IMPERIAL COLLEGE LONDON

M.Eng EXAMINATION IN CHEMICAL ENGINEERING 2019

PART III and IV

and

M.Sc. in ADVANCED CHEMICAL ENGINEERING

For Internal Students of Imperial College London

This paper is also taken for the relevant examination
for the Associateship

PRODUCT CHARACTERISATION

Monday 13th May 14:00-15:30

Answer all four questions

**THIS EXAMINATION PAPER HAS SIX PAGES IN TOTAL
WHICH INCLUDES THIS COVER SHEET**

Before starting, please make sure that the paper is complete. Ask the invigilator for a replacement if your copy is faulty

Question 1 carries 25 marks
Question 2 carries 25 marks
Question 3 carries 25 marks
Question 4 carries 25 marks

TURN OVER FOR QUESTIONS

Question 1 **[25 marks]**

A new fruit packaging allows the controlled release of plant growth regulator, namely methylcyclopropene. The packaging is made of a polymeric matrix, which is decorated with particles of a microporous and crystalline material that corresponds to a so-called metal organic framework (MOF). Owing to their porosity, the MOF particles can be loaded with methylcyclopropene.

(a) Sketch the profiles of the N_2 sorption isotherms at 77 K of the MOF particles before and after use of the food packaging (assuming some loss of the plant growth regulator). For these two isotherms, describe each part of the isotherm and explain any difference between them.

[6 marks]

(b) One of the product quality control steps of the food packaging manufacturing is a Differential Scanning Calorimetry (DSC) analysis of the polymeric matrix.

(i) Explain the principle of the DSC technique. **[3 marks]**

(ii) Sketch the DSC trace you expect for the polymeric matrix. Annotate the features. **[4 marks]**

[7 marks for part b in total]

(c) Discuss the possible thermogravimetric (TG) curve profiles for the entire fruit packaging – *i.e.* polymer, MOF, methylcyclopropene – before use (in N_2). Explain your reasoning. *Note:* a MOF contains an organic component and a metallic component.

[6 marks]

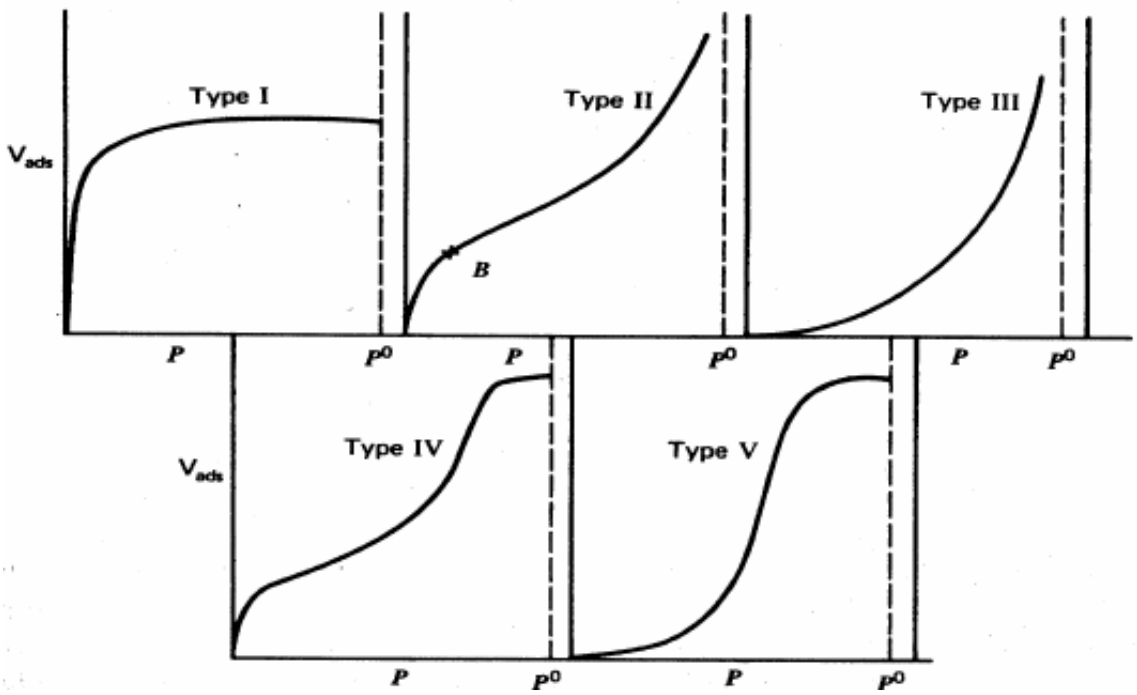
(d) A sensitive component of the food packaging is the MOF. If degraded, the MOF loses its ordered structure and porosity. How could one probe MOF degradation? Cite and describe at least two techniques.

[6 marks]

END OF QUESTION 1

Question 2 **[25 marks]**

Below are important diagrams relating to gas adsorption isotherms:



Answer the following questions:

(a) For determining the surface area of a porous sample, which isotherm(s) are best suited for doing this and why **[2 Marks]**

(b) Explain why nitrogen gas adsorption experiments are always conducted at 77 K rather than 298 K. If you wanted to BET characterise a material at 298 K propose, with a reason, a candidate molecule for such an experiment [**2 Marks**]

(c) You are currently developing a micro-porous catalyst <u>support</u> based on silica. Which of the above isotherm(s) could be observed for nitrogen adsorption on this material? **[2 Marks]**

(d) When Pt catalyst <u>particles</u> are added onto this <u>catalyst support</u>, making a complete catalyst, what type of isotherm is most likely to be observed for chemisorption onto the catalyst**?** **[2 Marks]**

QUESTION 2 CONTINUES

(e) Experimental BET analysis of your catalyst support and the catalyst support with Pt gave V_m values of 10 and 200 cm^3/gm respectively.

(i) What is the surface area of both samples? [**5 Marks**]

(ii) Are these estimates reasonable with respect to expected values ?

[**2 Marks**]

(iii) Would you expect the **c** constants to be different for both of these isotherms, and if so how? [**2 Marks**]

(f) Give an industrial or a practical example (non-catalyst) where the use of water vapour isotherms would be valuable in product characterisation. Clearly indicate why the data obtained would be critical in the characterisation of the specific product chosen. Describe briefly an experimental approach for the isotherm measurements

[8 Marks]

Data for Question 2:

(Name	Symbol	Value	Units, e.g.:)
Cross section area toluene	σ	34.3×10^{-20}	m^2
Avogadro's Constant	N_A	6.023×10^{23}	

Formulas for Question 2:

$$\frac{p}{V(p_o - p)} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c}\frac{p}{p_o}$$

p is the vapour pressure, p_o is the saturated vapour pressure, V is the volume of vapour adsorbed, V_m is the volume of vapour adsorbed at monolayer coverage and c measure of the heat of adsorption

END OF QUESTION 2

Question 3 **[25 marks]**

a) Many particulate systems are shear thinning in nature, i.e. their viscosity decreases as the shear rate increases, why is this so?

[5 Marks]

b) You are the manufacturer of a new cleaning product which is a suspension comprised of: water; an abrasive (calcium carbonate particles roughly 10 micron in size); a surfactant and a polymeric thickener. This suspension is non-Newtonian in nature.

You need to determine the rheological properties of this suspension under conditions corresponding to:

(i) The manufacturing process, which involves mixing and pumping;

(ii) The product simply sitting on the shelf, (a condition where no, or at least very minimal, sedimentation is occurring).

Describe **an** experiment for **each** of the above conditions which you would perform to determine the rheology of the suspension. Your answer should include the rationale for your choice, the equipment you would use and the type of data which you would expect to obtain.

[20 marks]

END OF QUESTION 3

Question 4

What two techniques would you choose to determine the particle size **and** particle size distribution of each of the following products? **In all cases**, explain your choice of methods **and** how you would conduct the experiments.

a) Sugar crystals in chocolate, believed to be around 20 μm in diameter.

[5 marks]

b) Carbon particles in car tyres, believed to be around 100 nm in diameter.

[5 marks]

c) Oil droplets in mayonnaise, believed to be around 10 μm in diameter.

[5 marks]

d) Gold nanoparticles used in homogeneous catalysis, believed to be around 10 nm in diameter.

[5 marks]

e) Titanium dioxide in paint, believed to be around 200 nm in diameter.

[5 marks]

END OF PAPER

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PRODUCT CHARACTERISATION

Wednesday 29th April 2020: 10:00 - 11:30

Answer all three questions

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Question 1 carries 25 marks
Question 2 carries 35 marks
Question 3 carries 40 marks

TURN OVER FOR QUESTION

Question 1 **[25 marks]**

Silica gel is an amorphous and porous form of silicon dioxide, SiO_2, with pores typically between 2 and 7 nm. Often manufactured in the form of small beads, it is commonly used as a desiccant. The beads can be doped with a moisture indicator that gradually changes colour when transitioning from the dry state to the moist state. An example of dopant is the organic molecule *methyl violet*.

(a) We first consider the thermogravimetric analysis of silica gel beads.

(i) **Sketch** the thermogravimetric curves under a N_2 atmosphere for the doped and un-doped forms of silica gel. **Label** the step(s).

(ii) **Explain** any change(s) to the curves observed for an analysis performed under air instead of N_2.

(iii) **Explain** any change(s) to the curves observed when using smaller beads of doped silica gel.

(iv) **Sketch** the thermogravimetric curve for the un-doped form of silica gel after months of usage (N_2 atmosphere). **Label** the step(s).

[8 marks]

(b) We now consider the porosity analysis of silica gel beads (Figure 1.1).

(i) **Calculate** the total volume of pores of the product.

(ii) Indicating any assumption(s) made, **derive** the maximum water uptake of the silica gel beads in mmol per gram of beads.

(iii) **Propose** an experiment one could conduct to determine the maximum water uptake of the silica gel beads.

[10 marks]

(c) Considering Figure 1.2, **determine** a lower bound for the energy required to desorb water from the silica gel beads. Explain your reasoning and indicate any assumption(s) made. *Hint: one needs to heat the product at the desired temperature.*

[7 marks]

QUESTION 1 CONTINUES
TURN OVER FOR data

Data for Question 1:

Name	Symbol	Value	Units
Gas constant	R	8.314	m^3 Pa mol^{-1} K^{-1}
Molar volume of liquid nitrogen at 77 K	V_M	34.65 x 10^{-6}	m^3 mol^{-1}
Molar mass of water		18	g mol^{-1}
Density of liquid water	ρ	1	g cm^{-3}

Figures for Question 1:

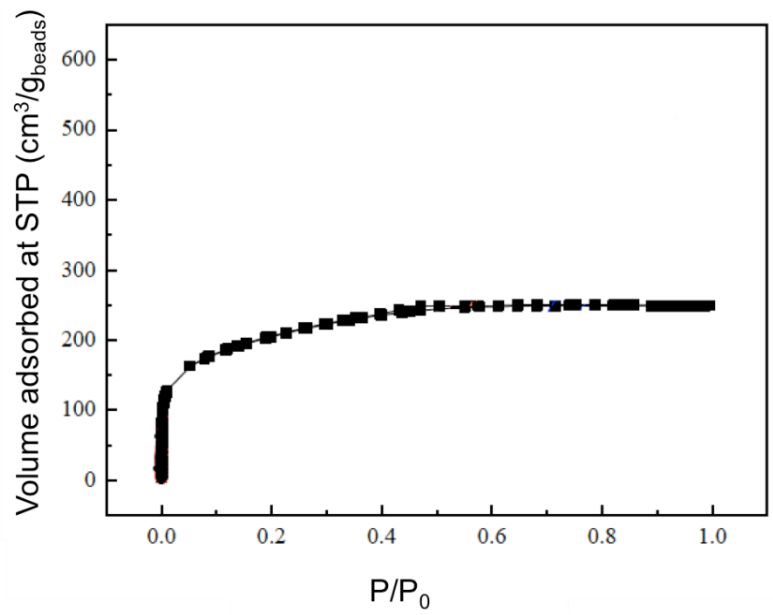

Figure 1.1. N_2 sorption isotherms for silica gel beads at 77 K (adapted from: *K L Yan and Q Wang 2018 IOP Conf. Ser.: Earth Environ. Sci.153 022010*).

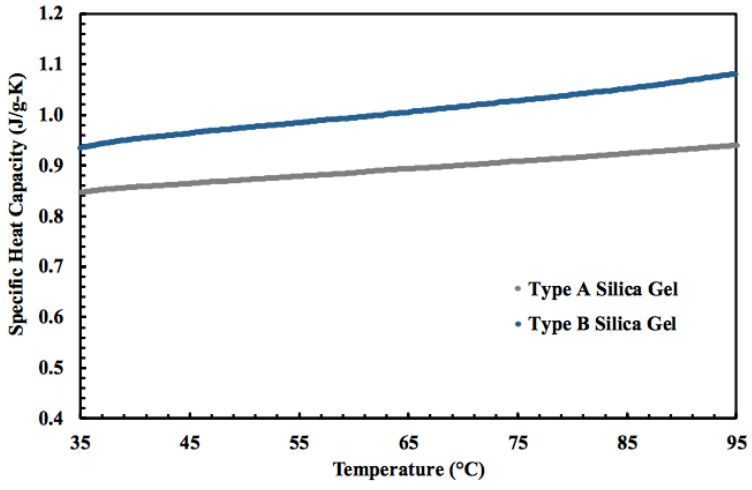

Figure 1.2. Heat capacity derived from DSC analyses for two types of silica gel (adapted from: *Islam et al. Proceedings of International Forum for Green Asia 2017, P-19*).

END OF QUESTION 1

TURN OVER

Question 2 **[35 marks]**

a) **Define** what is meant by the following rheological terms:

i) Stress
ii) Strain
iii) Strain rate
iv) Yield stress

[8 marks]

b) Figure 2.1 shows some rheological data for a micronized starch (MS) based wood adhesive (MSWA) which contains various amounts of the surfactant sodium dodecyl sulfate.Figure 2.1 A and 2.B were the result of an oscillatory shear experiment and plots the storage modulus, G' loss modulus, G" and tan(δ) as a function of the angular frequency.

i) **Describe** how such an experiment would be performed.

[5 marks]

ii) What is the inter-relation between the maximum stress and strain experienced during the oscillatory experiment and G', G" and tan(δ)?

[6 marks]

iii) What experiment should have been performed before the experiments reported in Figures 2.1A and 2.1B? **Explain** why this should be done.

[4 marks]

iv) Based on the rheological data, **describe** how the microstructure of the micronized starch adhesive is changing as the concentration of sodium dodecyl sulfate is increasing.

[6 marks]

v) **Indicate** which microscopy techniques could be used to study this product. **Explain** your answer.

[6 marks]

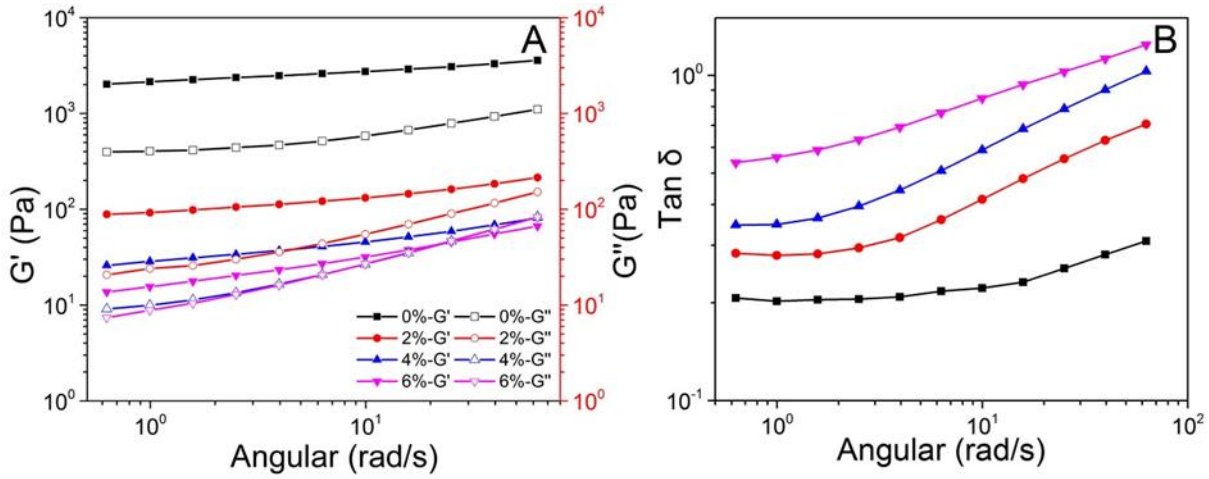

Figure 2.1. Result of an oscillatory shear experiment and plots the storage modulus, G' loss modulus, G" and tan(δ) as a function of the angular frequency and different sodium dodecyl concentrations. Adapted from a paper by Lei Chen Zhouyi Xiong, QingLi Ziaud Din and Hanguo Xiong, *International Journal of Biological Macromolecules* Volume 140, 1 November 2019, Pages 1026-1036.

END OF QUESTION 2

Question 3 **[40 marks]**

(a) **Sketch** the Infrared and Raman spectra of liquid CO_2. **Provide** notations for the axes; **indicate** the approximate positions of the spectral bands and briefly **explain** the origin of these spectral bands.

[10 marks]

(b) The ^{56}FeH diatomic molecule absorbs infrared light having a wavenumber of 1661.0 cm^{-1}. **Calculate** the wavenumber and frequency of light that ^{54}FeH would absorb. You may assume that mass of hydrogen atom is one atomic mass unit; velocity of light (c) = 2.998×10^8 m s^{-1}.

[5 marks]

(c) **Write** the expression for the Beer-Lambert Law in infrared absorption spectroscopy and **define** every term. The molar absorption coefficient (molar absorptivity) for an infrared band of a dye dissolved in 200 micrometres thick polymer film is 0.5×10^6 cm^2 mol^{-1}. The measured absorbance of this band is 0.1. **Calculate** the concentration of the dye in the polymer film.

[5 marks]

(d) How would you measure the distribution of substances during tablet dissolution using FTIR spectroscopic imaging? **Describe** the approach and relevant phenomena that can be studied using this approach. **Provide** approximate values for measured areas that can be analysed by this approach. **Support** your explanation with corresponding schematics and equations as appropriate.

[10 marks]

(e) Which spectroscopic technique would you use to differentiate single-walled carbon nanotubes of different diameters? **Explain** why.

[10 marks]

END OF QUESTION 3

END OF PAPER

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PRODUCT CHARACTERISATION

Thursday 6th May 2021: 10:00 - 11:30

Answer all three questions

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WHICH INCLUDES THIS COVER SHEET**

Question 1 carries 30 marks
Question 2 carries 30 marks
Question 3 carries 40 marks

TURN OVER FOR QUESTION

Question 1 **[30 marks]**

We consider a set of microporous zeolites which are used either to separate methanol and isopropanol (Zeolite A), or to separate n-hexane and 2,3-dimethlybutane (Zeolite B), or as a drug delivery carrier (Zeolite C).

(a) Using the data available below, **assign** the pore size distribution to zeolite A, zeolite, B and zeolite C. Justify your answer.

[5 marks]

(b) Some zeolites can also be used to adsorb CO_2 *via* a physisorption mechanism.
(i) **Sketch** the CO_2 adsorption isotherms at three different temperatures of your choice. Justify your answer.
(ii) **Explain** how the CO_2 adsorption isotherms might change if adsorption proceeds via a chemisorption mechanism.

[5 marks]

(c) The manufacturer of Zeolite A claims that its product can uptake up to 80 mmol of N_2 per gram of product. Using the data available to you, **demonstrate** that this claim is unfounded.

[5 marks]

(d) Zeolites can serve as catalysts. To enhance their performance as catalyst, they can be impregnated with a metal.
(i) **Sketch** the DSC profiles of a zeolite before and after impregnation with a metal.
(ii) **Propose** how one could use DSC to quantitatively assess the amount of metal impregnated.

[5 marks]

(e) A label for a Zeolite B used to uptake volatile organic compounds (VOCs) reads "a minimum energy of 235 J g^{-1} is required to desorb VOCs and regenerate the product". **Calculate** the minimum temperature at which the zeolite must be heated to be regenerated. Indicate any assumption(s) made.

[5 marks]

QUESTION 1 CONTINUES
TURN OVER FOR Part (f)

(f) We now consider the thermogravimetric analyses of zeolites. **Sketch** the thermogravimetric curves (from room temperature to 1000 ^{o}C) for these three cases, **label** the different steps and **justify** your answer:

(i) Pure zeolite under N_2 atmosphere;

(ii) Metal impregnated zeolite under O_2 atmosphere;

(iii) Amine impregnated zeolite under air atmosphere (note: the amine is an organic amine).

[5 marks]

Data for Question 1:

Name	Symbol	Value	Units
Kinetic diameter methanol	-	3.8	Å
Kinetic diameter isopropanol	-	4.7	Å
Kinetic diameter n-hexane	-	4.3	Å
Kinetic diameter 2,3-dimethlybutane	-	5.8	Å
Kinetic diameter of 5-fluorouracil (anticancer drug)	-	6	Å
Total volume of pores for zeolite A	V_{tot}	1.5	$cm^3\ g^{-1}$
Specific surface area for zeolite A	S_{BET}	855	$m^2\ g^{-1}$
Heat capacity of zeolite B at 298 K	C_p	0.75	$J\ g^{-1}\ K^{-1}$
Heat capacity of zeolite B at 373 K	C_p	0.85	$J\ g^{-1}\ K^{-1}$
Heat capacity of zeolite B at 473 K	C_p	0.95	$J\ g^{-1}\ K^{-1}$
Gas constant	R	8.314	$m^3\ Pa\ mol^{-1}\ K^{-1}$
Molar volume of liquid nitrogen at 77 K	V_M	34.65×10^{-6}	$m^3\ mol^{-1}$

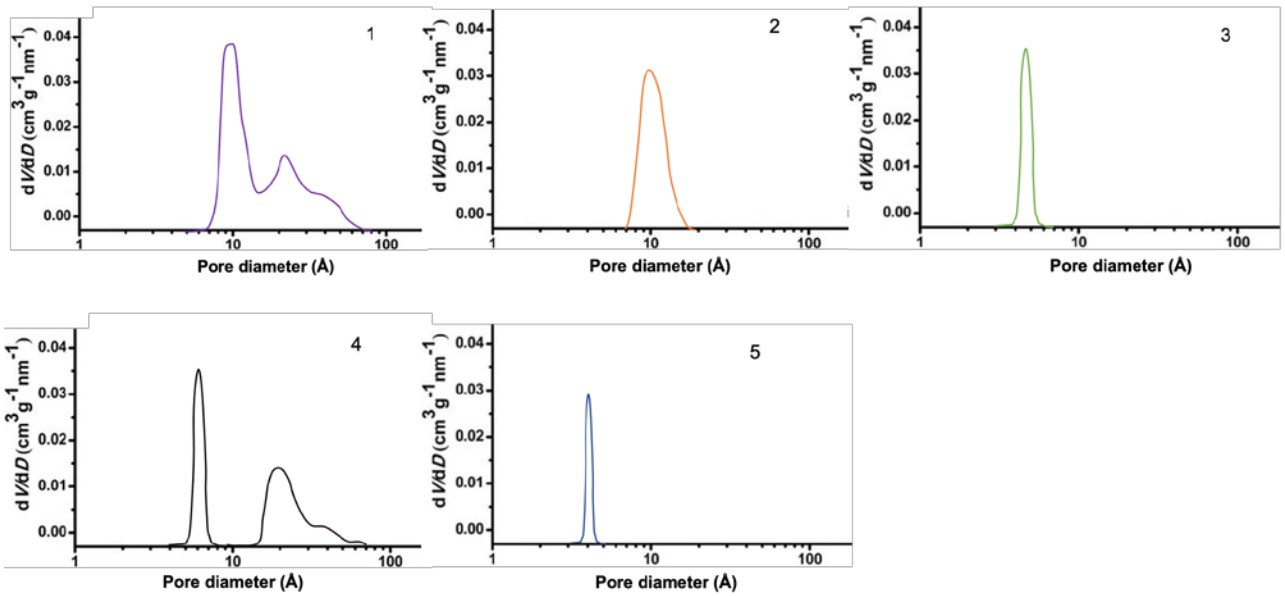

Fig. 1. Pore size distributions for various products.

END OF QUESTION 1

TURN OVER

Question 2 **[30 marks]**

You are to prepare a masonry paint consisting amongst other constituents of 5 micrometre diameter titania particles (density 4200 $kg \cdot m^{-3}$), which are sold as a powder and 200 nm diameter polymer latex particles (density 1200 $kg \cdot m^{-3}$), which are sold as a dispersion in water (density 1000 $kg.m^{-3}$). You purchase these particles, but need to ensure the quality of the particles regarding particle size.

(a) Briefly describe **two** techniques which you could use to size **each** of these particles.

[8 marks]

You formulate the water-based paint but find that the larger particles settle which is undesirable. You measure the rheology of the paint and find that it is Newtonian with a viscosity of 50 $mPa \cdot s^{-1}$.

(b) Calculate the sedimentation velocity of the titania particles and hence estimate how long it would take for all the particles to settle to the bottom of the can.

[8 marks]

(c) You want the paint to have a shelf life of 2 years, without more than 1 cm sedimentation of the particles.

(i) How would you achieve this? (Note that you cannot change the particle size of the titania as this would spoil the desired texture of the paint).

(ii) Sketch the rheological properties of the final paint, indicating, if you are able any values for the rheological parameters appropriate for your graphs.

[14 marks]

END OF QUESTION 2
TURN OVER

Question 3 **[40 marks]**

Vibrational spectroscopy is a major tool for characterising materials and products:

(a) Providing brief explanations for your selections, **indicate** which of the following 4 molecules, $^{37}Cl^{35}Cl$, H–C≡N (hydrogen cyanide), C_{60} fullerene and H_2O may show:

- Infrared absorption spectra?
- Raman spectra?
- Calculate the number of normal vibrations for each molecule.

[12 marks]

(b) Diffraction of visible or infrared light is the reason for a limited spatial resolution in the studies materials or products by Raman or Infrared spectroscopy combined with corresponding microscopes. **Describe** two approaches of overcoming diffraction limit to achieve high spatial resolution in Raman and Infrared spectroscopic imaging. **Provide** corresponding equations/schematics and examples of samples where such high spatial resolution was useful.

[13 marks]

(c) **Explain** the differences between Attenuated Total Reflection (ATR)–FTIR spectroscopy and confocal Raman microscopy when using these techniques to probe depths into polymeric samples. **Explain** how the range of the probing depth can be changed when using each of these approaches. **Support** your answers with corresponding equations or/and schematics as appropriate.

[15 marks]

END OF PAPER

IMPERIAL COLLEGE LONDON

M.Eng EXAMINATION IN CHEMICAL ENGINEERING 2022

PART III and IV

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M.Sc. in ADVANCED CHEMICAL ENGINEERING

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PRODUCT CHARACTERISATION

Monday 9th May 2022: 10:00 – 11:30

Answer all three questions

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Question 1 carries 20 marks
Question 2 carries 40 marks
Question 3 carries 40 marks

TURN OVER FOR QUESTION

Question 1 **[20 marks]**

A metal organic framework powder (MOF) is proposed to be used for CH_4 storage. The product specification sheet from the manufacturer includes the N_2 sorption isotherm at 77 K shown in Figure 1 and it states that the MOF can uptake 0.4 milligram of methane per gram of MOF at 298 K and 1 bar.

(a) **Evaluate** whether the methane storage claim from the manufacturer is plausible. **Justify** your answer and **comment** the result.

[7 marks]

(b) The MOF degrades over time with formation of atomic vacancies within its structure.
(i) **Determine** qualitatively what happens to the textural properties of the MOF.
(ii) **Identify** technique(s) you would use to evaluate these textural properties.

[5 marks]

(c) The MOF powder can be compacted and mixed with binders to form pellets. **Sketch** change(s) to the N_2 sorption isotherms of the MOF that may result from compaction and addition of binders. **Explain** your sketch(es) and **label** them appropriately.

[5 marks]

(d) Between BET and Langmuir, **select** the model that would lead to the best estimation of the surface area of the MOF powder. **Justify** your answer.

[3 marks]

Data for Question 1:

Name	Symbol	Value	Units
Gas constant	R	8.314	m^3 Pa mol^{-1} K^{-1}
Molar volume of liquid nitrogen at 77 K	V_M	34.65 x 10^{-6}	m^3 mol^{-1}
Molar mass of methane	M	16	g mol^{-1}
Molar volume of a gas at STP	V_M'	22.4	L mol^{-1}

QUESTION 1 CONTINUES
TURN OVER FOR Fig 1.1

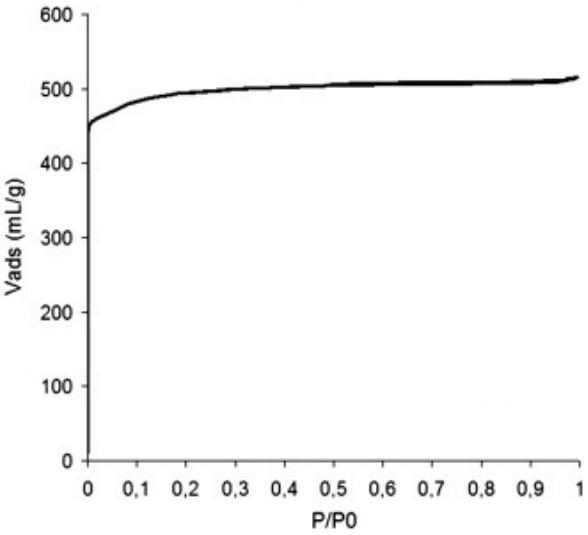

Fig. 1. N_2 sorption of the MOF at 77 K. The Y axis refers to the volume of gas uptake at standard temperature and pressure.

END OF QUESTION 1

Question 2 **[40 marks]**

a) Below in table 1 are some rheological data for some meat pate, (a paste)

i) Do the data fit the Bingham or power law models best? Hence, estimate the appropriate rheological parameters. (You may use graph paper, Excel, or any other software package to assess the data). **[15 Marks]**

ii) The pate is also viscoelastic, so you would wish to perform an oscillatory shear measurement as a function of frequency.
What rheological parameters would such an experiment tell you? **[3 Marks]**

iii) What experiment should be performed before doing this experiment? And why should such an experiment be carried out?

[4 Marks]

iv) Sketch the form of the resultant viscoelastic data as a function of frequency over an angular frequency of 10^{-1}-10^{1} Hz. **[3 Marks]**

b) You are working for a recently formed spin out company, which is making cosmetics. You have a new product, a mascara, which you are about to bring to market. Being a new company the laboratory where you are working is relatively poorly equipped and has no equipment costing over £40,000.
The mascara consists of water, a hydrocarbon oil, a surfactant, and some carbon black particles.
You need to determine some **physical** characteristics of this formulation for product control purposes.

i) For the mascara identify **three** characteristics which you should determine for the product and outline how you would achieve this? **[9 marks]**

ii) If you were working for a very well-equipped laboratory, what **additional** experiments could you perform to better characterise the product? **[6 marks]**

Question 2 table 1 continues next page

Table 1

Shear stress, Pa	Shear rate, s^{-1}
18.04	0.111
18.32	0.140
18.65	0.176
19.09	0.222
19.62	0.279
20.31	0.352
21.16	0.443
22.24	0.557
23.60	0.702
25.30	0.883
27.45	1.112
30.16	1.400
33.56	1.762
37.85	2.218
43.25	2.793
50.05	3.516
58.60	4.426
69.41	5.576
82.94	7.015
100.01	8.830
121.50	11.117
148.60	14.000

END OF QUESTION 2

Question 3 **[40 marks]**

Vibrational spectroscopy is a major tool for characterising materials and products:

(a) Based on the understanding of Infrared and Raman spectroscopy, and Hooke's law **arrange** the following stretching vibrations of functional groups in increasing order for their wavenumber, so lowest wavenumber ranks first. **Explain** your answers briefly:

(i) C-H (ii) C-F (iii) N-H (iv) O-H

[8 marks]

(b) For the polymeric sample analysed by Attenuated Total Reflection (ATR-FTIR) spectroscopy, (C=O) band has a depth of penetration equal to 3 μm. **Calculate** the depth of penetration for the C-O bond.

[5 marks]

(c) Carbon tetrachloride (CCl_4) has 3 Raman-active vibrations that occur at 218, 314 and 459 cm^{-1} away from the laser line. Draw a demonstration of the Raman spectrum of CCl_4 that includes both the Stokes and anti-Stokes lines with a **brief explanation**. **Explain** why the anti-Stokes bands of CCL_4 have the following order of intensity: 218 > 314 > 459 cm^{-1}.

[13 marks]

(d) **Explain** how the high spatial resolution achieved with micro ATR–FTIR spectroscopic imaging. **Compare** this spatial resolution with the spatial resolution achieved in FTIR spectroscopic imaging in transmission and **explain** the difference. **Explain** how the spatial resolution in transmission may be increased. **Support** your answers with corresponding equations or/and schematics as appropriate.

[14 marks]

END OF QUESTION 3

END OF PAPER