

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Tuesday, 9th June 1998, 9.30 a.m. to 12.30 p.m.

Candidates should answer *three* questions

The marks in square brackets indicate the weight the examiners expect to assign to each part of the question.

Speed of light, c	=	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant, h	=	$6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant, k_B	=	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Molar gas constant, R	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro number, N_A	=	6.022×10^{23}
1M	=	1 mol dm^{-3}
p^\ominus	=	$1 \text{ bar} = 10^5 \text{ Pa} \simeq 1 \text{ atm}$
V_m^\ominus	=	$24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K
Elementary charge, e	=	$1.602 \times 10^{-19} \text{ C}$
Atomic mass unit, u	=	$1.661 \times 10^{-27} \text{ kg}$
Electron mass, m_e	=	$9.109 \times 10^{-31} \text{ kg}$
Permittivity in vacuo, ϵ_0	=	$8.854 \times 10^{-12} \text{ F m}^{-1}$
$4\pi\epsilon_0$	=	$1.113 \times 10^{-10} \text{ F m}^{-1}$

1. Nuclear magnetic resonance
2. Surfaces
3. Dynamic electrochemistry
4. Atomic and molecular spectroscopy, dynamics
5. Photochemistry
6. Valence theory, spectroscopy, group theory
7. Statistical thermodynamics
8. Atmospheric chemistry, photochemistry, kinetics
9. Reaction dynamics
10. Quantum mechanics, NMR
11. Molecular interactions
12. Physico-chemical properties of the oxygen molecule

1. Answer **all** parts.

(a) Modern NMR spectrometers operate in a *pulsed* mode, where spectra are obtained by *Fourier transformation* of a signal from *free induction decay*. Explain clearly what is meant by this statement with particular attention to the italicised terms. Explain also why it is advantageous to record NMR spectra in a pulsed rather than a continuous mode. [40%]

(b) Give an account of the factors that make some nuclei more suitable than others for use in NMR.

EITHER explain why ^{13}C lines from atoms adjacent to the halogen atoms Cl, Br and I are affected in frequency but not split by spin-spin coupling, although all common isotopes of these halogens have non-zero nuclear spin.

OR explain why the ^1H spectrum of ammonium salts shows splitting into three lines by the ^{14}N nucleus, but spectra of primary amines show no such splitting of lines for protons bonded to the nitrogen atoms. [25%]

(c) Distinguish between spin-lattice and spin-spin relaxation in NMR. How can the spin-lattice relaxation time be measured?

Explain why the ^{13}C nuclear relaxation time for quaternary carbon atoms is much longer than that for carbon in $-\text{CH}=\text{}$ groups, which in turn is roughly twice as long as in $-\text{CH}_2-$ groups. Explain also why the relaxation time for carbon in methyl groups is relatively long and does not fit into this sequence. [35%]

2. Describe experimental methods which could be used to demonstrate the validity of **each** of the following statements indicating the *basis* of the methods you suggest and how the results obtained can be interpreted to support the statements given: [20% each]

- The clean surface atomic structure of single crystal solids often differs significantly from that expected from the simple truncation of the bulk crystal.
- The surface composition of many solids differs significantly from that in the bulk because of surface segregation and surface reaction with the ambient environment.
- The electronic and chemical structures of many adsorbate complexes at metal surfaces resemble those established in metal cluster chemistry.
- Lateral interactive forces often exist between neighbouring adsorbates at solid surfaces.
- The desorption activation energy of a substance adsorbed on a surface is often equal to the negative of the heat of adsorption.

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3. Answer all parts.

(a) Give an account of how current flow at an oxidation/reduction electrode depends on the electrode potential for fixed concentration of substrate near the electrode. [20%]

(b) Explain

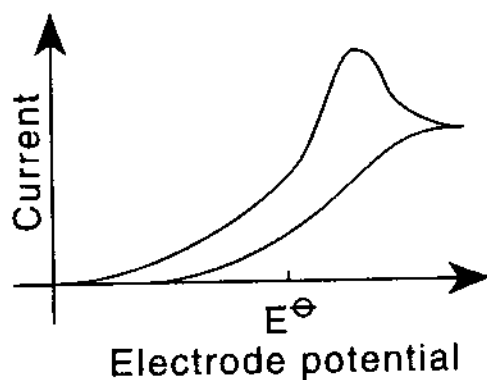
(i) why the current at a fixed electrode potential may vary with time,

(ii) why the use of *microelectrodes* is often advantageous in electrochemical studies of reaction kinetics,

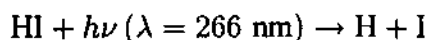
(iii) why some electron transfer processes at electrodes are fast and others are slow,

(iv) how fast and slow electron transfer processes can be distinguished experimentally using cyclic voltammetry. [50%]

(c) What can be deduced about the electrochemical and chemical processes at an electrode with the cyclic voltammogram shown below? Suggest further measurements which could be used to characterise them more fully. [30%]



4. The photodissociation of HI



has been studied by timing the flight of the H atoms to a detector 0.425 m away. Two strong peaks were found in the time-of-flight spectrum, one at 24.2 μs and the other at 37.4 μs .

(a) The H atom is formed in its ground state. Identify the two lowest energy states of the I atom, which give rise to the two peaks. [10%]

(b) Show that the total kinetic energy release (KER) in the reaction is given by the expression

$$\text{KER} = \frac{1}{2}m_{\text{H}}\{1 + m_{\text{H}}/m_{\text{I}}\}\{D/t\}^2$$

where m_{H} and m_{I} are the masses of the atoms, t is the time of flight and D is the flight distance, 0.425 m. Obtain total kinetic energy releases for the flight times of 24.2 μs and 37.4 μs , and hence determine the dissociation energy of HI and the spin-orbit splitting in the I atom. [30%]

(c) Deduce what you can about the lifetime of excited HI molecules from the following observations:

(i) If polarised light is used for dissociation, H atoms are ejected preferentially in a specific direction relative to the polarisation.

(ii) The absorption spectrum of HI at 266 nm is smooth, with no vibrational structure. (You can assume that, if it were not for lifetime broadening, the vibrational spacing would be the same as in ground state HI.) [20%]

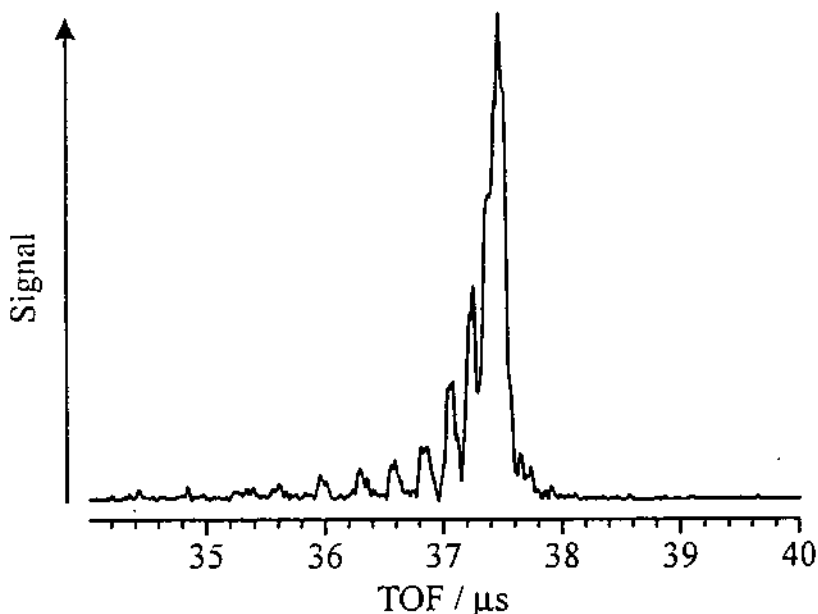
(d) Immediately after their formation, the H atoms were excited first to $n = 2$, then from there to a state of high principal quantum number so that they could be detected at the distant detector.

Show how you could work out the precise frequency needed to excite H atoms on an allowed transition from the ground state to $n = 2$. (No actual calculation is required. You should assume that the Rydberg constant R_{∞} is available and state what other information, if any, is needed.) [20%]

(e) Both time-of-flight peaks show fine structure due to thermal rotational energy of HI before photodissociation. Using the rotational constant given, determine the rotational quantum number for the subsidiary peak near 36 μs in the Figure, and deduce what you can about the rotational temperature of the HI. [20%]

RAM $I = 127$, $H = 1$. $B_0(\text{HI}) = 6.43 \text{ cm}^{-1}$. $1 \text{ cm}^{-1} = 1.988 \times 10^{-23} \text{ J molecule}^{-1}$

$\nu_0(\text{HI}) = 2308 \text{ cm}^{-1}$.



5. Discuss **all** of the following observations concerning non-radiative transitions in photochemistry in as much detail as possible.
- The rate constant for intersystem crossing from S_1 to T_1 in propanone is $5 \times 10^8 \text{ s}^{-1}$, but in benzophenone it is roughly 10^{11} s^{-1} .
 - The radiative lifetime of the first excited singlet state in benzene, of $^1B_{2u}$ symmetry, is 414 ns, but its measured lifetime in solution is much shorter. For anthracene the radiative and measured lifetimes of the first excited singlet state are both about 10 ns.
 - The fluorescence quantum yield of naphthalene in solution in hexane is 0.23, but for 1-bromonaphthalene it is 0.0016.
 - The quantum yield of phosphorescence of benzene- h_6 in a rigid glass at 80 K is 0.18, but for benzene- d_6 the yield is 0.24 under the same conditions.
 - The emission spectrum of a solution of pyrene in hexane at room temperature changes as a function of concentration. The emission from such a solution shows two lifetime components, one of the order of ns, the other of the order of ms.

[Each part will be given approximately equal weight.]

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Turn over

6. Construct the Walsh diagram for the triatomic molecule AH_2 where A is a first-row atom. Draw the molecular orbitals for the linear configuration on the left hand side and those for the 90° bond angle on the right hand side of the diagram. Label the orbitals with the irreducible representations of the appropriate point group.

Use the diagram to deduce the shape of the H_2O molecule in its ground electronic state and write down its electronic configuration. Deduce the spectroscopic term symbol for the ground electronic state. [30%]

Derive the symmetries of the vibrational (normal) coordinates of H_2O in its ground state. Sketch the form of these coordinates. Which of them are infrared active and which Raman active? Give reasons for your answer. [30%]

Use your Walsh diagram to derive the nature of the first excited singlet electronic state of H_2O . Is the transition to this state from the ground state allowed? How would you expect the geometry of the molecule to change in this excitation process? [20%]

The photoelectron spectrum of H_2O recorded with the He I line at 21.2 eV shows three transitions which correspond to the removal of an electron from each of the three highest occupied orbitals.

Deduce the nature of the corresponding electronic states of H_2O^+ produced by photoionization.

Explain why the transition to the lowest of these states has very little vibrational structure whereas the transitions to the other two both show strong excitation of the vibrational motion. [20%]

[Label your axes so that the out-of-plane, x axis transforms as a B_1 representation.]

7. Explain what is meant by a canonical ensemble in statistical thermodynamics. [10%]

(a) Consider a macroscopic sample at a temperature T of N independent Mn atoms in their ground 6S state. The sample is subjected to a magnetic field of variable flux density B . Each atom has a magnetic dipole moment which prefers to be oriented along the magnetic field with component m and an interaction energy of $-mB$. The energy levels of the atoms are given by

$$E(B) = E_0 + g_J \mu_B B M_J$$

where μ_B is the Bohr magneton, g_J is the g-factor and M_J is the component of the total electronic angular momentum J along the magnetic field. Explain why g_J is equal to 2.0 in this case.

Show that the electronic contribution q_{el} to the molecular partition function of Mn in a flux density B is given by

$$q_{el} = 2 \exp(-E_0/kT) \{ \cosh x + \cosh 3x + \cosh 5x \}$$

where $x = \mu_B B/kT$. [25%]

(b) Assuming a Boltzmann distribution, show that the mean magnetic moment \bar{m} of a Mn atom in the field direction is given by

$$\bar{m} = 2\mu_B \left\{ \frac{\sinh x + 3 \sinh 3x + 5 \sinh 5x}{\cosh x + \cosh 3x + \cosh 5x} \right\}.$$

For the sample, the total magnetization M is given by $N\bar{m}$. Show that, for small magnetic fields,

$$M = \chi B$$

where the paramagnetic susceptibility follows Curie's Law, $\chi = C/T$. Derive an expression for the constant C in this case. [20%]

(c) Given that the electronic contribution to the entropy of a system with energy E_{el} at temperature T and flux density B is

$$S_{el}(T, B) = Nk \ln q_{el} + E_{el}(T, B)/T,$$

show that, for the collection of Mn atoms,

$$S_{el}(T, B) = Nk \ln 2 + Nk \ln \{ \cosh x + \cosh 3x + \cosh 5x \} - \frac{N\mu_B B}{T} \left\{ \frac{\sinh x + 3 \sinh 3x + 5 \sinh 5x}{\cosh x + \cosh 3x + \cosh 5x} \right\}.$$

Obtain $S_{el}(T, B = 0)$ and comment on the physical significance of the result. [25%]

(d) Show that, for small fields, the field dependent contribution to the electronic entropy $\Delta S_{el}(T, B)$ is given by

$$\Delta S_{el}(T, B) = -\frac{1}{2} \chi B^2 / T.$$

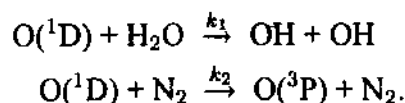
Comment on this result and its implications for cooling by adiabatic demagnetisation. [20%]

[$\cosh y = \frac{1}{2}(e^y + e^{-y})$, $\sinh y = \frac{1}{2}(e^y - e^{-y})$. For $y \ll 1$, $\sinh y \approx y$, $\cosh y \approx 1 + y^2/2$ and $\ln(1+y) \approx y$]

8. The *daytime* chemistry of the earth's atmosphere differs markedly from that at *night*. Explain why this is so, giving examples of some of the processes which are affected. [20%]

Ozone photolysis is an important process in the atmosphere, with an onset at $\lambda \simeq 310$ nm (in the ultraviolet). One of the products is atomic oxygen in the ^1D state. What is the other product, in what state is it principally formed and why?

During the daytime, a typical rate of absorption of radiation with $\lambda < 310$ nm by ozone in the lower atmosphere is 2.1×10^8 photons $\text{s}^{-1} \text{cm}^{-3}$ and the quantum yield for formation of $\text{O}(^1\text{D})$ is 0.9. The $\text{O}(^1\text{D})$ atoms are removed primarily by two processes



Calculate the rate of formation of OH radicals given that $k_1 = 2.2 \times 10^{-10}$ molecule $^{-1} \text{cm}^3 \text{s}^{-1}$ and $k_2 = 1.8 \times 10^{-11}$ molecule $^{-1} \text{cm}^3 \text{s}^{-1}$ at the appropriate temperature and that the mole fractions of H_2O and N_2 are 0.02 and 0.78 respectively. If the hydroxyl radical is removed in reactions for which the rate is given by the expression $60 [\text{OH}]$ molecule $\text{cm}^{-3} \text{s}^{-1}$, estimate the mean daytime concentration of OH under these conditions, given that its typical mole fraction is much less than 6×10^{-11} . [40%]

Isoprene is an important bio-organic hydrocarbon released by many types of vegetation. The rate constant for its reaction with the OH radical is 1.0×10^{-10} molecule $^{-1} \text{cm}^3 \text{s}^{-1}$. Calculate the lifetime of isoprene during the day from this removal process.

At night, attack on isoprene is mainly due to the reaction with ozone and the nitrate radical, NO_3 . The rate constants for the reactions with these two species are 1.3×10^{-17} molecule $^{-1} \text{cm}^3 \text{s}^{-1}$ and 6.8×10^{-15} molecule $^{-1} \text{cm}^3 \text{s}^{-1}$ respectively and the mole fractions of O_3 and NO_3 are 8×10^{-8} and 6×10^{-11} . If the supply of isoprene is suddenly cut off (for example, by a change of wind direction), calculate the fraction of isoprene removed near the ground by these two reactions during a 12 hour night. [40%]

$$\{1 \text{ atm} \equiv 2.5 \times 10^{19} \text{ molecule cm}^{-3}\}$$

9. Explain each of the following concepts in collision dynamics:

- (i) Impact parameter;
- (ii) Centrifugal barrier;
- (iii) Total cross-section;
- (iv) Differential cross-section.

[25%]

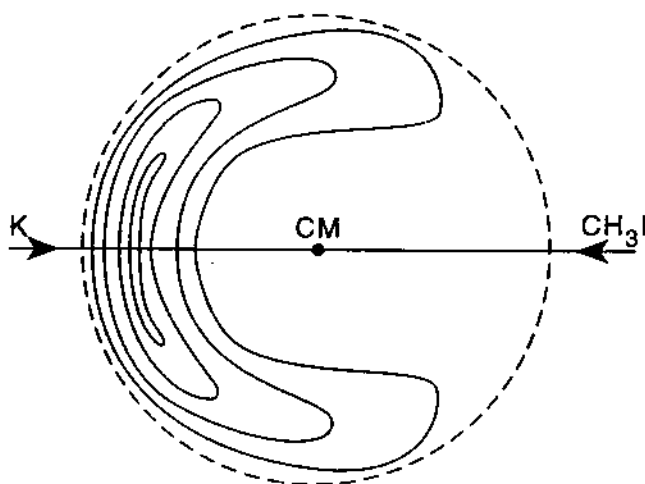
Answer three of the following parts:

[25% each]

(a) Discuss the behaviour of the collision cross-sections in elastic collisions. How can such cross-sections be used to provide detailed information on the intermolecular potential energy function?

(b) What is meant by the harpoon mechanism of chemical reactions? How can it be used to explain the large reaction cross-section and the product angular distribution? Given that the electron affinity of Br_2 is 246 kJ mol^{-1} and the ionisation energy of Rb is 403 kJ mol^{-1} , estimate the reaction cross-section for the $\text{Rb} + \text{Br}_2$ reaction.

(c) The following diagram shows the angle-velocity distribution of KI, produced by the collision of K atoms with CH_3I . Discuss the appearance of this diagram and comment on the fact that the majority of the energy available appears as product translational energy. How might the influence of the orientation of the CH_3I molecule on the collision dynamics be investigated?



(d) How do the shape of the potential energy surface, the position of the barrier to reaction and the masses of the particles involved affect the course of a reaction between an atom and a diatomic molecule? How can measurements of the vibrational, rotational or translational distributions of the product molecules be used to provide information on reaction dynamics?

10. What is meant by the terms *operator*, *eigenvalue* and *eigenfunction* in quantum mechanics? [20%]

What is the condition that a function is simultaneously an eigenfunction of two different operators? [10%]

Consider a system of two interacting nuclear spins in a magnetic field. The Hamiltonian for the system (in frequency units) is

$$H/h = -\nu_1 I_{1z} - \nu_2 I_{2z} + J I_1 \cdot I_2$$

where J is the spin-spin coupling constant and $\nu_i = (1 - \sigma_i)g_i\mu_N B/h$ is the frequency of an NMR transition in the absence of the spin-spin coupling.

Using the four possible products of the nuclear spin wavefunctions α_i and β_i , eigenfunctions of the z component of the spin operator, derive the secular equations and hence the full secular matrix for the Hamiltonian. The only non-zero matrix elements of I_x and I_y are:

$$\begin{aligned}\langle \alpha | I_x | \beta \rangle &= i \langle \alpha | I_y | \beta \rangle = \frac{1}{2} \\ \langle \beta | I_x | \alpha \rangle &= -i \langle \beta | I_y | \alpha \rangle = \frac{1}{2}\end{aligned}$$

Derive the energy levels when the coupling $J I_1 \cdot I_2$ is small compared with the chemical shift, $(\sigma_1 - \sigma_2)g_N\mu_N B$. What is the appearance of the NMR spectrum of this system under these conditions given that the selection rule for the transition of individual nuclei is $\Delta m_I = \pm 1$? [40%]

What are the effects of the *neglected* contribution of the spin-spin coupling on all eigenvalues and eigenfunctions?

How is the description simplified when the chemical shifts σ_1 and σ_2 are identical? Derive the new eigenvalues and eigenfunctions. Show that these eigenfunctions are simultaneously eigenfunctions of the operator $I^2 = (I_1 + I_2)^2$. How does this affect the appearance of the NMR spectrum? [20%]

What are the implications of these results for the interpretation of NMR spectra? [10%]

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11. How do interactions between molecules affect their concentrations and arrangement at the liquid-gas interface? [20%]

(a) The surface tension (γ) of ethanol-water mixtures at 298 K varies with mole fraction of ethanol (x_2) as follows:

x_2	0	0.011	0.021	0.047	0.092	0.146	0.208	0.283
$\gamma/\text{mN m}^{-1}$	72.2	60.8	54.9	46.0	37.5	32.3	29.6	27.9

The Gibbs isotherm for this system may be written

$$d\gamma = -\Gamma_2^{(1)} RT d \ln x_2$$

where $\Gamma_2^{(1)}$ is the surface excess of ethanol (defined relative to water). By drawing an appropriate graph, estimate the surface excess of ethanol at mole fractions of about 0.02, 0.10 and 0.25.

Suggest reasons why $\Gamma_2^{(1)}$ passes through a maximum.

How would you expect the surface tension and relative surface excess to vary as the concentration of ethanol continues to increase? [25%]

(b) State Raoult's Law. How must it be modified to include the effects of non-ideal behaviour?

The partial vapour pressure of ethanol (p_2) above ethanol/water mixtures at 298 K as a function of mole fraction of ethanol is as follows:

x_2	0	0.011	0.021	0.047	0.092	0.146	0.208	0.283	1.0
$p_2/\text{mm Hg}$	0.0	1.9	3.8	8.3	16.8	21.8	25.8	28.6	59.0

Use the values of the partial pressure in conjunction with Raoult's Law to determine the activity coefficient of ethanol in water at each concentration.

Suggest reasons for the deviation from ideal behaviour. [15%]

(c) How should the Gibbs isotherm be modified to include non-ideality?

Show that a more accurate representation of the Gibbs isotherm is

$$d\gamma = -\Gamma_2^{(1)} RT d \ln p_2$$

Use either the original isotherm and your values of the activity coefficient from (b) or the modified Gibbs isotherm to determine more accurately the surface excess of ethanol at a mole fraction of 0.25. [20%]

(d) From your value of the surface excess of ethanol obtained in (c) calculate the area occupied per ethanol molecule at a mole fraction of 0.25.

The areas occupied per molecule of butanol and hexanol at the surface of their solutions in water when the surface is fully saturated are respectively 0.25 and 0.28 nm². Comment on the values for the three molecules. [20%]

12. Comment in detail on **five** of the following observations which refer to the oxygen molecule. [20% each]

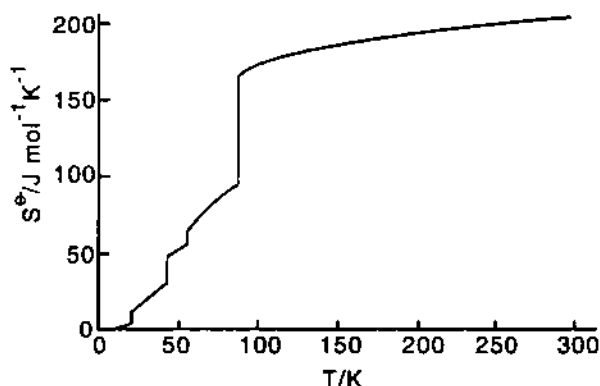
(a) O_2 has a pure rotational Raman spectrum with lines at the following shifts from the Rayleigh line:

$$14.38, 25.88, 37.38, 48.88 \text{ cm}^{-1}$$

(b) The electronic absorption spectrum of O_2 shows two very weak absorption features in the near infrared (origins at $7,918$ and $13,195 \text{ cm}^{-1}$) and a very strong band in the ultraviolet ($49,400 \text{ cm}^{-1}$).

(c) The reaction of O_2 with NO shows third order kinetics and the temperature dependence of the rate constant implies a negative activation energy.

(d) The heat capacity of oxygen shows the following variation with temperature:



(e) In both gaseous and liquid forms, oxygen is attracted into the strong-field region of an inhomogeneous magnetic field. In its lowest temperature solid form, it loses this property.

(f) The bond length decreases and the bond force constant and dissociation energy of oxygen both increase on excitation of an electron from the highest occupied valence orbital.

(g) The mass spectrum of oxygen shows strong peaks at roughly m/e 16 and 32 and weak peaks at m/e 18 and 34. There are further, even weaker peaks of which that with m/e of 17 is a close doublet. However when measured accurately the masses for the two strong peaks are 15.994366 and 31.989281, not integers.

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End of Examination