

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS - DECEMBER 2001
PHYSICAL CHEMISTRY FOR TEXTILE TECHNOLOGY - SCH 1122
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

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

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

SECTION A

- 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)
- 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)
- Arrange each of the following sets of elements in order of increasing atomic radius:
(a) Al, Mg, Na (b) Ca, Mg, Sr
(4 marks)
- The following thermal data were found for nitrogen:-

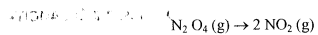
Heating	From (K)	To (K)	$\Delta S^\circ (\text{J K}^{-1} \text{ mol}^{-1})$
	0	35.61	27.2
	35.61	63.14	23.4
	63.14	77.32	11.4

Transition	Temperature (K)	$\Delta H^\circ (\text{kJ mol}^{-1})$
Solid/solid	35.61	0.229
Fusion	63.14	0.721
Boiling	77.32	5.58

Sketch the variation in absolute entropy of nitrogen with temperature from 0 K until the gas phase is reached.
(10 marks)

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5. At 328 K and 1 atm pressure the average molar mass of partially dissociated N_2O_4 is 61.2 g/mol. Calculate (a) the extent of reaction ξ , and (b) the equilibrium constant K for the reaction



at this temperature. (8 marks)

6. One mole of benzene (component 1) and 2 moles of toluene (component 2) are mixed. At 60°C the vapour pressures of benzene and toluene are 51.3 and 18.5 kPa respectively.

(a) As the pressure is reduced, at what pressure will boiling begin? (4 marks)

(b) What will be the composition of the first bubble of vapour? (4 marks)

7. A uniform tube of length L connects two very large containers, one containing pure water, the other an aqueous solution of concentration C . Initially there is a uniform concentration gradient in the tube. Measurements of the concentration are made in a small region about the midpoint of the tube. Initially

$$c = C/2 \quad \text{and} \quad \partial c / \partial x = C/L$$

What will be their values after a short time Δt ?

Describe the temporal and spatial variation of the solute flux in the tube.

(13 marks)

SECTION B

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

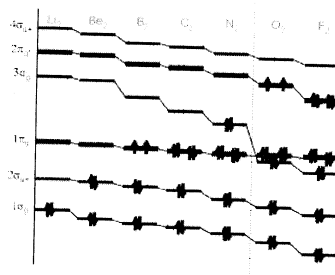
(b) Describe the geometry of the following species in detail, including a sketch and an estimate of the bond angles in each case: (i) ClF_3 (ii) $SeOF_4$ (iii) XeO_2F_2 (12 marks)

9. 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)

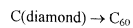


10. The allotropes of carbon include graphite, the stable phase under ambient conditions, and two metastable phases, diamond and buckminsterfullerene, C_{60} . The standard internal energy of combustion of C_{60} has been measured to be $-25.97 \text{ MJ mol}^{-1}$. (All data are at 298 K.)

(a) Calculate the standard enthalpy of combustion of C_{60} . (4 marks)

(b) Given that the standard enthalpy of combustion of C(graphite) is $-393.51 \text{ kJ mol}^{-1}$, calculate the standard enthalpies of formation of (i) CO_2 , (ii) C_{60} . (7 marks)

(c) Given that the standard enthalpy of formation of diamond is $1.895 \text{ kJ mol}^{-1}$, determine whether the process



is exothermic or endothermic.

(4 marks)

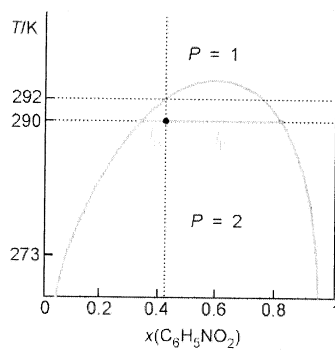
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11. Using the following data, graph the molar volume of $\text{ZnCl}_2/\text{H}_2\text{O}$ mixtures against molality of ZnCl_2 in the range indicated, and use it to determine the partial molar volumes of water and of zinc chloride in a one molal aqueous solution of ZnCl_2 :

Mass % ZnCl_2	2	6	10	14	18	
Density g cm^{-3}	1.0167	1.0532	1.0891	1.1275	1.1665	(15 marks)

12. The diagram below shows the liquid-liquid phase diagram for the system hexane/nitrobenzene at 1 atm pressure.

- (a) State the phase rule, and derive the number of degrees of freedom in each of the regions marked $P = 1$ and $P = 2$ on the diagram (4 marks)
- (b) Estimate from the diagram the upper consolute temperature and composition. (2 marks)
- (c) Describe what will happen as the system is heated at constant composition along the vertical dotted line on the diagram. (3 marks)
- (d) Estimate the compositions and amounts of the two phases present in (c) at 290 K. (I.e., shown by the black dot.) (6 marks)



END OF QUESTION PAPER!!!!

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