

FIRST PUBLIC EXAMINATION

Trinity Term 2003

Preliminary Examination in Chemistry

SUBJECT 3 : PHYSICAL CHEMISTRY

Wednesday, 11th June 2003, 9.30 am – 12.00 am

Time allowed: 2 ½ hours

Candidates should answer **ALL** questions in Section A and any **TWO** questions in Section B.

Use **SEPARATE** booklets for your answers to Section A and 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 × 10 ⁻³⁴ J s
Boltzmann constant, k _B	= 1.381 × 10 ⁻²³ J K ⁻¹
Speed of light, c	= 2.998 × 10 ⁸ m s ⁻¹
Avogadro number, N _A	= 6.022 × 10 ²³ mol ⁻¹
p [⊖]	= 1 bar = 1 × 10 ⁵ Pa
Electron mass, m _e	= 9.110 × 10 ⁻³¹ kg
Elementary charge, e	= 1.602 × 10 ⁻¹⁹ C
Faraday constant, F	= 9.648 × 10 ⁴ C mol ⁻¹
Atomic mass unit, u	= 1.661 × 10 ⁻²⁷ kg
Molar volume, V _m	= 24.79 dm ³ mol ⁻¹ at 298 K
1 electron volt	= 1.6022 × 10 ⁻¹⁹ J
Vacuum permittivity ε ₀	= 8.8542 × 10 ⁻¹² J ⁻¹ C ² m ⁻¹

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

SECTION A

Answer all six questions in this section

1. (a) (i) Show how *Coulomb's law of force* between two charges q_1 and q_2 separated by a distance r in vacuum can be used to derive an expression for the potential energy associated with the interaction between the charges.

[2]

- (ii) A proton and an electron in vacuum have an electrostatic potential energy of -5×10^{-18} J. By what distance are they separated?

[1]

- (b) Na has an atomic absorption line at 589.6 nm. A Na atom, which is initially travelling at 400 m s^{-1} in the opposite direction to light of this wavelength, is brought to rest by the absorption of light. Calculate the number of photons absorbed.

[atomic mass: Na 23 u]

[3]

- (c) The photoelectric effect results in electrons being emitted from a metal surface with a work function of 4.5 eV when it is irradiated with light with a wavelength of 185 nm. Calculate the maximum velocity of the emitted electrons.

[3]

2. (a) State the *second law of thermodynamics*.

[2]

- (b) Calculate the entropy changes occurring during the following processes.

- (i) 5 moles of an ideal gas undergo a volume expansion, such that the final volume is four times that of the initial volume.

[2]

- (ii) 1.5 moles of ice at 273.16 K melt to form water at this temperature.

[Enthalpy of fusion of water = $6.010 \text{ kJ mol}^{-1}$]

[2]

- (iii) 2 moles of Cu are heated from 300 K to 400 K.

[Heat capacity at constant pressure of Cu, $C_p = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$]

[2]

3. The chemical equilibrium



has an equilibrium constant denoted by K_p . Show that the fraction, α , of Cl_2 which is dissociated to atoms in a container at a total gas pressure p_{TOT} satisfies the equation

$$K_p = \frac{4\alpha^2 p_{TOT}}{(1-\alpha^2)p^\ominus} \quad [8]$$

4. (a) Describe within the *simple harmonic oscillator approximation* how the potential energy of a diatomic molecule varies with the change in bond length. How well does this approximation fit the actual behaviour observed? [4]

(b) The force constant for the H_2 molecule is 575 N m^{-1} . Calculate the zero point vibrational energy of H_2 .

[atomic mass: H 1 u] [2]

(c) Explain why you would expect the zero point energy of: (i) H_2^+ , and: (ii) D_2 to differ from that for H_2 . [2]

Turn Over

5. Two pure liquids **A** and **B** form an ideal solution when mixed together.
- (a) Describe how the partial vapour pressures of the two substances in the mixture will vary with changes in mixture composition. [2]
- (b) Draw graphs to illustrate how the Gibbs energy, the entropy and the enthalpy of mixing will vary with the mole fraction, x_B , of substance **B** in the solution. [2]
- (c) Calculate values for the Gibbs energy and entropy of mixing at 298 K when $x_B = 0.75$. [4]
6. (a) From the kinetic theory of gases, the number of gas species N striking a surface of area 1m^2 per second is given by the equation

$$N = \frac{p}{(2\pi mk_B T)^{1/2}}$$

where m is the mass of the species concerned, p is the gas pressure and T is the temperature.

Cs atoms at a temperature of 900 K and a pressure of 50 Pa, are lost from a vessel into a vacuum by effusion through a hole of diameter $10\ \mu\text{m}$. Calculate the rate at which atoms escape from the vessel.

[atomic mass: Cs 133 u]

- [4]
- (b) A hydrocarbon compound **A** undergoes chemical decomposition at elevated temperatures, and its concentration is found to decrease with time as shown in the table below.

Time / s	0	200	400	600	800
Concentration / $10^{-6}\ \text{mol dm}^{-3}$	8.0	6.2	4.8	3.7	2.9

Show that the decomposition rate exhibits a first order dependence on the concentration of **A** and calculate the rate constant for this reaction.

[5]

SECTION B

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

7. (a) Explain what is meant by the terms *rate equation*, *reaction order*, *molecularity*, and *activation energy*, which are encountered in chemical kinetics.

[8]

- (b) The rate of a particular chemical reaction is found to double when the temperature is raised from 420 K to 440 K. Calculate the activation energy.

[4]

- (c) Consider the following reaction



The concentration of NOBr (g) is found to fall off in time according to the following observations

Time / s	0	100	200	400	600
[NOBr] / $10^{-4} \text{ mol dm}^{-3}$	4.0	3.0	2.4	1.7	1.4

- (i) By integration of the rate equation, assuming the rate exhibits a second order dependence on the concentration of NOBr (g), derive an expression for the concentration of NOBr (g) as a function of time.

[5]

- (ii) Show graphically that the data recorded exhibits such a second order dependence.

[2]

- (iii) Determine the rate constant for the reaction.

[2]

- (iv) Derive an expression which describes the time required for the concentration of NOBr (g) to drop to half of its initial value, and calculate what this time would be for an initial concentration of $8 \times 10^{-4} \text{ mol dm}^{-3}$.

[4]

Turn over

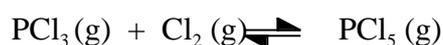
8. (a) Explain how the standard Gibbs energies of formation, $\Delta_f G^\ominus$, of the compounds involved in a chemical reaction at a particular temperature can be used to calculate the equilibrium constant of a reaction at that temperature.

[4]

$\Delta_f G^\ominus$ of the following compounds has been determined at the temperature of 298K.

Substance	$\Delta_f G^\ominus$ /kJ mol ⁻¹ at 298 K
PCl ₃ (g)	-267.8
PCl ₅ (g)	-305.0
Cl ₂ (g)	0

For the reaction



- (i) Calculate the equilibrium constant K_p at 298 K. [3]
- (ii) Calculate $\Delta_r H^\ominus$ assuming it is independent of temperature in the range 298-350K, given that $\Delta_r G^\ominus$ for the reaction is -20.2 kJ mol⁻¹ at 350 K. [4]
- (iii) Is the assumption that $\Delta_r H^\ominus$ is independent of temperature likely to be an accurate one? [2]

- (b) The slope of a phase boundary is described by the equation

$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

where $\Delta_{trs} V$ and $\Delta_{trs} S$ are the molar volume and entropy changes for the phase transition.

- (i) Explain why solid-liquid phase boundaries often appear approximately linear on p - T phase diagrams, whereas this is not true for liquid-vapour phase changes. [3]

QUESTION CONTINUES ON NEXT PAGE

- (ii) Describe how the above equation can be used to derive an equation for liquid-vapour phase changes which is of the form given below, noting any approximations made.

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

[6]

- (iii) A liquid exhibits a vapour pressure of 5.11 bar at 217 K, and a vapour pressure of 72.8 bar at 304 K.

Estimate the enthalpy of vaporisation of the substance.

[3]

Turn Over

9. (a) Explain how measurements of the potential of electrochemical cells can be used to determine thermodynamic parameters for chemical reactions. [7]

Consider the following electrochemical cell



At 298 K $E^\ominus (\text{Zn}^{2+} \text{ (aq)}, \text{Zn (s)}) = -0.763 \text{ V}$ and $E^\ominus (\text{Hg}, \text{Cl}^-, \text{Hg}_2\text{Cl}_2) = +0.268 \text{ V}$

- (b) Determine the overall cell reaction and calculate the equilibrium constant at 298 K. [6]
- (c) Measurement of the temperature variation of the standard potential of the cell shows it varies linearly, changing by -0.453 mV K^{-1} at temperatures near 298K.

Calculate the standard reaction entropy and standard reaction enthalpy for the cell reaction at 298 K.

- (d) Determine the cell potential at 298 K if the concentration of ZnCl_2 is $10^{-2} \text{ mol dm}^{-3}$. [8]
- [4]

10. (a) The table given below lists the wavenumbers (cm^{-1}) of one series of spectral lines that are observed in the emission spectrum of atomic hydrogen.

Wavenumber / cm^{-1}	5332	7799	9140	9948
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- (i) Explain the meaning of the quantum numbers which arise in the orbital description of the electronic properties of atomic hydrogen, and state the selection rules which apply to the emission spectrum. [7]
- (ii) Hence explain why the above emission lines are observed, and deduce the principal quantum numbers for the upper and lower states for each of the listed transitions. [7]

QUESTION CONTINUES ON NEXT PAGE

- (iii) Calculate the ionization energy of atomic hydrogen. [2]
- (iv) For the lowest energy transition noted above, estimate the wavenumber of the corresponding spectral line which would be observed in the emission spectrum of $\text{Li}^{2+}(\text{g})$. [4]
- (b) An electron which is trapped at a defect site in an alkali halide compound exhibits properties which closely conform to those predicted from the “particle-in-a-box” model, for a cubic box with sides of 0.6 nm length. Estimate the wavelength of the spectral transition for excitation of the electron from its ground state to the first excited state. [5]

END OF PAPER