2.2 Bonding and Structure: 2-hour Pack

AQA 7405 · Calculator allowed · about 120 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question is about electronegativity and bond polarity.

(a) Define the term electronegativity. **(1)**

(b) State and explain the general trend in electronegativity across Period 3, from sodium to chlorine. **(3)**

(c) Using these electronegativity values, H = 2.1, Cl = 3.0, F = 4.0, I = 2.5, rank the hydrogen halides HF, HCl and HI in order of increasing bond polarity, showing your working. **(3)**

(d) A student states: "Carbon dioxide, CO_2, has polar C=O bonds, so it must be a polar molecule." Evaluate this statement. **(3)**

(Total for Question 1 is 10 marks)

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2 This question is about intermolecular forces: London (dispersion) forces and permanent dipole-dipole forces.

(a) State what is meant by a London (dispersion) force. **(2)**

(b) Explain why the boiling points of the noble gases (He, Ne, Ar, Kr, Xe) increase down the group. **(3)**

(c) Hydrogen chloride, HCl (Mr = 36.5), has a higher boiling point than argon, Ar (Mr = 40), even though Ar has a slightly greater Mr. Explain why. **(3)**

(d) Given that the boiling point of argon is -186 C and the boiling point of HCl is -85 C, use this data to support your answer to part (c). **(2)**

(Total for Question 2 is 10 marks)

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3 This question is about hydrogen bonding and its effect on the properties of water.

(a) State the three conditions that must be met for hydrogen bonding to occur between molecules. **(3)**

(b) Describe how a hydrogen bond forms between two water molecules. **(2)**

(c) Explain, in terms of hydrogen bonding, why ice is less dense than liquid water. **(3)**

(d) The density of ice is 0.917 g/cm3 and the density of liquid water is 1.000 g/cm3 at 0 C. Calculate the percentage increase in volume when a fixed mass of water freezes to form ice. **(4)**

(Total for Question 3 is 12 marks)

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4 This question is about ionic polarisation and the bonding in aluminium chloride, $AlCl_3$.

(a) Explain, using the idea of ionic polarisation, why aluminium chloride, $AlCl_3$, has significant covalent character rather than being purely ionic. **(4)**

(b) Predict, with a reason, whether aluminium fluoride, AlF_3, or aluminium chloride, $AlCl_3$, has the greater ionic character. **(2)**

(c) State the type of structure adopted by solid aluminium chloride as a result of its covalent character. **(1)**

(d) Explain how the dative covalent bonds form within the Al_2Cl_6 dimer. **(2)**

(Total for Question 4 is 9 marks)

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5 Boron trifluoride, BF_3, reacts with ammonia, NH_3, to form the adduct $F_3B\text{-}NH_3$, in which a new dative covalent bond forms from the nitrogen atom to the boron atom.

(a) Suggest, with reasoning, the shape around the boron atom in the adduct $F_3B\text{-}NH_3$, given that BF_3 itself is trigonal planar. **(3)**

(b) Explain why BF_3 must have an incomplete octet (an empty orbital) on boron in order to accept the dative bond from nitrogen. **(2)**

(c) In the adduct $F_3B\text{-}NH_3$, the nitrogen atom's lone pair is now used in the dative bond to boron. Suggest how this affects the ability of $F_3B\text{-}NH_3$ molecules to hydrogen bond to one another, and hence compare the expected volatility of the adduct with that of a simple molecular compound of similar Mr that has no hydrogen bonding capability. **(2)**

(d) If ammonia, NH_3, were replaced with trimethylamine, $N(CH_3)_3$, in this reaction, a dative bond to boron would still form. Suggest why the melting point of the resulting adduct, $F_3B\text{-}N(CH_3)_3$, might differ from that of $F_3B\text{-}NH_3$, and in which direction you would expect this change. **(2)**

(Total for Question 5 is 9 marks)

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6 This synoptic question compares the structure, bonding and thermal behaviour of carbon dioxide and silicon dioxide, both Group 14 oxides.

(a) Carbon dioxide, CO_2, is a gas at room temperature and sublimes at -78°C. Silicon dioxide, SiO_2, is a solid that melts at about 1710°C. Describe the structure and bonding of solid CO_2 (dry ice) and of SiO_2. **(2)**

(b) Bond enthalpy data: C=O (in CO_2) = 805 kJ/mol; Si-O (in SiO_2) = 466 kJ/mol. Explain, using this data and the structures described in (a), why SiO_2 has a vastly higher melting point than the sublimation point of CO_2, even though the individual Si-O bond enthalpy is lower than the individual C=O bond enthalpy. **(4)**

(c) In the giant covalent lattice of SiO_2, there are 4 mol of Si-O bonds per mole of SiO_2 formula units. Using the Si-O bond enthalpy given, estimate the enthalpy needed to break all the covalent bonds in 1 mole of solid $SiO_2(s)$ into gaseous atoms, and state one limitation of using an average bond enthalpy for this estimate. **(4)**

(Total for Question 6 is 10 marks)

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7 This question uses ionic radii to compare the lattice enthalpies of the Group 2 oxides MgO, CaO and SrO.

(a) State how the magnitude of the lattice enthalpy of an ionic compound depends on (i) the charges of the ions and (ii) the sum of their ionic radii. **(2)**

(b) Ionic radii: Mg^{2+} = 72 pm, Ca^{2+} = 100 pm, Sr^{2+} = 118 pm, O^{2-} = 140 pm. Calculate the sum of ionic radii (r+ + r-) for MgO, CaO and SrO. **(3)**

(c) The product of the ionic charges (2 x 2 = 4) is the same for MgO, CaO and SrO. Using your answers to (b), predict the order of lattice enthalpy magnitude (most exothermic to least exothermic) for these three oxides, explaining your reasoning. **(3)**

(d) Calculate the ratio (r+ + r- for MgO) / (r+ + r- for CaO), giving your answer to 2 significant figures, and state what this ratio suggests about the relative magnitude of the lattice enthalpy of CaO compared with MgO. **(2)**

(Total for Question 7 is 10 marks)

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8 This question is about determining the density of solid sodium chloride from its unit cell dimensions, and the associated measurement uncertainty.

(a) Sodium chloride crystallises with a face-centred cubic unit cell of edge length a = 564.0 pm. Show that the volume of the unit cell is 1.79×10^{-22} cm^3. **(3)**

(b) Each unit cell contains 4 formula units of NaCl. Using density = (Z x M) / (NA x V), where Z is the number of formula units per unit cell, M is the molar mass of NaCl (58.5 g/mol) and NA = 6.02×10^{23} mol^{-1}, calculate the density of solid NaCl. Give your answer to 3 significant figures. **(3)**

(c) The edge length was measured as a = 564.0 pm ± 2 pm. Calculate the percentage uncertainty in a, and hence the percentage uncertainty in the density calculated in (b), given that density is proportional to $1/a^3$ (so the percentage uncertainty in density is 3 times the percentage uncertainty in a). **(3)**

(d) Express the density found in (b) together with its absolute uncertainty, quoted to an appropriate number of significant figures. **(3)**

(Total for Question 8 is 12 marks)

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9 Both ice (solid H_2O) and dry ice (solid CO_2) are solids formed from small covalent molecules, yet ice melts at 0°C while dry ice sublimes at -78°C at atmospheric pressure. Compare the structure and bonding in ice and dry ice, and use this to explain the large difference between their melting point and sublimation point.

(Total for Question 9 is 6 marks)

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Mark scheme · 2.2 Bonding and Structure: 2-hour Pack

Question 1

(a) the power (ability) of an atom to attract the bonding (shared) pair of electrons in a covalent bond oe **B1**

(a) Answer: The ability of an atom to attract the bonding pair of electrons in a covalent bond.

(b) electronegativity increases across Period 3 from Na to Cl **M1**

(b) nuclear charge (number of protons) increases across the period while the number of occupied shells (and shielding by inner shells) stays approximately constant oe **A1**

(b) atomic radius decreases, so there is a greater attraction for the bonding pair of electrons oe **A1**

(b) Answer: Electronegativity increases from Na to Cl because nuclear charge increases with roughly constant shielding, so atomic radius decreases and the attraction for bonding electrons increases.

(c) calculates the electronegativity difference for each: HF = 4.0-2.1 = 1.9; HCl = 3.0-2.1 = 0.9; HI = 2.5-2.1 = 0.4 **M1**

(c) correct order of increasing polarity: HI < HCl < HF **A1**

(c) correct justification: a greater electronegativity difference means a more polar bond oe **A1**

(c) Answer: Order of increasing bond polarity: HI < HCl < HF.

(d) the statement is not fully correct; the shape of the molecule must also be considered oe **M1**

(d) CO_2 is a linear, symmetrical molecule oe **M1**

(d) the two C=O bond dipoles are equal in size and point in exactly opposite directions, so they cancel out, giving no overall (net) molecular dipole: CO_2 is non-polar oe **A1**

(d) Answer: The statement is incorrect. CO_2 has polar bonds, but because the molecule is linear and symmetrical the bond dipoles cancel, so CO_2 itself is a non-polar molecule.

Question 2

(a) a weak intermolecular force caused by temporary (instantaneous) dipoles, arising from the random movement of electrons in an electron cloud oe **B1**

(a) the temporary dipole induces a dipole in a neighbouring molecule/atom, resulting in a weak force of attraction between them oe **B1**

(a) Answer: A weak attractive force caused by temporary dipoles (from random electron movement) inducing dipoles in neighbouring molecules.

(b) the number of electrons (and atomic size/Mr) increases down the group oe **B1**

(b) this increases the size of the electron cloud, so larger instantaneous and induced dipoles can form, increasing the strength of the London forces oe **B1**

(b) more energy is needed to overcome these stronger forces, so the boiling point increases down the group oe **B1**

(b) Answer: Boiling point increases down the group because more electrons give larger, stronger London forces, requiring more energy to overcome.

(c) HCl is a polar molecule (Cl is more electronegative than H), so it has a permanent dipole; Ar is non-polar oe **B1**

(c) HCl molecules experience permanent dipole-dipole forces in addition to London forces, whereas only London forces act between Ar atoms oe **B1**

(c) for molecules/atoms of similar Mr, the additional dipole-dipole forces are stronger overall than London forces alone, so more energy is needed to separate HCl molecules, giving a higher boiling point oe **B1**

(c) Answer: HCl has permanent dipole-dipole forces (from its polar bond) in addition to London forces, which are stronger overall than the London forces alone acting between non-polar Ar atoms, giving HCl a higher boiling point.

(d) calculates the difference in boiling point: -85 - (-186) = 101 C **M1**

(d) concludes that despite Ar having the greater Mr (and so stronger London forces alone), HCl boils 101 C higher, showing that permanent dipole-dipole forces make a significant additional contribution to intermolecular attraction in HCl oe **A1**

(d) Answer: HCl boils 101 C higher than Ar, showing the extra dipole-dipole forces in HCl contribute significantly more attraction than London forces alone.

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Question 3

(a) a hydrogen atom must be covalently bonded directly to a small, highly electronegative atom: nitrogen, oxygen or fluorine (N, O or F) oe **B1**

(a) the electronegative atom (N, O or F) must have at least one lone pair of electrons available oe **B1**

(a) the hydrogen bond forms between the delta+ hydrogen on one molecule and a lone pair on the N, O or F atom of a neighbouring molecule oe **B1**

(a) Answer: H must be bonded directly to N, O or F; that atom must have a lone pair; the hydrogen bond forms between the delta+ H and a lone pair on N/O/F of a neighbouring molecule.

(b) the delta+ hydrogen atom of one water molecule is attracted to a lone pair on the delta- oxygen atom of a neighbouring water molecule oe **B1**

(b) the hydrogen bond acts as a roughly linear, weak attraction (often shown as a dotted/dashed line) between the H and the lone pair, O-H...O oe **B1**

(b) Answer: The delta+ H of one water molecule is attracted to a lone pair on the delta- O of a neighbouring molecule, forming a roughly linear O-H...O hydrogen bond.

(c) in ice, hydrogen bonds hold water molecules in a rigid, open lattice, with each molecule hydrogen bonded to four neighbours oe **M1**

(c) this rigid, open structure creates more empty space between the molecules than in the liquid oe **M1**

(c) in liquid water, hydrogen bonds are constantly breaking and reforming, allowing molecules to pack more closely together, so liquid water is denser than ice oe **A1**

(c) Answer: Ice has a rigid, open hydrogen-bonded lattice with more space between molecules than liquid water, where molecules can pack more closely, making ice less dense.

(d) uses volume = mass / density for a fixed mass (e.g. 1 g): volume of water = 1/1.000 = 1.000 cm^3 **M1**

(d) volume of ice = 1/0.917 = 1.091 cm^3 (awrt 1.09) **M1**

(d) increase in volume = 1.091 - 1.000 = 0.091 cm^3 **M1**

(d) percentage increase = (0.091/1.000) x 100 = 9.1% (accept awrt 9.0-9.1%) cao **A1**

(d) Answer: Approximately 9.1% increase in volume (accept 9.0-9.1%).

Question 4

(a) Al^{3+} is a small ion with a high (3+) charge, so it has a high charge density (high polarising power) oe **M1**

(a) Cl^- is a relatively large ion, so its electron cloud is polarisable (easily distorted) oe **M1**

(a) the small, highly charged Al^{3+} ion distorts (polarises) the electron cloud of the Cl^- ion, pulling electron density towards itself oe **M1**

(a) this distortion means electron density is shared between the ions, giving the Al-Cl bond significant covalent character oe **A1**

(a) Answer: Al^{3+} has high charge density and strongly polarises the large, polarisable Cl^- ion, distorting its electron cloud and sharing electron density, giving the bond significant covalent character.

(b) AlF_3 has the greater ionic character **B1**

(b) correct reason: F^- is smaller and less polarisable than Cl^- (its electron cloud is held more tightly), so Al^{3+} causes less distortion, and the bonding remains closer to purely ionic oe **B1**

(b) Answer: AlF_3 has the greater ionic character, because F^- is smaller and less polarisable than Cl^-, so it is less distorted by Al^{3+}.

(c) a dimer, Al_2Cl_6 (two $AlCl_3$ units joined together) oe **B1**

(c) Answer: It exists as the dimer Al_2Cl_6.

(d) a chlorine atom on one $AlCl_3$ unit uses one of its lone pairs of electrons to form a new bond, donated to the aluminium atom of the neighbouring $AlCl_3$ unit, which has an empty orbital (only 6 electrons around Al in $AlCl_3$, an incomplete octet) oe **M1**

(d) two such dative bonds form (from two bridging chlorine atoms), joining the two $AlCl_3$ units into the dimer Al_2Cl_6 oe **A1**

(d) Answer: A lone pair from a Cl atom on one $AlCl_3$ unit is donated into the empty orbital on the Al atom of the other unit; two such dative bonds (bridging chlorines) form the Al_2Cl_6 dimer.

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Question 5

(a) in the adduct, boron now has four bonding pairs of electrons around it: the three original B-F bonds plus the new dative B<-N bond oe **M1**

(a) boron has four bonding pairs and no lone pairs oe **M1**

(a) the shape around boron becomes tetrahedral (bond angles approximately 109.5 degrees), rather than the trigonal planar (120 degree) shape in BF_3 itself oe **A1**

(a) Answer: Tetrahedral (bond angles approximately 109.5 degrees), because boron now has four bonding pairs and no lone pairs.

(b) boron has only three electrons in its outer shell (Group 13), so after forming three covalent bonds to fluorine it has only six electrons around it, an incomplete octet oe **M1**

(b) this leaves an empty orbital on boron, which can accept the lone pair of electrons donated by the nitrogen atom of NH_3, allowing the dative bond to form oe **A1**

(b) Answer: Boron has only 6 electrons around it in BF_3 (incomplete octet), leaving an empty orbital that can accept the nitrogen lone pair, forming the dative bond.

(c) because nitrogen's lone pair is now used in the dative bond to boron, it is no longer available to accept hydrogen bonds from the N-H hydrogens of neighbouring adduct molecules oe **M1**

(c) so the adduct cannot hydrogen bond extensively between its own molecules, and its volatility (boiling point) would be expected to be similar to other simple molecular compounds of comparable Mr (governed mainly by London and permanent dipole-dipole forces), rather than being anomalously raised as it would be if the lone pair were still free oe **A1**

(c) Answer: With the N lone pair used in the dative bond, the adduct molecules cannot hydrogen bond extensively to each other, so its volatility should resemble that of a similar-Mr compound relying on London/dipole-dipole forces, not an anomalously high-boiling hydrogen-bonded compound.

(d) nitrogen still has a lone pair available in $N(CH_3)_3$ (as in NH_3), so a dative bond to boron can still form oe **M1**

(d) the bulkier CH_3 groups increase the Mr, surface area and number of electrons of the molecule, increasing the strength of the London forces between adduct molecules, which would tend to raise the melting point of $F_3B\text{-}N(CH_3)_3$ compared with $F_3B\text{-}NH_3$ oe **A1**

(d) Answer: The dative bond still forms (N retains its lone pair), but the bulkier methyl groups increase Mr and London forces between molecules, tending to raise the melting point compared with $F_3B\text{-}NH_3$.

Question 6

(a) CO_2 has a simple molecular (covalent) structure: discrete, linear CO_2 molecules held together in the solid by weak van der Waals forces, oe **B1**

(a) SiO_2 has a giant covalent (macromolecular) structure in which every Si atom is covalently bonded to four O atoms (and every O atom to two Si atoms), forming a continuous, extended three-dimensional network, oe **B1**

(a) Answer: CO_2 is simple molecular; SiO_2 is giant covalent.

(b) subliming CO_2 only requires overcoming the weak van der Waals forces between molecules; the strong covalent C=O bonds within each molecule are not broken, oe **B1**

(b) melting SiO_2 requires breaking a very large number of strong covalent Si-O bonds throughout the giant covalent lattice, oe **B1**

(b) it is the type of force overcome (many strong covalent bonds throughout a lattice, versus weak van der Waals forces between separate molecules) that determines the melting/sublimation point, not the strength of one individual bond, oe **B1**

(b) so far more energy overall is required to melt SiO_2 than to sublime CO_2, giving SiO_2 its vastly higher melting point, oe **B1**

(b) Answer: Melting SiO_2 breaks many strong covalent bonds throughout a lattice, while subliming CO_2 only overcomes weak van der Waals forces between molecules.

(c) recognise that 4 mol of Si-O bonds must be broken per mole of SiO_2 **M1**

(c) correct substitution: 4 x 466 **M1**

(c) 1864 kJ/mol (accept 1860-1870), cao **A1**

(c) this is only an estimate because an average bond enthalpy assumes every Si-O bond in the lattice has identical strength/environment, which is not exactly true in the real crystal, oe **B1**

(c) Answer: Approximately 1864 kJ/mol; the value uses an average bond enthalpy, which assumes every Si-O bond is identical.

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Question 7

(a) the magnitude increases as the product of the ionic charges increases, oe **B1**

(a) the magnitude increases as the sum of the ionic radii decreases (the ions get closer together), oe **B1**

(a) Answer: Magnitude increases with greater ionic charge and with smaller sum of ionic radii.

(b) MgO: 212 pm **B1**

(b) CaO: 240 pm **B1**

(b) SrO: 258 pm **B1**

(b) Answer: MgO = 212 pm, CaO = 240 pm, SrO = 258 pm.

(c) recognise that, with the charge product constant, lattice enthalpy magnitude is approximately inversely related to r+ + r-, i.e. it decreases as r+ + r- increases **M1**

(c) correct order: MgO (most exothermic) > CaO > SrO (least exothermic) **A1**

(c) MgO has the smallest sum of ionic radii, so its ions can approach most closely, giving the strongest electrostatic attraction between oppositely charged ions and hence the most exothermic lattice enthalpy, oe **B1**

(c) Answer: MgO more exothermic than CaO, which is more exothermic than SrO.

(d) correct substitution: 212/240 **M1**

(d) 0.88 (cao, 2 sf), so the lattice enthalpy of CaO is predicted to be about 88% of the magnitude of that of MgO **A1**

(d) Answer: 0.88; CaO's lattice enthalpy magnitude is predicted to be about 88% of MgO's.

Question 8

(a) convert 564.0 pm to cm: 5.640×10^{-8} cm **M1**

(a) cube the edge length: $(5.640 \times 10^{-8})^3$ **M1**

(a) cso: 1.79×10^{-22} cm^3 (3 sf), as required **A1**

(a) Answer: 1.79×10^{-22} cm^3 (shown)

(b) correct identification of Z = 4 and M = 58.5 g/mol in the formula **M1**

(b) correct substitution: $(4 \times 58.5) / (6.02 \times 10^{23} \times 1.79 \times 10^{-22})$ **M1**

(b) 2.17 g/cm^3 (accept 2.16-2.17), cao **A1**

(b) Answer: 2.17 g/cm^3

(c) percentage uncertainty in a = (2/564.0) x 100 **M1**

(c) recognise percentage uncertainty in density = 3 x percentage uncertainty in a **M1**

(c) 1.1% (accept 1.0-1.1%), cao **A1**

(c) Answer: Approximately 1.1%

(d) absolute uncertainty = (1.1/100) x 2.17 **M1**

(d) 0.02 g/cm^3 (accept 0.02-0.03) **A1**

(d) density = (2.17 ± 0.02) g/cm^3, with the uncertainty quoted to the same number of decimal places as the density **B1**

(d) Answer: (2.17 ± 0.02) g/cm^3

Question 9

Level 3 A detailed and accurate comparison of the structure and bonding in ice and dry ice, correctly identifying the intermolecular forces present in each, with a clear and correct explanation of the large difference in melting/sublimation point. The answer is coherent and logically structured, using appropriate scientific terminology throughout. **5-6**

Level 2 A mostly correct comparison of structure and/or bonding in ice and dry ice, with a partially correct explanation of the temperature difference. There may be a minor inaccuracy or an underdeveloped link between structure/bonding and the observed properties. The answer shows some structure. **3-4**

Level 1 Some relevant, briefly stated points about the structure or bonding of ice and/or dry ice are given, but these are not linked into a coherent comparison or explanation of the temperature difference. **1-2**

Indicative content:

- Both ice and dry ice are simple molecular (covalent) lattices; the covalent bonds within each molecule (O-H in water, C=O in CO_2) are not broken when the solid melts or sublimes.
- CO_2 is a linear, non-polar molecule (the two C=O bond dipoles cancel by symmetry), so the only forces between CO_2 molecules in dry ice are relatively weak van der Waals (London/induced dipole-dipole) forces.
- In ice, each water molecule can form hydrogen bonds to up to four neighbouring water molecules (via its two O-H bonds and two oxygen lone pairs), in addition to van der Waals forces.
- Hydrogen bonds are considerably stronger than the van der Waals forces present in dry ice, so significantly more energy is needed to separate water molecules from the ice lattice than to separate CO_2 molecules from the dry ice lattice.
- This explains why ice has a much higher melting point (0°C) than the sublimation point of dry ice (-78°C): far less energy is needed to overcome the weak van der Waals forces in dry ice than to overcome the extensive hydrogen-bonded network (plus van der Waals forces) in ice.

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