

### Part III

#### Qu.1

Generally well answered. For part (a) a surprising number of candidates did not appreciate that powder methods permit much more accurate measurement of intensities. Part (b) caused no problems at all, and the only marks dropped here were through carelessness.. For part (c) they had to think, and most did it very well, although, in fairness, they had met similar problems before. Part (d) was mostly straightforward, but a surprising number of candidates seemed to find difficulty relating this to part (c).

No. of answers : 16

Average mark : 13.5/20

#### Qu.3

The 'Soft Matter' part of this question was short and required almost no calculations.

It assumed that the candidates knew how to compute the Debye-Hückel screening length (something that was treated in the lectures and the exercises).

Part (a) asked to explain/sketch how the screening changes as a monovalent salt is replaced by a divalent salt. Almost all candidates could sketch the effect, but quite a few did not get the numerical factor right.

Part (b) asked the candidates to sketch the effect of the refractive index of the medium on the dispersion forces between colloids. Again, most candidates had no problems with this question.

Finally, part (c) combined parts (a) and (b) and was, on the whole, answered very well.

#### Qu.4,

**Q 4a (paper 1)** 29 answers. This was reasonably well answered although the conformational depictions of the transition states were often distorted. Almost all identified the Ireland-Claisen rearrangement in the first example, but a good number could not assign the product stereochemistry correctly. In the second part, some candidates went for a chelation pathway but the majority proposed the correct Evans polar acyclic model – although some still got the stereochemistry wrong. Overall, this proved to be a good question for testing the manipulation of chiral structures in 3D and converting these into "zig-zag" stereochemical representations.

part (b), marked out of ten, for half the question

25 Answers

Generally good answers. Drawing the final structure in 3D is hard and there were a lot of good representations, although a few were missing carbon atoms, some showed six-membered rings as flat hexagons instead of chairs or boats, and getting all of the stereochemistry correct and consistent with the starting material is challenging. Cyclisation onto the triple bond goes to the kinetically favoured five-membered ring and not to a six-membered ring.

Mean mark - 6/10 - a small number of very low marks, probably from candidates who had timed the exam badly, depressed the average. Without four of the scripts, the average mark was almost 7/10, reflecting the high standard of most answers.

Q6

This question was attempted by 25 candidates.

Most candidates could correctly give the entropic and enthalpic arguments for the stability of vesicles (Part ai). However, a number could not do both. Parts aii and ii were both well answered with the vast majority able to address these correctly. Part b most could correctly identify that the ionic strength would reduce head to head repulsion inside the vesicle and made some sensible suggestions over what that would do, mainly a reduction in size, rather than budding. Part c was also reasonably well addressed with the hydrophobic effect identified and described in terms of water entropy. The effects of electrostatic interactions was also reasonably well covered and its secondary effect on the CMC.

Q7

Setter / marker Jane Clarke

17 scripts. Mark range 19.5/20 - 7/20

**Mean mark 13.4**

There were a similar number of 1<sup>st</sup> and 2:1 scripts with 2 @ 2:2 and 2 @ 3<sup>rd</sup> class.

Two candidates had near perfect scores (19.5/20) which pushed the mean up a little above the target.

Part (a) was very straightforward, book learning and most candidates got high marks (4 or 5 / 5)

(b) was surprisingly difficult. Many answers were trivial, without giving examples as asked. Given the weighting candidates should have noticed they were too superficial. Mark range 4.5 – 1 / 5 The best candidates really stood out here.

(c) I was very pleased at the way that most candidates did well on what I thought might be a difficult question.

I adjusted the marking scheme for this part. I had meant to mark / 20, but the two best scripts had answers that I could not fault and they had 13 marks.

Thus credit was given for each point made and this question was marked out of 13 and then adjusted to / 10.

Q8:

Most grasped that DABCO (B) should link the Zn-porphyrin-containing building blocks A and C together into three distinct structures, and that the hetero-structure is statistically favoured over the homo-structures. Some encountered difficulties when contemplating what the addition of Cu(I) would do to these structures, when the geometries of the building blocks precluded the formation of products having Cu(N)<sub>4</sub> coordination environments. Credit was given for reasonable inferences (across all questions marked) wherever these were made.

## Qu.9

Scripts: 35

Average mark: 12.9/20

Answers to this question varied in quality from 8/20 through to 18/20 so there was a good spread from which average mark was generated readily.

(a) (i) Hardly any candidates got full marks for this part, which was surprising as it was designed as a basic chemistry lead in that most should find to be 'easy marks'. It seemed that some had not read the question and so did not attempt to give a role for all the reagents and the solvent (hence losing marks straight away) and some simply did not know what the roles were. (4/20)

(ii) A variety of answers to this part, varying in credibility but each one marked on its own merits: most candidates scored at least one mark on this part and a good proportion ended up with 3 or 4 marks. (4/20)

(b) This was a mechanistic puzzle worth 8 marks and there were a good variety of pericyclic and ionic mechanisms, either noticing that the acetic anhydride was present or discounting it (and making life more difficult). Lots of scope here to differentiate between candidates: if an attempt was made, the marks given really ranged from 2/8 through to 8/8. (8/8)

## Q9a Report

This question was not done quite so well as I had expected it would be. The mean mark was 6.3/10.

Most candidates correctly saw that the imine would lithiate to give a tetramer. However quite a number also suggested that the amine would lithiate and then undergo limited laddering. This is in spite of the lectures explicitly covering the fact that the ether would prevent that and that a dimer should form.

Most candidates identified the correct site of metallation of the phosphane oxide in the next part. However, a very large number  $sp^2$  hybridized the deprotonated carbon in spite of being given a distinctly aliphatic chemical shift of 32 ppm in the  $^{13}C$  NMR spectrum (quite a few people seemed to ignore/not comment on this piece of data though a few clearly thought the shift was reasonable for  $sp^2$ ). Many candidates suggested a reasonable solid-state aggregate (a tetramer) though several seemed to suggest an extended network. The coupling to  $^{31}P$  and  $^6Li$  was handled very well.

## Qu.10

a) I was generally quite pleased about how students attempted this question. There are a number of different ways that the molecule could be synthesised and while the Sharpless asymmetric epoxidation is the best method to use in reality I also allowed other approaches. Using the SAE method, the main subsequent issue was construction of the [2.2.2] scaffold. Getting the order of steps correct can avoid selectivity issues, in particular when an epoxide and another leaving group are both available as electrophiles. For such an issue, very few students even commented that there would potentially be a competition. Attempting to construct the molecules using a Sharpless dihydroxylation was also common. This route could have some pitfalls including the amine itself binding to the Os catalyst and promoting a racemic background reaction but this could potentially be avoided by making a salt in practice. What I would have expected more attention on was how the molecule would fit into the mnemonic; this was often done incorrectly or the dihydroxylation precursor was misinterpreted as chiral. Other than that, most answers had some minor mistakes such as failure to include a base to activate the thiol as a nucleophile. This question is not overly difficult but was answered well nevertheless. Andy McNally.

**b) 10 Marks.** Some excellent answers, with candidates spotting the double allylation, RCM and Heck. There were a variety of plausible answers which perhaps contained flaws in chemo and regioselectivity but were given appropriate credit. A couple were clearly lost and scored quite poorly, even though all fragments needed to get to the product were given, which is surprising. The loss of two carbons on route to the product should have suggested loss of ethane as in RCM and in the course a fair amount of emphasis was placed on RCM, so it was hoped the student should spot this. Rob Phipps

Q10 – 25 scripts. Broad spread of marks, from 6/20 to 19/20. The average was 13/20.

Q.11 paper 1

Total number of scripts: 6

Marks: 16, 16.5, 20.5, 21, 23, 23.5

Mean: 20.1

Part (a): This part of the question about the common features and differences between diffusion in liquids and solids was surprisingly challenging for practically all the students. Thermally activated nature of diffusive motion both in liquids and solids was not spotted.

Part (b): For part (i), only a few students derived the expression for the mean squared displacement. The others just quoted the results.

For part (ii), none of the students noticed the the sum does not depend in index  $i$  due to translational invariance.

The rest of the question was answered correctly by the majority of the students.

**Q.11**

Total number of scripts: 9; Average mark: 14.9

Part (a): This part of the question about the direct-exchange mechanism of diffusion was attempted in all submitted scripts. Only several students answered this question correctly. The majority of the students described the interstitialcy mechanism instead.

Part (b): Note many students gave the derivation for the mean-squared displacement (which is very similar to that discussed in Question 6.1 after lecture 6) and just quoted the result. The rest of the question was answered mainly correctly.

Part (c): This section of the question on the atomic packing fraction of the fluorite crystal was attempted by all candidates. Most answered the question well, despite this particular derivation not having been

covered in lectures, with only a couple of students not being able to calculate the correct answer for the packing fraction.

#### Qu.12

This question was answered particularly well. The majority of students gave a coherent account of the XPS and NEXAFS techniques for part (a), which was essentially bookwork. The remaining parts of the question required students to combine XPS/NEXAFS information given in the question to deduce possible adsorption geometries for a particular molecule, and nearly everybody made a very creditable effort. Nobody managed to pick up on everything, but equally there were no poor attempts.

#### Qu.14 (parts a and b) (MS to add line or two about part c)

Parts (a) and (b) were well answered on the whole. Students understood that conservation of the angular momentum vector confines the scattering of two structureless particles to a plane, and were able to derive correctly the classical equations of motion describing this motion.

#### Qu.15

This question simply called for recall of some principles and examples which were covered in the lecture material. In general, this was not answered particularly well, probably as it was the last topic in the lecture series and has not generally been examined on, it was perceived as being unlikely to appear. Most candidates were able to identify at least some of the problems associated with using the precursors mentioned in the question and some the main advantages of single-source precursors. Stronger candidates could also give examples of the precursors used and identify the specific issues encountered when depositing group 13 nitrides.

#### Qu.17

Gave a good spread of marks for those that had time to do the question but quite a number of students appeared to only have time to give a partial answer.

In part (a) most got reasonable answers for getting to the linear C<sub>40</sub> precursor, though many got the rearrangement via a cyclopropyl cation (given in lectures) a bit wrong. For the cyclisation reactions a variety of plausible reactions were suggested though in most cases the answers were considerably more long-winded than the correct answer.

In part (b) most students knew (or got some sort of approximation of) the cyclo-oxygenase mechanism (which was from notes) but there were a spread of answers for the conversion of the initial prostaglandin intermediate to thromboxane, most of which involved unnecessary oxidation and reduction reactions.

#### Qu18

Answers to this question varied considerably. A surprising proportion of candidates could not provide a satisfactory answer to part (a), although it was straight from the lectures. Answers to part (b) were better, but only one candidate got it completely right. Part (c) was also rather surprising, as at least three candidates got this completely wrong, despite it being straight from lectures. By contrast, part (d), which required some thought, was very well answered, and most candidates also made a decent

attempt at describing the refinement of the metal atom co-ordinates, although not all appreciated the use of the difference density to locate the oxygen atoms.

No. of answers : 13

Average mark : 16.0/25

Qu.19

This question was only answered by about half of those taking the course. Part (a), which was straight from the lectures, was generally quite well done, but part (b) did cause some problems, indicating that the concept of the Power Spectrum did not go down too well. In particular, it appeared that the limitations due to chromatic aberration were only appreciated by less than half of those answering the question. Part (c) however, was surprisingly well answered, with four attempts scoring full marks and the rest being quite respectable. On the other hand, part (d), which definitely required a deeper understanding, was only successful for less than half of the candidates.

No. of answers : 8

Average mark : 18.3/25

Qu.23

All ingredients of this question had been treated either during lectures or exercises, but not in this combination.

Part (a) involved a simple integration and was done well by most candidates.

Part (b) required the candidates to know how to apply the Derjaguin approximation. This type of question had appeared in previous exams and was done well by most, but not all.

Part (c) went followed the excluded-volume route to compute depletion forces. It was a minor modification of an exercise – yet quite a few candidates made mistakes in computing the ‘doubly excluded’ volume.

Part (d) was answered well (although not necessarily eloquently).

Part (e) was answered very well by almost all candidates – as was to be expected, as this had been discussed during the exercises.

**Q 24 (paper 2)** 27 answers. This question was on the whole well done although there were only a few excellent answers. Almost all did well in the first part, involving an Evans syn glycolate aldol reaction. In the more testing part (b), only a few candidates came up with a chelated Z-enolate pathway and a rationalisation of the sense of stereoinduction was not attempted in most answers. In the final part of the question, a convincing exo transition structure to account for the outcome of the intramolecular Diels-Alder reaction was required. The artistic merits of the 3D conformational representations of transition states varied greatly.

Q25

12 Answers

A tough question, with a great deal to explain, and requiring knowledge of a wide range of chemistry. The standard of answers was high. Most candidates answered (a) and (b) well. For part (c), a number introduced a base which is not present in the reaction, and did not explain the regiochemistry of the

first step. However, the Julia-Julia-like process was analysed well. The NHC-dimerisation (d) followed by intramolecular ring-forming was usually analysed effectively. Part (e) was found to be the hardest, with only a few finding the interrupted-Pummerer mechanism which leads to a Claisen rearrangement to make the final product.

Mean mark - 18/25. This is rather high, but reflects a large amount of very high quality work. This question was clearly selected by students who are confident with the subject.

#### Q28 – Chemistry at small lengthscales

This question was attempted by 26 candidates and rather well answered by most.

Parts a and b were generally well answered by most candidates. There was a typo in one value in the table of data given but no-one seemed to have made any error based on this. One or two did not know the best concentration to estimate the area per molecule in a micelle. Most got a sensible area per molecule. Part c was also generally well answered with the insolubility of the surfactant, the area per molecule and the relation between Gibbs and Volmer approaches well presented. Other than some minor slips with calculations, most got the molecular volume correct and correctly determined the packing parameter in part d. The deductions about the expected shape were essentially correct although few delineated between the different possible inverted structures. Almost all candidates correctly identified the expected variation of the micelle shape with temperature in part e. Part f was the least well answered with rather superficial understanding of what information AFM and neutron reflection can provide.

#### Qu.29

This question was well answered with most students being comfortable with quantifying the nanoscale behaviour of polymers and describing key experimental techniques for their analysis.

#### Qu.30

Although only seven candidates answered this question, there was a wide range of marks from 8 to 23 out of 25, with a good spread in between. The lowest mark of 8 was mainly due to the candidate not answering half of the question. In this case, the answers for the parts of the question attempted were ok. At the other end of the scale the mark of 23 was for a near perfect answer to all sections. Many of the candidates gave poor answers to part b) which was disappointing as this was generally lecture material, however, many had misread/misinterpreted the question which asked how to characterise intermediate states not how to detect them (which was part a)). At this level I was surprised by the lack of understanding of the term characterise. The final parts of the question d)-f) were challenging and it was gratifying to see many good answers in this section. Even if the candidates did not propose the correct model in part d) they were able to logically think through the problems and their model and came up with good answers to parts e) and f). This showed generally an excellent understanding of complex kinetic schemes. Not including the mark of 8 (which was for a very complete answer), the average score was 16.2 (for all seven scripts this drops to 15). It was felt that for such a small number of scripts this was appropriate and reflected how well the question had been answered.

#### Q31

Setter / marker Jane Clarke

10 scripts. Mark range 23.5/25 - 10/25

### Mean mark 16.95

Part (a) was straightforward, with marks lost for not including units as asked (or getting units wrong!)

(b) was more tricky, but three candidates got full marks.

(c) was found by candidates to be the most difficult, The important point to work out was that protein folding is unimolecular and association is bi-molecular – another case of comparing units. Marks ranged from 10/10 to 0/10

(d) was more straightforward than I had & thought most candidates did well

(e) Most candidates could do this but many lost marks for not explaining their reasoning in detail.

There was no need to remark or reassign or reweight the marks.

### Q32:

Most students understood that molecular topology was at the heart of the question. Some did not grasp the significance of the MS fragmentation patterns on topology - this was key information. Those who were able to bring together NMR and MS information generally did quite well.

### Q33

Most understood the sandwich structure of the adduct between 1 and 2, but some did not grasp that 4 has a non-planar ground-state structure.

Understanding that binding between 2 and 4 destabilised the non-planar form 4 relative to its planar transition state to bowl inversion was the key to the final part of the question.

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### Question 34 (45 Minutes)

Scripts: 21

Average mark: 16.76/25

General comment: Answers to this question varied in quality but many candidates achieved a clear first class mark and there were fewer at the lower end (10 was the lowest mark).

(a) Almost without exception, candidates scored 3 or 4 marks on this question. Very well answered. (4/25)

(b) (i) Generally answered well: all candidates scored at least 1/2 available marks with many getting 2/2. (2/25)

(ii) Huge variation in the answers and suggested mechanisms for this part. Anything vaguely sensible got credit and very few candidates gave a fully correct answer. (4/25)



- (c) (i) Generally, the mechanistic part was answered very well, with some giving a much more concise explanation which was awarded equal credit to those who used up more time to draw duplicate diagrams. (3/25)
- (ii) Most candidates could provide one completely correct method for this and one method with a mistake or incorrect structure. This meant mainly candidates scored between 2/4 and 4/4. (4/25)
- (d) (i) Good variation in methods and explanations here leading to clear differentiation between candidates, marks varying between 1/5 and 5/5. (5/25)
- (ii) Class was divided on whether Champix is chiral, which was interesting (this was anticipated to be a 'give away mark') but even if they got that part wrong, they usually picked up the two remaining marks for this part, as there was a lot of scope for saying something reasonable (two reasonable facts generated two marks). (3/25)

### Question 35 (45 minutes)

Scripts: 24

Average: 16.37/25

Generally, this question was done well: 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 low marks (7-10) and the rest in the middle.

- (a) (i) Several different ideas put forward for this part with varying degrees of success. Most could score at least 3/5 with what they put down. (5/25)
- (ii) Memory work. Students could get one mark if they put down the basic definition of an agonist and an antagonist and two if they added a little extra information on rate of dissociation or the sub-divisions that there are within the broad definitions. (2/25)
- (iii) Also straight from the course material: one mark available for saying that clinical trials take many years and usually pick up most problems. The second mark available for then making a suggestion for why the problem might sometimes be picked up later, e.g. extreme adverse reaction in a small minority of the population. (2/25)
- (b) This question was generally well done and a correct answer, which mentioned stereochemistry was worth full marks. A correct answer which did not mention stereochemistry was given 3 marks and one which did not use a 1,3-dipolar

cycloaddition mechanism but was still relatively sensible (i.e. arrows pushed in the right direction) could still gain 2 marks. (4/25)

- (c) (i) The mechanistic part was not easy and credit was awarded evenly for all plausible possibilities for the cyclisation part, even if they were less likely than the electrocyclic mechanism proposed in the paper. (4/25)
- (ii) One mark available for suggesting  $^{15}\text{N}$  labelling and the second for a piece of additional information regarding the NMR and/or how this would help to answer the question of where the N atoms end up in the product. (2/25)
- (d) Variable answers to this question, with most candidates being awarded at least 3 marks. Unseen heterocycle type but most had a good go at it, which reflects well on the course being aimed towards students then being able to apply their knowledge of a group of known heterocycles to new situations. (6/25)

#### Qu.36

There was a broad spread of marks, from 4/25 to 22/25. The average was 16.3/25. Owing to the one script which was barely attempted (4/25), the whole average was brought down significantly – if this outlier were excluded, the average would be 17.3.

**a) 6 Marks.** This was intended to be Nicholas-type reaction. Whilst a number of students used the Nicholas reaction, identifying the giveaway propargylic alcohol, only one did it via the proposed oxonium formation/fragmentation. Most opted to do the fragmentation separately with TBAF. Two students didn't write anything for this question.

**b) 9 Marks.** Generally well done although fewer than expected got the hydrozirconation-transmetallation to copper. Many did conjugate addn of a cuprated alkyne followed by dissolving metal reduction, which is OK although this could present challenges wrt reduction of the ketone. Nearly everyone got the Suzuki coupling but a few opted to try to do a highly challenging  $\text{sp}^3\text{-sp}^3$  suzuki on a substrate likely to be very prone to beta-hydride elimination. Stereochemistry was generally well explained.

**c) 10 Marks.** Only one candidate saw that this can be achieved by most concisely and with high control via an alkyne-containing fragment via insertion and tandem Suzuki coupling. Most tried to do Suzuki/heck with a halogenated alkene fragment, which could also be valid but presents more challenges. Often this leads to stereochemical problems what looks like the correct haloalkene would actually lead to the wrong double bond isomer after rotation and beta hydride elimination. In some cases, no rationale was given for the double bond isomer obtained.

#### Qu.37

Again, I was generally pleased the answers to this question. In particular, students did very well in parts (b) and (c) and so the marking scheme was adjusted slightly to allow me to better differentiate

answers. Surprisingly, part (a) involving asymmetric hydrogenation caused some problems. Placing the molecule into the mnemonic should be straightforward based on the course notes but this was not always done properly. Few answers identified that the reaction is a dynamic kinetic resolution even though this should be realised from the information in the question and makes sense based on the pKa of the substrate and the reaction conditions. Part (d) is more open-ended and saw a variety of answers. A relatively simple disconnection returns a chiral benzylic alcohol and I was encouraged to see that a substantial amount of students could then identify the CBS reduction method as the most appropriate choice. Other catalytic asymmetric methods were allowed for full marks but often resulted in problems in the synthetic route and subsequently lower quality answers. Aside from some of the errors with asymmetric hydrogenation, students appear to be able to apply the catalytic asymmetric methods quite well. Andy McNally

22 scripts, average 16.9/25.

#### Q38 (L2: Solid Electrolytes)

This question tested candidates on their knowledge of defect reactions in oxide materials, resulting either from non-stoichiometry or aliovalent doping, as applied to titania. Much of the subject of the question had either been covered in lectures or was a straightforward development of such material. However, much of the question was rather badly answered.

a) All candidates answered this correctly.

b) All candidates answered the first part (i) correctly, but none got the second part (ii) correct: they all neglected the fact that oxygen vacancies are also created as well as titanium interstitials.

c) Most obtained the correct expression for the electron concentration resulting from the creation of just oxygen vacancies (i), but none got the correct formula in the case of the formation also of Ti interstitials (ii). Almost all correctly identified that the non-stoichiometric material would be n-type electronically.

d) All correctly wrote down the 2 alternative defect reactions each for the incorporation of aliovalent trivalent or pentavalent oxides in titania.

e) However, few managed to do well in this (rather straightforward) part of the question. Almost none recognised that the relative ionic radii given in the question meant that Ga and Nb ions could substitute readily for Ti ions, and none realized that the much larger size of Y ions meant that no defect reactions involving the substitution of them for Ti ions on lattice sites in titania would be likely to occur. And most candidates also failed to realize that vacancy-creation reactions would be more prevalent than the conjugate interstitial-creation reactions.

f) Most realized that oxygen-vacancy creation would lead to increased oxygen-ion conductivity, but failed to realize that the creation of oxygen interstitials would do the same.

Number of answers: 7. Average mark: 13.3

Qu.39

Total number of scripts: 6

Marks: 16, 16.5, 20.5, 21, 23, 23.5

Mean: 20.1

Part (a): This part of the question about the common features and differences between diffusion in liquids and solids was surprisingly challenging for practically all the students. Thermally activated nature of diffusive motion both in liquids and solids was not spotted.

Part (b): For part (i), only a few students derived the expression for the mean squared displacement. The others just quoted the results.

For part (ii), none of the students noticed the sum does not depend in index  $i$  due to translational invariance. The rest of the question was answered correctly by the majority of the students.

Qu.40

Again, this question was answered rather well. Part (a) was essentially bookwork, requiring a description of the Mott polarimeter and a discussion of its use in measurements of surface magnetism; this was uniformly handled well by the candidates. Similarly uniform results were obtained for part (b), which required a fairly straightforward application of standard ideas discussed in the course. Part (c) was potentially more taxing, but hidden beneath an unfamiliar context the solution really required only the use of a well-known trig identity; again, there was pretty much uniform success in tackling this section of the question. The main differentiation between candidates therefore arose in part (d), which again took a standard idea from the course into unfamiliar territory; here, around half the candidates achieved nearly full marks, while the other half gained very few. Overall, however, the performance on this question was gratifying.

#### Qu.41

This question was answered well by those students who attempted it. Nevertheless, the fact that there were only around half as many scripts as for the other surface science questions suggests that several candidates were put off by its apparent difficulty. Certainly, part (a) required candidates to apply their abstract understanding of projected bulk states to a concrete example, and this will have involved a degree of three-dimensional visualisation that some may have found daunting. In the event, only one candidate was entirely successful in this endeavour, with the others doing rather poorly. On the other hand, part (b) required a fairly substantial derivation to be replicated, covered only partially in the lecture notes and supervision questions; all but one candidate did very well here, and even the less successful attempt was creditable. Part (c) presented no problems, albeit it required only a brief qualitative statement following on from the previous quantitative sections. Finally, part (d) will have stretched the candidates into unfamiliar territory, but most succeeded in getting at least half-way to a solution. Again, the performance of candidates in this question was generally very good, albeit there appears to have been some self-selection that perhaps saw less confident candidates preferring other questions.

#### Q42 22 Scripts Average mark 16.82/25

Some pleasing answers across all parts of the question. The correlation in part (c) with regard to melting points was particularly well handled and some even considered whether a cocrystal would in fact be observed for the weaker halogen bonds. Part (d) had much more variation in quality of answer. Those who handled it well described the role of templating molecules well but in many instances the structures produced would have been more appropriate for dimerisation rather than polymerisation. The balance between h-bonding and X-bonding in many instances made well. Overall a well-handled question.

#### Q43 13 Scripts Average mark 17.0/25

In general each part was reasonably well handled although perhaps the weakest overall were part (c) and (e). The general process for CSP was well described and the use of energy minimisation and selection of space groups covered. In (b) the main criticism would be that few explained that it would be necessary when comparing energies of the anhydrate and hydrate to take the energy of water into account. Also in part (e) the actual process of relating observed diffraction pattern to putative diffraction patterns from low energy structures was rarely described well.

#### Q44

Part (a) was well answered, with students demonstrating a good understanding of the concept of a side-side time-correlation function, and its use for simulating reaction rates. Part (b) was less well answered, with students preferring to use qualitative reasoning to explain why the rate constant is

independent of dividing surface, rather than proving that it is so (i.e. deriving it mathematically). Part (c) was reasonably well answered, with candidates correctly identifying the saddle point on the given potential energy surface.

#### Qu.46

a)i) This introductory part of the question simply involved a recall of the different bonding descriptions of carbon-based alkenes and those of the heavier group 14 elements. This was answered well universally, with all candidates giving a sketch of the orbitals involved, their hybridization and dot/cross representations of the electrons involved in bonding.

ii) Descriptions of how these differences manifested themselves varied widely across the year group. Most indicated correctly that weak bonding resulted in monomer / dimer equilibrium with heavier group 14 derivatives reacting as monomers. A smaller proportion of candidates were able to recall that the different orbitals used in bonding compared to alkenes allowed for unusual cycloaddition reactions, giving examples. Some described the ability of monomer units to act as ligands to transition metals.

iii) This part of the question required a description of a bonding situation not previously encountered in the lectures, using principles learned in the course. This was generally answered extremely well, with candidates indicating the correct orbital hybridizations and source of bonding electrons.

b)The description of the bonding in these two systems was covered in detail in lectures. Most candidates indicated correctly the main principle that sp orbital mixing from bending lowered the energy of the  $a_{1g}$  antibonding orbital in the 14 electron system. The variation in answers was mainly down to the quality of molecular orbital diagrams drawn, with credit being given to correctly-indicated phases / nodal planes and symmetry labels.

c)i) This question required a recall of principles learned in 1B (Wade's Rules). A good proportion of candidates were able to apply these rules and predict a 14-electron *nido* structure but none went further to describe the types of molecular orbitals used.

ii) The alternative bonding description required the consideration of cyclobutadiene in a similar manner to cyclopentadiene, which was covered in lectures. The resulting MO diagrams are actually almost identical, but only the stronger candidates recognised this and drew the diagram correctly. Weaker answers showed just an interaction with the ligand  $\pi$  system and the metal. None showed the correct nodes in the MOs for the ligand, but this did not affect the final diagram for the ligand-metal complex.

#### Q47 Report

This question was generally well done. The mean mark was 16.5/25.

Almost all candidates got the maximum mark for the first part – though it was straightforward bookwork.

The second part of the question proved more variable. Most candidates got the right idea but were too vague in their answers. For example, recognising that Al had more outer electrons than Zn and that this prevented reaction, but not arguing precisely that for Zn you can get a 16-18-16 outer

electron count whereas for Al the outer shell is complete. Sketches of transition states were generally drawn too vaguely e.g. not clearly discriminating between full and partial (forming/breaking) bonds but rather just showing basic connectivities between atoms.

For part three of the question many candidates struggled with the cryoscopy and the implications of solvent loss for the formation of a C-Li bond in solution. Quite a few candidates also struggled with why the molecule exists in two forms. The NMR assignments were generally very well done though.

Qu.50

Only 3 scripts were received. All three seemed to be from talented and knowledgeable students. In part (a) one student got the answer almost completely right (except used alanine + phenethylamine instead of tryptophan), whereas the other two used more round-about approaches but still plausible chemistry for the most part. In part

(b) also, one student got the pathway exactly right (noticing that the alkaloid was one from the handout, though drawn differently) whereas the other two used more round-about approaches but still plausible chemistry. The resulting average mark was 18.0 out of 25.

Qu.51:

The question was answered well by most candidates, so a reasonably strict marking scheme was employed. In order to distinguish between the best answers, some marks were available for naming enzymes specific to type 2 PKS systems (eg cyclases and KSb, including its role which was briefly discussed in lectures), and full marks for the loss of an oxygen during biosynthesis of the aromatic core were only available to those who followed the type 2 route, rather than the dehydratase route employed by type 1 systems. Likewise, mention/demonstration of satellite peaks (part b), detection of  $^{18}\text{O}$  incorporation via shifts in the attached  $^{13}\text{C}$  chemical shift (part c) and sugar activation by NDP/TDP (part d) were required for full marks to be awarded.

Average mark obtained for this question : 16.8/25

### **IDP1**

A total of 25 students attempted this question. The average mark for the question was 16.78 out of 25 (67.1%), with a standard deviation of 2.83. The marks ranged from 10.5 to 22.5. As can be seen from the table below, no students scored under 10 (<40%), but 2 students scored between 40-50%.

The main point that a number of students neglected to mention in part (a) was the contrast in absorptive properties of the atmosphere between incoming solar visible radiation and outgoing emitted infrared radiation. Most students performed reasonably well in part (b) and gave several relevant points, although only a few students gave enough details to be awarded all of the marks. The vast majority of students performed very well on the calculations in parts (c), (d) and (e) and

received most of the available marks, with the exception of the additional explanation in (e) about the importance of the positive carbon cycle feedback for climate mitigation. However, part (f) proved to be challenging and only a few students managed to compute the integral and give the correct estimate the time for atmospheric CO<sub>2</sub> levels to return to present day values.

The marks used were (out of 25): (a) 5; (b) 6.5; (c) 4.0; (d) 2.0; (e) 1.25; and (f) 6.25. These were slightly amended from those given in the exam to account for the fact that almost all students performed very well on parts (c) and (d).

Range	Number
$x < 10$	0
$10 < x \leq 12.5$	2
$12.5 < x \leq 15$	3
$15 < x \leq 17.5$	11
$17.5 < x \leq 20$	7
$20 < x \leq 22.5$	2
$x > 22.5$	0

Part	Av mark
(a)	3.42/5
(b)	4.61/6.5
(c)	3.78/4
(d)	1.83/2
(e)	0.78/1.25
(f)	2.36/6.25



### **IDP3**

A total of 18 students attempted this question. The average mark for the question was 16.78 out of 25 (67.5%), with a standard deviation of 2.31. The marks ranged from 12.5 to 20.5. Only one student was awarded 50% or less.

In part (a), most students gave a couple of relevant points, but only a few gave enough detail in order to be awarded all available marks. Most students performed very well in parts (b) and (c) and gave accurate answers for the derivation and calculation. There were more mistakes in the calculations in part (e), where some students neglected to calculate the new tropopause temperature or account for the change in tropopause pressure in their calculation of the saturation vapour pressure under climate change. The main point that was missed in many of the answers to part (d) was that most transport into the stratosphere occurs in the tropics as a result of the stratospheric overturning circulation. In part (f), most people got the main effects of an increase in stratospheric water vapour on the production of HOx and therefore on the efficiency of the HOx catalytic cycle. However, many students failed to mention all of the other potential indirect effects in order to get all of the marks. It appears that a number of students may have run out of time in part (f).

The marks used were (out of 25): (a) 5.5; (b) 4; (c) 1.25; (d) 4; (e) 3.75; and (f) 6.5. These were slightly amended from those given in the exam to account for the fact that almost all students performed very well on parts (b) and (c).

<b>Range</b>	<b>Number</b>
$x < 10$	0
$10 < x \leq 12.5$	1
$12.5 < x \leq 15$	5
$15 < x \leq 17.5$	4
$17.5 < x \leq 20$	7
$20 < x \leq 22.5$	1
$x > 22.5$	0

<b>Part</b>	<b>Av mark</b>
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(a)	2.81/5.5
(b)	3.64/4
(c)	1.15/1.25
(d)	2.99/4
(e)	2.79/3.75
(f)	3.40/6.5