



UNIVERSITY OF  
CAMBRIDGE

**NATURAL SCIENCES TRIPOS Part IB**

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**Thursday 2nd June 2022      9:00 to 12:00**

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**CHEMISTRY A: PAPER 1**

*Candidates should attempt all five questions; where a question is divided into parts, candidates should answer all parts.*

Each question is marked out of 20. Where a question is divided into parts, the *approximate* number of marks available for each part is indicated thus **[*n*]**

**STATIONERY REQUIREMENTS**

Graph paper (4 sheets)  
Lined paper  
Rough work pad

**SPECIAL REQUIREMENTS**

Chemistry master cover sheet  
Department of Chemistry Data Book

Calculator – students are permitted to bring an approved calculator.

<p><b>You may not start to read the questions printed on the subsequent pages of this question paper until instructed that you may do so by the Invigilator.</b></p>
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**A1**

- (a) Define the *Hermitian conjugate*  $\hat{A}^\dagger$  of an operator  $\hat{A}$ , and show that

$$\int \Phi^* \hat{A} \Psi d\tau = \left[ \int \Psi^* \hat{A} \Phi d\tau \right]^*$$

if  $\hat{A}$  is *Hermitian* and if  $\Phi$  and  $\Psi$  satisfy appropriate boundary conditions (which you should specify).

[You are not expected to give explicit functional forms for  $\Phi$  and  $\Psi$ .] [3]

- (b) Assume that the hamiltonian  $\hat{H}$  can be written

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \dots$$

where  $\lambda$  is a small parameter, and  $\hat{H}^{(0)}$  is the hamiltonian of a simpler system, for which the normalised eigenfunctions  $\Psi_i^{(0)}$  and eigenvalues  $E_i^{(0)}$  (none of which are degenerate) are known.

- (i) Write out the equation relating  $\hat{H}^{(0)}$ ,  $\Psi_i^{(0)}$  and  $E_i^{(0)}$ . [1]  
(ii) Assuming that the eigenvalues  $E_i$  and eigenfunctions  $\Psi_i$  of  $\hat{H}$  can be similarly expanded as

$$\begin{aligned} E_i &= E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots \\ \Psi_i &= \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \dots \end{aligned}$$

show, by collecting together like powers of  $\lambda$ , that

$$\left[ \hat{H}^{(0)} - E_i^{(0)} \right] \Psi_i^{(1)} + \left[ \hat{H}^{(1)} - E_i^{(1)} \right] \Psi_i^{(0)} = 0$$

[3]

[Qu. A1 continued on next page]

[Continuation of Qu. A1]

- (iii) Use your answers to (b)(ii) and (a) to show that

$$E_i^{(1)} = \int \Psi_i^{(0)*} \hat{H}^{(1)} \Psi_i^{(0)} d\tau$$

[3]

- (iv) Calculate  $E_0^{(1)}$  for the hamiltonian

$$\begin{aligned} \hat{H} &= \hat{H}_0 + \lambda x^4 \\ \hat{H}_0 &= -\frac{1}{2} \frac{d^2}{dx^2} + \frac{x^2}{2} \end{aligned}$$

for which  $\Psi_0^{(0)} = \exp(-x^2/2)/\pi^{1/4}$ .

[2]

- (v) Assuming that  $\Psi_i^{(1)}$  can be expanded as

$$\Psi_i^{(1)} = \sum_{j \neq i} c_{ij} \Psi_j^{(0)}$$

derive an expression for  $c_{ij}$  in terms of the energies  $E_i^{(0)}$  and the integrals

$$H_{ij} = \int \Psi_i^{(0)*} \hat{H}^{(1)} \Psi_j^{(0)} d\tau$$

[8]

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**A2**

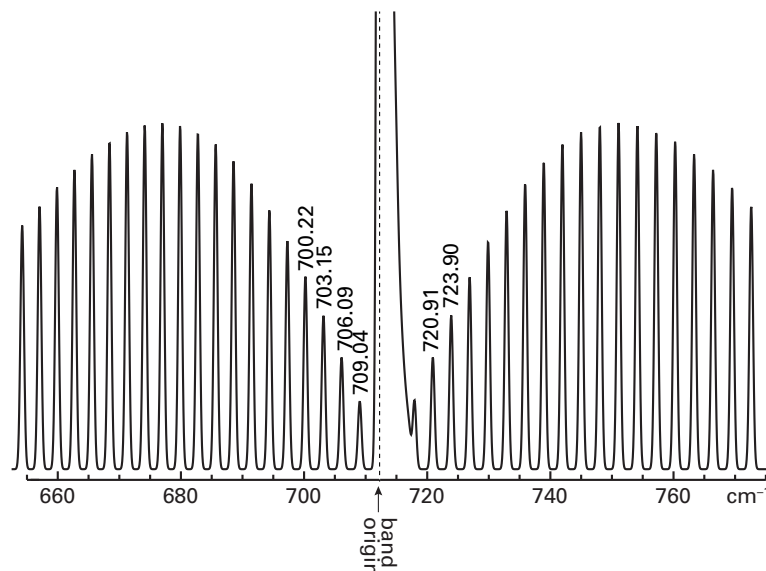
- (a) (i) State the Pauli principle as applied to electrons and use it to write out the appropriate linear combinations of spatial and spin orbitals in the singlet and triplet wave functions of the excited state configuration of He,  $1s2s$ . [3]
- (ii) Demonstrate mathematically that these functional forms are consistent with the Pauli exclusion principle, and with Hund's 1st rule. [2]
- (b) (i) What do the total angular momentum quantum numbers  $L$ ,  $M_L$ ,  $S$ ,  $M_S$  and  $J$  represent in a multi-electron atom? What is the permitted range of  $J$ ? How are  $M_L$  and  $M_S$  related to the quantum numbers of the individual electrons? [3]
- (ii) What do you understand by: 'configuration', 'term', 'level' and 'term symbol'? [2]
- (iii) Deduce the term symbols for the ground states of  $C(1s^2 2s^2 2p^2)$ ,  $V([Ar] 4s^2 3d^3)$  and  $Co([Ar] 4s^2 3d^7)$ , justifying each step of your reasoning. [4]
- (c) (i) Explain and justify the Born–Oppenheimer approximation.  
[Your answer should be brief and limited to bullet points and equations.] [3]
- (ii) The  $Li_2$  molecule has two excited electronic states, one a singlet, the other a triplet, which both dissociate into  $Li(1s^2 2s) + Li(1s^2 2p)$ . The potential curves of both states can be approximated (using atomic units) as

$$V(r) = 4\alpha \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

where  $r$  is the bond length, and the parameters  $(\sigma, \alpha)$  take values (3.4, 0.06) for one of the states and (4.9, 0.05) for the other state. Identify which state is the singlet and which the triplet, justifying your reasoning. [3]

## A3

- (a) Part of a band from the infra-red spectrum of HCN, recorded at moderate resolution, is shown below. The intensity of strong central feature has been truncated



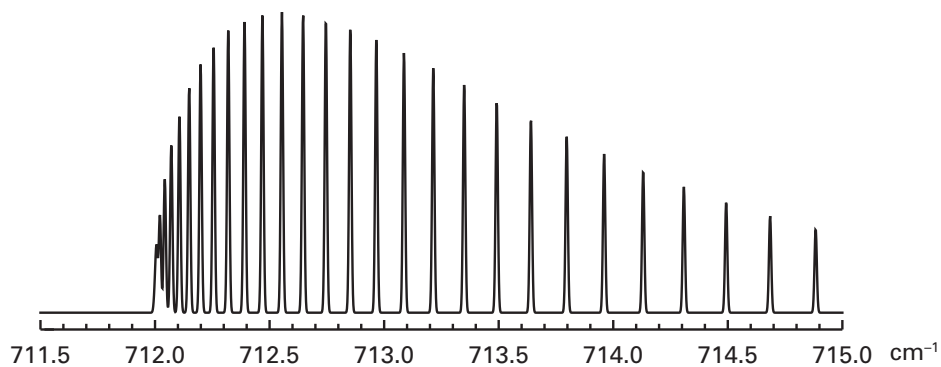
- (i) Explain the origin of the *resolved* fine structure seen in this band and identify the normal mode which is involved. [4]
- (ii) Assign the lines whose wavenumbers are indicated on the spectrum above, giving brief reasons for your answers. [3]
- (iii) Determine values of the two rotational constants relevant to this band, giving your answers in  $\text{cm}^{-1}$ . [In your analysis you should only use the lines whose wavenumbers are indicated; it is not necessary to draw a graph.]  
Comment on the values you obtain. [4]
- (iv) Determine a value for the equilibrium rotational constant and the corresponding moment of inertia, giving the latter in  $\text{kg m}^2$ . [2]

[Qu. A3 continued on next page]

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[Continuation of Qu. A3]

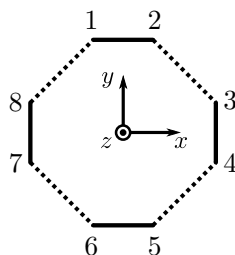
- (b) The strong central feature of the band in (a) was examined at very much higher resolution, giving the spectrum below (note the expanded scale).



- (i) Explain the form of the fine structure seen in this spectrum, including the intensity distribution. [3]
- (ii) Estimate the temperature of the sample, briefly explaining your method. [4]

**A4**

- (a) Consider the  $C_8H_8$  molecule shown below.



All eight carbon atoms lie in the  $xy$  plane, and there are two distinct bond lengths: short bonds are shown by solid lines; long bonds are shown by dotted lines. Use the coordinate system and labelling scheme indicated in the figure throughout your answer to this question.

- (i) Identify the point group of  $C_8H_8$  in the configuration shown above. [1]
  - (ii) Find and reduce the representation spanned by the carbon  $2p_z$  orbitals. [2]
- (b) To account for the different bond lengths, an extended version of Hückel theory will be used, in which the resonance integral between carbon atoms separated by a short bond is given by  $\beta_S$  and that between carbon atoms separated by a long bond is  $\beta_L$ . You may assume that  $|\beta_S| > |\beta_L|$ . The energy of the carbon  $2p_z$  orbital is  $\alpha$ , as in simple Hückel theory.

A non-degenerate symmetry orbital must transform in the way indicated by the characters of its irreducible representation. For example, for  $A_{1u}$  the characters of  $\sigma_v$  and  $\sigma_d$  are both  $-1$ , and therefore, the un-normalised symmetry orbital has the form

$$\phi^{(A_{1u})} \propto p_{z1} - p_{z2} + p_{z3} - p_{z4} + p_{z5} - p_{z6} + p_{z7} - p_{z8}.$$

You may find it useful to sketch the form of  $\phi^{(A_{1u})}$  and verify that it does indeed transform in the required way under the  $\sigma_v$  and  $\sigma_d$  mirror planes.

- (i) By considering the required behaviour under the  $\sigma_v$  and  $\sigma_d$  mirror planes, or otherwise, find the normalised symmetry orbitals for the other non-degenerate irreducible representations found in (a). Also find the energies of *all* nondegenerate molecular orbitals. [8]

[Qu. A4 continued on next page]

[TURN OVER]

[Continuation of Qu. A4]

- (ii) In addition there are four degenerate symmetry orbitals given by

$$\begin{aligned}\phi_1 &= \frac{1}{\sqrt{2}}(p_{z1} - p_{z5}) \\ \phi_2 &= \frac{1}{\sqrt{2}}(p_{z2} - p_{z6}) \\ \phi_3 &= \frac{1}{\sqrt{2}}(p_{z3} - p_{z7}) \\ \phi_4 &= \frac{1}{\sqrt{2}}(p_{z4} - p_{z8})\end{aligned}$$

Construct the secular determinant for these orbitals in terms of  $\alpha$ ,  $\beta_S$  and  $\beta_L$ .

[2]

- (iii) The energies of the degenerate molecular orbitals arising from the four symmetry orbitals in (ii) are given by  $E = \alpha \pm \sqrt{\beta_S^2 + \beta_L^2}$ . For  $\beta_L = 0$ , find the normalised degenerate molecular orbitals, expressed in terms of the  $p_{zi}$ .

[3]

- (c) (i) Calculate the total  $\pi$  electron energy for the cases: (1)  $\beta_S = \beta_L = \beta$ ; and (2)  $\beta_L = 0$ .
- (ii) Rationalise why, in the planar geometry,  $C_8H_8$  adopts a geometry with alternating short and long bonds, rather than one with equal bond lengths.

[2]



**A5**

The benzene molecule belongs to the point group  $\mathcal{D}_{6h}$ . The  $\sigma_v$  planes and the  $C_2$  axes pass through atoms on opposite sides of the ring; the  $\sigma_d$  planes and the  $C'_2$  axes pass through the mid-points of C–C bonds on opposite sides of the ring.

- (a) (i) Consider a basis consisting three orthogonal displacement vectors on each *carbon* atom. Form the representation and then reduce it. [4]  
 [You may consider all the vectors at once, or separate them into groups.]
- (ii) Hence find the irreducible representations of the normal modes of benzene. Confirm that these irreducible representations correspond to the expected number of normal modes. [3]
- (b) The intensity of a spectroscopic transition between a state with wavefunction  $\psi_i$  and another state with wavefunction  $\psi_j$  is proportional to the transition moment  $R_{ij}$  given by

$$R_{ij} = \int \psi_j^* \hat{\mu} \psi_i \, d\tau$$

where  $\hat{\mu}$  is the dipole moment operator.

- (i) Derive a simple rule for whether or not the fundamental of a normal mode with irreducible representation  $\Gamma^{(k)}$  is infra-red active. [3]
- (ii) Identify which normal modes of benzene are infra-red active. Assuming that each such mode gives a distinct band in the infra-red spectrum, how many such bands would you expect to see? [2]

[Qu. A5 continued on next page]

[TURN OVER

[Continuation of Qu. A5]

- (c) The *electronic* ground state of benzene is a singlet with symmetry  $A_{1g}$ . There are several excited singlet electronic states including one with symmetry  $E_{1u}$  and another with symmetry  $B_{2u}$ .

- (i) Explain why the transition from the ground electronic state to the  $E_{1u}$  state is allowed, but that to  $B_{2u}$  state is forbidden. [2]

The electronic transition  $B_{2u} \leftarrow A_{1g}$  can become weakly allowed if it is accompanied by a simultaneous change in vibrational state. The transition is then said to be from one ‘vibronic’ state to another.

The symmetry of a vibronic state is found by taking the direct product of the irreducible representation of the electronic state  $\Gamma^{(\text{elec})}$  with the irreducible representation of the vibrational state  $\Gamma^{(\text{vib})}$

$$\Gamma^{(\text{vibronic})} = \Gamma^{(\text{elec})} \otimes \Gamma^{(\text{vib})}$$

- (ii) Determine the irreducible representation of the vibronic state comprising the overall ground vibrational state and the ground electronic state. [1]
- (iii) Determine the irreducible representation of the vibronic state comprising a vibrational state with one quantum in an  $E_{2g}$  normal mode and the  $B_{2u}$  excited electronic state. [2]
- (iv) Hence show that the transition between these two vibronic states is allowed. [1]
- (v) Suppose that in addition to excitation of the  $E_{2g}$  normal mode one of the  $A_{1g}$  normal modes is also excited. Explain why the vibronic transition to this state is allowed for any number of quanta of excitation of the  $A_{1g}$  mode. [2]

END OF PAPER



UNIVERSITY OF  
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**NATURAL SCIENCES TRIPOS Part IB**

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**Wednesday 8th June 2022**

**9:00 to 12:00**

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**CHEMISTRY A: PAPER 2**

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**A6**

Consider a gas of atoms of mass  $m$  in equilibrium with a surface at temperature  $T$ ; each atom has an overall spin of  $1/2$ .  $N$  of these atoms are adsorbed onto a surface, and there are a total of  $M$  surface sites.

At the surface there is a magnetic field  $B$ , but there is no magnetic field in the bulk. The energy of interaction of the spin with the magnetic field is  $\pm\mu_B B$ , where the  $\pm$  refers to spin up and spin down and  $\mu_B$  is the Bohr magneton.

- (a) Write down an expression for the energy of an adsorbed atom assuming that this energy has a contribution which is independent of the magnetic field, and a contribution due to the interaction of the spin and the magnetic field. [1]
- (b) Write down an expression for the partition function  $q_{\text{ads}}$  for a single adsorbed atom on the surface. [2]
- (c) Using the simplest possible assumptions, which you should state, show that the partition function for the adsorbed molecules  $Q_N$  is given by

$$Q_N = q_{\text{ads}}^N f(M, N)$$

where you should determine the form of  $f(M, N)$ . [6]

- (d) Derive expressions for the chemical potential of the adsorbed and free atoms.  
[The translational partition function is  $q_{\text{trans}} = V/\Lambda^3$ , with  $\Lambda = (h^2/2\pi mkT)^{1/2}$ .] [4]
- (e) By equating these chemical potentials, show that the fractional surface coverage  $\theta$  satisfies the Langmuir equation

$$\theta = \frac{bp}{1 + bp}$$

and give an expression for  $b$ . [3]

- (f) Discuss, with the aid of a graph, how the adsorption is affected by changes in the magnetic field. [4]

**A7**

Consider the equilibrium between a neutral atom M and its ionised state consisting of a positively charged ion  $M^+$  and a free electron  $e^-$ .

The chemical potential of a species  $i$  is given by

$$\mu_i = -kT \ln(f_i/c_i) + \varepsilon_i$$

where  $f_i$  is the volume independent partition function given in general by

$$f_i = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$c_i = N_i/V$  is the concentration and  $\varepsilon_i$  is the energy of the electronic ground state with respect to a common origin.

- (a) By equating the relevant chemical potentials show that the equilibrium constant for ionisation of an atom is given by

$$K_c = \frac{f_e^- f_{M^+}}{f_M} \frac{1}{c^\circ} e^{-E_I/kT}$$

Be sure to define any additional symbols introduced. [4]

- (b) Show that this expression can be simplified to

$$K_c = \left( \frac{2\pi m_e k T}{h^2} \right)^{3/2} \frac{1}{c^\circ} \frac{2g_{M^+}}{g_M} e^{-E_I/kT}$$

where  $g_{M^+}$  and  $g_M$  are the electronic ground state degeneracies of M and  $M^+$ . State clearly the assumptions that you have made to arrive at this equation. [4]

- (c) According to the expression in (b), does  $K_c$  increase or decrease with temperature? Rationalise this result by considering the expected changes in entropy and energy on ionization. [2]

[Qu. A7 continued on next page]

[TURN OVER]

[Continuation of Qu. A7]

- (d) (i) Derive an expression for the degree of ionisation  $\alpha$  as a function of the equilibrium constant  $K_c$  assuming that the initial number density (number per unit volume) of neutral M atoms is  $c_{\text{tot}}$ . **[5]**
- (ii) Hence determine the value for the degree of ionisation of hydrogen at a temperature of 5000 K and with  $c_{\text{tot}} = 10^{22} \text{ m}^{-3}$ . Compare this with the value obtained for sodium at the same initial number density. **[5]**
- [The ionisation energy of hydrogen is 13.6 eV and that of sodium is 5.1 eV.]

**A8**

- (a) (i) Starting from the ‘bridge relation’,  $A = -kT \ln Q_N$ , derive the following expression for the translational contribution to the standard molar entropy of an ideal gas of non-interacting particles. Be sure to explain the assumptions you are making; further expressions you may need can be quoted without proof.

$$S_{\text{trans,m}}^{\circ}/R = \ln \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{RT}{p^{\circ}} \right\} - \ln N_A + \frac{5}{2}$$

[The translational partition function is given by  $q_{\text{trans}} = (2\pi mkT/h^2)^{3/2}V$ ;  $(\partial A/\partial T)_V = -S$ ]. **[5]**

- (ii) Derive a related expression for the rotational contribution of a *non-linear* molecule to the molar entropy assuming that the rotational partition function is  $q_{\text{rot}}$  and that the high-temperature limit applies. **[4]**

- (b) The values of the three rotational constants of  $\text{CH}^{35}\text{Cl}_3$  are

$$\tilde{A} = 0.110 \text{ cm}^{-1} \quad \tilde{B} = 0.110 \text{ cm}^{-1} \quad \tilde{C} = 0.0593 \text{ cm}^{-1}$$

The wavenumbers of the normal modes are (symmetry species given in parentheses)

$$\begin{array}{lll} 3034 \text{ cm}^{-1} (\text{A}_1) & 680 \text{ cm}^{-1} (\text{A}_1) & 363 \text{ cm}^{-1} (\text{A}_1) \\ 1220 \text{ cm}^{-1} (\text{E}) & 774 \text{ cm}^{-1} (\text{E}) & 261 \text{ cm}^{-1} (\text{E}) \end{array}$$

The rotational partition function of a non-linear molecule is given by

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\theta_{\text{rot},a}\theta_{\text{rot},b}\theta_{\text{rot},c}} \right)^{1/2}$$

where  $\sigma$  is the symmetry number and  $\theta_{\text{rot},a}$  is the rotational temperature corresponding to the rotational constant  $\tilde{A}$ ,  $\theta_{\text{rot},a} = \tilde{A}/k$ , and likewise for  $\theta_{\text{rot},b}$  and  $\theta_{\text{rot},c}$

- (i) Calculate the translational contribution to the standard molar entropy of  $\text{CH}^{35}\text{Cl}_3$  at 298 K, giving your answer in  $\text{J K}^{-1} \text{ mol}^{-1}$ . Use integer masses. **[3]**
- (ii) Calculate the rotational contribution to the standard molar entropy of  $\text{CH}^{35}\text{Cl}_3$  at 298 K, giving your answer in  $\text{J K}^{-1} \text{ mol}^{-1}$ . Make clear and justify any assumptions you make. **[4]**

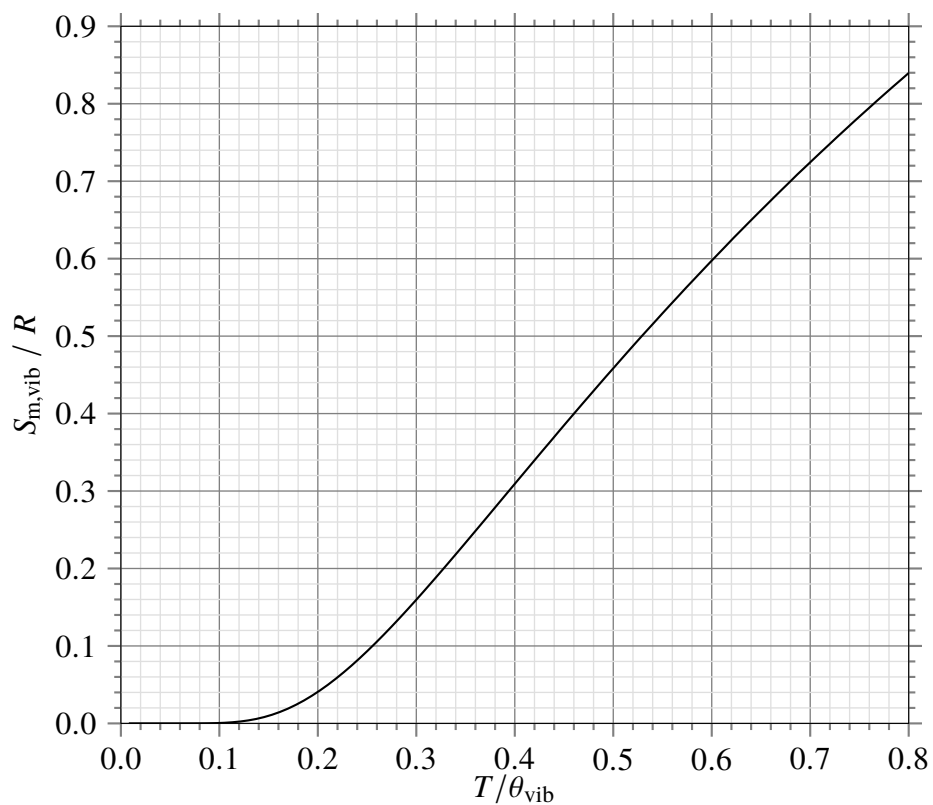
[You may find it useful to express the Boltzmann constant as  $0.695 \text{ cm}^{-1} \text{ K}^{-1}$ .]

[Qu. A8 continued on next page]

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[Continuation of Qu. A8]

- (iii) The plot below shows the contribution to the molar entropy made by a harmonic oscillator with vibrational wavenumber  $\tilde{\omega}$  expressed as a function of  $T/\theta_{\text{vib}}$ , where  $\theta_{\text{vib}} = \tilde{\omega}/k$  is the characteristic vibrational temperature.



Use the graph to estimate the contribution that each normal mode makes to the molar entropy at 298 K, and hence estimate the total vibrational entropy, giving your answer in  $\text{J K}^{-1} \text{mol}^{-1}$ . [4]



## A9

- (a) In the tight-binding model, and using the Hückel approximations, a one-dimensional band formed from the overlap of identical s orbitals with spacing  $a$  has energies

$$E_k = \alpha_s + 2\beta_s \cos(ka) \quad 0 \leq k \leq \pi/a$$

- (i) Explain what the parameters  $\alpha_s$  and  $\beta_s$  represent, and explain how this expression can be modified to describe a band formed from p orbitals overlapping head-on ( $\sigma$  overlap). [2]
  - (ii) On the same plot draw the dispersion curves for the s band and the p band, assuming that the atomic orbitals are well separated in energy, with the p higher in energy than the s. Label your plot with any relevant parameters and key values. [4]
  - (iii) Give expressions for the (energy) width of the two bands and the minimum band gap between them. Is this minimum band gap direct or indirect? [2]
- (b) If the energies of the s and p orbitals are sufficiently close it is possible for there to be mixing between adjacent s and p orbitals.

- (i) Describe the effect of this mixing on the dispersion curves for the case considered in (a)(ii), illustrating your answer with a sketch of the curves. [2]
- (ii) Now consider the special case where the s and p orbitals have the *same* energy and the same  $\beta$  parameter. Draw dispersion curves for the two bands for two cases: (1) where s–p mixing is ignored; (2) where s–p mixing is included. Comment on any special features of your plots. [3]
- (iii) The situation in (b)(ii) can be analysed within the Hückel framework to give the following expressions for energies of the two bands

$$E_{k,1} = +2 \{ \beta^2 \cos^2(ka) + \beta_{sp}^2 \sin^2(ka) \}^{1/2}$$

$$E_{k,2} = -2 \{ \beta^2 \cos^2(ka) + \beta_{sp}^2 \sin^2(ka) \}^{1/2}$$

where (for simplicity) the s and p orbital energies have been taken as zero,  $\beta$  is the parameter describing the interaction of adjacent s orbitals (the corresponding parameter for p orbitals has the same magnitude), and  $\beta_{sp}$  is the parameter describing the interaction between adjacent s and p orbitals. Assume  $|\beta_{sp}| < |\beta|$ . For each of  $E_{k,1}$  and  $E_{k,2}$  compute the energy for the points  $k = 0, \pi/2a, \pi/a$ , and hence make a sketch of the dispersion curves. Comment on the contributions that the atomic orbitals make to the bands as a function of  $k$ .

[4]

- (iv) Using your results from (iii), give expressions for the width of the two bands and the minimum band gap. Is this minimum band gap direct or indirect? [3]

[TURN OVER]

**A10**

- (a) (i) Make a sketch showing the arrangement of bands expected for a typical (intrinsic) semiconductor (such as Si or Ge), indicating on your diagram the band gap  $E_g$  and the likely location of the Fermi energy at a finite temperature. [2]
- (ii) Explain why the temperature dependence of the electrical conductivity  $\sigma$  of such a semiconductor is given by

$$\sigma \propto e^{-E_g/2k_B T}$$

Describe how this relationship can be used as the basis for the experimental determination of the band gap.

[The Fermi–Dirac distribution is

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

where  $E_F$  is the Fermi energy.] [4]

- (b) (i) Explain why doping Si with a few ppm of As results in a substantial increase in the conductivity at room temperature. [1]
- (ii) Describe how such doping affects the temperature dependence of the conductivity, giving reasons for your answer. [3]
- (iii) The material described in (b)(i), when examined at sufficiently low temperatures, shows a series of absorptions in the far IR spectra. The absorption line corresponding to lowest energy transition is at 7.97 meV, and there are also transitions observed at 9.44 meV and 9.97 meV, after which the spectrum shows a continuous absorption.

Account for these observations, being as quantitative as you can; you should assume that the effective electron mass is  $0.2 m_e$ .

[The Rydberg constant  $R_H$  is given by

$$R_H = \frac{e^4}{32\pi^2 \hbar^2} \times \frac{m_e}{\epsilon_0^2}$$

The value of this constant is 13.61 eV] [4]

- (iv) As the temperature is raised the transitions described in (b)(iii) become weaker and eventually disappear. Explain why this is so and give a rough estimate of the temperature at which you expect these transitions to start to weaken significantly. [3]

[Qu. A10 continued on next page]

[Continuation of Qu. **A10**]

- (c) Suppose that the Si is doped with Ga rather than As. Discuss what form the far IR spectrum of such a sample might take when recorded at low temperatures. **[3]**

END OF PAPER