EXAMINATION IN PHYSICAL CHEMISTRY

(in the exact style of a Prelims Paper)

Time allowed: 2.5 hours

Candidates should attempt \textit{ALL} questions in Section A and \textit{TWO} questions in Section B

[The numbers in square brackets indicate the relative weight the examiner anticipates assigning to each part of the question]

Attention is drawn to the table of constants provided on page 2 of this booklet.
### Fundamental Constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed of light in a vacuum ( c )</td>
<td>( 2.998 \times 10^8 \text{ m s}^{-1} )</td>
</tr>
<tr>
<td>Planck constant ( h )</td>
<td>( 6.626 \times 10^{-34} \text{ J s} )</td>
</tr>
<tr>
<td></td>
<td>( h = h/2\pi ) 1.055 \times 10^{-34} \text{ J s}</td>
</tr>
<tr>
<td>Boltzmann constant ( k_B )</td>
<td>( 1.381 \times 10^{-23} \text{ J K}^{-1} )</td>
</tr>
<tr>
<td>Gas constant ( R )</td>
<td>( 8.314 \text{ J K}^{-1} \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>Faraday constant ( F )</td>
<td>( 9.649 \times 10^{4} \text{ C mol}^{-1} )</td>
</tr>
<tr>
<td>Elementary charge ( e )</td>
<td>( 1.602 \times 10^{-19} \text{ C} )</td>
</tr>
<tr>
<td>Electron mass ( m_e )</td>
<td>( 9.109 \times 10^{-31} \text{ kg} )</td>
</tr>
<tr>
<td>Proton mass ( m_p )</td>
<td>( 1.673 \times 10^{-27} \text{ kg} )</td>
</tr>
<tr>
<td>Neutron mass ( m_n )</td>
<td>( 1.675 \times 10^{-27} \text{ kg} )</td>
</tr>
<tr>
<td>Electric constant ( \varepsilon_0 )</td>
<td>( 8.854 \times 10^{-12} \text{ F m}^{-1} )</td>
</tr>
<tr>
<td>Avogadro constant ( N_A )</td>
<td>( 6.022 \times 10^{23} \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>Atomic mass unit ( u )</td>
<td>( 1.661 \times 10^{-27} \text{ kg} )</td>
</tr>
<tr>
<td>Gravitational constant ( G )</td>
<td>( 6.674 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2} )</td>
</tr>
<tr>
<td>Gravitational acceleration ( g )</td>
<td>( 9.807 \text{ m s}^{-2} )</td>
</tr>
</tbody>
</table>

### Other conventions

- \( p^\circ = 1 \text{ bar} = 1 \times 10^5 \text{ Pa} \)
- 1 atm = 101.3 kPa = 760 Torr
- 1 D (Debye) = \( 3.336 \times 10^{-30} \text{ C m} \)
1. (a) Starting from the fundamental equation \( dG = Vdp - SdT \), and stating clearly any assumptions you make, derive the Clausius-Clapeyron equation for the variation of equilibrium vapour pressure of a liquid with temperature:

\[
\frac{d\ln p}{dT} = \frac{\Delta_{vap} H}{RT^2}
\]

(b) Calculate the vapour pressure of benzene at 373.2 K, stating any assumptions you make and given that the standard boiling point of benzene is 353.2 K, and \( \Delta_{vap} H^\circ = 30.8 \text{ kJ mol}^{-1} \).

2. Hydrogen chloride can be produced in the interstellar medium by the following series of elementary reactions:

\[
\begin{align*}
\text{Cl} + \text{H}_3^+ &\rightarrow \text{HCl}^+ + \text{H}_2 & k_1 = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \\
\text{HCl}^+ + \text{H}_2 &\rightarrow \text{H}_2\text{Cl}^+ + \text{H} & k_2 = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \\
\text{H}_2\text{Cl}^+ + \text{e}^- &\rightarrow \text{HCl} + \text{H} & k_3 = 1.5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}
\end{align*}
\]

(a) Use the steady-state approximation to derive expressions for the concentrations of \( \text{HCl}^+ \) and \( \text{H}_2\text{Cl}^+ \).

(b) Given the following concentrations (number densities): \( \rho_{\text{Cl}} = 4.0 \times 10^{-3} \text{ cm}^{-3} \), \( \rho_{\text{H}_3^+} = 1.0 \times 10^{-4} \text{ cm}^{-3} \), and \( \rho_{\text{e}^-} = 9.0 \times 10^{-5} \text{ cm}^{-3} \), estimate \( \rho_{\text{H}_2\text{Cl}^+} \).

3. Consider a titanium-sapphire laser tuned to a photon-energy of 1.91 eV.

(a) Convert this energy into SI units, then calculate the wavelength of the emitted light and the momentum of a single photon.

(b) How many photons would need to be absorbed per second by a polystyrene bead of mass 1 fg in order to levitate it?
4. (a) What is meant by the term *tunnelling* in quantum mechanics? 

The tunnelling probability, $P_T$, of a particle with mass $m$ and energy $E$ through a rectangular barrier is given by:

$$P_T \propto \exp \left( \frac{-2L}{\hbar} \sqrt{2m(V - E)} \right)$$

where $V$ and $L$ are the height and width of the barrier, respectively.

(b) Evaluate the ratio of tunnelling probabilities for a proton and deuteron, $P_{H^+}^T / P_{D^+}^T$, where $m_{D^+} = 3.3 \times 10^{-27}$ kg, $(V - E) = 1.6 \times 10^{-20}$ J, and $L = 1.0 \times 10^{-10}$ m.

(c) Comment on the implications for the rate of chemical reactions involving proton/deuteron transfer.

5. The interaction force between two point charges, $q_1$ and $q_2$, separated by a distance $r$ is given by Coulomb’s law:

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r r^2}$$

where $\epsilon_r$ is the relative permittivity of the medium.

(a) State the general relation between electrostatic force and electrostatic potential energy, and hence derive an expression for the potential energy of interaction between two point charges.

In a 0.01 M solution of NaCl in water at 298 K, the average distance between Na$^+$ and Cl$^-$ ions is 4.0 nm.

(b) Calculate the electrostatic interaction energy between Na$^+$ and Cl$^-$ ions at this separation, given that in water at 298 K, $\epsilon_r = 78$.

(c) Compare your answer to the thermal energy, $k_B T$, at 298 K, and comment.

6. (a) Describe, with the aid of a sketch, what is meant by the term *collision cross-section*.

(b) Calculate the collision cross-section for the collision of two argon atoms, given the atomic radius $a_{Ar} = 0.71$ Å.

(c) Calculate the collision cross-section of an argon atom with a helium atom ($a_{He} = 0.31$ Å).
7. Consider the following electrochemical cell:

\[ \text{Pt(s)|H}_2\text{(g, p = 1 bar)|HBr(aq, a = 1)|AgBr(s)|Ag(s)} \]

(a) Write down the half-cell reactions and the formal cell reaction.

(b) Determine \( E^\circ_{\text{cell}} \) at 298 K, and \( \Delta_r G^\circ \) for the cell reaction. [Note the standard reduction potential at 298 K: \( \text{AgBr(s)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^-, E^\circ = 0.0732 \text{ V} \)]

The following table shows how \( E^\circ_{\text{cell}} \) varies in the range 283 K to 313 K:

<table>
<thead>
<tr>
<th>( T/ \text{K} )</th>
<th>283</th>
<th>293</th>
<th>303</th>
<th>313</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^\circ_{\text{cell}}/\text{V} )</td>
<td>0.0807</td>
<td>0.0757</td>
<td>0.0707</td>
<td>0.0657</td>
</tr>
</tbody>
</table>

(c) Plot a graph to determine \( \left( \frac{\partial E}{\partial T} \right)_p \) in this temperature range.

(d) Hence, find \( \Delta_r S^\circ \) for the cell reaction.
SECTION B
Attempt any TWO questions

8. (a) Derive an integrated rate equation for the first-order reaction A \rightarrow B. \[3\]
(b) Hence show how the half-life is related to the rate constant in this case. \[2\]
Technetium-99m (\(^{99m}\)Tc) is a metastable nuclear isomer that is used as a radioactive tracer in medical diagnostics. \(^{99m}\)Tc decays to \(^{99}\)Tc by emitting \(\gamma\)-radiation, and then to \(^{99}\)Ru by \(\beta^-\)-emission, with the following characteristic radioactive-decay half-lives:

\[
\begin{align*}
^{99m}\text{Tc} & \xrightarrow{k_m} ^{99}\text{Tc} \\
\text{(}\frac{t_{1/2}}{2}\text{)} & = 6 \text{ hr} \\
^{99}\text{Tc} & \xrightarrow{k} ^{99}\text{Ru} \\
\text{(}\frac{t_{1/2}}{2}\text{)} & = 211000 \text{ yr}
\end{align*}
\]

In a competing reaction, both nuclear isomers of technetium are cleared from the body by a biological process that can be approximated by first-order kinetics, with rate constant \(k_{bio}\) and \(t_{1/2} = 24 \text{ hr}\).

(c) Calculate the rate constants \(k_{bio}\) and \(k\). \[2\]

A patient is injected with \(^{99m}\)Tc to give an initial concentration \([^{99m}\text{Tc}]_0 = 5.00 \mu\text{M}\), and scanned using single photon emission computed tomography.

(d) On a single graph, sketch how \([^{99m}\text{Tc}]\), \([^{99}\text{Tc}]\), and \([^{99}\text{Ru}]\) vary in the patient over the first four days after injection. \[4\]

(e) What is the concentration of \(^{99m}\)Tc after 20 min (the time of a typical scan)? \[4\]

(f) Express \(k_m\) as a multiple of \(k_{bio}\), and hence show that the rate equation for \(^{99}\)Tc can be written in the form:

\[
\frac{d[^{99}\text{Tc}]}{dt} + A[^{99}\text{Tc}] = 4k_{bio}[^{99m}\text{Tc}]_0 e^{-5k_{bio}t}
\]

and determine \(A\). \[5\]

The first-order linear differential equation above has the following solution:

\[
[^{99}\text{Tc}] = \frac{4k_{bio}[^{99m}\text{Tc}]_0}{A - 5k_{bio}} \left( e^{-5k_{bio}t} - e^{-At} \right)
\]

(g) Find the time at which \([^{99}\text{Tc}]\) reaches a maximum, and hence the maximum concentration of \(^{99}\)Tc. \[5\]
9. The Schrödinger equation (SE) for a one-dimensional harmonic oscillator is:

\[-\frac{\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2} kx^2 \psi(x) = E\psi(x)\]

(a) Sketch the potential energy of the oscillator for the given system and include on your diagram the wavefunctions for the three lowest energy levels. [3]

(b) On a separate graph, sketch the potential energy together with the probability densities for the first three energy levels. Use your sketch to illustrate differences between a classical and a quantum oscillator. [4]

(c) Find \(\alpha\) such that \(\psi_0 = N\exp^{-\alpha x^2/2}\) is a solution to the SE and determine the zero point energy, \(E_0\). [8]

(d) Normalize \(\psi_0(x)\). Note that: \(\int_{-\infty}^{\infty} e^{-ax^2} \, dx = \sqrt{\frac{\pi}{a}}\). [2]

The ground to first excited state vibrational energy gaps for hydrogen and iodine molecules are: \(\tilde{\nu}_{H_2} = 4161\) cm\(^{-1}\) and \(\tilde{\nu}_{I_2} = 207\) cm\(^{-1}\).

(e) Discuss why these values are different in the light of your answer to (c). [2]

(f) According to the Boltzmann distribution, the number of molecules, \(n_i\), found in a particular energy level, \(E_i\), can be expressed as:

\[n_i \propto \exp\left(-\frac{E_i}{k_B T}\right)\]

Use this expression to find the ratio of the number of molecules found in the first vibrational excited state compared to the ground state for both \(I_2\) and \(H_2\) at \(T = 600\) K. [4]

(g) In the light of your answer to (f), estimate the difference between the room temperature constant volume heat capacities of \(I_2\) and \(H_2\). State your reasons. [2]
10. Describe the uses of the van’t Hoff equation

\[
\frac{\text{d} \ln K}{\text{d}T} = \frac{\Delta_r H^\circ}{RT^2}
\]

in chemical thermodynamics. \[4\]

The water-gas shift reaction is represented by the chemical reaction

\[
\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}
\]

for which some thermodynamic parameters at 298 K are listed in the table below.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta_f H^\circ / \text{kJ mol}^{-1}$</th>
<th>$\Delta_f G^\circ / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(g)</td>
<td>-110.5</td>
<td>-137.2</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>-241.8</td>
<td>-228.6</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-393.5</td>
<td>-394.3</td>
</tr>
<tr>
<td>H$_2$(g)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(a) Calculate the equilibrium constant $K_p$ for this reaction at 298 K. \[4\]

(b) Industrially this reaction is normally utilised at high temperatures. Calculate $K_p$ at 650 K, taking $\Delta_r H^\circ$ to be constant over the temperature range. \[6\]

(c) A stoichiometric mixture of CO(g) and H$_2$O(g) is allowed to reach equilibrium at 650 K. If $x$ is the mole fraction of H$_2$(g) present, show that $K_p$ can be expressed in the form

\[
K_p = \frac{4x^2}{(1-2x)^2}.
\]

(d) Calculate the value of $x$ at $T = 650\text{K}$. \[4\]

(e) How could the accuracy of your calculation of $K_p$ at 650 K be improved if it was no longer assumed that $\Delta_r H^\circ$ was independent of temperature? \[3\]
11. (a) A concentration cell is an electrochemical cell in which the two electrodes are identical, but immersed in solutions of different concentrations.

(i) Suppose that the electrodes are metallic lead, immersed in solutions of lead (II) ions. If the two compartments have concentrations $m_R$ and $m_L$, find an equation for the cell emf using the Nernst equation. [5]

(ii) Why is the cell emf independent of the standard electrode potentials? [2]

(iii) Why is it necessary to include a salt bridge between the two compartments? [2]

The following three problems are all concerned with concentration cells in which metal electrodes are immersed in aqueous solutions of the corresponding cations at 298 K.

(b) A concentration cell is used to determine the concentration of lead in a contaminated water sample. The electrodes are metallic lead, the right hand compartment contains a standard 0.1 M solution of lead (II) nitrate, and the left hand compartment contains the solution of unknown concentration. The emf is measured to be 0.0233 V. Determine the concentration of lead in the unknown sample. [4]

(c) A concentration cell is set up with mercury electrodes, in which the right hand compartment contains mercury (I) nitrate of concentration, $m$. The left hand compartment contains a sample of the same solution that has been diluted to $m/10$. The emf of the cell is found to be 0.0296 V. Deduce the number of electrons required to reduce a mercury (I) ion. What does this imply about the chemical nature of the ion? [6]

(d) A concentration cell is set up with silver electrodes, in which the right hand compartment contains a standard solution of 0.1 M silver nitrate. The left hand compartment contains a total silver concentration of 0.01 M and 0.99 M aqueous ammonia. Silver complexes with ammonia according to the equilibrium

$$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+.$$ 

The emf of the cell is found to be 0.250 V. Evaluate the stability constant for this complex (i.e. the equilibrium constant for the equilibrium given). [6]