

Part III Examinations 2013

Q1

20 candidates (1 M.Phil candidate) answered this question and there were a diverse range of marks corresponding from very weak answers (8/20) to excellent (19/20). Despite the style of the question, it distinguished well those candidates who knew and had a very good understanding of the material to those that could remember some relevant bits of the course but who had clearly not understand some concepts. The best answers were concise and fully addressed the question and used appropriate examples with good levels of structural and mechanistic detail. The weaker answers tended to include irrelevant information, for example, descriptions of bacterial chaperones which are not linked to disease. In addition, the weaker scripts showed a poorer understanding of the when a protein forms fibrils which results in a loss of function (sickle cell anaemia) and those that aggregate and form fibrils which results in a gain of toxic function. The average was 12.8 and the scripts did not have to be remarked. I have not included the M.Phil candidate mark in the average.

Q4

- (a) Most students had no problem with this question. Apparently, inserting numbers in an equation is difficult, because here some students made mistakes.
- (b) All students who attempted this question gave the correct answers and showed a good understanding of what was happening.
- (c) Interestingly, all those who answered this question understood what had to be done, yet all of them managed to make a mistake somewhere along the line - even though no complicated algebra was needed to obtain the answer. The result was that not a single answer was 100% correct.

Q5a

38 answers.

This was generally well answered although the conformational depictions of the Diels-Alder transition states were often distorted. Most correctly identified the endo mode of cycloaddition in the first example, although a few went for a stepwise ionic mechanism. Some candidates also suggested a stepwise ionic process for the second part. A significant number offered "arrow-pushing" answers without a clear stereochemical analysis.

Q6

Candidate a

They answered parts (bi) and (bii) satisfactorily.

Candidate b

They answered part (bi) satisfactorily and part (bii) satisfactorily.

Candidate c

They answered parts (bi) and (bii) convincingly.

Candidate d

They answered parts (bi) and (bii) satisfactorily.

Candidate e

They answered parts (bi) and (bii) satisfactorily.

Candidate f

They answered parts (bi) and (bii) convincingly.

Candidate g

They answered part (bi) satisfactorily and (bii) convincingly.

Candidate h

They answered parts (bi) and (bii) satisfactorily.

Candidate i

They answered parts (bi) and (bii) satisfactorily.

Q7

Total number of scripts: 15

Marks:

19
17
16
17
14
13
13
12
12
10
11
10
6
7
3

Sum: 180

Mean: 12.0 (re-marked) (target mean mark is 13)

Part (a): This was a fairly standard piece of bookwork about obtaining structural information from diffraction experiments, but which was not answered well. The students tended not to answer the question directly, but instead concentrated on deriving the relevant equations instead of stressing what information could be derived from their use.

Part (b): This question on the use of quasi-elastic scattering to obtain information about atomic diffusion coefficients was well answered on the whole.

Part(c): This part of the paper about the single-particle and bulk diffusion coefficient was attempted in all submitted scripts.

Practically all the students answered correctly that the difference between these two diffusion coefficients is insignificant if there are no correlations in motion of diffusing atoms.

The main difficulty was in giving mathematical definitions for single-particle and bulk diffusion coefficients.

Q8 Part (a)

Mechanism of protein phosphorylation. Wide range of answers, some clear mechanistically (eg in line with inversion), some rather scruffy incomplete answers. Few mentioned role of metal.

Second part was to describe Shokat experiment. Some good answers, some careless e.g. 31P not 32P. Some feeding ATP into cells not to lysate etc.

Q9

Scripts: 42

Average mark: 12.95/20

Answers to this question varied in quality from 8/20 through to 18/20 so there was a good spread from which it was easy to find the right average mark.

(a) Most could define what was meant by an *in vitro* assay but to get three marks, it was also necessary to mention at least two kinds of measurements associated with this, e.g. IC_{50} and EC_{50} . (3/20)

(b) Anywhere between around 8 and 13 got the mark for this. Half a mark for those with the right reason, wrong value. About 3/4 of the answers were in the right ball-park. (1/20)

(c) No mechanisms were required explicitly for this answer so no credit could be given for correct mechanisms. Many candidates gave a good answer to this part, with much room to distinguish between the very good (who scored full marks) and the less knowledgeable. (4/20)

- (d) Again, much variation possible here in the mechanism and the full range of marks used accordingly. Most got at least 1 mark and many scored full marks on this part. The most common alternative mechanism given was to form an epoxide with the mCPBA rather than oxidising the less hindered N atom in the aromatic ring. (4/20)
- (e) Credit was awarded for all variations here as well, from just saying it kept the reaction neutral because it was a base and acid was produced, through to pointing out that the Boc group might be removed under acid conditions so it prevented that from happening, through to recognising that if the Boc group was removed, the nucleophilic N on the piperazine ring might then be acylated in an unwanted side-reaction. (3/20)
- (f) I was taken aback by the number of candidates who did not get the answer to this part correct (more than half did not), as it was put in as a kind of 'easy marks' question. One mark was awarded if candidates at least used the acid to protonate and activate the Boc group but after that, the only correct mechanism really was the decarboxylation mechanism. A large number of incorrect variations on this were given. (3/20)
- (g) Almost without exception, candidates got the mark for this part but some wrote a couple of lines, some wrote a page. Writing a page was not good use of the exam time for just 5% of the question. (1/20)
- (h) Also mainly correct answers to this part but fewer candidates wrote an essay to get the 5%. (1/20)

Q10

I was a little disappointed with the answers to this question. We have covered during the course that Michael additions, using this type of catalysis, will proceed via a hetero-Diels alder/ring opening pathway. The protic additive was also a clue and its role was also covered explicitly during the lectures. A much smaller proportion of students than I expected recognised this pathway. The majority of students chose a Michael addition pathway, which while being plausible required more justification in order to explain the stereochemical outcome. If students chose this type of answer then I was looking for a description of the potential stereochemical approaches of the nucleophile in the transition state - few students made these types of argument.

Q11

19 scripts.

Part a) was answered well by most candidates, with only a few difficulties arising from the use of zeta potential. Part b) was also well answered although candidates only tended to refer to one out of static or dynamic light scattering. Part c) Was also generally answered well although several

discussed polymer scaling well but didn't actually answer the question (the changes of polymer size with temperature).

Q12:

This question was generally well-answered, with marks ranging from 9 to 17, and an average mark of 13.7. Part (a) required candidates to work out the kinetic energy of photoelectrons in a particular experiment, and this was almost uniformly answered correctly. Similarly high marks were awarded for Part (b) in which the appropriate parameters for a cylindrical hemispherical analyser were to be obtained, given a desired absolute energy resolution. Part (c) required candidates to use concepts introduced in the course to deduce the behaviour of a system they had not seen before, and the marks were accordingly more varied. Multiple possible interpretations of the data provided were possible, and marks were given for any that were consistent; top marks went to candidates who discussed a number of options and/or who fully acknowledged areas of uncertainty. Finally, Part (d) was answered well by several candidates, but a number scored lower due to failing to recognise that the question asked for details of a photoemission experiment that accessed specific states, not simply generic states "at the Fermi level". Overall, however, the answers displayed a good grasp of the principles involved.

Q13a

Mean mark 5.5/10. This question was not quite so well done as I had hoped it would be. Part (a)i was very straightforward and the vast majority of candidates correctly recalled the exact structure.

Part (a)ii was more variable. A significant number of candidates missed the nucleophilic addition to give B though most candidates correctly identified C and D. That said, a significant number used the *i*Bu group as the base and, more worryingly, quite a few conducted an ortholithiation reaction - which missed the point about synergic bases.

Part (a)iii asked for the crystal structure of C when it is obtained from THF and this section was generally a bit of a letdown. Most candidates correctly placed Al on the ortho position of the arene but several suggested an Al-Li bond. A significant number incorporated the wrong amount of THF in the structure. The cryoscopy data was often vaguely interpreted.

The correct answer was that one of the three THFs present dissociate.

Q13b

Part (i) was a simple exercise in recalling the bonding within the Al_2Me_6 dimer. Most candidates produced good diagrams though some lost marks by not including electrons in the diagram or accompanying notes. Part (ii),(a) followed a similar pattern to above. Many candidates recognised orbitals and hybridisation but provided incorrect numbers of electrons for bonding. In (b) some students did not recognise the contribution of $\text{C}\equiv\text{C}$ pi-electrons to coordinate to vacant Al centres. Extra credit was given to the few who recalled that only the nearest *sp* carbon atoms are involved in bonding to Al. Part (iii) related the stability against dissociation to the number and availability of

electrons and steric effects in bridging groups. Although few candidates produced the full, correct series, marks were still awarded for almost correct orders and good explanations.

Q14

The question was well answered on the whole. In part (a) most students correctly identified the key steps needed to get from the scattering amplitude the thermal rate constant. Some students missed out important details (such as the ratio of velocities in the DCS, and the sum over final states). In part (b) all students wrote out the flux-side time-correlation function and more-or-less understood how it is used to get the rate, although quite a few students omitted to mention the importance of allowing a plateau time to be established. In part (c) everybody was able to evaluate the integral for the charging work. In 3 out of the 7 answers the vacuum and solvent work were interchanged in solvation free energy resulting in the wrong sign. Part (c) was probably too easy for the 50 percents of the marks it was worth.

Q15

Students were required to critically examine crystallographic data [*Science* 2010, **299**, 329], propose an alternative explanation based on their observations and propose additional experiments which could be undertaken. Students typically correctly identified problems with the bond lengths but their explanations ranged in quality and treatment of ESDs was generally missing. A range of alternative explanations were proposed, the best answers taking into account the bond lengths presented in the question and the simplest being that no reaction took place. A wide range of characterisation techniques were proposed, some of which were not suitable for characterisation of the compounds in the crystals, and explanations of how the data should be interpreted varied. Detailed criticisms of the paper can be found in the literature [e.g. *Science* **1047**, 330 (2010)].

Q17

22 Scripts

Marks

A	19
B	19
C	19
D	18
E	17.5
F	13.5
G	17.5

H	21
I	19.5
J	18.5
K	18.5
L	18.5
M	16
N	13
O	15
P	14.5
Q	14
R	15.5
S	9
T	14.5
U	18.5
V	14.5
Average	16.54 / 25

Overall this question was reasonably well answered. There were no exceptional answers but there was also on one disastrous attempt

The main failure was the ability to draw decent stereochemical diagrams. Surprising given that the question gives them the 3D structure. Most mistakes were made in stereochemistry.

This tested the application of something from the notes that would stretch their knowledge. I think most did reasonably well by chance rather than intellect ! Overall, a satisfactory outcome.

Q19

This question was answered by 7 candidates . Generally it was answered well and candidates could interpret the data to come up with a good structural and mechanistic model of what was happening in the system. One made a rather basic mistake regarding pKas of different amino acids which was disappointing to see at this level, but other than this the answers were all solid. Some of the candidates missed some of the detail, e.g, at low pH they attributed effects due to H^+ rather than X^- (in this case Cl^-) despite the clue in the question. The range of marks was 13-20 and the average was

16.7. Given the low number of candidates answering the question and the fact that all candidates had got at least a 2.1 in Part II it was felt that this distribution of marks was appropriate.

Q20

29 part III Chemistry candidates answered this question PLUS one MPhil (Scientific Computing) candidate.

Note: for the marks discussed I only count the Chemists. The MPhil Computing student did appallingly (3/25 marks). He/she cannot have had any supervisions or done any of the supervision work.

Part (a) was pretty straightforward and most candidates scored 8-10 / 10 for this question.

(b) was quite discriminating with marks varying from 2 - 15 / 15.

(c) was difficult for students to score full marks on. Most marks were, on first marking, below 1/3 of the marks (below 10 / 15).

(d) part d was again discriminating. The candidates could mostly with some thought get 6/10 but the best candidates were able to stretch the marks to 9 or 10 / 10.

On first marking the average mark was below the target significantly (15 / 25)

So I re-marked part c, out of 10, allowing credit for anything in the original mark scheme. A few candidates did so well they had a bonus point on this question.

Thus now the question was marked out of 45 instead of 50.

Now the average mark is 16.57 / 25. Very slightly below the target, but there were a significant number of poor candidates who brought this down.

I am satisfied that 1st class candidates all got 1st class marks and that all candidates who scored below 15 did not produce a 2:1 answer (There was a big gap between lowest 2:1 mark of 15 and next candidate who had 12.5/25).

Overall: Range 8/25 to 24.5/25

1st class 14/29 candidates

2:1 8/29 candidates

2:2 1/29

3rd 4/29

below 3rd 2/29

Q25

- (a) This question presented no problems to the students who attempted to answer it.
- (b) This question, although slightly more difficult than question a), was also well answered by all students.
- (c) Two students out of five read the question correctly. All others ignored the fact that the charge Q of the colloids had to be kept fixed. Of the two students who understood the question, one managed to get the calculation wrong.
- (d)
- i) This question was answered well.
- ii) This question provided no major problems. However, some of the answers were less than clear.
- iii) Only one student failed to answer this question correctly.

1

Q 27

33 answers.

This question was largely well done yet produced a good spread of marks. Several candidates ignored the requirement for an asymmetric allylation in the first part, simply using an allyl Grignard reagent. Almost all did well in the second part, involving redox chemistry and protecting group manipulations. In part (c) and the first part of (d), most candidates either came up with a chelation pathway or exploited the Evans polar model for 1,3-anti stereoselection. In the final and most testing part of the question, only a minority came up with the correct intramolecular Prins reaction for formation of the 2,6-cis tetrahydropyran. Others invoked Williamson ether type processes and couldn't convincingly account for the stereocontrol.

Q30

Candidate a

They answered parts (a) and (b) convincingly. In part (c) they made a reasonable attempt at answering the question but were unable to solve for B in terms of ζ .

Candidate b

They answered parts (a) and (b) convincingly. In part (c) the student appears to have confused the quantity $\delta F(t)$, which is a single quantity, with the Dirac delta function. I infer this from the fact that they convert $\delta F(t)$ to $F(t)$ after a few lines.

Candidate c

Part (a) was answered convincingly. Part (b)(i) was satisfactorily answered, defining the velocity in terms of the individual velocities would have been appropriate. Parts (b)(ii) and (b)(iii) were answered well.

Candidate d

They answered part (a) well. In Part (b)(i) they derive the incorrect equation for the instantaneous temperature. Part (b)(ii) was answered satisfactorily. In Part(b)(iii) also mentioning that the dynamics are deterministic in the Nose-Hoover method would have been appropriate, otherwise the question was answered satisfactorily.

Candidate e

Part (a) was answered well. In Part (b)(i) the quantity 'Nk_B' should have been in the denominator and there is an extra 'T' in the final equation. In part (b)(ii) it should have been mentioned that it does not produce a canonical distribution and (iii) should have mentioned the Nose-Hoover thermostat can reproduce the canonical ensemble; otherwise the questions were answered satisfactorily. In part (c) a reasonable attempt was made to answer this question, although the final expression is incorrect.

Candidate f

Parts (a) and (b) were answered convincingly. In part (c) a very good attempt was made at answering this question, although the final expression is incorrect.

Candidate g

Parts (a) and (b) were convincingly answered. In part (c) a reasonable attempt was made at answering this question, although the final expression is incorrect.

Q32

No of scripts: 14

Marks:

25

24.5

24

23.5

23.5

23

22

21

17.5

16.5

12

10

8

8

Sum: 248.5

Mean: 17.75 (target mean 16.75)

The question was relatively easy. Part (a) was attempted by all the students and the majority of them achieved the maximum number of marks (5). The same is for parts b(i) and b(ii). In part b(iii),

some of the students did not use the Taylor series expansion valid for low external field. In the final numerical exercise, some of the students forgot to use the Boltzmann constant to convert temperature to energy units.

Q33

(a) The mechanism of ribonucleotide reductase is from the notes, so many people got an average mark for remembering most of it. Although many answers had an idea about what the key experiments were, they were generally not well presented, showing a lack of understanding.

(b) The first part was bookwork. Some recapitulated the key points, many were OK but missed key details, at the other extreme were some sloppy sketchy outlines.

The mechanism of ring opening of 3 should have been straightforward but some people managed to get so confused they formed the wrong product. Almost no-one answered the question about the significance of the formation of product 3.

Formation of 4 was more testing and got a range of answers (several mechanisms are possible). In the final part almost everyone saw that the relative amount of 4 would increase, but assumed the ratio of 2:3 would be unchanged.

Q35

Question 35 (45 minutes)

Scripts: 28

Average: 16.79/25

Generally, this question was done very well and it was easy to mark and get close to the desired average. Many people scored very well on this, balanced out by a few with very low marks (6-8) and the rest in the middle.

(a) (i) Most people scored two marks on this question but didn't necessarily follow on to do part (ii) correctly. (2/25)

(ii) Several different orders of events could be considered in this case. Activation of indole by iodine and attack of the 1,2-diazole onto the activated indole in the 2-position was the most likely but there was variation here in which position on the 1,2-diazole reacted (comment was required to justify the given answer here, i.e. attack *via* C or N). Some answers used the iodine to activate the 1,2-diazole ring for attack by the indole in the 3-position, an answer which also got a lot of credit. Without an explanation as to what the

product was, just drawing the product was not enough (those who did this usually put it in the 3-position anyway. (3/25)

- (b) This was a difficult question mechanistically, made more difficult in cases where the CN group was drawn the wrong way round in the answer. Answers varied greatly, with some missing E1cB mechanisms (doing E2 or S_N2 instead) and some with an unlikely order of steps. Most got some credit but it varied a great deal. (7.5/25)
- (c) (i) Students either knew this or they didn't in general, with some answers getting half credit where it seemed they had guessed bp solv and max T correctly but weren't clear on the meaning of lines A and B. (2/25)
- (ii) Even those who didn't get part (i) completely right had a good try at part (ii) and most people got some credit for this question. (3/25)
- (d) (i) In order to get full credit for this part, both mechanisms to form product, as well as an explanation of which would be preferred based on orbital overlap considerations was necessary. Some people only put the mechanisms and automatically lost the explanation marks. (5/25)
- (ii) Most people only put down one suggestion here, which couldn't get 2.5 marks. At least two suggestions were needed to get all the marks.(2.5/25)

Q36

Scripts: 27

Average mark: 16.66/25

General comment: Answers to this question varied in quality with many candidates achieving a clear first class mark and fewer at the lower end (12 was the lowest mark).

- (a) (i) Variation in quality of answers here, with those ones achieving full marks that had annotated the correct mechanism. All mechanisms were considered and given credit according to how plausible they were. (5/25)
- (ii) Those who suggested the hydride shift got full marks here. Those who went for deprotonation could not have two marks because it disturbs the aromatic system and is less likely. (2/25)
- (b) A very mixed bag of answers in this part, with those who made any attempt at least scoring one mark for their efforts and many getting full marks for a variety of different solutions. Those who

wrote down an answer which they then expressed doubt about and gave reasons for their doubt were given credit for it: wrong answer right thinking. (5/25)

(c) (i) Any three issues and potential solutions could be mentioned here to get the full marks available for this part. Most people scored well. (3/25)

(ii) and (iii) Text book work. Most scored well. (1/25 and 3/25 respectively)

(iv) To get two marks, candidates needed to mention four of H-bonding, potential zwitterion formation, salt bridges, the inherent chirality of pregabalin or hydrophobic interactions. Generally done well. (2/25)

(v) As long as a good reason was given, candidates could answer advantage or disadvantage to this question. Most went for it being an advantage, which I would agree with, but 'disadvantage' was not marked as wrong, as long as they said why. (1/25)

(vi) To obtain three marks, candidates needed to correctly define undesired metabolism and suggest both the use of bioisosteres and prodrugs as potential solutions. (3/25)

Q37

a) Very few people identified the correct oxazaborolidine catalyst required for this question. I would have expected them to recognise that α,β -unsaturated ester with an α -vinylic proton (drawn in explicitly) should be a match for the Corey system based on what was covered in the lectures. A large proportion of students opted for iminium catalysis suggesting that there need to be more emphasis on what substrate classes are appropriate for each form of catalysis. A surprising number of students misread the structure of the starting material as a 1,2-ketoester possibly as this is a compatible motif with Evans bis-oxazoline catalysis.

b) Answered quite well. Most students provided a clear and logical structure to their answer and used the mnemonics for the Sharpless methods appropriately.

c) I thought that students would find this question most difficult due to the unusual form of the molecules that they were presented with. Under exam pressure they have to redraw these molecules (with three-dimensional) structure within the Sharpless mnemonic and recognise that steric features of each molecule would result in a kinetic preference for dihydroxylation. This was done very well and I was impressed with how many students answered this question at a high level. Top students recognised that this was a kinetic resolution (they have not seen Sharpless dihydroxylation in kinetic resolution mode during the course).

d) A mixed bag of answers to this question. While there was only one perfect answer I was impressed by the students capacity to work around some of the problems in their syntheses based on their wider knowledge of chemistry. Again, a critical aspect was that a significant proportion did not recognise the type of catalysis that was needed based on matching the catalyst structure (a secondary amine) with the α,β -unsaturated aldehyde.

Conclusions: A clear deficiency was recognising the motifs within substrates and applying the correct form of catalysis. There are probably less than ten of these that need to be committed to

memory during the course so I would expect most people to be capable of doing this. This is certainly an aspect of the course that I will place more emphasis on next year. Aside from this issue, some aspects answered very well such as the application of mnemonics in unusual situations and use of wider chemistry knowledge in synthetic planning.

Q38

14 Scripts

Marks

A	20.5
B	22
C	20.5
D	19
E	18
F	16.5
G	14.5
H	15.5
I	13.5
J	15
K	15
L	11
M	12.5
N	13
Average	16.17 / 25

This question should have been answered better than it was. It was all relatively straight forward but I had to mark generously. The spread of marks is fairly even with no one doing disastrously badly, but not many doing well.

Most people got part a although attention to detail let many down. No one got b completely correct and in general most failed to address any aspect of the stereochemical outcome. Part c was either very good or fundamentally flawed in their thinking, more good than bad though. Part d was routine, and part e was generally fine except the same problem of attention to detail throughout.

Overall, this could have been answered better but then I always think people should have done better.....

Q39

21 scripts.

Parts a) and b) were answered well by essentially every candidate, with only a few minor difficulties. Part c) was also generally answered well although several candidates could not identify the location of the cmc and took different parts of the graph to estimate the area per molecule in the micelle. Part d) was answered correctly by most candidates. Part e) was generally well attempted. Most candidates were aware of the packing parameter, even if they didn't call it that, and the divisions that delineated the different micellar shapes. Part f) was also reasonably well attempted. Several candidates did not know the difference between Gibbs and Langmuir layers although there were some nice answers with some discussion of which method gives a more representative value for the area per molecule of a surfactant.

Q40

Average for six scripts is 19.3/25.

This year the question was answered very well, and the general principles and applications of atomic force microscopy were well understood by all the students. The quantitative questions were also answered well, but in some cases the evaluation of the persistence length proved to be more challenging.

Q43

Mean mark 16.8/25. This question was generally quite well done. Part 1 was essentially bookwork but was done very well by most candidates - correctly identifying aggregation state and coordination mode.

Part 2 was a mixture of bookwork and deduction, though a surprising number of candidates did this part of the question only rather poorly. Only a small number perceived the relevance of hybridization at the carbon atom and the implications of this for the closure of a 4-membered chelate that would stabilize the metal. Most candidates opted instead for a rather vague steric argument.

The final section was based on candidates thinking beyond the scope of lectures. It was generally done to a better standard than I had expected.

Most candidates grasped the Fries rearrangement issue and understood the essentials of how heterometallic synergic bases operate. A significant number of candidates had a good go at the crystal structure of the final product, incorporating the amide ligand (and correctly identifying the

eliminated EtH). The main errors were in claiming that BuLi can successfully orthodeprotonate C and in the suggestion of incorrect aggregation states or stabilization modes in the structure of F.

Q41

This question was tackled well by most candidates, with scores ranging between 12 and 21, and an average mark of 17.2. Part (a) was very straightforward, and all but two candidates scored full marks here. Part (b) involved reproducing a derivation from the notes, and all but two candidates did a good job here too. The importance of using Auger ratios rather than absolute intensities was the subject of Part (c), and it was a little disappointing that there was some variation in the quality of answers here; some were clear and concise, while others were either clear or concise but not both. Finally, Part (d) required candidates to make use of the information given in the question, together with the expression quoted in Part (b), to estimate the thickness of a molecular overlayer; here again the answers were variable, due to an assortment of numerical slips and/or misapprehension of the fact that the expression to be used represents proportionality not equality. Nevertheless, the candidates generally showed a sound grasp of the concepts involved in this question.

Q42

This question was tackled well by all candidates, with marks ranging from 13 to 22, and an average mark of 18.0. Part (a) required the candidates to reproduce a derivation from the notes, commenting in particular upon how and why the resulting expression differs from the expression given in the question. All candidates managed to produce some reasonable version of the correct derivation, which is quite convoluted and involves multiple steps of logic, and the main point of discrimination therefore turned out to be the extent to which they fully brought out the two-dimensional aspect of their derivation versus the three-dimensional aspects that would have led to the expression given in the question. Part (b) asked the candidates to identify the likely nature of a set of three states observed in a hypothetical inverse photoemission experiment, to explain why such states ought to be quantised, and to deduce the work function of the surface. All candidates correctly identified the states as image states; the origin of quantisation was explained to varying degrees of validity; and the work function was evaluated correctly by only a few candidates. Overall, the answers revealed a pleasing level of understanding amongst the candidates.

Q44

Section (a) was intended to exhibit the candidates' knowledge and understanding of broadest principles of the course. Being the single section which carried the most weight, it also showed the widest variation in marks between answers. All candidates scored some marks. The weaker answers were generally restricted to a discussion on Wurtz coupling methods only. The stronger candidates were able to include techniques based on reaction of metastable M(I) and M(II) halides with carbon

nucleophiles, and mentioned the preferences of hexamer *versus* tetramer formation based on metal and ligand bulk. Very few recalled icosahedral clusters. Credit was given to those who gave examples of metal-metal multiple bonding and metallo-aromatic systems. Section (b) was highly structured but featured increasing levels of difficulty in order to differentiate between candidates. Part (i) was a simple example from the notes which almost universally was given full marks. Part (ii) was also from the lecture material and all students were able to recall the structure. Some included a simple valence-bond description of the bonding. Full marks were given to those who could also provide a molecular-orbital diagram and accompanying explanation. Compound (c) had not been featured in the notes but the stronger candidates were able to perform a cluster electron count and recognise it obeyed Wade's rules for *closo* compounds. Section (c) was generally answered well and most candidates were able to produce a simple molecular-orbital diagram showing the bonding within the fragment. Nearly all recognised the influence of the inert-pair effect on bonding with extra credit given to those who mentioned relativistic effects operating at the extreme bottom of the group. Section (d) was designed to test students' ability to apply some principles covered in the lecture material to an unfamiliar example and resulted in a wide spectrum of answers produced. A fair proportion described the back-bonding from iron d-orbitals into empty gallium p-orbitals though not many identified the maximum bond order of three. Only a few candidates recognised the competing pi donation from the Cp* fragment as the reason for the longer Ga-Fe bond length.

Q45

This question was rather poorly answered, with only one first class script (out of five). Most students coped well with part (a), giving good diagrams and formulae illustrating differential and integral cross sections, and explaining the role of phase shifts. Part (b) was less well answered, although several of the candidates did manage to get the correct asymptotic form of the radial wave function. Part (c) was answered very badly, despite part (i) having been a supervision question, which most students at the time had answered competently.

Q46

Conceptually everybody understood what was to be done. I was rather happy with that. Part (a) was no problem. All answers were essentially correct. (bi) amounts to evaluating the partition function over the reactant well, This is what everybody did although one student forgot to integrate over the negative coordinates (this gives the factor 1/2 in the expression for the probability). Part c(i) involves a very similar integral but now over the barrier region. Again, the integration splits up into two intervals, basically the same integral, but if you get it wrong, you won't recover the exponent of the activation energy, which is what happened in two cases. Part c(ii) was clearly somewhat too challenging. All answers mentioned that the friction must be high for Kramers theory to be valid, but finding the expression comparing the friction and drift force was asking for too much.

Q47

Students were required to apply their understanding of supramolecular principles, molecular components and data to determine the structures formed and explain the driving forces behind the

transformations that took place. Many students did not make use of the isotopomeric data in determining their answers to parts a) and b) and understanding of ligand exchange at the platinum centres was generally poor. Students did better in the second half of the paper (d-f) and were generally able to identify the role of the component presented and the rearrangement that was induced. Stronger answers explained the driving forces behind the transformations and used supramolecular terminology (e.g. [3]catenane, mechanical bond, cryptand etc.) to describe the products and processes. Literature reference [*JACS* 2013, **135**, 2084].

Q48

Students were required to apply their understanding of supramolecular chemistry principles, molecular components and data to determine the structures formed and explain the driving forces behind the transformations that took place. Students generally answered the question well, giving the structures expected in each step and explaining the observations that were made. In section b) better answers showed an appreciation of the dynamic nature of the bonding and addressed the experimental observations made. A wide range of kinetic and thermodynamic explanations were given to explain gel formation in d) with the best answers considering both enthalpic and entropic balances in the system. Answers in part f) were judged entirely on their own merit and good answers for the system being both reversible and non-reversible were given. Literature reference *JACS* 2011, **133**, 3158.

Q51

18 Scripts

Marks

A	20
B	17.5
C	21.5
D	19.5
E	19.5
F	17
G	17
H	16.5
I	18.5
J	14.5

K	19.5
L	14.5
M	18.5
N	7.5
O	13.5
P	14
Q	8.5
R	11.5
Average	16.06 / 25

Overall this question was about average. There were a few low marks that bring the average down but otherwise most scripts were of solid 2.1 and low 1st class. There were no exceptional answers.

Most people failed to address the first part correctly with only one person answering this well. Most overlooked the problem of stereochemistry. Some gave fairly crazy answers. Part b and c were generally fine but these were the 'give-away' marks of the question. D was moderate with no one really addressing the stereochemistry but most got the general idea. The final part was generally poor and should have been straightforward.

I thought this was a pretty decent question that provided an opportunity to show their knowledge and apply it. Not outstandingly answered but overall about average.

Q52

17 Scripts

Marks

A	22.5
B	18.5
C	17
D	20.5
E	21
F	14
G	16.5
H	15.5

I	14
J	17.5
K	16.5
L	18
M	14
N	14
O	13.5
P	16.5
Q	14
Average	16.67 / 25

Overall this question was reasonably well answered. There was one or two exceptional answers and no real disasters.

The main failure was the first question with only one person realising that it was an oxophilic Ti reagent that makes the reaction go 1,2 and the the 18-C-6 helps an oxy cope rearrangement. They should have done better with this. Otherwise everything else in the question was a reasonable spread.

This tested the application of something from the notes that would stretch their knowledge.

Overall, a satisfactory outcome.

Q53

The question was attempted in full by all candidates that chose it, indicating that it was not excessively hard or long. Part (a) required candidates to recall the fundamentals of polyketide biosynthesis, which was covered comprehensively in lectures. Generally, this was handled well, although in some cases excessive detail was provided (it is not necessary to provide a schematic of every round of chain extension, for example) and a few did not provide enough detail (steps or co-factors missing in the pathway). The timing of the unusual incorporation of glycerol was correctly predicted by all candidates, despite it being an unfamiliar pathway that required some invention. Marks were awarded for a detailed and logical pathway that used appropriate reagents/co-factors and accurate arrow pushing. Part (b) required students to identify inactive domains and unusual features in a polyketide synthase (PKS), and therefore required an interpretation that extended material given in the course. The inactive domains were identified by most students, although very few noted that the PKS had no thioesterase (TE) domain. TE domains are found in all type I PKSs described in the course, so an absence of this domain should have been noticed as being unusual. Alternative answers for this question were marked on merit. Part (c) required students to be inventive with an unfamiliar substrate. The ideal pathway involved a Diels-Alder reaction, which is a

step encountered in supervision material. Marks were awarded for correct arrow pushing and for a conformational analysis showing the production of the correct stereoisomer. Suitable oxidative biochemistry was required for the final step, which was an extension of lecture material. No arrow pushing was required for the oxidation but an appreciation of enzyme type and co-factor was expected. As before, alternative pathways were marked on merit.

Question IDP 1

This question was attempted by 31 candidates. Average mark was 16.2, with a standard deviation of 4.6, a maximum of 24 and a minimum of 3. The division of marks between sections was as advertised.

Section (a) was in general well answered, although the limitations were frequently dealt with very sketchily. For those attempting the question seriously, parts (b)-(e) were generally well understood and answered, the main problem being that candidates did not read the question carefully and therefore did not answer all parts (e.g. 'Explain why values.....' in part (b)). Apart from numerical slips, part (c) was well answered, although as part of the required comment candidates frequently did not account properly for the emissivity change and asserted (wrongly) that there did not appear to be a reduction in emission from the 'atmosphere'. This aspect should be clarified in the lectures.

There is an error/ambiguity in the wording of section (d) which should have asked the candidates to evaluate a revised atmospheric temperature (see below). Most candidates who attempted this section understood the intent and answered the question as intended, although 3 candidates expressed confusion in their scripts, and did not answer the section fully. These candidates were given an additional 2 marks (the entire section has 5 marks allocated).

There was a significant spread of answers to section (e).

Corrections for section (d) (shown in red).

Geo-engineering of the climate has been suggested as a means of mitigating the effects of increasing CO₂ amounts. One suggestion is to inject sulphate aerosol into the stratosphere in order to increase the Earth's albedo, thereby reducing incoming solar flux and offsetting the surface warming. Using the 1 layer model, determine what change in the Earth's albedo would be required in order to completely offset the reduction in IR transmission obtained in (c) **and compute the new atmospheric temperature**. Suggest two possible impacts of the revised atmospheric temperature **you obtained in (d)**.

Question IDP 2

This question was attempted by 21 candidates. Average mark was 16.7, with a standard deviation of 4.3, a maximum of 21 and a minimum of 7. The division of marks between sections was as advertised.

As is evident from the smaller spread of marks, there were no near perfect answers, largely because no candidate really grasped the detail of part (e).

There was a wide spread of comprehensiveness and relevance to the answers given to part (a) – again candidates should read the question. Part (b) was OK, except that the significance of the mixing time (that it must be quite high) was missed by many. For those who made a serious attempt, part (c) produced some good answers.

For those who made serious attempts, part (d) was well answered. The formalism of the continuity equation was properly understood, although several candidates made numerical errors, particularly in the conversion of the deposition velocity to a rate constant (which was hinted at in part (c)). The best candidates made plausible attempts at section (e), although no-one addressed it in the detail presented to them in the lectures.