UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Pertama
Sidang Akademik 2002/2003

September 2002

KAA 507 – Surface and Thermal Analysis

Time: 3 hours

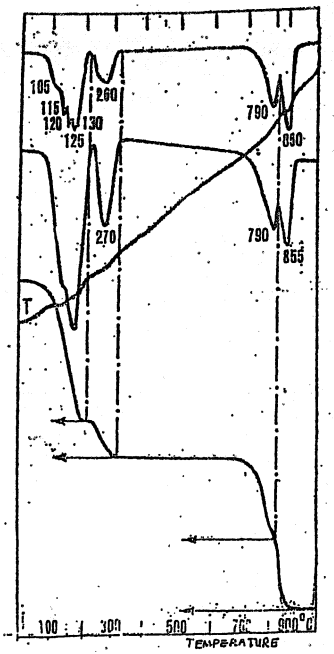
Please make sure this paper consists of FIVE printed pages before answering the questions.

Answer FIVE questions. Only the first five questions answered by the candidate will be marked.

1. (a) Differential thermogravimetric analysis (DTGA) and differential thermal analysis (DTA) are two methods commonly used in studying the sample behavior as a function of temperature. Describe briefly the differences between the two methods and explain the advantages and disadvantages of both in determining the melting point of a substance.

(4 marks)

(b) (i) In the figure given below are three thermograms corresponding to TGA, DTGA and DTA for hydrated copper sulphate ($CuSO_4.5H_2O$). Label and explain each of the thermogram.



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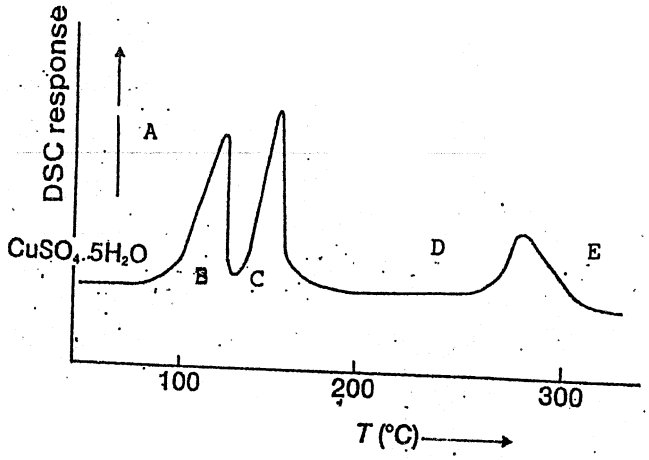
(ii) Using the DTGA and DTA results in question b(i), explain the changes at the region of A, B, C, D, E as shown in the DSC curve for $CuSO_4.5H_2O$ below:



(10 marks)

(c) High vacuum condition ($10^{-4} - 10^{-10}$ torr) is very essential in modern surface analysis especially those using electron and ion as a source of irradiation. Discuss briefly why high vacuum condition is essential?

(6 marks)

2. (a) What is the difference between heat-flux and power-compensated DSC? How do you interpret the results between the two methods?

(8 marks)

(b) What are the characteristics of material used as reference sample for DTA and DSC? Give two examples of reference materials for inorganic and polymer samples.

(5 marks)

(c) Transmission Electron Microscope (TEM) is capable of producing high resolutions images and selected area electron diffraction. Explain the basic principles of electron diffraction technique in structural determination of a material. What are the major advantages and disadvantages of electron diffraction technique?

(7 marks)

3. (a) The measurement of the expansion of solids and liquids caused by various imposed conditions at fixed temperatures is known as dilatometry. What are the differences of basic principle between thermodilatometry (TD) and thermo- mechanical analysis (TMA)?

(6 marks)

(b) TMA measurement is one of the methods used to monitor the effect of various modifications of polymerization, such as the glass transition temperature, Tg, of methyl methacrylate. What are the factors that you expect may increase the Tg of methyl methacrylate?

(8 marks)

(c) 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 including their advantages and disadvantages.

(6 marks)

4. (a) State four criteria that are used in distinguishing physical adsorption or chemical adsorption. Draw in the same diagram the schematic potential energy curve for (i) physical adsorption and (ii) chemical adsorption of a diatomic gas X_2 onto a surface of a metal M. Indicate the activation energy of chemisorption. Justify the shapes and relative position of the curves.

(8 marks)

(b) The following data list volumes of nitrogen gas adsorbed (reduced to S.T.P.) per gram activated charcoal at –196°C.

Pressure/mm Hg	50	100	200	400	600
Volume / $cm^3\ g^{-1}$	74	111	147	177	189

Show that the data fit a Langmuir adsorption isotherm expression and evaluate the constants. Calculate the specific surface area of the activated charcoal, if the cross section molecular area of nitrogen is $16.2\ \text{Å}^2$.

(6 marks)

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(c) The surface of a silicon is believed to be contaminated with SiO_2 and Cl^-. Discuss briefly the surface analytical techniques that are required to analyze the composition and the depth profile of the contaminants.

(6 marks)

5. (a) Sketch the five types of adsorption isotherm in the BET (Brunauer, Emmett and Teller) classification. The BET model of adsorption when the limiting number of adsorbed molecular layer is limited to a finite number of n at saturation, then BET treatment leads to the equation,

$$\frac{X}{X_m} = \frac{c(P/P_o)}{1-P/P_o} \cdot \frac{1-(n+1)(P/P_o)^n + n(P/P_o)^{n+1}}{1-(c+1)(P/P_o) - c(P/P_o)^{n+1}}$$

Where X is the amount adsorbed at relative pressure P/P_o, n is the number of adsorbed molecular layers and c is a constant.

Show that this equation can account for the Langmuir adsorption isotherm.

(12 marks)

(b) Auger Electron Spectroscopy (AES) is considered a real surface analytical technique.

(i) What is an Auger electron? How is it generated and analyzed?

(ii) Sketch the Auger transition of $L_1L_2M_1$ and KL_1M_1.

(iii) Both Auger electron and X-ray radiation are produced during the bombardment of electron onto a sample. Briefly explain how to minimize the effect of X-ray in Auger analysis.

(8 marks)

6. (a) Derive the Gibbs adsorption equation for gas-solid adsorption. What is the model of physical adsorption? Give ONE method of determining the specific surface area with the aid of the Gibbs equation.

(6 marks)

(b) At 90 K a 1.21g sample of a porous solid showed the following results for the adsorption of krypton.

Pressure / torr	1.110	3.078
Volume of Kr adsorbed / cm^3 (STP)	1.475	1.878

If the saturation vapour pressure and molecular cross-section area of krypton at this temperature are 19.0 torr and 21×10^{-20} m^2, respectively, calculate the specific surface area of the solid.

(6 marks)

(c) Secondary Ion Mass Spectrometry (SIMS) is one of the most sensitive surface analytical technique.

(i) What is secondary ion? How is it generated and analyzed?

(ii) Briefly explain the advantages and disadvantages of SIMS analysis.

(iii) What is the chemical image generated by SIMS? Discuss briefly the major differences of this image to that image produced by Scanning Electron Microscopy (SEM)?

(8 marks)

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