CPSS 4273

FIRST PUBLIC EXAMINATION

Long Vacation 1998

Preliminary Examination in Physical Sciences

SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Molecular and Cellular Biochemistry

Time allowed 2 ½ hours

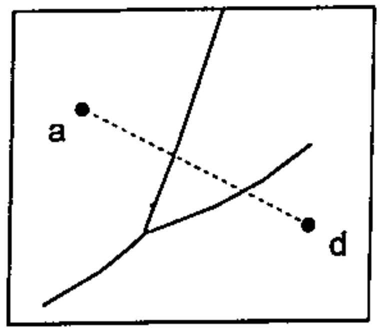
Candidates should answer FOUR *questions only.*

The numbers in the margin indicate the approximate weight the examiners expect to assign to each part of the question

R = 8.3145 J K^{-1} mol^{-1}
k = 1.3807 × 10^{-23} J K^{-1}
N_A = 6.0221 × 10^{23} mol^{-1}
h = 6.6261 × 10^{-34} J s
c = 2.9979 × 10^{8} m s^{-1}
F = 9.6485 × 10^{4} C mol^{-1}
1 u = 1.6605 × 10^{-27} kg
1 bar = 10^{5} Pa

You must not open this paper until instructed to do so by an invigilator.

1. An unlabelled phase diagram for carbon dioxide is shown in the figure below.



(a) Copy this diagram, labelling clearly the two axes, and the three regions into which it is divided by the phase boundary lines. [2]

(b) Define the terms *critical temperature* and *triple point.* [2]

(c) The Clapeyron equation defines the slopes of the lines in this diagram:

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

Outline the derivation of this equation, and explain the meaning of the symbols it contains. [6]

(d) Is the density of solid carbon dioxide greater than or less than that of liquid carbon dioxide? Justify your answer. [3]

(e) Describe the changes which could be observed if, starting from point **a** in the figure above, the conditions were gradually changed so that the system moved along the line **ad**. [6]

(f) At a pressure of 1 bar, water freezes at 273.16 K. At a pressure of 1000 bar, the freezing point is depressed by 7.3 K. The volume change on freezing is 1.6×10^{-6} m ^{3} mol $^{-1}$. Calculate the enthalpy of fusion of water at 273.16 K. [6]

2. **Answer any TWO of sections (a) to (d)** (all sections carry equal marks).

(a) Write down the Rydberg equation and explain briefly its value in analysis of atomic spectra of hydrogenic atoms. The lowest energy electronic transition in ground state hydrogen atoms occurs at a wavelength of 121.8 nm, and the lowest energy transition in ground state helium atoms occurs at a wavelength of 58.43 nm. Calculate the ratio of the Rydberg constants for hydrogen and helium.

(b) What is meant by a *radial probability distribution function* for an electron in an atom? In what way is it different from the *radial wavefunction*? Outline how a knowledge of the radial wavefunction can help explain the energy ordering of the s, p and d orbitals in an atom.

(c) If helium gas is excited in an electrical discharge, an emission spectrum showing a large number of spectral lines is observed. Many of these lines are absent from the absorption spectrum of helium. Explain this observation as fully as possible.

(d) What is the Uncertainty Principle? Describe one experiment which provides evidence for the Uncertainty Principle.

3. (a) Starting from the equations

$$\Delta_r G^\ominus = -RT \ln K$$

and

$$(\mathrm{d}/\mathrm{d}T)(\Delta_r G^\ominus/T) = -(\Delta_r H^\ominus / T^2)$$

derive an equation which shows how the equilibrium constant for a reaction, K, varies with temperature, stating any assumptions you make. [7]

(b) The vapour of pentane-2,4-dione consists of a mixture of two tautomers in equilibrium:

$$CH_3COCH_2COCH_3 \ \textit{(keto)} \rightleftharpoons CH_3COCH{=}C(OH)CH_3 \ \textit{(enol)}$$

The vapour contains 92% *enol* at 298 K and 84% *enol* at 373 K. Calculate the enthalpy of reaction and the entropy of reaction, assuming them to be independent of temperature. [9]

(c) For the equilibrium

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$$

in the temperature range 900 K to 1000 K

$$\ln K = 12.745 - 6341 / (T/\mathrm{K})$$

Calculate $\Delta_r H^\ominus$, $\Delta_r G^\ominus$ and $\Delta_r S^\ominus$ for this reaction at 1000 K. [9]

4. (a) State the second law of thermodynamics. [1]

(b) For each of the following processes, predict the entropy changes occurring during the process. Briefly justify your conclusions.

(i) 1 mole of calcium carbonate decomposes completely into calcium oxide and carbon dioxide upon heating. [4]

(ii) 1 mole of water is frozen rapidly at -5 °C and a pressure of 1 atmosphere. [4]

(c) Comment on your answer to part (ii) in the light of the second law of thermodynamics. [4]

(d) The molar heat capacity at constant pressure for He at 298 K is 20.79 J K^{-1}, while that of chlorine at the same temperature is 33.93 J K^{-1}.

(i) Predict the molar heat capacity at constant volume of argon at 298 K. [2]

(ii) Explain why the molar heat capacities of helium and chlorine differ. [5]

(iii) Halogens are often diluted with helium for use in experiments. Calculate the quantity of heat required to raise the temperature of 40 g of a mixture containing (by volume) 5% chlorine and 95% helium from 298 K to 305 K. Assume that the heat capacity of both gases is constant over this small temperature range, that the pressure remains constant, and that the gases do not interact with each other in any way.
[Atomic weights: He: 4, Cl: 35.5] [5]

5. (a) Distinguish between the *order* and the *molecularity* of a chemical reaction. [6]

(b) Outline one method by which the order of a chemical reaction can be determined experimentally. [6]

(c) The gas phase reaction of fluorine atoms with bromine follows the stoichiometric equation

$$F + Br_2 \rightarrow FBr + Br$$

The following concentrations of Br_2 were observed as a function of time at 298 K when the initial fluorine atom concentration $[F] = 4 \times 10^{-9}$ mol dm $^{-3}$.

Time / ms	0	0.7	1.3	2.7	3.9
$[Br_2]$ / 10^{-9} mol dm $^{-3}$	0.100	0.066	0.048	0.022	0.011

(i) Show that the reaction is first order with respect to Br_2. [9]

(ii) Given that the reaction is also first order with respect to F atoms, calculate the overall second-order rate constant. [4]

6. (a) Explain the meaning of the terms *standard electrode potential* and *insoluble salt electrode*. [6]

(b) The values of $E^{\ominus}$ for two half-reactions at 298 K are given below

$$AgI(s) + e^- = Ag(s) + I^-(aq) \qquad E^{\ominus} = -0.152\ V$$
$$Ag^+(aq) + e^- = Ag(s) \qquad E^{\ominus} = +0.799\ V$$

(i) Explain why it is necessary to measure the EMF of an electrochemical cell under conditions of zero current flow. [4]

(ii) Draw a diagram showing a cell in which the two half-reactions given above can be made to occur. [4]

(iii) Write down the overall cell reaction for the cell you have drawn. [3]

(iv) Write down the Nernst equation for the cell reaction. [3]

(v) Calculate $E^{\ominus}$ and $\Delta G^{\ominus}$ for the reaction occurring in the cell, and the solubility product of silver iodide at 298 K. [5]

7. (a) Explain what is meant by the terms ***eigenfunction***, ***eigenvalue*** and ***normalization constant***. [8]

(b) Show that

(i) e^{ibt}

(ii) $a.\cos(bt + c)$

in which a, b and c are constants, are eigenfunctions of the operator $\frac{d^2}{dt^2}$ and in each case determine the associated eigenvalue. [6]

(c) A simple model for the molecule β-carotene (whose structure is shown below) treats the π electrons as though they were confined to a one-dimensional box with infinitely high potential walls. The electrons can then be described according to the "particle-in-a-box" model, with each energy level able to accommodate a maximum of two electrons.

(i) What value must the wavefunction for the electrons in the box have at each end of the box? Why? [4]

(ii) β-carotene is orange; in what region of the visible spectrum does it absorb light? [2]

(iii) It is possible to synthesize molecules of structure similar to β-carotene, in which the length of the conjugated π system is greater than that in β-carotene. The energy of electrons confined to a one-dimensional box is given by

$$E = \frac{n^2h^2}{8mL^2}$$

in which n is a quantum number and L the length of the box. How would the wavelength of the light absorbed by the π electrons be affected if the length of the conjugated system were increased? Justify your answer. [5]