Country:	Language:

37th IChO Theoretical Examination

- use only the pen provided

- time	5 hours
- problem booklet	26 pages (including this cover sheet)
- answer sheets:	28 pages (including cover sheet, and fives pages at the end with only a box. Use if necessary. Write down the problem number inside the box
- draft paper (will not be marked):	5 sheets (more are available on request)
- total number of points:	279 (They are equally weighted in the final score)
- your name and student code	write on every answer sheet
- atomic masses	use only the periodic system given
- constants	use only the values given in the table
- answers	only in the appropriate boxes of the answer sheets. Nothing else will be marked
- questions ask for show works	no point will be given to no showing work
- restroom break	ask your supervisor
- official English-language version	available on request, for clarification only, ask your supervisor.
- after the stop signal	put your answer sheets in the correct order (if they aren't), put them in the envelope (don't seal), deliver them at the exit
- examination booklet	keep it, together with the pen and calculator.

G O O D   L U C K

Country:	Language:

Periodic table of elements
with atomic masses / u

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.01																	**2 He** 4.00
3 Li 6.94	**4 Be** 9.01											**5 B** 10.81	**6 C** 12.01	**7 N** 14.01	**8 O** 16.00	**9 F** 19.00	**10 Ne** 20.18
11 Na 22.99	**12 Mg** 24.31											**13 Al** 26.98	**14 Si** 28.09	**15 P** 30.97	**16 S** 32.07	**17 Cl** 35.45	**18 Ar** 39.95
19 K 39.10	**20 Ca** 40.08	**21 Sc** 44.96	**22 Ti** 47.88	**23 V** 50.94	**24 Cr** 52.00	**25 Mn** 54.94	**26 Fe** 55.85	**27 Co** 58.93	**28 Ni** 58.69	**29 Cu** 63.55	**30 Zn** 65.39	**31 Ga** 69.72	**32 Ge** 72.61	**33 As** 74.92	**34 Se** 78.96	**35 Br** 79.90	**36 Kr** 83.80
37 Rb 85.47	**38 Sr** 87.62	**39 Y** 88.91	**40 Zr** 91.22	**41 Nb** 92.91	**42 Mo** 95.94	**43 Tc** 98.91	**44 Ru** 101.07	**45 Rh** 102.91	**46 Pd** 106.42	**47 Ag** 107.87	**48 Cd** 112.41	**49 In** 114.82	**50 Sn** 118.71	**51 Sb** 121.76	**52 Te** 127.60	**53 I** 126.90	**54 Xe** 131.29
55 Cs 132.91	**56 Ba** 137.3	57-71	**72 Hf** 178.49	**73 Ta** 180.95	**74 W** 183.84	**75 Re** 186.21	**76 Os** 190.23	**77 Ir** 192.22	**78 Pt** 195.08	**79 Au** 196.97	**80 Hg** 200.59	**81 Tl** 204.38	**82 Pb** 207.19	**83 Bi** 208.98	**84 Po** 208.98	**85 At** 209.99	**86 Rn** 222.02
87 Fr 223	**88 Ra** 226	89-103	**104 Rf** 261	**105 Db** 262	**106 Sg** 263	**107 Bh** 264	**108 Hs** 265	**109 Mt** 268									

57-71	**57 La** 138.91	**58 Ce** 140.12	**59 Pr** 140.91	**60 Nd** 144.24	**61 Pm** 144.92	**62 Sm** 150.36	**63 Eu** 151.96	**64 Gd** 157.25	**65 Tb** 158.93	**66 Dy** 162.50	**67 Ho** 164.93	**68 Er** 167.26	**69 Tm** 168.93	**70 Yb** 173.04	**71 Lu** 174.97
89-103	**89 Ac** 227	**90 Th** 232	**91 Pa** 231	**92 U** 238	**93 Np** 237	**94 Pu** 244	**95 Am** 243	**96 Cm** 247	**97 Bk** 247	**98 Cf** 251	**99 Es** 252	**100 Fm** 257	**101 Md** 258	**102 No** 259	**103 Lr** 262

Fundamental Constants, Equations and Conversion Factors

Atomic mass unit	$1\ amu = 1.6605 \times 10^{-27}\ kg$
Avogadro's number	$N = 6.02 \times 10^{23}\ mol^{-1}$
Boltzmann's constant	$k = 1.3806503 \times 10^{-23}\ J\ K^{-1}$
Electron charge	$e = 1.6022 \times 10^{-19}\ C$
Faraday's constant	$F = 9.6485 \times 10^{4}\ C\ mol^{-1}$
Gas constant	$R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.08205\ L \cdot atm\ K^{-1}\ mol^{-1}$
Mass of electron	$m_e = 9.11 \times 10^{-31}\ kg$
Mass of neutron	$m_n = 1.67492716 \times 10^{-27}\ kg$
Mass of proton	$m_p = 1.67262158 \times 10^{-27}\ kg$
Planck's constant	$h = 6.63 \times 10^{-34}\ J\ s$
Speed of light	$c = 3 \times 10^{8}\ m\ s^{-1}$

Nernst equation (T = 298 K)	$E = E° - (0.0592 / n)\ \log K$
Arrhenius equation	$k = Ae^{-Ea/RT}$
Clausius-Clapeyron equation	$\ln P = -\Delta H_{vap} / RT + B$
De Broglie relation	$\ = h / mv$
Ideal gas equation	$PV = nRT$
Free energy	$G = H - TS$

$E = h\nu$

$\Delta G = \Delta G° + RT \ln Q$ $\Delta G = -nFE$

$\Delta U = q + w$ $w = -P\Delta V$

$V(cylinder) = \pi r^2 h$

$V(sphere) = 4/3\ \pi r^3$

$A(sphere) = 4\ \pi r^2$

$1\ \ = 10^{-10}\ m$	$1\ W = 1\ J\ s^{-1}$
$1\ J = 1\ kg\ m^2\ s^{-2}$	$1\ cal = 4.184\ J$
$1\ Pa = 1\ kg\ m^{-1}\ s^{-2} = 1\ N\ m^{-2}$	$1\ bar = 10^{5}\ Pa$

$1\ atm = 1.01325 \times 10^{5}\ Pa = 760\ mmHg\ (torr)$

$1\ eV\ /\ molecule = 96.4853\ kJ\ mol^{-1}$

Standard atmosphere	= 101325 Pa	
RT at 298.15 K	= $2.4790\ kJ\ mol^{-1}$	
Pi (π)	= 3.1415927	

Problem 1: Chemistry of Amides and Phenols

Total Scores: 38 points

	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8
Points	4	4	4	4	6	4	8	4

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms *N,N*-dimethylformamide (DMF), which can be described as the following resonance structures.

1-1 *Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide (CH$_3$CONHCH$_3$, compound **B**), and propionamide (CH$_3$CH$_2$CONH$_2$, compound **C**). Express your answer from high to low melting point as follows:*

____ > ____ > ____   *(Insert compound codes **A**, **B**, **C**)*

1-2 *Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.*
(a) 1660 cm^{-1} because of the shorter carbonyl bond length
(b) 1660 cm^{-1} because of the longer carbonyl bond length
(c) 1740 cm^{-1} because of the shorter carbonyl bond length
*(d) 1740 cm^{-1} because of the longer carbonyl bond length*

1-3   *Glycine (H_2N-CH_2-COOH) is an α-amino acid.   Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules.   Draw the structural formula of this tripeptide.*
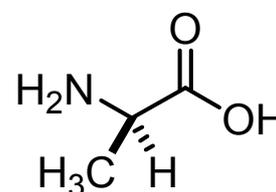
1-4   *When an α-amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers.   What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?*
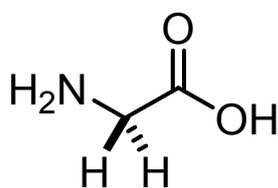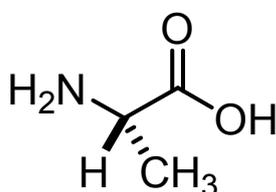
Glycine (Gly)   **L-Alanine (L-Ala)**   **D-Alanine (D-Ala)**

1-5   *Among the tripeptides synthesized in 1-4, how many are optically active?*

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids.   However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography.   The phenol compounds bearing different substituents have varied acidities.   The higher acidity results in stronger binding to PAGE gel.
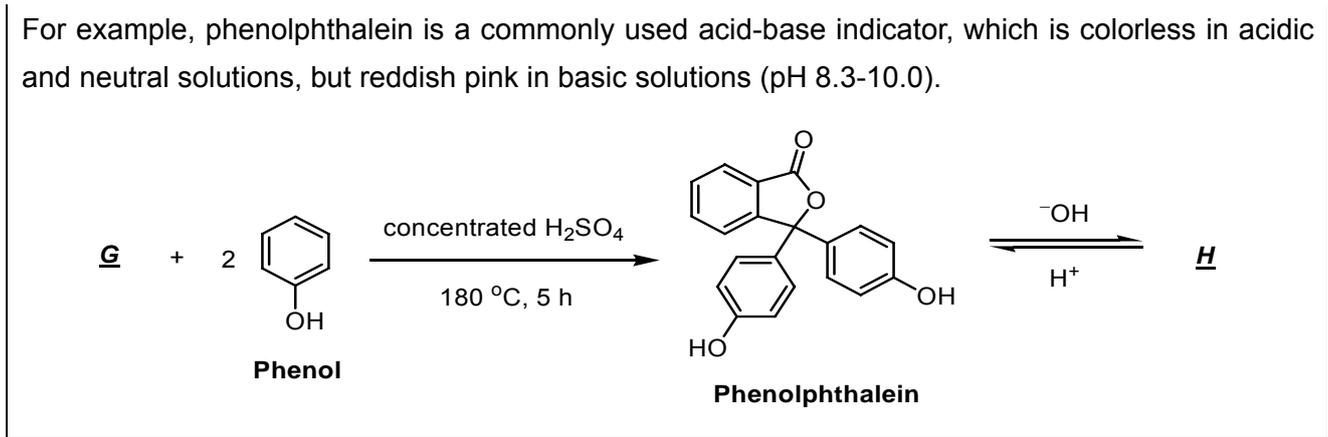
1-6   *Predict the binding affinity of phenol (compound D), 4-methylphenol (compound E) and 4-nitrophenol (compound F) with a polyamide gel.   Express your answer from high to low binding affinity as follows:*

　　_____ > _____ > _____   *(Insert compound codes D, E, and F)*

The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain.   A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary color.

For example, phenolphthalein is a commonly used acid-base indicator, which is colorless in acidic and neutral solutions, but reddish pink in basic solutions (pH 8.3-10.0).

**G** + 2 Phenol →(concentrated H_2SO_4, 180 °C, 5 h)→ **Phenolphthalein** ⇌(^-OH / H^+) **H**

Phenol   Phenolphthalein

For translation: concentrated

1-7 **Draw the structural formula of *H* derived from phenolphthalein that is attributable to the reddish pink color in aqueous NaOH solution.**

1-8 **A simple way to prepare phenolphthalein is via condensation of compound *G* with 2 equivalents of phenol. What is the most effective reagent for *G* to accomplish this transformation?   Select your answer from the following compounds.**
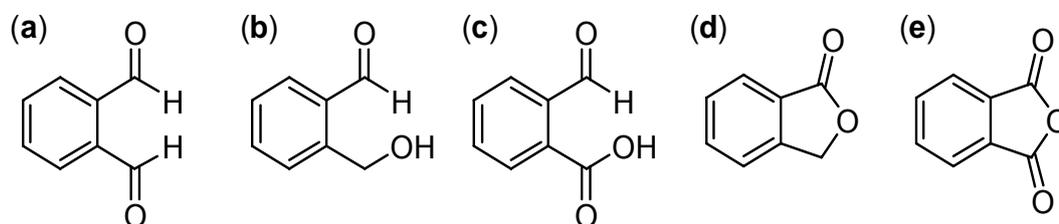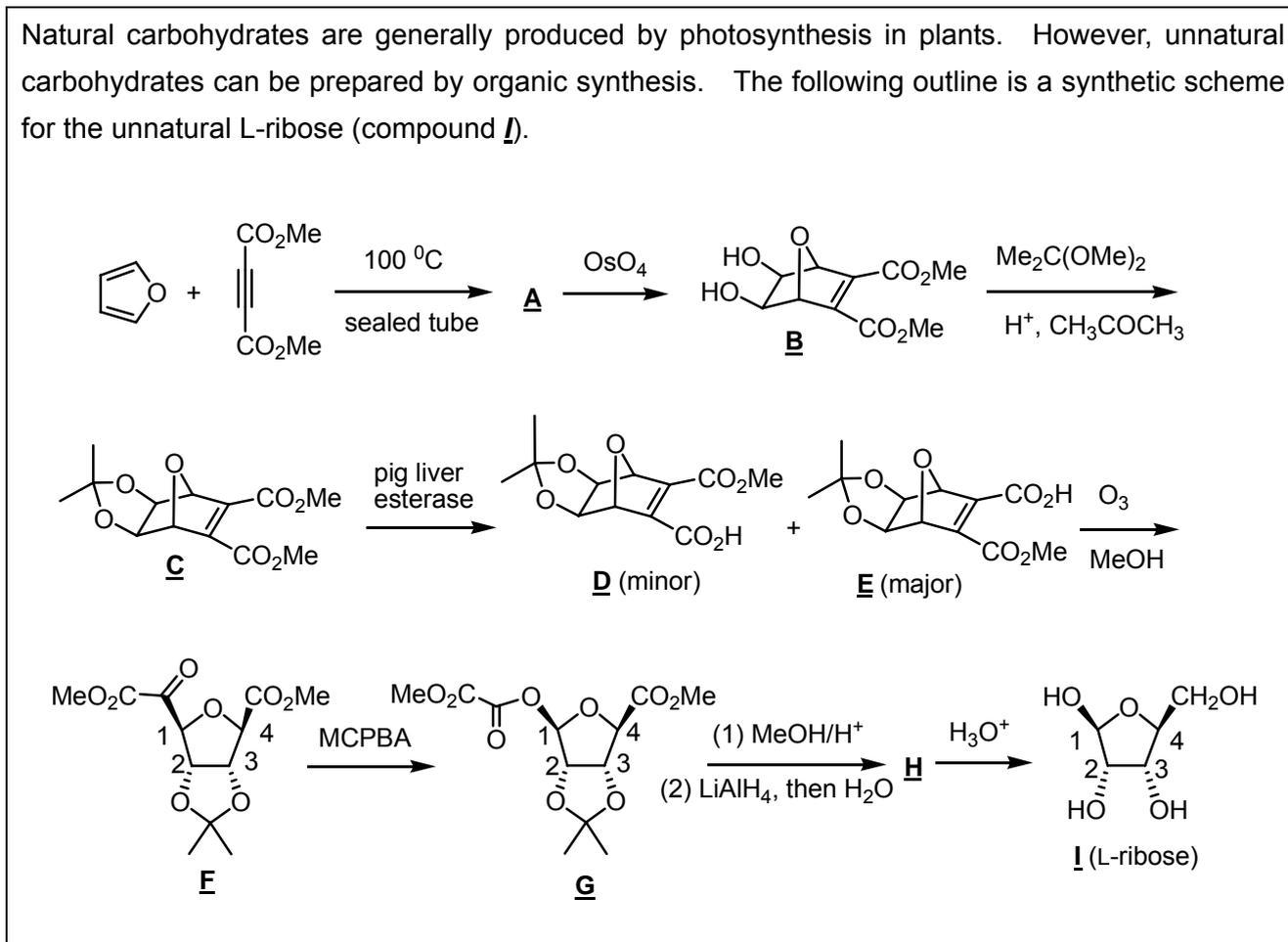
Problem 2: Organic Synthesis and Stereochemistry

Total Scores: 48 points

	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8
Points	4	8	6	6	6	8	6	4

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis.   The following outline is a synthetic scheme for the unnatural L-ribose (compound **I**).

For translation   sealed tube =   pig liver esterase =

(minor) =   (major) =

2-1   *Compound A has the molecular formula of $C_{10}H_{10}O_5$.   Draw the structural formula of A.*

2-2   *Given the chemistry described for reaction sequence A to C, indicate whether the following statements are true or false (Use T to represent true and F to represent false).*

    (a) OsO₄ is an oxidizing agent in the reaction of __A__ to __B__.

    (b) MeOH is generated as a by-product in the reaction of __B__ to __C__.

    (c) Protons act as the catalyst in the transformation of __B__ to __C__.

    (d) __C__ will still be formed albeit in lower yields in the absence of Me₂C(OMe)₂.

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20}$ = -37.1°. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20}$ = -49.0°.

2-3   *What is the molar ratio of __D/E__ in the product mixture before the recrystallization? Show your work.*

2-4   *Reaction of __F__ with meta-chloroperbenzoic acid (MCPBA) afforded __G__ as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).*

    (a) The reaction was to oxidize compound __F__.

    (b) The oxygen atom inserted originated from MCPBA.

    (c) The R/S notation of C-1 remained unchanged before and after the reaction.

The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows:

^{1}H NMR (CDCl₃) δ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, *J* = 6 Hz, 1H), 4.74 (d, *J* = 6 Hz, 1H), 4.89 (s, 1H).
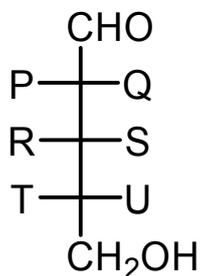

2-5   *Draw the configurational formula of __H__.*

2-6   *Assign R/S notations for compound __I__ at C-1, C-2, C-3 and C-4.   Give your answers as follows:*
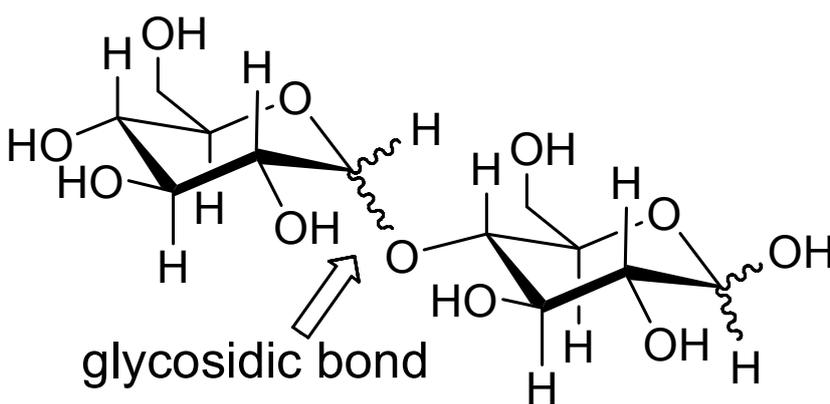
    C-1: ____; C-2: ____; C-3: ____; C-4: ____.

2-7 *What are the identities of P, Q, R, S, T and U in the Fischer projection of compound I (L-ribose)?*

$$
\begin{array}{c}
\text{CHO} \\
\text{P} \!-\!\!\!-\!\!\!-\! \text{Q} \\
\text{R} \!-\!\!\!-\!\!\!-\! \text{S} \\
\text{T} \!-\!\!\!-\!\!\!-\! \text{U} \\
\text{CH}_2\text{OH}
\end{array}
$$

Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:

glycosidic bond

2-8 How many diastereoisomers would be obtained for pentasaccharide J, if it is derived from five units of D-glucose?
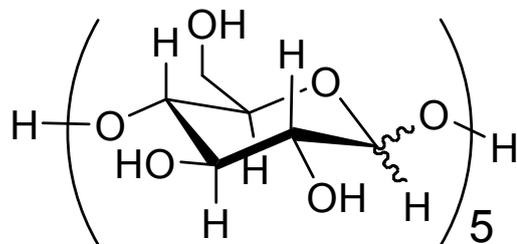
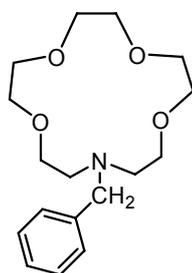pentasaccharide **J** derived from D-glucose

Problem 3: Organic Photochemistry and Photophysics

Total Scores: 36 points

	3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8
Points	8	4	4	4	4	4	4	4

Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns **A** and **B** exhibit different binding constants for Na^+, K^+, and Cs^+.

A   **B**
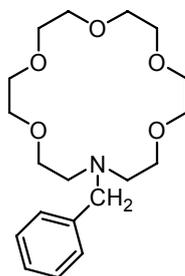
		Binding constant ($\log_{10} K$)	
Metal ion	Radius (pm)	Compound **A**	Compound **B**
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

For translation: Binding constant   Metal ion

     Radius (pm)   Compound

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

3-1 ***Provide the structural formula of C and D in the following synthesis.***

For translation: benzene: pyridine: toluene:

For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E, F, and G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.

F   **G**

3-2   *Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.*

(a) none of them   (b) E and F only   (c) G only   (d) all of them

3-3   *By adding one equivalent of potassium acetate into a dilute solution (10^{-5} M) of E, F, and G in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.*

(a) E   (b) F   (c) G

3-4 *Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.*

(a) sodium acetate   (b) potassium acetate   (c) cesium acetate   (d) doesn't make any difference

---

Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**.   Further oxidation of **I** gives phenanthrene.

For translation: [a]trans-Stilbene   [b]heat   [c]oxidation

3-5 *Draw the structural formula of compound **H**?*

3-6 *What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound **I**?*

Dihydroazulene derivative **J** exhibits interesting photochromic behavior.   Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**.   The vinylheptafulvene undergoes thermal reversion to dihydroazulene.

For translation: [a]heat

3-7 *Which compound will absorb light with longer wavelength? Select your answer from the following choices.*

(a) J   (b) K

3-8 *Compound K can react with one equivalent of CF_3CO_2H to generate a stable aromatic salt. Which position of K is most likely protonated? Select your answer from the following choices.*

(a) C-2   (b) C-3   (c) C-4   (d) C-5

Problem 4: Gold Capital of Asia

Total Score: 42 points

	4A-1	4A-2	4A-3	4A-4	4A-5	4A-6	4B-1	4B-2	4B-3	4B-4	4B-5
Points	2	4	4	2	6	2	2	2	2	8	8

A

Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy.   It was the site of one of the largest gold mines In Asia.   Accordingly, Chiufen is often referred to as the Gold Capital of Asia.   The compound KCN is traditionally used to extract gold from ore.   Gold dissolves in cyanide (CN^-) solutions in the presence of air to form $Au(CN)_2^-$, which is stable in aqueous solution.

$$4\,Au(s) +\ 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \rightleftharpoons 4\,Au(CN)_2^-(aq) + 4\,OH^-(aq)$$
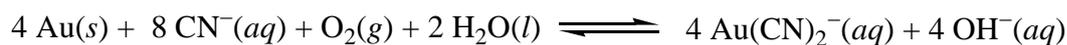
4A-1   Draw a structure for $Au(CN)_2^-$ showing the spatial arrangements of the atoms.

4A-2   How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

Aqua regia, a 3:1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to "dissolve" gold.   The process is actually a redox reaction with the following simplified chemical equation:
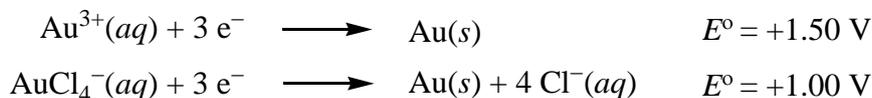
$$Au(s) +\ NO_3^-(aq) + Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + NO_2(g)$$
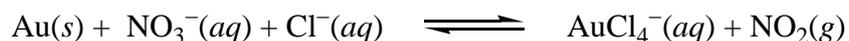
4A-3   Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4A-4   What are the oxidizing and reducing agents for 4A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion $AuCl_4^-$ forms. Consider the following half-reactions:

$$Au^{3+}(aq) + 3\ e^- \longrightarrow Au(s) \qquad E^o = +1.50\ V$$

$$AuCl_4^-(aq) + 3\ e^- \longrightarrow Au(s) + 4\ Cl^-(aq) \qquad E^o = +1.00\ V$$

An electrochemical cell can be formed from these two redox couples.

4A-5 *Calculate the formation constant for $AuCl_4^-$ at $25^{\circ}C$:*

$$K = [AuCl_4^-] / [Au^{3+}] [Cl^-]^4$$

4A-6 *The function of HCl is to provide Cl^-. What is the purpose of the Cl^- for the above reaction. Select your answer from the following choices.*
(a) Cl^- is an oxidizing agent
(b) Cl^- is a reducing agent
(c) Cl^- is a complexing agent
(d) Cl^- is a catalyst

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of $HAuCl_4$ is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of $NaBH_4$. Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4B-1 *Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.*
(a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
(b) bottom-up approach, which involves manipulating individual atoms and molecules

into nanostructures

4B-2 *The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry $AuCl_4^-$ from an aqueous phase to an organic phase. Which property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.*
(a) one side of the molecule is electropositive, the other side is electronegative.
(b) one side of the molecule is hydrophilic, the other side is hydrophobic.
(c) one side of the molecule is acidic, the other side is basic.

4B-3 *What is the function of $NaBH_4$ in this preparation? Select your answer from the following choices.*
(a) reducing agent
(b) oxidizing agent
(c) neutralization agent
(d) complexing agent

4B-4 *If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.*
(a) 10^2
(b) 10^3
(c) 10^4
(d) 10^5

4B-5 *What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.*
(a) 20-30%
(b) 40-50%
(c) 60-70%
(d) 80-90%

Problem 5: Lewis Structure

Total Score: 21 points

	5-1	5-2	5-3	5-4	5-5
Points	2	4	4	6	5

5-1 *Draw one Lewis structure for each of the following molecules.*
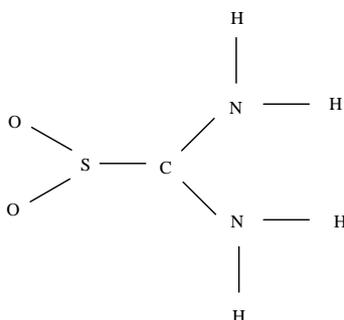
(a) N_2

(b) NH_3

(c) O_3

(d) SO_3

5-2 *Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.*

Thiourea-S,S-dioxide, $O_2SC(NH_2)_2$, has the following skeletal structure

---

5-3 *Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.*

5-4 *Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5-3?*

5-4a What is the geometry around the sulfur atom? Select your answer from the following choices.

(a) trigonal pyramidal

*(b) triangular planar*

(c) T-shape

5-4b *Similarly, what is the geometry around the C-atom? Select your answer from the following choices.*

(a) trigonal pyramidal

(b) triangular planar

(c) T-shape

5-4c *Finally, what is the geometry around the N-atom? Select your answer from the following choices.*

(a) trigonal pyramidal

(b) triangular planar

(c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:
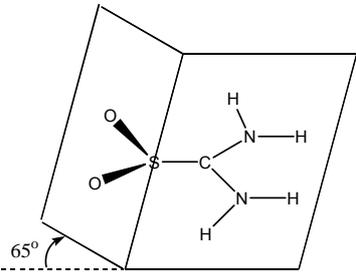
All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the $SC(NH_2)_2$ plane is $65°$.

5-5 *Draw the Lewis structure and resonance forms that are consistent with the geometry determined.*

Problem 6: Alkalinity of Water and Solubility of CO$_2$

Total Scores: 40 points

	6-1	*6-2*	*6-3*	*6-4*	*6-5*	*6-6*	*6-7*	*6-8*
Points	4	4	6	6	4	6	6	4

The capacity of water to accept H$^+$ ions is called alkalinity.   Alkalinity is important in water treatment and in the chemistry and biology of natural waters.   Generally, the basic species responsible for alkalinity in water are HCO$_3^-$, CO$_3^{2-}$, and OH$^-$.   At pH values below 7, H$^+$ in water detracts significantly from alkalinity.   Therefore, the complete equation for alkalinity in a medium where HCO$_3^-$, CO$_3^{2-}$, and OH$^-$ are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The contributions made by different species to alkalinity depend upon pH.   Relevant chemical equations and equilibrium constants (at 298 K) are shown below:

$$\text{CO}_{2(g)} \rightleftarrows \text{CO}_{2(aq)} \qquad\qquad K_{\text{CO}_2} = 3.44\text{x}10^{-2}$$

$$\text{CO}_{2(aq)} + \text{H}_2\text{O} \rightleftarrows \text{H}_2\text{CO}_3 \qquad\qquad K_{\text{H}_2\text{CO}_3} = 2.00\text{x}10^{-3}$$

$$\text{H}_2\text{CO}_3 \rightleftarrows \text{HCO}_3^- + \text{H}^+ \qquad\qquad K_{a1} = 2.23\text{x}10^{-4}$$

$$\text{HCO}_3^- \rightleftarrows \text{CO}_3^{2-} + \text{H}^+ \qquad\qquad K_{a2} = 4.69\text{x}10^{-11}$$

$$\text{CaCO}_{3(s)} \rightleftarrows \text{Ca}^{2+} + \text{CO}_3^{2-} \qquad\qquad K_{sp} = 4.50\text{x}10^{-9}$$

$$\text{H}_2\text{O} \rightleftarrows \text{H}^+ + \text{OH}^- \qquad\qquad K_w = 1.00\text{x}10^{-14}$$
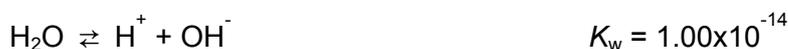
Note: Calculations must be shown.

6-1 *Natural waters (river or lake water) generally contain dissolved CO$_2$.   The ratio of [H$_2$CO$_3$] : [HCO$_3^-$] : [CO$_3^{2-}$] in a water at [H$^+$] = 1.00 × 10^{-7} M will be:*
     * (a)   : 1.00 :   (b) .   Calculate (a) and (b).*

6-2   *Gaseous CO_2 in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air.   Calculate the concentration of $CO_{2\,(aq)}$ (mol/L) in pure water that is in equilibrium with the unpolluted air at 1.01 x 10^5 Pa and 298 K containing 0.0360% (molar ratio) CO_2.* (assuming standard pressure = 1.01 x 10^5 Pa)
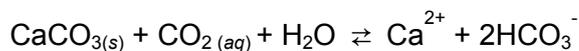
If you are unable to solve this problem, assume that concentration of $CO_{2\,(aq)}$ = $1.11x10^{-5}$ M for further calculations.

The solubility (S) of CO_2 in water can be defined as S = $[CO_{2(aq)}]$ + $[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$. The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01 x 10^5 Pa will vary with alkalinity.

6-3   *Find the solubility of atmospheric CO_2 in pure water (mol/L).   Neglect dissociation of water.*

6-4   *Find the solubility of atmospheric CO_2 in water (mol/L) initially containing $1.00x10^{-3}$ mol/L NaOH.*

At 298 K, 1.01 x 10^5 Pa unpolluted air is in equilibrium with natural water saturated with $CaCO_3$. The following main equilibrium may exist:

$$CaCO_{3(s)} + CO_{2\,(aq)} + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^-$$

6-5   *Calculate the equilibrium constant for the above equation.*

If you are unable to solve this problem, assume that equilibrium constant K_{eq} = $5.00x10^{-5}$ for further calculations.

6-6 *Calculate the concentration of Ca^{2+} (mg/L) in $CaCO_3$-saturated natural water that is in equilibrium with atmospheric CO_2.*

6-7 *Find the alkalinity (mol/L) of the above solution.*

6-8 *In an underground lake saturated with CaCO$_3$, the water has a high content of CO$_2$. The concentration of Ca^{2+} in this lake was found to be as high as 100 mg/L.   Assume the lake and the air above is a closed system, calculate the effective pressure of CO$_2$ (Pa) in air which is in equilibrium with this Ca^{2+} content.*

Problem 7: Kinetic Behavior of Ozone

Total Scores: 28oints

|	7-1	7-2	7-3	7-4	7-5
Points	6	6	6	4	6

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,

$$2O_3 \rightarrow 3O_2.$$

One of the proposed mechanisms is expressed as

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2 \qquad\qquad (1)$$

$$O_3 + O \xrightarrow{k_2} 2O_2 \qquad\qquad (2)$$
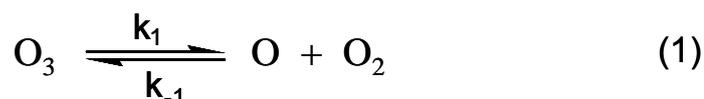
where k_1, k_{-1}, and k_2 are the rate constants.

7-1 *According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3, O_2, and O at time t, assuming step 2 is irreversible.*

7-2 *Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.*

7-3 *Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is d[O]/dt = 0, show that the rate equation is:*

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \rightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:

$$CCl_2F_2 \xrightarrow{\ h\nu\ } CF_2Cl + Cl \qquad (3)$$

7-4 *Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:*

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)} \qquad (4)$$

Assuming a two-step mechanism, propose the second step in the mechanism.

7-5 *The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ/mol, while the activation energy for the reaction without the presence of catalyst is 14.0 kJ/mol. Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25 °C. Assume the frequency factor is the same for each reaction.*

Problem 8: Protein Folding

Total Scores: 26 points

	8-1	8-2	8-3	8-4	8-5	8-6	8-7
Points	2	2	6	4	4	2	6

Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:

$$N \underset{}{\overset{K(T)}{\rightleftharpoons}} U$$

where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. K(T) is the equilibrium constant for the process at absolute temperature T.

8-1   *What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?*

8-2   *What is the standard free energy change of the process ($\Delta G°(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.*

8-3   *If $(C_N)_{eq}$ and $(C_U)_{eq}$ denote the equilibrium concentrations of N and U in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{eq}/C$. Deduce an expression for f_U in terms of the equilibrium constant K. Show all work on the answer sheet.*

Country:	Language:

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.
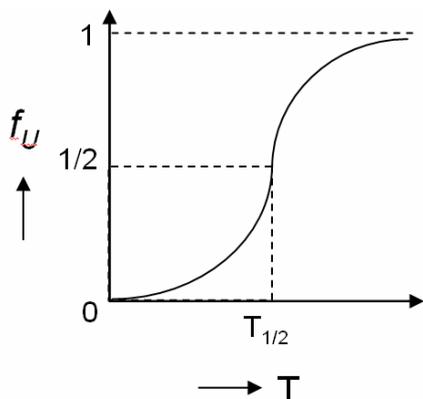
The mid-point of the denaturation curve is given by $f_U = \frac{1}{2}$ and $T = T_{\frac{1}{2}}$.   The latter is often referred to as the denaturation temperature.   At temperatures higher than $T_{\frac{1}{2}}$, f_U increases above $\frac{1}{2}$, but at temperatures lower than $T_{\frac{1}{2}}$, f_U decreases below $\frac{1}{2}$.

8-4 *What is the sign of ΔG°(T) at temperatures below and above $T_{\frac{1}{2}}$? Select your answer from the following choices.*
(a) Negative both below and above $T_{\frac{1}{2}}$
(b) Positive both below and above $T_{\frac{1}{2}}$
(c) Positive below $T_{\frac{1}{2}}$, but negative above $T_{\frac{1}{2}}$
(d) Negative below $T_{\frac{1}{2}}$, but positive above $T_{\frac{1}{2}}$.

8-5 *How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{1/2}$ and (ii) decreases below $T_{\frac{1}{2}}$?   Select your answer from the following choices.*
(a) Decrease in both cases.
(b) Increase in both cases.
(c) Increases above $T_{\frac{1}{2}}$, but decreases below $T_{\frac{1}{2}}$
(d) Decreases above $T_{\frac{1}{2}}$, but increases below $T_{\frac{1}{2}}$

Country:	Language:

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:

$$N \underset{k_b}{\overset{k_f}{\rightleftharpoons}} U$$

where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8-6 *For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b?*

8-7 *Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{eq}$.*