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Exam(s) 4th year Chemistry and 4th year Biopharmaceutical Chemistry
Module Code(s) CH429
Module(s) PHYSICAL CHEMISTRY
Paper No. 1
Repeat Paper
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Internal Examiner(s) Prof. P. Murphy Dr. W. M. Carroll, Dr. H. Curran, Dr. D. Leech, Dr. A. Ryder

Instructions: ANSWER THREE (3) QUESTIONS ONE FROM EACH SECTION

Duration Two (2) Hours
No. of Pages 5
Department(s) Chemistry
Course Co-ordinator(s) Dr. W. M. Carroll

Requirements:
MCQ Release to Library: Yes [ ] No [ ]
Statistical/ Log Tables x
Graph Paper x

Gas constant, $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Planck constant, $h = 6.624 \times 10^{-34} \text{ J s}$
Velocity of light, $c = 2.998 \times 10^8 \text{ m s}^{-1}$

Electronic charge, $e = 1.602 \times 10^{-19} \text{ C}$
Boltzmann constant, $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$

Electronic mass, $m = 9.109 \times 10^{-31} \text{ kg}$
Bohr magneton, $\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$

Faraday constant, $F = 96,485 \text{ C mol}^{-1}$
1 atmosphere $= 101,325 \text{ N m}^{-2}$
SECTION A

1. Answer all parts.

(a) Describe the differences between static and dynamic quenching of fluorescence. With the aid of diagrams how static and dynamic quenching can be discriminated by measurement of fluorescence parameters. [30 marks]

(b) Describe with the aid of diagrams how the effect of combined static and dynamic quenching might be discriminated using fluorescence measurements. [10 marks]

(c) Show with the use of the relevant equations how one would modify the Stern-Volmer equation to accommodate the two effects, and generate a straight line plot. [30 marks]

(d) The following normalized fluorescence data were obtained for quenching of fluorescence from an aqueous solution of an amino acid by KI water at near ambient temperatures. Construct a Stern-Volmer plot, and calculate the Stern-Volmer constant. Calculate the observed bimolecular quenching constant. The unquenched lifetime $\tau_0=4.3$ ns.

<table>
<thead>
<tr>
<th>KI [M]</th>
<th>0.0</th>
<th>0.04</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.50</th>
<th>0.80</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_0/I_F$</td>
<td>1.0</td>
<td>4.64</td>
<td>10.59</td>
<td>23.00</td>
<td>37.20</td>
<td>68.60</td>
<td>137.00</td>
</tr>
</tbody>
</table>

[30 marks]

2. In a flow study of the reaction between fluorine atoms and chlorine at 300 K, the concentration of Cl$_2$ was measured with a mass spectrometer being proportional to the signal $S$ obtained at various distances $d$ downstream from the point of mixing. The flow velocity was 53 ms$^{-1}$, at a total pressure of 150 Pa, and at an initial F$\cdot$ concentration of $1.70 \times 10^{12}$ atoms cm$^{-3}$ (much greater than that of Cl$_2$).

F$\cdot$ + Cl$_2$ $\rightarrow$ ClF + Cl$\cdot$

$S$ | 72.0 | 50.5 | 35.6 | 24.2 |
$d$ / mm | 65 | 135 | 200 | 275 |

Draw a schematic diagram of a flow tube apparatus that you would use to measure the F$\cdot$ + Cl$_2$ reaction under conditions where F$\cdot$ $\gg$ Cl$_2$ and Cl$_2$ is detected by mass spectrometry. Show in your figure how F$\cdot$ atoms are generated. [25 marks]

From the data provided above, find the rate constant for the reaction. [25 marks]

Compare your results with collision frequency. Collision radii of 135 and 165 pm may be assumed for F$\cdot$ and Cl$_2$, respectively. [40 marks]

Based on your comparison, is there a significant activation energy for this reaction? [10 marks]
SECTION B

3. Answer all parts.

(a) Define each of the terms in the Nernst-Planck equation below, used to describe the factors contributing to the flux of species penetrating a unit area of a plane as a function of time.

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]

[20 marks]

(b) Considering this equation, discuss the experimental conditions, in voltammetry, used to assure that the movement of the electroactive species is limited by diffusion. [20 marks]

(c) What does the term "electrochemical reversibility" mean? Give relevant examples of equations or parameters whose behaviour or condition lead to the "reversible" condition. Sketch cyclic voltammograms for reversible and irreversible, one-electron, redox processes to aid your discussion. [40 marks]

(d) Discuss briefly the effect of a follow-on catalytic chemical reaction, regenerating the initial electroactive reactant (EC'), on the shape of a reversible cyclic voltammogram, giving an example of an electrochemical device based on this mechanism. [20 marks]

4. Answer all parts:

(a) Ammonia is manufactured from hydrogen and nitrogen in the Haber process

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \quad \Delta H = -92 \text{ kJ mol}^{-1} \]

State the conditions employed industrially (including how raw materials are obtained) in the manufacture of ammonia and justify them on physico-chemical grounds. [25 marks]

(b) Why is the automotive exhaust catalyst called a three-way catalyst? Which metals are used in the automotive catalyst and what reactions do they catalyse? [25 marks]

(c) What are zeolites? What are the main possibilities for modifying zeolites and how do these modifications affect their catalytic abilities? [50 marks]
SECTION C

5. Answer (a) and (b):

(a) (i) Calculate the separation between the two lowest energy levels for an O₂ molecule in a one-dimensional box of length 5 nanometres. Give your answers in J mol⁻¹.

(ii) At what value of n does the energy of the molecule reach ½k_BT at 300K.

(b) When 0.316 g of glucose was burned in a bomb calorimeter the temperature rose by 7.7 K. In a separate experiment the calorimeter temperature rose by 5.6 K when a current of 10 A was allowed to flow for 30 s into an electric heater, powered using a 12 V power supply placed, within the calorimeter. Calculate the standard molar internal energy of combustion, the standard molar enthalpy of combustion and the standard enthalpy of formation of glucose. The standard molar enthalpy of formation of carbon dioxide is −393.5 kJ mol⁻¹ and of water is −285.8 kJ mol⁻¹.

Comment, by referring to entropy and free energy changes, on the spontaneity of the combustion reaction.

6. Answer (a) and (b):

(a) The standard reversible electrode potential for the reduction of H⁺ ions in aqueous solution at 298K is -0.241V (SCE) and yet hydrogen is evolved on the following surfaces at the potentials stated for a solution of 0.1 mol dm⁻³ aqueous HCl: Pt -0.321V (SCE), Hg -1.363V (SCE)

Explain this and how it relates to the choice of material for a cathode.

(b) For 1000 s, light at 430 nm was passed through a solution of dibromine and cinnamic acid in tetrachloromethane. The average power absorbed was 19.2 × 10⁻⁴ s⁻¹. Some of the dibromine reacted to form cinnamic acid dibromide and in this experiment the total dibromine content decreased by 4.24 × 10¹⁹ molecules.

Calculate the quantum yield.

Comment on the result.