

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

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**Wednesday 28th May 1997      1.30 to 4.30**

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**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.

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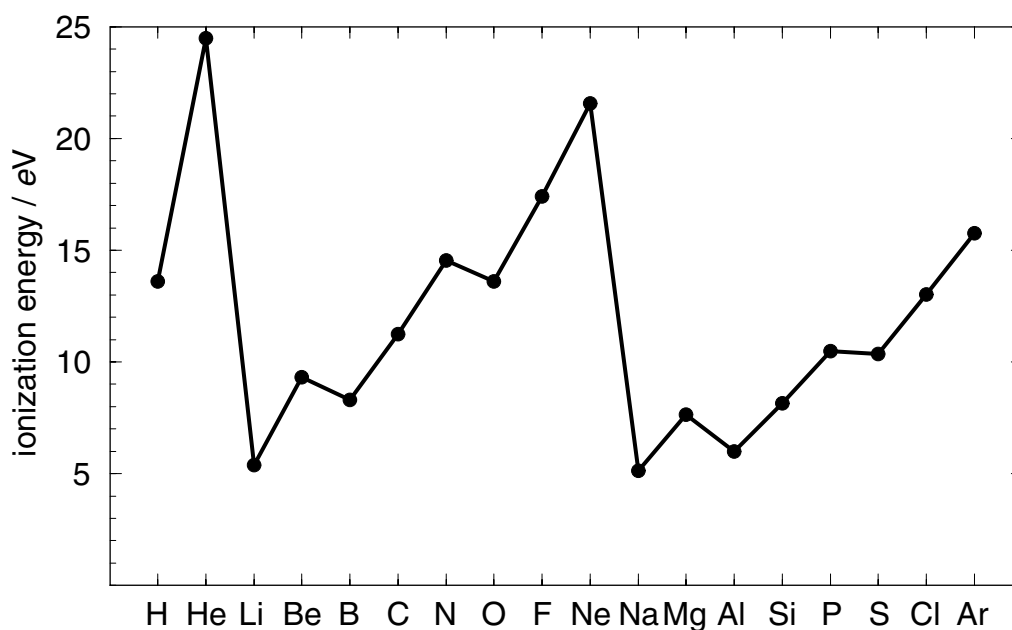
## SECTION A

### *Introduction to Quantum Mechanics*

#### A1

Answer **both** parts of this question:

- (a) Define the ionisation energy of a system. The diagram shows the variation of the first ionisation energy with atomic number. Explain in detail how the features shown are related to the atomic structure.



- (b) What qualitative features would you expect to see in the second ionisation energies of the elements He to Ne?

Approximate division of marks: (a) 80%, (b) 20%.

**A2**

Answer **all** parts of this question:

- (a) Find the energies and wavefunctions for a particle of mass  $m$  confined to a one-dimensional box of length  $L$ . Take the potential as being zero inside the box and infinity elsewhere. **Justify any assumptions that you make about the form of the wavefunction.**
- (b) A simplistic model for the  $\pi$  electrons in conjugated polyene chains assumes that each carbon atom contributes one electron and that these electrons then move freely in a box of length  $(N + 1)R$  where  $N$  is the number of atoms and  $R$  is an average bond length. Find expressions in terms of  $N$ ,  $R$  and fundamental constants for
- (i) the energy of the **highest** occupied level in such a system.
  - (ii) the energy of the **lowest** frequency electronic transition possible in such a system.
- (c) If a polyene absorbs at a frequency of  $3 \times 10^{14}$  Hz and has an average bond length of  $1.3 \text{ \AA}$ , approximately how many carbon atoms are in the chain?

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

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

Answer **both** parts of this question:

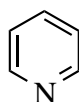
- (a) Describe the approximations which are used in Hückel theory. When are these likely to be inaccurate?
- (b) Consider two possible geometries for ozone,  $\text{O}_3$ : (i) an equilateral triangle; (ii) a bent geometry (with bond angle  $116^\circ$ ). Construct the Hückel secular equations for the  $\pi$  electrons in these two forms and hence find the orbital energies for both geometries and the orbital coefficients for the equilateral triangle geometry. Which of the two forms does Hückel theory predict to have the lower energy?

Approximate division of marks: (a) 30%, (b) 70%

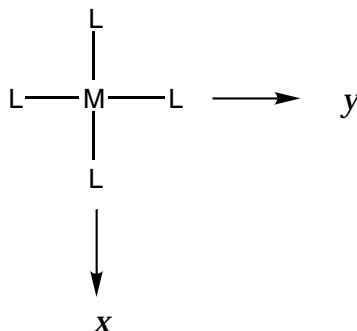
A4

Answer **both** parts of this question:

Ammonia and pyridine, **1**, can act as ligands towards transition metals, M, bonding through the nitrogen atom.

**1**

- (a) With respect to the local M–N axis, describe the symmetries of the orbitals of the nitrogen donor atom offered to the metal atom.
- (b) By considering the orientation of the ligand donor orbitals with respect to the metal d orbitals, predict the relative shifts of the metal d orbitals in each of the following square coordinated species,  $ML_4$ :



- (i)  $L = NH_3$ ;
- (ii)  $L = \text{pyridine}$ , with the plane of its ring oriented perpendicular to the  $xy$  coordination plane;
- (iii)  $L = \text{pyridine}$ , with the plane of its ring oriented parallel to the  $xy$  coordination plane.

Assume that the ligand orbitals lie at lower energies than the metal orbitals. ***There is no need to employ explicit Group Theory or to assign molecular symmetries to any orbitals.***

Approximate division of marks: (a) 20%, (b) 80%.

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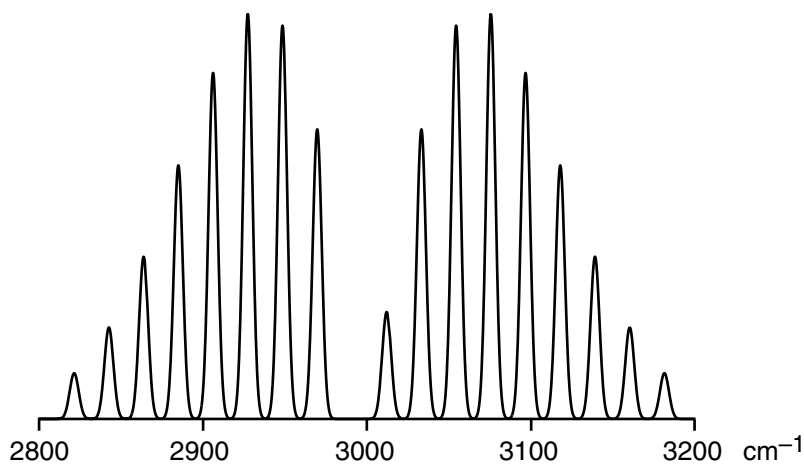
## SECTION C

*Molecular Energy Levels and Thermodynamics*

A5

Answer **all** parts of this question:

The figure shows a band in part of the idealised infra-red spectrum of  $^1\text{H}^{35}\text{Cl}$  gas, recorded at room temperature.



- (a) Explain how this band arises and the pattern of **frequencies** and **intensities** that are observed.
- (b) Four lines from this spectrum are seen at 2948.6, 2969.8, 3012.1 and 3033.3  $\text{cm}^{-1}$ . Assign these lines, explaining your reasoning, and hence find values for the rotational constant,  $B$ , (in  $\text{cm}^{-1}$ ), the bond length of  $^1\text{H}^{35}\text{Cl}$ , and the wavenumber of the band origin.
- (c) Explain where in the infra-red spectrum you would expect the corresponding band from  $^2\text{H}^{35}\text{Cl}$  to appear and in what ways this band would differ from that for  $^1\text{H}^{35}\text{Cl}$ . **Be as quantitative as you can in your answer.**

[Atomic masses:  $^1\text{H} = 1$ ,  $^2\text{H} = 2$ ,  $^{35}\text{Cl} = 35$  amu]

Approximate division of marks: (a) 60%, (b) 20%, (c) 20%.

**A6**

Answer **all** parts of this question:

- (a) Explain why and under what conditions the partition function,  $Q_N$ , for a system of  $N$  non-interacting indistinguishable particles (atoms or molecules) can be written as  $(q^N/N!)$ , where  $q$  is the partition function for one such particle.
- (b) The Helmholtz free energy,  $A$ , of a system is related to  $Q_N$  in the following way

$$A = -kT \ln Q_N$$

where  $k$  is the Boltzmann constant and  $T$  is the temperature. Starting from this relationship show that the translational entropy,  $S_{\text{trans}}$ , of a system of  $N$  non-interacting indistinguishable particles is given by

$$S_{\text{trans}} = Nk \left( \frac{5}{2} + \ln \frac{q_{\text{trans}}}{N} \right)$$

where  $q_{\text{trans}}$  is the translational partition function for one particle

$$q_{\text{trans}} = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V$$

and where  $V$  is the volume,  $m$  is the mass of the particle and  $h$  is Planck's constant.

- (c) Evaluate the molar entropy of  $^{84}\text{Kr}$  gas at 298 K and 1 atmosphere pressure.
- (d) Calculate the difference between the molar entropies of  $^{84}\text{Kr}$  gas and a gas consisting of  $^{84}\text{Kr}^+$  ions, both gases held under the same conditions of temperature and pressure.

[Atomic mass:  $^{84}\text{Kr} = 84$  amu]

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

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**SECTION D***Solids, Surfaces and Heterogeneous Catalysis***A7**

Answer **all** parts of this question:

- (a) Sketch the energy dependence of the Fermi-Dirac distribution function at zero Kelvin and at a finite temperature. Explain qualitatively why the curves have these shapes.
- (b) By analogy with the calculation for the corresponding three-dimensional case, show that the Fermi energy for a free-electron gas constrained to move in **two** dimensions only is

$$E_f = \frac{\hbar^2 \pi N}{m_e A}$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $m_e$  is the mass of the electron,  $N$  is the number of electrons and  $A$  is the area which they occupy.

Find the corresponding density of electron states,  $Z(E)$ .

- (c) Calculate the average (kinetic) energy of a two-dimensional free-electron gas and compare your result with that for a three-dimensional gas, commenting on any differences.

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



**A8**

Answer **both** parts of this question:

- (a) Obtain values for the surface energies,  $\gamma_{111}$  and  $\gamma_{100}$ , for both the (111) and (100) surfaces of fcc Cu (lattice parameter  $a = 3.61\text{\AA}$ ; latent heat of vaporisation  $\Delta H_v = 336\text{ kJ mol}^{-1}$ ). Why might experimental values of  $\gamma_{100}$  and  $\gamma_{111}$  be different from the theoretical estimates?
- (b) Explain what is meant by the **work function**,  $\phi$ , of a metal. How might this quantity be measured experimentally? Explain how the chemisorption or physisorption of layers of different atoms on the surface of a particular metal can change its work function. In this way, account for the sign and magnitude of the changes in work function  $\Delta\phi$  of the following metal/adsorbate systems:

System	$\Delta\phi / \text{eV}$
W/Ne	– 0.15
W/Xe	– 1.40
W/Cs	– 2.9
Ni/O	+ 0.3

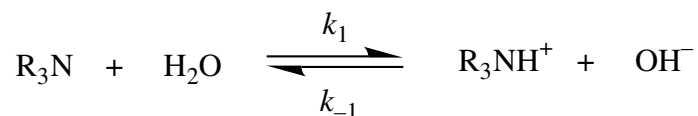
Approximate division of marks: (a) 50%, (b) 50%.

## SECTION E

*Reactivity and Solutions***A9**

Answer **both** parts of this question:

- (a) Describe how reaction rate constants may be determined for reactions in solution by (i) the stopped-flow method and (ii) the temperature-jump method.
- (b) In a pressure jump study of the reaction



the following relaxation times,  $\tau$ , were observed at 298K and various equilibrium concentrations of  $\text{R}_3\text{N}$ .

$[\text{R}_3\text{N}] / 10^{-3} \text{ M}$	0.39	1.31	2.84	6.69	15.46
$\tau / \text{s}$	0.313	0.224	0.177	0.127	0.089

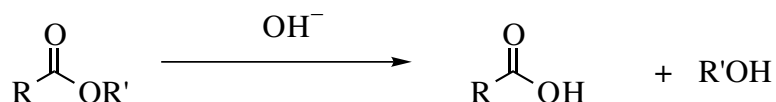
Determine the forward and reverse reaction rate constants, given that  $K = k_1/k_{-1} = 1.64 \times 10^{-3} \text{ M}$  at 298K.

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

**A10**

Answer **all** parts of this question:

- (a) Suggest a mechanism for the base catalysed hydrolysis of a carboxylic ester.



- (b) Explain how your mechanism is consistent with the following:

(i) the observed rate law,  $\text{rate} = k_2 [\text{RCO}_2\text{R}'] [\text{OH}^-]$ ;

(ii) for  $\text{MeCO}_2\text{Et}$  the entropy of activation,  $\Delta S^\ddagger$ , is  $-136 \text{ J K}^{-1} \text{ mol}^{-1}$ ;

(iii) hydrolysis of  $\text{R}-\overset{\text{O}}{\parallel}-^{18}\text{OR}'$  results in the isotope label appearing only in the alcohol;

(iv) the stereochemistry at  $\text{R}'$  is retained;

(v) the rate is strongly accelerated by electron withdrawing groups on  $\text{R}$ ;

(vi) hydrolysis of  $\text{R}-\overset{^{18}\text{O}}{\parallel}-\text{OR}'$  often results in part of the label being exchanged with solvent.

- (c) Draw a free energy profile that would be consistent with your mechanism indicating on it the reactants, the rate-limiting transition state, intermediates and products.

Approximate division of marks: (a) 20%, (b) 60% (approximately equally divided amongst the parts), (c) 20%.

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

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**Friday 30th May 1997      1.30 to 4.30**

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**CHEMISTRY A:      PAPER 2**

*Candidates should attempt ANY FIVE questions,*

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**A11**

Answer **all** parts of this question:

- (a) Write down the hamiltonian for a system with one electron and a nucleus of atomic number  $Z$ . Show that the wavefunction  $\psi = Ce^{-\alpha r}$  is an eigenfunction for a particular value of  $\alpha$ . Find the energy and the corresponding normalisation constant,  $C$ .
- (b) Show that  $\psi$  is not an eigenfunction of either the potential energy or the kinetic energy operators. What does this imply?
- (c) For this wavefunction, calculate the expectation values of the kinetic energy,  $\langle T \rangle$ , and the potential energy,  $\langle V \rangle$ . Hence show that  $\langle V \rangle = -2 \langle T \rangle$ .

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

[see the data book for the definition of the Laplacian,  $\nabla^2$ , and the necessary integrals]

**A12**

Answer **all** parts of this question:

- (a) Write down the spin function for a two-electron singlet state and the spin functions for a two-electron triplet state.
- (b) For a helium atom in which both electrons are in the 1s orbital, explain carefully which of the spin states are allowed.
- (c) Consider an excited state of the helium atom with the configuration (1s2s). Write down valid wavefunctions for the singlet and the triplet states arising from this configuration.

Show that the energy difference between the singlet and the triplet for this case is related to the exchange integral,  $K$ , given by

$$K = \int \psi_{1s}(1)\psi_{2s}(2) \frac{1}{r_{12}} \psi_{1s}(2)\psi_{2s}(1) \, dr_1 dr_2$$

where  $\psi_a(1)$  is the spatial wavefunction for electron 1 in orbital  $a$  and so on;  $r_{12}$  is the distance between the two electrons.

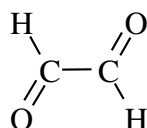
Which of Hund's rules is illustrated by this example?

Approximate division of marks: (a) 25%, (b) 25%, (c) 50%.

**A13**

Answer **all** parts of this question:

- (a) Why are symmetry orbitals useful?
- (b) The glyoxal molecule is planar with the following structure.



To which point group does this molecule belong?

What irreducible representations are spanned by

- (i) the 2p atomic orbitals in the plane of the molecule and  
 (ii) the 2p atomic orbitals perpendicular to the molecular plane?

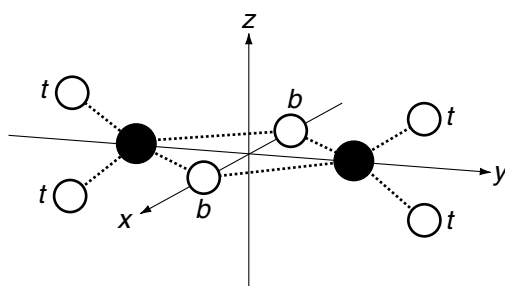
- (c) Construct symmetry orbitals for the  $\pi$  electrons in this molecule.
- (d) Using the Hückel approximation, construct the secular equations for these  $\pi$  orbitals and find the orbital energies in terms of the Hückel parameters  $\alpha_{\text{C}}$ ,  $\alpha_{\text{O}}$ ,  $\beta_{\text{CO}}$  and  $\beta_{\text{CC}}$ .

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

**A14**

Answer **all** parts of this question:

- (a) Briefly define the terms **atomic orbital**, **symmetry orbital**, **hybrid orbital** and **molecular orbital**.
- (b) Consider the following structure for  $B_2H_6$ , in which the boron and hydrogen atoms are shown by filled and open circles, respectively. The hydrogen atoms can be considered as bridging (marked *b*) or terminal (marked *t*).



Assuming that the bonding in this molecule may be described using  $sp^3$  hybrids on the boron atoms and  $s$  orbitals on the hydrogens, show that those  $sp^3$  hybrid orbitals which point to the centre of the molecule transform as  $a_g + b_{1g} + b_{2u} + b_{3u}$ , and that the orbitals of the two bridging hydrogens transform as  $a_g + b_{3u}$ .

- (c) Find the corresponding symmetry orbitals and use these to construct an approximate molecular energy level diagram. Does your diagram predict  $B_2H_6$  to be a "stable molecule"?

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



**A15**

Answer **all** parts of this question:

- (a) Show that the partition function,  $q$ , for a harmonic oscillator can be written

$$q = \frac{1}{1 - \exp[-\theta_{\text{vib}}/T]}$$

where  $\theta_{\text{vib}}$  is the vibrational temperature and  $T$  is the temperature.

Given that the internal energy of  $N$  such oscillators,  $U$ , is related to  $q$  by

$$U = NkT^2 \frac{1}{q} \frac{dq}{dT}$$

find an expression for the internal energy,  $U_{\text{vib}}$ , of a mole of harmonic oscillators.

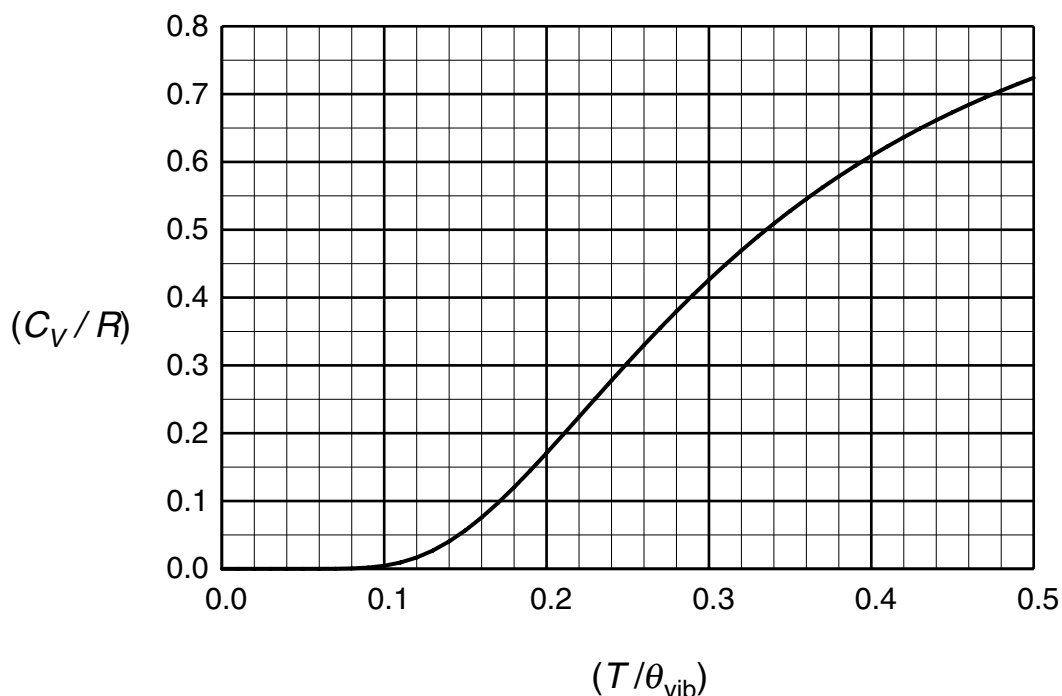
What value does  $U_{\text{vib}}$  take at low and high temperatures?

- (b) In discussing the vibrations of polyatomic molecules, what do you understand by the terms **normal mode** and **degeneracy**? How many normal modes are there in a molecule consisting of  $n$  atoms?

[question continued on the next page]

[continuation of question A15]

- (c) The following is a plot of  $(C_V/R)$ , where  $C_V$  is the constant volume heat capacity and  $R$  is the gas constant, against  $(T/\theta_{\text{vib}})$  for one mole of harmonic oscillators:



The following data refer to two gaseous triatomic molecules, A and B:

molecule	A	B
$C_V / \text{J K}^{-1} \text{ mol}^{-1}$ at 298 K	28.8	29.8
vibrational frequencies / $\text{cm}^{-1}$	667, 1330, 2349	710, 1043, 1740

**With the aid of the graph**, account for the observed values of the heat capacities and suggest likely geometries for A and B. (It is not necessary to calculate exact values for  $C_V$ ; approximate values taken from the graph will be sufficient).

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

[TURN OVER

**A16**

Answer **all** parts of this question:

- (a) Starting from the relationship between the partition function of a system,  $Q_N$ , and the Helmholtz free energy,  $A$ :

$$A = -kT \ln Q_N$$

where  $k$  is the Boltzmann constant and  $T$  is the temperature, show that the chemical potential,  $\mu$ , of an ideal gas is given by

$$\mu = -kT \ln \frac{q}{N}$$

where  $N$  is the number of particles (atoms or molecules) and  $q$  is the partition function for one such particle.

- (b) When considering chemical equilibrium, the chemical potential of species  $s$ ,  $\mu_s$ , is given by

$$\mu_s = -kT \ln \frac{q_s}{N_s} - \epsilon_0^{(s)}$$

where  $q_s$  is the partition function for species  $s$  and  $N_s$  is the number of particles of  $s$ . Explain why it is necessary to add the term  $\epsilon_0^{(s)}$  and the physical significance you ascribe to this quantity.

[question continued on the next page]

[continuation of question A16]

(c) For a chemical equilibrium of the form



where  $a$ ,  $b$  and  $c$  are the stoichiometric coefficients, the equilibrium constant,  $K_N$ , is given by

$$K_N = \frac{q_C^c}{q_A^a q_B^b} \exp[\Delta\epsilon_0/kT]$$

where  $\Delta\epsilon_0 = c\epsilon_0^{(C)} - a\epsilon_0^{(A)} - b\epsilon_0^{(B)}$ . Using this expression and the data given below, calculate the equilibrium constant for the following reaction at 298 K:



molecule	H <sub>2</sub>	I <sub>2</sub>	HI
molecular mass / amu	2	254	128
rotational temperature $\theta_{\text{rot}}$ / K	87.5	0.0538	9.43
vibrational temperature $\theta_{\text{vib}}$ / K	6330	308	3321
dissociation energy / kJ mol <sup>-1</sup>	432	147	295

You may assume that all of the molecules have non-degenerate electronic ground states.

Approximate division of marks: (a) 20%, (b) 20%, (c) 60%.

[TURN OVER

**A17**

Answer **all** parts of this question:

- (a) Explain what is meant by an **intrinsic** and an **extrinsic** semiconductor.
- (b) Sketch, on an Arrhenius plot (*i.e.*  $\ln(\text{quantity})$  vs  $1/T$ ), the temperature dependence of the charge carrier (electron or hole) concentration of an extrinsic semiconductor, accounting clearly for any differences in the temperature dependence found in different temperature regimes. On another plot, sketch the variation in the Fermi-level position with temperature. If the carrier mobility has the temperature dependence  $\mu(T) \propto T^{-3/2}$ , characteristic of electron-phonon scattering, sketch the temperature dependence of the electrical conductivity on an Arrhenius plot, giving your reasoning.
- (c) State how the following impurities, substituted in the tetrahedrally-coordinated semiconductors given, would behave as dopants:  
  

P in Si;    Ga in Ge;    Ge in GaAs;    Cd in InSb
- (d) An n-type doped semiconductor (band gap 1 eV; donor level 0.02 eV below the conduction band edge) absorbs IR light with a wavelength of  $6.2 \times 10^{-5}$  m at a temperature of 100K. What is the origin of this optical absorption? What happens to the optical absorption edge on increasing the temperature to 300K?

Approximate division of marks: (a) 15%, (b) 35%, (c) 25%, (d) 25%.

A18

Answer **both** parts of this question:

- (a) Derive the Langmuir isotherm for the non-dissociative adsorption of a single gas species A on a metal surface, stating clearly any assumptions made. Explain the origins of the activation energies for adsorption and desorption,  $E_{\text{ads}}$  and  $E_{\text{des}}$  respectively. How are these related to the enthalpy of adsorption  $\Delta H_{\text{ads}}$ ? Under what conditions are **zero-order** kinetics found for the unimolecular decomposition of A on the surface?
- (b) If **two** adsorbate species A and B are adsorbed non-dissociatively and in competition for the same sites, how is the Langmuir isotherm altered? For the case of the catalytic decomposition of ammonia on platinum at 1000°C, the rate of decomposition is found to follow the law

$$-\frac{dp_{\text{NH}_3}}{dt} = k \frac{p_{\text{NH}_3}}{p_{\text{H}_2}}$$

where  $p_{\text{NH}_3}$  and  $p_{\text{H}_2}$  are the partial pressures of  $\text{NH}_3$  and  $\text{H}_2$ , respectively.

Propose a mechanism that gives this form of rate law within the Langmuir model.

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

**A19**

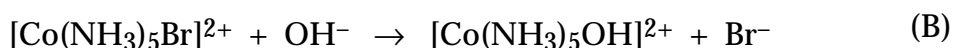
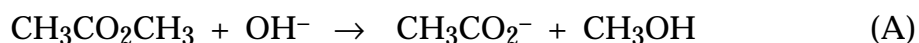
Answer **all** parts of this question:

- (a) Outline the derivation of the equation

$$k_r = \left( \frac{kT}{h} \right) K^\ddagger$$

for the rate constant,  $k_r$ , of a chemical reaction;  $k$  is the Boltzmann constant and  $T$  is the temperature. Explain the meaning of the equilibrium constant,  $K^\ddagger$ .

- (b) Derive an expression for the rate constant in terms of the entropy of activation,  $\Delta S^\ddagger$ , and the enthalpy of activation,  $\Delta H^\ddagger$ . Why is this expression more useful than an expression in terms of partition functions when considering reactions in solution?
- (c) The table below gives the rate constants,  $k_{\text{rel}}$ , for reactions A and B in aqueous solution at 298K as a function of pressure, in each case relative to the rate constant at one atmosphere.



$p$ / atmospheres	1	10	100	500	1000
$k_{\text{rel}}$ (A)	1.0	1.004	1.041	1.215	1.490
$k_{\text{rel}}$ (B)	1.0	0.9965	0.966	0.839	0.706

In each case calculate the volume of activation,  $\Delta V^\ddagger$ , of the reaction. Comment on your results.

Approximate division of marks: (a) 20%, (b) 25%, (c) 55%.

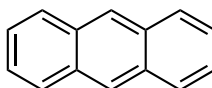
**A20**

Answer **all** parts of this question:

The rate of nitration of an aromatic substrate (ArH) by nitric acid in an organic solvent such as acetonitrile obeys the rate law:

$$\text{rate} \propto \frac{[\text{ArH}][\text{HNO}_3]^2}{[\text{NO}_3^-][\text{H}_2\text{O}]}$$

- Suggest a mechanism which is consistent with this and indicate the rate-limiting step.
- What effect would nitrate and water have on the rate?
- For benzene no primary kinetic isotope effect is observed, *i.e.*,  $k_{\text{H}}/k_{\text{D}} = 1.0$ . What does this tell you about the nature of the transition state?
- Draw a free energy profile for this reaction indicating on it the positions of the starting reactants, the rate-limiting transition state, intermediates and products.
- For the nitration of anthracene, **1**, by  $\text{NO}_2^+ \text{BF}_4^-$  in acetonitrile a large primary kinetic isotope effect is observed,  $k_{\text{H}}/k_{\text{D}} = 6$ . Explain this in terms of a change in the rate-determining step.



anthracene, **1**

Approximate division of marks: (a) 40%, (b) 10%, (c) 10%, (d) 20%, (e) 20%.