Part II

Qu.1

(a) Answered well with appropriate level of detail. Those that slipped up had not read the question and did not comment on both the numbers of electrons and orbitals, focussing instead on only one of these.

(b) Again this was answered well. Less than 5% of students had trouble with the counting of the Ru cluster.

(c) This question required application of Wade's Rules in a number of ways. Parts i) and iii) were straightforward and most candidates did not have any trouble in assigning the correct structure based on Wade's Rules. Those that were stumped by ii) had either counted wrong because they had substituted Rh for Ru Re or failed to notice that the Sb is an interstitial atom in this case. Part iv) required students to spot that the two carborane clusters were forming a Co(III) sandwich compound. This caused some confusion with less than 50% of students providing a sensible interpretation.

(d) i) This question features a nido borane based on an 11 vertex polyhedron with one missing vertex. No marks were awarded for remembering the shape of the polyhedron since this was not one of those that the students were asked to remember as part of the course. Compounds **A** and **B** ($B_{10}H_{14}$ and $[B_{10}H_{12}]^{2-}$) are both nido (they have the same electron count) so most found this part of the question straightforward. Many students struggled to come up with sensible structures for **C** and **D**. Marks were awarded for a number of different sensible interpretations and accompanying electron count and structure prediction.

ii) This is something that was covered in lectures. Most could remember it!

Qu.2(d)

The MO diagrams used to explain the geometries were generally done well.

The acidity of B12H14 was not generally recognised, leading to complicated cluster structures rather than a simple dication/dianion species.

The foundations of organic synthesis

General comment Q3&Q4

Twice as many students answered Q4 over Q3 probably due to the hidden Diels –Alder reaction in Q3. Both questions well answered with few of the “classic” errors that have been so common in previous years. Indicates a good basic understanding of the A2 Core course.

Qu.3

There were **36** answers to this question and the mean mark was **16.25**

No change in the published marking scheme

There were 17 first class answers but only 7 of these scoring 20 or above.

There was only 1 very poor answer but this was clearly due to candidate running out of time.

(a)

(i) Very well answered with the majority of answers offering explanation for the reagents or conditions that were suggested. Good to see most answers using a formal retro-synthesis even though not asked for.

(ii) This part was poorly answered with no answer using Danishefsky diene with the masked ketone. Perhaps a little too advanced for A2 and maybe more appropriate in B2 course.

(b)

Target molecule 3. Well answered with some very nice synthetic routes. Good understanding of the use of Wittig and alkyne anion chemistry to control double bond geometry.

Qu.4

There were **64** answers to this question and the mean mark was **16.5**

No change in the published marking scheme

There were 24 first class answers with 13 scripts scoring 20 or above – these were excellent answers. There was only 1 very poor answer but this was clearly due to candidate running out of time.

(a)

(i) Well answered with some very good routes to avoid using the azaenolate (which most seem to have forgotten about!!).

(ii) Good answers for this part with good use of Diels-Alder chemistry.

(b)

Target molecule 3. Generally well answered. Good retro-synthesis via Diels-Alder.

Qu. 5

(a)(i) Generally well answered

(ii) Generally OK, but a certain degree of muddle over how to derive the collision rate, and some people did not derive it but simply stated it.

(b)(i) Generally people understood that the slope was due to pressure broadening. Candidates attributed the intercept to natural or Doppler broadening, even though (as many stated) these are likely to be negligible for a microwave transition. Only one person got that it was the instrumental linewidth.

(ii) It was very depressing that people we so easily muddled by the use of MHz and □: even those who realised that they needed to change units tended to use the wrong factors. Depressing. [0.397 nm^2]

(c)(i) This was very straightforward, but even so some of the diagrams were pretty crummy, and people tended to forget the need to comment on the effect of the value of K.

(ii) Generally reasonably well done, although units once again caused problems. [62.4 MHz]

Moral of the story: pay more attention to units.

Qu. 6

(a) Was, on the whole, done very well, with many people achieving full marks for this part.

(b) (i) It was depressing how many silly errors there were in part, such as using *g*/*u* labels, the inability to count the number of electrons, not putting the electrons in the lowest energy orbitals (it is the ground state, after all).
(ii) Not that many people spotted that this is a PQR structure from a □□□ transition. Inexplicably, lots of people said that the lines in the R branch got further apart (which they don't – the R branch is on the high-frequency side, and the lines plainly get closer together). Very muddled answers to this part, all in all.
(iii) The band origin is clearly visible, so you can easily pick off the frequency separation of R0 and R1 (for example): it is them a simple matter to work out how this separation is relate to the rotational constants, and hence find B_{upper}. Very few people had any idea how to do this.

Moral of the story: pay more attention electronic spectroscopy.

Qu.7

The section about electron-electron interactions was extended this year from one to three lectures now also including example questions. What was added in the two additional lectures was a derivation of the Hartree Fock total energy expression and a detailed discussion of the application to two and three electron systems. This year was also the first time that the electron electron interaction energy was the subject of a 45min exam question. The question was a reformulation of an example problem, the He atom in the 1s2s configuration. It was answered by a third of the students who did very well. Almost everybody could do questions a and b. The main mistake was forgetting the minus sign in the expression for the exchange integral in question ci. Students who made this mistake had of course to find some way out to end up in ciii with a triple state lower in energy than the singlet state. This issue in practice determined the final mark.

Qu.8

This was a standard question about normal modes. The students who opted for this question (two thirds of the class) presumably did not have the courage or confidence to try the new subject about electron electron interaction. The marks showed the for A4 familiar bimodal distribution, with a relatively large fraction of firsts along with some rather bad work. Still, disregarding a small number of students who had put off this question till be very last moment and ran out of time, the answers were overall satisfatory with the most of the mistakes made in part c.

Qu. 9
Was attempted by six candidates. Average 16.6. Highest mark of 20.5, lowest of 12. The general significance of operators poorly explained, with a general difficulty to associate the eigenfunctions/eigenvalues with measurable quantities or to explain the significance of the expectation value. There was some strange notation in the variance question, but otherwise this was fine. The momentum part proved challenging, particularly the reason why the particle could not be.

Qu.10

Was attempted by three candidates. Average 16.6 Three satisfactory attempts with a high mark of 20.5. Numerical parts attempted well, most stating that beta was negative and rationalising choice of bonding MO. Descriptive parts less well done - rationale for LCAO-MO missing, constraints on coefficients in the LC, and the physical mechanism of lowering of energy mostly absent.

Qu. 11

Last year there were few answers to the corresponding ‘symmetry’ question, and they were all poor. It is therefore pleasing this year to see more answers, and answers of high quality. The question was generally very well answered, with in most cases a few marks being lost for failure to label the diagrams correctly. In retrospect the question was rather too easy.

Qu.12

Twenty four students attempted question 12. Part (a) dealt with the *trans*-effect in square planar complexes and this question was generally very well answered. Part (b) caused some problems, in particular recognition of the symmetry in the *fac*-complexes being the reason for two CO vibrations and analysis of the π-acceptor strengths of PF_3, PPh_3 and pyridine to justify the different CO wavenumbers for the Mo complexes. Part (c) was well answered with most students explaining the I_a mechanism satisfactory. However, most students did not recognize the stronger M-OH_2 bond in the Fe^{III} complex to justify the slower ligand exchange rate (on the other hand, steric arguments were well recognised). The quality in the answers to part (d) varied (as expected) widely. A mean mark of 16.54 was awarded (top mark was 24.5 out of 25).

Qu. 14

There were 74 answers to this question.
Mean mark = 15.6
Min. mark = 6
Max. mark = 23.5

This was a very popular question and there was a very wide spread of marks.

There were several very low scores that skewed the average mark. Some answers were excellent.

Despite a fair degree of generosity in the marking and extensive re-marking (taking several hours) it proved impossible to increase the average, because there were so many very low scores. The question was certainly sufficiently discriminating.

(a) Very similar to material from the lectures but only approximately a third of the students spotted the key issue of transition state stabilization. Most students presented an argument based on geometrical constraints to orbital overlap. Generous marking scheme adopted – correct approach automatically got 5 marks, ranging to 6 marks for additional comments. (6/25)

(b) Most students could draw the mechanism for carbene formation and cyclopropanation (book work). Not many commented upon the selectivity for the central alkene. The stereoselectivity in epoxidation was rationalised by most, though there were some poor mechanisms given for this step, which was very surprising. Only one student gave the correct explanation for the selectivity between the two alkenes in the conversion of C to D. [6 marks]

(c) The majority of students could provide a reasonable mechanism for the transformation (which taken alone scored half marks). A clear 3D diagram highlighting the interacting orbitals in the migration step, together with a comment on the comparative orbital overlap of the two possible migrating groups, was needed to get full marks. [4 marks]

(d) This part of the question was generally answered well. Most of the students spotted the correct reaction sequence and mechanisms were generally good. Woodward-Hoffmann rules were generally applied correctly. For the justification of endo selectivity, I would have liked to have seen better 3D diagrams (i.e. showing secondary orbital interactions) but marked leniently. A minority of students provided some truly odd mechanisms. Tried to be as lenient as possible with marking (within limits), some credit given for alternative mechanisms (if not too outlandish) and correct WH analysis and other comments even if incorrect mechanistic pathway followed. (9/25)

Qu.15

This question was reasonably well done. In part (a), the majority of the candidates were able to correctly propose a □-lactone for product **2**, supported by mechanistic reasoning and assigning the protons correctly, indicating their ability to process chemical shift and coupling constant data. However, there were quite a few erroneous structures proposed that were both mechanistically unsound and didn't fit all the NMR data. For part (b), most of the candidates correctly assigned the stereochemistry in the □-lactone but some failed to relate it back to the structure **1** without inverting stereocentres. Most candidates suggested a chair for **2** but the coupling data fits a boat conformation better. A fair proportion struggled with providing clear 3D drawings.

Qu.16

a 2 examples of nucleophilic catalysis - even though from notes, answers were uninspired and sketchy. Mainly looking for serine proteases, phosphatases, imines etc.

b Mechanism of mandelate racemase.
This was potentially quite a tough question under exam conditions, and needed clear thinking. Drawing a clear mechanism and recognising the differences presented by a His and a Lys on opposite faces was crucial, as was recognising the consequences of carrying reactions out in D2O, incorporating D then having a KIE Expected difficulties on part (iii) regarding the overshoot, but several made a reasonable attempt, recognising the effect of converting R to S led to D incorporation, and cosnequently slower conversion of the S form. Perturbation of pKa of lysine OK.

Qu. 17
Set and Marked by DRS
Answers = 33
Average mark = 16.61
SD = 4.97
Min mark = 5
Max mark = 22

The question was well answered by most candidates. Part (a) asked for the FAD mediated mechanism of the oxidation of phenylethylamine to the aldehyde. 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 exact SET mechanism required. Part (b) involved the suicide inhibitor selegiline, and it was pleasing to see so many excellent attempts to work out the covalent inhibition involved. Part (c) asked for the TPP mediated mechanism of G3P and L-Arg to give CEA, and was more variable in answers. Pleasingly the use of TPP was generally well understood, but the problem solving associated with further reactivity and sequence of events caused many problems.

Qu.18

This question was a little bit non-standard, although we had dealt with something slightly similar in the examples classes. Generally it was well answered. For part (a), most could demonstrate clearly why establishing the presence of a centre or not was essential to distinguish between the space groups, although some were rather hazy about the principles involved. Part (b) caused no real problems, but a surprising number of candidates could not locate the extra special positions. Part (c), which was absolutely standard, caused no problems, but only a few students could fully explain part (d), which was rather disappointing, and pulled the average mark down somewhat.

No. of attempts : 19 Average mark : 16.4/25

Qu.19

The first two parts of this question were straight from the lectures and examples classes and were, in general, very well answered, with several candidates obtaining full marks. Part (c) however, did show up some problems, insofar as some candidates had difficulty in applying the analysis of isomorphous replacement to a case of anomalous scattering, but almost all made a fair attempt. The problems really came with part (d), where only a very few candidates considered the possibility of calculating approximate phases from the heavy atom method and using this to solve the ambiguity, and of those that did, none failed to notice that the heavy atom contribution to beams with k odd was almost negligible.

No. of attempts : 19 Average mark : 16.2/25

Qu.20

Part (a) on the general structure of a clay such as montmorillonite was handled well and some clear descriptions of the important structural features given. The issue in part (b) was frequently poorly described with the effect of decreasing amounts of water on acidity as well as the potential collapse of the clay not clearly made. Part c-d were relatively good although perhaps part (c) frequently lacked a full perspective e.g. while gallery heights can be obtained quite easily the disordered nature of the interlayer means that actual in-plane arrangements less well determined. In part (e) some successfully considered the type of porosity that would be introduced in a clay after pillaring (i.e. still 2D compared to the 3D arrangement in a zeolite.

Qu.22
This was a relatively standard Langmuir adsorption question similar to those set in previous years. It attracted a large number of responses and was generally answered well by the candidates.

Part (a) was generally answered well, although a small minority of candidates failed to account for the total energy in the system by not multiplying epsilon_A by N_A and equivalently for B.

In (b), a significant proportion of candidates either neglected to indicate what the lower and upper bounds of the summation were, or were getting the bounds wrong, despite the very significant hint in the question itself. Many of those who did get the summation right failed to justify the reasons for their choice of bounds. One candidate (commendably) calculated the grand partition function for a single site, which helped them to avoid having to use the multinomial expansion altogether.

Part (c) was straightforward to do as the final answer was given.
However, despite being asked to derive an expression for the mean number of adsorbed particles of a gas, many candidates did not provide a derivation or even
a brief justification of their formula for the mean number of adsorption sites.
Nevertheless, the part was on the whole well answered.

Part (d) was a straightforward manipulation and was well-answered. A few candidates let themselves down by making simple algebraic mistakes in simplifying products of exponentials, although this was not penalised too harshly.

We intended part (e) to be slightly less familiar to candidates, as indeed it was.
Most candidates remembered that pV = kT log Xi, but many struggled with the simple differentiation required. The physical interpretation aspect of the question proved challenging. Disappointingly, no candidate spotted that the form of the entropy is that of the ideal entropy of mixing, despite one of the exercises covering this explicitly.

Qu.23

This polymer question was similar in style to those set in recent years. It was on the whole answered well by those who attempted it.

In part (a), almost all candidates got full marks, which was expected as this was a straight recall of a key result.

Most candidates had a good idea about how to approach part (b), with some beautiful derivations; however, many candidates simply went through the maths without a single word of explanation as to what they were doing or why. While their result may have been correct - this is not entirely surprising as the result was given - candidates did lose some marks for not explaining their steps.
Part (c) involved a very simple sketch of the free energy as a function of the polymer end-to-end distance for a polymer whose terminal monomers are charged.

Everyone was able to sketch the basic shape of this function. The question did not explicitly request a justification and, indeed, many candidates did not offer one.

Part (d) was mostly done well. Not all candidates explained why they were computing an extremum of the Helmholtz energy.

Part (e) proved to be somewhat more challenging. Most (but not all) candidates seemed unsure about how to address this question.

Qu. 24

This question presented problems on both the static and dynamic polarizability. Initially, the student was asked to derive the dynamic polarizability from time-independent perturbation theory (something which was presented in the lectures). This was then put in the context of the harmonic oscillator, for which ladder operators render the problem tractible (and indeed independent of the initial state). Finally, the problem was contrasted with the case of a static perturbation; the static polarizability was asked to be derived, and the result for the harmonic oscillator problem compared with the dynamic case. Only six scripts were marked for this question, although I believe that the difficulty of the question was about right. The average was 15.66 out of 25, with three answers of 1st class quality.

Qu.25

Parts a-c contained much bookwork, so I looked for the finer details in the answers and marked accordingly. Most of the scripts scored close to full marks on these parts.

Part d was answered much less well, in particular obtaining the irreps spanned by the normal modes of the cube. Part iii (energy level diagram) was also mis-labelled in a number of scripts. Nearly every script got the gist of the Jahn-Teller distortion in the cation, but because of errors made in earlier parts did not answer it fully correctly and lost a couple of marks accordingly.

Qu.28

Thirty one students attempted question 28. Part (a) dealt with the basics of dynamic voltammetry and reversibility criteria and shapes. As expected, the question was generally well answered. The photo-isomerisation of *E*- to *Z*-azoferrocene was (unexpectedly) only recognised by a few students. The class II mixed valency of in the CV of *E*-azoferrocene and the class I delocalisation in the product was recognized by most students. The quality in the answer to part (c) varied widely with some students achieving a full score. A mean mark of 17.05 was awarded (top mark was 25 out of 25).

Qu.29

Most candidates made competent attempts. Part (a) was framed so as to have candidates look for electron-nucleus interactions (important for the rest of the question) but this hint was not generally taken. On the whole the structures and assignments were sensible (albeit with some rather extreme outliers). Explanations for the remarkably high 1H chemical shifts in (c) were mostly focused on the wrong sort of paramagnetism. A decent number of candidates recognised that DMSO can act as a ligand but this did not always lead to an explanation of the changes observed.

Qu.30

There were 24 scripts in total and a wide range of marks obtained from 9/25 to 23/25. The average was 16.9 and this was close enough to the target value that remarking was not necessary. As usual, some of the answers were absolutely excellent and showed a thorough understanding of the course material and the ability to use that knowledge to think through unfamiliar questions. At the other end of the spectrum there were scripts which showed some basic knowledge which was directly related to that taught, but a lack of ability to go beyond that, or, in some cases, some misunderstanding of basic concepts. The lowest scoring scripts were usually incomplete in terms of answering all parts of the question.

candidate number	(a) 6	(b) 2.5	(c) 5	(d) 2.5	(e) 5	(f) 4	total
68474	3	0	3	3	3	0	12
6844W	5	2	4	3	3	3	20
6861R	6	2	2	3	3	2	18
6769Q	6	1	5	3	1	1	17
6771S	5	2	5	1	3	1	17
6772T	5	1	4	3	4	4	21
6775X	3	1	4	1	2	0	11
6779T	6	2	2	3	3	3	19
6784R	4	2	4	2	5	4	21
6789X	6	2	5	3	4	3	23
6794V	5	2	4	2	3	0	16
6796X	3	2	0	1	3	0	9
6811Q	5	1	4	1	3	3	17
6815V	3	2	1	2	3	3	14
6816W	4	2	4	3	3	3	19
6833R	5	1	4	2	3	0	15
6807T	4	2	3	3	4	1	17
6787V	5	2	5	2	1	2	17
6839Q	5	2	3	2	1	0	13
6843V	6	2	0	4	4	4	21
6855S	6	1	4	3	3	3	20
6856T	6	2	5	2	3	3	21
6863T	6	1	3	1	1	0	12
6867Q	5	1	5	0	3	2	16

Q32

A lot of good answers to this question. The balance between SN1 and SN2 and likely regioselectivity challenged a number of people in part (a). Part (b) separated the candidates between those who spotted the 1,6 relationship of two double bonds and correctly suggested a Claisen rearrangement, and those who did not and so struggled to connect starting materials and products.

Most people realised part (c) required a radical process, starting with attack on the alkyne pi-bond, but many accounts lacked a clear account of the regio and stereoselectivity involved in the processes. Part (d) was done well by most candidates, and the benzyne mechanism was found by the majority.

Qu.33

Set and Marked by DRS

Answers = 68

Average mark = 16.01

SD = 5.24
Min mark = 4
Max mark = 25

The question was generally well answered. Part (a) caused few problems, but a few did not get the order of addition correct/deprotonated the wrong position/used a MsCl mechanism for TsCl/could not translate the SN2 inversions to the correct stereochemistry. Part (b) required a 1,2-redution of the enone followed by the SN2 displacement of the mesylate. The mesylation mechanism was generally well reproduced. Part (c) required an addition of the carboxylate enolate to benzaldehyde via a cyclic transition state, cf. Zimmerman Traxler model that they had learnt. Most got this correct, but the weakest candidates just assumed that EtMgBr added to a carboxylic acid in the same way as if it was an ester, and could not get passed this assumption despite the product given. Part (d) proved to be the most problematic part. There were a few perfect answers, but not many. The initial transesterification confused a significant minority. The ‘rearrangement’ was often done incorrectly, with common mistake being not doubly deprotonating the acetoacetate or drawing a 3,5 sigmatropic rearrangement. The stereochemical outcome seemed easier to explain, along with the decarboxylation.

Qu.34

A total of 24 candidates attempted this question. The average mark for the question was 16.32 out of 25 (65.3%), with a standard deviation of 10% and a range of 10.5 to 21. A break down of the results is given in the table below.

The question was split into four sections. The following gives a summary of those sections.

a) This question dealt with a key concept in the course notes – the calculation of photolysis frequencies of species in the atmosphere. There were a number of subtle parts to the question that some but not all of the candidates picked up on. Specifically the question requires the inclusion of the column of the species under examination in the calculation of the optical depth and hence the species photolysis frequency. Not all students picked up on this. A large number (> 20%) of candidates made silly errors (unit related) in this question and so failed to score top marks on it. The average mark for this part of the question was 63%.
b) The question wants the candidates to extend their knowledge of the catalytic Ox destroying reactions covered in the lectures (HOx, NOx, ClOx, BrOx) to include the products of NF3 photolysis i.e. the FOx cycle. Almost all students achieved full marks for this question.
c) This question was used to test the knowledge that students have on the sources, sinks and reservoirs of F anf Br species and to explain why Ox loss is most important for Br rather than F. The key here is to note that the H-F bond is so strong such that the HF reservoir ends up acting as a sink. Whereas the reservoirs of Br are relatively unstable and hence Br is found mainly as BrO in the stratosphere and hence is able to destroy more Ox (on a molar basis). The average mark for this part of the question was 59%.
d) The question pushes the candidates to combine learning from the second part of the course by getting them to realize that the presence of a reactive C=C bond and a C-H bond mean that C2F2ClH will NOT be transported into the Stratosphere. The average mark for this part of the question was 64%.

Results summary:

Range	**Number**
x<10	0
10<x≤12.5	3
12.5<x≤15	7
15<x≤17.5	10
17.5<x≤20	10
20<x≤22.5	1
x>22.5	0

Qu.35

54 answers, mean mark 16.4

The three parts of the question were answered all equally well.
The 1st part asking about differences in photolysis regimes in the stratosphere and troposphere as answered the least well.
The 2nd very short part of the question on alkene/alkane oxidation schemes was very well answered.
The 3rd part of the question where reaction rates and lifetimes of atmospheric trace gases and heterogeneous reaction rates had to be calculated was answered on average satisfactory.

Qu.38
The marks for this question were wide ranging with a mean mark close to the target.

Parts (a) and (b) were reasonably well answered. The big differentiation was that some responses failed to recognise the structural context of the methylated site within DNA double helix.

There were some excellent answers to part (c) and also some that were poor. Part (c) proved to be the most discriminating part of this question.

Qu.40
40 candidates attempted this question and generally most did well. Part 1i and ii were pretty good with a few silly slips (giving diameter instead of radius and forgetting that to calculate the area of the hexagonal unit cell you need to include the angle). Part b was also pretty good with a couple of slips counting broken bonds but most doing well. Part c was also pretty good but some could not draw clear figures and indicate the fractional order spots. Most did not spot that a 2/3 coverage is also possible. In part d, most candidates came up with the reconstruction as a likely source of the square symmetry. Other sensible suggestions were also made.

Qu.42
(a) This was answered very well with more than 70% of students gaining full marks. Those that did not had not paid enough attention to the formula of the compound and so rationalised the bonding of a different molecule entirely.
(b) The cluster would need an additional two electrons to fit Wade's Rules. Those that did not

suggest this instead thought of an aromatic molecule and marks were given where the bonding for this was rationalised in a sensible manner.
(c) Many students plugged in the 5n rule where n = no. of vertices. There was an extra half mark available to those that noted that, since one electron is being provided by the CMe3 fragment, each boron needs only one extra electron to enable all bonds to become 2c-2e bonds. Most students were able to apply the 5n rule and get at least half marks for this part of the question.

Qu.43
i) Most students gave a good answer to this part of the question and explained that the bonding was predominantly ionic such that n = 1 giving M+ and R-. The extent of association depends on the size of R and most students used the (MeLi)4 example to discuss this.

ii) Depending on whether a cluster compound or a more discrete molecule (dimer) was chosen, students gave different interpretations for n and x. Marks were also awarded to those that spotted that the bonding here would be more covalent than for the group 1 metals and that it would also be electron deficient. Students lost marks in this part of the question for not discussing the type of bonding and instead focussing on rationalising their chosen values of n and x.

iii) Again, marks were given for sensible values of n and x and students answered this differently depending on whether they were thinking about cluster or discrete bonding. Marks were lost when students forgot to comment on the bonding which would be even more covalent here and, if MR4 discrete units were being considered, electron precise.

N.B. Whilst most interpreted the question as above, some answered with the transition metal groups 3 and 4 in mind which was understanable. Marks were given here for good discussions about how the metal oxidation states might change and how bonding to R groups would become more covalent for group 4 where the metals become more electronegative. Marks were also awarded for a sensible number of R groups around the central metal ions and for discussion of the likelihood and favourability of M-M bonding.

Qu.46
Most candidates recognised that the two species were taken from the extremes of the 4f-block and used this fact in their answer. Many attempted arguments based on ionicity vs covalency when simply considering the radii of the cations would have been more fruitful.
Proposing a repeat unit with correct empirical formula was done poorly.
A large proportion of candidates neglected to explain _all_ of the observations in the question.

Qu.47
Well answered: with majority of answers including a retrosynthesis as an aid to the question. Mean = 3.37

Qu.48
Well answered, with most of the answers showing good recall of simple Diels-Alder chemistry, epoxide (a^2 fragment) and reductive amination. Mean = 3.65

Qu.49
Well-answered and good understanding of the disconnections. Mean = 3.43

Qu.50
Poorly answered with poor recall of the nitro aldol reaction (Part IB) and some very sloppy reaction mechanisms . Mean = 2.91

Qu.51
Well answered and some good synthetic routes displaying good understanding of aldol reaction and regioselective alkylation of ketones. Mean = 3.48

Qu. 52
Not done very well at all, which is especially surprising at the expression for the spectral lines was given. There was the usual confusion over the difference between energy levels and transitions, plus the inability to evaluate correctly the formula for given values of *J* and *K*. [The lines are, in order of increasing frequency, (0,0), (1,1) and (1,0). *B* is 0.8518 cm^{-1}; the values of the centrifugal distortion constants are sensitive to the exact procedure by which they are fond but typical values for D_J and D_{JK} are 1.875 × 10^{-6} cm^{-1} and 1.5 × 10^{-5} cm^{-1}, respectively.]

Qu. 53
Done rather well: people either knew how to do it or did not. The final step in the proof required the use of the orthogonality of the wavefunctions, which needed to be stated explicitly for full marks.

Qu. 54
Done very well: in retrospect rather too easy. Some people attempted to use descent of symmetry (usually to C_{2v}) and came unstuck: such sophistication was not necessary as the direct product needed involved the totally symmetric irreducible representation, and so was trivial to find. [Mode 3 is IR active with PR structure, Mode 5 is IR active with PQR structure; the combination line has the same overall symmetry as the fundamental of Mode 5 and so is IR active with PQR structure.]

Qu. 55
This was done surprisingly poorly given that the derivation of D_e is an absolutely standard piece of work from Part IB Spectroscopy. There were lots of irrelevant “brain dumps” from the notes, and many trivial errors in algebra. Many people confused D_e and D_0. The last part, about the effect on D_0, hardly anybody got. [$D_e = \tilde{\omega}_e/4x_e$; D_e is unaffected by isotopic substitution; substituting e.g. a heavier atom lowers $\tilde{\omega}_e$, hence lowers the ZPE and hence *increases* D_0.]

Q56,57,58,59
Two of the 5-min questions, Q56 about Huckel theory, and Q59 about normal modes were standard. Answers were mostly correct with high average marks
(4 out of 5). This above average score was needed to offset the marks for
Q57 and Q58 which were more of a challenge. The majority of students understood what was asked in Q57 about the ionization potential and electron affinity of the H-atom. A good fraction among them, however, got the signs wrong, setting the ionization potential equal to the orbital energy or identifying the electron affinity with the difference between the energy of the anion relative to the atom. This of course made the last part of the question about the energy gap difficult to answer. Q58 about the atomic charges and bond order in the LiH dimer turned out to be the most difficult of the four, with on average rather disappointing answers.

Writing down the correct expressions for atomic charge (electronic plus nuclear) was evidently a challenge. Still there were a good number of full solutions including the proof of the relation between atomic charge and bond order.

Qu.60

49 students answered question 60, which asked to explain water exchange kinetics and electron transfer self-exchange in a couple of 3d transition metal ions. Most students recognized that factors such as LFAE and M-OH_2 bond strengths play an important role in explaining the water exchange kinetics. Although half of the students recognized the pure outer sphere electron transfer mechanism for the ET self-exchange, but a possible inner-sphere mechanism (in particular with bipy) was also often mistakenly mentioned. An average mark of 6.63 was awarded (top mark was 10 out of 10).

Qu. 61

This question was extremely popular (86 scripts) and the quality extremely variable (marks ranged from 0 to 9). I got the impression that not all the students who attempted the question had attended the course, as some answers were very ‘minimal’ and just provided a mechanism for the Diels-Alder step (which everyone will have encountered in the compulsory A2 course). Some answers were excellent.

The mean mark was 5.3. There were several very low scores (2.0 or below) that skewed the average mark. Even with a very generous marking scheme and extensive re-marking (taking several hours) it proved impossible to increase the average.

Most candidates spotted the Diels-Alder, but regioselectivity was not always discussed and only a handful of candidates attempted to explain the role of the Lewis acid. Most endo transition states were drawn the ‘wrong’ way round, though partial credit was given Mechanisms for the mesylation step were generally poor. Mechanisms for the Beckmann rearrangement were OK, though not many candidates talked about selective migration of the anti-periplanar group and even less commented upon retention of configuration in the migrating group. Credit was given for spotting the correct overall reaction sequence (Diels-Alder, activation of leaving group followed by Beckmann rearrangement).

Qu.62

Enoyl CoA hydratase question
Assignment of stereochemistry well done.
Mechanism of hydration generally well done. Needed to be explicit about orientation leading to stereochemistry.
Second part more problematical. Many answers had attack from top face and then 2 different protonation mechanisms. Some argued Glu could even move to catalyse this.
Some added glutamate as nucleophilic catalyst, then SN2 to invert at C3.
A few saw that by rotating C1-C2 bond of substrate could carry out normal catalytic reaction with opposite stereochemical outcome. This is the most probable explanation.

Qu.63

A fairly straightforward question, with the third part altered and made (I think) rather too easy. Most students had no real problems in drawing out the space group with the non-standard origin (part(a)) and few had any problems showing that the phases were 0 or pi (part(b)), although there were some silly mistakes. Determining the sign (part(c)) caused no problems at all, and all students obtained full marks for this. The marking scheme was therefore adjusted to give this part less weight.

No of attempts : 24 Average mark : 8.25/10

Qu.64

On the whole answered well with the definition of polymorphism and the outcome of solid state photochemistry illustrating topochemical control. Some answers were particularly clear in describing both the critical role of distances and orientation but only a few specified clearly that it was based on the limited motion possible within the close-packed crystal structure.

Question 65

This question was meant to be straightforward, but it seemed to cause many candidates quite a bit of difficulty.

The elementary maths involved in answering this question caused some candidates considerable problems. Many candidates could not evaluate a trivial integral. Others ignored the `hard-core' contribution to the second virial coefficient.

Furthermore, while a hint was provided that exp(x) is approximately 1+x for small x, most candidates failed to justify that x was indeed small for the exponential they were approximating. Going forward, it would be prudent for candidates answering theory questions in Chemistry Part II to brush up on their basic mathematics.

Qu.66

This question presented the candidate with derivation of some key equations in perturbation theory, concerning two perturbations of equal magnitude. This tested the core ideas of how a perturbation series is set up, and the manipulations required to derive equations for the desired quantities. From 24 papers received, the mean was 6.81/10, and was generally well answered.

Qu.70

Candidates were good at spotting the most acidic proton, explaining soft, Michael attack, showing the ring closing step and the Krapcho decarboxylation. The alternative route (enolisation of the other ester, cyclisation to give an regio-isomeric ester, then decarboxylation to the same product) was found by many people. Some credit was given for the less plausible secondary pathway of enolisation followed by thiolate attack. One of the Krapcho decarboxylations occurs on an ethyl group, unusually.

Qu.71
62 answers, mean mark 6.47

On average the question was well answered. Besides a number of students who got the maximum mark (10) there were also a few very poor answers where the students were not able to calculate the simple steady state concentration of N2O5, which had to be derived from a set of three reactions.
Not all students realised that there is a difference in the N2O5 chemistry in the troposphere and stratosphere, although most did answer this part of the question well.

Qu.73
29 candidates answered to this question, which was divided in part a) and b). The total mark was 10, 5 for part a) and 5 for part b). The range of marks was from 5 to 8.5 out of 10, with a good spread in between. Most candidates answered part a) in very well revealing an understanding of the structure of nucleic acids and their chemistry. The same was not true for part b) with many candidates only answering the question partially well. Part b) was certainly more challenging but some key concepts of the interactions of drugs with DNA which were discussed heavily in the lectures were missing with the candidates not being able to associate concepts with a concrete example.
The average score was 6.75. It was felt that for such number of scripts and the level of difficulty of the question this was appropriate and reflected how well the question had been answered by most candidates.

Qu.74
In general, attempts at this question were slightly disappointing, leading to an average mark of 5.8 despite relatively generous allocation of credit. Clarity of explanations and diagrams in part (a) was often poor, despite this material being covered explicitly in the lectures and supervisions. Two common misconceptions were apparent: (i) that charge transfer from the adsorbate significantly affects filling of the valence band, and (ii) that K arrives at the surface already ionised. Explanations of the high catalytic activity of Pt and low activity of Au (part (b)) were generally good (worryingly, a couple of candidates stated that Pt has a full d-band), but rather few candidates gave a cogent account of the relative activity of Cu.

Qu.75
Poor. Some failures to apply Huckel approximations correctly, particularly the definition for alpha and beta

QU.76
Most stated correct spatial wave functions, but did not link them with spin wave functions. Vanishing nature of triplet spatial wave function noted well, but continuous nature of wave functions only noted by one candidate.

Qu.77
Mostly well done, although few stated that m,n are required to be integers

Qu.78
Mostly well done, Hund's third rule proving the biggest challenge.

Average overall 3.19

Qu. 79–82 referred to Group Theory (from the A6) course. They were, on the whole, well done – in contrast to last year.

Qu. 79
The main problem here is that people simply did not know the geometries of the sulphur-containing species (somewhat shocking at this level). The fact that the supposed arrangement of bonds (e.g. single, double) is not relevant to the geometry of the molecules was not well-appreciated. [D_{4h}, C_{2v}, C_{2v}, D_{3h}, T_d]

Qu. 80
A set of very good answers. People knew what to do and did it accurately. [$E_{1g} + B_{2g} + A_{2u} + E_{2u}$]

Qu. 81
Certainly more difficult that Qu. 80, but several people achieved full marks, and those who attempted it at all obtained good marks. [Group 1+4: $B_{1g} + B_{2g}$; group 2+3+5+6: $B_{1u} + B_{2g} + B_{3g} + A_u$]

Qu. 82
Post people drew the MO diagram with confidence. More tricky was the effect of the ionisation. The main problem here is that people simply did not know the geometries of the sulphur-containing species (somewhat shocking at this level). The fact that the supposed arrangement of bonds (e.g. single, double) is not relevant to the geometry of the molecules was not well-appreciated. [Forming NH_3^+ involves ionizing a (largely) non-bonding electron from $2a_1$, so the effect is not large – possibly some change to the H-N-H bond angle (recalling that NH_3^{2+} is iso-electronic with planar BH_3].