

FIRST PUBLIC EXAMINATION

Long Vacation 1999

Preliminary Examination in Physical Sciences

SUBJECT 3: CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Biochemistry

WEDNESDAY 22 SEPTEMBER - 9.30am

Time Allowed 2 ½ hours

Candidates should answer all questions in Section A and any two questions in Section B.

(The numbers in square brackets indicate the weight that the Examiners expect to assign to each part of the question)

Molar gas constant, R	$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Planck constant, h	$= 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant, k_B	$= 1.381 \times 10^{-23} \text{ J K}^{-1}$
Speed of light, c	$= 2.998 \times 10^8 \text{ ms}^{-1}$
Avogadro number, N_A	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
p^\ominus	$= 1 \text{ bar} = 1 \times 10^5 \text{ Pa}$
Electron mass, m_e	$= 9.110 \times 10^{-31} \text{ kg}$
Elementary charge, e	$= 1.602 \times 10^{-19} \text{ C}$
Faraday constant, F	$= 9.648 \times 10^4 \text{ C mol}^{-1}$
Atomic mass unit, m_u	$= 1.661 \times 10^{-27} \text{ kg}$
Molar volume, V_m	$= 24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298K

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

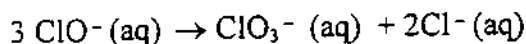
Section A

Answer all six questions in this section

1. (a) Draw the phase diagram for water (as a function of pressure and temperature), identifying clearly the triple point and critical point. [5]

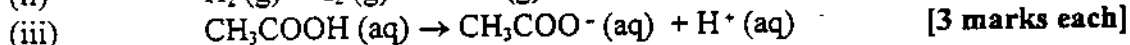
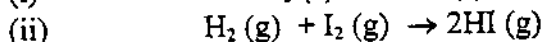
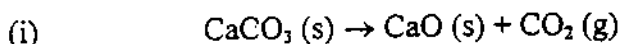
- (b) Materials can be “freeze-dried” by cooling them to temperatures below 0 °C and reducing the pressure. Use your diagram to explain how such a process removes water. [3]

2. The decomposition of hypochlorite ion in solution, shown below, obeys second order kinetics.



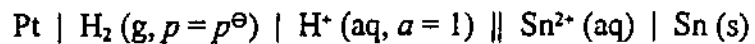
- (a) Write down the rate equation for the reaction. [1]
- (b) If concentrations are specified in mol dm⁻³, what are the units of the rate constant? [2]
- (c) Demonstrate that a plot of 1 / [ClO⁻] as a function of time should be linear. [5]

3. Discuss how the entropy of the system would change during each of the following reactions.



4. Write down and explain the atomic term symbols for lithium and boron in their lowest energy electronic states. [8]

5. For the following cell:



- (a) Write down the cell reaction. [3]
- (b) Give the Nernst equation for the cell reaction. [3]
- (c) Calculate the change in the standard cell potential when the activity of the Sn^{2+} is changed from $a = 1$ to $a = 0.1$ at a temperature of 298 K. [3]
6. Discuss fully **one** experiment which provides evidence for quantization. [8]

Turn over

Section B

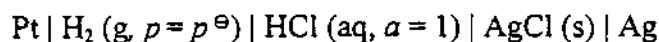
Answer any two questions in this section

7. The following data relate to the base-catalysed hydrolysis of an ester E:

[E] / mol dm ⁻³	[OH ⁻] / mol dm ⁻³	Initial rate of reaction / 10 ⁻⁴ mol dm ⁻³ s ⁻¹
0.071	0.239	0.014
0.142	0.241	0.027
0.142	0.481	0.054

- (a) Determine the rate equation for the reaction. [4]
- (b) In an experiment in which the concentration of ester was 0.24 mol dm⁻³, the initial rate of reaction was found to be 2.2×10^{-6} mol dm⁻³ s⁻¹. Determine the pH of the solution. [10]
- (c) Explain how a catalyst affects the rate of a reaction. [7]
- (d) Explain why, even though a catalyst is not consumed during a reaction, its concentration may still appear in the rate equation. [4]
8. (a) Explain how the standard EMF E^\ominus may be related to $\Delta_r G^\ominus$, $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for a reaction. [6]

- (b) For the cell



E^\ominus is given by the equation

$$(E^\ominus / \text{V}) = 0.2366 - 4.856 \times 10^{-4} (T - 273) - 3.421 \times 10^{-6} (T - 273)^2$$

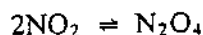
where T is in Kelvin.

- (i) Write down the half reactions and the overall cell reaction. [6]
- (ii) Write down the Nernst equation for the cell. [2]
- (iii) Calculate $\Delta_r G^\ominus$, $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ and the equilibrium constant for the reaction at 298 K. [11]

9. ANSWER EITHER PART I OR PART II

PART I:

Nitrogen (IV) oxide and dinitrogen tetroxide are in equilibrium according to the equation



At 298 K, $\Delta_r H^\ominus = -57.2 \text{ kJ mol}^{-1}$ and $\Delta_r S^\ominus = -175.8 \text{ J K}^{-1} \text{ mol}^{-1}$

- (a) Calculate $\Delta_r G^\ominus$ and the value of the equilibrium constant K_p at 298 K. [4]
- (b) 1 mole of NO_2 is confined to a container at 298 K and allowed to reach equilibrium. If the final pressure of the equilibrium mixture is 0.06 bar, calculate the mole fraction of N_2O_4 present. [7]
- (c) Make a sketch showing how the Gibbs Free Energy of the system at 298 K and at a constant pressure of 0.06 bar depends on the composition of the mixture, for compositions ranging from 100% N_2O_4 to 100% NO_2 . [8]
- (d) In what way does the change in Gibbs Free Energy help define the point at which a reaction has reached equilibrium? [2]
- (e) Reconcile your answer to part (d) with the value of $\Delta_r G^\ominus$ you found in part (a). [4]

PART II:

- (a) Derive, from first principles, the Clausius-Clapeyron equation, which relates the vapour pressure of a liquid to the absolute temperature. [6]
- (b) Comment as fully as possible on the data given in the table below. [19]

Liquid	Normal boiling point / K	Enthalpy of vaporization / kJ mol^{-1}	Entropy of vaporization / $\text{J K}^{-1} \text{ mol}^{-1}$
Helium	4.21	0.84	20
Nitrogen	77.3	5.56	72
Sulphur dioxide	263.1	24.92	95
Methanol	337.8	35.27	104
Ethanoic acid	391.4	24.39	62
Sodium chloride	1738	173.7	98

Turn over

10. A particle of mass m is constrained to move in a one-dimensional square well of length L . The potential energy of the system is given as

$$\begin{aligned} V(x) &= 0 & 0 \leq x \leq L \\ V(x) &= \infty & \text{for } x < 0 \text{ and } x > L \end{aligned}$$

- (a) Write down the Hamiltonian operator, \hat{H} for the system and show that the wavefunction

$$\psi = C \cos kx + D \sin kx$$

is an eigenfunction of \hat{H} . [6]

- (b) By using appropriate boundary conditions, derive expressions for the constants C , D and k and hence show that the energy of the system is quantized. [8]

- (c) Sketch the three lowest energy wavefunctions and comment on their properties. [5]

- (d) Derive a general expression for the probability that the particle will be found in the region

$$\frac{1}{2}L - \delta \leq x \leq \frac{1}{2}L + \delta \quad [6]$$