
UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2011/2012

January 2012

KAA 507 – Surface and Thermal Analysis
[Analisis Permukaan dan Terma]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of FOURTEEN pages of printed material before you begin the examination.

Instructions:

Answer **FIVE** (5) questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answer each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

In the event of any discrepancies, the English version shall be used.

Answer any **FIVE** (5) questions

1. (a) Show that the overall interaction energy, $\phi(z)$, of a gas molecule at a distance z from the surface of a solid may be represented by the general expression

$$\phi(z) = \phi_D + \phi_P + \phi_{F\mu} + \phi_R$$

where ϕ_D is the dispersion energy, ϕ_P the energy due to both solid and gas which are polar, $\phi_{F\mu}$ the energy due to dipole induced dipole, and ϕ_R the repulsion energy.

(10 marks)

- (b) Sketch the Brunauer, Emmette and Teller (BET) model for the adsorption of a gas on a surface of solid. State the assumptions made by the BET model for the formulation of the BET equation. From the BET equation, show how to estimate the values of the monolayer capacity, V_m and BET constant, c .

(10 marks)

2. (a) Pore size distribution analysis is one of the ways of characterizing the surface properties of a solid. Show in detail how to determine pore size distribution for a porous solid by the gas adsorption method and mercury porosimetry method. State the advantages and weaknesses of each method.

(10 marks)

- (b) The data below show the volume of H_2 that would occupy at STP ($0^\circ C$ and 1 atm) on the surface of 1.00 g of Cu at $0^\circ C$.

p / atm	0.050	0.100	0.150	0.200	0.250
V / mL	1.22	1.33	1.31	1.36	1.40

Identify what type of isotherm can be obtained from this data. Determine the volume of H_2 necessary to form a monolayer and estimate the surface area of the Cu sample. The density of liquid H_2 is 0.0708 g cm^{-3} .

(10 marks)

3. (a) Wavelength dispersive spectrometer (WDS) and energy dispersive spectrometer (EDS) are two types of X-ray detectors commonly used in surface analytical techniques. Discuss briefly the basic principle of these detectors and the advantages and disadvantages of each detector.
- (8 marks)
- (b) A solid sample is expected to consist of a mixture of FeS, Fe₃O₄ and CaCO₃.
- (i) Explain briefly the surface analytical techniques to determine the crystal structure of each compound in the sample.
- (ii) If the analysis is required to determine quantitatively the chemical composition on the surface of the sample, explain briefly what are the surface analytical techniques that are required to accomplish the analysis?
- (iii) If the analysis is required to determine the ratio of Fe²⁺ and Fe³⁺ in the sample, explain briefly what are the surface analytical techniques that is required to accomplish the analysis?
- (12 marks)
4. (a) Discuss briefly the factors affecting the interaction volume when a specimen is bombarded with an electron beam. Sketch the region of the interaction volume that generate the secondary electron, Auger electron and X-ray.
- (8 marks)
- (b) Consider the X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA).
- (i) Explain briefly the basic principles of XPS and EPMA with the emphasis on the source of irradiation, signal generated and the analysis capabilities.
- (ii) What is a chemical shift? Describe briefly, with an example, how the chemical shift can be used to determine the molecular structure.
- (iii) Both Auger electron and X-ray radiation are produced during the XPS analysis. Briefly explain how to minimize the effect of Auger electron during the XPS analysis.

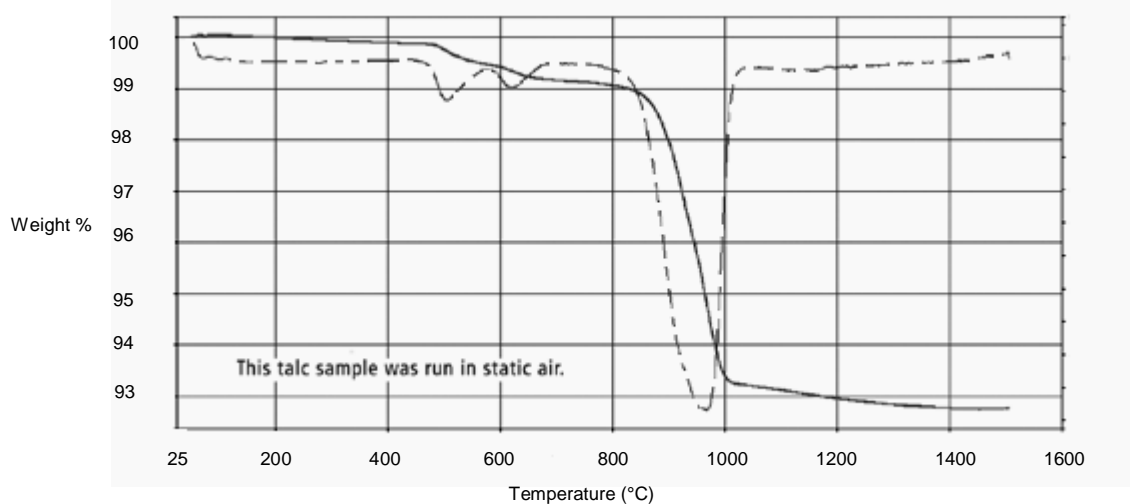
(12 marks)

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5. (a) The chemical composition of talcum powder is $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ and is known by its chemical name as hydrated magnesium silicate. The thermogravimetric analysis (TGA) spectrum of the sample, obtained in static air from 50 °C to 1500 °C in a TGA equipped with a high temperature furnace is shown below. The scanning rate was 10 °C min^{-1} . The derivative thermogram (DTG) is shown as a dotted line. Analyse the mass loss data and derive the decomposition pattern for the talcum powder.

[At. wt. of Mg, 24.3; Si, 28.1]



(8 marks)

- (b) The following are some of the thermogravimetric analyser (TGA) operating variables that contribute to the reproducibility of the thermogram:

- (i) Calibration
- (ii) Sample Preparation
- (iii) Temperature Scanning Rate
- (v) Sample Atmosphere

Give a brief account on how each of the variables affects the reproducibility of the TGA curve of a particular sample.

(6 marks)

...5/-

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- (c) Calcium salicylate is a unique detergent component which is a critical part of top tier passenger car and heavy-duty oil formulations. The thermogravimetric analysis carried out on the monohydrate (Figure 1) from 80 to 1000 °C shows 4 stages of decomposition. Identify the first and second decomposition products.

[At. wt. of Ca, 40.1]

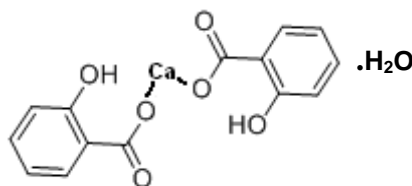


Figure 1 Structure of calcium salicylate monohydrate

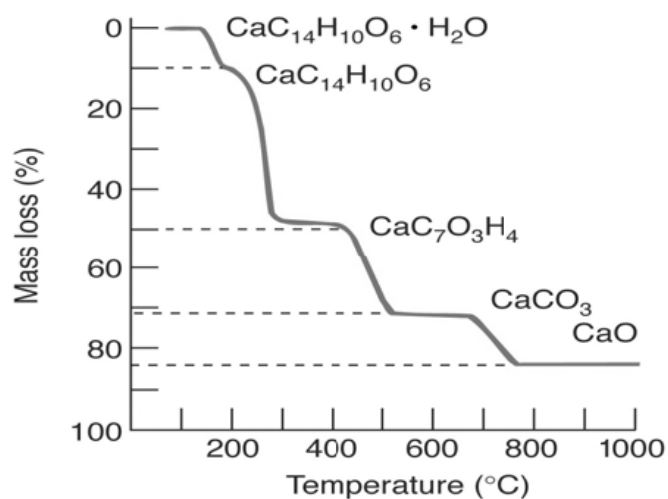


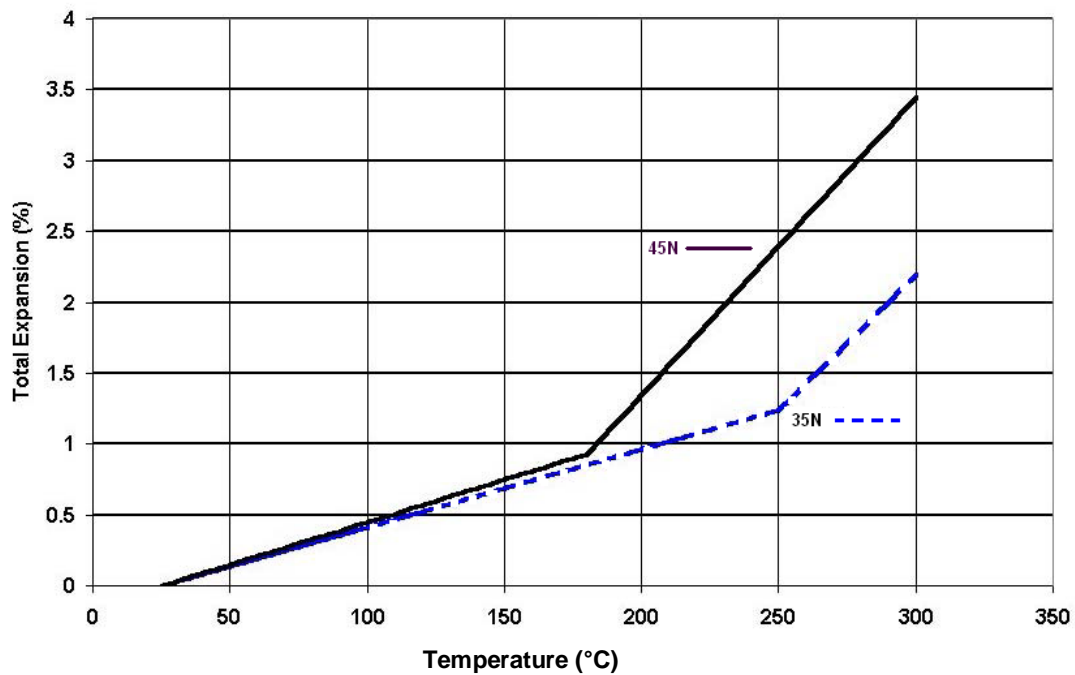
Figure 2 Thermogram of calcium salicylate monohydrate

(6 marks)

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6. (a) Draw a schematic diagram of a dynamic mechanical analysis (DMA) instrument and explain how the instrument may be used to measure the storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) for a material. (6 marks)
- (b) The glass transition (T_g) data for polyimide 45N and 35N were obtained from the thermal mechanical analysis (TMA) method based on the principles of thermal linear expansion with the thermogram shown below. Differential scanning calorimetric analysis (DSC) was run on the same samples based on the heat flow principle. Draw the DSC thermogram for the samples and explain the differences between the TMA and DSC methods.



(6 marks)

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- (c) Two samples of lactose were used for the study of T_g exhibited by amorphous and crystalline lactose. The first sample was a spray-dried lactose of 100 % amorphous content and the second was a fully crystalline sample of the α -lactose monohydrate. Sketch the DSC curves of both samples using a heating rate of $500\text{ }^\circ\text{C min}^{-1}$ with the T_g in the range of $80\text{-}100\text{ }^\circ\text{C}$. Explain the difference in the step height of the T_g for both samples.

(8 marks)

Jawab **LIMA** (5) soalan

1. (a) Tunjukkan tenaga saling tindak keseluruhan, $\phi(z)$, suatu molekul gas pada jarak z dari permukaan suatu pepejal dapat diwakilkan oleh ungakapan umum

$$\phi(z) = \phi_D + \phi_P + \phi_{F\mu} + \phi_R$$

bagi ϕ_D adalah tenaga penyebaran, ϕ_P tenaga berpunca daripada kedua-dua pepejal dan gas yang berketub, $\phi_{F\mu}$ tenaga berpunca daripada berketub mengaruh berketub dan ϕ_R tenaga penolakan.

(10 markah)

- (b) Lakarkan model Brunauer, Emmette and Teller (BET) bagi penjerapan suatu gas keatas suatu permukaan pepejal. Nyatakan anggapan yang dibuat oleh BET bagi pemformulaan persamaan BET. Daripada persamaan BET, tunjukkan bagaimana menganggarkan nilai muatan ekalapisan, V_m dan pemalar c , BET.

(10 markah)

2. (a) Kriteria bagi pencirian sifat permukaan suatu pepejal dapat ditunjukkan daripada analisis taburan saiz liang. Tunjukkan secara terperinci bagaimana menentukan taburan saiz liang bagi suatu pepejal berliang oleh kaedah penjerapan gas dan porosimetri merkuri. Nyatakan kelebihan dan kelemahan bagi setiap kaedah.

(10 markah)

- (b) Isipadu H_2 dalam data di bawah adalah isipadu gas pada STP ($0^\circ C$ dan 1 atm) yang akan memenuhi keatas permukaan 1.00 g tembaga pada $0^\circ C$.

p / atm	0.050	0.100	0.150	0.200	0.250
V / mL	1.22	1.33	1.31	1.36	1.40

Kenalpastikan apakah jenis isoterma yang diperolehi daripada data ini. Taksirkan isipadu H_2 yang diperlukan untuk membentuk suatu ekalapisan dan anggarkan luas permukaan sampel tembaga. Ketumpatan cecair H_2 adalah 0.0708 g cm^{-3} .

(10 markah)

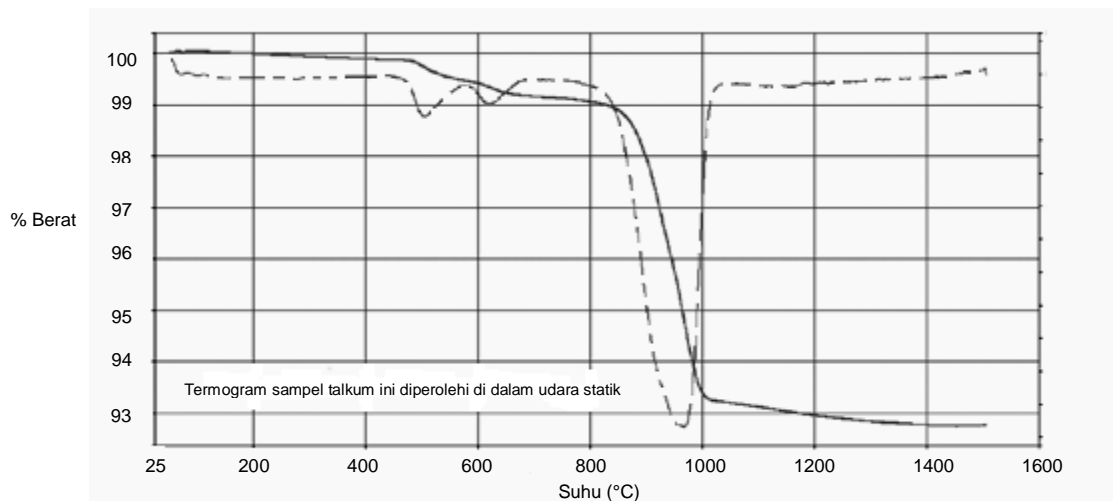
3. (a) Spektrometer serakan panjang gelombang (WDS) dan spektrometer serakan tenaga (EDS) merupakan dua jenis pengesan sinar-X yang biasa digunakan dalam kaedah analisis permukaan. Bincangkan dengan ringkas prinsip asas kedua-dua pengesan tersebut serta kelebihan dan kekurangannya bagi setiap pengesan. (8 markah)
- (b) Suatu sampel pepejal dijangka mengandungi campuran FeS, Fe₃O₄ and CaCO₃.
- (i) Jelaskan dengan ringkas kaedah analisis permukaan bagi menentukan struktur hablur setiap sebatian dalam sampel tersebut.
- (ii) Jika analisis memerlukan penentuan kuantitatif komposisi kimia pada permukaan sampel, jelaskan dengan ringkas apakah kaedah analisis permukaan yang diperlukan untuk melaksanakan analisis tersebut?
- (iii) Jika analisis memerlukan penentuan kadar Fe²⁺ dan Fe³⁺ di dalam sampel, jelaskan dengan ringkas apakah kaedah analisis permukaan yang diperlukan untuk melaksanakan analisis tersebut? (12 markah)
4. (a) Bincangkan dengan ringkas faktor-faktor yang mempengaruhi isipadu interaksi apabila suatu spesimen dibedil dengan pancaran elektron. Lakarkan kawasan isipadu interaksi yang memberikan isyarat bagi elektron sekunder, elektron Auger dan sinar-X. (8 markah)
- (b) Pertimbangkan spektroskopi fotoelektron sinar-X (XPS) dan mikroanalisis prob elektron (EPMA).
- (i) Jelaskan dengan ringkas prinsip asas XPS dan EPMA dengan penekanan kepada sumber pancaran, isyarat yang dihasilkan dan kemampuan analisis.
- (ii) Apakah yang dimaksudkan dengan anjakan kimia? Jelaskan dengan ringkas berserta contoh, bagaimana anjakan kimia boleh digunakan untuk menentukan struktur molekul.

- (iii) Elektron Auger dan pancaran sinar-X kedua-duanya dihasilkan semasa analisis XPS. Terangkan dengan ringkas bagaimana untuk meminimumkan kesan elektron Auger semasa analisis XPS.

(12 markah)

5. (a) Komposisi kimia bagi serbuk talkum ialah $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ dan ianya diketahui dengan nama kimianya sebagai magnesium silikat terhidrat. Spektrum analisis termogravimetrik (TGA) bagi sampel, diperolehi di dalam udara statik dari $50\text{ }^\circ\text{C}$ ke $1500\text{ }^\circ\text{C}$ di dalam suatu TGA yang dilengkapi dengan suatu relau suhu tinggi ditunjukkan di bawah. Kadar pengesanan ialah $10\text{ }^\circ\text{C min}^{-1}$. Termogram derivati (DTG) ditunjukkan sebagai suatu garis berputus. Analisiskan data kehilangan jisim dan perolehi corak penguraian bagi serbuk talkum tersebut.

[Berat atom bagi Mg, 24.3; Si, 28.1]



(8 markah)

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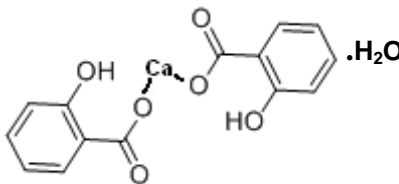
(b) Berikut adalah beberapa pembolehubah pengoperasian penganalisis termogravimetrik (TGA) yang menyumbang kepada ketersalinan sesuatu termogram:

- (i) Kalibrasi
- (ii) Penyediaan Sampel
- (iii) Kadar Pengskananan Suhu
- (iv) Atmosfera Sampel

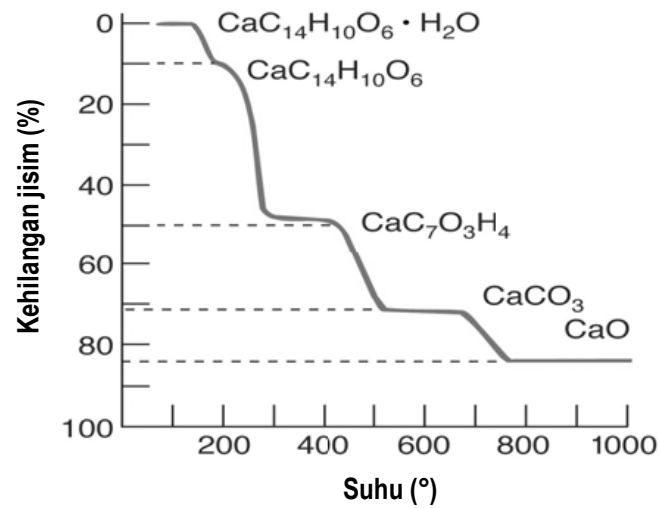
Jelaskan secara ringkas bagaimana setiap daripada pembolehubah tersebut dapat mempengaruhi keluk TGA bagi suatu sampel tertentu.

(6 markah)

(c) Kalsium salisilat merupakan suatu komponen bahan pembersih unggul yang menjadi bahagian yang kritikal bagi formulasi minyak pelincir kereta penumpang berprestasi tinggi dan kegunaan keadaan melampau. Analisis termogravimetrik (TGA) yang dijalankan pada monohydrate (Rajah 1) dari 80 hingga 1000 °C menunjukkan 4 peringkat penguraian. Kenalpastikan produk penguraian pertama dan kedua.



Rajah 1 Struktur bagi kalsium salisilat monohidrat



Rajah 2 Termogram bagi kalsium salisilat monohidrat

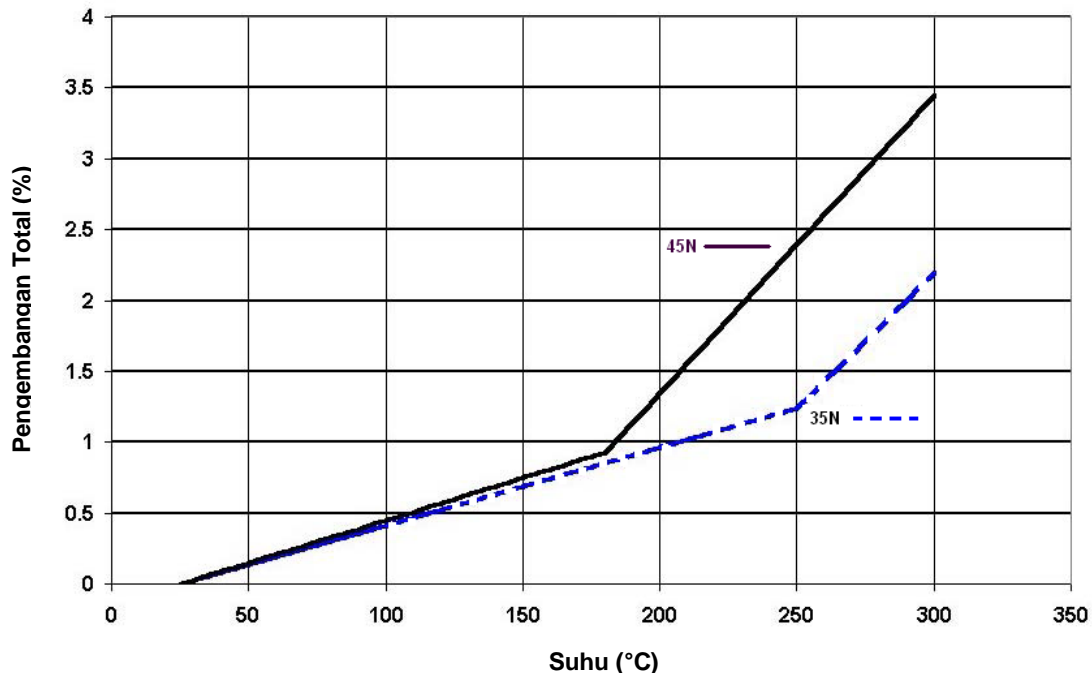
(6 markah)

6. (a) Lukiskan gambarajah skema bagi suatu penganalisis mekanikal dinamik (DMA) dan jelaskan bagaimana alat itu boleh digunakan untuk mengukur parameter modulus penstoran (E'), modulus kehilangan (E'') dan tangen kehilangan ($\tan \delta$) bagi suatu bahan.

(6 markah)

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- (b) Data peralihan kaca (T_g) bagi poliimida 45N dan 35N diperolehi daripada kaedah analisis mekanikal termal (TMA) berdasarkan pada prinsip pengembangan linear termal dengan termogram ditunjukkan di bawah. Analisis kalorimetrik pengesanan perbezaan (DSC) dilakukan pada sampel yang sama berdasarkan pada prinsip aliran haba. Lukiskan termogram DSC bagi sampel tersebut dan jelaskan perbezaan di antara kaedah TMA and DSC.



(6 markah)

- (c) Dua sampel laktosa digunakan untuk kajian T_g bagi laktosa amorfous dan berhablur. Sampel pertama adalah laktosa tersembur kering dengan kandungan 100% amorfous dan sampel kedua adalah sampel berhablur lengkap bagi α -laktosa monohidrat. Lakarkan keluk kalorimeter pengesanan diferensial (DSC) bagi kedua-dua sampel dengan menggunakan kadar pemanasan $500\text{ }^\circ\text{C min}^{-1}$ dengan T_g dalam julat $80\text{--}100\text{ }^\circ\text{C}$. Jelaskan perbezaan dalam ketinggian tingkat bagi T_g untuk kedua-dua sampel.

(8 markah)

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