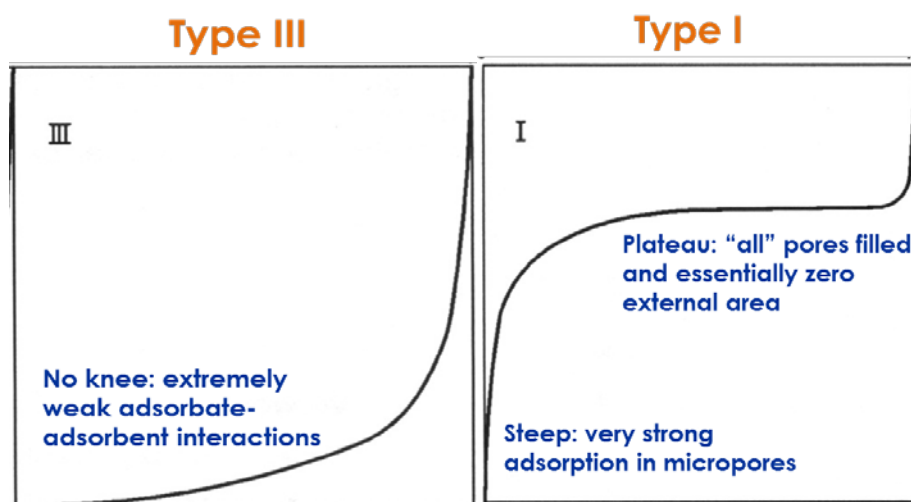


**Question 1****[25 marks]**

- (a) Prior to use, the MOF is loaded with methylcyclopropene, hence we expect low porosity. Methylcyclopropene may block entrance to the micropores and therefore the isotherm would be of type III. If not all pores are filled/blocked, we expect an intermediate between type I and II.

After use, assuming all the regulator has been released, we would observe a type I isotherms as the material is microporous.

**[6 marks]**

(b) (i)

DSC measures the energy changes occurring as a sample is heated, cooled or held isothermally, together with the temperature at which these changes are observed

In fact, DSC measures heat flow as a function of T.

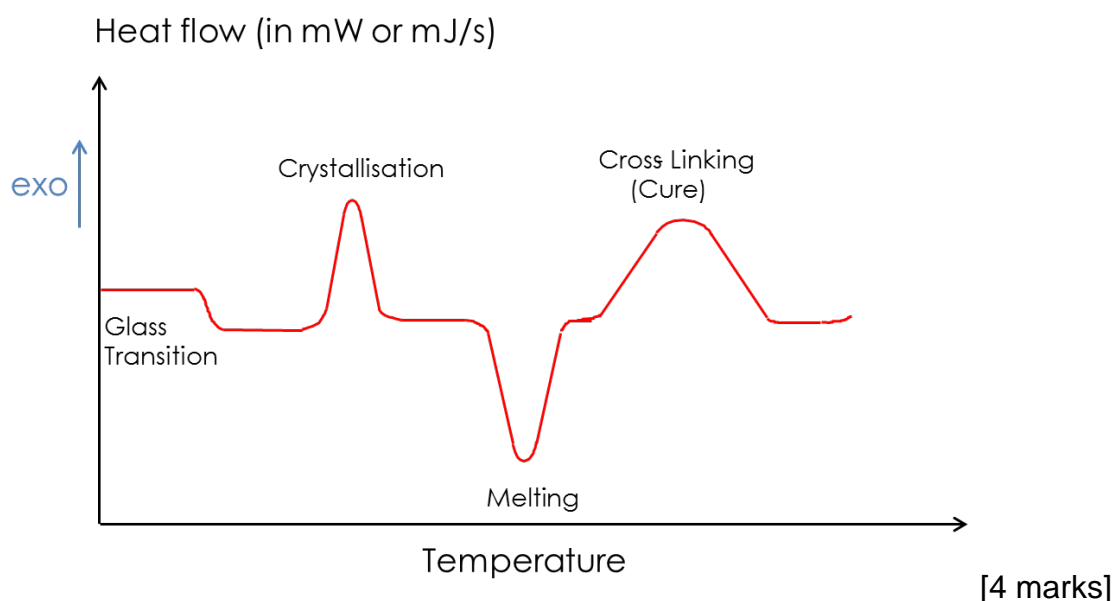
A reference must be used

The energy changes can be due to:

- Phase transition: melting, glass, crystalline phase
- Ferromagnetic–diamagnetic transition

**[3 marks]**

(ii)



(c) Given the information provided, we could expect 3 weight drops for the food packaging before use:

- first for the evaporation of the regulator < 200 °C.
- second and third drops for the decomposition of the MOF and polymer. Most likely between 250 and 450 °C.

The curve would not end at 0 wt% given the presence of the metals in the MOFs.

There could be 2 drops apparent and not 3 if the decomposition temperature of the MOFs and polymer are very close.

There could also be more drops if the polymer and/or MOF organic part decompose in several steps.

[6 marks]

(d)

N<sub>2</sub> sorption: N<sub>2</sub> or other gas molecules are adsorbed on the surface of a solid (here MOF) via physisorption. Knowing the dimension of the probing molecules, one can back calculate surface area and also pore volume. Some models are used for this – e.g. BET or Langmuir.

X-ray diffraction: is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline structure causes a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined.

Explain Bragg's law.

Peaks at a certain position before degradation. Change in peak intensity and/or position after degradation.

[6 marks]

## Question 2

- (a) This figure shows Brunauer's classification system for adsorption isotherms. Type II and III are best for BET analysis. [2 **Marks**]
- (b) At room temperature nitrogen is a gas and therefore has very weak surface adsorption. A molecule such as octane would be ideal for 298K (2 **Marks**)
- (c) Isotherms II and IV, and maybe I, could be expected for micro-porous solids. (2 **Marks**)
- (d) Type 1, Langmuir shaped isotherm, is usual for chemisorption (2 **Marks**)
- (e) Surface area =  $10/22400 \times 1.62 \times 10^{-20} \times 6.023 \times 10^{23} = 2.68 \text{ m}^2/\text{gm}$  and  $53.7 \text{ m}^2/\text{gm}$

These are in the range of 1-10 and 10-500  $\text{m}^2/\text{gm}$ , typical for supports and catalysts respectively

I would in the first case expect a low  $c$  ( $<10$ ) and the second case a higher one,  $c > 10$ .

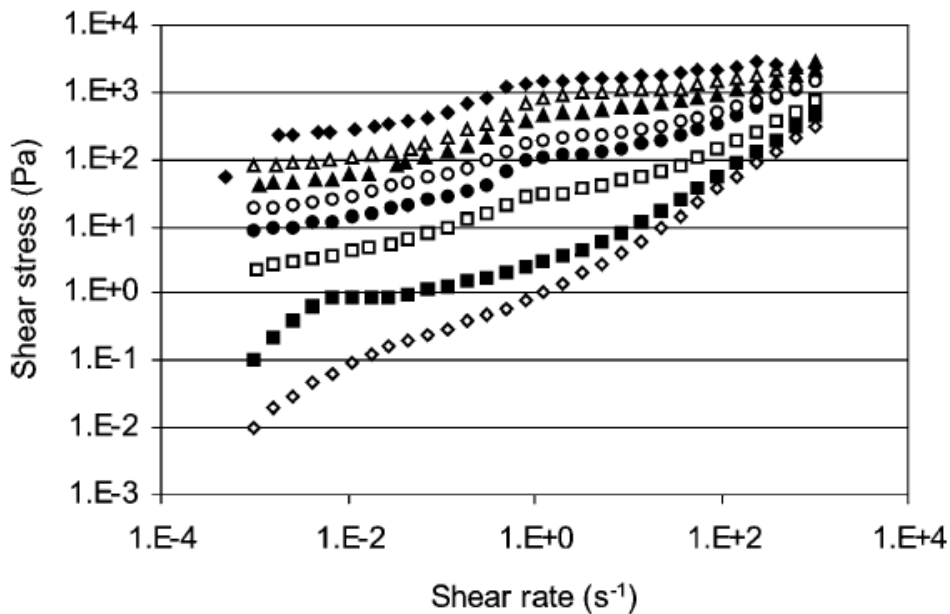
(9  
**Marks)**

- (f) One such example would be crystalline pharmaceutical solids. Many of these may be hydrates, and their existence and stability can be easily determined using water sorption isotherms. In the case of partially amorphous crystalline solids, the actual amorphous content can be determined from water sorption isotherms. The most common method for determining water sorption isotherms is the gravimetric DVS method where the sample is exposed to an inert gas flow which contains a known relative humidity and a known temperature. Following the sample mass changes as a function of time and relative humidity allows the water sorption isotherm to be obtained. (8 **Marks**)

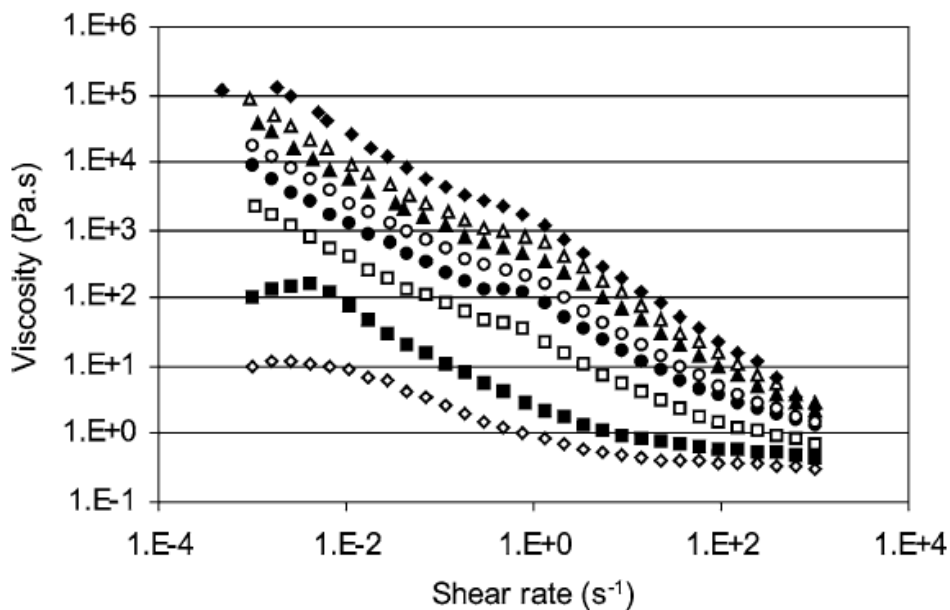
### Question 3

- a) Basically its because of particle interactions which are broken down at high shear rates, meaning smaller units are flowing hence the lower viscosity **[5 marks]**
- b) i) High shear experiments need to be formed here, for example shear stress versus shear rate ( and hence viscosity shear rate) but make sure the shear rate range is high, to mimic the processing conditions I would say do a linear shear rate range from 0-1000 s<sup>-1</sup>, or log 10 from 10-1000 s<sup>-1</sup>, using either concentric cylinder or cone and plate (parallel plate) geometries. **[5 marks]**

Data similar to those below expected, but only that from say 10<sup>1</sup> and higher required

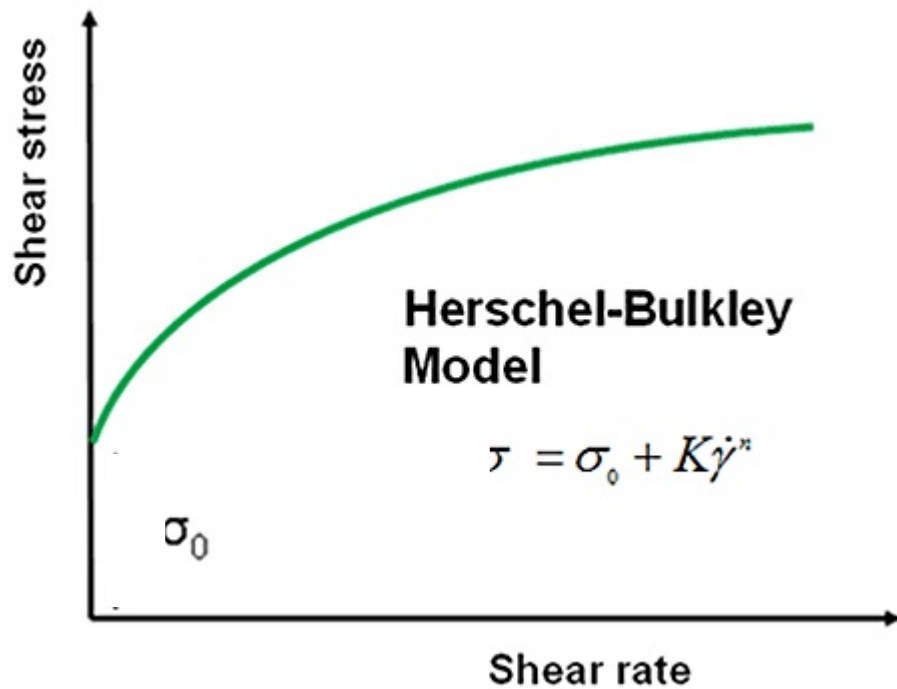


(a)



(b)

On a linear scale the following expected

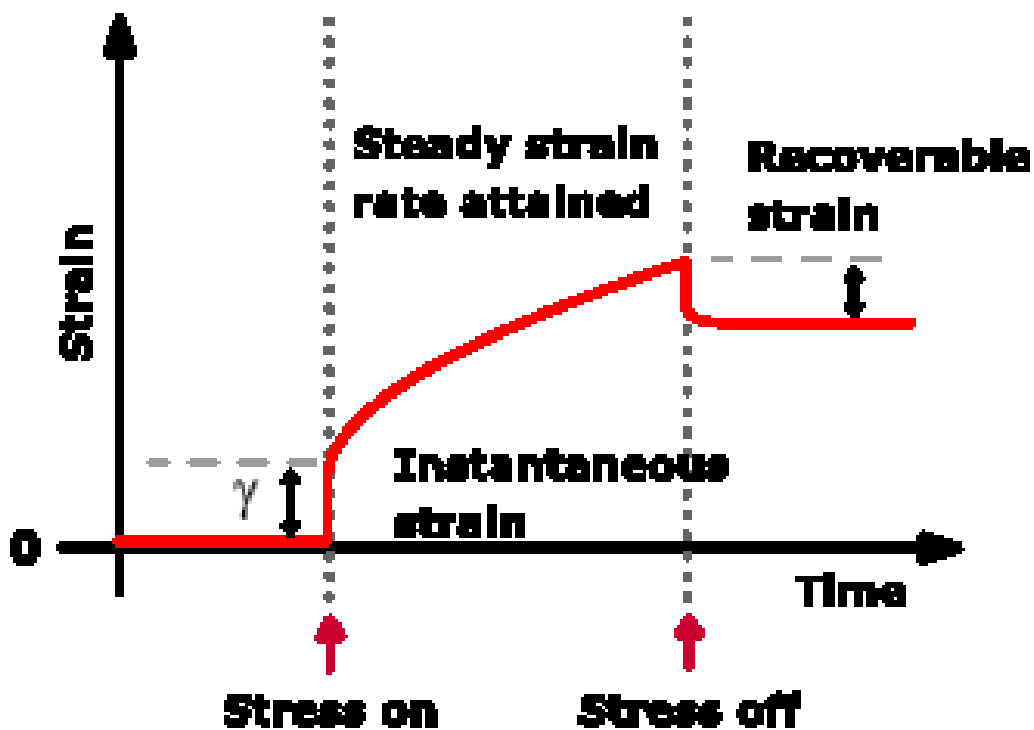


[5 marks]

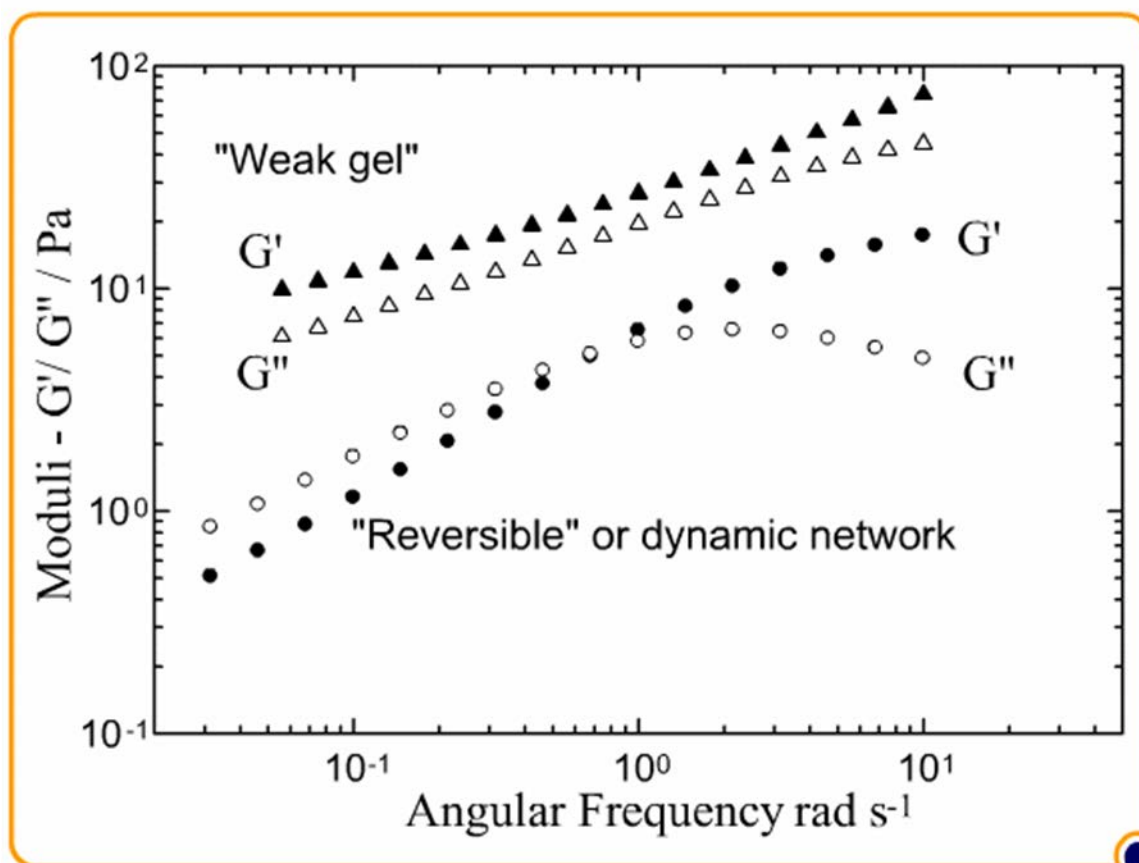
For product stability measurements we will need a low shear experiment either a creep type experiment or an oscillatory shear

[5 marks]

Typical creep data would look like



Oscillatory shear data like



[5 marks]

Question 4

**3 marks for 1<sup>st</sup> ,method 2 for second in all sections**

- a) optical microscopy and SEM, probably better to use dark field microscopy and SEM would need to be coated with a conducting material, preferably gold/chromium/carbon
- b) SEM or AFM, SEM again needs sputter coating, afm should work as it is. X-ray scattering just possible
- c) Optical microscopy (light field) and low angle light scattering
- d) Disc centrifuge, TEM, STM, dynamic light scattering, X-ray scattering or AFM all OK, not SEM or optical microscopy or neutron scattering
- e) Dynamic light scattering and TEM or SEM best, AFM OK, not optical techniques though, again x-ray scattering would be OK

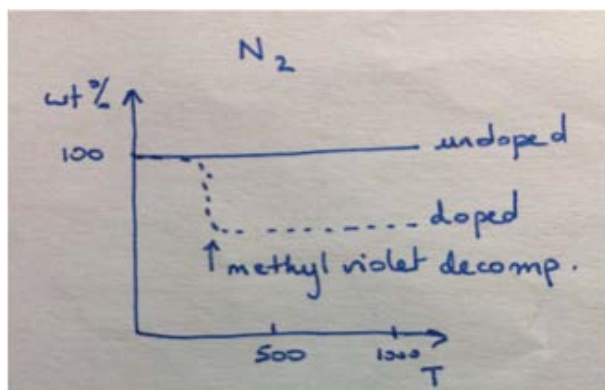
**Question 1****[25 marks]**

Silica gel is an amorphous and porous form of silicon dioxide,  $\text{SiO}_2$ , 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 change 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  $\text{N}_2$  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  $\text{N}_2$ .
  - (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 ( $\text{N}_2$  atmosphere). **Label** the step(s).

**[8 marks]**

(i)

**[2 marks]**

(ii)

No change for the undoped.

Earlier decomposition of the dopant for the doped sample.

**[2 marks]**

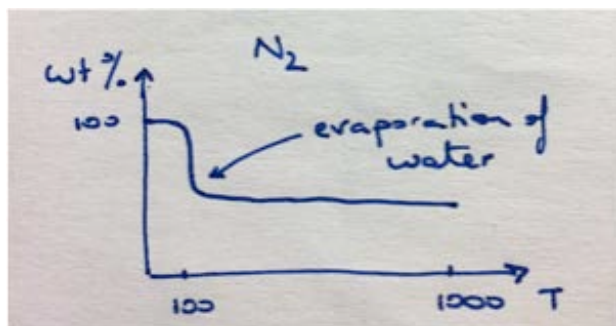
(iii)



Smaller beads mean greater heat transfer so earlier (lower T) decomposition of the dopant.

[2 marks]

(iv)



[2 marks]

- (b) We now consider the porosity analysis of silica gel beads (Figure 1.1).
- Calculate** the total volume of pores of the product.
  - Indicating any assumption(s) made, **derive** the maximum water uptake of the silica gel beads in mmol per gram of beads.
  - Propose** an experiment one could conduct to determine the maximum water uptake of the silica gel beads.

[10 marks]

(i) Use the derivation shown in the lecture on porosity analysis to find that:

$$V_{tot} = \frac{P_{standard} \times V_{adsorbed \text{ at STP}} \times V_M}{RT_{standard}} = \frac{10^5 \times 270 \times 34.65 \times 10^{-6}}{8.314 \times 298} = 0.378 \text{ cm}^3 \text{ g}^{-1}$$

[5 marks]

(ii) Assume no reaction of the product with water. All the water fills the pores. Pores are large enough to accommodate water (not entirely true).

$$V_{water} = V_{tot}$$

$$X_{water} = \frac{V_{tot} \times \rho}{M_{water}} = \frac{0.378 \times 1}{18} = 21 \text{ mmol/g(beads)}$$

[2 marks]

(iii) Expose a known amount of the beads to 100% humidity for 1 day, 10 days, 100 days. Analyse the three samples using TGA and derive the amount of water present. Determine when the plateau in uptake occurs.

Repeat for at least 3 samples to get an average value for the period determined for saturation.

[3 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]

If one wants to desorb water, a first step is to heat the beads at the desired temperature to desorb water.

We assume that this temperature is 100 °C.

We consider the type A silica gel as it has the lower heat capacity.

We assume that the heat capacity of type A silica gel at 100 °C is close to that at 95 °C. We take  $0.95 \text{ J g}^{-1} \text{ K}^{-1}$  as the value.

We assume that we start from an initial temperature of 25 °C.

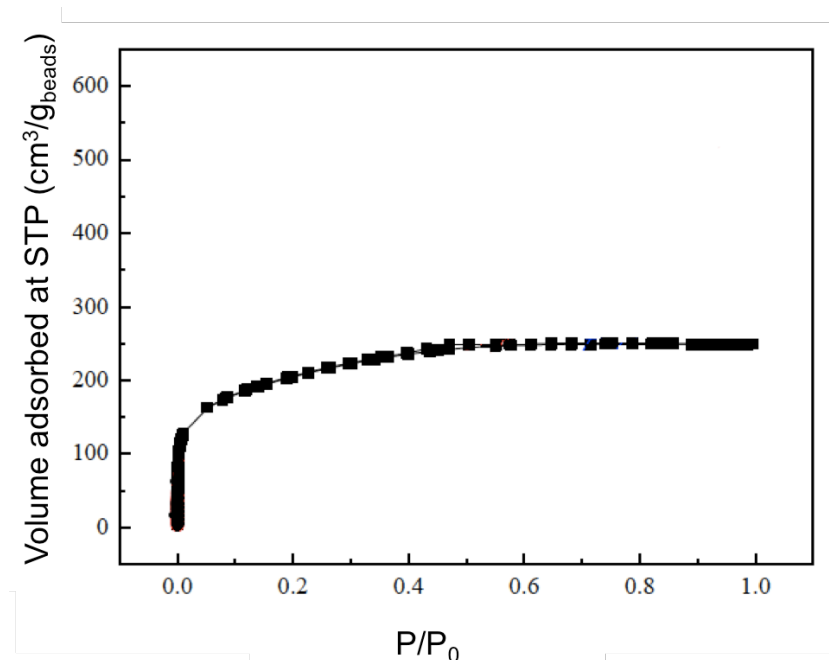
We perform the calculation for 1 kg of beads.

$$Q = m \times C_p \times \Delta T = 1000 \times 0.95 \times (273 + 100 - (273 + 25)) = 90 \text{ kJ}$$

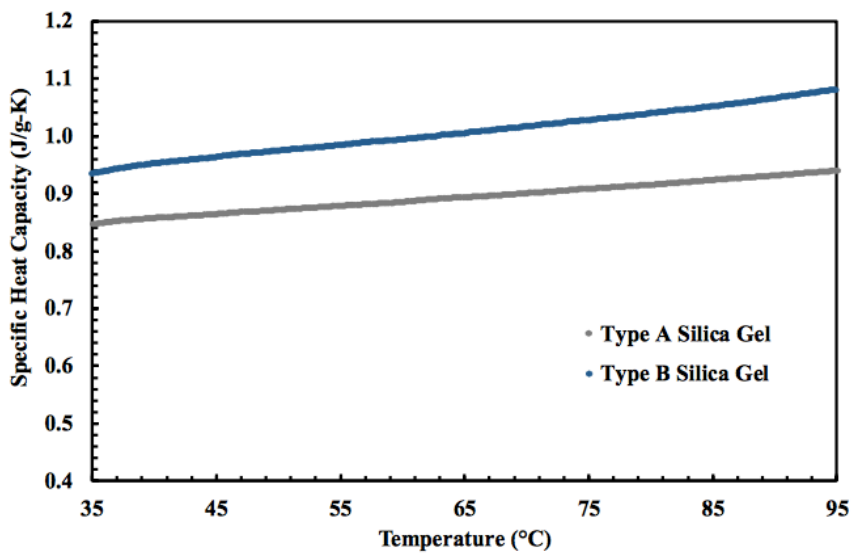
Data for Question 1:

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

Figures for Question 1:



**Figure 1.1.** N<sub>2</sub> 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 X.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*).

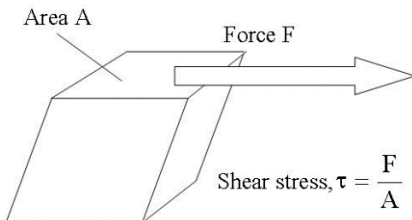
**END OF QUESTION 1**

## Question 2

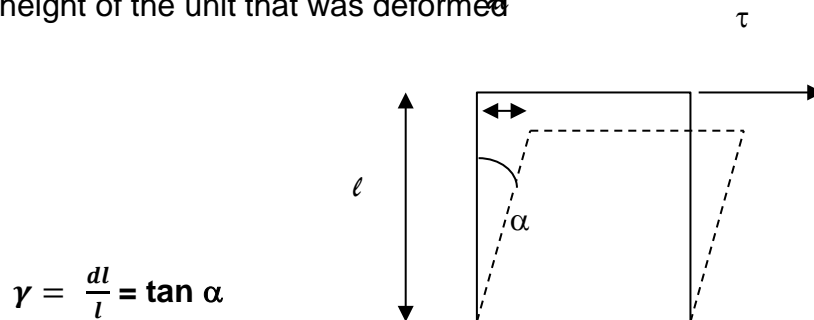
[35 marks]

a)

- i) **Shear stress**, is the force tending to cause deformation of a material by slippage along a plane or planes parallel to the imposed stress.



- ii) Strain, given the symbol  $\gamma$ , is a relative deformation. In a shear deformation it is defined as the distance moved in the direction of the deformation, divided by the height of the unit that was deformed



- iii) Strain Rate, or Shear Rate

This is the rate by which the strain is varying and is given by the rate at which the fluid is moving in relation to the walls of the container, divided by the gap between the walls of the container. It has units of 1/sec

- iv) Yield stress is the stress that needs to be exceeded in order for the fluid to flow

b)

- i) The fluid would be poured (or placed) into the rheometer (depending on the fluid this would be cone and plate for high modulus samples, concentric cylinder low modulus, and then an oscillatory shear at different frequencies applied

ii)  $G^* = \frac{\tau_0}{\gamma_0}$   $G' = \frac{\sigma_0}{\gamma_0} \cos \delta$   $G'' = \frac{\sigma_0}{\gamma_0} \sin \delta$

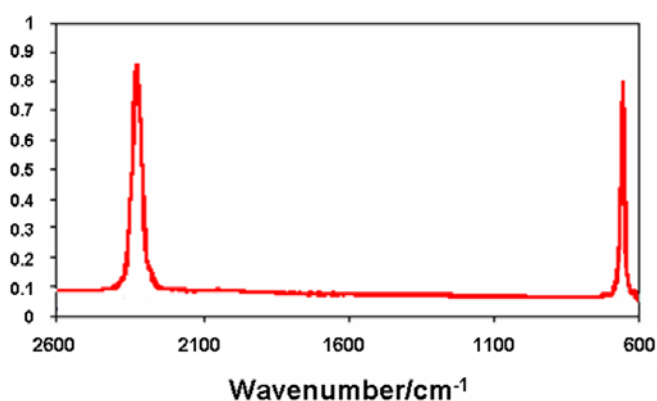
- iii) Its necessary to do an amplitude sweep and ensure that the experiment as a function of frequency is carried out in the linear viscoelastic region, where  $G'$  is constant with amplitude
- iv) In absence of surfactant we have a strong gel,  $G' \gg G''$  and virtually independent of frequency, as surfactant added initially more of a weak gel, but still  $G' > G''$ , but then it's a weak network with little gel like properties.
- v) Optical probably best, SEM but sample needs to be dried, AFM possible but again dry sample I feel. Not TEM

**END OF QUESTION 2**

### Question 3

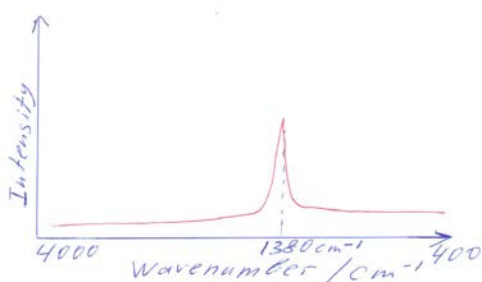
[40 marks]

- (a) The Infrared spectrum of liquid  $\text{CO}_2$  present two absorption bands, one corresponding to antisymmetric vibrational mode  $\nu_3$  at ca.  $2340 \text{ cm}^{-1}$  and another band at ca.  $670 \text{ cm}^{-1}$  corresponding to two double degenerate bending modes  $\nu_2$  of  $\text{CO}_2$ . The main selection rule for infrared active vibrations is that the dipole moment should change during the corresponding vibrations, which is the case for vibrations  $\nu_3$  and  $\nu_2$ . There is no rotational structures in these spectral bands because rotations are hindered in liquid phase of  $\text{CO}_2$ . Both these vibrations are IR active because dipole moment changes during vibrations. x-axis shows values of Wavenumber/ $\text{cm}^{-1}$  while y-axis shows absorbance (no units).



The Raman spectrum of liquid  $\text{CO}_2$  present one absorption band (as Fermi resonance was not taught in this course) of symmetric vibration  $\nu_1$   $\text{CO}_2$  ca.  $1380 \text{ cm}^{-1}$ . The main selection rule in Raman spectroscopy requires change of polarisability during molecular vibration:  $\frac{\partial \alpha}{\partial r} \neq 0$

Symmetric vibration of  $\text{CO}_2$   $\nu_1$  exhibits change in polarizability during vibration, while other vibrations do not change polarizability, so Raman inactive. [10 marks]



- (b) Solution should include discussion of diatomic molecule as harmonic oscillator.

Frequency of vibration of diatomic molecule is  $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  We need to

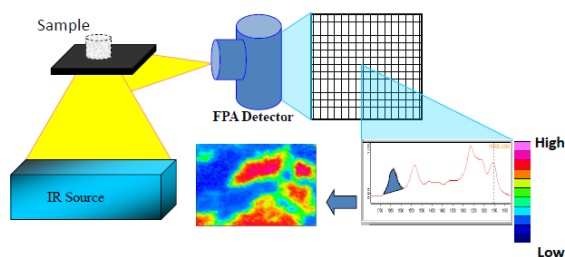
determine the reduced masses of  $^{56}\text{FeH}$  and  $^{54}\text{FeH}$ , assuming a mass of 1 for hydrogen:  
 For  $^{56}\text{FeH}$ , it is  $1 \times 56 / 57 = 0.9825\text{g}$ , for  $^{54}\text{FeH}$  it is  $1 \times 54 / 55 = 0.9818\text{g}$ .  $(0.9825 / 0.9818)^{1/2} = 1.00036$ ; so, wavenumber for  $^{54}\text{FeH} = 1661.0 \text{ cm}^{-1} \times 1.00036 = 1661.6 \text{ cm}^{-1}$ .  
 Frequency  $\nu = c \times \text{wavenumber}$ , so frequency is  $5 \times 10^{13} \text{ Hz}$ . There is no need to know exact value of atomic mass unit as it will be cancelled in the ratio of square root of reduced masses.

**[5 marks]**

(c) Beer-Lambert Law:  $A = \epsilon c l$ , where  $\epsilon$  is molar absorptivity,  $c$  is concentration and  $l$  is pathlength;  $A$  is absorbance (measured as a peak of the infrared band or as a area under the band, called integrated absorbance). Schematic diagram would also be helpful.  $0.1 = 0.5 \times 10^6 \text{ cm}^2/\text{mol} \times c \times 0.02 \text{ cm}$ ;  $c = 0.01 \text{ mol/L}$

**[5 marks]**

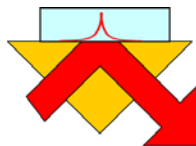
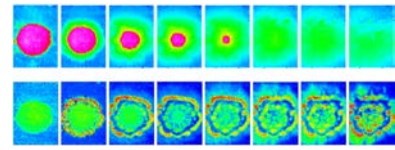
(c) First, principles of FTIR imaging should include discussion and a brief description of a combination of FTIR spectrometer with infrared array detector to measure thousands of spectra simultaneously from different locations within the sample. The simplest way to obtain chemical images is plotting absorbance of specific infrared bands as a function of all pixels:



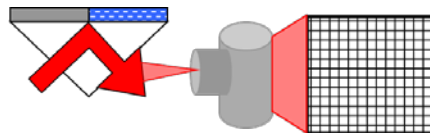
Combining FTIR spectrometer with a Focal Plane Array detector  
 (64 x 64 or 128 x 128 pixels)

The main approach to study tablet dissolution is macro ATR-FTIR imaging that uses ATR accessories with inverted prism (figure below) accommodated in a large sample compartment (or macro chamber) of a spectrometer. The main reason for the choice of ATR is because water strongly absorb IR radiation while ATR probes layer of only few micrometer thick (appropriate equation would be useful here). The inverted prism crystals made of ZnSe, diamond, Si or Ge. This results that macro ATR-FTIR imaging

measures different areas of studied tablets (from ca. 1 mm<sup>2</sup> to a few cm squared). This approach is suitable for studies of dynamic systems (e.g. dissolving tablet) to detect concentration profiles of drug, polymer and water within interfacial areas of tablet/aqueous medium. Main applications of macro ATR-FTIR imaging include studies of dissolution of tablets for understanding mechanism of drug release as it is capable detection drug crystallisation (figure below) during dissolution (because of shift of spectral bands).

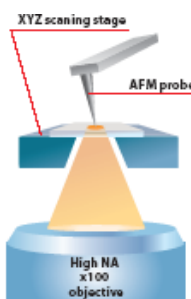
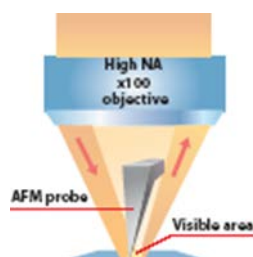
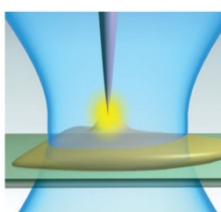


Macro ATR



[10 marks]

(d) The technique that can differentiate carbon nanotubes (SWCNT) of different diameters is TERS – tip-enhanced Raman spectroscopy, which is a novel technique that combines the high spatial resolution of atomic force microscopy (AFM) with the chemical information of Raman spectroscopy, thus breaking diffraction limit associated with confocal Raman microscopy. Brief discussion of principles of tip-enhanced Raman spectroscopy should include description of metal-tip covered with nano-particles gold (or silver) that produce surface-enhanced effect at the edge of the tip, as show in the figure on the left below. Therefore, the signal measured (yellow area in the figure) will be localised significantly better than the focus of laser beam in Raman microscopy, thus achieving spatial resolution on the order of nanometers, suitable for differentiation of carbon nanotubes (SWCNT). Discussion may also include mention of two approaches: upright illumination (for non-transparent samples) and inverted illumination (for transparent samples) and examples of differentiation of different carbon nanotubes by obtaining TERS spectra from the small area of dispersed nanotubes, where different Raman signals from bundles of carbon nanotubes of different diameters provided opportunity to differentiate their locations within the mixture. This is possible because wavenumber of the corresponding radial breathing modes (RBM) are directly related to the diameters of SWCNT, thus plotting distribution of intensity of RBM would allow to obtain image showing distribution of SWCNT of a particular diameter.



[10marks]



## Solutions of exam questions on Product Characterisation

### 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-dimethylbutane (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]

It is indicated that zeolites A, B and C are microporous so they can't have PSD 1 or 4.

Zeolite A distinguishes between molecules of size 3.8 Å and 4.7 Å so its pore size should be in between these two values. That leaves only PSD 5.

Zeolite B distinguishes between molecules of size 4.3 Å and 5.8 Å so its pore size should be in between these two values. That leaves only PSD 3.

Finally, zeolite C should have the capacity of adsorbing a molecule of size 6 Å so it leaves only PSD 2.

- (b) Some zeolites can also be used to adsorb CO<sub>2</sub> *via* a physisorption mechanism.
- (i) **Sketch** the CO<sub>2</sub> adsorption isotherms at three different temperatures of your choice. Justify your answer.
- (ii) **Explain** how the CO<sub>2</sub> adsorption isotherms might change if adsorption proceeds via a chemisorption mechanism.

[5 marks]

(i) Isotherms typically have a type I shape and the slopes will be increasing with lower temperature since physisorption is an exothermic process. [2 marks]

(ii) In the case of chemisorption, there is an activation step which means that energy needs to be provided before chemisorption occurs. So in that case, there might be a jump in uptake upon reaching a temperature and then a decrease as observed for physisorption. [3 marks]

- (c) The manufacturer of Zeolite A claims that its product can uptake up to 80 mmol of N<sub>2</sub> per gram of product. Using the data available to you, **demonstrate** that this claim is unfounded.

[5 marks]

QUESTION 1 CONTINUES

**TURN OVER FOR Part (d)**

From the data below, we get the total volume of pore of Zeolite A. This total volume would correspond to the volume of liquid N<sub>2</sub> one could store in zeolite A. If we apply a lot of pressure, then we might reach supercritical conditions, hence almost liquid state.

$$V_{tot} = n_{ads} \times V_M$$
$$n_{ads} = \frac{V_{tot}}{V_M} = \frac{1.5}{34.65} = 43 \text{ mmol/g}$$

The volume of liquid N<sub>2</sub> of 1.5 cm<sup>3</sup>/g translates into 43 mmol/g of N<sub>2</sub>. This value is lower than the value claimed by the manufacturer.

- (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]**

- (i) DSC profile of zeolite would be a flat line. No melting or crystallisation. However, in the case of a metal impregnated zeolite, one would expect to see a melting peak. [1 mark]
- (ii) One could use the enthalpy of melting of the metal to assess the amount of metal impregnated. To do, one would prepare a set of standard samples with known amount of metal impregnated in the zeolites. These samples would be characterised using DSC and the enthalpy of melting would be recorded for each of them. One could then build a calibration curve of enthalpy of melting vs amount of metal in the composite. Testing the actual sample, one would use the calibration curve to determine the amount of metal in their own sample. [4 marks]

- (e) A label for a Zeolite B used to uptake volatile organic compounds (VOCs) reads “a minimum energy of 235 J g<sup>-1</sup> 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]**

We assume that the heat capacity of the zeolite at the temperature of interest is an average of the heat capacity for the temperature range given, i.e. average of 0.75, 0.85 and 0.95, which is 0.85 J g<sup>-1</sup> K<sup>-1</sup>.

We assume that we start from room temperature, which we take as equal to 25 °C (298 K).

$$Q = C_p \times \Delta T = C_p \times (T_f - T_i) = C_p T_f - C_p T_i$$

$$T_f = \frac{1}{C_p} (Q + C_p T_i) = \frac{1}{0.85} (235 + 0.85 \times 298) = 574 \text{ K } (300 \text{ } ^\circ\text{C})$$

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

- (i) Pure zeolite under N<sub>2</sub> atmosphere;
- (ii) Metal impregnated zeolite under O<sub>2</sub> atmosphere;
- (iii) Amine impregnated zeolite under air atmosphere (note: the amine is an organic amine).

**[5 marks]**

(i) Flat line (or small drop at the start and then flat line). No decomposition below 1000 °C (zeolites are stable). Possibly removal of pre-adsorbed moisture below 150 °C (mass drop). [1 mark]

(ii) Flat line with a step showing a mass gain at high temperature related to metal oxidation. Possibly removal of pre-adsorbed moisture below 150 °C (mass drop). [1 mark]

(iii) Flat line up until 200-300 °C due to decomposition of the organic molecule. Then flat until 1000 °C. Possibly removal of pre-adsorbed moisture below 150 °C (mass drop). [2 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-dimethylbutane	-	5.8	Å
Kinetic diameter of 5-fluorouracil (anticancer drug)	-	6	Å
Total volume of pores for zeolite A	V <sub>tot</sub>	1.5	cm <sup>3</sup> g <sup>-1</sup>
Specific surface area for zeolite A	S <sub>BET</sub>	855	m <sup>2</sup> g <sup>-1</sup>
Heat capacity of zeolite B at 298 K	C <sub>p</sub>	0.75	J g <sup>-1</sup> K <sup>-1</sup>
Heat capacity of zeolite B at 373 K	C <sub>p</sub>	0.85	J g <sup>-1</sup> K <sup>-1</sup>
Heat capacity of zeolite B at 473 K	C <sub>p</sub>	0.95	J g <sup>-1</sup> K <sup>-1</sup>
Gas constant	R	8.314	m <sup>3</sup> Pa mol <sup>-1</sup> K <sup>-1</sup>
Molar volume of liquid nitrogen at 77 K	V <sub>M</sub>	34.65 x 10 <sup>-6</sup>	m <sup>3</sup> mol <sup>-1</sup>

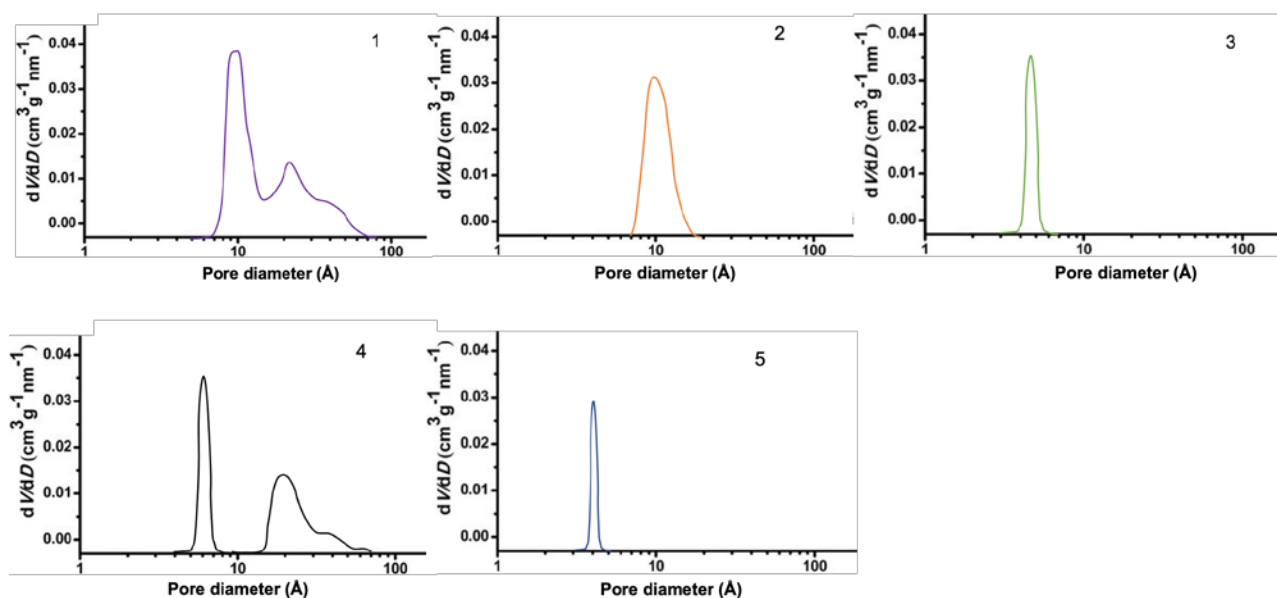


Fig. 1. Pore size distributions for various products.

**END OF QUESTION 1**

## Question 2

- (i) For small particles use dynamic light scattering and Transmission electron microscopy

DLS correlates the scattering at time  $t$  to a second scattering at time  $t+dt$ . Principle is based on diffusion of particles.

TEM is based on focusing electrons on a sample and essentially looking at the electron shadow

For the larger particles used low angle light scattering and TEM, or SEM. Light microscopy would not give high enough resolution.

**8 marks (2 for each suggestion with explanation)**

- (ii) Sedimentation velocity  $V$  is given by balancing gravitational force and Stokes drag, so that

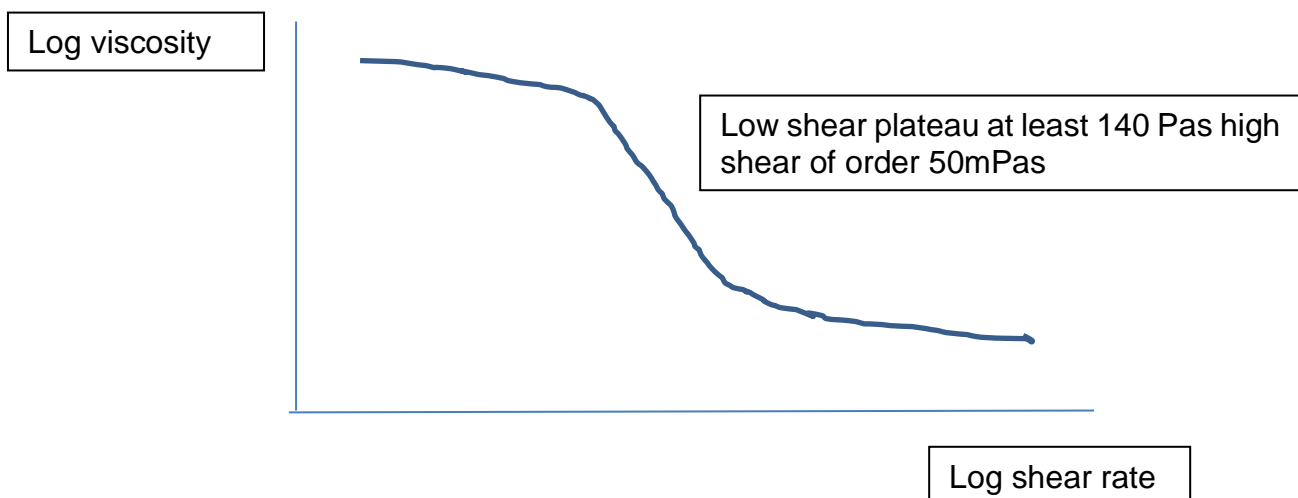
$$Vg = \frac{d^2 * (\Delta\rho) * g}{18 * \eta}$$

Such that in our case  $V = \frac{(5 \times 10^{-6})^2 (3200) \times 10}{18 \times 50 \times 10^{-3}} = 9.0 \times 10^{-7} \text{ m/s} = 900 \text{ nm/s}$

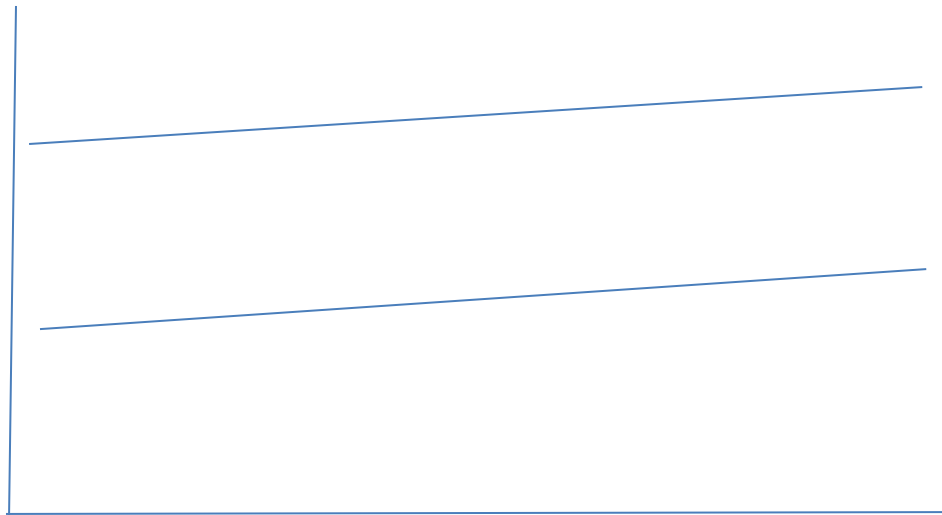
$= 2.2 \times 10^5 \text{ s} = 3.7 \times 10^3 \text{ minutes} = 61.8 \text{ hours}$

**8 marks**

- (iii) Rearrange above equation for viscosity putting the numbers in gives  $140 \text{ Pas}^{-1}$ . This would not function sensibly as a paint if it were Newtonian as you could not spread it easily. Therefore ought to be non-Newtonian.



Log Modulus



Log frequency

There are alternatives to these plots The first plot is crucial and **10 ,marks** for that if values are included,  
**4 marks for other plots**

### Question 3

[40 marks]

a) (a)

IR: All molecules apart from  $^{37}\text{Cl}^{35}\text{Cl}$  will show IR spectra because those molecules will have vibrations that change dipole moment of these molecules. The nonpolar  $^{37}\text{Cl}^{35}\text{Cl}$  molecule has one vibration which does not produce change of dipole moments because isotopes of Cl have the same charges.

Raman: All molecules will be active in Raman because their corresponding vibrations would change size or shape of molecules, thus leading to the change of polarizability.

The number of normal vibrations: **1** for  $^{37}\text{Cl}^{35}\text{Cl}$  and **4** for  $\text{H}-\text{C}\equiv\text{N}$  (hydrogen cyanide), as these both are linear molecules. For  $\text{C}_{60}$  fullerene one may expect **174** vibrations (mostly in far-infrared region with many generate vibrations) and there are **3** normal vibrational modes for  $\text{H}_2\text{O}$ .

**[12 marks, 3 marks for each molecules with explanation]**

b) In Infrared spectroscopic measurements the high-spatial resolution of micro-ATR

should be mentioned, which is defined is given by the Rayleigh criterion  $r = \frac{0.61\lambda}{NA}$

Where, NA is the numerical aperture of the system (the product of the refractive index,  $n$ , and  $\sin\theta$  and  $\theta$  is half the angle of the collection of light, thus  $NA = n \sin\theta$ ),  $\lambda$  is the wavelength of light and  $r$  is the minimal distance required to have a contrast of 26.4 % between two nearby objects (just resolved). Refractive index of Ge crystal is 4, thus it results in numerical aperture NA four times greater than it was in air, thus overcoming diffraction limit of IR measurements in transmissions by 4 times. Schematics of such microscope objective would be useful here.

In Raman spectroscopy it is possible to overcome diffraction limit of light by using near-field approaches, such as tip-enhanced Raman spectroscopy (TERS), which is a novel technique that combines the high spatial resolution of atomic force microscopy (AFM) with the chemical information of Raman spectroscopy, thus breaking diffraction limit associated with confocal Raman microscopy.

Discussion of principles of tip-enhanced Raman spectroscopy should be included. The schematic would be useful here.

**[13 marks]**

- c) One of the methods to obtain depth profile information about polymeric samples is **confocal Raman** microscopy, which provided a possibility of non-destructive approach. Measurements recorded below the surface, so Raman spectra and thus chemical information are obtained as a function of depth. Restriction of out of focus regions entering the detector is achieved by using a pin-hole that the light from other depths blocked. **Schematic** of confocal Raman microscope would be helpful here.

Spatial resolution for depth profiling ca. 2-3 micrometers and the probing depth for polymeric materials is ca 50-100 micrometers. A brief discussion of immersion lenses is needed here.

The depth profiling is achieved by using aperture and moving microscope stage in z-direction by selected distance, e.g. 2 micrometers. Stating the depth range of this approach should be included (ca. 100 micrometre deep). Alternatively, a polymeric sample may be cut and surface of cross-section to be mapped by steps of 1 micrometre.

A different vibrational spectroscopic method for obtaining information about depth information of polymeric samples would be FTIR spectroscopic imaging. First, micro ATR-FTIR spectroscopic imaging can be applied to study polymeric sample with high spatial resolution of few micrometres. Therefore, principles of FTIR imaging should include brief discussion and a brief description of a combination of FTIR spectrometer with infrared array detector to measure thousands of spectra simultaneously from different locations within the sample. The way to obtain chemical images should be briefly stated.

When imaging in ATR mode, IR light approaches the sample through a high refractive index material which provides an opportunity to increase the NA and thereby improve the spatial resolution, for example refractive index of Ge is 4 and it is infrared transparent materials, so using it will enhance spatial resolution by four times. This is achieved in micro ATR-FTIR spectroscopic imaging for studies of cross-section of polymeric sample. The cross-section provides insight into distribution of substances within the sample, but it is invasive approach. The depth profiling is achieved non-destructively using variable angles of incidence by gradually increasing the angle probing layers of different thickness within 1-3 micrometres



range. It is also possible to probe polymeric materials (such as laminates) using different angles of incidence in macro ATR imaging with different apertures (schematics is required)

**[15 marks]**

**Model answers:****Answer 1 (a):**

$$n_{ads} = \frac{P_{standard} V_{adsorbed}}{RT_{standard}} = \frac{10^5 [Pa] \times 5 \cdot 10^{-4} [m^3 g^{-1}]}{8.314 [Pa m^3 mol^{-1} K^{-1}] \times 273 [K]} = 22 mmol g^{-1}$$

$$V_{tot} = n_{ads} \times V_M = 22 \times 10^{-3} [mol g^{-1}] \times 34.65 \times 10^{-6} [m^3 mol^{-1}] = 762 cm^3 g^{-1}$$

At maximum, methane can occupy a volume of 0.152 cm<sup>3</sup> per gram of MOF.

At STP, this would correspond to a mass of methane of:

$$m = \frac{V_{tot}}{V_M} \times M = \frac{0.762 [cm^3 g^{-1}]}{22,400 [cm^3 mol^{-1}]} \times 16 [g mol^{-1}] = 0.544 mg/g$$

At 298 K, the adsorption would be even smaller (physical sorption is exothermic) and therefore the methane uptake value given by the manufacturer seems plausible.

However, one would conduct methane storage at high pressure and therefore it would be more valuable to look at the uptake at the high pressure range. **[7 marks]**

**Answer 1 (b):**

(i) The vacancies will create larger pores within the structure of the MOF. This will in turn:

- reduce the micropore volume
- increase the macropore and/or mesopore volume
- decrease the surface area. **[3 marks]**

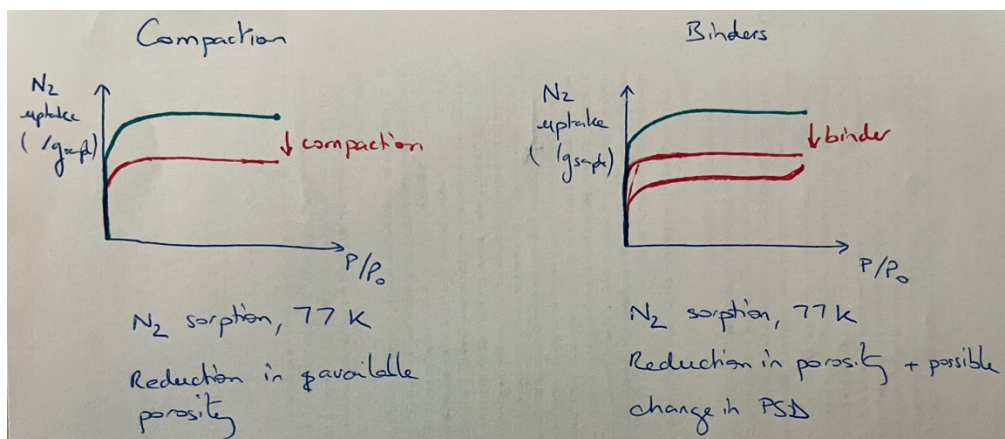
(ii) To prove these changes, one can use N<sub>2</sub> sorption at 77 K as well as mercury porosimetry. The former technique will inform on the changes in surface area and micro/mesopores volumes (and PDS). The latter will inform on the changes in macropore volume (and PSD) **[2 marks]**

**[5 marks]**

**Answer 1 (c):**

Both approaches will reduce the volume of pores and surface area of the MOF powder and its overall uptake per mass of sample.

They may also change the pore size distribution in the meso- and macropore ranges due to the formation of interparticle voids between the binder and the MOF..



**[5 marks]**

**Answer 1 (d):**

It is apparent from Figure X1 that the MOF is a microporous material (type I isotherm). Therefore, monolayer adsorption is anticipated. For this reason, the Langmuir model is best adapted as it assumes solely monolayer coverage.

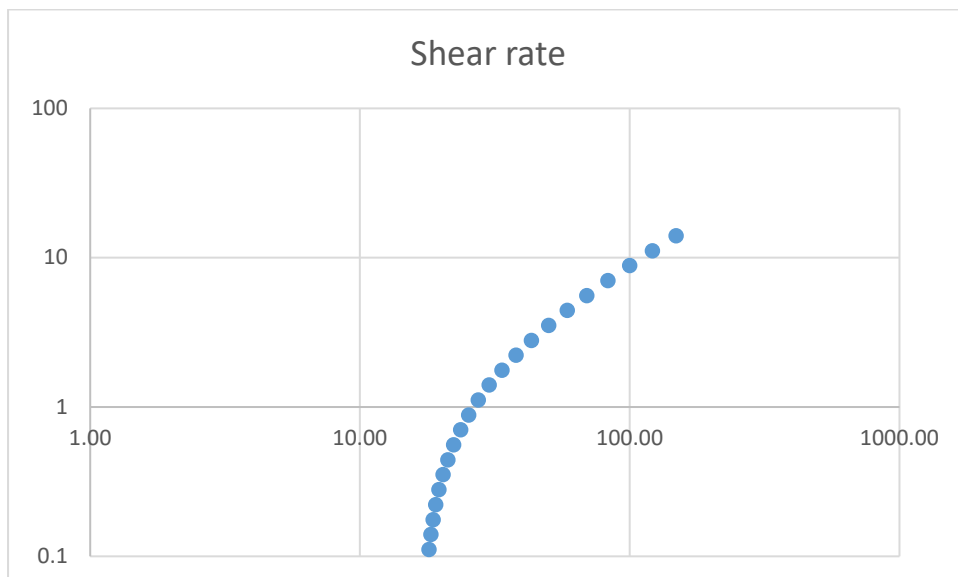
**[3 marks]**

## Answers 2

a) Bingham plot is



Power law plot is



The Bingham plot is clearly the better fit, as it is only at high shear rate that the power law fits

( 3 marks for each plot 4 marks for interpretation)

From the Bingham plot the yield stress is around 17.5 Pa and the plastic viscosity around 9Pas.

(5 marks each I would remove 4 marks if they also included the power law fits as that would imply they do not know which is the best)

It is possible that they would also plot the apparent viscosity. I would not expect this but would give extra credit if that was done, (I would give an extra 4 if that were done).

*ii) The elastic and loss modulus and the phase angle*

*iii) Need to do an amplitude sweep to ensure the frequency sweep would be in the linear viscoelastic region and then work below the critical stress/strain*

*iv) I would expect it to have constant  $G'$  and  $G''$  in this frequency range and to be separated by roughly an order of magnitude with  $G' > G''$*

*b) Carbon black particle size using DLS*

*Emulsion droplet size optical microscope*

*Viscosity as a function of rotation on Brookfield*

*Possibly interfacial tension of oil water / presence of surfactant using wilhelmy plate droplet shape analysis or similar*

*3 marks each*

*In a well-equipped lab, SEM/TEM of carbon particles*

*Viscoelastic measurements on a high end rheometer,  
possibly neutron scattering if well explained*

*6 marks in total*

### Answers/Solution for Question 3

(a)

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

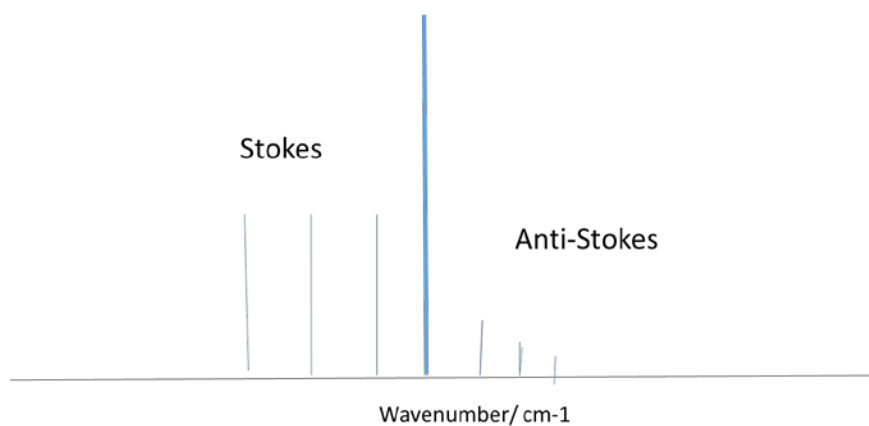
The position of wavenumber of stretching vibrations depends on masses of atoms involved and force constants, thus having heavy atom in (iii) will have lowest wavenumber (e.g. 1300-1100  $\text{cm}^{-1}$ ), followed by C-H (as much lighter atom H is involved), N-H has greater force constant than O-H.

So, the order should be (ii) C-F (i) C-H (iii) N-H (iv) O-H

(b) The depth of penetration in ATR depends on wavelength of the light (directly proportional).

Wavenumber of C=O band at around 1700  $\text{cm}^{-1}$ , while wavenumber of C-O band is around 1000  $\text{cm}^{-1}$ . Therefore, the depth of penetration for absorption at the C-O band will be  $3\text{ }\mu\text{m} \times 1.7 = 5.1\text{ }\mu\text{m}$ .

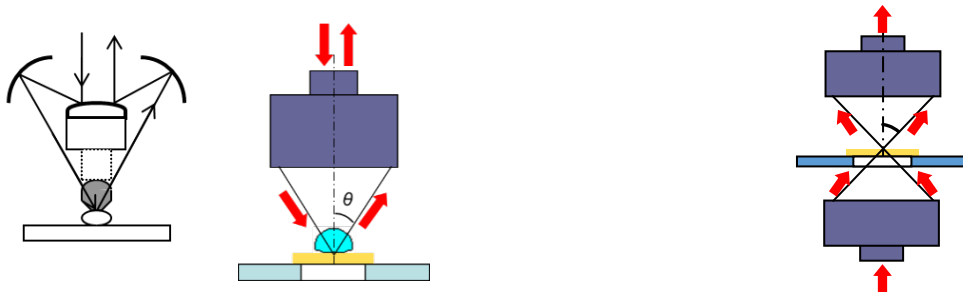
(c) The representation of incident line and corresponding Raman scattered lines should be presented, including Stokes and anti-Stokes (as in schematics below). The spacing from strong excitation line should be the same for both Stokes and anti-Stokes lines (which should have much smaller intensities because it involves vibrations at the first excitation level,  $v=1$  that has fewer molecules unlike Stokes lines which involves vibrations in fundamental level,  $v=0$ ). However, **Boltzmann distribution** will affect intensities of anti-Stokes because population of vibrational level with  $v=1$  at 218  $\text{cm}^{-1}$  will be greater than level at 314  $\text{cm}^{-1}$ , which will be greater than at the level at 459  $\text{cm}^{-1}$ .



(d) The micro ATR-FTIR imaging use microscope objective with Ge crystal (figure below on the left and centre) to increase numerical aperture and spatial resolution. This results that micro ATR-FTIR imaging provides a higher spatial resolution (2-3 micrometers) but images small area (50x50 or 60x60 micrometers squared).

Spatial resolution is defined is given by the Rayleigh criterion  $r = \frac{0.61\lambda}{NA}$

Where, NA is the numerical aperture of the system (the product of the refractive index,  $n$ , and  $\sin\theta$  and  $\theta$  is half the angle of the collection of light, thus  $NA = n \sin\theta$ ),  $\lambda$  is the wavelength of light and  $r$  is the minimal distance required to have a contrast of 26.4 % between two nearby objects (just resolved). When imaging in micro ATR-FTIR mode, IR light approaches the sample through a high refractive index material which provides an opportunity to increase the NA and thereby improve the spatial resolution, for example refractive index of Ge is 4 and it is infrared transparent materials, so using it will enhance spatial resolution by four times. This is achieved in micro ATR-FTIR spectroscopic imaging for studies of many different materials (polymer blends, cross-section of hair, live cells, etc.). In transmission,  $n=1$  (air) and spatial resolution 4 times worse than in micro ATR. Schematics of transmission in the figure below on the right. It is possible increase spatial resolution in transmission using objective with high NA, but also using solid immersion lens (refractive index of  $\text{CaF}_2$  is 1.4, thus 40% increase in spatial resolution), schematics is shown on the bottom.



Micro ATR

