Student Name	Student Code:

Text language:

Translator countries (if more than one):

Please do not translate this part and provide the required information in English.

35th International Chemistry Olympiad

Athens, Greece

Theoretical Examination

Thursday, 10 July 2003

The exam paper consists of 29 numbered pages in addition to this cover page and two appendix pages containing Fundamental Constants, useful expressions and conversion factors, and the Periodic Table of the Elements. Furthermore, you are provided with 5 yellow sheets of scratch paper, a pen and a scientific calculator.

Write your name at the top of this page and your code on every sheet. You should enter your answers in the space provided next to each question. Show all relevant work (calculations, structures, etc.) in the space provided. Give results with appropriate units. Do not write on the back side of the exam sheets.

You may separate your sheets from the clip while working on the exam, but you should assemble them in the proper order before putting them back in the envelope provided. You have 5 hours to work on the exam.

The exam consists of 35 questions divided in four sections:

Section	Category	Questions	Points
A	General	1 – 24	30.5
B	Physical	25 – 30	33.0
C	Organic	31 – 33	34.0
D	Inorganic	34 – 35	27.5
Totals		35	125.0

Questions 1 – 24 receive between 1 and 3 points each, as indicated on each question. No points are given or taken for incorrect or missing answers in multiple choice questions. In most questions, mark with √ your answer (only one) or circle the letters Y or N for correct or incorrect choices, unless instructed otherwise.

Questions 25 – 35 receive between 4 and 17.5 points per question as indicated on each one of them.

Good luck.

Student Code:

SECTION A: General

QUESTION 1 (1 point)

The molar solubility s (mol/L) of $Th(IO_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp}/ 128)^{1/4}$ ( )

(b) $s = (K_{sp}/ 256)^{1/5}$ ( )

(c) $s = 256\ K_{sp}^{1/4}$ ( )

(d) $s = (128\ K_{sp})^{1/4}$ ( )

(e) $s = (256\ K_{sp})^{1/5}$ ( )

(f) $s = (K_{sp}/128)^{1/5} / 2$ ( )

QUESTION 2 (1 point)

Which one of the following equations must be used for the exact calculation of $[H^+]$ of an aqueous HCl solution at any concentration c_{HCl}? ($K_w = 1\times10^{-14}\ M^2$).

(a) $[H^+] = c_{HCl}$ ( )

(b) $[H^+] = c_{HCl} + K_w/[H^+]$ ( )

(c) $[H^+] = c_{HCl} + K_w$ ( )

(d) $[H^+] = c_{HCl} - K_w/[H^+]$ ( )

QUESTION 3 (1 point)

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g/mol and N_A is the Avogadro constant. Which one of the following statements is not correct?

(a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 mL of solution. ( )

(b) 1.00 mmol amount of glucose has a mass of 180 mg. ( )

(c) A 0.0100 mole amount of glucose comprises of $0.0100\times24\times N_A$ atoms. ( )

(d) 90.0 g glucose contain $3\times N_A$ atoms of carbon. ( )

(e) 100 mL of a 0.10 M solution contain 18 g of glucose. ( )

QUESTION 4 (1 point)

If the density of a liquid compound B is ρ (in g/cm^3), M is the molar mass (in g/mol) of B and N_A is the Avogadro constant, then the number of molecules of B in 1 litre of this compound is:

(a) $(1000 \times \rho) / (M \times N_A)$ ( )

(b) $(1000 \times \rho \times N_A) / M$ ( )

(c) $(N_A \times \rho) / (M \times 1000)$ ( )

(d) $(N_A \times \rho \times M) / 1000$ ( )

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QUESTION 5 (1 point)
The equilibrium constant of the reaction:

$$Ag_2CrO_4(s) + 2Cl(aq)^- \rightleftharpoons 2AgCl(s) + CrO_4^{2-}(aq)$$

is given by the equation:

(a) $K = K_{sp(Ag2CrO4)} / K_{sp(AgCl)}{}^2$ ( )

(b) $K = K_{sp(Ag2CrO4)}\, K_{sp(AgCl)}{}^2$ ( )

(c) $K = K_{sp(AgCl)} / K_{sp(Ag2CrO4)}$ ( )

(d) $K = K_{sp(AgCl)}{}^2 / K_{sp(Ag2CrO4)}$ ( )

(e) $K = K_{sp(Ag2CrO4)} / K_{sp(AgCl)}$ ( )

QUESTION 6 (1 point)
How many mL of 1.00 M NaOH must be added to 100.0 mL of 0.100 M H_3PO_4 solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H_3PO_4 are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

(a) 5.0 mL ( )

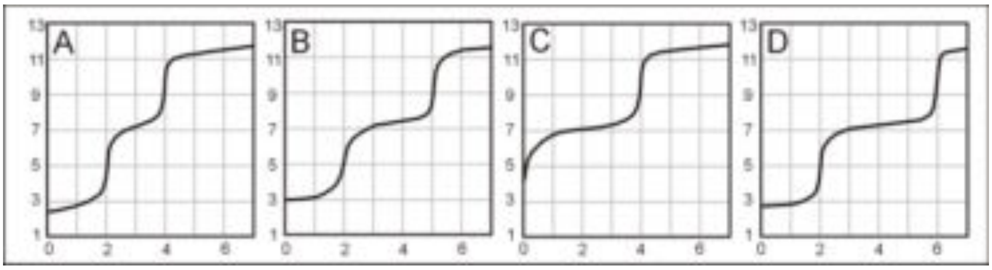
(b) 10.0 mL ( )

(c) 15.0 mL ( )

(d) 20.0 mL ( )

QUESTION 7 (1.5 point)
Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (pH vs. volume of titrant) shown in the figure. (for H_3PO_4: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

pH



Volume of titrant (mL)

(case a) The sample contains H_3PO_4 only.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case b) The sample contains both in a mole ratio $H_3PO_4 : NaH_2PO_4$ 2:1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case c) The sample contains both in a mole ratio $H_3PO_4 : NaH_2PO_4$ 1:1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

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QUESTION 8 (1 point)
A fuel/oxidant system consisting of N,N-dimethylhydrazine $(CH_3)_2NNH_2$ and N_2O_4 (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N_2, CO_2 and H_2O are the only products (all gases under the reaction conditions). How many moles of gases are produced from 1 mol of $(CH_3)_2NNH_2$?

(a) 8 ( )
(b) 9 ( )
(c) 10 ( )
(d) 11 ( )
(e) 12 ( )

QUESTION 9 (1 point)
The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

(a) F ( )
(b) (4/3) F ( )
(c) (3/2) F ( )
(d) 2 F ( )
(e) 3 F ( )

QUESTION 10 (2.5 points)
Identify particle X in each of the following nuclear reactions:

(case a)	${}^{68}_{30}Zn + {}^{1}_{0}n \rightarrow {}^{65}_{28}Ni + X$	alpha ( ), beta ( ), gamma ( ), neutron ( )
(case b)	${}^{130}_{52}Te + {}^{2}_{1}H \rightarrow {}^{131}_{53}I + X$	alpha ( ), beta ( ), gamma ( ), neutron ( )
(case c)	${}^{214}_{82}Pb \rightarrow {}^{214}_{83}Bi + X$	alpha ( ), beta ( ), gamma ( ), neutron ( )
(case d)	${}^{23}_{11}Na + {}^{1}_{0}n \rightarrow {}^{24}_{11}Na + X$	alpha ( ), beta ( ), gamma ( ), neutron ( )
(case e)	${}^{19}_{9}F + {}^{1}_{0}n \rightarrow {}^{20}_{9}F + X$	alpha ( ), beta ( ), gamma ( ), neutron ( )

QUESTION 11 (1 point)
10.0 mL of 0.50 M HCl and 10.0 mL of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 mL of 0.50 M NaOH were used instead of 10.0 mL. Thermal losses are negligible and the specific heats of both solutions are taken as equal.

(a) $(1/2) \times \Delta T$ ( )
(b) $(2/3) \times \Delta T$ ( )
(c) $(3/4) \times \Delta T$ ( )
(d) ΔT ( )

QUESTION 12 (1 point)
Natural antimony consists of the following 2 stable isotopes: ^{121}Sb, ^{123}Sb. Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. Natural hydrogen consists of the following 2 stable isotopes: ^{1}H, ^{2}H. How many peaks are expected in a low resolution mass spectrum for the ionic fragment $SbHCl^{+}$?

(a) 4 ( )

(b) 5 ( )

(c) 6 ( )

(d) 7 ( )

(e) 8 ( )

(f) 9 ( )

QUESTION 13 (1 point)
The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5°. Based on this we must expect a 2nd order diffraction from the same crystal at:

(a) 22.0 degrees ( )

(b) 22.5 degrees ( )

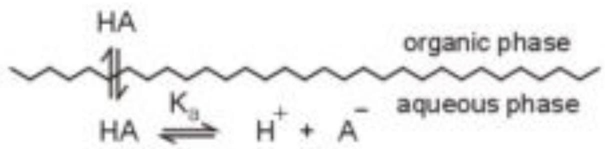
(c) 23.0 degrees ( )

(d) 23.5 degrees ( )

(e) 24.0 degrees ( )

(f) 24.5 degrees ( )

QUESTION 14 (1 point)
The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

(a) The distribution constant (K_D) of the acid HA depends on the pH of the aqueous phase. Y N

(b) HA can be efficiently extracted only from acidic aqueous solutions. Y N

(c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. Y N

(d) The distribution ratio (D) of the acid HA depends mainly on its concentration. Y N

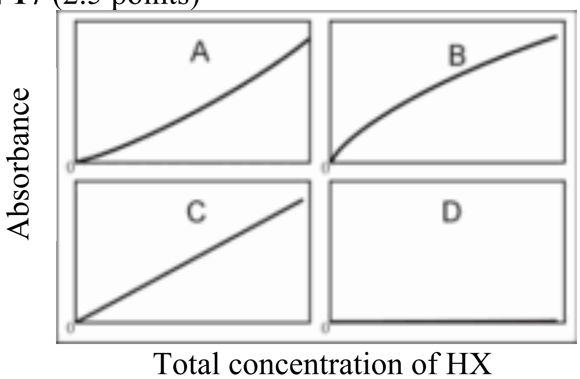
QUESTION 15 (1 point)
Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. Y N
(b) The absorbance is linearly related to the wavelength of the incident light. Y N
(c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. Y N
(d) The transmittance is inversely proportional to the logarithm of absorbance. Y N
(e) The transmittance is inversely proportional to the concentration of the absorbing compound. Y N

QUESTION 16 (1 point)
Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics

(case a) 3000 Å	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
(case b) 5×10^{14} Hz	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
(case c) 2000 cm^{-1}	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
(case d) 2×10^{6} GHz	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

QUESTION 17 (2.5 points)



The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:

(case a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

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QUESTION 18 (1 point)
Which of the following acids is the strongest?

(a) perchloric acid, $HClO_4$ ( )

(b) chloric acid, $HClO_3$ ( )

(c) chlorous acid, $HClO_2$ ( )

(d) hypochlorous, $HClO$ ( )

(e) All of them are equally strong because they all contain chlorine ( )

QUESTION 19 (1 point)
Which structure describes best the crystal system of iron in which the coordination number is 8?

(a) simple cubic ( )

(b) body-centered cubic ( )

(c) cubic closest packed ( )

(d) hexagonal closest packed ( )

(e) none of the above ( )

QUESTION 20 (1 point)
Which of the following elements has the largest third ionization energy?

(a) B ( )

(b) C ( )

(c) N ( )

(d) Mg ( )

(e) Al ( )

QUESTION 21 (1 point)
Which second period (row) element has the first six ionization energies (IE in electron volts, eV) listed below?

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

(a) B ( )

(b) C ( )

(c) N ( )

(d) O ( )

(e) F ( )

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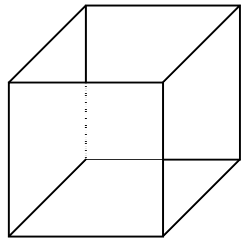
QUESTION 22 (3 points)
Silver metal exists as a face-centered cubic (fcc) packed solid.

(a) Draw an fcc unit cell.



(b) How many atoms are present in the fcc unit cell?

(c) The density of silver has been determined to be 10.5 g/cm^3 . What is the length of each edge of the unit cell?

(d) What is the atomic radius of the silver atoms in the crystal?

QUESTION 23 (1 point)
Are the following statements correct (Y) or not (N)?

(a) HF boils at a higher temperature than HCl. Y N

(b) HBr boils at a lower temperature than HI Y N

(c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. Y N

(d) Ammonia solutions are buffer solutions because they contain the conjugate pair $NH_3 – NH_4^+$. Y N

(e) Pure water at 80°C is acidic. Y N

(f) During electrolysis of an aqueous KI solution with graphite electrodes, the pH near the cathode is below 7. Y N

QUESTION 24 (2 points)
Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1:3. How many moles of HNO_3 are consumed by 1 mol of Zn?

(a) 2.2 ( )
(b) 2.4 ( )
(c) 2.6 ( )
(d) 2.8 ( )
(e) 3.0 ( )
(f) 3.2 ( )

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SECTION B: PHYSICAL

QUESTION 25: Muon (8 points)

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is :

$$\mu \rightarrow e + \bar{\nu}_e + \nu_\mu,$$

where $\bar{\nu}_e$ is the electron antineutrino, and ν_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + \nu_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of $1.4846\text{x}10^{-11}$ J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^{1}H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

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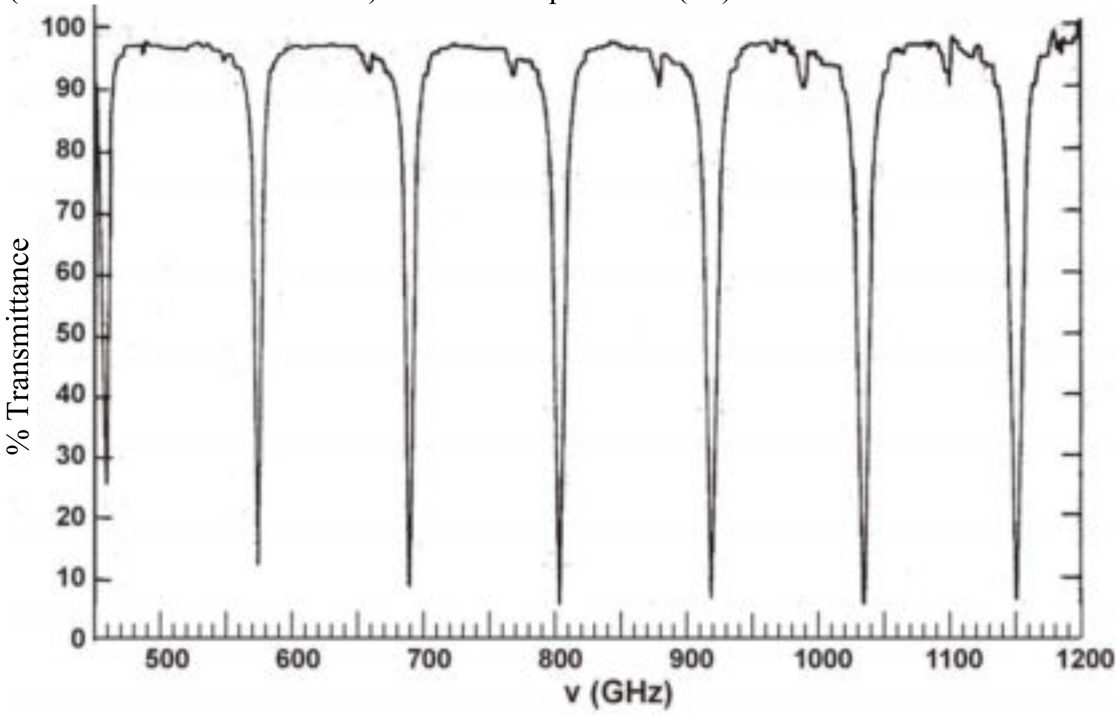
QUESTION 26: CO spectrum (5 points)

Rotational energy levels of diatomic molecules are well described by the formula $E_J = B\,J\,(J+1)$, where J is the rotational quantum number of the molecule and B its rotational constant. B is related to the reduced mass μ and the bond length R of the molecule through the equation $B = \frac{h^2}{8\pi^2 \mu R^2}$.

In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h\,\nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2\,B\,(J+1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h\,(\Delta\nu) = 2\,B$.



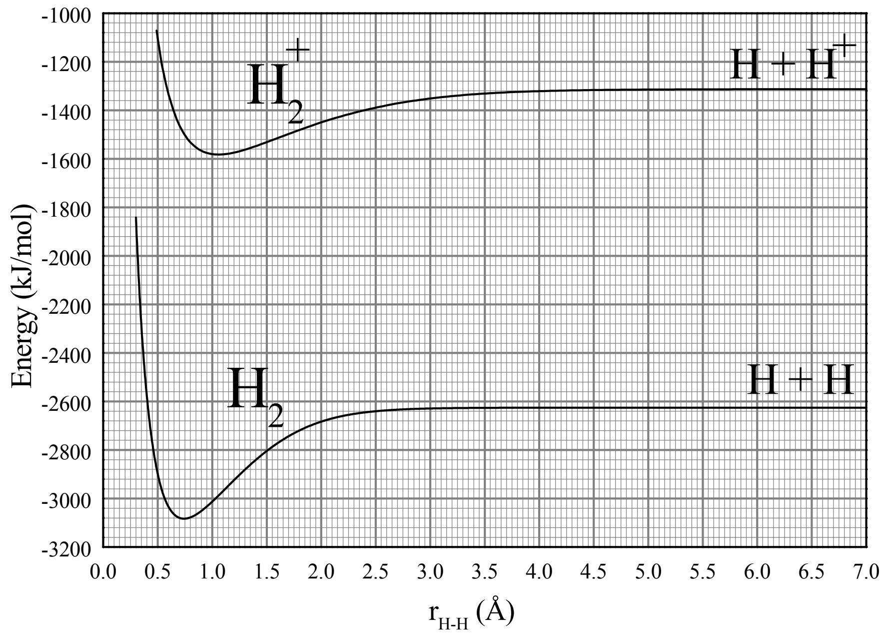
By inspecting the spectrum provided, determine the following quantities for $^{12}C^{16}O$ with appropriate units:

a) $\Delta\nu$

b) B

c) R

QUESTION 27: Hydrogen molecule (6 points)
In the following graph are presented potential energy curves of the H_2 molecule and its cation H_2^+.



Using the information provided on this graph, give numerical answers with appropriate units to the following questions:

1. What are the equilibrium bond lengths of H_2 and H_2^+?

2. What are the binding energies of H_2 and H_2^+?

3. What is the ionisation energy of the H_2 molecule?

4. What is the ionisation energy of the H atom?

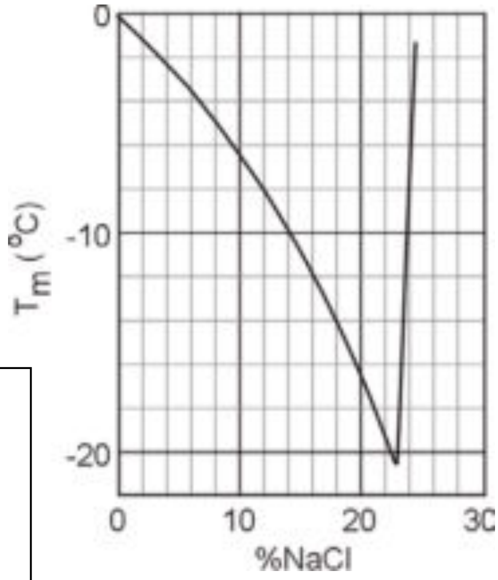
5. If we use electromagnetic radiation of frequency $3.9 \cdot 10^{15}$ Hz in order to ionise H_2, what will be the velocity of the extracted electrons? (ignore molecular vibrational energy)

QUESTION 28: Cryoscopy (4 points)

Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 °C) and well above the CO_2 sublimation point (−78 °C). In this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as −20 °C can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 °C with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

1. The mixing process is spontaneous
   Y N
2. The change of entropy during the mixing process is negative Y N
3. This diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is is the freezing point of the bath based on the diagram?



4. If an equal mass of $MgCl_2$ were used instead of NaCl, would the freezing point be higher? Y N

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QUESTION 29: Pool (5 points)
A very large swimming pool filled with water of temperature equal to 20°C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine the following quantities:

a) The heat delivered to the water

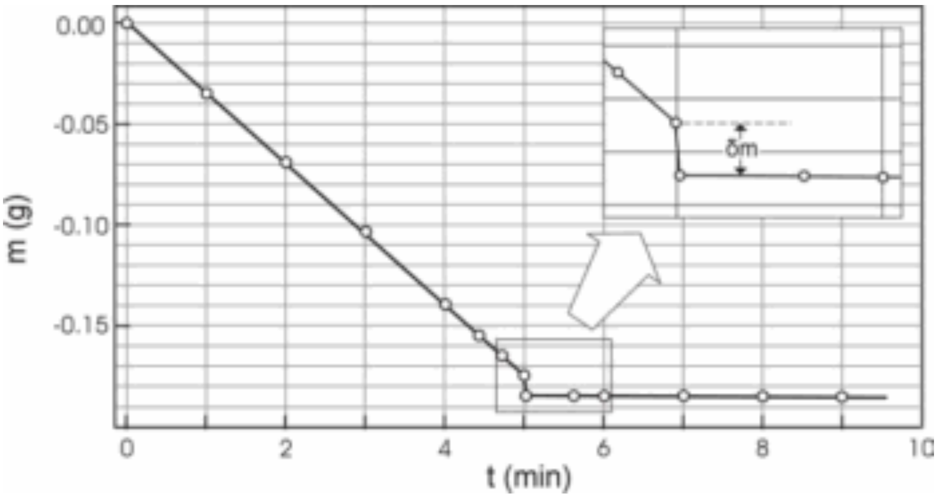
b) Is the change of entropy of the resistor positive, negative, or zero?
(i) $\Delta S_{res} > 0$ ( )
(ii) $\Delta S_{res} = 0$ ( )
(iii) $\Delta S_{res} < 0$ ( )

c) Is the change of entropy of the water positive, negative, or zero?
(i) $\Delta S_{pool} > 0$ ( )
(ii) $\Delta S_{pool} = 0$ ( )
(iii) $\Delta S_{pool} < 0$ ( )

d) Is the change of entropy of the system positive, negative, or zero?
(i) $\Delta S_{total} > 0$ ( )
(ii) $\Delta S_{total} = 0$ ( )
(iii) $\Delta S_{total} < 0$ ( )

e) Is the process reversible? Y N

QUESTION 30: Gas velocity (5 points)
The experiment described here gives a simple way to determine the mean velocity u of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time t=0. Balance readings are recorded as shown on



the diagram. At t = 5 min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δm. Therefore, the force exerted on the lid is f = δm g. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., f = ½ u dm/dt. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume g = 9.8 m s^{-2}.

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SECTION C: Organic

PROBLEM 31: Ester identification (14 points)

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 mL of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 mL of a 1.00 M HCl solution to titrate the unused NaOH, only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with I_2/NaOH to give a yellow precipitate and C_6H_5COONa.

The diacid **B** reacted with Br_2 in CCl_4 to give a single, optically inactive product (compound **D**).

Ozonolysis of **B** gave only one product.

1. Determine the molecular mass of compound **A**.

M_A =

2. Give the structural formulas of **A**, **B**, and **C** without stereochemical information.

A	B	C

3. Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.

Possible Stereochemical Formulas for C

4. Give the stereochemical formula for **D**, using a Fischer projection.

Stereochemical Formula for D

5. Give the stereochemical formula for **B**.

Stereochemical Formula for B

The diester **A** also reacted with Br_2 in CCl_4 and was converted to a mixture of two compounds (**E**, **F**) both optically active.

6. Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

Possible Stereochemical Formula(s) for E	**Possible Stereochemical Formula(s) for F**

If we use $Na^{18}OH$ for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

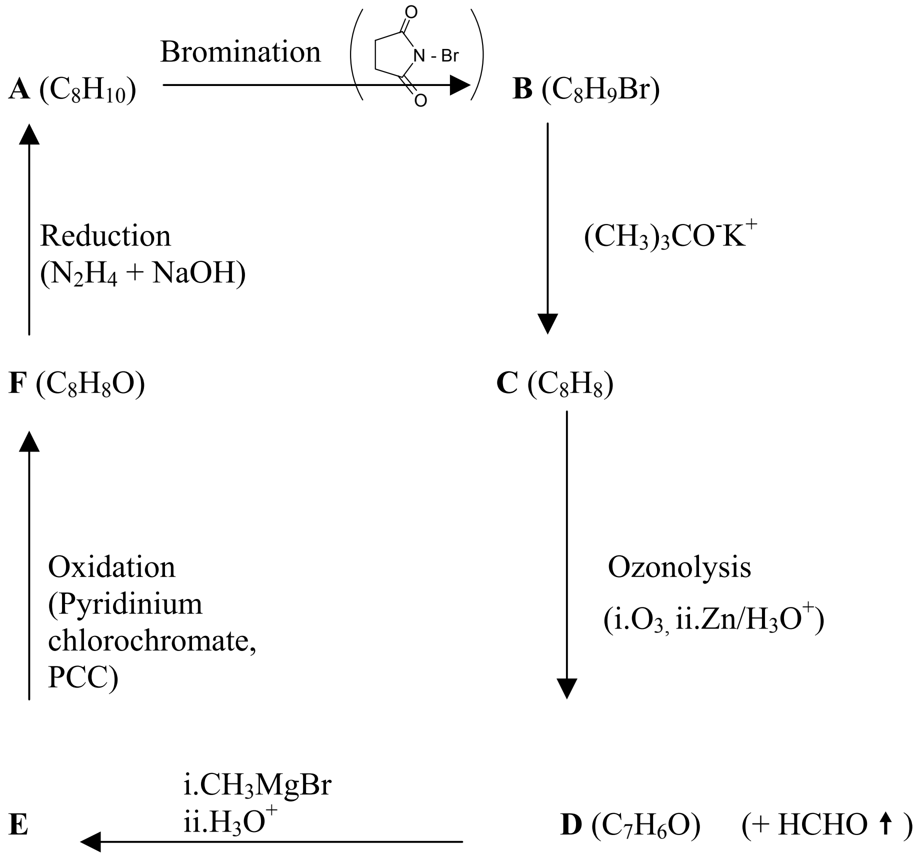
7. Mark the correct answer:

a. Only **B** ( )

b. Only **C** ( )

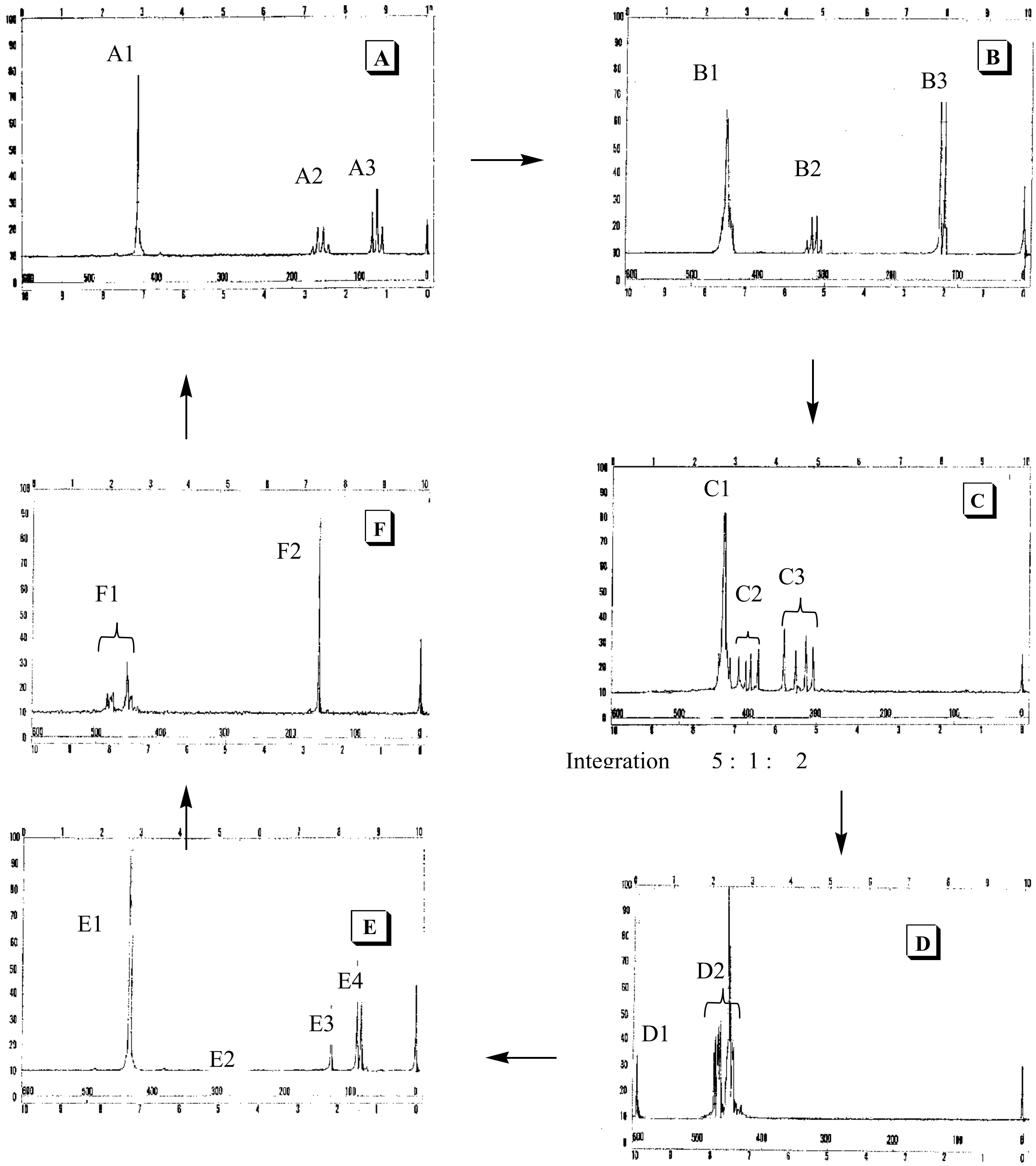
c. Both **B** and **C** ( )

PROBLEM 32: NMR puzzle (9 points)
An organic compound **A** (C_8H_{10}) gives the following chain of reactions:



Based on the ^{1}H-NMR spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding ^{1}H-NMR peaks, as shown in the example.

Student Code:



General remarks: NMR spectra were recorded in $CDCl_3$ on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in $CDCl_3$ solutions and catalyse rapid exchange of some particular protons.

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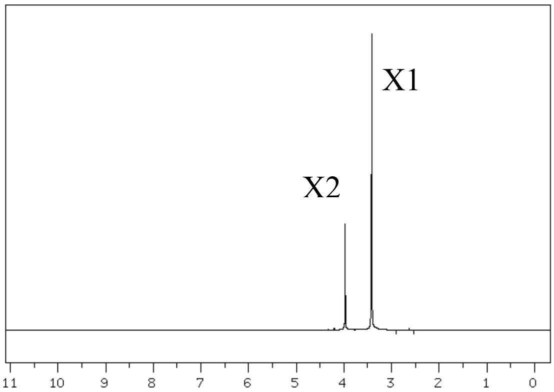
EXAMPLE

X1 X2
CH_3OH



A

B

F

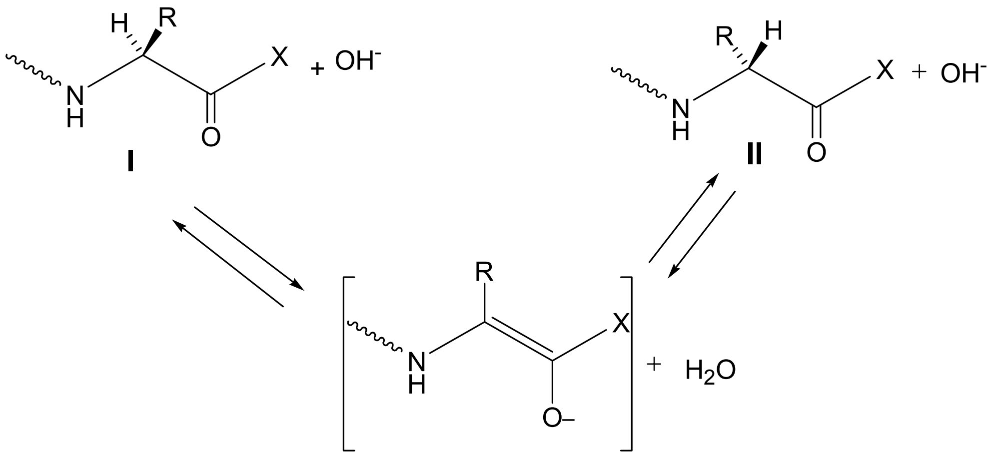
C

E

D

PROBLEM 33: Peptides (11 points)

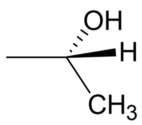
Racemization of α-aminoacids and peptides can occur by an α-enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:



intermediate

1. Draw stereochemical formulas I and II (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α-enolization mechanism described above operating on each of the following hydroxyaminoacids A and B:

A: serine (R = $–CH_2OH$)

B: (2*S*,3*R*)-threonine (R = )

A

I

II

B

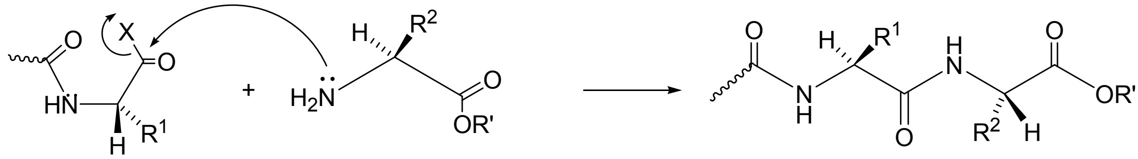
I

II

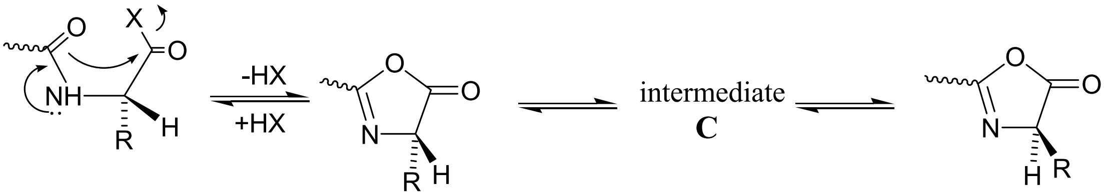
2. Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

	enantiomeric	diastereomeric
A $_{I, II}$	☐	☐
B $_{I, II}$	☐	☐

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:



It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:



azalactone azalactone

3. Write a structure for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center:

Intermediate **C**

Azalactones are very reactive substances that can still react with the amino group of an aminoacid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

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4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40˚C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$. (P_1)

A: Propose a structure for this substance.

P_1

B: Write the reaction product (s) of the substance you proposed above with *S*-alanine ethyl ester (P_2) (the side chain R of the aminoacid alanine is a methyl group) using stereochemical formulas (with bold and dashed bonds) for both reactants and product.

P_1 + **P_2** → Product

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SECTION D: Inorganic

QUESTION 34: Aluminium (17.5 points)

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al_2O_3) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $AlO_x(OH)_{3-2x}$ where $0<x<1$.

Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al_2O_3 40-60%, H_2O 12-30%, SiO_2 free and combined 1-15%, Fe_2O_3 7-30%, TiO_2 3-4%, F, P_2O_5, V_2O_5, etc., 0.05-0.2%). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200°C. Complete and balance the following chemical reactions of stage (i)

$$Al_2O_3 \; + \; OH^- \; + \qquad \rightarrow \; [Al(OH)_4(H_2O)_2]^-$$

$$SiO_2 \; + \; OH^- \qquad \rightarrow \; SiO_2(OH)_2^{2-}$$

$$SiO_2(OH)_2^{2-} \; + \qquad \rightarrow \; CaSiO_3\downarrow \; +$$

$$[Al(OH)_4(H_2O)_2]^- \; \rightarrow \qquad \downarrow \; + \; OH^- \; + \; H_2O$$

$$Al(OH)_3 \; \rightarrow \; Al_2O_3 \; +$$

ii) Héroult-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6. Typical electrolyte composition ranges are Na_3AlF_6 (80-85%), CaF_2 (5-7%), AlF_3 (5-7%), Al_2O_3 (2-8% intermittently recharged). Electrolysis is carried out at 940°C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:

$$Al_2O_3(l) \; + \; C(anode) \; \rightarrow \; Al(l) \; + \; CO_2(g)$$

Since cryolite is a rather rare mineral, it is prepared according to the following reaction. Complete and balance this reaction:

$$HF \; + \; Al(OH)_3 \; + \; NaOH \; \rightarrow \; Na_3AlF_6 \; +$$

During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.
iii) By using the thermodynamic data given below, which are taken to be independent of temperature, determine the thermodynamic quantities ΔH, ΔS and ΔG at 940°C for the reaction:

$$C(graphite) + CO_2(g) \rightarrow 2CO(g).$$

	Al(s)	Al_2O_3(s)	C (graphite)	CO(g)	CO_2(g)	O_2(g)
$\Delta_f H^o$ (kJ.mol^{-1})	0	−1676	0	−111	−394	
S^o (J.K^{-1}.mol^{-1})	28	51	6	198	214	205
$\Delta_{fus}H$ (kJ.mol^{-1})	11	109				

iv) At the same temperature and using the data from the table in part (iii) determine the quantities ΔH and ΔG for the reaction

$$2Al(l) + 3CO_2(g) \rightarrow Al_2O_3(l) + 3CO(g)$$

given that $\Delta S = -126$ J K^{-1} mol^{-1}. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[Al(H_2O)_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[Al(OH)_4]^-(aq)$. In both cases liberation of H_2 occurs. AlF_3 is made by treating Al_2O_3 with HF gas at 700°C, while the other trihalides, AlX_3, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The $AlCl_3$ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4°C) the structure changes to a 4-coordinate molecular dimer, Al_2Cl_6. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar $AlCl_3$ molecules.

For the molecular dimer Al_2Cl_6, in the gas phase, two different Al — Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al — Cl distances.

vii) What is the hybridization of the Al atom(s) in Al_2Cl_6 and $AlCl_3$?

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QUESTION 35: Kinetics (10 points)

The acid-catalyzed reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ was found to be first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by 0.010 mol L^{-1} was measured under various initial concentrations of the reactants.

i) Based on the information provided in the table, fill in the blanks.

$[CH_3COCH_3]$ (mol L^{-1})	$[I_2]$ (mol L^{-1})	Time (min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	…
1.50	…	…
…	…	0.36

ii) Derive the rate law for the reaction and calculate the observed rate constant.

iii) Calculate the time needed for 75% of CH_3COCH_3 to react in excess I_2.

iv) Show graphically the dependence of the rate on $[CH_3COCH_3]$ and on $[I_2]$, for fixed initial concentration of the other reagents.

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v) If the rate is doubled by raising the temperature by 10°C from 298 K, calculate the activation energy for this reaction.

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Fundamental constants

Quantity	Symbol	Value	Unit
Speed of light	c	299 792 458	m s^{-1}
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ = 12.566 370 614… x 10^{-7}	N A^{-2}
Permittivity of vacuum	ε_0	$1/\mu_0 c^2$ = 8.854 187 817 x 10^{-12}	C^2 m^{-2} N^{-1} or F m^{-1}
Planck constant	h	6.626 068 76 x 10^{-34}	J s
Electron charge	e	1.602 176 462 x 10^{-19}	C
Electron mass	m_e	9.109 381 88 x 10^{-31}	kg
Proton mass	m_p	1.672 621 58 x 10^{-27}	kg
Avogadro constant	N_A	6.022 141 99 x 10^{23}	mol^{-1}
Faraday constant	F	96 485.3415	C mol^{-1}
Boltzmann constant	k	1.380 650 3 x 10^{-23}	J K^{-1}
Molar gas constant	R	8.314 472	J K^{-1} mol^{-1}
Atomic mass unit	u	1.660 538 73 x 10^{-27}	kg

Source: *Physics Today* **55** BG6 (2002)

Common unit conversions

The unit 1 M is commonly used as an abbreviation for 1 mol dm^{-3}.

1 L = 1 dm^3 = 1000 cm^3

1 Å = 10^{-10} m

1 cal = 4.184 J

Useful formulas

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$E_n = \frac{-Z^2 e^2}{(4\pi\varepsilon_0) 2n^2 \alpha} \quad \text{with} \quad \alpha = \frac{\left(\frac{h}{2\pi}\right)^2 (4\pi\varepsilon_0)}{\mu e^2}$$

$$\text{Kinetic Energy} = \frac{1}{2} m v^2$$

$$E = m c^2$$

$$2\, d \sin\theta = n\, \lambda$$

$$k = A e^{-\frac{E_a}{RT}}$$