38th

ICHO

International Chemistry Olympiad

11 theoretical problems
3 practical problems

THE THIRTY-EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
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THEORETICAL PROBLEMS

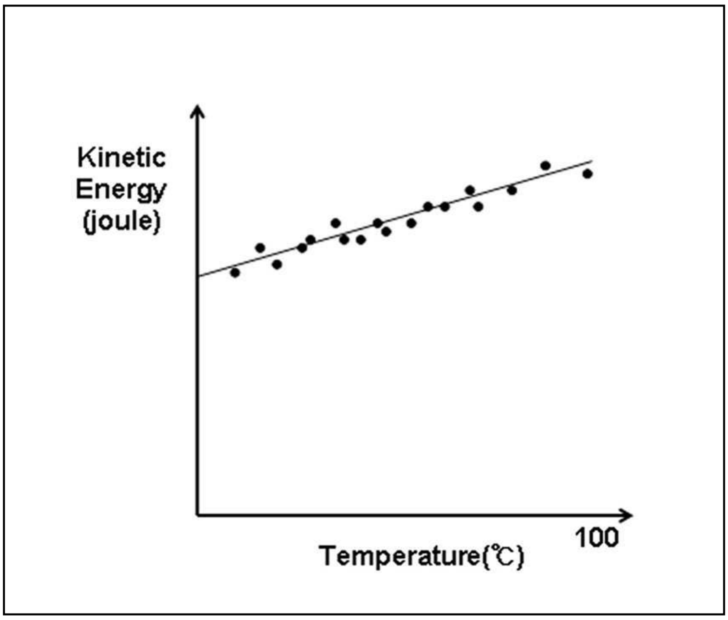
PROBLEM 1

Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27 ℃, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm s^{-1} at 27 ℃. The density of a water droplet is 1.0 g cm^{-3}.

1.1 Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27 ℃. The volume of a sphere is given by (4/3) π r^3 where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0 ℃ and 100 ℃ as a function of temperature is found to be linear. Assume that it remains linear below 0 ℃.



At thermal equlibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).

The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is 0.31 J g^{-1} K^{-1}.

1.2. Calculate Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

SOLUTION

1.1 The mass of a water droplet:

$m = V\rho = [(4/3)\ \pi\ r^3]\ \rho = (4/3)\ \pi\ (0.5\times10^{-6}\ \text{m})^3\ (1.0\ \text{g cm}^{-3}) = 5.2\times10^{-16}\ \text{kg}$

Average kinetic energy at 27 °C:

$$E_k = \frac{m\,v^2}{2} = \frac{(5.2\times10^{-16}\ \text{kg})\times(0.51\times10^{-2}\ \text{m/s})^2}{2} = 6.9\times10^{-21}\ \text{kg m}^2/\text{s}^2 = \underline{6.9\times10^{-21}\ \text{J}}$$

1.2 The average kinetic energy of an argon atom is the same as that of a water droplet. E_k becomes zero at –273 °C.

From the linear relationship in the figure, $E_k = a\,T$ (absolute temperature) where a is the increase in kinetic energy of an argon atom per degree.

$$a = \frac{E_k}{T} = \frac{6.9\times10^{-21}\ \text{J}}{(27+273)\ \text{K}} = 2.3\times10^{-23}\ \text{J K}^{-1}$$

S: specific heat of argon N: number of atoms in 1g of argon

$S = 0.31\ \text{J g}^{-1}\ \text{K}^{-1} = a\times N$

$$N = \frac{S}{a} = \frac{0.31\ \text{J g}^{-1}\ \text{K}^{-1}}{2.3\times10^{-23}\ \text{J K}^{-1}} = 1.4\times10^{22}\ \text{g}^{-1}$$

Avogadro's number (N_A) : Number of argon atoms in 40 g of argon

$N_A = 40\ \text{g mol}^{-1}\times1.4\times10^{22}\ \text{g}^{-1} = \underline{5.6\times10^{23}\ \text{mol}^{-1}}$

PROBLEM 2

Detection of hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

2.1 There are about 1×10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g cm^{-3}; 3/4 hydrogen and 1/4 helium by mass). Estimate the number of stellar protons in the universe to one significant figure.

In the 1920s Cecilia Payne discovered by spectral analysis of starlight that hydrogen is the most abundant element in most stars.

2.2 The electronic transition of a hydrogen atom is governed by $\Delta E(n_i \rightarrow n_f) = -C(1/n_f^2 - 1/n_i^2)$, where n is principle quantum number, and C is a constant. For detection of the $\Delta E(3\rightarrow2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the n = 2 state. Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1\rightarrow2)$ transition.

2.3 According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $\lambda T = 2.9\times10^{-3}$ m K. Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the $n = 1 \rightarrow n = 2$ excitation of hydrogen.

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

2.4 Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7 K, can cause the hyperfine transition. Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.

2.5 Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the “proton”. Fill in the blank.

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SOLUTION

2.1 Mass of a typical star = $(4/3) \times (3.1) \times (7\times10^{8}\text{ m})^{3} \times (1.4\times10^{6}\text{ g m}^{-3}) = 2\times10^{33}$ g

Mass of protons of a typical star = $(2\times10^{33}\text{ g}) \times (3/4 + 1/8) = 1.8\times10^{33}$ g

Number of protons of a typical star = $(1.8\times10^{33}\text{ g}) \times (6\times10^{23}\text{ g}^{-1}) = 1\times10^{57}$

Number of stellar protons in the universe = $(1\times10^{57}) \times (10^{23}) = \underline{1\times10^{80}}$

2.2 $\Delta E(2\rightarrow3) = C(1/4 – 1/9) = 0.1389\ C$ $\lambda(2\rightarrow3) = 656.3$ nm

$\Delta E(1\rightarrow2) = C(1/1 – 1/4) = 0.75\ C$

$\lambda(1\rightarrow2) = (656.3) \times (0.1389 / 0.75) = 121.5$ nm

2.3 $T = 2.9\times10^{-3}\text{ m K} / 1.215\times10^{-7}\text{ m} = 2.4\times10^{4}$ K

2.4 $\lambda = 3\times10^{8}\text{ m} / 1.42\times10^{9} = 0.21$ m

$T = 2.9\times10^{-3}\text{ m K} / 0.21\text{ m} = 0.014$ K

2.5 $^{14}N + {}^{4}He \rightarrow {}^{17}O + {}^{1}H$

PROBLEM 3

Interstellar chemistry

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either be desorbed from the surface or further react through surface migration with adsorbed H atoms to form CH_2, CH_3, etc.

Depending on how energetically a molecule "jumps" from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A\ \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

3.1 Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1\times10^{12}$ s^{-1} and E_{des} = 12 kJ mol^{-1}.

3.2 Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1}, and the IIG is a sphere with a 0.1 μm radius. Each migratory jump laterally advances the molecule by 0.3 nm. Show work and choose your answer from (a) – (e) below.

(a) $t \le 1$ day (b) 10 days $\le t \le 10^2$ yr c) 10^3 yr $\le t \le 10^6$ yr

(d) 10^7 yr $\le t \le 10^{10}$ yr (e) $t \ge 10^{11}$ yr

3.3 Consider the reaction of CO with H_2 to form H_2CO. The activation energy on a metal catalyst is 20 kJ mol^{-1} that is produced by formaldehyde at a rate of 1 molecule/s per site at 300 K. Estimate the rate of formaldehyde formation per site if the reaction takes place at 20 K.

3.4 Which is a set of all true statements? Circle one.

(a) Most CH species are desorbed from the IIG surface before encountering other reactants by surface migration.

(b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.

(c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

❑ (a) ❑ (b) ❑ (c) ❑ (a, b) ❑ (a, c) ❑ (b, c) ❑ (a, b, c)

SOLUTION

3.1 $k_{des} = A \exp(–E_{des}/RT) = (1\times10^{12}\ s^{-1}) \times (5\times10^{-32}) = 5\times10^{-20}\ s^{-1}$ at T = 20 K

surface residence time, $T_{residence} = 1 / k_{des} = 2\times10^{19}$ s = $\underline{6\times10^{11}\ yr}$

(full credit for $T_{half\text{-}life} = \ln 2 / k_{des} = 1\times10^{19}$ s = 4×10^{11} yr)

residence time = 2×10^{19} s

3.2 The distance to be traveled by a molecule: $x = \pi r$ = 300 nm.

$k_{mig} = A \exp(–E_{mig} / RT) = (1\times10^{12}\ s^{-1}) \times (2\times10^{-16}) = 2\times10^{-4}\ s^{-1}$ at T = 20 K

Average time between migratory jumps, $T = 1 / k_{mig} = 5\times10^{3}$ s

Time needed to move 300 nm = (300 nm / 0.3 nm) jumps × (5×10^{3} s/jump) =

= 5×10^{6} s = <u>50 days</u>

<u>The correct answer is (b).</u>

(Full credit for the calculation using a random-walk model. In this case:

$t = T\,(x/d)^{2} = 5\times10^{9}$ s = 160 yr. The answer is still (b).)

3.3 $k(20\ K) / k(300\ K) = \exp[(E/R)\,(1/T_1 – 1/T_2)] = e^{-112} = \sim 1\times10^{-49}$ for the given reaction

The rate of formaldehyde production at 20 K = = ~ 1×10^{-49} molecule/site/s =

= ~ 1×10^{-42} molecule/site/ yr

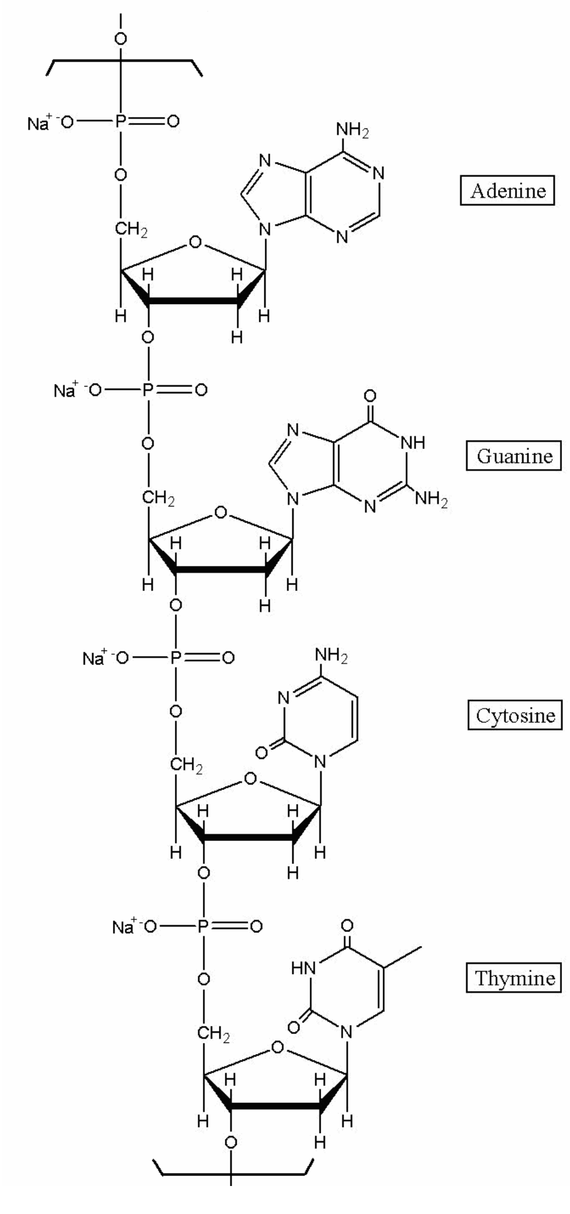
(The reaction will not occur at all during the age of the universe (1×10^{10} yr).)

3.4 The correct answer is <u>(b, c)</u>.

PROBLEM 4

The Chemistry of DNA

4.1 In 1944 Oswald Avery isolated a genetic material and showed by elemental analysis that it was a sodium salt of deoxyribonucleic acid. A segment of DNA with formula mass of 1323.72 is shown.



Assuming that equimolar amounts of the four bases are present in DNA, <u>write</u> the number of H atoms per P atom. <u>Calculate</u> (to 3 significant figures) the theoretical weight percentage of H expected upon elemental analysis of DNA.

4.2 Chargaff extracted the separated bases and determined their concentrations by measuring UV absorbance. The Beer-Lambert law was used to obtain the molar concentration. Chargaff discovered the following molar ratio for bases in DNA:

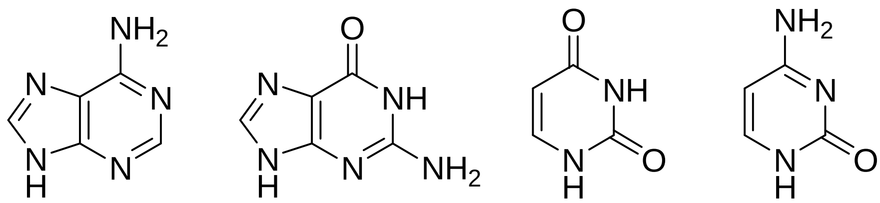
adenine to guanine = 1.43 thymine to cytosine = 1.43
adenine to thymine = 1.02 guanine to cytosine = 1.02

Chargaff's discovery suggested that the bases might exist as pairs in DNA. Watson and Crick mentioned in their celebrated 1953 paper in *Nature*: "It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material."

Draw structures of the specific pairing found in DNA. Indicate hydrogen bonds. Omit the sugar-phosphate backbone.

4.3 Mutation can occur through base pairings different from the above. Draw structures of any three alternative base pairs.

4.4 The plausibility of the formation of purine and pyrimidine bases in the prebiotic atmosphere of the Earth from HCN, NH_3, and H_2O has been demonstrated in the laboratory. Write the minimum number of HCN and H_2O molecules required for formation of the following compounds.



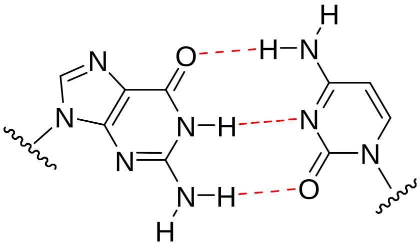
adenine guanine Uracil cytosine

SOLUTION

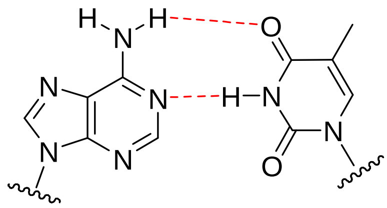
4.1

	H	P
Number of atoms:	11.3	1
theoretical wt %:	3.43	

4.2

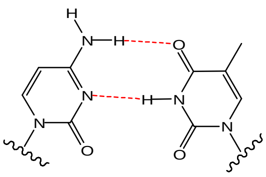


guanine cytosine

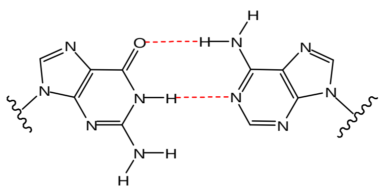


adenine thymine

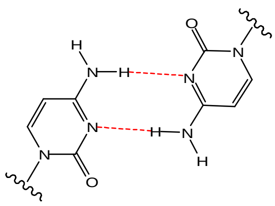
4.3



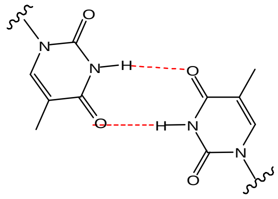
cytosine thymine



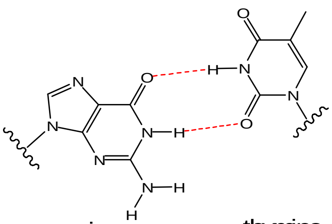
guanine adenine



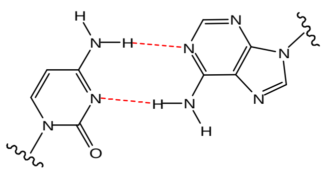
cytosine cytosine



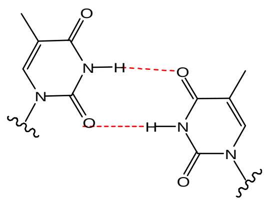
thymine thymine



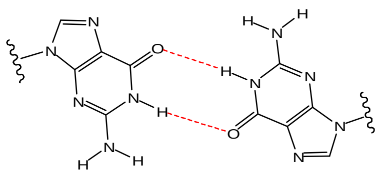
guanine thymine



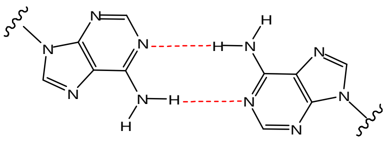
cytosine adenine



thymine thymine

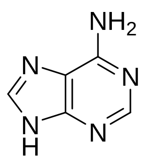
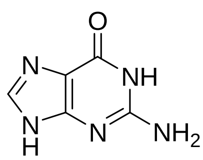
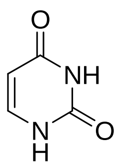
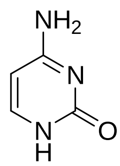


guanine guanine



adenine adenine

4.4

				
	adenine	guanine	Uracil	cytosine
HCN	(**5**)	(**5**)	(**4**)	(**4**)
H_2O	(**0**)	(**1**)	(**2**)	(**1**)

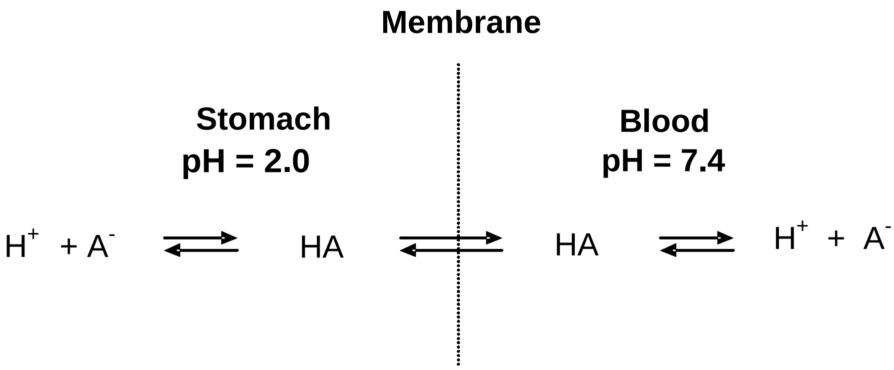
PROBLEM 5

Acid-Base Chemistry

5.1 Calculate $[H^+]$, $[OH^-]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in a 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0\times10^{-14}$, $K_2 = 1.2\times10^{-2}$ at 25 °C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.

5.2 Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm^3 aqueous solution containing 3.48 cm^3 of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm^3, M_r = 98.00) (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.44).

5.3 The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ([HA] + $[A^-]$) of aspirin (acetylsalicylic acid, pK = 3.52) in the blood to that in the stomach.

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SOLUTION

5.1 1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$[H_2SO_4] = 0$

2nd ionization: $[H^+][SO_4^{2-}] / [HSO_4^-] = K_2 = 1.2\times10^{-2}$ (1)

Mass balance: $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}] = 1.0\times10^{-7}$ (2)

Charge balance: $[H^+] = [HSO_4^-] + 2\,[SO_4^{2-}] + [OH^-]$ (3)

Degree of ionization is increased upon dilution.

$[H_2SO_4] = 0$

Assume $[H^+]_{H_2SO_4} = 2\times10^{-7}$

From (1): $[SO_4^{2-}] / [HSO_4^-] = 6\times10^4$ (2nd ionization is almost complete)

$[HSO_4^-] = 0$

From (2): $[SO_4^{2-}] = 1.0\times10^{-7}$

From (3): $[H^+] = (2\times10^{-7}) + 10^{-14} / [H^+]$

$[H^+] = 2.4\times10^{-7}$ (pH = 6.6)

$[OH^-] = 1\times10^{-14} / (2.4\times10^{-7}) = 4.1\times10^{-8}$

From (1):

$[HSO_4^-] = [H^+]\,[SO_4^{2-}] / K_2 = (2.4\times10^{-7}) \times (1.0\times10^{-7}) / (1.2\times10^{-2}) = 2.0\times10^{-12}$

Check charge balance:

$2.4\times10^{-7} \approx (2.0\times10^{-12}) + 2\,(1.0\times10^{-7}) + (4.1\times10^{-8})$

Check mass balance:

$0 + 2.0\times10^{-12} + 1.0\times10^{-7} \approx 1.0\times10^{-7}$

5.2 $n(H_3PO_4) = 0.85 \times 3.48\ cm^3 \times 1.69\ g\ cm^{-3} \times 1\ mol / 98.00\ g \times 1000 = 51.0\ mmol$

The desired pH is above pK_2.

A 1:1 mixture of $H_2PO_4^-$ and HPO_4^{2-} would have $pH = pK_2 = 7.20$.

If the *pH* is to be 7.40, there must be more HPO_4^{2-} than $H_2PO_4^-$.

We need to add NaOH to convert H_3PO_4 to $H_2PO_4^-$ and to convert to the right amount of $H_2PO_4^-$ to HPO_4^{2-}.

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

The volume of 0.80 NaOH needed to react with to convert H_3PO_4 to $H_2PO_4^-$ is:

51.0 mmol / 0.80 mol dm^{-3} = 63.75 cm^3

To get *pH* of 7.40 we need:

	$H_2PO_4^-$	+ OH^- →	HPO_4^{2-}
Initial mmol	51.0	x	0
Final mmol	51.0 – x	0	x

$pH = pK_2 + \log\,[HPO_4^{2-}] / [H_2PO_4^-]$

$7.40 = 7.20 + \log \{x / (51.0 – x)\}$; x = 31.27 mmol

The volume of NaOH needed to convert 31.27 mmol is:

31.27 mmol / 0.80 mol dm^{-3} = 39.09 cm^3

The total volume of NaOH = 63.75 + 39.09 = 102.84 cm^3 ≈ 103 cm^3

5.3 $pK = 3.52$

$pH = pK_a + \log ([A^-] / [HA])$

$[A^-] / [HA] = 10^{(pH-pKa)}$

In blood, $pH = 7.40$, $[A^-] / [HA] = 10^{(7.40-3.52)} = 7586$

Total ASA = 7586 + 1 = 7587

In stomach, $pH = 2.00$, $[A^-] / [HA] = 10^{(2.00 - 3.52)} = 3.02\times10^{-2}$

Total ASA = 1 + 3.02×10^{-2} = 1.03

Ratio of total aspirin in blood to that in stomach = 7587 / 1.03 = 7400

PROBLEM 6

Electrochemistry

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

6.1 Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic. Write a balanced half-reaction for the reduction of water.

6.2 Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write a balanced half-reaction for the oxidation of water.

6.3 When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis. Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

6.4 Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+ 0.340
Reduction of oxygen	– 2.710
Reduction of water	– 0.830
Reduction of sodium ion (Na^+)	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $Cu(OH)_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25 °C. Note that $K_w = 1.00 \times 10^{-14}$ at 25 °C.

6.5 Precipitation of $Cu(OH)_2$ begins at pH = 4.84. Determine the solubility product of $Cu(OH)_2$.

6.6 Calculate the standard reduction potential for $Cu(OH)_2(s) + 2 e^- \rightarrow Cu(s) + 2 OH^-$.

6.7 Calculate the electrode potential at *pH* = 1.00.

Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge recharge cycles, the following reversible half-reactions occur.

$LiCoO_2 \rightleftarrows Li_{1-x}\,CoO_2 + x\,Li^+ + x\,e^-$

$C + x\,Li^+ + x\,e^- \rightleftarrows CLi_x$

The total amount of energy a battery can store, is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

6.8 Graphite has lithium intercalation sites between its layers. Assuming a maximum 6 : 1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.

SOLUTION

6.1 $4 H_2O + 4 e^- \rightarrow 2 H_2(g) + 4 OH^-$ (or $2 H_2O + 2 e^- \rightarrow H_2(g) + 2 OH^-$)

6.2 $2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^-$ (or $H_2O \rightarrow 1/2\ O_2 + 2 H^+ + 2 e^-$)

6.3 $Cu \rightarrow Cu^{2+} + 2e^-$

6.4 Reduction of sodium ion seldom takes place.

It has a highly negative reduction potential of –2.710 V.

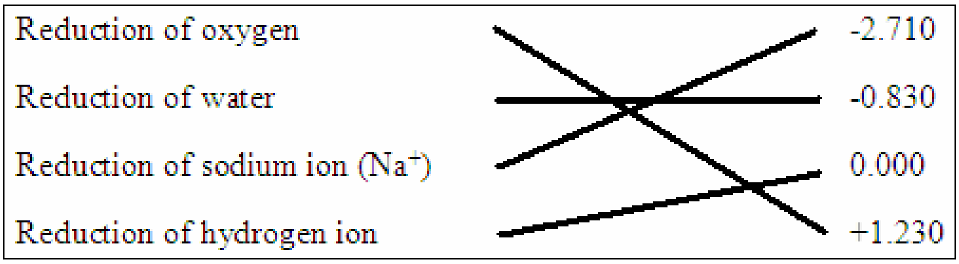
Reduction potential for water to hydrogen is negative (water is very stable).

But, it is not as negative as that for sodium ion. It is –0.830 V.

Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.

In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.

Reduction potential for hydrogen ion is defined as 0.000 V.



6.5 pOH = 14.00 – 4.84 = 9.16

$[OH^-] = 6.92\times10^{-10}$

$K_{sp} = [Cu^{2+}]\,[OH^-]^2 = 0.100 \times (6.92\times10^{-10}) = 4.79\times10^{-20}$

6.6 $E = E^o(Cu^{2+}/\,Cu) + (0.0592 / 2) \log [Cu^{2+}] = +0.340 + (0.0592/2) \log [Cu^{2+}] =$

$= +0.340 + (0.0592 / 2) \log (K_{sp} / [OH^-]^2)$

$= +0.340 + (0.0592 / 2) \log K_{sp} - (0.0592 / 2) \log [OH^-]^2$

$= +0.340 + (0.0592 / 2) \log K_{sp} - 0.0592 \log [OH^-]$,

By definition, the standard potential for

$Cu(OH)_2(s) + 2\ e^- \rightarrow Cu(s) + 2\ OH^-$

is the potential where $[OH^-] = 1.00$.

$E = E^o\left(Cu(OH)_2 / Cu\right) = + 0.340 + (0.0592/2) \log K_{sp}$

$= + 0.340 + (0.0592 / 2) \log (4.79\times10^{-20})$

$= + 0.340 – 0.572$

$= – 0.232$ V

One may solve this problem as follows.

Eqn 1: $Cu(OH)_2(s) + 2\ e^- \rightarrow Cu + 2\ OH^-$

$E_+^o = E^o\big(Cu(OH)_2 / Cu\big) = ?$

Eqn 2: $Cu(OH)_2(s) \rightarrow Cu^{2+} + 2\ OH^-$

$E^o = (0.05916 / n) \log K_{sp} = (0.05916 / 2) \log(4.79\times10^{-20}) = -\ 0.5715\ V$

Eqn 1 – Eqn 2 : $Cu^{2+} + 2\ e^- \rightarrow Cu$

$E_-^o = E_+^o - E^o = E^o\,(Cu^{2+} / Cu) = 0.34\ V$

Therefore, $E_+^o = E_-^o + E^o = + 0.34 + (-0.5715) = = -0.232\ V$

6.7 Below pH = 4.84, there is no effect of $Cu(OH)_2$ because of no precipitation.

Therefore,

$E = E\,(Cu^{2+} / Cu) = +0.340 + (0.0592 / 2) \log [Cu^{2+}] =$

$= +0.340 + (0.0592 / 2) \log 0.100 = +0.340 - 0.0296 = +0.310\ V$

6.8 1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge 96487 $\times$ 0.0139 = 1340 coulombs.

1340 coulombs / g = 1340 A sec / g = 1340 $\times$ 1000 mA $\times$ (1 / 3600) h =

= 372 mAh / g

PROBLEM 7

Hydrogen Economy

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7.1 Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, estimate the density of hydrogen in the cylinder in kg m^{-3}.

7.2 Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. ΔH_f^o [H_2O(l)] = -286 kJ/mol, ΔH_f^o [CO_2(g)] = -394 kJ/mol.

7.3 Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by [$1 - T_{cold}/T_{hot}$].

S^o_{298}[H_2(g)] = 131 J mol^{-1} K^{-1}

S^o_{298}[O_2(g)] = 205 J mol^{-1} K^{-1}

S^o_{298}[H_2O(l)] = 70 J mol^{-1} K^{-1}

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

SOLUTION

7.1 $$\frac{n}{V} = \frac{p}{RT} = \frac{80\times10^6 \text{ Pa}}{8,314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 32 \text{ kmol m}^{-3}$$

$$\rho = \frac{m}{V} = 32 \text{ kmol m}^{-3} \times 2 \text{ kg kmol}^{-1} = 64 \text{ kg m}^{-3}$$

7-2. $Hg_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta H_{rexn\text{-}1} = \Delta H_f\,[H_2O(l)] = -286\text{ kJ mol}^{-1} = -143\text{ kJ g}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H_{rexn\text{-}2} = \Delta H_f\,[CO_2(g)] = -394\text{ kJ mol}^{-1} = -33\text{ kJ g}^{-1}$

$$\frac{(-\Delta H_{rexn-1})}{(-\Delta H_{rexn-2})} = 4.3 \quad \text{or} \quad \frac{(-\Delta H_{rexn-2})}{(-\Delta H_{rexn-1})} = 0.23$$

7.3 $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$\Delta H_c = -286\text{ kJ mol}^{-1} = -143\text{ kJ g}^{-1} = -143\times10^3\text{ kJ kg}^{-1}$

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

$\Delta S_c = 70 - 131 - 205/2 = -163.5\text{ J mol}^{-1}\text{ K}^{-1}$

$\Delta G_c = -286\text{ kJ mol}^{-1} + 298\text{ K} \times 163.5\text{ J mol}^{-1}\text{ K}^{-1} = -237\text{ kJ mol}^{-1} = -1.2\times10^5\text{ kJ kg}^{-1}$

(a) electric motor: $W_{\max} = \Delta G_c \times 1\text{ kg} = -1.2\times10^5\text{ kJ}$

(b) heat engine: $W_{\max} = \text{efficiency} \times \Delta H_c$

$= (1 - 298 / 573) \times (-143\times10^3\text{ kJ}) = -6.9\times10^4\text{ kJ}$

$119\times10^3\text{ kJ} = 1\text{ W} \times t(\text{sec})$

$t = 1.2\times10^8\text{ s} = 3.3\times10^4\text{ h} = 1.4\times10^3\text{ days} = 46\text{ month} = 3.8\text{ yr}$

$\Delta G = -n\,F\,E$ n = number of electrons involved in the reaction

$F = 96.5\text{ kC mol}^{-1}$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ n = 2

$$E = \frac{-\Delta G}{n\,F} = \frac{237\text{ kJ mol}^{-1}}{2\times96.5\text{ kC mol}^{-1}} = 123\text{ V}$$

$$I = \frac{W}{E} = 0.81\text{ A}$$

PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

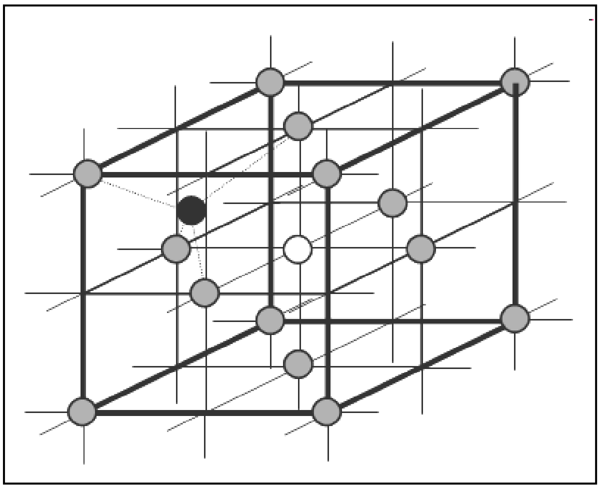
Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

$C(s) + O_2(g) \rightarrow CO_2(g)$	ΔH^0 = –393.51 kJ(/mol)	(1)
$CO_2(g) + C(s) \rightarrow 2\ CO(g)$	ΔH^0 = 172.46 kJ(/mol)	(2)
$Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$	ΔH^0 = ?	(3)

8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(Fe_2O_3(s))$ = –824.2 kJ mol^{-1},
S°(J mol^{-1} K^{-1}): Fe(s) = 27.28, Fe_2O_3(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO_2(g) = 213.74

In the manufacture of celadon pottery, Fe_2O_3 is partially reduced in a charcoal kiln to mixed oxides of Fe_3O_4 and FeO. The amount of the different oxides seems to be related to the "mystic" color of celadon ceramics. Fe_3O_4 (magnetite) itself is a mixed oxide containing Fe^{2+} and Fe^{3+} ions and belongs to a group of compounds with a general formula of AB_2O_4. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.



8.3 How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

8.4 What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4?

8.5 Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

8.1 (1): C (2): C (3): CO

8.2 Balanced equation (3): $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0_{(1)} = -393.51\ kJ = \Delta H_f^0\ (CO_2(g))$

(2) $CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0_{(2)} = 172.46\ kJ$

From (1) and (2):

$\Delta H_f^0(CO(g)) = (1/2)\ \{172.46 + (-393.51)\} = -110.525\ kJ$

$\Delta H_f^0(Fe_2O_3) = –824.2$ kJ

$\Delta H^0_{(3)} = 3 \times \Delta H_f^0(CO_2(g)) – \Delta H_f^0(Fe_2O_3) – 3 \times \Delta H_f^0(CO(g))$

$= [3 \times (–393.51)] – (–824.2) – [3 \times (–110.525)] = –24.8$ kJ

$\Delta S°_{(3)} = (2 \times 27.28) + (3 \times 213.74) – 87.4 – (3 \times 197.674) = 15.36$ J K^{-1}

$\Delta G^0_{(3)} = \Delta H^0 – T\Delta S^0 = –24.8$ kJ – (15.36 J K^{-1} × 1 kJ /1000 J × 1473.15 K) =

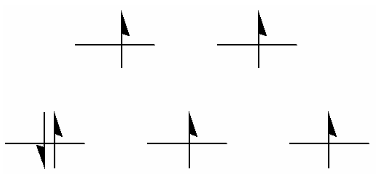
= – 47.43 kJ

$$K = e^{(-\Delta G°/RT)} = e^{(47430\,J\ /\ (8.314\ J\ K^{-1} \times 1473.15\,K))} = 48$$

8.3 One AB_2O_4 unit has available 4 (= 1 + (1/4 × 12) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) × 100 % = 12.5 % occupancy in available tetrahedral sites.

8.5

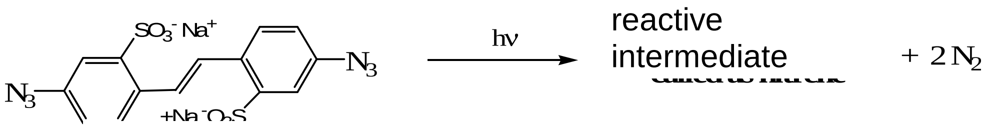


PROBLEM 9

Photolithographic process

Photolithography is a process used in semiconductor device fabrication to transfer a pattern from a photomask to the surface of a substrate. In a typical photolithography process, light is projected, through a mask that defines a particular circuitry, onto a silicon wafer coated with a thin layer of photoresist.

The earliest photoresists were based on the photochemistry that generates a reactive intermediates from bis(aryl azide). Patterning becomes possible through the cross-linking reaction of the nitrenes generated from the azides.



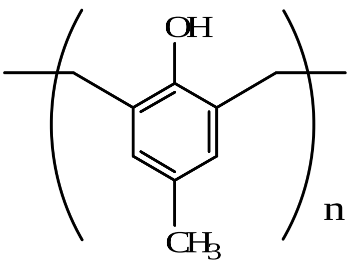
Bis(aryl azide)

9.1 Draw two possible Lewis structures of CH_3-N_3, the simplest compound having the same active functional group of bis(aryl azide). Assign formal charges.

9.2 Draw the Lewis structure of nitrene expected from CH_3-N.

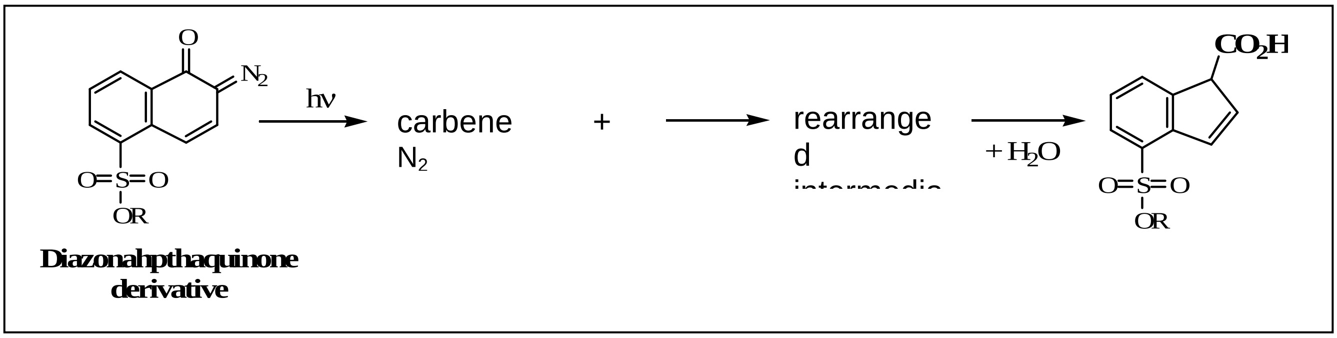
9.3 Draw the structures for two possible products, when this nitrene from CH_3-N_3 reacts with ethylene gas (CH_2CH_2).

Photoresists consisting of Novolak polymers, utilizes acid to change their solubility. The acid component can be produced photochemically from diazonaphthaquinone. In fact, “Novolaks” have been the representative “positive” photoresists of the modern microelectronic revolution.



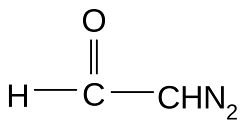
Novolak

When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.



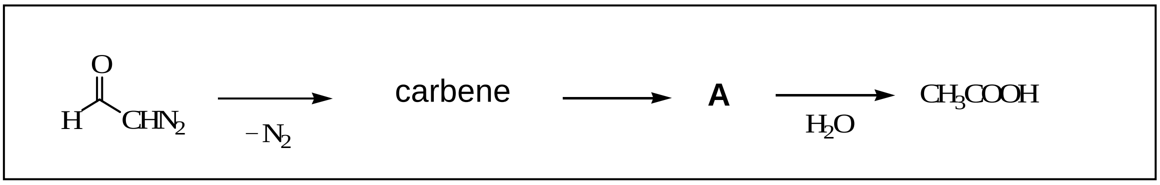
9.4 Draw three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.

Diazonaphthaquinone derivative

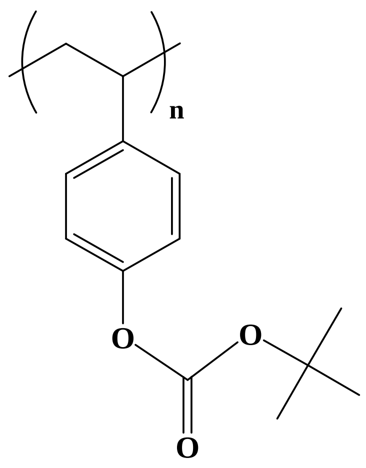


diazoacetaldehyde

9.5 Draw a Lewis structure of the rearranged intermediate, A (see below), generated from diazoacetaldehyde after losing N_2. A satisfies Lewis' octet rule and reacts with water to form acetic acid, CH_3COOH.

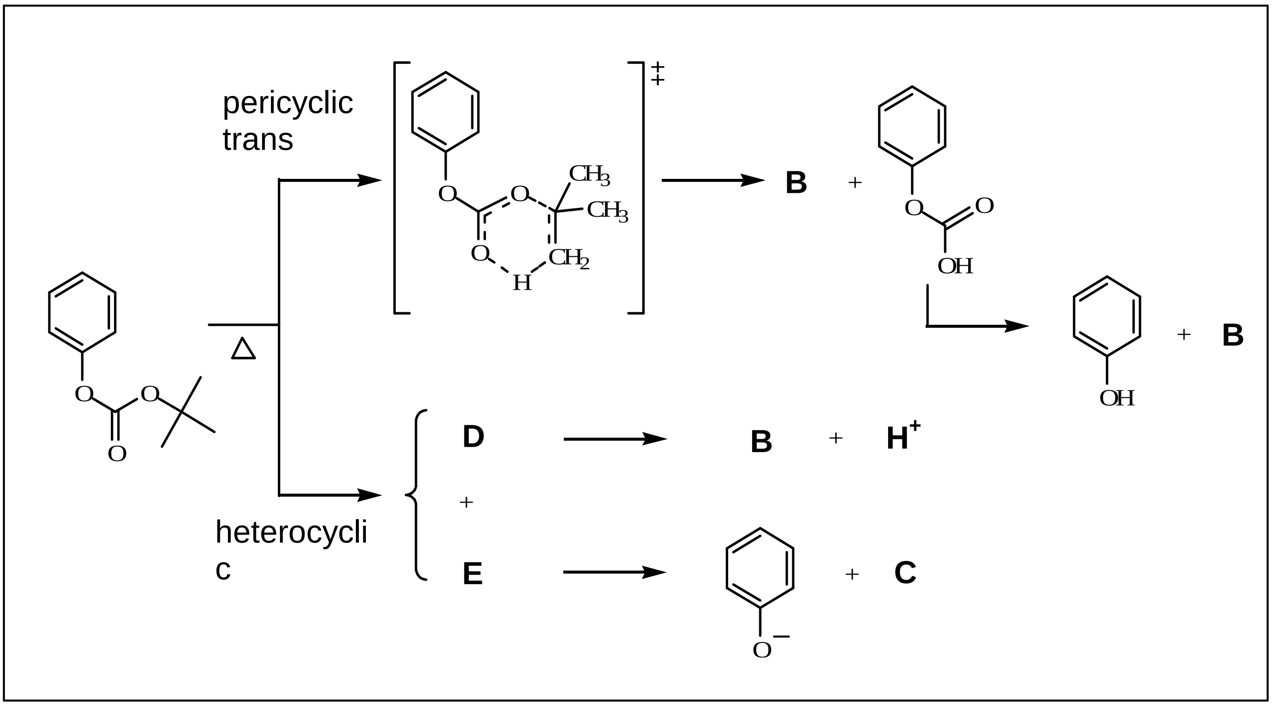


Advanced photoresists were invented in 1982 based on chemical amplification. The most popular chemical amplification for positive-tone involves the acid catalyzed deprotection of poly(*p*-hydroxystyrene) resin protected by various acid-sensitive protecting groups such as *t*-butyloxycarbonyl (*t*-BOC).

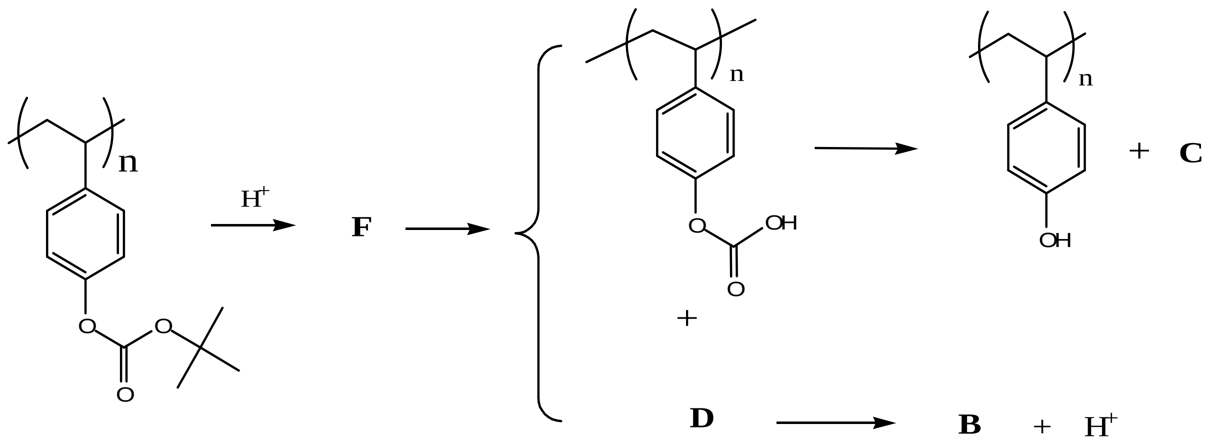


The thermal decomposition of carbonate ester itself normally occurs well above 150 °C.

9.6 Two plausible mechanisms have been suggested for this decomposition reaction having relatively high activation energy. Draw expected intermediates and products from this reaction.

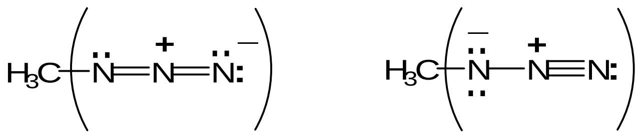


9.7 In the presence of a trace amount of acid, the reaction temperature can be reduced to below 100 °C. Draw expected intermediate F from the following chemical amplification process based on using *t*-BOC.

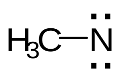


SOLUTION

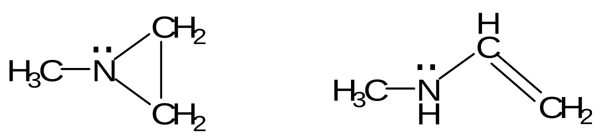
9.1



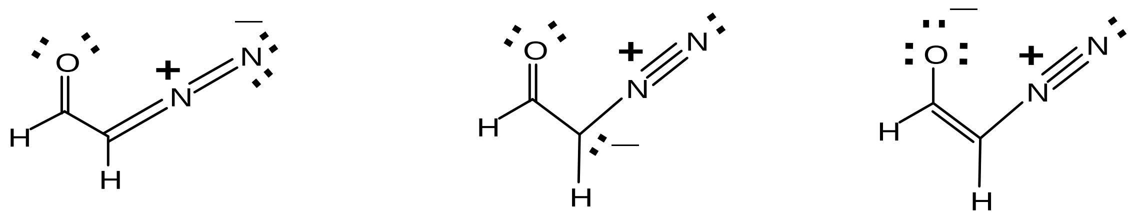
9.2



9.3



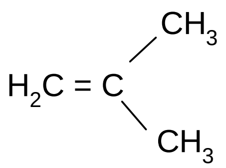
9.4



9.5

$O = C = CH_2$

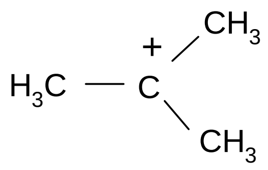
9.6



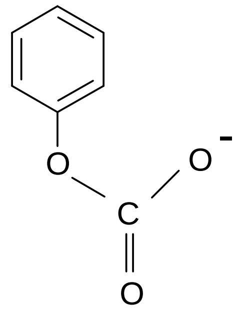
B

CO_2

C

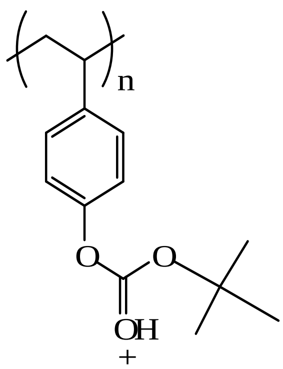


D



E

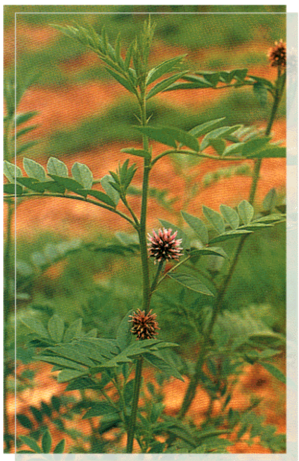
9.7



F

PROBLEM 10

Natural Products – Structural Analysis



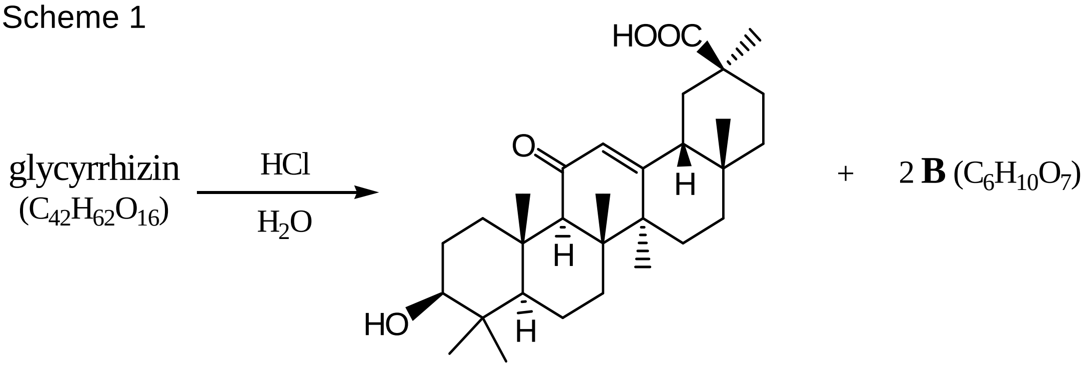
Licorice (Glycyrrhizia. Uralensis)

Licorice Root

The flavour extracted from the licorice root is 50 – 150 times sweeter than table sugar. The most important and abundant compound responsible for the sweetness and medicinal effects of licorice is *glycyrrhizin* ($C_{42}H_{62}O_{16}$).

Glycyrrhizin requires three equivalents of NaOH to effect neutralization. When *glycyrrhizin* was subjected to acid hydrolysis, *Glycyrrhizinic acid* (**A** ($C_{30}H_{46}O_4$)) and **B** ($C_6H_{10}O_7$) were obtainned in a 1:2 molar ratio (Scheme 1).

Scheme 1



A (Glycyrrhizinic acid)

When *glycyrrhizin* was methylated with methyl iodide (MeI) at every possible site before hydrolysis, hydrolysis produced **A'** (methyl glycyrrhizinate), **C** and **D** (Scheme 2). **B**, **C** and **D** exist as mixtures of anomers.

Scheme 2

$$\underset{(C_{42}H_{62}O_{16})}{\text{glycyrrhizin}} \xrightarrow[\text{ii) HCl / }H_2O]{\text{i) MeI, }Ag_2O} \mathbf{A'}\ (C_{31}H_{48}O_4) \quad + \quad \mathbf{C}\ (C_9H_{16}O_7) \quad + \quad \mathbf{D}\ (C_{10}H_{18}O_7)$$

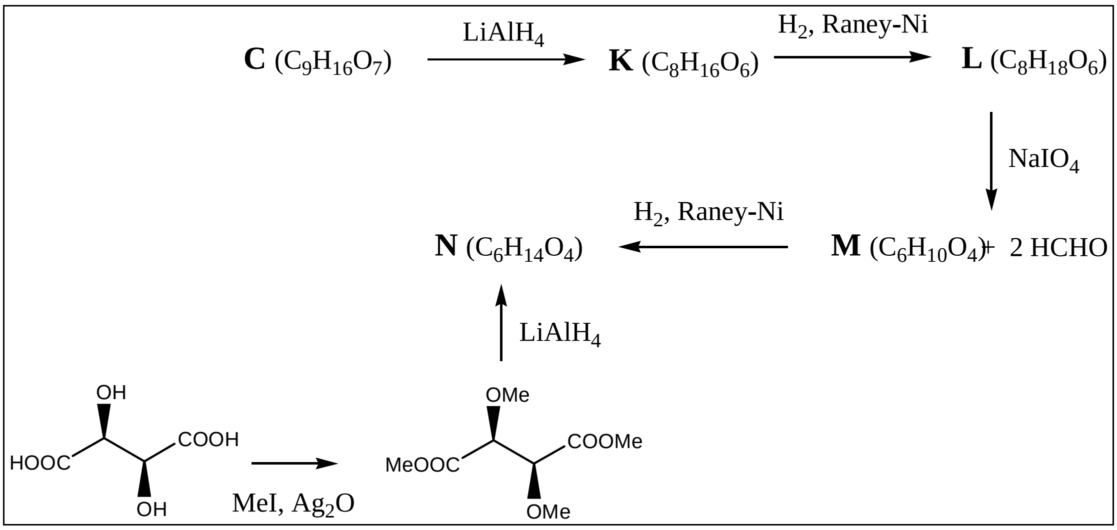
Methylation of **C** and **D** with MeI produced the same isomeric mixture of compounds, **J** (Scheme 3).

Scheme 3

$$\mathbf{C}\ (C_9H_{16}O_7) \xrightarrow{\text{MeI, }Ag_2O} \mathbf{J}\ (C_{11}H_{20}O_7) \xleftarrow{\text{MeI, }Ag_2O} \mathbf{D}\ (C_{10}H_{18}O_7)$$

C was reduced with $LiAlH_4$ to give **K**, and **L** was produced by the reduction of **K**. Oxidative cleavage of vicinal diol of **L** with $NaIO_4$ produced **M** and two equivalents of formaldehyde. Reduction of **M** produced **N**. The structure and stereochemistry of **N** was confirmed by the synthesis of **N** from D-(-)-tartaric acid through methylation followed by reduction (Scheme 4). A ^{1}H-NMR spectrum of **L** showed two distinct peaks for methyl groups. (There is no symmetry in L)

Scheme 4



10.1 <u>Complete</u> structures for **L , M, and N** in the answer sheet.

10.2 How many structures for **C** are possible? <u>Complete</u> possible structures for **C**.

To determine the correct structure of **C**, following set of reactions were performed. **J** was reduced to **E,** and acid hydrolysis of **E** produced **F**. Reduction of **F** generated **G,** and **G** was oxidized with $NaIO_4$ to **H** with formation of one equivalent of formaldehyde. **I** was obtained from **H** through reduction. Among all compounds from **A** to **I**, only **I** was optically inactive (Scheme 5).

Scheme 5

$$\mathbf{J}\ (C_{11}H_{20}O_7) \xrightarrow{LiAlH_4} \mathbf{E}\ (C_{10}H_{20}O_6) \xrightarrow[H_2O]{HCl} \mathbf{F}\ (C_9H_{18}O_6) \xrightarrow{H_2,\ \text{Raney-Ni}} \mathbf{G}\ (C_9H_{20}O_6)$$

$$\mathbf{G}\ (C_9H_{20}O_6) \xrightarrow{NaIO_4} \mathbf{H}\ (C_8H_{16}O_5) + HCHO$$

$$\mathbf{I}\ (C_8H_{18}O_5) \xleftarrow{H_2,\ \text{Raney-Ni}} \mathbf{H}\ (C_8H_{16}O_5)$$

optically inactive

10.3 Complete structures for **G** and **I**.

10.4 Which one is the correct structure for **C** among ones you have drawn in **10-2**?

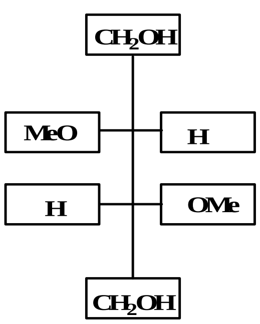
10.5 Complete structures for **B, D,** and **J**.

10.6 Complete the structure for Glycyrrhizin.

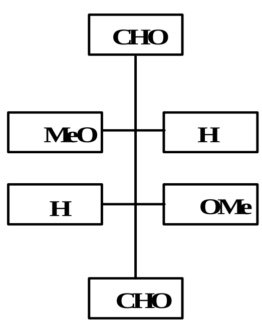
SOLUTION

10.1

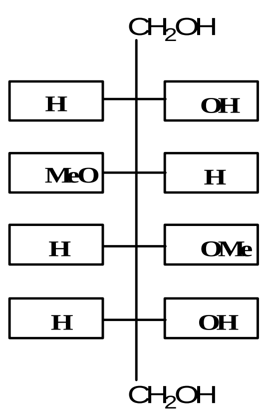
N



M

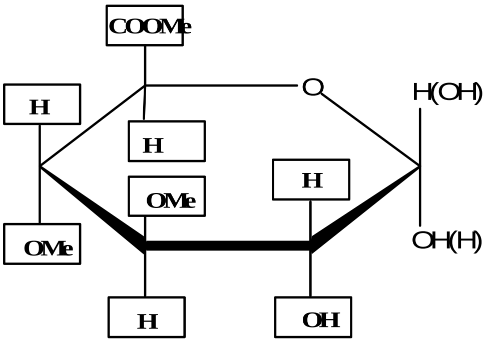


L

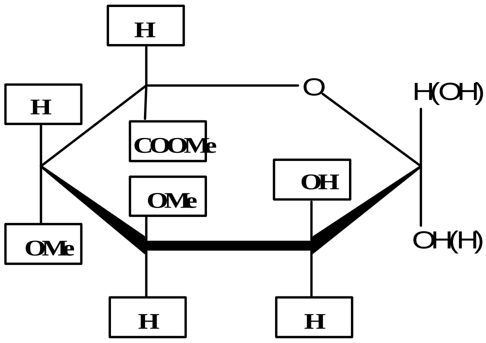


10.2 Number of possible structures **2**

1

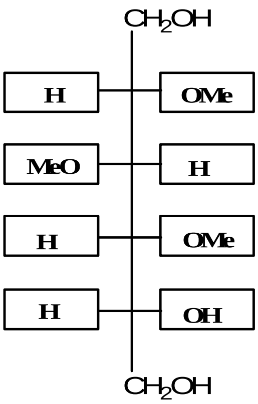


2

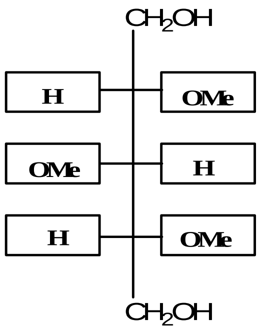


10.3

G



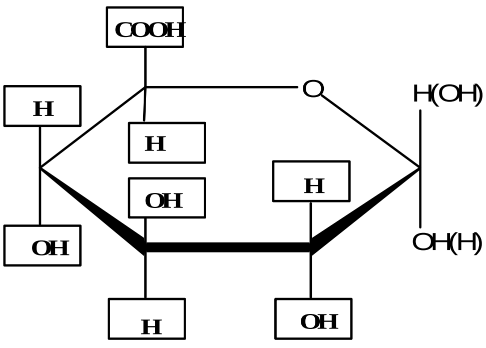
I



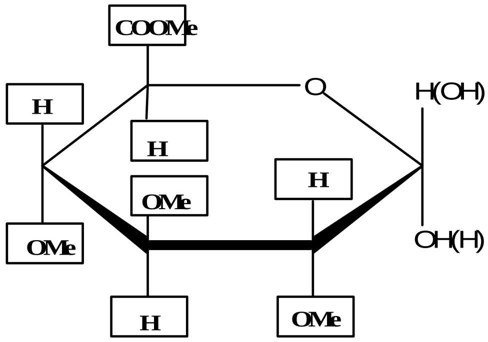
10.4

The correct structure for **C** from 10-2 is No. 1

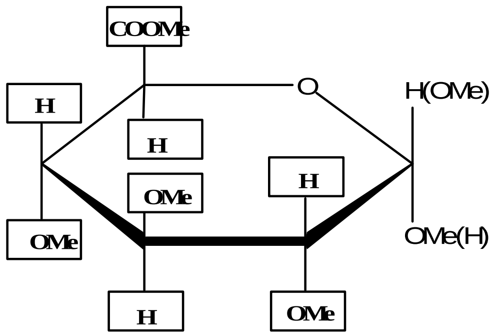
10.5 **B**



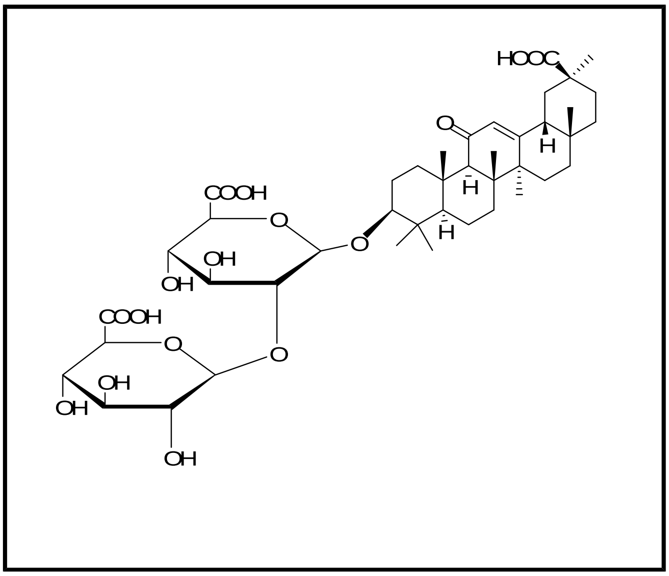
D


COOMe
H
H
OMe
H
H(OH)
OH(H)
OMe
H
OMe
O

J


COOMe
H
H
OMe
H
H(OMe)
OMe(H)
OMe
H
OMe
O

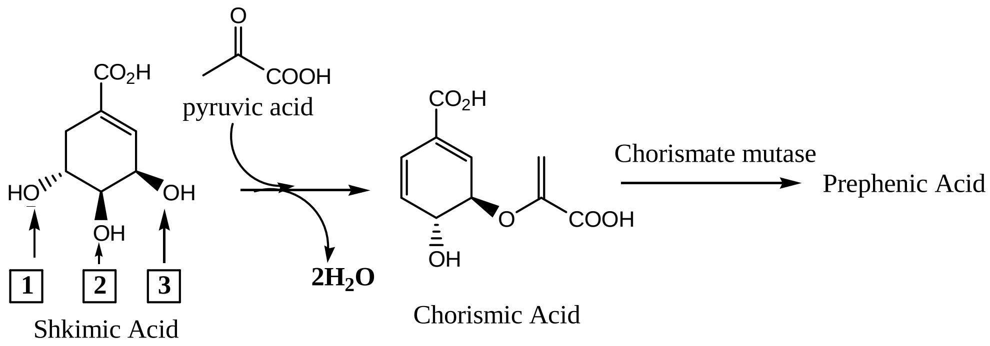
10.6


HOOC
O
H
H
H
COOH
O
OH
OH
O
COOH
O
O
OH
OH
OH

PROBLEM 11

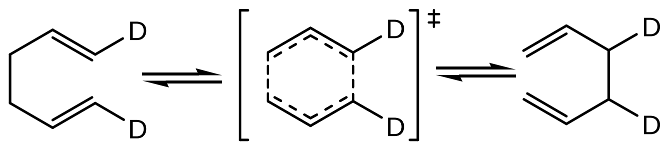
Enzyme Reaction

Shikimic acid biosynthesis is an important pathway for amino acids, alkaloids and heterocyclic natural product production. Nature converts shikimic acid to chorismic acid through a cascade of enzymatic reactions. Then chorismate mutase catalyzes the conversion of chorismic acid to prephenic acid at the branch point for the biosynthesis of aromatic amino acids such as tyrosine and phenylalanine.



11.1 During the transformation of shikimic acid to chorismic acid, dehydration is occurring. Choose the hydroxyl group in shikimic acid that is lost through above dehydration among all possible reactions.

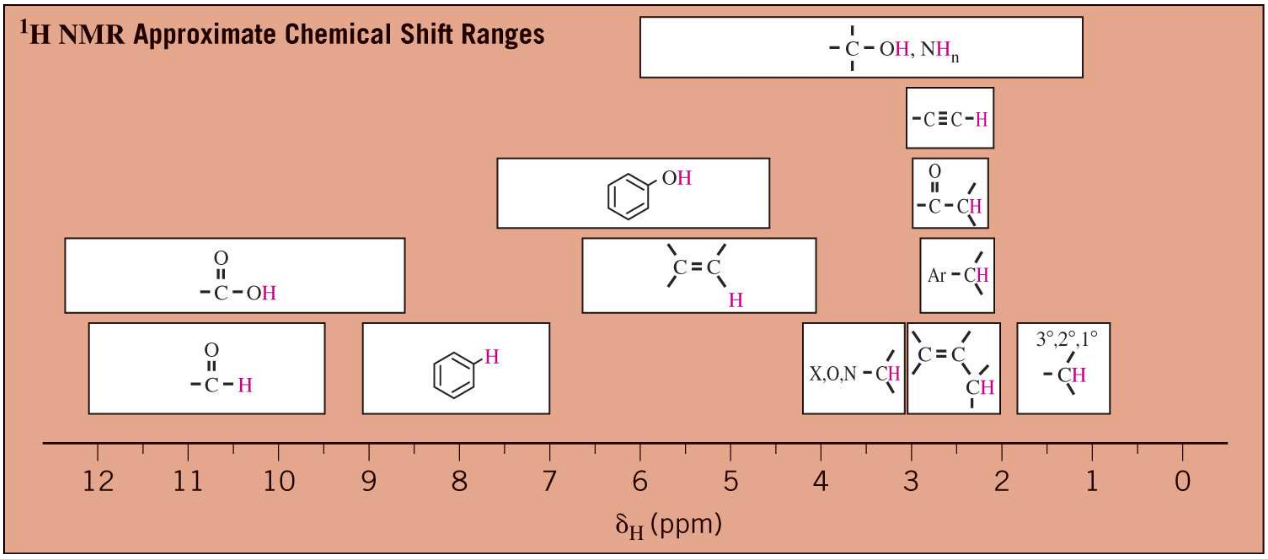
11.2 Chorismate mutase rearranges chorismic acid into prephenic acid without changing the molecular formula. Chorismic acid becomes prephenic acid through the Claisen rearrangement, a concerted pericyclic process like the Cope rearrangement as shown below:



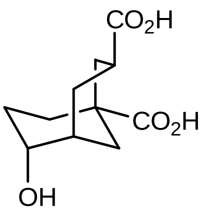
Based on the following spectral data, propose the structure of prephenic acid.

^{1}H-NMR (D_2O, 250 MHz): δ 6.01 (2H, d, J = 10.4 Hz), 5.92 (2H, dd J = 10.4, 3.1 Hz), 4.50 (1H, t, J = 3.1 Hz), 3.12 (2H, s). Note that there are three protons, which have been exchanged by D_2O very fast, and two protons at δ 3.12, which are exchanged slowly in prephenic acid. ^{13}C-NMR (D_2O, 75 MHz): δ 203, 178, 173, 132 (for two identical carbons), 127 (for two identical carbons), 65, 49, 48.

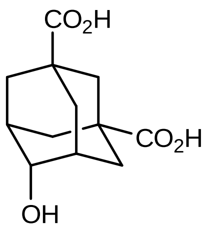
δ, chemical shift; H, integrals; d, doublet; dd, doublet of doublet; J, coupling constant; t, triplet; s, singlet



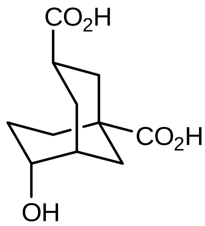
Chorismate mutase is believed to stabilize the transition state of Claisen rearrangement. Thus it is an interesting target for inhibitor design. Inhibitors, called transition state analog (TSA)s that resemble the transition state (TS, *e.g.*, the species in brackets "[ ]" above) of the reaction are designed to occupy the active site. Several inhibitors were designed and synthesized, and among them eight turned out to be potent inhibitors of the enzyme. The lower is the IC_{50} (inhibitor concentration of 50 % of the enzymatic activity) value, the better is the inhibitor.



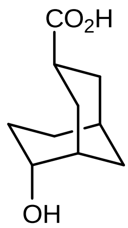
1
IC_{50} = 2.5 mM



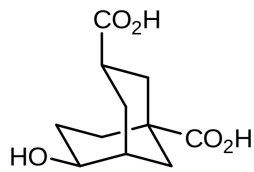
2
IC_{50} = 1.3 mM



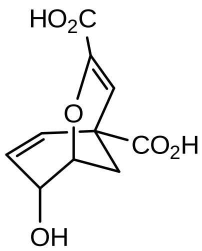
3
IC_{50} = 0.78 mM



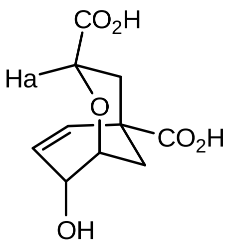
4
IC_{50} = 1.1 mM



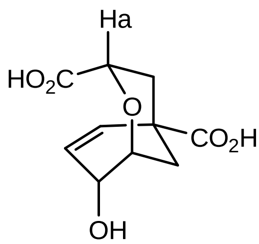
5
IC_{50} = 5.3 mM



6
IC_{50} = 0.017 mM



7
IC_{50} =0.0059 mM



8
IC_{50} = 0.00015 mM

11.3 Choose all correct statements based on the structures and IC_{50} values of above inhibitors. Increase of factor 5 is considered to be important.

(a) Configuration of the hydroxyl group plays an important role in the TS and inhibitor design.

(b) The presence of both carboxylic groups is important in the TS and inhibitor design.

(c) Transition state of the reaction contains two six-membered rings with one chair and one twist-boat conformation.

(d) **7** and **8** can be distinguished on the basis of the ^{1}H-NMR of H_a.

11.4 Draw the transition state of the transformation of chorismic acid to prephenic acid based on the TSA structures and their IC_{50} values.

11.5 Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid 1.0×10^6 fold at 25 °C by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at 25 °C.

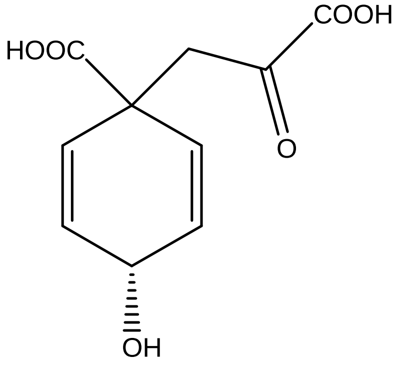
$\Delta H^{\neq}_{uncat}$ is 86,900 J mol^{-1} for the thermal conversion of chorismic acid to prephenic acid. At what temperature will the rate of the *uncatalyzed* thermal conversion be the same as that of the *enzyme-catalyzed* conversion at 25 °C, assuming that $E_a = \Delta H^{\neq}$.

____

SOLUTION

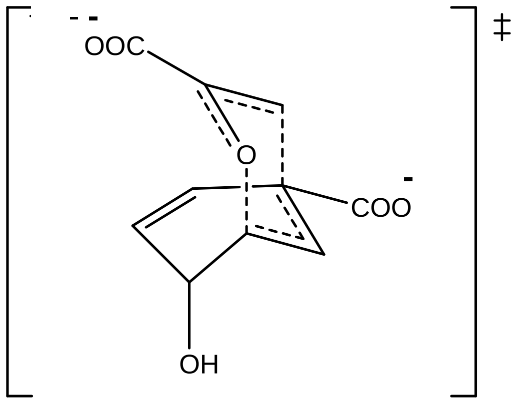
11.1 Hydroxyl group No. 3

11.2



11.3 Correct statements: (a), (c), (d).

11.4



Transition state

11.5 For the enzyme-catalyzed reaction, Arrhenius equation could be applied.

$$\frac{k_{cat}}{k_{uncat}} = \frac{A\ \exp\ (-E_{a,\ cat}\ /\ \mathrm{RT})}{A\ \exp\ (-E_{a,\ uncat}\ /\ \mathrm{RT})} = \exp\ [-\Delta E_{a,\ \text{cat-uncat}}\ /\ RT] =$$

$$= \frac{\exp\ (-\Delta E_{a,\ \text{cat}-\text{uncat}}\ (\mathrm{J\ mol^{-1}})}{2{,}480\ \mathrm{J\ mol^{-1}}} = 1\times10^{6}$$

Therefore, $-\Delta E_{a,\ \text{cat-uncat}}$ = 34,300 J mol^{-1}

$$\frac{k_{\text{uncat, T}}}{k_{\text{uncat, 298}}} = \frac{A\ \exp\ (-\Delta H^{\neq}{}_{\text{uncat}}\ /\ RT\ )}{A\ \exp\ (-\Delta H^{\neq}{}_{\text{uncat}}\ /\ 298\ R)} = \exp\left[\left(\frac{-\Delta H^{\neq}{}_{\text{uncat}}}{R}\right)\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$\frac{k_{\text{uncat, T}}}{k_{\text{uncat, 298}}} = 13.8 = \exp\left[\left(\frac{-86900}{8.32}\right)\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

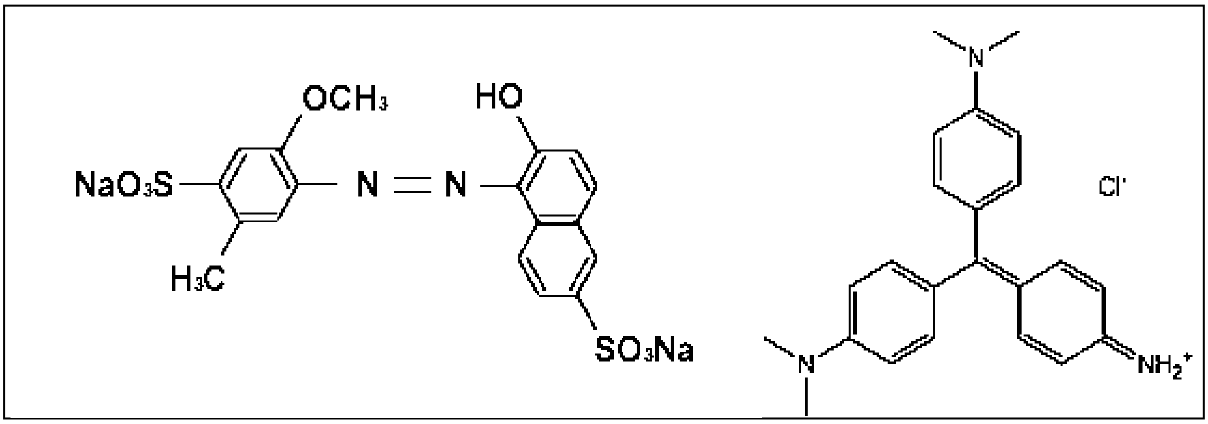
Therefore, T = 491 K, or 218 ^{o}C

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Reverse-phase Chromatography: Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the non-polar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



Food Red No. 40 Methyl Violet 2B

1.1 Spectrophotometric Analysis of R and B in a Mixed Solution

a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1.1).

b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1.1.

c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1.2 Chromatographic Separation Followed by Spectrophotometric Analysis

a) Elute the cartridge with about 10 cm^3 of Solution E using 10 cm^3 syringe (Fig. C).

b) Load 1.00 cm^3 of solution MD onto the cartridge (Fig. D).

c) Using 1 cm^3 syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 cm^3 volumetric flask. Repeat until the red compound is completely eluted and collected.

d) Fill the flask to the 10 cm^3 mark with Solution E and mix. Call this Solution F.

e) Obtain the absorption spectrum of solution F as in Experiment 1.1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1.1 in red ink.

f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1.2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.

g) Report the concentration of R in the original Solution MD.

h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.

PROBLEM 2 (Practical)

Reverse-phase Chromatography:

Acid-Base Titration of Acetic Acid and Salicylic Acid

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

a) Titrate 10 cm^3 of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 cm^3 of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.

b) Standardize NaOH solution with 2.00 cm^3 of the standard KHP (potassium hydrogen phthalate) solution (1.00×10^{-2} M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.

c) Withdraw 1.00 cm^3 of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 cm^3 of Solution MA.

2-2. Reverse-phase Separation and Titration

a) Elute a new C-18 cartridge with about 10 cm^3 of distilled water using 10 cm^3 syringe.

b) Load 1.00 cm^3 of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).

c) Elute with 1 cm^3 of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 cm^3 liquid in each tube.

d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.

e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.

f) Calculate the mole percent of AA in solution MA.

PROBLEM 3 (Practical)

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

Procedure

Helpful Comments

a) The weight of a spatula tip-full of a solid is about 15~20 mg.

b) Wipe spatula cleanly with Kimwipe between uses.

c) After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.

d) To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 cm^3 of CH_3CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 cm^3 of 95 % EtOH. (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulphuric acid and 95% ethanol (labelled as 2,4-DNPH).

Test 3: CAN test

Mix 3 cm^3 of the cerium(IV) ammonium nitrate solution in dilute HNO_3 (labelled as CAN) with 3 cm^3 of CH_3CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 cm^3 of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water first, and then add 1 cm^3 of CAN.) If there is a colour change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Bayer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of CH_3CN. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) To the solution, slowly add five drops of the 0.5 % $KMnO_4$ solution, drop by drop while shaking.

Test 5: *pH* test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of 95 % EtOH. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water). Measure the pH of the solution with pH paper.

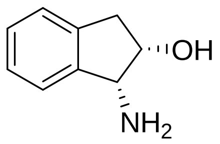
Test 6: Iron(III) chloride test

Take the solution from Test 5 and add five drops of a 2.5 % $FeCl_3$ solution.

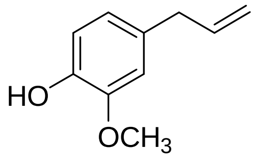
Results

1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.
2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

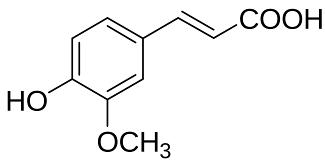
Possible Unknown Compounds (next page):



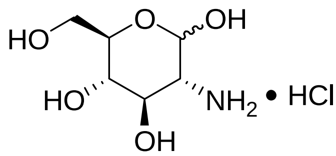
(A)



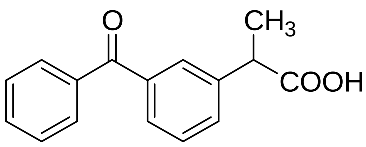
(E)



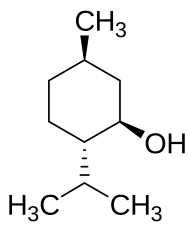
(F)



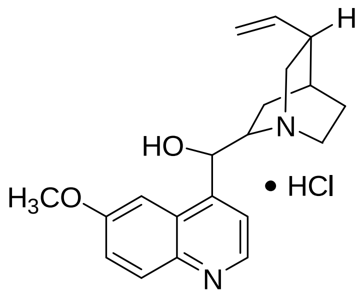
(G)



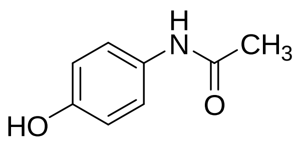
(K)



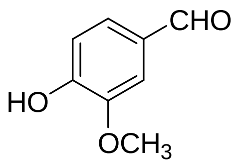
(M)



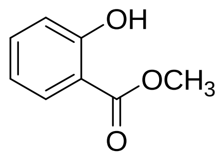
(Q)



(T)



(V)



(W)