

Report on Part 1A Inorganic Chemistry 2004

This was the first setting of the Part 1A paper and it was designed to be straightforward and adhered closely to the format already defined in a sample paper distributed in October 2003. The standard achieved by the students was pleasingly high, with an overall average of 65%, with marks on individual questions ranging from 100% to 5%. Virtually every candidate attempted 5 questions as required. There were signs that students avoided questions that were of a relatively new format and there was also the familiar tendency to pass over the more descriptive chemistry. Overall a pleasing outcome to this new examination.

Question 1 – Miscellaneous topics

The format here was familiar from past General II papers, and proved very popular, being attempted by 131 candidates (Max 20, min 1, mean 14). The vast majority were able to identify a correct molecular point group and to use group theory to deduce the number of IR active S-O stretches for SO_2 . The part on identifying the electron configuration of element 113 attracted few takers, but was fairly well done.

Question 2 – Transition metal chemistry

Another very popular question (125 takers, max 20, min 4, mean 13) which produced good answers on the whole. It was clear that the majority of the School had a firm grasp of the basics of ligand field theory. The number of students unable to assign the correct dimeric structure to $[\text{Cr}_2(\text{acetate})_4]$ was perhaps surprising in view of their having made it in the second year practicals.

Question 3 – Organometallic chemistry

This was attempted by far fewer students (45 takers, max 20, min 1, mean 11) probably due to the presence of a 'route map' question in the second part. Most candidates were able to deduce the structure of the alkyl complex and migratory insertion product but struggled with the sigma and pi bonded allyl complexes. The interpretation of the spectroscopic data was generally disappointing and too many just produced a structure without further rationale.

Question 4 – X-ray diffraction

Again this question followed a format used in Part 1 examinations and this familiarity attracted a large uptake. (115 takers, Max 20, min 2, mean 11). The majority of the candidates were well versed in the indexing of powder diffraction patterns and were able to cope well with the first four parts. Very few derived the correct U-O distance and even less made sensible comments about radius ratio rules or changes in radius with oxidation state in the final parts.

Question 5 – Molecular orbital theory

This format of question was new this year and perhaps due to the signposting in the sample paper proved to be the fifth most popular question (Takers 115, max 20, min 2, mean 15) and was well done by virtually all who attempted it.

Question 6 – Coordination chemistry

This question was based entirely on material in the lecture course but attracted very few answers. (Takers 21, max 15, min 1, mean 7), possibly as the format was somewhat different to that used for comparable material in Part 1. The rather poor marks suggested that this question was generally selected by the weaker candidates. The examples in the last part were drawn solely from the lecture course but only one or two candidates got anywhere close to the right answers.

Question 7 – Non-metal chemistry

This predominantly descriptive chemistry question was one of the less popular choices (Takers 69, max 19, min 4, mean 13). Nevertheless it was generally well answered and the majority proved capable of identifying most of the compounds A through G. There were a couple of near perfect answers, but many lost marks by not matching the given data to their proposed structures.

Question 8 – Lanthanide and actinide chemistry

The question style here again reverted to a style used in previous Part 1 papers and was second equal in terms of popularity (Takers 125, max 20, min 2, mean 14). Most have clearly prepared this topic well and produced some excellent answers, 12 achieving 19 or 20 out of 20.

JRD

8th October 2004

Part 1A, Organic Chemistry June 2004

This was the first year of the new Part IA examination, and the paper was set at a level intermediate between a Prelims paper, and the old General Organic I examination. The overall standard was extremely high, with an average of 66% and maximum and minimum marks of 98 and 33% respectively, most likely the result of a relatively easy paper, questions set largely on lecture material, and a very well prepared school, who only had past Part I papers as a guide for revision. All but one of the candidates completed all 5 questions, and all of these questions were done to a high standard; significantly, most candidates did what the question required, giving essay/descriptive type answers, mechanisms or explanations as asked for. A conscious effort was made to include one question from each Second year lecture series, as well as some First year material.

1. Reactive Intermediates (Answers: 133; Max mark: 20; min mark: 3; average: 14)

A popular easy starter question, on the whole very well done, especially Part C; however, a surprising number were unable to use SOCl_2 correctly. Ionic mechanisms involving carbocation intermediates with loss of nitrogen at the end of the reaction were popular alternatives in carbene reactions.

2. Heteroatom Chemistry (Answers: 113; Max mark: 19; min mark: 4; average: 12)

A very well handled question, with some excellent answers for Part C. There is clearly a good level of understanding of P, Si, S, and B chemistry in the School.

3. Aromatic Chemistry (Answers: 81; Max mark: 19; min mark: 2; average: 14)

Another very well handled question, drawn from the corresponding lecture course. Many answers for Part C(b), although correctly identifying a thermodynamic equilibration leading to the all-meta substituted product, did not provide a mechanism.

4. Conformational Chemistry (Answers: 133; Max mark: 20; min mark: 3; average: 13)

A very popular question, although non-specific "steric effects" or "transannular interactions" were frequently used to explain just about any phenomenon. Oddly, a number of candidates used methanol as a reagent in Part B(b) and ended up in a difficult tangle.

5. Umpolung Chemistry (Answers: 14; Max mark: 20; min mark: 3; average: 13)

This question was taken from the corresponding lecture course, and produced some excellent answers.

6. Polymer Chemistry (Answers: 30; Max mark: 19; min mark: 6; average: 13)

This straightforward question was also taken from the corresponding lecture course, and produced some excellent answers, although the alternative routes required in Part B(d)

generated some highly unconventional solutions, while simple alternatives tended to be ignored.

7. Spectroscopy (Answers: 136; Max mark: 20; min mark: 4; average: 14)

This question was very popular, although because it was based principally on chemical shift phenomena, required excellent recall of the appropriate data to be correctly done. It was clear that there is an excellent understanding of IR and ^{13}C phenomena, used in Part B(b).

8. Carbonyl and Heterocyclic Chemistry (Answers: 104; Max mark: 20; min mark: 2; average: 13)

This question was in part revision from First Year, and also included some Second Year material. The Fischer Indole Synthesis was frequently particularly very well done. There were, however, the expected problems with acetal formation.

MGM
July2004

Examiners Report, Physical Chemistry 1A 2004

The paper was set in a similar fashion to the Sample Paper, with choice within each question. The vast majority of candidates attempted five questions, with only a handful doing four (or six), and all felt able to stay until the end of the examination. Five questions were markedly more popular than three. The average mark, 69%, was higher than in the other two Part 1A papers, and may reflect the fact that candidates were given a wide choice. The standard deviation, 17% was also higher, partially because of the very low marks gained by a handful of candidates. A general comment is that mathematical derivations and manipulations were answered better than descriptive accounts of chemical phenomena. Interestingly the second year courses which are sometimes perceived as “hard” (Quantum Mechanics and Statistical Mechanics) gave rise to the two most popular questions.

1. **Thermodynamics.** 124 answers. Min: 4; Max: 20; Mean 17.

Straightforward and popular with a pleasing number of excellent answers. (b) was much more popular than (c). The most frequent mistakes were: sign errors in calculating $\Delta_r H$ and $\Delta_r S$ in (a)(iii); failure to convert kJ mol^{-1} to J mol^{-1} ; missing or incorrect stoichiometric coefficients in (c)(ii); Δ_r missing from $\Delta_r C_p$ in (b)(i). The final part of the question, (c)(ii) caused the greatest problems: many failed to realise that $x(\text{NO}) = 2x(\text{N}_2\text{O}_4)$ and that the three mole fractions must sum to unity.

2. **Liquids and solutions.** 35 answers. Min: 1; Max: 19; Mean 12.

A small number of attempts, with part (b) more popular than part (a) by a factor of about 2. Several people plotted a graph (with two points) for (a)(i). Many had little idea about either the θ -temperature or the number of monomer units that constitute a random flight segment, but picked up marks with often faultless answers to the quantitative parts of (a). In part (b)(i), many did not mention non-ideality or give the relation between activity, activity coefficient and concentration. Few mentioned ionic atmospheres in (b)(iv): entropic and solvation effects were frequently held to be responsible; a few discussed kinetic salt effects. A truly depressing number misinterpreted the notation $10^4 \text{S/mol dm}^{-3}$ and ended up with solubility products of $\sim 10^9$ for the sparingly soluble salt.

3. **Spectroscopy.** 122 answers Min:3; Max: 20; Mean 14.

A popular and generally well-answered question, with parts (a) and (b) being most popular. In (a)(i), not many candidates recognised that B_0 or B_1 were related to *average* bond lengths or more specifically to $\langle 1/r^2 \rangle_v$. In (a) (ii) several people calculated *differences* of transition frequencies rather than *absolute* frequencies. In part (b) the derivation was well known, but many muddled up D_e and D_0 . In part (c) very few could write a clear description of the Raman effect in terms of inelastic scattering of a photon. In (c)(ii) everybody seemed to know this had something to do with Raman being described as two-photon process, but not many explained the one-photon selection rule. In (iii) most candidates guessed that the spacings were $2B$ or $4B$ but had difficulty in giving or deriving formulae to show this.

4. **Quantum Mechanics:** 131 answers Min 3; Max 20; Mean 14.

It was very pleasing to see that this was the most popular question and there were many excellent answers. Common mistakes in part (a) were to include the normalization

constant with the eigenvalue in (i) and to fail to take the complex conjugate (i.e., to use ψ^2 rather than $\psi^*\psi$) in (ii) – despite the very obvious hint. Not many candidates stated that the probability density was independent of angle. In (a) (iv) rather few people clearly stated that the wavefunctions represented *equal magnitude* of the angular momentum, even when recognising that they had opposite direction, and few noted the important point that the coefficients in the summed wavefunction were *equal*, leading to the zero expectation value. Some candidates thought that the wavefunction represented *two* particles. Parts (b) and (c) were of roughly equal popularity. It was surprising how many people knew the ranges of the quantum numbers but failed to work out the correct number of combinations of l and m for $n = 4$. Part (c) was very well answered on the whole with some very good accounts of spin correlation.

5. **Valence:** 122 answers Min 2; Max 20; Mean 14.

Parts (a) and (c) were overwhelmingly popular compared to (b). The diatomic MO diagram was well known. More candidates should have used group theory to derive the term symbols rather than producing badly explained orbital diagrams. There were some dubious explanations of the + and – symbols for the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ terms; apparently the same configuration $\pi_x\pi_y$ gives a – sign for one term and + sign for the other....Part (b) was not very well answered, perhaps reflecting the fact that students are overall not so good at explaining concepts and writing short essay style answers in physical chemistry. Many wrote about LCAO rather than the orbital approximation and thus scored 0 marks for that part. The standard Huckel theory problem in part (c) was tackled successfully by almost all candidates attempting it.

6. **Statistical Thermodynamics:** 128 answers, Min 2; Max 20; Mean 13

Most answered Part (a), and the marks divided amongst the excellent (the majority) and a very poor minority getting less than 5 marks, and who really had no idea of the topic. The mathematical manipulations were generally done very well, although some tried to differentiate the Boltzmann distribution with respect to temperature in order to find the most probable value of J . Few mentioned the approximation of the distribution as a continuous function: many thought the approximation to a clearly stated rigid rotor case was the neglect of centrifugal distortion. A common statement about the shape of the rotational population curve was that this form was expected from the Maxwell Boltzmann distribution.

Part (b) was less well done, with the most common mistake being the neglect of the degeneracy in the bending motion. Manipulations of the numbers brought the not unexpected set of errors in converting cm^{-1} into energies with the use of the wrong value of c .

7. **Kinetics** 65 answers, Min 2; Max 20; Mean 12.

Kinetics lectures (and, presumably, tutorials) were given in Trinity term of the second year, and this may be the reason for the lower than expected number of answers. Part (a) was twice as popular as either (b) or (c), and the marks distributions were very similar. Although in part (a) there were many excellent answers, a number simply stopped after deriving zeroth and first order kinetics. In part (b) many wasted time in part (i) by deriving a complete isotopically dependent ratio for the rate constants. The calculation of the vibrational frequency for D_2 caused problems – some got it larger than that given for H_2 . Part (c) was straightforward, but again the calculation, this time of activation energies, got a fair number struggling with the manipulation of exponentials.

8. **Miscellaneous.** 16 answers. Min: 3; Max: 18; Mean 10.

An unpopular and generally poorly answered question, this seemed in many cases to be a refuge for the desperate. (b) and (e) had very few takers; the other bits were roughly equally popular. (a) Many candidates had no idea about band heads. Quite a number thought that the vibrational structure of electronic spectra is determined principally by anharmonicity. (b) No-one mentioned Boyle temperature or the virial equation. (c) Most were familiar with the selection rules for atomic spectroscopy. Not all discussed penetration/shielding effects for Na. (d) A variety of Nernst equations were proposed. Not all realised that the standard EMF of the cell is zero. (e) No-one knew that the molecular speeds are proportional to \sqrt{T} . (f) Most candidates recognized that this bit was about Raoult's and Henry's laws; not all discussed intermolecular forces.