Honour School of Natural Science

Chemistry Part I, Trinity Term 2004

Chairman's Report

1. Elementary data ('03 and '02 figures in parentheses)

Entry	174	(149, 164)
Withdrawals during the examination	3	(0, 0)
Candidates called for *viva voce* examination	0	(3, 2)
Results:		
Honours	168	(170, 162)
Pass	2	(0, 1)
Fail	1	(1, 1)
Numbers sitting individual Advanced papers:		
Inorganic	138	(108, 130)
Organic	109	(93, 97)
Physical	94	(95, 101)

No *viva voce* examinations were considered necessary. The candidate who failed had laboured under a substantial penalty for failure to complete the practical course.

2. Gibbs Prize

	S D Pritchard	(Hertford)	shared
	O M H Williams	(Oriel)	shared
proxime accessit	K B Ling	(New)	
book prizes	C Dyer-Smith	(Wadham)	
	A W Pilling	(Queen's)	

3. Marks

	I-1	I-2	O-1	O-2	P-1	P-2	I-A	O-A	P-A
minimum	17	29	16	14	31	26	29	15	32
maximum	87	91	99	100	98	97	95	97	100
mean	55	64	65	66	63	63	65	63	65
st.d.	16	13	17	20	13	15	12	19	14

The global average mark was 63.0, with a standard deviation (st.d.) of 13.1. This was a significant increase on the average mark of 61.25 (st.d. 15.25) awarded at Part I 2003 (and a further increase on preceding years). Happily, the average marks awarded for the advanced papers were in reasonable agreement, having a range of only 2.0 (and a mean of 64.3). No scaling of marks was carried out.

A histogram for the total mark distribution is appended.

The average total marks (8 papers) obtained by male and female candidates were:

Male (105): 511.9   Female (66): 491.5

– showing a *gender deficit* of 4.05 %, by no means an unusual figure but distinctly less than in the previous two years (7.8 and 8.1 %, respectively). The gender deficit for this year group at Prelims 2002, gauged in the same way, was 2.7 %. Its growth in the intervening two years is typical.

The *school deficit* (comparing state and private schools) was 5.2 % in favour of the state sector, as compared with −0.9 % for the same cohort at Prelims. But the general trend in the past has been variable.

4. Procedure

(a) *The written examinations*

As in recent years, the examinations were held in 6th (Thurs, Fri) and 7th (Mon, Tues, Wed) weeks. The question papers had the customary format.

All internal examiners invigilated throughout the sittings for the papers in their particular subject divisions.

(b) *Marking and examiners' meetings*

The internal examiners submitted their marks by Thursday of 8th week and the initial marks meeting was held on the Monday of 9th. There was unanimous agreement that no *vivas* were called for.

A final meeting was held on Tuesday of 9th week, and the lists signed and posted before lunchtime. (6 candidates had requested that their names be left of the published list.) Marks and rankings were sent to Colleges that afternoon in the usual way.

The External Examiners arrived on the Sunday in time to assess the (already marked) scripts of the weakest and strongest candidates. They had also the Monday afternoon to scrutinise more representative scripts of their choice.

(c) *Secondary marking*

All scripts were double-marked or checked by the internal examiners.

The External Examiners assessed some 10 – 15 % of the scripts *in toto* (third marking), but did not advise any but very minor changes in the marks awarded by the internals.

The examiners are again indebted to Mrs Nina Jupp for her adroit and indispensable help, showing as always great patience and good humour when under pressure.

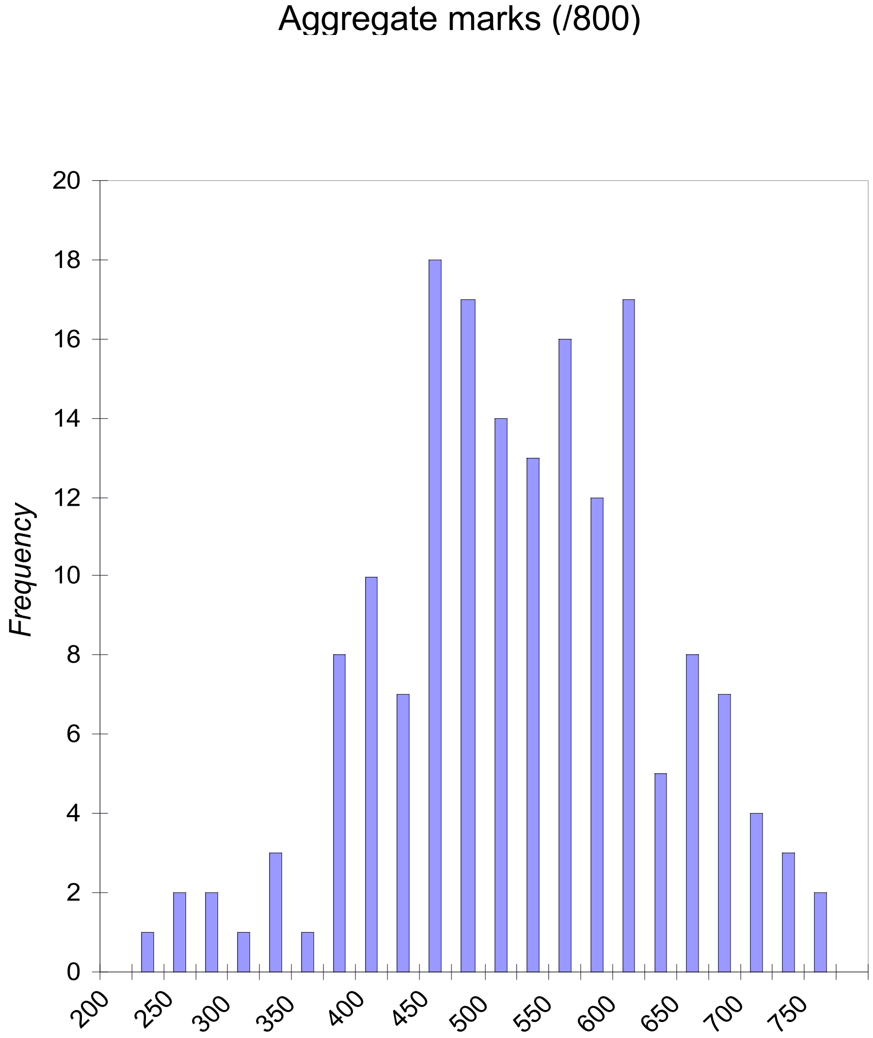
We should also recognise our debt to the staff of the Examination Schools for their efficient assistance, amiably rendered.

Finally, our thanks are also due to the external examiners – Profs. Ed Constable, Leo Salter and Jim Thomas – for their willingness to participate and for all their expert and frank contributions to the examination.

A F Orchard
Chairman

July 2004

Appendix



mean = 504 std = 105

Examiner's Report: General Inorganic Chemistry I 2004

A total of 173 candidates sat the paper

Highest Mark	**87**	**Lowest Mark**	**17**
Mean Mark	**55.0**	**Standard Deviation**	**15.6**

The table below gives a statistical breakdown of the marks.

Question	1	2	3	4	5	6	7	8
No. marked	84	131	171	47	147	107	31	141
Min. mark (/20)	3	1	2	1	1	1	1	0
Max. mark (/20)	19	20	20	20	18	20	18	20
Mean mark (/20) (mean % mark)	12 (60)	11 (55)	12 (60)	13 (65)	10 (50)	11 (55)	9 (45)	10 (50)
σ_(/20)	4	5	4	5	3	4	4	5

Q1 (Essay on comparison of elements)

Standard question. O vs S easily the most popular with some well rehearsed essays.

Q2 (Compounds of interest)

A popular question, although many candidates could write sensibly on two examples but very little on their other choices. There was certainly enough choice.

Q3 (Concepts)

The most popular question, attempted by all except two candidates. All concepts attracted answers, with 'hypervalence' being the least popular.

Q4 (Molecular orbitals)

Not very popular, and usually answered either extremely well or very badly. Many candidates gave little demonstration that they understood how to handle MO theory for simple symmetrical molecules.

Q5 Discussions of data

A very popular question; but few could answer four parts satisfactorily, hence the low average. Popularity: (c) >> (a) (d) > (b) >> (e). Most candidates could explain the principles of acid strength (c) and standard reduction potentials (a) and (d). Although the question on bond dissociation enthalpies (b) was attempted by many, no one offered any explanation for why bond dissociation enthalpies for $H_2E{=}EH_2$ may be lower than for $H_3E{-}EH_3$. Only a handful of candidates attempted the question on Ellingham diagrams.

Q6 *f*-block topics

Popularity (a) > (c) > (d) >> (b). Most candidates gave respectable answers to (a) and to a lesser extent (c). But few found much to write about coordination environments or nuclear synthesis. This again resulted in a low average mark.

Q7 Discussions of observations

By far the least popular question, with only SbF_5 attracting consistently good answers. Considering the likelihood of candidates preparing for a Q1 on N vs P, the answers presented on allotropes of P and N were poor, with little knowledge of the different forms adopted by P. One candidate confused *allotrope* with *isotope*.

Q8 Discussions of solid-state chemistry.

A popular question. Some very good discussions by those candidates attempting part (A), but candidates attempting (B) had difficulties in putting together three respectable answers. Thus while graphite intercalation (b) was generally well answered, there were surprisingly few good answers for AgI and TiO_2 and still fewer for zeolites or CuAu vs CsAu.

Fraser Armstrong
20th June 2004

Examiner's Report: General Inorganic Chemistry II 2004

A total of 173 candidates sat the paper

Highest Mark	**91**	**Lowest Mark**	**29**
Mean Mark	**64.1**	**Standard Deviation**	**13.0**

The table below gives a statistical breakdown of the marks.

Question	1	2	3	4	5	6	7	8
No. marked	170	17	61	44	166	134	143	125
Min. mark (/20)	3	10	1	1	5	1	2	1
Max. mark (/20)	20	19	20	17	19	19	20	20
Mean mark (/20) (mean % mark)	14.6 (73.1)	13.9 (69.4)	13.1 (65.4)	10.8 (54.2)	12.4 (61.9)	13.0 (65.1)	12.5 (62.3)	12.1 (60.4)
σ_(/20)	4	3	4	4	3	4	4	5

Q1 (symmetry, ν(CO), IR etc)

Very popular question. Popularity (a)>(d),(e)>(b),(c)
Part (a): $Os_3(CO)_{12}$ and $[Re_2Cl_8]^{2-}$ most popular. Question very well done and clearly familiar.
Part (b): Generally OK but no candidate realised that $[Ir(CO)_6]^{3+}$ has ν_CO) > free CO and very few recognised that the same applies for $[Hg(CO)_2]^{+}$.
Part (c): Again generally OK but the weaker candidates omitted to compare Δ_t and Δ_o on the same scale and some confused LFSE with LFSP.
Part (d): Clearly well prepared in general. Commonest error was in applying simple VSEPR methods (D_{3h} IF_3 for example instead of C_{2v}) and some candidates felt the need to do a full Γ_{xyz} analysis and then got a little lost. $[IF_2]^-$ was frequently worked out by inspection even though a bond stretch vector analysis is easily done.
Part (e): No systematic errors noted here. The majority of the school knew that NO can be either a 1e or 3e donor and chose wisely.

Q2 (Organometallic reaction sequences)

There were few takers for this question which should have been straightforward based on 2nd year lectures. Those who offered answers made light work of the problems given.

Q3 (bioinorganic and coordination chemistry)

Moderately popular. Popularity (c), (d) >> (a),(b)
Part (a): Well done where attempted with the Cu and Zn systems being the most frequently chosen topics. The FeS cluster exposed most lack of knowledge in this part.
Part (b): No candidate recognised 'D' as superoxide otherwise all OK.

Part (c): Generally well done and most candidates offered some sort of Irving-Williams / hard-soft composite explanation for the four ligands given.
Part (d): No significant weakness exposed in the answers for (i) with the chelate effect being fingered as the main culprit and statistical arguments advanced for dimishing *K*. Part (ii) drew scant insight from the school.

Q4 (chemistry of Pt)

Not very popular and typically very poorly handled by most of those who attempted it. Only compounds 'A', 'E', 'F' and 'G' tended to come close to being deduced, with astonishing transformations being proposed in some instances for the other products listed. This type of route-map/descriptive question continues to expose a lack of common chemical sense.

Q5 (spectroscopy and magnetism)

Popularity: (b) >> (e) > (c) > (a) > (d)
Almost universally popular. Part (b) on lanthanide magnetism was easily the most popular part within the question. Candidates universally found part (c) hard. Part (a) challenged them; most didn't realise that their skills in analysing d-d transitions with Orgel diagrams would have been better directed at part (d) (which sadly attracted only 10 answers!). Most thought that the bands with _ = 2000 were of "low intensity" and therefore attributed to "Laporte-forbidden d-d transitions". With identification of LMCT and MLCT not made the answers furnished were very difficult to sift for some credit to go to the more plausible statements. In (e) the main deficits were in identifying S_2F_4 and in a reluctance to venture explanations for the relative values of _/ppm.

Q6 (diffraction)

Pretty popular question. Generally straightforward, but with the usual errors and slips. In a few cases it was tackled last in a seeming final rush for a few extra marks, and some answered without seeming to know how to calculate d-spacings (strange to choose this question then!). Part (g) did its job in identifying the brightest and best, and in general answers to this part betrayed some very woolly thinking.

Q7 (Frost diagram and chemistry of Group 6)

A highly popular question. However, although most candidates could construct Frost diagrams (mostly the right way up) there were relatively few mature explanations of the trends in the aqueous chemistry of Cr, Mo, W revealed by the plots (e.g. trends in bond strengths, successive *IE*; ΔH_{atm}; ΔH_{solv}). Only a readjustment of the mark division between parts (a) and (b) avoided some embarassment. Many candidates were mislead into discussion of E^o values as function of pH in part (c) whereas a simple chromate/dichromate condensation explanation was sought. In part (d) a number of particularly creative candidates took "empirical formula" to imply that some cunning (often binuclear) structure other than the obvious C_{4v} $[Cl_4Cr{\equiv}N]^{2-}$ was expected.

Q8 (mechanisms)

Pretty popular question with parts **A** and **C** being the most populated and best answered (the main aspects of some of these questions being rather familiar from previous years perhaps). In Part **B** only one candidate recognised that the inverse dependence of k_{obs} on [PMe_3] was telling them something about the mechanism (and that it wasn't as simple as it looked at first sight). Some of the class would have activation energies for reductive elimination decreasing from Rh to Ir. Strangely, a handful of candidates thought that Δd in Part C refered to the ligand field splitting parameter…

To echo an examiner's report for General Inorganic Chemistry II from a previous year: overall, my impression was that we have some very clever students at the top end of the class, but that the tail is longer than it used to be. A lot of students appear to largely simply learn how to do past exam papers. Consequently, any question that resembles one from the recent past is well done, and any attempt to examine a particular topic in a new way, however straightforward, causes problems.

Philip Mountford
16th June 2004

General Organic Chemistry I 2004

There were 173 candidates who attained marks in the range 16-99%. The highest mark was 99% with 11 candidates scoring ≥ 90% with a mean mark of 64%. Five candidates attempted only 4 rather than 5 questions. The seven candidates who scored ≤ 30% showed no benefit from their 3 years of chemistry. The top 20 who scored ≥ 80% where excellent by anywhere's standard. The overall statistics are shown below:

Question No	1	2	3	4	5	6	7	8	Total
No. marked	85	157	19	118	144	64	169	104	173
Min mark	2	2	1	3	1	1	3	0	16
Max mark	20	20	17	20	20	20	20	20	99
Mean mark	13	13	10	12	12	13	15	13	64.3
St. deviation	4	4	5	4	5	5	3	5	17

Question 1: *Carbonyl Chemistry*: Not a very popular question although full of very standard carbonyl transformations. The Mannich reaction remains a mystery to many as do basic nitroalkane reactions.

Question 2: *Conformational Analysis*: Very popular question. Many candidates had trouble drawing cis-decalins and converting Fischer projections to 3D. Surprisingly, the majority of candidates did not seem to have come across phenonium ions.

Question 3: *Total Synthesis*: Least popular by far and least well answered question. Overall, Q.1, 3 and 6 show that the candidates are generally not very proficient at simple synthetic transformations.

Question 4: *Organometallic Chemistry*. Popular question with wide spectrum of quality of answers. Part A was either all correct or all wrong. Surprisingly, few knew the Reformatsky reaction and only a tiny number could attempt part D despite it occurring several times in the course.

Qustion 5*: Nitrogen Chemistry*: Third most popular question: Parts A and C were generally answered better than part B where the simple Vilsmeier reaction proved the most troublesome and few candidates understood the regioselectivity involved in the electrophilic additions.

Question 6: *Synthetic Methods*: The redox changes (step 5) were beyond most candidates whereas ester formations proved easy. Many candidates have trouble with acetal formation.

Question 7*: Radical Chemistry*: Most popular and best answered question with the most difficulty being found with the non-radical parts (polar addition of bromine and HBr to olefins).

Question 8: *NMR Spectroscopy*: Part A and B were well answered by many. The majority still do not understand diastereotopic protons or the temperature dependence of DMF. Part D was answered correctly or not attempted.

S.G. Davies

General Organic Chemistry II 2004

Of the 173 candidates, 19 scored 90% or higher and a further 26 scored between 80 and 89%; 20 candidates obtained less than 40%. The highest mark was 100% and the lowest 14%; the mean mark was 65.6% with a standard deviation of 19.7. Two candidates attempted only four questions; all others attempted five. The top quarter of the school displayed a mastery of a wide area of organic chemistry, with the best papers being outstanding. The bottom 10% of the school understand little chemistry and know less. Overall this is an impressive performance by Oxford undergraduates showing a good grip of both the facts and the ideas – a lot of students have clearly worked very hard and successfully. The statistics for the questions are:

Question no	1	2	3	4	5	6	7	8	TOTAL
No. marked	81	84	114	70	156	151	148	59	173
Min mark	1	3	1	3	3	1	1	3	14
Max mark	20	20	20	20	20	20	20	20	100
Mean mark	12	13	11	15	14	14	13	12	65.6
St. deviation	5	4	6	4	4	5	5	4	19.7

Question 1 **Sulfur Acids**.
Only a few candidates could make reasonable suggestion for the synthesis of simple sulfur compounds. The mechanistic aspects of the question were generally well handled with almost everyone knowing the Shapiro reaction.

Question 2 **Cyclopropanes and cyclobutanes**.
Generally good attempts at the synthetic part of the question. Almost all the answers chose between the Favorkii, acyloin and sulfur ylid problems – there was not a single successful attempt at the diazotransfer-Wolff rearrangement question

Question 3. **Nucleophilic and base initiated transformations**.
This question discriminated the abilities of candidates very well. While a number of good candidates could handle the aldol condensation in part (v), very few could see the tandem crossed Cannizarro reaction.

Question 4. **Protecting Groups**.
A well-answered question which presented few difficulties for candidates.

Question 5. **Pericyclic Reactions**.
The most popular question where most candidates displayed a high level of competence. The commonest error was to think that the dimethylhexadiene given in the question was the racemate rather than the *meso*-compound
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Question 6. **Polar Rearrangements**.
Many good answers – the commonest mistake was to involve nitrenes in the Schmidt reaction.

Question 7. **Phosphorus Chemistry**.
In Part A many candidates were not aware of the Appel reaction of an alcohol with triphenylphosphine and CBr4. The commonest error was to think that the diol in (iii) was the racemate rather than the *meso*-compound.

Question 8. **Aromatic Chemistry**.
This question was generally badly answered with the regiochemistry of nitration of aromatic acids presenting real difficulties for most candidates. Attempts at the synthesis of paracetamol and aspirin were generally poor. The mechanistic problems in part C were usually well-answered.
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EXAMINERS REPORT

GENERAL PHYSICAL CHEMISTRY I

Number of candidates: 172. Mean mark: 62.7%. S.D.: 13.2% .

It has for long been argued that our students in Oxford are good by national standards and that, although we freely admit to an often disappointing 'tail' of weaker candidates, those in the top third or so of the School are really rather impressive. The last time I examined Part I — two years ago — I echoed that view.

I cannot, however, repeat the sentiment at the end of this year,s Examination. The standard of candidates, including those not far from the top of the School, seems to me to have deteriorated markedly even in two years; it is certainly much lower than it was *eg* a decade or so ago. While each of us naturally has a different perspective on what Physical and Theoretical Chemistry may be, there is one thing on which there would be no dispute: our subject is quantitative, logical and deductive. It is precisely these characteristics that were in my eyes so vividly lacking in the answers produced by a significant fraction of this year's candidates. In many instances, an alarming number of students have no idea how to handle quantitative analysis of data, let alone cope with elementary algebra. Memory work, and rote regurgitation of facts, do not appear to cause particular difficulties; but deductive reasoning and coherent presentation of arguments were signally lacking in the 'typical' answer. I found this year's marking of examinations deeply dispiriting and can only hope that it was a passing aberration and not a foretaste of things to come.

Question l. Electrochemistry. Number of answers: 103. Mean: 9.8, max 19, min 3 .

A straightforward question, barely beyond Prelims level, in which a not inappreciable number of candidates were unable to deduce the cell reaction. Answers in general demonstrated a glaring inability to handle simple data analysis. Most candidates could not even figure out what to plot in part (c), and failed to appreciate that if $\ln(\gamma_{\pm}) \propto (m/m^{\circ})^{-}$, then a proportionality constant is involved. Only a few candidates were able to answer part (d); and none appreciated the significance of the negative second virial coefficient.

Question 2. Photochemistry. Number of answers: 132 . Mean: 12.4, max 20, min 3.

Quite popular, this question attracted some excellent answers (half a dozen or so scoring 19 or 20). Unfortunately, many of the weaker candidates just attempted parts (a) and (b). The former, straight bookwork, was done quite well by almost all candidates, although many thought that internal conversion referred to vibrational relaxation within the *same* electronic state. Part (c) evidently puzzled many candidates. Instead of the few lines of scaling expected, some candidates embarked on several pages of steady state calculations that failed to produce an answer. In part (d) too many candidates plotted I against t directly, forced a straight line through the curve, and were satisfied with the result. Of those who plotted the data logarithmically, quite a few forgot the times were in ns, and were content that their rate constant was a factor of 10^9 different from what many had anticipated in their comments in part (a). The final part, (e), offered relatively few difficulties for those who got that far.

Question 3. Statistical Mechanics. Number of answers: 104. Mean: 12.1, max 20, min 3.
Many answers to part (a) blithely ignored the difference between the internal energy and heat capacity; while the essential notion of characteristic temperature scales (θ_{rot} or θ_{vib}), required in part (b), appears to have eluded more than a few. In part (c) many candidates appeared to lack the notion of proof, while part (d) produced some physically absurd answers: students clearly need to be encouraged to check whether their answers make any sense. But a number of good answers were produced.

Question 4. Quantum mechanics. Number of answers 85: . Mean 13.4: , max 20, min 4.

A surprising number of candidates were unable to demonstrate that an eigenfunction of A is also an eigenfunction of A^2, and many made a mountain out of a molehill in dealing with the commutators of part (a). A significant number simply ignored the request to sketch the allowed eigenvalues in part (b), for reasons that were rarely clear; and part (c) defeated the majority of candidates. Overall, however, the question was answered reasonably competently by quite a few candidates, although very well by only a handful.

Qusetion 5. Liquid Kinetics. Number of answers 114: . Mean: 15.3, max 20, min 3.

Another quite popular question, which produced quite high marks, in part because of the high weighting given to part (a) — straight bookwork, well remembered by the majority of candidates. Part (b) required calculation of k_d, usually correctly done. However, candidates showed themselves worryingly unable to go on to substitute this value into the equation they had already derived and to solve for the required quantity. The section about viscosity at different temperature showed up both a lack of knowledge and an inability to apply what was known. One group of candidates thought the viscosity of a liquid would increase with increasing T. Others knew that η should decrease, but some of them assumed a $1/T$ dependence rather than an exponential. In either case, however, very few seemed able to find a way of using correctly their favoured form.

Question 6. Rotational and Vibrational Spectroscopy. Number of answers: 128. Mean: 13.1, max 20, min 2.

Most candidates were able to display a smattering of knowledge but very few gave completely secure answers to all parts. There were good answers to the calculation of rotational constants. There was great scope for confusion between different topics; for example, many people thought that residual motion at OK was associated with the Third Law of Thermodynamics.

Question 7. NMR. Number of answers: 101. Mean: 11.4, max 19, min 3.

A straightforward question on the proton NMR spectrum of ethanol. Although almost everyone gave the correct interpretation of the spectrum in acidic conditions, remarkably few gave explanations of the origin of the chemical shift and dipolar couplings. The remaining sections were well answered on the whole. Rather remarkably, everyone gave the correct definition of magnetically equivalent nuclei.

Question 8. Reaction Rates. Number of answers: 90. Mean: 13.1, max 20, min 3.

Only modestly popular, this question again drew some responses that gained very high marks, although the majority of answers were incomplete, muddled, or had calculational errors. The calculations of the time-dependent concentrations, for example, showed up an inability to manipulate numbers and functions in many candidates. Those who did get the correct numerical answers sometimes omitted an explanation of what they showed. Not all those who started the question answered part (b), but those who did try often did very well. There was tendency to guesswork, or not entirely rigorous thinking, in selection of the mechanism. In particular, the dependence of rate on [CO] was not considered explicitly in many cases. Calculation of the rate constant elicited a handful of very curious rate equations.

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EXAMINERS REPORT

GENERAL PHYSICAL CHEMISTRY II

Number of candidates: 172; mean mark: 63.0; standard deviation 15.3.

The general remarks made in connection with General Paper I apply with equal cogency to the present paper, and do not need repeating in detail. Although there were some clearly excellent answers to all questions, too often the candidates= recall was vague and muddled, and their powers of logic and reasoning apparently limited. It is clear that many candidates have great difficulty in applying even what they know to the solution of problems. An increasing worry is the inability of a sizeable proportion of the candidates to be able to carry through accurately relatively simple and straightforward arithmetical operations. This problem was compounded by the preference of many to use their calculators in floating-point mode, to quote answers with maybe 10 or 12 significant figures, but just two decimal places, and then to try to count by hand the power of ten with inevitable mistakes under examination pressure. In general, answers were often in error by many orders of magnitude. As usual, units were not quoted by far too many candidates. In a bizarre reversal of this fault, quite a few candidates spent what was evidently far too long working out dimensions and units from first principles, often ending up with inappropriate combinations of mass, length and time.

Question 1. Atomic spectroscopy
Attempted by 167 candidates. Mean mark 12.6, maximum 20, minimum 5.

A very popular question with disappointingly bad answers. Far too many people confused term values with transition wavenumbers. Very few people were even able to calculate the quantum defects. There was almost universal mis-spelling of principal (principle) and Rydberg (Rhydberg, Ryhdberg, Rydbergh, Y). Hardly anyone understood the cause of the isotope shift of ionisation energies (there were most incredible explanations including gravity and even weak nuclear forces!).

Question 2. Thermodynamics
Attempted by 147 candidates. Mean mark 12.8, maximum 20, minimum 2.

An entirely straightforward question that produced many dreadful answers. It was shocking to realise how few candidates, having chosen to answer this question, could demonstrate the basic knowledge of thermodynamics required in part (a). Nearly everyone managed to answer part (b), which required mere memory. Part (c) produced some bizarre answers: many candidates, having obtained the correct free energy change, were unable to exponentiate correctly to obtain the equilibrium constant. In part (d), the majority simply failed to appreciate the distinction between deriving the van't Hoff equation and stating it.

Question 3. Atmospheric Chemistry and Applied Kinetics
Attempted by 91 candidates. Mean mark 12.7, maximum 20, minimum 3.

Some candidates obviously chose this as a last-ditch question, but others gave some really excellent answers, (a) Rather too many candidates stated that O_2 photolysis was the source of O atoms (and thence O_3 and OH) in the *troposphere.* The source of OH was, in fact, quite poorly understood, with a good number of candidates citing the photolysis of H_2O, or the reaction of H_2O with NO or NO_2. (b) and (c) Several weird and wonderful schemes were devised for atmospheric oxidation (some of which appeared to convert CH_4 to CH_4!). Any that were remotely plausible chemically (if not thermochemically) attracted marks. (d) Was well done by a large number of those who attempted the question (and it was fortunate that a relatively high weighting of marks was given to the section). (e) The principle of obtaining the lifetime seemed to be generally appreciated, although rather too many candidates omitted to include the OH concentration in their calculations. Errors in numerical manipulation and in units produced a spread of atmospheric lifetimes for CH_4 ranging from nanoseconds to more than the lifetime of the universe. Fewer candidates seemed to understand how to translate the data provided into a rate of release of methane; again, those who had the correct method obtained numerical values that encompassed the grotesquely large or small as well as the correct values. As to the sources of methane, "cows breaking wind" (often expressed more earthily) seem to have impressed most candidates who answered; it is a moot point if the cows, or rice paddies, for that matter, are "natural".

Question 4. Valence
Attempted by 65 candidates. Mean mark 12.4, maximum 20, minimum 4.

This was a straightforward question on valence theory but was not very popular. Some of those that did tackle it found it difficult to solve the secular equations, producing pages of complicated algebra. The application to the electronic states of CO_2^+ was not in general very well tackled.

Question 5. Molecular Interactions
Attempted by 77 candidates. Mean mark 12.6, maximum 20, minimum 3.

A very simple question, addressed at the basics of particle–particle interactions, but a rather unpopular one. Despite marks being given for almost any answer that showed that the candidate had some knowledge, the mean mark was disappointingly low. (a) Most candidates sketched something of the correct shape, although a good number omitted to label the axes. Several avoided explaining what σ and ε might be; of those that did try, perhaps a majority thought that ε was the permittivity/dielectric constant "of free space" or "of the liquid between the atoms", while σ was variously the collision cross section (perhaps not so far off), the polarisability, the charge, the "shielding coefficient", and so on. (b) While there were some perfectly acceptable answers, too many candidates just wrote that one term was attractive and the other repulsive. Of those who did describe the "physical interactions", there were quite a few who suggested that the attractive force was a coulombic electron–nucleus interaction, while a handful referred to "gravitational forces".

(c) Only a couple of candidates knew the correct answer. Many omitted part (c) altogether, but those who did give an answer mostly thought that "because the repulsion tends to fall off exponentially" was an adequate response. (d) Most were able to get the correct answer, despite a good proportion believing that d/dr(1/r^{12}) = ✂12/r^{11} (and similarly for 1/r^6). (e) Only a very few seemed to remember what the Taylor(BMaclaurin) expansion is, but a few did the first part, which was intended to justify SHM and the use of a force constant, perfectly. Others started with the result for *U*(*r*), but got hopelessly lost on the way to deriving a value for *k*. (f) Quite apart from a general confusion between ω and ν (which was not penalised), a surprising number of ways were found to get the result wrong. 2, *n* and *h* appeared in a variety of places (or not at all) in the equations used, but perhaps the most recurrent error was the failure to square σ in the denominator of the equation for *k*.

Question 6. Polymers/Solution Thermodynamics
Attempted by 38 candidates. Mean mark 13.8, maximum 20, minimum 5.

An unpopular question, but easy, and generally quite well done by those who attempted it. (a) Surprisingly, it seemed to be part (a), and consequently part (b), that offered the greatest difficulty to the candidates who attempted the question. Many strange answers were given to why an average for *M* was required at all: there were references to "defects in the polymers", "some chains having one or two more or fewer units present than the average", and even discussion of how the radius of gyration affected colligative properties. Some rather peculiar formulations of M_n were given, (b) Without a proper definition of M_n, it was hard for candidates to attempt this part of the question. Many who tried the section had a vague idea of how to tackle it, and were given credit where possible. (c) Generally well done. A few candidates just tried to plot Π against *c,* but most gave the correct plot. The most common error was in taking *B* to be the slope of the Π/c *vs*. *c* plot, rather than (slope)/(intercept). (d) Any reasonable attempt at an explanation was given credit. Most people who had the values of *B* managed to get an answer for the temperature at which $B = 0$, although not all could have looked carefully at their values to see if they were reasonable.

Question 7. Statistical Mechanics
Attempted by 122 candidates. Mean mark 12.7, maximum 20, minimum 4.

A standard question on nuclear spin statistics – in D_2, although a number of candidates persisted in ignoring this fact and answered the question as if it concerned H_2. Parts (b) and (c) generated some feeble answers; some candidates appear to need instruction to the effect that repeating what is stated in a question does not constitute an answer. A strikingly small fraction of people were able to perform the simple sum required in the first part of (d). But a few good answers were produced.

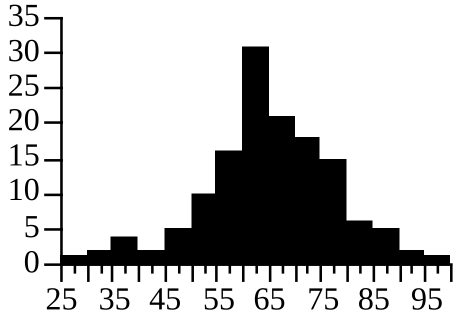
Question 8. Surfaces
Attempted by 146 candidates. Mean mark 13.2, maximum 20, minimum 3.

This was a hardy annual for which the majority of candidates were well prepared. There were reasonably sound derivations of the Langmuir isotherm. However, a depressingly large number of candidates were unable to re-arrange the isotherm so that it could be plotted as a straight line. A good knowledge of the experimental methods used to investigate the surface and the substrate was displayed.

RPW
21 June 2004

Examiner's Report, Advanced Inorganic Chemistry, 2004

No. of Candidates: **139**
Mean Mark: **64.6%**
Max. Mark: **95%**
Min. Mark: **29%**
St. Dev.: **12.6**



Overall impressions:
The most popular of the advanced papers and the marks suggest that inorganic chemistry is in good health at Oxford. The best answers to questions were extremely impressive, the average standard of answers was very good, but there were a few half-hearted attempts in evidence. Only two candidates didn't offer 3 questions, though there were some gaps in quite a few scripts. Clearly many candidates could have written much more than the time of 3 hours allowed. The one criticism I would make is that some evidently found it difficult to construct coherent written arguments – many might have scored more marks if they could have conveyed more effectively their understanding of the science!

Breakdown by Question:

Question	3	4	5	6	7	8	9	10	11	12	13	14
No. answers	3	45	11	56	45	17	6	61	82	63	18	8
Min.	22	6	15	2	7	5	19	7	11	10	5	10
Max.	27	33	31	30	32	34	33	32	32	32	30	28
Mean	24.3 73%	21.8 65.5%	22.6 68%	20.9 63%	22.1 66%	23.0 69%	25.0 75%	21.4 64%	21.8 65.5%	21.3 64%	20.2 60.5%	21.3 64%
St. Dev.	2.1	5.0	5.4	6.3	6.0	6.5	5.0	5.1	4.4	4.5	6.1	5.3

Qu. 1 (*Chemistry of a single element*)
No answers

Qu. 2 (*Comparative chemistry of pairs of elements)*
No answers

Qu. 3 (*Essays on miscellaneous topics*)
All 3 takers for this question wanted to demonstrate their knowledge of Xe chemistry, which they did successfully, and at great length, sometimes to the detriment of the other half of the question.

Qu. 4 (*Coordination chemistry*)
Popularity of the parts: (a) >> (c), (e) > (d) > (b)
(a) elicited a lot of generalised statements about the macrocyclic effect, some well-considered and others less so. Disappointingly few candidates really got to grips with the issues raised by the specific data provided. (b) and (e) attracted some fine answers with good recall of examples used in lectures, though many candidates didn't comment on how to sense that an anion had bound to a receptor. The significance of the 5-ring chelates to the size selectivity in (c) wasn't generally appreciated and 'hard/soft' raised an inappropriate head; surprisingly there were no comments on the identical gradients of

the correlations in the two data sets. Answers to part (d) were mostly poorly organised and betrayed confusion about the meaning of the data.

Qu. 5 (*Bioinorganic chemistry*)
The various parts were approximately equally popular. Most candidates for this question were well-drilled. This question was perhaps more focused than in previous years and it provided more focused responses from the candidates. The best answers came from (a) and (b). The more superficial accounts were most frequent in (c) and (d).

Qu. 6 (*Organometallic chemistry: structure & bonding*)
A and B equally popular. A few very poor answers detracted from the average mark, masking a good performance by the vast majority of candidates. In A, (a) and (b) were most popular, with well-organized and balanced essays for (a) especially. In (b) answers concentrated on transition metal Cp_2M systems, although bent metallocenes and pre- and post-transition metal compounds had been expected. (d) and to a lesser extent (c) attracted the weakest answers. In B, (a) was well anticipated, but more discussion of particular orbital interactions was merited. (b) was straightforward for most candidates but few remarked that the osmium compound must be η^6,η^4 (i.e. 18 VE) or noticed that $Ti(C_6H_6)_2$ is diamagnetic whereas $[V(C_6Me_3H_3)_2]^+$ is paramagnetic (both are d^4). Some answers failed to use the full d^n valence count for transition metal compounds (*e.g.* V(0) was d^3, Ti(0), d^2, and Fe(0) d^6) with all the unfortunate consequences this entails. (c) yielded generally inadequate answers – a discussion of how the two different ligands are activated was lacking. In (d) the relative electron-donating/ withdrawing effects of 6 x CO *vs* 2 x benzene on Cr(0) passed a number of the candidates by.

Qu. 7 (*Organometallic chemistry: reactions & mechanisms*)
Less popular than Qu. 6, but more consistently well answered. I more popular than II. (d) solicited some well-organized and often virtually perfect answers; (a) came a close second but there was a reluctance to explore life beyond metallocenes. There were some good answers for (c), and few answers for (d). In II, answers to (a) & (b) were disappointing, despite clear parallels with the more familiar Pd/Pt elimination/insertion reactions. (c) was more familiar to most candidates and for (d) most gave explanations for the relative stabilities of TiR_4 compounds. The "Cp_4Ti" system was clearly familiar to even the weaker candidates and was well done.

Qu. 8 (*Electronic & magnetic properties of solids*)
Option parts were answered in about equal proportion. There were some excellent answers, and candidates who answered this question tended to do well in the exam as a whole. The only notable issue that wasn't picked-up on in any of the answers was that the X-ray absorption edge spectra of $Ni_{1-x}Li_xO$ suggest that the holes may reside on O rather than, as more conventionally portrayed, Ni.

Qu. 9 (*Chemistry of solids: synthesis & properties*)
Not a popular question, but attracted some enthusiasts who provided outstanding answers. (a) was answered universally and often in more than enough detail. Surprisingly only two accounts of zeolite structures were solicited.

Qu. 10 (*Applications of NMR*)
Part A, popularity: (b) >>> (c) > (a)

In (b), neither fluxionality nor NMR time scale were generally well defined or explained. Can someone please convey the message (hopefully this is a good start?) that PF_5 is **NOT** a good example to use (its spectrum doesn't change with temperature, and although it is apparently "non-rigid", strictly speaking it is not "fluxional " – Cotton would be spinning if he had read some of the answers!).

Part B, popularity: (b) > (a) > (c) > (d)

In (b) few attempted to offer explanations of relative values of δ and J. Those that offered an opinion about the rigidity of Me_2PF_3 all thought it was caused by the steric bulk of Me – these barriers are electronic not steric! In (a) many thought that Pr^i_4NOH dealuminated natrolite – it is actually a template for forming Zeolite Y under typical conditions for hydrothermal zeolite synthesis. The best candidates worked-out that the ^{29}Si spectra related to different distributions of the same Si/Al ratio. Explanation of the spectra in (c) was elusive, but it should be a useful and challenging exercise for future tutorials!

Qu. 11 (*Crystal structures & diffraction*)

The most popular question – 79/82 for part B. In B, (a), (b) and (c) almost universally produced full marks. Candidates divided cleanly into those that quickly despatched the indexing, distance calculation and structure factor determination tasks and those that simply weren't up to the challenges. The majority couldn't spot the coordination environments and very few made much of the request for structural insights in parts (h) and (i).

Qu. 12 (*Applications of vibrational spectroscopy*)

Shock, horror – *not* the most popular question, as it has been in past years, indeed for as long as anyone can remember! Perhaps this is because the format of the problem section was relatively free-form compared to some previous questions? In A many candidates launched into their generalised essay on vibrational spectroscopy rather than focusing on the comparison and contrast of IR & Raman. In B, (a) was twice as popular as (b). In (a) many candidates failed to take note that the spectral area shown was exclusively the C–O *stretching* region, making life very complicated for themselves. Very few had much idea of how they might assign the bands due to a molecule with one of the CO's as ^{13}CO. Most would probably have done better with (b), where some candidates were able to produce plausible analyses that fit the spectral data on the basis of TeF_8^{2-} as a square prism (D_{4h}), although only one candidate posited (but didn't analyse) the correct geometry of a square antiprism (D_{4d}).

Qu. 13 (*Electronic absorption spectroscopy*)

The lowest average mark, reflecting blank spaces in many attempts. In (a) only a couple of candidates used an operator approach to the selection rules. In (b) several thought that B was magnetic field strength rather than a Racah parameter. Many didn't even attempt (d) and it confused most; only one candidate worked out which transition should be z-polarized.

Qu. 14 (*Photoelectron spectroscopy*)

(a), (b) and (c) were the most popular. There were no plausible MO diagrams for OsO_4. This question was tackled by some able candidates, but also by some who conjured-up orbitals and electrons at will in desperate attempts to produce MO diagrams that ultimately bore no resemblance to the number of bands in the PES spectrum! There was a popular movement suggesting that the PES spectra given might not be the best available, as implied by a frequent suggestion for further experiments using “high resolution PES spectroscopy”.

Favourite quote and a closing thought:
A candidate confirmed that his/her account of the preparation of a superconductor was correct thus, “I would choose this method …… because I have seen it work in the lab” – who said practicals aren’t useful?!

SJH 17th June 2004

Examiner's report – Advanced Organic Chemistry

All 109 candidates who sat the paper attempted three questions; the maximum mark was 97, the minimum 15, with a mean of 63 (s.d. 19). The paper followed the traditional pattern with specialist questions based on the third year lecture courses (9 questions), total synthesis (2 questions), and a general mechanistic problem. Predictably, most candidates answered one or more of the safe bets; Radicals and Pericyclics being by far the most popular with the honours for third place being almost evenly split between the Peptides and Transition Metal questions.

Question 1. **Free radical chemistry** (86 answers, min 7, max 32, mean 21)
No real surprises here; the most popular question. Most of the questions could have been answered solely on the basis of the lecture course in which polarity considerations are covered in some detail. Only a few of the better candidates commented on the anomalous usage of "nucleophilic" to describe certain organic free radicals. In general, the non-rider-specific marks were easily gained and most candidates were able to provide good examples of their own. Most of the riders were tackled reasonably but there were surprisingly many wrong answers to (f)—no marks were awarded for those in which a 1,5-H atom transfer was absent—and very few people understood the elements of polarity control in the brefeldin example, (g).

Question 2. **Bioorganic chemistry** (1 answer)
Most of the marks were gained on the basis of general bioorganic chemical knowledge rather than knowledge of the specific enzymes in question.

Question 3. **NMR** (7 answers, min 18, max 33, mean 26)
This ought to have been a popular question because almost half the marks were available simply on the basis of a very straightforward structure/spectrum matching exercise for which full marks were easily gained. As it was, those who dared to attempt this were rewarded with high marks and the mean was the highest for any of the questions. Part A was generally well answered; Part B less so although the four marks available for assigning resonance multiplicity to the carbon spectra confused some candidates who thought they'd missed the point (as it was so easy). Apart from one case, all those who attempted Part C successfully matched the amino acids with their corresponding spectra.

Question 4. **Catalysis** (6 answers, min 15, max 30, mean 19)
The definitions parts were well handled and most people were able to produce decent versions of accepted mechanisms for the now-classic cross-coupling processes. There needs to be some cross-checking between lecture courses to ensure that a consistent interpretation is presented of the terms "oxidative addition" and "reductive elimination". The riders were well handled although most answers to (iii) faltered after the Heck step, and there was really no satisfactory answer to rider (ii).

Question 5. **Mechanistic problems** (10 answers, min 3, max 25, mean 14)
Given that there were so many easy marks available on the rest of the paper, it was surprising to see even 10 answers to this question and a few candidates who attempted this really should have not. Part A was handled well, surprisingly so since no examples similar to these appear in the relevant lecture courses [with the possible exception of (a)]; even the [1,2]-silyl shift during nucleophilic attack of the allylic silane posed no

difficulties. Part B was not answered well and not a single correct answer to (a) was forthcoming (admittedly the nitrogen 'H' was missing); parts (b)–(f) [no (d), examiner's second mistake in this question] were all answered correctly by at least some of the candidates.

Question 6. **Total synthesis of cephalotaxine** (14 answers, min 4, max 27, mean 14)
Another generally poorly answered question and, again, one that was an inappropriate choice for some of the weakest candidates. Of the mechanistic parts in (a), the Reimer–Tiemann formylation seems to be well known, as does the Dakin reaction; the allylation/[2,3]-shift was usually spotted although few commented on the significance of this in controlling the regiochemistry of the allylation; no complete answer was forthcoming for step **G**. The reagents part (b) stimulated some creative (and lengthy) alternatives to the expected solutions and only step **C** usually gained the candidates most of the 7 available marks.

Question 7. **Organic materials** (9 answers, min 9, max 25, mean 18)
Most of the marks gained in this question were in the "suggest reagents/syntheses/mechanisms" sections with little evidence in the majority of answers of anything more than a superficial understanding of the compounds' behaviour as materials.

Question 8. **Peptide chemistry** (42 answers, min 10, max 30, mean 22)
A straightforward question with some very good answers but which also elicited some comments intended for the examiner. Thus, one candidate objected to the appearance of cyanogen bromide as a reagent on this question as "this was not covered in the lectures, which are supposed to be self-contained" or words to that effect; another objected to the use of the word "racemisation" in Part B, pointing out (wrongly) that this is an epimerisation. No one really got to the heart of the racemisation levels in the absence or presence of additives HOBt & HOCt (lead reference: *Tetrahedron,* **1998,** 14233).

Question 9. **Pericyclic chemistry** (75 answers, min 3, max 33, mean 22)
This, the second most popular question, was well-answered and there were 21 candidates scoring 28 or more. In Part A, only rider (f) was poorly answered, possibly because there is almost total reliance on the lecture course for examples and oxidopyrylium ylids are not specifically covered (although simple carbonyl ylids are). In Part B, part (c) was the least well answered but marks were given for either initial [4+6] or [4+2] (followed by [1,5]-alkyl shift) processes prior to extrusion of SO_2 and aromatisation. Orbital treatments of the ene reaction in B(d) were pleasingly good.

Question 10. **Total synthesis of quinine** (21 answers, min 10, max 28, mean 20)
This question produced pretty decent answers on the whole, the only sticking points being the stereochemical explanation in step **A**; forgetting to homologate the aldehyde in step **C**; suggesting a mechanism for the enolate oxidation step **G**. Everyone now knows the Swern (and, elsewhere, the Mitsunobu) reactions backwards; few are aware of the details of the Staudinger reaction (iminophosphorane reaction and aza-Wittig).

Question 11. **Transition metal chemistry** (40 answers, min 11, max 34, mean 23)
In terms of popularity, this gave Peptides a run for its money and was very well answered in the descriptive parts with a number of candidates achieving perfect marks over (a) and

(b). Marks were given in part (c)(iii) for any answers that showed that the candidate had spotted the use of TMS as a blocking group (provided the two positions—*ortho* to oxygen, or benzylic—were correctly chosen). About half of the candidates were aware of the spirocyclisation mechanism in part (e), the other half either chose to ignore the rate implications of the direct cyclisation or commented that maybe the exam paper contained an error.

Question 12. **Stereoselective synthesis** (16 answers, min 7, max 30, mean 21)
Few of the answers contained three conceptually different methods in part A(a), some simply providing three reagents for asymmetric reduction of a precursor α-keto-acid; some good answers were provided for the Sharpless kinetic resolution (including reasonable approximations of plausible catalytic assemblies). Part B produced a spread of acyclic stereocontrol models (Cornforth, Cram, Felkin–Anh) and all reasoned suggestions were rewarded; the Noyori reduction generated some essentially complete answers both in terms of mechanism and stereocontrol. Part C was well answered in (a)–(c) with full explanations of enolate stereochemistry, chelation, and facial selectivity; elements of stereocontrol in the Enders' example were not as well presented (e.g. fudged answers: wrong enolate stereochemistry and facial selectivity).

J Robertson
29-6-04

EXAMINERS REPORT
ADVANCED PHYSICAL CHEMISTRY

Number of candidates: 94 Mean mark: 64.9 Standard deviation: 13.8

This paper was the last of the “old-style” Advanced papers and contained the usual collection of predictable questions. There were some outstandingly good answers at the top end offset by some very weak ones at the bottom. Too often weaker candidates threw marks away by an inability to read the question carefully enough.

Question 1. Valence/Molecular Electronic Spectroscopy
Number of answers: 61. Mean 23.4, max 34, min 12.

A very straightforward question that, encouragingly, produced a significant number of good answers, particularly to parts (c–e). Parts (a) and (b) by contrast produced some very poor responses. Many candidates did not for example seem to know what an orbital is, leading them to produce endless irrelevant waffle; and there was widespread confusion between the orbital approximation and a linear combination of atomic orbitals. In part (b), while almost all candidates could draw the correct MO diagram for O_2, the general ability to discuss ‘features of note’ in it was disappointing.

Question 2. NMR
Number of answers: 20. Mean: 26.0, min 18, max 31.

This was a very straightforward question that was answered by surprisingly few candidates. Such answers as there were were of a very high standard. The discussion of the dipole–dipole interaction was too often restricted to the through-bond mechanism. The answers were sometimes spoiled by stating the answer baldly without justification or explanation.

Question 3. Ions in solution
Number of answers: 7. Mean mark 17.7, maximum 22, minimum 10.

This unpopular question produced six modest answers, and one rather poor one. Even part (a) produced some wrong definitions of ionic strength and poor explanations of the term in the denominator. Part (b) was tackled in essentially the correct manner in five cases, but no candidate completed the entire exercise without error. Part (c) was generally well done, but answers were marred by numerical slips. Part (d) was embarked on by some candidates in a reasonable way, but they either lost heart or ran out of time early on.

Question 4. Vibration–rotation spectroscopy
Number of answers: 40. Mean: 20.21, min 8, max 33.

This was a reasonably popular question although several candidates chose it as their third choice and produced incomplete answers. It was pleasing that the vast majority of answers recognised that only even J levels exist for CO_2 in its zero-point level. There were many numerical errors in the analysis of the three spectra and people were unsure of the method of combination differences. There was also a general failure to draw the appropriate energy level diagrams and to mark in the transitions.

Question 5. Electronic spectroscopy and group theory
Number of answers: 36. Mean: 20.7, min 12, max 33.

There were consistently good derivations of the irreducible representations of the vibrational modes of H_2CO. Knowledge of vibronically-induced transitions was rather patchy, however; all too often candidates relied on simple ideas from the theory of transition-metal complexes (Laporte rule, etc) with no mention of group theory at all. Only one candidate analysed the vibronic interaction in H_2CO properly and obtained the correct value for the out-of-plane vibrational frequency in the excited state.

Question 6. Thermodynamics.
Number of answers: 22. Mean 16.4, max 29, min 4.

A poorly answered question. In part (a) hardly anyone had the faintest idea about isotherms in the (P,V)-plane, which is odd given that the question was not compulsory. In the remaining parts of the question, the general level of competence in elementary algebra was parlous: most candidates seemed so bogged down in trivia that they failed to get the intended points — no one, for example, mentioned the law of corresponding states in part (b), few knew anything about intermolecular interactions in part (c) and nobody appreciated the physical significance of the divergent compressibility as the critical point is approached (in fact most failed to realise that $1/(t-1)$ diverges as $t \to 1$).

Question 7. Quantum Mechanics.
Number of answers: 11. Mean 21.2, max 29, min 8.

This question was something of a curate's egg. Parts (a), (b), (d) and (e) were quite well answered on the whole (albeit that some candidates appeared to think the hydrogen atom is 1-dimensional). The remaining parts of the question were by contrast poorly answered in general: for example, not a single candidate was able to obtain $E(Z)= Z^2 - 43Z/8$ in part (f), and part (g) even produced many answers that violated the variational principle. Not so long ago a question like this would have been devoured by our more theoretically inclined candidates.

Question 8. Interfacial kinetics
Number of answers: 6. Mean mark 17.8, maximum 26, minimum 14.

Another unpopular question, but answered sensibly, if not well, by those who attempted it. In part (a), candidates generally had a good idea of what η might be, but were stumped by j_0, and especially its physical meaning. The figure was explained reasonably well, although no candidate really got to grips with Region I and its linearity. Part (b) produced answers that were surprisingly incomplete or wrong in view of its request for a piece of straight bookwork. Candidates managed quite well with the plot required for Part (c), and several got the right, or nearly the right, answer for α; No-one, however, was able to get the right value of j_0 from the intercept, and some ridiculous values, of tens of amps, for example, were quoted. Part (d) seemed to be understood by the candidates, but only a couple made sensible progress; one candidate even got the correct answer!

Question 9. Statistical Mechanics.
Number of answers: 17. Mean 18.6, max 28, min 9.

A multi-component version of a standard statistical mechanics problem, answers to this question were on the whole unimpressive, albeit that there were a few good shots. Many candidates even made a meal out of parts (a) and (b), which were elementary demonstrations intended to get them off the ground. Part (c) was in general poorly answered, despite the 'intermediate results' given. Nobody was able to obtain correctly the $T = 0$ entropy in part (e), although one or two made sensible comments about the physical interpretation of the result.

Question 10. Atomic spectroscopy
Number of answers: 33. Mean: 23.21, min 7, max 34.

A straightforward question with some excellent answers at the top end. There was a great range of answers to the determination of the triplet states arising from the d^2 configuration. Full marks were given to those candidates who made use of the antisymmetric squares from the character tables. There was uniformly good knowledge of Hund's rules. There were also good attempts at the energy level diagrams in the presence of a magnetic field

Question 11. Theories of kinetics
Number of answers: 21. Mean mark 23.0, maximum 31, minimum 7.

This question attracted generally good answers, with some excellent ones balanced by some very poor ones. In part (a) a significant group of candidates stated merely that $E_a = E_c$, and did not recognise that the pre-exponential factor itself possesses a temperature dependence. Part (b) elicited the by-now familiar muddle in calculations and powers of ten. A good proportion of the candidates did, however, get the correct A-factor and value of P. The first section of Part (c) was generally dealt with efficiently, but the rest less convincingly: candidates seemed to have trouble converting from H to U. All manner of values were derived for the entropy, both positive and negative. Part (c) was generally tackled well. It was meant to be an extension to a standard bit of bookwork, but some candidates failed to recognise that the partition functions need to be raised to appropriate powers, while others attempted to work the whole thing out by calculating, for example, translational partition functions from the formula for each species.

Question 12. Molecular reaction dynamics
Number of answers: 8. Mean mark 15.9, maximum 21, minimum 11.

Attempted by only a few candidates, this question also produced a somewhat disappointing standard of answer. Things started badly in Part (a), since the candidates could hardly explain what a reaction cross section is, and often did not have a proper concept at all of the other quantities. Part (b) produced the best response, with almost everyone knowing what was going on. Just about any reasonable values for the collision radii of Cl and CH_4 were deemed acceptable. Part (c) generated greater difficulties! It is clear that all candidates had trouble with the A-level applied mathematics of section (v), although a couple were able to answer section (vi) in a qualitative way. Even those that did not get this far were nevertheless able to tackle section (viii), although not always obtaining the expected result.

JMB
20 June 2004