

NATURAL SCIENCES TRIPOS Part IB
NATURAL SCIENCES TRIPOS Part II (General)

Thursday 1st June 2000

1.30 to 4.30

CHEMISTRY A: PAPER 1

Candidates should attempt FIVE questions, ONE from each section

Where a question is divided into sections, the *approximate* division of marks between sections is indicated at the end of the question.

Linear graph paper is available if required.

A Periodic Table, the values of physical constants, character tables and selected mathematical formulae will be found in the data book provided.

Write on ONE side of the paper only.

The answers to each question should be returned separately.

A separate cover sheet for each question should be completed.

SECTION A

*Quantum Mechanics***A1**

Answer *all* parts of this question

- (a) Write down the Schrödinger equation for a harmonic oscillator which has a mass m and force constant k . Obtain the ground state wavefunction ψ_0 , assuming it has the form $e^{-\alpha x^2}$, and its energy E_0 .
- (b) What is meant by the statement that all wavefunctions $\psi_n(x)$ of the harmonic oscillator are orthogonal to each other? Assuming that $\psi_n(x) = H_n(x)e^{-\alpha x^2}$, where $H_n(x)$ is a polynomial of degree n , use nodal arguments to write down unnormalised forms for $\psi_1(x)$ and $\psi_2(x)$. Determine E_1 , the values of x for which $\psi_2(x) = 0$, and E_2 .

$$\left[\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{\pi}{2\alpha}} ; \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{8\alpha^3}} \right]$$

- (c) Discuss briefly the importance of the harmonic oscillator in understanding molecular vibrations, and outline the principal weakness of the model.

Approximate division of marks : (a) 30%, (b) 60%, (c) 10%.

A2

Answer *all* parts of this question

- (a) Define the angular momentum operators
- \hat{L}_x
- ,
- \hat{L}_y
- ,
- \hat{L}_z
- and
- \hat{L}^2
- .

In spherical polar coordinates r , θ , φ it may be shown that

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

Show that the four spherical harmonics (i) 1, (ii) $\sin \theta e^{i\varphi}$, (iii) $\sin \theta e^{-i\varphi}$ and (iv) $\cos \theta$ are eigenfunctions of \hat{L}_z and \hat{L}^2 . Hence attach labels m_l , l to these functions.

- (b) Describe how the spin functions α, β relate to the corresponding operators \hat{S}_z , \hat{S}^2 and the spin labels m_s , s .
- (c) The total angular momentum operator \hat{J} is defined to be $\hat{L} + \hat{S}$. Write down the two eigen equations involving \hat{J}_z and \hat{J}^2 which define the labels J , M_J .
- (d) Hence explain why the term symbols for the lowest states of the C atom are 3P_2 , 3P_1 , 3P_0 , 1D_2 , 1S_0 (the relative ordering is not requested).

Approximate division of marks: (a) 40%, (b) 10%, (c) 10%, (d) 40%.

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SECTION B*Symmetry and Bonding***A3**

Answer *all* parts of this question

- (a) What is the point group of the ethene molecule, C_2H_4 ? Sketch the effect on this molecule of: (i) the symmetry operation i ; (ii) one of the C_2 operations; and (iii) one of the σ operations.
- (b) Take the z-axis to be perpendicular to the plane of the molecule, and the x-axis to be directed along the C–C bond. Use any method to find the symmetry orbitals which can be constructed from the carbon $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals and to assign their symmetry labels.
- (c) Find the symmetry orbitals which can be formed from the four hydrogen $1s$ atomic orbitals.
- (d) Give approximate sketches of the bonding molecular orbitals which might be formed using only the hydrogen $1s$ and the carbon $2p_x$ and $2p_y$ atomic orbitals.

Approximate division of marks: (a) 20%, (b) 30%, (c) 30%, (d) 20%.

A4

Answer *all* parts of this question

- (a) Sketch the structures of the BH_3 and NH_3 molecules. Show the symmetry elements and assign the point groups for each molecule.
- (b) Deduce, assign, and sketch the hydrogen symmetry group orbitals for each molecule. Write down the irreducible representations for the 2s and 2p atomic orbitals on the B and N atoms, and hence construct qualitative molecular orbital diagrams for BH_3 and NH_3 .
- (c) Use your diagrams to explain why BH_3 and NH_3 adopt their respective structures, and why BH_3 is a Lewis acid whereas NH_3 is a Lewis base.

Approximate division of marks: (a) 30%, (b) 50%, (c) 20%.

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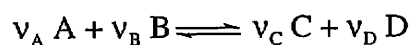
SECTION

Molecular Energy Levels and Thermodynamics

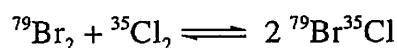
A5

Answer *all* parts of this question

- (a) Starting from the statistical thermodynamic expression for the chemical potential μ , derive an expression for the equilibrium constant K_c in terms of the partition functions of the reactants and products for the reaction:



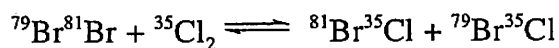
- (b) Consider the gaseous equilibrium:



Given the following information, calculate the equilibrium constant K_c at 298K explaining clearly what approximations or assumptions you make.

Molecule	$\theta_{\text{rot}} / \text{K}$	$\theta_{\text{vib}} / \text{K}$	$D_e / \text{kJ mol}^{-1}$
$^{79}\text{Br}_2$	0.118	465.0	195.8
$^{35}\text{Cl}_2$	0.351	813.5	246.0
$^{79}\text{Br}^{35}\text{Cl}$	0.219	619.1	221.4

- (c) Without detailed calculation, indicate how might you expect the equilibrium constant K_c at 298K to differ for the equilibrium:



Approximate division of marks: (a) 40%, (b) 40%, (c) 20%.

A6

Answer *all* parts of this question

- (a) What is the physical significance of the partition function q of a system? Indicate how the partition function can be used to evaluate thermodynamic properties of chemical systems.
- (b) Providing as much quantitative information as you can, plot how you would expect the internal energy U and the heat capacity C_v to vary with temperature for the following systems:
- (i) a diatomic molecule
 - (ii) a system containing particles with two non-degenerate energy levels
- (c) Given that the rotational constant and fundamental vibrational frequency of I_2 are 0.0374 cm^{-1} and 213.3 cm^{-1} respectively, evaluate the partition function q , the internal energy U and the heat capacity C_v for the I_2 molecule at 298K and 600K.
- [$I = 127 \text{ a.m.u.}$]
- (d) At higher temperatures, measured values of both U and C_v appear systematically higher than those calculated on the basis of the information given above. Provide an explanation and suggest what additional information would be required to account for this deviation.

Approximate division of marks: (a) 25%, (b) 30%, (c) 25%, (d) 20%.

[TURN OVER

SECTION D*Solids, Surfaces and Heterogeneous Catalysis***A7**Answer *all* parts of this question

- (a) The electronic properties of a trivalent metal are closely approximated by the free electron model. Explain the key approximations of this model and sketch (i) the dependence of electron energy on wavevector $E(\mathbf{k})$, (ii) the expected form of the Fermi surface, and (iii) the density of states $Z(E)$ of this metal.
- (b) The experimentally determined value for the Fermi energy (E_F) of this trivalent metal is 13.0 eV. By deriving an expression for E_F in the free electron limit, obtain an estimate for the atomic concentration in the metal.
- (c) According to free electron theory all solids should be electrical conductors. Explain concisely how the effects of lattice periodicity on electronic structure can account for the following facts:
- (i) Ba contains twice as many valence electrons per atom as Cs, yet its electrical conductivity is half that of Cs.
 - (ii) Pure diamond is an electrical insulator. Doping with either B or N causes diamond to behave as a semiconductor.

Approximate division of marks: (a) 20%, (b) 40%, (c) 40%.

A8

Answer *all* parts of this question

- (a) What are the assumptions that are made in deriving the Langmuir adsorption isotherm? Comment briefly on the likelihood of these assumptions being true in the general case. Derive expressions of the form $p_A = f(\theta_A, \theta_B)$ for the non-dissociative competitive adsorption of two gases on a solid surface when each gas obeys the Langmuir adsorption isotherm.
- (b) When adsorbed separately on the $\text{MgO}\{100\}$ single crystal surface, each of two alkane isomers (A, B) exhibits Langmuir adsorption. The adsorption is not activated and takes place without dissociation. At 77 K the fractional surface coverage of isomer A (θ_A) is 0.02 when its partial pressure is 10 kPa, whereas the coverage θ_B of isomer B reaches 0.02 when its partial pressure is only 1.0 kPa. Obtain an estimate for the difference in adsorption enthalpies of A and B, making clear any assumptions or approximations involved.
- (c) In another experiment, A and B are adsorbed competitively on the $\text{MgO}\{100\}$ surface at 77 K. At equilibrium, the partial pressures are identical and equal to 10 kPa. Obtain an estimate for the ratio of the coverages of A and B.

Approximate division of marks: (a) 30%, (b) 50%, (c) 20%.

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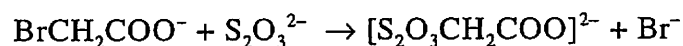
SECTION E

Reactivity and Solutions

A9

Answer *all* parts of this question

- (a) Discuss, briefly, how you would expect the kinetics of a reaction to be modified on moving from the gas phase to solution, distinguishing between diffusion and activation controlled kinetics. Mathematical details are not required.
- (b) For ionic reactants, what is meant by the primary kinetic salt effect?
- (c)
- (i) The second order reaction



was studied in solution at 25 °C; all species were present as their sodium salts. The kinetics were measured by taking 50 cm³ portions of the reaction mixture at specific times, adding 25 cm³ of iodine solution, and back titrating the excess with standard thiosulphate solution. In a particular run, with the initial concentration of both reactants equal to 5 × 10⁻⁴ mol dm⁻³, the excess iodine at the times t after starting the run were as follows:

t/min	0	2000	3500	4000
Excess iodine/cm ³	0.2	5.89	8.70	9.46

Calculate the second order rate constant for the reaction.

- (ii) The experiment was repeated, again with equal concentrations of reactants, for different initial reactant concentrations, yielding the results shown below:

Initial concentration/mol dm ⁻³	0.0007	0.0010	0.0014	0.0020
k ₂ /dm ³ mol ⁻¹ min ⁻¹	0.309	0.324	0.343	0.366

[Question A9 continues on the next page]

[Continuation of Question A9]

Determine the rate constant for the reaction when the activity coefficients are unity.
Confirm that the charges on the ions involved in the reaction are as expected.

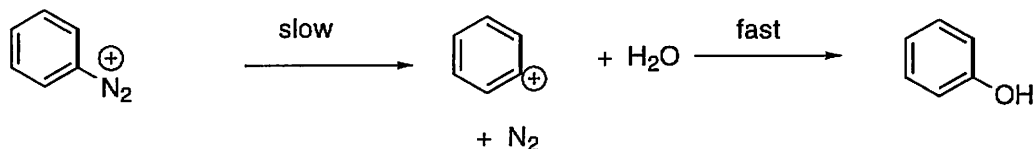
(Debye-Hückel constant 25 °C is $0.509 \text{ mol}^{-1/2} \text{ dm}^{3/2}$)

Approximate division of marks: (a) 30%, (b) 30%, (c) 40%.

[TURN OVER

A10Answer *all* parts of this question

A simple dissociative (S_N1) mechanism has been proposed for the decomposition of aryl diazonium salts in aqueous solution.



- Suggest a rate law equation for the mechanism.
- Suggest why the activation entropy for the reaction is $+45 \text{ J mol}^{-1} \text{ K}^{-1}$.
- Draw a schematic free energy profile for the reaction.
- The *p*MeO-substituted diazonium derivative reacts 10^4 times more slowly than the unsubstituted diazonium salt. By considering the effect of the substitution on the reactants, intermediates, and transition states, explain this result. Illustrate your answer by use of a free energy diagram.
- What happens to the activity of water at high H_2SO_4 concentration (e.g., 80%), and how can this property be used, in principle, to explore reaction mechanisms?

Approximate division of marks: (a) 10%, (b) 20%, (c) 20%, (d) 30%, (e) 20%.

END OF PAPER

NATURAL SCIENCES TRIPOS Part IB
NATURAL SCIENCES TRIPOS Part II (General)

Monday 5th June 2000	9.00 to 12.00
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CHEMISTRY A: PAPER 2

Candidates should attempt ANY FIVE questions.

Where a question is divided into sections, the *approximate* division of marks between sections is indicated at the end of the question.

Linear graph paper is available if required.

A Periodic Table, the values of physical constants, character tables and selected mathematical formulae will be found in the data book provided.

Write on ONE side of the paper only.

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A11

Answer *all* parts of this question

- (a) Write down, in atomic units, unnormalised, real forms for the 1s and 2p orbitals.
- (b) Molecular orbitals are linear combinations of atomic orbitals. Indicate how the diatomic molecular orbitals $\sigma_g 1s$, $\sigma_u 1s$, $\sigma_g 2s$, $\sigma_u 2s$, $\sigma_g 2p$, $\sigma_u 2p$, $\pi_g 2p$, $\pi_u 2p$ can be formed from atomic orbitals (e.g. $\sigma_g 1s = 1s_A + 1s_B$).
- (c) Then answer the following :
- Give the molecular orbital wavefunction for H_2 , and its term symbol.
 - Give the ground state configuration for O_2 , and its term symbol, with a justification.
 - It is found for C_2 that states with term symbols $^3\Pi_u$, $^3\Sigma_g^-$, $^1\Pi_u$, $^3\Sigma_u^+$ lie 716, 6434, 8391 and 13312 cm^{-1} above the $^1\Sigma_g^+$ ground state, respectively. Suggest electronic configurations for these five states which explain these observations.

Approximate division of marks: (a) 10%, (b) 20%, (c) 70%.

A12

Answer *all* parts of this question

- (a) Using SI units, write down the Schrödinger equation for the H atom. Show that a wavefunction of the form $e^{-\alpha r}$ is a solution of this equation for a particular value of α . Determine the corresponding energy and normalise the wavefunction.

$$\left[\text{Use } \nabla^2(e^{-\alpha r}) = \left(\alpha^2 - \frac{2\alpha}{r} \right) e^{-\alpha r} \right].$$

$$\left[\int_0^\infty r^2 e^{-2\alpha r} dr = (4\alpha^3)^{-1} \right].$$

- (b) Write down the probability that the electron is at a distance r from the proton. Find the most probable distance, and give its value in atomic units.
- (c) Using atomic units, sketch the electron-proton attraction potential; in your sketch also mark in the ground state energy. Show that the probability that the electron has tunnelled out of the classical region is $13e^{-4}$.

$$\left[\int_a^\infty r^2 e^{-br} dr = e^{-ab} \left\{ \frac{a^2}{b} + \frac{2a}{b^2} + \frac{2}{b^3} \right\} \right]$$

Approximate division of marks: (a) 40%, (b) 10%, (c) 50%.

[TURN OVER

A13

Answer *all* parts of this question

- (a) What are the molecular point groups of s-cis butadiene, and rectangular cyclobutadiene?
- (b) Construct the symmetry orbitals which can be formed from the p_π atomic orbitals in butadiene and assign their symmetries. Construct the Hückel secular determinants, find the π -electron energies, and draw an energy level diagram for s-cis butadiene.
- (c) Find the symmetry orbitals and π -electron energies in rectangular cyclobutadiene, and draw an energy level diagram.
- (d) According to Hückel theory, which of s-cis butadiene and rectangular cyclobutadiene is the more stable? Which has a triplet ground state?

Approximate division of marks: (a) 10%, (b) 40%, (c) 40%, (d) 10%.

A14

Answer *all* parts of this question

- (a) $[\text{NiL}_4]^{2+}$ complexes of neutral ligands L are found to exhibit tetrahedral and square planar geometries. Write down the point groups for the two types of complex and the irreducible representations corresponding to the Ni 3d orbitals in each case.
- (b) Assuming that each ligand L is a σ -donor and has no π -symmetry orbitals, and that Ni^{2+} uses 3d, 4s, and 4p orbitals, construct qualitative molecular orbital diagrams for tetrahedral and square planar $[\text{NiL}_4]^{2+}$ complexes. Explain your estimates of relative atomic and molecular orbital energies.
- (c) Use crystal field theory to derive d-orbital splitting diagrams for the above two geometries and compare them to the molecular orbital diagrams derived in (b).
- (d) By comparing the diagrams for tetrahedral and square planar $[\text{NiL}_4]^{2+}$ complexes in (b) or (c), discuss factors that favour the competing geometries.

Approximate division of marks: (a) 20%, (b) 40%, (c) 20%, (d) 20%.

[TURN OVER

A15

Answer *all* parts of this question

- (a) Starting from the statistical thermodynamic expression for the Helmholtz free energy or otherwise, derive expressions for the internal energy U and the entropy S for a system of N distinguishable and N indistinguishable particles. Comment on the expressions you obtain.

- (b) Show that for an ideal monatomic gas, the molar entropy can be written as

$$S = R \left[\ln q_{trans} - \ln(N_A) + 1 + T \left(\frac{\partial \ln q_{trans}}{\partial T} \right)_V \right]$$

- (c) Account, as quantitatively as you can, for the differences between the values of the molar entropies of the gases shown in the following table. The gases may be assumed to be in their electronic ground states at 1 bar and 298 K.

Gas	He	Ne	Ar	Ar ⁺	CO	N ₂	O ₂
Entropy /J mol ⁻¹ K ⁻¹	126.0	146.1	154.7	166.3	197.3	191.4	204.9

[Atomic masses (in a.m.u.) He = 4, Ne = 20, Ar = 40, C = 12, N = 14, O = 16]

Approximate division of marks: (a) 30%, (b) 30%, (c) 40%.

A16

Answer *all* parts of this question

- (a) Outline the general features which you would expect to be present in (i) pure rotation spectra and (ii) vibration-rotation spectra of a diatomic molecule. Indicate in your answer how the various features can be related quantitatively to properties of that molecule.
- (b) Low resolution spectroscopic measurements of a sample of nitric oxide $^{14}\text{N}^{16}\text{O}$ revealed absorption features as follows:

Wavenumber / cm^{-1}	Intensity
1848	weak
1876	strong
3668	very weak
3724	weak

Identify the transitions giving rise to these absorption features, giving your reasoning, and determine the vibrational frequency and the anharmonicity constant for the NO molecule.

- (c) At higher resolution, the absorption feature at 1876 cm^{-1} was resolved into a series of regularly spaced transitions, with the most intense transition being the 8th from the centre of the band. Given that the bond length of the $^{14}\text{N}^{16}\text{O}$ molecule is 0.1151 nm , estimate the temperature of the $^{14}\text{N}^{16}\text{O}$ sample.
- (d) How might you expect the intensities of the absorption features shown in the table above to change as the sample is warmed?

[N = 14 a.m.u., O = 16 a.m.u.]

Approximate division of marks: (a) 30%, (b) 30%, (c) 25%, (d) 15%.

[TURN OVER

A17

Answer *all* parts of this question.

- (a) Explain, with suitable examples, what you understand by the terms (i) clean surface reconstruction and (ii) adsorbate induced surface restructuring. In both cases, distinguish between displacive and substantial reorganisation of the surface atoms of the adsorbent. How may these effects be understood in terms of electronic surface states and resonances?
- (b) Define what is meant by the work function (ϕ) of a metal, explaining how the bulk and surface contributions to ϕ arise. Consider the adsorption of Cl, Cs, and Xe on the smooth, close-packed Pt{111} surface. In each case explain the nature of the adsorption bond, predict the sign of the change in work function ($\Delta\phi$) and indicate how $\Delta\phi$ varies with coverage.
- (c) What is the nature of the chemisorption bond between non-dissociatively adsorbed CO and the Pt{111} surface? How does the bonding change with adsorbate coverage and what is the associated behaviour of $\Delta\phi$? In contrast with its behaviour on Pt, CO dissociates readily on W surfaces. How do you account for this?

Approximate division of marks: (a) 20%, (b) 40%, (c) 40%.

A18

Answer *both* parts of this question

- (a) Sketch the energy band diagrams of p-type and n-type doped Si, indicating clearly the position of the Fermi level with respect to the impurity states. Explain what happens when p-type and n-type Si are brought into contact to form a p-n junction. Show how the properties of the p-n junction are altered by application of forward and reverse bias.
- (b) An intrinsic semiconductor has a band gap of 3.0 eV. An n-type dopant is introduced which gives rise to impurity levels 0.1 eV below the conduction band edge. Assuming that all carrier mobilities are the same, calculate the dopant concentration required to make the extrinsic conductivity 100 times greater than the intrinsic value, at 300 K. Explain any approximations made in your calculation. Sketch the temperature dependence of the number of electrons in the conduction band and the position of the Fermi level.

Approximate division of marks: (a) 50%, (b) 50%.

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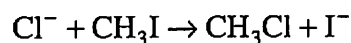
A19Answer *both* parts of this question

(a) Starting from the Eyring equation

$$k = \frac{k_B T}{h} K^\ddagger$$

develop an equation that indicates how the rate constant of a reaction may change when moving from one solvent to another. Provide an appropriate energy diagram to illustrate the changes that are taking place.

(b) In the following reaction at 298 K

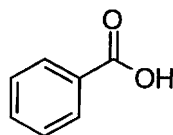


the changes in free energy on transfer from methanol to dimethylformamide for Cl^- ; CH_3I and the associated reaction activated complex are +37081, -2852 and +570 J mol⁻¹, respectively. Compute the change in rate constant when the reaction is carried out in dimethylformamide compared to methanol. Discuss the role of the solvents for this reaction.

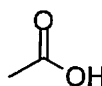
Approximate division of marks: (a) 40%, (b) 60%.

A20

Answer *all* parts of this question



benzoic acid



acetic acid

The pK_a values of benzoic acid and acetic acid in water are 4.2 and 4.8, respectively.

- (a) Using a simple equation explain what the pK_a value measures.
- (b) In aqueous solution there is a large entropic contribution to the ionisation constant. Explain this observation.
- (c) In the gas phase there is little entropic contribution to the ionisation constant, and the difference in pK_a values between benzoic and acetic acid is largely due to changes in enthalpy. In the gas phase, benzoic acid is *much* more acidic than acetic acid. Explain this observation.
- (d) Benzoic acids with different substituents on the benzene ring (e.g. p-Br, p-NO₂, p-MeO) have different pK_a values. These differences in pK_a values are much more pronounced in the gas phase than in aqueous solution. Why might this be?
- (e) What might one expect if the pK_a measurements described in (d) were made in DMSO (Me₂SO)?

Approximate division of marks: (a) 10%, (b) 20%, (c) 30%, (d) 30%, (e) 10%.

END OF PAPER