THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Series 2

38th – 42nd IChOs
2006 – 2010

Edited by Anton Sirota

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IUVENTA, Bratislava, 2017

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The preparatory problems from the 38th – 42nd IChOs

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42nd

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International Chemistry Olympiad

PREPARATORY PROBLEMS

Edited by Anton Sirota

31 theoretical problems
9 practical problems

2010

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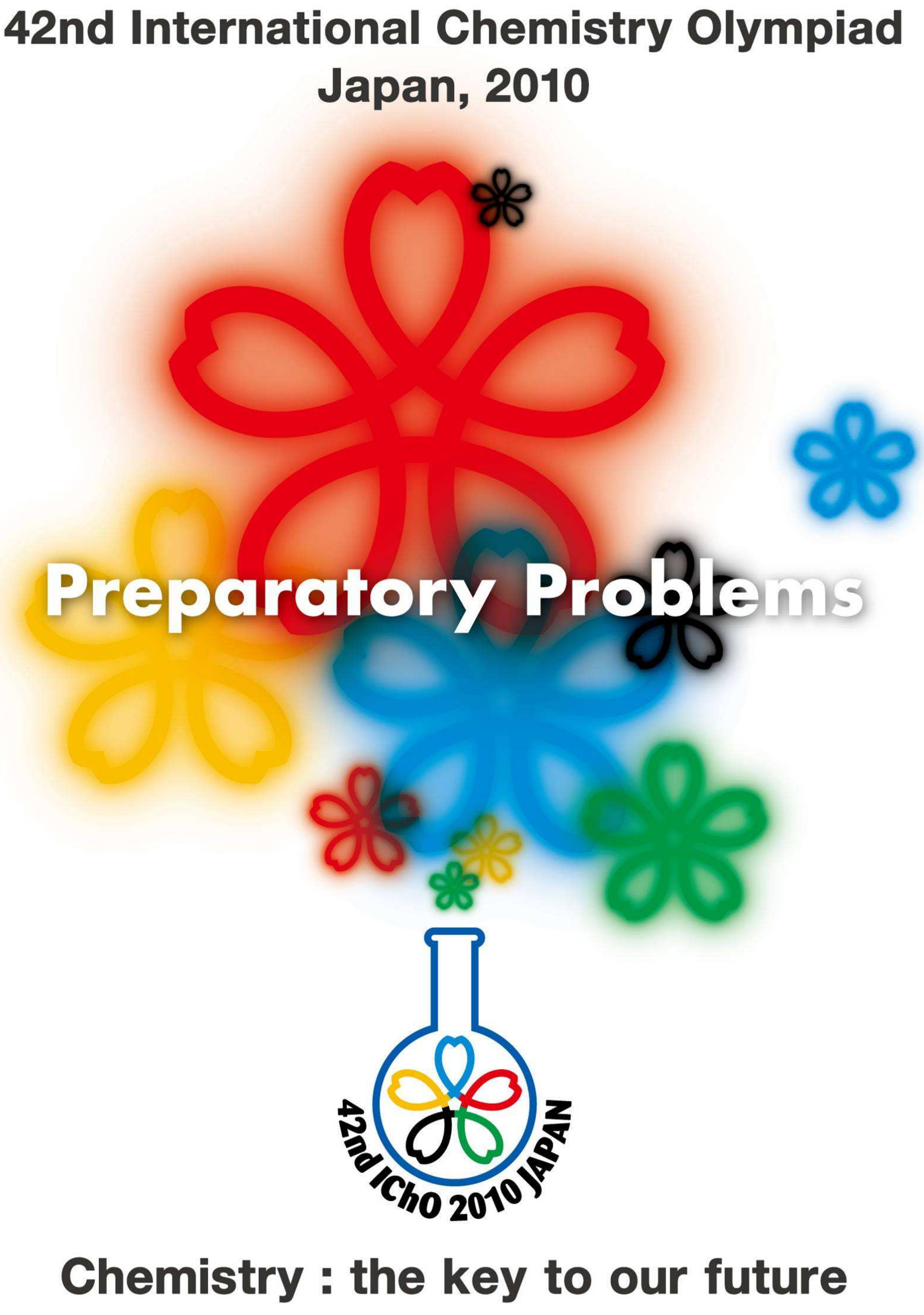

42nd International Chemistry Olympiad
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19 – 28 JULY 2010, TOKYO, JAPAN

PREPARATORY PROBLEMS

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Theoretical problems

Practical Problems

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PREPARATORY THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

Equilibrium constant

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

Half reaction	$E°$/ V (298 K)
$Sn^{2+} + 2\ e^- \rightarrow Sn$	–0.14
$Sn^{4+} + 2\ e^- \rightarrow Sn^{2+}$	+0.15
$Hg_2^{2+} + 2\ e^- \rightarrow 2\ Hg$	+0.79
$Hg_2Cl_2 + 2\ e^- \rightarrow 2\ Hg + 2\ Cl^-$	+0.27

1.1 Calculate the equilibrium constant, K, for the following reaction at 298 K

$Sn(s) + Sn^{4+}(aq) \rightleftarrows 2\ Sn^{2+}(aq)$

1.2 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+}.

1.3 Calculate the voltage, $E°$, of a fuel cell by using the following reaction involving two electrons.

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta_r G° = –237.1\ kJ\ mol^{-1}$

SOLUTION OF PREPARATORY PROBLEM 1

1.1 R: $Sn^{4+} + 2\,e^- \rightarrow Sn^{2+}$ + 0.15 V

L: $Sn^{2+} + 2\,e^- \rightarrow Sn$ – 0.14 V

$E° = +0.29$ V

$$\ln K = -\frac{\Delta_r G°}{RT} = \frac{nFE°}{RT} = \frac{2\,F \times 0.29}{R \times 298} = 22.59$$

$$K = \frac{[b_e(Sn^{2+})]^2}{b_e(Sn^{4+})} = \exp(22.59) = 6.4 \times 10^9.$$

1.2 R: $Hg_2Cl_2 + 2\,e^- \rightarrow 2\,Hg + 2\,Cl^-$ + 0.27

L: $Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg$ + 0.79

$E° = –0.52$ V

$$\ln K = -\frac{\Delta_r G°}{RT} = \frac{nFE°}{RT} = \frac{2\,F \times 0.52}{R \times 298} = -40.50$$

$K = b_e(Hg_2^{2+})\,[b_e(Cl^-)]^2 = \exp(-40.50) = 2.58 \times 10^{-18}$

let $x = b_e(Hg_2^{2+})$, then $b_e(Cl^-) = 2x$. Therefore, $K = x(2x)^2 = 4x^3$

Solving this equation for x gives: $x = (K / 4)^{1/3} = 8.6 \times 10^{-7}$

$S = x = 8.6 \times 10^{-7}$ mol kg^{-1}.

1.3 $$E° = -\frac{\Delta_r G°}{nF} = \frac{-(-237.1 \times 1000)}{2\,F} = 1.23 \text{ V}$$

THEORETICAL PROBLEM 2

Speed of sound

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

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

Here, R is the gas constant. The $C_{V,\ \mathrm{m}}$ 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.

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

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.

2.2 Estimate the speed of sound in Ne (neon), v_s(Ne), at room temperature.

SOLUTION OF PREPARATORY PROBLEM 2

2.1 Since the flight energy is zero at 0 K and it increases by $\frac{3}{2}R$ per unit temperature (per mol), the energy should be $\frac{3}{2}RT$ (per mol) at temperature T.

Thus, the total kinetic energy of one mole of gas is $\frac{1}{2}Mv^2 = \frac{3}{2}RT$.

This equation is solved for v:

$$v = \sqrt{\frac{3RT}{M}}$$

2.2 From the solution of problem 2.1, v, and therefore, v_s should be proportional to $M^{-1/2}$. Therefore, the speed of sound in Ne can be estimated as

$v_s(\mathrm{Ne}) = 1007 \times (20.18/4.003)^{-1/2} = 448$ m s^{-1}

$$v_s(\mathrm{Ne}) = 1007\ \frac{1}{\sqrt{\frac{20.18}{4.003}}} = 448\ \mathrm{m\ s^{-1}}$$

or $$v_s(\mathrm{Ne}) = 319\ \frac{1}{\sqrt{\frac{20.18}{39,95}}} = 449\ \mathrm{m\ s^{-1}}$$

THEORETICAL 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.

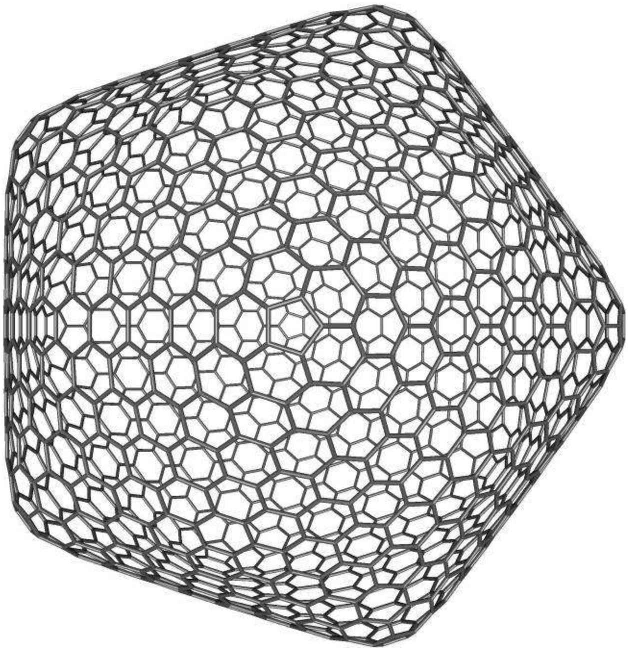


Fig. 1 Structure of a large C_{1500} fullerene

3.1 Calculate the surface area of fullerenes with *n* carbon atoms in terms of nm^2 (1 nm^2 ≡ 10^{-18} m^2).

3.2 Calculate the radius of fullerenes (in nm) as a function of *n* by considering the fullerene molecule as a perfect sphere.

3.3 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.

SOLUTION OF PREPARATORY PROBLEM 3

3.1 The areas of the hexagon and pentagon (S_6 and S_5) in the fullerenes are

$$S_6 = 0.14 \times 0.14/2 \text{ nm} \times \tan\left(\frac{180-360/6}{2}\right)/2 = 0.0509 \text{ nm}^2$$

$$\mathrm{S}_5 = 0.14 \times 0.14/2 \text{ nm} \times \tan\left(\frac{180-360/5}{2}\right)/2 = 0.0337 \text{ nm}^2,$$

respectively. Therefore, the total area of a fullerene with *n* carbon atoms is

$$S_{\text{total}} = 0.0337 \times 12 + 0.0509 \times \left(\frac{\mathrm{n}}{2} - 10\right) = 0.0255\,\mathrm{n} - 0.1046 \text{ nm}^2.$$

3.2 Since the total area of a perfect sphere is

$$S_{\text{sphere}} = 4\pi r^2,$$

and this area is equal to the area of the fullerene, the radius of the fullerene would be

$$r = \sqrt{\frac{0.0255\,n - 0.1046}{4\pi}} \text{ nm}.$$

3.3 The mass of the fullerene with *n* carbon atoms is

$$m = \frac{12.01}{N_{\text{A}} n}$$

Since the volume of a sphere with radius *r* is

$$V_{\text{sphere}} = \frac{4}{3}\pi r^3$$

which is also the volume of the fullerene, the density would be

$$d = \frac{12.01/N_A\, n}{\frac{4}{3}\pi\left(\frac{0.0255\,n - 0.1046}{4\pi}\right)^{\frac{3}{2}}} = \frac{12.0\sqrt{\pi}}{\left(0.0255 - \frac{0.1046}{n}\right) \times \sqrt{0.0255\,n - 0.1046}} \times 10^{-23} \text{ g nm}^{-3}$$

The density of air under standard conditions is

$$d_{\text{air}} = \frac{M}{V} = \frac{28.0 \times 0.8 + 32.0 \times 0.2}{\frac{RT}{p}} = \frac{28.8}{\frac{8.314 \times 298}{101325}} \times \frac{1}{\left(10^9\right)^3} = 1.18 \times 10^{-24} \text{ g nm}^{-3}$$.

This air density is larger than that of the fullerene with *n* carbon atoms, and *n* should be large enough so that

$$d_{\text{air}} > d \Rightarrow$$

$$1.18 \times 10^{-24} > \frac{12.0\sqrt{\pi}}{\left(0.0255 - \frac{0.1046}{\text{n}}\right) \times \sqrt{0.0255\text{n} - 0.1046}} \times 10^{-23} \gg 5.22\text{n}^{-1/2} \times 10^{-20} \text{ g nm}^{-3}$$

$$\text{n} > \left(\frac{5.22 \times 10^{-20}}{1.18 \times 10^{-24}}\right)^2 = 1.96 \times 10^9.$$

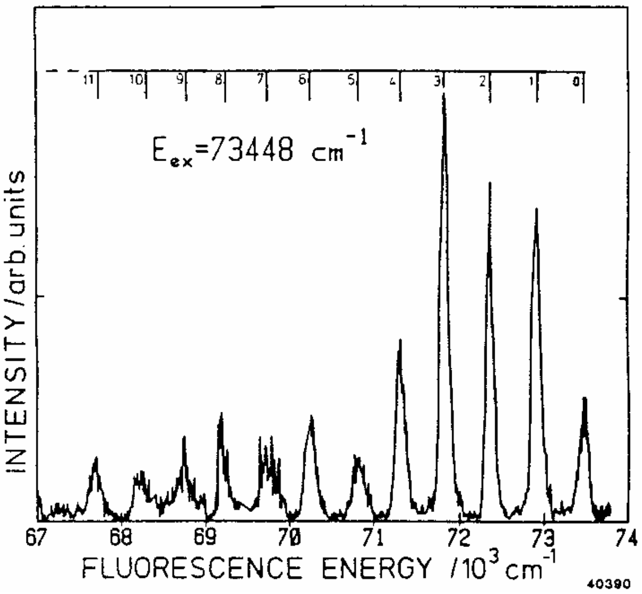
In this case, the minimum radius of the “molecular balloon” is

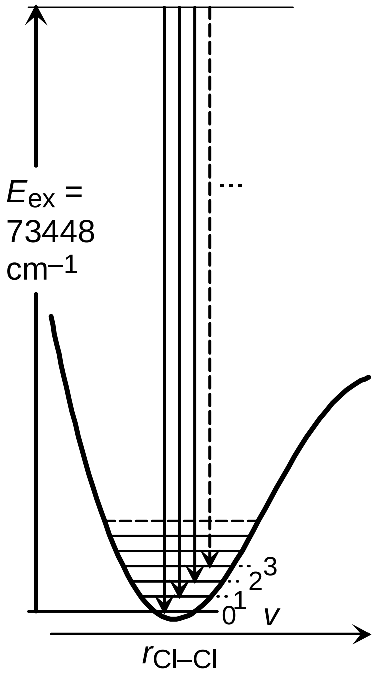
$$r = \sqrt{\frac{0.0255\,\text{n} - 0.1046}{4\,\pi}} = \sqrt{\frac{0.0255 \times 1.96 \times 10^9 - 0.1046}{4\,\pi}} = 1.99 \times 10^3 \text{ [nm]}.$$

THEORETICAL PROBLEM 4

Vibrational states of Cl_2

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 Cl_2 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,...).





4.1 Calculate the approximate energy spacing between the adjacent vibrational energy levels at the ground electronic state of Cl_2, E_v, in kJ mol^{-1}. You can choose any pair of adjacent peaks for calculation.

SOLUTION OF PREPARATORY PROBLEM 4

4.1 From the figure, the interval between the peaks can be determined to be 500 [480 – 550] cm^{-1}.

The corresponding wavelength $\lambda = 1\times10^{-2}$ / 500 [480 – 550] = 2.0 [1.82 – 2.08] $\times$ 10^{-5} m

Then, the corresponding energy $E_v = N_A hc$ / 2.0 [1.82 – 2.08]$\times10^{-5}$ = 6.0 [5.7 – 6.6] kJ mol^{-1}.

E_v = **6.0** [5.7 – 6.6] kJ mol^{-1}

THEORETICAL 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:

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

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.

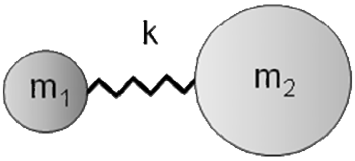


Figure I

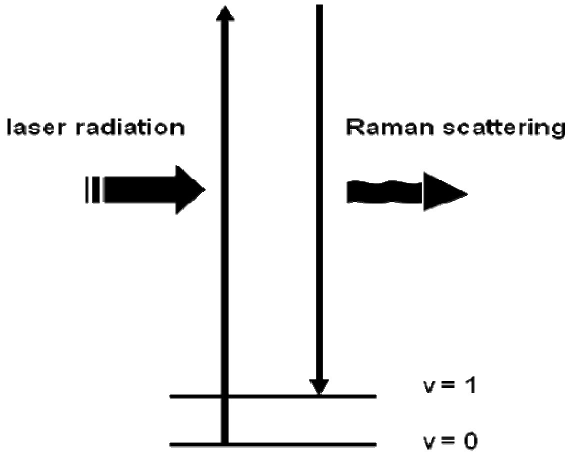


Figure II

5.1 Obtain the ratio of the reduced masses of H_2, N_2, and O_2:.

$\mu_{H_2} : \mu_{N_2} : \mu_{O_2} = 1 : \boxed{a} : \boxed{b}$

5.2 Wavelength λ (nm) and frequency ν (s^{-1} = 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.

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

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

5.3 The energy difference between $v = 0$ and $v = 1$ 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.

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

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

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

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

SOLUTION OF PREPARATORY PROBLEM 5

5.1 $\mu = \frac{m_1\, m_2}{m_1 + m_2}$; therefore, $\mu_{H_2} : \mu_{N_2} : \mu_{O_2} = \frac{1 \times 1}{1+1} : \frac{14 \times 14}{14+14} : \frac{16 \times 16}{16+16} = 1 : 14 : 16$

5.2 $\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\ \text{m s}^{-1}}{500 \times 10^{-9}\ \text{m}} = 6.010^{14}\ \text{s}^{-1}$

$$\text{wavenumber} = \frac{1}{500\ \text{nm}} = \frac{1}{500 \times 10^{-9}\ \text{m}} = \frac{1}{500 \times 10^{-7}\ \text{cm}} = 2.0 \times 10^{4}\ \text{cm}^{-1}$$

5.3 According to the energy-conservation principle, the wavenumber of the Raman scattering light should be 20000 – 4160 = 15840 cm^{-1}. The corresponding wavelength is ~631 nm.

5.4 $\sqrt{\frac{k_{O2}}{\mu_{O2}}} = \sqrt{\frac{2\, k_{H2}}{16\, \mu_{H2}}} = \frac{1}{2\sqrt{2}} \sqrt{\frac{k_{H2}}{\mu_{H2}}}$

The vibrational energy of the oxygen molecule is $\frac{1}{2\sqrt{2}}$ of the vibrational energy of the hydrogen molecule, that is, ~1475 cm^{-1}. According to energy-conservation principle, the wavenumber of Raman scattering light should be 20000 – 1470 = 18530 cm^{-1}.

The corresponding wavelength is ~540 nm.

THEORETICAL 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 $\nu = 6.26 \times 10^{11}\ s^{-1}$.

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

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

where μ and R_e are reduced mass**[1]** 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 $J' - J'' = \pm 1$.

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

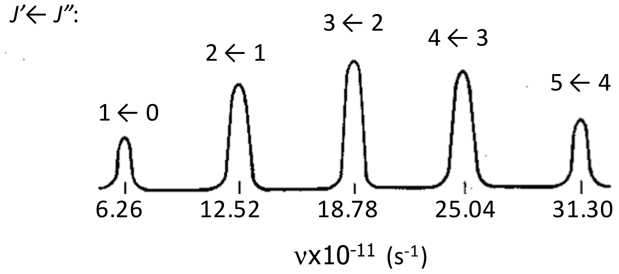


Fig. 1

Note:

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

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

SOLUTION OF PREPARATORY PROBLEM 6

6.1 According to the simple model (a rigid rotator model), the allowed frequencies for absorption ($J' = J'' + 1$) are

$$\nu = \frac{E_{J'} - E_{J''}}{h} = \frac{h}{8\,\pi^2 \mu\, R_e^{\;2}}\left[(J''+1)(J''+2) - J''(J''+1)\right] = \frac{h}{4\,\pi^2 \mu\, R_e^{\;2}}(J''+1)\,.$$

Hence, frequency of microwave resonant to the $J' = 1 \leftarrow J'' = 0$ transition is 6.26×10^{11} s^{-1}. As reduced mass of HCl^{35} is 1.61×10^{-27} kg,

$$R_e = \sqrt{\frac{h}{4\pi^2 \mu\, \nu}} = \sqrt{\frac{6.63 \times 10^{-34}}{4\pi^2 \times 1.61 \times 10^{-27} \times 6.26 \times 10^{11}}} = 1.29 \times 10^{-10} \text{ [m]}$$

THEORETICAL PROBLEM 7

Atomic and molecular orbitals

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

$$\varphi_a \propto 1s_A - 1s_B$$

$$\varphi_b \propto 1s_A + 1s_B$$

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.

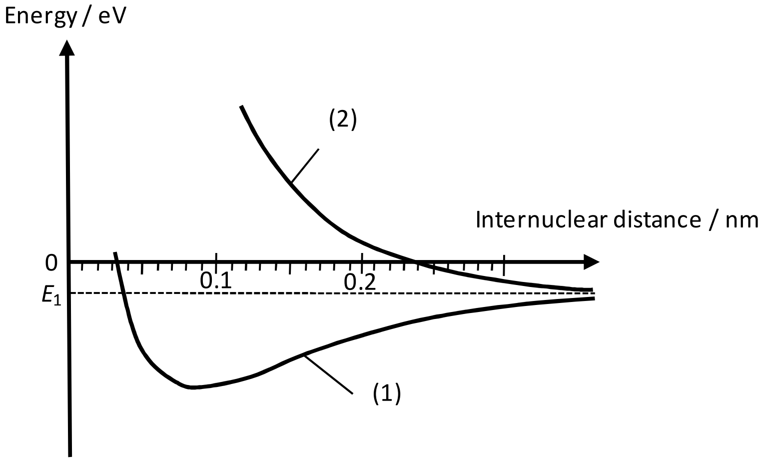


Fig. 1

7.2 Write the internuclear distance of stable H_2^+.

7.3 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.

SOLUTION OF PREPARATORY PROBLEM 7

7.1 The upper curve (2) in Fig. 1 shows the energy of the anti-bonding orbital, φ_a as a function of the internuclear distance.

7.2 The lower line in Fig. 1 shows the energy of the bonding orbital, φ_b. From the minimum of the energy curve, we are able to obtain the internuclear distance of stable H_2^+ to be 0.085 nm.

7.3 The two energy curves in Fig. 1 converge at E_1 as the internuclear distance becomes infinity. Here, H_2^+ is regarded as totally separated one hydrogen atom and one proton. Hence, $|E_1|$ is the same as the ionization potential of the hydrogen atom.

THEORETICAL PROBLEM 8

Electronic structure of polyene

The straight-chain polyene (····–CH=CH–CH=CH–CH=CH–····) 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:

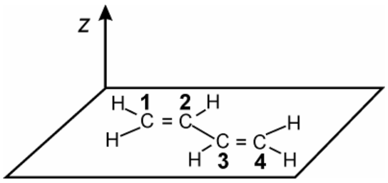


Fig. 8.1
Illustration of the chemical structure of 1,3-butadiene. Each carbon atom is numbered.

$$\psi_k = \sum_i c_i \varphi_i \qquad (1)$$

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:

$$\varepsilon_1 = \alpha - 1.62\,\beta \qquad \psi_1 = 0.37\varphi_1 - 0.60\,\varphi_2 + 0.60\,\varphi_3 - 0.37\varphi_4 \qquad (2)$$

$$\varepsilon_2 = \alpha - 0.62\,\beta \qquad \psi_2 = 0.60\varphi_1 - 0.37\varphi_2 - 0.37\varphi_3 + 0.60\varphi_4 \qquad (3)$$

$$\varepsilon_3 = \alpha + 0.62\,\beta \qquad \psi_3 = 0.60\varphi_1 + 0.37\varphi_2 - 0.37\varphi_3 - 0.60\varphi_4 \qquad (4)$$

$$\varepsilon_4 = \alpha + 1.62\,\beta \qquad \psi_4 = 0.37\varphi_1 + 0.60\varphi_2 + 0.60\varphi_3 + 0.37\varphi_4 \qquad (5)$$

8.1 Draw the energy levels of the molecular orbitals, and indicate the π electrons in the ground state using arrows while considering the spin direction.

8.2 Using α and β, calculate the photon energy necessary for excitation from the ground state to the first excited state of 1,3-butadiene.

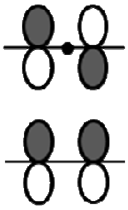


Fig. 8.2: Illustration of π molecular orbitals of ethylene. Solid circle represents a node.

8.3 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 behaviour 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 2 p_z orbitals that are aligned perpendicular to the chain with a spacing of α. If we assume a periodic boundary condition of $N\alpha$ along the chain, the energy state of the π electrons can be described by the following equation:

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

8.4 Calculate the energy width between the maximum and the minimum π-electron energy levels.

8.5 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

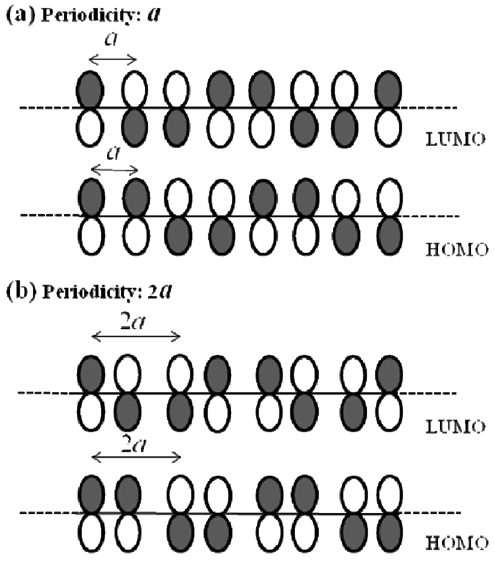


Fig. 8.3: Illustration for the LUMO and the HOMO of the 1D chain with a periodicity of a (upper) and $2a$ (lower).

periodicity changes from a to $2a$? Choose the correct answer from the following choices:

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.

8.6 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.

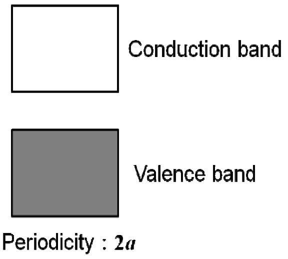
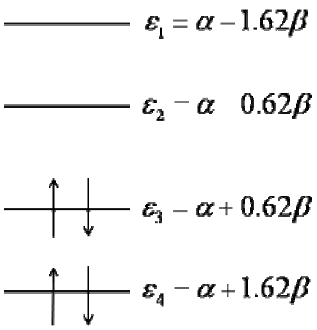


Fig. 4.
Illustration for the continuum electronic states of the 1D chain with a periodicity of $2a$.

SOLUTION OF PREPARATORY PROBLEM 8

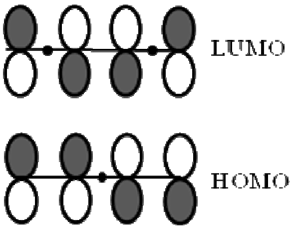
8.1



8.2

$$\Delta\varepsilon = \varepsilon_2 - \varepsilon_3 = \alpha - 0.62\,\beta - (\alpha + 0.62\,\beta) = -1.24\,\beta$$

8.3



8.4 $E_k(\text{max}) = \alpha - 2\beta$

$E_k(\text{min}) = \alpha + 2\beta$

Therefore, the energy width between E_k(max) and E_k(min) is -4β or $|4\beta|$

8.5 LUMO is destabilized due to proximity of two $2p_z$ orbitals with opposite signs.

HOMO is stabilized due to proximity of two $2p_z$ orbitals with same signs.

Answer: (b)

8.6 Br_2

THEORETICAL 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.

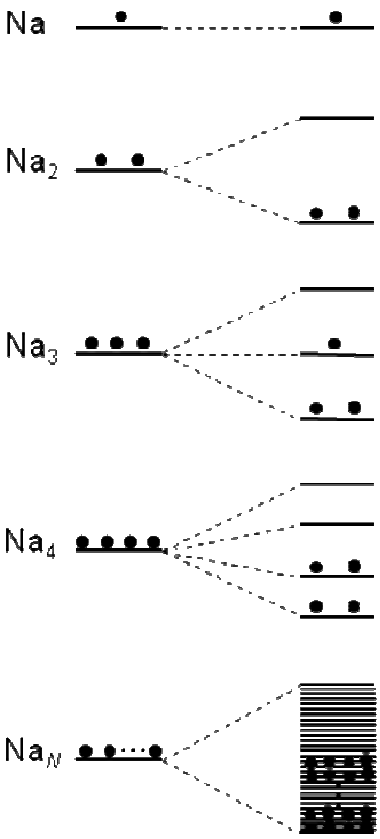


Fig. 9.1

9.1 The eigenenergy of the free particles confined in a 1D box is described as

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

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.

9.2 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.

9.3 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.

SOLUTION OF PREPARATORY PROBLEM 9

9.1 Since one eigenstate is occupied by two electrons with opposite spin directions (up-spin and down-spin), the quantum number n of the highest occupied level is $N/2$ for even N and $(N+1)/2$ for odd N. The length of the chain L is expressed as $a_0(N–1)$. On the basis of the given eigenenergy, the energy of the highest occupied level is written as

$$E_{\frac{N}{2}} = \frac{N^2 h^2}{32\, m a_0^2 (N-1)^2} \text{ for even } N \text{ and } E_{\frac{N+1}{2}} = \frac{(N+1)^2\, h^2}{32\, m a_0^2 (N-1)^2} \text{ for odd } N.$$

9.2 The number of Na atoms present in 1.00 mg of Na is

$$N = 6.02 \times 10^{23} \times \frac{1.00\times10^{-3}}{23.0} = 2.617\times10^{19}.$$

The energy width is expressed as $E_{\frac{N}{2}} - E_1 = \dfrac{h^2}{32\,\mathrm{m}\,\mathrm{a}_0^2}\left\{\dfrac{N^2-4}{(N-1)^2}\right\}$ for even N

and $E_{\frac{N+1}{2}} - E_1 = \dfrac{h^2}{32\, m\, a_0^2}\left\{\dfrac{(N+1)^2-4}{(N-1)^2}\right\}$ for odd N.

Since N is extremely large, the energy width is calculated as

$$\frac{h^2}{32\, m\, a_0^2} = 1.16\times10^{-19} \text{ J for the both cases.}$$

9.3 The energy gap for even N is $\Delta E = E_{\frac{N}{2}+1} - E_{\frac{N}{2}}$; using the equation obtained in (a), the equation for energy gap is rewritten as

$$\Delta E = \frac{h^2}{32\, m a_0^2}\left\{\frac{(N+2)^2 - N^2}{(N-1)^2}\right\} = \frac{h^2}{8 m\, a_0^2}\frac{(N+1)}{(N-1)^2}.$$

We solve the equation $\Delta E = \dfrac{h^2}{8 m a_0^2}\dfrac{(N+1)}{(N-1)^2} = E_{\text{Thermal}}$ (25 meV).

This equation is rewritten as $\dfrac{(N-1)^2}{N+1} = \dfrac{h^2}{8 m a_0^2\, E_{\text{Thermal}}} = 116.2$.

Thus, we obtain the quadratic equation $N^2 - 118.2\,N - 115.2 = 0$, and solve the equation to obtain N = 119.2.

Therefore, at least 120 Na atoms are required when the energy gap is smaller than the thermal energy 25 meV.

THEORETICAL 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.

10.1 Calculate the heat of reaction, Δ*H*°, 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 kJ mol^{-1}
Carbon dioxide:	: –393.5 kJ mol^{-1}
Water:	–285.8 kJ mol^{-1}

10.2 In a laboratory, we can generate carbon dioxide from calcium carbonate and hydrochloric acid. Calculate the volume, *V* (unite, cm^3), of generated carbon dioxide from 10.0 g of calcium carbonate and 50.0 cm^3 of 1.00 mol dm^{-3} 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.

SOLUTION OF PREPARATORY PROBLEM 10

10.1

Methane :	$C + 2\,H_2 \rightarrow CH_4$	$\Delta H^\circ_f = -74.82$ kJ mol^{-1}
Carbon dioxide :	$C + O_2 \rightarrow CO_2$	$\Delta H^\circ_f = -393.5$ kJ mol^{-1}
Water :	$H_2 + ½\,O_2 \rightarrow H_2O$	$\Delta H^\circ_f = -285.8$ kJ mol^{-1}

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \qquad \Delta H^\circ_f = -890.28 \text{ kJ mol}^{-1}$$

10.2 $$n(CaCO_3) = \frac{10.0\text{ g}}{100.1\text{ g mol}^{-1}} = 0.100\text{ mol}$$

$n(HCl) = 1.00\text{ mol dm}^{-3} \times 0.0500\text{ dm}^3 = 0.0500\text{mol}$

$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2$

The amount of generated carbon dioxide = 0.0250 mol

Calculation by use of an equation for ideal gas:

$$V(\mathrm{CO_2}) = \frac{0.0250\,\mathrm{mol} \times 8.31\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\ \mathrm{K}}{1013 \times 100\ \mathrm{Pa}} = 6.11 \times 10^{-4}\ \mathrm{m^3} = 611\ \mathrm{cm^3}$$

THEORETICAL 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.

11.1 Calculate the density of “Dry Ice”, ρ, when the edge length of the cubic unit cell of “Dry Ice” is 0.56 nm.

11.2 Calculate the number of carbon dioxide molecules, N, in the cuboid “Dry Ice” of 20 cm × 10 cm × 5.0 cm.

SOLUTION OF PREPARATORY PROBLEM 11

11.1 CO_2 (M = 44.0 g mol^{-1}): face-centered cubic lattice, 4 molecules per one unit lattice:

$$\rho = \frac{\dfrac{44.0\text{ g mol}^{-1}}{6.02\times10^{23}\text{ mol}^{-1}}\times 4}{(0.56\times10^{-9}\text{ m})^3} = \frac{44.0\times 4}{6.02\times(0.56)^3\times10^{(23\,-27)}} = \frac{176}{1.057\times10^{-4}} = 1.67\times10^{6}\text{ g m}^{-3}$$

11.2

$$N = \frac{(0.20\times0.10\times0.050)\times\rho_{\text{dry ice}}}{44.0}\times N_A$$

$$= \frac{(0.20\times0.10\times0.050)\times1.67\times10^{6}}{44.0}\times6.02\times10^{23}$$

$$= 2.28\times10^{25}$$

N = 2.3×10^{25} molecules

THEORETICAL 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 ($TiO(OH)_2$) 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.

12.1 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.

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

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

12.4 In a laboratory, 25.0 cm^3 of concentrated sulfuric acid (18.0 mol dm^{-3}) was used in order to obtain titanium dioxide from 10.0 g of pure ilmenite. Calculate the minimum mass of calcium carbonate that is necessary for neutralizing the surplus sulfuric acid when all of the processes (A) – (D) proceed completely.

SOLUTION OF PREPARATORY PROBLEM 12

12.1 Molar mass of ilmenite: $M(FeTiO_3)$ = 151.7 g mol^{-1}, and that of TiO_2: $M(TiO_2)$ = 79.9 g mol^{-1}

$$m(\text{FeTiO}_3) = \frac{m(\text{TiO}_2)}{79.9\ \text{g mol}^{-1}} \times 151.7\ \text{g mol}^{-1} = \frac{1000 \times 1000\ \text{g} \times 0.350}{79.9\ \text{g mol}^{-1}} \times 151.7\ \text{g mol}^{-1} = 664518\ \text{g} =$$

$m(FeTiO_3)$ = 665 kg

12.2 Processes (A) and (B):

$FeTiO_3 + 2\ H_2SO_4 + 5\ H_2O \rightarrow FeSO_4 \cdot 7\ H_2O\downarrow + TiOSO_4(aq)$

12.3 (C) $TiOSO_4(aq) + 2\ H_2O \rightarrow TiO(OH)_2 + H_2SO_4$

(D) $TiO(OH)_2 \rightarrow TiO_2 + H_2O$

From the answer 12.2:

(A) and (B), $FeTiO_3 + 2\ H_2SO_4 + 5\ H_2O \rightarrow FeSO_4 \cdot 7\ H_2O\downarrow + TiOSO_4(aq)$

Processes (A) – (D):

$FeTiO_3 + H_2SO_4 + 6\ H_2O \rightarrow FeSO_4 \cdot 7\ H_2O + TiO_2$

12.4 Chemical formula of the neutralization:

$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 \cdot 2\ H_2O + CO_2$

$M(H_2SO_4)$ = 98.08 g mol^{-1}; $M(CaCO_3)$ = 100.1 g mol^{-1}

The necessary amount of sulfuric acid for the reaction:

$$n(\text{H}_2\text{SO}_4) = \frac{m(\text{FeTiO}_3)}{151.7\ \text{g mol}^{-1}} \times 2 = \frac{10.0\ \text{g} \times 2}{151.7\ \text{g mol}^{-1}} = 0.132\ \text{mol}$$

The amount of surplus sulfuric acid:

$$n(\text{H}_2\text{SO}_4) = 18.00\ \text{mol dm}^{-3} \times 0.025\ \text{dm}^3 - 0.132\ \text{mol} = 0.318\ \text{mol}$$

The necessary amount of calcium carbonate for the neutralization:

$$m(\text{CaCO}_3) = 0.318\ \text{mol} \times 100.1\ \text{g mol}^{-1} = 31.8\ \text{g}$$

THEORETICAL 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.

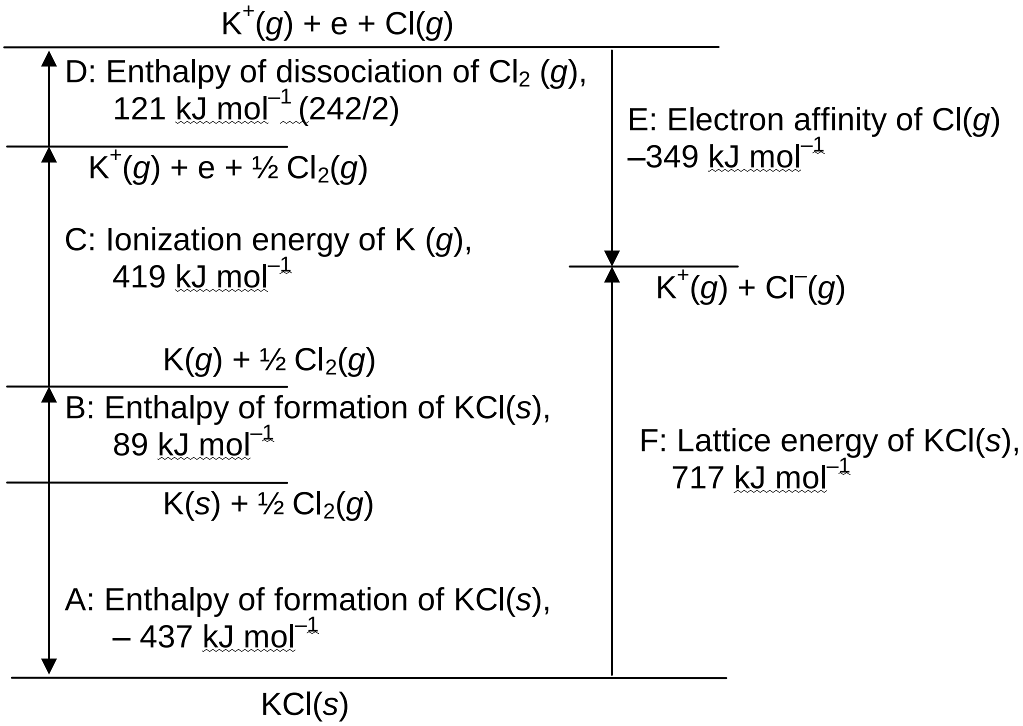
13.1 llustrate a Born-Haber cycle of potassium chloride (KCl) and calculate its lattice energy by use of the following thermodynamic data.

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.

SOLUTION OF PREPARATORY PROBLEM 13

13.1 B + C + D – A + E = 89 + 419 + 121 – (– 437) + (– 349) = 717 kJ mol^{-1}

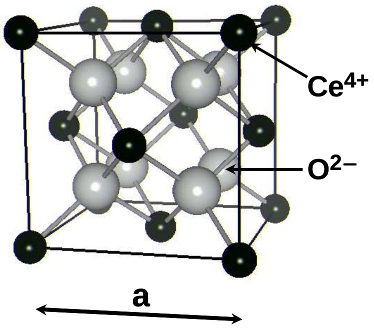


THEORETICAL PROBLEM 14

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 $Ce_{1-x}Y_xO_{2-y}$, 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.

14.1 Indicate how many cations and anions are present in the CaF_2 structure unit cell?



14.2 What is the ratio (%) of oxygen vacancies to the anion sites in the solid solution synthesized with the molar ratio of CeO_2 : Y_2O_3 = 0.8 : 0.1.?

14.3 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 1.36×10^{-22} cm^3.

SOLUTION OF PREPARATORY PROBLEM 14

14.1 Cations: 4 Anions: 8

14.2 $0.8(CeO_2) + 0.1(Y_2O_3) = Ce_{0.8}Y_{0.2}O_{1.9}$

$0.1 / 2.0 = 0.05$ 5 %

14.3 $1 / (1.36\times10^{-22}) \times 8 \times 0.05 = 2.94\times10^{21}$

THEORETICAL 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.

15.1 Represent reaction formulas at the cathode and the anode during oxygen pumping.

15.2 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 (cm^3) produced at the anode at 800 ºC and a pressure of 1.01×10^5 Pa. Given your answer to two significant figures.

15.3 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 ºC. Electronic conduction of the solid electrolyte can be ignored.

SOLUTION OF PREPARATORY PROBLEM 15

15.1 Cathode: $O_2 + 4\ e^- \rightarrow 2\ O^{2-}$

Anode: $2\ O^{2-} \rightarrow O_2 + 4\ e^-$

15.2 1/4 mol O_2 moves when 1 mole of electrons flows.

Moved O_2 : $n = (1.93 \times 500 / 96485) \times (1/4) = 2.5\times10^{-3}$ mol

$$V = \frac{n\,R\,T}{p} = \frac{2.5\times10^{-3}\times 8.314\times 1073}{1.01\times10^{5}} = 2.208\times10^{-4}\ \text{m}^3$$

$$= 2.208\times10^{2}\ \text{cm}^3$$

Answer: 2.2×10^{2} cm^3

15.3 In an oxygen concentration cell, ΔG^o and E^o are 0 and $z = 4$.

$$E = -\frac{R\,T}{4\,F}\ \ln\frac{p_{\text{ox}}}{p_{\text{red}}} = \frac{R\,T}{4\,F}\ \ln\frac{p_{\text{cathode}}}{p_{\text{anode}}} = 2.303\ \frac{R\,T}{4\,F}\ \lg\frac{p_1}{p_2}$$

$$= \frac{2.303\ \times\ 8{,}314\times 1073}{4\ \times\ 96485}\ \times 2 = 0.1064\ \text{V}$$

Answer: 1.1×10^{-1} V

THEORETICAL 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.

16.1 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.

16.2 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 $AgPb_2$.

16.3 Write the chemical reaction for lead in the alloy during the heating process of the alloy in the air at about 800 °C.

16.4 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.

16.5 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.

SOLUTION OF PREPARATORY PROBLEM 16

16.1 **Route 1**

$PbS + 2\ O_2 \rightarrow PbSO_4$

$PbS + PbSO_4 \rightarrow 2\ Pb + 2\ SO_2$

Route 2

$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$

$PbS + 2\ PbO \rightarrow 3\ Pb + SO_2$

16.2 **Route 1**

$AgS + 2\ PbSO_4 \rightarrow AgPb_2 + 2\ SO_2$

Route 2

$Ag_2S + 4\ PbO \rightarrow 2\ AgPb_2 + SO_2$

16.3 $2\ Pb + O_2 \rightarrow 2\ PbO$

16.4 B

16.5 E

THEORETICAL 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.

17.1 Write the coordination number and the coordination structure of the cobalt complex in the ethanol solution of cobalt(II) chloride anhydrate.

17.2 The blue colour remains when an amount of water double than that of the cobalt chloride was added to the ethanol solution of cobalt(II) chloride. Write the chemical formula of the major cobalt complex in the solution.

17.3 Write the chemical reaction when a large amount of water is added to the solution.

17.4 Write the coordination number and the coordination structure of the cobalt complex in the aqueous solution.

17.5 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.

17.6 Explain the color change if the temperature of the violet solution decreases.

17.7 Write the chemical formula of the cobalt complex in cobalt(II) chloride hexahydrate.

SOLUTION OF PREPARATORY PROBLEM 17

17.1 Coordination number: 4

Coordination structure: tetrahedral

17.2 $[CoCl_2(H_2O)_2]$

17.3 $[CoCl_2(H_2O)_2] + 4\ H_2O \rightarrow [Co(H_2O)_6]^{2+} + 2\ Cl^-$

17.4 Coordination number: 6

Coordination structure: octahedral

17.5 It becomes blue due to the formation of tetrahedral chlorocomplexes of Co(II)**.**

17.6 Heating causes a change in the structure of the complex. The solution becomes blue.

17.7 $[Co(H_2O)_6]Cl_2$

THEORETICAL PROBLEM 18

Redox titration

The chromium content of a stainless steel (a Fe-Cr alloy) sample was analyzed by the following procedure:

i) 0.1000 g of a stainless steel sample is dissolved in 20 cm^3 of heated sulfuric acid (c = 1.8 mol dm^{-3}).

ii) 4 cm^3 of conc. nitric acid is added to the solution and it is then heated for 10 min till the colour of the solution changes from blue to green.

iii) 10 cm^3 of 0.5 % silver nitrate aqueous solution and 6 g of ammonium persulfate ($(NH_4)_2S_2O_8$) 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 cm^3 of 5% NaCl aqueous solution is added.

v) 20 cm^3 of ammonium iron(II) sulfate ($FeSO_4 \cdot (NH_4)_2SO_4$) aqueous solution ($c$ = 1.00×10^{-1} mol dm^{-3}) is added with a volumetric pipette.

vi) Potassium permanganate ($KMnO_4$) aqueous solution (c = 2.00×10^{-2} mol dm^{-3}) is titrated using a burette. When the colour of the solution becomes light purple, it is presumed to be the final point.

Solve the problem according to the tasks 18.1 – 18.6. The relative atomic mass of Cr is assumed to be 52.00.

18.1 Describe the chemical reaction in process ii).

18.2 Trivalent chromium ion exists in the solution after process ii). How will it change after process iii)?

18.3 Describe the reaction which occurs in process iv). Moreover, mention the purpose of the process.

18.4 Describe the ionic reaction which occurs between heavy metal ions in process v). What color will the solution become in the process?

18.5 Describe the reaction which occurs in process vi).

18.6 The titrated amount in process vi) was 12.00 cm^3. Based on chemical equations and volumes of the solutions used calculate the chromium content of this stainless steel sample.

SOLUTION OF PREPARATORY PROBLEM 18

18.1 $6\ FeSO_4 + 2\ HNO_3 + 3\ H_2SO_4 \rightarrow 3\ Fe_2(SO_4)_3 + 4\ H_2O + 2\ NO$ ($Fe^{2+} \rightarrow Fe^{3+}$)

18.2 $Cr_2O_7^{2-}$

18.3 $Ag^+ + Cl^- \rightarrow AgCl\downarrow$

When the ammonium persulfate is not completely decomposed, the function of $AgNO_3$ (oxidation of the solution) will be prevented.

18.4 $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$

The color changes from orange to (light) blue green.

18.5 $MnO_4^- + 5\ Fe^{2+} + 8\ H^+ \rightarrow Mn^{2+} + 5\ Fe^{3+} + 4\ H_2O$

18.6 Based on the chemical equations in 18.1, 18.4 and 18.5 and considering the mass of the sample of the steel and volumes of the solutions used, one can calculate by simple stoichiometric calculations the content of chromium in the sample of steel.

THEORETICAL 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 19.1 – 19.5 with the provision that carbon content of the pig iron is 4.50 mass % and that a coke contains 90.0 mass % of C, 7 mass % of SiO_2, 3 mass % of Al_2O_3. The gas constant is 8.314 J K^{-1} mol^{-1}, and the relative atomic masses 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.

19.1 The main component of an iron ore is Fe_2O_3 and it will be reduced to form Fe and CO_2 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.

19.2 Iron ore also contains gangue (impurity materials), such as 7 mass % of SiO_2 and 3 mass % of Al_2O_3 other than 90 mass % Fe_2O_3. 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 SiO_2.

19.3 In a convertor process, carbon is eliminated by blowing O_2 gas onto pig iron. When the molar amounts of CO and CO_2 are identical, what is the volume (dm^3) of O_2 gas required for the complete removal of carbon from 1.00 kg of pig iron at 27 ^oC and 2.026×10^5 Pa?

19.4 When 1.00 kg of iron is produced from iron ore through BF and a convertor only via process (i) in the question 19.1, how many kg of CO_2 is generated? Assume that the CO gas (the same molar amount of CO_2) generated from the convertor is oxidized and exhausted as CO_2. In the calculation, include the CO_2 generated in the calcinations of $CaCO_3$ to produce the subsidiary material of CaO.

19.5 The crystal structure of iron is body center cubic (bcc). Derive the atomic radius of iron at room temperature.

SOLUTION OF PREPARATORY PROBLEM 19

19.1 (i) $Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$

(ii) $2\ Fe_2O_3 + 3\ C \rightarrow 4\ Fe + 3\ CO_2$

19.2 Mass of Fe_2O_3 required to obtain 1.00 kg of pig iron is 955 × (159.6 / 111.6) = 1365.75 g. And the amount of the slag generated from iron ore is 17 / 90, namely 257.98 g. Coke (392.29 g) also produces slag from the gangue 0.17 times as much as the coke, namely 66.69 g. Accordingly, the total amount of the slag generated becomes 324.67 g.

$\underline{m(Fe_2O_3) = 0.325\ \text{kg}}$

19.3 A half of the carbon (45 g) in the 1 kg of pig iron is oxidized into CO_2 and the rest into CO. Hence, 3/4 times of 45/12 mol of O_2 gas is required. Using $p\,V = nRT$, V can be obtained as 34.6 dm^3.

$\underline{V(O_2) = 34.6\ \text{dm}^3}$

19.4 Considering 1 kg of pig iron, the amount of moles of C required for the reduction is 1.5 times as much as that of Fe. Then, (955 / 55.8) × 3/2 × 12.0 = 308.06 g, which becomes 353.06 g together with the carbon dissolved in pig iron, 45 g.

As derived in the question 19.2, 324.67 g of the slag containing 7/17 of CaO is generated. When this amount of CaO is produced from $CaCO_3$, CO_2 is generated as much as 44/56.1 of CaO in weight bases. Hence, the total amount of CO_2 generation becomes (353.06 × 44 / 12) + (324.67 × 7 / 17) × 44 / 56.1 = 1399.41 g. Then, divided by 0.955, a value per 1 kg of iron can be obtained.

$\underline{m(CO_2) = 1.47\ \text{kg}}$

19.5 The atomic radius of the bcc is $\sqrt{3/4}$ times of the unit length, a. The volume of the unit structure, $a^3 = 55.8/7.90 \times 2/N_A = 23.4543\times10^{-24}\ \text{cm}^3$. Hence, $a = 2.8625\times10^{-8}$ cm.

$\underline{r(Fe) = 1.24\times10^{-10}\ \text{m}}$

THEORETICAL PROBLEM 20

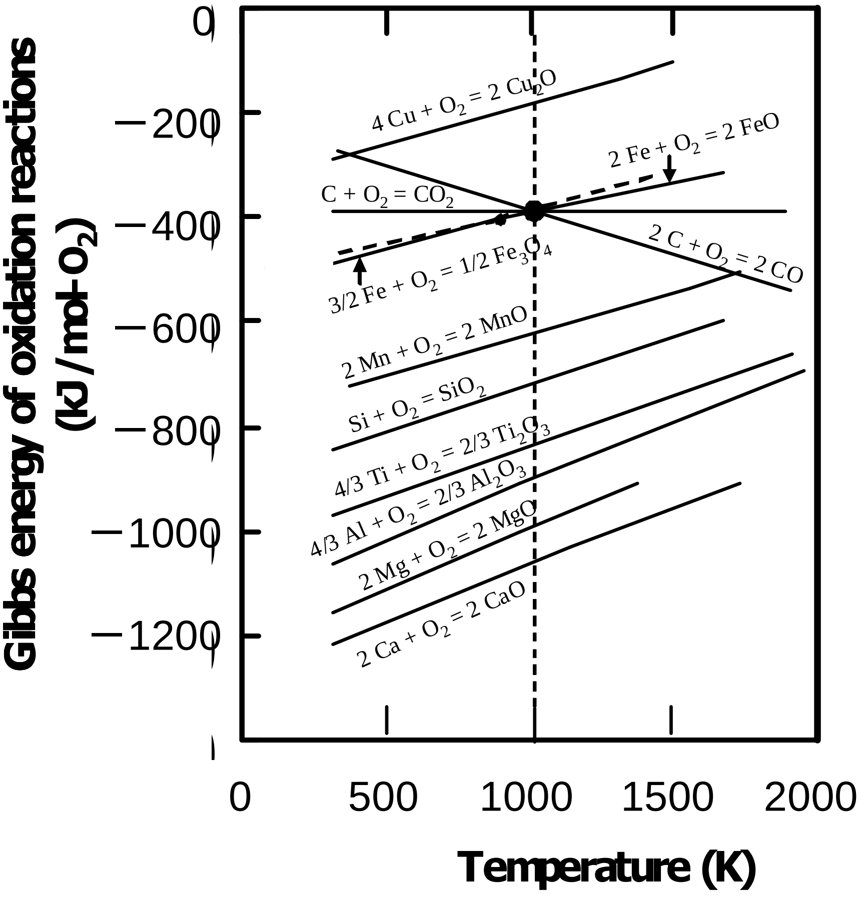
Gibbs energy of oxidation reaction

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

20.1 Fill (**i**) – (**vi**) 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^o, can be expressed as (**ii**) in terms of standard (**iii**) change, ΔH^o, and standard (**iv**) change, ΔS^o , 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_{O2} can be derived as (**v**) using ΔG^o and the gas constant *R*. The diagram where ΔG^o 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:



20.2 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.

20.3 Describe the chemical reaction when Cu_2O is reduced by Al.

20.4 Derive the heat of the reaction in the above question c) per mole of Al.

20.5 Show the points through which any lines of constant oxygen partial pressure p_{O2} and those with a constant value of the ratio of CO gas partial pressure to CO_2 gas partial pressure p_{CO}/p_{CO2} pass, respectively, in Figure 1.

20.6 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?

SOLUTION OF PREPARATORY PROBLEM 20

20.1

(i)	**(ii)**
m/2n M + O_2 = 2/n M_mO_n	$\Delta H^o - T\Delta S^o$
(iii)	**(iv)**
enthalpy	entropy
(v)	**(vi)**
$e^{(\Delta G^o/RT)}$	oxidized

20.2 In all the reactions except for the two C oxidations, 1 mole of the gas (oxygen), namely its entropy, is lost. This is why the slopes are almost identical. However, there are almost no changes in the entropy of the gas in the case of CO_2 gas formation, making the line horizontal, and causing the increase in 1mole of the gas in the case of CO formation showing the different sign with the same slope.

20.3 3 Cu_2O + 2 Al = 3 Cu + Al_2O_3

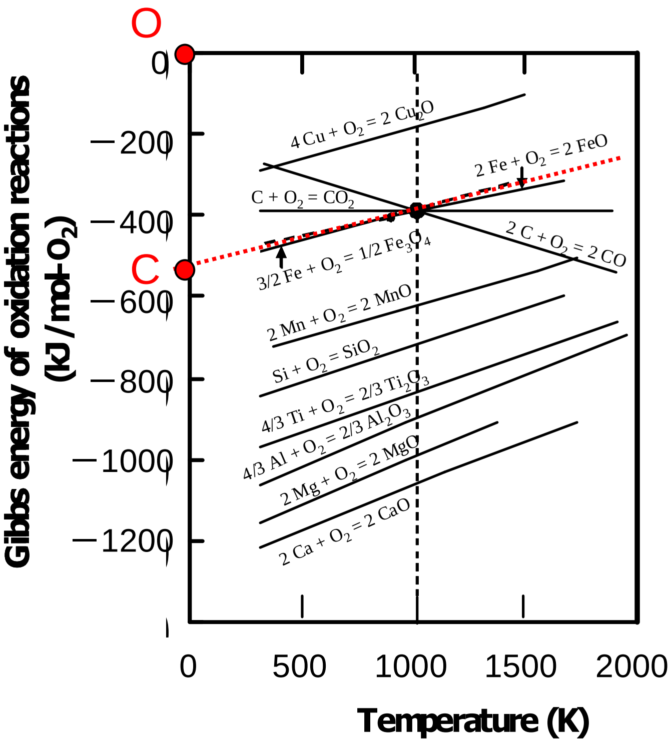
20.4 The heat generated (or absorbed) by the reaction per 1 mole of oxygen gas can be read from the difference in the values of the intercepts of the lines for Cu and Al. Hence, the value per 1 mole of Al can be obtained by multiplying 3/4. Then, the ΔH^o of the reaction can be read as –1130 – (–350) = –780 kJ per 1 mole of oxygen gas, and it will become –585 kJ per mole of Al.

Heat of 585 kJ will be generated by the reaction. (exothermic reaction)

20.5 Since the vertical axis shows $RT \ln p_{O2}$ value, any straight lines drawn through point "O" have the slope of $R \ln p_{O2}$. Hence, the value of p_{O2} is identical on such lines.

On the other hand, the line of the reaction: 2 CO + O_2 = 2 CO_2 can be drawn by the two oxidation reactions of C mentioned in the question b), and the intercept of the derived line is assumed to be "C" through which the line of constant p_{CO}/p_{CO2} value will go.

They are plotted in the figure as "O" and "C", respectively.



20.6 Two lines of 2 Fe + O_2 = FeO and 2 CO + O_2 = 2 CO_2 happen to cross at 1000 K, which means that the value of the ratio of p_{CO}/p_{CO2} is one when Fe and FeO coexist. Accordingly, the consumed fraction becomes 50 %.

THEORETICAL PROBLEM 21

Quantitative composition analysis of volcanic gas

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

Before sampling fumarolic gas, 20 cm^3 of 5 mol dm^{-3} 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 cm^3 and 38.0 cm^3, respectively.

A 10 cm^3 aliquot was collected from the 38.0 cm^3 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 cm^3 of 10% $BaCl_2$ solution to the solution resulted in a white precipitate. The precipitate was dried and weighed. Its mass was 0.30 g.

The volume of 1 mol of a gas is assumed to be 22.4 dm^3 in the standard condition (0 °C and 1013 hPa).

21.1 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 during the experiment constant (1.0 g cm^{-3}).

21.2 Calculate the quantity of sulfur (in mol) contained in the fumarolic gas collected into the syringe. Moreover, calculate the total volume (in cm^3) of H_2S and SO_2 gas components at the standard conditions (0 °C, 1013 hPa). Give the answer to two significant figures.

21.3 Mole ratios of H_2S to SO_2 are estimated utilizing the reactivity difference between H_2S and SO_2 gases. Fumarolic gas is bubbled into a testing tube which contains 30 cm^3 of KIO_3 – KI solution with a concentration of 0.03 mol dm^{-3} and 3 cm^3 of HCl solution (c = 4 mol dm^{-3}). Describe by chemical equations the reactions occurring for H_2S and SO_2 gases, respectively.

SOLUTION OF PREPARATORY PROBLEM 21

21.1 This corresponds to 1 mole of water.

The volume is 22.4 dm^3 at the standard condition.

$22.4 \times 1000 / (22.4 \times 1000 + 50.0 + 109.8 + 28.0) = 0.992$

$0.992 \times 100 = 99$ %

21.2 The precipitate is $BaSO_4$.

The formula mass is:

$M_r(BaSO_4) = 137.3 + 32.1 + 16.0 \times 4 = 233.2$

0.30 g of $BaSO_4$ corresponds to 0.30 g / 233.2 g mol^{-1} = 1.29×10^{-3} mol of $BaSO_4$

Total sulfur amount in the initial solution is

$n(S)_{total} = 1.29\times10^{-3} \times 38.0 / 10.0 = 4.90\times10^{-3}$ mol

The volume of the gas is

22.4 dm^3 $\times$ 4.90×10^{-3} mol = 109.8 cm^3 = 1.1×10^2 cm^3

21.3 $SO_2 + I_2 + 2\ H_2O \rightarrow SO_4^{2-} + 2\ I^- + 4\ H^+$

$H_2S + I_2 \rightarrow S + 2\ I^- + 2\ H^+$

THEORETICAL 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.

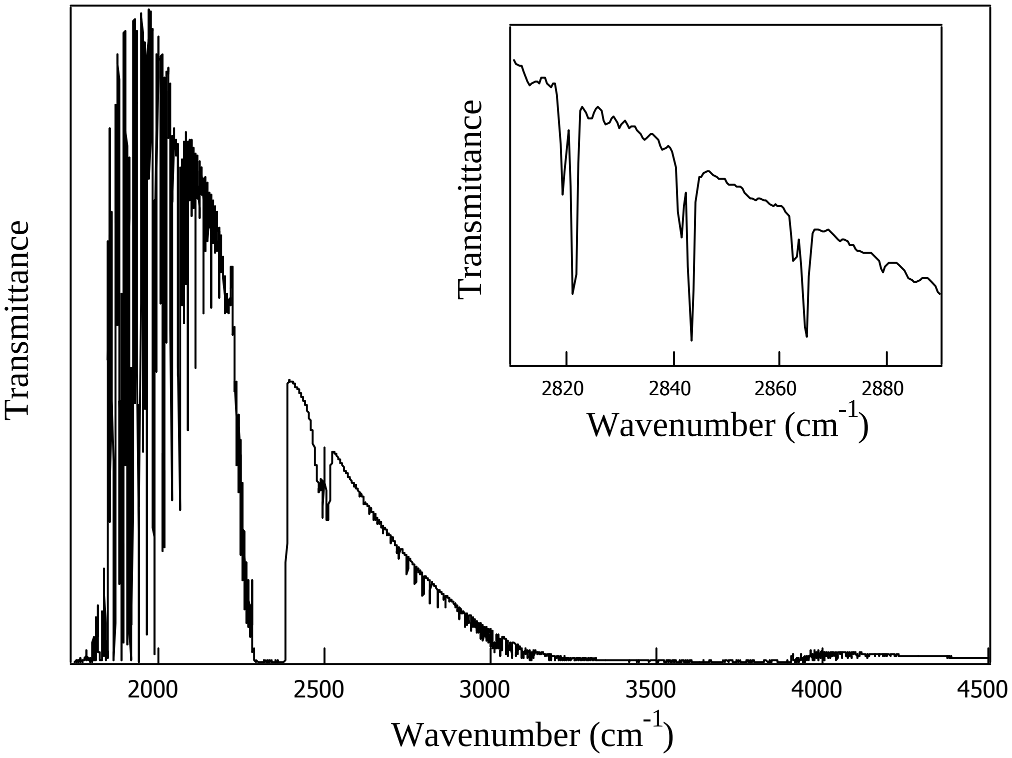


Figure: Infrared absorption spectrum of fumarolic gas obtained from a remote observation using an FTIR equipped with a telescope. X and Y denote hydrogen halides.

22.1 Describe chemical formula of X and Y.

22.2 As shown in the inset, the absorption bands of "X" are split. This split is caused by the isotopic composition of the halogen in "X". It has an isotope abundance ratio of 3 : 1. List the two isotopes in order of decreasing abundance.

SOLUTION OF PREPARATORY PROBLEM 22

22.1 **X** HCl **Y** HF

22.2 ^{35}Cl ^{37}Cl

THEORETICAL PROBLEM 23

Introduction to macromolecular chemistry

The presentation of concepts of macromolecules (often called "polymers") appeared in 1925 by the Nobel Prize chemist, Dr. H. Staudinger (Germany). He opened a fascinating world of new organic materials presently utilized as plastics, fibers, rubbers, etc. 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 H_2N-R-COOH (to give polyamides), HO-R-COOH (polyesters), H_2N-R-NH_2 + HOOC-R'-COOH (polyamides), HO-R-OH + 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 mass 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 would like to discuss the relation between the equilibrium state and the length of polymers derived from the stoichiometric mixture of bifunctional monomers. Equation 1 is a typical example of an esterification reaction where the equilibrium constant K is relatively small, such as K = 4.20 at 78 °C (boiling temperature of ethanol).

$$\begin{array}{lllll} \text{CH}_3\text{COOH} & \overset{K}{+} & \text{HOCH}_2\text{CH}_3 & \xrightarrow{K} & \text{CH}_3\text{CO-OCH}_2\text{CH}_3 \;+\; \text{H}_2\text{O} \\ \text{acetic acid)} & & \text{(ethanol)} & & \text{(ester: ethyl acetate)} \end{array} \qquad (1)$$

23.1 When the above esterification reaction (equation 1) is equilibrated from each 1.00 mol of starting material, calculate the mass of ethyl acetate.

By replace of the monofunctional molecules in equation 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 equation 2 supposing the same equilibrium constant in each step.

$$n\cdot HOOC\text{-}R^1\text{-}COOH + \cdot HO\text{-}R^2\text{-}OH \rightarrow HO\text{-}[COR^1CO\text{-}OR^2O]_n\text{-}H + (2n -1)\ H_2O \qquad (2)$$

(dicarboxylic acid) (diol) (polyester)

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 -COR^1CO-OR^2O- group is known as the repeating unit of which the structure is already a dimeric conjunction as described. Therefore, the unit molecular mass, M_u, in the case of eq. 2 is defined as follows ;

$$M_u = \frac{\text{molar mass of the repeating unit}}{2} \quad 2 \qquad (3)$$

When the average molecular mass of a polymer is represented by M *3), the relationship among XX, M and M_u is given as follows ;

$$X = \frac{M\ (\text{mass of end groups})}{M_u} \qquad M \qquad (4)$$

As understood from the calculation in 23.1 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 discussion, we define "the ***degree*** (***extent***) ***of reaction***" ***p*** as follows ;

$$\text{degree of reaction} = p = \frac{\text{amount of unreacted functional groups}}{\text{amount of initial functional groups}} \quad (\leq 1)1) \qquad (5)$$

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 failure, meanwhile. (●-● and o-o represent the dicarboxylic acid and diol residues, respectively.). X is ended with 5.0, in this case.

●-● – o-o – ●-● – o-o – ●-●…X...× or o-o – ●-● – o-o – ●-● – o-o…X ...×
↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑
OK OK OK OK fail OK OK OK OK fail

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

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

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 $X = 416.3$ (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 23.1, elaborative work is necessary to accomplish the reaction condition of $p \to 1$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 $p \to 1$. For easier consideration, let us simplify equation 2 into equation 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 p mol to a negligibly small amount, n_w mol.

$$\text{-COOH of dicarboxylic acid} + \text{-OH of diol} \overset{K}{\rightleftarrows} \text{-CO-O- of polyester} + \text{water} \qquad (7)$$

$$1 - p \; - p \qquad\qquad 1 - p \; - p \qquad\qquad p \; p \qquad\qquad p\ (\rightarrow n_w)$$

23.2 Represent K by using p and n_w.

23.3 From the equation derived in 23.2 and the Carothers equation represent X as a function of β (= K / n_w). If logically permitted, the equation should be simplified as far as possible, considering $pp \le 1$ and $\beta >> 1$.

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

Footnotes

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*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 H_2N-R-COOH or HO-R-COOH, because the repeating unit in such a polymer structure, H-[HN-R-CO]$_n$-OH or H-[O-R-CO]$_n$-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 weights and the number of the *i*-th macromolecular thread, respectively.

SOLUTION OF PREPARATORY PROBLEM 23

23.1 Let X be the amount of substance of the ester, then

$K = 4.20 = X^2 / (1.00 - X)^2$ and $X = 0.672$ mol.

The molar mass of the ester: $= (12.01 \times 4) + (1.01 \times 8) + (16.00 \times 2) = 88.12$ g mol^{-1},

therefore the quantity of the ester: $= 88.12 \times 0.672 = 59.2$ g

23.2 $K = \dfrac{p\, n_w}{(1 - p)^2}$

23.3 From 23.2: $\beta p^{2} - (2\beta + 1)\, p + \beta = 0$=

0 As $p \leq 1$, then

$$p = \frac{(2\beta+1) - [(2\beta+1)^2 - 4\beta^2]^{0.5}}{2\beta} = \frac{(2\beta+1) - (4\beta+1)^{0.5}}{2\beta}$$

p= Since $\beta \gg 1$, $2\beta + 1 \approx 2\beta$ and $4\beta + 1 \approx 4\beta$, therefore, p=

$$p = \frac{2\beta - 2\beta^{0.5}}{2\beta} = 1 - \beta^{-0.5}$$

Put this answer into the Carothers eq. [eq.(6)], $XX = \dfrac{1}{1 - p} = \beta^{0.5}$

23.4 In order to realize $X \geq 100$, $\beta^{0.5} = \left(\dfrac{K}{n_w}\right)^{0.5} \geq 100$.

At $K = 4.00$, $nn_w \leq 4.00\times10^{-4}$ (mol) or 4.00×10^{-2} mol %.

NOTE: The relation between n_w and X was estimated (at $K = 4.00$) and illustrated in Fig. 1. In order to produce PET with $M = 4.00\times10^{4}$ ($X = 416.3$), the same degree of polymerization discussed before, n_w should be less than 9.20×10^{-3} mol %. Careful removal of water is understood to be the key point.

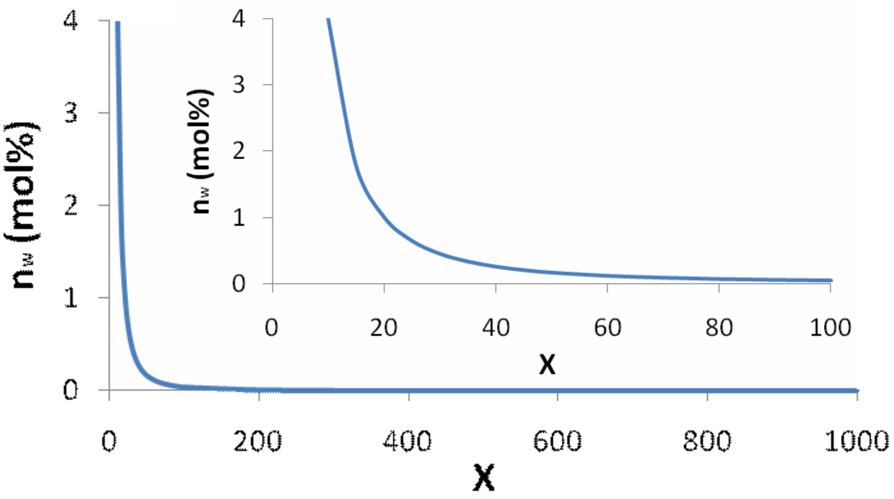
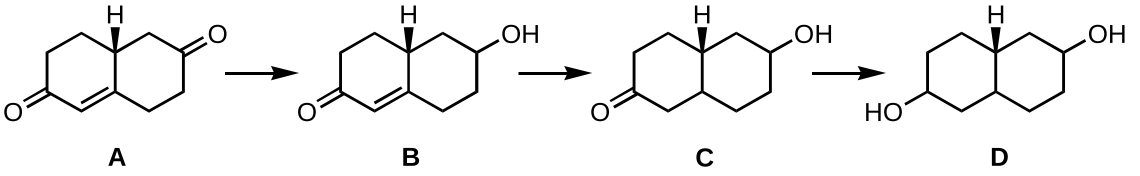


Figure 1. Relation between the (number-average) degree of polymerization ***X*** and the amount of residual water ***n*$_W$**

THEORETICAL 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 **Cij** (**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 **Dijk** (**i**, **j**, **k** = 1, 2) are obtained.



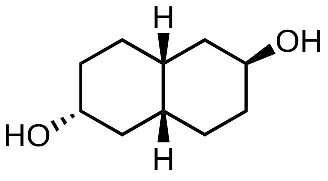
24.1 Are there any identical compounds in the eight kinds of products **Dijk** (**i**, **j**, **k** = 1, 2)? If so, draw the structures of all the compounds that meet the requirements.

24.2 Are there any compounds, in which optical rotation is principally zero degrees, in the eight kinds of products **Dijk** (**i**, **j**, **k** = 1, 2)? If so, draw the structures of all the compounds that meet the requirements.

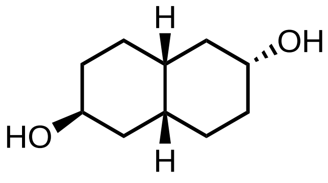
24.3 Are there any compounds which are a pair of optical isomers in the eight kinds of products **Dijk** (**i**, **j**, **k** = 1, 2)? If so, draw the structures of all the compounds that meet the requirements.

SOLUTION OF PREPARATORY PROBLEM 24

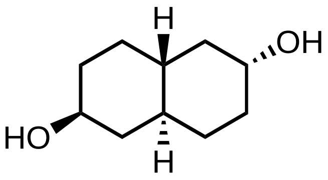
24.1

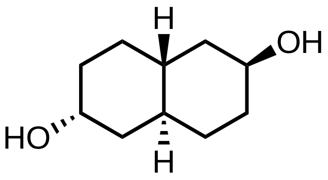


or

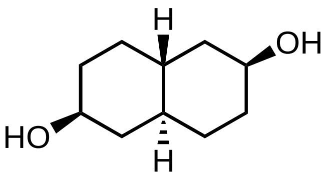


24.2

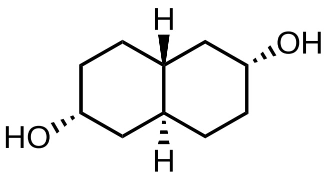




24.3



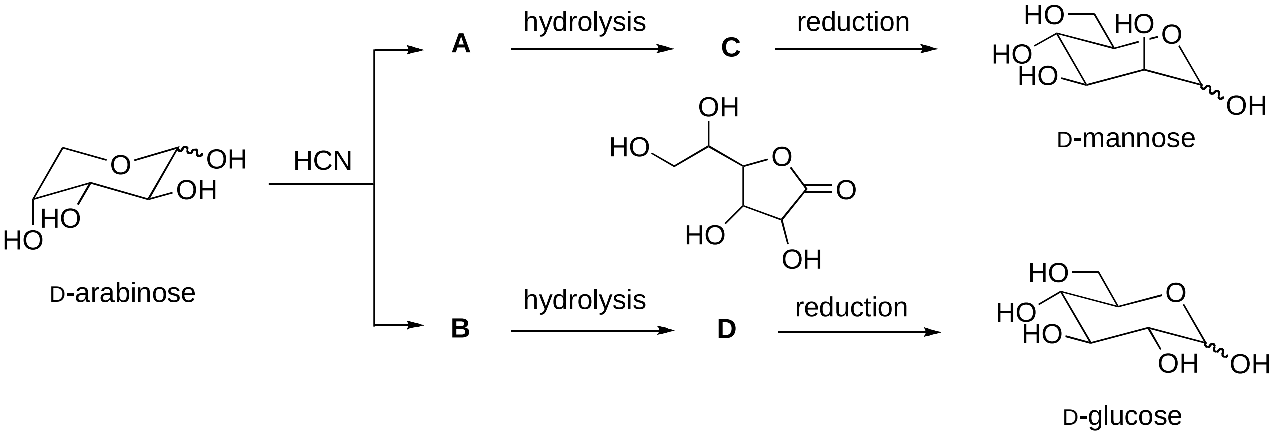
and



THEORETICAL 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.



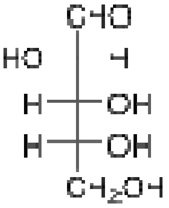
25.1 Draw a Fischer projection of the open-form of D-arabinose.

25.2 Draw Fischer projections of the cyanohydrins **A** and **B**.

25.3 Draw stereostructures of the lactones **C** and **D**.

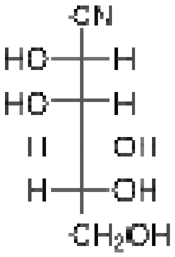
SOLUTION OF PREPARATORY PROBLEM 25

25.1

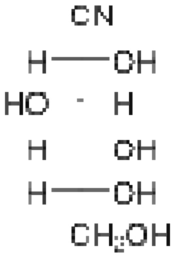


25.2

A

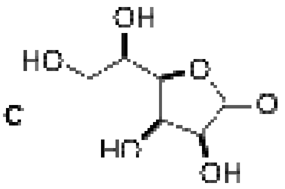


B

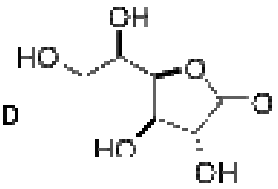


25.3

C



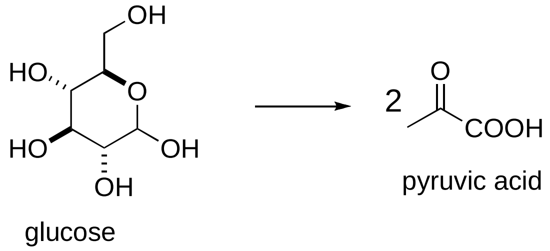
D



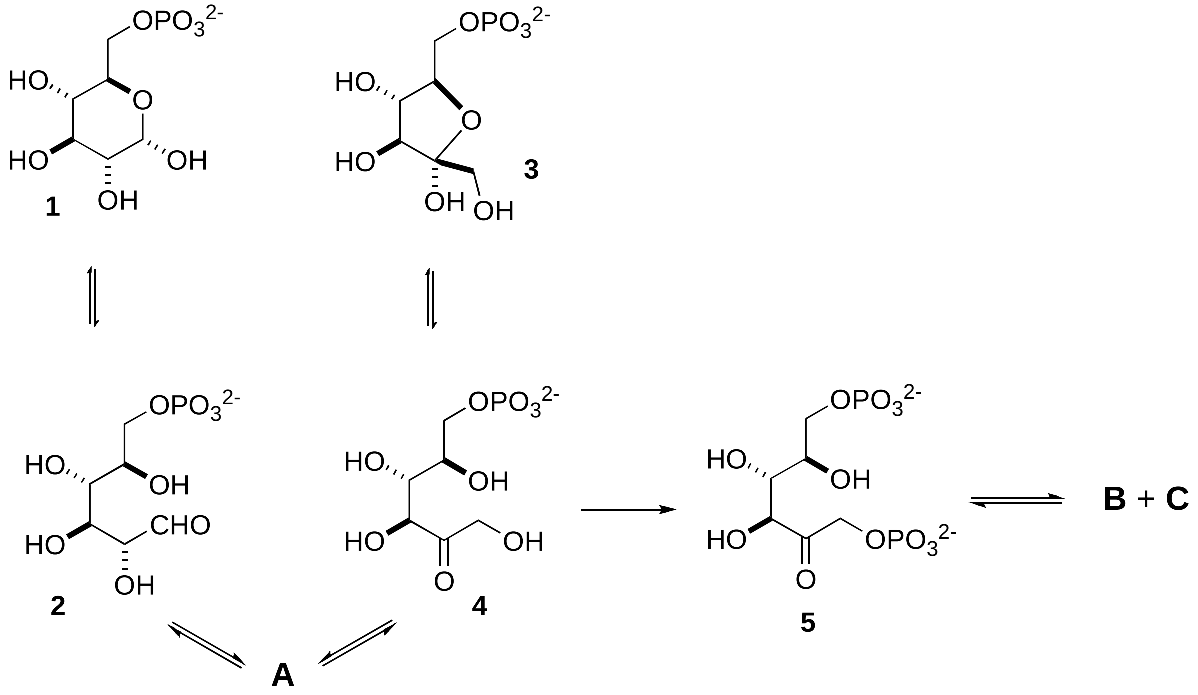
THEORETICAL PROBLEM 26

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.



26.1 A solution of glucose was treated with an equal amount of phenylhydrazine in acetic acid. Draw the structure of the major product.

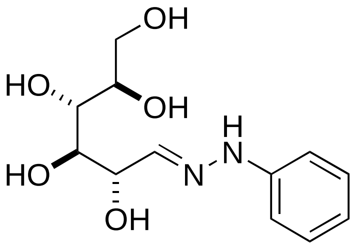
26.2 Draw Fischer projections of glucose-6-phosphate (**2**) and fructose-6-phosphate (**4**), respectively.

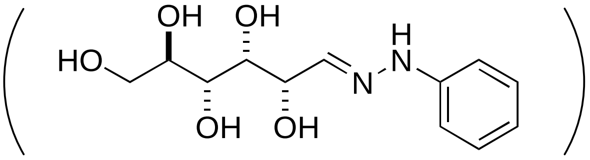
26.3 Draw the structure of tautomer **A**.

26.4 Draw the structures of carbonyl compounds **B** and **C**.

SOLUTION OF PREPARATORY PROBLEM 26

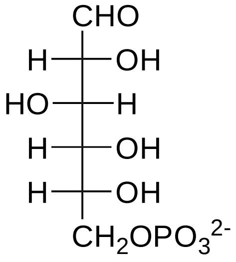
26.1

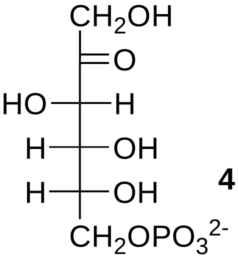




26.2

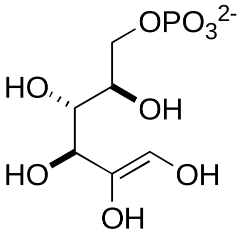
2



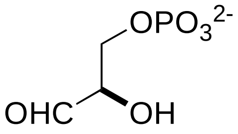


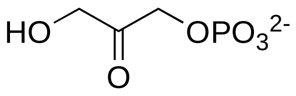
4

26.3



26.4

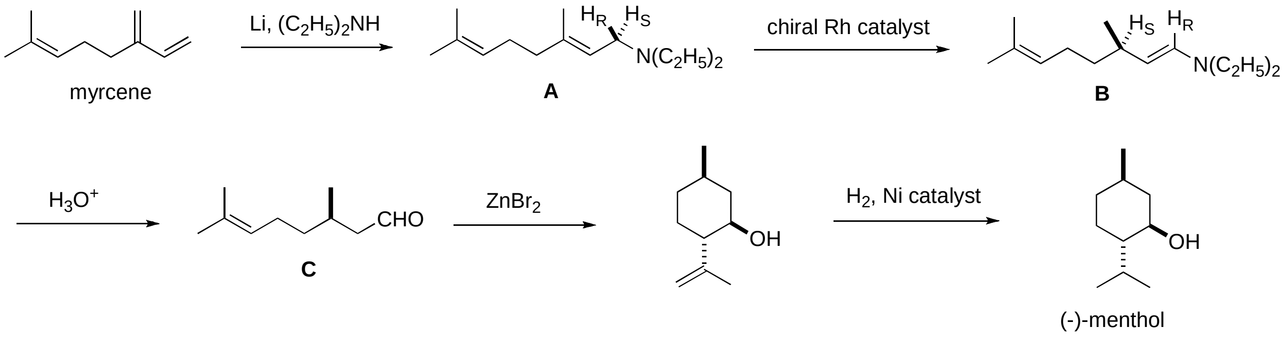




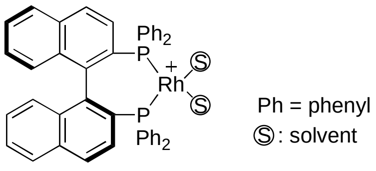
THEORETICAL PROBLEM 27

Menthol synthesis

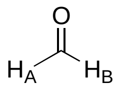
(-)-Menthol is a major component of the taste and fragrance of peppermint and is widely used in cakes, cosmetics, and tooth powder, etc. (-)-Menthol is anodyne and is used as medicine. (-)-Menthol can be supplied from natural resources such as peppermint oil, but is now synthesized industrially as shown 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**.



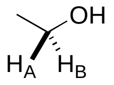
chiral Rh catalyst



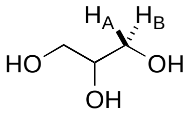
27.1 Which molecules include two enantiotopic hydrogens (H_A and H_B) that are stereochemically similar to two hydrogens (H_R and H_S) of amine **A**? Select your answer(s) from all the symbols of the following molecules **D** – **I**.



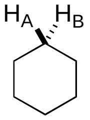
D



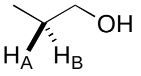
E



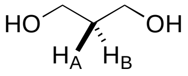
F



G



H



I

27.2 Propose a reasonable reaction mechanism of hydrolysis of enamine **B** to aldehyde **C**.

27.3 Draw the most stable conformer of (-)-menthol.

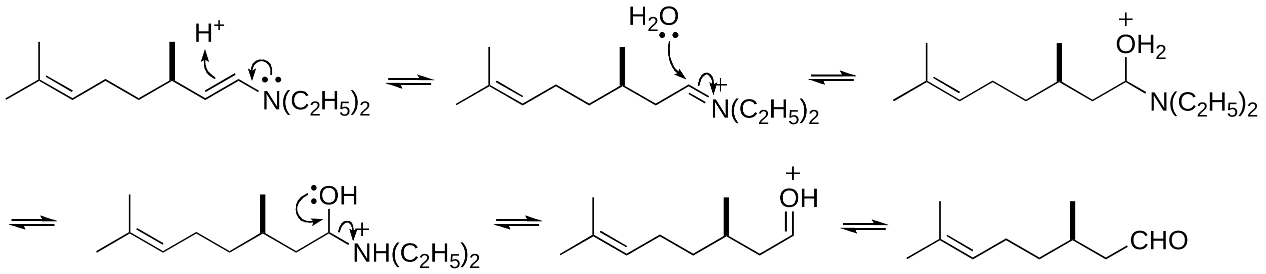
27.4 Treatment of (-)-menthol with dilute sulfuric acid causes a dehydration reaction. Predict the major product.

27.5 (-)-Menthol is a monoterpene composed of two isoprene units. Surround the isoprene unit of (-)-menthol in a line.

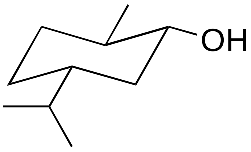
SOLUTION OF PREPARATORY PROBLEM 27

27.1 E, H

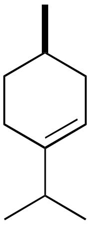
27.2



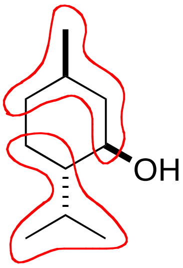
27.3



27.4



27.5

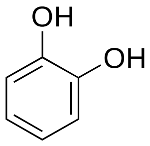


THEORETICAL PROBLEM 28

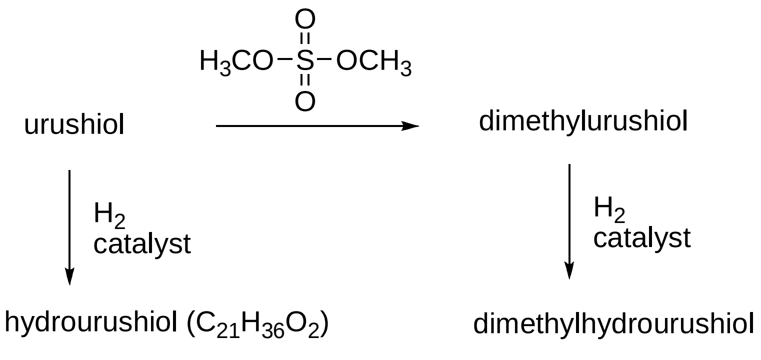
Structure studies of urushiol

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.



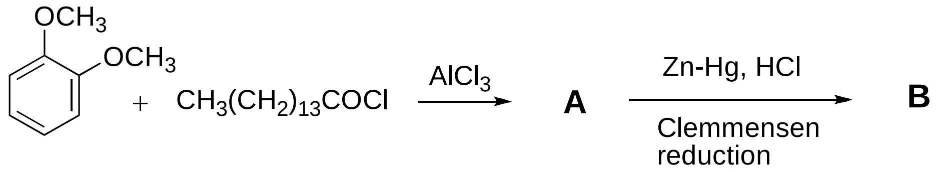
catecol (**1**)



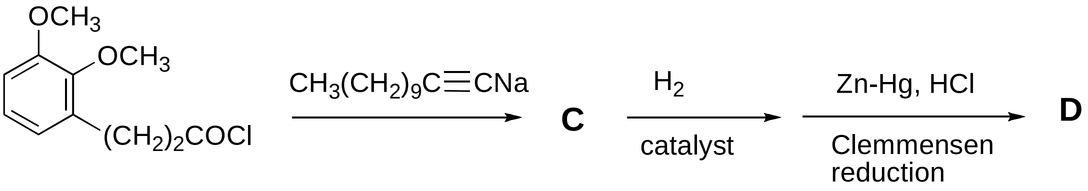
28.1 If the saturated alkyl chain of urushiol is one kind and is not branched, there are two possible structures for hydrourushiol. Draw each structure. Show the alkyl group such as $(CH_2)_n$-CH_3.

28.2 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**.

(I)



(II)



28.3 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 (OHC-CH_2-CO_2H and HOOC-CH_2-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**.

$$\text{OHC}-\text{CH}_2-\text{COOH} \longrightarrow \textbf{E} + \textbf{F}$$

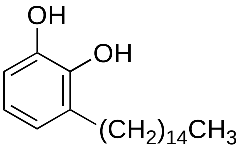
$$\text{HOOC}-\text{CH}_2-\text{COOH} \longrightarrow \textbf{G} + \textbf{F}$$

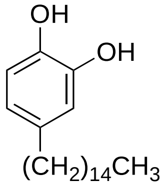
28.4 Carbonyl compounds obtained by ozonolysis of dimethylurushiol are shown below. You may assume that all of the double bonds and benzene rings were cleaved. Based on the experiment results, draw three structures of urushiol among possible urushiols. Show the unsaturated alkyl chain to determine the position of the double bond as in $(CH_2)_nCH=CH(CH_2)_nCH_3$. You do not need to consider the geometry of the double bond (cis or trans).

$$\text{dimethylurushiol} \xrightarrow{O_3} \begin{array}{lllll} HOOC(CH_2)_7COOH & CH_3(CH_2)_5COOH & (COOH)_2 & CO_2 & HCHO \\ HOOC(CH_2)_4COOH & CH_3(CH_2)_5CHO & CH_2CO_2H & CH_3CHO & HCOOH \end{array}$$

SOLUTION OF PREPARATORY PROBLEM 28

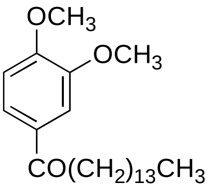
28.1



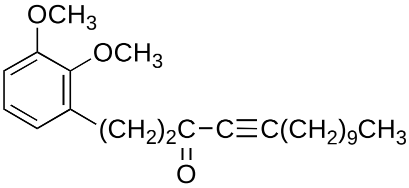


28.2

A



C



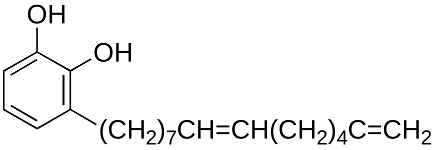
28.3

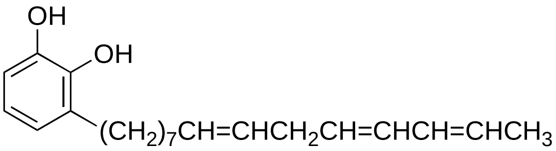
E CH_3CHO

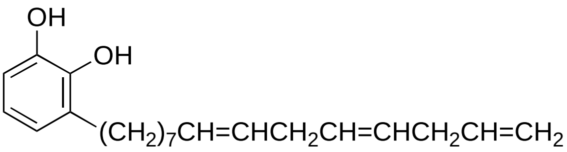
F CO_2

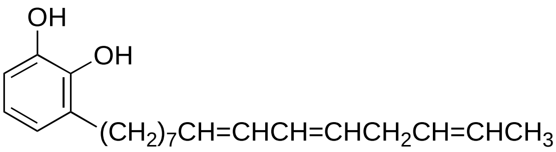
G CH_3COOH

28.4









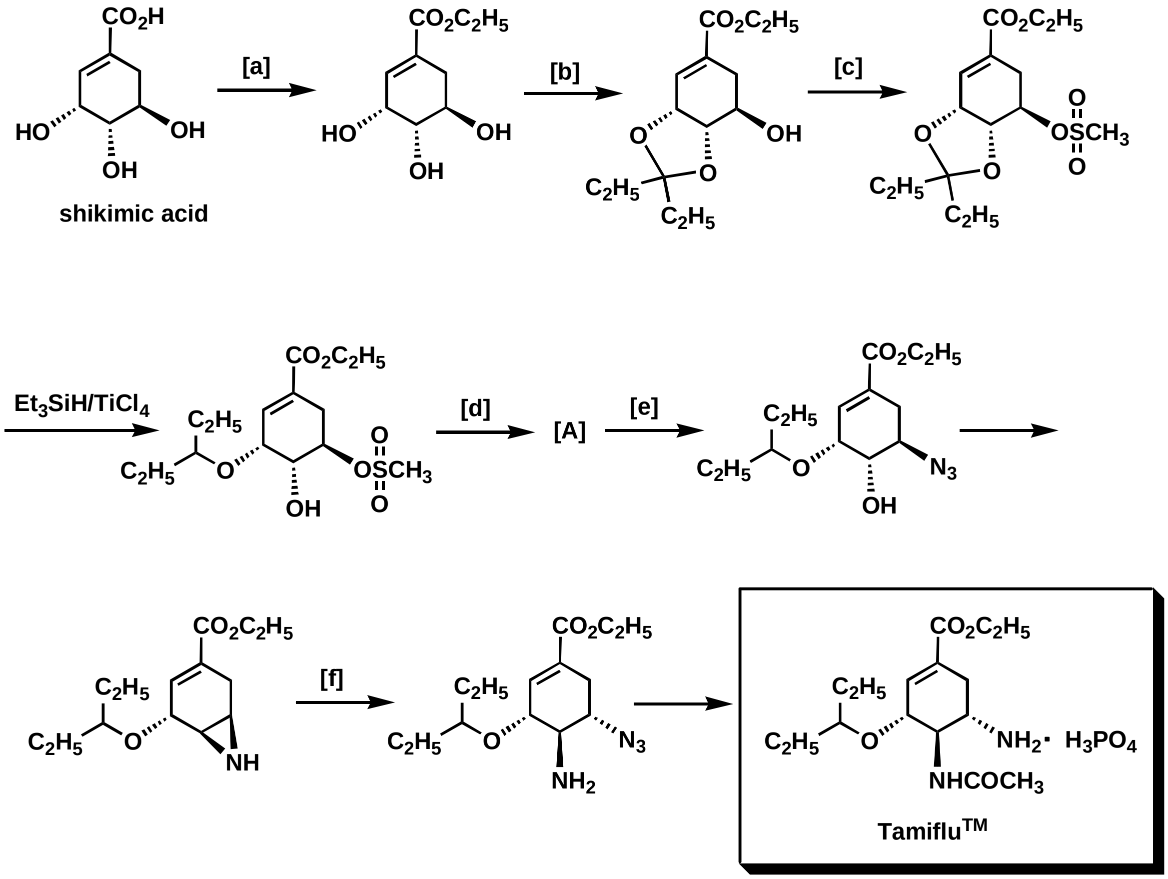
etc

THEORETICAL 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.



29.1 Show chemical reagents necessary for the transformations of **a**, **b**, **c**, **d**, **e**, and **f** in the above scheme.

29.2 Show the reaction mechanism for the transformation of **b**.

29.3 Show the molecular structure of intermediate **A**.

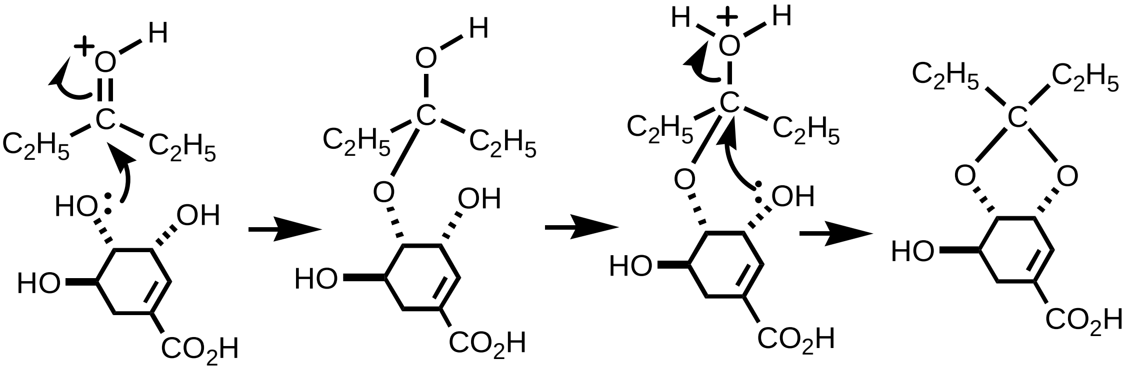
29.4 How many stereoisomers are possible in the molecular structure of Tamiflu?

SOLUTION OF PREPARATORY PROBLEM 29

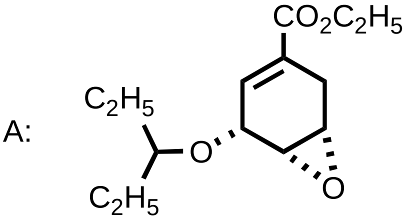
29.1 **a**: EtOH / $SOCl_2$ **b**: 3-pentanone / H^+ **c**: $MeSO_2Cl$ / Et_3N

d: $NaHCO_3$ **e**: NaN_3 / NH_4Cl **f**: NaN_3 / NH_4Cl

29.2



29.3



29.4 8 isomers

THEORETICAL PROBLEM 30

Nuclear magnetic resonance (NMR) spectra of isomers of C_4H_8

There are six isomers of C_4H_8.

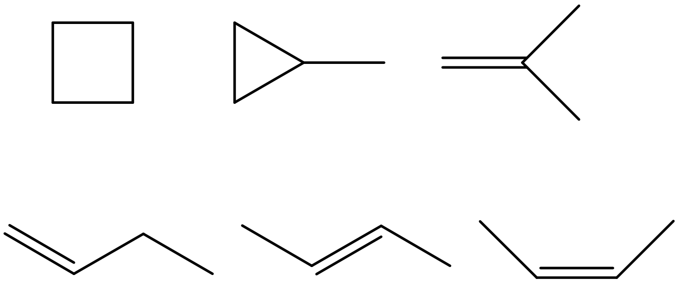
30.1 Draw the structural formulas of all the isomers.

30.2 One of the isomers has only one singlet peak in its proton NMR spectrum. Name this isomer.

30.3 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.

SOLUTION OF PREPARATORY PROBLEM 30

30.1



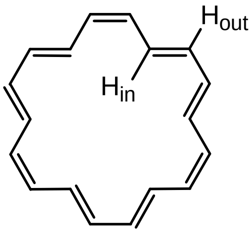
30.2 All the protons in this isomer are magnetically equivalent. Thus, the answer is cyclobutane.

30.3 This isomer has only two magnetically non-equivalent protons without spin-spin coupling. Thus, the answer is methylpropene (or isobutene, isobutylene). The numbers of two non-equivalent protons in methylpropene are two and six. Thus, the intensity ratio = 6/2 = 3 (or 2/6 = 1/3).

THEORETICAL 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. 31.1.



[18]annulene

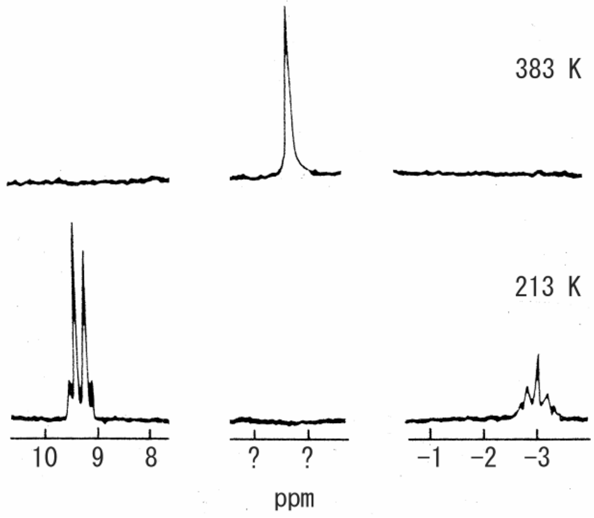


Fig. 31.1

31.1 In the spectrum obtained at 213 K, estimate the area ratio of the peaks at 9.3 and -3.0 ppm.

31.2 Explain why the spectrum obtained at 383 K has only one singlet peak while that obtained at 213 K has two multiplet peaks.

31.3 Estimate the position of the singlet peak in the spectrum obtained at 383 K.

SOLUTION OF PREPARATORY PROBLEM 31

31.1 [18]Annulene has 6 H_{in} and 12 H_{out}. Therefore, the larger resonance at 9.3 ppm can be assigned to H_{out}, while the smaller resonance at –3.0 ppm can be assigned to H_{in}.

Thus, A(9.3 ppm) / A(–3.0 ppm) = 12 / 6 = 2

Note:

The ring current from the aromatic 18π system of [18]annulene enhances the magnetic field outside the ring and diminishes the field inside the ring. This phenomenon is also responsible for the clear peak assignments. The downfield peaks (9.3 ppm) and the upfield peaks (-3.0 ppm) are assigned to H_{out} and H_{in}, respectively.

31.2 The conformarional mobility of [18]annulene allows the exchange of H_{in} and H_{out} by ring inversion. At 213 K, the slow exchange of H_{in} and H_{out} does not show any effect on the NMR spectra. Therefore, the H_{in} and H_{out} resonances are observed at -3.0 ppm and 9.3 ppm, respectively. In contrast, at 383 K, this exchange occurs rapidly and repeatedly; therefore, the resonance is observed at the weighted average of the chemical shifts of H_{in} and H_{out}.

31.3 [9.3 ppm × 12 + (–3.0 ppm) × 6] / [12 + 6] = 5.2 ppm

Notice the difference in the numbers of H_{in} and H_{out}.

PRACTICAL PREPARATORY PROBLEMS

PREPARATORY PROBLEM 32 (PRACTICAL)

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 and reagents

- acetic acid (c = 0.25 mol dm^{-3})
- benzyldimethyltetradecylammonium chloride (Zephiramine, Zeph; preferably with a concentration ranging from 5×10^{-5} to 8×10^{-5} mol dm^{-3})
- bromochlorophenol blue (BCPB; indicator)*$^{)}$
- potassium poly(vinylsulfate) solution (PVSK; titrant)**$^{)}$ (c = 0.0025 mol dm^{-3})
- sodium hydroxide (NaOH) solution, c = 0.01 mol dm^{-3}

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*) Prepare by dissolving the required amount of BCBP in 5 cm^3 of NaOH solution (c = 0.01 mol dm^{-3}) and diluting it with 200 cm^3 of water.

**) The concentration is defined as being that of its monomer unit, $C_2H_3SO_4K$. Its equivalent weight is 162.2, provided that the purity (degree of esterification) of PVSK is 100%.

Apparatus and glassware

- beaker (300 cm^3)
- burette (25 cm^3)
- conical beaker (200 cm^3)
- volumetric pipette (10 cm^3)

Procedures

1. Dissolve 0.048 g of BCPB in 5 cm^3 of a NaOH solution (c = 0.01 mol dm^{-3}) in a 300 cm^3 beaker, and dilute it with 200 cm^3 of water. The final concentration of BCPB should be ~ 4×10^{-4} mol dm^{-3}.
2. Take precisely an aliquot (10 cm^3) of the Zeph sample solution with a concentration at about 1.0×10^{-4} mol dm^{-3} and add it to a 200 cm^3 conical beaker using a volumetric pipette; then add 1 cm^3 of 0.25 mol dm^{-3} acetic acid and 1 cm^3 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 colour 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 colour should change to yellow.
4. Read the volume of the PVSK solution added.

Treatment of Data

32.1 Calculate the Zeph concentration in mg dm^{-3}. The reaction ratio of the monomer unit of PVSK to Zeph is 1 : 1.

32.2 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?

SOLUTION OF PREPARATORY PROBLEM 32

32.2 When the PVSK poly anion aqueous solution is added to the Zeph cation aqueous solution, both ions associate quantitatively through electrostatic interaction and yield non-polar ion pair species. In the early stage of titration with a large amount of free Zeph cations (known as a surfactant), the ion pairs are surrounded by Zeph cations to form cationic micelles. Near the equivalence point, the solution becomes cloudy due to generation of a precipitate of aggregates of the ion pairs, since the amount of free Zeph cations is not sufficient to maintain the micelles.

Beyond the equivalence point, when an excessively large number of PVSK anions is present in the solution, the solution becomes clear again, since the ion pairs are surrounded by PVSK anions and can be dispersed into the solution once more as anionic colloids.

PREPARATORY PROBLEM 33 (PRACTICAL)

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 mass.

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 cm^3 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 and reagents

- test solution (prepare as described above)
- acetic acid solution, c = 0.1 mol dm^{-3}
- ammonium fluoride
- ethylenediamine-*N,N,N',N'*-tetraacetic acid, c = 0.01 mol dm^{-3}, disodium dihydrate standard solution (accurately prepared)
- hexamethylenetetramine (hexamine) solution, 10 % (w/v)
- methyl orange (MO) solution, 0.1 %
- xylenol orange (XO) ethanol/water (20/80) solution, 0.1 %
- zinc(II) standard solution, c = 0.01 mol dm^{-3}, (accurately prepared, using $ZnSO_4 \cdot 7\ H_2O$),

Apparatus and glassware

- burette, 25 cm^3, 1 rack
- 5 Erlenmeyer flasks, 200 cm^3,
- hot-plate
- magnetic stirrer
- 4 Pasteur pipettes (droppers)
- pipette, 10 cm^3
- safety bulb
- 4 stirring bars (coated with Teflon)

Procedures

1. Pipette 10 cm^3 of the sample solution into a 200 cm^3 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 cm^3 of a EDTA standard solution (0.01 mol dm^{-3}). 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.
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 dm^{-3} acetic acid solution in drops until a clear yellow color reappears. Next, titrate the mixture using the standard Zn^{2+} solution with c = 0.01 mol dm^{-3} until the color turns to purple. The volume of titrant used in step 2 is defined as “A” cm^3. (Caution: Do not discard the titrated mixture; you will need to titrate it continuously in step 3.)

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.

3. Add ca. 1.0 g of NH_4F to the titrated mixture in step 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 dm^{-3} acetic acid solution dropwise until the color reappears. Next, titrate the mixture again using a 0.01 mol dm^{-3} Zn^{2+} standard solution. The volume of the titrant used in step 3 is defined as "B" cm^3.

Questions:

33.1 In steps 1 and 2, why is the pH adjusted to ca. 3.5 and ca. 5.5, respectively, in a stepwise manner? Explain the reason considering the difference in the stability of each metal-EDTA and –hydroxyl complex.

33.2 What is the role of ammonium fluoride added to the mixture in step 3?

33.3 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).

33.4 Calculate the concentrations (in mol cm^{-3}) of Al^{3+} and Zn^{2+} ions in the sample solution.

33.5 Assuming that the alloy contains only Al and Zn, calculate the composition of the alloy in percent by weight.

SOLUTION OF PREPARATORY PROBLEM 33

33.1 It makes it possible to avoid the formation of Al(III)-hydroxyl complex ions upon a reaction between EDTA and Al^{3+}.

In this procedure, all Al^{3+} and Zn^{2+} in the sample solution should be reacted with EDTA to obtain the total metal content using the back titration technique in step 1-2. To this end, adjusting the pH of the solution to around 5.5 is required to allow a quantitative reaction between Zn^{2+} and EDTA. At around pH 5.5, on the other hand, formation of an Al(III)-EDTA chelate complex is considerably suppressed by the formation of various Al(III)-hydroxyl complex ions, and the formation of the Al(III)-EDTA chelate complex would be incomplete (Al^{3+} forms various highly stable hydroxyl complex ions, even in weakly acidic media). Multi-nuclear complexes such as $[Al_2(OH)_2]^{4+}$ or $[Al_{13}(OH)_{32}]^{7+}$, especially, which are kinetically highly inert, are formed at pH 4 or above. In fact, only a limited amount of the Al(III)-EDTA chelate complex could be expected to be formed in this pH region in a reaction at room temperature. Al^{3+} must therefore be reacted with EDTA under boiling conditions after the pH is carefully adjusted to less than 4.

Hence, a lower aluminum content would be estimated due to incomplete formation of Al(III)-EDTA chelate if the pH of the sample solution was adjusted to pH 5.5 in one step.

33.2 Ammonium fluoride is used for the quantitative recover of Al^{3+} from the Al(III)-EDTA chelate complex. Fluoride ions react readily with aluminum ions to create a highly stable complex, $[AlF_6]^{3-}$. Adding a large amount of ammonium fluoride to the titration mixture and heating result in a quantitative exchange of EDTA ligands in the Al(III)-EDTA chelate with fluoride ions, as follows:

$$[Al(III)(edta)]^{-} + 6\ F^{-} \rightarrow [AlF_6]^{3-} + edta^{4-}$$

(The change in color of the XO indicator upon heating indicates that the free EDTA was released from the Al(III)-EDTA chelate complex by the reaction.) Hence, the contents of Al^{3+} in the mixture can be determined by titrating the released free EDTA ligands with the Zn^{2+} standard solution.

33.3 The total amount of substance of Al^{3+} and Zn^{2+} (in mol) in a 10 cm^3 sample solution is given by equation 33-1:

$$n(Al^{3+} + Zn^{2+}) = 0.01\ [\text{mol dm}^{-3}] \times f_{edta}\, f_{Zn} \times (6.00\text{-}A)\ [\text{cm}^3] \times 0.001 \qquad \text{(eq. 33.1)}$$

where f_{edta} and f_{Zn} are the factors for the standard solutions of 0.01 mol dm^{-3} EDTA and 0.01 mol dm^{-3} Zn^{2+} used, respectively.

The concentration of Al^{3+} in the sample solution is given by equation 33-2:

$$\text{Conc. of } Al^{3+} \text{ [mol]} = 0.01 \text{ [mol dm}^{-3}\text{]} \times f_{Zn} \times B \text{ [cm}^3\text{]} \times 0.001 / 0.010 \text{ [dm}^3\text{]} \quad \text{(eq. 33-2)}$$

The concentration of Zn^{2+} in the sample solution is given by equation 33-3:

$$\text{conc. of } Zn^{2+} \text{ [mol cm}^{-3}\text{]} = 0.001 \times 0.01 \text{ [mol dm}^{-3}\text{]} \times f_{Zn}\{f_{edta}\,(6.00 - A) \text{ [cm}^3\text{]} -$$

$$- 0.01 \text{ [mol dm}^{-3}\text{]} \times B \text{ [cm}^3\text{]}\} / 0.010 \text{ [dm}^3\text{]} \quad \text{(eq. 33-3)}$$

PREPARATORY PROBLEM 34 (PRACTICAL)

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

- hydrogen peroxide, 30%
- manganese dioxide
- potassium permanganate (after standardization), c = 0.02 mol dm^{-3}
- urea

Apparatuses and glassware

- test solution (prepare as described above)
- beaker (100 cm^3)
- burette (25 cm^3)
- conical flask (300 cm^3)
- Erlenmeyer flask (10 cm^3)
- filter paper
- graduated pipette
- test tube
- volumetric flask (100 cm^3)
- volumetric pipette (10 cm^3)

- water bath on a heating plate
- watch glass (preferably ca. 20 cm in diameter)

Procedure

1. Pipette about 3.4 cm^3 of 30% hydrogen peroxide into a 10 cm^3 Erlenmeyer flask using a volumetric pipette and add 1.2 g of urea (hydrogen peroxide : urea = 3 : 2 mole 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 cm^3 beaker. Add 50 cm^3 of water to dissolve the crystals. Transfer the solution to a 100 cm^3 volumetric flask and dilute it with water to the 100 cm^3 mark. Pipette 10 cm^3 of the solution into a 300 cm^3 conical flask. Add 200 cm^3 of water and 20 cm^3 of diluted sulfuric acid (10%).
5. Titrate the solution with standard 0.02 mol dm^{-3} potassium permanganate until a faint pink color persists for 15 s. Be sure to add the standard 0.02 mol dm^{-3} potassium permanganate slowly to prevent the formation of manganese dioxide. As a blank test, the same titration should be done without the crystals.

Questions

34.1 Calculate the hydrogen peroxide contents (mass %) in the crystals.

34.2 Write a balanced equation for the reaction.

34.3 Calculate the theoretical yield of urea-hydrogen peroxide.

34.4 Calculate the percentage yield.

SOLUTION OF PREPARATORY PROBLEM 34

34.2 $CO(NH_2)_2 + H_2O_2 \rightarrow CO(NH_2)_2{\times}H_2O_2$

34.3 (mass of urea [g] / 60.06 [g mol^{-1}]) $\times$ 94.07 [g mol^{-1}]

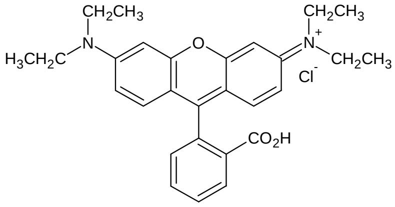
PREPARATORY PROBLEM 35 (PRACTICAL)

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

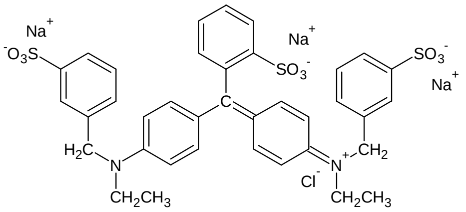
Since ancient times, organic dyes have been used for coloring cloth and leather. Numerous species of plants and animals have been used as sources of natural dyes. The extraction and purification of dyes as well as the dyeing process itself are sophisticated chemical processes. The first human-made (synthetic) 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.

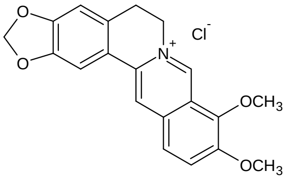
A



B



C



Chemicals

- organic dyes (respective names of dyes intentionally hidden)
- methanol
- developer (mixture of methanol and water (90/10 = v/v))

Apparatuses and glassware

- glass capillary
- wide-mouth bottle with cap (developing chamber) (× 3)
- TLC plates

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.
.
.
.
.

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

Note:

If P-2 and P-3 plates are not available, prepare them from modified silica gel and calcium sulphate ($CaSO_4 \cdot 1/2\ H_2O$; 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 vapour.
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.

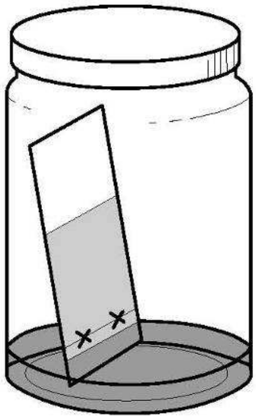


Fig. 35.1 TLC plate placed in a bottle with a cap.

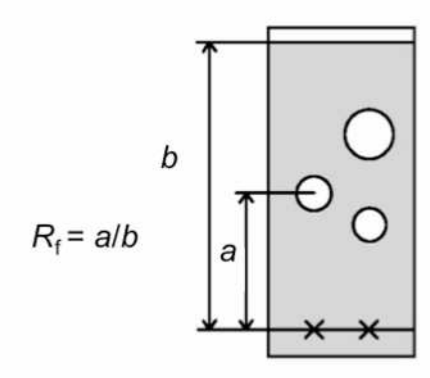


Fig. 35.2 TLC plate and developed spots.

Questions

I. TLC results

35.1 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.

35.2 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.

35.3 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 dm^{-3} 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.

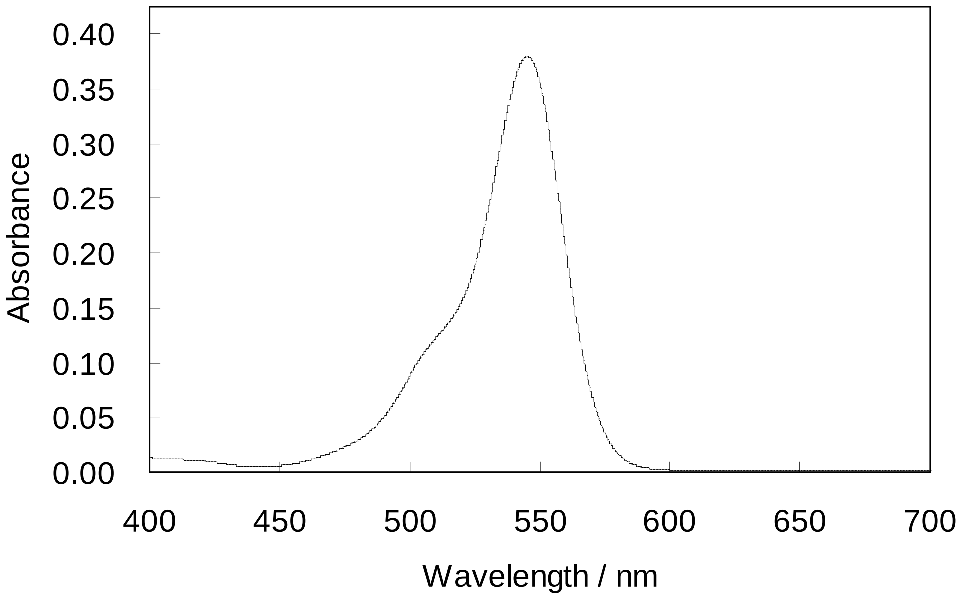


Fig. 35.3 Absorption spectrum of a dye.

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

35.4 Calculate the molar absorption coefficient of the dye at 545 nm.

35.5 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.

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

SOLUTION OF PREPARATORY PROBLEM 35

I. TLC results

35.2 Dye **A** (rhodamine B) is red, dye **B** (brilliant blue) is blue and dye **C** (berberine chloride) is yellow.

35.3 Judging from their structural formulae, dyes **A** and **B** have relatively larger numbers of dissociable sites than dye **C**. Obviously, dye **A** comprises cationic molecules and dye **B** anionic molecules, on the whole. Dye **C** also comprises cationic molecules but it should have weaker hydrophilicity than the others.

The TLC results indicate that (1) the red dye is strongly retained on the cation-exchange plate, (2) the blue dye is strongly retained on the anion-exchange plate, and (3) the yellow dye is strongly retained on both the cation-exchange and ODS-modified plates.

The conclusion entered in answer 2 was reached based on these observations.

II. Absorption spectra

35.4 According to the Beer–Lambert law, the absorbance, *A*, is given by following formula:

$$A = \varepsilon\ [\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}] \times c\ [\text{mol dm}^{-3}] \times l\ \ [\text{cm}]$$

The molar absorption coefficient of the dye at 545 nm is:

$$\varepsilon = \frac{0.380}{3.30\times10^{-6}\ \text{mol dm}^{-3} \times 1.0\ \text{cm}} = 1.15\times10^5\ [\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}]$$

35.5 According to Beer–Lambert law, the relationship between % transmittance and absorbance is given as follows:

$$\%T = 10^{-A} \times 100$$

Hence, the %*T* for the original dye solution, is 41.7 % and 79.4% at 545 and 503 nm, respectively.

35.6 When the concentration of dye is decreased to 50%, on the other hand, the absorbance will be decreased to 50%, since absorbance is proportional to the concentration of the species which absorbs the light. Hence, the absorbance will be 0.190 and 0.0500 at 545 and 503 nm respectively, and the %*T* calculated from the absorbance will be 64.6 % and 89.1 % at 545 and 503 nm, respectively.

Thus, by diluting the dye solution by 50%, the intensity of the transmitted light is increased by 1.55-fold and 1.12-fold at 545 nm and 503 nm, respectively. The above results suggest that wavelengths that show larger absorptivity are more sensitive to changes in the concentrations of species that absorb the light.

Since absorbance is proportional to the absorption pass length, when the pass length is increased 3-fold, the absorbance will be increased 3-fold. Hence, the absorbance will be 1.14, and the %*T* calculated from the absorbance will be 7.24 %.

PREPARATORY PROBLEM 36 (PRACTICAL)

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 sulphuric 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.

$$R^1COOR^2 + H_2O \xrightarrow{H^+} R^1COOH + R^2OH$$

Chemicals and reagents

- toluene, $C_6H_5CH_3$
- Amberlyst®-15 (H^+ form, dry)
- ethyl acetate, liquid,(reactant),
- phenolphthalein (0.5 wt.% solution in ethanol/water (1/1))
- sodium hydroxide (NaOH) standard solution, 0.02 mol dm^{-3}
  (concentration accurately determined)

Apparatuses and glassware

- burette (25 cm^3)
- Erlenmeyer flasks (100 $cm^3 \times 6$)
- glass vials (10 $cm^3 \times 6$; must be dried)
- graduated pipette (5 cm^3)
- magnetic stirrer
- stirring bar
- Pasteur pipette (dropper)
- reflux condenser
- silicone plug

- thermometer
- three-necked flask (250 cm^3)
- volumetric pipettes (1 cm^3 and 3 cm^3)
- 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 cm^3) 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 cm^3) to the flask. This will be the start time of the reaction.

(4) Charge six Erlenmeyer flasks with cold water (50 cm^3) and add a few drops of phenolphthalein to each flask. Keep the flasks at room temperature.

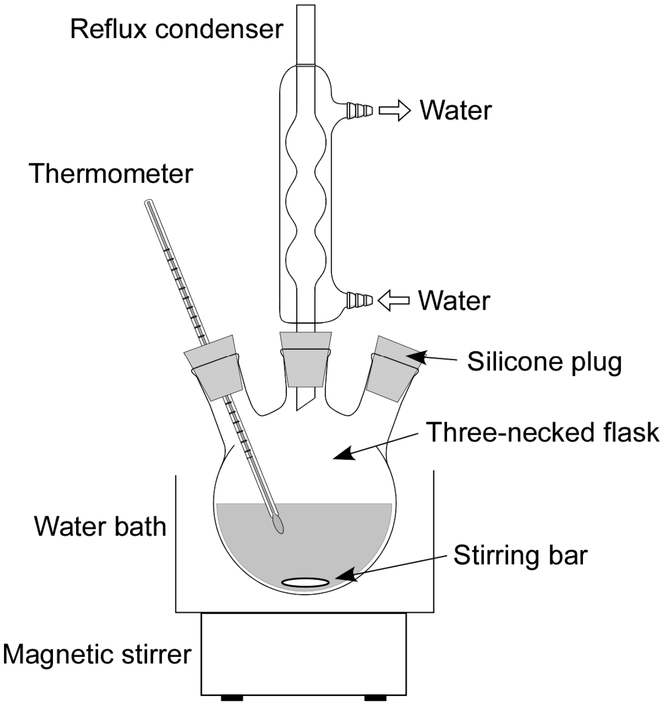


Fig. 36.1 Experimental setup.

(5) Fill a 25 cm^3 burette with the NaOH solution (0.3 mol dm^{-3}).

(6) Ten minutes after the start of the reaction, stop stirring the mixture in order to settle out the catalyst, and transfer about 5 cm^3 of the solution to a glass vial using a graduated pipette. Immediately, transfer 3 cm^3 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.

Treatment of Data

36.1 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}.

36.2 Plot $\log_{10}\frac{c_c}{c_c - c_t}$ against t, where c_c is the expected concentration for complete hydrolysis.

36.3 Estimate the first-order rate constant from the plot.

PREPARATORY PROBLEM 37 (PRACTICAL)

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+}.

$$Zn^{2+}, Fe^{2+} \xrightarrow{O_2, OH^-} (Zn^{II}_xFe^{II}_{1-x})Fe^{III}_2O_4$$

Chemicals

- acetic acid–sodium acetate buffer solution (pH 4)
- iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7\,H_2O$)
- sodium hydroxide solution, (c = 2 mol dm^{-3})
- zinc sulphate heptahydrate ($ZnSO_4 \cdot 7\,H_2O$)

Apparatuses and glassware

- air pump (flow rate 100 cm^3 min^{-1}) and tubing
- Büchner funnel
- Erlenmeyer flask (200 cm^3)
- glass microfiber filter (to capture particles of ca. 0.3 μm)
- graduated pipette (2 cm^3)
- 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.

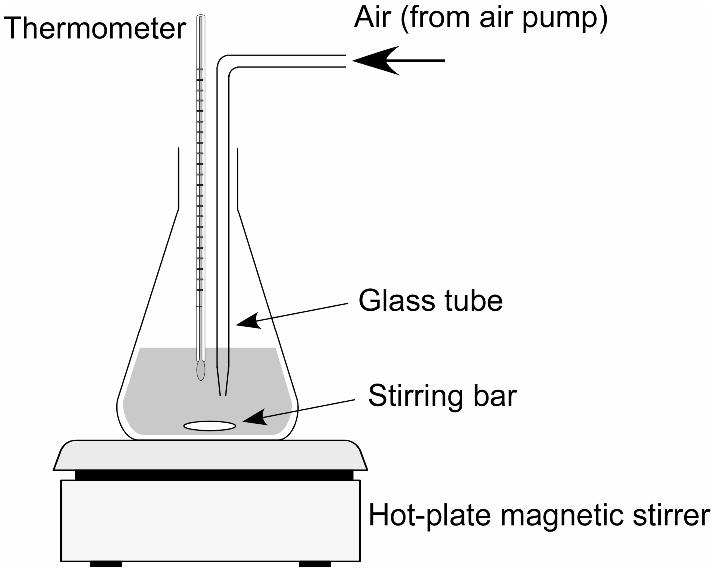


Fig. 37.1 Experimental setup.

(2) Dissolve $FeSO_4 \cdot 7\ H_2O$ (2.0 g) in water (40 cm^3) in the Erlenmeyer flask.

(3) Start stirring the solution.

(4) Dissolve $ZnSO_4 \cdot 7\ H_2O$ (0.20 g) in the solution.

(5) Start air bubbling through the glass tube (see Fig. 37.1).

(6) Heat the solution until the temperature reaches 65 – 75 ℃. Add around 6 cm^3 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 cm^3).

(12) Wash the precipitate with water, and then dry it at around 80 ℃ in an air oven.

(13) Weigh the precipitate.

Questions

37.1 Provide the theoretical yield of ferrite in grams.

37.2 Calculate the percentage yield of ferrite.

37.3 What analytical techniques can be used to detect the unreacted ferrous and zinc ions in the washing procedure (11)?

37.4 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).

SOLUTION OF PREPARATORY PROBLEM 37

37.1 Assume the weighed amounts of $ZnSO_4 \cdot 7H_2O$ (M = 287.56 g mol^{-1}) and $FeSO_4 \cdot 7H_2O$ (M = 278.01 g mol^{-1}) to be *x* and *y* (g), respectively.

Since all Zn ions are converted to $ZnFe_2O_4$ (M = 241.09 g mol^{-1}), the mass of $ZnFe_2O_4$ produced is $\frac{x}{287.56\text{ g mol}^{-1}} \times 241.09\text{ g mol}^{-1}$ [g].

The amount of Fe consumed in the formation of $ZnFe_2O_4$ is $\frac{2x}{287.56\text{ gmol}^{-1}}$ [mol]

The amount of Fe ions converted to Fe_3O_4 (M = 231.55 g mol^{-1}) is

$$\left(\frac{y}{278.01\text{g mol}^{-1}} - \frac{2x}{287.56\text{ g mol}^{-1}}\right) \text{(mol).}$$

Thus, the mass of Fe_3O_4 (g) produced is

$$\left(\frac{y}{278.01\text{g mol}^{-1}} - \frac{2x}{287.56\text{ g mol}^{-1}}\right) \times \frac{231.55\text{ g mol}^{-1}}{3}$$

The total theoretical yield (g) of the ferrites is consequently

$$\left(\frac{y}{278.01\,\text{g mol}^{-1}}-\frac{2\,x}{287.56\,\text{g mol}^{-1}}\right)\times\frac{231.55\,\text{g mol}^{-1}}{3}+\left(\frac{x}{287.56\,\text{g mol}^{-1}}\times 241.09\,\text{g mol}^{-1}\right)$$

37.3 Both the species can be detected by coloring test reactions. For Fe(II) ions, addition of a 4,4'-bipyridine or 1,10-phenanthroline solution gives a characteristic red color. For Zn(II) ions, addition of a zincon (1-(2-hydroxycarbonyl-phenyl)-5- (2-hydroxy-5-sulfophenyl)-3-phenylformazan, sodium salt) shows a blue color. Masking of the iron species is necessary for detection of Zn.

37.4 Cu^{2+}, Mg^{2+}, Ni^{2+}

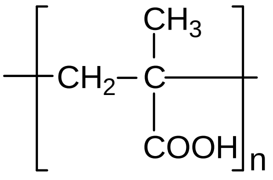
PREPARATORY PROBLEM 38 (PRACTICAL)

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.



$$\left[-CH_2-\overset{CH_3}{\underset{COOH}{C}}-\right]_n$$

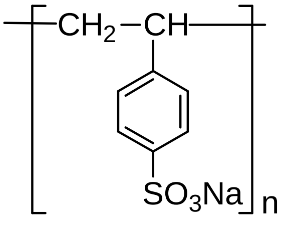
poly(methacrylic acid)

$HO-CH_2-CH_2-OH$

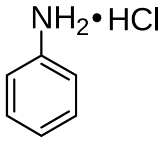
ethylene glycol

$HOOC-CH_2-CH_2-COOH$

succinic acid



poly(sodium 4-styrenesulfonate)



aniline hydrochloride

Chemicals

- anhydrous sodium carbonate (granular)
- aniline hydrochloride solution, c = 0.5 mol dm^{-3}
- ethylene glycol solution, c = 0.5 mol dm^{-3}
- poly(allylamine hydrochloride) (relative molar mass = 56,000) solution (monomer unit concentration: 0.1 mol dm^{-3})
- poly(ethylene oxide) (relative molar mass = 400,000) solution (monomer unit concentration: 0.1 mol dm^{-3})
- poly(methacrylic acid) (relative molar mass = 100,000) solution (monomer unit concentration: 0.1 mol dm^{-3})
- poly(sodium 4-styrenesulfonate) (relative molar mass = 70,000) solution (monomer unit concentration: 0.1 mol dm^{-3})
- succinic acid solution (c = 0.2 mol dm^{-3})

Glassware

- graduated pipettes
- test tubes

Procedures

(1) Add a small amount of anhydrous sodium carbonate (ca. 20 mg per 1 cm^3 of solution) to each solution.

(2) 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 cm^3 solution).

(3) 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.

Questions

38.1 Identify the compound in each solution from the results of procedures 1 and 2 above.

38.2 Give the equations for the reaction of aniline hydrochloride with anhydrous sodium carbonate and for the reaction of succinic acid with anhydrous sodium carbonate.

38.3 Is it possible to identify the compound by utilizing poly(ethyleneimine hydrochloride) instead of poly(allylamine hydrochloride)? Explain.

38.4 Report on the changes in appearance of the mixed solution in part 3 of the procedures and interpret these results.

SOLUTION OF PREPARATORY PROBLEM 38

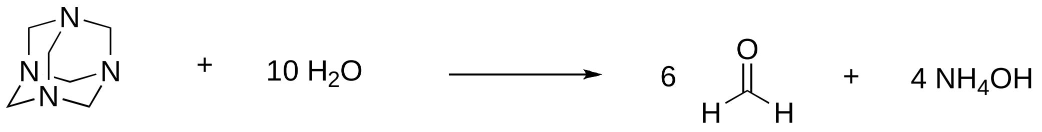
38.3 Yes. Poly(ethylene imine hydrochloride) (PEI) behaves as a polycation in an aqueous solution, where a polymer chain is positively charged like poly(allyamine hydrochloride). When the PEI solution is mixed with a solution of a polyanion such as poly(sodium 4-styrenesulfonate), a polymer – polymer complex is formed, and a precipitation is observed.

PREPARATORY PROBLEM 39 (PRACTICAL)

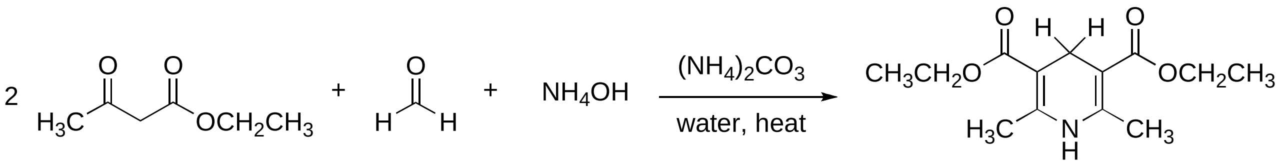
Synthesis of 1,4-dihydro-2,6-dimethylpyridine-3, 5-dicarboxylic acid diethyl ester (Hantzsch ester)

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.



hexamethylenetetramine



ethyl acetoacetate

Hantzsch ester

Chemicals

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

Apparatuses and glassware

- Büchner funnel
- glass capillary
- Erlenmeyer flasks (25 cm^3 and 100 cm^3)
- filter paper
- graduated pipette
- hot-plate magnetic stirrer (magnetic stirrer with heating plate)
- magnetic stirring bar
- suction flask
- test tube (100 cm^3)
- 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 cm^3 of water into a 100-cm^3 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 ℃ (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 LC 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

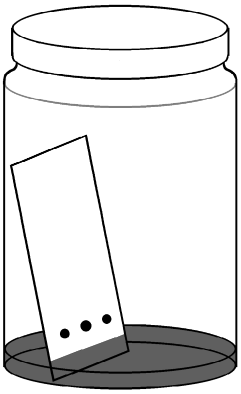
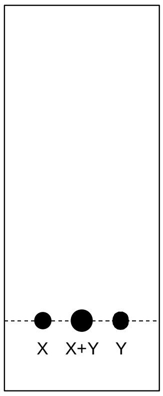


Fig. 39.1 TLC plate placed in a bottle with a cap.

TLC Plate



X: ethyl acetoacetate
Y: reaction mixture

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 cm^3 test tube. Add 10 cm^3 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 cm^3 Erlenmeyer flask using a graduated pipette. Repeat the extraction twice using ethyl acetate (2×5 cm^3) 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

39.1 Determine the total experimental yield of the isolated Hantzsch ester in grams.

39.2 Provide the theoretical yield of the Hantzsch ester in grams.

39.3 Calculate the percentage yield of the Hantzsch ester.

39.4 Determine the R_f values for the Hantzsch ester and ethyl acetoacetate.

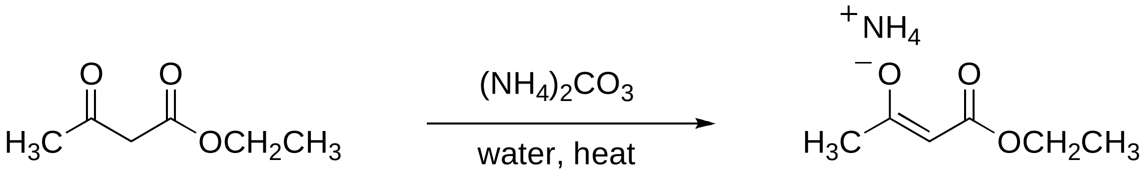
39.5 Explain why the ethyl acetoacetate becomes soluble in the aqueous ammonium carbonate solution.

39.6 Identify the origin of the C-4 carbon in the Hantzsch ester.

SOLUTION OF PREPARATORY PROBLEM 39

39.2 1/2 X (mass of ethyl acetoacetate [g]/130.1 [g mol^{-1}]) X 253.3 [g mol^{-1}]

39.5 Ethyl acetoacetate becomes more soluble in water in its enolate form produced under basic conditions.



enolate form

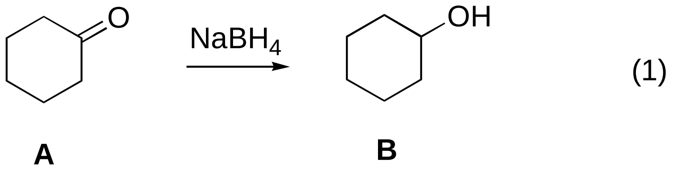
39.6 It is a carbon of formaldehyde generated in water, which is originally from a methylene carbon in hexamine.

PREPARATORY PROBLEM 40 (PRACTICAL)

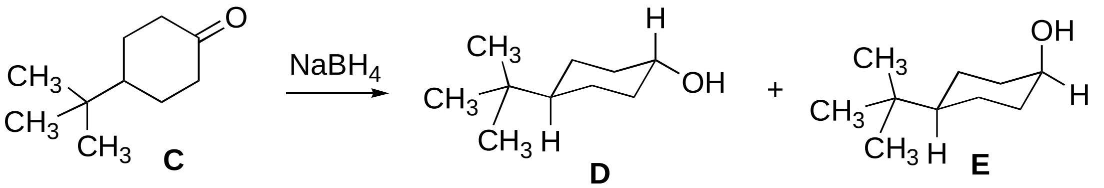
Reduction of a ketone with sodium borohydride

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).



(1)



(2)

Chemicals

- anhydrous sodium sulphate
- anisaldehyde stain (10% *p*-anisaldehyde and 5% H_2SO_4 in methanol)
- ethyl acetate, liquid
- ethanol
- hexane, liquid

- sodium borohydride, solid
- sulfuric acid solution
- 4-*tert*-butylcyclohexanone, solid

Apparatuses and glassware

- crystallization dish
- Erlenmeyer flask (30 cm^3)
- 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 cm^3) 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 ℃). 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 ℃ 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 cm^3) and hexane (3 cm^3) 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 cm^3) 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 cm^3). 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.

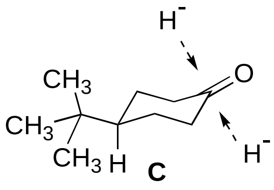
Questions

40.1 Calculate the theoretical yield of this reaction product.

40.2 Report the experimental yield, and calculate the percentage yield of this reaction product.

40.3 Sketch the TLC plate for the completed reaction and provide R_f values.

40.4 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.



C

Which is the alcohol for the prominent spot on the TLC, **D** or **E**?

SOLUTION OF PREPARATORY PROBLEM 40

40.1 (mass of 4-*tert*-butylcyclohexanone [g] / 154.2 g mol^{-1}) × 156.2 g mol^{-1}

40.4 Correct answer: **D**