

XCHA 2716

SECOND PUBLIC EXAMINATION
Honour School of Chemistry

CHEMISTRY PART IA

PHYSICAL CHEMISTRY

SAMPLE PAPER

Friday, -- June ----, 9.30 a.m. to 12.00 p.m.

Candidates should answer **SIX** questions.

Time allowed 2½ hours

Please start each question in a new booklet.

The numbers in square brackets indicate the approximate marks that examiners intend to assign to each part of the question.

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

Guide to Questions

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|--------------------------|-------------------------------|
| 1. Thermodynamics | 5. Valence |
| 2. Liquids and Solutions | 6. Statistical Thermodynamics |
| 3. Spectroscopy | 7. Rate Processes |
| 4. Quantum Mechanics | 8. Miscellaneous |

Do not turn over the page until you are told to do so.

Fundamental Constants

Speed of light	c	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054 \times 10^{-34} \text{ J s}$
Boltzmann constant	k_B	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	F	$9.649 \times 10^4 \text{ C mol}^{-1}$
Elementary charge	e	$1.602 \times 10^{-19} \text{ C}$
Electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Proton mass	m_p	$1.673 \times 10^{-27} \text{ kg}$
Vacuum permittivity	ϵ_0	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	u	$1.661 \times 10^{-27} \text{ kg}$
Bohr magneton	μ_B	$9.274 \times 10^{-24} \text{ J T}^{-1}$

Other conventions

$p^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$	$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr}$
$1 \text{ Da} = 1 \text{ g mol}^{-1}$	$1 \text{ L} = 1 \text{ dm}^3 \quad 1 \text{ M} = 1 \text{ mol L}^{-1}$

1. *Thermodynamics*

- (a) State, without proof, the Clapeyron equation for the gradient (dp/dT) of a phase boundary in the p - T phase diagram of a pure substance, explaining the meaning of the symbols used. [2]
- (b) (i) Sketch a typical p - T phase diagram of a substance such as benzene, and label the phases, the triple point and the critical point. [3]
- (ii) Comment, qualitatively, on the relative magnitudes of the gradients of the different phase boundaries. [3]
- (c) The temperature-dependence of the vapour pressure of solid and liquid benzene is given below.

	T / K	p / kPa
Solid	265	1.83
	275	3.88
Liquid	280	5.40
	290	9.05

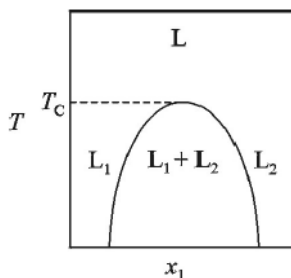
Use the Clausius-Clapeyron equation for the vapour pressure above a liquid or solid:

$$\frac{d \ln p}{dT} = \frac{\Delta_u H}{RT^2}$$

to estimate the enthalpies of sublimation and vaporization of benzene, identifying any approximations that you use. [7]

2. Liquids and Solutions

- (a) What is meant by an *ideal solution*? Using the expression for the chemical potential in an ideal solution determine an equation for the molar Gibbs free energy of mixing, $\Delta_{\text{mix}}G$, in a two-component mixture. [5]
- (b) In the regular solution model of non-ideal mixtures, the molar entropy of mixing, $\Delta_{\text{mix}}S$, is assumed to be ideal and the molar enthalpy of mixing, $\Delta_{\text{mix}}H$, is given by $\beta x_1 x_2$, where x_1 and x_2 are the mole fractions of the two components and the constant β is independent of temperature.
- (i) Describe a simple physical model for a non-ideal mixture that would behave as a regular solution. [A mathematical derivation is not required.] [3]
- (ii) The phase diagram for a mixture that behaves as a regular solution is shown below.



Sketch how $-T\Delta_{\text{mix}}S$, $\Delta_{\text{mix}}H$ and $\Delta_{\text{mix}}G$ vary with composition for mixtures at temperatures above and below the upper critical solution temperature, T_C . [5]

- (iii) Use your diagrams to explain why two liquids may only be partially miscible even though $\Delta_{\text{mix}}G < 0$ for all compositions. [2]

3. Spectroscopy

- (a) Explain briefly what is meant by the *Raman effect* and state both the gross and specific selection rules associated with a pure rotational Raman spectrum. [4]
- (b) The energy levels for a rigid rotor in vibrational level v are given by the following formula

$$E_v(J) = hcB_v J(J + 1) ,$$

where J is the rotational angular momentum quantum number and B_v is the rotational constant for vibrational level v .

- (i) Show that the wavenumbers of the Stokes lines, $\tilde{\nu}_S$, in a pure rotational Raman spectrum are given by:

$$\tilde{\nu}_S = \tilde{\nu}_I - 2B_v (2J + 3) ,$$

where $\tilde{\nu}_I$ is the wavenumber of the incident radiation. [4]

- (ii) The following consecutive Stokes lines are observed within the rotational Raman spectrum of $^{14}\text{N}_2$ (note that there may be other rotational transitions outside this range):

$$(\tilde{\nu}_I - \tilde{\nu}_S)/\text{cm}^{-1} = 35.808; \quad 43.766; \quad 51.724; \quad 59.682.$$

By considering the separations of successive transitions, determine a value for the rotational constant B_0 and assign the four transitions. [4]

- (iii) Discuss what additional information, if any, would be required to determine the *equilibrium* bond length, r_e , of $^{14}\text{N}_2$. [3]

Note: The nuclear spin quantum number, I , for ^{14}N is non-zero.

4. *Quantum Mechanics*

The wave function of the $2p_z$ orbital in a hydrogen atom is

$$\Psi(r, \theta) = N \cos \theta \, r e^{-r/2a_0}$$

in which a_0 is the Bohr radius and N is a normalisation constant with

$$\frac{4\pi}{3} N^2 = \frac{1}{4! a_0^5}$$

The radial distribution function, $P(r)$, for a $2p_z$ orbital is given by

$$P(r) = \int_0^{2\pi} \int_0^\pi \Psi(r, \theta)^2 r^2 \sin \theta \, d\theta \, d\phi$$

(a) Explain what is meant by the term *radial distribution function*. [2]

(b) Show that

$$P(r) = \frac{4\pi}{3} N^2 r^4 e^{-r/a_0}$$

Note that: $\int_0^\infty x^p e^{-x/b} dx = p! b^{p+1}$ and $\int_0^\infty P(r) dr = 1$ [7]

(c) Using the above expression for $P(r)$, and the normalization constant given, derive the following expression for the mean value of r^m

$$\langle r^m \rangle = \frac{(m+4)!}{4!} a_0^m$$
 [4]

(d) Hence determine the mean distance of a $2p_z$ electron from the nucleus. [2]

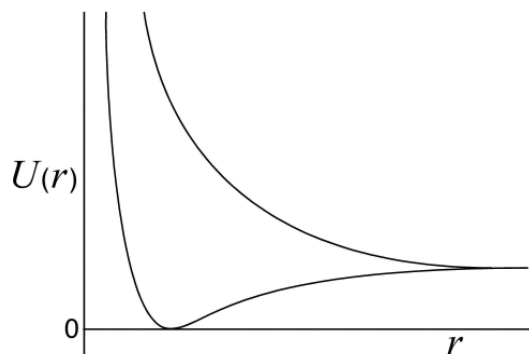
5. Valence

- (a) The energies, $U(r)$, of the lowest two electronic states of the H_2^+ ion as a function of internuclear separation, r , are given approximately by

$$U_1(r) = A \{1 - \exp[-\alpha(r - r_e)]\}^2$$

$$U_2(r) = A + Br^{-2}$$

Identify which state is which on the diagram below, mark on a copy of the diagram the values of A and r_e and account briefly for the shapes of the two curves in terms of molecular orbital theory. [5]



- (b) Given that, per molecule, $A = 4.25 \times 10^{-19} \text{ J}$ and $B = 1.96 \times 10^{-38} \text{ J m}^2$, calculate the energy difference E between the two states at $r = r_e = 1.06 \times 10^{-10} \text{ m}$. [2]
- (c) By expanding $\exp[-\alpha(r - r_e)]$ for $r \approx r_e$ show that $U_1(r)$ can be rewritten

$$U_1(r) = A\alpha^2(r - r_e)^2$$

[4]

- (d) The equation

$$U_1(r) = \frac{1}{2}k(r - r_e)^2$$

is the potential energy for a harmonic oscillator with force constant k . Given that $\alpha = 1.37 \times 10^{10} \text{ m}^{-1}$, calculate the vibrational frequency of H_2^+ , and hence show that the zero point energy is small compared to E (from part (b)). [4]

6. Statistical Thermodynamics

For a system of N independent, indistinguishable particles, the canonical partition function, $Q \equiv Q(N, V, T)$, is related to the molecular partition function, q , by the relationship $Q = q^N / N!$

Furthermore, Q can be related to the internal energy and Helmholtz free energy as follows:

$$E(T) = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad \text{and} \quad A(T) = -k_B T \ln Q$$

The three-dimensional translational partition function for particles of mass m can be written in the following form:

$$q = A(mT)^{3/2} V,$$

where A is a constant, T is the temperature of the system and V is the volume of the container (box).

In the following, consider a monatomic gas of independent particles (in which the electronic degrees of freedom may also be neglected).

- (a) Show that the internal energy is given by

$$E(T) = \frac{3}{2} N k_B T. \quad [4]$$

- (b) Hence show that the entropy $S(T)$ is given by

$$S(T) = N k_B \ln \left(\frac{q e^{5/2}}{N} \right)$$

Note: Stirling's approximation is $\ln N! \approx N \ln N - N$ for $N \gg 1$. [5]

- (c) Show that the translational contribution to $S(T)$ may be expressed in the form

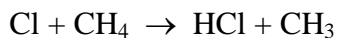
$$S(T) = N k_B \left(B + \frac{3}{2} \ln m \right)$$

where m is the relative atomic mass, and B is independent of the chemical identity of the gas. [3]

- (d) Hence account for the fact that the *difference* in the standard molar entropies of ^{131}Xe and ^4He at $T = 298 \text{ K}$ is $43.5 \text{ J K}^{-1} \text{ mol}^{-1}$. Take the relative atomic masses as $m(\text{He}) = 4$, $m(\text{Xe}) = 131$. [3]

7. Rate Processes

The reaction



has been studied by forming Cl atoms with a laser pulse in excess methane, and observing the concentration of HCl as a function of time.

- (a) Show that the HCl concentration, $[\text{HCl}]$, varies with time t as

$$[\text{HCl}] = [\text{HCl}]_{\infty} \{1 - \exp(-k_1 [\text{CH}_4] t)\}$$

where $[\text{CH}_4]$ is the methane concentration, $[\text{HCl}]_{\infty}$ is the concentration of HCl at $t = \infty$ and k_1 is the rate constant. [5]

- (b) The following data apply to the reaction at 298 K with $[\text{CH}_4] = 10^{15} \text{ molecule cm}^{-3}$.

t / ms	$[\text{HCl}] / 10^{10} \text{ molecule cm}^{-3}$
2	0.57
4	1.05
8	1.74
12	2.19
16	2.46
∞	3.00

Evaluate k_1 . [6]

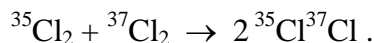
- (c) Rate constants have been measured for various isotopic forms of methane. Explain, using transition state theory, why the rate constant may depend on isotopic substitution. [4]

8. *Miscellaneous*

Answer *THREE* parts only from parts (a), (b), (c), (d), and (e).

Each part carries equal weight

- (a) Explaining your reasoning, use statistical mechanical arguments to estimate K_p , $\Delta_r G^\circ(298)$, and $\Delta_r S^\circ(298)$ for the reaction



You may assume that all three diatomic molecules have the same vibrational frequencies and equilibrium bond-lengths.

- (b) A typical time-dependent signal in Fourier transform nuclear magnetic resonance spectroscopy has the form

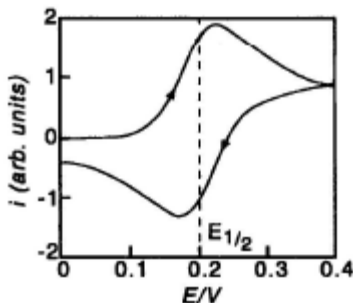
$$f(t) = e^{-\alpha t} \cos(\omega_0 t).$$

The (approximate) Fourier transform may be written

$$F(\omega) \approx \sqrt{\frac{2}{\pi}} \frac{\alpha}{\alpha^2 + (\omega - \omega_0)^2}.$$

State the Fourier transform equation relating $f(t)$ and $F(\omega)$ and sketch the two functions, indicating the effect on both of variation in α and ω_0 .

- (c) The figure below shows the first sweep of a cyclic voltammogram for the oxidation of species A to A^+ at an electrode when the kinetics are fast (“reversible” electrode kinetics).



Explain the shape of the voltammogram. Explain how the voltammogram would differ if the electrode reactions were slow (“irreversible” electrode kinetics)?

Question continues...

- (d) Consider a particle of mass μ confined in a two-dimensional box of sides L , bounded by $0 \leq x \leq L$ and $0 \leq y \leq L$, and with potential energy $V = 0$ inside the box and infinity elsewhere. Inside the box, the Hamiltonian is

$$\hat{H} = \frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right).$$

Assuming a *separable* wavefunction of the form

$$\psi(x, y) = X(x)Y(y),$$

with

$$X(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$Y(y) = \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi y}{L}\right),$$

solve the Schrödinger equation, and show that

$$E = \frac{\pi^2 \hbar^2}{2\mu L^2} (n^2 + m^2).$$

State the possible values of m and n , and identify under what circumstances you would expect to find degeneracy.

- (e) The one-dimensional diffusion equation may be written as

$$\frac{\partial \rho(x, t)}{\partial t} = D \frac{\partial^2 \rho(x, t)}{\partial x^2},$$

where D is the diffusion coefficient and $\rho(x, t)$ is the concentration. Find a solution to this equation given the conditions that $\rho(x, t) \rightarrow 0$ as $t \rightarrow \infty$ and $\rho(0, t) = \rho_0$.

End of Examination