

FIRST PUBLIC EXAMINATION

Trinity Term 2002

Preliminary Examination in Chemistry

SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Molecular and Cellular Biochemistry

Wednesday, 5th June 2002, 2.30 pm – 5.00 pm

Time allowed: 2½ 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	$= 2.998 \times 10^8 \text{ m s}^{-1}$
Avogadro number, N_A	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
p^\ominus	$= 1 \text{ bar} = 760 \text{ Torr} = 1 \times 10^5 \text{ Pa}$
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, u	$= 1.661 \times 10^{-27} \text{ kg}$
Molar volume, V_m	$= 24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K
1 electron volt	$= 1.6022 \times 10^{-19} \text{ J}$

Do not turn over until instructed to do so by an invigilator.

SECTION A

Answer all six questions in this section

1. (a) At 843 K and 1 bar pressure, a crystalline substance undergoes a phase transition to a new crystal structure. If the pressure is raised to 80 bar, the phase transition occurs at 854 K. The volume change which accompanies the phase change is $+6.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ at each pressure. Calculate the molar enthalpy change of the phase transition, given it is independent of temperature.

[4]

- (b) At 1 bar pressure, benzene boils at 353 K and the enthalpy of vaporisation is 30.8 kJ mol^{-1} .

(i) Calculate the molar *entropy* of vaporisation at this boiling point and comment on its value.

[2]

(ii) Calculate the vapour pressure of benzene at 343 K, noting any approximations in the equations, which you use.

[3]

2. 1% of F_2 (g) molecules are dissociated to form F (g) atoms at equilibrium, when heated to a particular temperature in a vessel, containing only fluorine, at a total pressure of 10 Pa.

Use the information provided to calculate the equilibrium constant K_p at this temperature for the reaction



and discuss how the fraction of dissociated molecules would vary if the amount of fluorine in the vessel was increased.

[8]

3. (a) The quantum mechanical formula for the energy E , of a particle of mass m , trapped in a one-dimensional box of length L , within which the potential is zero, is

$$E = \frac{n^2 h^2}{8 m L^2} \quad n = 1, 2, 3 \dots$$

What would be the corresponding expression for a particle trapped in a two-dimensional box, of dimensions $L \times L$?

[2]

- (b) A semiconductor material incorporates an electron trapped in a two-dimensional square box of side 10 nm, within which the potential can be taken as zero. Calculate the zero point energy of the electron in this structure.

[3]

- (c) What is meant by the term *degeneracy* in quantum mechanics? What are the degeneracies of the lowest and second lowest energy levels in the system described in part (b) above?

[3]

4. (a) Discuss how well the vibrational properties of diatomic molecules can be understood using the harmonic oscillator model for vibrational motion.

[3]

- (b) How do such vibrational properties compare to those of a classical body undergoing harmonic motion?

[2]

- (c) The energy difference between the lowest two vibrational energy levels of the oxygen molecule is 3.14×10^{-20} J. Estimate the vibrational force constant, k .

[3]

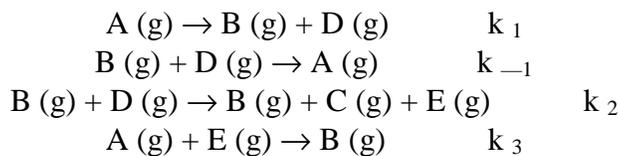
[atomic mass: O 16 u]

Turn Over

5. The overall reaction



is postulated to occur via the following mechanism



where D(g) and E(g) are reactive intermediates.

- (a) Explain what is meant by the *steady state approximation* in reaction kinetics. [2]
 (b) Use this approximation to show that the concentration of E is given by

$$[E] = \frac{k_1 k_2}{(k_{-1} + k_2) k_3} \quad [6]$$

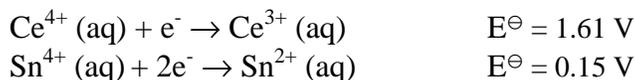
6. Consider the following electrochemical cell at 298 K



which is prepared such that all species have unit activity.

- (a) Determine the EMF of the cell, the cell reaction and the value of the equilibrium constant at 298 K. [6]
 (b) What would be the new cell EMF at 298 K, if the activity of the Ce^{3+} species was reduced to 0.5, with the activity of the other species remaining unchanged? [3]

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



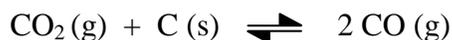
SECTION B

Answer any two questions in this section
All questions in this section carry equal marks

7. (a) Explain how the standard molar heat capacities at constant pressure of the substances involved in a chemical reaction can be used to calculate the variation with temperature of the standard enthalpy change for the reaction. [5]
- (b) Standard molar heat capacities at constant pressure, C_p^i , are provided in the table below for the substances indicated, at 298 K. The heat capacities given can be assumed to be constant over the temperature range 298-600 K.

Substance	$C_p^i / \text{J mol}^{-1} \text{K}^{-1}$
C (s)	8.5
CO ₂ (g)	37.1
CO (g)	29.1

For the reaction



ΔG^\ominus is $120.02 \text{ kJ mol}^{-1}$ and ΔH^\ominus is $172.45 \text{ kJ mol}^{-1}$, both measured at a temperature of 298 K. For this reaction, calculate:

- (i) ΔS^\ominus and the equilibrium constant K_p both at 298 K. [6]
- (ii) ΔH^\ominus at 600 K. [7]
- (iii) the equilibrium constant K_p at 600 K. [7]

Turn over

8. (a) How is an *ideal solution* defined? [3]
- (b) Explain whether you would expect liquid mixtures of (i) methylbenzene and benzene (ii) propanone and carbon disulphide, to exhibit properties which conform closely to those expected of an ideal solution. [4]
- (c) Assume the systems considered below exhibit properties expected of ideal solutions.
- (i) At 300 K, pure substances *A* and *B* exist in liquid form, with vapour pressures of 43.3 kPa and 11.3 kPa respectively. Calculate the total vapour pressure and the composition of the vapour phase above a mixture of these two liquids, at 300 K with a mole fraction $x_A = 0.3$. [6]
- (ii) Calculate the Gibbs energy of mixing and the entropy of mixing when 71 g of decane ($C_{10}H_{22}$ (l)) is added to 129 g of hexane (C_6H_{14} (l)) at a temperature of 300 K. What is the enthalpy of mixing for this process? [6]
- (iii) A substance *C* has a freezing point of 343 K and an enthalpy of fusion of 3.9 kJ mol^{-1} . A saturated solution of *C* has a mole fraction $x_C = 0.73$. What is the temperature? [6]

[atomic masses: C 12 *u* ; H 1 *u*]

9. Explain the meaning of the following concepts, which arise in the description of the electronic properties of the alkali metal atoms: *atomic orbital*, *electron configuration*, *radial distribution function*, *penetration*, *quantum defect*, *selection rule*. [9]
- (a) The lowest energy transition, in the electronic absorption spectrum of atomic hydrogen from the electronic ground state, occurs at $82\,259 \text{ cm}^{-1}$. Calculate the ionisation energy of atomic hydrogen. The electronic emission spectrum of atomic hydrogen exhibits a series of strong lines at $5\,331.6$, $7\,799.4$ and $9\,139.9 \text{ cm}^{-1}$. Explain in detail the origin of these lines. [5]
- (b) How would you expect the observed wavenumbers for the same transitions in the electronic emission spectrum of deuterium to compare with those measured for hydrogen in (a) above? [4]
- (c) How would you expect the ionisation energies of (i) He^+ , (ii) He , to compare with the value for atomic hydrogen calculated in (a) above? [4]
- (d) The yellow line observed in the electronic emission spectrum of sodium is split into two components, separated by approximately 17 cm^{-1} . Explain why this is so. [3]

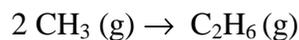
10. (a) Explain what is meant by the terms *reaction order*, *half-life*, and *activation energy*, which are encountered in chemical kinetics.

[6]

- (b) How can the rates of chemical reactions be measured experimentally? Include in your answer a consideration of “slow” and “fast” reactions.

[4]

- (c) The concentration of methyl radicals, CH₃, in a container is found to vary with time, as indicated below, as a result of the gas phase reaction.



The rate of reaction does not depend on temperature.

[CH ₃] / 10 ⁻⁷ mol dm ⁻³	4.1	3.0	2.4	2.0	1.7
Time / 10 ⁻⁶ s	0	40	80	120	160

- (i) Show the reaction rate is second order with respect to [CH₃]. (ii) Calculate the rate constant for the above reaction. (iii) What is the activation energy for this reaction?

[8]

- (d) The initial rate of reaction, *R*, for the thermal decomposition of cyclopropane to form propene is measured for a fixed reactant concentration at differing temperatures, and the results are indicated below.

<i>R</i> / 10 ⁻⁵ mol dm ⁻³ s ⁻¹	2.7	19	74	260
Temperature / K	800	840	870	900

Calculate the activation energy for this reaction.

[5]

Suggest an explanation for the differences arising in the activation energies calculated in your answers to (c) and (d).

[2]

END OF PAPER