**Summer Examinations 2013**

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<th>Exam Code</th>
<th>Chemistry CH301</th>
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<tr>
<td>Exam</td>
<td>3rd Year Chemistry</td>
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<tr>
<td>Module Code(s)</td>
<td>CH313</td>
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<td>Module</td>
<td>Physical Chemistry</td>
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<td>Repeat Paper</td>
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<td>External Examiner(s)</td>
<td>Professor Paul Seakins</td>
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<tr>
<td>Internal Examiner(s)</td>
<td>Dr William Carroll, Dr Henry Curran, Dr Dónal Leech, Dr Alan Ryder</td>
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**Instructions:**
- All questions carry equal marks, distributed as shown
- Answer four (4) questions
- One (1) from each Section

**Duration:** 2 hrs

**No. of Pages** | Chemistry

**Department(s):** Chemistry

**Course Co-ordinator(s):** Dr. Henry Curran

**Requirements:**
- MCQ Release to Library: Yes [ ] No [ ]
- Handout
- Statistical/ Log Tables: Yes
- Cambridge Tables: Yes
- Graph Paper: Yes
- Log Graph Paper: Yes
- Other Materials: Calculator

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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, $h = 6.626 \times 10^{-34} \ \text{J s}$

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, $k = 1.381 \times 10^{-23} \ \text{J K}^{-1}$

Electronic mass, $m = 9.109 \times 10^{-31} \ \text{kg}$

Faraday constant, $F = 96,485 \ \text{C mol}^{-1}$

1 atmosphere = 101,325 N m$^{-2}$

Vacuum permittivity, $\varepsilon_0 = 8.854 \times 10^{-12} \ \text{J}^{-1} \ \text{C}^2 \ \text{m}^{-1}$
Section A

1. Answer (a), (b), (c), (d), (e) and (f). For answers (a), (b), (d) and (e), illustrate your answer with at least one example.

(a) What is meant by a Van der Waals force? [4 marks]

(b) Define the term dipole moment. [4 marks]

(c) Give the equation for the potential energy of interaction between two dipoles that are fixed (non-rotating) and give a typical energy of interaction in kJ mol⁻¹? [4 marks]

(d) What is a hydrogen bond? [4 marks]

(e) Define the term polarizability? [4 marks]

(f) What strength of electric field is required to induce an electric dipole moment of 5 mD in a molecule of polarizability volume 2.5 × 10⁻³¹ m³? [5 marks]

2. Answer (a), (b), and (c)

(a) Write a brief account about the uses and advantages of a continuously-stirred spherical flow reactor. [8 marks]

The following is a diagram of a representation of a gas flow through a continuously-stirred spherical flow reactor:

![Diagram](image)

where $[A]_i =$ inlet concentration of $A$, $[A]_o =$ outlet concentration of $A$, $V$ is the volume of the reactor and $v$ is the flow rate or the flow velocity.

(b) Derive an equation for the dependence of the concentrations on the flow rate for a 1st-order reaction in a stirred reactor: [10 marks]

(c) Reactant $A$ flows into a continuously-stirred flow reactor with an inlet concentration of $2.0 \times 10^{-4}$ mol dm⁻³ and must flow out with an outlet concentration no greater than $4 \times 10^{-6}$ mol dm⁻³. If the rate constant for this reaction is $98$ s⁻¹, how long should each reactant molecule spend, on average, inside the reactor? [7 marks]
Section B

3. Answer (a) and (b)

A plot of the variation in vapour pressure of CS\textsubscript{2}, propanone and total pressure as a function of mole fraction of CS\textsubscript{2} is presented below.

(a) Discuss the use of Raoult’s and Henry’s laws to describe the solvent and solute vapour pressure behaviour for this solution, providing an interpretation for any deviation from ideal solution behaviour.

[15 marks]

(b) From the plot, estimate the activity, and activity coefficient of the solvent component for solutions of (i) CS\textsubscript{2} mole fraction of 0.8 and (ii) propanone mole fraction of 0.8. Comment on your results.

[10 marks]

4. Answer (a) and (b)

(a) Describe the main factors which influence the magnitude of the glass transition temperature, \( T_g \) in polymer systems.

[12 marks]

(b) The flow times in an Ostwald viscometer for solutions of polymethyl methacrylate in benzene at 298 K are as follows:

<table>
<thead>
<tr>
<th>Conc. / (g / 100 cm\textsuperscript{3})</th>
<th>0.0</th>
<th>0.3</th>
<th>0.6</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow time / s</td>
<td>44.7</td>
<td>56.6</td>
<td>68.8</td>
<td>85.6</td>
</tr>
</tbody>
</table>

Assuming a constant density for the solutions, determine the intrinsic viscosity, and use the equation:

\[
[\eta] = 0.94 \times 10^{-5} \text{ M}^{0.76} \text{ m}^3 \text{ kg}^{-1}
\]

to calculate the average molar mass for the polymethyl methacrylate sample.

[13 marks]
5. **Answer (a) and (b)**

(a) Describe the important role diffusion processes can play in electrode reactions, including corrosion reactions.  

[12 marks]

(b) What is the least negative potential which must be applied to a copper cathode immersed in 0.6 M CuSO$_4$ at 298 K in order to deposit copper from solution at a current density 61.7 A m$^{-2}$? Assume that concentration polarisation can be neglected. The equilibrium exchange current density ($i_0$) is 0.30 A m$^{-2}$ and the transfer coefficient ($\alpha$) is 0.46.  

$E^{0}_{Cu^{2+}/Cu} = 0.34$ V  

[13 marks]

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6. **Answer (a), (b), (c) and (d)**

(a) Describe the drop weight method for measuring the surface tension of a liquid.  

[6 marks]

(b) How does the addition of sodium chloride to water influence its surface tension? Give reasons for your answer.  

[5 marks]

(c) The data below are for the chemisorption of hydrogen on copper powder at 25$^\circ$C. Confirm that they fit the Langmuir isotherm at low coverages.  

<table>
<thead>
<tr>
<th>$p$/Pa</th>
<th>25</th>
<th>129</th>
<th>253</th>
<th>540</th>
<th>1000</th>
<th>1593</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$/cm$^3$</td>
<td>0.042</td>
<td>0.163</td>
<td>0.221</td>
<td>0.321</td>
<td>0.411</td>
<td>0.471</td>
</tr>
</tbody>
</table>

Then find the value of $K$ for the adsorption equilibrium and the adsorption volume corresponding to complete monolayer coverage.  

[9 marks]

(d) Show how the adsorption volume corresponding to complete monolayer coverage ($V_{\infty}$) can be used to obtain the surface area of adsorbent.  

[5 marks]
7. Answer (a), (b), and (c)

(a) What is scanning tunnelling microscopy and what aspect of quantum theory makes it happen?

[7 marks]

(b) Calculate the energy difference between the ground state and the first excited state of a single helium atom trapped in a one-dimensional box of length 40 pico-metres. Give your answers in J mol⁻¹.

[14 marks]

(c) What wavelength of light (in wavenumber units) would be required to effect this transition? What type of optical spectroscopy could you use to measure the transitions?

[4 marks]

8. Answer (a), (b) and (c)

(a) Give a concise explanation of rotational Raman spectroscopy. Explain the gross and specific selection rules, and describe with words and sketches the general appearance of the spectra.

[10 marks]

(b) The rotational constant B is given by: \[ B = \frac{\hbar}{8 \pi^2 c}, \text{ units } \text{cm}^{-1} \], fill in the blanks, explain all the terms in the equation.

[3 marks]

(c) The rotational Raman spectrum of \( ^{35}\text{Cl}_2 \) (m(\(^{35}\text{Cl}) = 34.9688 \text{ u} \)) shows a series of Stokes lines separated by 0.9752 cm⁻¹ and a similar series of anti-Stokes lines. Calculate the bond length of the molecule.

[12 marks]