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

$$3\ ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$$

   (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.

   (i) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
   (ii) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
   (iii) $CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H^+(aq)$ **[3 marks each]**

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:

$$\mathrm{Pt} \mid \mathrm{H_2}\,(\mathrm{g}, p = p^{\ominus}) \mid \mathrm{H^+}\,(\mathrm{aq}, a = 1) \parallel \mathrm{Sn^{2+}}\,(\mathrm{aq}) \mid \mathrm{Sn}\,(\mathrm{s})$$

(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]

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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

$$Pt \mid H_2 (g, p = p^\ominus) \mid HCl (aq, a = 1) \mid AgCl (s) \mid Ag$$

$E^\ominus$ is given by the equation

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

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

$$2NO_2 \rightleftharpoons N_2O_4$$

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

$$V(x) = 0 \qquad 0 \leqslant x \leqslant L$$
$$V(x) = \infty \qquad \text{for } x < 0 \text{ and } x > L$$

(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

$$\tfrac{1}{2}L - \delta \leqslant x \leqslant \tfrac{1}{2}L + \delta$$ **[6]**