FIRST PUBLIC EXAMINATION
Long Vacation 2002
Preliminary Examination in Chemistry
SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY
also
Preliminary Examination in Molecular and Cellular Biochemistry
24th September 2002, 9.30 am – 12.00 pm
Time allowed: 2.5 hours

Candidates should answer all questions in Section A and any two questions in Section B.
The numbers in square brackets indicate the weight that the Examiners expect to assign to each part of the question.

Molar gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Planck constant, $h = 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant, $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Speed of light, $c = 2.998 \times 10^8 \text{ m s}^{-1}$
Avogadro number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$p^\oplus = 1 \text{ bar} = 760 \text{ Torr} = 1 \times 10^5 \text{ Pa}$
Electron mass, $m_e = 9.110 \times 10^{-31} \text{ kg}$
Elementary charge, $e = 1.602 \times 10^{-19} \text{ C}$
Faraday constant, $F = 9.648 \times 10^4 \text{ C mol}^{-1}$
Atomic mass unit, $u = 1.661 \times 10^{-27} \text{ kg}$
Molar volume, $V_m = 24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K
1 electron volt $= 1.6022 \times 10^{-19} \text{ J}$

Do not turn over until instructed to do so by an invigilator.
SECTION A
Answer all questions in this section

1. (a) For an ideal solution containing two components, sketch the dependence of the total vapour pressure on composition. [4]

(b) AgCl has a solubility product of $1.6 \times 10^{-10}$ at 298 K. Calculate the concentration of Ag$^+$ ions in a saturated solution prepared by dissolving AgCl in 0.01 mol dm$^{-3}$ NaCl solution. [4]

2. (a) Describe the difference between the order and molecularity of a chemical reaction. [2]

(b) For a second order process, $2A \rightarrow B$, show that the integrated form of the rate law is given by

$$
\frac{1}{[A]} - \frac{1}{[A_o]} = kt
$$

[3]

(c) Define what is meant by the half life, $t_{1/2}$, of a reaction and derive an expression for this quantity for the second order rate process above. [3]

3. A section of the emission spectrum of hydrogen shows a series of lines corresponding to the electron returning to the $n = 3$ state, the Paschen Series.

(a) Describe the appearance of this spectrum and illustrate, using an energy level diagram, the transitions observed. [3]

(b) The Paschen series converges to a transition at 12186 cm$^{-1}$. Calculate the Rydberg constant for hydrogen, $R_H$, and use this to calculate the ionization energy from the electronic ground state, $n = 1$. [3]

(c) State the selection rules for observed transitions in atomic spectra. [2]

4. (a) The van’t Hoff equation provides a relationship between an equilibrium constant and temperature.

$$
\frac{\text{d} \ln K}{\text{d}(1/T)} = -\frac{\Delta H^\Theta}{R}
$$

For a reaction at equilibrium show that the temperature dependence of the equilibrium constant, $K$, is given by

$$
\ln \frac{K_2}{K_1} = -\frac{\Delta H^\Theta}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
$$

[3]

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(b) The equilibrium constants for a particular chemical reaction at a series of temperatures are given in the Table. Determine the values of $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ at 298 K. [5]

<table>
<thead>
<tr>
<th>T/K</th>
<th>289</th>
<th>294</th>
<th>298</th>
<th>305</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K/10^3$</td>
<td>7.25</td>
<td>5.25</td>
<td>4.17</td>
<td>2.66</td>
<td>2.00</td>
</tr>
</tbody>
</table>

5. A particle undergoing free translational motion, subject to zero potential, can be described by the wavefunction

$$\psi = C \sin kx + D \cos kx,$$

(a) Use this equation to derive a suitable solution if the particle is confined in a one-dimensional box of length $L$, subject to an infinite potential at $x = 0$ and $x = L$, and zero potential for $0 < x < L$. [3]

(b) What is meant by normalization of a wavefunction? [2]

c) Show that the normalization constant for the wavefunction derived in (a) is $\left(\frac{2}{L}\right)^{\frac{1}{2}}$. [2]

d) Calculate the mean kinetic energy of this particle in its lowest energy state. [3]

6. The standard emf of the cell

$$\text{Zn}(s)\|\text{Zn}^{2+}(aq)\|\text{Fe}^{3+}(aq),\text{Fe}^{2+}(aq)\|\text{Pt}(s)$$

is 1.53 V at 298 K and 1.55 V at 323 K.

(a) Sketch the cell. [3]

(b) Write down the equation for the cell reaction. [2]

(c) Calculate $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ for the cell at 323 K. [3]
SECTION B
Answer any two questions from this section
All questions in this section carry equal marks

7. (a) Describe the approximations used to derive a reaction rate using the steady state approximation. For the reaction A → B → C, derive a general expression for [B], assuming it is a steady state intermediate. [5]

(b) For the following reaction

$$\text{H}^+ + \text{HNO}_2 + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br}^-} \text{C}_6\text{H}_5\text{N}_2^+ + 2\text{H}_2\text{O}$$

The observed rate law is

$$v = k[\text{H}^+][\text{HNO}_2][\text{Br}^-] \quad (1)$$

A mechanism has been proposed containing the following elementary steps

$$\begin{align*}
\text{H}^+ + \text{HNO}_2 & \xrightarrow{k_1} \text{H}_2\text{NO}_2^+ \\
\text{H}_2\text{NO}_2^+ & \xrightarrow{k_2} \text{H}^+ + \text{HNO}_2 \\
\text{H}_2\text{NO}_2^+ + \text{Br}^- & \xrightarrow{k_i} \text{ONBr} + \text{H}_2\text{O} \\
\text{ONBr} + \text{C}_6\text{H}_5\text{NH}_2 & \xrightarrow{k_i} \text{C}_6\text{H}_5\text{N}_2^+ + \text{H}_2\text{O} + \text{Br}^- 
\end{align*}$$

Use the steady state approximation to show that the above mechanism produces the following rate law [16]

$$v = \frac{k_1k_2[\text{H}^+][\text{HNO}_2][\text{Br}^-]}{k_{-1} + k_1[\text{Br}^-]} \quad (2)$$

(c) Compare the two rate expressions, (1) and (2), and deduce the relative sizes of the rate constants $k_{-1}$ and $k_1$ relative to $[\text{Br}^-]$. [4]

8. For a particle of mass $m$ undergoing simple harmonic motion, with respect to a fixed origin, the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2\psi = E\psi$$

where $k$ is a constant.

(a) Give the energy levels associated with solutions to this equation. Comment on the energy of the lowest level and show that the energy difference between consecutive energy levels is given by

$$E_{v+1} - E_v = \hbar\nu$$

where $\nu$ is the frequency. [5]
(b) Eigenfunctions for the harmonic oscillator contain three components: a normalization constant $N$; a Hermite polynomial $H_v(x)$, and a Gaussian function of the form $e^{-x^2}$. Calculate the normalization constant for the general eigenfunction when $v = 1$. 

$$\psi_v(x) = H_v(x)e^{-x^2/2}$$ [4]

(c) Sketch the wavefunctions of the four lowest levels for the harmonic oscillator. On a separate diagram show the probability distributions, $|\psi|^2$, for these states of the system. Comment on the expected probability distribution at very large values of the quantum number $v$. [8]

(d) Hydrogen iodide (HI) exhibits a force constant $k = 313.8 \text{ N m}^{-1}$ for vibrational motion. Calculate the energies of the lowest four energy levels and the energy of a photon required to produce an allowed transition. (the relative atomic mass of I is 127) [8]

$$\text{note } \int_{-\infty}^{\infty} H_v(x)e^{-x^2} \, dx = \pi^{v/2}2^v v! , \text{ if } v' = v$$

[atomic masses: H 1 u; I 127 u]

9. (a) The table below gives the standard entropies of vaporization for a number of liquids

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta_vap S^\circ$/J K$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>+87.2</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>+85.8</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>+85.1</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>+87.9</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>+109.1</td>
</tr>
</tbody>
</table>

With reference to Trouton’s rule, discuss the discrepancy between the value obtained for H$_2$O and those for the other liquids. What would you expect for $\Delta_vap S^\circ$(ethanol)? [6]

(b) If we assume that the constant pressure heat capacity remains constant over a given temperature range, show that the variation in entropy between two temperatures, $T_i$ and $T_f$, is given by the expression

$$S_{T_f} - S_{T_i} = C_p \ln \left( \frac{T_f}{T_i} \right)$$ [6]

(c) We now describe the temperature dependence of the heat capacity ($C_p$) by the polynomial $a + bT + c/T^2$. How is the temperature dependence of the entropy now described? [3]

(d) For liquid naphthalene, $a = 79.5$, $b = 0.4075 \times 10^{-3}$ and $c = 0.0$. The coefficients for solid naphthalene are $-115.9$, $3.92$ and $0.00$. Evaluate the entropy difference between 10 K and the boiling point (490.9 K) per mole of liquid naphthalene. The standard enthalpy of fusion at the freezing point (354 K) is 18.80 kJ mol$^{-1}$. [8]

(e) Polynomials of the type given in (c) cannot be used at temperatures approaching 0 K. How is the entropy calculated at these very low temperatures. [2]

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Turn over
10. The following cell has been used to determine the acid dissociation constant of the ammonium ion.

\[
\text{Pt(s)} | \text{H}_2(\text{g}) (P = 1 \text{ bar}) | \text{NH}_3(\text{aq}) \ (0.0212 \text{ M}), \text{NH}_4\text{Cl} \ (\text{aq}) \ (0.0212 \text{ M}) | \text{AgCl(s)} | \text{Ag(s)}
\]

The measured emf value for the cell is 0.8759 V at 298 K when the cell is prepared using the shown concentrations; \( E_{\text{Ag/AgCl}}^{\text{c}} \) is 0.2223 V.

(a) Identify the half reactions and give the equation describing the overall reaction. [5]

(b) Write down the Nernst equation for this process. [5]

(c) Give an expression for the acid dissociation constant, \( K_a \), and calculate its value under the conditions given above. [15]