Q1

This question was answered well with many people scoring first class marks.

(a) (i) – Most students recognised that $[Te]^{6+}$ is an electron precise cluster and could suggest an appropriate bonding model. Those that lost marks suggested bonding models that could not support such an electron precise cluster with sp^3 hybridisation (for example, octahedral clusters in which each Te would need to form four bonds to other Te atoms as well as support a lone pair).

(ii) The same mistakes were made in this part of the question – wrong structures suggested that did not fit the bonding model.

(b) (i) Answered very well. This is a core component of the course. Most students obtained full marks.

(ii) The important point to note here is that the number of cluster electron pairs remains the same, even though a vertex is removed, for a closo,nido,arachno series. Marks were awarded for any sensible clusters that provided the right number of electrons (for example the nido clusters B_6H_{10} and $[B_6H_8]^{2-}$ were equally valid). Marks were deducted where the charges on the clusters were so large that supporting such a charge over few boron and hydrogen atoms was likely to be very unstable.

(c) (i) The electron counting in this question did not cause any problems, however, few students had thought about why the bonding models were different. Most could present the two models (delocalised cluster bonding for the borane, electron precise sigma system with a delocalised pi system for the allyl anion) but almost no-one suggested why the two are different. The reason is that the borane has too many hydrogens to support so cannot adopt a localised valence bond model. The allyl anion has sufficient electrons left over after constructing bonds to hydrogen to form a pi system (with bond order 1.5).

(ii) Careful use of Wade's rules for both boranes and organometallic species was needed here. Marks were lost through lack of care with counting electrons or for assumptions of charges which were incorrect.

(iii) Most students were confident that availability of d orbitals was at the core of this question. Not everyone also included steric pressure in their discussion.

Question 2 (6 answers): Generally well answered. Part (a) was not as well answered as might have been expected given how central to the course this topic is and how much discussed. There was a variety of approaches to (b), but most were insightful. Part (c) was universally well answered.

Q2(d)
The candidates who attempted this part of the question produced answers of variable quality. Those of lesser quality were mostly a result of writing answers that did not address the specific points in the question. There were some very good, lucid attempts that directly addressed all the points required by the question.

General comment – Q3&4

Both questions less well answered than in previous years; the macro-lactones in both questions causing problems. Few top class answers plus more very poor answers. That said the majority of answers were satisfactory indicating a good basic understanding of the A2 Core course.

Q3

There were **35** answers to this question and the mean mark was **14.7**

No change in the published marking scheme

There were 9 first class answers but only 4 of these scoring 20 or above.

There were 8 very poor answers but in each case this seemed due to the candidates running out of time.

Target molecule 1. Well answered with the majority of answers using a classical 1,5-dicarbonyl strategy. The formal requirement for a retrosynthetic analysis seemed to have helped organise thoughts.

Target molecule 2. This part was less well answered with many answers displaying poor understanding of the Diels-Alder reaction.

Target molecule 3. This part was less well answered with the macro-lactone causing far more problems than expected especially with the use of protecting groups (when needed and methods of selective de-protection). The best answers came up with some excellent synthetic routes (very impressive in a examination).

Q4

There were **68** answers to this question and the mean mark was **15.9**

No change in the published marking scheme

There were 21 first class answers with 6 scripts scoring 20 or above – these were excellent answers. There were only 2 very poor answers but this was clearly due to candidates running out of time.

Target molecule 1. Well answered with the majority of answers using a 1,5-dicarbonyl strategy and intramolecular aldol. The formal requirement for a retrosynthetic analysis seemed to have helped organise thoughts.

Target molecule 2. This part was less well answered with many answers displaying poor understanding of the Diels-Alder reaction (the lack of a double bond clearly causing more problems than expected although the use of an FGI to reveal the Diels-Alder is in the problem sheet!).

Target molecule 3. This part was reasonably well answered with the macro-lactone causing fewer problems than in Question 3 (probably due to the *cis*-alkene and the lactone providing obvious disconnection points). As in Q3 many answers showed up problems with the use of protecting groups (when needed and methods of selective de-protection). The best answers came up with some excellent synthetic routes (very impressive in a examination).

Q5

In retrospect this question was too easy. (a) Well answered, but often at too great a length. (b) Well answered with many people getting out both the assignment and the spectroscopic constants ($\widetilde{D}_J = 1.96 \times 10^{-6}\ \mathrm{cm}^{-1}$, $\widetilde{D}_{JK} = 1.46 \times 10^{-5}\ \mathrm{cm}^{-1}$, and $\tilde{B} = 0.852\ \mathrm{cm}^{-1}$; the exact values depend on the method used). (c) Generally well done, although a lot of fudging to get the target expression. (d) On the whole people knew what to do but many got into a muddle with the units ($E = 1.93 \times 10^4$ V m^{-1}).

Qu. 6

In retrospect this question was too easy. (a) Well answered, but often at way too great a length and in a scruffy, disordered kind of way. (b) Most people got the point, but not everyone commented on the fact that quenching has to be assumed to be pseudo first order i.e. [Q] effectively constant. Plotting the graph was appalling, with many people getting into a muddle over the units ($k_Q = 4.35 \times 10^9$ mol^{-1} dm^3 s^{-1}. (c) Generally fine, although quite a few people failed to spot that τ_0 requires a time-resolved measurement.

Q7 (51 answers)
This was the question preferred by most students and done rather well. Almost all could do part a and b. The most common mistake was the infamous error of equating the ionization potential to the orbital energy for which two marks were subtracted (the students have been repeatedly warned for this in the lectures and again in the examples). Part c caused more difficulties (as it was meant to) but, in spite of this, was attempted by the majority of the students. Most mistakes were made in setting up the perturbation matrix forgetting to insert a -beta for one or both bonds of the benzene reference missing in the ascorbate anion.

Q8 (35 answers)
It evidently always takes a bit of courage to opt for a question about normal modes which seemes to be not very popular among students. Virtually everybody could construct the Hessian of CH_4 (pat ai). Also the frequencies were mostly correct. The corresponding T2 normal modes aked for in aii were however frequently not the obvious x, z and z mode but some bizarre linear combination of it (sometimes not orthogonal to each other, but still orthogonal to the A1, so the frequency was still correct). The answers to bi were almost all correct. Part bi could only be done by those with a clear understanding of the normal modes displacements. The errors in the relatively few answers to biii were mostly calculation errors. There were however a couple of correct results.

Q11

A total number of four students chose to answer Question 11, so the result may not be very statistical. The highest score achieved is 15 while the lowest is only a disappointing 4 (honestly I don’t think this student has grasped the idea of course well; most of the fundamental understanding is lacking on him/her).

(a) Most students managed to assign the point group well except one. I take it as a pure negligence (by this student) as he/she seems to be the only one who is able to sketch nearly all of the SOs. Most students didn’t appreciate the power of using “Cartesian function-like” idea to assist in sketching SOs – which I think should be emphasised/highlighted in future lecturing.
None of the students manages to rank the energies of the SOs based on the number of nodes in them. This then affects their ability to draw a flaw-free MO diagram - despite that most of them are aware of pairing SOs/AOs of the same symmetry to form MO.
(b) Most students manage to locate “easy” axes such as C_8, S_{16} and ⍰$_d$, but only one of them finds the “hidden” C_2'. The majority have also answered (ii) well.
(c) Most students struggle to find a plausible explanation except one. They should be reminded in future lecturing that to energy separation as well as spatial overlap are two “other” important factors (apart from pure symmetry considerations) that decide whether different AOs/SOs can interact effectively.

Q12:

Most answers were of decent quality and all parts of the question received excellent answers from at least one candidate i.e. there was no part of the question that was impossible.

Most candidates did a decent job of extrapolating their knowledge of heterogeneous and homogeneous reactions to the new situation of a polymer-immobilised catalyst. There were also some good and inventive suggestions for how the active site could be made chiral. A few candidates got side tracked onto a discussion of how a polymer immobilised catalyst could be used to produce isotactic or syndiotactic polypropene. When discussing the mechanism lots of candidates fell into the small trap of using propene as a model substrate when this will not give chiral reduction products. Most candidates struggled to see that polymer immobilisation is likely to be detrimental to chiral induction due to subtle differences in active site structure due to its interaction with the support.

Part (b)(i) was very accurately answered and there were many good answers to parts (ii) and (iii) but a large minority of candidates would have benefitted from numbering the atoms in the substrate so that they ensured none were lost or acquired in the polymerisation reaction. Even though the final part was worth only 10 % many discussions of ROMP versus ADMET could have been more specific.

Q13

The 33 scripts are read through once to gauge the quality of the answers and then marked according to a marking scheme which fairly represented the balance of completeness of the answers for the four parts.

Mean Mark: 16.21/25 (this excludes three scripts in which only one part of the question was answered or in which the candidates presented single sentence answers to parts of the questions).

Grade Distribution: 27% First (9/33); 30% II.1 (10/33); 24% II.2 (8/33); 12% III (4/33); 6% Fail (2/33)

Q13a: this question seemed to challenge the candidates the most, and offered the most diverse range of answers. Three stood out as addressing the key elements of the question, but marks were offered for answers that gave credibly interpretation of the data and made use of the material presented in the lectures. Marked as 7/25

Q13b: of the four parts this is the one that with little effort provided an opportunity for candidates to 'bank' most of the marks on offer. The answer was in the question itself, so candidates needed to identify the trends in the trans-effect and if possible show the intermediate steps and give an energy profile to address the features of these effect. Marked as 6/25

Q13c: only three candidates got the subtlety of the solvent mediated step, but on the whole most candidates gave reasonable and credible answers with good use of the material offered in the lectures and one of the supervision questions. Part (ii) of the question invited interesting answers, but nobody used the data to provide the preferred answer. Marked as 7/25

Q13d: this standard electrochemical question generated some excellent (and complete) answers which were rewarded accordingly with the full marks, Most candidates at the very least addressed some of the data, however surprisingly few exploited the opportunity to address all four of the reductants. Marked as 5/25

Q14

There were 71 answers to this question.

Mean mark = 16.3

Min. mark = 9.5

Max. mark = 23

This was a very popular question and there was a decent spread of marks. Some answers were excellent.

(a) Generally well answered, diagrams and orbital labels required for full marks – similar example in the notes, though this one had the added complication of ketone versus ester enolate which did confuse some candidates. [6 marks]

(b) This part of the question proved to be challenging and enabled effective discrimination between the candidates. Relatively generous marking scheme adopted with most high-scoring answers proceeding via a Baeyer-Villiger process rather than direct fragmentation of the addition-adduct (which is the suggested mechanism in the literature). [5 marks]

(c) Most candidates coped well with this 'standard' example, though a not insignificant number made errors in the final step (attack of methoxide into the isocyanate). [4 marks]

(d) The vast majority of candidates recognized the two pericyclic steps involved, though most had them in the wrong order (i.e. cycloaddition first followed by a 4 electron electrocyclization). Relatively few had the correct sequence (6 electron electrocyclization followed by a Diels-Alder cycloaddition on the less hindered face) which accounts for the observed stereochemistry in the product. WH rules were generally applied correctly. [10 marks]

Q 15

50 answers. The first half of this question (leading to approx 50% of the marks) was well done with essentially everyone working out the correct stereochemistry and conformation from the relevant NMR data. The second part of (b) proved more testing, with many candidates knowing little or nothing about the Mosher ester method for configurational assignment of alcohols. In part (c), which was intended as the most challenging part, few candidates came up with a conformational explanation for the NMR signal doubling – presumably, they didn't look close enough to find the amide bond in the structure of **1**. In part (d), most of the candidates suggested an alternative explanation based on the same tautomeric equilibrium with the ring-opened hydroxy ketone but didn't consider that this could close on to the C14 ketone to give the observed 7-membered hemiacetal ring as opposed to the 13-epi 6-membered hemiacetal (which would be very high in energy and unlikely). This question was designed to test the candidates understanding of stereochemistry and conformation in the real life setting of a complex natural product like **1** (= rapamycin).

Q16

Only answered by 5 questions. Of these two were good, one average, one poor and one unfinished. Seemed a reasonable question but the low number of people answering it suggests that most of the class concentrated solely on the other half of the course. Average mark was 16.9 out of 25 until the unfinished script came in late which lowered it to 15.4.

Question 17

Answers = 31

Average mark = 16.90

SD = 4.46

Min mark = 7

Max mark = 25

The question was well answered by most candidates. Part (a) asked for the PLP mediated mechanism of gamma-aminobutyrate amino transferase. This was similar to transformations that they had seen before, and so almost every answer started on the right lines. The problems that the students seemed to have were not remembering the structure of PMP. Part (b) involved the mechanism of the suicide inhibitor, and it was pleasing to see so many excellent attempts to work out the covalent inhibition involved, although there were only a few who managed to see an aromatic product was possible. Part (c) asked for the $FMNH_2$ mediated mechanism to give chorismate, and was more variable in answers. Pleasingly many answers used variations of SET and H-atom abstraction to get the required product.

Q17

Answered by 23 and mostly badly (and with many unfinished answers). Part (a) simply involved reproducing the mechanism in the notes but the majority had not learnt it and guessed, and most of these produced impossible mechanisms to try to get to the product. Part (b) only involved a minor alteration to the mechanism in part (a), so people who got (a) wrong would not get (b) right. Nevertheless any workable mechanism got credit. The question was marked as generously as possible but still the average was only 5 out 10.

Q18

This question was attempted by 13 candidates

Part a was generally well answered with most candidates identifying the reduction in variables to be determined as the key aspect. The coordinates and implications of the mirror plane were also generally well answered. The statistical approach for the COS was generally reproduced well. Some candidates also referred to anomalous scattering. Part b was well attempted although a surprisingly significant number of candidates struggled with x= 1/3. Parts c and d were good with only one or two not correctly identifying the systematic absences. Most candidates could schematically illustrate the 00l reflections in part e. But only one or two correctly gave the positions of the peaks from the HCP and FCC and hence deduced the indistinguishability of the FCC and HCP structures.

Q19

Most students answered part (a) from the "top down", appending a statement of the phase problem at the end. This probably indicates that the whole question was not read before starting to answer. The best answers started by outlining the phase problem and its implications for making the required inverse Fourier transform, then showed how the heavy atom method is applied.

The numerical parts (b), (c), (d) and (e) were straightforward and answered well by most.

In part (f), most students stated that the phase indication for Pt is correct, but incorrect for Ni. This was related to the relative scattering power of Pt *vs* Ni, but with varying degrees of clarity. The key point was that the probability of getting a correct phase indication for any structure factor must be greater for Pt than for Ni, so the iterative heavy atom method should converge more rapidly for **A**(Pt) than for **A**(Ni).

For part (g), the best answers described the difference between the two isomorphous compounds explicitly using the structure factor equation. Too many students discussed the general (non-centrosymmetric) case, despite being asked to discuss only the centrosymmetric case! The discussions on how to deduce the phase from the known difference were generally lacking in clarity.

Question 20 (15 answers): Generally very good answers so had to be re-marked three times to achieve a more reasonable average. Parts (a), (c) and (d), relating to aspects of collagen molecular structure or collagenous tissue structure were very well-answered, in particular, part (d) which I expected to be tricky. Answers to part (b) were generally a little muddled – most trying to pull in understanding from solution state NMR spectroscopy and not always successfully.

Q 21

Generally answered well. (a) most students got the right answers varied in their level of detail of explanation. (b) Contained many errors in the scheme of the chirality of the molecule . While (c) and (d) were generally well understood and explained in the first part while the second part was not always complete and correct. Average Mark – 17.5

Q22

[14 responses, mean 16.4, min 10.25, max 24.25, stddev 4.3, median 15.6; 5 I, 4 II(i), 3 II(ii), 2 III]

The mean marks for the subparts were as follows:

(a) (i) 3.7/5, (ii) 4.0/5, (iii) 4.4/6.25, (iv) 0.5/1.25, (b) (i) 1.6/2.5, (ii) 1.0/2.5, (iii) 1.1/2.5

This question on a simple model of DNA unzipping was fairly popular, but it proved much harder than envisaged. The question was marked very generously in order to attain the target mean of 65%.

In part (a), some candidates struggled with the straightforward aspects of the question (such as noticing the geometric series or explaining why there is no degeneracy factor in the sum over the Boltzmann factors in part (i)). A good handful made life difficult for themselves by going through some pretty awful algebra in part (ii) instead of expanding the logarithm in the first step, which would have made the calculation straightforward. A few candidates blatantly tried to bluff their way to the answer given, with consecutive equations not following on from each other. In part (iii), the physical reasons for the high temperature limit were as a rule not explained very convincingly. Almost no one managed to answer part (iv) particularly well: many (but not all) spotted what the physically reasonable limit should be, but the resolution offered was often that we would need to allow the number of broken bonds to go all the way to N (is N/2 really that much better than (N-1)/2 as an estimate?). I expected that chemists might be quick to pick up on the fact that there are more orientational degrees of freedom around the broken bonds, since the two bases involved no longer need to point at each other but can freely rotate about the bond connecting them to the rest of the DNA strand. However, only a single candidate spotted this additional source of entropy that will, of course, dominate at high temperatures. However, as this was intended to be a challenging part of the question, it was intentionally given a low weighting in order not to disadvantage candidates too much.

Part (b) was a 'wordy' question, which is rather unusual for a theory question, and candidates were far less well prepared to tackle it. It was included following the external examiners' suggestion last year, and perhaps with good reason: it is apparent that while most of our students are well prepared to answer mathematically quite challenging questions, their knowledge of some of the fundamental concepts introduced in the course is perhaps somewhat less impressive, and a number of candidates skipped this part altogether. This is not to say that it was all bad: some candidates offered truly excellent suggestions for correcting the statements given, but the mean marks for this part were considerably lower than for part (a). I wonder if some of the 8 candidates who only answered Q22 might have been better off answering Q23 instead, which did not involve nearly as many descriptive parts.

Q23 B6 Statistical mechanics

[13 responses, mean 18.5, min 10, max 24.5, stddev 4.3, median 20.3; 8 I, 2 II(i), 1 II(ii), 2 III]

The mean marks for the subparts were as follows:

(a) 3.7/5, (b) 3.2/3.75, (c) 3.5/5, (d) 4.9/6.25, (e) 3.3/5

This question on mean-field theory attracted a number of answers. It may have looked rather unfamiliar, as candidates are unlikely ever to have seen examples of mean-field theory with two distinct effective fields, but the question guided the candidates along and they could check their answer at every stage. The question was answered extremely well by those who attempted it. It is reassuring that our students seem to have a very firm grasp of mean-field theory, even though it has not been examined in nearly a decade. Overall, a very pleasing result.

In part (a), a number of candidates said that because the spins at y=+1 and y=-1 are in the same environment, h_{-1}=h_{+1} and s_{i,-1}=s_{i,+1}. The first conclusion holds, but the second one does not: the potential energy can be specified for any given configuration of spins. A number of candidates lost a mark because they did not explicitly state that the reason we can write Q as a product of molecular partition functions is that the spins are non-interacting: they were invited to compute molecular partition functions by the question, but a brief justification was still expected.

In part (c), many candidates lost marks because they did not (or could not) explain where their expression for <U_1>_0 came from: a clear explanation of the number of neighbours of each type that each environment has was required. It seemed that a handful of candidates reverse-engineered the result provided, but did not seem to be able to justify the expression they ended up with.

As the instructions were so comprehensive, part (d) was marked relatively harshly. Rather too many candidates lost marks because they differentiated A_1, which is the true Helmholtz energy of the system, rather than a trial (mean-field) Helmholtz energy. Of course A_1 <= A_MF, but it is A_MF that should be minimised, not A_1 (which, in any case, is not known).

Finally, the last part of (e), which required a bit of careful thinking, proved tricky for a number of candidates, but I was very impressed by how many students were able to work out the correct answer.

Q24 B7 Perturbation theory

[12 responses, mean 17.3, min 8, max 24.5, stddev 4.2, median 18.3; 8 I, 1 II(i), 2 II(ii), 0 III, 1 F]

The mean marks for the subparts were as follows:

(a) 2.2/2.5, (b) 5.2/7.5, (c) 1.5/2.5, (d) 4.0/5, (e) 4.3/7.5

This was a well answered question on multiple degenerate perturbation theory in the context of a hydrogen atom in a magnetic and an electric field. This context was certainly unfamiliar, but the question did not prove to be overly challenging for the majority of candidates.

Part (a) involved computing a curl and a divergence, and was almost universally well done. It is very encouraging that candidates do not appear to have forgotten their Part IA vector calculus.

In part (b), the commutativity part of the question seemed to confuse a surprising number of candidates. It was important to remember [as indeed the question made abundantly clear by giving an explicit expression and by using 'hats', which were otherwise not used in the course] that p is an operator, so to find the commutator, it is usual to use a 'ghost' function so as to make it harder to miss the product rule required. This is very similar to finding the commutator [p_x, x] that is a staple of Part IB Chemistry questions, so it was rather disappointing to see just how many candidates were completely stumped by this part of the question: more than one candidate decided that p.A is always 0 because of the Coulomb gauge condition. Most candidates failed to note that the charge of an electron is q=-e.

In part (c), a number of candidates seemed not to remember that L = r x p. Using r=(x,y,z) and p=(p_x,p_y,p_z), we can find an explicit expression for L_z just by computing the cross product. Using A=(B/2)(-y,x,0) and dotting it with p=(p_x,p_y,p_z) gives us an expression for H^(1) to compare to. It was not necessary to express the p_i operators in terms of derivatives. Alternative approaches, though more difficult, were of course also given credit.

In part (d), some candidates were confused about the n=2 states of hydrogen, thinking for example that |2,1,-1> was the 2p_x orbital, which is not the case (the p_x and p_y orbitals are linear combinations of the orbitals considered here). However, this confusion did not lead anyone astray, since the eigenfunction equation for L_z was given. A small number of candidates lost some marks because they made absolutely no comment on why they were within their rights to use (effectively) non-degenerate perturbation theory and did not show that the perturbation hamiltonian was diagonal in the basis set given. Some candidates derived the secular equations from first principles: while it is impressive they they were able to do so without any guidance, this was certainly not required, and no credit was given for doing so.

In part (e), a surprising number of candidates failed to notice that this question was not written in atomic units (with hbar, the electron mass and the Bohr radius appearing in various equations). A number also could not recall the expression for the energy of a dipole moment in an electric field, and got the sign of their perturbation hamiltonian wrong, or even just used x as the perturbation hamiltonian, with no dependence on the electric field at all. But on the whole, candidates had a good idea about what needed to be done, even though multiple degenerate perturbation theory was not considered explicitly in the lecture course.

Overall, the question was very well done: our students are clearly very good at problem solving.

Q25

12 scripts.

Parts a and b were largely bookwork send very well answered (for a maximum of 7.5 marks).
Part c was also surprisingly well answered, given that it was most definitely **not** bookwork, and that they had not met a similar question before. In retrospect, the giveaway was the "show the largest multipole moment is J=6", rather than the original "work out the largest multipole moment". Many of the respondents gave correct answers (working effectively to this hint), and therefore scored well (out of the total of 10 marks for this part).

Part d was a mixed bag. Clearly several candidates did not read the question, and answered only part of what was requested (for example, worked things out for either benzene or pyridine, but not both). Also, some candidates worked out what wasn't requested (the number of non-zero components, rather than independent components) and obviously did not receive credit for this.

Overall, however, these were a very good set of scripts, with most candidates scoring at or above the 17.5 mark (1st class).

Q26

(a) Both cases generally well done. Still surprising that there were errors in the observed rate constants, given this is IA material.

(b) This part was not well done. Some clearly worked out what the plot must looked like and got full marks. The plots for others were all over the place, some with no kink at all. Almost all candidates did realise that the Brønsted plot would be more relevant in this case.

(c) This part was generally not well done, despite being straight from the notes and after we had spent a whole lecture on this type of change. Virtually everyone recognised that there was a change in the RDS, but most got the order of the changeover wrong, arguing that the worse nucleophiles made step 1 rate-determining. They did not realise that the poorer the nucleophile, the better it is as leaving and so it leaves in preference to the chloride ion from the tetrahedral intermediate, thus making step 2 the RDS.

(d) Again, this part was not well done since many seemed to want dinitrophenolate to be a better leaving group than chloride and then, inexplicably, p-nitrophenolate to be better still.

(e) Few people got the numerical parts correct, but some carry-forward marking was allowed for the majority who got the steps the wrong way round in (c). The important point was recognising that step 1 was the RDS on the RHS of the graph and hence told us the relative magnitudes of k_1.

27

(a) Generally well done. Almost everyone appreciated the form of the energy profiles and when the steady-state approximation was and was not applicable.

(b) Despite realising that the SS was not applicable for Case A, most students then went on to use it in some form! Very few appreciated that if the equilibrium is heavily over to the right, the concentration of the intermediate is essentially the concentration of the aldehyde. There were also far too many errors with the basic kinetics. Many students misunderstood what pseudo-first-order kinetics meant, often thinking that the concentration of the borane could simply be ignored. This meant that only around a quarter or so got the different rate expressions and hence understood the significance of (b)iii.

(c) This part was well done with almost everyone getting full marks.

(d) This part was not well attempted with few candidates realising that if the complex is readily formed, it is the second step that depends far more on the nature of the substituent and so will give a positive -value.

(e) Again, only the minority realised that with aluminium, Case A is now seen with the complex readily formed.

Q28

Thirty-seven students attempted question 28. Part (a) and (b) dealt with the basics of dynamic voltammetry, in particular reversibility criteria and shapes with a diffusional and adsorbed analyte. As expected, this part of the question was generally well answered (topic covered in depth during lectures and supervision). Part (c) dealt with the assignment of redox waves for a Mn complex. The reversible Mn^{I}/Mn^{0} redox couple (waves C and D) was recognised by most students, but the nature of wave E (reduction of Mn^{0} complex, followed by release of cyanide from the Mn ion – EC mechanism) was less well answered. Only very few students assigned waves B and A to the oxidation of the five-coordinate $[Mn(bipy)(CO)_3]^{-}$ and $[Mn(bipy)(CO)_3]^{0}$, respectively. Part (d) concerned electrocatalytic CO_2 reduction with the doubly reduced Mn complex at wave E and photoelectrochemistry. Many students had problems giving an adequate description/sketch of the two-electron nature of the CO_2 reduction and the electrochemical response on a semiconductor electrode during irradiation. General observation: Labelling of graphs and sufficiently detailed explanation of graphs/sketches was often missing. A mean mark of 16.46 was awarded (top mark was 25 out of 25).

Q29

For the first parts of the question some candidates were not very clear about the conditions needed for magnetic equivalence and so proposed spectra that were more complicated than they should have been. The structure of the Ru complex did not prove too difficult but the final assignment was frequently unclear. Many candidates did not spot the magnetic inequivalence in the Pt complex and thus were not able to explain the second-order effects in its spectrum.

Q30

29 scripts

Initial marking according to the strict mark scheme came out low so mark scheme was adjusted and all scripts were remarked. New mark scheme attached. Each part (a / b) now awarded equal marks. This was unbalanced in original mark scheme because I had originally had a longer part (a) and downgraded part a when I shortened the paper. This had been an error.

This question had 2 parts (a / b) now awarded equal marks

Part a had 3 sections, **each was now marked out of 5**

(i) was challenging (ii) pretty well answered by most (iii) really discriminated the best from the rest

Marks for **a** were totalled (/15) and then adjusted to / 12.5 (50% of total)

Part b had 4 sections, marked out of 5 / 5 / 6 / 4

(i) was straightforward (ii) caught some people out, a problem some did could not figure how to solve (iii) a few great answers, but the poorer students really struggled (iv) very easy for most

Marks for **b** were totalled (/20) and then adjusted to / 12.5 (50% of total)

Overall mean mark 15.3 Range 24/25 - 6/ 25

This is lower than the target but it is justifiable:

- All 1st class papers have 1st class marks 12/ 29 candidates
- 17 / 29 have 1st / 2:1 marks
- There is a very long tail: 7/29 candidates have 10/25 or lower. This disproportionally lowers the mean mark.

Q31

Only 7 students attempted this question so the distribution is not statistically significant.

The marks were spread over all classes, including fail. Parts a) and b) were recall of standard enzyme mechanisms and were straightforward, although the replacement of a Zinc with an Iron . The discriminator part c) worked well. I worried that no-one would spot the obvious, but unprecedented, key to the answer but in fact two students did just that and one student addressed more of the enzyme mechanism than was required and I gave it maximum marks for the whole question.

If fact, that highlighted the only real problem with this question in that the final part c) required little written answer and it seemed to provoke the idea in the students heads that more detail, of exactly how the pre-TTQ was crosslinked into TTQ, was reqruied. In retrospect, the question could have stated that the mechanism of conversion of preTTQ to TTQ was not needed. It was implicit in the question that asked “Propose a mechanism for reaction of peroxide with MauG…” but 4 of the 7 students did not pick that up.

Q32, C3
A challenging question which was generally tackled well, leading to a relatively high average mark; many good attempts. Most people were able to make good suggestions at most of the targets, although D and F are rather hard.

Q33

Answers = 49

Average mark = 16.02

SD = 3.86

Min mark = 9

Max mark = 23

The question was clearly difficult for the majority of candidates. Part (a) caused the least problems, and marks were given for any reasonable prediction of the resulting stereochemistry. Part (b) required the opening of the anomeric centre by the Lewis acid Ph_2AlCl, followed by addition of the Ph group to the resultant oxonium ion. Part (c) required the formation of a $Bu_3Sn\bullet$ (radical) for the start of the propagation steps. Most got this correct, but then things usually went wrong. Due to the cyclised product, most answers suggested a hydrogen atom abstraction first, rather than the bromine atom abstraction. Another common slip was not to suggest any diastereoselectivity. Part (d) proved to be the most problematic part. Most thought the mild H^+ step would deprotect the ketal, despite the later steps would then be unselective or impossible. In fact the ketal remains and the phenol is formed. The Lewis acid BF_3 step contained the cascade cyclisation, although most answers seemed to think the final basic step was where all the bonds were made. Disappointingly few candidates tried to shine any light on the stereochemical outcome.

Q34

60 students attempted Q34, which was a question about the atmospheric chemistry of ozone in the stratosphere. The question started by (a) asking the students to rationalise the vertical profile of O3 in the atmosphere. This was generally well answered (average mark for this part of the question was 78%), however, there were a number of students who did not read the question properly and gave an account of everything they knew about O3 in the stratosphere rather than answering the question (one student even taking it upon themselves to throw in some literature references).
Part (b) then asked the students to use the Chapman mechanism to derive an expression for O3. At first sight, this is very trivial and several students wrote a very trivial expression for steady state [O3]. With more thought, the higher scoring students saw that the expression could be further simplified to one that only involves the rate constants of the mechanism, the mixing ratio of O2 and [M]. This was something we did in the lectures as a "live" exercise.
Part (c) then wanted the student to calculate the missing rate constants, J1 and J2, and the [O2] and so [M] at 40km. Largely, this was well answered. The most common mistake was (i) not to included the O2 column in calculation of J1 and (ii) to not spot the units of H (km NOT cm!).
Part (d) then required the students to think about how changes in [O2] would change dJ1/dz. Many of the answers were very good and linked well with the expectation that the maximum in O3 would raise/lower with increases/decreases in O2.
Finally, part (2) asked how the very strong GHG N2O could impact O3 directly and indirectly. There were some very poor answers to this part of the question (the average for this part was 50%). Some of the worst answers did not even have balanced chemical reactions.
The overall average mark for the question was 16.4 and the range was 5-24.

Q36

The first and last parts of this question were the derivation of MP2 and size consistency which were covered in the lectures/handout. The hard part of the question was substituting in values using the 6-31G HF integrals. The resulting values do not give agreement with the exact answer due to the small basis set. Overall, there were many answers that were of a high standard and giving a complete discussion of most of the points that were hoped for: from all the finer points of the derivation and matrix elements to the discussion of the orbitals/integrals in the problem of size consistency. The only area that caused problem was in the definition of the eigenvalues, with respect to the integrals, as this was not in the previous part of the question and should have been worked out.

Q37

Although the question starts with some relatively simple matrix elements, which all the people who tackled the question were able to do, the second half is really quite unfamiliar and difficult. The construction of the exact functional rearranges the first two parts to give the expression in the question. Even if this could not be done, then the last part (just by differentiating the given expression) could be carried out. Several people tackled the question and a couple of answers were extremely impressive to both derive and use the exact functional.

Q38

27 Scripts marked to an average mark of 16.22.

Part (a) was generally answered well and to a good average score by most candidates, as expected, given the material was covered explicitly in the lectures.

Part (b) was more of s ‘stretch’ question that extended beyond the material given in lectures. There were a small number of very strong answers, especially for parts (i) and (ii). Candidates found part (ii) the most challenging and most failed to see a mechanism involving loss of nucleobase.

Q40

This question was attempted by 41 candidates

Part a was generally answered well by all but a tiny handful of candidates. Part b was a reasonably standard Gibbs isotherm equation which was again answered well by the majority of candidates. Most candidates also made a reasonable attempt at Part c and correctly deduced equation of the line to plot with appropriate graphs. Some difficulties with extrapolation led to a range of values for ao but credit was given for a sensible comment on the value obtained. The last part on the BET isotherms was a little disappointing with a significant number of candidates not clear about the meanings of Po and C. Only seven candidates could correctly give the form of the straight line plot used to extract Vi and C.

Q41

15 candidates attempted this question.

A rather mixed bag of answers. Part a was straight from notes/lectures and was addressed well by most candidates. Part b was also answered well by all but a few, who forgot that soap bubbles have two interfaces each. The calculation of the amount of liquid and vapour in part c was also generally solid. However, parts d and e were much less robustly answered with only about half correctly predicting the behaviour. Some candidates gave essentially model answers for Part f (again straight from the notes and lectures). Quite a few could not recall the molar volume of the liquid and its value for water. Although expressly asked for in the question almost no one clearly defined all the variables. The last part, g, was a relatively straightforward calculation requiring a little care and approximately half the candidates got the correct answer.

Q42

(a) Almost all students correctly determined the number of electron pairs for cluster bonding in $C_4B_2H_6$ although some mistakenly assigned the formula as $B_4C_2H_6$. Those with the correct formula went on to classify the structure as nido and to suggest a pentagonal bipyramidal structure.

(b) The second half of this question was answered much less convincingly. Most students spoke of some multiple bonding character for the planar compound but could not explain how it might come about. Students did not do simple things to assess the bonding, such as assign hybridisation states, count pi electrons. Few students spotted that the F atoms can pi donate into the ring, which would not be possible in the case of exo H atoms, hence the preference to adopt cluster bonding for the cluster in part (a) rather than localised multiple bonding scheme seen for the compound in part (b).

Question 44: Very well answered; had to mark strictly on how well-explained answers were to differentiate.

Question 45: Either very well answered or badly answered, little in the middle. Poor answers did not appreciate the difference in LF splitting between 1st and 3rd row transition metal complexes, did not appreciate the role of ligand-ligand repulsion, over-emphasised the role of electron spin-pairing in the difference in tetrahedral v square-planar geometries, did not explain the prevalence of square planar geometries for d^8 complexes.

Q46

Many candidates produced really good answers. However, a distressingly large number were not clear about the number of valence electrons, and electron configurations, of Eu and Np (in spite of having the Data Book with them in the exam) and so produced some very elaborate but incorrect answers.

Q47

Well answered: with majority of disconnections via reductive amination and ester alkylation. Mean = 4.0

Q48

Well answered, with most of the answers showing good recall of controlling alkene geometry via the Wittig reaction. Mean = 3.6

Q49

Well answered, with most of the answers showing good recall of controlling the alkylation of aldehydes and ketones. Mean = 3.1

Q50

Well answered with good recall of the aldol condensation and the epoxidation of electron deficient alkenes. Mean = 3.5

Q51

Well-answered with good recall of some key reactions (Diels-Alder and Baeyer-Villiger). Mean = 3.7

Q52

Not especially well answered. People failed to spot that the only likely source of broadening in the microwave was pressure broadening (not natural lifetime broadening, which would be utterly negligible in the microwave). The value given for the infrared is thus the pressure broadening (which is constant with frequency) and a new contribution, likely to be Doppler – since this increases with frequency. At 20,000 cm^{-1}, the Doppler will be 10 × that at 2000 cm^{-1} i.e. $10 \times (0.006 - 0.003) = 0.03\ \text{cm}^{-1}$.

Q53

Was way too easy.

Q54

Most people knew how to get to the expression for the Q branch lines, but too many left out any contribution for the pure vibrational transition. Most people got that $\tilde{B} = 9.44\ \text{cm}^{-1}$, but people then got into a muddle with how to interpret the spacing in the Q branch, which is $|2(\tilde{C} - \tilde{B})| = 6.446\ \text{cm}^{-1}$. The correct value is $\tilde{C} = 6.19\ \text{cm}^{-1}$. Many people got a value for $\tilde{C}$ which was larger than that for $\tilde{B}$, which is plainly not possible given the definition of the moments of inertia.

Q55

Quite well done, with most people knowing what the configurations had to be, but what was less well done was the explanation of why the proposed configuration gave the required term symbol. There was much confusion between *l*, *L*, *λ*, and *Λ*, and similarly rather muddled ideas about how to combine the spin quantum numbers. Many people worried about whether or not the terms would arise from allowed spectroscopic transitions from the ground state, which was simply not a relevant issue.

Q56

Almost everybody got the energy levels right. Most marks were lost in using the wrong populations in the expression for the total energy. I was somewhat surprised to see that this didn't prevent the students identifying B as the stable configuration (this is probably the "chemical intuition" acquired in other courses)

Q57

The large number of correct answers to this question (and corresponding above average score) was way beyond my expectations. Evidently the students did pick up the concept of a Slater determinant and how to manipulate them.

Q58

The errors here, as expected, were in the sign, positive orbital energy and negative interaction energy. Evidently this is (still) not felt as alarming. However if followed through consistently, the absolute energies are correct, which gave still a 60% mark.

Q59

The large number of wrong answers to this question are further confirmation of the general lack of intuition for normal modes. Many answers started by setting up the Hessian and deriving the normal mode frequencies instead of just scaling them.

Q60

The 57 scripts are read through once to gauge the quality of the answers and ten key points were identified which helped formulate a marking scheme out of 10. The scripts were marked once according to the marking scheme which fairly represented the balance of completeness of the answers, and then marked a second time to make sure that the mean mark reflected a suitable spread from the best to the least-best answers.

Mean Mark: 6.36/10

Only a handful of candidates (9/57) used the available time to give a clear indication of their understanding of what the question was asking and carefully presenting insightful and creative answers (i.e. being marked 8 or 9/10). A surprising number of candidates (18/57) presented the minimum information (one or two relevant points) or invested too much time labouring to overstate the information that was in the question without really showing a sound understanding of what the question was relating to in the course (i.e. being marked 5 or lower/10). In marking the scripts, candidates (the 30/57 achieving a mark of 6 or 7/10) were rewarded for stating key words or concepts even if they were not developed as well as in the best scripts.

Q61

B2 Structure and reactivity

This questions was very popular (73 scripts) and the quality extremely variable (marks ranged from 0 to 10).

The mean mark was 5.5. There were several very low marks (0.5 or below) that skewed the mean considerably (several scripts did not contain a single mechanistically correct step of any description). Even with a very generous marking scheme and extensive re-marking (taking several hours) it proved impossible to increase the average. Removal of scores of 0.5 or below leads to a mean mark of 6.1.

Most candidates recognised that the role of the base was to remove a proton from the CH_2 group adjacent to the nitrogen. Several candidates provided answers that featured mistakes in the valency of atoms (pentavalent carbons were more common than I would have expected). The route adopted by most candidates involved deprotonation of the CH_2 group adjacent to the nitrogen followed by intramolecular nucleophilic attack of the resultant anion on the alkene and subsequent protonation. A relatively small proportion of candidates spotted the possibility of electrocyclic ring closure followed by protonation. Those that did tended to score very highly.

Q63

26 candidates attempted this question.

Most candidates were able to identify the connection between the experimental intensity and the Patterson function and the appropriate mathematical relation. Almost all were able to sketch the trigonal bipyramidal PCl5 molecular shape and assign the experimental peaks to give the relevant bond lengths on the figure. Almost everyone correctly calculated the missing peak weight. Most were able to identify that there would be same number of peaks in the Patterson function for the square based pyramid and that the relative intensities would be needed to distinguish them.

Q 64

Overall, the questions was generally well answered with varying degrees of detail and care in the answers and mechanisms. (a) most of them got the answer correctly (b) was also well answered but with a less success, while only few student were able to correctly answer to (c). Average Mark – 6.8

Q65 B6 Statistical mechanics

[23 responses, mean 6.6, min 2.75, max 10, stddev 1.9, median 7.0; 12 I, 3 II(i), 4 II(ii), 2 III, 2 F]

This question on the concentration entropy of diffusing particles was very popular. It was well answered on the whole, although the physical interpretation of the result given and the microscopic interpretation of Fick's 1st law both proved rather more challenging than working through the simple maths in the derivation itself.

In order to examine the candidates' ability to communicate their work in a clear fashion, the question specifically asked for a careful explanation of each step taken, and so some marks were deducted if candidates did not provide one. In the derivation, some candidates neglected to write the variable of integration (dx) in their integrals, and then got confused and integrated in t rather than x. In fact, several candidates seemed to be confused by the set-up, writing comments such as 'as t increases, x increases' - but the integral given is over all x, so this makes no sense.

Many candidates did not explain why one of the terms that they obtained by integrating by parts vanishes: ln(c)*(dc/dx) as x tends to positive or negative infinity is not 'obviously' zero, since c tends to zero at such values of x, and ln(0) tends to negative infinity. It is important to note that (dc/dx) vanishes faster (i.e. exponentially) than ln(c) rises in magnitude, but only two or three candidates commented on this.

Many of the lower marks were obtained by candidates who had clearly run out of time; those candidates who made a serious attempt at the entire question generally did very well.

Q66
Most scripts got the dimensionality part (2J1+1)(2J2+1) correct, as the direct products implied by f$^{\wedge 2}$ and d^1f$^{\wedge 2}$. Also, most got the identification of the singlet and triplet states associated with f$^{\wedge 2}$. However, the J values were in general poorly worked out, resulting in a lose of about 2-3 marks out of 10, depending on the working shown.

Q68
The majority tackled this question well, with good summaries of the factors contributing to shielding. The assignments and explanations for chemical shifts of PhMgBr were generally acceptable but the presentation of the arguments often lacked coherency and sometimes important details were omitted.

Q69

30 Scripts.   Average 6.1 StdDev 1.8

On the whole, I was disappointed with the bulk of the scripts. In the first run through marking gave an everage of 5.5, so I ran through again and remarked and managed to get the average up to 6.1. Three low scores of 2 or 3 bring the average down from 6.5 to 6.1, so I do not think this low average disadvantages the majority of students.

Part a) required discussion of the thermodynamics of the thermal stability of proteins and how it can be altered by small molecule binding. I think only about 20% of answers recognised this, even though I thought that would be quite obvious. Most students just did a core dump of what they had learned about the interactions that stabilise proteins (mainly from Jane's part of the course). Only one student discussed the key point which is how the T_m varies with small molecule concentration. Several others eluded to it by presenting sensible ⍰G vs T curves which also got good marks.

The answers to part b were also frustrating, although generally better quality. The majority of students pointed out that denatured states of proteins have many more accessible ligands (including the polypeptide backbone itself) for metals, which is the key to the question, but they did not say what the ligands were which was also really needed for a full answer.

There were some excellent answers that attracted scores above 8.0 but I did not feel there were any perfect answers and so the maximum mark I could give was 9.5.

I do not suggest changes to either of theses questions before deposition in the Past Papers archive.

Q70, C3
DABCO is widely believed to be a strong non-nucleophilic base. Was it being confused with DBU, perhaps? The mechanism in the paper is the formation of an allene in a six-membered ring. This is the mechanism produced by many candidates. A Baylis-Hilman process, however, seems much more likely, as DABCO is a good nucleophile and this would explain the stereochemistry more naturally. Credit given for both mechanisms.

Q72

A relatively standard question on basic knowledge from the course for the Kohn-Sham equation and a simple functional derivative. Most people did well on these parts, especially describing in good detail all the points that were hoped for. The last part of (b) was a one orbital system and rearranging the KS equation of the first part to give an expression. Most people got some of the way along this part but nobody fully simplified down to the von-Weizsacker expression.

Q74:

This question was answered quite well, with an average mark of 6.2 (over 49 scripts) brought a little below the target mark mainly due to a handful of attempts that were clearly compromised by time pressure; all bar three candidates scored in the range between 4 and 9 marks. The majority of candidates correctly identified the (1x2) and (2x1) unit cells in Part (a), but several did not demonstrate a clear understanding of the difference between (2x2) and c(2x2) cells. Performance in Part (b) seemed to correlate fairly well with that in the earlier section, so most candidates again did reasonably well but not perfectly. Finally, in Part (c) most candidates described either the experimental geometry of LEED, or the interpretation of LEED in terms of the Ewald sphere, but only a handful did both; full marks here were correspondingly rare, but few candidates failed to gain at least half marks. Overall, most candidates showed reasonably good understanding of the subject matter, dropping marks mainly on the details.

Q75

Quite well done for the first part, but people struggled with the interpretation. Most commonly missing was the idea that in this case each measurement gave the *same* eigenvalue and that this was the eigenvalue corresponding to the given eigenfunction.

Q76

Surprisingly poorly done, given that this is a very standard piece of work. Several people failed to compute the differentials correctly, and so went completely wrong.

Q77

Most people were able to deal with d^2 and d^8, but d^5s^1 was more of a challenge and not everyone spotted how to extend the 'box' to cope with this configuration.

Q78

In principle a very straightforward question, but one which needs people to keep a clear head about the sign of the various terms. Despite the clear statement that $\alpha_1 < \alpha_2$, several thought that $(\alpha_2 - \alpha_1)$ was negative!

Q79

A very standard piece of work, but several people tripped up by forgetting that the normalization integral is $\int_0^{2\pi} \psi^* \psi \, d\phi$ and/or forgetting how to take the complex conjugate of $e^{i\phi}$ and/or forgetting that $e^{i\phi}e^{-i\phi} = 1$.