

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY  
SUPPLEMENTARY EXAMINATIONS - MARCH 2003  
INORGANIC CHEMISTRY I - SCH1101  
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

Answer ALL questions from Section A and ANY THREE from Section B.

Periodic Tables Required

Planck's Constant  $h = 6.626 \times 10^{-34} \text{ J s}$       Velocity of light  $c = 2.998 \times 10^8 \text{ m s}^{-1}$   
Charge on the electron  $e = 1.602 \times 10^{-19} \text{ C}$

SECTION A

- (a) Specify the set of quantum numbers used to describe an electron in an atom, and state what values of each are possible. (8 marks)

(b) State the Exclusion Principle in a form relevant to atomic structure. Show how it leads to the conclusion that in a given shell there can only be two s, six p and ten d electrons. (5 marks)
- The  $\text{Li}^{2+}$  ion has a Lyman series at  $740747 \text{ cm}^{-1}$ ,  $877924 \text{ cm}^{-1}$ ,  $925933 \text{ cm}^{-1}$ , and beyond.

(a) Show that the energy levels are of the form  $-hcR/n^2$ . (6 marks)

(b) Calculate the value of R for this ion. (4 marks)
- Using VSEPR Theory, predict the geometry of the following interhalogen species:

(a)  $\text{BrF}_3$ , (b)  $\text{IF}_3$ , (c)  $\text{IBr}_2^-$  (9 marks)
- (a) The terms (i) first ionisation energy, (ii) electron affinity, refer to the enthalpies of which processes? (2 marks)

(b) The Mulliken definition relates the electronegativity of an element to both its first ionisation energy and electron affinity. State Mulliken's formula, and explain its significance. (6 marks)

< 1 >

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5. The ionic radius of  $O^{2-}$  is 140 pm. Which of the following Group II ions would be predicted to form 4-, which 6- and which 8-co-ordination in their oxides?  
Mg<sup>2+</sup> 72 pm, Ca<sup>2+</sup> 100 pm, Sr<sup>2+</sup> 116 pm, Ba<sup>2+</sup> 136 pm. (6 marks)
6. Draw Lewis diagrams for each of the equivalent resonance structures for the carbonate  $CO_3^{2-}$  and for the hydrogencarbonate  $HCO_3^-$  ion. Two of the bonds in hydrogencarbonate are shorter than in those in carbonate, while one is longer. Explain. (9 marks)

#### SECTION B

7. Draw the possible Kekulé' structures for naphthalene  $C_{10}H_8$ , which consists of two fused benzene rings. Identify the four types of non-equivalent C-C bonds in this molecule, and predict the bond-order of each based on the assumption that each Kekulé' structure has equal weight in forming the resonance hybrid. (15 marks)
8. The bond angle in water,  $H_2O$ , is  $104.5^\circ$ .
- (a) Explain this observation using VSEPR theory. (5 marks)
- (b) Using a sketch, predict the orientation of the dipole moment in the water molecule. If the magnitude of the dipole moment is  $6.17 \times 10^{-30}$  C m and the O-H bond length 103 pm, estimate the bond dipole and the fractional charges on the atoms. (10 marks)
9. (a) The metallic radii of molybdenum, Mo, and tungsten, W, are both 136 pm. How does this observation differ from the normal behaviour of the atomic radius within a Group, and what is the explanation? (3 marks)
- (b) If elemental Mo and W both have body-centred cubic crystal structures, calculate the unit cell edge length  $a$  for each. (5 marks)
- (c) Show that the density of Mo is  $10.3 \text{ g cm}^{-3}$ , and calculate the density of W. (7 marks)

10. In the Huckel approximation the  $\pi$ -electron energies of a homonuclear ring system are given by the formula

$$E_j = \alpha + 2\beta \cos(2\pi j/n)$$

$$\text{where } j = 0, \pm 1, \pm 2, \dots, n/2 \quad n \text{ even,} \\ \dots, \pm(n-1)/2 \quad n \text{ odd,}$$

$n$  is the ring size, and  $\alpha$  and  $\beta$  have their usual meanings.

- (a) Sketch the energy level diagrams for  $n = 4, 5, 6, 7$  and  $8$ . (5 marks)
- (b) Calculate the delocalisation energy (if any) of the following cyclic species, and state which would be considered aromatic:- (10 marks)
- (i)  $C_4H_4$ , (ii)  $C_5H_5^-$ , (iii)  $C_6H_6$ , (iv)  $C_7H_7^+$ , (v)  $C_8H_8$ .
11. (a) Explain the theoretical Born-Mayer expression for the lattice energy of an ionic crystal. Illustrate how the Madelung constant arises by writing down the first three terms for the sodium chloride crystal structure. (7 marks)
- (b) Show how the lattice enthalpy is determined experimentally by sketching the Born-Haber cycle for NaCl. (8 marks)

**END OF QUESTION PAPER!!!!**