**37th IChO Theoretical Examination**

1. - use only the pen provided
2. - time 5 hours
3. - problem booklet 26 pages (including this cover sheet)
4. - answer sheets: 23 pages (including cover sheet, more available on request)
5. - draft paper (will not be marked): 5 sheets (more are available on request)
6. - total number of points: 279 (They are equally weighted in the final score)
7. - 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

1. - 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

1. - restroom break ask your supervisor
2. - official English-language version available on request, for clarification only, ask your supervisor.
3. - 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



**Fundamental Constants, Equations and Conversion Factors**

Atomic mass unit 1 amu = 1.6605 × 10-27 kg

Avogadro’s number *N*= 6.02 × 1023 mol-1

Boltzmann’s constant *k* = 1.3806503 × 10-23 J K -1

Electron charge *e* = 1.6022 × 10-19 C

Faraday’s constant *F* = 9.6485 × 104 C mol -1

Gas constant *R* = 8.314 J K-1 mol-1 = 0.08205 L • atm K-1 mol-1

Mass of electron *me* = 9.11 × 10-31 kg

Mass of neutron *mn* = 1.67492716 × 10-27 kg

Mass of proton *mp* = 1.67262158 × 10-27 kg

Planck’s constant *h* = 6.63 × 10-34 J s

Speed of light *c* = 3 × 108 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* = - Δ*Hvap / RT + B*

De Broglie relation **= *h / mv*

Ideal gas equation *PV* = *nRT*

Free energy *G* = *H – TS*

*E = hv*

Δ*G* = Δ*G˚* + *RT* ln *Q* Δ*G* = *- nFE*

ΔU = *q + w* w = *- P*Δ*V*

V(cylinder) = πr2h

V(sphere) = 4/3 πr3

A(sphere) = 4 πr2

1 Å = 10-10 m 1 W = 1 J s-1

1 J = 1 kg m2 s-2 1 cal = 4.184 J

1 Pa = 1 kg m-1 s-2 = 1 N m-2 1 bar = 105 Pa

1 atm = 1.01325 × 105 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 (**) = 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 (CH3CONHCH3, compound B), and propionamide (CH3CH2CONH2, 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 (H2N-CH2-COOH) is an -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. ***When an -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?***



***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).



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. ***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 C10H10O5. 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 []D20 = -37.1o. Further purification by recrystallization gave pure **E** with the optical rotation []D20 = -49.0o.

***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 C9H16O5. Proton NMR data of **H** are listed as follows:

1H NMR (CDCl3)  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: \_\_\_\_.***

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



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:



* 1. ***How many diastereoisomers would be obtained for pentasaccharide J, if it is derived from five units of 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+.



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.



***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: atrans-Stilbene bheat coxidation

***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: aheat

***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 CF3CO2H 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.



***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:



***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forms. Consider the following half-reactions:



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

***4A-5 Calculate the formation constant for AuCl******at 25°C:***

 ***K = [AuCl] / [Au3+] [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 HAuCl4 is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of NaBH4. 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 AuCl4¯ 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 NaBH4 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) 102***

***(b) 103***

***(c) 104***

***(d) 105***

***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) N2***

***(b) NH3***

***(c) O3***

***(d) SO3***

* 1. ***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, O2SC(NH2)2, has the following skeletal structure



* 1. ***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(NH2)2 plane is 65°.

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

**Problem 6: Alkalinity of Water and Solubility of CO2**

**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 HCO3-, CO32-, and OH-. At pH values below 7, H+ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO3-, CO32-, and OH- are the only contributors to alkalinity can be expressed as

 alkalinity = [HCO3-] + 2[CO32-] + [OH-] – [H+]

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

 CO2(*g*) ⇄ CO2(*aq*) *K*CO2 = 3.44x10-2

 CO2(*aq*) + H2O ⇄ H2CO3 *K*H2CO3 = 2.00x10-3

 H2CO3 ⇄ HCO3- + H+ *K*a1 = 2.23x10-4

 HCO3- ⇄ CO32- + H+*K*a2 = 4.69x10-11

 CaCO3(*s*) ⇄ Ca2+ + CO32- *K*sp = 4.50x10-9

 H2O ⇄ H+ + OH- *K*w = 1.00x10-14

**Note: Calculations must be shown.**

***6-1 Natural waters (river or lake water) generally contain dissolved CO2.*** ***The ratio of [H2CO3 ] : [HCO3-] : [CO32-] in a water at [H+] = 1.00 × 10-7 M will be:***

 ***(a) : 1.00 : (b) . Calculate (a) and (b).***

***6-2 Gaseous CO2 in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air.*** ***Calculate the concentration of CO2 (aq) (mol/L) in pure water that is in equilibrium with the unpolluted air at 1.01 x 105 Pa and 298 K containing 0.0360% (molar ratio) CO2.*** (assuming standard pressure = 1.01 x 105 Pa)

***If you are unable to solve this problem, assume that concentration of CO2 (aq) = 1.11x10-5 Mfor further calculations.***

Thesolubility (S) of CO2 in water can be defined as S = [CO2(*aq*)] + [H2CO3] + [HCO3-] + [CO32-]. The solubility of atmospheric CO2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01 x 105 Pa will vary with alkalinity.

***6-3 Find the solubility of atmospheric CO2 in pure water (mol/L). Neglect dissociation of water.***

***6-4 Find the solubility of atmospheric CO2 in water (mol/L) initially containing 1.00x10-3 mol/L NaOH.***

At 298 K, 1.01 x 105 Pa unpolluted air is in equilibrium with natural water saturated with CaCO3. The following main equilibrium may exist:

CaCO3(*s*) + CO2 (*aq*) + H2O ⇄ Ca2+ + 2HCO3-

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

***If you are unable to solve this problem, assume that equilibrium constant Keq = 5.00x10-5for further calculations.***

* 1. ***Calculate the concentration of Ca2+ (mg/L) in CaCO3-saturated natural water that is in equilibrium with atmospheric CO2.***

***If you are unable to solve this problem, assume that concentration of Ca2+ (aq) = 40.1 mg/Lfor further calculations.***

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

***6-8 In an underground lake saturated with CaCO3, the water has a high content of CO2. The concentration of Ca2+ 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 CO2 (Pa) in air which is in equilibrium with this Ca2+ 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 (O3) 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,

2O3  3O2.

One of the proposed mechanisms is expressed as

 

 

where k1, k-1, and k2 are the rate constants.

***7-1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O3, O2, and O at time t, assuming step 2 is irreversible.***

* 1. ***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 O3 depletion as a function of O2 and O3 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:*** .

One pathway for the destruction of ozone (2O3 🡪 3O2) in the upper atmosphere is catalyzed by Freons. For instance, when CCl2F2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl2F2 may give rise to Cl atoms according to the following reaction:

******

***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) + O3(g) → ClO(g) + O2(g) (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 oC. 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:



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 (ΔG°(T)) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.***

***8-3 If (CN)eq and (CU)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 fU = (CU)eq/C. Deduce an expression for fU in terms of the equilibrium constant K. Show all work on the answer sheet.***

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 fU = ½ and T = T½. The latter is often referred to as the denaturation temperature. At temperatures higher than T½, fU increases above ½, but at temperatures lower than T½ , fU decreases below ½.

***8-4 What is the sign of ΔG°(T) at temperatures below and above T½? Select your answer from the following choices.***

***(a) Negative both below and above T½***

***(b) Positive both below and above T½***

***(c) Positive below T½, but negative above T½***

***(d) Negative below T½, but positive above T½.***

***8-5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above T1/2 and (ii) decreases below T½? Select your answer from the following choices.***

***(a) Decrease in both cases.***

***(b) Increase in both cases.***

***(c) Increases above T½ , but decreases below T½***

***(d) Decreases above T½ , but increases below T½***

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:



where kf and kb 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 kf and kb?***

***8-7*** ***Derive a rate law for the overall process, that is dCU/dt in terms of only rate constants, CU and (CU)eq.***

**37th IChO Theoretical Examination Answer Sheets**

**Problem 1: Chemistry of Amides and Phenols**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***1-1*** | ***1-2*** | ***1-3*** | ***1-4*** | ***1-5*** | ***1-6*** | ***1-7*** | ***1-8*** | **∑** |
| **Total Points** | **4** | **4** | **4** | **4** | **6** | **4** | **8** | **4** | **38** |
| **Received** |  |  |  |  |  |  |  |  |  |

**Problem 2: Organic Synthesis and Stereochemistry**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***2-1*** | ***2-2*** | ***2-3*** | ***2-4*** | ***2-5*** | ***2-6*** | ***2-7*** | ***2-8*** | **∑** |
| **Total Points** | **4** | **8** | **6** | **6** | **6** | **8** | **6** | **4** | **48** |
| **Received** |  |  |  |  |  |  |  |  |  |

**Problem 3: Organic Photochemistry and Photophysics**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***3-1*** | ***3-2*** | ***3-3*** | ***3-4*** | ***3-5*** | ***3-6*** | ***3-7*** | ***3-8*** | **∑** |
| **Total Points** | **8** | **4** | **4** | **4** | **4** | **4** | **4** | **4** | **36** |
| **Received** |  |  |  |  |  |  |  |  |  |

# **Problem 4: Gold Capital of Asia**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***4A-1*** | ***4A-2*** | ***4A-3*** | ***4A-4*** | ***4A-5*** | ***4A-6*** | ***4B-1*** | ***4B-2*** | ***4B-3*** | ***4B-4*** | ***4B-5*** | **∑** |
| **Total Points** | **2** | **4** | **4** | **2** | **6** | **2** | **2** | **2** | **2** | **8** | **8** | **42** |
| **Received** |  |  |  |  |  |  |  |  |  |  |  |  |

**Problem 5: Lewis Structure**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | ***5-1*** | ***5-2*** | ***5-3*** | ***5-4*** | ***5-5*** | **∑** |
| **Total Points** | **2** | **4** | **4** | **6** | **5** | **21** |
| **Received** |  |  |  |  |  |  |

**Problem 6: Alkalinity of Water and Solubility of CO2**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***6-1*** | ***6-2*** | ***6-3*** | ***6-4*** | ***6-5*** | ***6-6*** | ***6-7*** | ***6-8*** | **∑** |
| **Total Points** | **4** | **4** | **6** | **6** | **4** | **6** | **6** | **4** | **40** |
| **Received** |  |  |  |  |  |  |  |  |  |

**Problem 7: Kinetic Behavior of Ozone**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | ***7-1*** | ***7-2*** | ***7-3*** | ***7-4*** | ***7-5*** | **∑** |
| **Total Points** | **6** | **6** | **6** | **4** | **6** | **28** |
| **Received** |  |  |  |  |  |  |

**Problem 8: Protein Folding**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***8-1*** | ***8-2*** | ***8-3*** | ***8-4*** | ***8-5*** | ***8-6*** | ***8-7*** | **∑** |
| **Total Points** | **2** | **2** | **6** | **4** | **4** | **2** | **6** | **26** |
| **Received** |  |  |  |  |  |  |  |  |

**Problem 1: Chemistry of Amides and Phenols**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***1-1*** | ***1-2*** | ***1-3*** | ***1-4*** | ***1-5*** | ***1-6*** | ***1-7*** | ***1-8*** | **∑** |
| **Total Points** | **4** | **4** | **4** | **4** | **6** | **4** | **8** | **4** | **38** |
| **Received** |  |  |  |  |  |  |  |  |  |

|  |
| --- |
| ***1-1*** |
| *Express your answer from high to low melting point as follows:* *> > (Insert compound codes A, B, C)* |

|  |
| --- |
| ***1-2*** *Answer for multiple choice question:* |

|  |
| --- |
| * 1. *Draw the structural formula of tripeptide Gly-Gly-Gly*
 |

|  |
| --- |
| ***1-4*** |
| *The number of all possible linear tripeptides is:*  |

|  |
| --- |
| ***1-5****The number of optically active linear tripeptides is:*  |

|  |
| --- |
| ***1-6*** *Express your answer from high to low binding affinity as follows:* *> > (Insert compound codes D, E, and F)* |

|  |
| --- |
| ***1-7*** *Draw the structural formula of compound H:* |
|  |

 ***1-8*** *Answer for multiple choice question****:***

**Problem 2: Organic Synthesis and Stereochemistry**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***2-1*** | ***2-2*** | ***2-3*** | ***2-4*** | ***2-5*** | ***2-6*** | ***2-7*** | ***2-8*** | **∑** |
| **Total Points** | **4** | **8** | **6** | **6** | **6** | **8** | **6** | **4** | **48** |
| **Received** |  |  |  |  |  |  |  |  |  |

|  |
| --- |
| ***2-1*** *Draw the structural formula of compound A.* |
|  |

|  |
| --- |
| ***2-2*** T or F *(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.* |

|  |
| --- |
| ***2-3***  *D/E ratio before recrystallization:* *Show your work here* |
|  |

|  |
| --- |
| ***2-4*** T or F  *(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.* |

|  |
| --- |
| ***2-5***  *Draw the configurational formula of compound H.* |
|  |
|  |

|  |
| --- |
| ***2-6*** *Give your answers as follows* *C-1: \_\_\_\_; C-2: \_\_\_\_; C-3: \_\_\_\_; C-4: \_\_\_\_.* |

|  |
| --- |
| ***2-7*** |
|  *P:**Q:**R:**S:**T:**U:* |

|  |
| --- |
| ***2-8*** *The number of diastereoisomers of pentasaccharide is:* |

**Problem 3: Organic Photochemistry and Photophysics**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***3-1*** | ***3-2*** | ***3-3*** | ***3-4*** | ***3-5*** | ***3-6*** | ***3-7*** | ***3-8*** | **∑** |
| **Total Points** | **8** | **4** | **4** | **4** | **4** | **4** | **4** | **4** | **36** |
| **Received** |  |  |  |  |  |  |  |  |  |

|  |
| --- |
| * 1. *Draw the**structural formula of C and D*
 |

|  |
| --- |
| ***3-2*** *Answer for multiple choice question****:*** |

|  |
| --- |
| ***3-3*** *Answer for multiple choice question****:*** |

|  |
| --- |
| ***3-4*** *Answer for multiple choice question****:*** |

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

|  |
| --- |
| ***3-6***  *(cis or trans)* |

|  |
| --- |
| ***3-7*** *Answer for multiple choice question****:*** |

|  |
| --- |
| ***3-8*** *Answer for multiple choice question****:*** |

# **Problem 4: Gold Capital of Asia**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***4A-1*** | ***4A-2*** | ***4A-3*** | ***4A-4*** | ***4A-5*** | ***4A-6*** | ***4B-1*** | ***4B-2*** | ***4B-3*** | ***4B-4*** | ***4B-5*** | **∑** |
| **Total Points** | **2** | **4** | **4** | **2** | **6** | **2** | **2** | **2** | **2** | **8** | **8** | **42** |
| **Received** |  |  |  |  |  |  |  |  |  |  |  |  |

|  |
| --- |
| ***4A-1*** *Draw a structure for Au(CN)2-* |
|  |

|  |
| --- |
| ***4A-2*** *Weight for KCN: g* |
| *Show your work here* |

|  |
| --- |
| ***4A-3*** |
|  |

|  |
| --- |
| ***4A-4*** *oxidizing agent:* *reducing agent:* |

|  |
| --- |
| ***4A-5*** *Formation constant K:* |
| *Show your calculations here* |
|  |

|  |
| --- |
| ***4A-6*** *Answer for multiple choice question****:*** |

|  |
| --- |
| ***4B-1*** *Answer for multiple choice question****:*** |

|  |
| --- |
| ***4B-2*** *Answer for multiple choice question****:*** |
|  |

|  |
| --- |
| ***4B-3*** *Answer for multiple choice question****:*** |

|  |
| --- |
| ***4B-4*** *Answer for multiple choice question****:*** |
| *Show your work here* |

|  |
| --- |
| ***4B-5*** *Answer for multiple choice question****:*** |
| *Show your work here* |

**Problem 5: Lewis Structure**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | ***5-1*** | ***5-2*** | ***5-3*** | ***5-4*** | ***5-5*** | **∑** |
| **Total Points** | **2** | **4** | **4** | **6** | **5** | **21** |
| **Received** |  |  |  |  |  |  |

|  |
| --- |
| ***5-1*** |
|  |
|  |
|  |

|  |
| --- |
| ***5-2*** |
|   |

|  |
| --- |
| ***5-3*** |
|  |
|  |

|  |
| --- |
| ***5-4****Answer for multiple choice question 5-4a:* *Answer for multiple choice question 5-4b:* *Answer for multiple choice question 5-4c:* |

|  |
| --- |
| ***5-5*** |
|  |
|  |

**Problem 6: Alkalinity of Water and Solubility of CO2**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***6-1*** | ***6-2*** | ***6-3*** | ***6-4*** | ***6-5*** | ***6-6*** | ***6-7*** | ***6-8*** | **∑** |
| **Total Points** | **4** | **4** | **6** | **6** | **4** | **6** | **6** | **4** | **40** |
| **Received** |  |  |  |  |  |  |  |  |  |

|  |
| --- |
| ***6-1***  *[H2CO3 ] : [HCO3-] : [CO32-] = : 1.00 :*  *(a) (b)* |
| *Show your work here* |

|  |
| --- |
| ***6-2*** |
|  |

|  |
| --- |
| ***6-3*** |
|  |

|  |
| --- |
| ***6-4*** |
|  |

|  |
| --- |
| ***6-5*** |
|  |

|  |
| --- |
| ***6-6*** |
|  |

|  |
| --- |
| ***6-7*** |
|  |

|  |
| --- |
| ***6-8*** |
|  |

**Problem 7: Kinetic Behavior of Ozone**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | ***7-1*** | ***7-2*** | ***7-3*** | ***7-4*** | ***7-5*** | **∑** |
| **Total Points** | **6** | **6** | **6** | **4** | **6** | **28** |
| **Received** |  |  |  |  |  |  |

|  |
| --- |
| **7*-1***  |
|    |

|  |
| --- |
| **7*-2***   |
|  |

|  |
| --- |
| ***7-4*** |

|  |
| --- |
| **7*-5***  |

**Problem 8: Protein Folding**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***8-1*** | ***8-2*** | ***8-3*** | ***8-4*** | ***8-5*** | ***8-6*** | ***8-7*** | **∑** |
| **Total Points** | **2** | **2** | **6** | **4** | **4** | **2** | **6** | **26** |
| **Received** |  |  |  |  |  |  |  |  |

|  |
| --- |
| ***8-1***  |

|  |
| --- |
| ***8-2***  |

|  |
| --- |
| ***8-3***  |

|  |
| --- |
| **8*-4*** *Answer for multiple choice question****:*** |

|  |
| --- |
| **8*-5*** *Answer for multiple choice question****:*** |

|  |
| --- |
| **8*-6***  |

|  |
| --- |
| **8*-7***  |

**37th International Chemistry Olympiad**

**Taipei, Taiwan**

**Practical Examination
Tuesday, 19 July 2005**

**Important Remarks**

* The plastic bag you got upon entering the laboratory is the unknown samples for experiment 2. Put it inside the basket on your bench for later use.
* At all times while you are in the laboratory you should wear safety spectacles or your own spectacles if they have been approved.
* Eating of any kind of food is strictly prohibited in the laboratory.
* When you enter the laboratory, check the place of the safety shower.
* Participants are expected to work safely, to behave socially and to keep equipment and work environment clean. Do not hesitate to ask a laboratory assistant if you have any questions concerning safety issues.
* **Work may only begin when the start signal is given.**
* You have 5 hours to complete all of the experimental tasks, and record your results on the answer sheets. There will be a pre-warning 30 minutes before the end of your time. You must stop your work immediately after the stop command is given. A delay in doing this by 5 minutes will lead to cancellation of the current task and will result in zero points for that task.
* **This practical examination comprises two experiments. In order to use the available time efficiently, you will start working on the organic chemistry experiment up to the point where you are instructed to work on the analytical chemistry experiment. Then you will finish the work on the organic chemistry experiment. The second part of the organic experiment (experiment 1) will need at least 1 hour.**
* **Use only the pen and calculator provided.**
* Write your name and personal identification code (in the back of your name card) on every answer sheets.
* All results must be written in the answer boxes on the answer sheets. Data written elsewhere will not be marked. Do not write anything in the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the laboratory assistant.
* When you have finished the examination, you must put all answer sheets into the envelope provided. Only papers in the envelope will be marked.
* Do not leave the examination room until you have permission to do so.
* Use only the tools provided.
* There are total **5** pages of answer sheets, **4** for organic and **1** for analytical experiment, respectively.
* 4 blank draft papers (will not be marked) are provided,more are available on request
* An official English-language version is available only on request.

**Disposal of waste chemicals, spills, and glassware**

There are three waste containers in the lab, one for organic filtrates and organic washings, one for solid wastes, and one for broken glass.

**Cleaning up**

Please keep your work area clean. Wipe your lab bench with a wet tissue when you are finished.



**Organic synthesis**

**Equipment list**

|  |  |  |  |
| --- | --- | --- | --- |
| equipment | No. | equipment | No. |
| Hot plate/stirrer with stand | 1 | Weighing paper | 10 |
| Stirrer | 2 | Sample vial (20 mL)(**blue label** labelled with your student code and 1H NMR) | 1 |
| Stirrer retriever | Shared by 2 persons  | Sample vial (20 mL)(**pink label** labelled with your student code and []D) | 1 |
| Filtration pump | Shared by 2 persons | Glass rod | 1 |
| Clamp with holder | 3 | Spatula | 2 |
| thermometer | 1 | Septa  | 2 |
| Pasteur pipette | 5 | Water bath (stainless steel) | 1 |
| Pipette bulb | 2 | Ice bath (Styrofoam) | 1 |
| Graduated cylinder (10 mL) | 1 | Needle | 1 |
| Graduated cylinder(25 mL) | 1 | Water bottle with Deionized H2O | 1 |
| Round bottom flask (25 mL) | 1 | Glove (cotton) | 1 pair |
| Round bottom flask (50 mL) | 1 | Glove (latex) on central bench |  |
| Filter, Fritted (50 mL)(labelled with your student code) | 1 | Flask holder | 1 pc |
| Filter, Fritted (70 mL)(labelled with your student code) | 1 | Paper towel | 1 roll |
| Filtration flask with rubber (250 mL) | 1 | Kimwipes | 1 box  |
| Condenser | 1 | Glass funnel | 1 |
| Teflon sleeve for condenser*(you can trim off 1 cm from the smaller end for a better fit)* | 1 | Beaker (800 mL) | 1 |
| Safety goggles | 1 | Beaker (400 mL) | 1 |

**Chemical list**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| chemicals | formula | formula weight | amount | Risk statements | Safety statements |
| ethanol  | C2H5OH | 46.07 | 50 mL | 11 | 7-16 |
| pre-mixed solventsethylene glycol:ethanol (2:9) | (CH2OH)2 | - | 50 mL | 22 | - |
| benzoylformic acid | C8H6O3 | 150.13 | written on sample vial | 36/37/38 | 26-28-36 |
| ammonium formate | HCO2NH4 | 63.06 | 7.57 g | 36/37/38 | 26-36 |
| D,L-phenylglycine | C8H9NO2 | 151.16 | written on sample vial (to be provided for step 2)  | - | 22-24/25 |
| Pentamethylcyclopentadienyl-rhodium(III) chloride, dimer | [(CH3)5C5RhCl2]2 | - | 37.2 mg | 20/21/22, 36/37/38 | 26, 36 |
| (1*S*)-(+)-10-camphorsulfonic acid (+)-(CSA) | C10H16O4S | 232.30 | 1.80 g | 34 | 26-36/37/39-45 |

Risk statements

R 11 Highly flammable.

R 20 Harmful by inhalation.

R 22 Harmful if swallowed.

R 25 Toxic if swallowed.

R 31 Contact with acids liberates toxic gas.

R 32 Contact with acid liberates very toxic gas.

R 34 Causes burns.

R 35 Causes severe burns.

R 36 Irritating to eyes.

R 37 Irritating to respiratory system.

R 38 Irritating to skin.

R 40 Limited evidence of a carcinogenic effect

R 41 Risk of serious damage to the eyes.

R 43 May cause sensitization by skin contact.

R 50 Very toxic to aquatic organisms.

R 52 Harmful to aquatic organisms.

R 53 May cause long-term adverse effects in the aquatic environment.

Combination of risk statements

R 20/21/22 Harmful by inhalation, in contact with skin, and if swallowed.

R 36/37/38 Irritating to eyes, respiratory system and skin.

Safety statements

S 7 Keep container tightly closed.

S 13 Keep away from food, drink and animal foodstuffs.

S 16 Keep away from sources of ignition - No smoking.

S 22 Do not breathe dust.

S 23 Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).

S 23.2 Do not breathe vapor.

S 24 Avoid contact with skin.

S 26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S 28 After contact with skin, wash immediately with plenty of soap-suds.

S 30 Never add water to this product.

S 36 Wear suitable protective clothing.

S 37 Wear suitable gloves.

S39 Wear eye / face protection.

S 41 In case of fire and/or explosion do not breathe fumes.

S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

S 60 This material and its container must be disposed of as hazardous waste.

S 61 Avoid release to the environment. Refer to special instructions / Safety data sheets.

Combination of safety statements

S 24/25 Avoid contact with skin and eyes.

S 36/37/39 Wear suitable protective clothing, gloves and eye/face protection.

S 36/37 Wear suitable protective clothing and gloves.

S 37/39 Wear suitable gloves and eye/face protection.

**Experiment 1**

**The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution**

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of -lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH3 following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



 Benzaldehyde D,L-phenylglycine Benzoylformic acid

 In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as R- and S- isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H2O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H2O at 25 °C. The chemical yield and the optical purity of the diastereomeric salt will be measured.

**EXPERIMENTAL PROCEDURE**

**Caution: You have to wear latex gloves during all operation for practical task 1.**

**Step 1. Preparation of D,L-phenylglycine**

|  |
| --- |
| ***The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].*** |

1. To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (**NOTE:** ***irritant, do not contact with skin***), 7.57 g of ammonium formate (HCO2NH4), 37.2 mg of Rh catalyst (**NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!**) and 22 mL of the pre-mixed solvents at ambient temperature.

2. Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (**NOTE: the solvent is air cooled, so there is no tap water running through the condenser.**) The temperature of the water bath needs to be maintained in the range of 68 to 72 °C by adjusting the thermostat of the hot plate/stirrer.

3. The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.

4. Add 15 mL of deionized water to the resulting mixture and stir for 10 minutes.

5. Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 mL each). For each washing, ***break the aspirator pressure***, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.

1. For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 °C for 1.5 hour.

|  |
| --- |
| ***During the drying period you can start working on Experiment 2 (Analytical Experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.*** |

1. Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by 1H NMR spectrum analysis. Turn in the product in a vial (**blue label** with 1H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

**Step 2. Enantiomeric resolution of D,L-phenylglycine by (+)-camphorsulfonic acid [(+)-CSA]**

1. To a 25 mL round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 mL) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.

2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.

3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 mL each).

4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).

5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (**pink label** labelled with [α]D and your student code)and give the sample vial to the lab assistant**.** The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

*The organization committee will weigh the resolved product (from the fritted glass funnel) for students who fail to finish the procedure in time. However, 15 penalty points will be taken.*

**Experiment 2**

**Identification of Unknown Inorganic Samples**

**Note**

(1) This practical exercise is a kind of “spot test”. You can do it on the pallet or on a sheet of black film (for white precipitate).

(2) Please check all items written in theequipment and reagent list.

(3) **Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.**

(4) The volume of each unknown solution is about 1.5 mL (about 30 drops). **No more reagents or samples will be provided**.

(5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.

(6) Make sure the switch on the battery box is closed.

(7) **You will get 8 points for each correct identification.**

**Introduction**

There are 12 unknown samples in your plastic bag：9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the **List of Unknown Inorganic Samples** carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 mL solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol/L).

The unknown samples are as follows:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| HCl | H2O2 | H2SO4 | ZnCl2 | NH4SCN |
| NaOH | Na2CO3 | Na2SO3 | BaCl2 | K4Fe(CN)6 |

**Note**

(1) Two unknown samples are duplicates.

(2) The hydrated H2O of crystal is omitted in the formulas listed above.

On your lab bench, there is a plastic basket which contains the equipments, unknown samples, and reagents to be used in this task.

Equipment list

|  |  |  |  |
| --- | --- | --- | --- |
| equipment | No. | equipment | No. |
| Pt wire electrode | 1 | Au wire electrode | 1 |
| Battery case | 1 | Battery | 2 |
| Pallet | 1 | Black film (round) | 1 |
| Scissors | 1 | Dropper (1 mL) | 5 |
| Coffee stirrer | 2 |  |  |

Reagent list

|  |  |  |  |
| --- | --- | --- | --- |
| Reagent | Conc. | Reagent | Conc. |
| KI | 0.1M | pp (phenolphthalein) | 0.01％ |
| FeCl3 | 0.1M | Starch solution | 0.01％ |

Risk and safety statements

|  |  |  |  |
| --- | --- | --- | --- |
| Chemicals  | Formula  | Risk statements | Safety statements |
| Hydrochloric acid  | HCl  | 36/37/38  | 26  |
| Sulfuric acid  | H2SO4  | 35  | 26-30-45  |
| Sodium hydroxide solution  | NaOH  | 35  | 26-36/37/39-45  |
| Hydrogen peroxide solution | H2O2 | 22-41 | 26-39 |
| Sodium carbonate solution | Na2CO3 | 36 | 22-26 |
| Barium chloride solution  | BaCl2 | 20-25  | 45  |
| Sodium sulfite solution | Na2SO3 | 31-36/37/38 | 26-36 |
| Zinc chloride solution | ZnCl2 | 22-34-50/53 | 26-36/37/39-45-60-61 |
| Potassium hexacyanoferrate (II) solution | K4Fe(CN)6 | 32 | 22-24/25 |
| Ammonium thiocyanate solution  | NH4SCN | 20/21/22-32-52/53 | 13-61 |
| Iron (III) chloride (solid) | FeCl3 | 22-34 | 26-36/37/39-45 |
| Potassium iodide (solid) | KI  | -  | 22-24/25 \*  |
| Starch solution  | -  | -  | -  |
| Phenolphthalein indicator |  | 40 | 36/37 |

***2-1*** Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

**Note**

After you have finished your work, please put the two electrodes (Pt and Au wires) and two batteries back in their original plastic bags, respectively, then return all equipment and reagents (include unknown samples) to the original places (in the plastic basket).

***2-2*** In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is ZnCl2.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).