NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
SUPPLEMENTARY EXAMINATIONS - JULY 2004
PHYSICAL CHEMISTRY FOR TEXTILE TECHNOLOGY - SCH1122
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

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

Gas Constant R = 8.314 J K^{-1} mol^{-1} = 0.0821 L atm K^{-1} mol^{-1}
Avogadro's Number $N_A = 6.022 \times 10^{23}$ mol^{-1}
Graph Paper and Periodic Tables Required

SECTION A

1. List all the possible combinations of quantum numbers corresponding to the *5f*-subshell in an atom. How many electrons in total can be accommodated in this subshell? (7 marks)

2. The greatest probability of finding an electron in a small volume element of the *1s*-orbital of the hydrogen atom is at the nucleus, yet the most probable distance of the electron from the nucleus is 53 pm. How can these two statements be reconciled? (5 marks)

3. Combustion of diborane, B_2H_6, at constant pressure, proceeds according to the equation:

$$B_2H_6\,(g) + 3\,O_2\,(g) \rightarrow B_2O_3\,(s) + 3\,H_2O\,(\ell) \quad \Delta H_{298} = -2020\ kJ\ mol^{-1}$$

Given that the standard enthalpies of formation of B_2O_3 (s) and H_2O (ℓ) at this temperature are -1264 kJ mol^{-1} and -286 kJ mol^{-1} respectively, and the enthalpy of vaporisation of water is 41 kJ mol^{-1}, calculate the standard molar enthalpy of formation of B_2H_6(g). (8 marks)

4. The heat capacity of chloroform, $CHCl_3$, is given in the range 240 K to 330 K by

$$C_p\ (J\ K^{-1}\ mol^{-1}) = 91.47 + 0.075\ (T/K).$$

Calculate the change in molar enthalpy, and in molar entropy, in heating a sample of chloroform from 273 K to 300 K. (10 marks)

odd no's

5. The standard reaction Gibbs energy of isomerisation of *cis*-2-pentene (C_5H_{10}) to *trans*-2-pentene is -3.67 kJ mol^{-1} at 400 K. Calculate:

(a) The equilibrium constant for reaction, (4 marks)

(b) The equilibrium mole fraction of the two isomers. (4 marks)

6. The vapour pressure of pure liquid A at 300 K is 575 Torr, and that of pure liquid B 390 Torr. These compounds form ideal liquid and vapour mixtures. Consider equilibrium in a mixture with vapour composition $y_A = 0.35$. Calculate the total pressure of the vapour, and the composition of the liquid. (9 marks)

7. At 300 K the partial pressure of HCl gas in equilibrium with its solution in liquid $GeCl_4$ are as follows:

x(HCl)	0.005	0.012	0.019
p(HCl) (kPa)	32.0	76.9	121.8

(a) Show graphically that the solution obeys Henry's Law in this range, and calculate the Henry's Law constant at 300 K. (8 marks)

SECTION B

8. (a) Describe in detail the bonding in ethene (ethylene, C_2H_4). Include explanations of the terms hybrid orbital, σ-bond and π-bond. (10 marks)

(b) The lowest energy unoccupied molecular orbital (LUMO) in ethene is π^* in character. Describe, with the aid of a sketch, how this orbital is formed from atomic orbitals. (5 marks)

9. (a) Describe the geometry of a trigonal bipyramid. (3 marks)

(b) Describe the geometry of the following species in detail, including a sketch and an estimate of the bond angles in each case: (i) ClF_3 (ii) $SeOF_4$ (iii) IF_5 (12 marks)

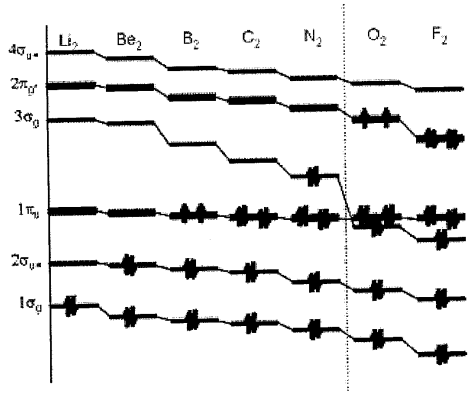
even no's

10. The diagram below shows the electronic configurations of the homonuclear diatomic molecules of the Second Row elements.

(a) Define bond order in molecular orbital terms. Which molecule may we conclude to be unstable to dissociation into its constituent atoms, and why? (4 marks)

(b) Which two molecules shown are paramagnetic, and why? What property must the highest occupied molecular orbital (HOMO) have, in order for a species with an even number of electrons to be paramagnetic? (6 marks)

(c) Explain, with the aid of diagrams, why the antibonding σ-orbitals have **u** symmetry labels, while the antibonding π-orbitals have **g** labels. (5 marks)



11. (a) Calculate the standard enthalpy change of combustion of methane, CH_4 , given the following standard enthalpy changes of formation (all data at 298K):

$\Delta H^\circ_{formation}(H_2O) = -285.53$ kJ mol^{-1}
$\Delta H^\circ_{formation}(CO_2) = -393.51$ kJ mol^{-1}
$\Delta H^\circ_{formation}(CH_4) = -74.81$ kJ mol^{-1}

(6 marks)

(b) Use the following heat capacity data to convert your answer from part (a) to 323K.

$C_P(O_2) = 20.95$ J K^{-1} mol^{-1}
$C_P(H_2O) = 75.29$ J K^{-1} mol^{-1}
$C_P(CO_2) = 29.12$ J K^{-1} mol^{-1}
$C_P(CH_4) = 35.31$ J K^{-1} mol^{-1}

(9 marks)

odd no's

12. The following table gives the volume of nitrogen (reduced to 1 atm) adsorbed per gram of active carbon at 0 °C at various pressures.

p (Pa)	524	1731	3058	4534	7497
v (cm^3/g)	0.987	3.04	5.08	7.04	10.31

(a) Plot the data according to the Langmuir isotherm, and determine the constants. (10 marks)

(b) Estimate the pressure of nitrogen which would result in a fractional coverage of 0.5. (5 marks)

END OF QUESTION PAPER!!!!

even no's