



## FACULTY OF SCIENCE

### DEPARTMENT OF CHEMICAL SCIENCES

<b>MODULE:</b>	<b>CEM0087/CEM8X06</b> STRUCTURAL CHEMISTRY
<b>CAMPUS:</b>	APK
<b>TEST:</b>	<b>SUPPLEMENTARY EXAMINATION</b>
<b>DATE:</b>	JANUARY 2020
<b>SESSION:</b>	
<b>ASSESSORS:</b>	PROF A. MULLER
<b>MODERATOR:</b>	PROF B.O. OWAGA (UKZN)
<b>DURATION:</b>	3 HOURS
<b>MARKS:</b>	100

**NUMBER OF PAGES**      7 PAGES, INCLUDING COVER PAGE

**INSTRUCTIONS**      ANSWER ALL QUESTIONS ON ANSWER SHEETS

APPLY CORRECT USE OF SIGNIFICANT FIGURES  
WHERE APPLICABLE.

CALCULATORS MAY BE USED TO ANSWER  
QUESTIONS.

BOTH QUESTION AND ANSWER SHEETS MUST  
BE HANDED IN AT THE END OF THE EXAM

ALL QUESTIONS REQUIRE THAT YOU SHOW THE  
INDIVIDUAL STEPS ON HOW YOU ARRIVED AT  
THE ANSWER.

**QUESTION 1****[8]**

Consider an atom at fractional coordinates  $x, y, z$ .

When operated on by the following symmetry elements, what are the fractional coordinates of the symmetry related atoms?

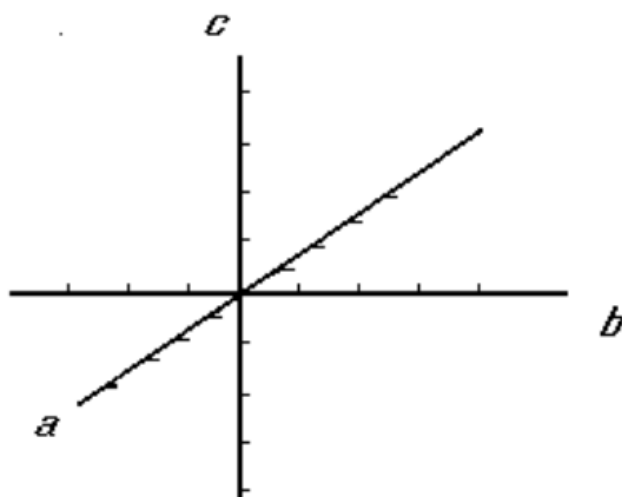
- a) 2 along  $b$
- b)  $\bar{1}$  at coordinate  $(0,0,0)$
- c)  $m$  perpendicular to  $b$
- d)  $2_1$  along  $a$

**QUESTION 2****[6]**

At low temperatures, methane crystallizes in a cubic cell with  $a = 5.89 \text{ \AA}$ . Assuming that the density of the solid methane is similar to or greater than that of liquid methane ( $d = 0.466 \text{ g cm}^{-3}$ ), determine whether methane adopts a primitive, body-centered or face-centered structure.

**QUESTION 3****[6]**

Illustrated below are a set of orthogonal crystallographic axes with tic marks at  $1 \text{ \AA}$  along each axis. Indicate the lattice plane formed by the Miller indices  $(0 \ 3 \ 1)$  from a unit cell with  $a = 4 \text{ \AA}$ ,  $b = 3 \text{ \AA}$  and  $c = 2 \text{ \AA}$ . You may either answer directly on the question paper or redraw the axis in your exam book.



**QUESTION 4****[9]**

Without drawing space group diagrams, explain in detail the information implied by the following space group symbols:

- a)  $P2_12_12_1$
- b)  $Fd3m$

**QUESTION 5****[5]**

In the monoclinic Bravais lattice the  $b$  axis is perpendicular to  $a$  and  $c$  and is referred to as the unique axis. Using structure diagrams explain why a 2-fold rotation axis can only be parallel to the  $b$  axis and why a mirror plane can only be perpendicular to the  $b$  axis.

**QUESTION 6****[2]**

$\text{Me}_3\text{NHCl}$  crystallizes in a monoclinic space group, with  $a = 6.09$ ,  $b = 7.03$ ,  $c = 7.03 \text{ \AA}$ ,  $\beta = 95.73$  and  $Z = 2$ . The only limiting condition found from the Miller indices is that  $0k0$   $k = 2n+1$  is absent. Use this information and predict a possible space group.

**QUESTION 7****[10]**

The successful interpretation of the  $F_o$ - $F_c$  map is usually followed by anisotropic refinement of all non-hydrogen atoms.

Briefly answer the following:

- a) Explain what is meant by anisotropic refinement. (2 marks)
- b) Describe the shortcomings of refining hydrogen atoms from a Fourier electron density difference map and how this can be overcome. Also, provide an example of instances where the use of the Fourier electron density difference map for placement of the hydrogen atom is still useful. (6 marks)
- c) Refinement of data can be checked for correctness inside the software used and also online. Provide short explanations on what these entail. (2 marks)

**QUESTION 8****[5]**

Pure nickel metal crystallizes in a face centred cubic lattice with an unit cell length of 3.524 Å.

Calculate the d-spacing and Bragg diffraction angle of the (100) and (110) planes.  
(Assume Cu K $\alpha$  = 1.5418 Å was used)

**QUESTION 9****[7]**

Briefly detail the parameters encountered during refinement of single crystal data.

**QUESTION 10****[7]**

Using an analogy with a visible light microscope, provide a brief description what is meant by the “phase problem” in crystallography, and what can be done to find a solution to this problem.

**QUESTION 11****[4]**

Discuss the difference between Patterson and Direct methods for solving crystal structures.

**QUESTION 12****[2]**

Give a brief description on the meaning of bi- and trifurcated hydrogen bonding.

**QUESTION 13****[8]**

List and describe the four interactions types a hydrogen bond can transition to.

**QUESTION 14****[10]**

Discuss the experimental requirements for charge density studies.

**QUESTION 15****[6]**

Briefly describe the design aspects to consider for spherical recognition in supramolecular chemistry.

**QUESTION 16****[3]**

List three non-covalent interactions found in supramolecular chemistry.

**QUESTION 17****[2]**

Explain the difference between supermolecules and supramolecular assemblies.

**TOTAL = 100 marks**

## Supplementary information

### Selected systematic absences

Unit cell	Absent
A	$hkl, k+l = 2n+1$ (odd)
B	$hkl, h+l = 2n+1$
C	$hkl, h+k = 2n+1$
I	$hkl, h+k+l = 2n+1$
F	$hkl$ , mixed (not all even or all odd)

Glide planes	Absent
a-glide	$h0l, h = 2n+1$
c-glide	$h0l, l = 2n+1$
n-glide	$h0l, h+l = 2n+1$
d-glide	$hhl, 2h+l = 4n+1$

screw axes	Absent
$2_1$ parallel to a	$h00, h = 2n+1$
$2_1$ parallel to b	$0k0, k = 2n+1$
$2_1$ parallel to c	$00l, l = 2n+1$
$4_1$ parallel to c	$00l, l = 4n+1$

## Constants and formulas:

Avogadro number ( $N_A$ ) =  $6.023 \times 10^{23} \text{ mol}^{-1}$

Distances between planes in a cubic lattice: 
$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2} (h^2 + k^2 + l^2)$$

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