

42nd International Chemistry Olympiad Japan, 2010

Preparatory Problems



Chemistry : the key to our future



Contents

Constants, Formulae, and Periodic Table	3
Theoretical Problems	4
Advanced Level Fields	5
Problem 1: Equilibrium constant	6
Problem 2: Speed of sound	7
Problem 3: Structures of nanomaterials	8
Problem 4: Vibrational states of Cl ₂	9
Problem 5: Raman spectroscopy	10
Problem 6: Internuclear distance of a hetero-nuclear diatomic molecule	12
Problem 7: Atomic and molecular orbitals	13
Problem 8: Electronic structure of polyene	14
Problem 9: Electronic structure of condensed matter	17
Problem 10: Carbon dioxide I	18
Problem 11: Carbon dioxide II	19
Problem 12: Synthesis of titanium dioxide	20
Problem 13: Born-Haber cycle	21
Problem 14: Solid state structure	22
Problem 15: Oxide-ion conductors	23
Problem 16: Silver smelting and refining	24
Problem 17: Cobalt(II) complexes	26
Problem 18: Red-ox titration	27
Problem 19: Iron-making and crystal structure	28
Problem 20: Gibbs energy of oxidation reaction	29
Problem 21: Quantitative composition analysis of volcanic gas	31
Problem 22: Vibrational and rotational spectra of volcanic gas	32
Problem 23: Introduction of macromolecular chemistry	33
Problem 24: Reduction of carbonyl compounds	37
Problem 25: Kiliani-Fischer synthesis	38
Problem 26: Glycolysis	39
Problem 27: Menthol synthesis	40
Problem 28: Structure studies of urushiol	41



Problem 29: Synthesis of Tamiflu	43
Problem 30: Nuclear magnetic resonance (NMR) spectra of isomers of C ₄ H ₈	44
Problem 31: Nuclear magnetic resonance (NMR) spectrum of [18]annulene	45
Practical Problems	46
Advanced Level Fields	47
Problem 32: Colloid titration: titration of a cationic surfactant with polyanion ...	48
Problem 33: Analysis of zinc-aluminum alloy by EDTA titration	50
Problem 34: Preparation of urea-hydrogen peroxide	53
Problem 35: Separation of a dye mixture using thin-layer chromatography (TLC)	55
Problem 36: Hydrolysis of ethyl acetate over a solid acid catalyst	59
Problem 37: Synthesis of a zinc ferrite	61
Problem 38: Identification of polymers and small organic molecules by qualitative analysis	63
Problem 39: Synthesis of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (Hantzsch ester)	65
Problem 40: Reduction of a ketone with sodium borohydride	68



Constants and Formulae

Avogadro constant:	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	$\Delta_r G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$	
Planck constant:	$h = 6.626 \times 10^{-34} \text{ J s}$	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \ln \frac{P_{\text{ox}}}{P_{\text{red}}}$
Speed of light:	$c = 3.000 \times 10^8 \text{ m s}^{-1}$	Logarithm:	$\ln x = 2.303 \log x$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log \frac{I_0}{I} = \epsilon cl$

In equilibrium constant calculations, all concentrations are referenced to a standard concentration of 1 mol L^{-1} . Consider all gases ideal throughout the exam.

Periodic Table with Relative Atomic Masses

1 H 1.01																	18 He 4.00
3 Li 6.94	4 Be 9.01											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 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 -	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	57-71	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 -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	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
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -



Theoretical Problems



Advanced Level Fields

Theoretical

Solid state structures: metals, metal salts

Thermodynamics: electrochemical cells, the relationship between equilibrium constants, electromotive force and standard Gibbs energy, the variation of the equilibrium constant with temperature

Quantum chemistry: quantized energy, related spectroscopy

Electronic structures: atomic and molecular orbitals, π electrons and electrical conductivity

Nuclear Magnetic Resonance (NMR): interpretation of ^1H NMR spectra; chemical shifts, multiplicities, coupling constants and integrals

Chemistry of saccharides: equilibrium between linear and cyclic forms, pyranoses and furanoses, and Haworth projection and conformational formulae, reactions

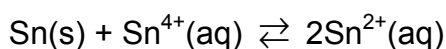


Problem 1: Equilibrium constant

Answer the following questions using the standard potential, E° , values given in the table.

Half reaction	E°/V (298 K)
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.79
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27

- a) Calculate the equilibrium constant, K , for the following reaction at 298 K



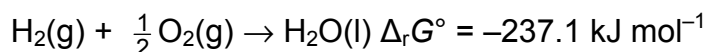
$K =$

- b) Calculate the solubility, S , of Hg_2Cl_2 in water at 298 K (units for S , mol kg^{-1}). The mercury cation in the aqueous phase is Hg_2^{2+} .

$S =$

mol kg^{-1}

- c) Calculate the voltage, E° , of a fuel cell by using the following reaction involving two electrons.



$E^\circ =$

V



Problem 2: Speed of sound

The heat capacity, $C_{V,m}$, of 1 mole of monoatomic gases such as helium at a constant-volume condition is expressed by the following equation:

$$C_{V,m} = \frac{3}{2}R$$

Here, R is the gas constant. The $C_{V,m}$ value corresponds to the increase in the energy of flying motion of gaseous atoms per unit temperature, and the flight speed of the atoms is expected to reduce to zero (0) at 0 K.

- a) Derive the mean flight speed, v , of gaseous atoms with molar mass M at temperature T .

$$v =$$

The speed of sound, v_s , in monoatomic gases is proportional (and roughly equal) to the flight speed, v , of the gaseous atoms. The speeds of sound in He (helium) and Ar (argon) at room temperature are 1007 m s^{-1} and 319 m s^{-1} , respectively.

- b) Estimate the speed of sound in Ne (neon), $v_s(\text{Ne})$, at room temperature.

$$v_s(\text{Ne}) = \quad \text{m s}^{-1}$$

Problem 3: Structures of nanomaterials

Fullerenes are a group of well-known novel nanomaterials with hollow spherical structures; these nanomaterials are novel allotropes of carbon. Fullerenes with n carbon atoms have 12 pentagons and $(n/2-10)$ hexagons, where n is an even number and 20 or more.

Answer the following questions by assuming that the length of each carbon-carbon bond in fullerene is 0.14 nm and that the carbon atoms are point masses.

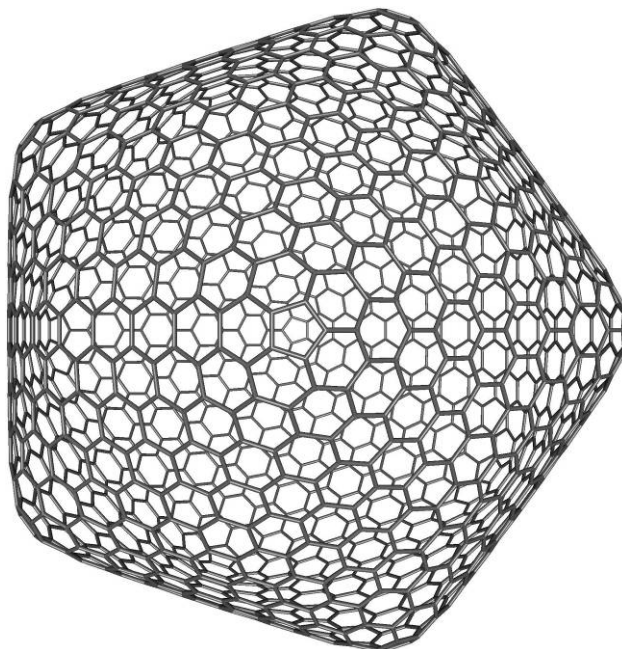
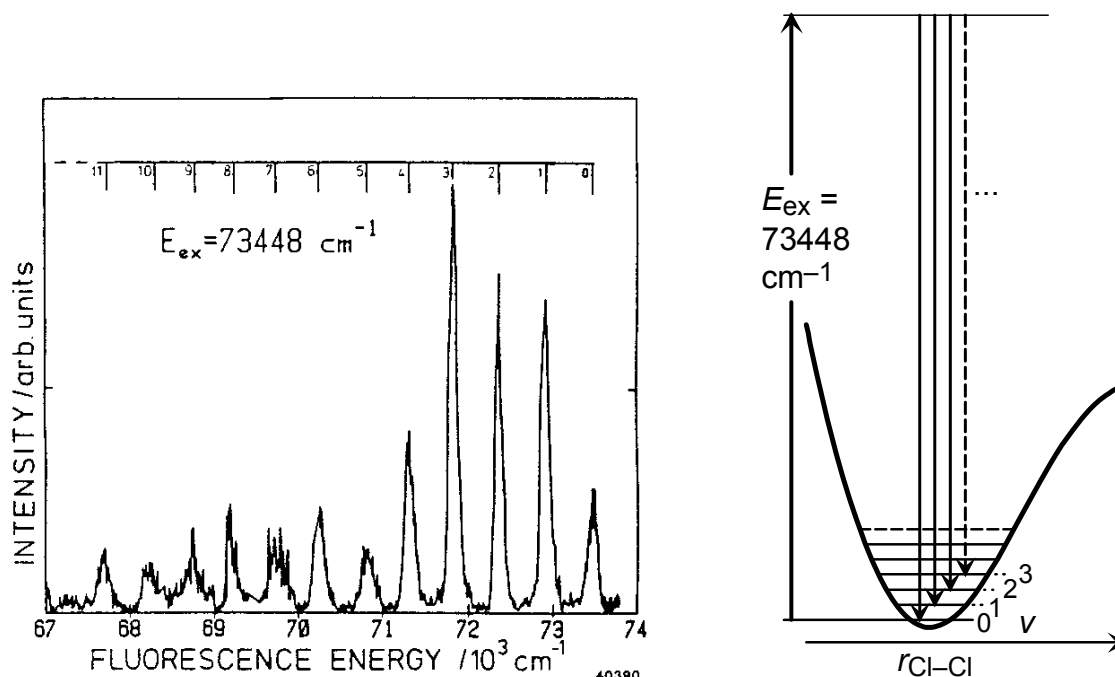


Fig. 1 Structure of a large C_{1500} fullerene

- a) Calculate the surface area of fullerenes with n carbon atoms in terms of nm^2 ($1 \text{ nm}^2 \equiv 10^{-18} \text{ m}^2$).
- b) Calculate the radius of fullerenes (in nm) as a function of n by considering the fullerene molecule as a perfect sphere.
- c) Figure 1 shows a large fullerene with C_{1500} . One of hypothetical applications of these large fullerenes is as a “molecular balloon” that can float in air. At 300 K and 101325 Pa, the density of these hollow spherical molecules can be smaller than that of air (80% N_2 and 20% O_2). Calculate the minimum number of carbon atoms and the minimum radius of the fullerene (in nm) required to satisfy this condition. Here, the fullerene molecule is rigid enough to retain its structure under air pressure and is considered to be a perfect hollow sphere.

Problem 4: Vibrational states of Cl₂

The wavenumber (cm^{-1}), the reciprocal of the wavelength, is often used as a measure of energy and is equal to the energy of a photon with the corresponding wavelength. The following figure shows the emission spectrum of gaseous Cl₂ excited at 73448 cm^{-1} . The spectrum shows a sequence of peaks, and each peak corresponds to the fluorescence at the vibrational state with the quantum number v ($= 0, 1, 2, \dots$).



- a) Calculate the approximate energy spacing between the adjacent vibrational energy levels at the ground electronic state of Cl₂, E_v , in kJ mol^{-1} . You can choose any pair of adjacent peaks for calculation.

$$E_v = \quad \text{kJ mol}^{-1}$$

Problem 5: Raman spectroscopy

The vibration in a diatomic molecule can be considered analogous to the stretching and compression of a spring, as shown in Figure I. The strength of this hypothetical spring is expressed by the force constant, k , which is large for strong bonds and small for weak bonds. Quantum mechanical analysis of the vibrational motion of diatomic molecules shows that the vibrational energy can be expressed in discrete values. The vibrational energy E_v is expressed by the following equation:

$$E_v = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right) \quad h: \text{Planck's constant}$$

Here, v is the vibrational quantum number, which can be any integral value 0, 1, 2, ..., and μ represents the reduced mass of the molecule ($\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$: m_1 and m_2 are the atomic masses).

When the molecule is irradiated with intense radiation such as laser light, light with energy different from that of the incident radiation is scattered; this optical phenomenon is called Raman scattering. In this optical process, the difference between the energy of the Raman scattering light and the incident laser light is the vibrational energy of the molecule, as shown in Figure II.

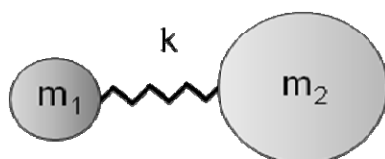


Figure I

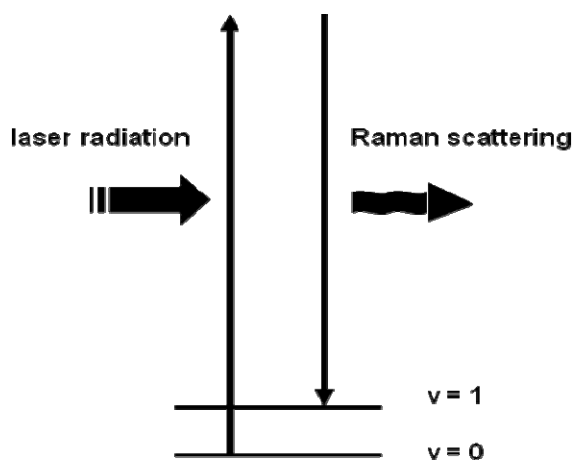


Figure II



- a) Obtain the ratio of the reduced masses of H_2 , N_2 , and O_2 .

$$\mu_{\text{H}_2} : \mu_{\text{N}_2} : \mu_{\text{O}_2} = 1 : \boxed{\text{a}} : \boxed{\text{b}}$$

- b) Wavelength λ (nm) and frequency ν ($\text{s}^{-1} = \text{Hz}$) are used to characterize light (radiation). In spectroscopy, the wavenumber (cm^{-1}), which corresponds to the number of waves per cm, is also employed frequently. Calculate the frequency and wavenumber of green light at 500 nm.

$$\text{Frequency} = \boxed{\text{c}} \text{ s}^{-1}$$

$$\text{Wavenumber} = \boxed{\text{d}} \text{ cm}^{-1}$$

- c) The energy difference between $\nu = 0$ and $\nu = 1$ for H_2 is 4160 cm^{-1} . Obtain the wavelength of Raman scattering light when H_2 is irradiated with laser light at 500 nm.

$$\text{The wavelength of Raman scattering light} = \boxed{\text{e}} \text{ nm}$$

- d) Assuming that the force constant for O_2 is twice that for H_2 , estimate the energy difference between $\nu = 0$ and $\nu = 1$ for O_2 . Obtain the wavelength of Raman scattering light when O_2 is irradiated with laser light at 500 nm.

$$\text{The energy difference} = \boxed{\text{f}} \text{ cm}^{-1}$$

$$\text{The wavelength of Raman scattering light} = \boxed{\text{g}} \text{ nm}$$

Problem 6: Internuclear distance of a hetero-nuclear diatomic molecule

Structure of simple molecules has been determined by spectroscopy, where the interaction between the radiation and the molecules is observed as a function of wavelength. The rotational spectrum of molecules appears in the far infrared or microwave region. Since microwave frequencies can be measured very precisely, internuclear distance of a diatomic molecule with a permanent dipole moment can be determined with high accuracy. A spectrum for the H^{35}Cl molecule is shown in Fig. 1. The rotational lines are separated by $\nu = 6.26 \times 10^{11} \text{ s}^{-1}$.

According to the simple model of a rotating diatomic molecule, the rotational energy, E_J , is discrete, which can be written as

$$E_J = \frac{h^2}{8\pi^2 \mu R_e^2} J(J+1) \quad J = 0, 1, 2, \dots$$

where μ and R_e are reduced mass¹ and internuclear distance, respectively. The rotational energy depends on the quantum number J . Under irradiation of microwave, transitions between rotational levels from the rotational state J'' to the rotational state J' are allowed, if

$$J' - J'' = \pm 1.$$

Calculate internuclear distance, R_e , of H^{35}Cl .

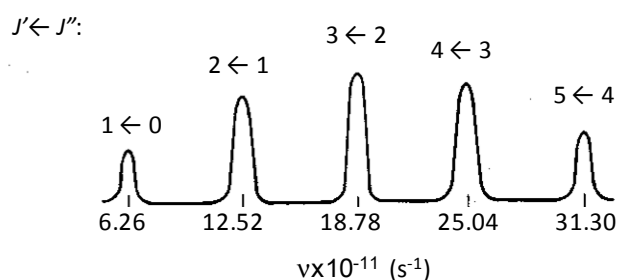


Fig. 1

Note

- ¹ Reduced mass, μ , is the effective [inertial mass](#) appearing in the [two-body problem](#). For two bodies, one with mass, m_1 , and the other with mass m_2 , it is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}.$$

Problem 7: Atomic and molecular orbitals

a) It is known that molecular orbitals of H_2^+ are represented by the linear combination of atomic orbitals (LCAO). The molecular orbitals are

$$\phi_a \propto 1s_A - 1s_B$$

$$\phi_b \propto 1s_A + 1s_B$$

where $1s_A$ is a ground-state hydrogen orbital centered on nucleus A, and $1s_B$ is centered on nucleus B. The energies for the molecular orbitals are shown in Figure 1 as a function of the internuclear distance of H_2^+ . (Note that the potential energy between an electron and a proton is set zero, when an electron and proton is fully separated.) Write which energy curve is for ϕ_a .

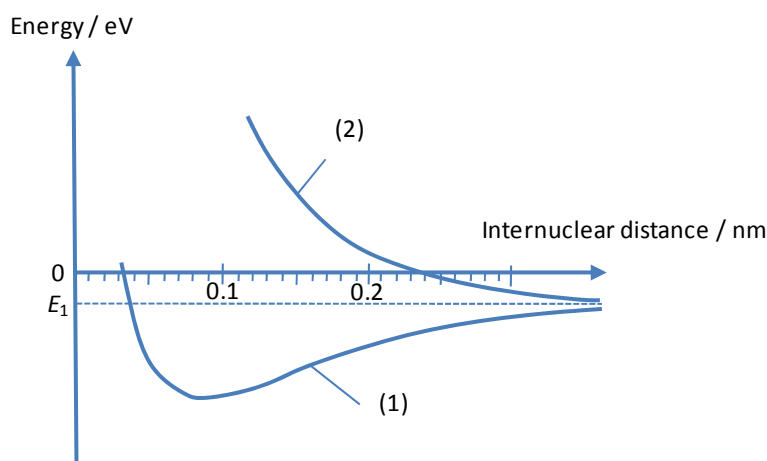


Fig. 1

b) Write the internuclear distance of stable H_2^+ .

c) The two energy curves in Fig. 1 converge at E_1 as the internuclear distance becomes infinity. Write which physical parameter of the hydrogen atom the energy $|E_1|$ equals to.

Problem 8: Electronic structure of polyene

The straight-chain polyene ($\cdots\text{—CH=CH—CH=CH—CH=CH—}\cdots$) is a chemical moiety present in the molecules that absorb visible light. Let us consider the behavior of π electrons in the straight-chain polyene.

First, for the sake of simplicity, we use the Hückel approximation to assess the π electrons of 1,3-butadiene, which contains four carbon atoms. We define the normal to the carbon-backbone plane as the z -axis and the atomic orbital ($2p_z$ orbital) of each carbon atom as ϕ_i ($i = 1, 2, 3, 4$). The molecular orbital ψ_k is expressed as the linear combination of these atomic orbitals according to the following equation:

$$\psi_k = \sum_i c_i \phi_i \quad (1)$$

The coulomb integral is defined as α and the resonance integral between adjacent atoms is defined as β , where α is the energy of the $2p_z$ orbital of an isolated carbon atom, and β can be determined from the overlap between adjacent $2p_z$ orbitals. The eigenenergy ε_k and the corresponding molecular orbital are obtained by the variation method, as shown in the following sets:

$$\varepsilon_1 = \alpha - 1.62\beta \quad \psi_1 = 0.37\phi_1 - 0.60\phi_2 + 0.60\phi_3 - 0.37\phi_4 \quad (2)$$

$$\varepsilon_2 = \alpha - 0.62\beta \quad \psi_2 = 0.60\phi_1 - 0.37\phi_2 - 0.37\phi_3 + 0.60\phi_4 \quad (3)$$

$$\varepsilon_3 = \alpha + 0.62\beta \quad \psi_3 = 0.60\phi_1 + 0.37\phi_2 - 0.37\phi_3 - 0.60\phi_4 \quad (4)$$

$$\varepsilon_4 = \alpha + 1.62\beta \quad \psi_4 = 0.37\phi_1 + 0.60\phi_2 + 0.60\phi_3 + 0.37\phi_4 \quad (5)$$

- a) Draw the energy levels of the molecular orbitals, and indicate the π electrons in the ground state using arrows while considering the spin direction.
- b) Using α and β , calculate the photon energy necessary for excitation from the ground state to the first excited state of 1,3-butadiene.

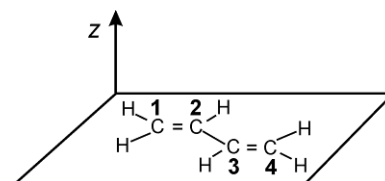


Fig. 1 : Illustration of the chemical structure of 1,3-butadiene. Each carbon atom is numbered.

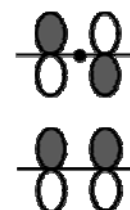


Fig. 2: Illustration of π molecular orbitals of ethylene. Solid circle represents a node.

- c) Draw the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 1,3-butadiene on the basis of the example for ethylene shown in Fig. 2, i.e., draw four $2p_z$ orbitals perpendicular to a horizontal line and indicate the sign for each orbital in black and white. Further, represent nodes by using solid circles. Note that you do not need to consider the differences in the contribution of each $2p_z$ orbital to the molecular orbitals.

Next, consider the behavior of π electrons in a system where the number of carbon atoms is extremely large, i.e., polyacetylene. Consider a one-dimensional (1D) chain of a certain number (N) of $2p_z$ orbitals that are aligned perpendicular to the chain with a spacing of a . If we assume a periodic boundary condition of Na along the chain, the energy state of the π electrons can be described by the following equation:

$$E_k = \alpha + 2\beta \cos ka \quad k = \frac{2\pi p}{Na}, p = 0, \pm 1, \pm 2, \dots \quad \left(-\frac{\pi}{a} \leq k < \frac{\pi}{a} \right) \quad (6)$$

- d) Calculate the energy width between the maximum and the minimum π -electron energy levels.
- e) Since the energy-level spacing of the 1D chain is extremely small, the energy levels form continuum states. Therefore, thermal excitation from HOMO to LUMO is easily induced at room temperature. Although such thermally excited electrons are mobile in the chain and can contribute to electric conductivity, pure polyacetylene is a poor conductor of electricity. This is because the carbon atoms in polyacetylene are not arranged with a periodicity of a ; instead, these atoms are arranged with a periodicity of $2a$ because of the alternating arrangement of single and double bonds. If the HOMO and LUMO of the 1D chain with periodicities of a and $2a$ are assumed as shown in Fig. 3(a) and (b), respectively, how do the energy levels of the HOMO and LUMO alter when the periodicity changes from a to $2a$? Choose the correct answer from the following choices.

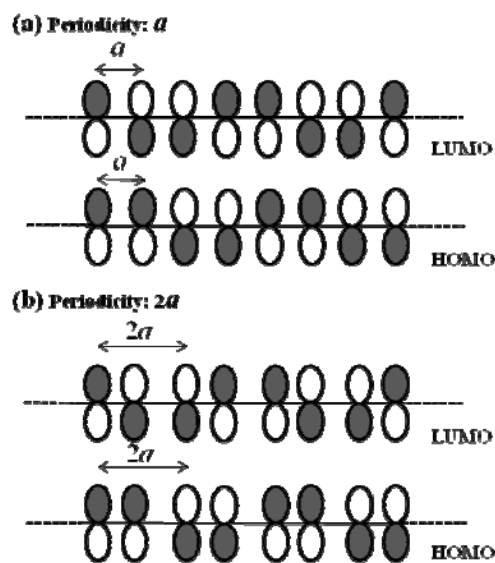


Fig. 3 : Illustration for the LUMO and the HOMO of the 1D chain with a periodicity of a (upper) and $2a$ (lower).



- (a) HOMO is destabilized, while LUMO is stabilized.
- (b) HOMO is stabilized, while LUMO is destabilized.
- (c) Both HOMO and LUMO are stabilized.
- (d) Both HOMO and LUMO are destabilized.

f) The 1D chain with a periodicity of $2a$ shows a gap between continuum states, which results in the formation of a filled valence band and an unfilled conduction band, as illustrated in Fig. 4. Since the valence band is filled with electrons and no unoccupied states are available for conduction, polyacetylene is an insulator. When a chemical substance is added to polyacetylene, the valence electrons become mobile. This chemical is obtained by oxidation of an aqueous solution of an alkali halide, and the number of inner-shell electrons in its constituent atoms is the same as that in argon. Write the chemical formula of this substance.

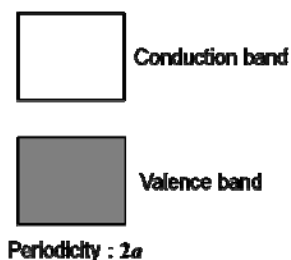


Fig. 4 : Illustration for the continuum electronic states of the 1D chain with a periodicity of $2a$.

Problem 9: Electronic structure of condensed matter

The electronic structure of condensed matter is usually different from that of an isolated atom. For example, the energy levels of a one-dimensional (1D) chain of Na atoms are illustrated in Figure 1. Here, the energy-level changes of the 3s-derived states of Na are shown. The energy-level spacing decreases as the number of Na atoms (N) increases. At an extremely large N , the energy-level spacing becomes negligibly smaller than the thermal energy, and the set of 3s-derived levels can be considered as a “band” of energy levels (last image in Figure 1). Na 3s electrons occupying the band of energy levels delocalize over the chain leading to a metallic character. Therefore, the 3s electrons can be assumed to be free particles confined in a 1D box.

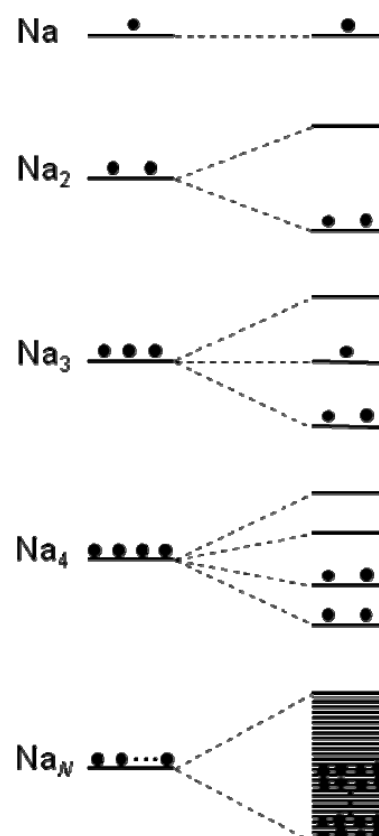


Fig. 1

- d) The eigenenergy of the free particles confined in a 1D box is described as

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (n = 1, 2, 3, \dots)$$

where n is the quantum number, h is the Planck constant, m is the weight of the electron, and L is the length of the 1D Na chain. Assuming that the chain length $L = a_0(N-1)$, where N is the number of Na atoms and a_0 is the nearest-neighbor interatomic distance, calculate the energy of the highest occupied level.

- e) We assume that 1.00 mg of Na forms a 1D chain with $a_0 = 0.360$ nm. Calculate the energy width from the lowest occupied level to the highest occupied level.
- f) If the thermal energy at room temperature is assumed to be 25 meV, how many Na atoms are required when the energy gap between the highest occupied level and the lowest unoccupied level is smaller than the thermal energy (25 meV)? Calculate the least number of Na atoms required assuming that the number is even.



Problem 10: Carbon dioxide I

Oxidation and combustion of organic compounds are exothermic reactions. The heat of reaction due to the combustion of fossil fuels such as oil, coal and natural gas has been utilized as main sources of energy.

- a) Calculate the heat of reaction, ΔH° , due to the complete combustion of 1 mol of methane at 298 K in the atmosphere, using the following data of the standard enthalpy of formation of methane, carbon dioxide and water.

Methane	: $-74.82 \text{ kJ mol}^{-1}$
Carbon dioxide	: $-393.5 \text{ kJ mol}^{-1}$
Water	: $-285.8 \text{ kJ mol}^{-1}$

- b) In a laboratory, we can generate carbon dioxide from calcium carbonate and hydrochloric acid. Calculate the volume, V (unite, mL), of generated carbon dioxide from 10.0 g of calcium carbonate and 50.0 mL of 1.00 mol L^{-1} aqueous hydrochloric acid at 298 K and 1013 hPa, assuming that the reaction proceeds completely and the generated carbon dioxide acts as an ideal gas.



Problem 11: Carbon dioxide II

Solid carbon dioxide is called “Dry Ice”. The “Dry Ice” is molecular crystal and the unit cell thereof is a face center cubic structure consisting of carbon dioxide molecules.

- a) Calculate a density of “Dry Ice”, ρ , when the edge length of the cubic unit cell of “Dry Ice” is 0.56 nm.
- b) Calculate the number of carbon dioxide molecules, N , in the cuboid “Dry Ice” of 20 cm \times 10 cm \times 5.0 cm.



Problem 12: Synthesis of titanium dioxide

One of the important minerals for a raw material of titanium dioxide is ilmenite (FeTiO_3). A model process of the synthesis of titanium dioxide (sulfate process) is divided into the following processes, (A)-(D).

- (A) Iron (II) sulfate and titanyl sulfate (TiOSO_4) aqueous solution is prepared by dissolving ilmenite in a concentrated sulfuric acid with heating.
- (B) Iron (II) sulfate heptahydrate is precipitated by controlling the concentration of the solution and cooling it.
- (C) After the precipitate of iron (II) sulfate heptahydrate is filtered out, titanium hydroxide ($\text{TiO}(\text{OH})_2$) is precipitated by heating the filtered solution and subsequently carrying out hydrolysis reaction.
- (D) Titanium dioxide is prepared by the calcination of titanium hydroxide.

The obtained Iron (II) sulfate is utilized as the source of some ferrite. The surplus sulfate acid is neutralized with limestone (calcium carbonate). The obtained gypsum (calcium sulfate dihydrate) is utilized as a by-product.

- a) Natural ilmenite ore contains lots of impurities. Assuming that the titanium content is 35.0 mass% in the natural ilmenite ore when titanium is converted into titanium dioxide and that the impurities in the ore contain no titanium component except for ilmenite, calculate the mass of ilmenite, m , in 1000 kg of the natural ilmenite ore.

- b) Show the chemical reaction which proceeds through the processes (A) and (B) described above as the form of one chemical formula.

- c) Show the chemical reaction through all of the processes (A)-(D) described above as the form of one chemical formula.

- d) In a laboratory, 25.0 mL of concentrated sulfuric acid (18.0 mol L^{-1}) was used in order to obtain titanium dioxide from 10.0 g of pure ilmenite. Calculate the minimum amount of calcium carbonate in terms of mass, m , that is necessary for neutralizing the surplus sulfuric acid when all of the processes (A)-(D) proceed completely.



Problem 13: Born-Haber cycle

Energy is produced by the formation of 1 mol of ion pairs from gaseous ions which approach each other from infinity. This evolved energy at 0 K under normal atmospheric pressure is defined as the lattice energy. The lattice energy of an ionic crystal is indirectly obtained by applying Hess's law to its enthalpy of formation.

- a) Illustrate a Born-Haber cycle of potassium chloride (KCl) and calculate its lattice energy by use of the following thermodynamic data.

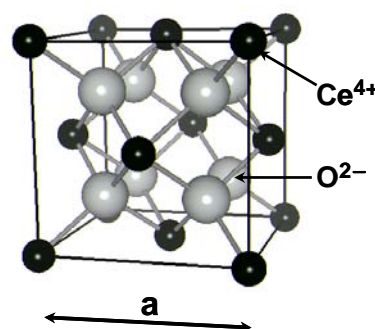
Enthalpy of formation of KCl (s)	- 437 kJ mol ⁻¹
Enthalpy of sublimation of K (s)	89 kJ mol ⁻¹
Ionization energy of K (g)	419 kJ mol ⁻¹
Enthalpy of dissociation of Cl ₂ (g)	242 kJ mol ⁻¹
Electron affinity of Cl (g)	- 349 kJ mol ⁻¹

The marks of "g" and "s" represent "gas" and "solid" state, respectively.

Problem 14: Solid state structure

The unit cell of the CaF_2 crystal structure is shown in the Figure. The addition of a small amount of Y_2O_3 to CeO_2 with the CaF_2 crystal structure and heating give a solid solution $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-y}$, in which Ce^{4+} and Y^{3+} are homogeneously distributed at the cation sites and oxygen vacancies are formed at the anion sites. Here, the valence of the cerium ions is assumed to be constant at +4.

- a) Indicate how many cations and anions are present in the CaF_2 structure unit cell?



- b) What is the ratio (%) of oxygen vacancies to the anion sites in the solid solution synthesized with the molar ratio of $\text{CeO}_2 : \text{Y}_2\text{O}_3 = 0.8 : 0.1$?
- c) Calculate the number of oxygen vacancies contained in 1.00 cm^3 of the above solid solution. Here, the unit cell volume a^3 is $1.36 \times 10^{-22} \text{ cm}^3$.



Problem 15: Oxide-ion conductors

Oxides with a CaF_2 crystal structure containing a high concentration of oxygen vacancies show oxide-ion conduction when heated at high temperatures, and these oxides are often called solid electrolytes. A cell using a solid electrolyte with porous Pt electrodes on both sides can be applied to oxygen sensors, oxygen pumps and fuel cells etc.

In the oxygen pump, oxygen molecules are reduced to oxide ions at the cathode, and the oxide ions move to the anode and are oxidized to oxygen molecules at the anode, by an applied voltage. Meanwhile, when the oxygen partial pressures are different at two electrodes which are not short-circuited, an electromotive force is generated between both electrodes, and this phenomenon is used for the oxygen sensor.

- a) Represent reaction formulas at the cathode and the anode during oxygen pumping.

- b) An electric current of 1.93 A was flowed for 500 s to move oxygen ions from the cathode to the anode. Calculate the volume of oxygen gas (mL) produced at the anode at 800 °C under 1.01×10^5 Pa. Given your answer to two significant figures.

- c) Calculate the electromotive force (V) when the ratio of the oxygen partial pressures P_1 and P_2 at both electrodes is maintained to be $P_1/P_2 = 100$ at 800 °C. Electronic conduction of the solid electrolyte can be ignored.



Problem 16: Silver smelting and refining

The Iwami-Ginzan Silver Mine in Japan produced a large volume of silver from the sixteenth to the seventeenth centuries. The ores included natural silver and argentite (silver sulfide). To obtain pure silver from the ores, galena (lead sulfide) was used for the smelting. In the method, the silver ore was mixed with lead sulfide and then melted in a container. During the heating process, an alloy of silver and lead was formed and pooled at the bottom of the container due to the high density of the alloy. The obtained alloy was put on an unglazed porous ceramic sheet and heated under an air flow. The alloy was melted and formed a droplet on the sheet. Lead in the alloy reacted chemically with the air and was removed from the alloy. The other impurities were also removed simultaneously and silver metal could be obtained.

- a) Write the 2-step chemical reactions from lead sulfide to lead metal. Lead sulfide is heated under an air flow in the first step of the process, and then heated while blocking the air in the second step. You should provide the possible two routes with the different intermediate compounds in your answer.
- b) If the same procedure is carried out with the presence of silver sulfide, an alloy of silver and lead is obtained. Write the chemical reactions between silver sulfide and the intermediate compounds of question 1. In general, the composition of the alloy can be changed continuously and the chemical formula of the alloy cannot be written stoichiometrically. Answer the question assuming the chemical formula of the obtained alloy to be AgPb_2 .
- c) Write the chemical reaction for lead in the alloy during the heating process of the alloy in the air at about $800\text{ }^\circ\text{C}$.



d) Which is the reason that best describes why the lead compound obtained in question 3 can be removed from the alloy. Choose one from the following choices.

A: The lead compound reacts chemically with the ceramic sheet and is removed from the alloy.

B: The lead compound wets the ceramic sheet and is sponged into the porous ceramics due to a capillary action.

C: The lead compound evaporates and is removed from the alloy.

D: The lead compound is separated from the silver due to the low density of the compound.

E: The lead compound is separated from the silver due to the high density of the compound.

e) What happens, if gold is included in the ores? Choose one from the following choices.

A: Silver is oxidized when gold is precipitated.

B: Gold is precipitated at the bottom of the alloy and can be separated from silver.

C: Gold covers the surface of the alloy and can be separated from silver.

D: Gold is precipitated at the center of the alloy and can be separated from silver.

E: Gold remains in the silver metal as a uniform alloy and cannot be separated from silver.



Problem 17: Cobalt(II) complexes

Cobalt chloride is widely used as an indicator of silica gel activity. The dried state is shown by a blue color and the red color indicates the absorption of water. In the case of pure compounds, cobalt(II) chloride anhydrate is blue and the hexahydrate is red. The aqueous solutions of both compounds are shown by a red color. On the other hand, the ethanol solution of cobalt(II) chloride anhydrate is shown by a blue color. The color changes to red with the addition of water.

- a) Write the coordination number and the coordination structure of the cobalt complex in the ethanol solution of cobalt(II) chloride anhydrate.
- b) The blue color remains when an amount of water double that of the cobalt chloride was added to the ethanol solution of cobalt(II) chloride anhydrate. Write the chemical formula of the major cobalt complex in the solution.
- c) Write the chemical reaction when a large amount of water is added to the solution.
- d) Write the coordination number and the coordination structure of the cobalt complex in the aqueous solution.
- e) If a certain amount of water is added to the ethanol solution, the solution becomes violet. Explain the color change if a small amount of concentrated hydrochloric acid is added to the violet solution.
- f) Explain the color change if the temperature of the violet solution decreases.
- g) Write the chemical formula of the cobalt complex in cobalt(II) chloride hexahydrate.
- g) Write the chemical formula of the cobalt complex in cobalt(II) chloride hexahydrate.



Problem 18: Red-ox titration

The chromium content of a stainless steel (a Fe-Cr alloy) sample was analyzed by the following procedure. Answer the questions a) - f). Here, the atomic weight of Cr is assumed to be 52.00.

- i) 0.1000 g of a stainless steel sample is dissolved into 20 mL of heated sulfuric acid (1.8 mol L^{-1}).
- ii) 4 mL of conc. nitric acid is added to the solution and heated for 10 min, when the color of the solution changes from blue to green.
- iii) 10 mL of 0.5% silver nitrate aqueous solution and 6 g of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) are simultaneously added to the solution, it is heated for 20 min until the decomposition of ammonium persulfate is terminated, when color of the solution turns orange.
- iv) 10 mL of 5% NaCl aqueous solution is added.
- v) 20 mL of $1.00 \times 10^{-1} \text{ mol L}^{-1}$ ammonium iron(II) sulfate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$) aqueous solution is added with a volumetric pipette.
- vi) $2.00 \times 10^{-2} \text{ mol L}^{-1}$ potassium permanganate (KMnO_4) aqueous solution is titrated using a burette. When the color of the solution becomes light purple, it is presumed to be the final point.

- a) Describe the chemical reaction in process ii).
- b) Trivalent chromium ion exists in the solution after process ii). What kind of form will the chromium ion take after process iii)?
- c) Describe the reaction which occurs in process iv). Also mention the purpose of the process.
- d) Describe the ionic reaction which occurs between heavy metal ions in process v). What color will the solution become in the process?
- e) Describe the reaction which occurs in process vi).
- f) The titrated amount in process vi) was 12.00 mL. Derive the chromium content of this stainless steel sample.



Problem 19: Iron-making and crystal structure

Iron is generally produced from an iron ore resource by reducing it with carbon. The main production process is through a blast furnace (BF) and a convertor. Pig iron (molten Fe-C alloy) is produced by feeding iron ore resource, subsidiary materials (CaO) and cokes from the top of the BF and by blowing heated air from the bottom. Then, molten steel is obtained by oxidizing the pig iron in a vessel such as a convertor in order to remove impurities as well as carbon. Answer the questions a) - e), with the provision that carbon content of the pig iron is 4.50 mass% and that a coke contains 90.0 mass% C, 7 mass% SiO₂, 3 mass% Al₂O₃. The gas constant is 8.314 J K⁻¹ mol⁻¹), and the atomic weights of C, O, Ca and Fe are 12.0, 16.0, 40.1 and 55.8, respectively. The density of iron is 7.90 g cm⁻³ at room temperature.

- a) The main component of an iron ore is Fe₂O₃ and it will be reduced to form Fe and CO₂ by (i) CO gas produced by the reaction between the cokes and the heated air or (ii) carbon in the cokes. Describe each chemical reaction.
- b) Iron ore also contains gangue (impurity materials), such as 7 mass% SiO₂ and 3 mass% Al₂O₃ other than 90 mass% Fe₂O₃. It will react with the gangue in the coke and the subsidiary material CaO, forming the oxide melts which will be exhausted as slag. How many kg of the slag is produced as a byproduct to obtain 1 kg of pig iron? Assume that the subsidiary material is added so that the mass of CaO is equal to that of SiO₂.
- c) In a convertor process, carbon is eliminated by blowing O₂ gas onto pig iron. When the molar amounts of CO and CO₂ are identical, what is the volume (L) of O₂ gas required for the complete removal of carbon from 1.00 kg of pig iron at 27 °C and 2.026 × 10⁵ Pa?
- d) When 1.00 kg of iron is produced from iron ore through BF and a convertor only via process (i) in the question a), how many kg of CO₂ is generated? Assume that the CO gas (the same molar amount of CO₂) generated from the convertor is oxidized and exhausted as CO₂. In the calculation, include the CO₂ generated in the calcinations of CaCO₃ to produce the subsidiary material of CaO.
- e) The crystal structure of iron is body center cubic (bcc). Derive the atomic radius of iron at room temperature.

Problem 20: Gibbs energy of oxidation reaction

Answer the following questions on the Gibbs energy of oxidation reactions.

a) Fill the blanks in the following sentences with suitable terms or chemical formulae.

When metal “M” is oxidized by one mole of oxygen gas to form an oxide M_mO_n (m, n : integers), the reaction can be expressed as (i). The standard Gibbs energy change of this reaction, ΔG° , can be expressed as (ii) in terms of standard (iii) change, ΔH° , and standard (iv) change, ΔS° , of this reaction at an absolute temperature T . On the other hand, when a pure metal M and a pure oxide M_mO_n are in equilibrium state at an absolute temperature T , the oxygen partial pressure p_{O_2} can be derived as (v) using ΔG° and the gas constant R . The diagram where ΔG° values for various oxidation reactions are drawn as a function of absolute temperature is called an “Ellingham Diagram” (Figure 1). As can be seen in the figure, most relations are drawn by a straight line and the metals existing in the lower part tend to be (vi) compared to those in the upper part.

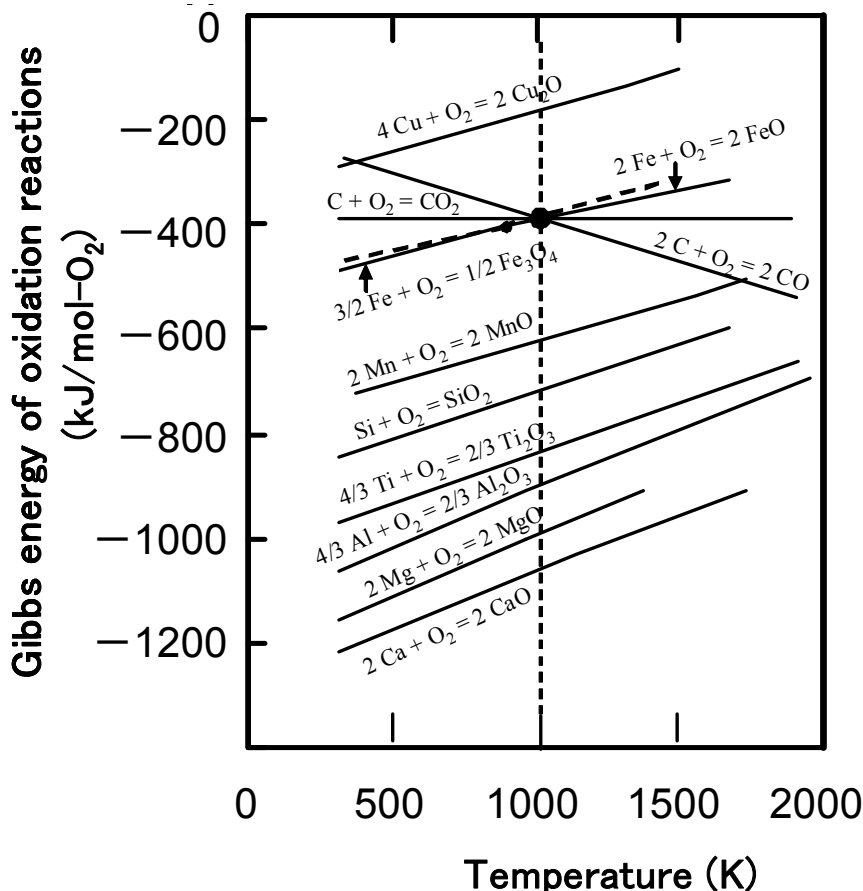


Figure 1. Gibbs energy of oxidation reaction – temperature diagram. (Ellingham Diagram)



- b) When both the reactants and the products are in the condensed state (solid or liquid) in Figure 1, the slope of each line in the diagram shows an almost identical value. The line is horizontal in the case of CO_2 gas, and the slope shows a different sign with the same absolute value in the case of CO gas. Explain why.
- c) Describe the chemical reaction when Cu_2O is reduced by Al.
- d) Derive the heat of the reaction in the above question c) per mole of Al.
- e) Show the points through which any lines of constant oxygen partial pressure p_{O_2} and those with a constant value of the ratio of CO gas partial pressure to CO_2 gas partial pressure $p_{\text{CO}}/p_{\text{CO}_2}$ pass, respectively, in Figure 1.
- f) When solid FeO is reduced to Fe by flowing CO gas at 1000 K in equilibrium state, how much % of the CO gas will be consumed?



Problem 21: Quantitative composition analysis of volcanic gas

Answer the questions a) - c) on composition determination of fumarolic gas.

Before sampling fumarolic gas, 20 mL of 5 mol L⁻¹ NaOH solution was loaded in a syringe and air was removed from the syringe. A titanium tube was inserted into a fumarole and the tube was sufficiently heated by the hot fumarolic gas to prevent condensation of fumarolic gas in the tube. By connecting the titanium tube with the syringe using a rubber tube, the fumarolic gas was introduced into the syringe by slow drawing. During the sampling procedure, the syringe was cooled with a wet towel. After completing the gas collection, the syringe was equilibrated with the surrounding mountain atmosphere condition (0 °C, 1013 hPa) and the volumes of gas and liquid components recorded from the scale on the syringe were 50.0 mL and 38.0 mL, respectively.

A 10 mL aliquot was collected from the 38.0 mL solution in the syringe, and all the sulfur species were oxidized to sulfate ion using an oxidant. After adding diluted HCl into the solution and making the solution slightly acidic, the addition of 20 mL of 10% BaCl₂ solution to the solution resulted in a white precipitate. The precipitate was dried and weighed to be 0.30 g.

The volume of 1 mol of a gas is assumed to be 22.4 L in the standard condition (0 °C and 1013 hPa).

- Calculate the volume component of water vapor (in %) in the collected fumarolic gas assuming that the volume of NaOH solution did not change by absorption of gases other than water vapor. The density of NaOH solution was at a constant, 1.0 g mL⁻¹, during the experiment.
- Calculate the quantity of sulfur (in mol) contained in the fumarolic gas collected into the syringe. Moreover, calculate the total volume (in mL) of H₂S and SO₂ gas components in the standard condition (0 °C, 1013 hPa). Give the answer to two significant figures.
- Molar ratios of H₂S to SO₂ are estimated utilizing the reactivity difference between H₂S and SO₂ gases. Fumarolic gas is bubbled into a testing tube which contains 30 mL of 0.03 mol L⁻¹ KIO₃-KI solution and 3 mL of 4M HCl solution. Describe the chemical reaction equations occurring for H₂S and SO₂ gases, respectively.

Problem 22: Vibrational and rotational spectra of volcanic gas

Recently, the chemical composition of fumarolic gas has been determined using remote spectroscopic methods. The figure shown below is an infrared absorption spectrum (vibration-rotation spectrum) of fumarolic gas. “X” and “Y” in the figures represent two hydrogen halide species. Y is known to dissolve silicate.

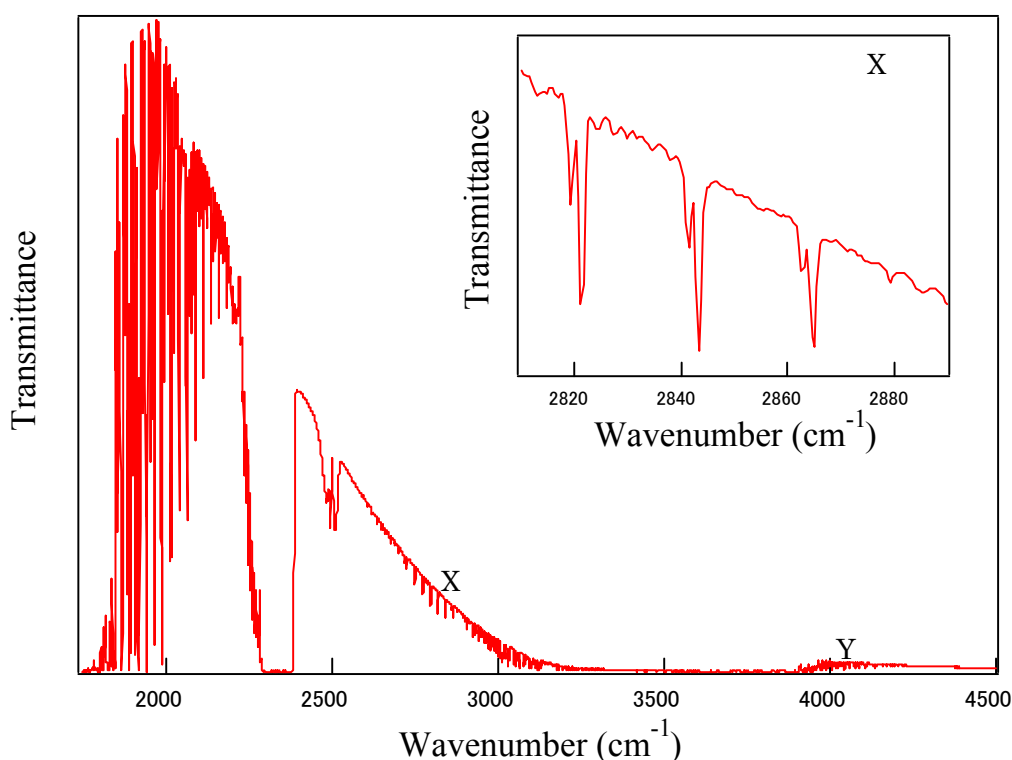


Figure Infrared absorption spectrum of fumarolic gas obtained from a remote observation using an FTIR equipped with a telescope. X and Y denote hydrogen halides.

- a) Describe chemical formula of X and Y.
- b) As shown in the inset, the absorption bands of “X” split. This split is caused by the isotopic composition of the halogen in “X” has an isotope abundance ratio of 3:1. List the two isotopes in order of decreasing abundance.

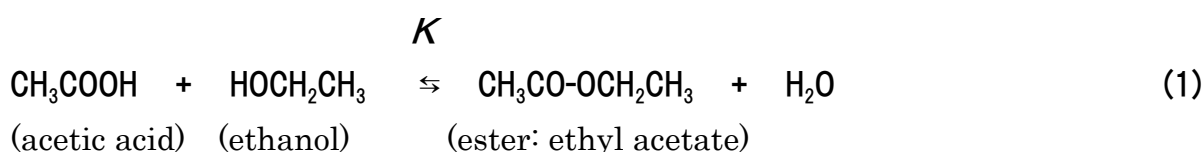


Problem 23: Introduction to macromolecular chemistry

The presentation of concepts of macromolecules (often called “polymers”) in 1925 by the Nobel Prize chemist, Dr. H. Staudinger (Germany), opened a fascinating world of new organic materials presently utilized as plastics, fibers, rubbers and so on.

Macromolecules are roughly classified into two categories, vinyl and non-vinyl polymers. Unlike the former, which are usually prepared from corresponding vinyl monomers (= α -olefins) by the chain polymerization processes in the presence of initiators or catalysts, the latter are usually obtained by the step polymerizations of (combination of) bifunctional monomers, such as $\text{H}_2\text{N-R-COOH}$ (to give polyamides), HO-R-COOH (polyesters), $\text{H}_2\text{N-R-NH}_2 + \text{HOOC-R'-COOH}$ (polyamides), $\text{HO-R-OH} + \text{HOOC-R'-COOH}$ (polyesters), etc. As easily understood from the last two instances of the step polymerization between the bifunctional monomers, the stoichiometric balance of component monomers is one of the most important factors in obtaining high molecular weight polymers.

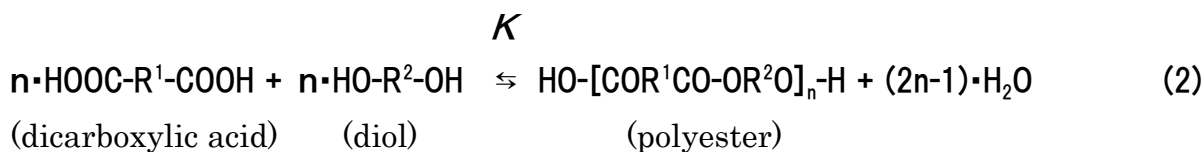
When the elementary processes of step polymerization are reversible, such as esterification equilibria, it is also a matter of importance to shift the equilibria rightward. Here, we'd like to discuss the relation between the equilibrium state and the length of polymers derived from the stoichiometric mixture of bifunctional monomers. Eq.(1) is a typical example of an esterification reaction where the equilibrium constant is relatively small, such as $K \rightleftharpoons 4.20$ at 78°C (boiling temperature of ethanol).



a) **When the esterification reaction of eq.(1) is equilibrated from each 1.00 mol of starting material, calculate the amount of ethyl acetate (g).**

Replace the monofunctional molecules in eq.(1) with a dicarboxylic acid and a diol, the corresponding polycondensation reaction may produce linear chain polyesters.

Although the polycondensation is composed of multi-step equilibria, the representation is often simplified as eq.(2) supposing the same equilibrium constant in each step.



The **length** of polymer chain is very important in respect to material chemistry. The long chain polymers may provide enough mechanical strength to fabricate textiles and thin films. In turn, the shorter ones are useful as adhesives, coatings, detergents, etc. In order to discuss on the polymer **length**, it is easier to think about the **degree of polymerization** (abb. X)^{*1)} rather than the molecular weight of which calculation is dependent on the structures of R^1 and R^2 . For instance in eq.(2), X is equal to 1 for the dicarboxylic acid or the diol, whereas it is $2n$ for the polyester (note that the structure in the brackets is already “dimer”)^{*2)}. Because a polymer is a mixture of long, middle and short chain molecules, X is the averaged number^{*1)}. The HO- and -H groups attached out of the brackets in eq.(2) are known as the end groups, and the -COR¹CO-OR²O- group is known as the repeating unit of which the structure is already a dimeric conjunction as described. Therefore, the **unit molecular weight**, M_u , in the case of eq.(2) is defined as follows ;

$$M_u = \text{molecular weight of the repeating unit} \div 2 \quad (3)$$

When the average molecular weight of a polymer is represented by M ^{*3)}, the relationship among X , M and M_u is given as follows ;

$$X = (M - \text{weight of end groups}) / M_u \quad (4)$$

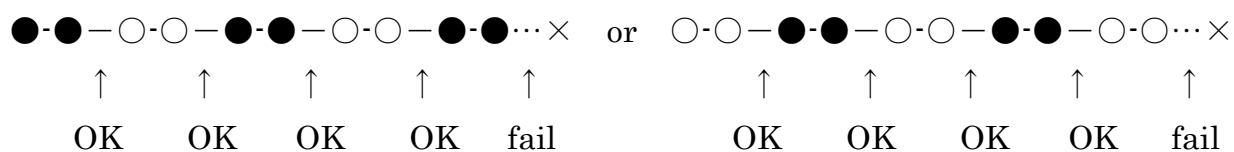
As understood from the calculation in a), when the equilibrium constant of the designated reaction is relatively small, considerable amounts of starting materials remain unreacted even at the equilibrium state. The quantity of product can be determined by the analysis of the consumption of functional groups. Before making discussions, we define “the **degree (extent) of reaction**”, p , as follows ;

$$\begin{array}{l}
 \text{degree of reaction} = p (\leq 1) = \\
 [\text{amount of unreacted functional groups}] \div [\text{amount of initial functional groups}] \quad (5)
 \end{array}$$



For instance, in eq.(1), starting from each 1.00 mol of bifunctional monomers and reaching $p = 0.80$ after being reacted for a certain period, then 0.80 mol of the ester is obtained.

In organic syntheses, $p \times 100$ is equal to the yield (%). If one can achieve $p = 0.80$, it is generally satisfactorily high yield. However, $p = 0.80$ is not good enough in the step polymerization syntheses. As represented below, $p = 0.80$ means concomitant success 4 out of 5-times — with one failuer, meanwhile. (●-● and ○-○ represent the dicarboxylic acid and diol residues, respectively.). X is ended with **5.0**, in this case.



Consequently, $p \rightarrow 1$ should be realized to prepare the polymers with large X . Dr. Wallace H. Carothers (USA) had studied the relationship between X and p , and presented eq.(6) in conclusion.

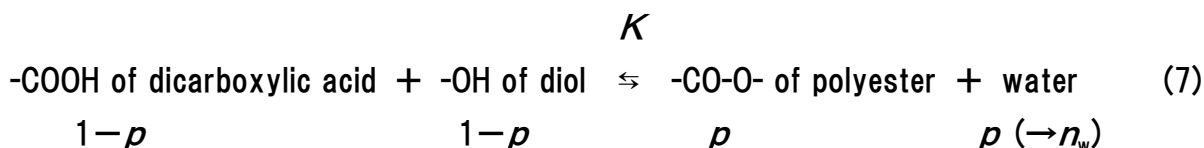
$$X = 1/(1-p) \quad [\text{Carothers eq.}] \quad (6)$$

Although even amateurs can easily prepare vinyl polymers, such as polystyrene, with $M \geq 10^6$ (corresponding to $X \geq 10^4$) by the chain polymerization of α -olefin monomers, exquisitely fabricated commercial polycondensation polymers, such as nylon-6,6 or PET [=poly(ethylene terephthalate), or poly(oxyethyleneoxyterephthaloyl)], carry M of merely $1 \sim 8 \times 10^4$. Typically, M of ordinary PET is 4.000×10^4 , corresponding to $X \doteq 416.3$ (cf. $M_u = 96.09$), where the p value of the polycondensation between terephthalic acid and 1,2-ethanediol should exceed 0.9976 [since $416.3 \geq 1/(1-p)$ from eq.(6)]. It is understood that much effort is necessary for the production of step polymerization polymers with high M or X .

As estimated in a), elaborative work is necessary to accomplish the reaction condition of $p \rightarrow 1$ since K is relatively small in the case of esterification polycondensation. The by-product removal in accordance with the reaction progress is one of the schemes to realize $p \rightarrow 1$. For easier consideration, let us simplify eq.(2) into eq.(7); starting from each (exactly) 1 mol of -COOH (of dicarboxylic acid) and -OH (of diol), p mol of ester linkage is formed at the equilibrium, whereas each $(1-p)$ mol of -COOH and -OH groups



remain unreacted. To shift the equilibrium rightward, the quantity of water should be diminished from ρ mol to a negligibly small amount, n_w mol.



b) Represent K by using ρ and n_w .

c) From the eq. derived in b) and the Carothers eq., represent X as a function of β ($= K/n_w$). If logically permitted, the equation should be simplified as far as possible, considering $\rho \leq 1$ and $\beta \gg 1$.

d) Calculate the upper limit of n_w in order to accomplish $X \geq 100$, supposing $[-\text{COOH}]_0 = [-\text{OH}]_0 = 1.00$ mol and $K = 4.00$. The answer should be given as three significant figures.

Footnotes

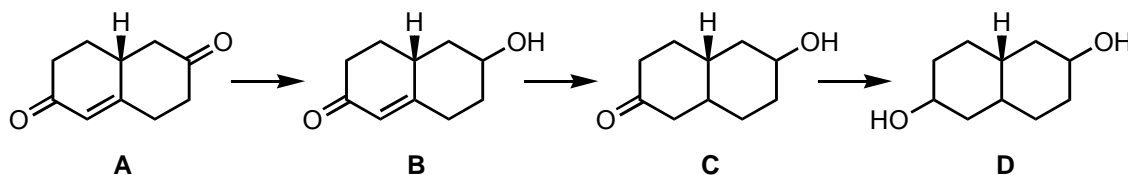
*1) It is usually represented as “the number-average degree of polymerization” and abbreviated by X_n .

*2) In the case of polymers derived from bifunctional monomers carrying different kinds of functionalities such as $\text{H}_2\text{N-R-COOH}$ or HO-R-COOH , because the repeating unit in such a polymer structure, $\text{H} \cdot [\text{HN-R-CO}]_n \cdot \text{OH}$ or $\text{H} \cdot [\text{O-R-CO}]_n \cdot \text{OH}$, is *monomeric*, the value of n directly corresponds to X .

*3) It is usually represented as “the number-average molecular weight (molecular mass)” and abbreviated by M_n . Definition : $M_n = (\sum M_i N_i / \sum N_i)$, where M_i and N_i are the molecular weight and the number of the i -th macromolecular thread, respectively.

Problem 24: Reduction of carbonyl compounds

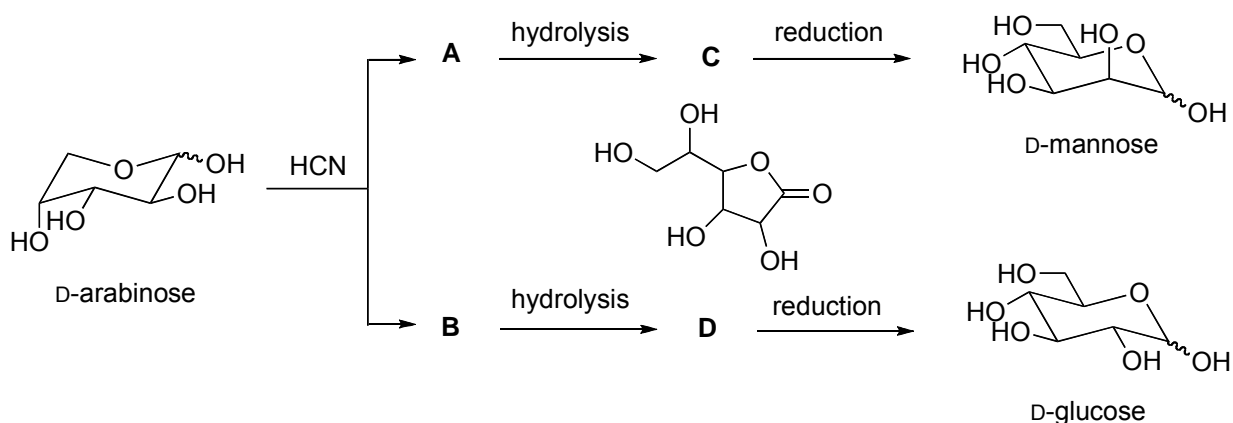
Reduction of the one of the carbonyl groups in compound **A** gives compound **B**, which contains two stereoisomers, **B1** and **B2**. After separation of these isomers, the reductions of carbon-carbon bond are carried out to give compound **C**, as a mixture of two kinds of stereoisomers, respectively from **B1** and **B2**. By the separation of the isomers, four kinds of products **C_{ij}** ($i, j = 1, 2$) are obtained. Furthermore, these four products are applied to the reduction of another carbonyl group to give compound **D**, which is again a mixture of two kinds of stereoisomers in each reaction. After the separation of stereoisomers of each reaction, eight kinds of products **D_{ijk}** ($i, j, k = 1, 2$) are obtained.



- Are there any identical compounds in the eight kinds of products **D_{ijk}** ($i, j, k = 1, 2$)? If so, draw the structures of all the compounds that meet the requirements.
- Are there any compounds, in which optical rotation is principally zero degrees, in the eight kinds of products **D_{ijk}** ($i, j, k = 1, 2$)? If so, draw the structures of all the compounds that meet the requirements.
- Are there any compounds which are a pair of optical isomers in the eight kinds of products **D_{ijk}** ($i, j, k = 1, 2$)? If so, draw the structures of all the compounds that meet the requirements.

Problem 25: Kiliani-Fischer synthesis

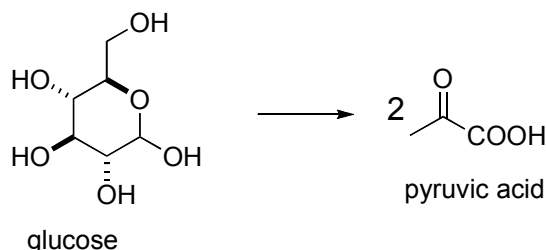
D-Arabinose is predominantly found in the cyclic form, which is in equilibrium with a minute amount of the open form. Treatment of D-arabinose with hydrogen cyanide (HCN) yields a diastereomeric mixture of cyanohydrins **A** and **B**. Hydrolysis of cyanohydrins **A** and **B** yields their corresponding carboxylic acids, which lactonize on heating and form the 5-membered lactones **C** and **D** (the planar structures of the lactones are shown below), respectively. The lactones **C** and **D** can be reduced with sodium amalgam (or sodium borohydride) to yield D-mannose and D-glucose, respectively. This chain-extension procedure is known as Kiliani-Fischer synthesis.



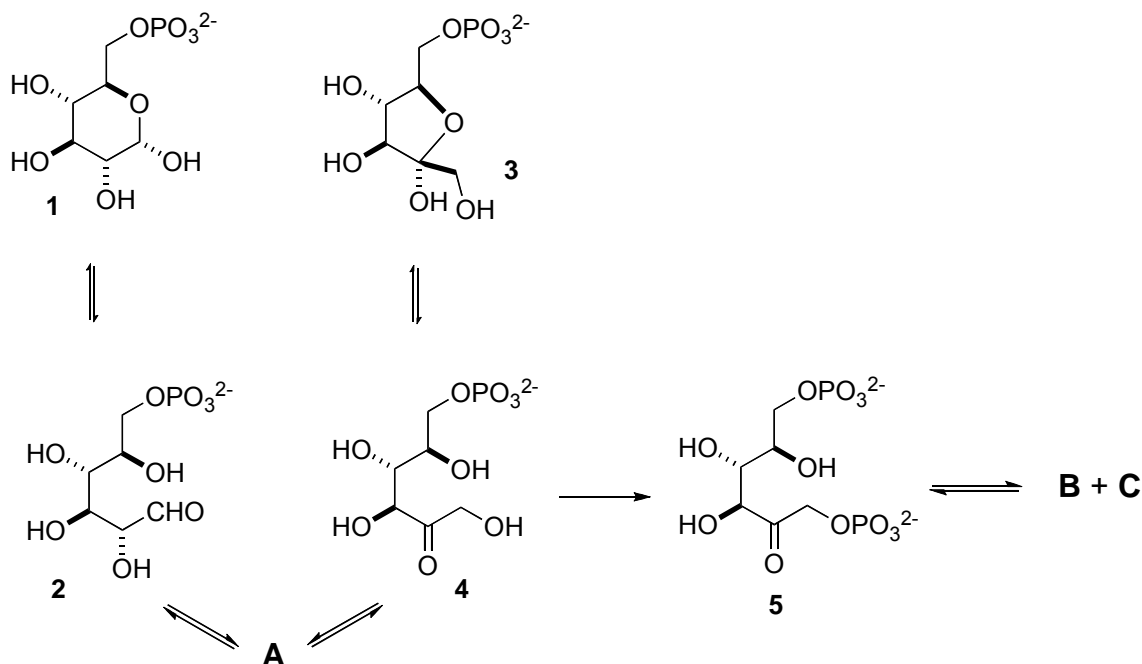
- Draw a Fischer projection of the open-form D-arabinose.
- Draw Fischer projections of the cyanohydrins **A** and **B**.
- Draw stereostructures of the lactones **C** and **D**.

Problem 26: Glycolysis

Glucose is used as an energy source for short-term activity in most organisms. Glucose is metabolized into pyruvic acid via a series of reactions catalyzed by various enzymes.



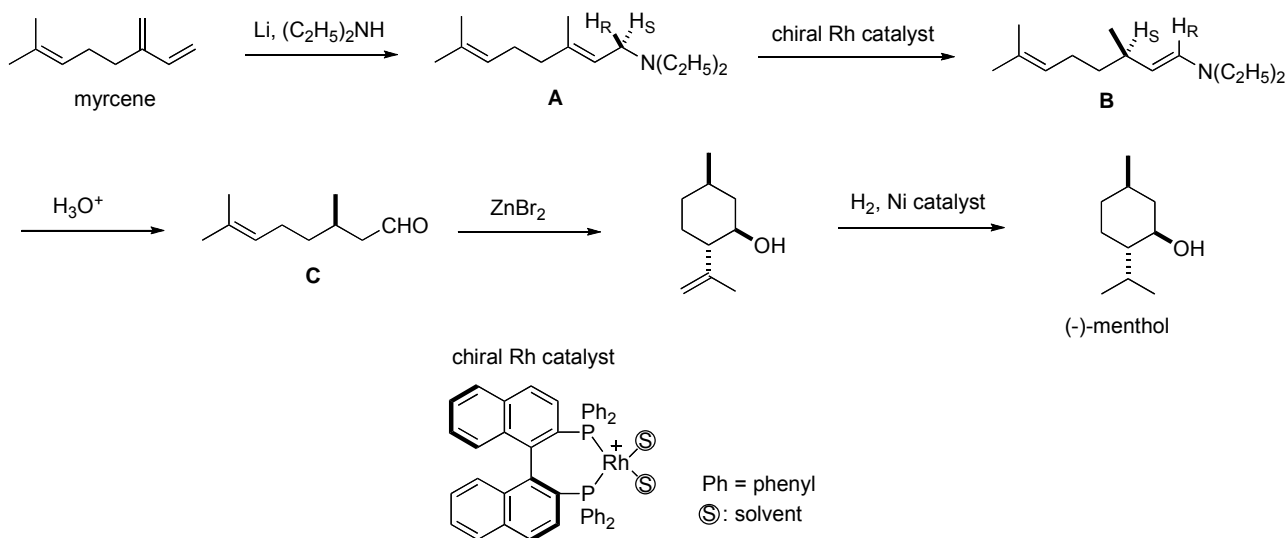
The first half of the metabolic pathway proceeds as follows. The first step is the phosphorylation of α -glucose to form α -glucose-6-phosphate (**1**). Next, **1** is transformed into open-form glucose-6-phosphate (**2**), which isomerizes to open-form fructose-6-phosphate (**4**). This isomerization reaction occurs through the tautomer **A** of **2** and **4**. Phosphorylation of **4** affords fructose-1,6-diphosphate (**5**), which cleaves into carbonyl compounds **B** and **C** by retro-aldol reaction. Compounds **B** and **C** are able to interconvert via the common tautomer as similar to **2** and **4**, and both produce pyruvic acid.



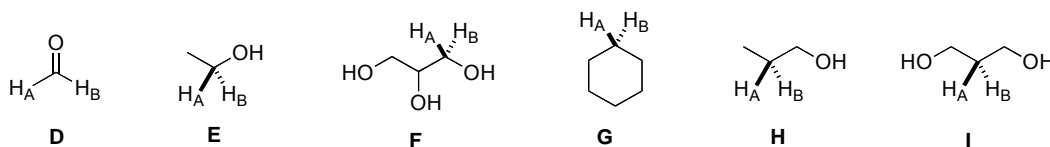
- A solution of glucose was treated with an equal amount of phenylhydrazine in acetic acid. Draw the structure of the major product.
- Draw Fischer projections of glucose-6-phosphate (**2**) and fructose-6-phosphate (**4**), respectively.
- Draw the structure of tautomer **A**.
- Draw the structures of carbonyl compounds **B** and **C**.

Problem 27: Menthol synthesis

(-)-Menthol is a major component of the taste and fragrance of peppermint and is widely used in cakes, cosmetics, and tooth powder, etc. (-)-Menthol is anodyne and is used as medicine. (-)-Menthol can be supplied from natural resources such as peppermint oil, but is now synthesized industrially as shown below. It is said that the synthesis supplies about 1/3 of the world demand of (-)-menthol. A key step of the synthesis is 1,3-asymmetric hydrogen migration reaction from amine **A** to enamine **B**. A rhodium catalyst with a chiral bidentate ligand developed by Ryoji Noyori (Nobel Prize Winner, 2001, Chemistry) can precisely distinguish enantiotopic hydrogens, H_R and H_S , and selective migration of H_S provides optically pure enamine **B**.



- a) Which molecules include two enantiotopic hydrogens (H_A and H_B) that are stereochemically similar to two hydrogens (H_R and H_S) of amine **A**? Select your answer(s) from all the symbols of the following molecules **D-I**.

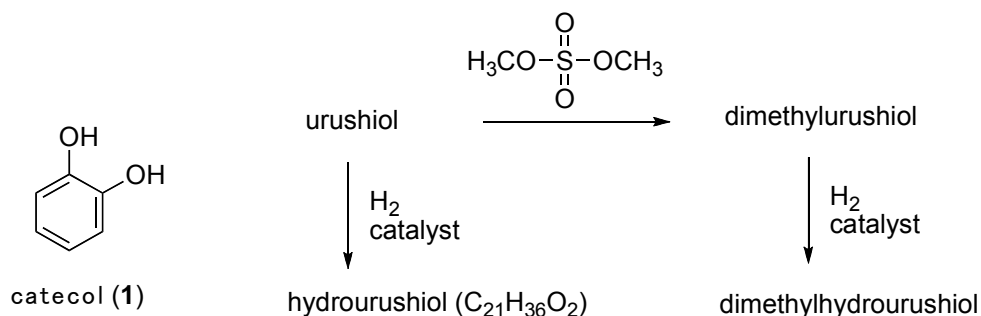


- b) Propose a reasonable reaction mechanism of hydrolysis of enamine **B** to aldehyde **C**.
 c) Draw the most stable conformer of (-)-menthol.
 d) Treatment of (-)-menthol with dilute sulfuric acid causes a dehydration reaction. Predict the major product.
 e) (-)-Menthol is a monoterpene composed of two isoprene units. Surround the isoprene unit of (-)-menthol in a line.

Problem 28: Structure studies of urushiol

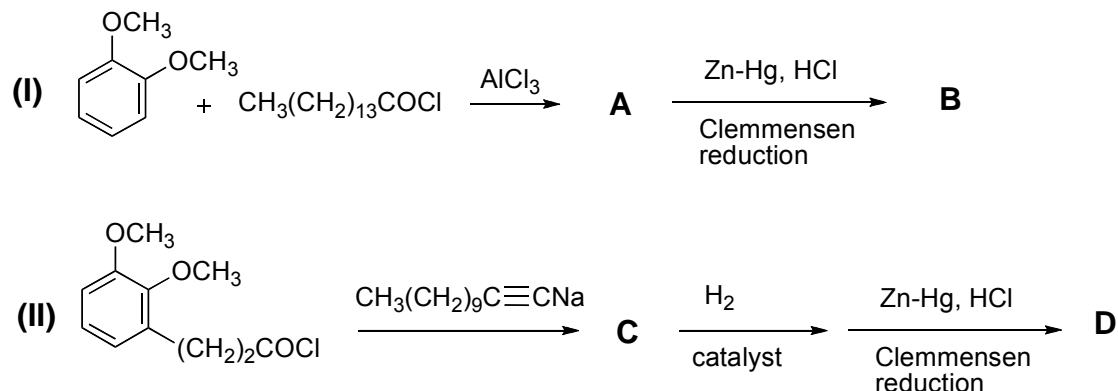
Japanese lacquer (Urushi in Japanese) is a natural paint that has been used since ancient times and is made from the sap of the lacquer tree. Japanese lacquer is glossy and beautiful and is used for lacquer ware and traditional craft objects. The major component of the sap of the lacquer tree is urushiol. Oxidation and polymerization of urushiol catalyzed by the enzyme (laccase) contained in a lacquer tree solidify the sap of the lacquer.

The chemical structure of urushiol has been studied from the beginning of 20th century and was determined by Professor Rikou Majima in 1918. Urushiol was a mixture of compounds with similar chemical structures, and even determination of its molecular formula is very difficult because it was very unstable substance that polymerized easily. Since destructive distillation of urushiol gave a mixture of catechol (**1**) and unsaturated hydrocarbons, urushiol seemed to be catechol derivatives with unsaturated alkyl chains. In addition, treatment of urushiol with dimethyl sulfate afforded dimethylurushiol. Furthermore, catalytic hydrogenation of urushiol under ordinary hydrogen pressure just developed by Willstätter at that time provided pure hydrourushiol as crystals, and the molecular formula of hydrourushiol was determined as $C_{21}H_{36}O_2$. This advanced structure studies of urushiol greatly.

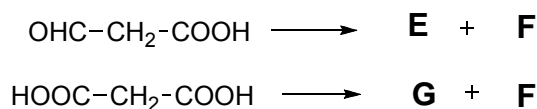


- a) If the saturated alkyl chain of urushiol is one kind and is not branched, there are two possible structures for hydrourushiol. Draw each structure. Show the alkyl group such as $(CH_2)_n-CH_3$.
- b) To determine the structure of hydrourushiol, the following two syntheses (**I**) and (**II**) were performed. Among synthesized compounds **B** and **D**, compound **D** was identical to dimethylhydrourushiol derived from natural urushiol. Thus, the location of the

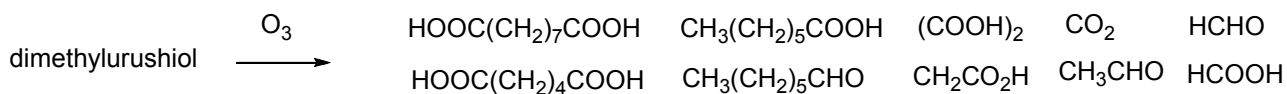
unsaturated alkyl group of urushiol was determined. Draw the structure of the synthetic intermediates **A** and **C**.



- c) To determine a number and a position of the double bonds of the unsaturated alkyl chain of urushiol, ozonolysis of dimethylurushiol was carried out. Because urushiol was a mixture, various carbonyl compounds were provided by this experiment (question 4, see below). However, carbonyl compounds with three carbons ($\text{OHC-CH}_2\text{-CO}_2\text{H}$ and $\text{HOOC-CH}_2\text{-COOH}$) are not detected by this experiment. This is because both carbonyl compounds decompose as in the following equations. Show the chemical formula of **E**, **F**, and **G**.



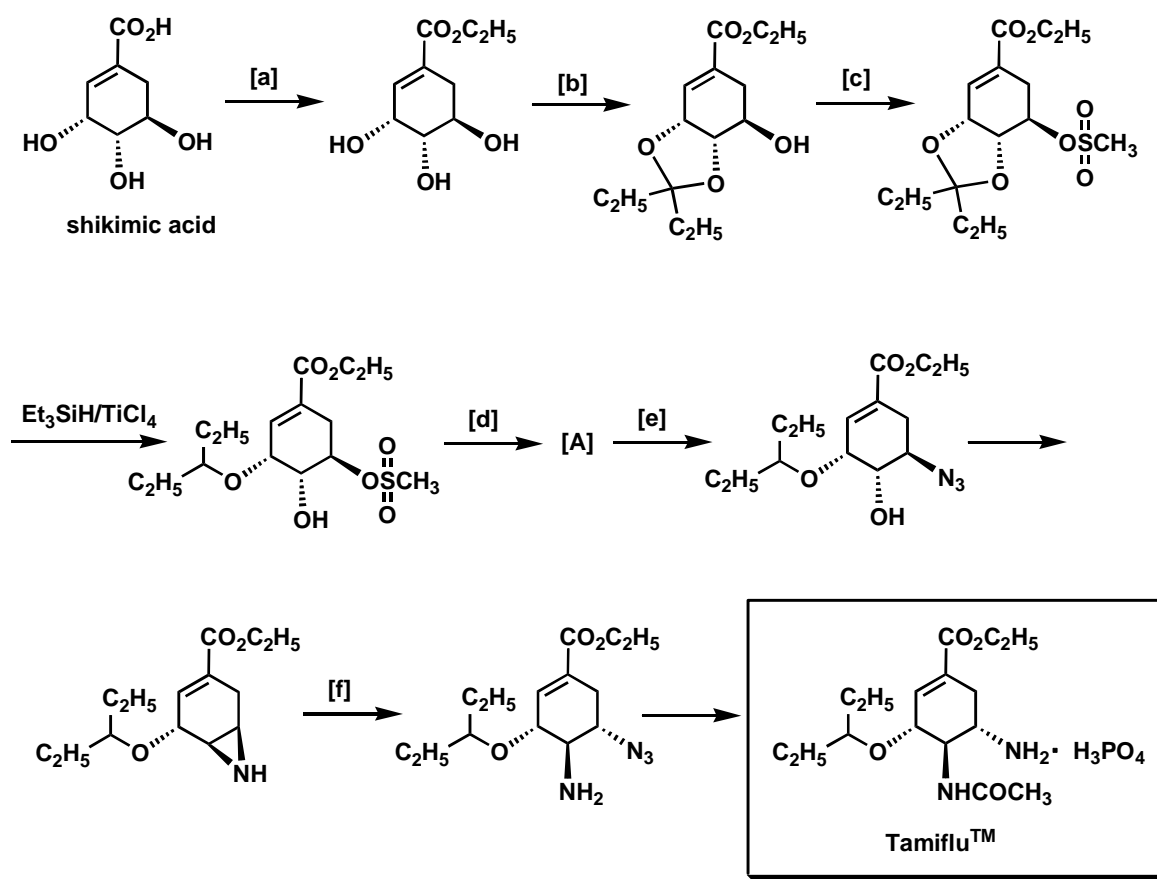
- d) Carbonyl compounds obtained by ozonolysis of dimethylurushiol are shown below. You may assume that all of the double bonds and benzene rings were cleaved. Based on the experiment results, draw three structures of urushiol among possible urushiols. Show the unsaturated alkyl chain to determine the position of the double bond as in $(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{CH}_3$. You do not need to consider the geometry of the double bond (cis or trans).



Problem 29: Synthesis of Tamiflu

Shikimic acid is not only an important intermediate in biosynthesis, but also a useful chiral reagent leading to the production of various valuable medicines because the molecule of shikimic acid contains several chiral carbons.

Tamiflu is now a specific medicine for the inhibition of influenza virus propagation, and can be synthesized starting from shikimic acid which was derived from natural Star anise (*Illicium verum*). A part of the synthetic scheme is shown below.



- Show chemical reagents necessary for the transformations of **a**, **b**, **c**, **d**, **e**, and **f** in the above scheme.
- Show the reaction mechanism for the transformation of **b**.
- Show the molecular structure of intermediate **A**.
- How many stereoisomers are possible in the molecular structure of Tamiflu?



Problem 30: Nuclear magnetic resonance (NMR) spectra of isomers of C_4H_8

There are six isomers of C_4H_8 .

- Draw the structural formulas of all the isomers.
- One of the isomers has only one singlet peak in its proton NMR spectrum. Name this isomer.
- One of the isomers has two singlet peaks in its proton NMR spectrum. Name this isomer. Also estimate the area ratio of the two peaks.

Problem 31: Nuclear magnetic resonance (NMR) spectrum of [18]annulene

[18]Annulene is an aromatic compound containing 18 carbon atoms. The annulene molecule has an almost planar structure with 6 inner hydrogens (H_{in}) and 12 outer hydrogens (H_{out}). The 1H NMR spectra of [18]annulene at 213 K and 383 K are shown in Fig. 1.

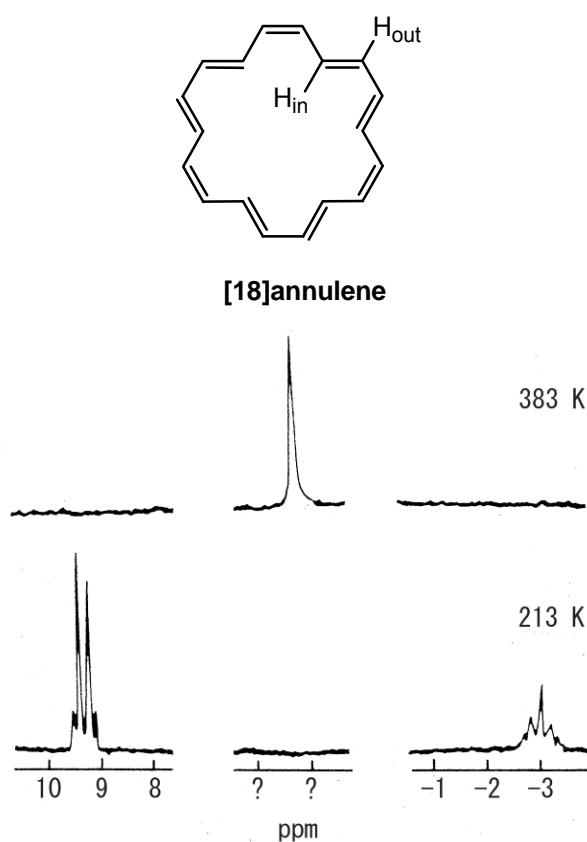


Fig.1

- In the spectrum obtained at 213 K, estimate the area ratio of the peaks at 9.3 and -3.0 ppm.
- Explain why the spectrum obtained at 383 K has only one singlet peak while that obtained at 213 K has two multiplet peaks.
- Estimate the position of the singlet peak in the spectrum obtained at 383 K.



Practical Problems



Advanced Level Fields

Practical

1. Synthesis techniques: filtrations, drying of precipitates, thin layer chromatography
2. Theory and practice of extraction with immiscible solvents

Safety

- The safety (S) and risk (R) phrases associated with the substances used are provided in each problem. See Appendix B of the Regulations for the meanings of the phrases.
- The experiments are designed to be carried out only in properly equipped chemical laboratories under competent supervision.
- Safety cautions must be provided by the Mentors. Major cautions are shown below.
 - ✓ Protect the eyes and body in an appropriate manner.
 - ✓ Never pipette solutions using mouth suction.
 - ✓ Use a fume hood if indicated.
- Disposal procedures are not included in the Preparatory Problems, as regulations are different in each country.



Problem 32:

Colloid titration: titration of a cationic surfactant with polyanion

Colloid titration was first proposed by Hiroshi Terayama in 1948 and has been developed primarily in Japan. Colloid titration is based on the interactions of charged colloids (charged polymers, polycations, and polyanions) with inversely-charged colloids (charged polymers and molecules capable of forming colloids). The reactions employed for colloid titration entail rapid precipitation, which leads to a cloudy suspension. Precipitation is completed when the positive and negative charges are equal. The end point of colloid titration is detected by changes in the color of dyes upon interaction with colloids—typically the adsorption and desorption of dyes on colloids as well as the association of dyes with colloids. Colloid titration can be employed for the quantitative analysis of various colloidal species, such as surfactants, as well as for the determination of the charges of natural colloids, such as clay particles and humic acid.

In this experiment, you will determine the amount of a cationic surfactant, benzyldimethyltetradecylammonium chloride, using standard potassium poly(vinylsulfate) (PVSK). The end point is detected using bromochlorophenol blue (BCPB). BCPB is initially associated with the cationic surfactant, and its color changes upon release from the cationic surfactant, which completely interacts with PVSK at the end point.

Chemicals

- 0.25 mol L⁻¹ acetic acid
- benzyldimethyltetradecylammonium chloride (Zephiramine, Zeph; preferably with a concentration ranging from 5×10^{-5} to 8×10^{-5} mol L⁻¹)
- bromochlorophenol blue (BCPB; indicator)*
- 0.0025 mol L⁻¹ potassium poly(vinylsulfate) (PVSK; titrant)**
- 0.01 mol L⁻¹ sodium hydroxide (NaOH)

* Prepare by dissolving the required amount of BCBP in 5 mL of 0.01 mol L⁻¹ NaOH solution and diluting it with 200 mL of water.

** The concentration is defined as being that of its monomer unit, C₂H₃SO₄K. Its equivalent weight is 162.2, provided that the purity (degree of esterification) of PVSK is 100%.

Glassware

- beaker (300 mL)
- burette (25 mL)
- conical beaker (200 mL)
- volumetric pipette (10 mL)



Procedures

- (1) Dissolve 0.048 g of BCPB in 5 mL of 0.01 mol L⁻¹ NaOH solution in a 300 mL beaker, and dilute it with 200 mL of water. The final concentration of BCPB should be $\sim 4 \times 10^{-4}$ mol L⁻¹.
- (2) Take precisely an aliquot (10 mL) of the Zeph sample solution at about 1.0×10^{-4} mol L⁻¹ and add it to a 200 mL conical beaker using a volumetric pipette; then add 1 mL of 0.25 mol L⁻¹ acetic acid and 1 mL of the BCPB solution. Check the pH of the solution using pH test paper. If the pH is not around 3.3, add acetic acid or NaOH solution to achieve the desired pH of 3.3.
- (3) The initial color is blue. Carefully drop the standard PVSK solution into the sample solution while stirring continually. Before the end point is reached, the solution may become somewhat cloudy. If the solution becomes cloudy, drop the standard PVSK solution in slowly. At the end point, the color should change to yellow.
- (4) Read the volume of the PVSK solution added.

Questions

1. Calculate the Zeph concentration in mg L⁻¹. The reaction ratio of the monomer unit of PVSK to Zeph is 1:1.
2. Why does the solution become cloudy, as the end point is approached? Why does the solution become clear again after the end point is reached?

Substance		R phrases	S phrases
acetic acid	0.25 mol L ⁻¹	10-35	23-26-45
benzyltrimethyltetradecylammonium chloride (Zephiramine)	$\sim 5-8 \times 10^{-5}$ mol L ⁻¹ aq. solution	21/22-34-50	36/37/39-45-61
bromochlorophenol blue (BCPB)	solid	none listed	none listed
potassium poly(vinylsulfate) (PVSK; or poly(vinyl sulfate) potassium salt)	0.0025 mol L ⁻¹ aq. solution	36/37/38	26-36
sodium hydroxide	0.01 mol L ⁻¹ aq. solution	35	26-37/39-45



Problem 33:

Analysis of zinc-aluminum alloy by EDTA titration

Alloys containing aluminum and zinc as primary alloying elements have been developed in Japan for use in industry. The most famous example—extra super duralumin “7075”—is the strongest aluminum alloy used in aircraft manufacturing. Recently, a novel zinc-aluminum alloy that exhibits an interesting mechanical property has also been developed. The alloy exists as a solid at room temperature but is easily spread like a starch syrup under appropriate mechanical tension. This property is known as “super-plasticity,” which facilitates industrial uses of the alloy, including use as a high-performance and semi-permanent seismic damper for protecting buildings from earthquakes. This unique property arises from the alloy’s fine-grained microstructure containing 7%–50% aluminum by weight.

Composition is a fundamental parameter for developing such advanced alloys. In this experiment, assuming the composition assay of this type of alloy, you will be given a test solution which simulates a digested sample of the alloy; 50 mL of the solution contains 30–35 mg of zinc and 10–15 mg of aluminum, and is acidified to pH 1 using hydrochloric acid. You will be required to determine the concentrations of Zn^{2+} and Al^{3+} in the sample solution by titration utilizing ethylenediaminetetraacetic acid (EDTA) as a chelating agent. Masking and back-titration techniques should also be employed.

Chemicals

- test solution (prepare as described above)
- 0.1 mol L⁻¹ acetic acid solution
- ammonium fluoride
- 0.01 mol L⁻¹ ethylenediamine-*N,N,N',N'*-tetraacetic acid, disodium salt, dihydrate (EDTA2Na•2H₂O) standard solution (accurately prepared)
- 10% (w/v) hexamethylenetetramine (hexamine) solution
- 0.1% methyl orange (MO) solution
- 0.1% xylenol orange (XO) ethanol/water (20/80) solution
- 0.01 mol L⁻¹ Zn²⁺ standard solution (accurately prepared using ZnSO₄•7H₂O)

Apparatuses and glassware

- burette (25 mL, 1 rack)
- Erlenmeyer flask (200 ml × 5)
- hot-plate × 1
- magnetic stirrer × 1
- Pasteur pipette (dropper) × 4
- pipette (10 mL × 2, 30 mL × 1)
- safety bulb × 1
- stirring bar (coated with Teflon) × 4



Procedures

- (1-1) Pipette 10 mL of the sample solution into a 200 mL Erlenmeyer flask and place a stirring bar in the flask. Start stirring the solution on a magnetic stirrer and add a few drops of MO indicator. Add 30 mL of a 0.01 mol L^{-1} EDTA standard solution. To adjust the pH of the mixture to ca. 3.5, introduce (dropwise) a 10% hexamine solution into the flask until the MO indicator shows a slight color change, from red to orange. Place the flask on a hot-plate and boil the mixture for a few minutes; then place the flask in an ice bath to cool the mixture. After cooling, place the flask on the magnetic stirrer and add a few drops of the XO indicator solution to the mixture.
- (1-2) Adjust the pH to ca. 5.5 as follows: stir the mixture gently, deliver the 10% hexamine solution dropwise into the flask until the XO indicator changes color from yellow to slightly purplish, and then, add a 0.1 mol L^{-1} acetic acid solution in drops until a clear yellow color reappears. Next, titrate the mixture using $0.01 \text{ mol L}^{-1} \text{ Zn}^{2+}$ standard solution until the color turns to purple. The volume of titrant used in step 1-2 is defined as "A" mL. (Caution: Do not discard the titrated mixture; you will need to titrate it continuously in step 2-1.)

Note:

Determining the end point is somewhat difficult, since the color changes gradually from yellow to purple as the end point is approached. When the color is close to purple, read the burette and then add another drop of titrant; if there is a perceptible color change, read the burette again and add another drop. Repeat this process until a drop of titrant causes no color change, and then record the preceding burette reading. If EDTA is still present, the yellow color will return; add more titrant until the color remains purple for at least one minute.

- (2-1) Add ca. 1.0 g of NH_4F to the titrated mixture in step 1-1, and heat it on the hot-plate until the mixture boils; note that heating results in the mixture's color returning to yellow. Remove the flask to an ice bath, and after the mixture cools, place the flask on the magnetic stirrer. If the clear yellow color has disappeared after cooling, add a 0.1 mol L^{-1} acetic acid solution dropwise until the color reappears. Next, titrate the mixture again using a $0.01 \text{ mol L}^{-1} \text{ Zn}^{2+}$ standard solution. The volume of the titrant used in step 2-1 is defined as "B" mL.



Questions:

1. In steps 1-1 and 1-2, why is the pH adjusted to ca. 3.5 and ca. 5.5 in a stepwise manner? Explain the reason considering the difference in the stability of each metal-EDTA and -hydroxyl complex.
2. What is the role played by the ammonium fluoride added to the mixture in step 2-1?
3. Show the formula for calculating the concentration of the Al^{3+} and Zn^{2+} ions in the sample solution based on the results of each titration (A and B).
4. Calculate the concentrations of Al^{3+} and Zn^{2+} ions in the sample solution in mol L^{-1} .
5. Assuming that the alloy contains only Al and Zn, calculate the composition of the alloy in percent by weight.

Substance		R phrases	S phrases
acetic acid	0.1 mol L^{-1} aq. solution	10-35	23-26-45
ammonium fluoride		23/24/25	26-45
ethylenediamine- <i>N,N,N',N'</i> - tetraacetic acid, disodium salt, dihydrate	0.01 mol L^{-1} aq. solution	none listed	none listed
Hexamethylenetetramine	10% aq. solution	11-42/43	16-22-24-37
methyl orange	0.1% aq. solution	25	45
ethanol	liquid	11	7-16
xlenol orange	0.1% ethanol (20%) / aq. solution	none listed	none listed
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.01 mol L^{-1} aq. solution	22-41-50/53	22-26-39-46- 60-61



Problem 34:

Preparation of urea-hydrogen peroxide

Hydrogen peroxide (H_2O_2), which can oxidize a variety of inorganic and organic compounds under mild reaction conditions, is widely used in industry, particularly the chemical industry. Because water is the only degradation product of H_2O_2 , it is an environmentally friendly oxidant. The adduct of hydrogen peroxide with urea through hydrogen bonding is considered to be a useful “solid form” of hydrogen peroxide (urea-hydrogen peroxide: UHP). UHP is an inexpensive and safe oxidant similar to aqueous hydrogen peroxide. Since UHP is a stable solid, it is more convenient to use than aqueous hydrogen peroxide.

In this experiment, you will prepare UHP by mixing urea and aqueous hydrogen peroxide. UHP will be obtained as white needle crystals via slow evaporation. The hydrogen peroxide content will be determined by redox titration using potassium permanganate.

Chemicals

- 30% hydrogen peroxide
- manganese dioxide
- 0.02 mol L^{-1} potassium permanganate (after standardization)
- urea

Apparatuses and glassware

- beaker (100 mL)
- burette (25 mL)
- conical flask (300 mL)
- Erlenmeyer flask (10 mL)
- filter paper
- graduated pipette
- test tube
- volumetric flask (100 mL)
- volumetric pipette (10 mL)
- water bath on a heating plate
- watch glass (preferably ca. 20 cm in diameter)



Procedures

- (1) Pipette about 3.4 mL of 30% hydrogen peroxide into a 10 mL Erlenmeyer flask using a volumetric pipette and add 1.2 g of urea (hydrogen peroxide : urea = 3 : 2 molar ratio). Heat a water bath to 60 °C (taking care to regulate the temperature to avoid hydrolysis of urea). Place the Erlenmeyer flask containing the mixture in the water bath and heat it for a few minutes to yield a clear, colorless solution. Transfer the solution to a watch glass for slow evaporation.
- (2) Needle-like crystals will gradually develop from the solution. After the crystallization is completed, place the needle-like crystals on a filter paper to remove the moisture. Weigh the crystals.
- (3) Place about 0.1 g of the crystals in a test tube and add water. Put a trace of manganese dioxide in the test tube to confirm the formation of an oxygen bubble.
- (4) Accurately weigh approximately 0.62 g of the crystals and transfer them to a 100-mL beaker. Add 50 mL of water to dissolve the crystals. Transfer the solution to a 100-mL volumetric flask and dilute it with water to the 100 mL mark. Pipette 10 mL of the solution into a 300-mL conical flask. Add 200 mL of water and 20 mL of diluted sulfuric acid (10%).
- (5) Titrate the solution with standard 0.02 mol L⁻¹ potassium permanganate until a faint pink color persists for 15 s. Be sure to add the standard 0.02 mol L⁻¹ potassium permanganate slowly to prevent the formation of manganese dioxide. As a blank test, the same titration should be done without the crystals.

Questions

1. Calculate the hydrogen peroxide contents (mass %) in the crystals.
2. Write a balanced equation for the reaction.
3. Calculate the theoretical yield of urea-hydrogen peroxide.
4. Calculate the percentage yield.

Substance		R phrases	S phrases
hydrogen peroxide	30% aq. solution	22-41	26-39
manganese dioxide	solid	20/22	25
potassium permanganate	0.02 mol L ⁻¹ aq. solution	51/53	61
urea	solid	none listed	none listed

Problem 35:

Separation of a dye mixture using thin-layer chromatography (TLC)

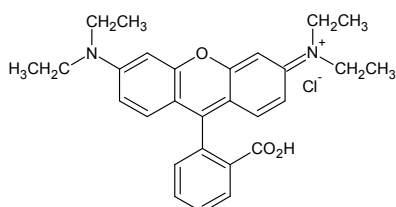
Since ancient times, organic dyes have been used for coloring cloth and leather. Numerous species of plants and animals have been used as sources of natural dyes. The extraction and purification of dyes as well as the dyeing process itself are sophisticated chemical processes. The first human-made (synthetic) organic dye, mauveine, was discovered as late as the 19th century. Since then, however, thousands of synthetic dyes have been used for various purposes extending beyond coloring, including indispensable uses for digital photo-recording media such as compact discs (CDs) and digital versatile discs (DVDs). The apparent color of a dye solution comes from the absorption of light preferred by the dye molecule. When a dye solution in a transparent vessel is seen against a white background, the complementary color of its absorption can be recognized.

In this experiment, you will learn the basic principles and procedures for separating and distinguishing individual dyes from their mixture.

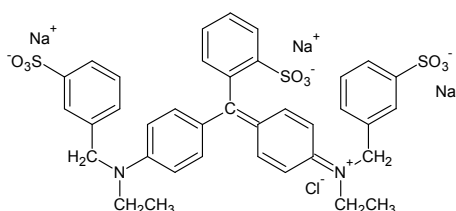
Chemicals

- organic dyes (respective names of dyes intentionally hidden)

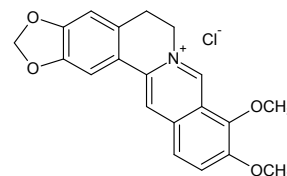
A



B



C



- methanol
- developer (mixture of methanol and water (90/10 = v/v))

Apparatuses and glassware

- glass capillary
- TLC plates

Code	Stationary phase
P-1	Silica modified by octadecylsilyl ligands
P-2	Silica modified by anion-exchange ligand
P-3	Silica modified by cation-exchange ligand

- wide-mouth bottle with cap (developing chamber) (× 3)

- *If P-2 and P-3 plates are not available, prepare them from modified silica gel and calcium sulphate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$; binder) (you can use silica gel with calcium sulphate instead of pure calcium sulphate). Typically, slurry modified silica gel and calcium sulphate in a methanol/water mixture (2/18) and homogenize the slurry using an electric blender. Spread the slurry on a glass plate. Dry and then activate it at 110-130 °C.

Procedures

Using a pencil, draw a starting line approximately 10 mm above the shorter edge of a silica gel plate.

- (1) Draw cross marks on the line as chromatography starting points.
- (2) Use a glass capillary to collect some of the sample solution, spot the solution lightly on one of the starting points, and dry the spot with a dryer, if necessary. Repeat this operation a few times to concentrate the sample in a small spot, measuring less than 2 mm in diameter.
- (3) Pour developing solvent into the respective wide-mouth bottles about 5 mm in height.
- (4) Close the caps and wait a few minutes until the bottles are saturated with solvent vapor.
- (5) Open the cap of one bottle and grip the upper edge of a TLC plate with tweezers. Place the TLC plate in the bottle so that the bottom of the plate is immersed in the solvent and the top of the plate is leaning against the wall of the bottle. The solvent should be drawn straight up.
- (6) Finish the development when the solvent front reaches about 10 mm below the upper edge of the TLC plate.
- (7) Take the TLC plate out and immediately mark the front line of the developing solvent with a pencil.
- (8) Record the shapes and colors of the spots.
- (9) Use the same steps to develop the other TLC plates.

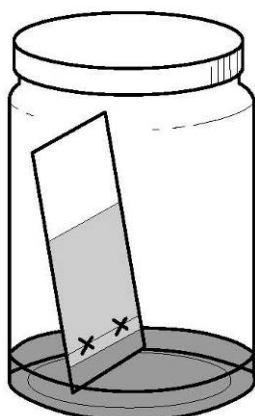


Fig. 35.1 TLC plate placed in a bottle with a cap.

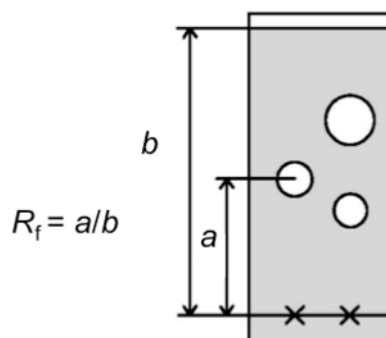


Fig. 35.2 TLC plate and developed spots.

Questions

I. TLC results

1. From the spots recorded on the TLC plates, calculate the R_f value of each dye on each plate.

$$R_f = a/b$$

a = distance from the starting point to the center of gravity of the sample spot.

b = distance from the starting point to the front of the developing solvent.

2. Determine the color of dyes **A**, **B**, and **C** by considering the nature of the surface of the TLC plate and the properties of the molecules (acidic or basic and hydrophilic or hydrophobic) anticipated by the structural formulae.
3. Explain concisely how you reached your conclusion.

II. Absorption spectra

The apparent color of a dye solution comes from the light absorption preferred by the dye molecule. We can obtain more in-depth information on dyes from their optical absorption spectra. The figure shows the absorption spectrum obtained by measuring the 3.30×10^{-6} mol L⁻¹ solution of one of dyes **A–C** using a cuvette with a 10-mm optical path length. Maximum absorbance (0.380) is observed at 545 nm, which corresponds to the wavelength of yellow-green light.

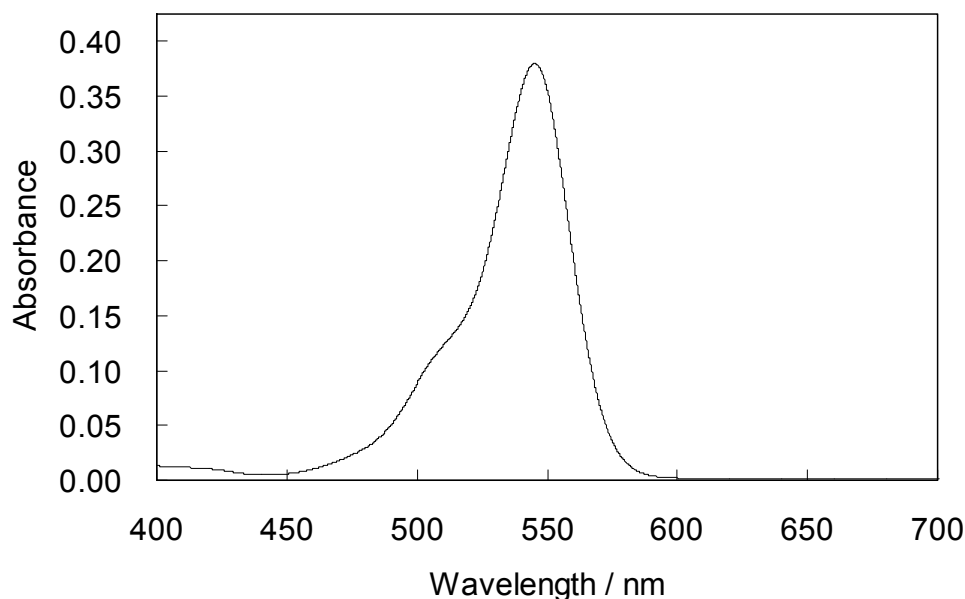


Fig. 35.3 Absorption spectrum of a dye.

The following are questions concerning the phenomena of light absorption and the Beer–Lambert law.

1. Calculate the molar absorption coefficient of the dye at 545 nm.
2. Calculate the % transmittance of the dye solution at 545 and 503 nm (the absorbance is 0.100 at 503 nm). Then calculate the % transmittance that will be measured at



each wavelength when the dye solution is diluted by 50%. By comparing these results, estimate which wavelength of the light source results in a more sensitive change in transmittance when the concentration of the dye solution is modified.

3. Calculate both the absorbance and % transmittance obtained for the original dye solution at 545 nm using a cuvette with a 30-mm path length.

Substance		R phrases	S phrases
methanol	liquid	11-23/24/25-39 /23/24/25	7-16-36/37-45
silica	solid	none listed	none listed
silica modified by octadecylsilyl ligands (ODS-modified silica)	solid	none listed	22-24/25
Silica modified by anion-exchange ligands	solid	36/37/38	26
Silica modified by cation-exchange ligands	solid	34	26-36/37/39-45
Dye A	solid	22-41	26-39
Dye B	solid	68	36/37
Dye C	solid	none listed	none listed

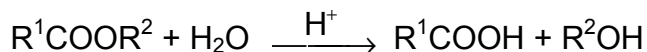


Problem 36:

Hydrolysis of ethyl acetate over a solid acid catalyst

A catalyst is a key material used in efficient chemical conversions. Today, about 90% of chemical processes use catalysts. Large-scale catalytic processes are employed, for example, in oil refining and petrochemical processes. In the petroleum industry, soluble liquid acids, such as sulfuric acid, are often used as catalysts in homogeneous systems. Since liquid acids are difficult to recover, however, insoluble solid acids are welcome for use in environmentally benign processes.

Various solid materials are capable of releasing H^+ ions into liquids, and such materials can be utilized as solid acid catalysts. H^+ -type cation-exchange resins are typical examples of solid acids. In this experiment, you will examine the catalysis of an H^+ -type cation-exchange resin for hydrolysis of ethyl acetate.



Chemicals

- Amberlyst[®]-15 (H^+ form, dry)
- ethyl acetate (reactant)
- phenolphthalein (0.5 wt.% solution in ethanol/water (1/1))
- 0.02 mol L⁻¹ sodium hydroxide (NaOH) standard solution
(concentration accurately determined)

Apparatuses and glassware

- burette (25 mL)
- Erlenmeyer flasks (100 mL × 6)
- glass vials (10 mL × 6; must be dried)
- graduated pipette (5 mL)
- magnetic stirrer
- stirring bar
- Pasteur pipette (dropper)
- reflux condenser
- silicone plug
- thermometer
- three-necked flask (250 mL)
- volumetric pipettes (1 mL and 3 mL)
- water bath

Procedure

- (1) Assemble the experimental setup as shown in Fig. 36.1. The chemicals will be charged through the unequipped neck.
- (2) Charge water (100 mL) and Amberlyst-15 (1.0 g) into the three-necked flask. Then heat and stir the solution.
- (3) When the solution reaches a constant temperature of 60 °C, add ethyl acetate (5 mL) to

the flask. This will be the start time of the reaction.

- (4) Charge six Erlenmeyer flasks with cold water (50 mL) and add a few drops of phenolphthalein to each flask. Keep the flasks at room temperature.
- (5) Fill a 25-mL burette with the 0.3 mol L^{-1} NaOH solution.
- (6) Ten minutes after the start of the reaction, stop stirring the mixture in order to settle out the catalyst, and transfer about 5 mL of the solution to a glass vial using a graduated pipette. Immediately, transfer 3 mL of the solution to an Erlenmeyer flask charged with water with a volumetric pipette. (You can directly transfer the solution from the reactor to the Erlenmeyer flask, depending on your skill level). Stir the solution again.
- (7) Repeat procedure (6) at intervals of 10 min until 60 min have elapsed from the start of the reaction. Then similarly prepare five more samples for titration in Erlenmeyer flasks.
- (8) Titrate six samples in the Erlenmeyer flasks with the NaOH solution. It is recommended that you calculate the amount of the NaOH solution required for complete hydrolysis of ethyl acetate prior to the titration.

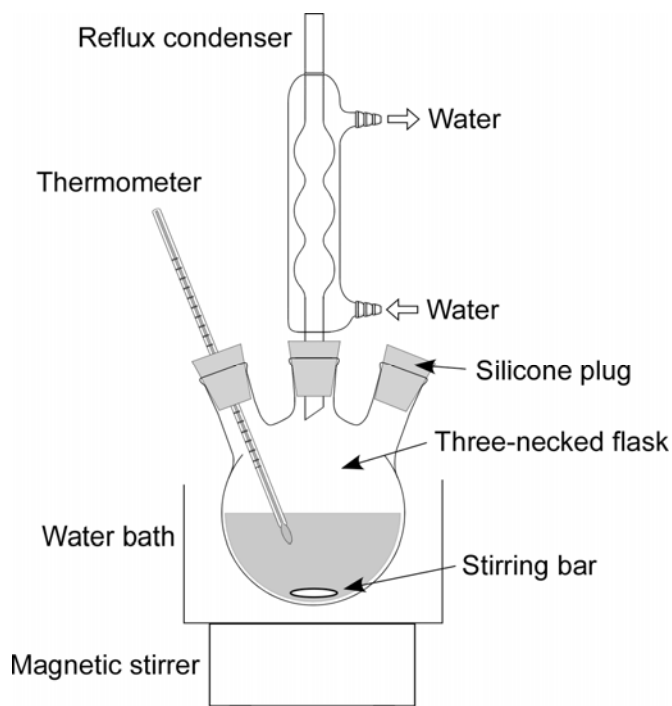


Fig. 36.1 Experimental setup.

Analysis

1. Determine the concentration of acetic acid in the solution at each reaction time t , defined as C_t , from the titration results. The density of ethyl acetate is 0.900 g cm^{-3} .
2. Plot $\log_{10} \frac{C_c}{C_c - C_t}$ against t , where C_c is the expected concentration for complete hydrolysis.
3. Estimate the first-order rate constant from the plot.

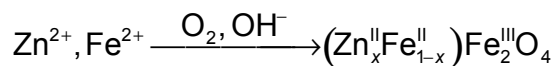
Substance		R phrases	S phrases
ethyl acetate	liquid	11-36-66-67	16-26-33
Amberlyst [®] -15	solid (granular)	36	26-36
phenolphthalein	0.5 wt.% solution in ethanol/water (1/1)	10	7-16
sodium hydroxide	0.3 mol L^{-1} aq. solution	36/38	26



Problem 37: Synthesis of a zinc ferrite

Ferrites were invented by Yogoro Kato and Takeshi Takei in Japan in 1930. They are magnetic mixed oxides of iron and divalent metals (M) expressed as MFe_2O_4 . A representative example of ferrites is Fe_3O_4 , where $M^{2+} = Fe^{2+}$, and many divalent cations can form ferrites with Fe^{3+} cations. Today, ferrites are very important magnetic materials used in electronics.

Ferrites are also important in waste water treatment, where they are used for the removal of heavy metal cations. This is related to the synthetic process of ferrites. Ferrites can easily be prepared by a wet precipitation technique from a solution containing M^{2+} and iron (Fe^{2+} and/or Fe^{3+}) cations under oxidative conditions and with a controlled pH and temperature. In this experiment, you will prepare a ferrite, $ZnFe_2O_4$, from a solution of Zn^{2+} and Fe^{2+} .



Chemicals

- acetic acid–sodium acetate buffer solution (pH 4)
- iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$)
- sodium hydroxide (2 mol L^{-1} solution)
- zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$)

Apparatuses and glassware

- air pump (flow rate 100 mL min^{-1}) and tubing
- Büchner funnel
- Erlenmeyer flask (200 mL)
- glass microfiber filter (to capture particles of ca. 0.3 μm)
- graduated pipette (2 mL)
- hot-plate magnetic stirrer
- magnet
- pH test paper (effective for pH 7–11)
- stirring bar
- thermometer
- suction flask
- tweezers

Procedures

- (1) Assemble the experimental setup as shown in Fig. 37.1.
- (2) Dissolve $FeSO_4 \cdot 7H_2O$ (2.0 g) in water (40 mL) in the Erlenmeyer flask.
- (3) Start stirring the solution.
- (4) Dissolve $ZnSO_4 \cdot 7H_2O$ (0.20 g) in the solution.
- (5) Start air bubbling through the glass tube (see Fig. 1).
- (6) Heat the solution until the temperature reaches 65–75 °C. Add around 6 mL of the sodium hydroxide solution and confirm that the solution pH reaches 9–11. If not, add

more of the solution until the pH has reached 9–11. The time when the pH is adjusted is the reaction start time.

- (7) Add the sodium hydroxide solution at appropriate intervals to maintain the pH at 9–11 while maintaining the solution's temperature. The color of the precipitate will gradually turn deep black.
- (8) One hour after the start of the reaction, stop stirring, air bubbling, and heating.
- (9) Place the magnet on the outer wall of the flask and confirm that the magnet attracts the precipitate.
- (10) Separate the precipitate by suction filtration using a glass microfiber filter. Recover the precipitate appropriately (it may be difficult to recover the fine particles that stick to the flask wall).
- (11) Wash the precipitate with the acetate buffer (50 mL).
- (12) Wash the precipitate with water, and then dry it at around 80 °C in an air oven.
- (13) Weigh the precipitate.

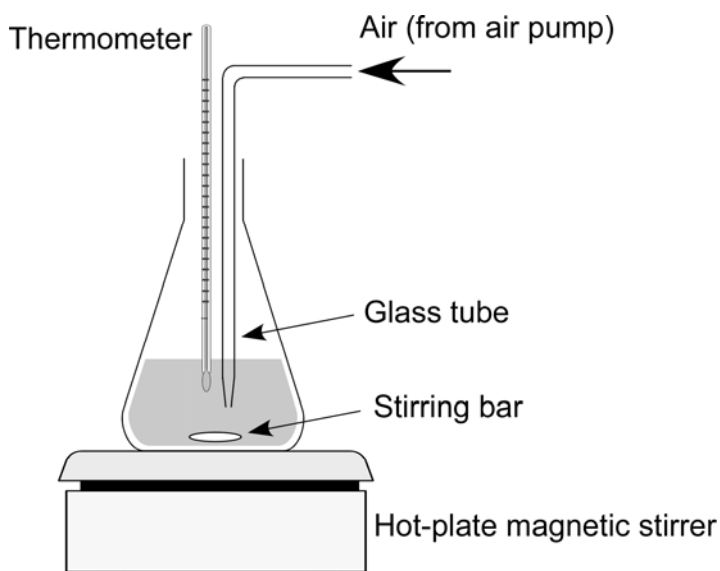


Fig. 37.1 Experimental setup.

Questions

1. Provide the theoretical yield of ferrite in grams.
2. Calculate the percentage yield of ferrite.
3. What analytical techniques can be used to detect the unreacted ferrous and zinc ions in the washing procedure (11)?
4. Choose the species that would be precipitated with ferric ions to form ferrites in a way similar to Zn^{2+} (ionic radius 0.074 nm) (the values in parentheses are ionic radii of the cations):
 Al^{3+} (0.051 nm), Ba^{2+} (0.134 nm), Ca^{2+} (0.099 nm), Cs^{+} (0.167 nm), Cu^{2+} (0.072 nm), Hg^{2+} (0.110 nm), Mg^{2+} (0.066 nm), Ni^{2+} (0.068 nm)

Substance		R phrases	S phrases
acetic acid–sodium acetate buffer solution (pH 4)	liquid	none listed	none listed
iron(II) sulfate heptahydrate	solid	22	36/37/39
sodium hydroxide	2 mol L ⁻¹ aq. solution	34	26-37/39-45
zinc sulfate heptahydrate	solid	22-41-50/53	22-26-39-46 -60-61

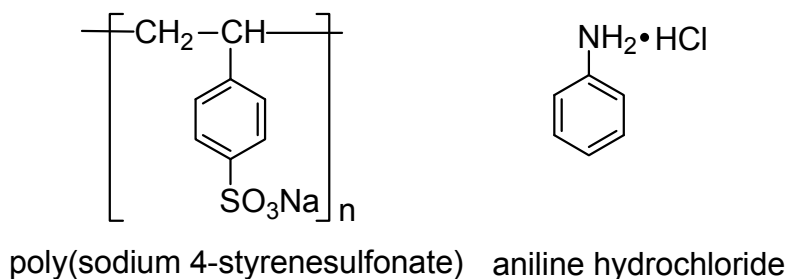
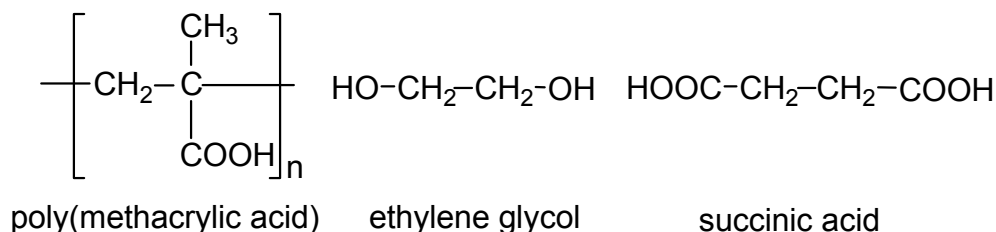
Problem 38:

Identification of polymers and small organic molecules by qualitative analysis

Simple chemical tests are often utilized for qualitative analyses of inorganic and organic compounds. Identification of unknown compounds requires a wide range of chemical knowledge. In order to identify inorganic compounds, unknown compounds are classified on the basis of their behavior to reagents which bring about acid-base, and/or redox reactions, sometimes producing precipitations. For organic compounds, the chemical reactions of functional groups present in the molecule are used for identification purposes. For polymeric compounds, the additional effects characteristic of macromolecules should be taken into consideration in order to identify the compounds.

Suppose that a polymer solution with a functional group A in each repeating unit is mixed with a solution of a chemically complementary polymer with a functional group B, and that there are attractive interactions between A and B. Due to the presence of a large number of the repeating units, the intermolecular attractive interactions inherent in polymers are stronger than those of the corresponding small molecules. Combining such polymers forms a polymer-polymer complex. The complex usually shows lower solubility than the individual polymers, and precipitation of the complex is often observed.

In this experiment, you will have five unknown aqueous solutions (A–E), each containing one of the compounds below (all of which are used). Carry out the following experiments and answer the questions.



Chemicals

- anhydrous sodium carbonate (granular)
- 0.5 mol L⁻¹ aniline hydrochloride solution
- 0.5 mol L⁻¹ ethylene glycol solution
- poly(allylamine hydrochloride) (MW = 56,000) solution
(monomer unit concentration: 0.1 mol L⁻¹)



- poly(ethylene oxide) (MW = 400,000) solution
(monomer unit concentration: 0.1 mol L^{-1})
- poly(methacrylic acid) (MW = 100,000) solution
(monomer unit concentration: 0.1 mol L^{-1})
- poly(sodium 4-styrenesulfonate) (MW = 70,000) solution
(monomer unit concentration: 0.1 mol L^{-1})
- 0.2 mol L^{-1} succinic acid solution

Glassware

- graduated pipettes
- test tubes

Procedures & Questions

- (1) Identify the compound in each solution from the results of procedures a) and b) below.
 - a) Add a small amount of anhydrous sodium carbonate (ca. 20 mg per 1 mL of solution) to each solution.
 - b) Add the poly(allylamine hydrochloride) solution (approximately 1:1 in volume) to each solution. If no precipitation is observed, add a small amount of anhydrous sodium carbonate (ca. 10 mg per 1 mL solution).
- (2) Give the equations for the reaction of aniline hydrochloride with anhydrous sodium carbonate and for the reaction of succinic acid with anhydrous sodium carbonate.
- (3) Is it possible to identify the compound by utilizing poly(ethyleneimine hydrochloride) instead of poly(allylamine hydrochloride)? Explain.
- (4) Mix the poly(ethylene oxide) solution with an equal amount of the poly(methacrylic acid) solution. Then add a small amount of anhydrous sodium carbonate. Report on the changes in appearance of the mixed solution and interpret these results.

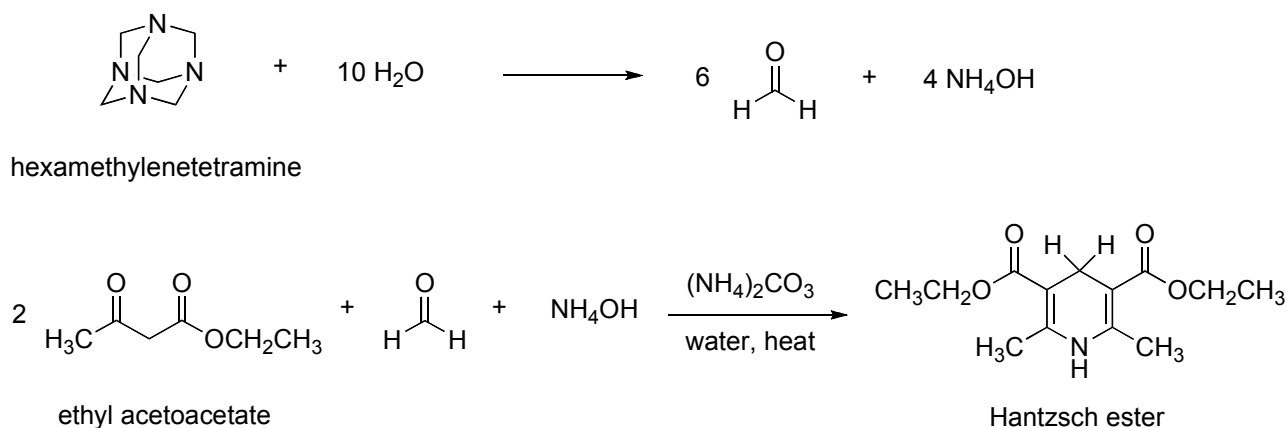
Substance		R phrases	S phrases
anhydrous sodium carbonate	Solid (granular)	36	22-26
aniline hydrochloride	solid	23/24/25-40-41-43-4 8/23/24/25-50-68	26-27-36/37/ 39-45-61-63
ethylene glycol	liquid	22	none listed
poly(allylamine hydrochloride)	solid	22-43	36/37
poly(ethylene oxide)	solid	none listed	none listed
poly(methacrylic acid)	solid	none listed	none listed
poly(sodium 4-styrenesulfonate)	solid	none listed	none listed
succinic acid	solid	37/38-41	26-36/37/39

Problem 39:

Synthesis of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (Hantzsch ester)

1,4-Dihydropyridine and its derivatives (1,4-DHPs) are ubiquitous in nature and common to a number of bioactive molecules that include antitumor, antimutagenic, and antidiabetic agents. 1,4-DHPs are also known as therapeutic agents of an important class of calcium channel blockers. Recently, 1,4-DHPs have played a new role in organic chemistry—as alternative hydrogen sources. They have been used instead of gaseous hydrogen to reduce various organic compounds containing C=C, C=N, and C=O bonds, with or without the aid of appropriate catalysts.

A Hantzsch 1,4-DHP ester (or simply a Hantzsch ester), represented by 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester, is one such compound in which synthesis is accomplished conveniently by a one-pot multi-component reaction of commercially available reagents. In this experiment, you will synthesize the Hantzsch ester according to the scheme illustrated below.



Chemicals

- ammonium carbonate
- anhydrous sodium sulfate
- 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester
- ethyl acetate
- ethyl acetoacetate
- hexamethylenetetramine (hexamine)
- toluene

Apparatuses and glassware

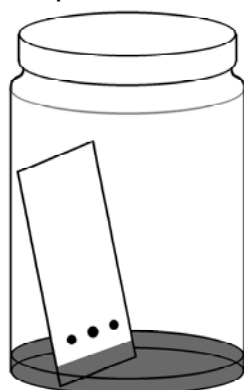
- Büchner funnel
- glass capillary
- Erlenmeyer flasks (25 mL and 100 mL)
- filter paper

- graduated pipette
- hot-plate magnetic stirrer (magnetic stirrer with heating plate)
- magnetic stirring bar
- suction flask
- test tube (100 mL)
- thermometer
- thin layer chromatography plate
(silica gel 60 F254; layer thickness: 0.25 mm on a glass support)
- UV lamp equipped with short and long waves (254 and 365 nm)
- water aspirator (or diaphragm vacuum pump)
- wide-mouth bottle with cap (developing chamber)

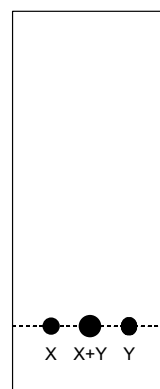
Procedure

- (1) In a fume hood, enter 1.30 g of ethyl acetoacetate and 50 mL of water into a 100-mL Erlenmeyer flask. Add 1.00 g of ammonium carbonate powder and place the magnetic stirring bar in the flask; stir at room temperature on a hot-plate magnetic stirrer until the ethyl acetoacetate is completely dissolved. Add 7.00 g of hexamethylenetetramine and place a cork stopper on the flask. Heat the mixture to 70 °C (use a thermometer) while stirring on a preheated hot-plate magnetic stirrer. After heating for 1 h, cool the mixture to room temperature by removing it from the hot-plate stirrer.
- (2) As the mixture cools down, take a small portion of the reaction mixture using a glass capillary and load it to make two spots in the center and right positions on a thin layer chromatography (TLC) plate. Load an appropriate amount of ethyl acetoacetate in the center and left positions, so that there are three spots on the plate, the central of which spots contains both the reaction mixture and ethyl acetoacetate. Develop the TLC plate using hexane/ethyl acetate (2/1) as a developer. Use a pencil to trace the outlines of the spots detected using a UV lamp (254 and 365 nm).

Development chamber



TLC Plate



X: ethyl acetoacetate
Y: reaction mixture

Fig. 39.1 TLC plate placed in a bottle with a cap.

Fig. 39.2 Spots on the TLC plate before development.

- (3) After a crystalline product has been precipitated out of the reaction mixture, filter the product through a Büchner funnel under reduced pressure, wash the solid product obtained with small portions of water, and dry it in order to weigh the product. Identify



the product with the authentic Hantzsch ester by TLC analysis as described above. Use hexane/ethyl acetate (2/1) as a developer.

- (4) Place the filtrate and your magnetic stirring bar in a 100-mL test tube. Add 10 mL of ethyl acetate to the test tube and stir the solution vigorously for 30 s over a magnetic stirrer. Stop stirring and wait for the solution to separate into two layers. Transfer the upper organic layer into a 25-mL Erlenmeyer flask using a graduated pipette. Repeat the extraction twice using ethyl acetate (2×5 mL) and add anhydrous sodium sulfate (1 g) to the Erlenmeyer flask to dry the combined organic layer. Check the organic layer with TLC to determine whether or not it still contains the Hantzsch ester.

Questions

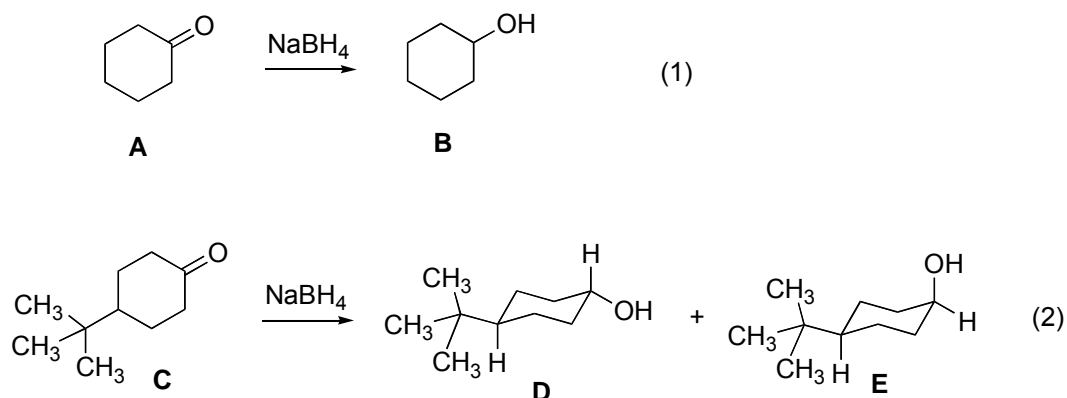
1. Determine the total experimental yield of the isolated Hantzsch ester in grams.
2. Provide the theoretical yield of the Hantzsch ester in grams.
3. Calculate the percentage yield of the Hantzsch ester.
4. Determine the R_f values for the Hantzsch ester and ethyl acetoacetate.
5. Explain why the ethyl acetoacetate becomes soluble in the aqueous ammonium carbonate solution.
6. Identify the origin of the C-4 carbon in the Hantzsch ester.

Substance		R phrases	S phrases
ammonium carbonate	solid	22	none listed
anhydrous sodium sulfate	solid	none listed	none listed
1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester	solid	36/37/38	26
ethyl acetate	liquid	11-36-66-67	16-26-33
ethyl acetoacetate	liquid	36	26
hexamethylenetetramine (hexamine)	solid	11-42/43	16-22-24-37
hexane	liquid	11-38-48/20-51/53-62-65-67	9-16-29-33-36/37-61-62

Problem 40: Reduction of a ketone with sodium borohydride

Alcohols are ubiquitous in biologically active organic compounds as well as industrially useful materials. A key method of preparing alcohols in synthetic organic chemistry is to reduce carbonyl compounds such as aldehydes and ketones. A variety of reagents have been developed for such conversions, and one of the most common reagents used in laboratories is sodium borohydride. This reagent is a mild and selective reducing agent for ketones and aldehydes. Reduction of cyclohexanone (**A**) with sodium borohydride gives cyclohexanol (**B**), for example, with a good yield and as a single product (eq. 1). Sodium borohydride can also reduce 4-*tert*-butylcyclohexanone (**C**) to 4-*tert*-butylcyclohexanol, a mixture of two isomers **D** and **E** (eq. 2). This can be understood based on the existence of two approach pathways for the hydride in sodium borohydride, i.e., the axial and equatorial directions.

In this experiment, you will reduce the 4-*tert*-butylcyclohexanone (**C**) with sodium borohydride and analyze the products on thin layer chromatography (TLC).



Chemicals

- anhydrous sodium sulfate
- anisaldehyde stain (10% *p*-anisaldehyde and 5% H₂SO₄ in methanol)
- ethyl acetate
- ethanol
- hexane
- sodium borohydride
- sulfuric acid
- 4-*tert*-butylcyclohexanone

Apparatuses and glassware

- crystallization dish
- Erlenmeyer flask (30 mL)
- filter paper
- glass capillary



- glass funnel
- magnetic stirrer
- magnetic stirring bar (1.5 cm long)
- oven (or hot-plate)
- test tube (diameter: ca. 2 cm, height: ca. 20 cm or taller)
- TLC plate (silica gel 60; layer thickness: 0.25 mm, on a glass support)
- tweezers
- water bath
- wide-mouth bottle with cap (developing chamber)
- wide-mouth bottle (anisaldehyde stain container)
- graduated pipette

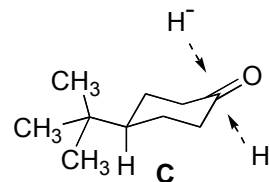
Procedures

- (1) Inside a fume hood, add 4-*tert*-butylcyclohexanone (1.0 g) and ethanol (1 mL) to a test tube fitted with a stirring bar. Place the test tube in a water bath on a magnetic stirrer. Stir the mixture to form a clear solution at room temperature (ca. 25 °C). Add sodium borohydride (0.1 g) to the resulting solution, in a few portions. Take care to regulate the temperature.
- (2) Monitor the progress of this reaction with TLC according to the procedure described in Problem 39 above. Develop TLC plates with an developer of hexane/ethyl acetate = 4/1. Dip the TLC plates fully in the anisaldehyde stain solution stored in a wide-mouth bottle for a few seconds. Take the plates out of the solution and heat them in an oven at 150 °C or above for 15 min (or heat them on a hot-plate until the spots become visible). Use tweezers for these processes. Check the completion of the reaction by TLC.
- (3) Remove the water bath. Add water (3 mL) and hexane (3 mL) to the reaction mixture. Vigorously stir the entire mixture for 5 min. Then transfer the upper layer (organic phase) to an Erlenmeyer flask using a graduated pipette.
- (4) Add hexane (3 mL) to the test tube with the remaining lower layer (aqueous phase) and stir the mixture vigorously for 5 min. Transfer the upper layer (organic phase) to the same Erlenmeyer flask using the graduated pipette. Repeat this extraction process again.
- (5) Add anhydrous sodium sulfate (1 g) to the Erlenmeyer flask containing the organic phase. Filter this mixture using filter paper and a glass funnel to remove the solids. Transfer the filtrate to a crystallization dish. Rinse the residual solids with hexane (2 mL). Transfer the washing to the crystallization dish.
- (6) Evaporate the ethanol and hexane in the fume hood at room temperature (it will take several hours) to obtain a white solid. Weigh the amount of solids.



Questions

1. Calculate the theoretical yield of this reaction product.
2. Report the experimental yield, and calculate the percentage yield of this reaction product.
3. Sketch the TLC plate for the completed reaction and provide R_f values.
4. In this reduction, the steric environment is different for both faces of the carbonyl group of 4-*tert*-butylcyclohexanone. Thus, two reduced alcohol compounds, i.e., *cis*- and *trans*-alcohols against the *tert*-butyl group, are generated. Since sodium borohydride is a relatively small reagent, a hydride preferentially approaches it from the axial direction. Which is the alcohol for the prominent spot on the TLC, **D** or **E**?



Substance		R phrases	S phrases
anhydrous sodium sulfate	solid	none listed	none listed
anisaldehyde	liquid	22-36/37/38	26-36
ethanol	liquid	11	7-16
ethyl acetate	liquid	11-36-66-67	16-26-33
hexane	liquid	11-38-48/20-51/53-62-65-67	9-16-29-33-36/37-61-62
methanol	liquid	11-23/24/25-39/23/24/25	7-16-36/37-45
sodium borohydride	solid	15-24/25-34	22-26-36/37/39-43-45
4- <i>tert</i> -butylcyclohexanone	solid	36/37/38	26-36
sulfuric acid	liquid	35	26-30-45