



RIO TINTO AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL EXAMINATION — PART B

1999

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 candidates

- (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) You must attempt **all** 5 questions. All questions are of equal value.
- (4) Appropriate data can be found 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 **each page** of your examination booklet.
- (8) Use **only black** or **blue pen** for your written answers, **pencil or other coloured pens are not acceptable**.

Question 1

Note: Data for this question can be found at the end of the question.

- a) The acidity of a water sample is influenced by gas absorption. The most important gas, in this respect, is generally carbon dioxide.
 - (i) Give a set of three reaction equations which demonstrate the effect of atmospheric CO_2 upon water acidity.
 - (ii) Arrange the following gas mixtures in order of their tendency for CO_2 (g) to dissolve in aqueous solution (percentages given are mole %):
 - (A) 90% Ar, 10% CO_2
 - (B) 80% Ar, 10% CO_2 , 10% NH_3
 - (C) 80% Ar, 10% CO_2 , 10% Cl_2

Write equations for any chemical reactions occurring in the aqueous phase on exposure to these gas mixtures.

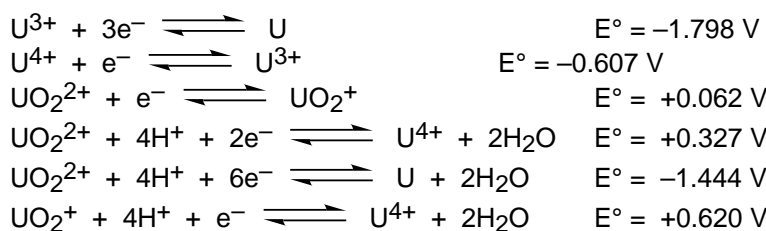
(iii) Arrange the following aqueous systems in order of their ability to dissolve CO_2 . Assume that, prior to exposure to 10% CO_2 in Ar, they have been allowed to equilibrate with air:

- (A) distilled water
- (B) 1 M HCl solution
- (C) 1 mM sodium acetate solution

(iv) Assuming an atmospheric content of 350 ppm CO_2 (by volume), and assuming that equilibration has been reached between gaseous and aqueous CO_2 , calculate the pH of a raindrop at atmospheric pressure.

(v) Calculate the pH of a bottle of carbonated water ($P_{\text{CO}_2(\text{g})} = 1 \text{ atm}$)

b) The following half-reactions relate to the speciation of uranium in aqueous solutions:



(i) Assign oxidation states to the various uranium-containing species appearing in the above half-equations.

(ii) By analysis of the above half-reactions, determine the ultimate chemical fate of a small piece of solid uranium placed in contact with a 1 molar solution of a strong, monoprotic acid HX, and in the presence of 1 atm of hydrogen, all at 298 K. Provide balanced reactions and electrode potentials for all reactions. It can be assumed that the conjugate base X^- does not react perceptibly with uranium or with its compounds.

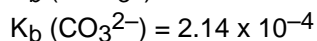
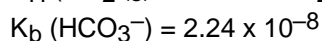
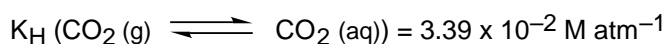
(iii) What is the most stable uranium-containing species at pH = 6.0 (and otherwise standard conditions)?

(iv) Determine the pH range, for acidic or neutral solutions, under which a 1 molar solution of UO_2^+ would be stable:

(A) under otherwise standard conditions (ie. $P_{\text{H}_2} = 1.0 \text{ atm}$); concentrations of other uranium-containing species = 1.0 M)

(B) with $P_{\text{H}_2} = 1.0 \times 10^{-6} \text{ atm}$, and with conditions otherwise standard.

DATA: (all at 298K)



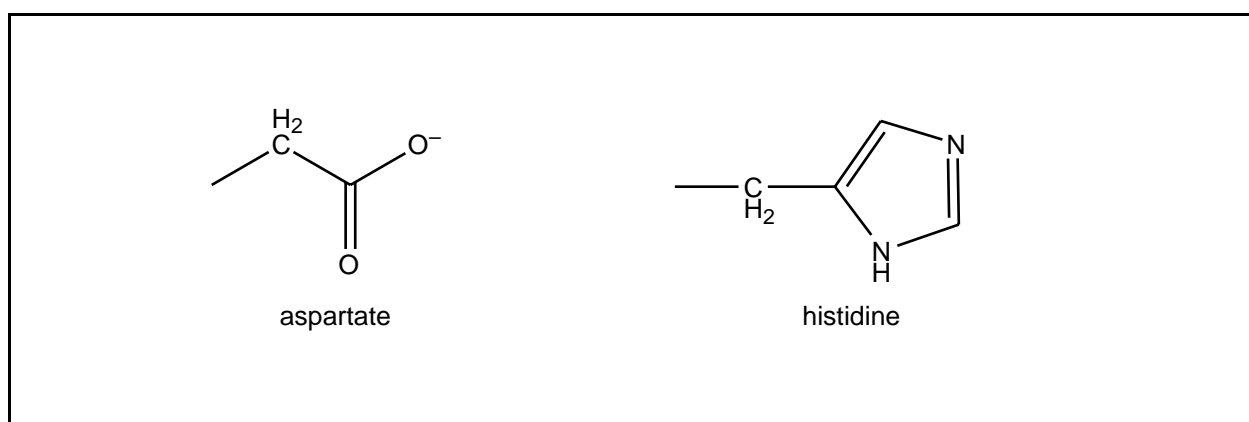
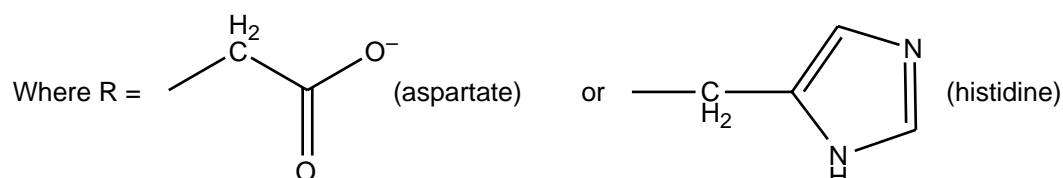
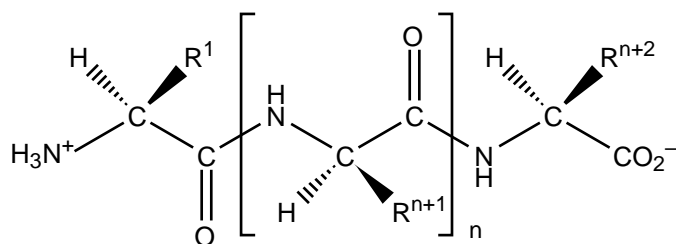
Question 2

Urease is a nickel-containing enzyme that catalyses the hydrolysis of urea (H_2NCONH_2) to ammonium ion and carbamate ion (H_2NCOO^-). The carbamate ion is subsequently hydrolysed further in a spontaneous process that is not catalysed by urease.

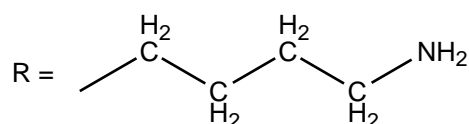
a) Write the equation for the hydrolysis reaction of carbamate ion.

b) Each protein subunit of the urease tertiary structure contains two nickel(II) ions. These metal ions are coordinated to relevant donor atoms on the side chains of amino acids of the protein

primary structure. Given the structural formulas for a generalised protein chain and the side chains of aspartate and histidine, circle potential donor atoms in each of the two side chains.



- c) The two nickel(II) centres of urease are also linked by a bridging carboxylate group and a bridging water molecule. The bridging carboxylate group belongs to a lysine chain that has been modified into a carbamate derivative. Given the structural formula of the lysine side chain,



draw the structural formula for the lysine side chain **carbamate** derivative.

- d) Write the electronic configuration of the nickel(II) ion.
- e) A number of coordination geometries are known for nickel(II) complexes. In octahedral coordination geometry the d orbitals are distributed between two energy levels. Indicate which of the five d orbitals in octahedral geometry occupy the higher and lower energy levels, respectively. Give a qualitative explanation for your answer based on a comparison of the d orbital spatial distributions.
- f) Certain nickel(II) complexes also display square planar coordination geometry, which is the dominant geometry of complexes of the palladium(II) and platinum(II) metal ions. Draw the two isomers of square planar [Ni(SCH₂CH₂NH₂)₂] and label each isomer as *cis* or *trans*. How many stereoisomers would you expect for a tetrahedral complex containing the same ligand set? Explain.
- g) Draw all geometrical isomers of square planar [Pt BrCl(NH₃)(C₆H₅N)].
- h) How many stereoisomers would you expect for the complex ions



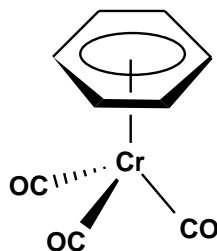
Sketch them. How many stereoisomers would you expect for tetrahedral complexes containing the same ligand set? Explain.

Question 3

This question has two parts, Theoretical chemistry and Thermodynamics, both parts are of equal value.

a) Theoretical chemistry

- (i) Benzene has a delocalised π -system of 6 electrons. Using the linear combination of atomic orbitals (LCAO) approach on the 6 carbon 2p orbitals, draw the three lowest-energy π -system molecular orbitals (MOs). Be careful to indicate all important information about the MOs (e.g. symmetry, nodes, etc.) (**Hint:** some degeneracy exists) Rationalise the order of the energies of these MOs.
- (ii) Draw and label the valence atomic orbitals of chromium being careful to indicate all useful information (e.g. phase, relative orientation, etc.)
- (iii) Hexacarbonylchromium(0) reacts with benzene to form a chromium complex of formula $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ whose structure is indicated below. This structure has 3 planes of symmetry. Indicate which of the AOs of chromium and bonding MOs of benzene can be mixed in the LCAO approach to form MOs. (**Hint:** ignore the carbonyl ligands, and number your orbitals in your answers to a) and b) to help you answer this part)

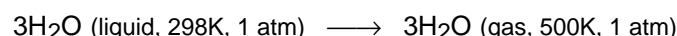


b) Thermodynamics

- (i) If the internal energy of a system would change as a result of a process, is the magnitude and sign of that change an indicator that the process is spontaneous? Why/why not?
- (ii) Define the infinitesimal entropy change associated with a reversible process at a temperature T (an equation is sufficient). Simplify the previous expression if the process occurred at constant pressure. Write the equivalent expression for a finite entropy change where no phase transition occurs.

Hint:
$$\int_{x_1}^{x_2} dx/x = \ln(x_2 / x_1)$$

- (iii) Calculate ΔS for the process



if the molar enthalpy of vaporisation is $\Delta H_m^0 = +40.58 \text{ kJ mol}^{-1}$ at 373K and the molar heat capacities of liquid and gaseous H_2O at 1 atm are 75.3 and 33.9 $\text{kJ K}^{-1} \text{ mol}^{-1}$, respectively.

- (iv) Armchair scientists sometimes dispute the Second Law of Thermodynamics by asserting that biologically-important chemical systems are in very low-entropy states, being assemblies of tens of thousands of atoms that are organised to be able to interact in ways whose emergent properties are those we identify as life. Life has spontaneously occurred on Earth and always features these low-entropy chemical assemblies, which is an apparent contradiction of the Second Law. State the Second Law and argue for or against the above perspective.

Question 4

Cane sugar is one of the most pure foods available, however as soon as it is dissolved in water it begins to hydrolyse. This disaccharide undergoes acid catalysed cleavage into its component simple sugars; glucose and fructose. A convenient way of measuring the degree of hydrolysis is to monitor the change in optical activity of the solution. A solution of pure sucrose will rotate the plane of polarised light to the right, whereas an equi-molar solution of glucose and fructose will rotate the polarised light towards the left. The amount of rotation depends on concentration and the optical path length for a particular sugar. Thus using monochromatic light from a sodium lamp (at 20°C) a 1g mL⁻¹ solution of sucrose in a 10 cm long cuvette will rotate plane polarised light +66.53°. Similarly, glucose will rotate the plane by +52.7° and fructose by -92.4°.

- a) The hydrolysis was followed at 25°C and the following changes in the plane of the polarised light recorded as a function of time.

t / min	0	10	20	40	80	180	300	∞
Rotation / °	6.60	6.17	5.79	5.00	3.71	1.40	-0.24	-1.98

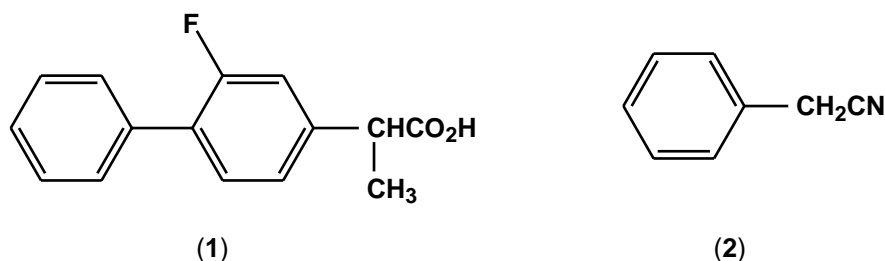
Determine the overall order of the reaction and estimate the rate constant.

Data: Universal gas constant = 8.314 J K⁻¹ mol⁻¹. Ignore the temperature effect on the rotation of plane polarised light.

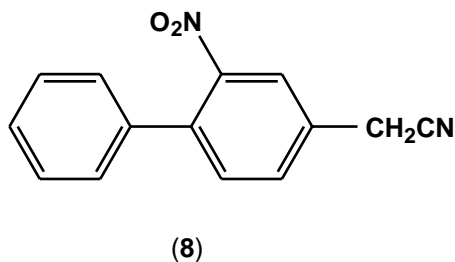
- b) In 0.1M HCl the rate is doubled by increasing the temperature from 25°C to 30°C. Calculate the activation energy of hydrolysis.

Question 5

Benzofluoroprofen (**1**) is a potent anti-inflammatory drug which can be synthesised in a series of steps from the nitrile (**2**).



Nitration of (**2**) with a mixture of nitric acid and sulfuric acids affords two isomers, the major product (**3**) being taken into the synthesis further. Reduction of (**3**) with iron and aqueous ammonium chloride yields (**4**) C₈H₈N₂ which reacts with acetic anhydride (ethanoic anhydride) to afford (**5**) C₁₀H₁₀N₂O. Further nitration of (**5**) yields (**6**) which undergoes acid catalysed hydrolysis to afford (**7**) C₈H₇N₃O₂. Diazotization of (**7**) under aprotic conditions followed by copper catalysed addition to benzene affords (**8**), the structure of which is shown below.



- a) Deduce the structures (**3**) to (**7**).
- b) Provide mechanism for the conversion of (**2**) to (**3**).

- c) Reaction of (8) with Zn in the presence of acid affords (9) which when diazotised in the presence of tetrafluoroboric acid (HBF_4) affords a salt (10) $\text{C}_{14}\text{H}_{10}\text{N}_3\text{BF}_4$. On heating this salt affords a single organic product (11) together with nitrogen and boron trifluoride. Controlled reaction of (11) with CH_3Br and base yields (12) which upon saponification (basic hydrolysis) followed by neutralisation affords (1).

Identify the remaining structures (7) to (12).

- e) How many optical isomers of (1) are possible and what are their structures?