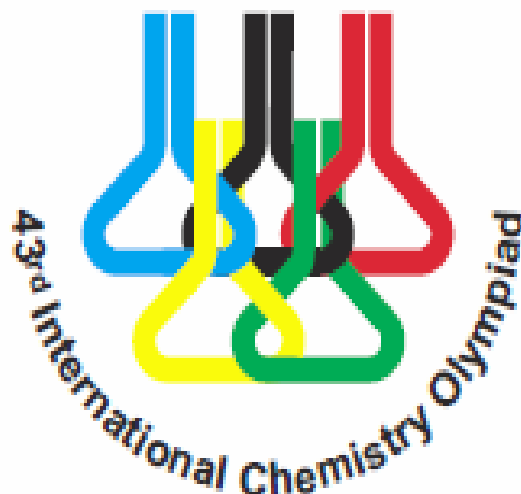


Name:

Code:

2011 Ankara, TURKEY



43rd International Chemistry Olympiad

Practical Tasks

**12 July 2011
Ankara, Turkey**

Name:

Code:

Instructions

- This examination has **9** pages for practical tasks and **8** pages of answer sheets (2+2 for Task 1, 3+3 for Task 2, and 4+3 for Task 3).
- You have 15 minutes to read this booklet before starting the experiments.
- You have **5 hours** for the practical examination. **Tasks 2 and 3** require the use of the same magnetic stirrer. In **Task 3**, there are waiting periods of 30 and 60 minutes.
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is announced. A delay in doing this by 5 minutes will lead to cancellation of your practical exam. After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following items should be **left on your bench**:
 - The problem booklet (this booklet)
 - The answer booklet
 - TLC1 and TLC2 plates in zipper storage bags with your student number and code (from Task 3)
- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own glasses if they have been approved. Use the **pipette filler bulb** provided. You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- You are allowed to work only in the space allocated for you.
- Use only the pen provided, not a pencil, for writing the answers.
- Use the calculator provided.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded. Use the back side of the sheets if you need scratch paper.
- Use the **container** labeled as "**Aqueous Waste**" to dispose the waste solutions in Task 1.
- Use the **container** labeled as "**Organic Waste**" to dispose the waste solutions in Task 3.
- Chemicals and labware will not be **refilled or replaced** without penalty except the first incident. Each further incident will result in the **loss of 1 point** from your 40 practical points.
- The official English version of this examination is available on request only for clarification.

Name:

Code:

Apparatus

On each desk	For common use in the lab
PET bottle 500 mL with water	Distilled water in jugs for refill
Goggles	Latex gloves (ask for proper size)
Pencil, ruler and permanent marker	Aqueous Waste container for Task 1
Magnetic Stirrer	Organic Waste container for Task 3
	Containers for broken glass and capillaries

Task 1
On the desk
Pipettes (3) 1, 10, 25 mL
Funnels (2), plastic
Burettes (2) connected to a stand by clamps, 50 mL
In the box inside the cabinet
Erlenmeyer flasks (2), 250 mL
Filler bulb (1)

Task 2	
On the desk	
Set-up	Graduated tube (marks indicate the volume in mL)
	Schlenk tube with a valve, a septum and a stir bar, 50 mL
	Tygon tubing connecting the graduated tube to a Schlenk tube and to a bulb
In the box inside the cabinet	
Funnel (1)	
Chronometer (timer) (1), ask supervisor about operation if needed	
Syringe (1), 2.0 mL	

Task 3
On the desk
Pipette (1), 2 mL
Graduated cylinder (1), 250 mL
Flash column with glass stopper connected to a stand by clamp (1)
In the box inside the cabinet
TLC plates (2) TLC1 and TLC2 in zipper bag
TLC developing chamber (1) and a lid
Capillary tubes (6)
Erlenmeyer flasks: (3)100 mL, (1) 250 mL
Graduated cylinder (1), 50 mL
Volumetric flask with a plastic stopper (1), 10 mL
UV-vis cells (2), path length 1.0 cm
Pressure applying bulb with an adapter (1) and clamp (1)
Syringe (2), 2.0 mL
Pasteur pipettes (6) and a bulb
Tweezers (1)

Name:

Code:

Chemicals

		R Phrase	S Phrase
Task 1	Unknown solution 100 mL	36 38	26 37 39
	Dextrin in Eppendorf tubes (3) in a zipper bag		
	Dichlorofluorescein indicator	36 37 38	26 36
	AgNO₃ solution, 0.1 M*, 100 mL	8 22 34 50 53	26 45
	EDTA , 0.01 M*, 100 mL	36	26
	pH 10 buffer (NH₃/NH₄Cl) , 5 mL	10 23 24 34 50	9 16 26 33 36 37 39 45 61
	EBT indicator	36 37 38	26
Task 2	Solution-A H ₃ NBH ₃ , 29.5 mg in 10 mL H ₂ O	5	15
	Solution-B poly(4-styrenesulfonic acid-co-maleic acid) 137.7 mg in 9 mL H ₂ O	26	26 36
	Solution-C Potassium tetrachloropalladate(II), K ₂ [PdCl ₄], 6.7 mg in 1 mL H ₂ O	36/38	26 37/39
Task 3	Rxn RB 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one and a stir bar		
	V1 1.0 mmol triethylamine in 1.0 mL CHCl ₃	11 20 21 22 35 38 40 48	3 16 26 29 36 37 39 45
	V2 1.0 mmol (<i>R</i>)-1-phenylethanamine in 0.5 mL CHCl ₃	11 20 21 22 34 35 38 40 48	6 26 28 29 36 37 39 45
	SM 2,3-dibromo-1-ferrocenylpropan-1-one, reference starting material for TLC		
	ELUENT 3:2 heptane:ethyl acetate mixture, 500 mL	11 20 22 36 66 67	16 23 29 33

*Exact value is given on the label

Name:

Code:

Risk and Safety Phrases

- R5 Heating may cause an explosion.
R8 Contact with combustible material may cause fire.
R10 Flammable.
R11 Highly flammable.
R20 Harmful by inhalation.
R21 Harmful in contact with skin.
R22 Harmful if swallowed.
R23 Toxic by inhalation.
R24 Toxic in contact with skin.
R26 Very toxic by inhalation.
R34 Causes burns.
R35 Causes severe burns.
R36 Irritating to eyes.
R37 Irritating to respiratory system.
R38 Irritating to skin.
R40 Limited evidence of a carcinogenic effect.
R48 Danger of serious damage to health by prolonged exposure.
R50 Very toxic to aquatic organisms.
R53 May cause long-term adverse effects in the aquatic environment.
R66 Repeated exposure may cause skin dryness or cracking.
R67 Vapours may cause drowsiness and dizziness.
- S3 Keep in a cool place.
S9 Keep container in a well-ventilated place.
S15 Keep away from heat.
S16 Keep away from sources of ignition.
S23 Do not breathe vapour.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S29 Do not empty into drains.
S33 Take precautionary measures against static discharges.
S36 Wear suitable protective clothing.
S37 Wear suitable gloves.
S39 Wear eye / face protection.
S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible.)
S61 Avoid release to the environment. Refer to special instructions / safety data sheets

Name:

Code:

Ideal gas equation: $PV = nRT$

Gas constant: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1}$

Zero of Celsius scale: 273.15 K

Beer-Lambert equation $A = \epsilon b c$

$1 \text{ atm} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa}$

Periodic Table of Elements with Relative Atomic Masses

1																	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											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 47.87	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 65.38	31 Ga 69.72	32 Ge 72.64	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 95.96	43 Tc [98]	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 137.33	57 La 138.91	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 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac (227)	104 Rf (261)	105 Ha (262)													
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	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 173.05	71 Lu 174.97				
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (257)				

Task 1

Analysis of Chloride Mixtures

Composition of a solution containing only MgCl_2 and NaCl can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. In this argentometric procedure, silver nitrate is used as the titrant to precipitate the chloride ions present in the solution. The end point is detected through the use of an adsorption indicator, typically dichlorofluorescein, a weak organic acid. Prior to the end point, silver chloride particles are negatively charged because of the adsorption of excess chloride ions present in solution. The indicator anions are repelled by the negatively charged surface of the silver chloride particles imparting a yellow-green color to the solution. Beyond the equivalence point, however, silver chloride particles adsorb silver ions. Thus a positively charged layer is formed and it attracts the dichlorofluoresceinate ions displaying a pink-red color. Dextrin is used to stabilize the silver chloride particles against the coagulation.

On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. As a hexadentate ligand, EDTA forms chelates with all metal ions, except alkali metal ions, in a 1:1 ratio regardless of the charge of the cation. Eriochrome Black T (EBT) is a common indicator used for EDTA titrations. When $\text{pH} > 7.00$ EBT imparts a blue color to the solution in the absence of metal ions and forms a red color when coordinated to metal ions.

In this experiment the chloride content of the solution containing MgCl_2 and NaCl will be determined by Fajans method. Magnesium ion concentration will be determined by EDTA titration.

A 100 mL solution prepared by dissolving MgCl_2 and NaCl in water is given as the unknown sample. The objective is to determine the concentration of MgCl_2 and NaCl in g/100 mL.

A. Determination of total chloride by Fajans Method

1. Using a 10-mL pipette, transfer 10.0 mL aliquot from the bottle labeled as **unknown solution** into a 250-mL Erlenmeyer flask. Complete the volume to approximately 100 mL by adding distilled water.
2. Take one of the Eppendorf tubes given in the zipper bag labeled as **dextrin** and transfer all its content into the Erlenmeyer flask.
3. Add 5 drops of dichlorofluorescein indicator solution.
4. Record the exact concentration of AgNO_3 in standard solution.
5. Fill one of the burettes with the standard AgNO_3 solution.

Name:

Code:

6. Titrate the unknown solution until the whole solution has pink-red color.
7. Record the volume of AgNO_3 used, in mL.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the **Aqueous Waste** container and rinse it twice with distilled water.

B. Determination of Mg^{2+} by direct titration with EDTA

1. Fill the second burette with the standard EDTA solution.
2. Record the exact concentration of EDTA in standard solution.
3. Using a 25-mL pipette, transfer a 25.0 mL aliquot of unknown solution into a 250-mL Erlenmeyer flask. Complete the volume to approximately 100 mL by adding distilled water.
4. Using a 1-mL pipette, add 1.0 mL of pH 10 buffer.
5. Add 3-4 drops of EBT indicator solution.
6. Titrate the unknown solution with standard EDTA solution until the color changes from red to blue.
7. Record the volume of EDTA solution used, in mL.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the **Aqueous Waste** container and rinse it twice with water.

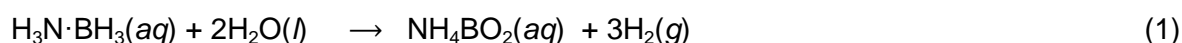
Treatment of Data

1. Determine the amount of Cl^- ion in millimoles in 100 mL unknown solution.
2. Determine the amount of Mg^{2+} ion in millimoles 100 mL unknown solution.
3. Calculate the concentration of MgCl_2 and NaCl in the unknown solution, in g/100 mL.

Task 2

Hydrogen generation from ammonia borane

Hydrogen has been considered as a clean and environmentally benign new energy carrier in the way towards a sustainable energy future. An effective and safe storage of hydrogen is one of the key issues of the hydrogen economy. Among the chemical hydrides, considered as potent solid hydrogen storage materials, ammonia-borane ($\text{H}_3\text{N}\cdot\text{BH}_3$) has been attracting a great deal of attention due to its high hydrogen content and stability under fuel cell operating conditions. Ammonia borane can release hydrogen upon hydrolysis, Equation 1:



Aqueous solution of ammonia borane is stable and its hydrolysis occurs only in the presence of a suitable catalyst. Recent studies have shown that palladium(0) nanoclusters stabilized by water soluble polymers are highly active catalyst in the hydrolysis of ammonia borane. Palladium(0) nanoclusters are generated in situ by the reduction of potassium tetrachloropalladate(II) with ammonia borane in the presence of poly(4-styrenesulfonic acid-co-maleic acid).

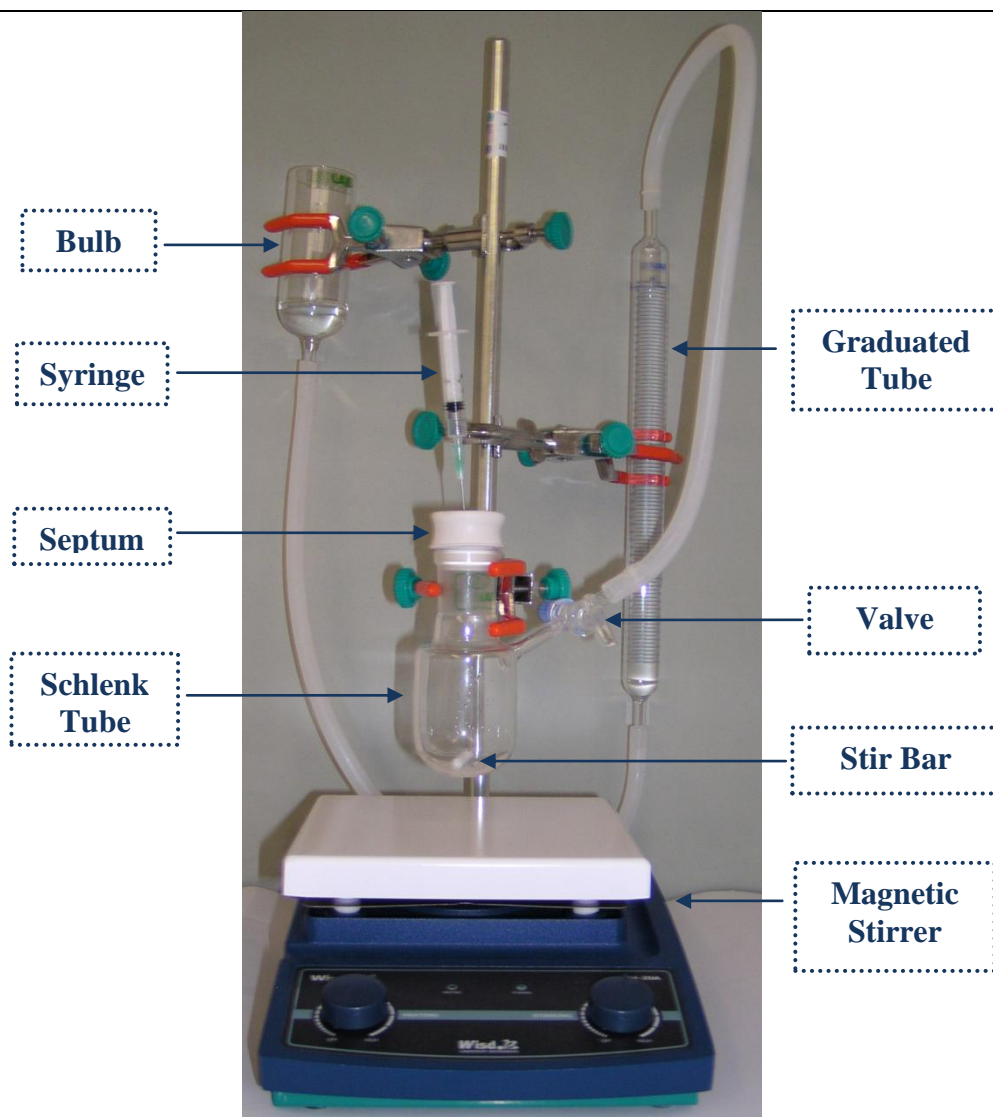
In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane and palladium(0) nanoclusters will be formed and stabilized by poly(4-styrenesulfonic acid-co-maleic acid). These nanoclusters will catalyze the hydrolysis of ammonia borane.

I. Preparation of the Experimental Set-up

1. Check that the experimental setup, shown below, is held on a support, the graduated tube is connected to the Schlenk tube by Tygon tubing, and a stir bar is in the Schlenk tube.
2. Make sure that the septum is off and the valve is open.
3. By changing the bulb height adjust the water level in the graduated tube to zero.
4. Close the valve on the Schlenk tube.

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Experimental Set-up

II. Hydrolysis of ammonia borane

A. In the absence of catalyst

1. Transfer all of the ammonia-borane solution (**Solution-A**) from the glass vial to the Schlenk tube through the funnel,
2. Add the polymer solution (**Solution-B**) from the glass vial to the Schlenk tube through the funnel.
3. Close the Schlenk tube with the septum, turn the stirring on at 600 rpm (as marked on the stirrer), and open the valve connecting to the graduated tube. Record the water level as V_0 at time zero. Start the timer.
4. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Name:

Code:

B. In the presence of catalyst

1. While stirring, transfer all of the potassium tetrachloropalladate(II) solution (**Solution-C**) from the glass vial to the Schlenk tube by injecting through the septum using a 2.0 mL syringe. Keep the syringe inserted in the septum throughout the experiment. Start the timer.
2. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Treatment of Data

A. Reaction of ammonia-borane without catalyst

1. Plot the volume of gas recorded versus time in Graph 1.
2. Report the volume of gas evolved as $V_{\text{uncatalyzed}}$.

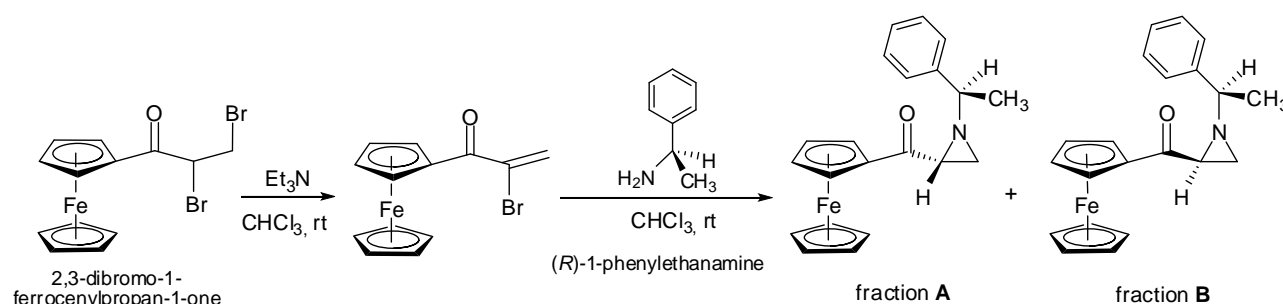
B. Reaction of ammonia-borane with catalyst

1. Plot the volume of gas generated versus time in Graph 2.
2. Calculate the maximum number of moles and the maximum volume (mL) of hydrogen gas which will be evolved theoretically from the hydrolysis of 29.5 mg ammonia borane with a purity of 97% w/w at 25 °C. The atmospheric pressure is 690 torr.
3. Calculate the rate of hydrogen generation in your experiment
 - i) in mL H₂/ min.
 - ii) in mmol H₂/ min by assuming that the temperature is 25 °C. The atmospheric pressure is 690 torr.
4. Calculate the rate of hydrogen production per mole of palladium in (mol H₂)·(mol Pd)⁻¹·(min)⁻¹ in your experiment. The purity of potassium tetrachloropalladate(II) is 98% w/w.

Task 3

Synthesis, purification and separation of a diastereomeric mixture

Nature has many compounds in the form of a single enantiomer or diastereomer such as sugars, amino acids, steroids, etc. Some of these compounds are biologically active and used as drugs. Therefore, the asymmetric synthesis of organic compounds is important. One of the methods for the asymmetric synthesis of organic compounds employs a metal-catalyst, in which the metal is coordinated to a chiral organic molecule named as chiral ligand. In this experiment two chiral ligands will be synthesized.



A. Synthesis

1. Transfer the triethylamine solution in vial 1 (**V1**) using a syringe to the 10 mL round bottom reaction flask (**Rxn RB**) containing 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one through the septum.
2. Stir the mixture at room temperature for 30 min using the magnetic stirrer at 600 rpm (as marked on the stirrer).
3. At the end of 30 min, transfer the (*R*)-1-phenylethylamine solution in vial 2 (**V2**) to the reaction flask using the same syringe through the septum.
4. Stir the mixture for additional 60 min at room temperature.
5. At the end of 60 min turn off the magnetic stirrer and perform a Thin Layer Chromatography, TLC, analysis as follows:
 - i) Check your TLC plates before use. Damaged plates will be replaced upon request without penalty.
 - ii) Draw a start line on the lower portion of TLC plate with a pencil (Fig. 2.1).
 - iii) Apply starting material from the vial labeled as **SM** two times to the spot on the left and then two times to the spot in the middle of plate. To the same plate, apply the reaction mixture (**RM**) taken from the reaction flask once to the spot on the right and then once to the spot in the middle as shown in Figure 2.1 (use a different capillary tube for each sample).
 - iv) Develop TLC plate in the TLC chamber with the eluent. Mark the solvent front with the pencil.
 - v) When the TLC plate is dry, place it in a zipper storage bag marked as **TLC1**.

Name: _____

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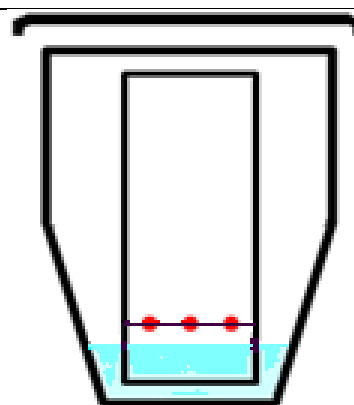
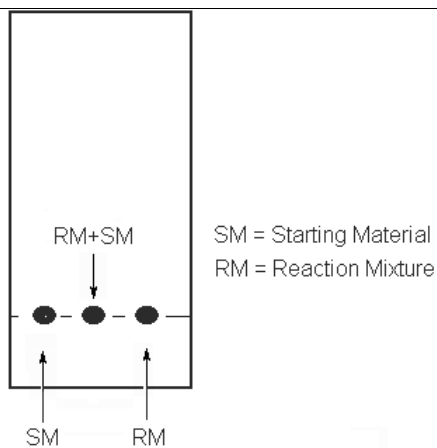


Figure 2.1. A TLC plate

Fig. 2.2 A TLC plate placed in the TLC developing chamber.

B. Flash Column Chromatography

1. Remove the stopper, open the valve, and bring the eluent level at top of column to the upper level of silica gel.
2. Close the valve and load the content of reaction flask on the top of flash column using a Pasteur pipette (Fig. 2.3).

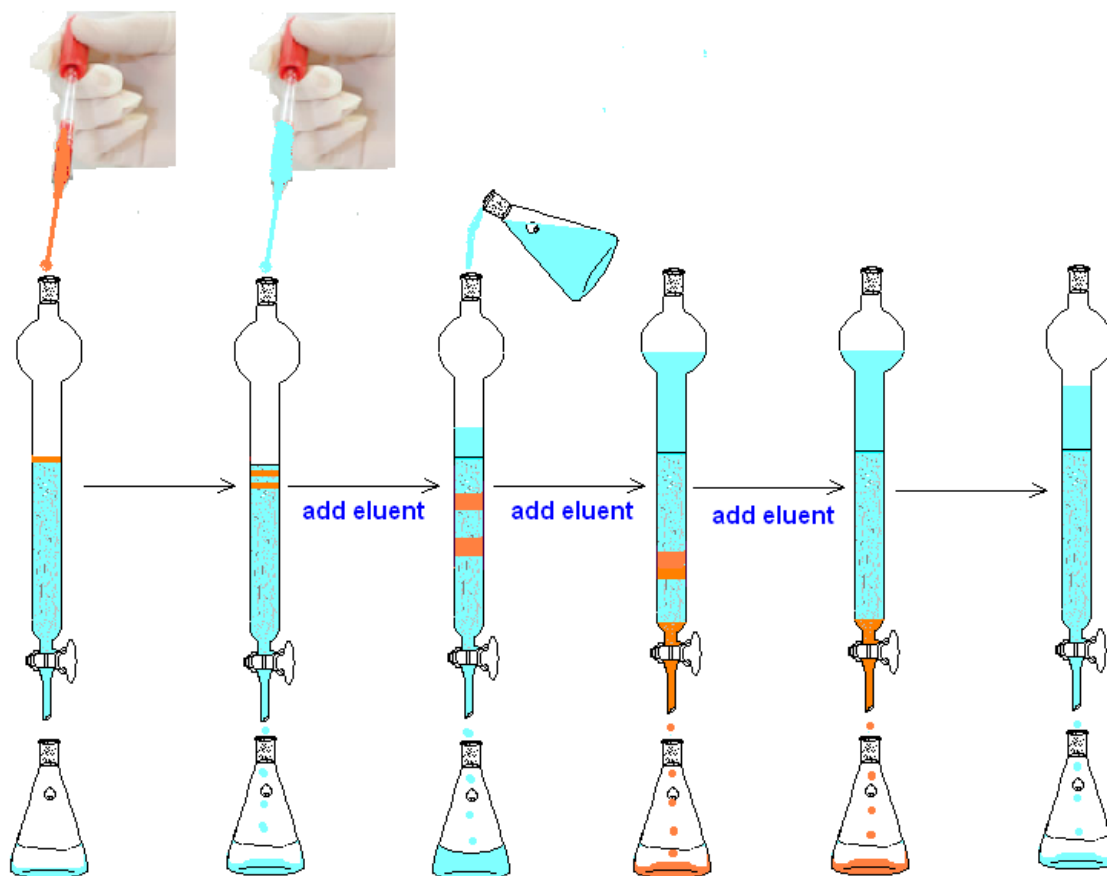


Figure 2.3. Flash Column Chromatography

Name:

Code:

3. Rinse the reaction flask with 0.5 mL eluent taken from the bottle labeled as **ELUENT** using a clean syringe. Using the same Pasteur pipette, load the washings also on the top of column.
4. Open the valve of the column and let the solvent run down to the upper level of silica gel.
5. Close the valve and add 1.0 mL eluent by a Pasteur pipette. Open the valve. When the eluent is at the upper level of silica gel, add 2-3 mL eluent slowly without closing the valve.
6. Fill the column by adding more eluent. **CAUTION: Be careful during the addition of eluent; do not disturb silica gel.**
7. In order to speed up the purification, apply little pressure by connecting the pressure applying bulb with an adapter on top of the column. **CAUTION: Be careful not to apply too much pressure. Add eluent time to time to avoid silica gel run dry.**
8. You are expected to collect two major fractions **A** and **B**. Discard any material which elutes before major fraction **A** and between **A** and **B** into the container labeled as **Organic Waste**.
9. Collect the first major fraction into a 100 mL Erlenmeyer flask and label it as fraction **A**.
10. Collect the second major fraction into a 250 mL Erlenmeyer flask and label it as fraction **B**.
11. After collecting fraction **B** stop the elution by closing the valve.

C. Analysis

1. Perform another TLC by applying the starting material (**SM**) two times to the spot on the left, apply fraction **A** two times to the spot in the middle, and then fraction **B** five times to the spot on the right. After development, when the TLC plate is dry, place it in a zipper storage bag marked **TLC2**.
2. Measure the volume of fraction **A** using 50 mL graduated cylinder and record the volume to your answer sheet.
3. Measure the volume of fraction **B** using 250 mL graduated cylinder and record the volume to your answer sheet.
4. Using a 2-mL pipette transfer 2.0 mL of fraction **A** into the 10 mL volumetric flask and complete the volume to 10 mL by adding eluent. After shaking the flask, fill out the UV-visible cell (at least $\frac{3}{4}$ of its volume) by using a Pasteur pipette. Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.
5. Using fraction **B**, fill out (at least $\frac{3}{4}$ of its volume) the other UV-visible cell by a Pasteur pipette (no need for dilution). Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

Treatment of Data

1. Copy (sketch) the TLC1 plate on your answer sheet.
2. Copy (sketch) the TLC2 plate on your answer sheet.

Name:

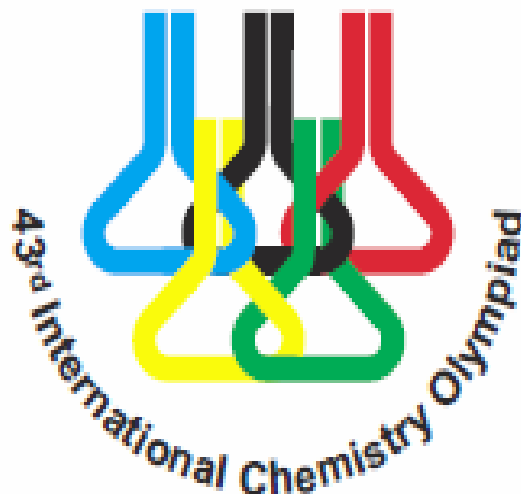
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3. Calculate and record the R_f values of the spots (fraction **A**, fraction **B**, and starting material **SM**) using the TLC2 plate.
 4. The molar extinction coefficient, ϵ , is $404 \text{ Lmol}^{-1} \text{ cm}^{-1}$ for **A** and $400 \text{ Lmol}^{-1} \text{ cm}^{-1}$ for **B** at 450 nm. Calculate:
 - i) The percent yield of fraction **A** based on the starting material.
 - ii) The percent yield of fraction **B** based on the starting material.

Name:

Code:

2011 Ankara, TURKEY



43rd International Chemistry Olympiad

Theoretical Problems

**14 July 2011
Ankara, Turkey**

Name:

Code:

Instructions

- Write your name and code on each page.
- This examination has 8 problems and 32 pages.
- You have 5 hours to work on the problems. **Begin** only when the **START** command is given.
- Use only the pen and the calculator provided.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. Full points will be given for right answers with working.
- When you have finished the examination, put your papers into the envelope provided. Do not seal the envelope.
- You must **stop** your work when the **STOP** command is given.
- Do not leave your seat until permitted by the supervisors.
- The official English version of this examination is available on request only for clarification.

Name:

Code:

Constants and Formulae

Avogadro constant: $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$ Ideal gas equation: $PV = nRT$ Gas constant: $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $0.08205 \text{ atm} \cdot \text{L} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ Energy of a photon: $E = \frac{hc}{\lambda}$ Faraday constant: $F = 96485 \text{ C} \cdot \text{mol}^{-1}$ Gibbs free energy: $G = H - TS$ Planck constant: $h = 6.6261 \times 10^{-34} \text{ J} \cdot \text{s}$ $\Delta_r G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$ $\Delta H = \Delta E + \Delta nRT$ Speed of light: $c = 3.000 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ Faraday equation: $Q = it$

Zero of Celsius scale: 273.15 K

Arrhenius equation: $k = Ae^{-E_a/RT}$ 1 N = 1 kg m s⁻² 1 eV = 1.602 × 10⁻¹⁹ J $K_w = 1.0 \times 10^{-14}$ at 25 °C1 atm = 760 torr = 1.01325 × 10⁵ Pa

Integrated rate law for the zero order reaction:

 $[A] = [A]_0 - kt$

Integrated rate law for the first order reaction:

 $\ln [A] = \ln [A]_0 - kt$

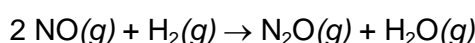
Periodic Table of Elements with Relative Atomic Masses

1																	18
1 H 1.008	2											13	14	15	16	17	2
3 Li 6.941	4 Be 9.012											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	3	4	5	6	7	8	9	10	11	12	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 47.87	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 65.38	31 Ga 69.72	32 Ge 72.64	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 95.96	43 Tc [98]	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 137.33	57 La 138.91	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 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac (227)	104 Rf (261)	105 Ha (262)													
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	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 173.05	71 Lu 174.97				
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (257)				

Problem 1**7.0 % of the total**

a	b	c	d			e	Problem 1	x%
			i	ii	iii			
3	2	6	6	1.5	1	2.5	22	7.0

Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO₂. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures NO reacts with H₂ to produce nitrous oxide, N₂O, a greenhouse gas.



To study the kinetics of this reaction at 820 °C, initial rates for the formation of N₂O were measured using various initial partial pressures of NO and H₂.

Exp.	Initial pressure, torr		Initial rate of production of N ₂ O, torr·s ⁻¹
	P _{NO}	P _{H₂}	
1	120.0	60.0	8.66×10 ⁻²
2	60.0	60.0	2.17×10 ⁻²
3	60.0	180.0	6.62×10 ⁻²

Throughout this problem do not use concentrations. Use units of pressure in torr and time in seconds.

a. Determine the experimental rate law and calculate the rate constant.

$$\text{Rate} = R = k(P_{\text{NO}})^a(P_{\text{H}_2})^b$$

$$\frac{R_1}{R_2} = \frac{8.66 \times 10^{-2}}{2.17 \times 10^{-2}} = 3.99 = \frac{k \times 120^a \times 60^b}{k \times 60^a \times 60^b} \quad 2^a = 3.99 \Rightarrow a = 2$$

$$\frac{R_3}{R_2} = \frac{6.62 \times 10^{-2}}{2.17 \times 10^{-2}} = 3.05 = \frac{k \times 60^a \times 180^b}{k \times 60^a \times 60^b} \quad 3^b = 3.05 \Rightarrow b = 1$$

$$\text{Rate} = k(P_{\text{NO}})^2(P_{\text{H}_2})$$

$$k = \frac{8.66 \times 10^{-2}}{120^2 \times 60} = 1.00 \times 10^{-7} \text{ torr}^{-2} \cdot \text{s}^{-1} \quad (2.5 + 0.5 \text{ pt})$$

Name:

Code:

- b. Calculate the initial rate of disappearance of NO, if 2.00×10^2 torr NO and 1.00×10^2 torr H_2 are mixed at $820^\circ C$. (If you do not have the value for the rate constant then use 2×10^{-7} in appropriate unit.)

$$\text{Rate} = \frac{\Delta P_{N_2O}}{\Delta t} = -1/2 \frac{\Delta P_{NO}}{\Delta t} = 1.0 \times 10^{-7} \times 200^2 \times 100 = 0.40 \text{ torr} \cdot \text{s}^{-1}$$

$$-\frac{\Delta P_{NO}}{\Delta t} = 0.80 \text{ torr} \cdot \text{s}^{-1} \quad (1.5+0.5 \text{ pt})$$

- c. Calculate the time elapsed to reduce the partial pressure of H_2 to the half of its initial value, if 8.00×10^2 torr NO and 1.0 torr of H_2 are mixed at $820^\circ C$. (If you do not have the value for the rate constant then use 2×10^{-7} in appropriate unit.)

$$\text{Rate} = k(P_{NO})^2 P_{H_2}$$

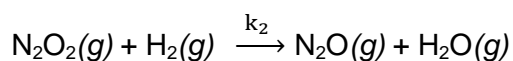
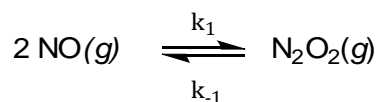
$$\text{as } P_{NO} \gg P_{H_2}$$

$$\text{Rate} = k' P_{H_2} \Rightarrow k' = k(P_{NO})^2$$

$$k' = 1.0 \times 10^{-7} \times (8.00 \times 10^2)^2 = 0.064 \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k'} = 10.8 \text{ s} \quad (5.5+0.5 \text{ pt})$$

- d. A proposed mechanism for the reaction between NO and H_2 is given below:



Name:

Code:

- i. Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

$$\frac{\Delta P_{N_2O}}{\Delta t} = k_2(P_{N_2O_2})(P_{H_2})$$

steady state approximation for N_2O_2

$$\frac{\Delta P_{N_2O_2}}{\Delta t} = 0 = k_1(P_{NO})^2 - k_{-1}P_{N_2O_2} - k_2P_{N_2O_2}P_{H_2} = 0$$

$$P_{N_2O_2} = \frac{k_1(P_{NO})^2}{k_{-1} + k_2P_{H_2}}$$

$$\frac{\Delta P_{N_2O}}{\Delta t} = k_2P_{H_2} \frac{k_1(P_{NO})^2}{k_{-1} + k_2P_{H_2}}$$

$$\text{Rate} = \frac{\Delta P_{N_2O}}{\Delta t} = k_1 k_2 \frac{(P_{NO})^2 P_{H_2}}{k_{-1} + k_2 P_{H_2}} \quad (6 \text{ pt})$$

- ii. Under what condition does this rate law reduce to the experimentally determined rate law found in Part a?

If $k_{-1} \ll k_2 P_{H_2}$

If $k_{-1} \gg k_2 P_{H_2}$

If $k_{-1} > k_2$

If $k_1 > k_{-1}$

(1.5 pt)

Name:

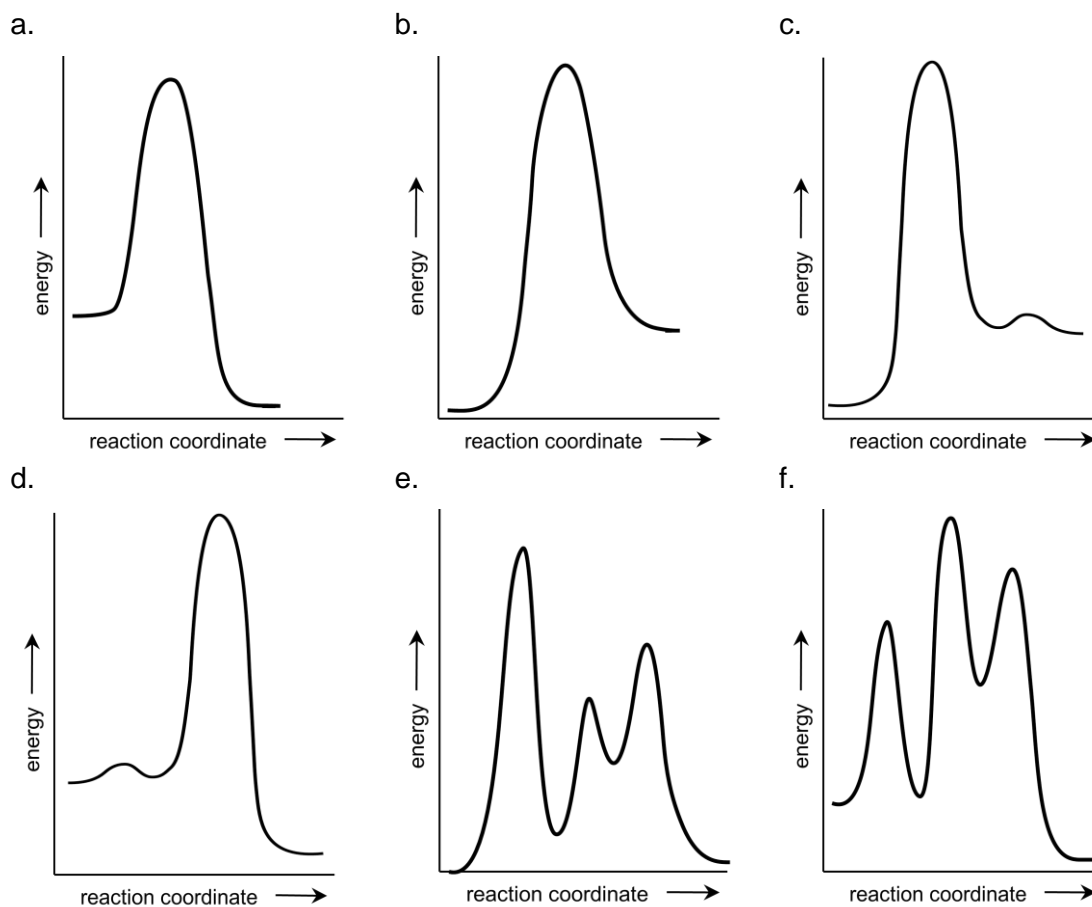
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iii. Express the experimentally determined rate constant k in terms of k_1 , k_{-1} and k_2 .

$$k = \frac{k_1 k_2}{k_{-1}}$$

(1 pt)

e. Select the schematic energy diagram that is consistent with the proposed reaction mechanism and experimental rate law.



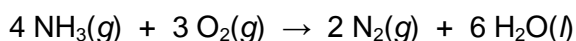
a) b) c) ✓ d) e) f) (2.5 pt)

Problem 2**7.0 % of the total**

a	b			Problem 2	x%
	i	ii	iii		
6	9	6	2	23	7.0

Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel. It produces no greenhouse gases on combustion.

In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the equation given below.



The initial and final states are at 298 K. After combustion with 14.40 g of O_2 , some of NH_3 remains unreacted.

- a. Calculate the heat given out during the process.

Given: $\Delta_f H^\circ(\text{NH}_3(g)) = -46.11 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\text{H}_2\text{O}(l)) = -285.83 \text{ kJ}\cdot\text{mol}^{-1}$

$$q_v = \Delta E = \Delta H - \Delta n_g RT$$

for 1 mole of NH_3

$$\Delta H = 3/2 \times (-285.83) - (-46.11) = -382.64 \text{ kJ}$$

$$\Delta n_g = -1.25 \text{ mol}$$

$$\Delta E = -382.64 - (-1.25) \times 8.314 \times 298 \times 10^{-3}$$

$$= -379.5 \text{ kJ for 1 mol of NH}_3$$

$$n(\text{O}_2) = \frac{14.40}{32.0} = 0.450 \text{ mol}$$

$$n(\text{NH}_3) \text{ reacted} = 0.450 \left(\frac{4}{3} \right) = 0.600 \text{ mol}$$

$$q_v = \Delta E = 0.600 \times (-379.5) = -227.7 \text{ kJ} = -228 \text{ kJ}$$

heat given out = **228 kJ**

(6 pt)

Name:

Code:

- b. To determine the amount of NH_3 gas dissolved in water, produced during the combustion process, a 10.00 mL sample of the aqueous solution was withdrawn from the reaction vessel and added to 15.0 mL of 0.0100 M H_2SO_4 solution. The resulting solution was titrated with 0.0200 M standard NaOH solution and the equivalence point was reached at 10.64 mL. ($K_b(\text{NH}_3) = 1.8 \times 10^{-5}$; $K_a(\text{HSO}_4^-) = 1.1 \times 10^{-2}$)
- i. Calculate pH of the solution in the container after combustion.

$$\text{Total mmol H}_2\text{SO}_4 = (15.00 \text{ mL})(0.0100 \text{ mol}\cdot\text{L}^{-1}) = 0.150 \text{ mmol H}_2\text{SO}_4$$



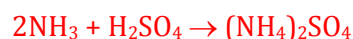
After back titration with NaOH,

$$\text{mmol H}_2\text{SO}_4 \text{ reacted} = \frac{1}{2}(\text{mmol NaOH reacted}) = \frac{1}{2} (10.64 \text{ mL} \times 0.0200 \text{ mol}\cdot\text{L}^{-1})$$

$$\text{mmol H}_2\text{SO}_4 \text{ reacted} = 0.1064 \text{ mmol H}_2\text{SO}_4$$

$$\text{Total mmol H}_2\text{SO}_4 = 0.1064 \text{ mmol} + \text{mmol H}_2\text{SO}_4 \text{ reacted with NH}_3 = 0.150 \text{ mmol H}_2\text{SO}_4$$

$$\text{mmol H}_2\text{SO}_4 \text{ reacted with NH}_3 = 0.0436 \text{ mmol H}_2\text{SO}_4$$



$$\text{mmol NH}_3 = 2(\text{mmol H}_2\text{SO}_4 \text{ reacted with NH}_3) = 2(0.0436 \text{ mmol NH}_3) = 0.0872 \text{ mmol NH}_3$$

$$[\text{NH}_3] = \frac{0.0872 \text{ mmol}}{10.0 \text{ mL}} = 8.72 \times 10^{-3} \text{ M}$$



$$[\text{NH}_3]_0 - x \qquad \qquad \qquad x \qquad \qquad x$$

$$K_b = 1.8 \times 10^{-5} = \frac{x^2}{(0.00872 - x)}$$

$$-1.57 \times 10^{-7} + 1.8 \times 10^{-5} x + x^2 = 0$$

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 1.57 \times 10^{-7}}}{2}$$

$$x = [\text{OH}^-] = 3.96 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = 3.41$$

$$\text{pH} = 14.00 - 3.41 = 10.59$$

(9 pt)

Name:

Code:

- ii. At the end point of titration, NH_4^+ and SO_4^{2-} ions are present in the solution. Write the equations for the relevant equilibria to show how the presence of these two ions affect the pH and calculate their equilibrium constant(s).



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.1 \times 10^{-13}$$



$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

(6 pt)

- iii. Circle the correct statement for the pH of solution at the equivalence point.

(2 pt)

pH > 7.0

pH = 7.0

pH < 7.0

Problem 3**8.0 % of the total**

a	b	c		d	Problem 3	x%
		i	ii			
7	4	2	5	5	23	8.0

At 0 K, the total energy of a gaseous diatomic molecule AB is approximately given by:

$$E = E_0 + E_{\text{vib}}$$

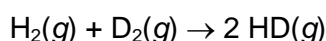
where E_0 is the electronic energy of the ground state, and E_{vib} is the vibrational energy.

Allowed values of the vibrational energies are given by the expression:

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) \varepsilon \quad v = 0, 1, 2, \dots \quad \varepsilon = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu(\text{AB}) = \frac{m_A m_B}{m_A + m_B}$$

where h is the Planck's constant, v is the vibrational quantum number, k is the force constant, and μ is the reduced mass of the molecule. At 0 K, it may be safely assumed that v is zero, and E_0 and k are independent of isotopic substitution in the molecule.

- a. Calculate the enthalpy change, ΔH , in $\text{kJ}\cdot\text{mol}^{-1}$ for the following reaction at 0 K.



Deuterium, D, is an isotope of hydrogen atom with mass number 2. For the H_2 molecule, k is $575.11 \text{ N}\cdot\text{m}^{-1}$, and the isotopic molar masses of H and D are 1.0078 and $2.0141 \text{ g}\cdot\text{mol}^{-1}$, respectively. Given: $\varepsilon_{\text{H}_2} = 1.1546 \varepsilon_{\text{HD}}$ and $\varepsilon_{\text{D}_2} = 0.8167 \varepsilon_{\text{HD}}$ at 0 K.



$$\Delta H = \Delta E + \Delta n_g RT \quad \Delta n_g = 0 \quad \text{Thus } \Delta H = \Delta E$$

$$\Delta E = 2E(\text{HD}) - E(\text{H}_2) - E(\text{D}_2)$$

$$E_{\text{vib}} = \frac{1}{2} \varepsilon \quad \text{as } v = 0 \text{ at } 0 \text{ K}$$

$$\Delta E = 2\left(E_0 + \frac{\varepsilon_{\text{HD}}}{2}\right) - \left(E_0 + \frac{\varepsilon_{\text{H}_2}}{2}\right) - \left(E_0 + \frac{\varepsilon_{\text{D}_2}}{2}\right) = \varepsilon_{\text{HD}} - \frac{1}{2}(\varepsilon_{\text{H}_2} + \varepsilon_{\text{D}_2})$$

$$\Delta E = \varepsilon_{\text{HD}} \left(1 - \frac{1}{2}(1.1546 + 0.8167)\right) = 0.01435 \varepsilon_{\text{HD}}$$

$$\mu(\text{HD}) = \frac{m_{\text{H}} m_{\text{D}}}{m_{\text{H}} + m_{\text{D}}}$$

$$= \frac{1.0078 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1} \times 2.0141 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1} / N_A^2}{(1.0078 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1} + 2.0141 \times 10^{-3} \text{ kg}) / N_A}$$

$$= 1.1154 \times 10^{-27} \text{ kg}$$

$$\varepsilon_{\text{HD}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{6.6261 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi} \times \sqrt{\frac{575.11 \text{ N} \cdot \text{m}^{-1}}{1.1154 \times 10^{-27} \text{ kg}}}$$

$$= 7.5724 \times 10^{-20} \text{ J}$$

$$\varepsilon_{\text{HD}} = 7.5724 \times 10^{-20} \text{ J} \times N_A$$

$$= 7.5724 \times 10^{-20} \text{ J} \times 6.0221 \times 10^{23} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= 45.600 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H = \Delta E = 0.01435 \varepsilon_{\text{HD}} = 0.6544 \text{ kJ} \cdot \text{mol}^{-1} \quad (7 \text{ pt})$$

- b. Calculate the frequency in s^{-1} of infrared photons that can be absorbed by HD molecule. (If you do not have the value for ε_{HD} then use $8.000 \times 10^{-20} \text{ J}$ for the calculation.)

$$h\nu = \Delta E$$

$$\Delta E = E_{v1} - E_{v0} = \left(\frac{3}{2} - \frac{1}{2}\right) \varepsilon_{\text{HD}} = \varepsilon_{\text{HD}}$$

$$h\nu = \varepsilon_{\text{HD}} \quad \Rightarrow \quad \nu = \frac{\varepsilon_{\text{HD}}}{h}$$

$$\varepsilon_{\text{HD}} = 7.5724 \times 10^{-20} \text{ J} \text{ from part a}$$

$$\nu = \frac{7.5724 \times 10^{-20} \text{ J}}{6.6261 \times 10^{-34} \text{ J} \cdot \text{s}} = 1.1428 \times 10^{14} \text{ s}^{-1} \quad (4 \text{ pt})$$

- c. The allowed electronic energies of H atom are given by the expression

$$E = -\frac{R_H}{n^2}, \quad n = 1, 2, \dots \quad \text{where } R_H = 13.5984 \text{ eV}, \quad 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

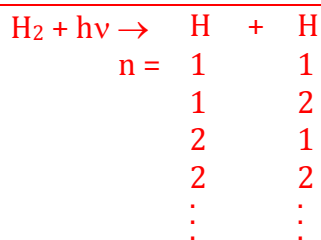
- i. The total energy of H₂ molecule in its ground state is -31.675 eV, relative to the same reference as that of hydrogen atom. Calculate the dissociation energy in eV of a hydrogen molecule in its ground state such that both H atoms are produced in their ground states.



$$\text{For } n = 1, \Delta E = 2(-13.5984) - (-31.675) = 4.478 \text{ eV}$$

(2 pt)

- ii. A H₂ molecule in the ground state dissociates into its atoms after absorbing a photon of wavelength 77.0 nm. Determine all possibilities for the electronic states of H atoms produced. In each case, what is the total kinetic energy in eV of the dissociated hydrogen atoms?



The energy of H₂ molecule in its ground state is -31.675 eV

$\lambda = 77.0 \text{ nm}$

$$E(\text{photon}) = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34})(3.00 \times 10^8)}{77.0 \times 10^{-9}} = 2.58 \times 10^{-18} \text{ J}$$

$$= 2.58 \times 10^{-18} \text{ J} \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 16.1 \text{ eV}$$

$$\Delta E = E_{n_1} + E_{n_2} - E_{\text{H}_2} = -\frac{R_H}{n_1^2} - \frac{R_H}{n_2^2} - (-31.675) < 16.1 \text{ eV}$$

$$n_1 = 1, n_2 = 1,$$

$$\Delta E = -\frac{13.5984}{1^2} - \frac{13.5984}{1^2} + 31.675 = 4.478 \text{ eV};$$

$$\text{K.E.} = 16.1 - 4.478 = 11.6 \text{ eV}$$

$$n_1 = 1, n_2 = 2 \text{ or } n_1 = 2, n_2 = 1,$$

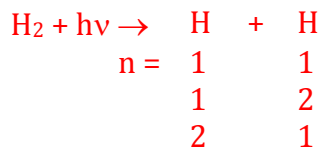
$$\Delta E = -\frac{13.5984}{1^2} - \frac{13.5984}{2^2} + 31.675 = 14.677 \text{ eV};$$

$$\text{K.E.} = 16.1 - 14.677 = 1.4 \text{ eV}$$

$$n_1 = 2, n_2 = 2, \quad \Delta E = -\frac{13.5984}{2^2} - \frac{13.5984}{2^2} + 31.675 = 24.880 \text{ eV} > 16.1 \text{ eV}$$

(5 pt)

Thus possibilities are



Name:

Code:

- d. Calculate the electron affinity of H_2^+ ion in eV if its dissociation energy is 2.650 eV. (If you do not have the value for the dissociation energy for H_2 then use 4.500 eV for the calculation.)

$$\text{IP}(\text{H}) = \Delta E_{n \rightarrow \infty} = -\frac{13.5984}{\infty^2} - \frac{-13.5984}{1^2} = 13.598 \text{ eV}$$



$$\text{EA}(\text{H}_2^+) = \text{DE}(\text{H}_2^+) - \text{IP}(\text{H}) - \text{DE}(\text{H}_2) = 2.650 - 13.598 - 4.478 = -15.426 \text{ eV}$$

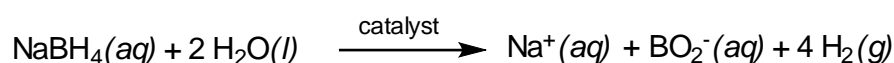
Electron affinity = -15.426 eV

(5 pt)

Problem 4**9.0% of the total**

a	b	c	d	e	f	g	Problem 4	x%
4	3	6	3	4	6	4	30	9.0

For sustainable energy, hydrogen appears to be the best energy carrier. The most efficient way of using hydrogen is generation of electrical energy in a fuel cell. However, storing hydrogen in large quantities is a challenge in fuel cell applications. Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride (NaBH_4), being nontoxic, stable and environmentally benign, appears to be the most promising one. The hydrolysis of sodium borohydride that releases H_2 gas is a slow reaction at ambient temperature and, therefore, needs to be catalyzed.



Colloidal ruthenium(0) nanoclusters are the most active catalysts in this hydrolysis even at room temperature and lead to a complete H_2 release from sodium borohydride. Kinetic studies show that the catalytic hydrolysis of NaBH_4 is first order with respect to the catalyst, but zero order with respect to the substrate. The rate of hydrogen production per mole of ruthenium is $92 \text{ mol H}_2 \cdot (\text{mol Ru})^{-1} \cdot \text{min}^{-1}$ at 25°C .

- a. Calculate the amount of ruthenium catalyst (in mg) which must be added to 0.100 L solution of $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaBH_4 to supply the hydrogen gas at a rate of $0.100 \text{ L} \cdot \text{min}^{-1}$ at 25°C and 1.0 atm , that is required for a portable fuel cell.

$$n_{\text{H}_2} = \frac{(100 \times 10^{-3} \text{ L} \cdot \text{min}^{-1}) \times (1.0 \text{ atm})}{(0.082 \text{ atm} \cdot \text{L} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 4.1 \times 10^{-3} \text{ mol H}_2 \cdot \text{min}^{-1}$$

$$\frac{(4.1 \times 10^{-3} \text{ mol H}_2 \cdot \text{min}^{-1})}{(92 \text{ mol H}_2 \cdot (\text{mol Ru})^{-1} \cdot \text{min}^{-1})} = 4.5 \times 10^{-5} \text{ mol Ru}$$

$$(4.5 \times 10^{-5} \text{ mol Ru}) \times (101.07 \text{ g} \cdot \text{mol}^{-1}) = 4.5 \times 10^{-3} \text{ g Ru} = 4.5 \text{ mg Ru}$$

(4 pt)

Name:

Code:

b. For how many minutes will this system supply hydrogen gas at this rate?

$$(1.00 \times 10^{-1} \text{L}) \times (1.0 \text{ mol} \cdot \text{L}^{-1}) = 0.10 \text{ mol NaBH}_4$$

$$(0.10 \text{ mol NaBH}_4) \times 4 \text{ mol H}_2 \cdot (\text{mol NaBH}_4)^{-1} = 0.40 \text{ mol H}_2 \text{ to be released}$$

$$\frac{(0.40 \text{ mol H}_2)}{(4.1 \times 10^{-3} \text{ mol H}_2 \cdot \text{min}^{-1})} = 98 \text{ min}$$

(3 pt)

c. The Arrhenius activation energy for this catalytic hydrolysis of sodium borohydride is $E_a = 42.0 \text{ kJ} \cdot \text{mol}^{-1}$. Calculate the temperature required to achieve the same rate of hydrogen evolution by using half the amount of ruthenium catalyst used at $25.0 \text{ }^\circ\text{C}$.

$$\text{Rate} = k[\text{Ru}] = (Ae^{-E_a/RT})[\text{Ru}]$$

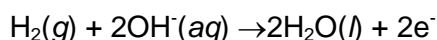
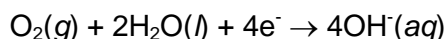
$$\frac{(e^{-E_a/R298})}{(e^{-E_a/RT})} = \frac{1}{2}$$

$$-\frac{E_a}{R} \left(\frac{1}{298} - \frac{1}{T} \right) = \ln\left(\frac{1}{2}\right), \quad \frac{4.20 \times 10^4 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \left(\frac{1}{298} - \frac{1}{T} \right) = \ln(2),$$

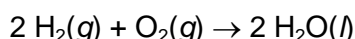
$$T = 311 \text{ K or } T = 38 \text{ }^\circ\text{C}$$

(6 pt)

d. A fuel cell is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments.

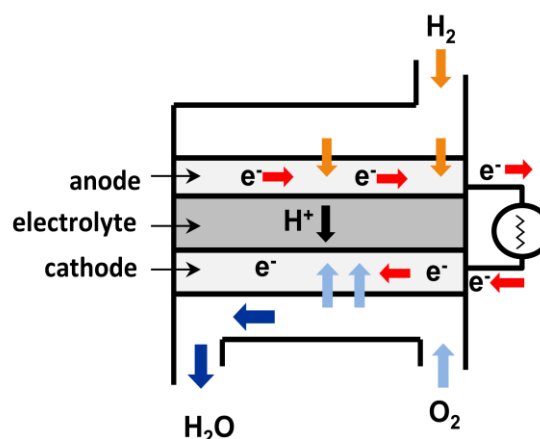


The net result of the two reactions is



The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride.

Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is -0.83 V and $\Delta_f G^\circ (\text{H}_2\text{O}(\text{l}))$ is $-237 \text{ kJ} \cdot \text{mol}^{-1}$.



Name:

Code:

Since $\Delta G^\circ = -nFE^\circ$

$$2(-2.37 \times 10^5) = -4 \times 96485 \times E^\circ_{\text{cell}} \quad E^\circ_{\text{cell}} = +1.23 \text{ V}$$

$$1.23 \text{ V} = E^\circ_{\text{cathode}} - (-0.83) \quad E^\circ_{\text{cathode}} = +0.40 \text{ V} \quad (3 \text{ pt})$$

- e. Calculate the volume of air at 25 °C and 1.0 atm needed to generate a constant current of 2.5 A for 3.0 h in this fuel cell. Assume that air contains 20% by volume $\text{O}_2(\text{g})$.

$$(2.5 \text{ A}) \times (3.0 \text{ h}) \times (3600 \text{ s} \cdot \text{h}^{-1}) = 27000 \text{ C}$$

$$n(\text{O}_2) = (27000 \text{ C}) \times \left(\frac{1 \text{ mol O}_2}{4 \times 96485 \text{ C}} \right) = 0.070 \text{ mol}$$

$$V(\text{O}_2) = \frac{(0.070 \text{ mol}) \times (0.082 \text{ atm} \cdot \text{L} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times (298 \text{ K})}{(1.0 \text{ atm})} = 1.7 \text{ L} \quad V_{\text{air}} = 8.6 \text{ L} \quad (4 \text{ pt})$$

- f. The efficiency of a fuel cell is given by the ratio of the work produced to the heat dissipated by the cell reaction. Thus, the maximum efficiency for a fuel cell is given by:

$$\eta_{\text{fuel cell}} = \frac{\text{work}}{\text{heat}}$$

Calculate the maximum efficiency for the fuel cell using the data given below at 25 °C and standard pressure.

	S° ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
$\text{H}_2(\text{g})$	130.7
$\text{O}_2(\text{g})$	205.2
$\text{H}_2\text{O}(\text{l})$	70.0

$$\Delta_{\text{rxn}}G^\circ = \Delta_{\text{rxn}}H^\circ - T\Delta_{\text{rxn}}S^\circ$$

$$\Delta_{\text{rxn}}S^\circ = [2 \times S^\circ(\text{H}_2\text{O}(l))] - [2S^\circ(\text{H}_2(g)) + S^\circ(\text{O}_2(g))] = 2 \times 70.0 - (2 \times 130.7 + 205.2) =$$

$$\Delta_{\text{rxn}}S^\circ = -326.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

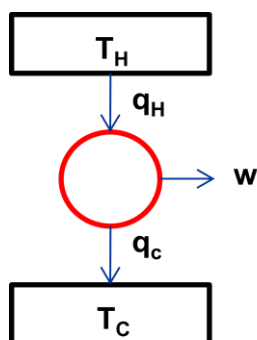
$$\Delta_{\text{rxn}}H^\circ = \Delta_{\text{rxn}}G^\circ + T\Delta_{\text{rxn}}S^\circ = (-474) + 298.15 \times (-326.6 \times 10^{-3}) = -571.4 \text{ kJ}$$

$$\text{maximum } w = \Delta_{\text{rxn}}G^\circ = -474 \text{ kJ}$$

$$\eta = \frac{-474000 \text{ J}}{-571400 \text{ J}} = 0.83$$

(6 pt)

- g. The second law of thermodynamics states that it is impossible to convert all of the heat, q_H , from a high-temperature reservoir at T_H into work. At least, some of the energy, q_C , must be transferred to a low-temperature reservoir at T_C . Thus, a heat engine with 100% efficiency is thermodynamically impossible. When the heat engine is working reversibly, as in a Carnot cycle, the efficiency will be maximum.



For a heat engine working reversibly between two reservoirs the following relations applies:

$$q_H = w + q_C$$

and

$$\frac{q_H}{T_H} = \frac{q_C}{T_C}$$

What should be the temperature of the hot reservoir, T_H , of a Carnot heat engine to maintain the efficiency of the fuel cell calculated in part (f), if the temperature of cold reservoir T_C is 40°C ? (If you do not have the value for the efficiency then use 0.80)

$$\eta_{\text{engine}} = \frac{w}{q_H} = \frac{q_H - q_C}{q_H} = 1 - \frac{q_C}{q_H}$$

$$\text{Since } \frac{q_H}{T_H} = \frac{q_C}{T_C} \quad \frac{q_C}{q_H} = \frac{T_C}{T_H}$$

$$\text{Thus; } \eta_{\text{engine}} = 1 - \frac{T_C}{T_H}$$

$$0.83 = 1 - \frac{313}{T_H} \quad T_H = 1.8 \times 10^3 \text{ K or } T_H = 1.6 \times 10^3 \text{ }^\circ\text{C}$$

(4 pt)

Problem 5**7.0% of the total**

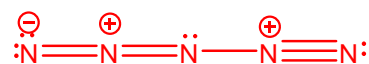
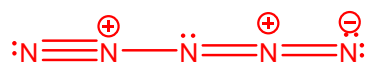
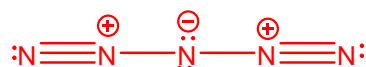
a		b	c	d	e	f	g	Problem 5	x%
i	ii	1	6	5	2	2	6	30	7.0
5	3								

Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amount of energy is released from their decomposition or reactions leading to more stable products. The only known polynitrogen species are N_2 , N_3^- and N_5^+ , isolated in 1772, 1890 and 1999, respectively, and the recently reported cyclic anion, N_5^- .

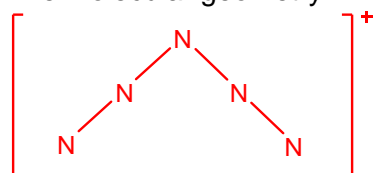
- a. (i) Write the Lewis structure for N_5^+ with three energetically favorable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of N_5^+ .

 N_5^+

Lewis Structure



The molecular geometry



5 point

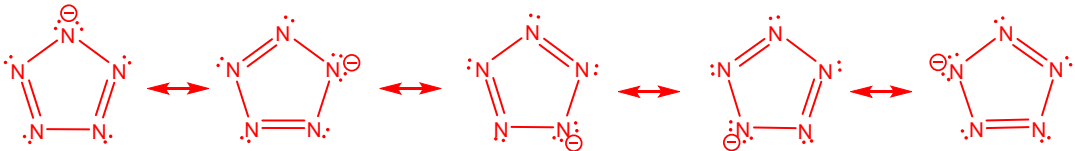
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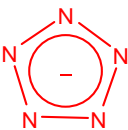
(ii) Write the Lewis structures for cyclic N_5^- with five energetically favorable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of cyclic N_5^- .

Cyclic N_5^-

Lewis Structure

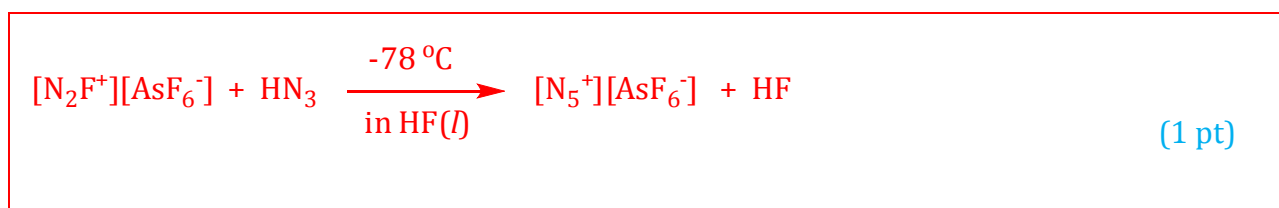


The molecular geometry

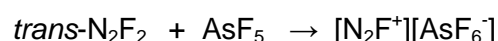
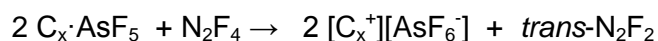


(3 pt)

b. The synthesis of $[N_5^+][AsF_6^-]$, a white ionic solid, was achieved by reacting $[N_2F^+][AsF_6^-]$ with hydrazoic acid, HN_3 , in liquid HF at $-78\text{ }^\circ\text{C}$. Write the balanced chemical equation for this reaction.

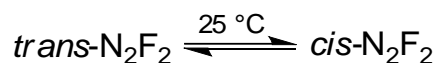


The preparation of $[N_2F^+][AsF_6^-]$ requires the reaction of N_2F_2 with strong Lewis acid, AsF_5 , as follows:



In the synthesis of N_2F_2 , the *trans* isomer is formed, which is thermodynamically less stable than *cis*- N_2F_2 . However, conversion of *trans*- N_2F_2 to *cis*- N_2F_2 requires surmounting a high energy barrier of 251 kJ/mol, so that equilibration between the *cis* and the *trans* isomers does not significantly take place without a suitable catalyst.

When *trans*- N_2F_2 is maintained in a closed container for 6 days at room temperature, in the presence of a small amount of SbF_5 as a catalyst, *cis*-*trans* thermal equilibrium is established.



The standard enthalpies of formation of *trans*- and *cis*-N₂F₂ are 67.31 and 62.03 kJ/mol, respectively, and their standard entropies at 25 °C are 262.10 and 266.50 J·K⁻¹·mol⁻¹, respectively.

- c. Find the ratio of the number of *cis*-N₂F₂ molecules over that of the *trans*-N₂F₂ molecules in an equilibrium mixture at 25 °C.

The desired ratio is the value of the equilibrium constant, *K*, of the *trans*→*cis* reaction shown above.

$$K = \frac{[\text{cis}]}{[\text{trans}]}$$

$$\Delta G^\circ = -RT \ln K$$

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

$$\Delta H^\circ = 62.03 - 67.31 = -5.28 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S^\circ = 266.50 - 262.10 = 4.40 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta G^\circ = -5.28 \times 10^3 - (298)(4.40) = -6.59 \times 10^3 \text{ J}\cdot\text{mol}^{-1}$$

$$K = e^{-\Delta G^\circ/RT} = e^{-(-6.59 \times 10^3)/(8.314 \times 298)} = 14.3$$

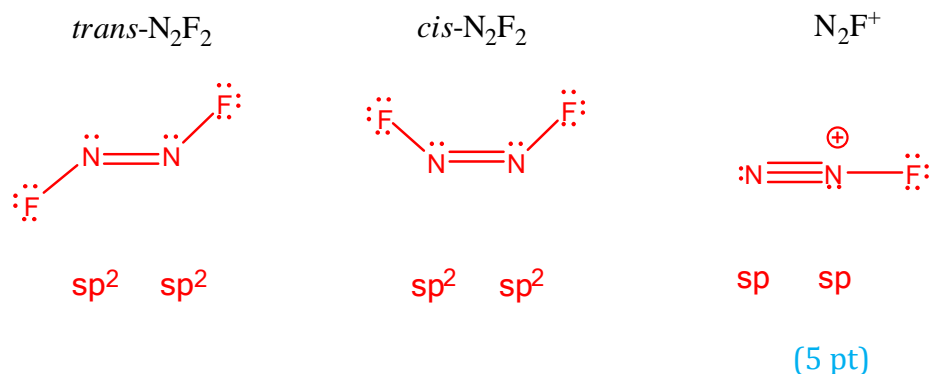
$$\frac{[\text{cis}]}{[\text{trans}]} = 14.3 \text{ at } 25\text{ }^\circ\text{C}.$$

(6 pt)

- d. Write the Lewis structures showing the geometry of the N₂F⁺ ion and of the *trans*- and *cis*-isomers of N₂F₂. Include all lone pairs and formal charges. Suggest an appropriate hybridization for each nitrogen atom in N₂F₂ and N₂F⁺.

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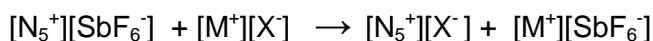


Solid $[\text{N}_5^+][\text{AsF}_6^-]$ is marginally stable at room temperature but reacts explosively with water to produce arsenic pentafluoride, hydrogen fluoride, molecular nitrogen and oxygen.

e. Write a balanced equation for the reaction between $[\text{N}_5^+][\text{AsF}_6^-]$ and water.



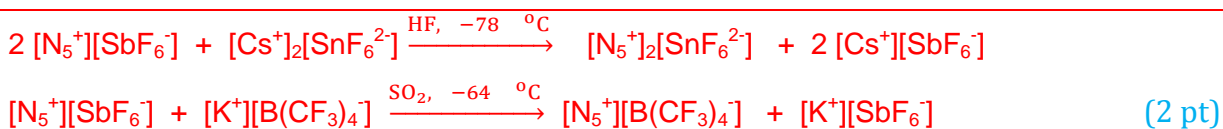
Conversion of $[\text{N}_5^+][\text{SbF}_6^-]$ into other N_5^+ salts can be achieved by a metathesis reaction:



$\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Cs}^+$; $\text{X}^- = \text{large anion such as } \text{SnF}_6^{2-} \text{ and } \text{B}(\text{CF}_3)_4^-$.

Since $[\text{Cs}^+][\text{SbF}_6^-]$ has a low solubility in anhydrous HF, and $[\text{K}^+][\text{SbF}_6^-]$ has a low solubility in SO_2 , these two solvents were used extensively to carry out metathesis reactions at -78°C and -64°C , respectively.

f. Write the balanced equation for the preparation of $[\text{N}_5^+]_2[\text{SnF}_6^{2-}]$ and $[\text{N}_5^+][\text{B}(\text{CF}_3)_4^-]$ in solution starting with $[\text{Cs}^+]_2[\text{SnF}_6^{2-}]$ and $[\text{K}^+][\text{B}(\text{CF}_3)_4^-]$, respectively. Indicate the appropriate solvent.

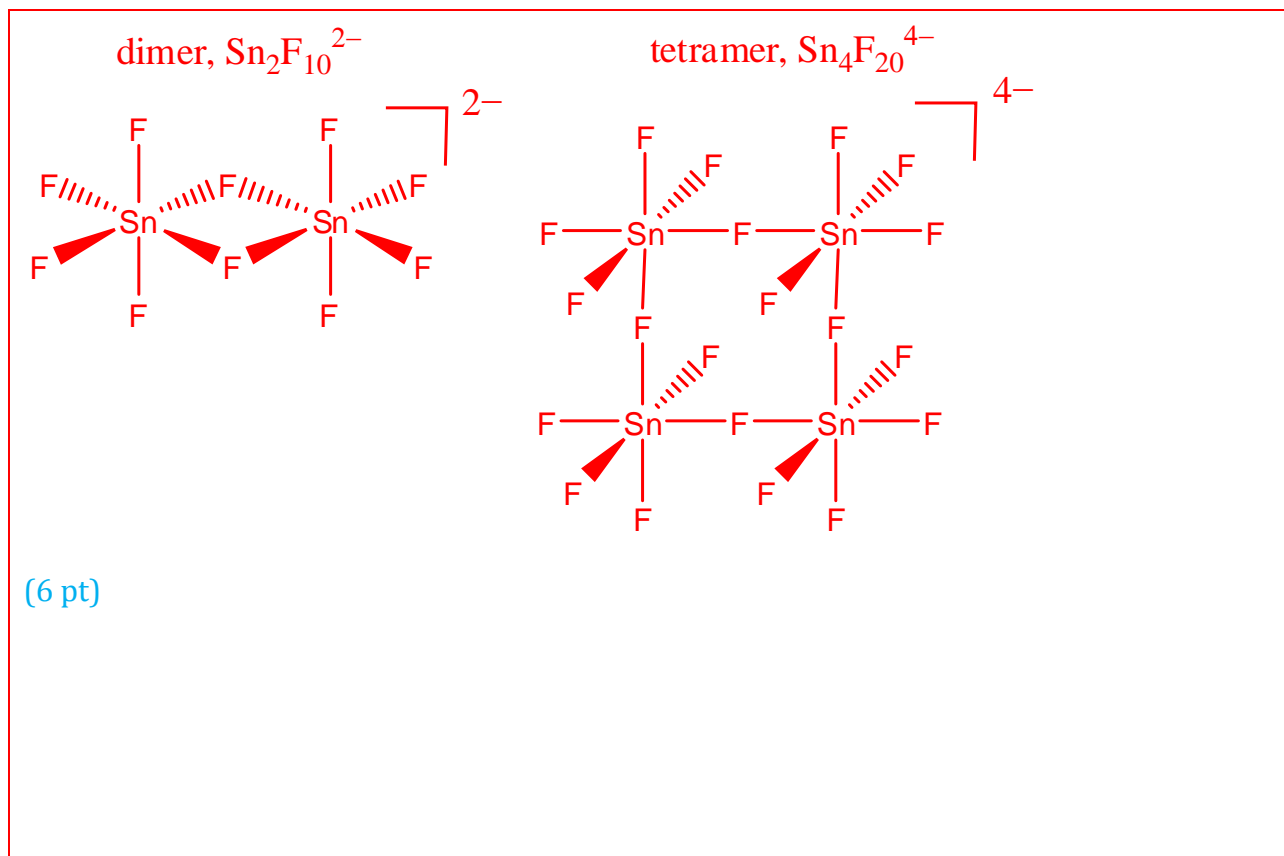


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When $[\text{N}_5^+]_2[\text{SnF}_6^{2-}]$ decomposes under carefully controlled conditions at 25-30 °C, $[\text{N}_5^+][\text{SnF}_5^-]$ and N_5F are formed. The $[\text{N}_5^+][\text{SnF}_5^-]$ salt is a white solid and has a thermal stability comparable to that of $[\text{N}_5^+][\text{SbF}_6^-]$ (50 – 60 °C). The solution ^{119}Sn NMR spectrum has shown that the SnF_5^- anion in this compound is, in fact, a mixture of dimeric and tetrameric polyanions. In both of these polyanions the coordination number of Sn atom is 6 and there are bridging fluorine atoms.

g. Draw the structures of dimeric and tetrameric polyanions.



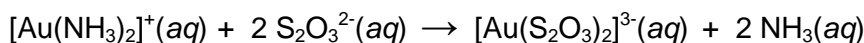
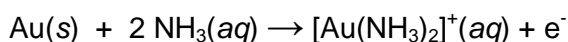
Problem 6**7.0% of the total**

a	b	c	d	e	f	g	Problem 6	x%
5	3	4	2	5	3	1	23	7.0

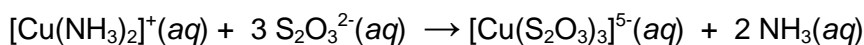
Extraction of gold using sodium cyanide, a very poisonous chemical, causes environmental problems and gives rise to serious public concern about the use of this so called “cyanide process”. Thiosulfate leaching of gold has been considered as an alternative. In this process, the main reagent is ammonium thiosulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_3$, which is relatively nontoxic. Although this process appears to be environmentally benign, the chemistry involved is very complex and needs to be studied thoroughly. The solution used for leaching gold contains $\text{S}_2\text{O}_3^{2-}$, Cu^{2+} , NH_3 , and dissolved O_2 . The solution must have a pH greater than 8.5 to allow free ammonia to be present.

According to the proposed mechanism, a local voltaic micro-cell forms on the surface of gold particles during the leaching process and operates as follows:

Anode:

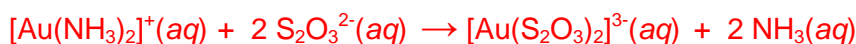


Cathode:



a. Write the overall cell reaction for this voltaic cell.

Net anode half reaction:



Net cathode half reaction:



Name:

Code:



Overall cell reaction:



(5 pt)

- b. In the presence of ammonia, O_2 oxidizes $[\text{Cu}(\text{S}_2\text{O}_3)_3]^{5-}$ back to $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Write a balanced equation for this oxidation-reduction reaction in basic solution.

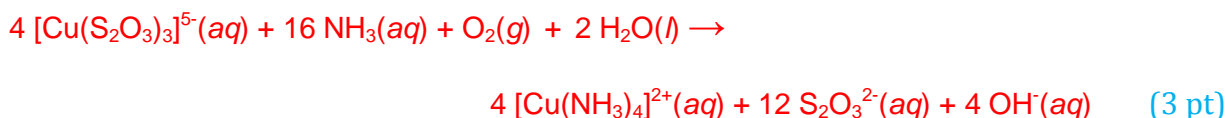
Oxidation half reaction:



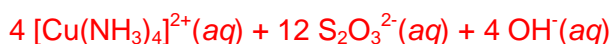
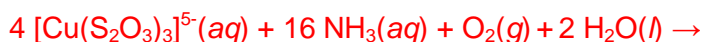
Reduction half reaction:



Oxidation-Reduction Reaction:



- c. In this leaching process, the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion functions as catalyst and speeds up the dissolution of gold. Write the net overall oxidation-reduction reaction for dissolution of the gold metal, which is catalyzed by $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion.



Name:

Code:

- d. Draw the coordination geometries of the metal in $[\text{Au}(\text{NH}_3)_2]^+$ and $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ complex ions, indicating the coordinating atoms.

	$[\text{Au}(\text{NH}_3)_2]^+$	$[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$
Coordination geometry	$[\text{H}_3\text{N}-\text{Au}-\text{NH}_3]^+$	$[\text{O}_3\text{S}-\text{S}-\text{Au}-\text{S}-\text{SO}_3]^{3-}$
	(2 pt)	

- e. The formation constants, K_f , of $[\text{Au}(\text{NH}_3)_2]^+$ and $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ complexes are 1.00×10^{26} and 1.00×10^{28} , respectively. Consider a leaching solution, in which the equilibrium concentrations of the species are as follows:

$$[\text{S}_2\text{O}_3^{2-}] = 0.100 \text{ M}; [\text{NH}_3] = 0.100 \text{ M}; \text{total concentration of gold(I) species} = 5.50 \times 10^{-5} \text{ M}.$$

Calculate the percentage of gold(I) ion, which exists in the form of thiosulfate complex.



$$K_{\text{eq}} = K_f(2)/K_f(1) = 1.00 \times 10^2$$

$$[\text{Au}(\text{NH}_3)_2]^+ + [\text{Au}(\text{S}_2\text{O}_3)_2]^{3-} = 5.50 \times 10^{-5} \text{ M}$$

$$K_{\text{eq}} = \frac{(0.100)^2 x}{(5.50 \times 10^{-5} - x)(0.100)^2} = 1.00 \times 10^2, \quad x = 5.445 \times 10^{-5} \text{ M}$$

$$\frac{5.445 \times 10^{-5}}{5.50 \times 10^{-5}} \times 100 = 99.0 \text{ \% of Au(I) in the form of } [\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$$

(5 pt)

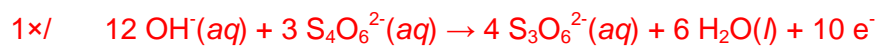
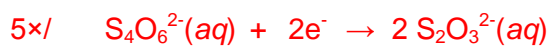
- f. When the concentration of O_2 is not high enough and $\text{pH} > 10$, $\text{S}_2\text{O}_3^{2-}$ reduces $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to $[\text{Cu}(\text{S}_2\text{O}_3)_3]^{5-}$ with the formation of tetrathionate ion, $\text{S}_4\text{O}_6^{2-}$:



In basic solution tetrathionate disproportionates to trithionate, $\text{S}_3\text{O}_6^{2-}$, and thiosulfate. Write a balanced equation for this disproportionation reaction.

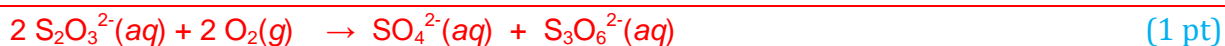
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(3 pt)

- g.** When the O_2 concentration is too high it oxidizes $\text{S}_2\text{O}_3^{2-}$ to yield trithionate and sulfate ions. Write a balanced equation for this reaction.

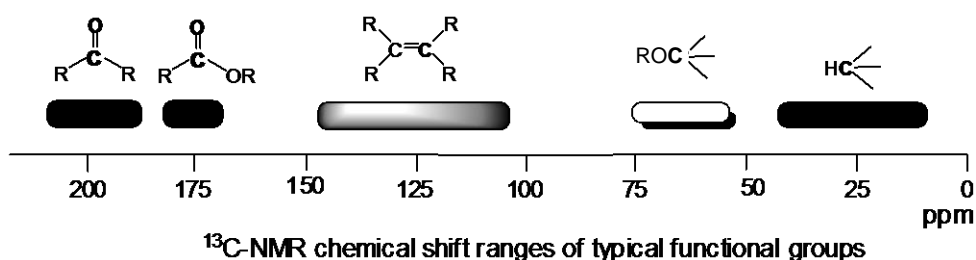


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Problem 7 8.5% of the total

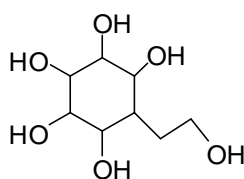
A	S	B	C	D	E	F	G ₁	G ₂	H	I	J	K	L	M	1a	1b	Problem 7	x%
2	2	2	2	2	2	1	1	1	2	2	2	1	1	1	1	1	26	8.5



Synthesis of a carbasugar

Carbohydrates are essential components of living cells and a source of energy for animals. They include simple sugars with small molecules as well as macromolecular substances. When the ring oxygen (endocyclic oxygen) in sugars is replaced by a methylene group, the compounds formed are called as **pseudosugars** or **carbasugars**. Since carbasugars are hydrolytically stable towards acids and enzymes, several carbasugars have found application in the field of glycosidase inhibition.

The total syntheses of two isomeric carbasugar having skeleton **1** are described below.



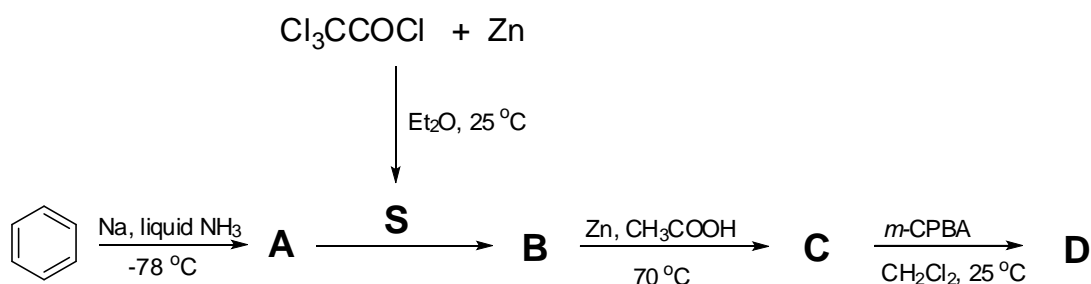
1

The total synthesis of **1** starts with a reduction of benzene by sodium in liquid ammonia to give **A**. The C-13 NMR spectrum of **A** consists of two signals at 124.0 and 26.0 ppm.

Trichloroacetyl chloride in the presence of Zn gives a reactive species **S**. One equivalent of **S** undergoes [2+2] cycloaddition with **A** to form a racemic product **B**. The reaction of **B** with Zn in acetic acid gives **C**. Compound **C** contains only carbon, hydrogen and oxygen: The C-13 NMR spectrum of **C** exhibits three sp² carbon signals at 210.0, 126.5 and 125.3 ppm.

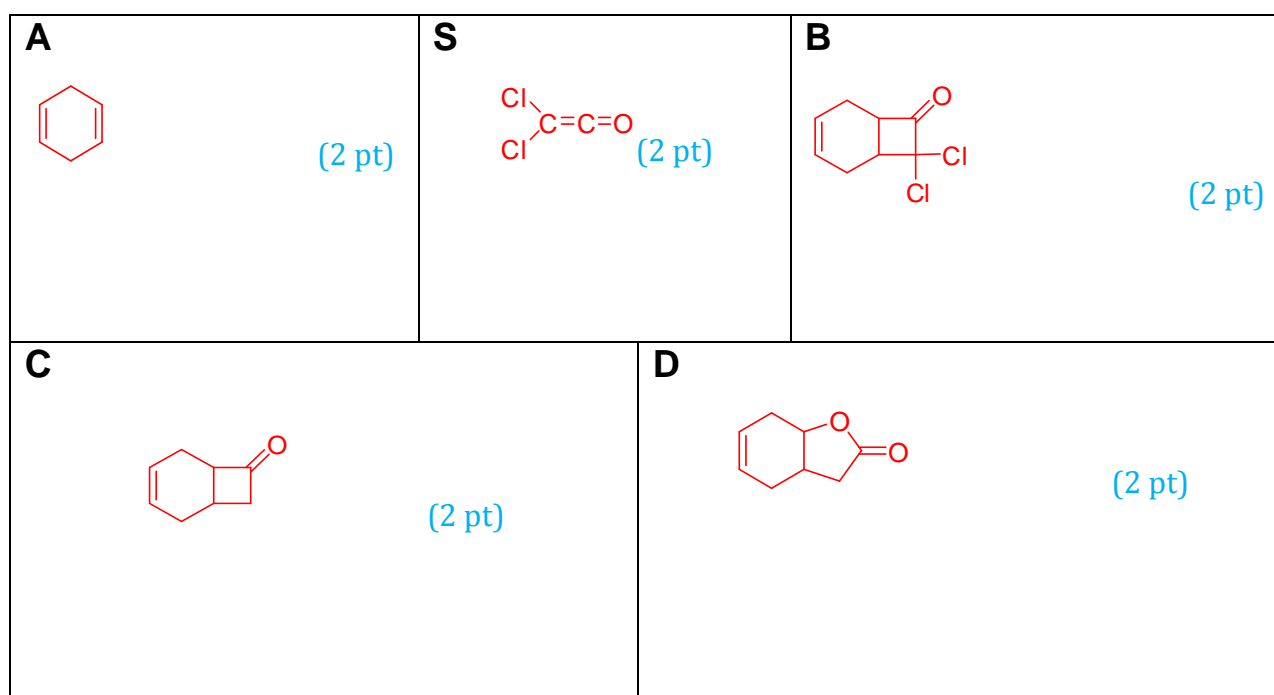
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The reaction of **C** with one equivalent *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride gives **D** as a major product. The C-13 NMR spectrum of **D** exhibits also three signals in the sp² region at 177.0, 125.8, 124.0 ppm.

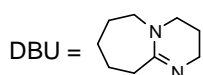
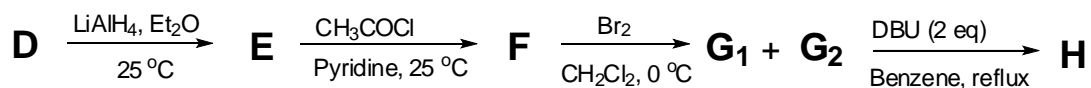
Draw the structures of **A**, **B**, **C**, **D**, and the intermediate **S**.



Reduction of **D** with LiAlH₄ yields **E**, which reacts with excess acetyl chloride in pyridine to give **F**. Draw the structures (use one enantiomer) of **E** and **F** using dashed-wedged line notation. Assign the configurations (*R* or *S*) at the asymmetric carbon atoms in **E**.

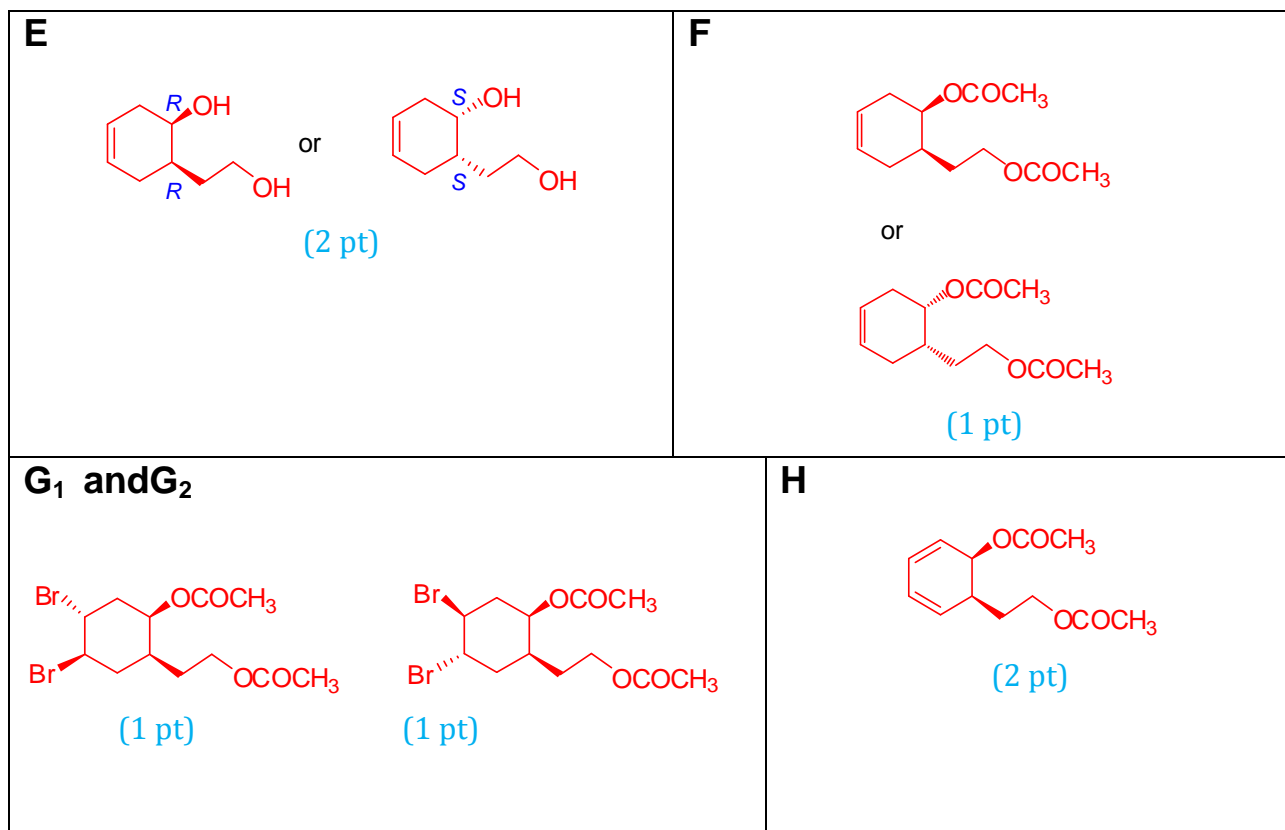
The compound **F** (use the drawn enantiomer) is reacted with bromine to give the stereoisomers **G**₁ and **G**₂. Draw the structures of **G**₁ and **G**₂ using dashed-wedged line notation.

A mixture of **G**₁ and **G**₂ is reacted with two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which is a strong amine base, to afford **H**. Draw the structure of **H** using dashed-wedged line notation.



Name:

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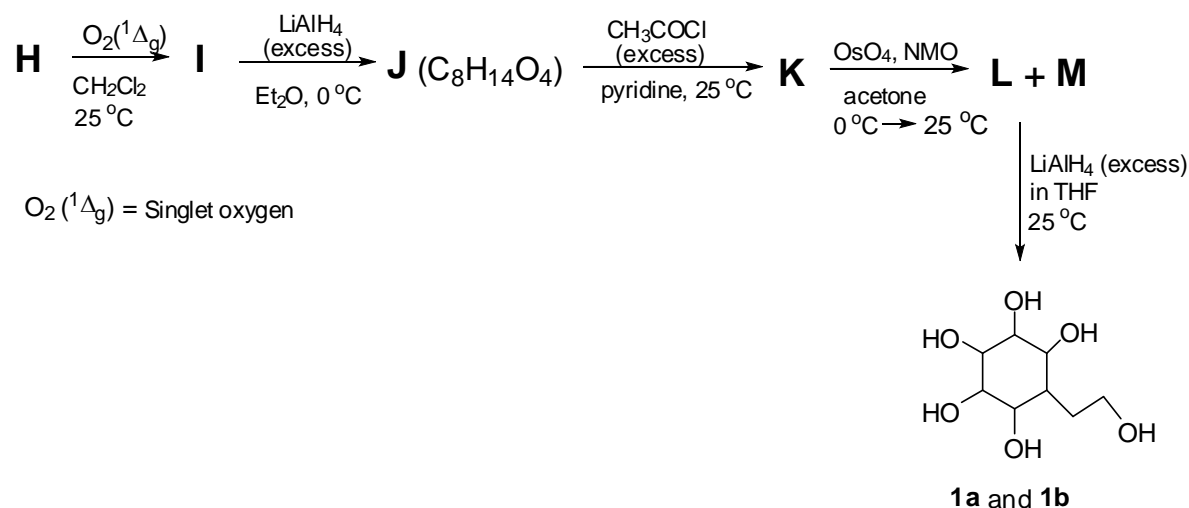


Reaction of **H** with singlet oxygen (in situ generated) affords **I**. Although two isomers are theoretically possible, **I** is formed as the single isomer due to steric hindrance and electronic repulsion.

The reaction of **I** with excess LiAlH_4 results in the formation of **J**. The C-13 NMR spectrum of **J** shows 8 signals, two in the sp^2 region.

Reaction of **J** with excess acetyl chloride in the presence of pyridine yields **K**. Subsequent reaction of **K** with OsO_4 in the presence of 4-methylmorpholine 4-oxide (NMO) gives stereoisomers **L** and **M**.

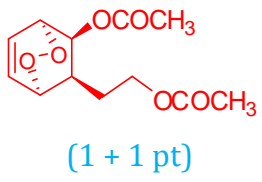
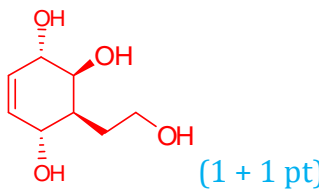
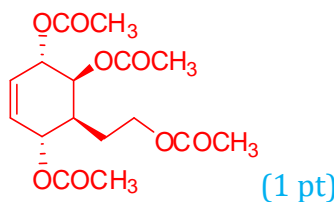
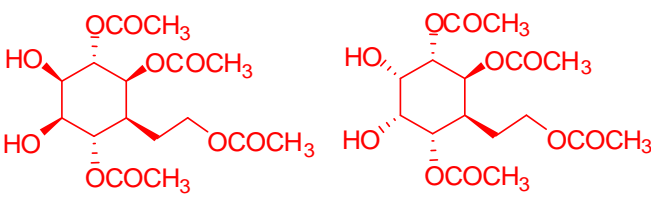
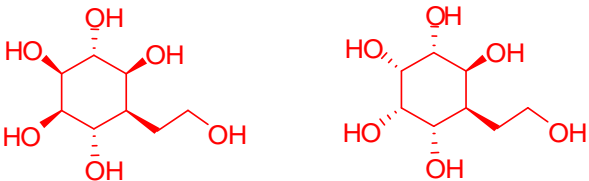
Upon reduction with excess LiAlH_4 , **L** and **M** give the stereoisomers **1a** and **1b**, respectively.



Name:

Code:

Draw the structures of **I**, **J**, **K**, **L**, **M**, **1a**, and **1b** using dashed-wedged line notation.

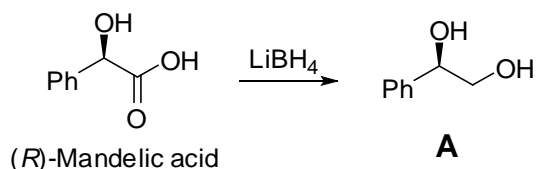
<p>I</p>  <p>(1 + 1 pt)</p>	<p>J</p>  <p>(1 + 1 pt)</p>
<p>K</p>  <p>(1 pt)</p>	<p>L and M (1 + 1 pt)</p> 
<p>1a and 1b (1 + 1 pt)</p> 	

Problem 8 6.5% of the total

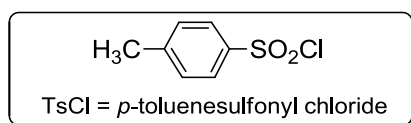
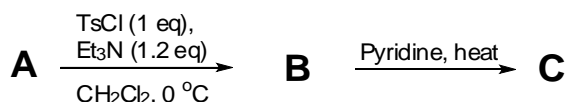
B	C	D	E	F	G	H	I	J	K	L	M	Problem 8	x%
2	2	2	2	1	1	1	1	1.5	1.5	1.5	1.5	18	6.5

Click chemistry is a chemical concept introduced by K. B. Sharpless in 2001 and describes a set of chemical reactions that generate substances quickly, reliably and quantitatively by joining molecules through small units under mild conditions. This methodology has recently been applied as a key step in the following synthesis of bicyclic compounds.

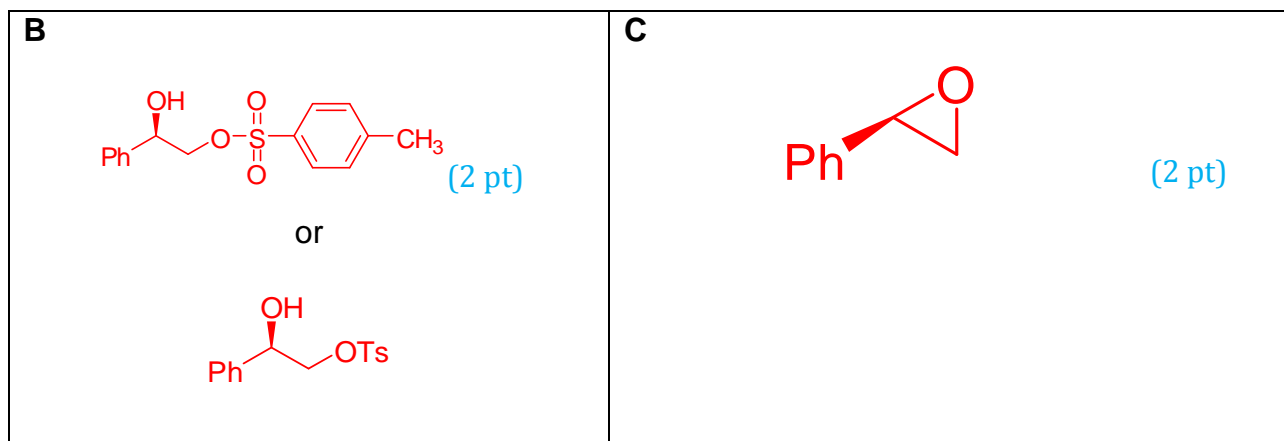
Mandelic acid is a versatile natural compound and widely used as a "chiral pool" in synthesis. The reduction of (*R*)-mandelic acid with LiBH_4 affords **A**.



Reaction of **A** with 1 equivalent *p*-toluenesulfonyl chloride gives **B**. Heating **B** in pyridine yields **C**. During this transformation, compounds **B** and **C** retain their absolute configurations.



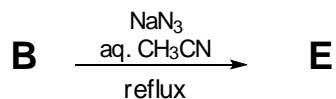
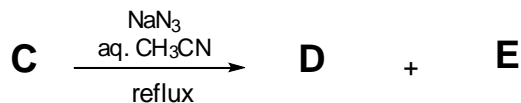
Draw the structures of **B** and **C** with the correct stereochemistry. Use dashed-wedged line notation throughout this problem.



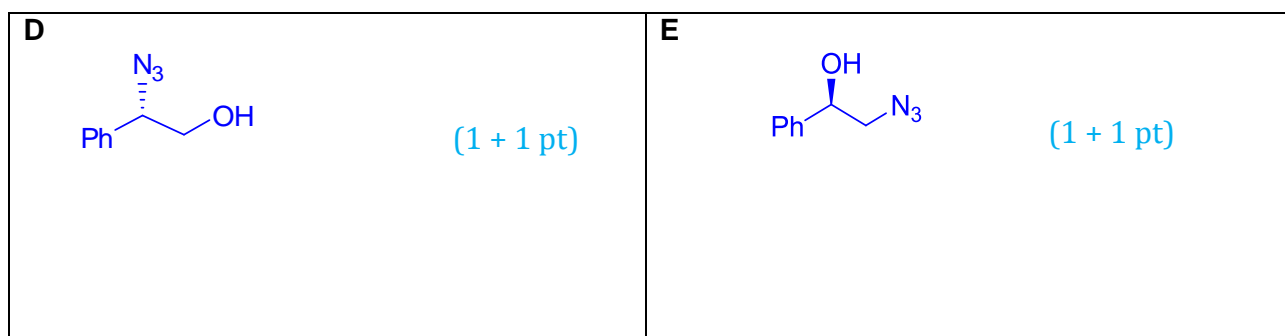
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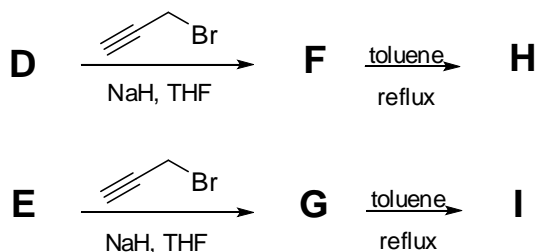
Reaction of **C** with sodium azide in aqueous acetonitrile gives a mixture of enantiopure regioisomers **D** and **E** in a ratio of 3:1. On the other hand, the compound **B** affords **E** as the sole product under the same condition.



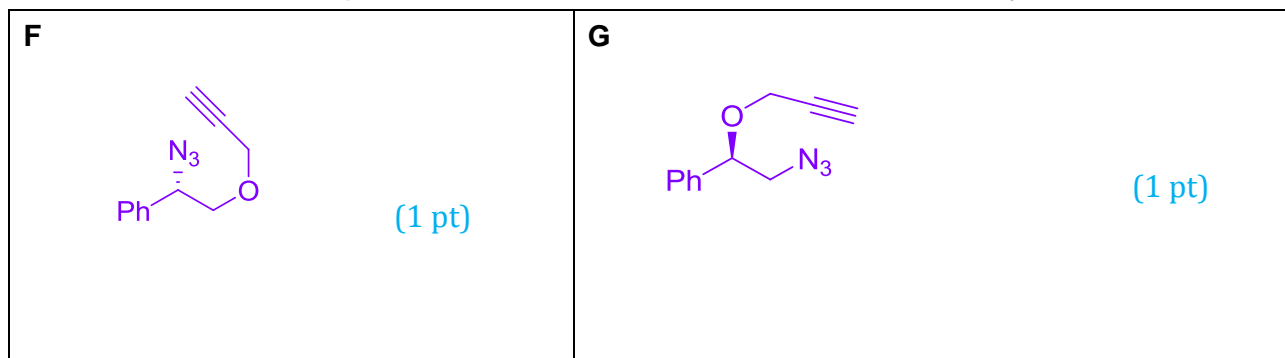
Draw the structures of **D** and **E** with the correct stereochemistry.



Part I: Compounds **D** and **E** are separately subjected to NaH mediated reaction with 3-bromoprop-1-yne to afford **F** and **G**, respectively. Heating **F** and **G** separately in toluene gives the bicyclic products **H** and **I**, respectively.

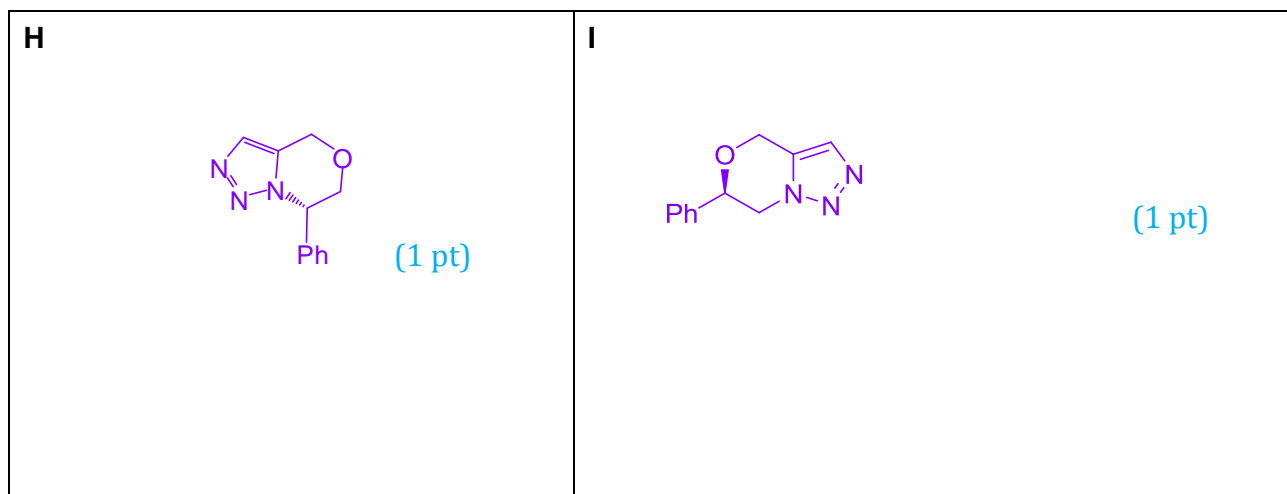


Draw the structure of compounds **F**, **G**, **H** and **I** with the correct stereochemistry.

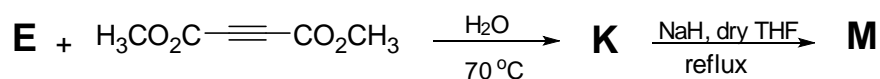
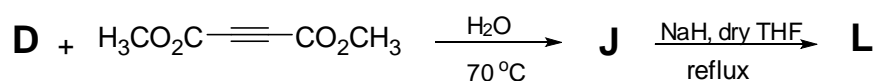


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Part II: Reaction of **D** and **E** separately with dimethyl acetylenedicarboxylate in water at 70°C forms the optically active monocyclic regioisomers **J** and **K**, respectively. Subsequent treatment of **J** and **K** with NaH gives final bicyclic products **L** and **M**, respectively, both having the formula $C_{13}H_{11}N_3O_4$.



Draw the structures of compound **J**, **K**, **L** and **M** with the correct stereochemistry.

