# FIRST PUBLIC EXAMINATION

Trinity Term 1999

Preliminary Examination in Physical Sciences

SUBJECT 3: CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Molecular and Cellular Biochemistry

Thursday, 10th June 1999, 2.30 p.m. to 5.00 p.m.

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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 298 K |

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

## Section A

Answer **all six** questions in this section

1. Reactant A is converted into product C according to the mechanism:

$$A \rightarrow B \qquad (1)$$
$$B \rightarrow C \qquad (2)$$

with respective rate constants for the two reactions of $k_1$ and $k_2$.

(a) Assuming that $k_1$ and $k_2$ are approximately equal, that $[A]_0 = 1.0$ M and that $[B]_0 = [C]_0 = 0.0$ M, sketch how the concentrations of A, B and C vary with time. **[6]**

(b) To which of the species A, B and C, if any, could the *Steady State Approximation* be applied? Briefly justify your answer. **[3]**

2. Briefly explain the meaning of the following terms

(i) *State function*
(ii) *Heat capacity*
(iii) *Phase diagram* **[8]**

3. For the cell

$$Zn(s) \mid Zn^{2+}(aq, a) \parallel Cu^{2+}(aq, a) \mid Cu(s)$$

determine the cell reaction, the standard EMF and the value of the equilibrium constant for the cell reaction at 298 K, assuming unit activity for all species.

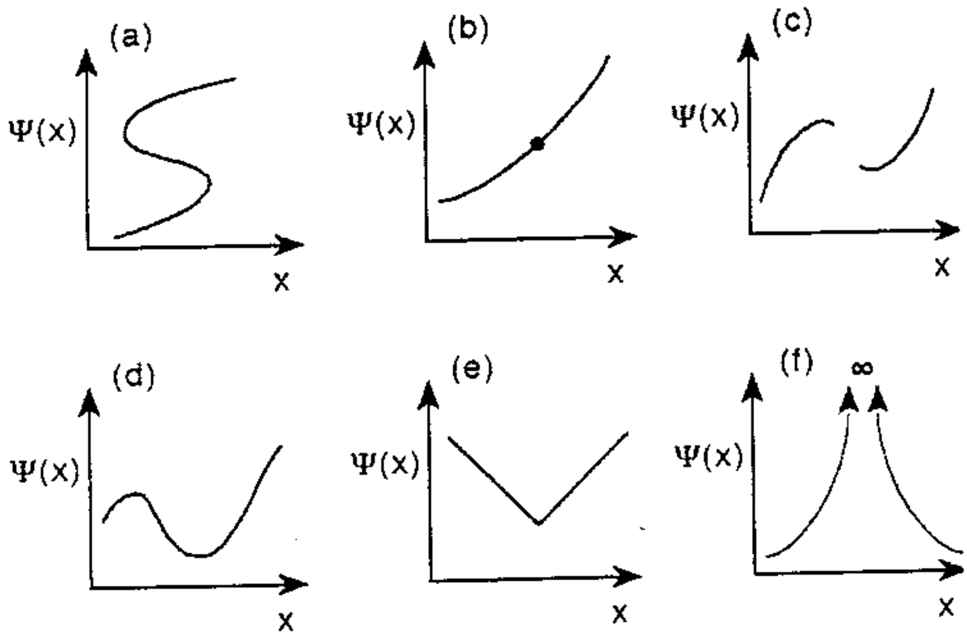
You may use the following standard reduction potentials measured at 298 K

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^\ominus = 0.337 \text{ V}$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^\ominus = -0.763 \text{ V}$$

**[9]**

4. The wavefunction for the hydrogen atom in its ground state ($n$ = 1) is of the form $\psi = Ne^{-r/a_o}$ where $r$ is the distance from the nucleus to the electron and $a_o$ the Bohr radius. Evaluate the normalisation factor $N$.
[You may need the standard integral $\int_0^\infty x^2 e^{-kx} dx = \{2/k^3\}$ ] **[8]**

5. The figure below shows portions of several functions, some of which might be solutions to the Schrodinger wave equation. Identify those functions which are *not* acceptable solutions, and explain why these functions are disallowed. **[8]**




6. Heptane ($C_7H_{16}$) and octane ($C_8H_{18}$) dissolve to form ideal solutions. At 313 K the vapour pressures of heptane and octane are 0.121 bar and 0.041 bar respectively.

(a) Calculate the total vapour pressure of a solution at 313 K which consists of equal weights of heptane and octane. [RAM: H = 1; C = 12] **[3]**

(b) To a solution of 50.0 g heptane and 50.0 g octane at 313 K is added 5.0 g of a non-dissociating, involatile solute. The total vapour pressure of the resulting solution is found to be 0.0828 bar. Assuming that the solution behaves ideally, calculate the molecular weight of the solute. **[3]**

(c) How will the addition of solute affect the normal boiling point of the solution? **[2]**

**Turn over**

## Section B

Answer **any two** questions from this section

7. (a) Why does the rate of most chemical reactions increase as the temperature is raised? [5]

(b) The rate constant for the decomposition of HI into $H_2$ + $I_2$ shows the following temperature dependence:

| $k$ / dm$^3$ mol$^{-1}$ s$^{-1}$ | $3.16 \times 10^{-6}$ | $7.90 \times 10^{-5}$ | $3.20 \times 10^{-3}$ | 0.10 |
|---|---|---|---|---|
| $T$ / K | 550 | 625 | 700 | 830 |

Determine the activation energy for the reaction, and the pre-exponential factor A in the Arrhenius equation. [5]

(c) What is the overall reaction order for the decomposition? What justification do the data in the table above give for the form of the rate equation? [4]

(d) The reaction between hydrogen and iodine to form hydrogen iodide is believed to proceed *via* a chain mechanism. Using this reaction as an example, explain the meanings of the terms *Initiation*, *Propagation* and *Termination.* [6]

(e) For the reaction between nitric oxide and oxygen

$$2\,NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

the rate law is

$$\text{Rate} = k\,[NO]^2\,[O_2]$$

The rate of reaction is found to *fall* as the temperature is increased. Propose a mechanism for the reaction, and show how it explains both the rate law and the temperature dependence of the reaction. [5]

8. (a) Write an expression for the equilibrium constant for the gas-phase reaction: [2]

$$H_2\,(g) + \tfrac{1}{2}\,S_2\,(g) \rightleftharpoons H_2S\,(g)$$

(b) Sketch how the mole fraction of hydrogen sulphide varies as a function of pressure, for an arbitrary temperature, $T_1$. Demonstrate how the shape of the plot can be related to your expression for $K_p$. [4]

(c) At a total pressure of 1 bar, the equilibrium constant for the reaction has been found to vary with temperature as follows:

| $T$ / K | 400 | 600 | 800 | 1000 |
|---|---|---|---|---|
| $K_p$ | $8.33 \times 10^8$ | $1.54 \times 10^5$ | 1960 | 137 |

– Determine the enthalpy of reaction near 700 K. [6]

(d) Add a line to your sketch from part (b) showing how the mole fraction of hydrogen sulphide would vary with pressure for a second temperature $T_2 > T_1$. [3]

(e) What conditions of temperature and pressure favour dissociation of hydrogen sulphide? [2]

(f) At 600 K, without changing the size of the container, 1 mole of nitrogen is added to the equilibrium mixture. What effect, if any, would this have on the position of equilibrium? Justify your answer as completely as possible. [8]

9. (a) Write notes explaining the meanings of the quantum numbers $n$, $l$, $m_l$ and $s$ for the electron of a hydrogen atom. [8]

(b) The emission spectrum of atomic deuterium shows lines at 15238, 20571, 23029 and 24380 $cm^{-1}$. Determine the ionization energy of the lower state, and the value of the Rydberg constant for deuterium, $R_D$. [8]

(c) What is meant by the *radial distribution function* of an atomic orbital? [4]

(d) The wavefunction for a hydrogenic 1s orbital is

$$P(r) = 2(Z/a_o)^{\frac{3}{2}} e^{-\rho/2}$$

in which $\rho = 2Zr/na_o$ and Z is the atomic number.

Calculate the most probable radius at which the electron will be found when it occupies the 1s orbital of $Li^{2+}$. [$a_o$ = 52.9 pm.] [5]

**Turn over**

10. (a) Explain what is meant by a *reference electrode* and comment on the properties needed to ensure an electrode acts as a good reference electrode. **[8]**

(b) Write down the cell reaction and the Nernst equation for the Harned cell (shown below). **[4]**

$$\mathrm{Pt} \mid H_2\,(g)\,(p = p^{\ominus}) \mid \mathrm{HCl}\,(aq, a) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

(c) Explain briefly how one could determine the standard reduction potential for a half cell. [3]

(d) Solid silver chloride conducts electricity sufficiently well that the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid Cl_2\,(g) \mid \mathrm{Pt}$$

is reversible for both solid and liquid silver chloride. The variation of the standard potential of the cell with temperature is as follows:

| $T$ / K | 550 | 625 | 680 | 730 | 770 | 820 | 890 |
|---|---|---|---|---|---|---|---|
| $E$ / V | 1.012 | 0.974 | 0.946 | 0.920 | 0.905 | 0.888 | 0.865 |

Determine the enthalpy and entropy of fusion, and the melting point of silver chloride. **[10]**