CARIBBEAN EXAMINATIONS COUNCIL

REPORT ON CANDIDATES' WORK IN THE CARIBBEAN ADVANCED PROFICIENCY EXAMINATION

MAY/JUNE 2004

CHEMISTRY

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GENERAL COMMENTS

UNIT 1

Candidates again demonstrated a weakness in the comprehension of the Organic Chemistry theory and the application in mechanistic questions. The performance of the candidates in Module 2 was below satisfactory.

Many candidates experienced difficulty in constructing both molecular and ionic equations.

UNIT 2

The candidates demonstrated knowledge of the syllabus objectives in this unit. However, candidates' performance reflected inattention to descriptive details and a weakness in explaining underlying principles and concepts.

INTERNAL ASSESSMENT

The overall level of performance in the internal assessment was satisfactory. However, there are several recurring problems that require urgent attention.

A. <u>Projects</u> (Analysis and Interpretation)

This component was poorly done. Teachers are again reminded that the candidates are required to carry out individual analysis of the data acquired and not be given credit for simply regurgitating aspects of the literature review.

Examples of points for consideration in the analysis and interpretation section of the project are

- limitations of the application(s)
- historical, social and economic impact
- expected outcomes.

B. Laboratory Practicals

Teachers are reminded that the Planning and Design (P&D) assignments should be structured so as to pose the students with a problem from which a hypothesis can be developed. The hypothesis will then form the basis for the design of the chemical investigation to solve the problem.

P&D problems continued to be too simple or vague in their structure. In addition, mark schemes were inappropriate. In some instances, candidates were not given credit for feasible designs because the mark scheme was too rigid. In other instances mark schemes did not adequately assess the skills required for P&D.

Teachers are also reminded that each skill, for example, Manipulation and Measurement (M/M) or Observation, Recording and Reporting (ORR) must be assessed twice to avoid placing the candidates at a disadvantage.

All mark schemes used to assess the skills per module must be submitted. The absence of appropriate mark schemes was especially noted in practical assignments involving qualitative analysis of unknown compounds. General schemes for marking ORR and AI in such practical assessments proved inadequate for moderation. It is essential that all unknowns be identified in the mark schemes provided.

DETAILED COMMENTS

UNIT 1

PAPER 01

Question 1

Candidates were expected to demonstrate their understanding of the underlying principles of dynamic chemical equilibrium.

Most candidates were able to give a partial explanation of the term ‘dynamic equilibrium’. However, candidates were unsure of the requirement of a closed system. Many candidates stated that a closed vessel or container was a requirement.

Another common error made was the inclusion of the $NH_4Cl(s)$ in the expression for the equilibrium constant.

Question 2

This question required candidates to use the kinetic model to explain the properties of the liquid state. In addition, the properties of an ideal gas had to be applied in a calculation.

Generally, performance on this question was satisfactory. However, candidates demonstrated some difficulty in clearly describing the nature of the liquid state in terms of the strength of the intermolecular forces and energies of particles.

The calculation posed little difficulty in terms of manipulation of the appropriate mathematical expression. However, too many candidates omitted to convert the given temperatures to the Kelvin scale.

Many candidates were unable to deduce that the balloon would burst as the gas expanded under reduced pressure.

Question 3

The application of the concepts of reduction and oxidation formed the basis of this question. Candidates were required to **explicitly** explain redox in terms of the reaction between sodium and bromine.

Surprisingly, the performance on this question was below the acceptable standard for advanced proficiency. Many candidates simply stated that sodium was oxidized and bromine was reduced without subsequently explaining the changes that actually occurred, for example, sodium lost one electron and was oxidized while bromine gained one electron and was reduced **OR** sodium showed an increase in oxidation number from 0 to +1 and was oxidized while bromine showed a decrease in oxidation number from 0 to –1 and was reduced.

Many candidates were unsure of the direction of electron transfer and some thought that the reaction was initiated by the ionic species of the elements.

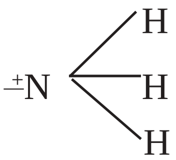
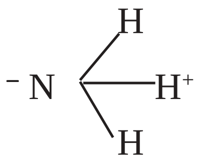
Some difficulty was encountered by candidates in writing the equation for the reaction between zinc and nitric acid. Many candidates were unable to explain the difference in the reactions of the acids with zinc in terms of the oxidizing power of the nitrate (V) ion.

Question 4

This question focused on the dipolar nature of amino acids and their acidic and basic character.

The performance on this question was generally unsatisfactory. Candidates demonstrated deficiencies in a number of areas including inability to draw an accurate displayed formula of the zwitterion, including the correct assignment of charges.

Common errors were

- writing  as  or $^-NH_3^+$ instead of placing the positive charge on the nitrogen

- lack of knowledge of the properties of amino acids in terms of the consequences of ionic bonding between zwitterions

- lack of knowledge of the response of the acidic and basic functional groups to change in pH. Many candidates ignored using the zwitterionic form of the amino acid in the reactions

Candidates had difficulty in identifying the functional groups of the amino acid. Some did not know the difference between the CARBONYL and CARBOXYL GROUPS.

A few candidates also identified the amine group as the amide group.

Question 5

Candidates were required to demonstrate their knowledge and understanding of addition and condensation polymerization.

The performance on this question was generally good. Most candidates were able to score 5-8 marks out of the total of 10. The area of greatest difficulty in this question was the drawing of the repeat unit of nylon 6,6 or nylon 6.

Also, the determination of the structure of the monomer from the given repeat unit in Part (c) proved challenging to some candidates.

Candidates did not write the displayed formula to show the bonding between the O-H and tended to write it as OH. Candidates need to be reminded that in the displayed formula all bonds must be shown.

Question 6

This question required candidates to demonstrate their understanding of the relationship between structural features of amines and amides and their basic character.

This question was poorly done. Candidates were unable to relate the pK_b to the basic strength of the species given and were therefore unable to identify the strongest base as that with the lowest pK_b value.

Candidates were also unable to relate the pK_b values to the structures of phenylamine, ethylamine and ethanamide and several misconceptions were brought forward including

- the alkyl group as electron withdrawing
- the benzene ring as electron releasing.

They failed to realize that the lone pair on the nitrogen becomes unavailable for accepting a proton due to the presence of the carbonyl group in ethanamide and the phenyl group in phenylamine.

Question 7

This question required candidates to show their knowledge of the electromagnetic spectrum and the transitions occurring on absorption of specific wavelengths of radiation by molecules.

Most candidates scored in the range of 0-5 marks out of the total of 10 for this question.

Knowledge of the radiation sequence in the electromagnetic spectrum and the relationship between wavelength and frequency /energy was notably lacking.

Many candidates were unable to account for the curves in the ultraviolet and visible spectra in Part (b)(i), in terms of the absorption that occurs over a band of wavelengths.

Most candidates were unaware of the contribution of vibrational modes to the absorption spectrum in (b)(ii).

Many candidates were unable to clearly explain molecular excitation in terms of electron promotion from a molecular orbital of lower energy to one of higher energy. Few candidates demonstrated knowledge of electron promotion occurring between bonding and antibonding molecular orbitals.

Question 8

Knowledge and understanding of the application of Atomic Absorption Spectroscopy (AAS) in quantitative analysis were required in this question.

Performance in this question was satisfactory. However, weaknesses were noted in knowledge of the theory underlying the application of AAS. Identification of potential sources of error proved to be challenging for some candidates. Many candidates were unaware of the direct relationship between detection limit and the standard deviation.

Candidates require practice in the use of calibration curves.

Question 9

This question dealt with the application of thin layer chromatography.

The performance on this question was very variable.

The advantages of thin layer chromatography over paper chromatography were not well known.

Many candidates showed little knowledge of two-dimensional chromatography as required in Part (d).

UNIT 1

PAPER 02

Question 1

Candidates were required to apply their knowledge of titrimetric analysis in this question.

Performance here was generally good.

Candidates, however, displayed difficulty in completing the equation using the formula H_2X for the acid. Many candidates gave the formula of the salt as NaX.

Surprisingly, a few candidates suggested the use of a measuring cylinder as appropriate for the quantitative measurement of the wine.

It is recommended that students be given adequate practice in this area of analysis and the use of proper techniques.

Question 2

This question tested the candidates' knowledge of the acidity of phenols, alcohols and carboxylic acids.

Performance on this question was unexpectedly below standard. The use of pKa as an indicator of relative acidity proved difficult for most candidates.

In many instances, appropriate observations were not given for the reaction between the organic acids and sodium carbonate. A common error was the use of inferences instead of observations.

The test for carbon dioxide was not known by some candidates and therefore reagents such as lime juice, soda lime water, calcium carbonate, soda lime were given. A few candidates wrote the formula for calcium hydroxide as CaOH.

In addition, candidates persisted to describe the result of the test for carbon dioxide with lime water as a 'milky' or 'cloudy' precipitate. It must be stressed that this is not acceptable. Furthermore, the use of 'no reaction' for an observation is also not an acceptable response. Candidates should have stated explicitly that no effervescence would have been observed for both reactions with phenol and ethanol.

The responses to this question reflected a poor foundation in structure-activity relationships for the organic compounds.

Question 3

The application of solvent extraction as a separation technique was the focus of this question.

All aspects of this question proved challenging to the candidates.

Noted deficiencies included:

- Lack of knowledge of the use of solvent extraction in the separation of organic compounds

- Limited comprehension of the process of separation involving the reaction between the organic acid and the sodium carbonate and the subsequent dissolving of the product in the aqueous layer

- Limited knowledge of the use of anhydrous sodium sulphate as an agent to remove water and the use of inorganic solvents to remove inorganic residues from organic solutions

It is recommended that students be given adequate practice in the separation techniques taught in Module 3.

Question 4

This question tested the candidates' knowledge and understanding of the concepts of chemical energetics and proved to be unpopular. Performance, however, was generally satisfactory.

Some errors were made in the definitions for enthalpy and enthalpy change. Most candidates were unaware of the need for constant pressure as a required condition in the definitions.

In addition, candidates were unsure of the solution to the calculation which involved the application of Hess's Law. See Appendix 1 for solution.

Question 5

This popular question dealt with periodicity of ionization energy and required candidates to demonstrate proficiency in writing electron configurations.

Most candidates did fairly well on this question. However, a few errors were noted:

- Candidates also had difficulty writing the electronic configuration given the atomic number. Many candidates were unable to determine the correct electronic configuration of the ion formed as they did not realize that the elecctrons would be lost from the 4s orbital instead of the 3d.
- Candidates were often unable to explain the periodic anomalies due to the presence of the electron entering a new sub level for Aluminium and the stability of a half-filled sub level for Phosphorus relative to the repulsion caused by the pairing in the sub level of Sulphur.
- Candidates must be reminded of using an appropriate scale when plotting graphs which should see the graph occupying more than half of the page and be convenient for plotting of points.
- Many candidates had difficulty in explaining the shape of the graph. Some were able to identify the three different energy levels but were unable to explain the pattern with respect to the increase in the effective nuclear charge as each electron was removed.

Question 6

This question expected candidates to demonstrate their knowledge of the reactions of organic functional groups and the results of successive treatment with specific arrangements.

Candidates lost marks readily in this question when asked to give equations for specific functional group conversions. In some instances, knowledge of the functional group conversion was demonstrated but the chemical change of the reagent was unknown. For example, the treatment of the given organic molecule, vanillin, with Fehling's reagent was correctly identified to cause oxidation of the aldehyde functional group but the conversion of copper ions to copper(I) oxide was unknown by many. Many candidates thought that copper(II) oxide was the inorganic product.

This was a common error for all the equations required and, in addition, knowledge of the details of the reactions was limited.

Candidates also found it challenging to focus on the reactions of the individual functional groups and seemed confused by the complexity of the vanillin structure as presented. The structure of the 2,4-dinitrophenylhydrazone product of the reaction between vanillin and 2,4-dinitrophenylhydrazine was correctly illustrated by few candidates.

Candidates continue to display severe weaknesses in the reactions and mechanisms of organic functional groups. Teachers are advised to ensure that students are given adequate practice in writing organic reactions and mechanisms for consolidation of the concepts involved.

<u>Question 7</u>

This question proved to be challenging to the candidates and was answered by few. Knowledge and understanding of the unimolecualr and bimolecular mechanisms of the nucleophilic substitution reactions of the halogenoalkanes were tested.

Again, this was a weak area for most candidates. In Part(a), candidates demonstrated knowledge of the details of the SN1 and SN2 mechanisms but were unable to provide an appropriate structure for the corresponding halogenoalkane.

Part(b) challenged the candidates, as an appreciation of the stereochemistry of the mechanisms was required. Little knowledge of the inversion of stereochemistry associated with the SN2 mechanism was demonstrated. In many instances the use of the mechanistic arrows was incorrect.

These features of organic reaction mechanisms need to be reinforced. Candidates must recognize that mechanistic arrows always flow from the site of the electron pair to the electron deficient site being attacked.

<u>Question 8</u>

The principles of gravimetric analysis formed the basis of this question. Generally, candidates experienced difficulty with this question.

Most candidates were unaware of the principles of gravimetric analysis.

Surprisingly, in Part (b), writing the equation for the reaction between free chloride and silver nitrate proved to be difficult for some candidates. In many instances, marks were lost for the absence of state symbols or the use of incorrect state symbols. The subsequent calculation of the mass of chloride present in the analyte sample was poorly done. See Appendix 2 for solution.

This performance suggests that students need reinforcement in the underlying principles of gravimetry as a quantitative method of analysis.

<u>Question 9</u>

This question tested the knowledge and understanding of titrimetric and AAS methods of analysis. Performance was satisfactory. Most candidates were knowledgeable on the requirements of a primary standard. However, some common errors were noted. These included:

- Inability to identify titrimetric operations that would impact on accuracy or precision

- Incorrect plotting and drawing of the calibration curve

- Taking incorrect readings from the graph

- Giving readings taken from the graph to too few or too many decimal places

- Incorrect calculation of the standard deviation

- Inappropriate use of the rules for assigning significant figures

It is recommended that students be given more practice in the statistical analysis of quantitative data.

UNIT 2

PAPER 01

<u>Question 1</u>

The focus of this question was acid/base equilibria. The candidates' performance was quite satisfactory.

A common error, however, was the recognition that the dilute NaOH solution would not be a strong alkali and hence the titration would actually be more of a weak acid / weak base titration where no indicator would adequately signal the equivalence point.

Question 2

Candidates were expected to demonstrate their knowledge and understanding of the principles of buffer systems.

Performance was satisfactory but candidates still demonstrate a weakness in manipulation of the acid equilibrium expression to calculate the pH of the buffer system. See Appendix 3 for solution.

Question 3

This question tested candidates' knowledge and understanding of standard electrode potential and standard cell potential.

This question was fairly well done.

Candidates were able to correctly define the standard electrode potential but many candidates omitted the conditions of 25^{o}C and 1 atmosphere.

Teachers are reminded that candidates need to practice calculations involving standard electrode potentials.

Question 4

This question examined the trends and properties of Group II compounds including the carbonates, sulphates and oxides.

This question was done fairly well.

Few candidates, for Part (c), did not know the formula for quicklime (CaO) and therefore could not get the equation for the reaction with water. Some did not recognize the reaction with water to be exothermic and wrote that the quicklime reacted with the boat to start fires.

Question 5

In this question candidates were expected to show their knowledge of the qualitative tests for iron(II), iron(III), chloride and bromide ions.
Candidates were quite familiar with the results of the test for iron (II) and iron(III) with NaOH and also the test for the halides with $AgNO_3$. However, some candidates were unable to write the equation for the reaction of the silver chloride with NH_3(aq).

Question 6

This question dealt with the chemistry of the halogens including oxidizing power and reaction with $AgNO_3$. Candidates were, however, expected to apply their knowledge of standard electrode potentials.

Most candidates were able to predict the oxidizing power of the halogens down the group.

In Part (b) (i), candidates misinterpreted the required response and therefore gave descriptions of the product for the reactions as observations and did not identify the reactions as displacement or oxidation/reduction reactions.

Quite a few candidates wrote incorrect statements such as 'the bromide ion displaced iodine' instead of bromine displacing iodide ions.

In (b)(ii), few candidates were able to write the balanced equation for the reaction between the bromide ion and chlorine and hence calculate E_{cell} for the reaction.

Question 7

Knowledge of the natural recycling of carbon was required for this question.

The performance was generally good.

The term 'sinks', however, seemed unfamiliar to some candidates and led to incorrect responses. The concepts of negative and positive feedback also proved challenging to many candidates.

Question 8

The industrial synthesis of ammonia formed the basis of this question and most candidates performed well.

Question 9

Candidates were tested on their understanding of the concepts of reduce, reuse and recycle in environmental management.

Performance was satisfactory.

UNIT 2

PAPER 02

Question 1

The candidates' understanding of the theory of reaction kinetics was examined in this question.

The overall performance on this question was not satisfactory. Some of the candidates wrote the rate equation as k = [A] instead of rate = k[A].

The mechanism for the reaction was poorly done. Candidates seem unfamiliar with writing mechanism for a reaction and where mechanisms were given the rate determining step was not identified.

Question 2

This question again proved challenging. Candidates failed to apply the underlying chemistry of complex formation, ligand displacement and stability constants in Part(a), to explain the reaction between CO and haemoglobin. The competitive nature of CO as a ligand in comparison to O_2 especially at low O_2 concentration and hence its higher stability constant was recognized by only a few candidates.

Most candidates were, however, aware that the inhalation of CO could lead to oxygen starvation and eventually death.

Some candidates were unable to write the equation for the reaction between Cu^{2+} ions and NH_3(aq).

Question 3

Part (a) of this question required knowledge of the natural recycling of nitrogen in the environment. Part(b) involved the application of spectrophotometry in the quantitative estimation of nitrate(V).

This question was also poorly done. Common deficiencies were:

- Limited knowledge of the chemistry of the nitrogen cycle
- The reaction of NO_2 and H_2O was not well known
- Incorrect interpolation from the graph

Question 4

This question required candidates to apply the concepts of chemical equilibrium to the formation of precipitates. Calculation of k_{sp} and the explanation of the common ion effect were also components of the question.

This was not a popular question but some of the candidates who attempted it did fairly well.

Most candidates were able to write the expression for the K_{sp} of AgCl. However, some included the AgCl(s) in the expression.

Few candidates were able to say how they would have calculated the $[OH^-]$ and hence the K_{sp} value for $Ca(OH)_2$. The stoichiometry of the reaction was also ignored in the expression.

Some candidates were able to recognize the introduction of a common ion. However, they were then unable to explain the observation in terms of the equilibrium shifting to favour the formation of a precipitate.

Question 5

This question dealt with the conditions under which the dynamic equilibrium between N_2O_4 and NO_2 exists and the macroscopic properties of the system.

Candidates confused equilibrium position with rate of reaction. For Parts (c) (i)and (iii) candidates did not mention observations. Instead, they stated that more of NO_2 or more of N_2O_4 were produced.

Few candidates wrote K_c in terms of partial pressures, failing to realize that concentration should be used.

Question 6

Knowledge of the periodicity of the Period 3 oxides and chlorides was examined in this question.

This question was the favourite in this section but also showed some weaknesses.

- Candidates did not mention all of the oxidation states and instead wrote ranges. Some even wrote negative oxidation states for Cl and P not realizing that oxygen, being higher in electronegativity, would give those elements positive oxi dation states.

- Candidates found it difficult to relate the acid/base behaviour of the oxides to their structure and bonding. Few candidates incorrectly wrote metallic bond ing for ionic oxides. Although some mentioned the type of bond, they did not refer to the structure. Some candidates also referred to the metal Al being amphoteric instead of the oxide.

<u>Question 7</u>

The chemistry of the Group IV elements, as required in this question, also proved challenging to the candidates.

Most candidates failed in (b)(ii) to relate the electronegativity of silicon and chlorine to the polar nature of the Si-Cl bond. Instead they made reference to chlorine being able to attract the water molecule to itself.

<u>Question 8</u>

The industrial extraction of aluminium and the properties of the metal were the fundamentals of Question 8.

This question was the favourite from this section. Surprisingly, candidates did not score marks easily for this familiar process. They lost marks readily for being vague in their responses and inattention to the details of the process. In addition:

- Labelling of the diagram was unsatisfactory.
- Few of the candidates gave the correct anode equation.

<u>Question 9</u>

The limited knowledge of the petroleum and petrochemical industries and their environmental impact and regulation, as demonstrated by the candidates, was again troubling. These objectives are clearly stated in the syllabus, yet the percentage of candidates showing unfamiliarity with the material was too high.

- Candidates could identify the fractional distillation process, however, they were unable to explain how the process works.

- Four benefits of petroleum refining could not be identified by many candidates

- Candidates did not show awareness of the environmental problems associated with the industries.

- Many candidates did not know what was meant by the term ‘photochemical’ in relation to the formation of smog. They commonly omitted to mention the presence of sunlight/UV light being a necessary condition. Candidates also did not realize that in peak hour traffic there would be maximum photochemical activity.