Instructions: All questions carry equal marks, distributed as shown
Answer four (4) questions
One (1) from each Section

Duration: 2 hrs
No. of Pages: 2
Department(s): Chemistry
Course Co-ordinator(s): Prof Henry Curran

Requirements:
MCQ: Release to Library: Yes ☐ No ☐
Handout: Yes
Statistical/ Log Tables: Yes
Cambridge Tables: Yes
Graph Paper: Yes
Log Graph Paper: Yes
Other Materials: Calculator

Gas constant, $R = 8.3143 \ \text{J K}^{-1} \text{mol}^{-1}$
Planck constant, $h = 6.626 \times 10^{-34} \ \text{J s}$
Electronic charge, $e = 1.602 \times 10^{-19} \ \text{C}$
Electronic mass, $m = 9.109 \times 10^{-31} \ \text{kg}$
1 atmosphere = $101,325 \ \text{N m}^{-2}$
Avogadro constant, $N_A = 6.022 \times 10^{23} \ \text{mol}^{-1}$
Velocity of light, $c = 2.998 \times 10^8 \ \text{m s}^{-1}$
Boltzmann constant, $k = 1.381 \times 10^{-23} \ \text{J K}^{-1}$
Faraday constant, $F = 96,485 \ \text{C mol}^{-1}$
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), and (e)

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

(b) Explain, with the aid of illustrations, why ozone has a dipole moment whereas carbon dioxide does not. [4 marks]

(c) Please complete, in your answer book, the table below describing how the potential energy of interaction of two ions or charged particles depends on the charge separation, r, and the typical energy resulting from the interaction.

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>Distance dependence of potential energy</th>
<th>Typical energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion-dipole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole-dipole (stationary)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole-dipole (rotating)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[8 marks]

(d) Give the equation for the potential energy of interaction between two dipoles that are fixed (non-rotating). [4 marks]

(e) Calculate the molar potential energy of the dipolar interaction between two fixed peptide links separated by 5.0 nm in different regions of a polypeptide chain at an angle, \(\theta = 135^\circ\), \(\mu_1 = \mu_2 = 2.4\) D, corresponding to \(8.0 \times 10^{-30}\) C m. [5 marks]

2. Answer (a) and (b)

(a) Make an appropriate Arrhenius plot of the following data for the conversion of cyclopropane to propene and calculate the activation energy for the reaction:

<table>
<thead>
<tr>
<th>(T/\text{K})</th>
<th>750</th>
<th>800</th>
<th>850</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k/\text{s}^{-1})</td>
<td>(1.8 \times 10^{-4})</td>
<td>(2.7 \times 10^{-3})</td>
<td>(3.0 \times 10^{-2})</td>
<td>0.26</td>
</tr>
</tbody>
</table>

[15 marks]

(b) The rate constant for a reaction increases by a factor of 1.23 when the temperature is increased from 20\(^\circ\)C to 27\(^\circ\)C. What is the activation energy of the reaction? [10 marks]
Section B

3. Answer (a), (b), (c) and (d)

(a) Define each term in the expression for the chemical potential of a component, B, in an ideal solution: \( \mu_B = \mu_B^* + RT \ln x_B \)  

(b) Use the plot presented below to discuss the use of Raoult’s and Henry’s laws to describe the solvent and solute vapour pressure, providing an interpretation for any deviation from ideality for solvent and solute.

(c) From the plot, estimate the activity, and activity coefficient of the solvent B for a solution containing 0.5 mole of a non-volatile solute, A, in 2 mole of solvent B, if the vapour pressure of the pure solvent, B, is 50 kPa.

4. Answer (a) and (b)

(a) Explain the difference between (i) low density polyethylene (LDPE), (ii) high density polyethylene (HDPE) and (iii) ultra-high molecular weight polyethylene (UHMWPE).

(b) Consider the following polymer size fraction of a given polymer sample:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Molecular Weight</th>
<th>Number of Chains</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5,000</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>10,000</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>1,000,000</td>
<td>3</td>
</tr>
</tbody>
</table>

i. Calculate the number-average molecular weight of the polymer.
ii. Calculate the weight-average molecular weight of the polymer.
iii. Calculate the polydispersity index of the polymer.
Section C

5. Answer (a) and (b)

The room temperature free energy of formation of liquid water is $-237 \text{ kJ/mol}$ yet an electrochemical cell for the room temperature electrolysis of water requires $1.87 \text{ V}$ cell working voltage to produce oxygen and hydrogen gas.

\[
\begin{align*}
2 \text{H}^+ + 2\text{e}^- &\rightarrow \text{H}_2 & E^0 &= 0.00 \text{ V} \\
\tfrac{1}{2}\text{O}_2 + 2 \text{H}^+ + 2\text{e}^- &\rightarrow \text{H}_2\text{O} & E^0 &= 1.23 \text{ V}
\end{align*}
\]

(a) Discuss the contribution of overpotential(s) to the cell working voltage for water electrolysis.

(b) What additional voltage would be required to sustain a $1 \text{ mA}$ constant current for water electrolysis if the cathode contact resistance is $2 \Omega$, the anode contact resistance $3 \Omega$ and the solution resistance $1600 \Omega$, when the electrodes are $10 \text{ cm}$ apart?

(c) Suggest how this additional voltage requirement might be minimised.

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

The Gibbs adsorption isotherm can be written as

\[
\Gamma = -\frac{1}{RT} \left( \frac{d\gamma}{d \ln C} \right)
\]

(a) Define each term in the equation, explaining what is meant by each term.

(b) Describe one method that can be used to measure surface tension, and explain how the addition of a surfactant to water influences the surface tension.

(c) The data below are for the surface tension of solutions of hexanol in water at $25 ^\circ \text{C}$. From the data estimate $\Gamma$ for hexanol in water, and use this value to estimate the area occupied per molecule of hexanol in a monolayer on water.

<table>
<thead>
<tr>
<th>Surface tension/mN m$^{-1}$</th>
<th>65</th>
<th>59</th>
<th>52</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration/mol dm$^{-3}$</td>
<td>0.0022</td>
<td>0.005</td>
<td>0.009</td>
<td>0.016</td>
</tr>
</tbody>
</table>
Section D

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

(a) Consider you have an electron trapped in a one-dimensional “box” 15 pm long with walls of infinite potential. What would be the wavelength (in pm) of radiation required to make the electron undergo a transition from the fourth to the fifth energy level?

[17 marks]

(b) Sketch the first 4 normalised wavefunctions for a particle confined in a hypothetical 1 dimensional box.

[4 marks]

(c) Explain the Born Interpretation in the context of understanding wavefunctions.

[4 marks]

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

$^{1}\text{H}^{79}\text{Br}$ gas was analysed using an IR absorption spectrometer. A fundamental vibration at 2575.15 cm$^{-1}$ and an overtone band at 5022.78 cm$^{-1}$ were measured.

(a) Calculate the equilibrium oscillation frequency (in cm$^{-1}$) and the anharmonicity constant.

[15 marks]

(b) Explain how you could measure the equilibrium bond distance of $^{1}\text{H}^{79}\text{Br}$ with a high degree of accuracy using a different spectroscopic technique? Provide appropriate equations to illustrate your answer.

[6 marks]

(c) In the high resolution vibrational spectrum of $^{1}\text{H}^{79}\text{Br}$, the separation between the lines in the P and R branches of the spectrum are different. Explain why this is so.

[4 marks]