

CCHE 4273  
CMET 4273

FIRST PUBLIC EXAMINATION

Trinity Term 2001

Preliminary Examination in Physical Sciences

SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY

Wednesday, 6th June 2001, 2.30 - 5.00 pm

Time allowed: 2 ½ hours

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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, $N_A$	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
$p^\ominus$	$= 1 \text{ bar} = 1 \times 10^5 \text{ Pa}$
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, $m_u$	$= 1.661 \times 10^{-27} \text{ kg}$
Molar volume, $V_m$	$= 24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298K
1 electron volt	$= 1.602 \times 10^{-19} \text{ J}$

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

## SECTION A

Answer all six questions in this section

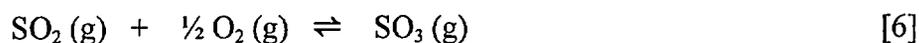
1. (a) Hess' law is most commonly stated in terms of the enthalpy change for a set of reactions, but it can equally well be applied to changes in Gibbs' free energy or entropy; why is this? [2]

(b) The standard enthalpy of formation of sulfur dioxide at 298 K is  $-296.6 \text{ kJ mol}^{-1}$ , and that of sulfur trioxide is  $-394.8 \text{ kJ mol}^{-1}$ .

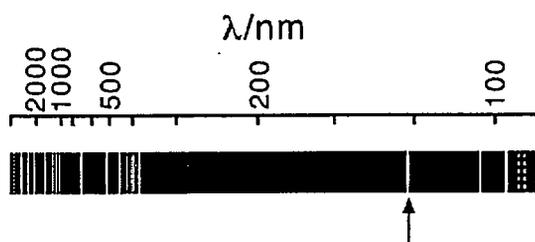
Given the following standard entropies at 298 K:

$\text{O}_2$ :  $204.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\text{SO}_2$ :  $247.9 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\text{SO}_3$ :  $256.4 \text{ J K}^{-1} \text{ mol}^{-1}$

calculate the value of the equilibrium constant  $K_p$  at 298 K for the reaction

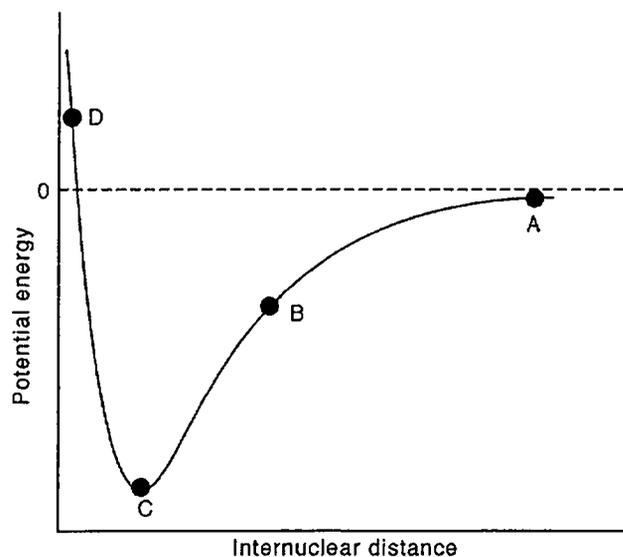


2. The figure below shows a portion of the atomic emission spectrum of hydrogen.

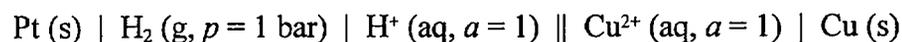


- (a) Explain briefly how atomic emission spectra provide evidence for quantisation. [3]
- (b) The line marked with an arrow is the lowest energy line in the so-called Lyman series, in which the electronic transitions terminate at the 1s level in the hydrogen atom. What is the upper state from which this transition originates? [2]
- (c) The energy of the line marked with an arrow is 10.2 eV; calculate the ionization energy of the ground state hydrogen atom. [3]

3. The figure below shows how the potential energy of the  $N_2$  molecule depends on the separation between the two nitrogen atoms.



- (a) For each of points A, B, C and D state whether the force which the atoms exert on each other at that point is attractive, repulsive, or approximately zero. [4]
- (b) Why does the potential energy of the  $N_2$  molecule rise very rapidly as the internuclear distance diminishes to small values? [2]
- (c) The potential energy curve for  $I_2$  has the same general appearance as that shown above for  $N_2$  but differs in detail. On a single diagram, sketch potential energy curves for **both**  $N_2$  **and**  $I_2$  and comment on the differences. [3]
4. (a) What is a salt bridge? Why is one often used in the construction of electrochemical cells? [4]
- (b) The measured EMF for the cell



is +0.337V. Write down the cell reaction, and calculate the value of  $\Delta G^\ominus$  for this reaction. [4]

5. (a) Nitric oxide can react to form nitrogen and oxygen according to the equation:



The rate equation for the forward reaction is second order in the pressure of nitric oxide. Write down the rate equation for the forward reaction, and give the units of the rate constant  $k$ . [4]

(b) The standard enthalpy of formation of NO (g) at temperatures near 1400 K is 90.2 kJ mol<sup>-1</sup>. In which direction will the position of equilibrium in the reaction move if the temperature is lowered? Explain your answer. [4]

6. Explain, using examples where possible, what is meant by the terms *radial distribution function*, *excited state*, *degenerate orbital*. [9]

## SECTION B

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

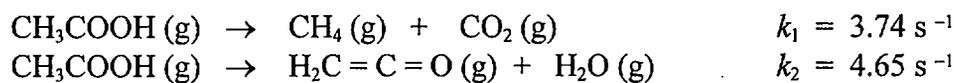
7. (a) Explain what is meant by the terms *kinetic mechanism*, *rate law* and *molecularity*. [9]

(b) A substance decomposes according to the following parallel 1st-order reactions:



The ratio  $k_1/k_2$  is 10 at 283 K and 0.1 at 313 K. Assuming that the pre-exponential factor,  $A$ , has the same value for each reaction, calculate the difference in activation energy for the two reactions. Which reaction has the higher activation energy? [6]

(c) The gas phase decomposition of ethanoic acid at 1189 K proceeds via two parallel 1st-order reactions:



Calculate the expected percentage yield of methane at this temperature. [4]

(d) Determine the half-life for the decomposition of ethanoic acid at 1189 K. [6]

8. An electrochemical cell is prepared at 298 K by connecting a standard hydrogen electrode to a half-cell in which a Pt | H<sub>2</sub> ( $p = 1$  bar) electrode dips into an aqueous solution of an organic acid of unit molality.

(a) Make a sketch of the cell. [6]

(b) Explain why the EMF of the cell must be measured under conditions of zero current flow. [5]

(c)  $K_a$  for the organic acid is 0.27 at 298 K. Assuming that the acid behaves ideally, determine the EMF of the cell at 298 K. [7]

(d) In reality the acid is unlikely to behave ideally at this concentration. Explain as fully as possible what effect non-ideal behaviour would have on the EMF of the cell. [7]

9. (a) Arrange the following materials in order of increasing heat capacity at 298 K:

O<sub>2</sub>, CH<sub>4</sub>, He, Ar, benzene [3]

(b) Briefly justify the order in which you have placed the molecules in part (a). [5]

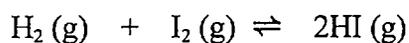
(c) The molar heat capacity  $C_p$  of H<sub>2</sub>O (l) has the value 75.4 J K<sup>-1</sup> mol<sup>-1</sup> (which you may assume to be constant) between 273 K and 373 K. The enthalpy of vaporisation of water at 373 K,  $\Delta_{\text{vap}}H^\ominus$ , is 40.7 kJ mol<sup>-1</sup>. Calculate the change in entropy when five moles of water at 273 K are converted to water vapour at 373 K, its normal boiling point at a pressure of 1 bar.

[10]

(d) The van't Hoff Isochore is

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$$

Values of the equilibrium constant for the reaction



are given in the table below

$T / \text{K}$	500	750	1000	1250	1500
$K_p$	144	51.1	28.5	19.1	14.8

Calculate the enthalpy change for the forward reaction. [5]

(e) The enthalpy of the reaction shown above is not completely independent of temperature; why is this? [2]

10. The normalised wavefunction for an electron trapped in a one-dimensional box of length  $L$  with infinitely high walls positioned at  $x = 0$  and  $x = L$  is:

$$\psi_n = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right)$$

- (a) Two electrons are present in *each* of the three lowest energy levels in such a box. Calculate the total electron density at the following positions:

$$x = 0 L \quad x = 0.1 L \quad x = 0.2 L \quad x = 0.3 L \quad x = 0.4 L \quad x = 0.5 L. \quad [8]$$

- (b) Use the values you have calculated in Part (a) to plot the total electron density across the whole box. [4]

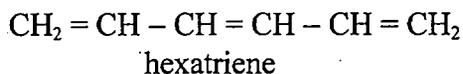
- (c) The energy of an electron trapped in a box of length  $L$  is given by

$$E = \frac{n^2 h^2}{8mL^2}$$

Give an expression for the total energy of the six electrons in the box.

[3]

- (d) In hexatriene, the six electrons in the conjugated  $\Pi$  system move within the molecular framework provided by the carbon atoms. The electrons can be treated, to a first approximation, as being confined to a one-dimensional box, whose length is the distance between the two terminal carbons plus one single C – C bond (to take account of the fact that the electrons can move slightly beyond each end of the carbon chain).



Assuming that the C = C bond length is 0.135 nm and that the C – C bond length is 0.154 nm, calculate the smallest amount of energy required to excite one of these  $\Pi$  electrons to the first available excited energy level. ( $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ )

[6]

- (e) In the light of the plot of electron density you have prepared in part (b), comment on the possible strength of the different carbon-carbon bonds in hexatriene. [4]