

Instructions

Examination Procedures

- You have **5 hours** to complete **Tasks 1, 2, and 3**. You may perform the tasks in any order you choose.
- There will be an additional **15 minutes reading time** before the start.
- **DO NOT** begin working on the tasks until the **START command** is given.
- When the **STOP command** is given **at the end of the 5 hours**, you must **stop** your work on the tasks **immediately**. **A delay in doing so may lead to your disqualification from the examination.**
- 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 behind**:
 - ✓ The problem booklet (this booklet)
 - ✓ The answer booklet
 - ✓ Your chosen TLC plates in zipper storage bags A and B with your student code (from Task 1)
 - ✓ Your product and glass microfiber filter sheet in a crystallization dish with a lid in zipper storage bag C with your student code (from Task 1)
- **Do not leave** the examination hall until you are instructed to do so by the supervisors.

Safety

- **Safety** is the most important issue in the laboratory. You are expected to follow the safety rules given in the IChO regulations. **Safety glasses** and **lab coats** must be worn at **ALL TIMES**.
- If you behave in an unsafe manner, you will receive **one warning** before you are asked to leave the laboratory. If required to leave due to a second warning, you will receive a score of zero for the entire experimental examination.
- **NO eating or drinking** is allowed in the laboratory.
- In case of emergency, follow the instructions given by the supervisors.

Notes on the booklets and answer methods

- The **problem booklet** comprises 23 pages including cover page.
- The **answer booklet** comprises 6 pages. Do not attempt to separate the sheets.

- You should confirm **your student code** inscribed on the booklets and write **your name and student code on every answer sheet**.
- Use only the pen provided for filling in the **answer sheets**. You may also use the calculator and the ruler provided. Use the mechanical pencil provided only for experiments in Task 1. Do not use the mechanical pencil for filling in the **answer sheets**.
- All results must be written in the appropriate areas on the answer sheets. Results written elsewhere will not be graded. If you need to do **rough calculations, etc.**, use the back of the sheets.
- You should take care to report answers to an appropriate number of significant figures.
- Keep your answer booklet in the envelope provided. Take out the booklet only when you write the answers. Do not seal the envelope.

Notes on the Examination

- You may need to reuse some glassware during the examination. If this is the case, clean it carefully in the sink closest to you.
- Contact a supervisor near you if you have any **questions** regarding the tasks or if you need a **refreshment/toilet break**.
- Use the labeled **waste containers** under the hood or near the windows for disposal of liquids and solids. A waste container (plastic beaker) is also available on each bench for aqueous waste. Discard used glass capillaries into a labeled plastic tube.
- **Replacement of chemicals and laboratory ware** will be provided if necessary. Other than the first, for which you will be pardoned, each such incident will result in the **loss of 1 point** from your 40 practical points. Refilling of washbottle water is permitted with no loss of points.
- An official English version of this examination is available upon request if you require clarification.

Periodic table with relative atomic masses

1 H 1.01	2 He 4.00																
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 -	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	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	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
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

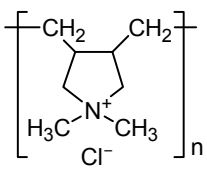
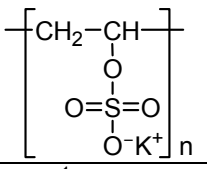
Apparatuses

Apparatuses	Number
For multiple tasks (on the desk or in Box 1):	
20-mL beaker for taking a small portion of liquid to rinse inside of glassware	1
Paper	3
2-mL pipette bulb	1
5-mL pipette bulb	1
Pipette rack	1
200-mL plastic beaker for waste	1
Safety bulb	1
Spatula	1
Stand	1
100-mL washbottle	1
500-mL washbottle	1
For Task 1 (in Box 1, on the desk or on pipette rack):	
Büchner funnel with rubber adapter	1
Clamp with muff (clamp holder)	1
200-mL conical beaker	1
300-mL conical beaker	1
Diaphragm vacuum pump with tubing and connector	1
Glass capillary tube (in a plastic tube)	8
Glass microfiber filter sheet in a crystallization dish with lid	1
2-mL graduated pipette	3
5-mL graduated pipette	1
Magnetic stirrer	1
10-mm magnetic stirring bar	1
22-mm magnetic stirring bar	1
10-mL measuring glass	1
pH test paper (in a zipper storage bag)	3
10-mL plastic graduated cylinder	1
Plastic tube for used glass capillary	1
Suction flask	1
10-mL test tube	1

100-mL test tube	1
TLC developing chamber with lid	1
TLC plate (in a zipper storage bag)	4
Tweezers	1
Zipper storage bags A and B for submission of TLC plates	1 for each
Zipper storage bag C for submission of glass microfiber filter sheet in a crystallization dish	1
For Task 2 (in Box 2, on the desk or on pipette rack):	
2-mL graduated pipette	1
5-mL graduated pipette	1
Label (in a zipper storage bag)	4
LED light box (in a zipper storage bag: do not remove from the bag at any time.)	1
Nessler tube	5
Nessler tube rack	1
50-mL volumetric flask	2
5-mL volumetric pipette	1
10-mL volumetric pipette	1
For Task 3.1 (in Box 2 or on pipette rack):	
Burette	1
Burette clamp	1
100-mL conical beaker	6
Glass funnel (for transferring chemicals to a burette)	1
1-mL graduated pipette	2
5-mL volumetric pipette	1
20-mL volumetric pipette	1
For Task 3.2 (in Box 2):	
10-mL vial (in a zipper storage bag)	10
Plastic Pasteur pipette	1
Shared equipment:	
Gloves of various sizes	
UV lamp	
Cleaning tissue	

Chemicals on Each Desk

Chemical	Quantity	Container	R phrases	S phrases
For multiple tasks (in Box 1):				
0.5 mol L ⁻¹ hydrochloric acid (0.5 mol L ⁻¹ HCl)	50 mL	Plastic bottle	None listed	None listed
For Task 1 (in Box 1):				
1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (C ₁₃ H ₁₉ NO ₄ ; 1,4-DHP_powder)	1 g	Vial	36/37/38	26
1,4-DHP for TLC (1,4-DHP_TLC)	3 mg	Vial	36/37/38	26
Ethanol (C ₂ H ₅ OH)	10 mL	Glass bottle	11	7-16
Ethyl acetate (CH ₃ COOC ₂ H ₅)	25 mL	Glass bottle	11-36-66-67	16-26-33
Heptane (C ₇ H ₁₆)	20 mL	Glass bottle	11-38-50/53-65-67	9-16-29-33-60-61-62
Potassium iodide (KI)	150 mg	Glass bottle	None listed	None listed
Sodium metabisulfite (Na ₂ S ₂ O ₅)	1 g	Glass bottle	22-31-41	26-39-46
Saturated sodium hydrogencarbonate solution (Sat. NaHCO ₃ solution)	25 mL	Glass bottle	None listed	None listed
Urea hydrogen peroxide (CH ₄ N ₂ O•H ₂ O ₂ ; UHP)	1 g	Vial	8-34	17-26-36/37/39-45
For Task 2 (in Box 2):				
Sample solution (labeled as "Sample solution")	30 mL	Plastic bottle	None listed	None listed
Standard Fe(bpy) ₃ ²⁺ solution 1 (containing 2.0 mg of iron in 1 L solution) (labeled as "Standard Fe(bpy) ₃ ²⁺ solution 1")	50 mL	Plastic bottle	None listed	None listed
Standard Fe(bpy) ₃ ²⁺ solution 2 (containing 3.0 mg of iron in 1 L solution) (labeled as "Standard Fe(bpy) ₃ ²⁺ solution 2")	50 mL	Plastic bottle	None listed	None listed
Acetate buffer solution (pH 4.6, 1:1 mixture of acetic acid and sodium acetate; CH ₃ COOH-CH ₃ COONa solution)	50 mL	Plastic bottle	None listed	None listed

0.1 mol L ⁻¹ disodium hydrogenphosphate solution (0.1 mol L⁻¹ Na₂HPO₄)	25 mL	Plastic bottle	None listed	None listed
0.2 % (w/v) 2,2'-bipyridine aqueous solution (0.2 % (w/v) C₁₀N₂H₈)	25 mL	Plastic bottle	None listed	None listed
Sodium thioglycolate (C₂H₃NaO₂S)	20 mg	Vial	22-38	36
For Task 3.1 (in Box 2 or on the desk):				
Polysaccharide solution (labeled as " Polysaccharide solution ")	50 mL	Plastic bottle	None listed	None listed
Poly(diallyldimethylammonium chloride) aqueous solution (PDAC) 	240 mL	Glass bottle	None listed	None listed
Potassium poly(vinyl sulfate) aqueous solution (0.0025 mol L ⁻¹ ; monomer unit concentration) (0.0025 mol L⁻¹ PVSK) 	240 mL	Glass bottle	36/37/38	26-36
0.5 mol L ⁻¹ sodium hydroxide aqueous solution (0.5 mol L⁻¹ NaOH)	50 mL	Plastic bottle	34	26-37/39-45
1 g L ⁻¹ toluidine blue (TB) aqueous solution (1 g L⁻¹ C₁₅H₁₆N₃SCI)	6 mL	Dropper bottle	None listed	None listed

For Task 3.2 (in Box 2):				
Solution X-1 (X: A-H)	10 mL	Dropper bottle	36/37/38	26-36
Solution X-2 (X: A-H)	10 mL	Dropper bottle		
Solution X-3 (X: A-H)	10 mL	Dropper bottle		
Solution X-4 (X: A-H)	10 mL	Dropper bottle		
Solution X-5 (X: A-H)	10 mL	Dropper bottle		

Risk Phrases

Number	Special Risks
8	Contact with combustible material may cause fire.
11	Highly flammable
22	Harmful if swallowed
31	Contact with acids liberates toxic gas.
34	Causes burns
36	Irritating to eyes
38	Irritating to skin
41	Risk of serious damage to eyes
65	Harmful: may cause lung damage if swallowed.
66	Repeated exposure may cause skin dryness or cracking.
67	Vapors may cause drowsiness and dizziness.
36/37/38	Irritating to eyes, respiratory system and skin
50/53	Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment.

Safety Phrases

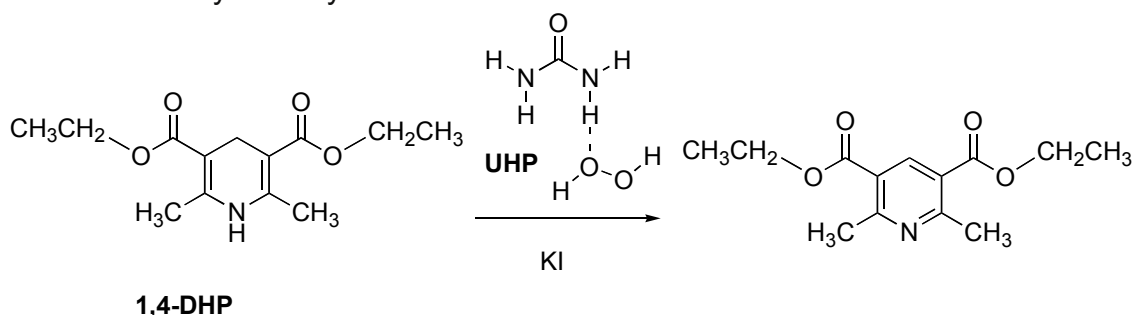
Number	Safety Recommendations
7	Keep container tightly closed.
9	Keep container in a well ventilated place.
16	Keep away from sources of ignition - No Smoking.
17	Keep away from combustible material.
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
29	Do not empty into drains.
33	Take precautionary measures against static discharges.
36	Wear suitable protective clothing.
37	Wear suitable gloves.
39	Wear eye/face protection.
45	In case of accident or if you feel unwell, seek medical advice immediately. (Show the label where possible.)
46	If swallowed, seek medical advice immediately and show the container or label.
60	This material and its container must be disposed of as hazardous waste.
61	Avoid release to the environment. Refer to special instructions/ material safety data sheet.
62	If swallowed, do not induce vomiting: seek medical advice immediately and show the container or label
24/25	Avoid contact with skin and eyes.
36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
37/39	Wear suitable gloves and eye/face protection

Task 1

1a	1b	1c	1d	1e			Total
				i	ii	iii	
4	4	2	2	2	2	24	40

Reaction of Hantzsch Ester with Urea Hydrogen Peroxide

In this experiment, you are required to synthesize a pyridinedicarboxylate derivative from 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (1,4-DHP or Hantzsch ester) by oxidation with urea hydrogen peroxide (UHP), an environmentally-friendly oxidant.



Procedures

- (1) Place a 22-mm magnetic stirring bar in a 100-mL test tube. Fix the test tube on a magnetic stirrer using a clamp. Add 1,4-DHP (1 g) (labeled as 1,4-DHP_powder), and potassium iodide (150 mg) to the test tube, followed by ethanol (5 mL), with a 5-mL graduated pipette.
- (2) Add 1 g UHP (wear gloves) and stir the mixture. (**Caution: this reaction is exothermic.**)
- (3) For thin layer chromatography (TLC) analysis, prepare a mixture of ethyl acetate:heptane (1:2 in volume) with a measuring glass and place an appropriate amount of the mixture in a TLC developing chamber. Add 1 mL of ethyl acetate to the vial (labeled as 1,4-DHP_TLC) to dissolve 1,4-DHP (3 mg).
- (4) Check your TLC plates before using. If they are damaged, they can be replaced without penalty. Draw a start line on the lower portion of a TLC plate with a pencil (see Fig. 1.1).
- (5) During the reaction, the reaction mixture becomes clear (usually within 20 min). When the reaction mixture becomes clear (the precipitates may form when it cools, but precipitates will not affect the TLC analysis), take a small portion of the mixture using a

glass capillary and load it to make two spots in the center and right positions on the TLC plate. Load an appropriate amount of the 1,4-DHP solution prepared in procedure (3) in the center and left positions, so that there are three spots on the plate, with the center spot containing both the reaction mixture and 1,4-DHP (see Fig. 1.1). Develop the TLC plate in the TLC chamber (see Figs. 1.1 and 1.2). Mark the solvent front with the pencil. Visualize the spots using a UV lamp (254 nm) and draw a line around the UV-active spots on the TLC clearly with the pencil. Assess the completion of the reaction based on the TLC results. Repeat the TLC analysis after ten minutes, if you find significant amounts of 1,4-DHP in the reaction mixture. [Note that you will perform TLC analysis again in procedure (8).] Place the last TLC plate in a zipper storage bag marked "A."



Fig. 1.1 Spots on the TLC plate before development;
X: 1,4-DHP, Y: Reaction mixture.

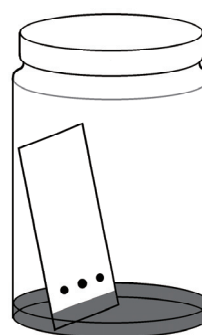


Fig. 1.2 TLC plate placed in the TLC developing chamber.

(6) Set up the suction filtration equipment (see Fig. 1.3).

Connect the suction flask to the diaphragm vacuum pump. Place a Büchner funnel fitted with a rubber adapter onto the suction flask. Place a glass microfiber filter sheet on the funnel.

(7) Add water (5 mL) to the reaction mixture using a 10-mL plastic graduated cylinder. Add sodium metabisulfite (1 g), transfer the contents of the tube (including the stirring bar) into a 200-mL conical beaker and wash the test tube with water (30 mL). Place the 200-mL conical beaker on the magnetic stirrer

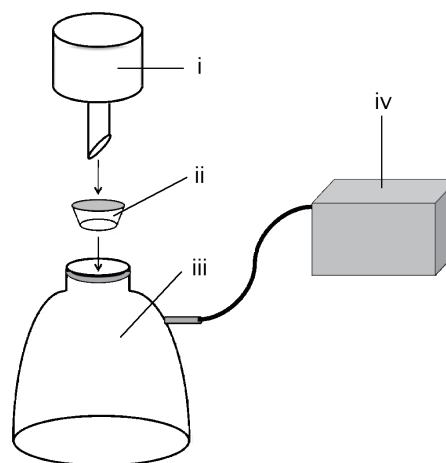


Fig. 1.3 Suction filtration equipment: i, Büchner funnel; ii, rubber adapter; iii, suction flask; iv, diaphragm vacuum pump.

and stir the solution. Add saturated sodium hydrogencarbonate solution in small portions using a 2-mL graduated pipette until the pH of the aqueous phase becomes just over 7 (check the pH with pH test paper). Filter the precipitate formed through the Büchner funnel with suction using the diaphragm vacuum pump, and wash the precipitate with a small portion of water. Suck air through the precipitates for a minute to dry the product.

- (8) Transfer the filtrate from the suction flask to a 300-mL conical beaker. Transfer the filtrate (2 mL) to a 10-mL test tube using a 2-mL graduated pipette. Place a 10-mm magnetic stirring bar in the test tube and fix it securely with the clamp. Add 1 mL of ethyl acetate to the test tube using a 2-mL graduated pipette and stir the solution vigorously for 30 seconds on the magnetic stirrer. Stop stirring and wait for the solution to separate into two layers. Analyze the upper layer by TLC to see if there is any product remaining in the filtrates. Spot the filtrates on the plate in the same way as procedure (5). Mark the solvent front and the spot(s), if any. Place the TLC plate in a zipper storage bag marked "B." If you detect the product on the TLC plate, add more saturated sodium hydrogencarbonate solution.
- (9) At this stage, if you find a precipitate formed, filter and wash it. If you find no precipitate, skip this filtration process.
- (10) Suck air through the precipitate for 10 minutes to dry the product. Place your product and the glass microfiber filter sheet in the crystallization dish. Cover the dish with the lid marked with your code. Avoid placing the stirring bar in the dish. Place the crystallization dish with the lid in a zipper storage bag marked "C."

a) Copy (sketch) the TLC plate in bag "A" on your answer sheet.

Indicate the solvent front line and the base line.

- 1) If there are less than three spots loaded on the base line, 3 points will be subtracted.
- 2) If the spots are not separated on the TLC after development, 2 points will be subtracted.
- 3) If the solvent front line and/or the base line is missing, 1 point will be subtracted for each.



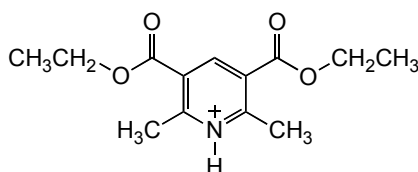
- b) Determine and record the R_f values (to the 2nd decimal place) of the spots on the TLC plate in bag "A."

Spot	R_f value
1,4-DHP	0.32-0.42
Product	0.61-0.71

Two points each will be awarded for R_f values (to the 2nd decimal place) in the ranges shown above. No points will be awarded for values outside the ranges. A score of 1 will be given if the value is reported down to the 1st decimal place.

- c) Draw the structural formula of the organic cation before adding sodium hydrogencarbonate.

If the correct structural formula is drawn as is shown below, 2 points will be awarded.



- d) What is (are) the final product(s) derived from UHP? Give the chemical formula(e) of the product(s).

If correct chemical formulae are written as shown below, 1 point each will be awarded.

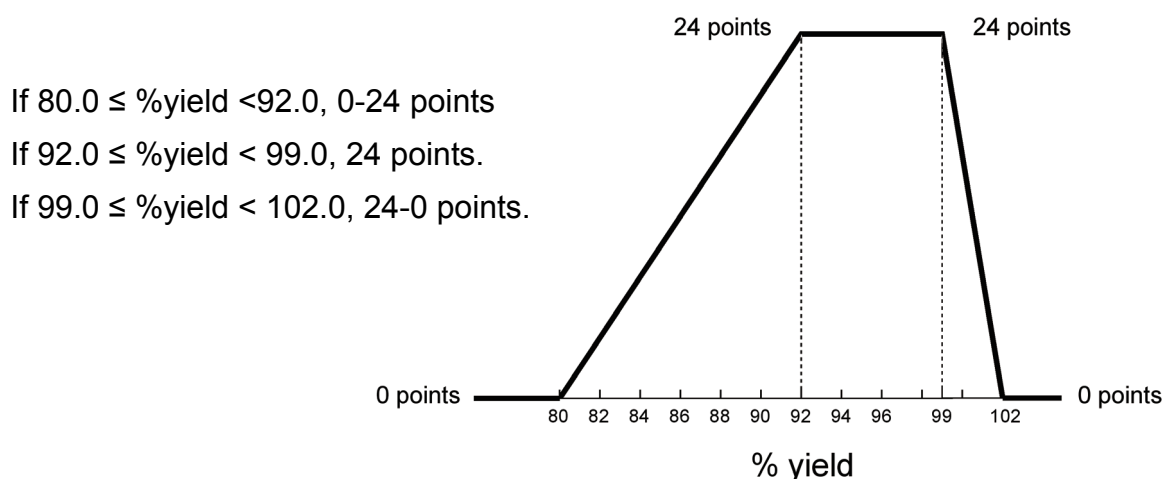


- e) Submit the following:

- TLC plate in bag "A"
- TLC plate in bag "B"
- Your product and filter paper in the crystallization dish placed in bag "C"
- TLC plate in bag "A"

If the outline to be drawn with a pencil around the UV-active spots is unclear or missing, 1 point will be subtracted.

- v) TLC plate in bag “B”
- 1) If the outline to be drawn with a pencil around the UV-active spots is unclear or missing, 1 point will be subtracted.
 - 2) If the solvent front line and/or the base line is missing, minus 1 point for each will be subtracted.
- vi) Your product and filter paper in the crystallization dish stored in bag “C”
- 1) The scientific committee will measure the percent yield after drying at 60 °C.
 - 2) In most cases, the sample is pure and dissolved in CDCl_3 completely. The following calculation based on the percent yields obtained will be applied only if no 1,4-DHP or byproducts is observed in the ^1H NMR spectrum and the product is completely soluble in CDCl_3 .



- 3) If there are peaks of 1,4-DHP (ca δ 2.19 ppm) and the corresponding pyridine product (ca δ 2.85 ppm) in the ^1H NMR spectrum and the percent yield is 100% or less, the actual percent yield is calculated by the following equation:

$$\frac{\text{Sample mass (g)}}{\text{Theoretical yield (g)}} \times \frac{(\text{Integral at } \delta \text{ 2.85 ppm}) \times 251.3}{(\text{integral at } \delta \text{ 2.19}) \times 253.3 + (\text{integral at } \delta \text{ 2.85 ppm}) \times 251.3} \times 100$$

- 4) If insoluble material remains after the addition of CDCl_3 for ^1H NMR measurement, 6 points will be subtracted.
- 5) If byproducts are detected evidently in the ^1H NMR spectrum, 6 points will be subtracted.

Task 2

2a	2b	2c	2d	2e	2f		Total
					i	ii	
2	2	15	15	3	3	5	45

Determination of Fe(II) and Fe(III) by visual colorimetry

In this experiment, you are required to determine Fe(II) and Fe(III) in a given sample solution which simulates a dissolved magnetite ore by visual colorimetric analysis involving a color reaction between Fe(II) and 2,2'-bipyridine (bpy) to form an intensely red complex, $\text{Fe}(\text{bpy})_3^{2+}$.

The amount of $\text{Fe}(\text{bpy})_3^{2+}$ complex can be quantified by visual colorimetric measurement using Nessler tubes. This is a quite simple technique that was employed before photoelectric instruments were generally available, but an accuracy of less than $\pm 5\%$ can be achieved. In this technique, a pair of Nessler tubes is used; one is filled with a reference solution, and the other is filled with a solution to be tested. The depths of colors of the two solutions are balanced by adjusting the heights of liquid columns of the solutions.

When the colors look the same, the concentration can be calculated from that of the reference solution with a known concentration and the height of the column of each solution based on the Lambert-Beer law:

$$A = \varepsilon cl$$

where A is the absorbance, c is the concentration, l is the path length and ε is the molar absorption coefficient. First, you will learn to employ this technique by conducting **measurements A** and **B**, and then you will determine the concentrations of Fe(II) and Fe(III) with **measurements C** and **D**.

Procedures

- (1) Add 5 mL of acetate buffer solution, 5 mL of disodium hydrogenphosphate solution (to mask Fe(III)), 5 mL of 2,2'-bipyridine solution and 10.00 mL of sample solution into a 50-mL volumetric flask using appropriate pipettes for each and dilute the resulting solution with water to the 50-mL mark. Then stopper the flask and mix the solution well. Allow it to stand for at least **20 min** to fully develop color. This solution is named "**sample 1**."
- (2) Add 5 mL of acetate buffer solution, 5 mL of 2,2'-bipyridine solution and 5.00 mL of sample solution into a 50-mL volumetric flask. Then add 20 mg of sodium thioglycolate

powder (in excess) to reduce Fe(III) to Fe(II). Dilute the solution with water to the 50-mL mark, stopper the flask and mix the solution well. Allow it to stand for at least **20 min**. This solution is named “**sample 2**.”

- (3) Perform visual colorimetric measurements A – D based on the “Instructions for visual colorimetric measurement” shown below.

Instructions for visual colorimetric measurement

Set a pair of Nessler tubes on a Nessler tube rack placed on an LED light box (do not remove it from the bag at any time) and turn on the light (see Fig. 2.1). Pour the provided “**standard Fe(bpy)₃²⁺ solution 1**” into one tube to an appropriate height (70 – 90 mm is recommended) from the bottom (etched marks on the tube indicate fixed heights from the bottom in mm) and use this as a reference for **measurements A - D**. Pour the solution to be measured into the other tube, and then compare its depth of color with that of the reference solution by looking downward through the solutions toward the LED light box.

Adjust the height of the liquid column of the test solution by adding or removing the solution with a graduated pipette until the depth of color in the two tubes is identical. Estimate your reading to at least 1 mm.

Note that the depths of color in a certain range may be recognized as identical to human eyes. The appropriate value for the height of the test solution, *h*, should be determined by taking the range into the consideration. For example, if you adjust the height of the liquid column of the test solution only by increasing (or decreasing) the volume, you could reach a lower (or higher) value than the true one. A possible way to estimate the true value is to take an average between the values of lower and higher limits.

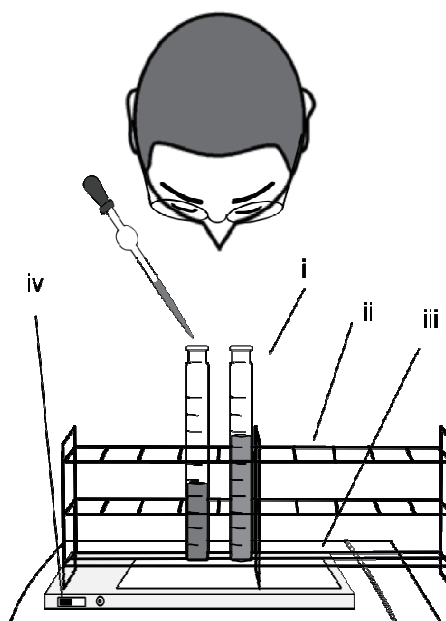


Fig. 2.1 Visual colorimetric measurement: i, Nessler tube; ii, Nessler tube rack; iii, LED light box in a zipper storage bag; iv, power switch.

Measurement A: Perform a measurement using “**standard Fe(bpy)₃²⁺ solution 1**” as both the reference and the test solutions. In this measurement, pour the reference

solution into a Nessler tube to achieve an appropriate height, and then pour the test solution into the other Nessler tube until the colors of the two solutions match each other. (When the colors match, the heights should IDEALLY be the same.) Then add more test solution until you recognize that the colors have become different from each other. Report both the lower and higher limits of the height of the liquid column of test solution with the same depth of color as the reference solution.

a) Report your results for **measurement A** using the table provided on the answer sheet.

	h' (height of standard solution 1) / mm	Lower limit of h / mm	Higher limit of h / mm	h (estimated height of test solution) / mm
Measurement A	Any value	Any value	Any value	Any value

Two points will be awarded, except when there is no answer.

Measurement B: Perform a measurement of “**standard $\text{Fe}(\text{bpy})_3^{2+}$ solution 2**” as a test solution using “**standard $\text{Fe}(\text{bpy})_3^{2+}$ solution 1**” as a reference.

b) Report your results for **measurement B** using the table provided on the answer sheet.

	h' (height of standard solution 1) / mm	h (estimated height of test solution) / mm
Measurement B	Any value	Any value

Two points will be awarded, except when there is no answer.

Measurement C: Perform measurement of **sample 1**.

c) Report your results for **measurement C** using the table provided on the answer sheet.

	h' (height of standard solution 1) / mm	h (estimated height of test solution) / mm
Measurement C	Experimental value of h'	sample 1: $1.23 h'$
		sample 2: $1.16 h'$
		sample 3: $1.10 h'$

Measurement D: Perform measurement of **sample 2**.

d) Report your results for **measurement D** using the table provided on the answer sheet.

	h' (height of standard solution 1) / mm	h (estimated height of test solution) / mm
Measurement D	Experimental value of h'	sample 1: $0.763 h'$
		sample 2: $0.725 h'$
		sample 3: $0.749 h'$

For 2c and 2d, a full score of 15 points will be awarded for values within a $\pm 5\%$ error range. A score of zero will be given if the absolute error is 15% or more. A linear point scale will be applied for scores from zero to 15; points will be calculated by the following equation:

$$P = 15 \left[1 - \frac{|MV - h| - MV \cdot 0.05}{(MV \cdot 0.15) - (MV \cdot 0.05)} \right]$$

$$MV = \frac{h' \cdot 2.0 \text{ (mg L}^{-1}\text{)}}{c}$$

P : Points (no negative value; zero if $P < 0$)

MV : Master value of h (mm)

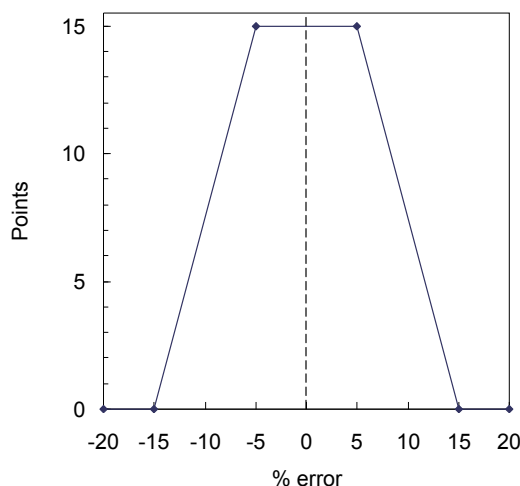
h : Experimental height of liquid column of the test solution (mm)

h' : Experimental height of liquid column of reference solution (mm)

c : Concentration of Fe in correctly prepared test solutions (mg L^{-1})

for 2c, $c = 1.63, 1.72$ and 1.82 for Sample 1, 2 and 3, respectively.

for 2d, $c = 2.62, 2.76$, and 2.67 for Sample 1, 2 and 3, respectively.



e) Express the concentration of the test solution, c , using the concentration of the reference solution, c' , and the height of each liquid column, h and h' .

$$c = \frac{c' h'}{h}$$

3 points. Any equivalent formula is acceptable.

- f) Calculate the concentrations of Fe(II) and Fe(III) in the original sample solution in mg L⁻¹.

For Fe²⁺,

$$[\text{Fe}^{2+}] = \frac{2.0(\text{mg L}^{-1}) \times h'_C \times 50(\text{mL})}{h_C \times 10(\text{mL})}$$

[Fe²⁺]: concentration of Fe²⁺ in the sample solution (mg L⁻¹)

h_C : experimental height (mm) of the liquid column of the test solution in the measurement C

h'_C : experimental height (mm) of the liquid column of the standard solution in the measurement C

If the concentrations are calculated correctly from the experimental data, full marks will be awarded 3 points.

For Fe³⁺

$$[\text{Fe}^{3+}] = \frac{2.0(\text{mg L}^{-1}) \times h'_D \times 50(\text{mL})}{h_D \times 5(\text{mL})} - [\text{Fe}^{2+}]$$

[Fe³⁺]: concentration of Fe³⁺ in the sample solution (mg L⁻¹)

h_D : experimental height (mm) of the liquid column of the test solution in the measurement D

h'_D : experimental height (mm) of the liquid column of the standard solution in the measurement D

If the concentrations are calculated correctly from the experimental data, full marks will be awarded 5 points.

Concentrations of Fe²⁺ and Fe³⁺ in each *original* sample solution

	[Fe ²⁺] / mg L ⁻¹	[Fe ³⁺] / mg L ⁻¹
Sample 1	8.16	18.0
Sample 2	8.60	19.0
Sample 3	9.08	17.7

Task 3

3.1a	3.1b	3.1c	3.1d	3.1e	3.1f	3.2	Total
4	10	1	10	1	4	20	50

Polymers in Analysis

Polymers can be used in various analyses. In this task, you are first required to analyze a polysaccharide using a polymer-polymer interaction, which will then be utilized to identify polymers in the second part.

3.1 Analysis of Polysaccharide by Colloid Titration

You are provided with a solution of a polysaccharide containing sulfonate ($-\text{SO}_3^-$) and carboxylate ($-\text{COO}^-$) groups. You are asked to determine the concentrations of these two groups by colloid titration under the basic and acidic conditions based on the differences in the protonation behavior of these acid groups. A back-titration technique is utilized.

When these acid groups are ionized, the polysaccharide becomes a polyanion. Upon addition of polycation, poly(diallyldimethylammonium) (provided as its chloride salt, PDAC), it forms a polyion complex. PDAC solution is standardized using the standard solution of potassium poly(vinyl sulfate) (PVSK). At the endpoint of colloid titration, the number of anionic groups becomes equal to that of cationic groups.

Procedures

(1) Take precisely 20 mL of the PDAC solution using a volumetric pipette into a 100-mL conical beaker. Add 2 drops of toluidine blue (TB) into the conical beaker. Titrate the resulting blue solution with the $0.0025 \text{ mol L}^{-1}$ PVSK (monomer unit concentration) standard solution. At the endpoint, the color turns purple. Note that the solution becomes gradually turbid as the endpoint approaches. The endpoint is determined when the color remains purple for 15-20 seconds. Repeat if necessary.

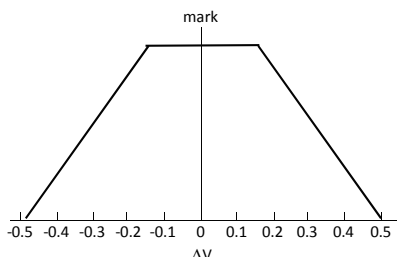
1a) Report the PVSK solution volume (in mL) consumed in the standardization of PDAC. Record your reading to 0.05 mL.

PVSK solution volume consumed in the standardization of PDAC:

z mL

$$MV(z) = 20.06 \text{ mL}$$

A full score of 4 points will be awarded if the answer is $MV(z) \pm 0.15$ mL. (*MV*: Master Value)
 A score of zero will be given if the answer is less than $(MV(z) - 0.5)$ mL or greater than $(MV(z) + 0.5)$ mL. A linear point scale will be applied for answers in between.
 Two points will be subtracted if the value is not reported down to the 2nd decimal place (in mL).



(2) Take precisely 5 mL of the polysaccharide solution and 20 mL of the PDAC solution using volumetric pipettes into another conical beaker. Add 0.4 mL of 0.5 mol L^{-1} NaOH and 2 drops of TB to the solution. Titrate the resulting blue solution with the PVSK standard solution in a similar manner. Repeat if necessary. (The appearance of coagulation may be different, depending on the pH of the solution.)

1b) Report the PVSK solution volume (in mL) consumed in the titration under basic conditions. Record your reading to 0.05 mL.

PVSK solution volume consumed under basic conditions: <div style="text-align: right; margin-right: 20px;">x mL</div>
--

Sample A: $MV(x) = 13.14$ mL

Sample B: $MV(x) = 12.07$ mL

Sample C: $MV(x) = 10.91$ mL

A full score of 10 points will be awarded if the answer is $MV(x) \pm 0.25$ mL.
 A score of zero will be given if the answer is less than $(MV(x) - 0.6)$ mL or greater than $(MV(x) + 0.6)$ mL. A linear point scale will be applied for answers in between.
 Two points will be subtracted if the value is not reported down to the 2nd decimal place (in mL). A score of zero will be applied if the value becomes negative after the subtraction.

1c) Mark the acid group(s) ionized under the basic conditions on the answer sheet.

conditions	acid group	
basic	<input checked="" type="checkbox"/> $-\text{SO}_3\text{H}$	<input checked="" type="checkbox"/> $-\text{COOH}$

Total 1 point.

(3) Repeat procedure 2 above with the addition of 0.5 mL of 0.5 mol L^{-1} HCl instead of 0.5 mol L^{-1} NaOH.

- 1d)** Report the PVSK solution volume (in mL) consumed in the titration under acidic conditions. Record your reading to 0.05 mL.

PVSK solution volume consumed under the acidic conditions: <p style="text-align: right;">y mL</p>
--

Sample A: $MV(y) = 15.26$ mL

Sample B: $MV(y) = 14.61$ mL

Sample C: $MV(y) = 13.59$ mL

A full score of 10 points will be awarded if the answer is $MV(y) \pm 0.25$ mL.

A score of zero will be given if the answer is less than $(MV(y) - 0.6)$ mL or greater than $(MV(y) + 0.6)$ mL. A linear point scale will be applied for answers in between.

Two points will be subtracted if the value is not reported down to the 2nd place of decimals (in mL). A score of zero will be applied if the value becomes negative after the subtraction.

- 1e)** Mark the acid group(s) fully ionized under acidic conditions on the answer sheet.

conditions	acid group	
acidic	<input checked="" type="checkbox"/> $-\text{SO}_3\text{H}$	<input type="checkbox"/> $-\text{COOH}$

Total 1 point.

- 1f)** Calculate the concentrations of the $-\text{SO}_3^-$ (or $-\text{SO}_3\text{H}$) groups and the $-\text{COO}^-$ (or $-\text{COOH}$) groups (in mol L^{-1}) in the given polysaccharide solution.

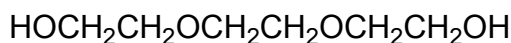
$-\text{SO}_3^-$ (or $-\text{SO}_3\text{H}$) group: $0.0005(z - y)$ <p style="text-align: right;">mol L^{-1}</p>
$-\text{COO}^-$ (or $-\text{COOH}$) group: $0.0005(y - x)$ <p style="text-align: right;">mol L^{-1}</p>

Total 4 points, 2 points for each.

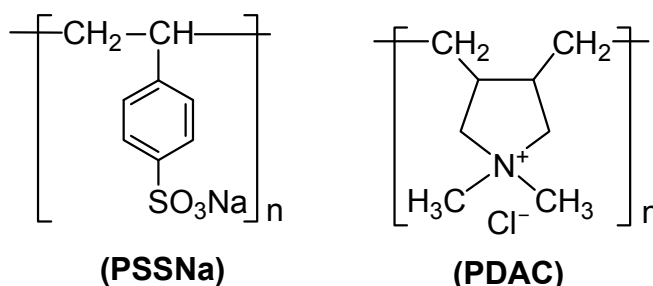
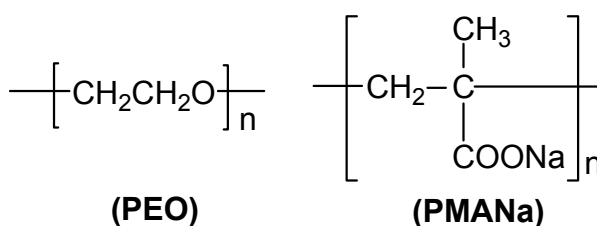
A score of 2 is given to the values within (calculated value) ± 0.2 . A score of 1 is given to the values which were outside the above allowance ($\pm 0.2 \text{ mol L}^{-1}$) and within (calculated value) $\pm 0.5 \text{ mol L}^{-1}$.

3.2 Identification of compounds

You are provided with five solutions (**X-1~5**, “**X**” designates your sample code, which is a letter in the Roman alphabet from **A** to **H**), and each solution contains one of the compounds below (all of which are used). The concentration is 0.05 mol L⁻¹ (for polymers, monomer unit concentration). Your task is to identify all the compounds by carrying out the following procedures.



(**TEG**)



[Abbreviations: **TEG**, triethylene glycol; **PEO**, poly(ethylene oxide); **PMANa**, poly(sodium methacrylate); **PSSNa**, poly(sodium 4-styrenesulfonate); **PDAC**, poly(diallyldimethylammonium chloride) MW. stands for molecular weight.]

Helpful comments

- 1) Aggregates observed in **Task 3.1** could be observed when mixing two polymer solutions in an appropriate combination, in which an interaction takes place between the two polymers. They can be utilized to identify polymer samples.
- 2) The volume of a solution measuring 5 mm in height from the bottom of the vial is approximately 1 mL. Remind that you have only 10 mL of each solution.

Procedures

- (1) Mix similar volumes of two solutions together in a vial.
- (2) If necessary, you can acidify the resulting mixture. Ten drops of hydrochloric acid ($0.5 \text{ mol L}^{-1} \text{ HCl}$) from a plastic Pasteur pipette are sufficient for this purpose.

Identify the compound in each solution based on the experimental results. For each solution, mark one of the five boxes to indicate your identification. You are also asked to fill in the blanks with one of the letters in the Roman alphabet, from A to H, to indicate your sample code.

Sample code					
<input type="text"/> -1	<input type="checkbox"/> TEG	<input type="checkbox"/> PEO	<input type="checkbox"/> PMANa	<input type="checkbox"/> PSSNa	<input type="checkbox"/> PDAC
<input type="text"/> -2	<input type="checkbox"/> TEG	<input type="checkbox"/> PEO	<input type="checkbox"/> PMANa	<input type="checkbox"/> PSSNa	<input type="checkbox"/> PDAC
<input type="text"/> -3	<input type="checkbox"/> TEG	<input type="checkbox"/> PEO	<input type="checkbox"/> PMANa	<input type="checkbox"/> PSSNa	<input type="checkbox"/> PDAC
<input type="text"/> -4	<input type="checkbox"/> TEG	<input type="checkbox"/> PEO	<input type="checkbox"/> PMANa	<input type="checkbox"/> PSSNa	<input type="checkbox"/> PDAC
<input type="text"/> -5	<input type="checkbox"/> TEG	<input type="checkbox"/> PEO	<input type="checkbox"/> PMANa	<input type="checkbox"/> PSSNa	<input type="checkbox"/> PDAC

Before (upper rows) and after (lower rows) the addition of HCl

	TEG	PEO	PMANa	PSSNa	PDAC
TEG					
PEO	- -				
PMANa	- -	- +			
PSSNa	- -	- -	- -		
PDAC	- -	- -	+ -	+ +	

+: Precipitation, -: No precipitation (or the precipitate disappears)

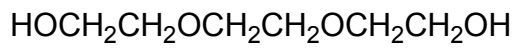
PMANa and PSSNa are polyanions, and they interact with a polycation (PDAC) to form a precipitate. Under acidic conditions, the carboxylate ($-\text{COO}^-$) groups in PMANa undergo protonation, and PMANa changes to protonated poly(methacrylic acid) (PMA). The resulting carboxy ($-\text{COOH}$) groups interact with the ether oxygen atoms in PEO through hydrogen bonding to form a precipitate. Since protonated PMA is no longer a polyanion, the precipitate (the complex between PMANa and PDAC) disappears after the addition of HCl.

On the other hand, PSSNa does not exist as the protonated form, even under acidic conditions, and no precipitate is observed with PEO at a lower pH. Since TEG is a small molecule, its interaction with PMA is not strong enough to form a precipitate.

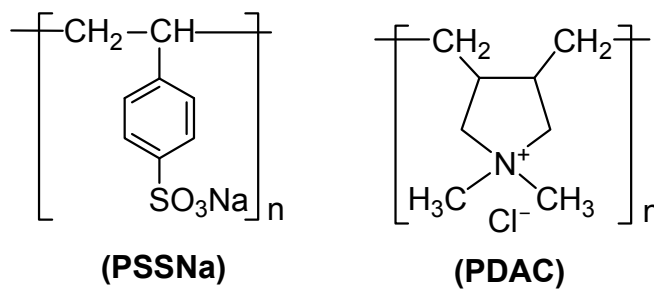
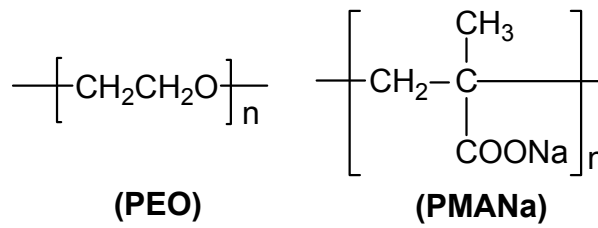
- 1) For each correct answer, 4 points will be awarded.
- 2) If two or more boxes are marked for one sample, 0 points will be given for that sample even if the correct answer is included in the marked compounds.
- 3) If the same box is marked for more than two samples, 0 points will be given for these samples even if the correct answer is included in the marked samples.

Table List of samples in Task 3.2

TEG	PEO	PMANa	PSSNa	PDAC
A-3	A-2	A-1	A-4	A-5
B-2	B-1	B-5	B-3	B-4
C-1	C-5	C-4	C-2	C-3
D-5	D-4	D-3	D-1	D-2
E-3	E-2	E-1	E-4	E-5
F-2	F-1	F-5	F-3	F-4
G-1	G-5	G-4	G-2	G-3
H-5	H-4	H-3	H-1	H-2



(TEG)



[Abbreviations: **TEG**, triethylene glycol; **PEO**, poly(ethylene oxide);
PMANa, poly(sodium methacrylate); **PSSNa**, poly(sodium 4-styrenesulfonate);
PDAC, poly(diallyldimethylammonium chloride)]

Instructions

- Ensure that your name and student code are written in the spaces provided at the top of each answer sheet.
- You have 5 hours to work on the problems.
- 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 any relevant calculations in the appropriate boxes when necessary. If you provide no working and only the correct result for a complicated calculation, you will receive no marks.
- Numerical answers are meaningless without the appropriate units. You will be heavily penalized if units are not given where required.
- You must stop work immediately when the STOP command is given. A delay in doing this may lead to your disqualification from the exam.
- When you have finished the examination, you must put your papers into the envelope provided, and seal the envelope by yourself.
- Do not leave your seat until permitted by the supervisors.
- This examination has 22 pages. The answer booklet comprises 17 pages.
- The official English version of this examination is available on request only for clarification.

Constants and Formulae

Avogadro constant:	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	$\Delta_r G^\circ = -RT \log_e K = -nFE_{\text{cell}}^\circ$	
Planck constant:	$h = 6.626 \times 10^{-34} \text{ J s}$	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \log_e \frac{c_{\text{ox}}}{c_{\text{red}}}$
Speed of light:	$c = 2.998 \times 10^8 \text{ m s}^{-1}$	Energy of a photon:	$E = \frac{hc}{\lambda} = h\nu$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log_{10} \frac{I_0}{I} = \epsilon cl$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol L^{-1} . Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1																	18
1 H 1.01											2 He 4.00						
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 -	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	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	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
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Problem 1

8% of the total

1a	1b	1c	1d	1e	1f	1g	1h	1i	Task 1
2	4	2	1	1	1	3	2	1	17

In 1894, Lord Rayleigh reported that the mass of chemically prepared nitrogen was different from that of nitrogen extracted from the atmosphere, as shown in Tables 1 and 2. Later, this difference was attributed to the presence of argon in *atmospheric nitrogen*. The masses of gases were measured by using a glass vessel with a known volume under atmospheric pressure (1.013×10^5 Pa).

Table 1. Mass of *Chemical Nitrogen in the Vessel*

From nitric oxide	2.3001 g
From nitrous oxide	2.2990 g
From ammonium nitrite purified at a red heat	2.2987 g
From urea	2.2985 g
From ammonium nitrite purified in the cold	2.2987 g
Mean	2.2990 g

Table 2. Mass of *Atmospheric Nitrogen in the Vessel*

O ₂ was removed by hot copper (1892)	2.3103 g
O ₂ was removed by hot iron (1893)	2.3100 g
O ₂ was removed by ferrous hydrate (1894)	2.3102 g
Mean	2.3102 g

- a) Calculate the volume V [m³] of the vessel used by Rayleigh from the mean mass of *chemical nitrogen*, which must have been pure nitrogen. Assume that the measurements were carried out at a temperature of 15.0 °C.

The amount n of the pure nitrogen (*chemical nitrogen*), $M = 28.02$ g mol⁻¹, is

$$n = \frac{m}{M} = \frac{2.2990}{28.02} = 8.205 \times 10^{-2} \text{ mol.} \quad \text{[or equivalent]} \quad (1 \text{ pt})$$

Then, from the ideal gas law, $V = \frac{nRT}{p}$

$$= \frac{8.205 \cdot 10^{-2} \times 8.314 \times 288.15}{1.013 \cdot 10^5} = \underline{1.940 \times 10^{-3} \text{ m}^3}. \quad (1 \text{ pt})$$

$$V = \quad \text{m}^3$$

- b) Estimate the mole fraction x of argon in Rayleigh's *atmospheric nitrogen*, by assuming that argon and nitrogen were the only constituents. Use the mean masses of the *atmospheric* and *chemical nitrogen* for the calculation.

The equation for the ratio of the mass of *atmospheric* nitrogen to the mass of *chemical* nitrogen is

$$\frac{28.02(1-x) + 39.95x}{28.02} = \frac{2.3102}{2.2990} \quad \text{[or equivalent]} \quad (1 \text{ pt})$$

Transformation gives

$$x = \frac{(2.3102 - 2.2990) / 2.2990}{39.95 - 28.02} \times 28.02 \quad \text{[or equivalent]} \quad (2 \text{ pt})$$

$$= \underline{1.14 \times 10^{-2}} \quad (\text{or } 1.14\%) \quad (1 \text{ pt})$$

$x =$

Ramsay and Clève discovered helium in cleveite (a mineral consisting of uranium oxide and oxides of lead, thorium, and rare earths; an impure variety of uraninite) independently and virtually simultaneously in 1895. The gas extracted from the rock showed a unique spectroscopic line at around 588 nm (indicated by D₃ in Figure 1), which was first observed in the spectrum of solar prominence during a total eclipse in 1868, near the well-known D₁ and D₂ lines of sodium.

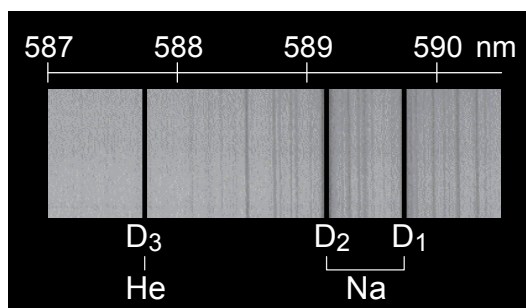


Figure 1. Spectral lines around 588 nm

- c) Calculate the energy E [J] of a photon with the wavelength of the D₃ line of helium shown in Figure 1.

According to Figure 1, the wavelength of the D₃ line is approximately 587.7 nm (no punishment if 587.8 or 588 is used).

The corresponding photon energy is $E = \frac{hc}{\lambda}$

$$= \frac{6.626 \cdot 10^{-34} \times 2.998 \cdot 10^8}{587.7 \cdot 10^{-9}} \quad (1 \text{ pt})$$

$$= \underline{3.380 \times 10^{-19} \text{ J}} \quad (1 \text{ pt})$$

$E =$

J

Figure 2 shows an energy diagram of the atomic orbitals of helium. The arrows indicate the "allowed" transitions according to the spectroscopic principle.

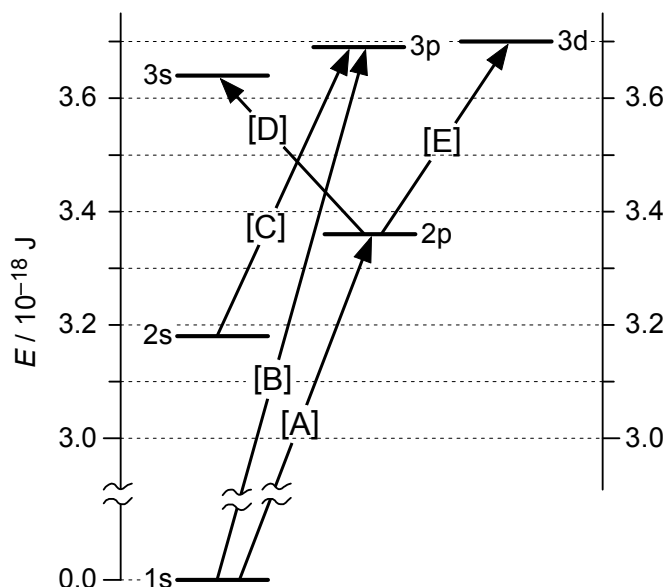
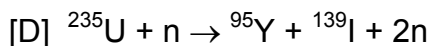
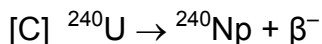
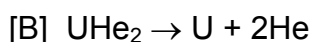
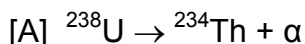


Figure 2. Energy diagram of atomic orbitals of helium when an electron resides in the 1s orbital.

- d) Identify the transition relevant to the D₃ line of helium among the transitions [A] to [E] indicated in Figure 2. Mark one on the answer sheet:

[E] The energy, 3.382×10^{-19} J, matches with the energy of the transition [E] between the 2p and 3d orbitals. (1 pt)
cf.) Energy difference [10^{-19} J] = [A]:33.6, [B]:36.9, [C]:5.1, [D]:2.8, [E]:3.4

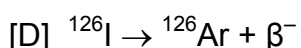
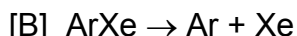
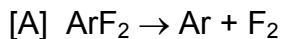
- e) Which equation explains the occurrence of helium in cleveite among [A] to [D] below? Mark one on the answer sheet:



[A] Considering that the α particle is the nucleus of helium, α -decay [A] is the relevant source of helium in such rocks. No compound of He such as UHe_2 in [B] is known to be stable at ambient temperature. [C] is a radio active decay of ^{240}U in the thorium series. [D] is a nuclear fission reaction of ^{235}U occurring in nuclear reactors. The correct answer is [A]. (1 pt)

Argon is also found in minerals such as *malacon*.

- f) Which equation explains the occurrence of argon in rocks among [A] to [D] below? Mark one on the answer sheet.



[C] [C] is a well-known radioactive decay reaction occurring with a half-life of the order of the age of the earth. No stable compound of Ar, such as ArF_2 or ArXe , can be expected. Products of [D] should be $^{126}\text{Xe} + \beta^-$. The correct answer is [C]. (1 pt)

One of the strongest evidences for the monoatomicity of argon and helium is the ratio of the heat capacity under constant pressure to that at constant volume, $\gamma = C_p / C_v$, which is exactly 5/3 (1.67 ± 0.01) for a monoatomic gas. The ratio was derived from the measurement of speed of sound v_s by using the following equation, where f and λ are the frequency and wavelength of the sound, and R , T , and M denote the molar gas constant, absolute temperature, and molar mass, respectively.

$$v_s = f\lambda = \sqrt{\frac{\gamma RT}{M}}$$

For an unknown gas sample, the wavelength of the sound was measured to be $\lambda = 0.116$ m at a frequency of $f = 3520$ Hz ($\text{Hz} = \text{s}^{-1}$) and temperature of 15.0 °C and under atmospheric pressure (1.013×10^5 Pa). The density ρ of the gas for these conditions was measured to be 0.850 ± 0.005 kg m^{-3} .

- g) Calculate the molar mass M [kg mol^{-1}] of this gas.

The density ρ is given by $\rho = \frac{nM}{V}$. [or equivalent] (1 pt)

By combining with the ideal gas law gives:

$$M = \frac{\rho RT}{p} = \frac{0.850 \times 8.314 \times 288.15}{1.013 \cdot 10^5}$$
 [or equivalent] (1 pt)

$$= \underline{2.01 \times 10^{-2}} \text{ kg mol}^{-1}. (20.1 \text{ g mol}^{-1})$$
 (1 pt)

$M =$ kg mol^{-1}

h) Calculate the heat capacity ratio γ for this gas sample.

From the equation for the sonic velocity, $f\lambda = \sqrt{\frac{\gamma RT}{M}}$,

$$\gamma = \frac{M}{RT} (f\lambda)^2 = \frac{2.01 \cdot 10^{-2}}{8.314 \times 288.15} (3520 \times 0.116)^2 \quad [\text{or equivalent}] \quad (1 \text{ pt})$$

$$= \underline{1.40} \quad (1 \text{ pt})$$

$$\text{(or, using } \frac{M}{RT} = \frac{\rho}{p}, \gamma = \frac{\rho}{p} (f\lambda)^2 = \frac{0.850}{1.013 \cdot 10^5} (3520 \times 0.116)^2 = 1.40)$$

$$\gamma =$$

i) Which is this gas among [A] to [D]? Mark one on the answer sheet:

[A] HCl

[B] HF

[C] Ne

[D] Ar

[B] From $M = 20.1 \text{ g mol}^{-1}$, this gas must be HF or Ne.

From $\gamma = 1.4 (\neq 5/3 \approx 1.67)$, this is NOT a monoatomic gas (*i.e.*, HCl or HF).

Thus, this gas must be [B] HF. (1 pt)

Note: It is not possible to distinguish between HF ($M = 20.01$) and Ne ($M = 20.18$) from the molar mass only, which is 20.10 ± 0.12 by taking into account the uncertainty of $\rho (\pm 0.005 / 0.850 = \pm 0.6\%)$. However, the precision of $\gamma = 1.40$ is enough to exclude the possibility of monoatomic gas ($\gamma = 5/3 \approx 1.67$).

Problem 2

6% of the total

2a	2b	2c	2d	2e	Task 2
4	4	4	3	5	20

Crystal structure of alkali metal halide

In crystals of ionic compounds, cations are generally arranged in the interstices of the closest packed lattice of anions. The structure of an ionic crystal such as sodium chloride becomes stable when the cations are in contact with the nearest anions.

- a) In the crystal of sodium chloride, both Na^+ and Cl^- ions form a face-centered cubic lattice. Give the numbers of Na^+ and Cl^- ions in a unit cell and the coordination numbers of Na^+ and Cl^- ions in sodium chloride crystal.

Number of ions	Na^+ : 4	Cl^- : 4
Coordination number	Na^+ : 6	Cl^- : 6

[Total 4 pts]

[2 pt] Both number of Na^+ and Cl^- ions are correct.

[1 pt] Each coordination number of Na^+ and Cl^- ions is correct.

- b) The ionic radii of Na^+ and Cl^- ions in the crystal of sodium chloride are 0.102 nm and 0.181 nm, respectively. Calculate the density [kg m^{-3}] of the sodium chloride crystal.

[Total 4 pts]

Length of lattice l : $l = 0.102 \times 2 + 0.181 \times 2 = 0.566 \text{ nm}$ [2 pt]

Density ρ :

$$\rho = \frac{(22.99 + 35.45) \times 4}{(0.566 \times 10^{-9})^3 \times 6.022 \times 10^{23}} = 2.14_{08} \times 10^6 \text{ g m}^{-3} = 2.14 \times 10^3 \text{ kg m}^{-3}$$

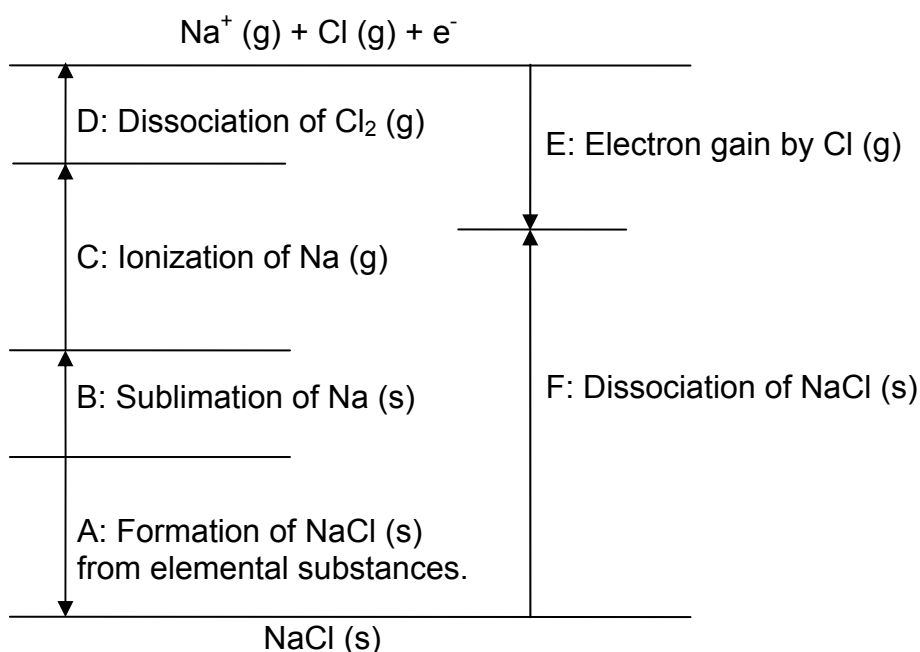
[1 pt for the equation of density, 1 pt for final answer.]

Density of NaCl crystal (kg m^{-3}): $2.14 \times 10^3 \text{ kg m}^{-3}$

Born-Haber cycle and lattice enthalpy

In ionic inorganic compounds such as sodium chloride, the heat of lattice formation from gaseous ions is very high, and the contribution of the change in entropy is small. Therefore, the lattice formation enthalpy is estimated from enthalpy data by using a Born-Haber cycle.

- c) The figure below shows the Born-Haber cycle of NaCl. The labels “g” and “s” represent “gas” and “solid” states respectively. Show chemical equations in the A and F steps.



- d) Calculate the enthalpy of the lattice formation of NaCl [kJ mol^{-1}] by using the following enthalpy data of the respective steps in the above Born-Haber cycle.

Formation of NaCl (s)	Sublimation of Na (s)	Ionization of Na (g)	Dissociation of Cl ₂ (g)	Electron gain by Cl (g)
-411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	-349 kJ mol^{-1}

[Total 3 pts]

Enthalpy conservation condition: $-\text{A} + \text{B} + \text{C} + \text{D}/2 = \text{F} - \text{E}$ [1 pt]

From the above equation, $-(-411) + 109 + 496 + (242/2) = \text{F} + 349$, thus, $\text{F}=788$ [1 pt]

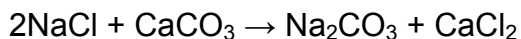
The lattice formation enthalpy of NaCl is $-\text{F}$, thus, -788 kJ mol^{-1} [1 pt]

Lattice formation enthalpy of NaCl (kJ mol^{-1}): -788 kJ mol^{-1}

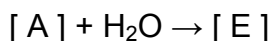
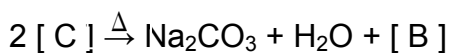
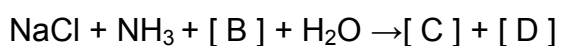
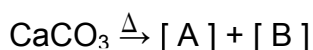
Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

e) The total chemical reaction in the ammonia-soda process is represented as follows:



This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions involving ammonia:



where Δ represents applying heat treatment. Insert the chemical formulas of the appropriate compounds in the blank spaces [A]–[E] in the above reactions.

A: **CaO**

B: **CO₂**

C: **NaHCO₃**

D: **NH₄Cl**

E: **Ca(OH)₂**

[Total 5 pts]

1 pt for one correct chemical formula.

Problem 3

7% of the total

3a	3b	3c	3d	Task 3
2	3	1	3	9

The chemical oxygen demand (COD) refers to the amount of oxidizable substance, such as organic compounds, in a sample solution, and it is used as an indication of water quality in seas, lakes, and marshes. For example, the COD of service water is kept below 1 mg L^{-1} . The COD (mg L^{-1}) is represented by mass of O_2 (mg) which accepts the same amount of electrons which would be accepted by the strong oxidizing agent when 1 L of a sample solution is treated with it. An example of the operation is presented below.

Analytical Operation

A 1.00-L sample solution was acidified with a sufficient amount of sulfuric acid, and chloride ions were removed by the addition of silver nitrate solution. To the sample solution, $1.00 \times 10^{-1} \text{ L}$ of $5.00 \times 10^{-3} \text{ mol L}^{-1}$ potassium permanganate solution was added, and the mixture was heated for 30 min. Further, $1.00 \times 10^{-1} \text{ L}$ of $1.25 \times 10^{-2} \text{ mol L}^{-1}$ disodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$ or NaOOC-COONa) standard solution was added, and the mixture was stirred well. Oxalate ions that remained unreacted were titrated with $5.00 \times 10^{-3} \text{ mol L}^{-1}$ potassium permanganate solution; $3.00 \times 10^{-2} \text{ L}$ of the solution was used for the titration.

- a) Give the equation of the redox reaction of potassium permanganate and disodium oxalate.



or



or



[Total 2 pts]

- b) Calculate the amount of O_2 (mg) that will oxidize the same number of moles of oxidizable substance as $1.00 \times 10^{-3} \text{ L}$ of $5.00 \times 10^{-3} \text{ mol L}^{-1}$ potassium permanganate does.

The reactions of potassium permanganate and O_2 are as follows:



Hence, 1 mol of KMnO_4 amounts to 1.25 mol of O_2 .

$$\frac{5 \times 5.00 \times 10^{-3} (\text{mol L}^{-1}) \times 10^{-3} (\text{L}) = 4 \times X / 32 (\text{mol})}{\text{where } X \text{ is the amount of } \text{O}_2 (\text{g}).}$$

[Underlined (or equivalent) equation: 2 pt]

Thus, $X = 2.00 \times 10^{-4} \text{ g.} \quad \rightarrow \quad 2.00 \times 10^{-1} \text{ mg}$

[1 pt]

[Total 3 pts]

c) From the following choices, select the most appropriate reason for the removal of chloride ions:

[A] Some of the chloride ions react with potassium permanganate, resulting in an error in COD.

[B] Some of the chloride ions react with disodium oxalate, resulting in an error in COD.

[C] Some of the chloride ions react with organic compounds in the sample solution, resulting in an error in COD.

[D] A color is developed during titration, resulting in an error in COD.

[A]

[Total 1 pt]

d) Calculate the COD (mg L^{-1}) of the sample solution described in the analytical operation above.

The amounts of electron used for reduction and oxidation are equal, then

$$\frac{5 \times 5.00 \times 10^{-3} (\text{mol L}^{-1}) \times (1.00 \times 10^{-1} + A) (\text{L}) =$$

$$\frac{2 \times 1.25 \times 10^{-2} (\text{mol L}^{-1}) \times 1.00 \times 10^{-1} (\text{L}) + X}{(1)} \quad \text{[Underlined (or equivalent) equation: 2 pt]}$$

where A (mL) is the amount of potassium permanganate used for the final titration, and X (mol) is the amount of electron for the oxidizable substance.

Eq.(1) gives $X = 2.50 \times 10^{-2} \times A$.

At $A = 3.00 \times 10^{-2} (\text{L})$, $X = 7.50 \times 10^{-4} (\text{mol})$.

$$\text{Hence, COD} = (32/4) (\text{g mol}^{-1}) \times 7.50 \times 10^{-4} (\text{mol}) \times 10^3 (\text{mg/g}) \times 1/1 (\text{L}^{-1}) = 6.00 \text{ mg L}^{-1}.$$

[1 pt]

[Total 3 pts]

or

The amount of potassium permanganate consumed for the oxidizable substance, B (mL), is

$$\frac{5 \times 5.00 \times 10^{-3} \times (1.00 \times 10^{-1} + A - B) = 2 \times (1.25 \times 10^{-2}) \times (1.00 \times 10^{-1})}{[2 \text{ pt}]}$$

At $A = 3.00 \times 10^{-2} \text{ L}$, B equals to $3.00 \times 10^{-2} \text{ L}$.

From the solution to question b) above,

$$\text{COD} = (2.00 \times 10^{-1}) / (1.00 \times 10^{-3}) (\text{mg/L}) \times 3.00 \times 10^{-2} (\text{L}) \times 1/1 (\text{L}^{-1}) = 6.00 \text{ mg L}^{-1}.$$

[1 pt]

[Total 3 pts]

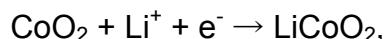
Problem 4

6% of the total

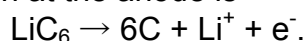
4a	4b	4c	4d	Task 4
2	3	2	1	8

The rechargeable lithium ion battery has been developed in Japan.

The standard electromotive force of the battery is 3.70 V. Assume that the half-reaction at the cathode is



and the half-reaction at the anode is



- a) Write the total reaction equation of the battery and calculate the value of the standard Gibbs energy of the reaction [kJ mol^{-1}].

Total reaction equation:



The standard Gibbs energy of the reaction:

$\Delta G^0 = -nFE^0 = -1 \times 96485 \text{ C mol}^{-1} \times 3.70 \text{ V} = -357 \text{ kJ mol}^{-1}$ (1 pt)

- b) The battery cell is constructed using LiCoO_2 and graphite (C) as the electrode materials. Calculate the mass of the anode in the completely charged state and that in completely discharged state if 10.00 g of LiCoO_2 and 10.00 g of graphite (C) are present initially.

In the completely charged state: 10.71 g (2 pt)

The amount of LiCoO_2 is $10.00/97.87 = 0.1022 \text{ mol}$.

The amount of C is $10.00/12.01 = 0.8326 \text{ mol}$, which is larger than $0.1022 \text{ mol} \times 6 = 0.6132 \text{ mol}$.

Thus, the mass in the completely charged state of the anode is $10.00 + 0.1022 \times 6.94 = 10.709 \text{ g} = \underline{10.71 \text{ g}}$.

In the completely discharged state: 10.00 g (1 pt)

- c) Calculate the maximum energy generated per mass of the lithium ion battery cell [kJ kg^{-1}]. Assume that the correct ratio for complete reaction between the cathode and anode materials is used and the sum of the mass of electrodes is 50.0% of the total mass of the battery cell. In comparison, the energy density of lead-acid batteries used for vehicles is about 200 kJ kg^{-1} .

The mass of 1 mol LiCoO_2 is 97.87 g

The mass of 6 mol C is $12.01 \times 6 \text{ g} = 72.06 \text{ g}$

The total mass of the electrode is $(97.87 + 72.06) \text{ g} = 169.93 \text{ g}$

The mass of the cell is $169.93 / 0.500 \text{ g} = 340 \text{ g}$

The maximum energy generated is 357 kJ.

Thus, the maximum energy per unit mass of the cell is 1050 kJ kg^{-1} (2 pts)

- d) Because an aqueous solution cannot be used as an electrolyte, an organic solution is used in the lithium ion battery cell. Give the chemical formula of the gas generated if water is present in the electrolyte.

H_2 or H_2 and O_2 (1 pt)

Problem 5

7% of the total

5a-1	5a-2	5b	5c	5d	5e	5f	Task 5
1	1	2	2	3	4	5	18

When an atom X absorbs radiation with a photon energy greater than the ionization energy of the atom, the atom is ionized to generate an ion X^+ and the electron (called a photoelectron) is ejected at the same time. In this event, the energy is conserved as shown in Figure 1, that is,

Photon energy ($h\nu$) = ionization energy (IE) of X + kinetic energy of photoelectron.

When a molecule, for example, H_2 , absorbs short-wavelength light, the photoelectron is ejected and an H_2^+ ion with a variety of vibrational states is produced. A photoelectron spectrum is a plot of the number of photoelectrons as a function of the kinetic energy of the photoelectrons. Figure 2 shows a typical photoelectron spectrum when H_2 in the lowest vibrational level is irradiated by monochromatic light of 21.2 eV. No photoelectrons are detected above 6.0 eV. eV is a unit of energy and 1.0 eV is equal to 1.6×10^{-19} J.

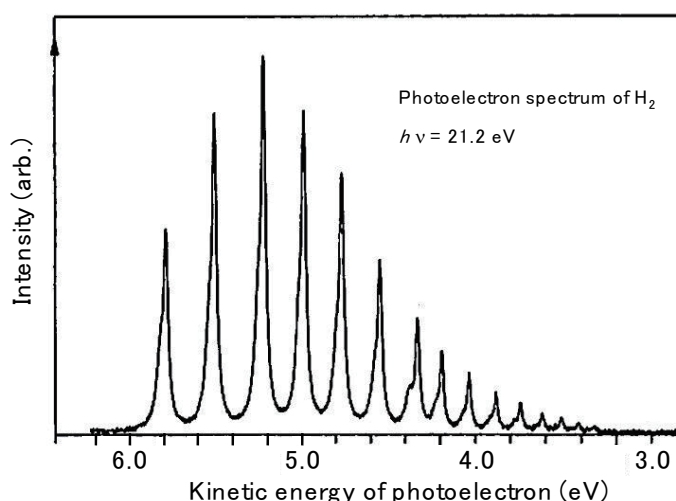
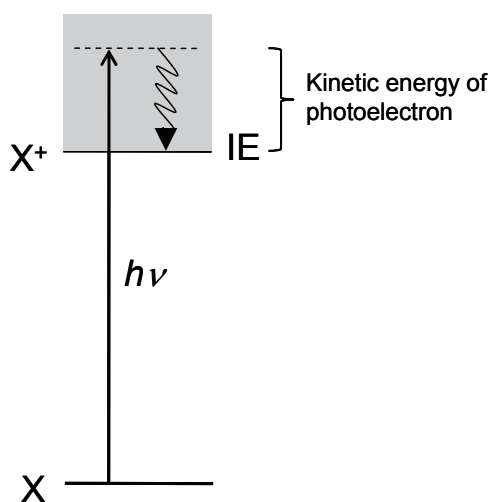


Figure 1. Schematic diagram of photoelectron spectroscopy.

Figure 2. Photoelectron spectrum of H_2 . The energy of the incident light is 21.2 eV.

a-1) Determine the energy difference ΔE_{A1} (eV) between H_2 ($v = 0$) and H_2^+ ($v_{ion} = 0$) to the first decimal place. v and v_{ion} denote the vibrational quantum numbers of H_2 and H_2^+ , respectively.

a-2) Determine the energy difference ΔE_{A2} (eV) between H_2^+ ($v_{ion} = 0$) and H_2^+ ($v_{ion} = 3$) to the first decimal place.

a-1) & a-2)

The spectral peak at 5.8 eV in Fig. 2 corresponds to the electron with the highest kinetic energy, which is generated by the reaction $H_2(v = 0) \rightarrow H_2^+(v_{ion} = 0) + e$. Accordingly,

$$\Delta E_{A1} = 21.2 \text{ eV} - 5.8 \text{ eV} = 15.4 \text{ eV}$$

One can estimate from Fig. 2 that the energy difference ΔE_{A2} between H_2^+ ($v_{ion} = 0$) and H_2^+ ($v_{ion} = 3$) is approximately 0.8 eV.

$$\Delta E_{A1} \text{ (eV)} = 15.4 \text{ eV} \quad 1 \text{ pt}$$

$$\Delta E_{A2} \text{ (eV)} = 0.8 \text{ eV} \quad 1 \text{ pt}$$

b) The electronic energy levels E_n^H of a hydrogen atom are given by the equation

$$E_n^H = -\frac{Ry}{n^2} \quad (n = 1, 2, 3 \dots)$$

Here n is a principal quantum number, and Ry is a constant with dimensions of energy. The energy from $n = 1$ to $n = 2$ of the hydrogen atom is 10.2 eV. Calculate the ionization energy E_B (eV) of the hydrogen atom to the first decimal place.

The ionization energy corresponds to $n = \infty$. Accordingly,

$$\Delta E_{n=2 \leftarrow n=1} = \frac{3}{4} Ry$$

$$\Delta E_{n=\infty \leftarrow n=1} = Ry$$

Thus, the energy required for the ionization is 4/3 times larger than the transition energy of the Lyman α line.

$$E_B = 10.2 \text{ eV} \times \frac{4}{3} = 13.6 \text{ eV}$$

$$E_B \text{ (eV)} = 13.6 \text{ eV} \quad 2 \text{ pts}$$

- c) The energy threshold for the generation of two electronically excited hydrogen atoms H^* ($n = 2$) from H_2 ($v = 0$) has been derived to be 24.9 eV by an experiment. Determine the bond energy E_C (eV) of H_2 to the first decimal place.

24.9 eV = the binding energy of a hydrogen molecule + 10.2 eV + 10.2 eV.
Thus, the binding energy of a hydrogen molecule = $E_C = 4.5$ eV.

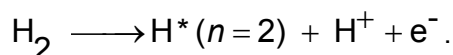
E_C (eV) = 4.5 eV 2 pts

- d) Considering an energy cycle, determine the bond energy E_D (eV) of H_2^+ to the first decimal place. If you don't have the values for E_B and E_C , then use 15.0 eV and 5.0 eV for E_B and E_C , respectively.

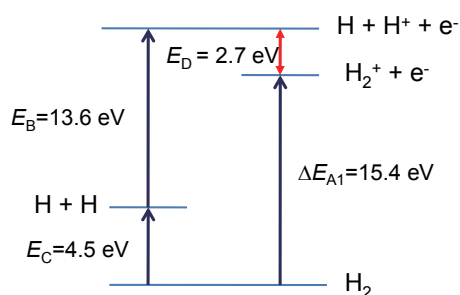
From Figure 3 below,
 $E_D = E_B + E_C - \Delta E_{A1} = 13.6 + 4.5 - 15.4 = 2.7$ eV.

E_D (eV) = 2.7 eV 3 pts

- e) Calculate the threshold energy E_E (eV) of the following dissociative ionization reaction to the first decimal place:



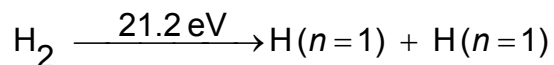
If you don't have the values for E_B and E_C , then use 15.0 eV and 5.0 eV for E_B and E_C , respectively.



From Figure 3 above, the threshold energy for the dissociative ionization reaction $H_2 \rightarrow H^*(n=2) + H^+ + e^-$ is $E_B + E_C + 10.2$ eV = 13.6 + 4.5 + 10.2 = 28.3 eV.

E_E (eV) = 28.3 eV 4 pts

- f) When H_2 absorbs monochromatic light of 21.2 eV, the following dissociation process occurs at the same time.



Two hydrogen atoms move in opposite directions with the same speed. Calculate the speed u (m s^{-1}) of the hydrogen atoms generated in the above reaction. H_2 is assumed to be at rest. If you don't have the value for E_C , then use 5.0 eV for E_C .

The excess energy is 16.7 eV (= 21.2 eV – 4.5 eV). Because two hydrogen atoms are generated upon photodissociation, half of this excess energy is released as translational energy of the hydrogen atoms.

$$\frac{1}{2}mu^2 = 8.35 \text{ eV} = 1.34 \times 10^{-18} \text{ J}$$

(2 pts)

$$m = \frac{1.008 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.67 \times 10^{-27} \text{ kg}$$

Then,

$$u^2 = 1.6 \times 10^9 \text{ m}^2 \text{ s}^{-2} \quad u \approx 4.0 \times 10^4 \text{ m s}^{-1}$$

$$u \text{ (m/s)} = 4.0 \times 10^4 \text{ m/s} \quad 5 \text{ pts}$$

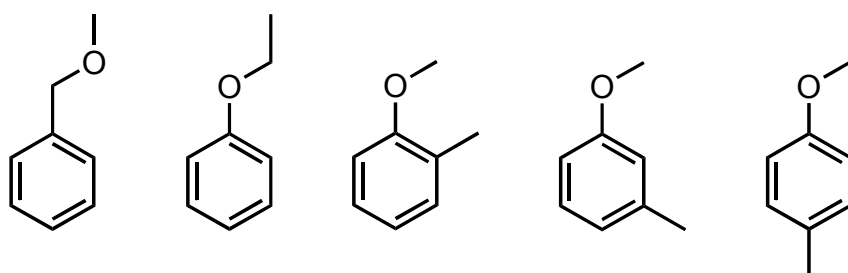
Problem 6

6 % of the total

6a	6b	6c	6d	Task 6
5	4	6	11	26

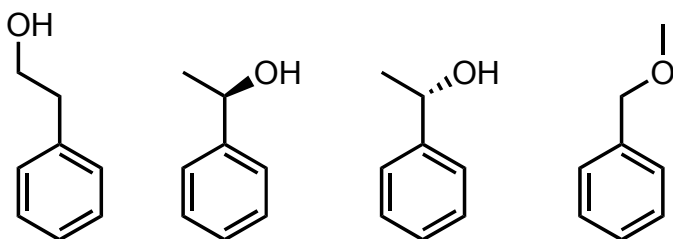
Read the description of four kinds of isomeric organic compounds of **A**, **B**, **C**, and **D**. All have $C_8H_{10}O$ and contain a benzene ring. Answer the questions that follow. If there are stereoisomers, give all structural formulas. Note that any wrong isomers will be penalized.

- (1) At room temperature, a piece of sodium metal was added to **A**, **B**, and **C** in test tubes and the evolution of hydrogen gas was observed only in the case of **C**.
 - When an iron(III) chloride aqueous solution was added to **C** and **D**, no coloration was observed in **C**, whereas **D** was colored.
 - **A** was oxidized when (2) aqueous potassium permanganate was added to it and the mixture was heated; the acidification of the heated mixture and its isolation afforded benzoic acid.
 - Let's imagine that (3) a hydrogen atom in the benzene ring is replaced by a chlorine atom, it is possible to obtain four kinds of monochlorinated structural isomers from **B**, while only two kinds of such isomers can be obtained from **D**.
 - Hydrogenation of the benzene ring in **C** and **D** using a catalyst gave saturated alcohol(s). It was found that the saturated alcohol(s) obtained from **C** has no stereogenic carbons, but the one(s) from **D** has stereogenic carbon(s).
- a) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that do NOT yield hydrogen gas in the underlined procedure (1), in which a piece of sodium is added to the neat samples in the case of the liquid samples and to the concentrated solution of the samples in an aprotic solvent in the case of the solid ones.



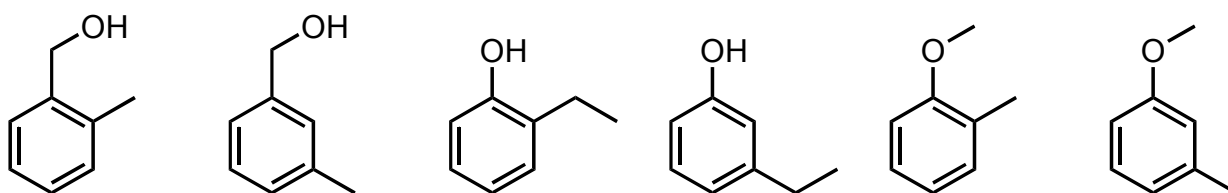
1pt each
wrong isomer: -1pt each
total pts ≥ 0 (not negative)

- b) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that yield benzoic acid in the underlined procedure (2).



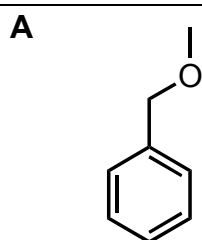
1pt each
 wrong isomer: -1pt each
 total pts ≥ 0 (not negative)

- c) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that could yield four different mono-chlorinated structural isomers when the underlined transformation in (3) is performed.

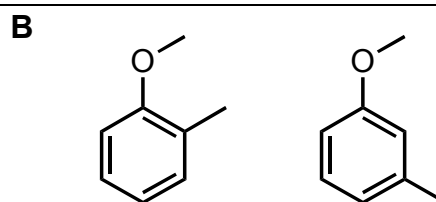


1pt each
 wrong isomer: -1pt each
 total pts ≥ 0 (not negative)

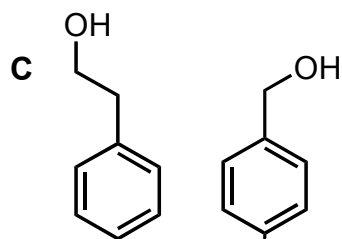
- d) Give the structural formulas of **A**, **B**, **C**, and **D**. When several isomers can be considered, give the structural formulas of all of them.



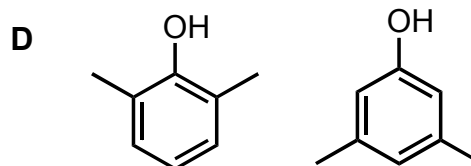
1pt
 wrong isomer: -1pt each
 total pts ≥ 0 (not negative)



1pt each
 wrong isomer: -1pt each
 total pts ≥ 0 (not negative)



2pts each
 wrong alcohol/phenol: -1pt each
 ether: -2pts each
 total pts ≥ 0 (not negative)



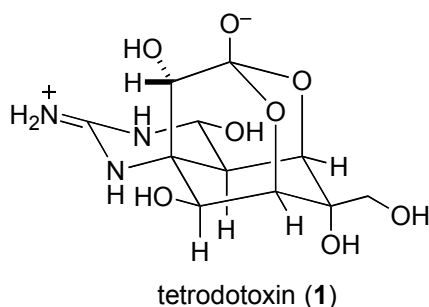
2pts each
 wrong alcohol/phenol: -1pt each
 ether: -2pts each
 total pts ≥ 0 (not negative)

Problem 7

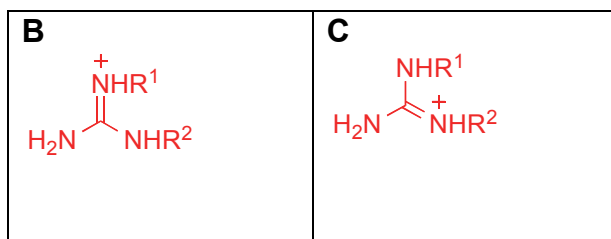
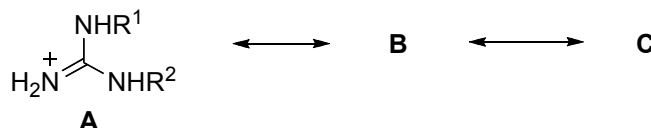
7% of the total

7a	7b	7c	7d	Task 7
4	9	6	5	24

Certain varieties of puffer fish, *Fugu* in Japanese, are highly prized as foods in Japan. Since the viscera (especially ovaries and livers) of the fish contain a potent toxin (tetrodotoxin), food poisoning often results from its ingestion. Studies on tetrodotoxin (**1**) have been performed from the beginning in the 20th century; its chemical structure was elucidated in 1964.

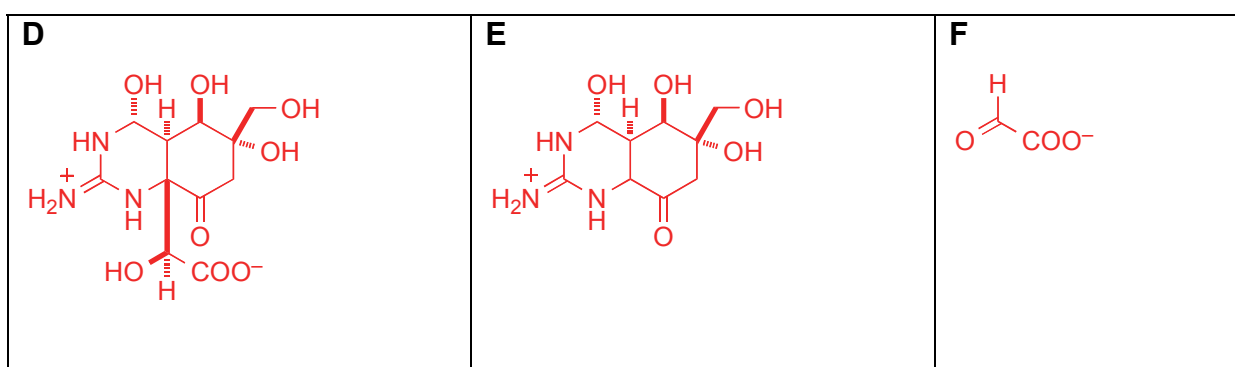
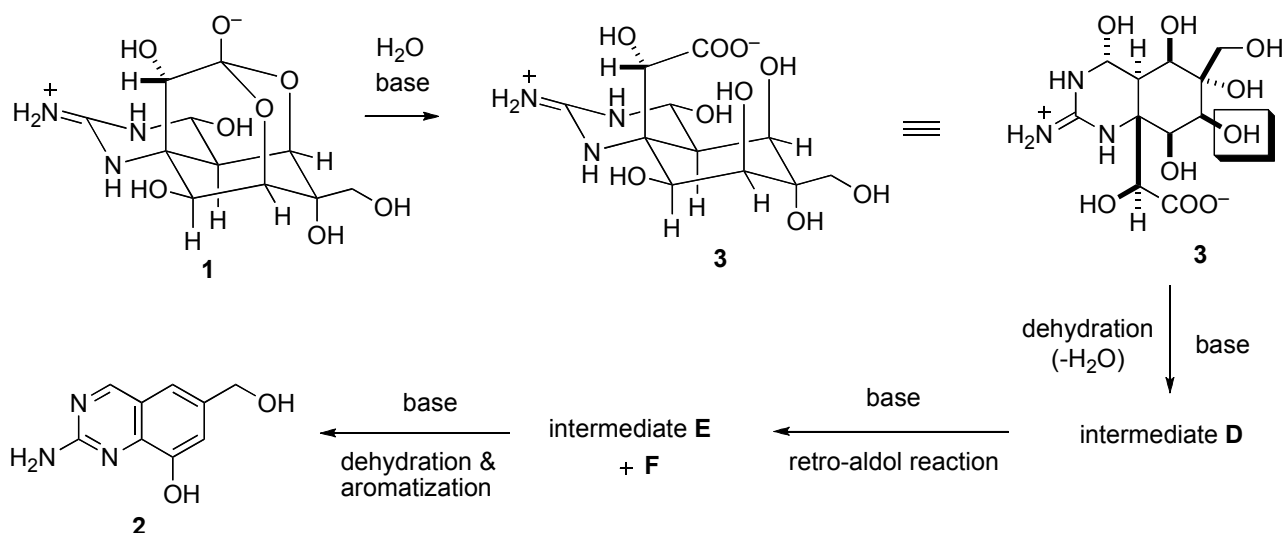


- a) The guanidine group in tetrodotoxin exhibits strong basicity. The guanidinium ion resulting from protonation on the guanidine group is stabilized by the existence of the following resonance. Draw two resonance structures **B** and **C**.



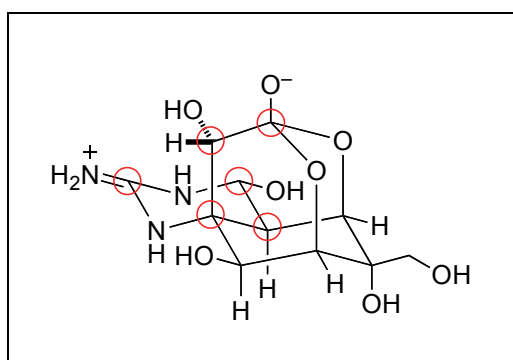
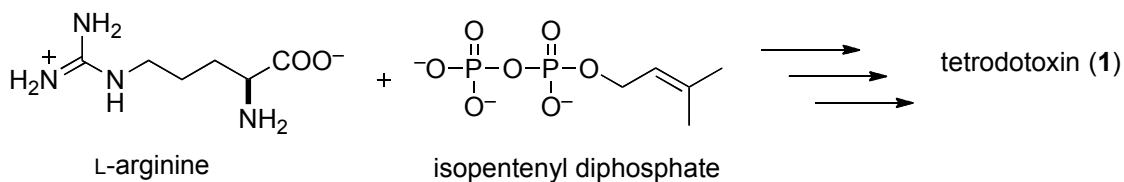
2 pts each.

- b) Many derivatization reactions were performed in structure studies of tetrodotoxin. Treatment of tetrodotoxin (**1**) with ethanolic potassium hydroxide upon heating afforded quinazoline derivative **2**, which provided an insight into the nature of the fundamental skeleton of tetrodotoxin. The reaction mechanism can be described as follows. First, tetrodotoxin is hydrolyzed into carboxylate **3**. Then the hydroxyl group highlighted with a frame is eliminated by the base to give intermediate **D**. A retro-aldol reaction of **D** cleaves a carbon-carbon bond to provide intermediates **E** and **F**. Finally, dehydration and aromatization from **E** produce quinazoline derivative **2**. Draw structures of the postulated intermediates **D**, **E**, and **F**.



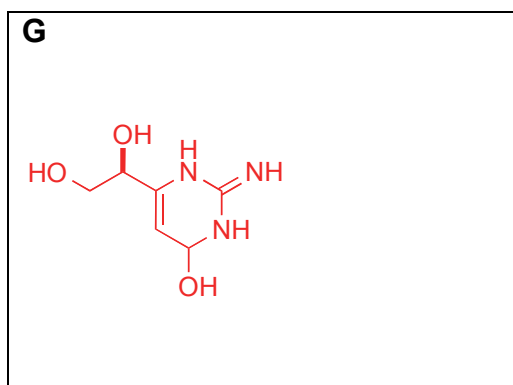
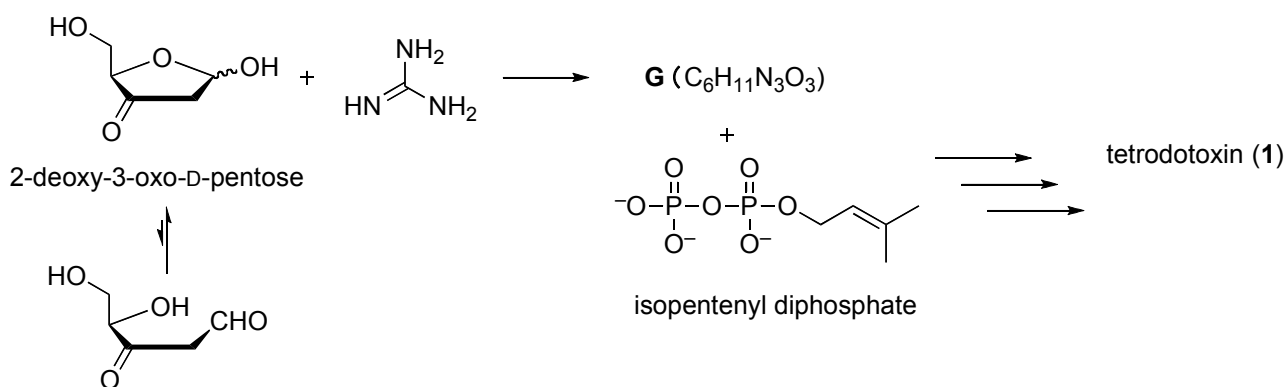
3 pts each. Other stereoisomers are acceptable. Each free form is acceptable. Tautomers concerning guanidine moiety are all acceptable. Enol form is acceptable. E: dehydrated products and zwitterionic structure are acceptable.

- c) Although biosynthesis of tetrodotoxin still remains to be clarified, it is proposed that tetrodotoxin may be biologically synthesized from L-arginine and isopentenyl diphosphate. Among the carbons included in tetrodotoxin, circle all the carbons that are expected to be of L-arginine origin.

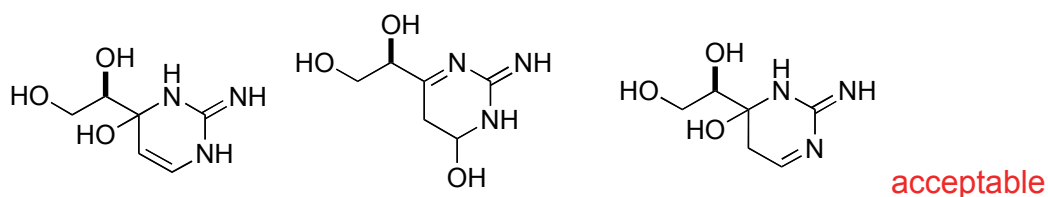


6 pts. 1 pt each for correct carbon. Deduct 1 pt for each carbon over 6. 0 pts for all carbons circled.

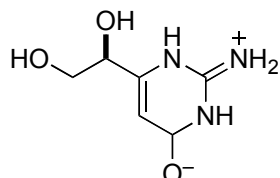
- d) In the 1990s, an alternative biosynthetic pathway of tetrodotoxin was proposed. Condensation between 2-deoxy-3-oxo-D-pentose and guanidine provides intermediate **G** with cyclic guanidine moiety (molecular formula $C_6H_{11}N_3O_3$). Tetrodotoxin may be biologically synthesized from intermediate **G** and isopentenyl diphosphate. Draw a structure of the postulated intermediate **G** showing the stereochemistry.



5 pts (enantiomer at C4, 3 pts, C4 stereochemistry is unclear, 3 pts).



Each zwitterionic structure (and protonated structure) like below is acceptable.



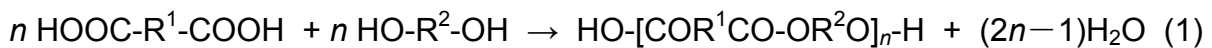
Tautomers concerning guanidine moiety are all acceptable.

Problem 8

6% of the total

8a-1	8a-2	8a-3	8b-1	8b-2	Task 8
2	4	3	4	7	20

The esterification reaction between bi-functional molecules gives one of the typical linear chain polymers as shown in eq.(1) by polycondensation (often called “condensation polymerization”). The control of polymerization conditions and procedures determines the length of polymer strands, i.e., *the average degree of polymerization*, X (note that $X = 2n$ in the present instance). Because X (and also n) is an averaged number, it is not always an integer but a value with decimal figures.



X can be estimated from the consumption of functional groups (here, -COOH and -OH). Let us define the degree of reaction, p , as $p = (N_0 - N) / N_0 (\leq 1)$, where N_0 and N denote the total numbers of functional groups before and after the polymerization, respectively. For each functional group of the dicarboxylic acid molecules (**A**) and diol molecules (**B**), we add the suffixes of “A” or “B” such as N_{A0} , N_{B0} , N_A or N_B , respectively, i.e., $N_0 = N_{A0} + N_{B0}$ and $N = N_A + N_B$. When the initial feed is unbalanced such as $N_{A0} \leq N_{B0}$, X is expressed by p_A and r as shown in eq.(2), where $r = N_{A0} / N_{B0} (\leq 1)$ and $p_A = (N_{A0} - N_A) / N_{A0}$. If $r = 1$, p_A is identical to p and eq.(2) becomes the same to the Carothers equation.

$$X = (1 + r) / (1 + r - 2p_A r) \quad (2)$$

a) Some nylon-6,6 sample was prepared by polycondensation between an *equimolar* mixture of adipic acid (hexanedioic acid) and hexamethylenediamine (hexane-1,6-diamine).

a-1) Show the chemical structure of this nylon-6,6 sample. [Caution: what are the end groups when polycondensation was started from the *equimolar* mixture?]

HO-[CO(CH₂)₄CO-NH(CH₂)₆NH]_n-H or equivalent structures are all OK.
Total 2 pts. -0.5 pt for lacking “n,” another -0.5 pt for lacking each of the end group(s).

- a-2) When this nylon-6,6 sample carries an average molecular weight, M , of 5507.25 (g mol^{-1}), give its X value to the second decimal place.

Calculation procedures must be shown by suitable equation(s) (otherwise, no score will be provided):

The unit molecular weight, M_u , is calculated to be,

$$M_u = (12.01 \times 12 + 1.01 \times 22 + 14.01 \times 2 + 16.00 \times 2) / 2 = 226.36 / 2 = 113.18$$

$$X = (5507.25 - 18.02) / M_u = (5507.25 - 18.02) / 113.18 = 48.50, \text{ or}$$

$$X = 2n = 2 \times [(5507.25 - 18.02) / 226.36] = 48.50$$

$$X = 48.50$$

Black parts are prewritten in the answer boxes (same to all questions in Problem 8). Underlined (or equivalent) calculation procedures are required. Total 4 pts. -1 pt for calculation mistakes.

- a-3) Give the p value necessary to prepare this nylon-6,6 sample of $M = 5507.25$ (g mol^{-1}) to the fifth decimal place. If you get no numerical answer in a-2), use 52.50 instead.

From eq.(3) at $r = 1$ (Carothers eq.), $X = 48.50 = 1 / (1 - p)$, then $p = 0.97938_1$
 $\doteq 0.97938$

$$p = 0.97938 \text{ (0.98095 when } X = 52.50.)$$

Total 3 pts. -1 pt for calculation mistakes.

- b) The low-molecular-weight polyester (oligoester) is prepared from the mixture of 36.54 (g) of adipic acid (hexanedioic acid) and an unknown amount [W (g)] of butane-1,4-diol (Bdiol). Under the condition of $p_A \rightarrow 1$, the oligoester with $X = 11.00$ carrying Bdiol units in both chain ends is obtained.

- b-1) Show the precise chemical structure of this oligoester of $X = 11.00$.

$[\text{HO}(\text{CH}_2)_4\text{O}]_{1.000}-[\text{CO}(\text{CH}_2)_4\text{CO}-\text{O}(\text{CH}_2)_4\text{O}]_{5.000}-\text{H}$ or
 $\text{HO}(\text{CH}_2)_4\text{O}-[\text{CO}(\text{CH}_2)_4\text{CO}-\text{O}(\text{CH}_2)_4\text{O}]_{5.000}-\text{H}$ is accurate, however,
 $\text{HO}(\text{CH}_2)_4\text{O}-[\text{CO}(\text{CH}_2)_4\text{CO}-\text{O}(\text{CH}_2)_4\text{O}]_5-\text{H}$ is acceptable.

Total 4 pts, -1 pt for lacking the number of unit repeating or writing " n " instead of "5.00 (or 5)". Another -1 pt for lacking HO- and/or -H end group(s). No point if lacking the left-most $\text{HO}(\text{CH}_2)_4\text{O}-$ group.

b-2) Calculate the unknown amount, W (g), to the first decimal place.

Calculation procedures must be shown by suitable equation(s) (otherwise, no score will be provided):

$$Mw(\text{adipic acid}) = 146.16, Mw(\text{Bdiol}) = 90.14$$

Ans.1 Since $X = 11.00$, the oligoester contains 5.00 units of adipate and 6.00 units of Bdiol. [cf) $5.00 + 6.00 = 11.00 = X$] When $p_A \rightarrow 1$, the initial molar feed ratio of the monomers is equal to the molar composition of the resulting oligoester.

$$[\text{adipic acid}]_0 / [\text{Bdiol}]_0 = 5.00 / 6.00, \underline{W = 90.14 \times (6.00 / 5.00) \times (36.54 / 146.16) = 27.042 \doteq 27.0 \text{ (g)}}$$

Ans.2 From eq.(2), when $p_A \rightarrow 1$, $X = (1 + r) / (1 - r)$. Therefore,

$$\underline{11.00 = [1 + \{(36.54 / 146.16) / (W / 90.14)\}] / [1 - \{(36.54 / 146.16) / (W / 90.14)\}]} \\ = [(W / 90.14) + 0.2500] / [(W / 90.14) - 0.2500]$$

$$\underline{11.00 \times [(W / 90.14) - 0.2500] = [(W / 90.14) + 0.2500], 10.00 \times (W / 90.14) = 3.000}$$

$$\underline{W = 3.000 \times 90.14 / 10.00 = 27.042 \doteq 27.0 \text{ (g)}}$$

$$\underline{W = 27.0 \text{ (g)}}$$

Either calculation procedures are acceptable. Underlined (or equivalent) calculation procedures are required. Total 7 pts, -1 pt for calculation mistakes.

Problem 9

7% of the total

9a	9b	9c	9d	9e	9f	Task 9
4	2	8	4	8	8	34

α -Cyclodextrin (α CyD), which is a cyclic oligosaccharide of six $\alpha(1 \rightarrow 4)$ linked α -D-glucopyranoside units, can be topologically represented as toroids (Figure 1). α -D-glucopyranoside units in α CyD are usually in the most stable chair conformation.

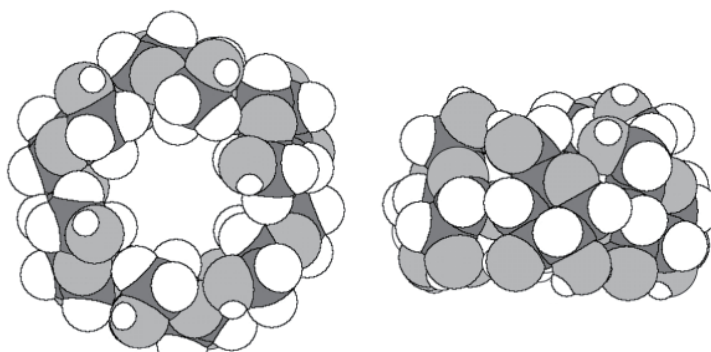
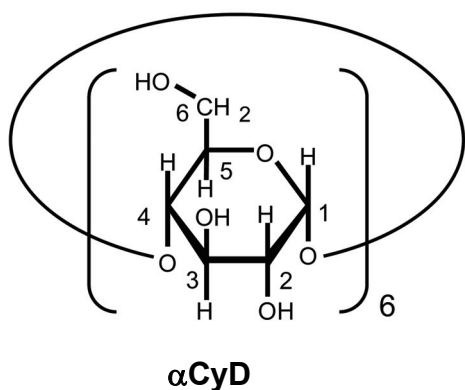
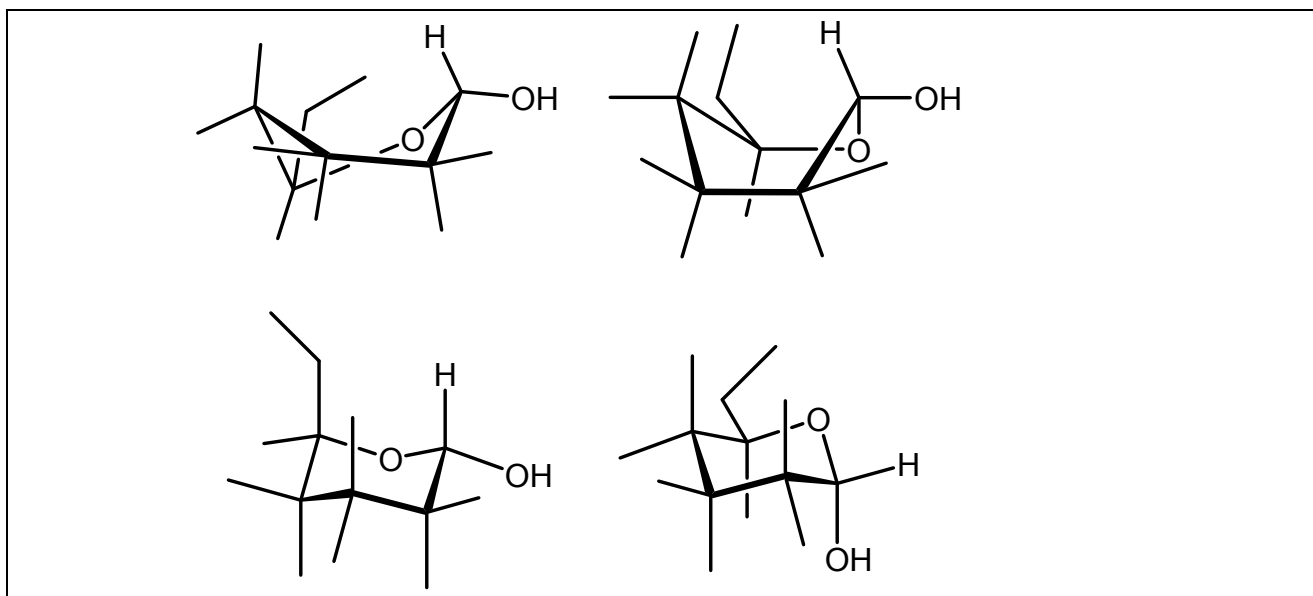


Figure 1. Space filling model of α CyD. Left: view through the hole. Right: side view.

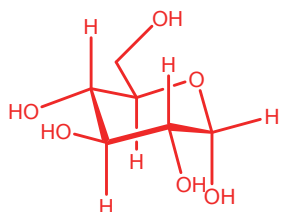
- a) Give the absolute configuration (*R* or *S*) at stereogenic carbons C-2 and C-5 of D-glucose. Also, draw a stereostructure of the open chain form of D-glucose.

Absolute configuration at C-2: <div style="display: flex; justify-content: space-between; align-items: center; margin-top: 10px;"> <i>R</i> 1 pt </div>	Chain form: <div style="text-align: center; margin-top: 20px;"> </div> <div style="text-align: center; margin-top: 5px;"> or </div> <div style="text-align: center; margin-top: 10px;"> 2 pts (carbon skeleton: 1 pt; others: 1 pt) </div>
Absolute configuration at C-5: <div style="display: flex; justify-content: space-between; align-items: center; margin-top: 10px;"> <i>R</i> 1 pt </div>	

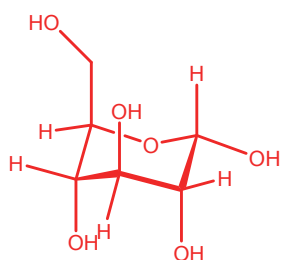
b) Choose the most stable conformation from the four incomplete α -D-glucopyranose formulas given in the answer box and enclose it in a box. Also, add four OH groups and four H atoms to complete the α -D-glucopyranose formula.



Answer:



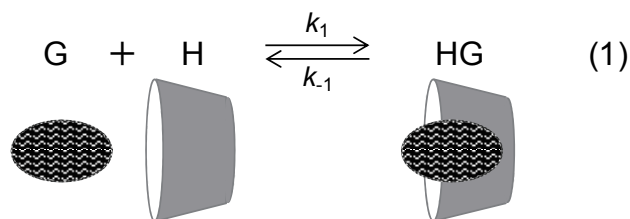
2 pts (4C_1 : 1 pt; -OH: 1 pt)



1 pts (4C_1 : 0 pt; -OH: 1 pt)

Others 0 pt

α CyD in water is able to host hydrophobic molecules. When the host/guest (H/G) stoichiometry is 1/1, the inclusion complexation can be given by the following equilibrium.



where k_1 and k_{-1} are the rate constant for the forward and backward reaction, respectively. The complexation of a guest to α CyD causes a chemical shift change in ^1H NMR spectra. Figure 2 shows a part of ^1H NMR spectra (signals from H-1 of α CyD) showing the chemical shift change in the presence of varying amounts of 1,10-bis(trimethylammonium)decane diiodide (BTAD). The doublet peak at 5.06 ppm is from H-1 of free α CyD, while the doublet at 5.14 ppm is from H-1 of α CyD complexed with BTAD. (Note that the spectra given in Figure 2 were measured in the complexation equilibrium state.)

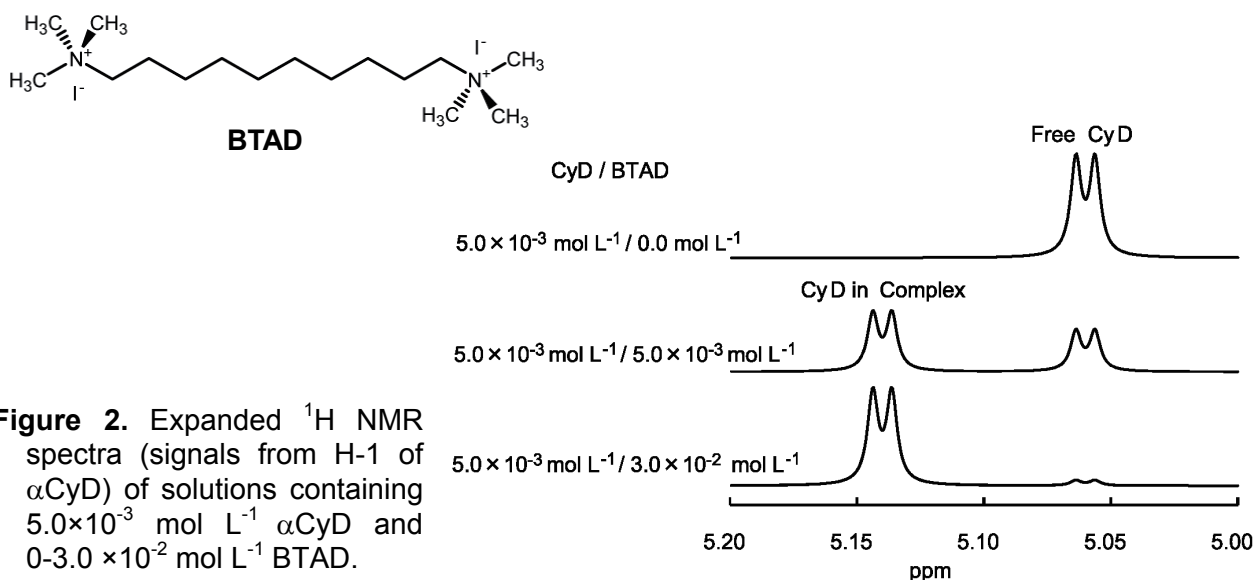


Figure 2. Expanded ^1H NMR spectra (signals from H-1 of α CyD) of solutions containing $5.0 \times 10^{-3} \text{ mol L}^{-1}$ α CyD and $0-3.0 \times 10^{-2} \text{ mol L}^{-1}$ BTAD.

- c) In the spectrum of $5.0 \times 10^{-3} \text{ mol L}^{-1} / 5.0 \times 10^{-3} \text{ mol L}^{-1}$ α CyD/BTAD, the relative peak areas of the doublets at 5.06 and 5.14 ppm are 0.41 and 0.59, respectively. Calculate, to 2 significant figures, the concentration equilibrium constant, K for the inclusion complexation of α CyD/BTAD.

$$K = \frac{[\text{HG}]}{[\text{H}][\text{G}]} = \frac{[\alpha\text{CyD}]_0 \times a_{5.14}}{[\alpha\text{CyD}]_0 \times a_{5.06} \times \{[\text{BTAD}]_0 - [\alpha\text{CyD}]_0 \times a_{5.14}\}} = \frac{5.0 \times 10^{-3} \text{ M} \times 0.59}{(5.0 \times 10^{-3} \text{ M} \times 0.41)^2} = 0.70 \times 10^3$$

1 pt

3 pts

3 pts

1 pt

$a_{5.06}$: relative area of the peak at 5.06 ppm = mole fraction of free α CyD

$a_{5.14}$: relative area of the peak at 5.14 ppm = mole fraction of α CyD complexed with BTAD

K: 7.0×10^2

8 pts in total

Complexation of α CyD with hexyltrimethylammonium bromide (HTAB) appears in NMR spectra in a way different from the α CyD/BTAD complexation. Figure 3 shows a part of ^1H NMR spectra (H-6 signal of HTAB) in α CyD/HTAB solutions. The signal appears as one triplet (not two triplets), which shifts depending on the concentration of α CyD from the position of free HTAB to the position of α CyD/HTAB in proportion to the fraction of the complex in the solution. The H-6 signals from free HTAB and HTAB complexed with α CyD are triplets at 0.740 ppm and 0.860 ppm, respectively.

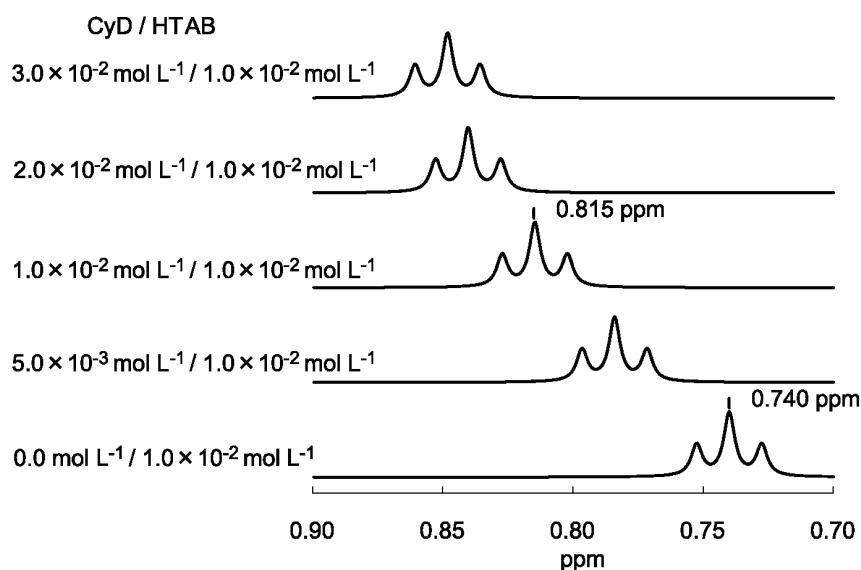
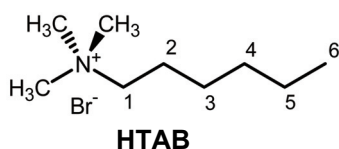


Figure 3. Expanded ^1H NMR spectra (H-6 signal of HTAB) of solutions containing $1.0 \times 10^{-2} \text{ mol L}^{-1}$ HTAB and 0 – $3.0 \times 10^{-2} \text{ mol L}^{-1}$ α CyD.

- d) The signal of HTAB in α CyD/HTAB solutions appears as one triplet, which shifts depending on the concentration of α CyD. Choose the rational interpretation(s) just from these spectra.

hint: When a guest molecule move in and out of α CyD rapidly and repeatedly, only one signal of the guest is observed at the weighted average of the chemical shifts of the free guest and the shift of the guest included in α CyD.

- k_1 of α CyD/HTAB $>$ k_1 of α CyD/BTAD
- k_1 of α CyD/HTAB $<$ k_1 of α CyD/BTAD
- K of α CyD/HTAB $>$ K of α CyD/BTAD
- K of α CyD/HTAB $<$ K of α CyD/BTAD

a 4 pts (additional choice : -2 pts for each)

- e) The signals of HTAB in $1.0 \times 10^{-2} \text{ mol L}^{-1}/1.0 \times 10^{-2} \text{ mol L}^{-1}$ $\alpha\text{CyD}/\text{HTAB}$ are positioned at 0.815 ppm. Calculate, to 2 significant figures, K for the complexation of $\alpha\text{CyD}/\text{HTAB}$.

In $1.0 \times 10^{-2} \text{ mol L}^{-1}/1.0 \times 10^{-2} \text{ mol L}^{-1}$ $\alpha\text{CyD}/\text{HTAB}$,

$$f_{10/10} = \frac{S_{10/10} - S_{\text{free}}}{S_{\text{complex}} - S_{\text{free}}} = \frac{0.815 - 0.740}{0.860 - 0.740} = 0.625$$

3 pts

S_{free} , S_{complex} : chemical shift of HTAB in free, and complexed state

$S_{10/10}$: chemical shift of HTAB in 10.0 mM/10.0 mM $\alpha\text{CyD}/\text{HTAB}$

$f_{10/10}$: mole fraction of complexed HTAB in 10.0 mM/10.0 mM $\alpha\text{CyD}/\text{HTAB}$

$$K = \frac{[\text{HG}]}{[\text{H}][\text{G}]}$$

$$= \frac{[\text{HTAB}]_0 \times f_{10/10}}{\{[\alpha\text{CyD}]_0 - f_{10/10} [\text{HTAB}]_0\} [\text{HTAB}]_0 (1 - f_{10/10})} = \frac{1.0 \times 10^{-2} \text{ mol L}^{-1} \times 0.625}{[1.0 \times 10^{-2} \text{ mol L}^{-1} \times (1 - 0.625)]^2}$$

2 pts

2 pts

$$= 4.4 \times 10^2$$

$$K: 4.4 \times 10^2$$

1 pt

8 pts in total

- f) At 40.0 °C and 60.0 °C, K for the complexation of $\alpha\text{CyD}/\text{HTAB}$ are 3.12×10^2 and 2.09×10^2 respectively. Calculate, to 2 significant figures, the enthalpy change, ΔH° [kJ mol^{-1}], and the entropy change, ΔS° [$\text{J K}^{-1} \text{ mol}^{-1}$]. (Ignore the temperature dependence of ΔH° and ΔS° .)

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

$$\Delta G^\circ (40.0 \text{ }^\circ\text{C}) = -8.314 \times 313.2 \ln (3.12 \times 10^2) = -14.94 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta G^\circ (60.0 \text{ }^\circ\text{C}) = -8.314 \times 333.2 \ln (2.09 \times 10^2) = -14.79 \times 10^3 \text{ J mol}^{-1}$$

2 pts each

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

$$-14.94 \times 10^3 = \Delta H^\circ - 313.2 \times \Delta S^\circ$$

$$-14.79 \times 10^3 = \Delta H^\circ - 333.2 \times \Delta S^\circ$$

2 pts

$$\Delta S^\circ = -7.5 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta H^\circ = -17 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ: -7.5 \text{ J K}^{-1} \text{ mol}^{-1} \quad 1\text{pt}$$

$$\Delta H^\circ: -17 \text{ kJ mol}^{-1} \quad 1\text{pt}$$

8 pts in total