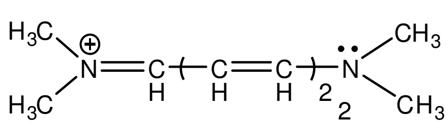
The energy levels for a system with 8 free electrons, N=8

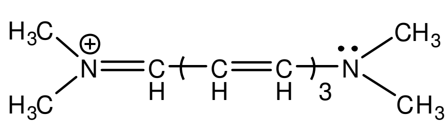
The lowest energy electronic transition for such a system involves the excitation of one of the electrons in level n = 4 (N/2) to the level n = 5 (N/2 + 1). For this transition to be affected by light absorption, the wavelength λ of light must be such that

$$\Delta E = \frac{hc}{\lambda}, \qquad \Delta E = \frac{h^2}{8mL^2}\left[\left(\frac{N}{2}+1\right)^2 - \left(\frac{N}{2}\right)^2\right] = \frac{h^2}{8mL^2}(N+1)$$

Cyanine, pinacyanol, and dicarbocyanine shown below, are dye molecules that have a conjugated chain between the two ends.


cyanine


pinacyanol


dicarbocyanine

a) Draw the resonance forms of these three molecules.

b) The delocalized electrons can move freely along the central chain of the molecule, between the two terminal nitrogen atoms but not more than one bond length beyond the nitrogen atom. Particle in a box model can be applied to calculate the quantized energy levels of these delocalized electrons. The box length can be taken as the distance between the two nitrogen atoms, measured along the carbon-carbon bonds, plus one bond length on either side of each nitrogen atom. Determine the number N of delocalized electrons in each dye molecule.

c) Experimentally, the electronic absorption band maxima of these molecules, λ_{max}, are recorded at 525, 605 and 705 nm for cyanine, pinacyanol and dicarbocyanine, respectively. Calculate ΔE for cyanine, pinacyanol and dicarbocyanine.

d) Predict the chain length where the electrons can move freely in these molecules.

e) As the conjugated π electrons are free to move along the polyene carbon backbone, but not allowed to leave the molecule, they can be viewed as particles in a box defined by the carbon backbone of a linear polyene. The average carbon-carbon bond length in a hydrocarbon chain of alternating single and double bonds can be approximated to 140 pm. The length of carbon chain, the box length, is approximately $L = 2j \times 140$ pm, where j is the number of double bonds in the polyene chain. Determine the number N of delocalized electrons and the box length L for 1,3-butadiene and 1,3,5-hexatriene.

f) Estimate the frequencies and wavelengths of the lowest electronic transition for 1,3-butadiene and 1,3,5-hexatriene.

Problem 23 Radioactive decay

Although twenty three isotopes of phosphorus are known (all the possible isotopes from ^{24}P up to ^{46}P), only ^{31}P, with spin 1/2, is stable and is therefore present at 100% abundance. The half-integer spin and high abundance of ^{31}P make it useful for nuclear magnetic resonance (NMR) spectroscopic studies of biomolecules, particularly DNA. Two radioactive isotopes of phosphorus have half-lives that make them useful for scientific experiments. ^{32}P has a half-life of 14.3 days and ^{33}P has a half-life of 25.3 days. Both radioisotopes of phosphorous, ^{32}P and ^{33}P, are beta emitters and they decay as shown in the following nuclear reactions;

$^{32}_{15}\mathrm{P} \rightarrow {}^{32}_{16}\mathrm{S} + \beta$ $\qquad$ $^{33}_{15}\mathrm{P} \rightarrow {}^{33}_{16}\mathrm{S} + \beta$

Isotope	isotopic masses (amu)
^{32}P	31.97390727
^{33}P	32.9717255
^{32}S	31.97207100
^{33}S	32.97145876

a) Calculate the energy of β particles emitted in the decay reactions of ^{32}P and ^{33}P.

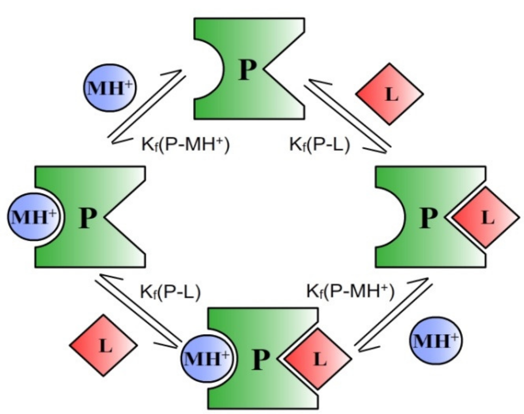
b) To shield beta radiation usually lead is used. However, secondary emission of X-rays takes place *via* a process known as Bremsstrahlung in the case of high energy β-emission, Therefore shielding must be accomplished with low density materials, e.g. Plexiglas, Lucite, plastic, wood, or water. During shielding of β-emission from ^{32}P, X-ray photons of λ = 0.1175 nm are produced. Calculate the energy of X-ray photons in eV.

c) Find the mass of ^{32}P which has activity of 0.10 Ci (1 Ci = 3.7×10^{10} disintegration/s).

d) A sample containing both radioisotopes ^{32}P and ^{33}P has an initial activity of 9136.2 Ci. If the activity decreases to 4569.7 Ci after 14.3 days, calculate the $^{32}P/^{33}P$ ratio initially present in the sample.

Problem 24 Enzyme-substrate interaction

In biological systems, it is very common for proteins such as enzymes or receptors to bind to multiple ligands or substrates at the same time. Binding of the first ligand usually affects the binding of the second ligand either positively or negatively. In this question, imagine that there is a protein **P** which can bind to two different ligands **L** and **MH$^+$** as shown in the figure given below.



For simplicity, assume that the binding of these two ligands are independent of each other; i.e. binding of the first ligand does not change the binding constant (complex formation constant) for the second ligand.

a) Equal volumes of 100 μM solutions of ligand **L** and protein **P** are mixed in a buffer solution of pH 9.50. The formation constant is K_f**(P-L)** = 2.22×10^4. Calculate molar concentration for all the species present in this solution. What percentage of the protein **P** is complexed with the ligand **L**?

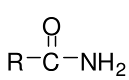
b) Ligand **M** has a free amine group and only its protonated form, *i.e.* **MH**$^+$, can bind to protein **P**. What percentage of the ligand **M** is protonated at pH 9.50? pK_a(**MH**$^+$) = 10.00.

c) Equal volumes of 100 μM solutions of ligand **M** and protein **P** are mixed in a buffer solution of pH 9.50. Calculate molar concentration for all the species present in this solution. What percentage of the protein **P** is complexed with the ligand **MH**$^+$**?** K_f(**P**-**MH**$^+$) = 5.26×10^5.

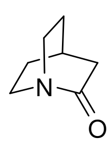
d) 100 μL of 100 μM protein **P**, 50 μL of 200 μM of ligand **L** and 50 μL of 200 μM of ligand **M** are mixed in a buffer solution of pH 9.50. What percentage of the protein **P** is bound to (i) only **L**, (ii) only **MH**$^+$ and (iii) both **L** and **MH**$^+$? Calculate molar concentration for all the species present in this solution.

Problem 25 Amides

The amide functional group is one of the most fundamental motifs found in chemistry and biology. Typical acyclic amides **1** are planar and stable, while the cyclic amides (bridgehead lactams) are unstable.

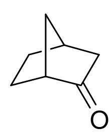


1



2-quinuclidone

2

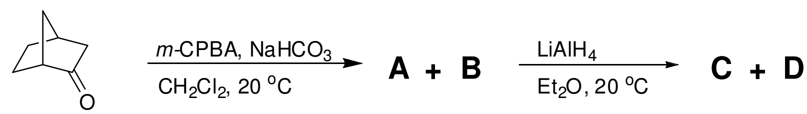


norcamphor

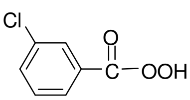
3

2-Quinuclidone (**2**), a typical example of bridgehead lactams, is very unstable due to the improper alignment of nitrogen lone pair and carbonyl group for π-interaction. As a consequence, the amide group resembles an amine as evidenced by the ease of salt formation. The organic synthesis of the tetrafluoroborate salt of 2-quinuclidone (**2**) is a six-step synthesis starting from norcamphor (**3**) and the final step being an azide-ketone Schmidt reaction.

a) The reaction of enantiopure norcamphor (**3**) with *m*-chloroperbenzoic acid (*m*-CPBA) gives **A** and **B**. **A** is formed as the major product in 78% yield, whereas the second isomer **B** is formed as the minor product. The reaction of **A** with lithium aluminum hydride results in the formation of **C**, whereas the reduction of **B** yields optically inactive compound **D.** Give the structures of the compounds **A, B, C, D** and determine the absolute configurations (*R/S*) of the stereogenic carbon atoms in **A, B, C** and **D**.



norcamphor
3

m-CPBA = 

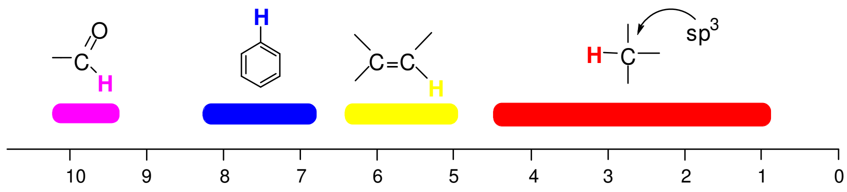
b) Treatment of **C** with 1 equiv. of tosyl chloride (TsCl) yields the compound **E**, which is converted into **F** by reaction with 1 equiv. of NaN_3 in dimethylformamide. Give the structures of **E** and **F**.

c) **F** is subjected to pyridinium chlorochromate (PCC) oxidation reaction to form the precursor **G** of the target compound. Finally, **G** is exposed to tetrafluoroboric acid (HBF_4). The target compound **H** is isolated as its tetrafluoroborate salt. Beside this product a second isomer **I** is formed as the minor product. Give the structures of **G, H** and **I**.

Problem 26   NMR Spectroscopy

^{1}H-NMR Spectroscopy

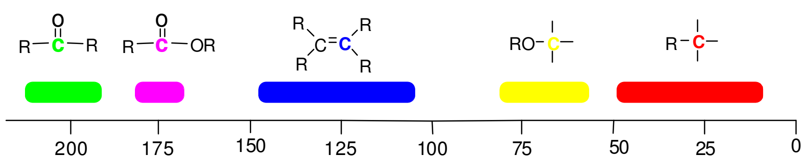
The ^{1}H-NMR spectroscopy allows the identification of hydrogen atoms in organic molecules. From the position of the signals (chemical shift) and the splitting of the signals, the type and connectivity of the hydrogen atoms can be recognized. Some characteristic hydrogen atom resonances are given below.



^{1}H-NMR Resonance ranges of typical functional groups in ppm relative to TMS

^{13}C-NMR Spectroscopy

The ^{13}C-NMR is analogous to ^{1}H-NMR and allows the identification of carbon atoms in organic molecules. The ^{13}C-NMR spectrum of a given compound shows as many signals (singlets) as the number of the different carbon atoms. The relative intensities of all kinds of carbon (primary, secondary, tertiary, and quaternary) signals will be assumed to be equal. Some characteristic carbon resonances are given below.



^{13}C-NMR Resonance ranges of typical functional groups in ppm relative to TMS

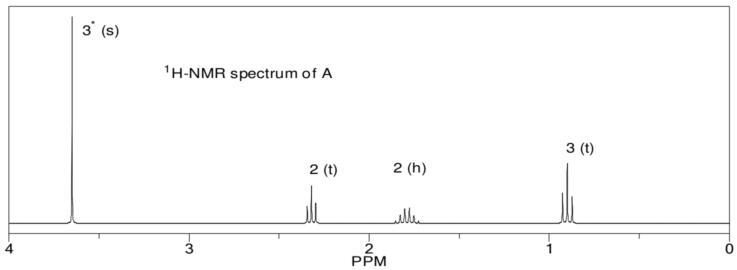
Description of six isomeric (constitutional) compounds (**A, B, C, D, E** and **F**) having the formula $C_5H_{10}O_2$ is as follows

- None of the compounds is branched.
- There is no O-H absorbance in the IR spectra of the isomers.
- In each compound, one oxygen atom is sp^2- and the other is sp^3-hybridized.

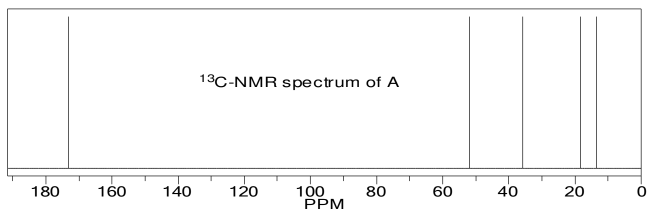
Determine the structures of all isomers by using the information given above and analyzing the ^{1}H- and ^{13}C-NMR spectra given below.

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, h = hextet.

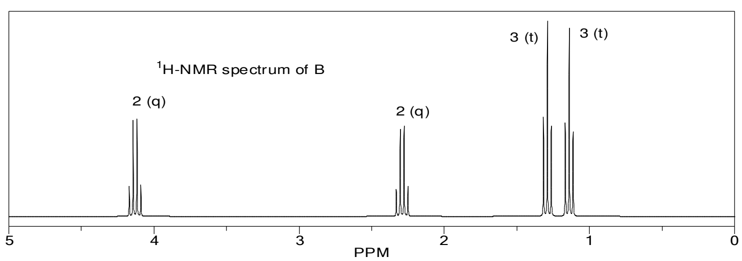
Compound A

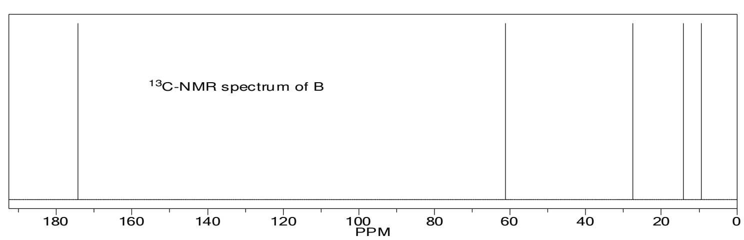


*) The numbers on the signals give the number of the resonating protons

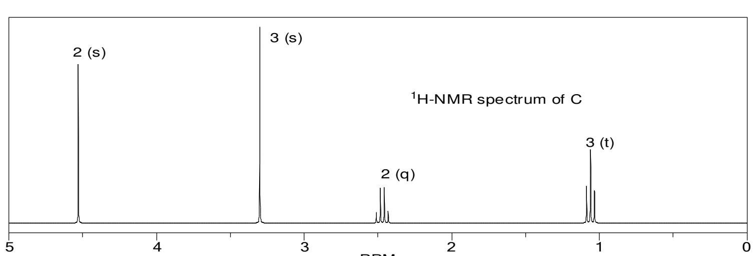


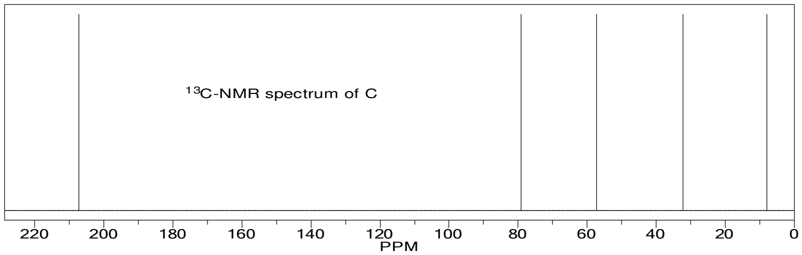
Compound B



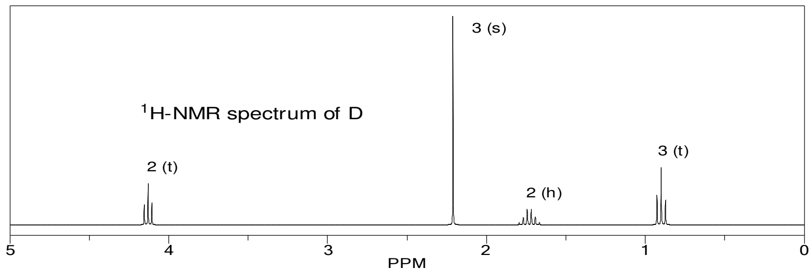


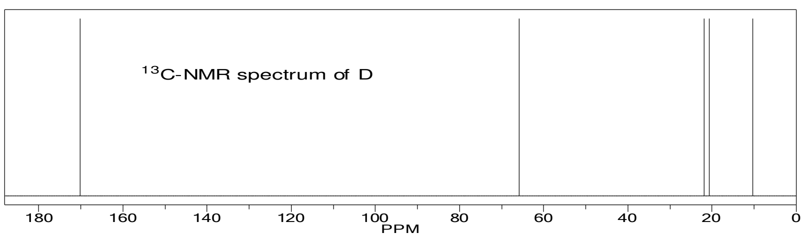
Compound C



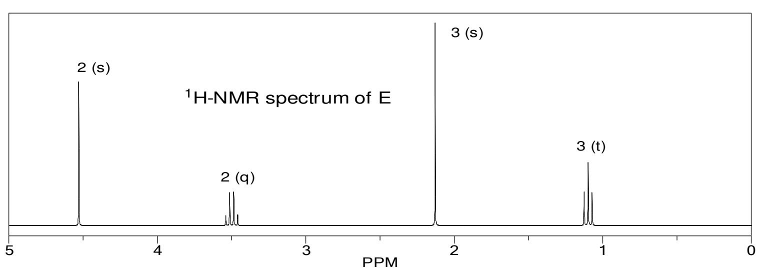


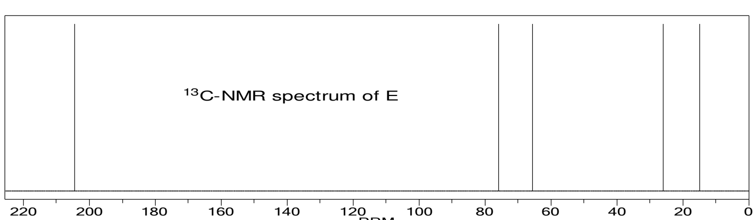
Compound D



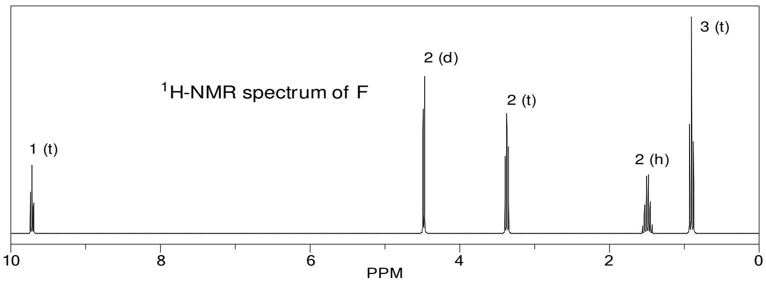


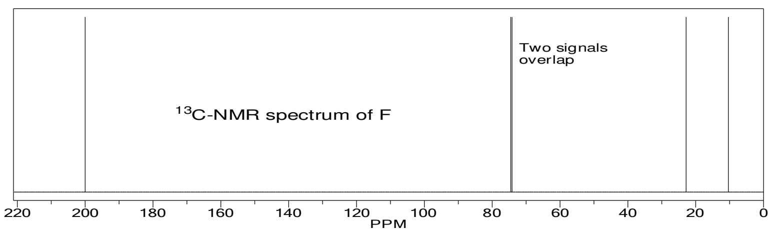
Compound E





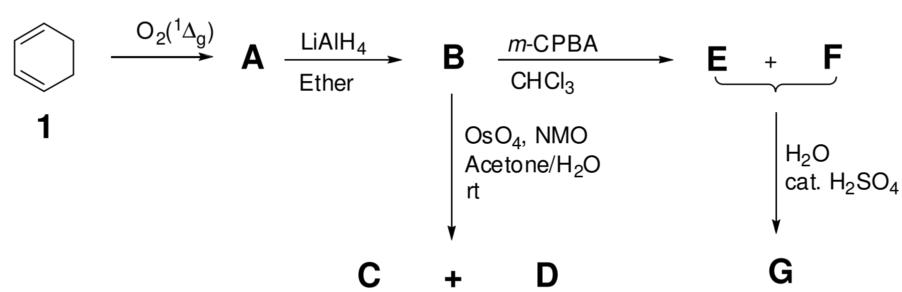
Compound F





Problem 27 Cyclitols

Cyclitols have recently attracted a great deal of attention due to their diverse biological activities and their versatilities as synthetic intermediates. Polyhydroxy cyclohexanes, such as inositols, quercitols, and conduritols, belong to the family of cyclitols. These compounds can exist in a number of different stereoisomers; inositols, quercitols, and conduritols have 9, 16, and 6 possible stereoisomers, respectively. Cyclohexa-1,3-diene (**1**) is an important key compound for the synthesis of versatile cyclitol derivatives. The total synthesis of isomeric cyclitols having the molecular formula **$C_6H_{12}O_4$** is shown below.

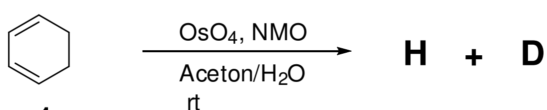


- The reaction of cyclohexa-1,3-diene (**1**) with singlet oxygen $O_2(^1\Delta_g)$, generated in situ by irradiation of oxygen molecule in the presence of a sensitizer, yields an unstable bicyclic compound **A**. The reaction of **A** with $LiAlH_4$ in ether results in the formation of **B**, whose ^{13}C-NMR spectrum shows 3 resonances. One of them appears in the sp^2 region.

- Osmylation of **B** in the presence of an excess of NMO (*N*-morpholine oxide) (more than 2 equiv.) at room temperature in acetone/H_2O leads to the isomeric mixture of **C** and **D** where the compound **C** is formed as the major product.
- Oxidation of **B** with *m*-chloroperbenzoic acid (*m*-CPBA) gives a diastereomeric mixture of **E** and **F**. Treatment of this mixture with H_2O in the presence of a catalytic amount of H_2SO_4 affords only compound **G** as a racemic mixture having the molecular formula of $C_6H_{12}O_4$.

a) Draw the structures of **A, B, C, D, E, F,** and **G** using dashed-wedged line notation to indicate the relative configurations.

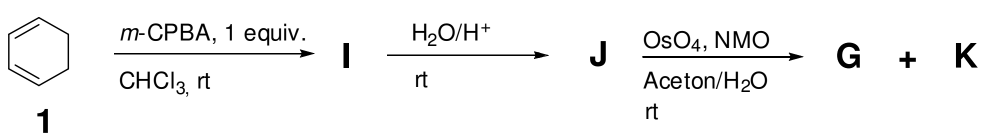
b) Osmylation of **1** in the presence of an excess of NMO (*N*-morpholine oxide) (more than 2 equiv.) at room temperature in acetone/H_2O leads to the formation of a diastereomeric mixture of **H** and **D** where the compound **H is** formed as the major product.



1

Draw the structure of **H** using dashed-wedged line notation.

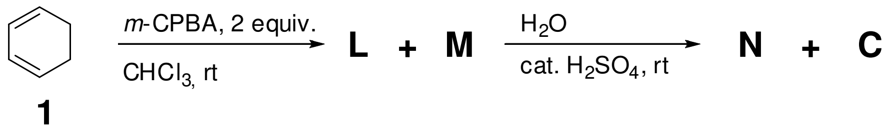
c) Reaction of cyclohexa-1,3-diene (**1**) with 1 equiv. *m*-chloroperbenzoic acid (*m*-CPBA) gives a single product **I**, which is reacted with H_2O in the presence of a catalytic amount of H_2SO_4 to provide **J** (There is no rearranged product). Osmylation of **J** in the presence of excess of NMO (*N*-morpholine oxide) (more than 1 equiv.) at room temperature in acetone/H_2O leads to formation of isomeric **G** and **K**.



1

Draw the structures of **I, J,** and **K** using dashed-wedged line notation.

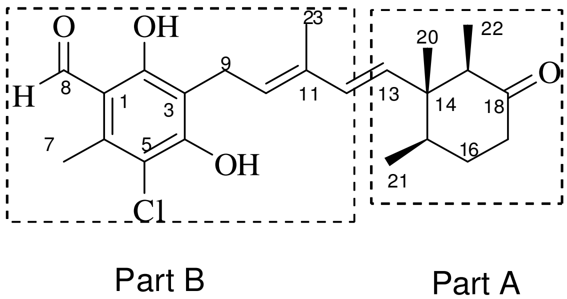
d) Reaction of cyclohexa-1,3-diene (**1**) with 2 equiv. of *m*-chloroperbenzoic acid (*m*-CPBA) gives a diastereomeric mixture of **L** and **M.** Reaction of this mixture (**L** and **M**) with H_2O in the presence of a catalytic amount of H_2SO_4 yields a mixture of **N** and **C**.



Draw the structures of **L, M, and N** using dashed-wedged line notation.

Problem 28 Antiviral antibiotic

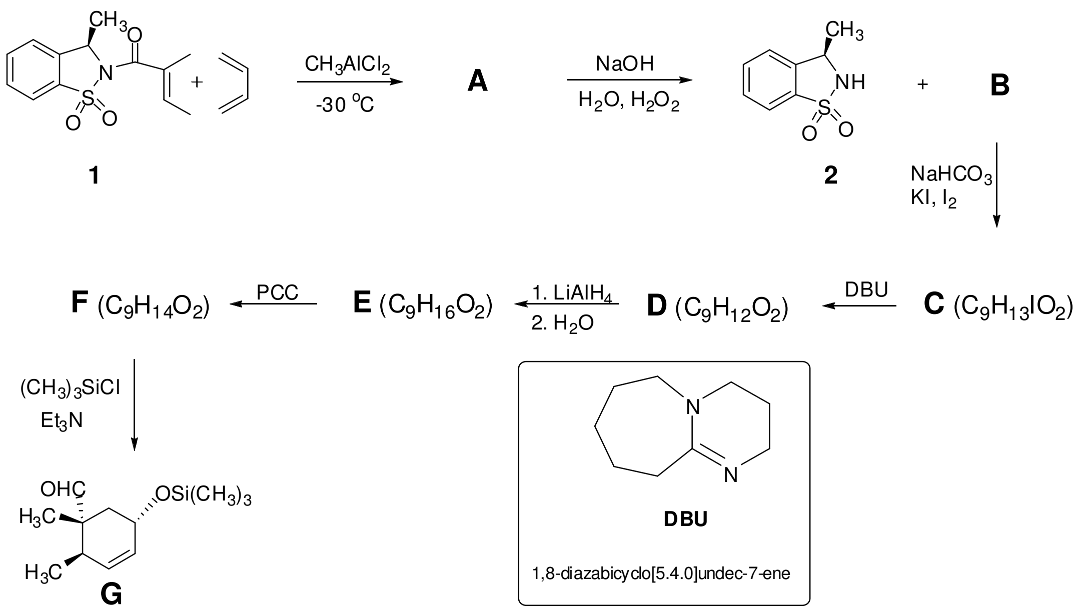
Ascochlorin (antiviral antibiotic)



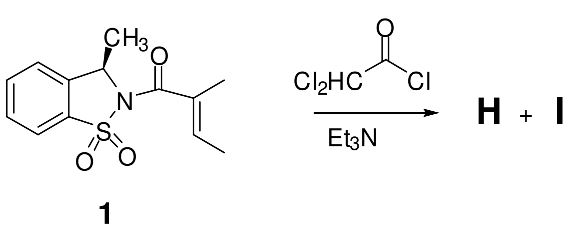
Ascochlorin is an antiviral antibiotic obtained from the filter cake of the fermented broth of *Ascochyta viciae* Libert. It has a strong inhibitory effect on viral growth in cultured cells. The absolute stereochemistry of this antibiotic was determined by X-ray analysis. Due to high biological activity, the ascochlorin family has attracted the attention of synthetic organic chemists.

Part A (Synthesis of right side of ascochlorin)

Synthesis of cyclohexanone unit (right side of ascochlorin) starts with Diels-Alder reaction which is a [4+2] cycloaddition reaction. Reaction of 1,3-butadiene and chiral dienophile **1** gives the cycloadduct **A** with the desired stereochemistry of cyclohexanone unit. Basic hydrolysis of **A** affords the sultam **2** and the chiral carboxylic acid **B**. This carboxylic acid **B** undergoes iodolactonization reaction (initial step is the formation of an iodonium ion intermediate) to form the δ-iodolactone **C**. Treatment of **C** with DBU (non nucleophilic base) forms the compound **D**. Reduction of **D** with $LiAlH_4$ and then hydrolysis with water produces the diol **E**. Selective oxidation of **E** with pyridinium chlorochromate (PCC) leads to the product **F**. Subsequent protection of the hydroxy group with $(CH_3)_3SiCl$ produces the compound **G**.



Besides [4+2] cycloadditon reaction, the compound **1** can also undergo [2+2] cycloadditon reactions. For example, the dienophile **1** undergoes a cycloaddition reaction with ketene (general formula, $R_2C{=}C{=}O$). When the dienophile **1** is reacted with 2,2-dichloroacetyl chloride (ketene equivalent) in the presence of a base, an isomeric mixture of **H** and **I** is formed.



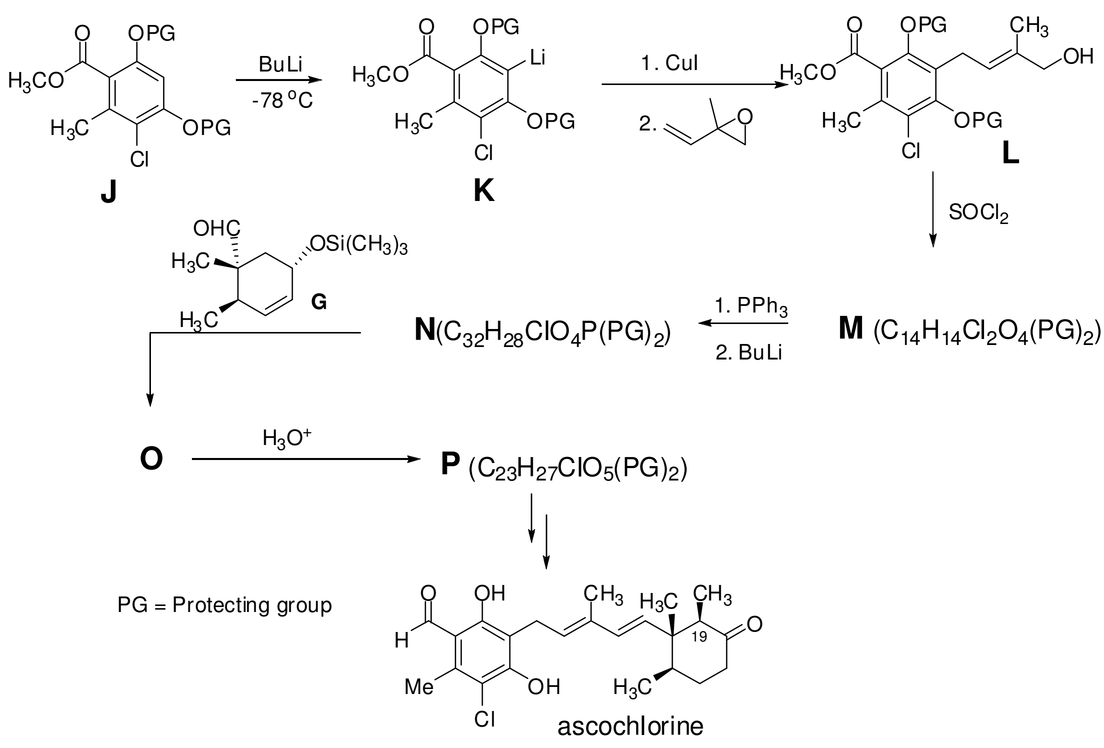
a) Draw the structures of compounds **A**, **B**, **C**, **D**, **E**, and **F** with the correct stereochemistry.

b) Draw the structure of ketene obtained *in situ* from 2,2-dichloroacetyl chloride.

c) Draw the structures of **H** and **I**.

Part B (Synthesis of left side of ascochlorin)

In order to synthesize the left side of the molecule (Part B), the aromatic compound **J** is used as starting material (PG is a protecting group for OH). Reaction of **J** with strong base (butyllithium, BuLi) forms the lithiated compound **K**. Treatment of this intermediate with copper(I) iodide and then with epoxide gives compound **L**. Reaction of this compound with thionyl chloride ($SOCl_2$) produces compound **M**. In order to combine part A and part B, Wittig reaction is planned. For this purpose compound **M** is reacted with triphenylphosphine (PPh_3) and then the product of this reaction is treated with BuLi to get the intermediate Wittig reactant **N**. Finally coupling is achieved by reaction of **N** with aldehyde **G**, which yields **O**, the main skeleton of ascochlorine. In order to remove $(CH_3)_3Si$ group, **O** is treated with dilute acid solution which gives compound **P**. The ascochlorine synthesis is completed by five more steps.



a) Propose a mechanism for the conversion of **K** to **L**.

b) Draw the structures of compounds **M**, **N, O**, and **P**.

c) The ascochlorin synthesis from compound **P** is completed by performing five more steps:

   i) Oxidation of OH group on the cyclohexyl unit.

   ii) Introduction of the methyl group to C19 (do not worry about the correct stereochemistry).

iii) Conversion of ester group on the aromatic unit to aldehyde.

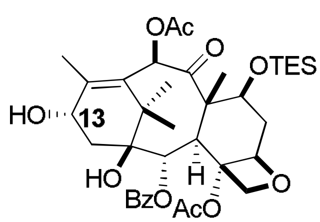
iv) Selective reduction of α,β-unsaturated double bond of cyclohexenone unit.

v) Removal of protecting groups (PG) which can be achieved by using Bu_4NF.

Write the reagents used for the steps i, ii, and iii.

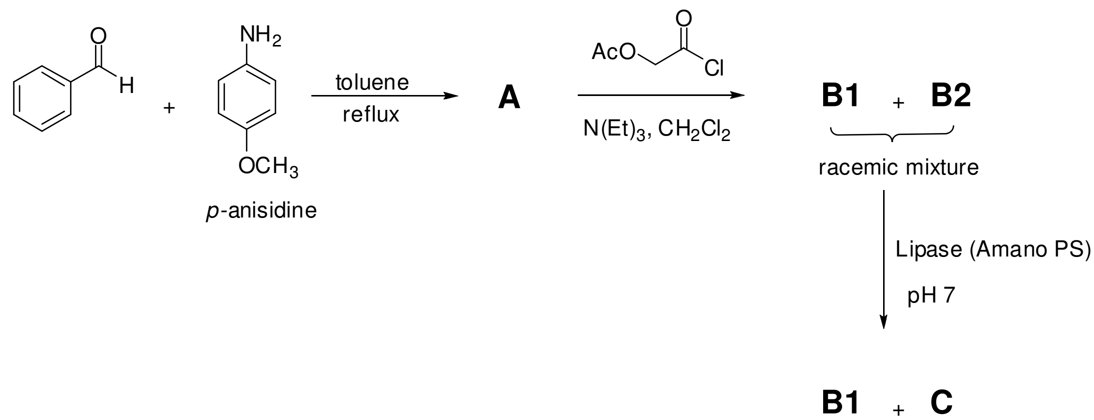
Problem 29 Acyclic β-amino acids

In recent years, acyclic β-amino acids have attracted attention especially following their recognition as an important class of compounds in the design and synthesis of potential pharmaceutical drugs such as Taxol® (paclitaxel) and its analogue Taxotere® (docetaxel), currently considered to be among the most important drugs in cancer chemotheraphy. The only source of Taxol is the bark of the pacific yew tree, *Taxus brevifolia*, but its Taxol content is relatively low. In efforts to overcome this supply problem, chemists have been working on semi-syntheses. These methods involve synthetic side-chain coupling to C13-OH of the more readily available Baccatin III derivatives as given below, which can be isolated in higher yield from the needles of various Taxus species (e.g. *Taxus baccata*).



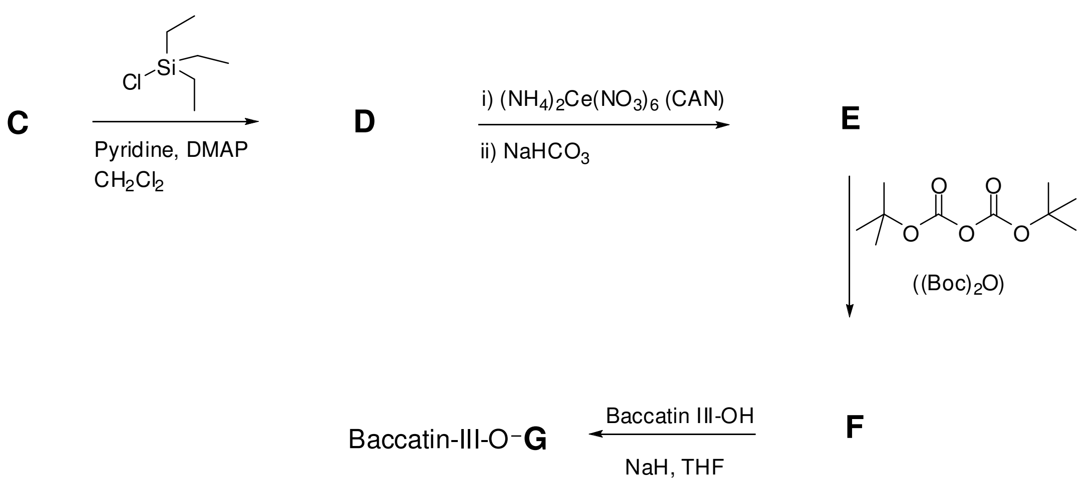
Baccatin III derivative

a) The racemic synthesis of side chain is started by refluxing benzaldehyde with *p*-anisidine in toluene to afford compound **A**. Subsequent reaction of compound **A** with acetoxyacetyl chloride in the presence of triethylamine gives the racemic mixture of cyclic compounds **B1** and **B2** with the molecular formula ($C_{18}H_{17}NO_4$). The resultant racemic mixture of **B1** and **B2** is subjected to enzymatic resolution by using Lipase (Amano PS). Lipases are well known biocatalysts to hydrolyze the ester units. They selectively hydrolyze only one enantiomer of a racemic mixture. As a result of this hydrolysis, **B1** (as the unreacted enantiomer) and **C** (hydrolysis product) are isolated. **B1** has absolute configuration **3*R*,4*S*** whereas, **C** has **3*S*,4*R***.



Draw the structures of compounds **A**, **B1**, **B2**, and **C** with the correct stereochemistry where applicable.

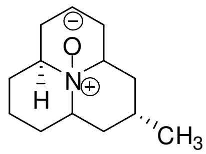
b) Hydroxy unit of compound **C** is protected with triethylsilyl chloride in the presence of pyridine and 4-dimethylaminopyridine (DMAP) to give the compound **D**. Treatment of **D** with cerium(IV) ammonium nitrate (CAN), a feasible reagent for the oxidative cleavage of *N*-aryl bond, followed by neutralization with $NaHCO_3$ solution yields the desired compound **E**. The target β-lactam *N*-unit is protected with bis(*tert*-butyl)dicarbonate $(Boc)_2O$ to afford the compound **F**. In the final step, Baccatin III derivative is coupled with the compound **F** in the presence of NaH in THF.



Draw the structures of compound **D**, **E**, **F** and **G** with the correct stereochemistry.

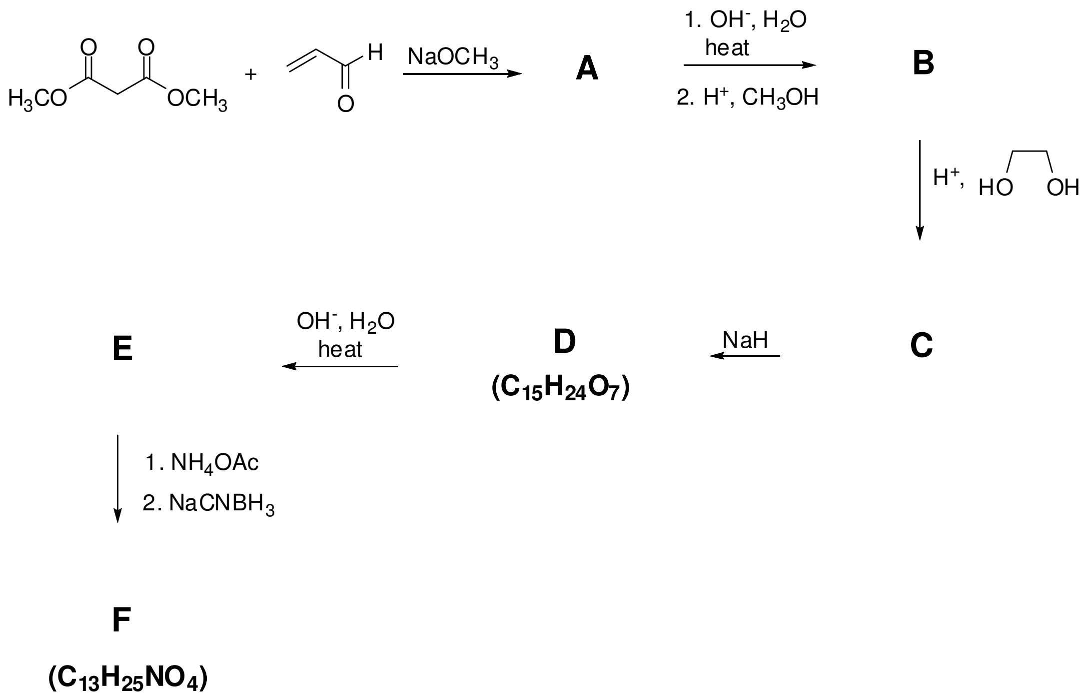
Problem 30 Life of Ladybug

In nature, there are many known species of the ladybug family (*Coccinellidae*). Besides their cuteness, they play a beneficial ecological role in controlling populations of some harmful insects. When molested or disturbed, they emit droplets of a fluid from their joints. This process known as "reflex bleeding", serves as an efficient deterrent. This fluid was isolated, characterized and termed as coccinelline. The structure of coccinelline is given below.



Coccinelline

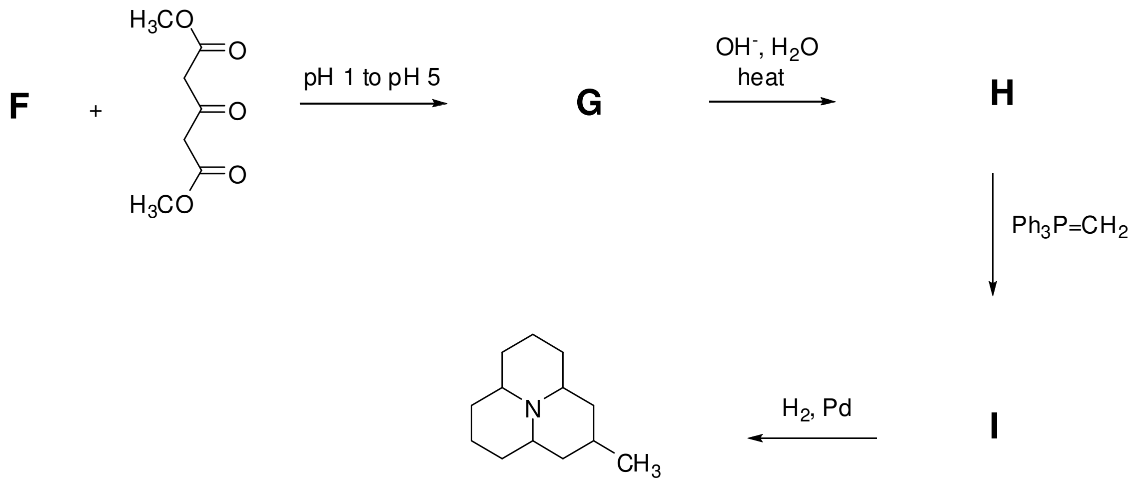
a) In laboratory synthesis of coccinelline, very common and readily available starting compounds are chosen. The reaction between dimethyl malonate and acrolein in the presence of sodium methoxide yields compound **A**. Subsequently, it is heated in basic solution followed by esterification with methanol under acidic condition to afford compound **B**. The ^{13}C-NMR spectrum of compound **B** shows two characteristic signals at around 170 and 200 ppm. Then, the compound **B** is treated with ethane-1,2-diol under slightly acidic condition to give compound **C**. The signal of compound **B** at around 200 ppm disappears in the ^{13}C-NMR spectrum of compound **C**. Compound **C** undergoes a self condensation reaction in the presence of NaH to yield compound **D**. Decarboxylation reaction of compound **D** affords compound **E**. In the next step, compound **E** is first reacted with ammonium acetate followed by reduction with sodium cyanoborohydride. In this step, compound **F** is formed *via* the reductive amination of the compound **E**.



Draw the structures of the compounds **A**, **B**, **C**, **D**, **E** and **F**.

b) In the next part of synthesis, compound **F** is first deprotected at pH 1 and, then, the pH is adjusted to 5 followed by the addition of acetone dicarboxylic ester which can easily be enolizable. As a result of this step, the **tricyclic** compound **G** is isolated as the sole product. Draw the structure of compound **G**. Propose a plausible mechanism for the formation of compound **G**. (***Hint:*** *After deprotection step, iminium ion is formed and reacted with enolizable acetone dicarboxylic ester.*)

c) The final part of synthesis involves the decarboxylation of compound **G** under basic condition to afford compound **H**. The ^{13}C-NMR spectrum of compound **H** shows the characteristic signal at around 200 ppm. The reaction of compound **H** with methylene triphenylphosphorane yields compound **I** which is subsequently hydrogenated to afford precoccinelline. In the final step, precoccinelline is oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to get coccinelline.



Precoccinelline

Draw the structures of **H** and **I**.

Practical Problems

Safety

The participants of the Olympiad must be prepared to work in a chemical laboratory and be aware of the necessary rules and safety procedures. The organizers will enforce the safety rules given in *Appendix A* of the IChO Regulations during the Olympiad.

The Preparatory Problems are designed to be carried out only in a properly equipped chemistry laboratory under competent supervision. Since each country has own regulations for safety and disposables, detailed instructions are not included herein. Mentors must carefully adapt the problems accordingly.

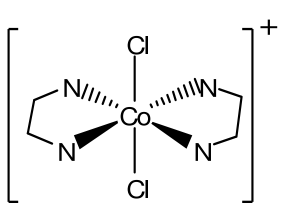
The safety (S) and risk (R) phrases associated with the materials used are indicated in the problems. See the Appendix A and B of the Regulations for the meaning of the phrases. The Regulations are available on the website http://www.icho43.metu.edu.tr

Safety cautions for the practical questions must be provided by the Mentors. Major cautions are:

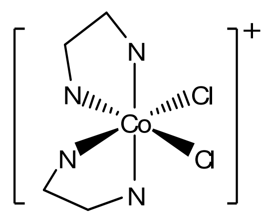
- Use fume hoods if indicated.
- Safety goggles and laboratory coat should be worn at all times in the laboratory.
- Never pipette solutions using mouth suction.
- Dispose reagents into the appropriate waste containers in the laboratory.

Problem 31 Preparation of trans-dichlorobis(ethylenediamine)-cobalt(III)chloride and kinetics of its acid hydrolysis

Geometrical isomers differ in the spatial arrangement of atoms or groups around a central atom. Geometrical isomers usually have distinctive physical and chemical properties. The *cis*- and *trans*-isomers of octahedral cobalt complexes are among the most well known examples. The complexes of Co(III) ion are sufficiently stable and occur in separable isomeric forms. For example, dichlorobis(ethylenediamine)cobalt(III) ion, $[Co(en)_2Cl_2]^+$ can exist in either *cis*- or *trans*-form as shown below. Ethylenediamine (en) is a bidentate ligand, which coordinates to the metal through both of its nitrogen atoms. The *cis* complex is dark purple, whereas the *trans* complex is green.



trans



cis

At low concentrations the green *trans*-$[Co(en)_2Cl_2]^+$ ion undergoes a first order acid hydrolysis reaction, and a red mixture of the *cis* and *trans* isomers of $[Co(en)_2(H_2O)Cl]^{2+}$ complex ion are formed as shown below.

$$\textit{trans}\text{-}[Co(en)_2Cl_2]^+ + H_2O \rightarrow \textit{cis}\text{- and }\textit{trans}\text{-}[Co(en)_2(H_2O)Cl]^{2+}$$

green red mixture

In this experiment, the chloride salt of *trans*-dichlorobis(ethylenediamine)cobalt(III) complex will be prepared and the rate constant of its acid hydrolysis reaction will be determined.

Chemicals and reagents

- Ethylenediamine, $H_2NC_2H_4NH_2$, 10% (v/v)
- Cobalt(II)chloride hexahydrate, $CoCl_2{\cdot}6H_2O$
- Hydrochloric acid, HCl(*aq*), concentrated solution
- Sulfuric acid, H_2SO_4(*aq*), 1.0 $mol{\cdot}L^{-1}$

Substance	**Phase**	R Phrase	S Phrase
$H_2NC_2H_4NH_2$	Liquid, 10% (v/v)	11 20 21 22 35	3 16 26 29 36 37 39 45
$CoCl_2$•$6H_2O$	Solid	22 42 43 49 50 53	22 45 53 60 61
HCl (*aq*)	Concentrated sol.	23 24 25 34 36 37 38	26 36 37 39 45
H_2SO_4 (*aq*)	1.0 mol·L^{-1}	23 24 25 35 36 37 38 49	23 30 36 37 39 45

Apparatus and glassware

- Evaporating dish
- Steam bath
- Beakers, 25 mL (2)
- Pipette, 10 mL
- Stirring rod
- Graduated cyclinder, 25 mL
- Colorimeter or UV-Vis spectrometer
- Cell for colorimeter

A. Preparation of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride

1. In a fume hood, dissolve 1.6 g of cobalt(II) chloride hexahydrate in 5.0 mL of water in an evaporating dish.
2. Add 9.0 mL of 10% v/v solution of ethylenediamine into the evaporating dish.
3. Place the dish on a steam bath and stir for 40 min maintaining the volume of the solution by adding small portions of hot water. During this process, Co(II) is oxidized to Co(III) by the oxygen of the air, therefore good agitation is necessary to promote the dissolution of oxygen in the solution.
4. Add 10 mL of concentrated HCl solution and continue heating and stirring (without adding water) until a thin slurry of crystals forms.
5. Dry the crystals on the steam bath to eliminate HCl and H_2O.
6. Weigh and calculate the yield.

B. Kinetics of acid hydrolysis of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride

1. Dissolve 0.10 g of *trans*-$[Co(en)_2Cl_2]Cl$ in 5.0 mL of water in a test tube.
2. Transfer about 2 mL of the solution into the absorbance cell using a pipette and record the absorbance of the solution at 620 nm using a colorimeter or spectrometer,

with the help of your assistant or technician. Record absorbance value as A_o at t_o, 0.0 min into the Table given below.

3. Place 0.20 g of *trans*-$[Co(en)_2Cl_2]Cl$ in a beaker and add 10.0 mL of 1.0 M H_2SO_4 solution into the beaker..
4. Transfer about 2 mL of the solution into the absorbance cell using a pipette and with the help of your assistant or technician record the absorbance of the solution at 620 nm at intervals of about 10 min as t_i for 90 minutes into the table given below.

Time	Min	Absorbance A
t_o	0.0	
t_1		
t_2		
t_3		
t_4		
t_5		
t_6		
t_7		
t_8		
t_9		
t_{10}		

Treatment of Data

A. 1. Calculate the percent yield of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride.

B. 1. Plot ln $\frac{A_0}{A_i}$ versus time.

2. Estimate the first order rate constant from the plot.
3. Explain why absorbance values can directly be used for concentrations.

Problem 32 Analysis of calcium salts

Several different salts of calcium are available in nature. Carbonate, chloride and sulfate salts are among the most common ones. Unlike the carbonate and sulfate salts, calcium chloride is soluble in water. Calcium carbonate reacts with Brönsted acids releasing carbon dioxide:

$CaCO_3(s) + 2\ H^+(aq) \longrightarrow Ca^{2+}(aq)\ +\ H_2O(l) + CO_2(g)$

In this experiment, the composition of a mixture of calcium salts will be determined based on solubility, and reaction of $CaCO_3$ with a strong acid.

Chemicals and reagents

- A mixture of calcium salts: 40.0% wt $CaCO_3$, 5.0% wt $CaCl_2$ and 55.0% wt $CaSO_4$ (Any mixture can be used. The amount of sample and the hydrochloric acid can be adjusted for a desired volume of carbon dioxide gas.)
- Hydrochloric acid, HCl(*aq*) 3.0 mol·L^{-1}
- Sodium chloride, NaCl
- Acetone, CH_3COCH_3

Substance	Phase	R Phrase	S Phrase
$CaCO_3$	Solid	36 37 38	37 38 41
$CaCl_2$	Solid	36	22 24
$CaSO_4$	Solid	-	22 24 25
HCl(*aq*)	3.0 mol·L^{-1}	23 24 25 34 36 37 38	26 36 37 39 45
NaCl	Solid	36	26 36
CH_3COCH_3	Liquid	11 36 66 67	2 9 16 26

Apparatus and glassware

- Apparatus shown in Figure 32-1
- Ice bath
- Pipette, 10 mL
- Graduated cyclinder, 25 mL
- Funnel
- Filter paper (Whatman 42)
- Stirring bar
- Stirrer
- Septum

A. Preparation of ice-*bath*

1. Add sufficient amount of NaCl in an ice-bath containing about 300 mL of ice-water mixture to obtain a solution at a temperature below -5 ºC. Use ice at a temperature below -10 ºC.

B. Reaction with hydrochloric acid

1. Assemble the experimental setup as shown in Figure 32-1 in a hood. Check that the experimental set up is held on a support and the graduated tube is connected to the Schlenk tube by a Tygon tubing.

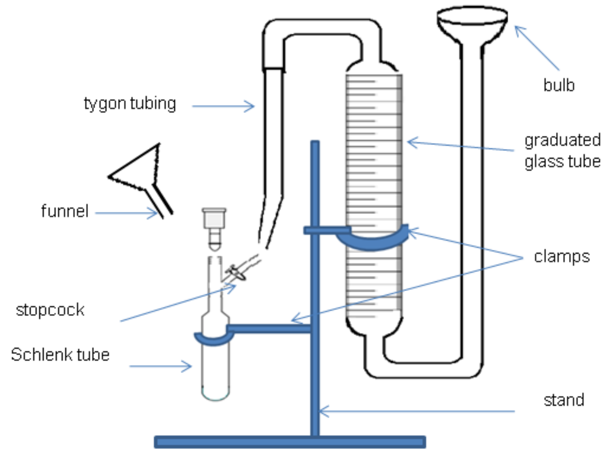


Figure 32-1 Apparatus for measuring the volume of gas evolved from the reaction.

2. Fill the graduated glass tube with water by pouring water through the bulb opening.
3. Transfer exactly 1.00 g of the salt mixture from the glass vial to the Schlenk tube through the funnel. Put a magnetic stirring bar into the Schlenk tube.
4. Rinse the funnel with about 3-4 mL water to get all the sample down to Schlenk tube.
5. Freeze the water by immersing the bottom of the Schlenk tube into the ice-bath.
6. Add 10.0 mL of 3.00 mol·L^{-1} HCl solution into the Schlenk tube and close the Schlenk tube with a septum.
7. By changing the bulb height adjust the water level in the graduated tube to zero.
8. Open the stopcock connecting the Schlenk tube to the graduated tube and remove the ice bath.
9. When the ice in the Schlenk tube melts, the acid rapidly reacts with $CaCO_3$ liberating carbon dioxide gas. Stir the solution vigorously.
10. Wait until no more change in the level of water inside the graduated tube takes place. When no more gas evolution is observed, record the volume of the gas evolved.

11. Open the Schlenk tube and filter the solution. Wash the solid with distilled water and then rinse with acetone. Decant the filtrate into the waste acid container.
12. Record the mass of calcium sulfate dried.

Treatement of data

1. Calculate the number of moles of carbon dioxide gas liberated. (Vapor pressure of the acid solution at the temperature of experiment has to be considered).
2. Calculate the amount of $CaCO_3$ reacted.
3. Calculate the weight percentage of $CaSO_4$ present in the sample.
4. Calculate the weight percentages of $CaCO_3$ and $CaCl_2$ present in the salt mixture.
5. Discuss the possible sources of experimental error.

Problem 33 Potassium bisoxalatocuprate(II) dihydrate: Preparation and analysis

The high natural abundance and high concentrations of copper and copper ores make copper an economical choice for many industrial applications. Copper may exist in three oxidation states, +1, +2, and +3. However, most copper compounds are commonly encountered as salts of Cu^{2+}, while Cu^{3+} is the least stable form. Copper, being a transition metal, also forms coordination compounds.

In this experiment, potassium bisoxalatocuprate(II) dihydrate will be prepared by reaction of copper(II) sulfate pentahydrate with potassium oxalate.

$CuSO_4{\cdot}5H_2O(aq) + 2\ K_2C_2O_4(aq) \rightarrow K_2Cu(C_2O_4)_2{\cdot}2H_2O(s) + K_2SO_4(\mathrm{aq}) + 3\ H_2O(l)$

The number of oxalato ligands in the complex ion will be determined by titration with standard permanganate solution. The copper content of the complex ion will be determined by iodine-thiosulfate titration.

Chemicals and reagents

- Copper(II) sulfate pentahydrate, $CuSO_4.5H_2O$
- Potassium oxalate monohydrate, $K_2C_2O_4.H_2O$
- Sulfuric acid, $H_2SO_4(aq)$, 2.5 mol.L^{-1}
- Potassium permanganate, $KMnO_4$, 0.020 mol.L^{-1}
- Sodium carbonate, Na_2CO_3

- Acetic acid, CH_3COOH, dilute
- Potassium iodide, KI
- Sodium thiosulfate, $Na_2S_2O_3$, 0.020 $mol{\cdot}L^{-1}$
- Starch indicator (freshly prepared, 5% w/v)
- Potassium thiocyanate, KSCN
- Ethanol, C_2H_5OH
- Acetone, CH_3COCH_3

Substance	State	R Phrase	S Phrase
$CuSO_4.5H_2O$	Solid	22 36 38 50 53	22 60 61
$K_2C_2O_4.H_2O$	Solid	21 22	24 25
H_2SO_4	2.5 $mol{\cdot}L^{-1}$	35	26-30-45
$KMnO_4$	0.020 $mol{\cdot}L^{-1}$	8 22 50 53	60 61
Na_2CO_3	Solid	36 37 38	2 22 26
CH_3COOH	dilute solution	10 35	24 25 26 36 37 39 45 51 60
KI	Solid	36 38 42 43 61	26 36 37 39 45
KSCN	Solid	21 22	24 25
C_2H_5OH	Liquid	11	7 9 16 33
CH_3COCH_3	Liquid	11 36 66 67	2 9 16 26

Apparatus and glassware

- Erlenmeyers, 250 mL (2)
- Beakers, 50 mL (2)
- Funnel
- Pipettes, 5 mL, 10 mL
- Graduated cylinder, 50 mL
- Burettes (2)
- Stirring rod
- Stirring bar
- Ice-bath
- Washing bottle

- Filter paper
- Heater-stirrer

A. Preparation of potassium bisoxalatocuprate(II) dihydrate

1. Dissolve 4.1 g copper(II) sulfate hexahydrate**,** $CuS0_4.5H_20$ in 8.0 mL of water and heat the solution to 90 °C.
2. Gradually add the hot solution, while stirring, to a solution (also at 90 °C) of 12.3 g $K_2C_2O_4.H_2O$ in 35 mL of water.
3. Allow the solution to cool down to room temperature and then cool in an ice-bath to 10°C. Filter off the solid*,* wash with ice cold water followed by ethanol and then acetone. Dry at 40 °C in air for 1 h.
4. Weigh the dried sample.

B. Determination of oxalate in the prepared compound

1. Transfer an accurately known amount (0.16-0.18 g) of potassium bisoxalatocuprate(II) dihydrate prepared in Part A into a 250-mL erlenmeyer flask, and dissolve the complex by adding about 25 mL of water.
2. Add 20 mL of 2.5 M sulfuric acid and heat the solution to about 80 °C.

$$H_2SO_4(aq) + K_2Cu(C_2O_4)_2{\cdot}2H_2O(s)(aq) \rightarrow K_2C_2O_4(aq) + CuSO_4(aq) + H_2C_2O_4(aq) + 2\ H_2O(l)$$

3. Titrate the solution with standardized 0.020 mol.L^{-1} potassium permanganate solution, until the color of the solution becomes pink persistent for 1-2 minutes (end-point). Record the volume of standard $KMnO_4$ solution used.

$$16\ H^+(aq) + 2\ MnO_4^-(aq) + 5\ C_2O_4^{2-}(aq) \rightarrow 10\ CO_2(g) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$$

C. Determination of copper in the prepared compound

1. Add solid Na_2CO_3 to the solution obtained in Part B-2 until a precipitate first appears. Then add dilute acetic acid (10% w/v) until the pH is about 5. Finally, add about 1 g of solid potassium iodide into the solution.

$Na_2CO_3(aq) + CuSO_4(aq) \rightarrow Na_2SO_4(aq) + CuCO_3(s)$

$2\,Cu^{2+}(aq) + 5\,I^-(aq) \rightarrow 2CuI(s) + I_3^-(aq)$

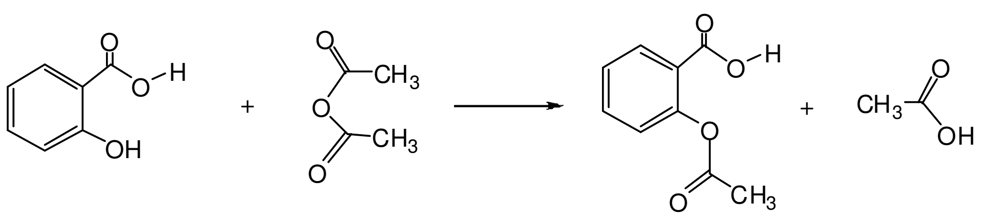
2. Titrate the liberated iodine which forms the I_3^- ion with standardized 0.020 M sodium thiosulfate solution using freshly prepared 5% (w/v) starch solution as indicator. A sharper end-point is obtained by the addition of 1-2 g potassium thiocyanate as the end-point is approached.

Treatment of data

1. Calculate the % yield of potassium bisoxalatocuprate(II) dihydrate prepared.
2. Calculate the weight % of oxalate present in potassium bisoxalatocuprate(II) dihydrate complex. Compare the experimental value with the theoretical value.
3. Write the oxidation reduction reactions involved for the determination of copper content.
4. Calculate the weight % of copper present in potassium bisoxalatocuprate(II) dihydrate. Compare the experimental value with the theoretical value.

Problem 34 Synthesis and analysis of Aspirin

Aspirin, acetylsalicylic acid is both an organic ester and an organic acid. It is used extensively in medicine as an analgesic, pain releiver and as a fever-reducing drug. It is generally prepared by reaction of salicylic acid with acetic anhydride according to the following reaction.



salicylic acid acetic anhydride acetylsalicylic acid acetic acid

The amount of acetylsalicylic acid can be determined by titrating with a strong base such as sodium hydroxide.

$CH_3CO_2C_6H_4CO_2H(aq) + OH^-(aq) \rightarrow CH_3COOC_6H_4COO^-(aq) + H_2O(l)$

However, being an ester acetylsalicylic acid is easily hydrolyzed, hence, during a normal titration with a strong base the alkaline conditions break it down leading to errors in analysis. Thus, a back titration method is applied, in which in the first step, all the acid present in solution is completely hydrolyzed by excess strong base such as NaOH. The aspirin/NaOH acid-base reaction consumes one mole of hydroxide per mole of aspirin. The slow aspirin/NaOH hydrolysis reaction also consumes one mole of hydroxide per mole of aspirin, Thus, the number of moles of NaOH added should be more than twice that of aspirin. Then, the amount of excess hydroxide is determined by titration with standard acid solution.

In this experiment, acetylsalicylic acid will be prepared. The total amount of acid present will be determined by using a back titration method.

Chemicals and reagents

- Salicylic acid, $CH_3CO_2C_6H_4CO_2H$
- Acetic anhydride, $CH_3C_2O_3CH_3$
- Phosphoric acid, H_3PO_4 or sulfuric acid, H_2SO_4, concentrated
- Ethanol, C_2H_5OH
- Sodium hydroxide, NaOH 0.50 mol·L^{-1}
- Hydrochloric acid, HCl 0.30 mol·L^{-1}
- Phenolphthalein indicator

Substance	Phase	R Phrase	S Phrase
$CH_3CO_2C_6H_4CO_2H$	Solid	22 36 37 38 41 61	22 26 36 37 39
$CH_3C_2O_3CH_3$	Liquid	10 20 22 34	26 36 37 39 45
H_3PO_4	Concentrated	23 24 25 35 36 37 38 49	23 30 36 37 39 45
H_2SO_4	Concentrated	23 24 25 35 36 37 38 49	23 30 36 37 39 45
C_2H_5OH	Liquid	11 20 21 22 36 37 38 40	7 16 24 25 36 37 39 45
NaOH(aq)	0.50 mol·L^{-1}	35	26 37 39 45
HCl(aq)	0.30 mol·L^{-1}	23 25 34 38	26 36 37 39 45

Apparatus and glassware

- Beakers, 100 mL,
- Erlenmeyer, 250 mL (2)
- Pipettes, 5 mL and 10 mL
- Graduated cylinder, 50 mL

- Burette, 50 mL
- Stirring rod
- Watch glass
- Buchner funnel
- Filter paper
- Vacuum filtration flask
- Melting point capillary tube
- Thermometer, 110 °C
- Melting point apparatus
- Washing bottle

A. Synthesis of Aspirin, acetylsalicylic acid

1. Place accurately weighed 3.00 g of salicylic acid in a 100 mL Erlenmeyer flask.
2. Add 6.0 mL of acetic anhydride and 4 to 8 drops phosphoric acid to the flask and swirl to mix everything thoroughly.
3. Heat the solution to about 80-100 °C by placing the flask in hot water for about 15 minutes.
4. Add 2 mL of cold water dropwise until the decomposition of acetic anhydride is completed and then 40 mL of water and cool the solution in ice bath. If crystals do not appear, scratch the walls of the flask with a stirring rod to induce crystallization.
5. Weigh the filter paper that will be used in filtration. Filter the solid by suction filtration through a Buchner funnel and wash the crystals with a few milliliters of ice cold water at about -5 °C.
6. For recrystallization, transfer by dissolving the crystals into a beaker and add 10 mL ethanol and then add 25 mL warm water.
7. Cover the beaker with a watch glass and once crystallization has started place the beaker in an ice bath to complete the recrystallization.
8. Apply suction filtration as described in step 5.
9. Place the filter paper with the product onto a watch glass and dry in oven at 100 °C for about 1 h and weigh the product.
10. Determine the melting point (135 °C) to verify purity.

Determination of amount of acetylsalicylic acid

1. Dissolve 0.5 g of aspirin in 15 mL of ethanol in a 250 mL Erlenmeyer flask.
2. Add 20 mL of 0.50 mol·L^{-1} NaOH solution.
3. In order to speed up the hydrolysis reaction, heat the sample in a water bath about 15 min after addition of two or three boiling chips to the flask swirling the flask occasionally. **Caution: Avoid boiling, because the sample may decompose.**
4. Cool the sample to room temperature and add 2-4 drops of phenolphthalein indicator to the flask. The color of the solution should be faint pink. If the solution is colorless add 5 mL of 0.50 mol·L^{-1} NaOH solution and repeat the steps 3 and 4.
5. Record the total volume of 0.50 mol·L^{-1} NaOH solution added.
6. Titrate the excess base in the solution with 0.30 mol·L^{-1} HCl solution until the pink color just dissappears and the solution becomes cloudy.
7. Record the volume of 0.30 mol·L^{-1} HCl solution added.
8. Repeat the titration two more times using two new samples.

Treatment of data

1. Calculate the yield of aspirin prepared.
2. Calculate the amount of acetylsalicylic acid present in the Aspirin sample.
3. Calculate the purity of aspirin and express in weight percentage.

Problem 35 Determination of iron and copper by iodometric titration

Master alloys are formed by mixing a base metal such as Al, Ni or Cu with a high percentage of one or two other metals. Master alloys are widely used in industry as semi-finished products. In metallurgical plants, master alloys are added to other molten metal mixtures for some purposes such as alteration of the composition to achieve certain chemical, electrical or mechanical properties in the final product.

In this experiment, a sample solution of master alloy containing iron and copper ions will be analyzed by a two stage titrimetric method. First, the amount of Fe(III) ions will be determined by precipitation with pyrophosphate in acidic solution and then, the amount of Cu(II) will be calculated from the total amount of ions present in solution determined by an indirect iodometric titration with standard sodium thiosulfate solution.

Chemicals and reagents:

- Test solution 0.10 M (simulating a digested sample of alloy containing both Fe^{3+} and Cu^{2+} ions in 4-6 g·L^{-1})
- Sodium thiosulfate standard solution, $Na_2S_2O_3$, 0.050 mol·L^{-1}
- Sodium pyrophosphate solution, $Na_4P_2O_7$, 5.0% (w/v)
- Hydrochloric acid solution, HCl(*aq*), 4.5 mol·L^{-1}
- Potassium iodide solution, KI, 10 %(w/v)
- Starch solution, 5.0% (w/v).

Substance	Phase	R Phrase	S Phrase
HCl solution	4.5 mol·L^{-1}	23 25 34 38	26 36 37 39 45
KI solution	10% (w/v)	36 38 42 43 61	

Apparatus and glassware

- Burette, 50 mL
- Graduated cylinder, 50 mL
- Erlenmeyer flask, 250 mL (2)
- Pipettes, 5 mL and 10 mL
- Watch glasses (2)

A. Determination of copper(II) ion

1. Transfer 10.0 mL of the test solution into a 250 mL Erlenmeyer flask, add 50 mL water and mix thoroughly.
2. To the same flask add 20 mL of 5.0% (w/v) pyrophosphate, 5.0 mL of 4.5 mol·L^{-1} HCl and 40 mL of 10% (w/v) KI. When pyrophosphate is added a precipitate may form.
3. Close the flask with a watch glass and leave in dark for 3-5 min for the formation of white precipitate.
4. Titrate the content of the flask with standard 0.020 mol·L^{-1} $Na_2S_2O_3$ until a pale yellow color is obtained.
5. At this point, add 5 mL of starch indicator (5%w/v) and titrate until the color of solution changes from dark blue to milky white.
6. Record the volume of sodium thiosulfate solution added.

B. Determination of total amount of copper(II) and iron(III) ions

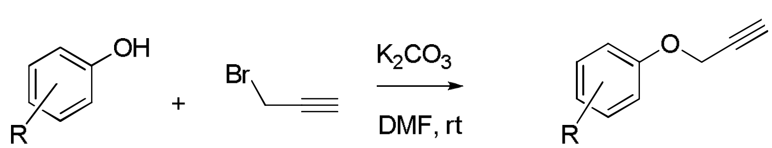
1. Transfer 10.0 mL of the test solution into 250 mL Erlenmeyer flask, add 50 mL water and mix thoroughly.
2. To the same flask add 2 mL of 4.5 $mol \cdot L^{-1}$ HCl and 40 mL of 10% (w/v) KI into the solution and mix thoroughly.
3. Close the flask with a watch glass and leave in dark for 3-5 min. A small amount of white precipitate may be observed.
4. Titrate the solution with a standard 0.050 $mol \cdot L^{-1}$ $Na_2S_2O_3$ until a pale yellow color is obtained.
5. At this point, add 5.0 mL of 5.0 % (w/v) starch indicator and titrate until the color of the solution changes from dark blue to milky white.
6. Record the volume of sodium thiosulfate solution added.

Treatment of data and questions

1. Write the equations for the titration processes.
2. Explain why the solution is acidified.
3. Explain why starch is added close to the end of titration.
4. Calculate the number of moles of Cu^{2+} and Fe^{3+} ions present in the test solution.
5. Calculate the mass ratio of Cu^{2+} and Fe^{3+} ions.

Problem 36 Phenol propargylation: Synthesis of 1-nitro-4-(prop-2-ynyloxy)benzene and (prop-2-ynyloxy)benzene

Propargyl unit can be anchored to phenolic substances via a S_N2 type reaction under slightly basic condition. The resultant products can be feasible candidates as substrates for the following Huisgen dipolar cycloaddition reaction.



R: H, 4-nitro

In this experiment, two parallel experiments, using phenol as a reactant in one of them, and 4-nitrophenol as a reactant in the other, will be performed under the same conditions. Both experiments will be stopped after 3 h as indicated in the following procedure.

Chemicals and reagents

- Phenol, C_6H_5OH
- 4-Nitrophenol, $NO_2C_6H_4OH$
- Propargyl bromide, $CH{\equiv}CCH_2Br$
- Toluene, $C_6H_5CH_3$
- DMF, dimethylformamide, $(CH_3)_2NCHO$
- Potassium carbonate, K_2CO_3
- Ethyl acetate, $CH_3COOC_2H_5$
- Heptane, C_7H_{16}
- Ether, $C_2H_5OC_2H_5$
- Brine, saturated NaCl solution
- Anhydrous sodium sulfate Na_2SO_4

Substance	Phase	R Phrase	S Phrase
C_6H_5OH	liquid	24 25 34 R36/37/38.	28 45
$NO_2C_6H_4OH$	solid	*23 24 25 34*	*28*
$CH{\equiv}CCH_2Br$	liquid	11 20 25 36/37/38 63 67	16 26 28A 37/39
$C_6H_5CH_3$	liquid	11 20 48 63 65 67	16 25 29 33
$(CH_3)_2NCO$	liquid	20 21 36 61	45 53
K_2CO_3	solid	22 36 37 38	-
$CH_3COOC_2H_5$	liquid	11 36 66 67	16 23 29 33
C_7H_{16}	liquid	9 11 20 22	9 16 23 29 33
$C_2H_5OC_2H_5$	liquid	12 19 22 66 67	9 16 29 33

Apparatus and glassware

- Round bottom flask, 50 mL
- Pipettes
- Magnetic stirrer

- TLC precoated silica gel plates (Silica Gel PF-254)
- UV-lamp
- Flash column chromatography, thick-walled glass column filled with a flash grade Silica Gel 60.

Prelaboratory work. Before starting the experiment, estimate the phenolic substrate that would undergo a faster reaction. Explain the reason.

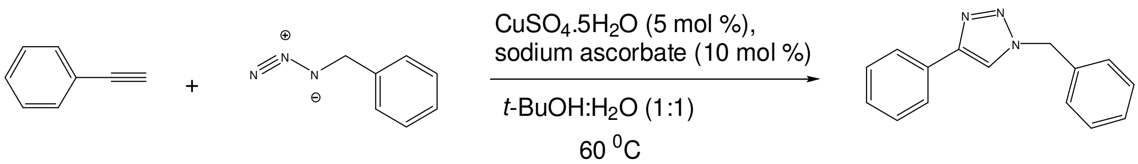
1. Place 1.0 mmol 4-nitrophenol (or phenol) to a 50 mL round bottom flask containing 1.0 mL DMF. Stir the mixture at room temperature for 5 min and then add 1.2 mmol propargyl bromide (80% weight solution in toluene) and 1.2 mmol potassium carbonate.
2. Stir the resulting mixture at room temperature for 3 hrs until TLC analysis indicates the completion of the reaction. For TLC, use precoated silica gel plates (Silica Gel PF-254) and visualize the spots by UV-light. Use ethyl acetate: heptane 1:3 mixture as an eluent.
3. Dilute the reaction mixture with 1.0 mL of water and extract with 10.0 mL of ether. Wash the organic phase 3 times with 1.5 mL of brine, then dry over anhydrous sodium sulfate.
4. Evaporate the solvent to afford the crude corresponding propargyl ether and weigh the product.
5. Purify the crude product of (prop-2-ynyloxy)benzene by flash column chromatography which is performed by using thick-walled glass column with a flash grade Silica Gel 60.

Treatment of data

1. Calculate the R_f values of 4-nitrophenol and 1-nitro-4-(prop-2-ynyloxy)benzene. Repeat the same calculations for phenol and (prop-2-ynyloxy)benzene.
2. Calculate the chemical yield of 1-nitro-4-(prop-2-ynyloxy)benzene isolated as a solid substance. Measure the melting point of this substance.
3. Calculate the chemical yield of (prop-2-ynyloxy)benzene.

Problem 37 Huisgen dipolar cycloaddition: Copper(I)-catalyzed triazole formation

One of the most popular reactions within the “click chemistry” concept is the azide-alkyne Huisgen dipolar cycloaddition using a copper(I) catalyst. The procedure given below is an example for copper(I) catalyzed triazole formation considered as a “click chemistry” concept.



Chemicals and reagents

- Benzyl azide, $C_6H_5CH_2N_3$
- Phenyl acetylene, $C_6H_5C{\equiv}CH$
- Copper(II) sulfate pentahydrate, $CuSO_4{\cdot}5H_2O$
- Sodium ascorbate, $NaC_6H_7O_6$
- Aqueous ammonia solution, NH_3(*aq*), 10% wt
- *tertiary*-Butylalcohol, $(CH_3)_3COH$

Substance	Phase	R Phrase	S Phrase
$C_6H_5CH_2N_3$	Liquid	10 20 21 22	26 36 37 39
$C_6H_5C{\equiv}CH$	Liquid	10 36 37 38	16 33 60
$CuSO_4$ $5H_2O$	1.0 mol·L^{-1}	22 36 38 50 53	22 60 61
$NaC_6H_7O_6$	Solid	-	24 25
NH_3	10% wt solution	10 23 24 34 50	9 16 26 33 36 37 39 45 61
$(CH_3)_3COH$	liquid	11 20	9 16

Apparatus and glassware

- Screw-top vial 20 mL
- Pasteur pipettes
- Stirring bar
- Plastic syringes (1 and 2 mL)
- Graduated cylinder
- Thermometer
- TLC precoated silica gel plates (Silica Gel PF-254)
- Heater and stirrer

- Buchner funnel

1. Dissolve 133 mg (1 mmol) of benzyl azide in 1mL of ^{t}BuOH:water (1:1) solution and add via syringe in a 20 mL screw-top vial having a stirring bar.
2. Close the cap and add followings to the reaction vial via a syringe through PTFE (cap liner) of the cap.

   a) 1 mmol of phenyl acetylene dissolved in 1.0 mL of ^{t}BuOH:water (1:1) solution.

   b) 9.8 mg (10 mol %) of sodium ascorbate in 0.5 mL of ^{t}BuOH:water (1:1) solution.

   c) 2-3 Drops (~5 mol %) of 1.0 mol/L aqeous copper(II) sulfate pentahydrate.
3. Stir the mixture at 60 °C for 1-2 h until completion by TLC (use ethyl acetate: heptane 1:2 mixture as an eluent).
4. Dilute the reaction mixture with 10 mL of ice water and add 2.0 mL of 10% wt aqueous ammonia solution. Stir for another 5 min and collect the solid precipitate with a Buchner filter and air-dry overnight.

Treatment of data

1. Calculate the yield of the product.