# Autumn Examinations 2013/2014

**Exam Code(s)**  
4BS, 4BPC

**Exam(s)**  
Final Examination for the Degree of B.Sc. Honours

**Module Code(s)**  
CH429

**Module(s)**  
PHYSICAL CHEMISTRY

**Paper No.**  
1

**Repeat Paper**  
1

**External Examiner(s)**  
Prof. Tia Keyes

**Internal Examiner(s)**  
Prof. P. Murphy, Prof. H. Curran, Prof. D. Leech, Dr. A. Ryder, Prof. R. Woods

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**Instructions:**  
ANSWER THREE (3) QUESTIONS

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**Duration**  
Two (2) Hours

**No. of Pages**  
3

**Department(s)**  
Chemistry

**Course Co-ordinator(s)**  
Prof. D. LEECH

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**Requirements:**

- **MCQ**  
  Release to Library: Yes  
  Gas constant, $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$  
  Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

- **Statistical/ Log Tables**  
  x

- **Graph Paper**  
  x

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<table>
<thead>
<tr>
<th>Physical Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planck constant, $h$</td>
<td>$6.624 \times 10^{-34} \text{ J s}$</td>
</tr>
<tr>
<td>Velocity of light, $c$</td>
<td>$2.998 \times 10^{8} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Electronic charge, $e$</td>
<td>$1.602 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>Boltzmann constant, $k$</td>
<td>$1.381 \times 10^{-23} \text{ J K}^{-1}$</td>
</tr>
<tr>
<td>Bohr magneton, $\mu_B$</td>
<td>$9.274 \times 10^{-24} \text{ J T}^{-1}$</td>
</tr>
<tr>
<td>Faraday constant, $F$</td>
<td>$96,485 \text{ C mol}^{-1}$</td>
</tr>
<tr>
<td>1 atm = 101,325 N m$^{-2}$ = 101,325 Pa</td>
<td></td>
</tr>
</tbody>
</table>
1. **Spectroscopy**

**Answer each of the following:**

a) Explain using appropriate diagrams and formulae the phenomenon of **Fluorescence Anisotropy**. Clearly explain all the terms in the equations used to describe the phenomenon. Give two specific and different examples of the use of this technique in the biological sciences.  

[50 marks]

b) A protein which has been labeled with a fluorophore has a molecular weight of 22 kDa and a rotational correlation time of 9.3 ns. If this fluorophore has a lifetime of 30 ns, and a fundamental (max.) anisotropy of 0.25, what is the anisotropy of the fluorophore-protein complex? If this protein binds to an anti-body with a molecular weight of 125 kDa and a rotational correlation time of 60.7 ns, what is the anisotropy of the labelled protein/anti-body complex? Explain your answer.  

[20 marks]

c) Using appropriately labelled diagrams, describe the potential effects of solvent on fluorophore emission.  

[30 marks]

2. **Thermodynamics**

Now that summer is upon us, let’s consider how sweating helps moderate body temperature. How much heat is removed (per mol) when liquid water evaporates from human skin? (i.e. how effective is sweating?)

You may assume the following:

- skin temp = 35°C,
- \( C_p \) (liquid water) = 75.2 \( \text{JK}^{-1}\text{mol}^{-1} \),
- \( C_p \) (gaseous water) = 33.6 \( \text{JK}^{-1}\text{mol}^{-1} \),
- \( \Delta H \) for vapourisation of water at 100°C = 40.7 \( \text{kJmol}^{-1} \).

[100 marks]
3. Analytical Electrochemistry

Answer each of the following:

a) Briefly describe the principles of operation and applications of potentiometric ion-selective electrodes. Factors to consider include:
   • construction of the electrochemical cell
   • reference electrode choice
   • filling solution electrolyte
   • signal response and interferences
   • and analytical parameters.

   [50 marks]

b) Give a simple description of the electrical double layer at an electrode-electrolyte interface. Describe, using examples, how the existence of the double layer limits the analytical utility of linear sweep and cyclic voltammetric techniques and outline how the pulsed voltammetric techniques improve upon this technique.

   [50 marks]

4. Kinetics

Answer each of the following:

(a) A shock tube study was carried out on the reaction of carbon atoms with nitric oxide by heating a mixture of carbon suboxide, nitric oxide and oxygen. Following the shock, carbon suboxide, $C_3O_2$, is rapidly pyrolysed:

   $C_3O_2 \rightarrow C + 2CO_2$

   and the C atoms then react with an excess of NO.

   The relative concentrations of carbon atoms, $S_C$, were determined using mass spectroscopy. From the data in the table below, confirm that the reaction obeys first order kinetics and calculate the first order rate constant.

<table>
<thead>
<tr>
<th>Time / µs</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_C$</td>
<td>5.74</td>
<td>4.33</td>
<td>3.13</td>
<td>2.33</td>
<td>1.83</td>
<td>1.40</td>
</tr>
</tbody>
</table>

   [50 marks]

(b) Draw a diagram of a shock tube and explain how it can be/is used for chemical kinetic studies.

   [30 marks]

(c) Why is the study being carried out in a shock tube? What is the advantage in having an excess of NO present?

   [20 marks]