

PART A

2002

Please note that this answer book will be photocopied when returned and then split so that answers are sent to the appropriate markers.

For this reason it is extremely important that you observe instructions 6 to 8.

Instructions to Student

1. You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.
2. You are **not** permitted to refer to books, notes or periodic tables but you may use a non programmable electronic calculator.
3. All questions to be attempted. A guide for time allocation is supplied at the beginning of each question.
4. Data is supplied, where necessary, with each question.
5. Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
6. Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.
7. Ensure that your name is written in the appropriate place on **ALL** of the pages in this examination booklet.
8. Use only **black** or **blue pen** for your written answers, **pencil or other coloured pens are not acceptable**.

Supervisor Declaration

I certify that the final selection examination was carried out under strict examination conditions and that no improper actions occurred during the examination period.

Name of Exam Supervisor: *(please print)*

Signed: Date:

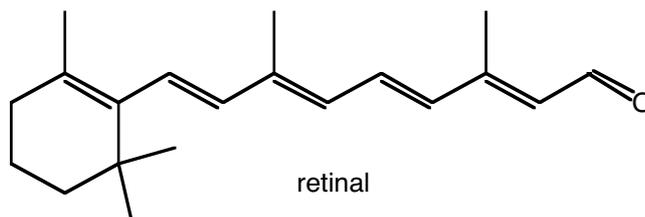
Please use the enclosed pre-addressed Express Post Envelope to return the Examination.
(Mr R W Switzer, RTASO Chemistry program, PO Box 589, Mudgeeraba QLD 4213).

EXAMINATIONS MUST BE RECEIVED BY
FRIDAY 21st MARCH 2003.

Question 1 (20 minutes)

Data:	Rydberg constant	$R_{\text{H}} = 1.097 \times 10^7 \text{ m}^{-1}$
	Planck's constant	$h = 6.626 \times 10^{-34} \text{ J s}$
	Speed of light in vacuum	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
	Mass of electron	$m_e = 9.110 \times 10^{-31} \text{ kg}$
	Charge of electron	$-e = -1.602 \times 10^{-19} \text{ C}$
	Ångström	$1 \text{ Å} = 10^{-10} \text{ m}$
	Energy levels for a particle of mass m confined to a one-dimensional box of zero potential and length L	$E = \frac{n^2 h^2}{8mL^2}, n = 1, 2, 3, \dots$

- (a) Helium is the only member of the periodic table to have been detected within an extraterrestrial object (the solar corona) prior to its isolation within the laboratory. In fact, for almost thirty years, the solar spectrum was the sole source of information on this novel element. Its presence was detected from several series of spectral lines in sunlight, including the Pickering series, which arises from electrons in He^+ ions falling from higher energy levels to the orbit with $n = 4$.
- Give a formula for the wavelength of the lines in the Pickering series.
 - What is the shortest wavelength in this series?
 - Calculate the energy (in eV) and momentum of a photon with this wavelength. What is the chemical significance of this energy?
 - How many electrons in a single atom can have $n = 4$?
- (b) β -carotene, the orange pigment with which AChO students are so familiar, is also responsible for carrots' famed ability to enable diners to see in the dark. When eaten, this pigment is broken down into Vitamin A, which in turn is oxidised to retinal (see below). This is the principal substance which, by absorbing light in our eyes, is responsible for black-and-white vision.



The actual mechanism by which light detection occurs is very complicated, but surprisingly accurate predictions can be made using nothing more than the particle-in-a-box model.

- Using this model, sketch the wavefunctions for the lowest energy level and the HOMO of the π -system.
- Take the average bond length in retinal to be 1.4 Å and the bond angle for sp^2 -hybridised carbon to be 120° , and use the particle-in-a-box model to predict the wavelengths of light which this system is capable of absorbing. Hence estimate the colour of light to which our eyes are most sensitive.

Question 2 (25 minutes)

- Write ground state valence electron configurations for each of the following species: P^{3-} , Sn^{2+} , V^{3+} , Bi^{3+} and Pt^{4+} .
- Name the following coordination compounds: $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$, $\text{Cs}[\text{FeCl}_4]$, $\text{K}_2[\text{Pt}(\text{C}_2\text{O}_4)_2]$ and $[\text{Cu}(\text{en})_3](\text{BF}_4)_2$.
- For each of the transition metal ions in part b) construct a clearly labeled d-orbital splitting diagram and calculate the crystal field stabilization energy in terms of Δ_o .
- Which, if any, of the complexes in part (b) would be expected to exist in stereoisomeric forms? Sketch them. How many stereoisomers are expected for the following species: $[\text{Pt}(\text{dmen})\{(\text{S})\text{-pn}\}]^{2+}$ and $[\text{Co}\{(\text{S})\text{-pn}\}_3]^{3+}$ [where $\text{dmen} = \text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ and $\text{pn} = \text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{NH}_2$]? Sketch them.

Question 3 (45 minutes)

Data (at 298.15 K) for (a): H_3PO_4 : $\text{p}K_{\text{a}1} = 2.12$, $\text{p}K_{\text{a}2} = 7.21$, $\text{p}K_{\text{a}3} = 12.32$

$$\text{FW}(\text{H}_3\text{PO}_4) = 97.99 \text{ g mol}^{-1}$$

$$K_{\text{sp}} \text{ of zinc phosphate} = 9.10 \times 10^{-33}$$

- (a) Phosphoric acid is of great importance in fertiliser production. In addition, phosphoric acid and its various salts have a number of applications in metal treatment, food, detergent and toothpaste industries.
- (i) Write down the conjugate base of the dihydrogen phosphate ion and determine its $\text{p}K_{\text{b}}$ value (at 298.15 K).
- Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and root beers. A cola having a density of 1.00 g mL^{-1} contains 0.0500% by weight of phosphoric acid.
- (ii) Determine the pH of cola. Assume that the acidity of the cola arises only from phosphoric acid. State and justify any assumptions made in your calculations.
- Phosphoric acid is also used as a fertiliser for agriculture. 1.00×10^{-3} moles of phosphoric acid is added to an 1.00 L aqueous soil suspension and the pH was found to be 7.00.
- (iii) Write out the expressions for the dissociation constants of phosphoric acid.
- (iv) Express $[\text{HPO}_4^{2-}]$, $[\text{H}_2\text{PO}_4^-]$, and $[\text{H}_3\text{PO}_4]$ in terms of $[\text{PO}_4^{3-}]$. Leave the coefficients in terms of $[\text{H}^+]$ and the dissociation constants.
- (v) Determine the fractional concentration (ie expressed as a fraction of the total amount of phosphate added) of all the different phosphate species present in the solution. Assume that no component of the soil interacts with any of the phosphate species.
- Zinc is an essential micronutrient for plant growth. Plants can absorb zinc in water-soluble form only. In a given sample of soil water with $\text{pH} = 7.00$, zinc phosphate was found to be the only source of zinc and phosphate.
- (vi) Write out the expression for the solubility product of zinc phosphate.
- (vii) What is the relationship between $[\text{Zn}^{2+}]$ and $[\text{PO}_4^{3-}]_{\text{TOTAL}}$?
- (viii) What is the relationship between $[\text{Zn}^{2+}]$ and $[\text{PO}_4^{3-}]$?
- (ix) Calculate the concentration of $[\text{Zn}^{2+}]$, $[\text{H}_3\text{PO}_4]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$, and $[\text{PO}_4^{3-}]$ in the solution.
- (x) Qualitatively, describe what will occur to the solubility of zinc phosphate when you increase and decrease the pH of the soil. If the plant you are cultivating requires a high level of zinc to sustain growth, how should you alter the pH?

Data (at 298.15 K) for (b): $K_{\text{sp}}(\text{Hg}_2\text{Cl}_2) = 1.32 \times 10^{-18}$ $\text{FW}(\text{Hg}_2\text{Cl}_2) = 472.1 \text{ g mol}^{-1}$
 $E^\circ(\text{SCE}) = 0.242 \text{ V}$ $\text{FW}(\text{KCl}) = 74.55 \text{ g mol}^{-1}$
 $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.154 \text{ V}$ $R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$
 $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.771 \text{ V}$ $F = 96485.3415 \text{ C mol}^{-1}$
 Solubility of KCl = 35.0 g in 100 mL H_2O

- (b) Although the standard reduction potentials of compounds are referenced according to the standard hydrogen electrode (SHE) it is often not practical to set one up to measure the potentials of redox systems. Numerous alternative standard electrodes have been constructed that are more practical to use. Of these, the most commonly used is the saturated calomel electrode (SCE). This consists of a platinum wire immersed in a ball of mercury in contact with a Hg_2Cl_2 paste, with the entire apparatus bathed in a saturated solution of KCl.

- (i) If the SCE is hooked up to the SHE to form a galvanic cell, what is the line notation for the cell?
- (ii) What is the solubility of Hg_2Cl_2 in the SCE and in pure water (in g 100 mL^{-1})?

When measuring the potential of a redox system with the SCE, the potential of the SCE has to be subtracted, in other words:

$$E_{\text{measured}} = E_{\text{cell}} - E_{\text{SCE}}^\circ$$

A solution containing Sn^{2+} ions is titrated potentiometrically with Fe^{3+} .

- (iii) Write down the overall reaction and calculate the E_{cell}° and ΔG° for the system.
- (iv) Determine the equilibrium constant of the reaction (in the spontaneous direction).
- 20 mL of 0.100 M Sn^{2+} is titrated with 0.200 M Fe^{3+} solution.

- (v) Write down the Nerst equation that describes the voltage of the $\text{Sn}^{4+}/\text{Sn}^{2+}$ redox pair relative to the SCE.
- (vi) Write down the Nerst equation that describes the voltage of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox pair relative to the SCE.
- (vii) What is the relationship between these two equations?
- (viii) Calculate the voltage of the system relative to the SCE when
- 5 mL of Fe^{3+} solution is added.
 - 30 mL of Fe^{3+} solution is added.
- (ix) Calculate the concentration of all species at the equivalence point. State any assumptions you have made.
- (x) What is the potential at equivalence point relative to the SCE?

Question 4 (45 minutes)

- (a) A particular drug decomposes by first order kinetics, with an activation energy of 80kJ mol^{-1} . The expiry date for a preparation containing the drug is given as 1 year away from purchase if it is refrigerated at 5°C . If the product is accidentally stored for one month at room temperature (25°C), what should the new expiry date be?

Data for (b): $0^\circ\text{C} = 273.15\text{K}$

$1\text{ atm} = 101.3\text{ kPa}$

$$\text{Clausius-Clapeyron equation: } \ln\left(\frac{p_2^{\text{vap}}}{p_1^{\text{vap}}}\right) = -\frac{\Delta_{\text{vap}}H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta_{\text{vap}}H^\circ(\text{C}_2\text{H}_5\text{OH}) = 39.3\text{kJ mol}^{-1}$$

$$\Delta_{\text{vap}}H^\circ(\text{H}_2\text{O}) = 40.7\text{kJ mol}^{-1}$$

Atomic mass: H (1.008) C (12.01) O (16.00)

- (b) Alcoholic beverages are created when yeasts produce ethanol from glucose in aqueous solution, in the absence of oxygen. The ethanol kills the yeast at about 15 mass percent and to increase alcohol concentration the mixture must be distilled. Although water and ethanol do not always behave as an ideal mixture, under these conditions Raoult's Law can be assumed to apply.

At 20°C the vapour pressure of water = 2.67kPa and that of ethanol = 6.66kPa .

- (i) If our starting solution boils at 99.5°C and 1 atm, what is the mass percentage of ethanol? (Assume the mixture contains only ethanol and water).
- (ii) What is the mass composition of the first drop of liquid distilled over?

Data for (c): Heat capacities can be assumed constant over the range of conditions considered.

$$\overline{C}_p(\text{ice}) = 76.1\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\overline{C}_p(\text{liquid water}) = 37.15\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_{\text{fus}}H^\circ(\text{H}_2\text{O}) = 6.01\text{ kJ mol}^{-1}$$

$$\Delta S = n\overline{C}_p \ln(T_2/T_1) \text{ for constant pressure processes}$$

- (c) Consider 28.5g of supercooled (liquid) water at -12.0°C and 1.00 bar. This metastable state suddenly freezes to ice at the same temperature and pressure. **Hint:** Find a three step pathway.
- (i) Treat the metastable state as an equilibrium state and calculate the heat released in this process.
- (ii) What is the change in entropy of the system?
- (iii) What is the change in entropy of the surroundings? Determine the total entropy change of the universe in the process and show that the answer is consistent with the second law of thermodynamics. Take the surroundings to be at -12.0°C .

Organic Section (45 minutes)

Question 5 (15 minutes)

Draw **and name** all products formed when 1-methylcyclohexene is treated with the following reagents. Pay particular attention to the stereochemical and regiochemical consequences of each reaction. Where more than one stereoisomer is possible, name only one and indicate clearly which structure you have named.

- (a) Ozone, followed by Zn/DMS
- (b) Hot concentrated KMnO_4
- (c) Cold dilute KMnO_4
- (d) Br_2 in H_2O

Question 6 (10 minutes)

Explain using resonance structures (Whelan intermediates) why bromination of benzoic acid gives predominately meta-bromobenzoic acid and little of the ortho or para isomers. You may consider Br^+ to be the attacking electrophile.

Question 7 (10 minutes)

Draw the products, and the mechanism for each reaction when (a) butanone and (b) ethyl ethanoate are reduced with the Grignard reagent phenyl magnesium bromide. In (b), explain why the reduction of ethyl ethanoate proceeds via a different mechanism.

Question 8 (10 minutes)

Red blood cells contain the globular (water soluble) protein haemoglobin which is used to transport oxygen about the body.

- (a) Where would you expect to find the largest proportion of hydrophobic and hydrophilic amino acids in the native structure (i.e. as found in the body) of haemoglobin? Explain briefly why haemoglobin adopts its native 3D structure with these properties?

Sickle-cell anaemia is a disease caused by a single amino acid residue in haemoglobin being mutated (changed), resulting in a misfolding of haemoglobin. The residue in question, located on the surface of the haemoglobin structure, is a glutamic acid ($-\text{CH}_2\text{CH}_2\text{COOH}$ sidechain) in normal haemoglobin, whereas in mutated "S"-haemoglobin it is changed to a valine (isopropyl sidechain).

- (b) Explain using your answer to (a) how this mutation may cause haemoglobin to misfold.