**Autumn Examinations 2014**

Exam Code(s)  
Exam(s)  
Module Code(s)  
Module(s)  

<table>
<thead>
<tr>
<th>Paper No.</th>
<th>Repeat Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>II</td>
</tr>
</tbody>
</table>

External Examiner(s)  
Internal Examiner(s)  

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

**Duration**  
Two (2) Hours

<table>
<thead>
<tr>
<th>No. of Pages</th>
<th>Department(s)</th>
<th>Course Co-ordinator(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Chemistry</td>
<td>Prof. D. LEECH</td>
</tr>
</tbody>
</table>

**Requirements:**  
MCQ  
Release to Library: Yes  
Statistical/ Log Tables: x  
Graph Paper: x  

<table>
<thead>
<tr>
<th>Gas constant, ( R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} )</th>
<th>Avogadro constant, ( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planck constant, ( h = 6.624 \times 10^{-34} \text{ J s} )</td>
<td>Velocity of light, ( c = 2.998 \times 10^{8} \text{ m s}^{-1} )</td>
</tr>
<tr>
<td>Electronic charge, ( e = 1.602 \times 10^{-19} \text{ C} )</td>
<td>Boltzmann constant, ( k = 1.381 \times 10^{-23} \text{ J K}^{-1} )</td>
</tr>
<tr>
<td>Electronic mass, ( m = 9.109 \times 10^{-31} \text{ kg} )</td>
<td>Bohr magneton, ( \mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1} )</td>
</tr>
<tr>
<td>Faraday constant, ( F = 96,485 \text{ C mol}^{-1} )</td>
<td>1 atm = 101,325 N m(^{-2}) = 101,325 Pa</td>
</tr>
</tbody>
</table>
1. Quantum Chemistry
(a) What are the most likely locations of particle in a box of length L in the state n=3? [30 marks]

(b) Discuss the approximations built into the Hückel method. [30 marks]

(c) For the linear configurations of H$_3$, apply a variant of the Hückel theory based on hydrogen 1s orbitals.

(i) Write down the secular determinants for linear H$_3$ in terms of the Coulomb integrals $\alpha$ and the resonance integrals $\beta$. [40 marks]

(ii) Find the roots of the secular determinant for linear H$_3$ in terms of the Coulomb integrals $\alpha$ and the resonance integrals $\beta$.

2. Statistical Thermodynamics
(a) A certain system is composed of 1 mole of identical, non-interacting, indistinguishable molecules. Each molecule has available to it only three energy levels, whose energies and degeneracies are $\varepsilon_1 = 0, g_1 = 1$; $\varepsilon_2/k = 250$ K, $g_2 = 2$; $\varepsilon_3/k = 500$ K, $g_3 = 3$ (k is Boltzmann’s constant).

(i) Calculate the molecular partition function ($q$) at 1000 K. [25 marks]

(ii) Calculate the average number of molecules in each level at 1000 K. [25 marks]

(iii) Calculate the average number of molecules in each level in the limit $T \rightarrow \infty$. [25 marks]

(b) Given that the vibration heat capacity has the formula:

$$C_{vib,m} = R \frac{u^2 e^u}{(e^u - 1)^2}$$

where: $u = \frac{\hbar v \theta_{vib}}{kT}$

calculate the vibrational heat capacity of carbon monoxide (CO) at 500 K and 5000 K given that its characteristic vibrational temperature $\theta_{vib}$ is 3084 K. Comment on the results you obtain. [25 marks]
3. **Surface Chemistry**

(a) Compare and contrast physisorption and chemisorption. In your answer discuss adsorbent-adsorbate interactions and energetics, and models used to represent each type of adsorption behaviour.

[30 marks]

(b) Identify all of the terms in the two equations below.

\[ \lambda = \frac{kT}{\sqrt{2\sigma p}}, \quad m \]

\[ z = \frac{p}{\sqrt{2\pi nkT}}, \text{ particles m}^{-2}\text{s}^{-1} \]

[15 marks]

(i) Estimate the mean free path of carbon monoxide in a vessel under medium vacuum conditions \((10^{-4} \text{ Pa})\) and a temperature of 25°C, given a collision cross section of 0.42 nm\(^2\) for CO.

[15 marks]

(ii) Estimate the time taken to achieve monolayer coverage of a metal substrate by carbon monoxide in a vessel under medium vacuum conditions \((10^{-4} \text{ Pa})\) and a temperature of 25°C, assuming associative adsorption, unity sticking co-efficient, a surface atomic density of 10\(^{19}\) atoms/m\(^2\) and using a value of 1.66 \(\times\) 10\(^{-27}\) kg for the unified atomic mass unit, detailing any simplifying assumption(s) in your estimation.

[20 marks]

(iii) Use your results in (i) and (ii) above to justify requirement of UHV conditions in surface science.

[20 marks]

4. **Drug Delivery**

**Answer any two of the following:**

(a) Define the term bioavailability and describe the differences between (i) relative bioavailability and (ii) absolute bioavailability. Plot a graph of the concentration of drug in plasma against time following administration of a single dose.

[50 marks]

(b) Explain the term zero-order release. Plot a graph of the cumulative mass of drug release against time. Explain how the drug release rate depends on drug diffusivity and the concentration gradient.

[50 marks]

(c) List the main components of the transdermal patch. Describe the advantages and disadvantages of transdermal drug delivery over other routes of drug delivery.

[50 marks]