

**FIRST PUBLIC EXAMINATION**

**Trinity Term 1998**

**Preliminary Examination in Physical Sciences**

**SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY**

also

Preliminary Examination in Molecular and Cellular Biochemistry

Thursday, 11 June 1998. 2.30 p.m. – 5.00 p.m.

Time allowed: 2 ½ hours

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*Candidates should answer **FOUR** questions only.*

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

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$$

$$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.6261 \times 10^{-34} \text{ J s}$$

$$c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

$$F = 9.6485 \times 10^4 \text{ C mol}^{-1}$$

$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

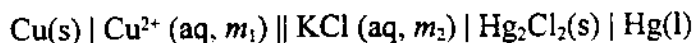
$$1 \text{ bar} = 10^5 \text{ Pa}$$

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

1. (a) Explain how the standard EMF of a cell and its variation with temperature can be used to derive  $\Delta_r G^\ominus$ ,  $\Delta_r H^\ominus$  and  $\Delta_r S^\ominus$  for the cell reaction. [7]

- (b) Consider the following electrochemical cell at 298.15 K



- (i) Write down the two electrode reactions and, hence, derive the overall cell reaction. [6]

- (ii) Starting from the equation

$$E = E^\ominus - [RT/nF] \ln Q$$

and assuming ideal behaviour, derive an equation giving the dependence of the overall cell EMF on the solute concentrations and on the two standard electrode potentials. [6]

- (iii) Given that the standard electrode potentials for the  $\text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$  and  $\text{KCl(aq)} \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg(l)}$  electrodes are 0.337 V and 0.268 V respectively, determine which of the two electrodes is positive if  $m_1 = m_2 = 0.01 \text{ mol kg}^{-1}$ . [6]

2. (a) With reference to atoms, explain the meanings of the terms *first ionization potential*, *orbital* and *shielding*. [9]

- (b) Given that the ionization energy of a ground state hydrogen atom is 13.6 eV, calculate the ionization energy of the electron from the 2s orbital in a hydrogen atom. [4]

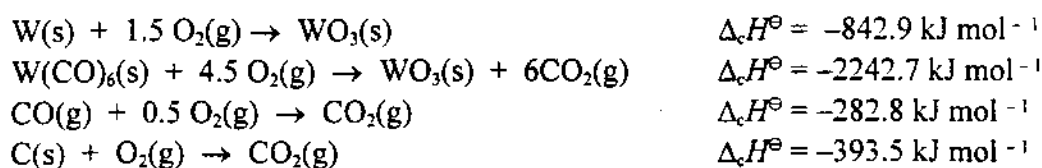
- (c) Using diagrams where appropriate, compare the wavefunction and energy for an electron in the 2s orbital of the hydrogen atom, with the wavefunction and energy for an electron in the 2s orbital in the helium ion ( $\text{He}^+$ ). [7]

- (d) Would you expect the energy of an electron in the 2p orbital of an excited hydrogen atom to be equal to the energy of an electron in the 2s orbital of an excited hydrogen atom? Justify your answer as fully as possible. [5]

3. (a) State the *First Law of Thermodynamics*, and explain what is meant by the term *state function*. [6]

(b) Explain clearly the distinction between a *bond dissociation enthalpy* and a *mean bond dissociation enthalpy*. [5]

(c) The following enthalpies of combustion have been measured at 298 K.



(i) Calculate the enthalpy of formation of  $\text{W(CO)}_6(\text{s})$ . [8]

(ii) At 298 K, the enthalpies of sublimation of  $\text{W(CO)}_6(\text{s})$  and of  $\text{W(s)}$  are 75.6 and 849.4  $\text{kJ mol}^{-1}$ , respectively. Calculate the mean (W—CO) bond dissociation enthalpy in  $\text{W(CO)}_6$ . [6]

4. Values of some thermodynamic parameters for Br<sub>2</sub>, Cl<sub>2</sub> and BrCl at 298 K are given below.

Material	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
Br <sub>2</sub> (l)	0	152.3
Cl <sub>2</sub> (g)	0	223.0
BrCl(g)	14.69	239.9

- (a) Why are the enthalpies of formation of chlorine and bromine equal to zero? [1]
- (b) Calculate  $\Delta_r H^\ominus$  and  $\Delta_r S^\ominus$  for the reaction at 298 K  
$$\text{Br}_2(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{BrCl}(\text{g})$$
 [5]
- (c) Comment on the value you have obtained for  $\Delta_r S^\ominus$ . [2]
- (d) Calculate  $\Delta_r G^\ominus$  and  $K_p$  for the reaction at 298 K. [6]
- (e) Explain how a change in (i) pressure and (ii) temperature might affect the relative amounts of reactants and products at equilibrium. [6]
- (f) Discuss the effect that a catalyst for this reaction would have on the rate of the forward and reverse reactions and on the position of equilibrium. [5]

5. A particle is confined within a one-dimensional box of uniform zero potential energy by infinitely high potential energy barriers at  $x = 0$  and  $x = L$ . The wavefunction for  $n$ th state of the particle is:

$$\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L) \quad n = 1, 2, 3, 4, \dots$$

- (a) Explain the origin of the term  $(2/L)^{1/2}$  in this expression [3]
- (b) Why is  $n = 1$  the lowest acceptable value of  $n$ ? [2]
- (c) Sketch the wavefunctions and energies of the wavefunctions for  $n = 1, 2, 3$  and  $4$ . [7]
- (d) Derive a general expression applicable to any value of  $n$  for the probability that the particle will be found in the region  $1/4 L \leq x \leq 3/4 L$  [8]
- [ You may need the expression  $\int (\sin^2 ax) dx = \frac{1}{2} x - \frac{1}{4a} \sin 2ax$  ]
- (e) Using your expression from part (d), determine the smallest value of  $n$  for which there is exactly a 50% chance that the particle will be found between the limits  $1/4 L \leq x \leq 3/4 L$  and show qualitatively that this is in accord with the wavefunctions you have drawn for part (c). [5]

6. (a) Explain the meaning of the terms *rate equation*, *reaction order* and *molecularity*, which occur in chemical kinetics. [8]
- (b) At 300 K the numerical value of the rate constant for a certain first order gas phase reaction is 0.00125.
- (i) If the pressure of the gas is measured in Torr and time in seconds, what units does the rate constant have? [1]
- (ii) The activation energy for the reaction is  $290 \text{ kJ mol}^{-1}$ . At what temperature would the numerical value of the rate constant be 0.0025? [4]
- (c) The decomposition of gas-phase  $\text{N}_2\text{O}$  into its elements is catalyzed by gold surfaces. At low pressures of  $\text{N}_2\text{O}$  the reaction is first order with respect to  $\text{N}_2\text{O}$ , while at high pressures of  $\text{N}_2\text{O}$  it is zero order with respect to  $\text{N}_2\text{O}$ .
- (i) Write a balanced equation for the decomposition of  $\text{N}_2\text{O}$  on a gold surface. [1]
- (ii) Write rate equations for the decomposition at low  $\text{N}_2\text{O}$  pressure and for the decomposition at high  $\text{N}_2\text{O}$  pressure. [4]
- (iii) A sample of  $\text{N}_2\text{O}$  at high pressure is sealed into a container with a gold surface to act as catalyst for the decomposition. Sketch a graph showing how the *rate of reaction* varies with time. You may assume that the products of the reaction have no influence upon the rate of reaction. Your diagram should show clearly how the rate varies both at the start of the reaction and when the reaction is nearly complete. [7]

7. (a) Starting from the Clapeyron equation,

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

derive the integrated form of the Clausius-Clapeyron equation, which shows how the vapour pressure of a solid or liquid varies with temperature. State clearly any assumptions which you make. [6]

(b) An organic liquid for which the boiling temperature at 1 bar is 410K has at this temperature an enthalpy of vaporization of 36 kJ mol<sup>-1</sup>. Calculate the vapour pressure of the liquid at 320K. [6]

(c) Given the following vapour pressures as functions of temperature

$$\text{Benzene (l): } \ln(p/\text{Pa}) = -4108 / (T/\text{K}) + 23.225$$

$$\text{Benzene (s): } \ln(p/\text{Pa}) = -5314 / (T/\text{K}) + 27.564$$

calculate:

(i) the entropy of vaporization of liquid benzene at its boiling point at 1 bar. [7]

(ii) the entropy of fusion of solid benzene at the triple-point temperature. [6]