FACULTY OF SCIENCE

DEPARTMENT OF CHEMICAL SCIENCES

MODULE:	**CEM0087/CEM8X06**
	STRUCTURAL CHEMISTRY
CAMPUS:	APK
TEST:	**EXAMINATION**
DATE:	NOVEMBER 2019
SESSION:	
ASSESSORS:	PROF A. MULLER
MODERATOR:	PROF B.O. OWAGA (UKZN)
DURATION:	3 HOURS
MARKS:	100

NUMBER OF PAGES	**7** PAGES, INCLUDING COVER PAGE AND SUPPLEMENTARY INFORMATION
INSTRUCTIONS	ANSWER ALL QUESTIONS
	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 **[7]**

Briefly describe the crystallization technique of vapour diffusion to grow single crystals.

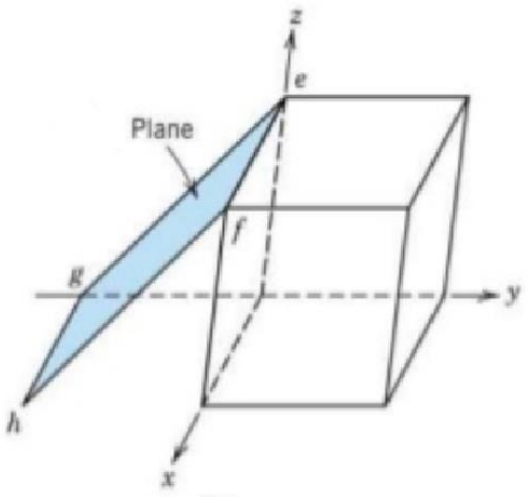
QUESTION 2 **[11]**

Describe the following terms as used in crystallography:

a) I-centred lattice (*3 marks*)
b) Braggs Law (*3 marks*)
c) Space group diagram (*3 marks*)
d) Systematic absence (*2 marks*)

QUESTION 3 **[4]**

Assign the Miller indices of the diffraction plane indicated below:



QUESTION 4 **[6]**

The ionic compound $[(C_{11}H_{20}N_2)_2P][Cl]\cdot n(C_7H_8)$ crystallizes in the space group $P\bar{1}$ with a = 10.134(3), b = 12.243(3), c = 13.037(3) Å, α = 103.358(4), β = 99.906(5), γ = 100.772(4)°, V = 1506.31Å^3. Given that the measured density is 1.145g cm^{-3}, what conclusions can you draw about the structure?

QUESTION 5 **[16]**

a) State all the information that can be extracted from the Herman-Mauguin notation, $P2_1$ space group. *(5 marks)*
b) Construct a 2-D space group diagram of $P2_1$. Include the following details below the diagram: *(11 marks)*
    i. number of equivalent positions contained in the unit cell and their position(s) in crystallographic coordinates,
    ii. if the space group is enantiomorphous or non-enantiomorphous,
    iii. if the space group is centrosymmetric or non-centrosymmetric, and
    iv. the reduced multiplicity of the special position(s) if present

QUESTION 6 **[7]**

What systematic absences are expected if the following symmetry elements are present?

a) I centered lattice
b) c glide perpendicular to a-axis
c) mirror perpendicular to b-axis
d) 2_1 along c-axis

QUESTION 7 **[11]**

Powder X-ray data can be collected through the Debye-Scherrer method.

a) Explain the origin of the Debye rings observed with the method. (*3 marks*)
b) Briefly describe how data is extracted from this method. (*3 marks*)
c) Briefly discuss the refinement methodology for powder diffraction data. (*3 marks*)
d) Name and briefly describe another method available to collect X-ray powder diffraction data. (*2 marks*)

QUESTION 8 **[8]**

The success of single crystal X-ray data refinement relies on the correct interpretation of the F_o-F_c map, and usually results in a model where all atoms are normalized to have the same size. Deviations from these may indicate the presence of disorder in the data.

Briefly answer the following:

a) List another cause that can also be responsible for atom sizes not to be normalized properly, and explain why. (*2 marks*)
b) Briefly describe how disorders are treated during refinement. (*2 marks*)
c) Refinement of a disorder is usually also accompanied by inclusion of restraints or constraints, briefly explain what these are. (*4 marks*)

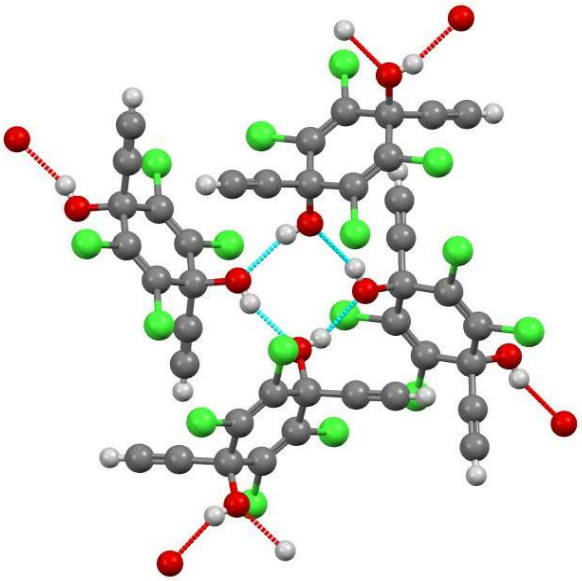
QUESTION 9 **[4]**

List three interactions, in order of increasing strength, which may be present in crystal packing.

QUESTION 10 **[10]**

The crystal structure of 2,3,5,6-tetrachloro-trans-1,4-diethynylcyclohexa-2,5-diene-1,4-dione show intermolecular interactions as shown below. Take careful note of the intermolecular interactions, (in red and light blue) and:

a) Circle these interactions on your question paper
b) Provide a graph set notation for each.



QUESTION 11 **[6]**

Give a description on pi-pi stacking observed in crystal packing. Include in your discussion a detailed picture to illustrate various geometrical aspects that should be taken into account when analysing this interaction.

QUESTION 12 **[6]**

List and briefly describe three types of supramolecular polymers.

QUESTION 13 **[4]**

List and briefly detail the two models developed for the use in charge-density mapping.

TOTAL [100]

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)

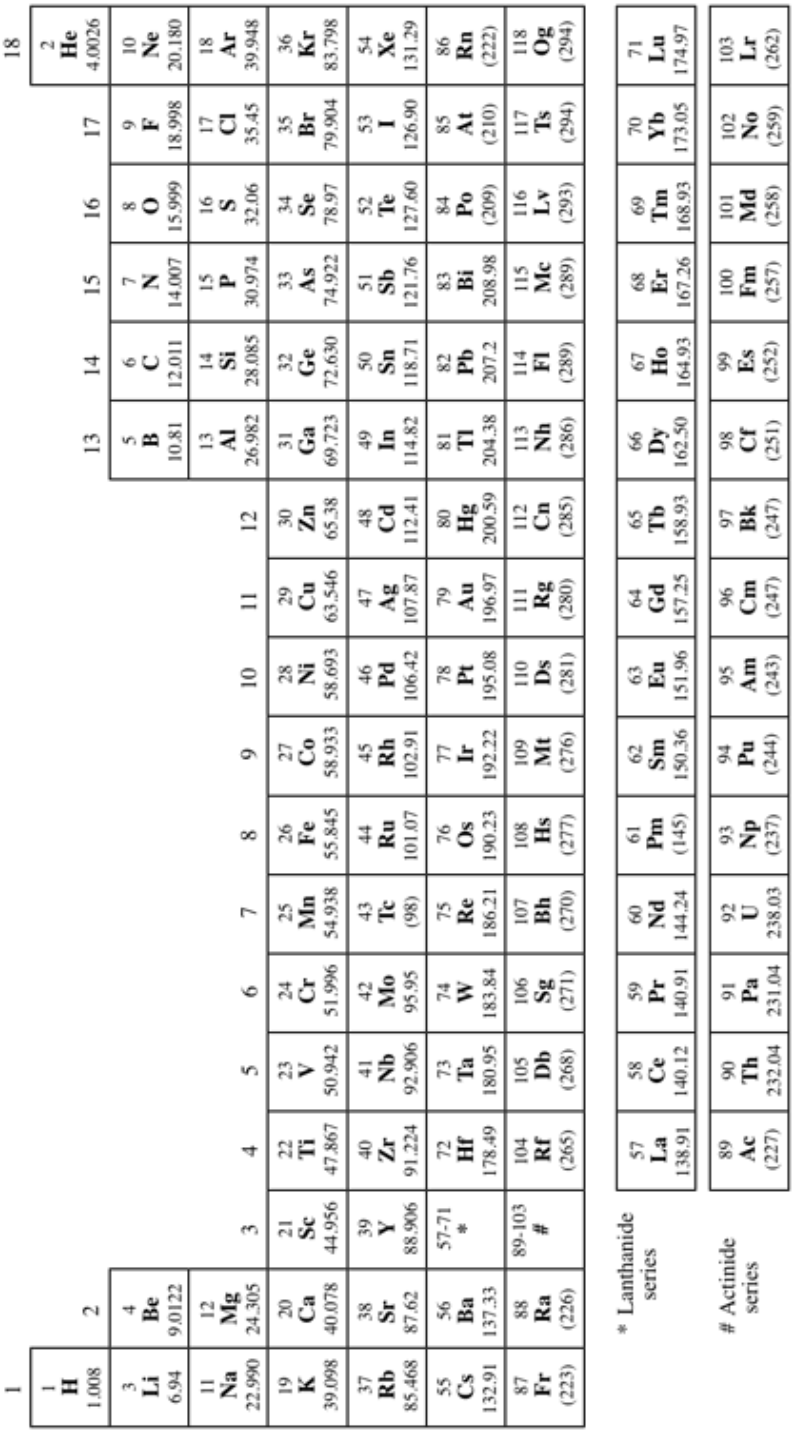
Glide planes	Absent
a-glide	h0l, h = 2n+1
c-glide	h0l, l = 2n+1
n-glide	h0l, h+l = 2n+1
d-glide	hhl, 2h+l = 4n+1

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) = 6.023×10^{23} mol^{-1}

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



1																	18
1 **H** 1.008	2											13	14	15	16	17	2 **He** 4.0026
3 **Li** 6.94	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305	3	4	5	6	7	8	9	10	11	12	13 **Al** 26.982	14 **Si** 28.085	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.630	33 **As** 74.922	34 **Se** 78.97	35 **Br** 79.904	36 **Kr** 83.798
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89-103 #	104 **Rf** (265)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

* Lanthanide series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.05	71 **Lu** 174.97
# Actinide series	89 **Ac** (227)	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)