THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Series 2

38th – 42nd IChOs
2006 – 2010

Edited by Anton Sirota

IChO International Information Centre
IUVENTA, Bratislava, 2017

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The preparatory problems from the 38th – 42nd IChOs

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ISBN 978-80-8072-171-8

Issued by IUVENTA in 2017
with the financial support of the Ministry of Education of the Slovak Republic

Number of copies: 200
Not for sale.

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38th

International Chemistry Olympiad

PREPARATORY PROBLEMS

Edited by Anton Sirota

30 theoretical problems
6 practical problems

2006

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The original title page:

38th International Chemistry Olympiad

Preparatory Problems

2–11 July 2006
Gyeongsan, Korea

" Chemistry for Life,
Chemistry for Better Life"

KOREAN CHEMICAL SOCIETY

KOREA SCIENCE AND ENGINEERING FOUNDATION

THE THIRTY–EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2 – 11 JULY 2006, GYEONGSAN, KOREA

PREPARATORY PROBLEMS

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PREPARATORY THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

"A brief history" of life in the universe

Chemistry is the language of life. Life is based on atoms, molecules and complex chemical reactions involving atoms and molecules. It is only natural then to ask where atoms came from. According to a widely accepted model, the universe began about 15 billion years ago in a big bang and has been expanding ever since. The history of the universe as a whole can be viewed in terms of a series of condensations from elementary to complex particles as the universe cooled. Of course, life as we know it today is a special phenomenon that takes place at moderate temperatures of the Earth.

Light elements, mostly hydrogen and helium, were formed during the first several minutes after the big bang in the rapidly expanding and, therefore, rapidly cooling early universe. Stars are special objects in space, because temperature drop is reversed during star formation. Stars are important in chemistry, because heavy elements essential for life are made inside stars, where the temperature exceeds tens of millions of degrees.

The temperature of the expanding universe can be estimated simply using:

$$T = \frac{1\times 10^{10}}{t^{1/2}}$$

where T is the average temperature of the universe in Kelvin (K) and t is the time (age of the universe) in seconds. Answer 1.1 through 1.4 with one significant figure. Round off if you want.

1.1 Estimate the temperature of the universe when it was 1 second old at which time the temperature was too high for fusion of protons and neutrons into helium nuclei to occur.

1.2 Estimate the temperature of the universe when it was about 3 minutes old and the nuclear synthesis of helium was nearly complete.

1.3 Estimate the age of the universe when the temperature was about 3,000 K and the first neutral atoms were formed by the combination of hydrogen and helium nuclei with electrons.

1.4 The first stable molecules in the universe were possible only after the temperature of the expanding universe became sufficiently low (approximately 1,000 K) to allow atoms in molecules to remain bonded. Estimate the age of the universe when the temperature was about 1,000 K.

1.5 Estimate the average temperature of the universe when the universe was about 300 million years old and the first stars and galaxies were born.

1.6 Estimate the temperature of the universe presently and note that it is roughly the same as the cosmic microwave background measurement (3 K).

1.7 Order the following key condensations logically, consistent with the fact that over 99 % of atoms in the expanding universe are hydrogen or helium.

(a) – ( ) – ( ) – ( ) – ( ) – ( ) – ( ) – ( ) – ( ) – ( )

a. quarks → proton, neutron
b. 1×10^{14} cells → human being
c. H, C, N, O → H_2, CH_4, NH_3, H_2O (in interstellar space)
d. proton, helium nucleus + electron → neutral H, He atoms
e. proteins, nucleic acids, membrane → first cell
f. proton, neutron → helium nucleus
g. H_2, He, CH_4, NH_3, H_2O, dust → solar system
h. H, He atoms → reionization, first generation stars and galaxies
i. proton, helium nucleus (light elements) → heavy elements such as C, N, O, P, S, Fe, U; supernova explosion
j. H_2, CH_4, NH_3, H_2O, etc. → amino acids, sugars, nucleotide bases, phospholipids on Earth

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SOLUTION OF PREPARATORY PROBLEM 1

1.1 $T = 1\times10^{10} / (1)^{1/2} = 1\times10^{10}$ K (10 billion degrees)

1.2 $T = 1\times10^{10} / (180)^{1/2} = 0.7\times10^{9} \approx 1\times10^{9}$ K (1 billion degrees)

1.3 $t = [1\times10^{10} / (3\times10^{3})]^{2}$ s $= 1\times10^{13}$ s $= 3\times10^{5}$ yr

1.4. $t = (1\times10^{10} / 1\times10^{3})^{2}$ s $= 10^{14}$ s $= 3\times10^{6}$ yr

1.5 100 K

1.6 10 K

1.7 (a) – (f) – (d) – (h) – (i) – (c) – (g) – (j) – (e) – (b)

THEORETICAL PROBLEM 2

Hydrogen in outer space

Hydrogen is the most abundant element in the universe constituting about 75 % of its elemental mass. The rest is mostly helium with small amounts of other elements. Hydrogen is not only abundant. It is the building block of all other elements.

Hydrogen is abundant in stars such as the sun. Thus the Milky Way galaxy, consisting of over 100 billion stars, is rich in hydrogen. The distance between stars is several light years on the average. Hydrogen is also the major constituent of the interstellar space. There are about 100 billion galaxies in the universe. The empty space between galaxies is vast. For example, the Milky Way galaxy is separated from its nearest neighbor, the Andromeda galaxy, by 2 million light years. Hydrogen again is the primary constituent of the intergalactic space even though the number density is much less than in the interstellar space. The average density of matter in the intergalactic space, where the current temperature is the cosmic background energy of 2.7 K, is about 1 atom per m^3.

2.1 Calculate the average speed, $(8\ RT\ /\ \pi\ M)^{1/2}$, of a hydrogen atom in the intergalactic space.

2.2 Calculate the volume of a collision cylinder swept out by a hydrogen atom in one second by multiplying the cross–sectional area, πd^2, by its speed where d is the diameter of a hydrogen atom (1×10^{-8} cm). Molecules whose centers are within the cylinder would undergo collision.

2.3 Calculate the number of collisions per second experienced by a hydrogen atom by multiplying the above volume by the number density. How many years does it take for a hydrogen atom to meet another atom in the intergalactic space?

2.4 Calculate the mean free path λ of hydrogen in the intergalactic space. λ is the average distance traveled by a particle between collisions.

Hydrogen atoms are relatively abundant in interstellar regions within a galaxy, there being about 1 atom per cm^3. The estimated temperature is about 40 K.

2.5 Calculate the average speed of hydrogen atom in the interstellar space.

2.6 Calculate the mean free path (λ) of hydrogen in the interstellar space.

2.7 What do these results imply regarding the probability of chemical reactions in space?

SOLUTION OF PREPARATORY PROBLEM 2

2.1 $\sqrt{\dfrac{8 \times 8.3\ \text{J K}^{-1}\ \text{mol}^{-1} \times 2.7\ \text{K}}{3.14 \times 1.0\times10^{-3}\ \text{kg mol}^{-1}}} = 240\ \text{m s}^{-1}$

2.2 Volume of cylinder = $(2)^{1/2}\,(3.14)(1.0\times10^{-8}\ \text{cm})^2(2.4\times10^4\ \text{cm s}^{-1}) = 1.1\times10^{-11}\ \text{cm}^3\ \text{s}^{-1}$

2.3. Collision / sec = (volume of cylinder) × (atoms / unit volume) =

$= (1.1\times10^{-11}\ \text{cm}^3\ \text{s}^{-1}) \times (\,1.0\times10^{-6}\ \text{cm}^{-3}) = 1.1\times10^{-17}\ \text{s}^{-1}$

Time between collisions = $\dfrac{1}{1.1\times10^{-17}\ \text{s}^{-1}} = 9\times10^{16}\ \text{s}$ = about 3 billion years

2.4. $(240\ \text{m s}^{-1}) \times (9\times10^{16}\ \text{s}) = 2.2\times10^{19}\ \text{m}$ (about 2,000 light years)

2.5. Speed is proportional to the square root of the temperature.

$(240\ \text{m s}^{-1}) \times (40 / 2.7)^{1/2} = 920\ \text{m s}^{-1}$

2.6. Volume of cylinder =

$= (2)^{1/2} \times (3.14) \times (1.0\times10^{-8}\ \text{cm})^2 \times (9.2\times10^4\ \text{cm s}^{-1}) = 4.1\times10^{-11}\ \text{cm}^3\ \text{s}^{-1}$

Collision / sec = (volume swept per second) × (atoms/unit volume)

$= 4.1\times10^{-11}\ \text{cm}^3\ \text{s}^{-1} \times 1\ \text{cm}^{-3} = 4.1\times10^{-11}\ \text{s}^{-1}$

Time between collisions = $\dfrac{1}{4.1\times10^{-11}\ \text{s}^{-1})} = 2.4\times10^{10}\ \text{s}$ = about 800 years

Mean Free path = $(920\ \text{m s}^{-1})(2.4\times10^{10}\ \text{s}) = 2.2\times10^{13}\ \text{m}$

(intergalactic space)/λ(interstellar space)

$\dfrac{2.2\times10^{19}\ \text{m}}{2.2\times10^{13}\ \text{m}}$ = about a million

2.7. very small

THEORETICAL PROBLEM 3

Spectroscopy of interstellar molecules

Atoms in interstellar space seldom meet. When they do (most likely on ice surfaces), they produce radicals and molecules. These species, some of which presumably played a role in the origin of life, have been identified through the use of different spectroscopic methods. Absorption spectra of interstellar species can be observed by using the background radiation as the energy of excitation. Emission spectra from excited species have also been observed. Simple diatomic fragments such as CH and CN were identified in interstellar space over 60 years ago.

3.1 The background electromagnetic radiation in the interstellar space has a characteristic energy distribution related to the temperature of a blackbody source. According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $T\lambda = 2.9\times10^{-3}$ m K. Let's consider a region near a star where the temperature is 100 K. What is the energy in joule of a photon corresponding to the peak emission from a blackbody at 100 K?

When molecules with non–zero dipole moments rotate, electromagnetic radiation can be absorbed or emitted. The spectroscopy related to molecular rotation is called microwave spectroscopy, because the electromagnetic radiation involved is in the microwave region. The rotational energy level of a diatomic molecule is given by $E_J = J(J+1)h^2 / 8\pi^2$ where J is the rotational quantum number, h is the Planck constant, I is the moment of inertia, μR^2. The quantum number J is an integer increasing from 0 and the reduced mass μ is given by $m_1m_2 / (m_1+m_2)$ for diatomic molecules (m_1 and m_2 are masses of the two atoms of the molecule). R is the distance between the two bonded atoms (bond length).

3.2 Carbon monoxide is the second most abundant interstellar molecule after the hydrogen molecule. What is the rotational transition (change of J quantum number) with the minimum transition energy? What is the minimum transition energy of the $^{12}C^{16}O$ rotation in joules? The bond length of CO is 113 pm. Compare the transition energy of CO with the radiation energy in problem 3.1. What does the result imply?

The distribution of molecules in different energy levels is related to the background temperature, which affects the absorption and emission spectra.

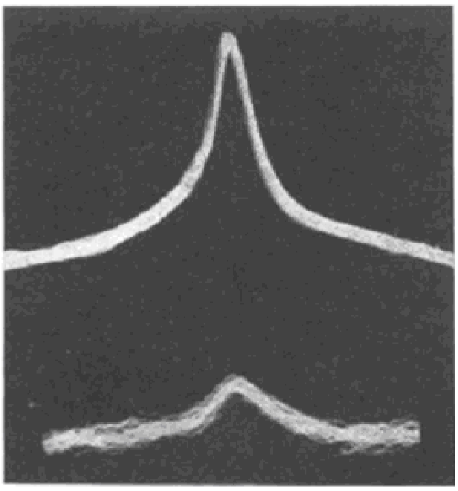


Figure 3–1. Oscillogram for the lowest rotational transition of $^{12}C^{16}O$ at 115,270 MHz. The upper curve was taken at the temperature of liquid air, the lower at the temperature of dry ice. (Reference: O. R. Gilliam, C. M. Johnson and W. Gordy. *Phys. Rev.* vol. 78 (1950) p.140.)

3.3 The equation for the rotational energy level is applicable to the rotation of the hydrogen molecule. However, it has no dipole moment so that the transition of $\Delta J = 1$ by radiation is not allowed. Instead a very weak radiative transition of $\Delta J = 2$ is observed. Calculate the temperature of interstellar space where the photon energy at the maximum intensity is the same as the transition energy of the hydrogen molecule ($^1H_2$) between $J = 0$ and 2. The H–H bond length is 74 pm.

SOLUTION OF PREPARATORY PROBLEM 3

3.1. $100\,\lambda = 2.9\times10^{-3}$ m K $\qquad \lambda = 2.9\times10^{-5}$ m

$$E(\text{photon}) = \frac{hc}{\lambda} = \frac{(6.63\times10^{-34}\ \text{J s}) \times (3.0\times10^{8}\ \text{m s}^{-1})}{2.9\times10^{-5}\ \text{m}} = 6.9\times10^{-21}\ \text{J}$$

3.2. J: $0 \leftrightarrow 1$

$$\mu = 12\times\frac{16}{28}\times 1.66\times10^{-27}\ \text{kg} = 1.14\times10^{-26}\ \text{kg}$$

$\text{I} = \mu\text{R}^2 = (1.14\times10^{-26}\ \text{kg})\ (1.13\times10^{-10}\ \text{m})^2 = 1.\ 45\times10^{-46}\ \text{kg m}^2$

$$E(0\leftrightarrow1) = \frac{2\,h^2}{8\pi^2 I} = \frac{2\,(6.63\times10^{-34}\ \text{J s})^2}{8\pi^2\,(1.45\times10^{-46}\ \text{kg m}^2)} = 7.68\times10^{-23}\ \text{J}$$

E(photon) of problem 3.1 = 6.9×10^{-21} J > $E(0\leftrightarrow1) = 7.68\times10^{-23}$ J Rotational excitation by the background radiation is feasible.

3.3 $E(0\leftrightarrow2) = \dfrac{6\,h^2}{8\,\pi^2 I} = \dfrac{hc}{\lambda}$ $\qquad\qquad \lambda = \dfrac{8\,\pi^2 c\,I}{6h}$

$\text{I} = \mu\text{R}^2 = [(1/2)\times 1.\ 66\times10^{-27}\ \text{kg}]\ (0.74\times10^{-10}\ \text{m})^2 = 4.55\times10^{-48}\ \text{kg m}^2$

$$\lambda = \frac{8\,\pi^2 c\,I}{6h} = \frac{8\,\pi^2\ \times\ 4.55\times10^{-48}\ \text{kg m}^2\ \times\ 3\times10^{8}\ \text{m s}^{-1}}{6\ \times\ 6.63\times10^{-34}\ \text{J s}} = 2.71\times10^{-5}\ \text{m}$$

$$T = \frac{2.9\times10^{-3}\ \text{m K}}{\lambda} = \frac{2.9\times10^{-3}\ \text{m K}}{2.71\times10^{-5}\ \text{m}} = 107\ \text{K}$$

Observation of hydrogen rotational spectra is feasible at 100 K.

THEORETICAL PROBLEM 4

Ideal gas law at the core of the sun

Life on Earth has been made possible by the energy from the sun. The sun is a typical star belonging to a group of hydrogen–burning (nuclear fusion, not oxidation) stars called main sequence stars. The core of the sun is 36 % hydrogen (^{1}H) and 64 % helium (^{4}He) by mass. Under the high temperature and pressure inside the sun, atoms lose all their electrons and the nuclear structure of a neutral atom becomes irrelevant. The vast space inside atoms that was available only for electrons in a neutral atom becomes equally available for protons, helium nuclei, and electrons. Such a state is called plasma. At the core of the sun, the estimated density is 158 g cm^{-3} and pressure 2.5×10^{11} atm.

4.1 Calculate the total number of moles of protons, helium nuclei, and electrons combined per cm^3 at the core of the sun.

4.2 Calculate the percentage of space occupied by particles in hydrogen gas at 300 K and 1 atm, in liquid hydrogen, and in the plasma at the core of the sun. The density of liquid hydrogen is 0.09 g cm^{-3}. The radius of a nuclear particle can be estimated from $r = (1.4\times10^{-13}$ cm) (mass number)$^{1/3}$. Assume that the volume of a hydrogen molecule is twice that of a hydrogen atom, and the hydrogen atom is a sphere with the Bohr radius (0.53×10^{-8} cm). Estimate your answer to 2 significant figures.

4.3 Using the ideal gas law, estimate the temperature at the core of the sun and compare your result with the temperature required for the fusion of hydrogen into helium (1.5×10^7 K).

SOLUTION OF PREPARATORY PROBLEM 4

4.1 Protons: (158 g cm^{-3} × 0.36) / (1.0 g mol^{-1}) = 57 mol cm^{-3}

Helium nuclei: (158 g cm^{-3} × 0.64) / (4.0 g mol^{-1}) = 25 mol cm^{-3}

Electrons: 57 + (25 × 2) = 107 mol cm^{-3}

Total: 189 mol cm^{-3}

4.2 Volume of a hydrogen molecule = 2 (4/3) πr^3

$= 2 \times (4/3)\, \pi \times (0.53\times10^{-8}\ \text{cm})^3 = 1.2\times10^{-24}\ \text{cm}^3$

Hydrogen gas:

$$\frac{V}{n} = \frac{RT}{p} = \frac{8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 300\ \text{K}}{101.325\ \text{kPa}} = 24.6\ \text{dm}^3\ \text{mol}^{-1} = 4.1\times10^{-23}\ \text{dm}^3\ /\ \text{molecule}$$

$= 4.1\times10^{-20}\ \text{cm}^3$ / molecule

$$\frac{1.2\times10^{-24}\ \text{cm}^3}{4.1\times10^{-20}\ \text{cm}^3} = 3.0\ \times10^{-5} = 0.003\ \%$$

Liquid hydrogen: (2 g mol^{-1}) / (0.09 g / cm^{-3}) / (6$\times$10^{23} molecule mol^{-1}) = 3.7$\times$10^{-23} cm^3

(1.2$\times$10^{-24} cm^3) / (3.7$\times$10^{-23} cm^3) = 0.030 = 3.0 %

Solar plasma: (neglect volume of electrons)

4/3 π (1.4$\times$10^{-13} cm)^3 (1$\times$ 57 mol cm^{-3} + 4 $\times$ 25 mol cm^{-3}) (6$\times$10^{23} mol^{-1}) = 1.1$\times$10^{-12} = 1.1$\times$10^{-10} %

Volume occupied is extremely small and ideal gas law is applicable.

4.3 From 4.1 we know that there are 189 moles of particles per cm^3.

$$T = \frac{pV}{nR} = \frac{2.5\times10^{11} \times 1\times10^{-3}}{189 \times 0.082} = 1.6\times10^{7}\ \text{K}$$

THEORETICAL PROBLEM 5

Atmosphere of the planets

The solar system was born about 4.6 billion years ago out of an interstellar gas cloud, which is mostly hydrogen and helium with small amounts of other gases and dust.

5.1 The age of the solar system can be estimated by determining the mass ratio between Pb–206 and U–238 in lunar rocks. Write the overall nuclear reaction for the decay of U–238 into Pb–206.

5.2 The half–life for the overall reaction is governed by the first alpha–decay of U–238 ($^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$), which is the slowest of all reactions involved. The half–life for this reaction is 4.51×10^{9} years. Estimate the mass ratio of Pb–206 and U–238 in lunar rocks that led to the estimation of the age of the solar system.

Elemental hydrogen and helium are rare on Earth, because they escaped from the early Earth. Escape velocity is the minimum velocity of a particle or object (*e.g.*, a gas molecule or a rocket) needed to become free from the gravitational attraction of a planet. Escape velocity of an object with mass m from the Earth can be determined by equating the gravitational potential energy, $-G\,M\,m\,/\,R$, to the kinetic energy, $(1/2)\,m\,v^2$, of the object. Note that the m's on both sides cancel and, therefore, the escape velocity is independent of the mass of the object. However, it still depends on the mass of the planet.

The universal constant of gravitation $G = 6.67\times10^{-11}$ N m^2 kg^{-2}
The Earth's mass $M = 5.98\times10^{24}$ kg
The Earth's radius $R = 6.37\times10^{6}$ m

5.3 Calculate the escape velocity for the Earth.

5.4 Calculate the average speed, $(8RT\,/\,\pi M)^{1/2}$, of a hydrogen atom and a nitrogen molecule at ambient temperature. Compare these with the escape velocity for the Earth. Note that the temperature of the upper atmosphere where gases can escape into space will be somewhat different. Also note that photolysis of water vapor by ultraviolet radiation can yield hydrogen atoms. Explain why hydrogen atoms escape more readily than nitrogen molecules even though the escape velocity is independent of the mass of the escaping object.

The chemical composition of the atmosphere of a planet depends on the temperature of the planet's atmosphere (which in turn depends on the distance from the sun, internal temperature, etc.), tectonic activity, and the existence of life.

As the sun generated heat, light, and solar wind through nuclear fusion of hydrogen to helium, the primitive inner planets (Mercury, Venus, Earth, and Mars) lost most of their gaseous matter (hydrogen, helium, methane, nitrogen, water, carbon monoxide, etc.). As the heavy elements such as iron and nickel were concentrated at the core through gravity and radioactive decay produced heat, internal temperature of the planets increased. Trapped gases, such as carbon dioxide and water, then migrated to the surface. The subsequent escape of gases from the planet with a given escape velocity into space depends on the speed distribution. The greater the proportion of gas molecules with speed exceeding the escape velocity, the more likely the gas is to escape over time.

5.5 Circle the planet name where the atmospheric pressure and composition are consistent with the given data. Explain.

The average surface temperatures and the radii of the planets are as follows:

Venus: 730 K; 6 052 km
Earth: 288 K; 6 378 km
Mars: 218 K; 3 393 km
Jupiter: 165 K; 71,400 km
Pluto: 42 K; 1,160 km

	pressure (in atm)	composition (%)	planet
a.	> 100	H_2(82); He(17)	(Venus, Earth, Mars, Jupiter, Pluto)
b.	90	CO_2(96.4); N_2(3.4)	(Venus, Earth, Mars, Jupiter, Pluto)
c.	0.007	CO_2(95.7); N_2(2.7)	(Venus, Earth, Mars, Jupiter, Pluto)
d.	1	N_2(78); O_2(21)	(Venus, Earth, Mars, Jupiter, Pluto)
e.	$1.\ 10^{-5}$	CH_4(100)	(Venus, Earth, Mars, Jupiter, Pluto)

5.6 Write the Lewis structures for H_2, He, CO_2, N_2, O_2, and CH_4. Depict all valence electrons.

All of the above atmospheric components of the planets are atoms and molecules with low boiling point. Boiling point is primarily determined by the overall polarity of the molecule, which is determined by bond polarity and molecular geometry. Non–polar molecules interact with dispersion force only and, therefore, have low boiling points. Yet there are differences in boiling points among nonpolar molecules.

5.7 Arrange H_2, He, N_2, O_2, and CH_4 in the order of increasing boiling point. Explain the order.

SOLUTION OF PREPARATORY PROBLEM 5

5.1 $^{238}_{92}U \rightarrow {}^{206}_{82}Pb + 8\ {}^{4}_{2}He + 6\ {}^{0}_{-1}e$

5.2 After almost one half–life, the molar ratio between ^{206}Pb and ^{238}U is 1.

Mass ratio: $\dfrac{M_r\left({}^{206}Pb\right)}{M_r\ \left({}^{238}U\right)} = \dfrac{206}{238} = 0.87$

5.3 $(1/2)\ m\ v_e^2 = \dfrac{G\,M\,m}{R}$

$$v_e^2 = \frac{2\,G\,M}{R} = \frac{2 \times 6.67{\times}10^{-11}\ \text{N m}^2\,\text{kg}^{-2} \times 5.98{\times}10^{24}\ \text{kg}}{6.37{\times}10^{6}\ \text{m}}$$

$v_e = 1.12{\times}10^4\ \text{m s}^{-1}$

5.4 Hydrogen atom: $\sqrt{\dfrac{8\,RT}{\pi\,M}} = \sqrt{\dfrac{8 \times 8.3145\ \text{kg m}^2\ \text{s}^{-2}\ \text{mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{3.14\ \times\ 1.008{\times}10^{-3}\ \text{kg mol}^{-1}}} = 2500\ \text{m s}^{-1}$

(22 % of the escape velocity)

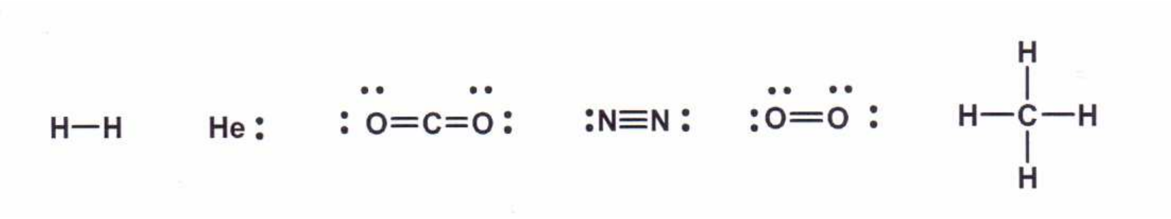
Nitrogen molecule:

$2500\ \text{m s}^{-1} \times (1/28)^{1/2} = 470\ \text{m s}^{-1}$ (4 % of the escape velocity)

The fraction with speed exceeding the escape velocity is much greater for hydrogen atoms than for nitrogen molecules.

5.5
a. Jupiter: large mass, low temperature, H/He retained at high pressure
b. Venus: lost light elements, rich in carbon dioxide, high pressure
c. Mars: small mass, rich in carbon dioxide, low pressure
d. Earth: lost light elements, carbon dioxide converted to oxygen through photosynthesis
e. Pluto: very small mass, lost light elements, very low atmospheric pressure

5.6



5.7 He (4 K) < H_2 (20 K) < N_2 (77 K) < O_2 (90 K) < CH_4 (112 K)

Dispersion force is greater for larger molecules.

Nitrogen with the triple bond has a smaller bond length than oxygen.

Nitrogen also has less lone pair electrons to be involved in dispersion.

THEORETICAL PROBLEM 6

Discovery of the noble gases

Molecules such as H_2, N_2, O_2, CO_2, and CH_4 in Problem 5 are formed through chemical bonding of atoms. Even though valency was known in the 19th century, the underlying principle behind chemical bonding had not been understood for a long time. Ironically, the discovery of the noble gases with practically zero chemical reactivity provided a clue as to why elements other than the noble gases combine chemically. In 1882, Rayleigh decided to redetermine accurately gas densities in order to test Prout's hypothesis.

6.1 What is Prout's hypothesis? What evidence did he use to support his hypothesis? (Search the Internet or other sources.)

To remove oxygen and prepare pure nitrogen, Rayleigh used a method recommended by Ramsay. Air was bubbled through liquid ammonia and was passed through a tube containing copper at red heat where the oxygen of the air was consumed by hydrogen of the ammonia. Excess ammonia was removed with sulfuric acid. Water was also removed. The copper served to increase the surface area and to act as an indicator. As long as the copper remained bright, one could tell that the ammonia had done its work.

6.2 Write a balanced equation for the consumption of oxygen in air by hydrogen from ammonia. Assume that air is 78 % of nitrogen, 21 % of oxygen, and 1 % of argon by volume (unknown to Rayleigh) and show nitrogen and argon from the air in your equation.

6.3 Calculate the molecular mass of nitrogen one would get from the density measurement of nitrogen prepared as above. Note that argon in the sample, initially unknown to Rayleigh, did contribute to the measured density.
(Atomic masses: $A_r(N) = 14.0067$, and $A_r(Ar) = 39.948$).

Rayleigh also prepared nitrogen by passing air directly over red–hot copper.

6.4 Write a balanced equation for the removal of oxygen from air by red–hot copper. Again show nitrogen and argon from the air in your equation.

6.5 Calculate the molecular mass of nitrogen one would get from the density measurement of the nitrogen prepared by the second method.

6.6 To Rayleigh's surprise, the densities obtained by the two methods differed by a thousandth part – a difference small but reproducible. Verify the difference from your answers in 6.3 and 6.5.

6.7 To magnify this discrepancy, Rayleigh used pure oxygen instead of air in the ammonia method. How would this change the discrepancy?

6.8 Nitrogen as well as oxygen in the air was removed by the reaction with heated Mg (more reactive than copper). Then a new gas occupying about 1 % of air was isolated. The density of the new gas was about x–times that of air. Calculate x.

6.9 A previously unseen line spectrum was observed from this new gas separated from 5 cm^3 of air. The most remarkable feature of the gas was the ratio of its specific heats (C_p/C_v), which proved to be 5/3, i. e. the highest possible,. The observation showed that the whole of the molecular motion was (*). Thus, argon is a monatomic gas.

Choose (*): (1) electronic (2) vibrational (3) rotational (4) translational

6.10 Calculate the mass of argon in a 10 m×10 m×10 m hall at STP.

In 1894, Rayleigh and Ramsay announced the discovery of Ar. Discovery of other noble gases (He, Ne, Kr, Xe) followed and a new group was added to the periodic table. As a result, Rayleigh and Ramsay received the Nobel Prizes in physics and in chemistry, respectively, in 1904.

6.11 Element names sometimes have Greek or Latin origin and provide clues as to their properties or means of discovery. Match the element name with its meaning.

Helium •
Neon •
Argon •
Krypton •
Xenon •

• new
• stranger
• lazy
• hidden
• sun

SOLUTION OF PREPARATORY PROBLEM 6

6.1. In 1816 Prout published a hypothesis that all matter is composed ultimately of hydrogen. (Later, Harlow Shapley, an eminent astronomer, said that if God did create the world by a word, the word would have been hydrogen.) Prout cited as evidence the fact that the specific gravities of gaseous elements appeared to be whole–number multiples of the value for hydrogen.

6.2. $28\ NH_3 + 21\ O_2 + 78\ N_2 + Ar \rightarrow 92\ N_2 + 42\ H_2O + Ar$

6.3. $\dfrac{(92 \times 2 \times 14.0067)\ +\ 39.948}{93} = 28.142$

6.4. $78\ N_2 + 21\ O_2 + Ar + 42\ Cu \rightarrow 78\ N_2 + 42\ CuO + Ar$

6.5. $\dfrac{(78 \times 2 \times 14.0067)\ +\ 39.948}{79} = 28.164$

6.6. $\dfrac{28.164}{28.142} = 1.0008$ (about 0.1%)

6.7. $4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$

The relative molecular mass of pure nitrogen = $2 \times 14.0067 = 28.013$

$\dfrac{28.164}{28.013} = 1.0054$

The discrepancy would increase about 7–fold (0.0054 / 0.0008).

6.8. 40 : 29 = 1.4

6.9 5 R : 3 R = 1.67 translational

6.10 Volume of air = 1000 m^3 = $\dfrac{1.0 \times 10^6\ dm^3}{22.4} = 4.5 \times 10^4$ mol of air

Mass of argon = $4.5 \times 10^4 \times 0.01 \times 40 = 1.8 \times 10^4$ g = 18 kg

6.11 helium – sun
neon – new
argon – lazy
krypton – hidden
xenon – stranger

THEORETICAL PROBLEM 7

Solubility of salts

The solubility of metals and their salts played an important role in Earth's history changing the shape of the Earth's surface. Furthermore, solubility was instrumental in changing the Earth's atmosphere. The atmosphere of the primitive Earth was rich in carbon dioxide. Surface temperature of the early Earth was maintained above the boiling point of water due to continued bombardment by asteroids. When the Earth cooled, it rained and a primitive ocean was formed. As metals and their salts dissolved the ocean became alkaline and a large amount of carbon dioxide from the air dissolved in the ocean. The CO_2 part of most carbonate minerals is derived from this primitive atmosphere.

As life arose about 3.8 billion years ago and photosynthetic bacteria evolved about 3 billion years ago, molecular oxygen was produced as a by–product of photosynthesis. As oxygen reacted with the metal ions in the ocean, metal oxides with low solubility were deposited on the ocean floor which later became dry land through plate tectonic motion. Iron and aluminum ores were, and still are, of particular importance as raw materials in human civilization.

Let's consider a solubility problem using silver halides. K_{sp} values for AgCl and AgBr are 1.8×10^{-10} and 3.3×10^{-13}, respectively.

7.1 Excess AgCl was added to deionized water. Calculate the concentration of Cl^- in equilibrium with solid AgCl. Repeat the calculation for Br^- assuming that AgBr was added instead of AgCl.

7.2 Assume that 0.100 dm^3 of Ag^+ solution ($c = 1.00\times10^{-3}$ mol dm^{-3}) is added to a Cl^- solution of the same volume and concentration. What is the concentration of Cl^- in the solution once equilibrium has been established? What is percentage of the total chloride in solution?

7.3 Assume that 0.100 dm^3 of Ag^+ solution ($c = 1.00\times10^{-3}$ mol dm^{-3}) is added to a Br^- solution of the same volume and concentration. What is the concentration of Br^- in the solution once equilibrium has been established? What is percentage of the total bromide solution?

7.4 Experimental verification of the answers in 7.2 and 7.3 is difficult, because the exact volume and concentration of the solutions are unknown. Repeat the calculations in 7.2

and 7.3 assuming that the concentration of the Ag^+ solution is 1.01×10^{-3} mol dm^{-3}.

Now let's assume that Ag^+ solution (c = 1.00×10^{-3} mol dm^{-3}) is slowly added with constant stirring to a 0.100 dm^3 solution containing both Cl^- and Br^- at a concentration of 1.00×10^{-3} mol dm^{-3}.

7.5 Which silver halide will precipitate first? Describe the situation when the first precipitate appears.

7.6 Determine the percentage of Cl^-, Br^- and Ag^+ ions in the solution and in the precipitate after addition of 100, 200, and 300 cm^3 of Ag^+ solution.

V_{add}	% Br in solution	% Br in precipitate	% Cl in solution	% Cl in precipitate	% Ag in solution	% Ag in precipitate
100 cm^3						
200 cm^3						
300 cm^3						

SOLUTION OF PREPARATORY PROBLEM 7

7.1 $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$

$K_{sp} = [Ag^+][Cl^-] = x^2 = 1.8\times10^{-10} \Rightarrow [Ag^+] = [Cl^-] = 1.34\times10^{-5}$

$AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$

$K_{sp} = [Ag^+][Br^-] = x^2 = 3.3\times10^{-13} \Rightarrow [Ag^+] = [Br^-] = 5.74\times10^{-7}$

7.2 In this hypothetical case, $[Ag^+] = [Cl^-] = 1.34\times10^{-5}$ just as in 7.1.

$$\frac{Cl^-(aq)}{Cl\,(total)} = \frac{Cl^-(aq)}{Cl^-(aq)\ +\ AgCl(s)} = \frac{1.3\times10^{-5}\ \text{mol dm}^{-3}\times\ 0.200\ \text{dm}^3}{1.00\times10^{-4}\ \text{mol}} = 0.027 = 2.7\ \%$$

7.3 Similarly, $[Ag^+] = [Br^-] = 5.7\times10^{-7}$ just as in 7.1.

$$\frac{Br^-(aq)}{Br\ (total)} = \frac{Br^-(aq)}{Br^-(aq)\ +\ AgBr(s)} = \frac{5.7\times10^{-5}\ mol\ dm^{-3}\times\ 0.200\ dm^3}{1.00\times10^{-4}\ mol} =$$

$$= 1.1\times10^{-3} = 0.11\ \%$$

7.4 Assume that 1.00×10^{-4} mol of AgCl is precipitated, and 1.00×10^{-6} mol of Ag^+ ions remains in solution. Then a portion of AgCl dissolves.

$[Ag^+] = 5.0\times10^{-6} + x$, $[Cl^-] = x$

$K_{sp} = [Ag^+][Cl^-] = (5.0\times10^{-6} + x)\ x = 1.8\times10^{-10}$

⇒ $[Cl^-] = 1.1\times10^{-5}$ (slightly decreased)

$[Ag^+] = 1.6\times10^{-5}$ (slightly increased)

$$\frac{Cl^-(aq)}{Cl\ (total)} = \frac{Cl^-(aq)}{Cl^-(aq)\ +\ AgCl(s)} = \frac{1.1\times10^{-5}\ mol\ dm^{-3}\times\ 0.200\ dm^3}{1.00\times10^{-4}\ mol} = 0.022 = 2.2\ \%$$

Similarly,

$[Ag^+] = 5.0\times10^{-6} + x$, $[Br^-] = x$

$K_{sp} = [Ag^+][Br^-] = (5.0\times10^{-6} + x)\ x = 3.3\times10^{-13}$

$x < 5.0\times10^{-6}$; therefore, $(5.0\times10^{-6})\ x = 3.3\times10^{-13}$

⇒ $[Br^-] = 6.6\times10^{-8}$ significant decrease from 5.7×10^{-7}

$[Ag^+] = 5.1\times10^{-6}$ significant increase from 5.7×10^{-7}

$$\frac{Br^-(aq)}{Br\ (total)} = \frac{Br^-(aq)}{Br^-(aq)\ +\ AgBr(s)} = \frac{6.5\times10^{-8}\ mol\ dm^{-3}\times\ 0.200\ dm^3}{1.00\times10^{-4}\ mol} =$$

$$= 1.3\times10^{-4} = 0.013\ \%$$

7.5 AgBr will precipitate first. Theoretically, AgBr will begin to precipitate when the Ag^+ concentration reaches 3.3×10^{-10} mol dm^{-3}. At this concentration of Ag^+, AgCl will not precipitate.

AgBr: $[Ag^+] = \dfrac{K_{sp}}{\left[Br^-\right]} = \dfrac{3.3\times10^{-13}}{1.0\times10^{-3}} = 3.3\times10^{-10}$

This corresponds to 3.3×10^{-8} dm^3 of the Ag^+ solution, which is much less than the smallest volume one can deliver with a micropipet.

7.6 This problem can be solved using the mass conservation relations. However, the solution can be simplified as shown below.

A = total amount of Ag = $[Ag^+]_0\ V_{add} = (1.00\times10^{-3}\ mol\ dm^{-3})\ V_{add}$

B = total amount of Br^- = $[Br^-]_0\ V_{orignal}$ = (1.00×10^{-3} mol dm^{-3}) (0.100 dm^3) =

= 1.00×10^{-4} mol

C = total amount of Cl = $[Cl^-]_0V_{orignal}$ = 1.00×10^{-3} mol dm^{-3} × 0.100 dm^3 =

= 1.00×10^{-4} mol

$A = [Ag^+]\ V_{tot} + n_{AgCl(s)} + n_{AgBr(s)}$ (1)

$B = [Br^-]\ V_{tot} + n_{AgBr(s)}$ (2)

$C = [Cl^-]\ V_{tot} + n_{AgCl(s)}$ (3)

$K_{sp}(AgBr) = [Ag^+][Br^-]$ (4)

$K_{sp}(AgCl) = [Ag^+][Cl^-]$ (5)

▸ V_{add} = 100 cm^3,

V_{tot} = 200 cm^3 (total n(Ag) = 1.00×10^{-4} mol). Assume that all Ag^+ are used to precipitate Br^- as AgBr(s).

$[Ag^+] = [Br^-] = 0$, $[Cl^-] = 5.0\times10^{-4}$ n(AgBr) = 1.00×10^{-4} mol, n(AgCl) = 0

At equilibrium:

$[Ag^+] = K_{sp}(AgCl) / [Cl^-] = 3.6\times10^{-7}$

$[Br^-] = K_{sp}(AgBr) / [Ag^+] = 9.2\times10^{-7}$

Total Ag = $Ag^+(aq)$ + AgBr + AgCl, total Br = Br^- (aq) + AgBr

Since total Ag = total Br, $Ag^+(aq)$ + AgCl = $Br^-(aq)$

n(AgCl) = $([Br^-] - [Ag^+])V_{tot}$ = [(9.2 – 3.6)×10^{-7} mol dm^{-3}] × 0.200 dm^3 =

= 1.1×10^{-7} mol (0.11 % of the total Cl)

$[Cl^-] = 5.0\times10^{-4}$ (still valid, because very little AgCl is formed) n(AgBr) = 1.00×10^{-4} mol (still valid, because $[Br^-]$ is small)

▸ V_{add} = 200 cm^3,

V_{tot} = 300 cm^3 (total n(Ag) = 2.00×10^{-4} mol)

Assume complete precipitation of Br^- and Cl^- with Ag^+

$[Ag^+] = [Br^-] = [Cl^-] = 0$, n(AgBr) = 1.0×10^{-4} mol, n(AgCl) = 1.0×10^{-4} mol

At equilibrium:

$$[Ag^+] = [Br^-] + [Cl^-] = \frac{K_{sp}(AgBr)}{[Ag^+]} + \frac{K_{sp}(AgCl)}{[Ag^+]}$$

$[Ag^+] = 1.3\times10^{-5}$

$$[Br^-] = \frac{K_{sp}(AgBr)}{[Ag^+]} = 2.5\times10^{-8}$$

$$[Cl^-] = \frac{K_{sp}(AgCl)}{[Ag^+]} = 1.3\times10^{-5}$$

$n(AgBr) = 1.00\times10^{-4}$ mol – $c(Br^-)\ V_{tot} = 1.00\times10^{-4}$ mol

$n(AgCl) = 1.00\times10^{-4}$ mol – $c(Cl^-)\ V_{tot} = 9.6\times10^{-5}$ mol

▸ $V_{add} = 300$ cm^3

$V_{tot} = 400$ cm^3 (total $n(Ag) = 3.00\times10^{-4}$ mol)

Assume complete precipitation of Br^- and Cl^- with Ag^+.

$[Ag^+] = 2.5\times10^{-4}$, $[Br^-] = [Cl^-] = 0$, $n(AgBr) = 1.0\times10^{-4}$ mol, $n(AgCl) = 1.0\times10^{-4}$ mol

$$[Br^-] = \frac{K_{sp}(AgBr)}{[Ag^+]} = 1.3\times10^{-9}$$

$$[Cl^-] = \frac{K_{sp}(AgCl)}{[Ag^+]} = 7.2\times10^{-7}$$

$n(AgBr) = 1.00\times10^{-4}$ mol – $c(Br^-)\ V_{tot} = 1.00\times10^{-4}$ mol

$n(AgCl) = 1.00\times10^{-4}$ mol – $c(Cl^-)\ V_{tot} = 9.97\times10^{-5}$ mol

V_{add}	% Br in solution	% Br in precipitate	% Cl in solution	% Cl in precipitate	% Ag in solution	% Ag in precipitate
100 cm^3	0.18	99.8	99.9	0.11	0.07	99.9
200 cm^3	0.007	100	4.0	96.0	2.0	98.0
300 cm^3	0.0005	100	0.3	99.7	33.3	66.7

THEORETICAL PROBLEM 8

Physical methods for determination of Avogadro's number

Avogadro's number is a fundamental constant in chemistry. However, an accurate determination of this value took a long time. Avogadro (1776–1856) himself did not know Avogadro's number as it is known today. At about the time of his death, Avogadro's number determined from gas properties, such as diffusion coefficient and viscosity, approached 5×10^{22}. Avogadro's number as we know it today (6.02×10^{23}) became available only in the early 20th century. Let's consider three separate approaches.

8.1 At thermal equilibrium, the probability of finding a molecule with a mass m at height h is proportional to the Boltzmann factor, $\exp(-E(h) / k_BT)$, where $E(h)$ is the gravitational potential energy (mgh, where g is 9.81 m s^{-2}) and k_B is the Boltzmann constant. Thus, the number density at h follows "barometric" distribution:

$$\frac{\rho(h)}{\rho(h_o)} = \exp\left(-\frac{mg\,(h-h_o)}{k_B\,T}\right)$$

(**a**) Spherical particles of diameter 0.5 μm and density 1.10 g cm^{-3} are suspended in water (density 1.00 g cm^{-3}) at 20 °C. Calculate the effective mass m of the particles corrected for buoyancy.

(**b**) Now the number density of the particles with effective mass will follow barometric distribution. In an experiment where a vertical distribution of such particles was measured, it was observed that the number density at h decreased to 1/e times the number density at h_o over a vertical distance of 6.40×10^{-3} cm. Calculate Boltzmann's constant.

(**c**) Calculate Avogadro's number using Boltzmann's constant and the gas constant. (R = 8.314 J mol^{-1}K^{-1})

8.2 Avogadro's number can also be determined by single crystal X–ray crystallography. The density of sodium chloride crystal is 2.165 g cm^{-3}. The sodium chloride lattice is shown below (Figure 8.1). The distance between the centers of adjacent Na^+ and Cl^- ions was determined to be 2.819×10^{-8} cm. Calculate the Avogadro's number.

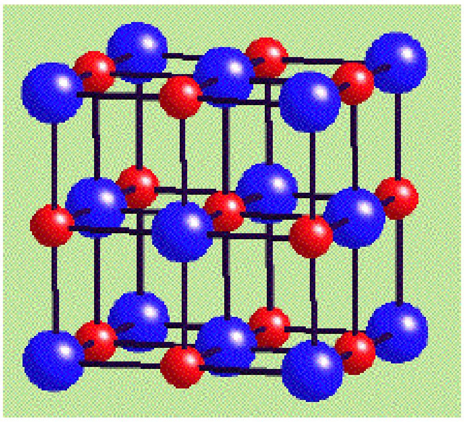


Figure 8–1. Lattice structure of sodium chloride

In the rock–salt structure one finds a face–centered cubic array of anions and the same array of cations. The two arrays interpenetrate each other. A unit cell contains 4 anions (8 centered at the apexes are each shared by 8 unit cells thus giving 1 anion, and 6 positioned at the face centers are each shared by 2 unit cells giving 3 anions). A unit cell also contains 4 cations.

8.3 In a well known oil drop experiment, Millikan determined in 1913 that the basic unit of electric charge is 1.593×10^{-19} C. Calculate Avogadro's number from this value and Faraday charge, which is electric charge per equivalent (1 Faraday = 96,496 coulomb as used by Millikan).

SOLUTION OF PREPARATORY PROBLEM 8

8.1. (a) Volume of the particle = $(4/\,3 \times 3.14)\,(0.5{\times}10^{-6}\,/\,2)^3\ \text{m}^3 = 6.54{\times}10^{-14}\ \text{cm}^3$

Effective mass = $(6.54{\times}10^{-14}\ \text{cm}^3)\,(1.10 - 1.00)\ \text{g cm}^{-3} = 6.54{\times}10^{-15}\ \text{g}$

(b) $$\frac{m\,g\,(h-h_\text{o})}{k_\text{B}\,T} = 1$$

$$k_\text{B} = \frac{6.54{\times}10^{-18}\ \text{kg} \times 9.81\,\text{m s}^{-2} \times 6.40{\times}10^{-5}\ \text{m}}{293.15\ \text{K}} = 1.40{\times}10^{-23}\ \text{J K}^{-1}$$

(c) Avogadro's number = $R\,/\,k_\text{B} = \dfrac{8.314\ \text{J mol}^{-1}\text{K}^{-1}}{140{\times}10^{-23}\ \text{J K}^{-1}} = 5.94{\times}10^{23}\ \text{mol}^{-1}$

8.2 Length of the edge of the unit cell = $2 \times 2.819{\times}10^{-8}\ \text{cm} = 5.638{\times}10^{-8}\ \text{cm}$

Volume of the unit cell = $(5.638{\times}10^{-8}\ \text{cm})^3 = 1.792 \times 10^{-22}\ \text{cm}^3$

Volume per Na^+ plus Cl^- = $1.792{\times}10^{-22}\ \text{cm}^3\,/\,4 = 4.480{\times}10^{-23}\ \text{cm}^3$

Formula mass of NaCl = 22.99 + 35.45 = 58.44

Molar volume of the crystal = $58.44\ \text{g}\,/\,2.165\ \text{g cm}^{-3} = 26.99\ \text{cm}^3$

Avogadro's number = $26.99\ \text{cm}^3\,/\,4.480{\times}10^{-23}\ \text{cm}^3 = 6.025{\times}10^{23}$

8.3 Avogadro’s number = $96496\ \text{C mol}^{-1}\,/\,1.593{\times}10^{-19}\ \text{C} = 6.058{\times}10^{23}\ \text{mol}^{-1}$

THEORETICAL PROBLEM 9

An electrochemical method for determination of Avogadro's number

By definition, Avogadro's number is the number of atoms in exactly 12 g of carbon ^{12}C. Avogadro's number recommended by CODATA (Committee on Data for Science and Technology) in 2002 is $6.0221415(10) \times 10^{23}$ mol^{-1}, where the number in parenthesis represents one standard deviation in the last two digits.

Avogadro's number can be determined electrolytically. Current and time are measured in order to obtain the number of electrons passing through the electrochemical cell from $Q = I\,t$ (charge = current × time). Copper electrodes were used for electrolysis of H_2SO_4 solution (c = 0.5 mol dm^{-3}). During electrolysis, copper is lost from the anode as the copper atoms are converted to copper ions. The copper ions pass through the solution. At the surface of the cathode, hydrogen gas is liberated through reduction of hydrogen ions in the acidic solution. Experimental results are as follows:

decrease in anode mass: 0.3554 g
constant current: 0.601 A
time of electrolysis: 1802 s

Note that 1 A = 1 C s^{-1} or 1 A s = 1 C and the charge of one electron is 1.602×10^{-19} C.

9.1 Write the reactions at both the anode and cathode.

9.2 Calculate the total charge that passed through the circuit.

9.3 Calculate the number of electrons involved in the electrolysis.

9.4 Calculate the mass of a copper atom.

9.5 Determine Avogadro's number. Molar mass of copper is 63.546 g mol^{-1}.

9.6 It is also possible in principle to collect the hydrogen gas evolved and use its mass to determine Avogadro's number. Calculate the mass. What is the percent error in this measurement of Avogadro's number?

9.7 It is also possible in principle to collect the hydrogen gas evolved and use its mass to determine Avogadro's number. Calculate the mass of evolved hydrogen gas. Is this determination of Avogadro's number from the mass of evolved hydrogen practical?

SOLUTION OF PREPARATORY PROBLEM 9

9.1 Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$; cathode : $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$

9.2 Total charge = (0.601 A × 1 C s^{-1}) / 1 A × 1802 s = 1083 C

9.3 Number of electrons = (1083 C × 1 electron) / 1.602×10^{19} C = 6.760×10^{21}

9.4 Number of copper atoms = 6.760×10^{21} / 2 = 3.380×10^{21}

Mass of a copper atom = 0.3554 g / 3.380×10^{21} = 1.051×10^{-22} g

9.5 Avogadro's number = 63.546 g / 1.051×10^{-22} g = 6.046×10^{23}

9.6 Error (in %): ($6.046 \times 10^{23} - 6.022 \times 10^{23}$) / 6.022×10^{23} = 0.4 %

9.7 Mass of H_2 evolved = 1 g × 6.760×10^{21} / 6.02×10^{23} = 0.011 g

Collecting and weighing such a small amount of any gas is not practical considering buoyancy correction.

THEORETICAL PROBLEM 10

Enthalpy, entropy, and stability

All chemical changes in living and non–living systems obey laws of thermodynamics. The equilibrium constant of a given reaction is determined by changes in Gibbs free energy, which is in turn determined by enthalpy change, entropy change, and the temperature.

10.1 Fill in the blanks (a–f) with all that apply from the following:

equilibrium constant, K_{eq}
entropy change, ΔS
enthalpy change, ΔH
free energy change, ΔG

(a) strongly temperature–dependent ( )
(b) closely related to bond strength ( )
(c) measure of change in randomness ( )
(d) related to the quantity of reactants and products ( )
(e) measure of spontaneity of a reaction ( )
(f) measure of heat released or absorbed ( )

The following equilibrium exists in the vapor phase dissociation of molecular addition compounds of donor molecules, D, and boron compounds, BX_3.

$$D\cdot BX_3(g) \leftrightarrow D(g) + BX_3(g)$$

$$K_p = \frac{[D][BX_3]}{[D\cdot BX_3]}$$

10.2 Dissociation constants (K_p) of the molecular addition compounds $Me_3N\cdot BMe_3$ and $Me_3P\cdot BMe_3$ at 100 °C are 0.472 and 0.128, respectively. Calculate the standard free energy change of dissociation at 100 °C for both compounds. Which complex is more stable at this temperature?

10.3 The standard entropy change of dissociation, $\Delta S°$, is 45.7 cal mol^{-1} K^{-1} for $Me_3N\cdot BMe_3$ and 40.0 cal mol^{-1} K^{-1} for $Me_3P\cdot BMe_3$. Calculate the standard enthalpy change of dissociation for both compounds. Which compound has the stronger central bond? Assume that ΔH and ΔS are temperature–independent.

10.4 Which is more critical in determining the overall stability of these addition compounds at 100°C, enthalpy term (ΔH) or entropy term ($T\,\Delta S$)?

10.5 At what temperature does $Me_3N{\cdot}BMe_3$ become more thermodynamically stable than $Me_3P{\cdot}BMe_3$? Assume that ΔH and ΔS are temperature–independent.

SOLUTION OF PREOPARATRY PROBLEM 10

10.1 (a) K_{eq} and ΔG

(b) ΔH

(c) ΔS

(d) K_{eq}

(e) ΔG

(f) ΔH

10.2 From $\Delta G = -RT \ln K_p$,

ΔG is 1.52 kcal mol^{-1} for $Me_3P{\cdot}BMe_3$ and 0.56 kcal mol^{-1} for $Me_3N{\cdot}BMe_3$.

$Me_3P{\cdot}BMe_3$ is more stable (less likely to dissociate) than $Me_3N{\cdot}BMe_3$ at 100°C.

10.3 $\Delta G = \Delta H - T\,\Delta S$

$\Delta H_{373} = \Delta G_{373} + 373\ \Delta S_{373} \approx \Delta G_{373} + 373\ \Delta S°$,

$Me_3N{\cdot}BMe_3$: $\Delta H = 0.56\ \text{kcal mol}^{-1} + (373\ \text{K} \times 45.7\ \text{cal mol}^{-1}\ \text{K}^{-1}) = 17.6\ \text{kcal mol}^{-1}$

$Me_3P{\cdot}BMe_3$: $\Delta H = 1.52\ \text{kcal mol}^{-1} + (373\ \text{K} \times 40.0\ \text{cal mol}^{-1}\ \text{K}^{-1}) = 16.4\ \text{kcal mol}^{-1}$

More heat is needed to dissociate $Me_3N{\cdot}BMe_3$. Therefore, the N–B central bond is stronger.

10.4 $Me_3N{\cdot}BMe_3$:

$\Delta H = 17.6\ \text{kcal mol}^{-1}$ $\quad -T\,\Delta S = -\ 373\ \text{K} \times 45.7\ \text{cal mol}^{-1}\ \text{K}^{-1} = -17.05\ \text{kcal mol}^{-1}$

$\Delta G = 0.56\ \text{kcal mol}^{-1}$

$Me_3P \cdot BMe_3$:

$\Delta G = 16.4 \text{ kcal mol}^{-1}$ $\quad - T\,\Delta S = -\,373 \text{ K} \times 40.0 \text{ cal mol}^{-1}\text{ K}^{-1} = -14.92 \text{ kcal mol}^{-1}$

$\Delta G = 1.52 \text{ kcal mol}^{-1}$

Enthalpy change is larger for $Me_3N \cdot BMe_3$, however, larger increase in the entropy term leads to a smaller increase in Gibbs free energy for $Me_3N \cdot BMe_3$.

10.5 $17\,600 \text{ cal mol}^{-1} - (45.7 \text{ cal mol}^{-1}\text{K})\, T > 16\,400 \text{ cal mol}^{-1} - (40.0 \text{ cal mol}^{-1}\text{K})\, T$

$5.7 \text{ (cal mol}^{-1}\text{K) T} < 1\,200 \text{ cal mol}^{-1}$

$\text{T} < 210\text{K} \ (-\,63 \text{ °C})$

THEORETICAL PROBLEM 11

Lewis acids and bases

Acids and bases are essential for life. Amino acids have both acidic and basic groups. DNA and RNA are nucleic acids that contain bases such as adenine, guanine, thymine, cytosine, and uracil. Thus, understanding acid–base chemistry is essential for understanding life. Oxygen was so named by Lavoisier because of its acid–forming nature; the acid–forming nature of oxygen is a manifestation of its high electronegativity. Lewis extended the definition of acids and bases, and electronegativity is again central in understanding Lewis acidity and basicity.

11.1 Describe the molecular structure of BX_3. What is the hybridization of the boron orbitals?

11.2 How does this hybridization change when the boron halide forms an adduct with a base such as pyridine (C_5H_5N)? Is the structural change around boron upon adduct formation more favorable when X is F or I? List BF_3, BCl_3, and BBr_3 in the order of increasing Lewis acidity based on the above structural consideration.

11.3 Electronegativity is another important consideration in predicting Lewis acidity. List BF_3, BCl_3, and BBr_3 in the order of increasing Lewis acidity, based only on the electronegativity of the halogen elements (inductive effect).

11.4 Is adduct formation between the boron halide (Lewis acid) and pyridine (Lewis base) exothermic or endothermic? Which Lewis acid will show the greatest enthalpy change upon adduct formation?

Although the gaseous state would be best for computing the relative strengths of the three boron halides under consideration, the liquid state of these materials could be used as a satisfactory reference state since the boron halides are relatively non–polar liquids or gases.

11.5 The enthalpy changes when mixing liquid boron halide with nitrobenzene, ΔH_1, and when mixing the nitrobenzene–boron halide solution with pyridine also in nitrobenzene, ΔH_2, are given below.

$$BX_3(l) + C_6H_5NO_2(l) \rightarrow C_6H_5NO_2 \cdot BX_3(soln) \qquad \Delta H_1$$

$$C_6H_5NO_2 \cdot BX_3(soln) + C_5H_5N(soln) \rightarrow C_5H_5N \cdot BX_3(soln) + C_6H_5NO_2(soln) \qquad \Delta H_2$$

	BF_3	BCl_3	BBr_3
ΔH_1 (kcal mol^{-1})	– 6.7	– 8.7	– 12.5
ΔH_2 (kcal mol^{-1})	– 25.0	– 30.8	– 32.0

Calculate ΔH_3 for the following reactions. Do they agree with your prediction in 11.4?

$$BX_3(l) + C_5H_5N(soln.) \rightarrow C_5H_5N{\cdot}BX_3(soln.)$$

11.6 Boron halides also show very different reactivity with water. BF_3 forms stable addition compounds whereas BCl_3 and BBr_3 react violently with H_2O at temperatures below 20°℃. Predict the products, **A**, **B**, and **C**, for the following reactions:

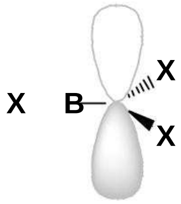
$BF_3 + H_2O \rightarrow$ **A**

BCl_3 (or BBr_3) + 3 $H_2O \rightarrow$ **B** + **C**

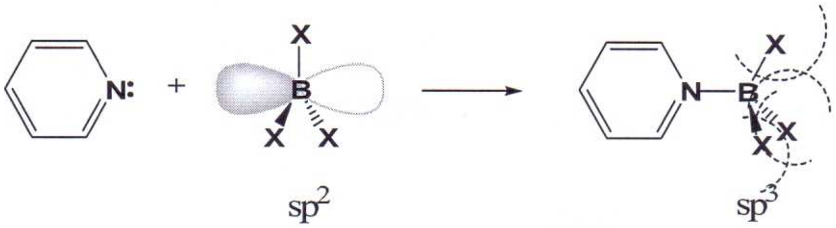
11.7 What kind of extra bond can be formed in BX_3 between the central boron and one of its halides possessing lone pair electrons in order to fulfill the 'octet rule'? Explain how this extra bond affects the Lewis acidity of BX_3.

SOLUTION OF PREPARATORY PROBLEM 11

11.1 Central B has sp^2 hybridization and BX_3 is triangular.



11.2 When an adduct is formed with pyridine, the structure around the central boron becomes tetragonal sp^3 hybrid type (tetrahedron) structure. This structural change will induce steric hindrance around boron which is more pronounced with larger groups (i.e., iodine atoms) and adduct formation is not preferred. Therefore, BF_3 is predicted to show the greatest preference to form adduct. (BF_3 is expected to show the strongest Lewis acidity)



11.3 The more electronegative halogen is expected to remove effectively electron density from the central boron and increase acidity.

Lewis acidity: $BF_3 > BCl_3 > BBr_3$

11.4 Like neutralization that occurs between HCl and NaOH, the reaction producing stable acid–base adduct is expected to be exothermic. The enthalpy change will be the largest for the strongest Lewis acid, BF_3.

11.5

	BF_3	BCl_3	BBr_3
$\Delta H_3 = \Delta H_1 + \Delta H_2$ (kcal mol^{-1})	–31.7	–39.5	–44.5

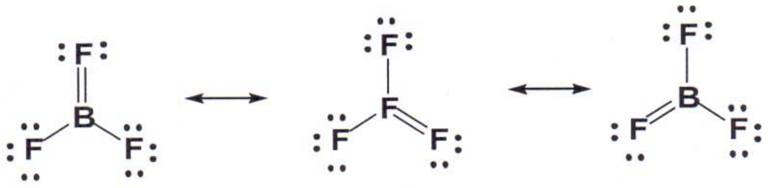
The actual order of acidity is opposite from prediction based on the electro–negativity of the halides.

11.6 A = $BF_3 \cdot H_2O$

B = $B(OH)_3$, C = 3 HX (3 HCl or 3 HBr)

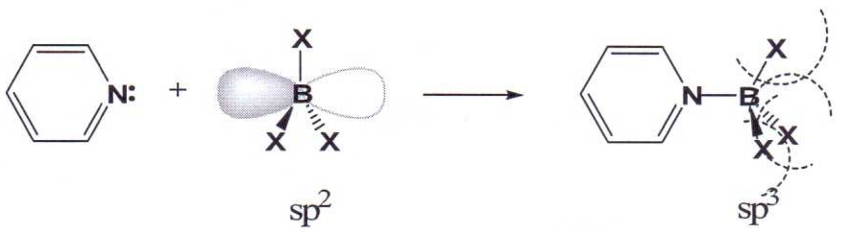
Strong Lewis acids such as BCl_3 and BBr_3 can activate O–H bonds in H_2O molecule to produce $B(OH)_3$ by releasing HX. Dative π–bonding with lone pair electrons of O, which have a similar energy level, can stabilize $B(OH)_3$ as explained in 11.7.

11.7 Empty p_z–orbital in boron can accept a dative π–bond from the lone pair electrons of fluorine, which satisfies the 'octet rule' for boron and shortens the boron–fluorine bond distance.



Since resonance structures of this kind are not possible in the adduct compounds, effective resonance will reduce the tendency for pyridine adduct formation.

The ability to form dative π–bonding appears to decrease sharply in the heavier elements due to the energy differences between B and X. Resonance of this dative π–bonding should be of lesser importance in the chloride and least importance in the bromide. These resonance structures having dative π–bonding are sufficiently large so as to reverse the trend expected from the relative inductive effects and the steric effects from the adduct formations.



THEORETICAL PROBLEM 12

Solubility equilibrium in a buffer solution

Biochemical reactions take place in buffered aqueous environments. For example, the pH of the blood is maintained around 7.4 by the buffering action of carbonate, phosphate, and proteins. Many chemical reactions in the laboratory are also carried out in buffer solutions. In this problem, let's consider the solubility equilibrium in a buffer solution.

12.1 H_2S gas with a volume of 440 cm^3 at STP can be dissolved in 100 cm^3 of water at 25 °C. Calculate the concentration of H_2S (mol dm^{-3}) in water saturated with H_2S. Assume that there is no volume change in water upon dissolution of H_2S.

12.2 Assume that equilibrium is established after a $FeCl_2$ solution with a concentration of 1.0×10^{-8} mol dm^{-3} is saturated with H_2S by continuously bubbling of H_2S into the solution.

$K_{sp}(FeS) = [Fe^{2+}][S^{2-}] = 8.0\times10^{-19}$ at 25 °C (1)

For acid dissociation of H_2S,

$$K_1 = \frac{[H^+]\,[HS^-]}{[H_2S]} = 9.5\times10^{-8} \qquad (2)$$

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = 1.3\times10^{-14} \qquad (3)$$

For autoprotolysis of water:

$K_w = [H^+][OH^-] = 1\times10^{-14}$ (4)

In the solution, the positive charge is balanced by the negative charge:

$[H^+] + 2\,[Fe^{2+}] = [Cl^-] + [OH^-] + [HS^-] + 2\,[S^{2-}]$ (5)

Cross out terms that are negligibly small in the charge balance equation (5), in order to determine $[H^+]$ and $[Fe^{2+}]$. Would you increase or decrease the pH of the solution to precipitate more FeS? How does the increase of pH by 1 affect the concentration of Fe^{2+} ion?

12.3 How would you adjust the final pH of the solution saturated with H_2S to reduce the concentration of Fe^{2+} from 0.010 mol dm^{-3} to 1.0×10^{-8} mol dm^{-3}?

12.4 You want to use acetic acid (HAc) / sodium acetate (NaAc) buffer to achieve concentration of Fe^{2+} 1.0×10^{-8} mol dm^{-3} as described above. Suppose that you are making the buffer by mixing acetic acid and sodium acetate in water in a volumetric flask. Enough acetic acid was added to make the initial concentration 0.10 mol dm^{-3}. Considering that the precipitation reaction produces H^+ ($Fe^{2+} + H_2S \rightarrow FeS(s) + 2\ H^+$), how would you adjust the initial concentration of sodium acetate to obtain concentration of Fe^{2+} equal to 1.0×10^{-8} mol dm^{-3} after equilibrium is established?

The dissociation constant for acetic acid at 25 °C is 1.8×10^{-5}.

12.5 What is the pH of the buffer before H_2S is introduced and FeS is precipitated?

SOLUTION OF PREPARATORY PROBLEM 12

12.1 440 cm^3 H_2S in 100 cm^3 of water = 4.4 dm^3 H_2S in 1 dm^3 of water = 0.20 mol dm^{-3}

12.2 For approximation, the concentration of all anions with the exception of $[Cl^-]$, which is 0.02, can be omitted in eq. (5). Thus

$[H^+] + 2\,[Fe^{2+}] = [Cl^-] = 0.020$ (6)

Combine (2) and (3): $[H^+]^2\,[S^{2-}]\,/\,[H_2S] = 1.24\times10^{-21}$

Since $[H_2S] = 0.2$, one gets $[H^+]^2\,[S^{2-}] = 2.48\times10^{-22}$ (7)

Combine (1) and (7): $[H^+]^2\,(8.0\times10^{-19})\,/\,[Fe^{2+}] = 2.48\times10^{-22}$

$[H^+]^2 = 3.1\times10^{-4}\,[Fe^{2+}]$ (8)

Combine (6) and (8) and solve for $[H^+]$:

$[H^+] = 0.0176$ pH = 1.75

$[Fe^{2+}] = (0.020 - 0.0176)\,/\,2 = 0.0012$ (12 % remains in solution)

Check: $[HS^-] = (9.5\times10^{-8})\,[H_2S]\,/\,[H^+] = 1.1\times10^{-6} << [Cl^-] = 0.02$

$[S^{2-}] = (1.3\times10^{-14})\,[HS^-]\,/\,[H^+] = 2.5\times10^{-18}$

$[OH^-] = 5.7\times10^{-13}$

Eq. (8) shows that 10–fold decrease in $[H^+]$ increases $[Fe^{2+}]$ 180–fold.

12.3 From $[H^+]^2 = 3.1\times10^{-4}\,[Fe^{2+}]$,

$[H^+] = [(3.1\times10^{-4})\,(1\times10^{-8})]^{1/2} = 1.76\times10^{-6}$ pH = 5.75

12.4 Original $n(HAc) = 0.10$ mol $dm^{-3}\times 100$ cm^3 = 10 mmol

Henderson–Hasselbach equation for the HAc / Ac^- buffer at pH = 5.75:

pH = 5.75 = pK + log $[Ac^-]\,/\,[HAc]$ = 4.74 + log $[Ac^-]\,/\,[HAc]$

initial $n(Fe^{2+})$ = 0.01 mol $dm^{-3}\times 100$ cm^3 = 1 mmol

$n(H^+)$ produced upon precipitation of 1 mmol Fe^{2+} = 2 mmol Ac^-

consumed by H^+ produced = 2 mmol

log $[Ac^-]\,/\,[HAc]$ = 5.75 – 4.74 = 1.01

Let x = original $n(Ac^-)$

$(x – 2) / (10 + 2) = 10^{1.01} = 10.2$,

$x = 124$ mmol $[Ac^-] = 124$ mmol / 100 $cm^3 = 1.24$ mol dm^{-3}

12.5 $pH = 4.74 + \log (1.24 / 0.10) = 5.83$

THEORETICAL PROBLEM 13

Redox potential, Gibbs free energy, and solubility

The proton, neutron, and electron are the three sub–atomic particles important in chemistry. These particles occupy two regions. Proton and neutron occupy the central place of the nucleus and electron the vast space outside the nucleus.

Neutron transfer does not take place in ordinary chemical reactions. Proton (hydrogen ion) transfer constitutes acid–base reactions. Electron transfer constitutes oxidation–reduction reactions. Oxidation–reduction reactions are essential for life. Photosynthesis and respiration are two prime examples. Oxidation–reduction reactions also allow key thermodynamics quantities to be measured as demonstrated in this problem.

The following information is given:

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = 0.7996$ V

$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$ $E° = 0.0713$ V

$\Delta_f G^\circ(NH_3(aq)) = -26.50 \text{ kJ mol}^{-1}$

$\Delta_f G^\circ(Ag(NH_3)_2^+(aq)) = -17.12 \text{ kJ mol}^{-1}$

$$\begin{tikzcd}
BrO_3^-(aq) \arrow[r, "+1.491\text{ V}"] \arrow[rrr, bend left, "+1.441\text{ V}"] & HOBr \arrow[r, "+1.584\text{ V}"] & Br_2(aq) \arrow[r, "?"] & Br^-(aq)
\end{tikzcd}$$

13.1 Calculate $\Delta_f G^\circ(Ag^+(aq))$.

13.2 Calculate the equilibrium constant for the following reaction at 25 °C:

$$Ag^+(aq) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$$

13.3 Calculate the K_{sp} value of AgBr(*s*) at 25°C.

13.4 Calculate the solubility of AgBr in an aqueous solution of ammonia at 25°C.
$c(NH_3) = 0.100 \text{ mol dm}^{-3}$

13.5 A galvanic cell using the standard hydrogen electrode as an anode is constructed in which the overall reaction is

$$Br_2(l) + H_2(g) + 2\,H_2O(l) \rightarrow 2\,Br^-(aq) + 2\,H_3O^+(aq).$$

Silver ions are added until AgBr precipitates at the cathode and $[Ag^+]$ reaches a concentration of 0.0600 mol dm^{-3}. The cell voltage is then measured to be 1.721 V. Calculate $\Delta E°$ for the galvanic cell.

13.6 Calculate the solubility of bromine in the form of $Br_2(aq)$ in water at 25℃.

SOLUTION OF PREPARATORY PROBLEM 13

13.1. $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = 0.7996$ V

$\Delta G° = \Delta G_f°(Ag(s)) + \Delta G_f°(e^-) - \Delta G_f°(Ag^+(aq)) = -\Delta_f G°(Ag^+(aq)) = -F\,\Delta E°$

Therefore, $\Delta_f G°(Ag^+(aq)) = F\,\Delta E° = 77.15$ kJ mol^{-1}

13.2 $Ag^+(aq) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$

$\Delta G° = \Delta_f G°(Ag(NH_3)_2^+(aq)) - \Delta_f G°(Ag^+(aq)) - 2\,\Delta_f G°(NH_3(aq)) =$

$= -17.12$ kJ $- 77.15$ kJ $- 2\,(-26.50)$ kJ $= -41.27$ kJ

$$\ln K_f = \frac{-\Delta G^o}{RT} = 16.65 \qquad K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+]\,[NH_3]^2} = e^{16.65} = 1.7\times10^7$$

13.3 $AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$ $\Delta E° = (0.0713 - 0.7996)$ V $= -0.7283$ V

$$\ln K_{sp} = \frac{-\Delta G^0}{RT} = \frac{n\,F\,\Delta E^0}{RT} = -28.17$$

$K_{sp} = [Ag^+]\,[Br^-] = e^{-28.347} = 4.9\times10^{-13}$

13.4 Let us assume: $[Ag^+] << [Ag(NH_3)_2^+]$.

$AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$ $K_{sp} = 4.9\times10^{-13}$

$Ag^+(aq) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$ $K_f = 1.7\times10^7$

$AgBr(s) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Br^-(aq)$ $K = K_{sp}\,K_f = 8.31\times10^{-6}$

Initial Change	0.100 –2 *S*	0 +*S*	0 +*S*
Equilibrium	0.100 – 2S	*S*	*S*

$$K = \frac{S^2}{(0.1 - 2S)^2} = 8.31\times10^{-6} \quad \Rightarrow \quad \frac{S}{(0.1 - 2S)} = 2.88\times10^{-3}$$

$S = [Ag(NH_3)_2^+] = [Br^-] = 2.9\times10^{-4}$ (mol dm^{-3})

$[Ag^+] = K_{sp} / [Br^-] = 1.7\times10^{-10} << [Ag(NH_3)_2^+]$

Thus, the solubility of AgBr is 2.9×10^{-4} mol dm^{-3}

13.5 $[Br^-] = K_{sp} / [Ag^+] = 4.89\times10^{-13} / 0.0600 = 8.15\times10^{-12}$

$$\Delta E^o = \Delta E + \frac{RT}{nF}\ln\frac{[Br^-]^2[H_3O^+]^2}{p_{H_2}}$$

$$= 1.721 + \frac{0.0592}{2}\log_{10}\frac{(8.15\times10^{-12})^2(1)^2}{1} = 1.065\text{ V}$$

13.6 In order to estimate the solubility of $Br_2(aq)$, we need to calculate the Gibbs free energy of the reaction:

$Br_2(l) \rightarrow Br_2(aq)$ $\Delta G° = ?$

$Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)$

$E_1° = 1.065$ V, $\Delta G_1° = -2\,F E_1° = -2.130$ F V

Let us first calculate $E_2°$ for the half–cell reaction:

$Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)$, $\Delta G_2° = -2\,F E_2°$

From the Latimer diagram:,

$BrO_3^-(aq) + 6\,H_3O^+(aq) + 6\,e^- \rightarrow Br^-(aq) + 9\,H_2O(l)$ $E_3° = 1.441$ V

$BrO_3^-(aq) + 5\,H_3O^+(aq) + 4\,e^- \rightarrow HOBr(aq) + 7\,H_2O(l)$ $E_4° = 1.491$ V

$2\,HOBr(aq) + 2\,H_3O^+(aq) + 2\,e^- \rightarrow Br_2(aq) + 4\,H_2O(l)$ $E_5° = 1.584$ V

Then, $2\,BrO_3^-(aq) + 12\,H_3O^+(aq) + 10\,e^- \rightarrow Br_2(aq) + 18\,H_2O(l)$

$E_6° = (2 \times 4\,E_4° + 2\,E_5°) / 10 = 1.5096$ V

Similarly, $Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)$

$E_2° = (2 \times 6\,E_3° - 10\,E_6°) / 2 = 1.098$ V

(Note that $6 \times E_3° = 4 \times E_4° + 1 \times E_5° + 1 \times E_2°$)

Then, $\Delta G_2° = -2\,\Delta E_2° = -2.196$ F V

Finally, $\Delta G° = \Delta G_1° - \Delta G_2° = 0.066$ F V = 6368 J mol^{-1}

Therefore,

$$[Br_2(aq)] = K = e^{\frac{-\Delta G^o}{RT}} = e^{-2.569} = 0.077\ (\text{mol dm}^{-3})$$

THEORETICAL PROBLEM 14

Measuring the ozone level in air

Ozone both helps protect and leads to damage of life forms. As the oxygen level in the Earth's atmosphere built up significantly about 2 billions years ago during which time the, ozone level in the upper atmosphere also increased. This ozone layer effectively blocked ultraviolet radiation and made life on land possible. Today, the ozone layer appears to be depleting – developing a large hole – thus, the fate of this layer is of great concern. On the other hand, ozone is a health hazard in our immediate environment at ground level. It is a key constituent of photochemical smog.

A simple method for measuring the concentration of ozone in the ground–level atmosphere is as follows. Air is bubbled through an acidic aqueous solution containing iodide and the atmospheric ozone oxidizes iodide to triiodide via the following unbalanced reaction:

$$O_3(g) + I^-(aq) \rightarrow I_3^- (aq) + O_2(g) \qquad (1)$$

At the end of the sampling period, the triiodide concentration is determined with a UV–VIS spectrophotometer at 254 nm.

Air was bubbled during 30.0 min into 10 cm^3 of an aqueous solution containing excess of KI under the following atmospheric conditions: pressure = 750 torr, temperature = 298 K, flow rate = 250 cm^3 min^{-1}. The absorbance of the resulting I_3^- solution was measured in a 1.1 cm cell by using a spectrophotometer equipped with a photocell. The photocell resistance is inversely proportional to the light intensity. Resistance values for the blank and the sample solution were 12.1 kΩ and 19.4 kΩ, respectively. The molar absorption coefficient of the I_3^- solution was determined to be 2.4×10^5 (mol dm^{-3})$^{-1}$ cm^{-1}. In various useful units, the universal gas constant is: $R = 8.314472$ J K^{-1} mol^{-1} = 0.08205746 L atm K^{-1} mol^{-1} = 62.3637 L torr K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1}

14.1 Balance equation (1).

14.2 Draw the Lewis structure for ozone.

14.3 Calculate the amount of substance of ozone in the sample of the air.

14.4 Assuming that the gases behave ideally under the conditions used, calculate the concentration in *ppb* of ozone present in the sampled air.

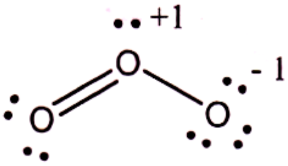
SOLUTION OF PREPARATORY PROBLEM 14

14.1 $3\,I^- \rightarrow I_3^- + 2\,e^-$

$O_3 + 2\,H^+ + 2\,e^- \rightarrow O_2 + H_2O$

$3\,I^- + O_3 + 2\,H^+ \rightarrow I_3^- + O_2 + H_2O$

14.2



14.3 The absorbance is given by

$$A = -\log T = -\log(I_{\text{sample}}/\,I_{\text{blank}}) = \log(\text{R}_{\text{sample}}\,/\,\text{R}_{\text{blank}})$$

$$\text{A} = \log\frac{19.4\text{ k}}{12.1\text{ k}} = 0.205$$

$$c(\text{I}_3^-) = \frac{A}{\varepsilon\,b} = \frac{0.205}{240{,}000\ (\text{mol dm}^{-3})^{-1}\text{cm}^{-1} \times 1.1\ \text{cm}} = 7.76\times10^{-7}\ \text{mol dm}^{-3}$$

$$n(\text{O}_3) = V_{\text{sample}}\ c(\text{I}_3^-) = 0.01\ \text{dm}^3 \times 7.76\times10^{-7}\ \text{mol} = 7.76\times10^{-9}\ \text{mol}$$

14.4 The amount of substance of air sampled:

$$n = \frac{p\,V}{R\,T} = \frac{p\left(t_{\text{sampling}}\ F\right)}{R\,T} = \frac{750\ \text{torr} \times 30\ \text{min} \times 0.250\ \text{dm}^3\,\text{min}^{-1}}{62.4\ \text{torr dm}^3\text{mol}^{-1}\text{K}^{-1} \times 298\ \text{K}} = 0.302\ \text{mol}$$

The concentration of O_3 in ppb = 7.76×10^{-9} mol / (0.302 mol $\times 10^9$) = 25.7

THEORETICAL PROBLEM 15

Lifesaving chemistry of the airbag

Certain chemical reactions can protect people from serious injury or death. The following chemical reactions used to be utilized to rapidly produce large amounts of nitrogen gas inside an automobile airbag:

$2\ NaN_3 \rightarrow 2\ Na + 3\ N_2(g)$ (1)
$10\ Na + 2\ KNO_3 \rightarrow K_2O + 5\ Na_2O + N_2(g)$ (2)
$K_2O + Na_2O + SiO_2 \rightarrow$ alkaline silicate (“glass") (3)

15.1 Write the Lewis structure for the azide anion and nitrogen molecule.

15.2 How many grams of sodium azide are needed to generate enough nitrogen to fill an airbag with a volume of 15,0 dm^3 at a temperature of 50 °C and a pressure of 126,6 kPa?

15.3 Separately, write a balanced equation for the decomposition of nitroglycerine. Finally, write a balanced equation for the decomposition of lead azide used for detonation. In what ways are the reactions for sodium azide, nitroglycerine and lead azide similar?

15.4 Write a balanced equation for the reaction of sodium azide with sulfuric acid to form hydrazoic acid (HN_3) and sodium sulfate.

15.5 How many grams of hydrazoic acid are produced if 60,0 g of sodium azide reacts with 100 cm^3 of sulfuric acid (c = 3,00 mol dm^{-3})?

SOLUTION OF PREPARATORY PROBLEM 15

15.1

15.2 $n(N_2) = \dfrac{pV}{RT} = \dfrac{126.6\ \text{kPa} \times 15{,}0\ \text{dm}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 323\ \text{K}} = 0.707\ \text{mol}$

Mass of sodium azide needed to generate 0.707 moles of nitrogen:

$n(NaN_3) = 2/3 \times 0.707\ \text{mol} = 0.471\ \text{mol}$

$m(NaN_3) = 0.471\ \text{mol} \times 65{,}0099\ \text{g mol}^{-1} = 30.6\ \text{g}$

15.3 $4\ C_3H_5(NO_3)_3 \rightarrow 6\ N_2 + O_2 + 12\ CO_2 + 10\ H_2O$

$Pb(N_3)_2 \rightarrow Pb + 3\ N_2$

In all three reactions, the reactants are solid or liquid with small volume. A large volume of nitrogen gas is produced. Nitroglycerin produces other gases. The nitrogen molecule has a triple bond and is very stable. Thus, the reactions are highly exothermic, so that gases produced expand rapidly.

l

15.4 $2\ NaN_3 + H_2SO_4 \rightarrow 2\ HN_3 + Na_2SO_4$

15.5 $n(NaN_3) = \dfrac{60.0\ \text{g}}{65.0099\ \text{g mol}^{-1}} = 0.923\ \text{mol}$

$n(H_2SO_4) = 3{,}00\ \text{mol dm}^{-3} \times 0.100\ \text{dm}^3 = 0.300\ \text{mol}$

$m(HN_3) = 2 \times 0.300\ \text{mol} \times 43.028\ \text{g mol}^{-1}) = 25{,}8\ \text{g}$

THEORETICAL PROBLEM 16

Catalysts for the synthesis of ammonia

The synthesis of ammonia is a prime example of how chemistry can be used to improve human life. Even though primitive living systems had been "fixing" nitrogen to make compounds of nitrogen for hundreds of millions of years, human beings learned to prepare ammonia only about 100 years ago.

Ammonia is a source of nitrogen atom required for all amino acids and is essential in the production of fertilizer. Amino groups can be easily transformed into nitro groups found commonly in explosives such as TNT. More than 100 million tons of ammonia are produced annually worldwide, second only to sulfuric acid. However, Nature produces even more ammonia than the chemical industry. Ammonia is synthesized from nitrogen and hydrogen, however, the chemical bond of the nitrogen molecule is extremely stable, keeping ammonia from being synthesized without proper conditions or use of catalyst. In the early 20th century, Haber–Bosch method was developed for ammonia synthesis using high pressure and temperature, which is still employed in today's chemical industry. Haber (1918) and Bosch (1931) were awarded the Nobel Prize in chemistry for these contributions.

16.1 First, let us see if the reaction is feasible from a thermodynamic standpoint. Calculate the standard entropy change of the system in the following reaction:

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

The standard entropy is 191.6, 130.7, and 192.5 J $K^{-1}mol^{-1}$ for N_2, H_2, and NH_3, respectively. Does the entropy of the system increase or decrease? If it decreases, what must be the case for the reaction to proceed spontaneously?

16.2 In order to see whether the reaction is likely to be exothermic, consider a similar reaction between oxygen and hydrogen to form water. Is that reaction exothermic? Match the compounds with the standard enthalpy of formation ($\Delta_f H^{\,o}$) in kJ mol^{-1} .

$H_2O(g)$ • • – 46.11
HF(g) • • –241.82
$NH_3(g)$ • • –271.1

16.3 Using the value of $\Delta_f H^o$ you selected above, calculate the entropy change at 25 °C of the system and the surroundings combined.

16.4 Consider now the rate of the reaction. The rate determining step of the reaction, $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ is the atomization of the nitrogen molecule. Assuming that the activation energy of the atomization is the bond energy of the nitrogen molecule (940 kJ mol^{-1}) and that the A factor of the rate determining step is 1×10^{13} sec^{-1}, calculate the rate constant of atomization at 800 °C using the Arrhenius rate law. Calculate the rate constant at the same temperature when the activation energy is lowered by half with a catalyst.

The amount of catalyst used by the chemical industry is enormous. More than 100 tons of catalyst are used in a factory where 1000 tons of ammonia can be produced daily. In addition to the Fe catalyst that has been used since Haber and Bosch, a Ru catalyst is used in ammonia synthesis. Metal complex binding with elemental nitrogen and hydrogen is also studied as homogeneous catalyst for ammonia synthesis in solution.

16.5 Reactions between reactants and undissolved metal catalyst can occur at the metal surface so that the catalyst surface area affects the catalysis rate. Calculate the amount of substance of nitrogen N_2 adsorbed on 1.00 kg of Fe catalyst. Assume that the catalyst is composed of a 1 μm^3 cube (very fine powder) and that all six faces of the cube are available for nitrogen adsorption. The density of Fe is 7.86 g cm^{-3} and the adsorption area for a nitrogen molecule is 0.16 nm^2.

16.6 If a soluble, homogeneous catalyst with a molar mass of 500 g mol^{-1} is synthesized for nitrogen molecule binding, calculate how many nitrogen molecules bind to 1.00 kg of catalyst? Assume that one catalyst molecule binds one nitrogen molecule. Compare the result with the number of nitrogen molecules adsorbed on the Fe surface in problem 16.2.

16.7 While ammonia is synthesized under high pressure and temperature in the chemical industry, natural ammonia is synthesized from atmospheric nitrogen, ~0.8 atm. Enzymes for ammonia synthesis in nature called nitrogenases are proteins with cofactors that contain Fe or Mo. The ammonia synthesis reaction by nitrogenases is an electron transfer reaction: $N_2(g) + 8\ H^+ + 8\ e^- \rightarrow 2\ NH_3(g) + H_2(g)$. 16 ATP molecules are consumed in the reaction. ATP molecule decomposes into ADP and inorganic phosphate, and releases an energy of 30.5 kJ mol^{-1}. Calculate the energy required to synthesize 1 mol of ammonia using nitrogenase. At least 400 kJ of energy is used for the synthesis of 1 mol of ammonia in the chemical industry these days.

SOLUTION OF PREPARATORY PROBLEM 16

16.1 $S^0 = (2 \times 192.5) - (191.6 + 3\times130.7) = -198.7$ J K^{-1} mol^{-1}

The reaction must be exothermic and produce enough heat to increase the entropy of the surroundings and thereby offset the decrease in system entropy.

16.2 Combination of hydrogen with a more electronegative element will be more exothermic.

$H_2O(g)$: – 241.82 kJ mol^{-1}

$HF(g)$: – 271.1 kJ mol^{-1}

$NH_3(g)$: – 46.11 kJ mol^{-1}

16.3 $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} = \Delta S_{sys} - \Delta H_{sys} / T$

$$= -198.7 \text{ J mol}^{-1}\text{ K}^{-1} + \frac{92.22\times10^3 \text{ J mol}^{-1}}{298 \text{ K}} = +111 \text{ J mol}^{-1}\text{K}^{-1}$$

16.4 $NH_3(g)$: – 46.11 kJ mol^{-1}

$$k_1 = A \exp(-\frac{E_a}{R\,T}) = 1\times10^{13} \times \exp(-\frac{940\times10^3}{8.3145 \times 1073}) = 1.74\times10^{-33} \text{ sec}^{-1}$$

$$k_2 = A \exp(-\frac{E_a}{R\,T}) = 1\times10^{13} \times \exp(-\frac{470\times10^3}{8.3145 \times 1073}) = 1.32\times10^{-10} \text{ sec}^{-1}$$

$k_2/k_1 = 7.6\times10^{22}$

16.5 Mass of cube = 7.86 g cm^{-3} × $(1.00\times10^{-4}\text{ cm})^3 = 7.86\times10^{-15}$ kg

$$\text{Number of cubes in 1 kg} = \frac{1.00 \text{ kg}}{7.86\times10^{-15} \text{ kg}} = 1.27\times10^{14}$$

Surface area of Fe powder = 6×10^{-12} m^2 × 1.27×10^{14} = 763 m^2

Area for N_2 adsorption = 0.16×10^{-18} m^2

$$n = \frac{\text{area of Fe powder}}{\text{area for N}_2} = 4.77\times10^{21} = 7.92\times10^{-3} \text{ mol}$$

16.6 1.00 kg / 0.500 kg mol^{-1} = 2.00 mol ⇨ $N(N_2) = 1.20\times10^{24}$

16.7 8 × 30.5 kg mol^{-1} = 244 kJ

E(nitrogenase) < E(chemical industry)

THEORETICAL PROBLEM 17

From sand to semiconductors

Chemistry enables life. Chemistry also enriches life. For thousands of years, human beings have been putting sand to good use. Glass was made from sand. Lenses were made from glass and were used to make telescopes, microscopes, eyeglasses, and glassware for chemical experiments.

More recently, sand became a starting material for semiconductors. One of the most abundant elements in the Earth's crust is silicon, which is found in compounds containing Si–O bonds. Silica (SiO_2) is present in abundance at the earth's surface.

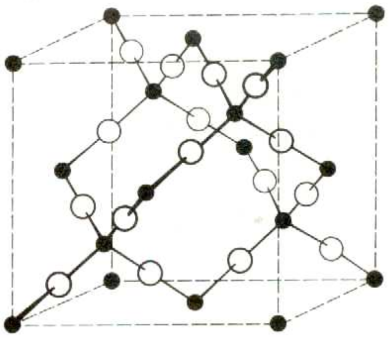


Figure 17–1. β–cristobalite, one structure of silica.

17.1 How many Si and O atoms exist in the unit cell of β–cristobalite?

17.2 Suggest the hybridized orbital of Si for this structure and guess the bond angle of O–Si–O.

SiO_2 is very unreactive, yet it reacts with HF. The reaction with HF may be used to etch glass or in semiconductor manufacturing:

$$SiO_2(s) + 6\ HF(aq) \rightarrow \mathbf{A}(aq) + 2\ H^+(aq) + 2\ H_2O(l)$$

17.3 Draw the molecular structure of **A**.

Silicon can be obtained by heating silica and coke (a form of carbon) at 3000 °C in an electric arc furnace.

17.4 Write a balanced equation for the reaction of SiO_2 with carbon. In this case, assume that only one kind of gas is formed whose Lewis structure should show formal charges.

17.5 Sketch the molecular orbitals of the gas formed from the reaction above.

To obtain ultrapure silicon, crude silicon is treated either with Cl_2 gas to give **B** or with HCl gas to give **C**.

17.6 Write a balanced equation for the reaction of Si with Cl_2.

17.7 Predict the molecular structure of **B**.

17.8 Is the product **C** from the following reaction (1) polar or not? Draw the three–dimensional structure of **C** and sketch the direction of its dipole moment, if any:

$$\text{Si}(s) + 3\ \text{HCl}(g) \rightarrow \mathbf{C}(g) + \text{H}_2(g) \qquad (1)$$

The reverse reaction of (1) is spontaneous at 1000 ℃, depositing ultrapure silicon. The final purification of the silicon takes place by a melting process called zone refining. This process depends on the fact that the impurities are more soluble in the liquid phase than in the solid phase (Figure 17.2). The zone refining procedure can be repeated until the desired level of purity (less than 0.1 ppb impurity) is obtained.

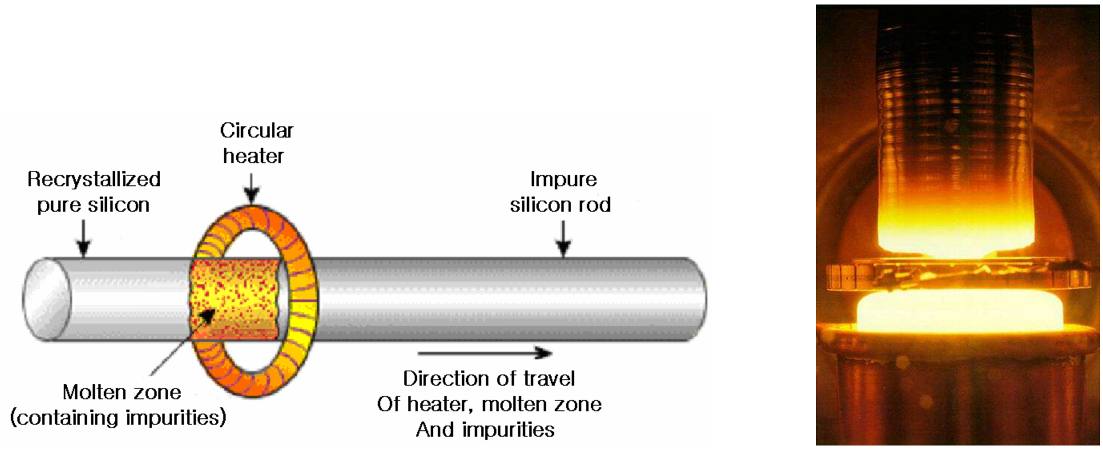


Figure 17.2. Zone refining of silicon

17.9 How many atoms per gram in the silicon wafer have been replaced by impurity atoms when the impurity level is 0.1 ppb?

Like all semiconductors, high–purity silicon fails to conduct electrical current until a minimum electrical voltage is applied, but at higher voltages it conducts moderately well. Semiconducting properties of silicon can be improved significantly by doping. Doping is the addition of a minor amount of a different element.

17.10 When a small number of boron atoms replace silicon atoms in solid silicon, what is the charge carrier? What is the name for this type of doped–semiconductor?

17.11 Draw a band diagram that can explain conductivity improvement upon replacement of some silicon atoms with boron atoms. Show in your drawing the band gap change after doping.

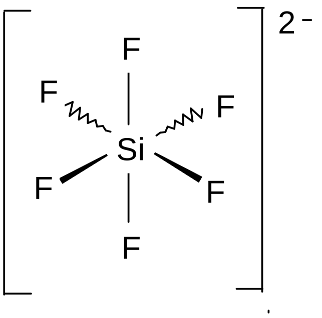
SOLUTION OF PREPARATORY PROBLEM 17

17.1 Si : (1/ 8 × 8) + (1/ 2 × 6) + (1 × 4) = 8

O : 1 × 16 = 16

17.2 sp^3 ; 109.5°

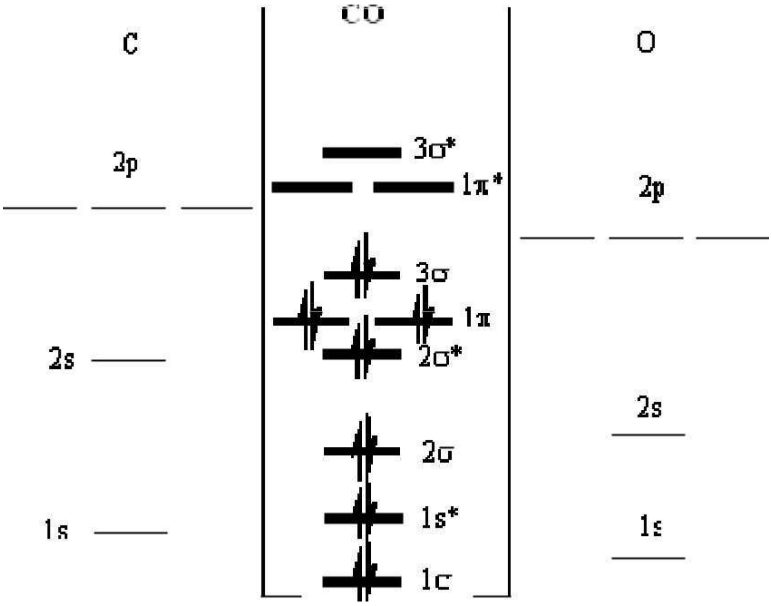
17.3 octahedral:



17.4 Since Lewis structure of the gas shows the formal charges, it should not be O=C=O, but :C≡O: where atom C has the formal charge of –1 and atom O has the formal charge of +1. Therefore, the balanced equation for the reaction is

$$SiO_2(s) + 2\ C(s) \rightarrow Si(s) + 2\ CO(g)$$

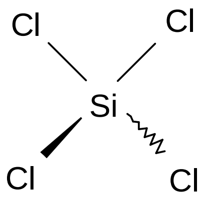
17.5



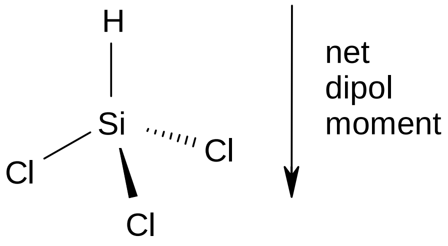
17.6 $Si(s) + 2\ Cl_2(g) \rightarrow SiCl_4(l)$: from the Merck Index

Schenk in Handbook of Preparative Inorganic Chemistry Vol. 1, G. Brauer, Ed. (Academic Press, New York, 2nd ed., 1963) pp 682–683.

17.7 Tetrahedral



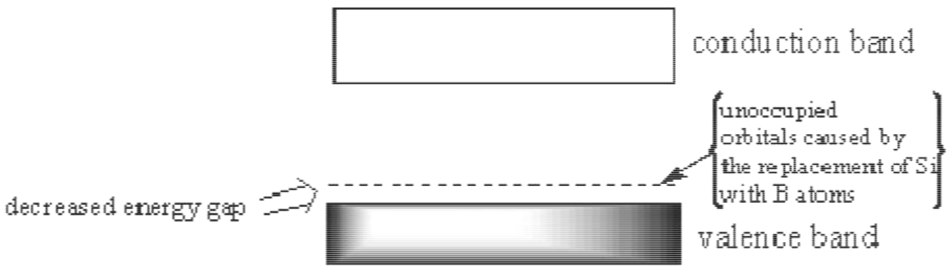
17.8 **C**: $SiHCl_3$, polar



17.9 $(1\ \text{g} / 32.066\ \text{g mol}^{-1}) \times 0.1\times10^{-9} \times 6.02\times10^{23} = 1.9\times10^{12}$

17.10 In a Si wafer doped with B atoms, holes exist that neighboring electrons can move into, thus causing electrical conductivity. Therefore, holes are the charge carriers. This kind of doped–semiconductor is the p–type semiconductor.

17.11.

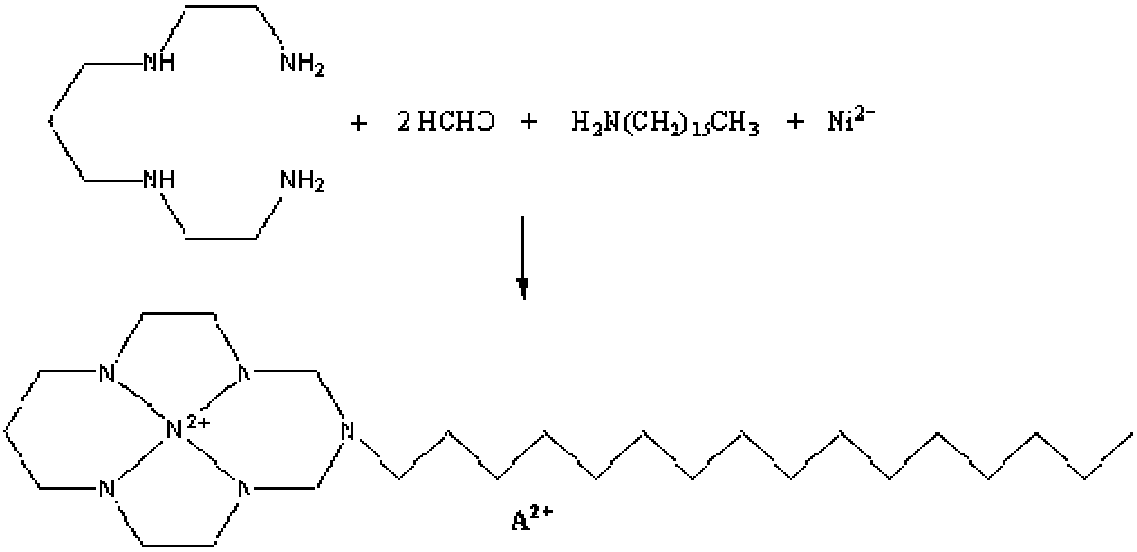


THEORETICAL PROBLEM 18

Self–assembly

Useful and essential structures can be made by self–assembly. In fact, life–forms were first made possible by the self–assembly of cell membranes about 4 billion years ago. Self–assembly is a fundamental principle that generates structural organization on all scales from molecules to galaxies. Self–assembly is defined as reversible processes in which pre–existing parts or disordered components of a pre–existing system form stable structures of well–defined patterns.

Some transition metal complexes can participate in the self–assembly. For example, a Ni complex with a long alkyl chain can be formed from many separate parts in the following reaction.



18.1 Predict the structure around the Ni(II) cation.

18.2 Determine whether A^{2+} is paramagnetic or not, using the d–orbital splitting pattern of Ni(II) in this structure.

18.3 Indicate the hydrophobic portion in A^{2+}.

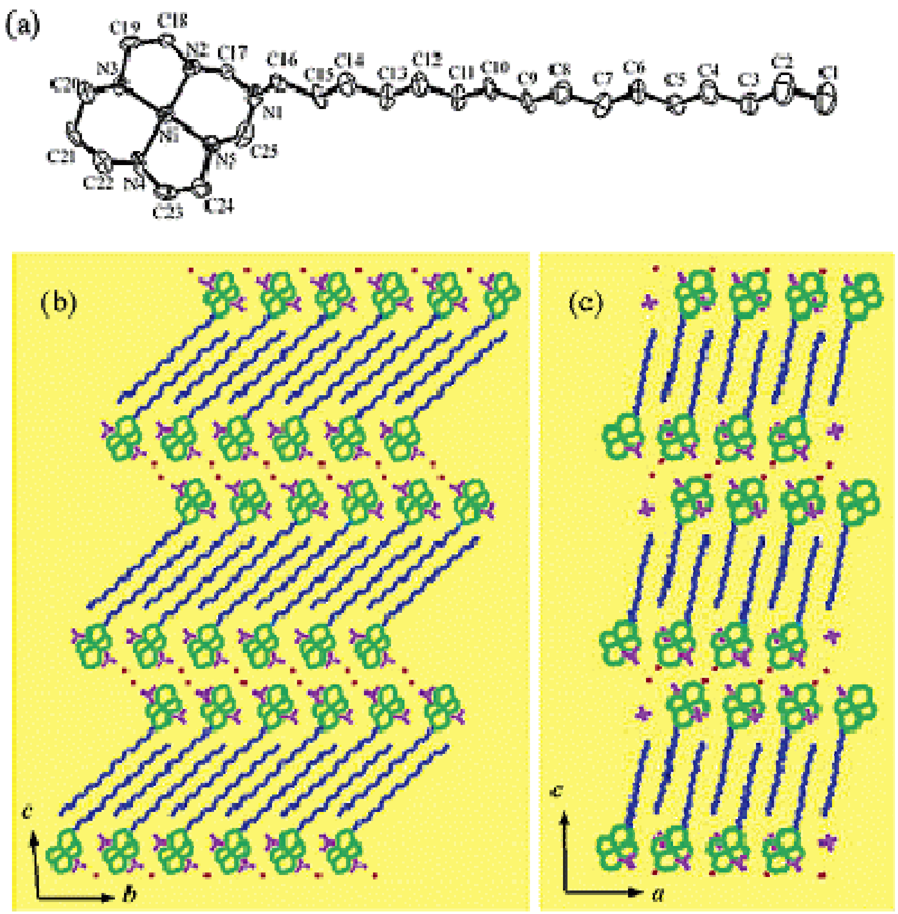
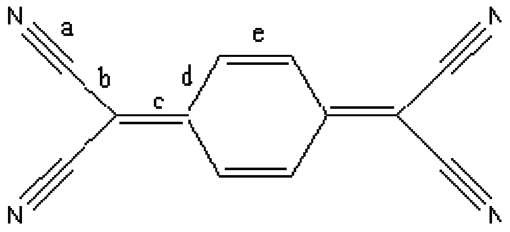


Figure 18.1. The molecular structure for A^{2+} and the packing structure of $A(ClO_4)_2 \cdot H_2O$.

18.4 What is the driving force for such assembly? (Hint: Its ionic compound, $A(ClO_4)_2 \cdot H_2O$, is found to float on the surface of water although its density is greater than 1.0 g cm^{-3}.)

Metal complexes of TCNQ (7,7,8,8–tetracyano–p–quinodimethane) have been studied due to magnetic and electric conducting properties.

(TCNQ) =



The infrared spectrum is diagnostic for the formal oxidation state and the coordinative status of the TCNQ molecules.

18.5 For TCNQ as pictured, which bond (among a – e) has the highest vibrational frequency?

18.6 Point out the bond(s) (among a – e) which might be shortened when TCNQ is reduced to form the radical anion.

The TCNQ derivative of A^{2+} ($[A^{2+}(TCNQ)_2](TCNQ)\cdot(CH_3COCH_3)$) also shows an interesting structural feature as shown in Figure 18–2.

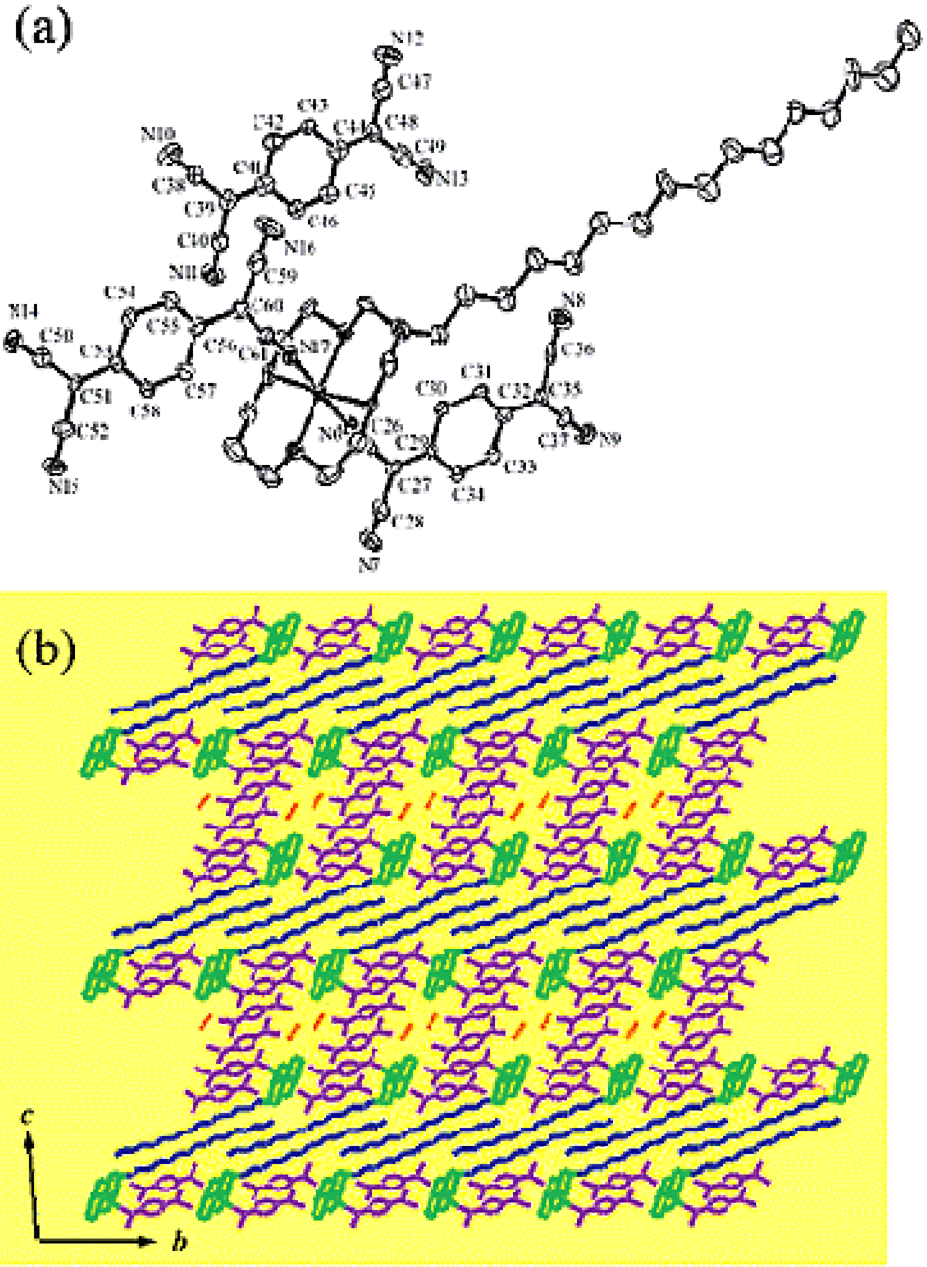


Figure 18.2. The molecular structure for A^{2+} and the packing structure of $[A^{2+}(TCNQ)_2](TCNQ\cdot CH_3COCH_3)$

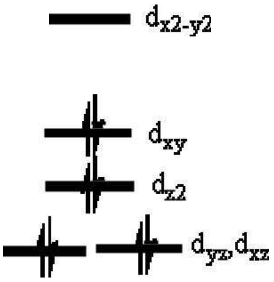
18.7 What is the coordination number for atom Ni in the TCNQ derivative of A^{2+}?

18.8 In this structure, TCNQ molecules overlap one another. What is the driving force for such organization?

SOLUTION OF PREPARATORY PROBLEM 18

18.1 square planar

18.2 Ni^{2+}, d^8, square planar, diamagnetic



18.3 a long alkyl side chain: $–C_{16}H_{33}$.

18.4 hydrophobicity due to the long alkyl chains

18–5 bond a

18.6 bonds b and d are shortened upon reduction.

18.7 coordination number 6

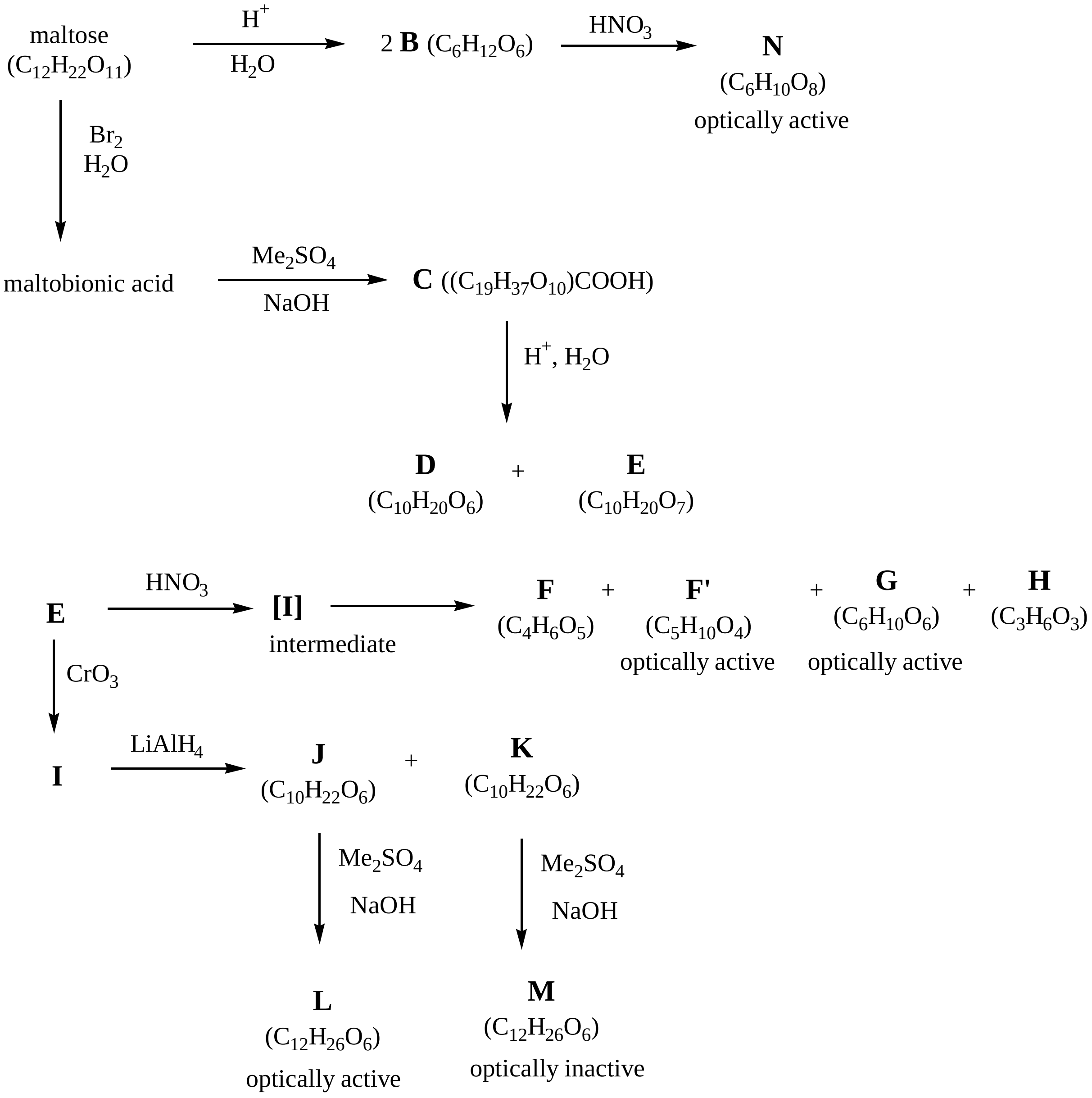
18.8 $\pi – \pi$ stacking interactions

THEORETICAL PROBLEM 19

Stereochemistry (Organic synthesis – 1)

The fermentation of starch with malt produces ethyl alcohol. During this process, the hydrolysis of starch is catalyzed by the enzyme diastase present in malt to produce maltose, a disaccharide.

Maltose ($C_{12}H_{22}O_{11}$) reduces Tollens' and Fehling's reagents and it is oxidized by bromine in water to maltobionic acid (($C_{11}H_{21}O_{10}$)COOH), a mono carboxylic acid. In order to deduce its structure, maltose was subjected to series of reactions:



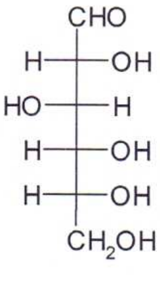
19.1 Draw structures **B**, **D** – **N** in a Fisher projection.

19.2 Draw structures for maltose, maltobionic acid and **C** in a Haworth projection.

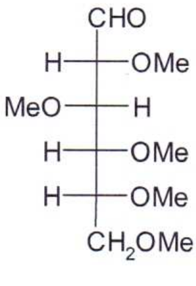
SOLUTION OF PREPARATORY PROBLEM 19

19.1

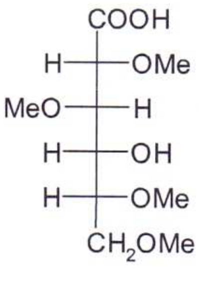
B



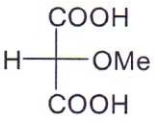
D



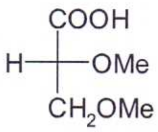
E



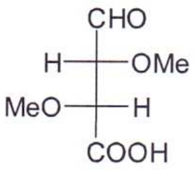
F



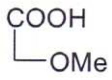
F'



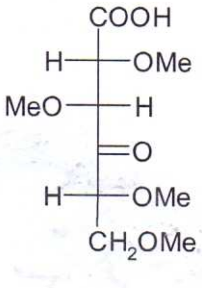
G



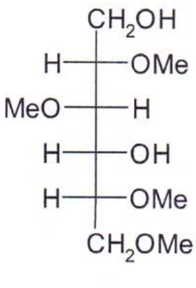
H



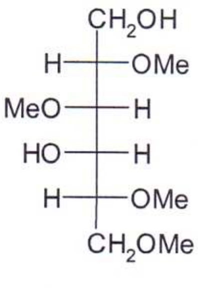
I



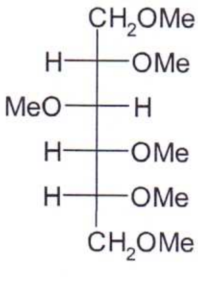
J



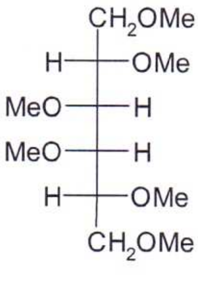
K



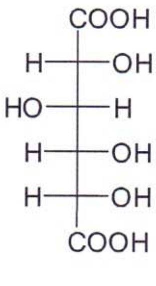
L



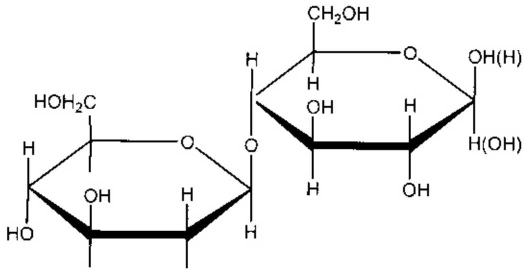
M



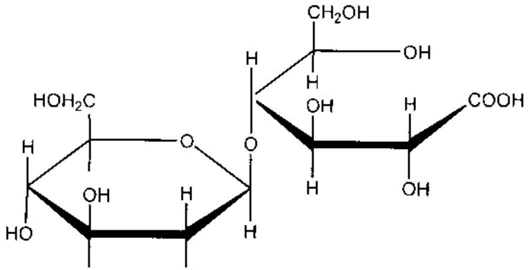
N



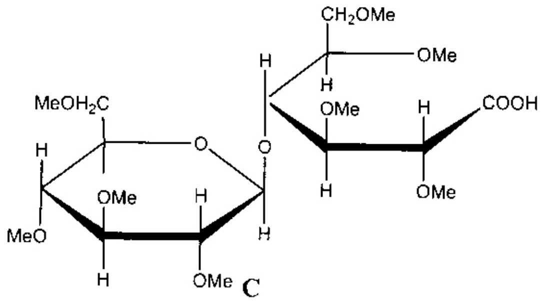
19.2



maltose



maltobionic acid

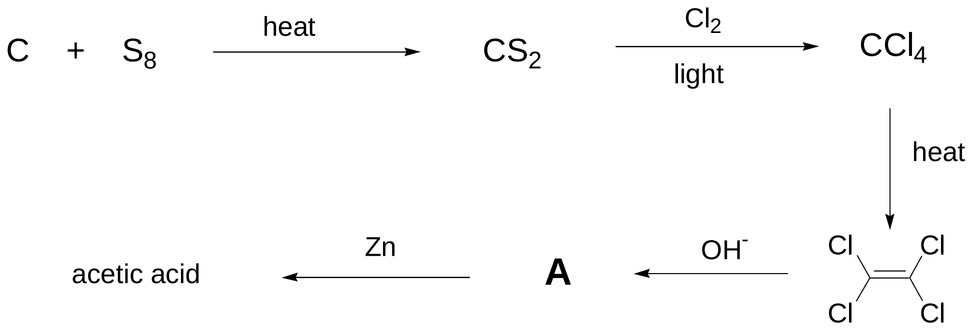


C

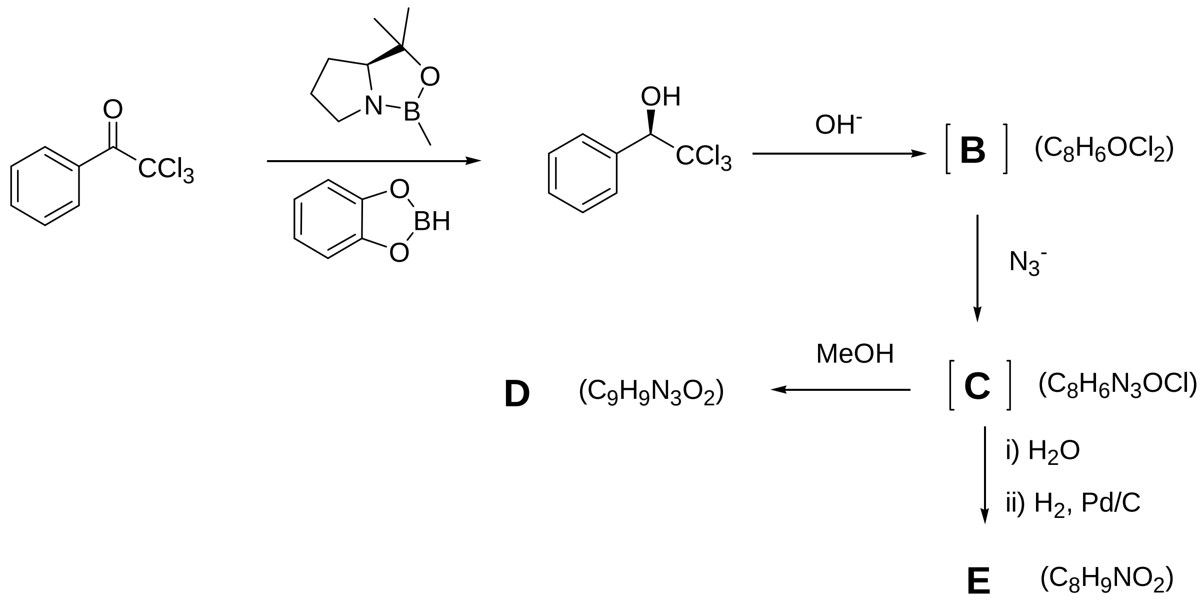
THEORETICAL PROBLEM 20

Total synthesis (Organic synthesis – 2)

The first total synthesis of an organic compound was accomplished in the 19th century by Kolbe starting from carbon and sulfur as depicted in the following scheme.



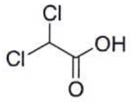
Even in modern organic synthesis, a similar synthetic strategy has been applied in the synthesis of amino acids.



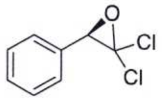
20.1 Draw the structures of **A**–**E** and designate the *absolute* stereochemistry of **D** and **E** using the R/S convention.

SOLUTION OF PREPARATORY PROBLEM 20

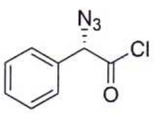
20.1



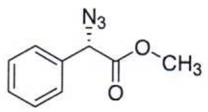
A



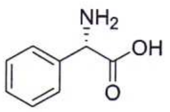
B



C



D



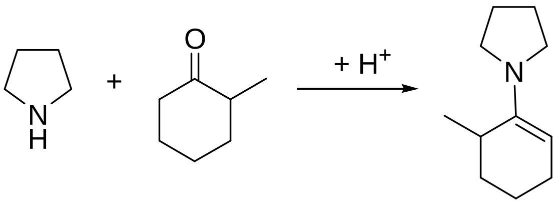
E

configuration : S

THEORETICAL PROBLEM 21

Enamine chemistry (Organic synthesis – 3)

Enamine is formed between ketone and secondary amine in the presence of acid catalyst.

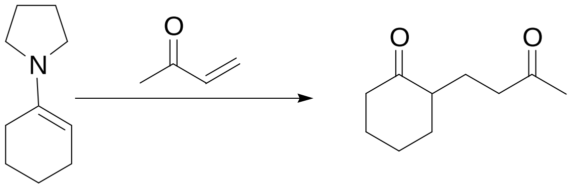


(1)

21.1 Propose a mechanism for enamine formation in the presence of acid catalyst (eq. 1).

21.2 This process exhibits a bell–shaped pH dependence in the presence of acid catalyst. The maximum rate of formation occurs at pH 3–4. Propose a plausible reason why this dependence occurs.

21.3 Enamine reacts with conjugated enones such as methylvinylketone to form a 1,5–dicarbonyl compound after the hydrolysis of enamine (equation 2).

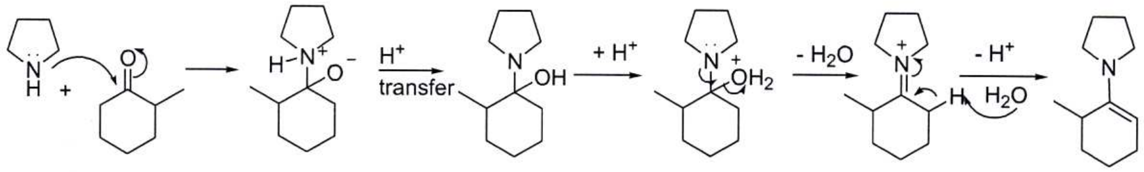


(2)

The product of this reaction now has one chiral center. Suggest conditions of special amine to make stereospecific product as shown in equation 2.

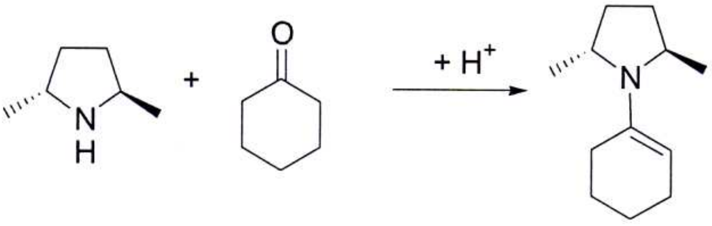
SOLUTION OF PREPARATORY PROBLEM 21

21.1



21.2. Normally, acid catalyzes the enamine formation as shown in 21.1. However, if too much acid is present, the basic amine (nucleophile) is completely protonated so the initial nucleophilic addition step cannot occur.

21.3 An enamine prepared from a single enantiomer of the chiral secondary amine is chiral, and thus the Michael addition reaction can proceed from only one side of enamine to yield a single enantiomeric product.

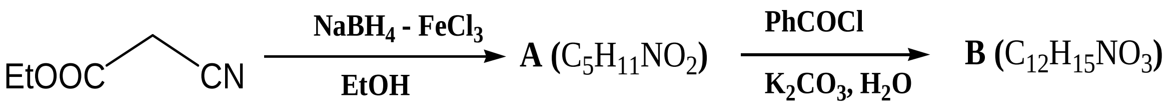


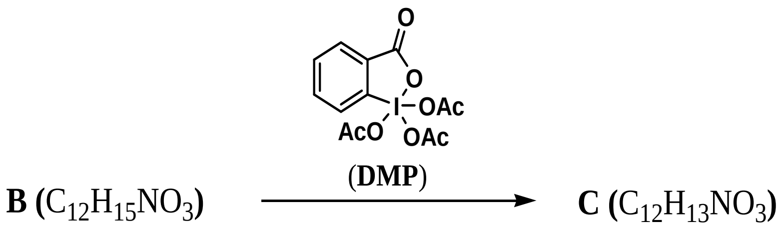
THEORETICAL PROBLEM 22

Oxidation and reduction in organic synthesis

In the manipulation of organic compounds, oxidation reaction and reduction reaction are the most important reactions. Especially, a chemo–selective, region–selective or stereo–selective reduction/oxidation is very important in designing an efficient organic synthesis of a target molecule. While nature achieves such selectivity through specific design of active sites of enzymes, chemical transformation mostly relies on subtle difference in reactivity by changing the nature of reagents.

The following scheme is a good example of chemo–selective reduction and oxidation reactions starting from ethyl cyanoacetate.

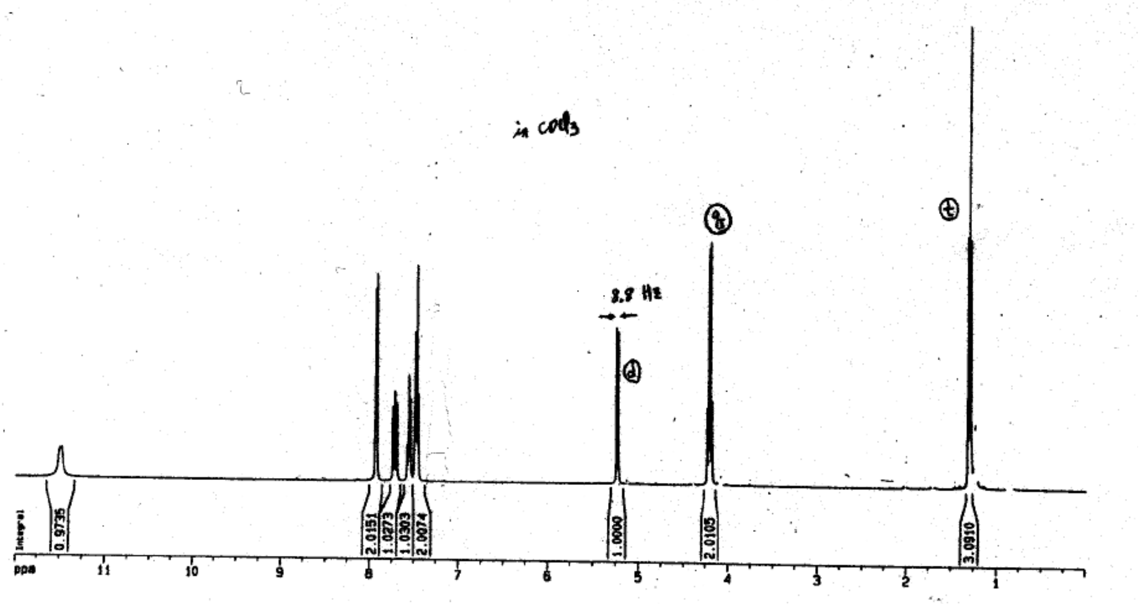




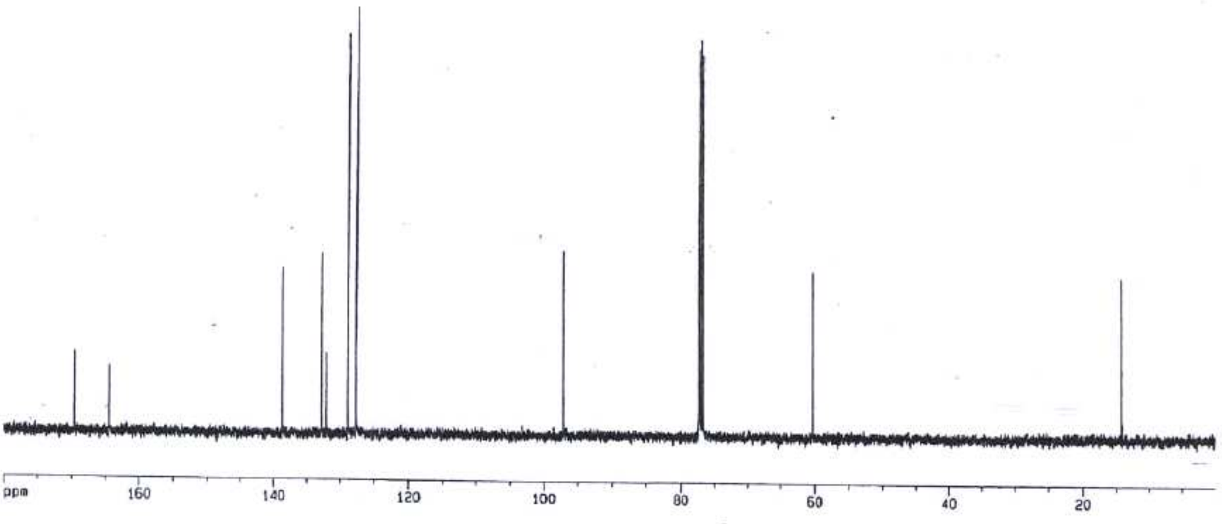
22.1 When ethyl cyanoacetate was treated with a reducing agent $NaBH_4$ in presence of $FeCl_3$, a selective reduction of a functional group was observed. When the product A was reacted with benzoyl chloride, 1 equivalent of benzoyl chloride was consumed to form B. What are the structures of A and B?

22.2 Dess–Martin Periodinane (DMP) is a strong but mild oxidizing agent, and can oxidize various functional groups in a selective manner. When B was oxidized with DMP a clean oxidation occurred to form C. ^{1}H–NMR, ^{13}C–NMR, IR and mass spectra were obtained. These spectra showed that a clean transformation occurred to form a single product. In the ^{1}H–NMR a doublet between 5~6 ppm shows the coupling constant J = 8.8 Hz. Draw the structure of C.

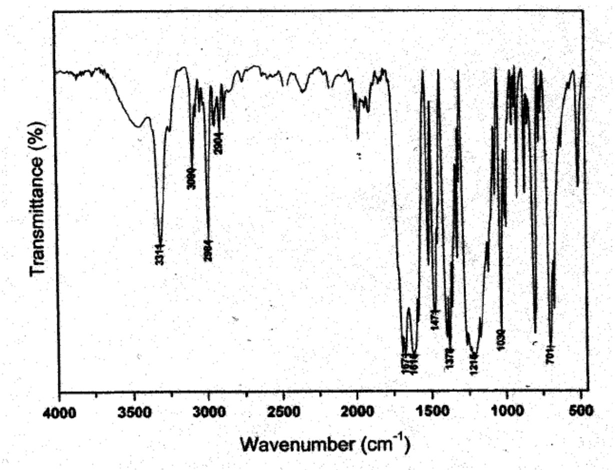
22.3 In the ^{1}H–NMR, the chemical shift of one peak showed up near δ= 11.5 ppm. Assign the proton in the structure C for this chemical shift. What is the reason for the chemical shift for the assigned proton that does not appear in the region (δ = ~ 8 ppm) for ordinary protons of that functional group?



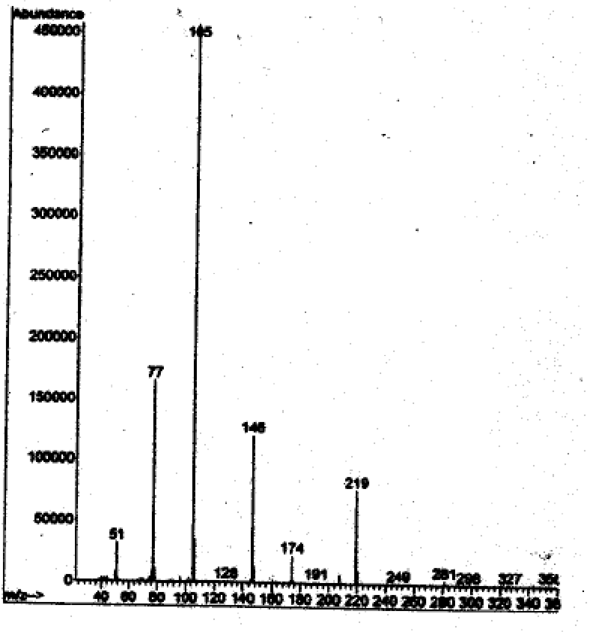
1H–NMR of C



13C–NMR of C



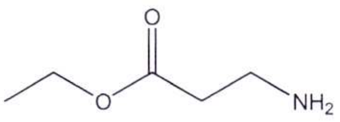
IR of C



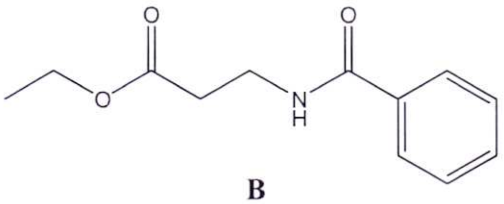
Mass spectrum of C

SOLUTION OF PREPARATORY PROBLEM 22

22.1

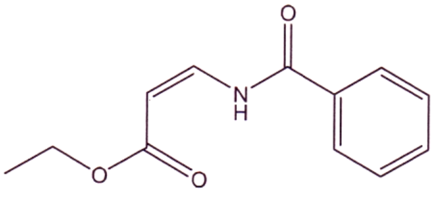


A



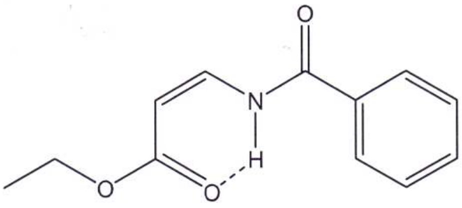
B

22.2



C

22.3 The cis-configuration of the olefin allows a strong hydrogen bonding between the proton of the amide and the carbonyl oxygen of the ester as shown in he following structure.



The strong hydrogen bonding moved the chemical shift of the amide proton toward further down-field.

THEORETICAL PROBLEM 23

Antifreeze proteins

The temperature below 0 °C occurs commonly on earth. How can organisms survive in conditions where water freezes? For many insects exposed to prolonged subfreezing conditions, cryoprotectant synthesis begins in their bodies during early autumn, and these substances are cleared in early spring. Figure 1 shows the seasonal content of glycerol in a freeze–avoiding insect.

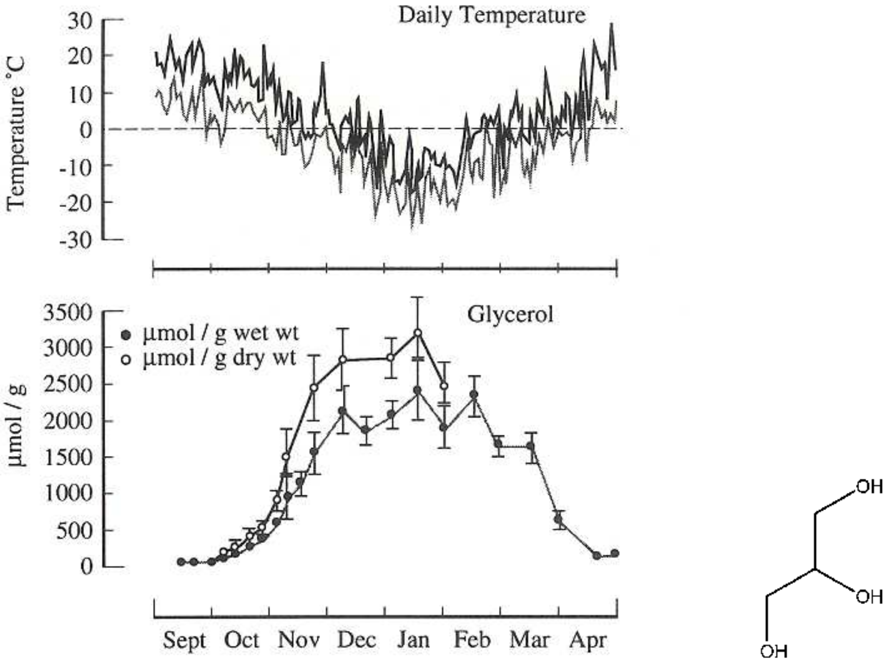
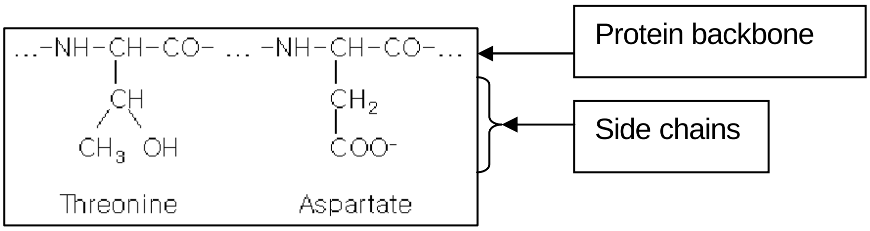


Figure 23.1. Daily maximum and minimum temperatures and glycerol content in the freeze–avoiding larvae of the goldenrod gall moth. The structure of glycerol is given on the right. (Reference: K.B. Storey and J.M. Story 1988 Physiol. Rev. 68:27)

23.1 What is the mass percent of glycerol in the insect if it could avoid freezing at –20.0 °C due to glycerol concentration alone? Assume the insect behaves as an ideal solution. What would be the osmotic pressure at this glycerol concentration? Comment on the resulting values. The freezing point depression constant for water is $K_f = 1.86$ °C (mol/kg)$^{-1}$.

23.2 What is the actual fraction of glycerol in the insect's wet mass in January? What would be the freezing point of water in the insect in January considering the amount of glycerol alone?

23.3 In addition to freezing point depressants, “antifreeze proteins” are known to act to avoid freezing in animals including cold–water fish and many insects. The colligative freezing point depression due to antifreeze proteins is quite small. Experiments suggest that antifreeze proteins inhibit the growth of small ice particles. If some threonine or aspartate side chains composing the protein are chemically modified, the antifreeze activity disappears. What kind of interactions between antifreeze proteins and ice particles are probably responsible for the antifreeze activity?



SOLUTION OF PREPARATORY PROBLEM 23

23.1 For freezing point depression, $\Delta T = -K_f\ m$

The molal concentration (molality) m is obtained by

$-20.0 = -1.86\ m$,

$m = 10.75 \text{ mol kg}^{-1}$

The mass of the glycerol in 1 kg of water is

$m(\text{glycerol}) = \textit{molality} \times M(\text{glycerol}) = 10.75 \text{ mol kg}^{-1} \times 92.10 \text{ g mol}^{-1} = 990 \text{ g}$.

Therefore, glycerol would be about 50 % by mass.

This is a ridiculously large number indicating that something else is also required to avoid freezing.

Osmotic pressure is obtained from the van’t Hoff equation, $\pi = c\ R\ T$. Assuming that the molar concentration c is approximately the same as the molality obtained above,

osmotic pressure $\pi = 10.75 \text{ mol dm}^{-3} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 253 \text{ K} = 22\ 612 \text{ kPa}$

The osmotic pressure is extremely high, and the organism may not be stable.

23.2 From Figure 1, the glycerol content in January is

2500 µmol g^{-1} = 2.5 mol kg^{-1} = 230 g of glycerol / 1 kg water.

Therefore, the glycerol mass fraction is 0.187 (18.7 mass %)

Freezing point depression at this concentration is

$$-2.5 \times 1.86 = -4.7\ ^\circ C,$$

i. e. significantly higher than the temperature in January.

23.3 Threonine and aspartate side chains can contact each other through their oxygen and hydrogen groups to form stable hydrogen bonds. The hydrogen bonds of these side chains might preferably interact with water molecules of the ice particle surfaces, thus inhibiting ice crystal growth.

THEORETICAL PROBLEM 24

The human body

The human body consists of cells, which in turn consist of atoms. About two thirds of body mass is water, which means that about two thirds of cell mass is water.

24.1 Estimate the approximate number of atoms 10^x in a human body weighing 60 kg (estimate number x.) Consider the average atomic mass of the three atoms in a water molecule. For your own information, consider the average atomic mass of atoms in other molecules such as proteins, fats, and carbohydrates.

24.2 A human body consists of about 100 trillion (10^{14}) cells. Assume that all human cells are cubic and identical in size. Estimate the size of an average human cell (length of the edge of the cube) in one significant figure.

24.3 Assume that all atoms in a cell are uniformly distributed. Estimate the distance between two atomic nuclei in a cell.

24.4 Estimate the distance between the centers of mass of two water molecules in pure water.

24.5 Estimate the average distance between atomic nuclei in pure water. Compare your result with answers in 24.3 and 24.4.

SOLUTION OF PREPARATORY PROBLEM 24

24.1 The **a**verage relative atomic mass of the three atoms in a water molecule = 18 / 3 = 6, the average relative atomic masses of atoms in other molecules are about the same.

For example, consider carbohydrate, $C(H_2O)$. 30 / 4 = 7.5

So, let's assume that the human body is composed of only water.

60 kg of water = 10,000 moles of atoms = 6×10^{27} atoms or about 10^{28} atoms

24.2 Assume that the density of the human body is 1 g cm^{-3}.

Volume of body = 6×10^{-2} m^3

Volume of a cell = 6×10^{-16} m^3

Length of a cell = 8×10^{-6} m (about 10 micrometers)

24.3 Number of atoms in a cell = $10^{28} / 10^{14} = 10^{14}$

Volume per atom in a cell = 6×10^{-16} m^3 / 10^{14} = 6×10^{-30} m^3

Distance between two atomic nuclei = 2×10^{-10} m = 2 Angstroms

24.4 Volume of a mole of water = 18×10^{-6} m^3

Average volume occupied by a water molecule = 3×10^{-29} m^3

Distance between centers of mass of two water molecules = 3×10^{-10} m = 3 Angstroms

24.5 Volume of a mole of water = 18×10^{-6} m^3

Number of atoms in a mole of water = 18×10^{23}

Average volume occupied by an atom in water = 10^{-29} m^3

Average distance between atomic nuclei in water = 2×10^{-10} m = 2 Å (angstroms)

THEORETICAL PROBLEM 25

Hemoglobin

Another important class of compounds in the human body is proteins. Many proteins carry out catalytic functions. Hemoglobin, on the other hand, transports oxygen from the lung to remote parts of the body.

25.1 The molecular mass of hemoglobin is about 67000 g mol^{-1}. The average mass of hemoglobin in erythrocytes in 100 cm^3 of blood is 15 g. Calculate the concentration of hemoglobin in blood (in mol dm^{-3}).

25.2 Estimate the average distance between two oxygen molecules in the air we breathe. Assume frigid air at 0 °C in which 21 vol. % of air is oxygen.

25.3 According to Henry's law

$$\text{solubility} = k_H \times \text{partial pressure}$$

$$(k_H = \text{Henry's constant})$$

Henry's constant for oxygen is 1.3×10^{-3} mol dm^{-3} atm^{-1}. Estimate the average distance between two oxygen molecules in water in equilibrium with air.

25.4 A hemoglobin molecule can bind up to four oxygen molecules. Estimate the average distance between two oxygen molecules in blood when hemoglobin is saturated with oxygen. Compare your result with answers in 25.2 and 25.3 and note how efficiently hemoglobin concentrates and transports oxygen to tissues where the partial pressure of oxygen is low.

25.5 There are about (   ) amino acids in hemoglobin. (Fill in the number in the bracket.) Estimate using average molecular mass of amino acids and check against literature values.

25.6 There are about (   ) different kinds of amino acids in hemoglobin.

25.7 Trypsin hydrolyzes peptide bonds at the carboxyl group of arginine and lysine. Consider, for example, the following peptide.

H_3N^+–gly–phe–**arg**–ala–ala–tyr–leu–phe–his–pro–**lys**–gly–trp–glu–ile–asp–phe–COO–

Upon complete hydrolysis by trypsin, the following set of peptides will result.

H_3N^+–gly–phe–**arg**–COO^-

H_3N^+–ala–ala–tyr–leu–phe–his–pro–**lys**–COO^-

H_3N^+–gly–trp–glu–ile–asp–phe–COO^-

Upon complete hydrolysis of hemoglobin after reduction of the disulfide bonds and alkylation, you expect to find on the average about (   ) amino acids in a tryptic peptide (peptide resulting from hydrolysis by trypsin).

25.8 The average molecular mass of the tryptic peptides is about (   ).

SOLUTION OF PREPARATORY PROBLEM 25

25.1 150 g haemoglobin in 1 dm^3

n(haemoglobin) = 150 g / 67,000 g mol^{-1} = 0.0022 mol

concentration: 0.0022 mol dm^{-3}

25.2 Volume of 1 mol of air = 22.4×10^{-3} m^3

Number of oxygen molecules in the above volume =

= (6.02×10^{23}) (0.21) = 1.26×10^{23}

Volume of air per oxygen molecule = $(22.4\times10^{-3}\ m^3)/(1.26\times10^{23}) = 1.78\times10^{-25}\ m^3$

Average distance between oxygen molecules = 5.6×10^{-9} m

25.3 Solubility = $(1.3\times10^{-3}\ mol\ dm^{-3}\ atm^{-1})$ (0.21 atm) = 2.7×10^{-4} mol dm^{-3}

Number of oxygen molecules in a liter of water

= $(6\times10^{23}\ mol^{-1})$ (2.7×10^{-4} mol) = 1.6×10^{20}

Volume of water per oxygen molecule

= $(1\times10^{-3}\ m^3) / (1.6\times10^{20}) = 6.3\times10^{-24}\ m^3$

Average distance between oxygen molecules = 1.8×10^{-8} m

25.4 Number of oxygen molecules in 1 dm^3 of blood = $4 \times 0.0022 \times 6\times10^{23} = 5.3\times10^{21}$

Volume of blood per oxygen molecule = $1.0\times10^{-3}\ m^3 / 5.3\times10^{21} = 1.9\times10^{-25}\ m^3$

Distance between oxygen molecules = 5.7×10^{-9} m

25.5 The average relative molecular mass of amino acids is about 130. Water is removed upon peptide bond formation. 67,000 / (130 – 18) = 600 amino acid residues.

Actually hemoglobin has two alpha and two beta chains, each of which consists of 141 residues.

25.6 All life–forms on earth use 20 common amino acids.

25.7 Trypsin hydrolyzes after 2 amino acid residues (arginine and lysine) out of 20 different kinds of amino acids. So, on average the enzyme breaks every tenth peptide bond.

The number of amino acid residues in an average tryptic peptide = 20 / 2 = 10

25.8 When considering the removal of water in the peptide bond formation:

$(130 - 8) \times 10 + 18 = 1{,}140$ = about 1,000

THEORETICAL PROBLEM 26

Mass spectrometry of hemoglobin

26.1 If you lived in the 19th century, what method would you use to determine the molecular mass of hemoglobin? Explain.

Breakthroughs in molecular mass determinations of biopolymers such as proteins were recognized with the 2002 Nobel Prize in chemistry awarded to Fenn for developing electrospray ionization mass spectrometry (ESI MS) and to Tanaka for pioneering work leading to matrix–assisted laser desorption/ionization time–of–flight mass spectrometry (MALDI–TOF MS). In MALDI–TOF MS, proteins are embedded in a crystal of UV–absorbing matrix molecules and desorbed/ionized upon irradiation with a UV laser pulse. Singly charged protonated protein ion, $[M+H]^+$, is produced as a major species from a protein with mass M.

26.2 Consider hemoglobin with a 67,434 Da molecular mass. After desorption / ionization, the $[M+H]^+$ ion is accelerated by 20.000 kV. Calculate the energy of the protein ion in joule. (coulomb × volt = joule)($e = 1.60218 \times 10^{-19}$ coulomb)

26.3 The accelerated protein ion is then allowed to travel 1.0000 m in an evacuated flight tube to a detector. All electrical energy is converted to kinetic energy (mv^2 / 2). If the flight time of the protein ion was determined to be 1.3219×10^{-4} s, what is the molar mass of hemoglobin calculated from the flight time measurement? What is the mass accuracy in ppm?

26.4 The flight tube is maintained under a high vacuum at 25 °C. What is the residual pressure in the flight tube at which the mean free path of air molecules is the same as the length of the flight tube? See Problem 2 for definition of mean free path. Assume that all air molecules are spheres with a diameter of 2 angstroms.

SOLUTION OF PREPARATORY PROBLEM 26

26.1 Osmotic pressure (freezing point depression is too small, mass spectrometry is not available)

26.2 For a singly charged protein ion (67,435 Da)

Electrical energy = $e\,V = 1.60218\times10^{-19}$ C × 2.0000×10^{4} V = 3.20436×10^{-15} J

26.3 $mv^2 / 2$ = electrical energy

m = (2)(electrical energy) / v^2

$= 2\,(3.20436\times10^{-15}\text{ J}) / (1.0000\text{ m} / 1.3219\times10^{-4}\text{ s})^2 = 1.11987\times10^{-22}$ kg

$M\,[\text{M+H}]^+ = 1.11987\times10^{-22}\text{ kg} \times 6.0221\times10^{23} = 67.440\text{ kg mol}^{-1}$

Molar mass M of haemoglobin = 67,440 – 1 = 67,439 kg mol^{-1}

mass accuracy = 67,439 / 67,434 = 1.000074 74 ppm

26.4 Volume of collision cylinder = $\pi\,d^2\,v$

Number of molecules in unit volume: $N / V = p\,N_0 / RT$

Collision / sec = (volume of collision cylinder)(molecules / unit volume) =

$= (\pi d^2\,v)\,(p\,N_0 / RT)$

Time between collisions = $1 / [(\pi d^2\,v)\,(pN_0 / RT)]$

mean free path = speed / time between collisions

$= v / [(\pi d^2\,v) \times (pN_0 / RT)] = 1$ m

$p = (RT / N_0) / [(\pi d^2)(1\text{ m})]$

$= (8.314\text{ J mol}^{-1}\text{ K}^{-1})\,(298\text{ K}) / [(6.02\times10^{23}\text{ mol}^{-1})\,(3.14)\,(2\times10^{-10}\text{ m})^2\,(1\text{ m})]$

$= 3.3\times10^{-2}\text{ Pa} = 3.2\times10^{-7}$ atm

THEORETICAL PROBLEM 27

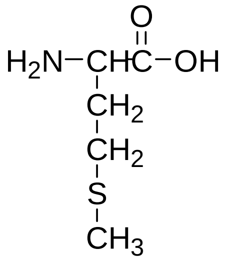
Post–translational modification

Nature uses 20 amino acids to make diverse proteins. However, since the diversity from 20 amino acids sometimes is not enough, chemical modifications are carried out mostly at the side chains of amino acids to generate more diverse functional groups by many natural enzymes. Many types of these post–translational modifications are important in recognition of protein–protein, protein–DNA, protein–RNA molecules. These modifications are used as turn–on (off) switches, transferring messages, known as signal transduction in living cells.

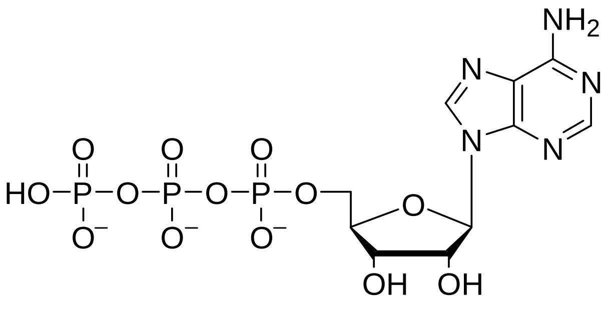
Recently, methylation was found to be as important as other known post–translational modifications, such as phosphorylation and glycosylation. Like other modifications, there is a reverse reaction, demethylation. The two processes work oppositely, turning signals on and off (off and on), like phosphorylation and glycosylation. However, processes of methylation and demethylation in nature are quite different. In other words, the mechanisms of the two facilitating enzymes are not the reverse of each other.

27.1 Considering the functional groups of side chains existing in 20 amino acids, what kind of functionality is suitable for generating more diversity owing to methylation and demethylation? Name two amino acids.

27.2 In methylation of an amino acid side chain, S–adenosylmethionine (SAM) is used as a cofactor. SAM is made from methionine and ATP. Deduce the structure of SAM.



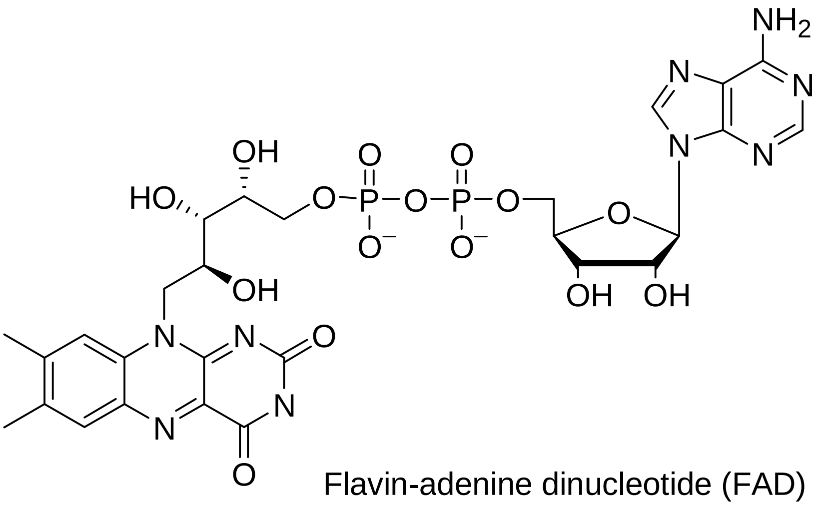
Methionine (Met)



Adenosine triphosphate (ATP)

27.3 Propose a mechanism of amino acid methylation with SAM.

27.4 Two steps make up the proposed mechanism for demethylation. The enzyme uses FAD as a cofactor for the first step. Propose plausible mechanisms for demethylation.

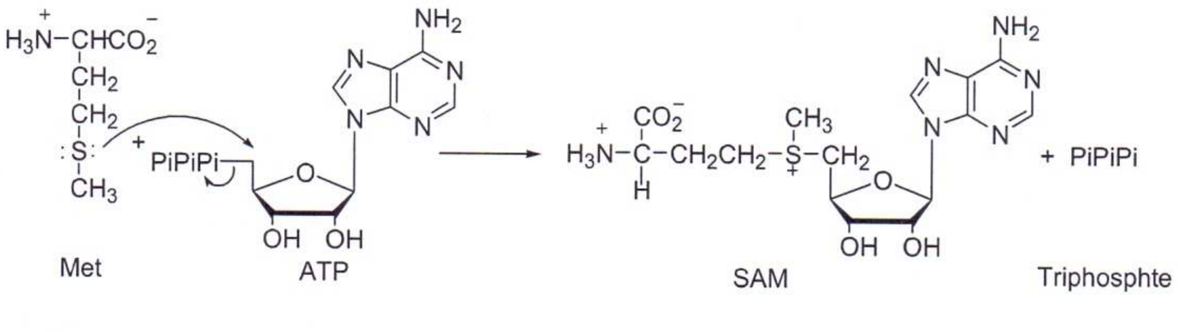


Flavin-adenine dinucleotide (FAD)

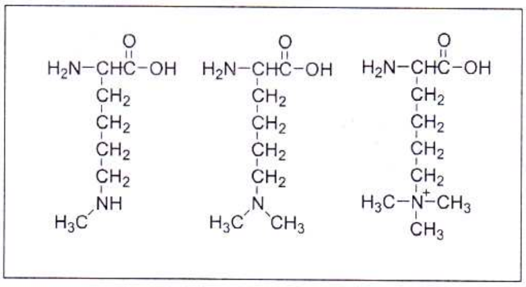
SOLUTION OF PREPARATORY PROBLEM 27

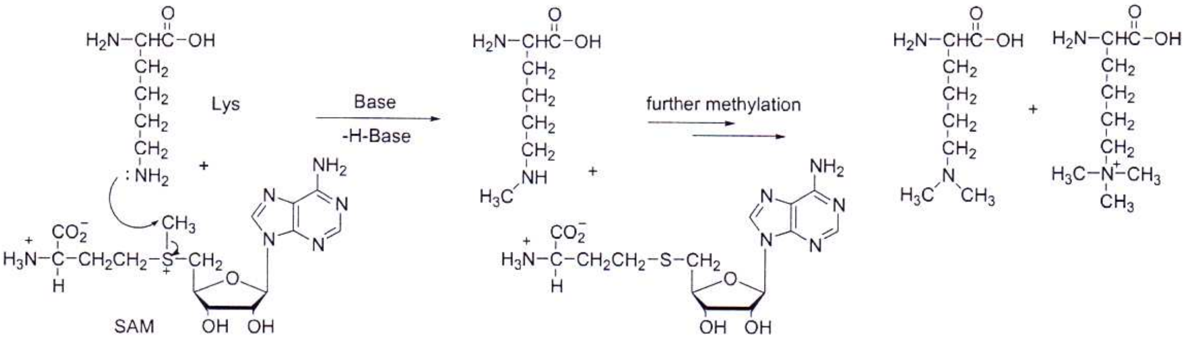
27.1 Lys (K) and Arg (R) provide plausible methylation sites at their side chains, because they can accept more than one methyl groups. Other amino acids side chains with oxygen nucleophile can hold only one methylation.

27.2 Triphosphate group is a good leaving group and sulfur is a good nucleophile. Sulfur of methionine undergoes S_N2 type reaction with ATP with triphosphate as the leaving group to form SAM.

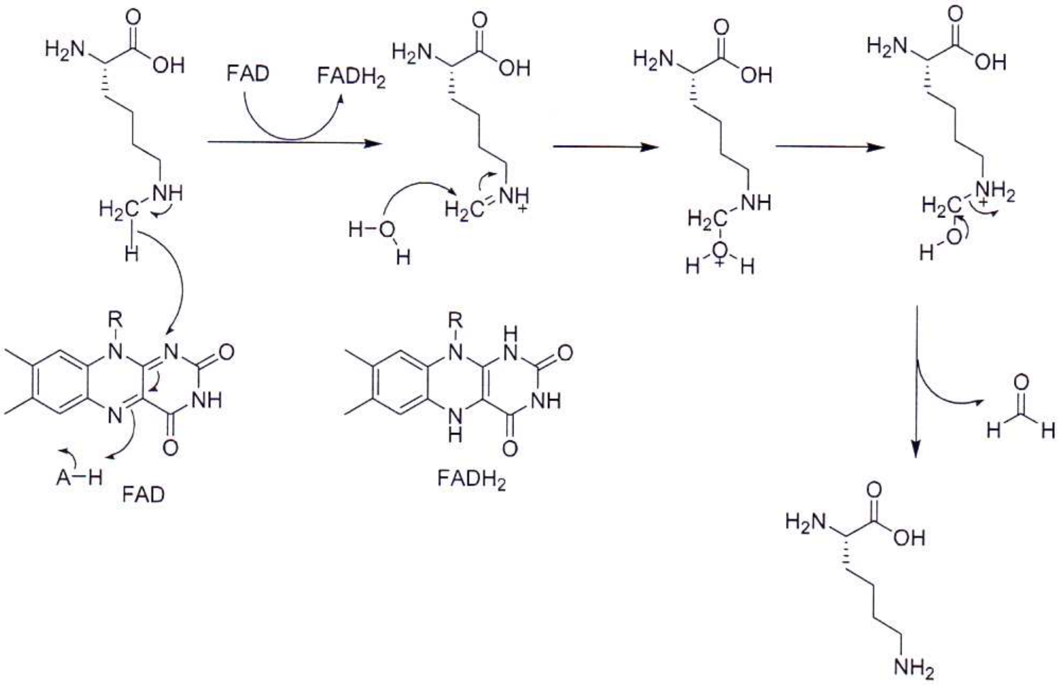


27.3





27.4



THEORETICAL PROBLEM 28

Transition state in enzymatic reactions

Enzymes are catalysts for living organisms. They have evolved to enable specific chemical reactions necessary for life to thrive more efficiently. In the active site of an enzyme, amino acid residues including side chains have evolved to provide space for the transition state (TS) of the chemical transformation to exist with conformational and electrostatic match. Thus, the binding affinity of this TS to the enzyme is expected to be very high (if one can calculate), stabilizing the energy of the transition state through an enzyme–TS complex. This lowers the activation energy of the reaction and creates rate acceleration. If one can calculate the binding constant owing to the complex formation, one could readily deduce how efficient the enzyme is by calculating k_{cat} / k_{uncat}.

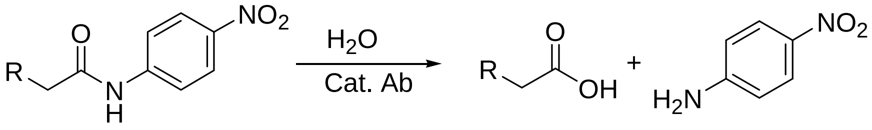
Man–made enzymes are holy grails for some chemists, because they can give insight about the behavior of natural enzymes and can be used as useful synthetic and therapeutic tools. Catalytic antibodies can be one of these kinds of artificial enzymes. Antibodies have antigen–binding sites, in which the target antigen binds with high affinity ($K_D = 10^{-9} - 10^{-11}$) and with great specificity. These properties can be exploited as active sites in artificial enzymes. Antigen–binding sites may serve to specifically recognize substrates and perform certain chemical reactions.

Since these catalytic antibodies need to accommodate transition state (TS) structures in chemical transformations, an antigen that triggers the production of the catalytic antibody must be designed and synthesized just like the TS structure. However, chemists cannot prepare a transition state structure because it is transient. Instead, one can synthesize a stable compound that resembles the structure of the transition state. This newly designed compound is called a transition state analogue (TSA). Once a TSA is made, it can be injected into mice to generate antibodies. The half–life of the TSA should be longer than 2 weeks at physiological conditions to obtain an adequate immune response. After generating as many antibodies as possible, the most tightly binding and specific antibodies are selected as candidates for antibody catalysts.

28.1 If one of the selected antibodies has $K_D = 1\times10^{-13}$ against the TSA, comparing with normal antibody ($K_D = 1\times10^{-6}$) how much stabilization energy can the TSA gain from the binding to this specific antibody?

28.2 Let us assume that the TSA can be considered as the real transition state (TS). Then, how much rate enhancement will be obtained when we will use this catalytic antibody for the intended chemical transformation? Describe this enhancement by k_{cat} / k_{uncat}.

Most scientists are interested in the specific hydrolysis of the pathogenic proteins or peptides such as β–amyloid as the intended chemical reaction by catalytic antibodies. Assuming that the following reaction is the intended reaction by catalytic antibody, TS of the hydrolysis of the amide bond should be considered to make a plausible TSA.



28.3 What is the transition state or reactive intermediate of the above amide bond hydrolysis?

28.4 Design a stable TSA suitable for replacing the TS. Remember that the TSA should be stable and structurally close to the TS.

SOLUTION OF PREPARATORY PROBLEM 28

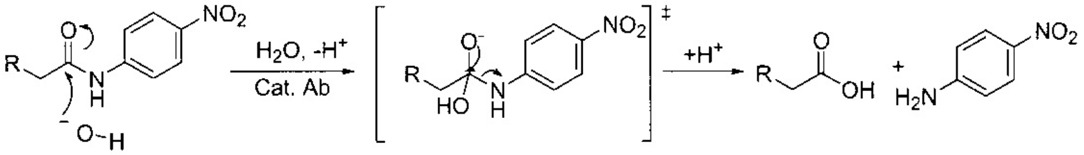
28.1 The reduced energy of the transition state can be calculated by comparing ΔG^o ($\Delta G^o = -RT \ln K_{eq}$) values between K_D of selected antibody and normal antibody.

$G^o = (-RT \ln K_{D,\text{ selected}}) - (-RT \ln K_{D,\text{ normal}}) = -RT (\ln K_{D,\text{ selected}} - \ln K_{D,\text{ normal}})$

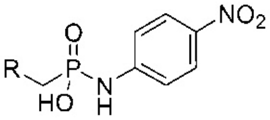
$= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310 \text{ K} \times \ln (10^{-13}/10^{-6}) = 41.6 \text{ kJ mol}^{-1}$

28.2 $k_{cat} / k_{uncat} = \exp(E_{uncat} - E_{cat} / RT)$ by Arrhenius equation ($k = A \exp(-Ea / RT)$)
$k_{cat} / k_{uncat} = \exp (41{,}600 \text{ J mol}^{-1} / 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310 \text{ K}) \approx 1\times10^{7;}$ (reciprocal value of K_D)

28.3



28.4

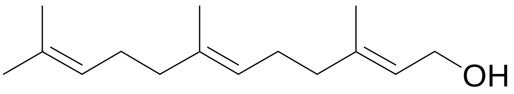


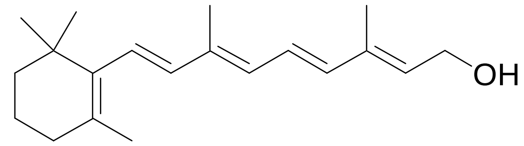
THEORETICAL PROBLEM 29

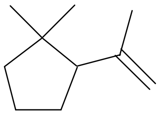
Nature's building blocks

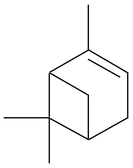
Natural rubber is a polymer composed of isoprene, the conjugated diene 2–methyl–1,3–butadiene. Isoprene can be found not only in rubber but in a wide range of natural products called terpenes, most of which have carbon skeletons made up of isoprene units joined head–to–tail. Recognition of this fact – the isoprene rule – has been great help in working out structures and determining the biosynthetic origin of terpenes.

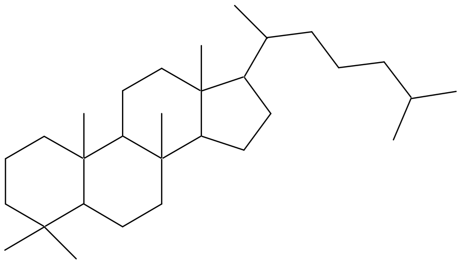
29.1 Find the isoprene units in the following terpenoid natural products.

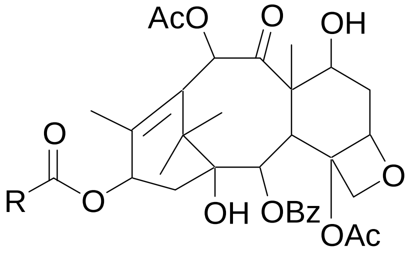






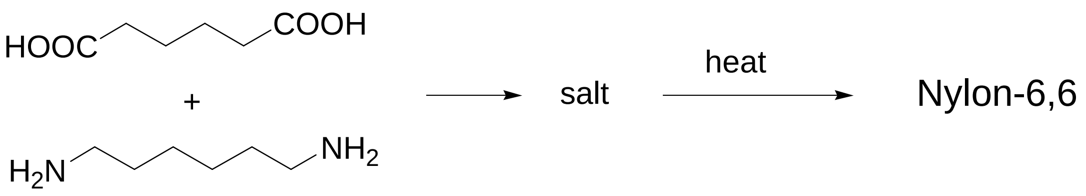


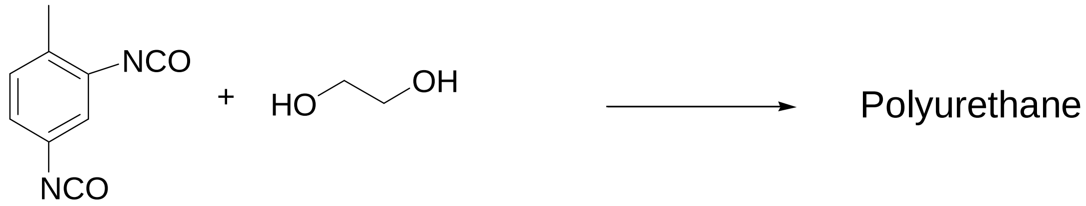


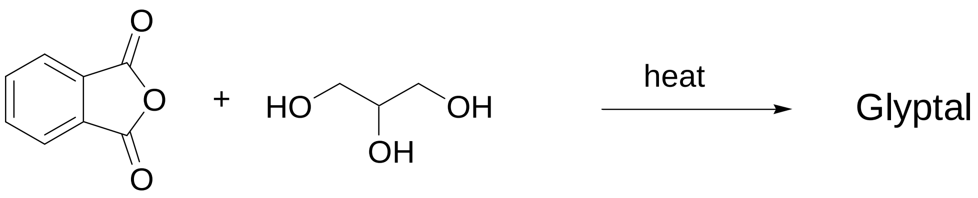


In polymer chemistry, the repeating unit is called a monomer and the repeating units are joined together through chain reaction polymerization or step–reaction polymerization. A few examples of step–reaction polymerization are provided below.

29.2 Draw the repeating unit in each polymer product.

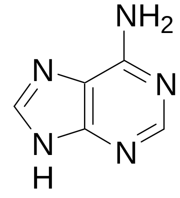


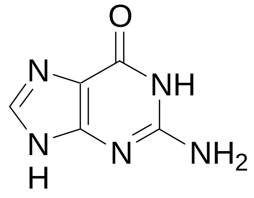


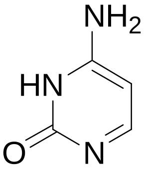


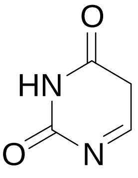
Nature also was suspected to have used basic building blocks such as HCN, NH_3 and water that are observed in interstellar space to produce adenine, guanine, cytosine and uracil in the "prebiotic system" as Oro has demonstrated in 1960.

29.3 Identify the origin of each carbon and nitrogen atoms of these bases from HCN, NH_3 and H_2O



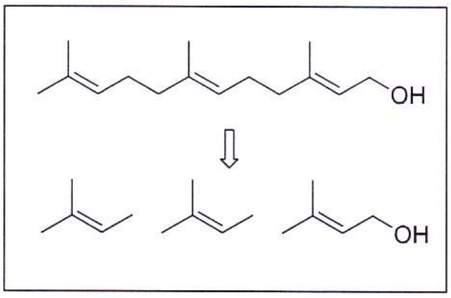


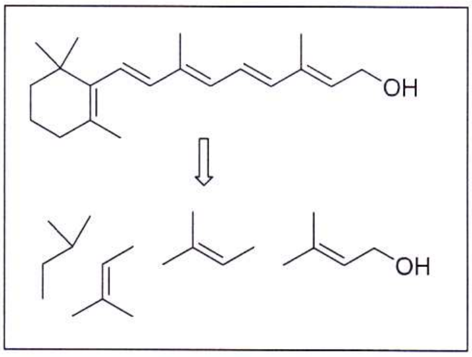


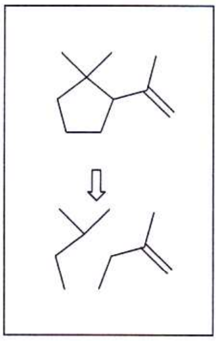


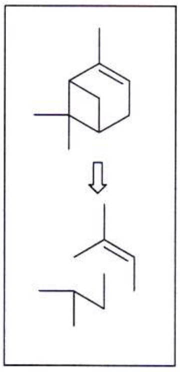
SOLUTION OF PREPARATORY PROBLEM 29

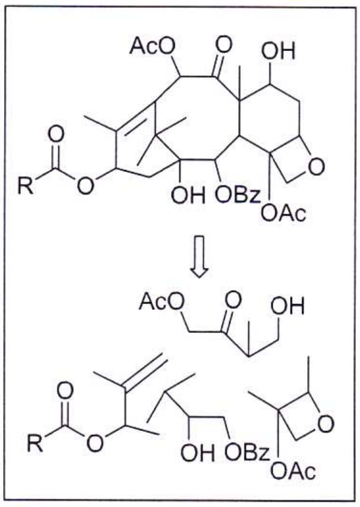
29.1

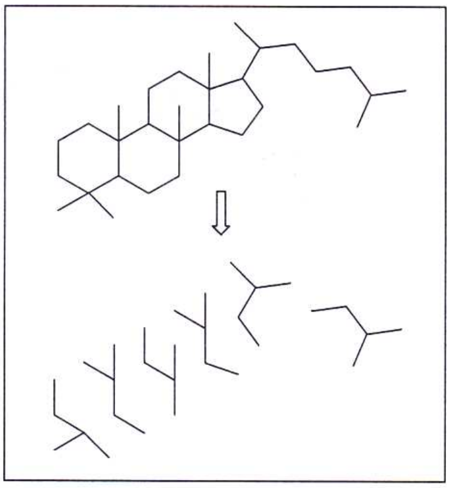






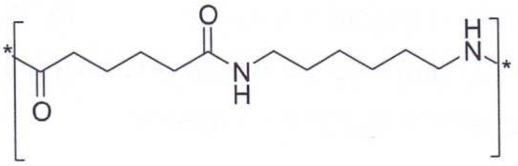




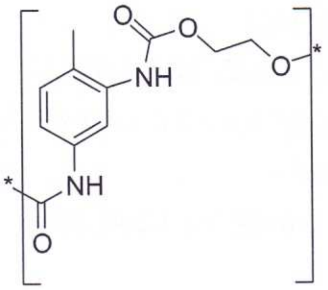


29.2

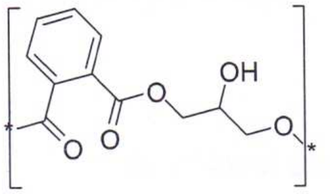
Nylon-6,6



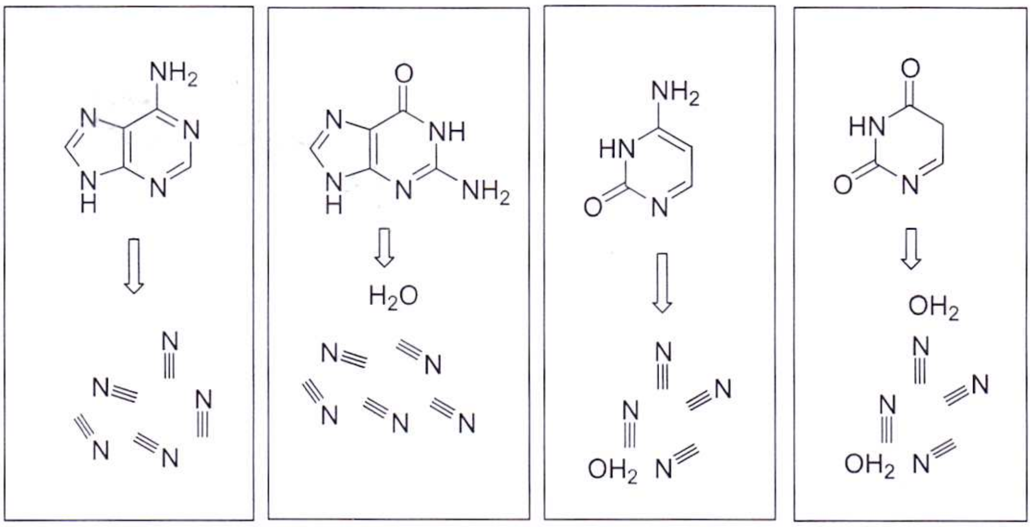
Polyurethane



Glyptal



29.3



THEORETICAL PROBLEM 30

True or false

30.1 Hydrogen is the most abundant element at the core of the sun.

30.2 Hydrogen is the only element in the periodic table that can exist without a neutron. This suggests that a neutron is essential for binding positively charged protons in the nucleus.

30.3 The number of neutrons for heavy nuclei exceeds the number of protons, because the electrostatic repulsion between protons is long–range whereas the strong nuclear force among the protons and the neutrons is short–range.

30.4 Helium is the second–most abundant element in the universe. The molar ratio between hydrogen nuclei (proton) and helium nuclei (α–particle) is about 3 to 1.

30.5 Helium was first made in the interior of the first star in the history of the universe.

30.6 The mass of an α–particle = 2 × (proton mass + neutron mass).

30.7 Neutral atoms were first made before the birth of the first star in the history of the universe.

30.8 The discovery of argon precedes the discovery of the octet rule.

30.9 Mendeleev's periodic table precedes the discovery of argon.

30.10 The discovery of proton precedes the discovery of electron.

30.11 The ionization energy of hydrogen is greater than the bond energy of the hydrogen molecule.

30.12 The enthalpy of formation of CO_2(g) is about the same as twice the enthalpy of formation of H_2O(g), because there are two electronegative oxygen atoms in CO_2 whereas there is only one in H_2O.

SOLUTION OF PREPARATORY PROBLEM 30

True: 30.2, 30.3, 30.7, 30.8, 30.9, 30.11

False: 30.1, 30.4, 30.5, 30.6, 30.10, 30.12

PRACTICAL PROBLEMS

PREPARATORY PROBLEM 31 (PRACTICAL)

Molecular mass determination of carbon dioxide from density measurements

Introduction

Avogadro's principle (1811) is fundamental. For example, molecular mass determinations from gas densities are based on this principle. Cannizzaro showed in 1858 that molecular masses determined from gas density measurements can be used to determine relative atomic mass. For example, the relative molecular mass of nitric oxide, nitrous oxide, and nitrogen dioxide relative to that of hydrogen gas, which Cannizzaro defined to be 2, is 30, 44, and 46, respectively. From a large body of such data, one could deduce the relative atomic masses of different elements.

Gas density measurements led to another major breakthrough in the 19th century. Rayleigh and Ramsay discovered argon while determining the density of nitrogen gas (see Problem 6). Soon a new group was added to help complete the periodic table. Avogadro's principle is exemplified in the following experiment which involves determining the molar mass of carbon dioxide from density measurements. This experiment also uses the ideal gas law.

Materials

- Dry ice, water

Apparatus and glassware

- balance with at least 0.01 g accuracy
- two 500 cm^3 flasks with sidearm
- rubber tubing
- rubber stopper
- aluminum foil
- cylinder
- thermometer
- barometer

Experimental Design

31.1 Devise two separate procedures for determining the density of carbon dioxide at room temperature and atmospheric pressure using dry ice as the source of carbon dioxide.

31.2 Indicate possible sources of error and suggest ways to minimize these errors.

31.3 Calculate the molar mass of carbon dioxide (i) from its density relative to that of air and (ii) using the ideal gas law.

Procedure A

(1) Record the ambient temperature (T) and atmospheric pressure (p).

(2) Weigh a flask. Record m_1.

$$m_1 = m(\text{flask}) + m(\text{air}) \qquad (1)$$

(3) Place crushed dry ice at the bottom of the flask and allow time for sublimation to occur. After a while, make sure that there is no solid dry ice remaining and measure the temperature inside the flask. Wait until temperature is equalized with the openings loosely covered with aluminum foil to let carbon dioxide at room temperature and atmospheric pressure fill the flask, wipe out condensed water on the outer surface of the flask, and weigh. Record m_2.

$$m_2 = m(\text{flask}) + m(CO_2) \qquad (2)$$

(4) Seal the opening of the side arm with a rubber stopper. Fill the flask to the rim with water and measure volume of the water with a graduated cylinder. This is the volume of carbon dioxide in the flask (V). Calculate the mass of air, m(air), occupying this volume under the experimental conditions. Assume that 78 % of air is nitrogen, 21 % oxygen, and 1 % argon. The mass of 1 mol of air is 29.0 g. Calculate m(flask) from (1) and m(air). Then calculate $m(CO_2)$ from (2) and m(flask).

(5) Determine the molecular mass of carbon dioxide from $m(CO_2)$ and m(air).

$$M(CO_2) = 29.0\ \text{g mol}^{-1}\ \frac{m(CO_2)}{m(\text{air})}$$

(6) Also determine the molecular mass of carbon dioxide using the ideal gas law.

$$p\,V = \frac{m(CO_2)\,R\,T}{M(CO_2)}$$

Procedure B

(1) Connect two flasks through their side arm with one piece of rubber tube. Elevate one flask and place a sufficient amount of crushed dry ice at the bottom of this flask. Seal the opening of this elevated flask with a rubber stopper and let carbon dioxide gas overflow through its side arm, and fill the receiving (lower) flask.

(2) Once a sufficient amount of carbon dioxide has overflowed, weigh the receiving flask filled with carbon dioxide after covering its openings with aluminum foil. The advantage of this procedure is that carbon dioxide in the receiving flask is at room temperature and atmospheric pressure.

(3) Determine the volume, *V*, and mass of the flask as in Procedure A.

(4) Repeat until consistent mass of carbon dioxide in the flask is obtained.

(5) Determine the molar mass of carbon dioxide as above.

PREPARATORY PROBLEM 32 (PRACTICAL)

Determination of molar mass by freezing point depression

Introduction

Accurate measurement of gas density was used for the determination of molecular masses of gaseous compounds in the 19th century. For liquid and solid compounds, however, colligative properties had to be used. Here, freezing point depression will be used to demonstrate how 19th century chemists estimated the molar mass of an unknown compound and determined the molecular formula from a given empirical formula. Freezing point depression also can be used to test Arrhenius's theory of electrolytic dissociation.

Chemicals and materials

- Ice
- sodium chloride
- unknown compound A (glucose),
- unknown compound B (sucrose),
- wire

Apparatus and glassware

- thermometer or digital temperature sensor (0.1 °C accuracy),
- beaker,
- test tube,
- wire

Procedure

(1) Mix enough sodium chloride with ice and water in a beaker to bring the temperature of the ice water down to about –8 to –10 °C. Add more ice and salt as necessary to maintain this temperature range.

(2) Add several milliliters of water to the test tube (2~3 cm in diameter). Place a thermometer or digital temperature sensor and a wire bent at one end to form a ring to facilitate mixing. Then immerse the lower half of the test tube assembly into the ice bath and monitor the temperature change for about 10 min while vigorously agitating the water with the wire. The temperature will drop sharply to a point of super–cooling and

increase slightly to the freezing point, where the temperature will remain steady. Calibrate the thermometer or the temperature sensor to 0 ℃ at the freezing point of water.

(3) Prepare 1.00 and 2.00 molal solutions of sodium chloride in water. Determine the freezing point of these solutions following the procedure above. Using the three data points (origin from zero point calibration, 1.00 and 2.00 molal concentration), construct a curve showing freezing point vs. molal concentration. Determine freezing point constant, K_f, of water from the slope and the van't Hoff *i* factor for sodium chloride.

$– \Delta T_\mathrm{f} = K_\mathrm{f}\, m\, I$

(4) Dissolve 20 g of unknown compound in 80 g of water. Similarly dissolve 20 g of unknown compound B in 80 g of water. Determine the freezing point depression of these solutions and calculate molality.

(5) From the calculated molality and the number of grams of the compound in 1,000 g of solvent, calculate the molar masses of both compounds.

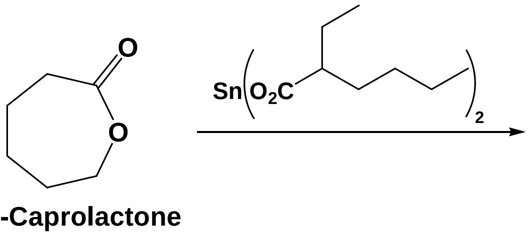
(6) Elemental analysis showed that the compounds are simple carbohydrates. The mass percentages of C, H, and O (by difference) for both compounds were similar within experimental error (C: 40 ~ 42 %, H: 6 ~ 7 %, O: 51 ~ 54 %). Suggest molecular formulas for compounds A and B.

PREPARATORY PROBLEM 33 (PRACTICAL)

Molar mass determination of polymer by titration

Introduction

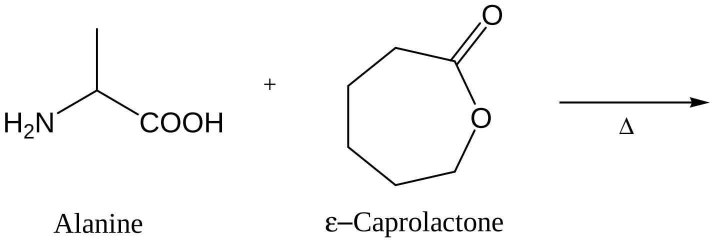
Polycaprolactone (PCL) is a biodegradable polyester with a low melting point (~60 °C) typically prepared by ring opening polymerization (ROP) of ε–caprolactone (ε–CL) using a catalyst such as tin(II) 2–ethylhexanoate (stannous octanoate).



PCL is fully biodegradable. Furthermore its low melting point makes PCL a useful component of a composite biodegradable material. For example, PCL mixed with starch is used to make cheap biodegradable trash bags.

PCL is degraded by hydrolysis of its ester linkages under physiological conditions and, therefore, has also received a great deal of attention for use as an implantable biomaterial. PCL has been approved in certain countries for use in the human body, and may be potentially used in drug delivery, sutures, adhesion barriers and scaffolds for tissue repair. So far, a variety of drugs have been encapsulated within PCL beads for controlled release and targeted drug delivery.

Recently, it has been reported that the ROP of ε–CL can proceed with a heat in the presence of natural amino acids. Therefore, the biocompatibility and in vivo safety of PCL thus–obtained could be satisfying for medical and pharmaceutical purposes.



In this experiment, four ROP reactions will be carried out for different time intervals to prepare polymer samples with varying molecular masses. Since the degree of polymerization (DP) of these samples is relatively low and each polymer molecule contains an end–group suitable for simple acid–base titration, the average molecular mass of the polymers can be determined by end–group analysis. A main problem in such an approach for molecular mass determination is finding a solvent for the polymer that is compatible with the titration. Fortunately, an appropriate solvent system is available for PCL. PCL can be titrated with KOH in isopropyl alcohol/1,4–dioxane solvent (*v*/*v*=1/4) using 1% phenolphthalein solution in pyridine as an indicator. The average molar mass, Mn, of the polymer can be calculated as follows from the sample mass and the number of moles of the end group:

M_n = mass of polymer sample in g / amount of substance (in moles) from end group analysis

The degree of polymerization (DP) at specific reaction time can be obtained from M_n for each polymer sample.

DP = M_t / M_0,
M_t – molar mass at time t
M_0 – molar mass of one monomeric unit

Chemicals and materials

- L–alanine,
- ε–caprolactone
- KOH
- Tetrahydrofuran
- Methanol
- isopropyl alcohol
- 1,4–dioxane
- 1% phenolphthalein solution in pyridine

Apparatus and glassware

- Balance with at least 0.01 g accuracy,
- four 50 cm^3 one–neck round bottom flasks,

- four 250 cm^3 beakers,
- test tubes,
- 50 cm^3 burrette,
- Pasteur pipette,
- oil bath,
- hot plate stirrer,
- vacuum oven,
- mg–scale balance

Procedure 1: Neat ring–opening polymerization

(1) In each of four 50 cm^3 one–neck round bottom flasks (RBF), mix 0.13 g L–alanine (1.5 mmol) and 5.13 g ε–caprolactone (45 mmol) and stir the mixture at 160 °C in an oil bath. Connect the flasks to nitrogen line to release any pressure developed during the heating.

(2) After 1, 5, 12, and 24 h, remove one of the flasks from the bath and cool it down to room temperature. Dissolve the mixture in 5 cm^3 tetrahydrofuran (THF) and precipitate the polymer product by pouring the solution into 80 cm^3 methanol/H_2O (v / v = 4 / 1) solution.

(3) Filter the precipitated polymer products and dry in a vacuum oven for several hours. Measure the mass of dried polymer products.

Procedure 2: Titration with KOH

(1) Prepare a standardized solution of KOH with a concentration of about 0.008 mol dm^{-3} in isopropyl alcohol / 1,4–dioxane (v / v = 1 / 4).

(2) Dissolve each polymer sample obtained above in 5.0 cm^3 of isopropyl alcohol / 1,4–dioxane (v / v = 1 / 4). Add 4 drops of 1% phenolphthalein / pyridine solution to 1.0 cm^3 aliquot of each polymer solution and titrate with the standardized KOH solution. Repeat this titration.

(3) Calculate the average experimental molar mass (g mol^{-1}) of the sample from the average volume of the titrant.

(4) Repeat steps 2 and 3 for other polymer samples.

Questions

Assume that 100% conversion of monomer is obtained after 24 h, and all the amino acid (alanine) is incorporated into the polymer.

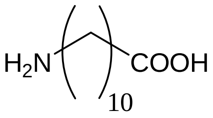
33.1 What is the structure of the resulting compound if alanine attacks the caprolactone? Explain the meaning of titration with KOH.

33.2 At times of 1, 5, 12, and 24 h, calculate yields, amounts of KOH in moles used in titration, the number of polymer chain, average experimental molar mass value (g mol^{-1}) of polymer (M_n), and degree of polymerization.

	1 h sample	2 h sample	5 h sample	24 h sample
Polymer yield (g)				
Volume of KOH solution (cm^3)				
Amount of KOH (mmol)				
Amount of polymer (mmol)				
M_n (g mol^{-1})				
Degree of polymerization				

33.3 Draw each polymeric product from the 1, 5, 12, and 24 h trials. The repeat unit in polymer chain can be expressed as an example showed below.

Example) 11–aminoundecanoic acid

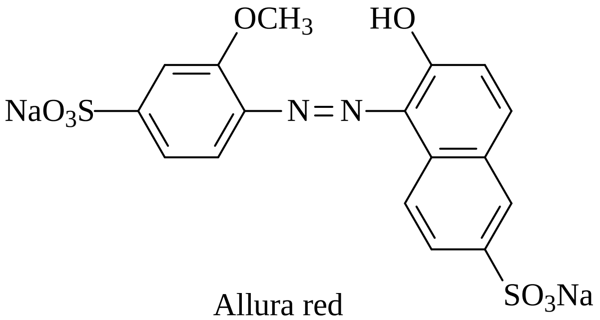


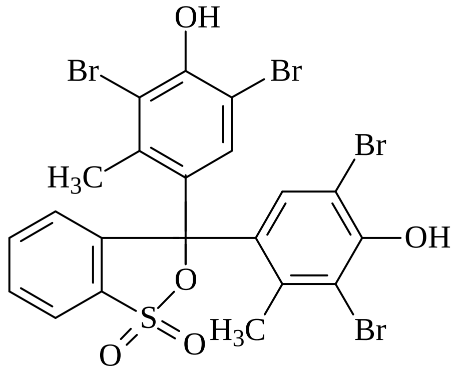
PREPARATORY PROBLEM 34 (PRACTICAL)

Separation and quantitative determination of dyes by column chromatography and spectrophotometry

Introduction

In this experiment, students receive small volumes of unknown liquid which is a mixture of allura red ($C_{17}H_{12}N_2O_8S_2Na_2$, *abbrev*. AR) and bromocresol green ($C_{21}H_{14}Br_4O_5S$, *abbrev*. BCG) in their basic forms. An aliquot is placed on a small silica gel column, which students prepare by filling silica gel in a Pasteur pipet. The students separate the dyes by *stepwise* elution with the solvents listed in Table 1. The students choose two eluents that are expected to give the best separation of the dyes. The samples are then diluted to a known volume and quantified by visible spectrophotometry. The components of the entire experiment – column preparation, separation, calibration curves, and analysis of the unknown – can be undertaken easily if students know how to perform quantitative serial dilution, operate a spectro–photometer, and know how to select the analytical wavelengths for the dyes.


Allura red


Bromocresol green

Chemicals and materials

- allura red, solid,
- bromocresol green, solid,
- hydrochloric acid, *w*(HCl) = 0.35,
- triethylamine,
- methanol,
- ethyl acetate,
- silica gel, solid,

Apparatus and glassware

- visible spectrophotometer,
- analytical balance,
- sample cell (10–mm pathlength),
- twelve 10 cm^3 volumetric flasks,
- two 50 cm^3 volumetric flasks,
- two 50 cm^3 beakers,
- three 2 cm^3 Pasteur pipets,
- one micropipette (0.1 cm^3),
- pipet filler.

Procedures:

I. Preparation of stock solutions of dyes

These dye solutions tend to decompose over extended periods of time, so they should be prepared just prior to the experiment.

(1) Bromocresol green. An accurately weighed sample (300 mg) is dissolved in ethyl acetate in a 50 cm^3 volumetric flask to which sufficient triethylamine is added to produce the purple basic form.

(2) Allura red. An accurately weighed sample (about 100 mg) is dissolved in about 30 cm^3 of methanol in a 50 cm^3 volumetric flask to which triethylamine is added dropwise until the dye is completely dissolved. Methanol is then added to the mark to dilute the mixture.

Note: Allura red should be pre–purified as follows: Dissolve the sodium salt of allura red in methanol and then filter the mixture. Add an excess of concentrated HCl to the filtrate obtained. After about 30 min the resulting crystals of the protonated form can be filtered off.

II. Preparation of standard solutions of dyes

Prepare five standard solutions for each dye by diluting the stock solution in the same solvents used for the preparation of the stock solutions in 10 cm^3 volumetric flasks. To the allura red standard solutions 3–4 drops of concentrated HCl are added to obtain the dye in its acidic form. The concentration of the standard solutions should be in the range of one tenth to nine tenths of the original concentration of the stock solution.

III. Preparation of calibration curves of dyes

Prepare a calibration curve for each dye using its absorbances at respective peak maximum *vs*. concentration in ppm.

IV. Preparation of a chromatographic column

Prepare a chromatographic column by placing a small plug of glass wool (or cotton) at the constriction of a 2 cm^3 Pasteur pipet. Silica gel (45/70 mesh) slurried in ethyl acetate is added to the pipet to produce 4–5 cm of packed gel in the column.

V. Column chromatography and quantification

(1) Transfer a 40 μdm^3 aliquot of unknown liquid to the column.

(2) Rinse the walls of the column with a few drops of an eluent selected from Table 1, pass the eluent through the column and collect the eluate in a 10 cm^3 volumetric flask containing 2–3 drops of triethylamine.

(3) Pass a second eluent through the column selected from Table 1, and collect the eluate in a separate 10 cm^3 volumetric flask containing 3 – 4 drops of concentrated HCl. A small band of impurity may be left behind at the top of the column.

(4) Dilute the first fraction in its purple, basic form to volume with the first eluent.

(5) Dilute the second fraction in its acidic, red form to volume with the second eluent.

(6) Find the concentration of each sample, and thus the amount (mg) of each dye in the unknown from the calibration curve for each dye.

Table 34.1 Possible eluent systems

Eluent No.	Eluent Set I	Eluent Set II
1	ethyl acetate	methanol
2	methanol	ethyl acetate
3	ethyl acetate–HCl[a)] (200 : 1 v/v)	methanol–HCl (200 : 1 v/v)
4	ethyl acetate–TEA (200 : 1 v/v)	methanol–TEA (200 : 1 v/v)
5	methanol–HCl (200 : 1 v/v)	ethyl acetate–HCl (200 : 1 v/v)
6	methanol–TEA (200 : 1 v/v)	ethyl acetate–TEA (200 : 1 v/v)

a) concentrated hydrochloric acid.

Questions

34.1 What are the concentrations in ppm of AR and BCG in your sample?

34.2 Note that separation is performed in the normal phase LC mode. Considering the structures of the dyes, which dye would you want to elute first for best results? Which eluent would you use for eluting the first–eluting dye? Explain.

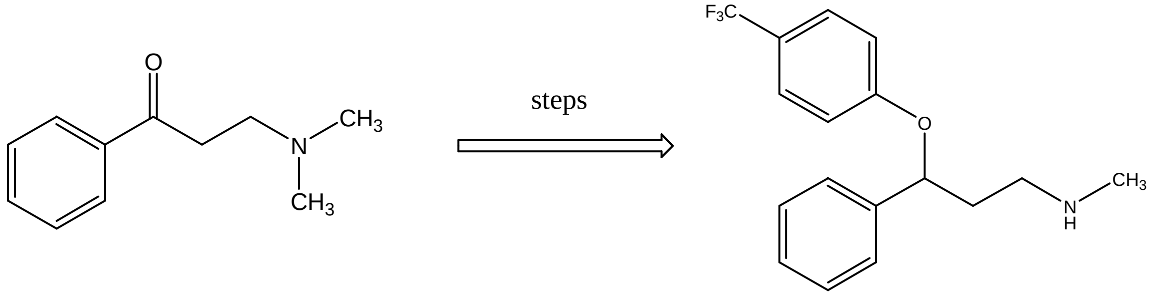
34.3 Which dye would be eluted second? Which eluent would you use for eluting the second dye? Explain.

PREPARATORY PROBLEM 35 (PRACTICAL)

Synthesis of ββ–dimethylaminopropiophenone hydrochloride

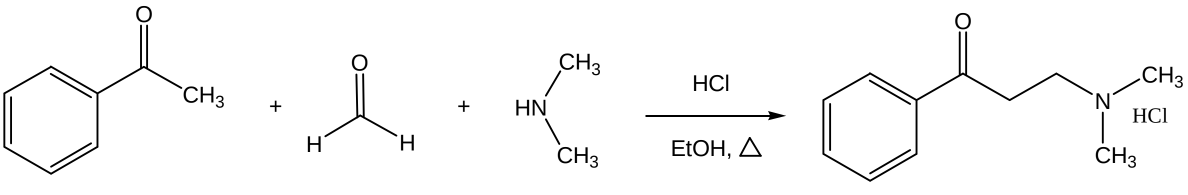
Introduction

Prozac is a famous antidepressant, also known as the "happy drug" as it can help alleviate depression. The active ingredient in Prozac is fluoxetine. Fluoxetine is prepared from β–dimethylaminopropiophenone in a four step sequence.



fluoxetin (Prozac)

The target molecule can be obtained by a one–pot reaction involving three or more starting compounds also known as a multicomponent reaction (MCR). Among MCRs classic name reactions have developed into popular chemical reactions in the pharmaceutical industry for the preparation of compound libraries of low molecular drug–like compounds. For example, the Mannich reaction is a "one pot" combination reaction of three synthetic fragments to make a single product. This multicomponent reaction can be applied to the synthesis of β–dimethylaminopropiophenone, as paraformaldehyde and dimethylamine hydrochloride are combined in the presence of acetophenone to produce directly β–dimethyl–aminopropiophenone.



Experimental

Chemicals

- Acetophenone, liquid,
- concentrated HCl aqueous solution,
- dimethylamine hydrochloride, solid,
- paraformaldehyde, solid,
- ethanol, 95 % aqueous solution,
- ethyl ether,
- hexane,
- methanol,
- ethyl acetate,
- acetone,
- $NaHCO_3$, aqueous solution,
- $KMnO_4$, aqueous solution, 0.1 mol dm^{-3},
- $ZnCl_2$, solid,
- $FeCl_3$, 2.5% aqueous solution,
- $AgNO_3$, 5% aqueous solution,
- NaOH, 10% aqueous solution,
- NH_3, aqueous solution (c = 2 mol dm^{-3}),
- 2,4–dinitrophenylhydrazine,
- conc. sulfuric acid.

Apparatus and glassware

- round–bottomed flask, 25 cm^3,
- Erlenmeyer flask, 50 cm^3,
- stirrer,
- temperature controller,
- heating mantle,
- sand,
- support stand,
- clamp and clamp holder,
- melting point apparatus,
- capillary tubes,

- magnetic bar,
- reflux condenser,
- hose,
- Büchner funnel,
- suction flask,
- glass rod,
- filter paper,
- beaker, 100 cm^3,
- TLC plate (silica gel 60 F_{254}, layer thickness: 250 µm, on glass support),
- micro–syringe,
- developing chamber with a lid,
- UV lamp.

Procedure

Inside a fume hood, add 2 cm^3 of acetophenone, 0.65 g of dimethylamine hydrochloride and 1.76 g of paraformaldehyde into a 25 cm^3 round–bottom flask. Add 4 cm^3 of 95% ethanol to the flask, followed by 40 $µdm^3$ of concentrated HCl. Add your magnetic bar and equip the flask with a reflux condenser. Reflux the mixture for 2 hours by placing the flask in a sand bath preheated to 120 ℃. Allow the reaction mixture to cool slightly (to 50~80 ℃) and transfer it to a small Erlenmeyer flask (pour, do not pipette since the material may freeze in the pipette). Add 16 cm^3 of acetone and allow the flask to cool to room temperature. Mix thoroughly with a glass stirring rod. Cool the mixture in an ice–bath to complete the crystallization. Filter by suction using a Büchner funnel with a filter flask and wash the solids with 4 cm^3 of acetone. (You can use 1 cm^3 acetone to help transfer the last of the solid in the flask.) Let the product dry for at least 20 minutes on the funnel. Weigh the products and determine their melting point.

Extract a free amine into the organic solvent with aqueous $NaHCO_3$ solution for developing TLC. Dissolve about 0.1 g of the product with distilled water and then transfer the solution into a small separatory funnel. Add ethyl ether as an organic solvent. Neutralize the water layer with aqueous $NaHCO_3$ solution. Use a pH paper. Obtain the organic layer for TLC. Develop a TLC plate in ethyl acetate: hexane (2 : 1, *v*/*v*) or ethyl acetate: methanol (2 : 1, *v*/*v*).

Qualitative Tests

Perform the following tests with the product and report the observation.

1) The Bayer Test (Potassium permanganate); ALKENES AND ALKYNES

(This test is useful for indicating the presence of most olefinic or acetylenic functional groups.)

Dissolve 30 mg of the product in 2 cm^3 of water. Add dropwise aqueous solution of $KMnO_4$, (c = 0.1 mol dm^{-3}) report the results.

2) Lucas test; ALCOHOLS

(This test is useful for distinguishing among lower molar mass of primary, secondary, and tertiary alcohols.)

Prepare Lucas's reagent by dissolving 136 g of zinc chloride in 89 cm^3 of conc. HCl with cooling in ice bath. Add 2 cm^3 of Lucas's reagent to 30 mg of the product in a test tube. Note the time required to form the insoluble alkyl chloride, which appears as a layer or emulsion.

3) Ferric chloride test; PHENOLS

(This test is useful for the recognition of phenols.)

Dissolve 30 mg of the product in 2 cm^3 of water or a mixture of ethanol and water, and add up to 3 drops of the 2.5% aqueous ferric chloride solution. Most phenols produce red, blue, purple, or green coloration; enols give red, violet, or tan coloration.

4) Tollen's reagent (silver–ammonia complex ion); ALDEHYDES

(This test is useful for distinguishing aldehydes from ketones and other carbonyl compounds.)

To a clean test tube, add 2 cm^3 of the 5% silver nitrate solution and 1 drop of the 10% sodium hydroxide solution. Add aqueous ammonia solution (c = 2 mol dm^{-3}) drop by drop with good shaking until the dark precipitated silver oxide just dissolves. Add 1 drop of the liquid or 30 mg of the product to be tested, shake the tube to mix, and allow it to stand at room temperature for 20 minutes. If nothing happens, heat the tube in a beaker of water at 35 °C for five minutes.

5) Test with 2,4–dinitrophenylhydrazine; ALDEHYDES AND KETONES

(This test is useful for identifying aldehydes and ketones.)

Prepare 2,4–dinitrophenylhydrazine reagent by dissolving 3 g of 2,4–dinitrophenylhydrazine in 15 cm^3 of conc. sulfuric acid and adding this solution , with good stirring, to a mixture of 20 cm^3 of water and 70 cm^3 of 95% ethanol. Dissolve 100 mg of a solid product in 2 cm^3 of 95%

ethanol, and add this solution to 2 cm^3 of the 2,4–dinitrophenylhydrazine reagent. Shake the mixture vigorously; if a precipitate does not form immediately, let the solution stand for 15 min.

Results

– **Reagents & Products** (Show calculations)

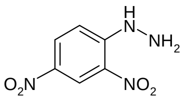
Reagents (compound names)	M (g mol^{-1})	m (g) or V (cm^3) used	mmole used	equivalent	physical properties
Product: [M = g mol^{-1}] Mass: ________________ g Yield: ________________ %					

– **Melting Point**: ________________ °C (Observed)

________________ °C (Reported in the literature)

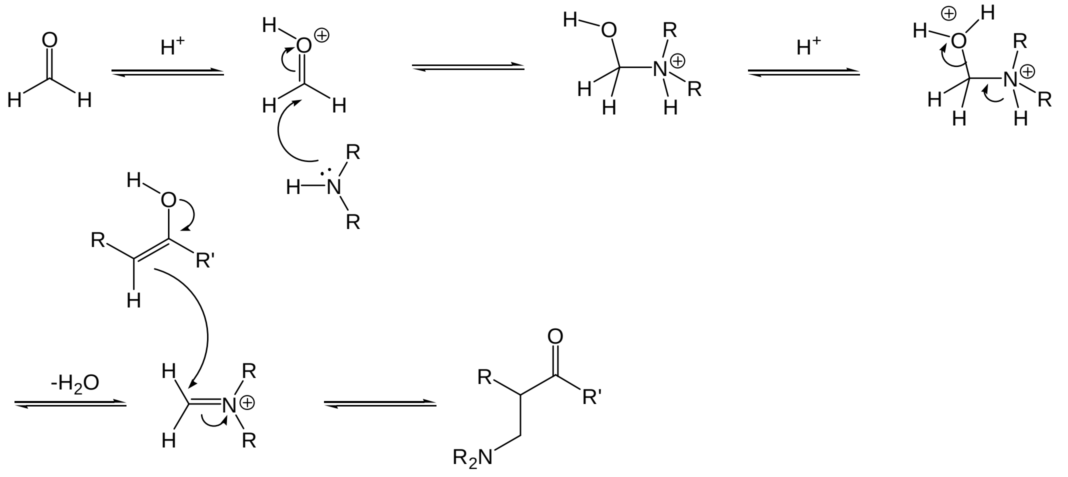
– ***R*$_f$ values** (Record the R_f values and the size and shape of each spots):

(Show calculations)

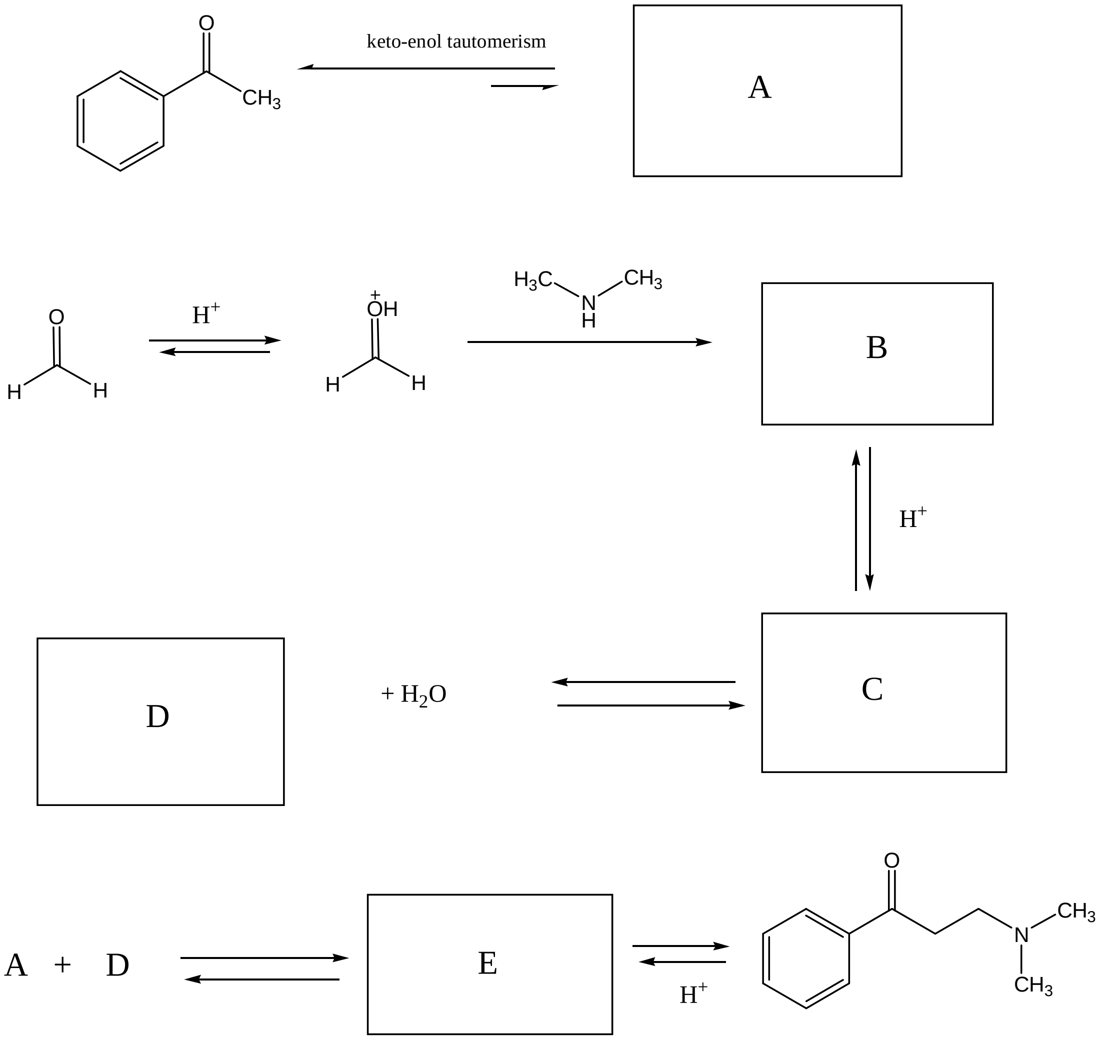
Test Reagent	Test result	
	Observed	expected
1) $KMnO_4$ (Bayer's test)		
2) HCl, $ZnCl_2$ (Lucas's test)		
3) $FeCl_3$ (Ferric chloride solution)		
4) $AgNO_3$ / NaOH / NH_3 (Tollen's reagent)		
5) 2,4–dinitrophenylhydrazine 		

Question

The general mechanism for a Mannich reaction is given below as an illustrative example.



Account for the overall reaction in a stepwise fashion. Try depicting the mechanism (i.e., electron "pushing") for the reaction carried out in the test.

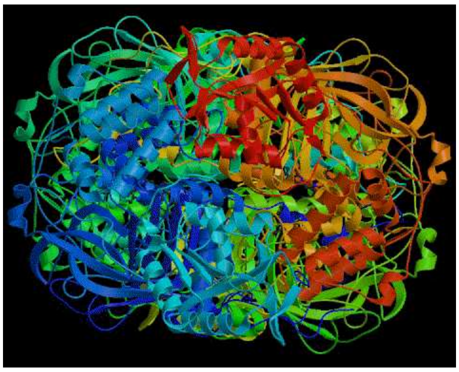


PREPARATORY PROBLEM 36 (PRACTICAL)

Enzyme kinetics by catalase

Introduction

Catalysis is a central concept in chemistry and biology, essential in life and industrial processes. Enzymes are catalysts for biochemical reactions. In this experiment, the Michaelis–Menten kinetics of hydrogen peroxide decomposition ($2\ H_2O_2 \rightarrow 2\ H_2O + O_2$) by catalase in potato juice will be investigated. Catalase is well known for its extremely high reaction rate. One catalase molecule can decompose 40 million hydrogen peroxide molecules in one second. Such a high rate is needed to scavenge reactive oxygen species and protect cellular components in the oxidative environment. The figure below shows a 3–dimensional structure of catalase from *E. coli* determined by X–ray crystallography.



The number of moles of the evolved oxygen gas can be determined from its volume measured using a buret or from the pressure change in an enclosed reaction vessel. Reaction rate can be expressed as the number of moles of oxygen per unit time.

An enzyme (E) combines with a substrate (S) and produces an enzyme–substrate complex (ES) with a rate constant k_1. ES could be decomposed back to E and S with a rate constant k_2 or concerted to a product (P) with a rate constant k_3. The steady state condition for ES can be determined by solving the following rate equations:

$$d[ES] / dt = k_1([E]_{tot} – [ES]) [S] , \quad \text{where} \quad [E]_{tot} = [E] + [ES]$$

$$– d[ES]/dt = k_2 [ES] + k_3 [ES]$$

$$[S]([E]_{tot} – [ES]) / [ES] = (k_2 + k_3) / k_1$$

$(k_2 + k_3) / k_1$ is defined as the Michaelis–Menten constant, K_M.

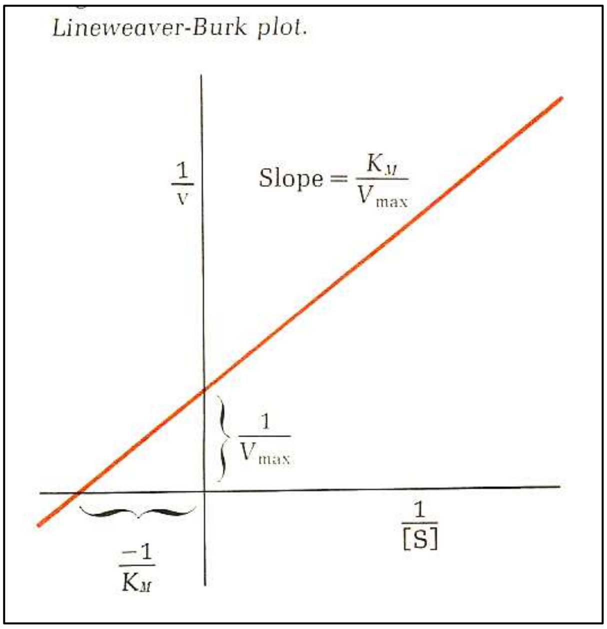
Solving the last equation for [ES] one gives [ES] = [E] [S] / (K_M + [S]).

Let v is the initial rate for the evolution of oxygen: $v = k_3$ [ES]. If the enzyme is present only as ES, v will approach to a maximum value, $v_{max} = k_3\,[E]_{tot}$. From these relations, one gets the Michaelis–Menten equation.

$$v = \frac{v_{max}[S]}{K_M + [S]}$$

Obviously, K_M is the value of [S] when $v = v_{max} / 2$. Taking the inverse of the Michaelis–Menten equation one gets the celebrated Lineweaver–Burk equation (see Figure), which is one of the most frequently used equations in chemistry.

$$1/v = (K_M / v_{max}) (1 / [S]) + 1 / v_{max}$$

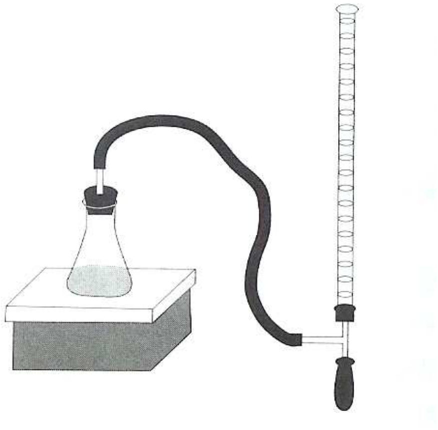


Chemicals and materials

- hydrogen peroxide,
- fresh potato,
- catalase

Apparatus

- blender,
- ice bath,
- boiling water bath



Procedure

(1) Prepare 0.5, 1, 2, 3, 4, 6% solution of hydrogen peroxide by diluting the given 30% hydrogen peroxide with deionized water.

(2) Make potato juice by blending pieces of potato with approximately equal mass of water. Squeeze the juice with cheesecloth. Keep the juice in an ice bath.

(3) Add 2 cm^3 of the juice to 30 cm^3 of the diluted hydrogen peroxide solutions and shake. As a control, use 30 cm^3 of deionized water.

(4) Measure the volume of oxygen produced using a set–up shown below. Make a soap bubble with the rubber bulb and measure time needed to produce a certain volume (20 cm^3 for example) of oxygen gas at room temperature.

(5) Repeat with 6% hydrogen peroxide using the juice heated in boiling water bath for 10 min to denature the enzyme.

(6) If pure catalase is available, repeat the whole experiment using catalase at a known concentration (1 micromolar, for example).

Treatment of data and questions

36.1 Calculate the molar concentration of hydrogen peroxide, [S].

36.2 Calculate the amount of substance of oxygen produced in a given time for each [S].

36.3 Calculate v for each [S].

36.4 Plot v against [S] and see if it approaches a maximum value.

36.5 Develop a Lineweaver–Burk plot to determine K_M and V_{max}.

36.6 If $[E]_{tot}$ is known, calculate k_3 from $V_{max} = k_3\,[E]_{tot}$. What is the turn–over number of catalase per second?