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Topic 2.7: VSEPR and Hybridization

Worksheet · AP Chemistry

Unit 2 · Compound Structure and Properties

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How to Use This Worksheet

Work through the sections in order. Section A checks the ideas, Section B builds fluency with individual molecules and ions, and Section C mixes geometry, hybridization, bonding and polarity the way an exam would.

For every central atom, use the same working sequence and write down every step: count the bonding domains, count the lone pairs, add them to get the total electron domains, name the electron geometry, name the molecular geometry, state the expected bond angle, and only then assign hybridization. A double or triple bond is one bonding domain, and a lone pair is one domain.

Do not look at the answer key until you have attempted every question. The key gives full working, so compare your method, not just your final answer.

Section A: Recall and Concepts

A1. Define an electron domain. Explain why a double bond and a triple bond each count as only one domain, and apply the definition to the carbon atom in CO_2: state its domains, electron geometry, molecular geometry and bond angle.

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A2. Distinguish electron geometry from molecular geometry. Use NH_3 to show how one species can have a tetrahedral electron geometry but a trigonal pyramidal molecular geometry, and state its total domains and approximate H-N-H bond angle.

A3. State the order of repulsion between lone pairs and bonding pairs, strongest first. Then rank CH_4, NH_3 and H_2O in order of increasing bond angle, giving the domain count, molecular geometry and approximate angle of each.

A4. Complete the hybridization pattern for two, three and four electron domains: for each, state the hybridization, the electron geometry and the ideal bond angle. Then explain why the oxygen atom in H_2O is sp^3 even though the molecular geometry of water is bent.

A5. State the sigma and pi composition of a single bond, a double bond and a triple bond. Explain why a sigma bond is stronger than a pi bond and why a pi bond restricts rotation, using the carbon atoms of ethene as your example: include their domains, geometry and approximate bond angles.

Section B: Core Practice

B1. The chlorate ion, ClO_3^-, has chlorine bonded to three oxygen atoms, with one lone pair on chlorine. One resonance contributor gives chlorine one double bond and two single bonds. (a) Count the bonding domains, lone pairs and total electron domains on chlorine. (b) State the electron geometry, the molecular geometry and the approximate Cl-O bond angles. (c) State the hybridization of chlorine.

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B2. Sulfur dioxide, SO_2, is drawn with sulfur bonded to two oxygen atoms and one lone pair on sulfur; its resonance contributors swap a double bond between the two S-O positions. (a) Count the electron domains on sulfur. (b) State the electron geometry, the molecular geometry and the approximate O-S-O bond angle. (c) State the hybridization of sulfur, and explain why resonance does not change any of your answers.

B3. Compare CO_2 and BF_3. (a) For each central atom, count the electron domains and state the electron geometry, molecular geometry, bond angle and hybridization. (b) Both molecules contain polar bonds. Determine whether each molecule is polar or nonpolar, and justify each answer using its geometry.

B4. Xenon tetrafluoride, XeF_4, has xenon bonded to four fluorine atoms, with two lone pairs on xenon. (a) Count the electron domains on xenon. (b) State the electron geometry and the molecular geometry, and explain where the two lone pairs sit. (c) State the F-Xe-F bond angles in the molecular geometry. (d) State whether an sp, sp^2 or sp^3 label should be assigned to xenon in the AP Chemistry CED treatment, and why.

B5. Ethene, C_2H_4, has each carbon bonded to two hydrogen atoms and double bonded to the other carbon. (a) For one carbon atom, count the electron domains and state the electron geometry, the molecular geometry around that carbon, the approximate bond angles and the hybridization. (b) Count the total sigma and pi bonds in the whole molecule. (c) Explain why rotation about the C=C bond is restricted.

B6. Acetic acid, CH_3COOH, contains a methyl carbon bonded to three hydrogens and to the second carbon, and a carbonyl carbon bonded to the methyl carbon, double bonded to one oxygen and single bonded to the other oxygen. Neither carbon carries a lone pair. (a) Analyse the methyl carbon: domains, electron geometry, molecular geometry, bond angle and hybridization. (b)

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Analyse the carbonyl carbon: domains, electron geometry, molecular geometry, bond angle and hybridization. (c) State the sigma and pi composition of the C=O bond.

Section C: Exam Style

C1. Hydrogen cyanide, HCN, has the connectivity H-C≡N, and nitrogen carries one lone pair. Nitrogen gas, N_2, has a triple bond and one lone pair on each nitrogen. (a) For the carbon atom in HCN, count the electron domains and state the electron geometry, molecular geometry, bond angle and hybridization. (b) For each nitrogen atom in N_2, count the electron domains and state the hybridization. State the bond angle situation for a diatomic molecule. (c) State the sigma and pi composition of each triple bond, and explain what that composition means for rotation about the bond.

C2. Sulfur hexafluoride, SF_6, bromine pentafluoride, BrF_5, and xenon tetrafluoride, XeF_4, all have six electron domains around the central atom. SF_6 has no lone pair, BrF_5 has one lone pair, and XeF_4 has two lone pairs. (a) State the electron geometry shared by all three species. (b) State the molecular geometry of each species, explaining the lone pair placements in BrF_5 and XeF_4. (c) State the ideal bond angles for SF_6, and explain how the lone pair changes the angles in BrF_5 and in XeF_4. (d) A student labels all three central atoms sp^3d^2. State how this should be handled in AP Chemistry CED terms.

C3. A student makes three claims about CH_4, NH_3 and H_2O: (1) all three central atoms have the same electron geometry and the same hybridization; (2) all three molecules have the same molecular geometry; (3) all three bond angles equal 109.5°. (a) Evaluate claim (1): give the domain count, electron geometry and hybridization of the central atom in each species. (b) Evaluate claim (2): state the molecular geometry of each species. (c) Evaluate claim (3): state the approximate

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bond angle in each species and explain the order using lone pair repulsion. (d) State which of the three molecules are polar and which is nonpolar, justifying each answer from its geometry.

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Answer Key

A1. An electron domain is one region of electron density around an atom: one bond of any order, or one lone pair. A double or triple bond places its shared electrons in the same region, along the same direction from the central atom, so it counts once even though it contains more electrons than a single bond. In CO_2 the carbon has two bonding domains (the two C=O bonds) and no lone pair, a total of 2 electron domains. Its electron geometry is linear, its molecular geometry is also linear because there are no lone pairs, and the O-C-O bond angle is 180°.

A2. Electron geometry is the arrangement of all electron domains, bonding and nonbonding. Molecular geometry is the arrangement of the bonded atoms only, with lone pairs left out of the description. In NH_3 nitrogen has three N-H bonding domains and one lone pair, a total of 4 electron domains, arranged tetrahedrally, so the electron geometry is tetrahedral. Only the three hydrogen atoms are counted in the molecular geometry, and three atoms at the base of a pyramid with nitrogen at the apex give a trigonal pyramidal molecular geometry. The lone pair compresses the H-N-H bond angle from the ideal 109.5° to about 107°.

A3. The repulsion order, strongest first, is lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair, because a lone pair is held by one nucleus only and its density spreads closer to the central atom. All three species have 4 electron domains and tetrahedral electron geometry, so the differences come only from lone pairs. CH_4 has no lone pair, a tetrahedral molecular geometry and an angle of 109.5°. NH_3 has one lone pair, a trigonal pyramidal molecular geometry and an angle of about 107°. H_2O has two lone pairs, a bent molecular geometry and an angle of about 104.5°. Increasing bond angle: H_2O (about 104.5°) < NH_3 (about 107°) < CH_4 (109.5°).

A4. Two electron domains: sp hybridization, linear electron geometry, ideal angle 180°. Three electron domains: sp^2 hybridization, trigonal planar electron geometry, ideal angle 120°. Four electron domains: sp^3 hybridization, tetrahedral electron geometry, ideal angle 109.5°. Hybridization is set by the total domain count, not by the molecular geometry name. The oxygen in H_2O has two O-H bonding domains and two lone pairs, a total of 4 electron domains, so it is sp^3 and its electron geometry is tetrahedral. Its molecular geometry is bent, with an H-O-H angle of about 104.5°, because only the two hydrogen atoms are counted once the lone pairs are set aside.

A5. A single bond is 1 sigma bond. A double bond is 1 sigma bond and 1 pi bond. A triple bond is 1 sigma bond and 2 pi bonds. A sigma bond forms by overlap along the internuclear axis, directly between the nuclei; a pi bond forms by side to side overlap of unhybridized p orbitals, which is less direct, so an individual pi bond is weaker than an individual sigma bond. Rotating one atom of a pi bonded pair about the bond axis would twist the p orbitals out of alignment and break the pi overlap, so rotation is restricted. In ethene each carbon has 3 electron domains (two C-H bonds and the C=C bond counted once), a trigonal planar electron geometry and a trigonal planar

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arrangement of its three bonded atoms, approximate bond angles of 120°, and sp^2 hybridization; the C=C bond itself is 1 sigma bond and 1 pi bond.

B1. (a) Chlorine has three bonding domains, one to each oxygen; whether a bond is drawn single or double does not change the count. It also has one lone pair. Total electron domains: 3 + 1 = 4. (b) Four domains give a tetrahedral electron geometry. Counting only the three oxygen atoms gives a trigonal pyramidal molecular geometry, the same pattern as NH_3. The lone pair compresses the O-Cl-O bond angles below the ideal tetrahedral value, to about 107°. (c) Four electron domains mean chlorine is sp^3 hybridized.

B2. (a) Sulfur has two bonding domains and one lone pair, a total of 3 electron domains. (b) Three domains give a trigonal planar electron geometry. Counting only the two oxygen atoms gives a bent molecular geometry. The lone pair repels the two bonding domains, so the O-S-O bond angle is a little less than the ideal 120°, about 119°. (c) Three electron domains mean sulfur is sp^2 hybridized. Resonance swaps which S-O bond is drawn double, but in every contributor sulfur still has two bonding domains and one lone pair, so the domain count, both geometries, the angle and the hybridization are unchanged.

B3. (a) In CO_2 carbon has 2 electron domains (two double bonds, no lone pair): linear electron geometry, linear molecular geometry, bond angle 180°, sp hybridization. In BF_3 boron has 3 electron domains (three single bonds, no lone pair): trigonal planar electron geometry, trigonal planar molecular geometry, bond angles 120°, sp^2 hybridization. (b) CO_2 is nonpolar: its two polar C=O bond dipoles are equal and point in exactly opposite directions along the linear geometry, so they cancel. BF_3 is also nonpolar: its three polar B-F bond dipoles are equal, arranged symmetrically at 120° in the trigonal planar geometry, so they cancel. Neither molecule is polar; in both, polar bonds are arranged so symmetrically that no net dipole survives.

B4. (a) Xenon has four bonding domains and two lone pairs, a total of 6 electron domains. (b) Six domains give an octahedral electron geometry. The two lone pairs sit opposite each other, above and below the plane of the four fluorine atoms, because that placement keeps the strongest lone pair-lone pair repulsion as far apart as possible, at 180°. Counting only atoms, the molecular geometry is square planar. (c) In the square planar molecular geometry, adjacent F-Xe-F bond angles are 90° and opposite F-Xe-F angles are 180°. (d) No sp, sp^2 or sp^3 label is assigned. The CED hybridization sequence covers two, three and four domains only; the geometry of XeF_4 is justified by its 6 electron domains, octahedral electron geometry and opposite lone pairs, not by a d orbital hybrid label.

B5. (a) Each carbon has three bonding domains: two C-H single bonds and the C=C double bond counted once. It has no lone pair, so the total is 3 electron domains. The electron geometry is trigonal planar, the arrangement of the three bonded atoms around the carbon is also trigonal planar, the bond angles are approximately 120°, and the carbon is sp^2 hybridized. (b) Sigma bonds: four C-H bonds contribute 4, and the C=C bond contributes 1, for a total of 5 sigma bonds. Pi

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bonds: the C=C bond contributes 1. Ethene therefore has 5 sigma bonds and 1 pi bond. (c) The pi bond is made by side to side overlap of the unhybridized p orbitals on the two carbons, one above and one below the plane of the molecule. Rotating one carbon about the C=C axis would misalign those p orbitals and break the pi bond, so rotation is restricted; the sigma bond alone, by contrast, is symmetrical about the axis and would allow rotation.

B6. (a) The methyl carbon has four bonding domains (three C-H bonds and one C-C bond) and no lone pair, a total of 4 electron domains. Its electron geometry is tetrahedral, its molecular geometry is tetrahedral, its bond angles are about 109.5°, and it is sp^3 hybridized. (b) The carbonyl carbon has three bonding domains (the C-C bond, the C=O double bond counted once, and the C-O bond) and no lone pair, a total of 3 electron domains. Its electron geometry is trigonal planar, its molecular geometry is trigonal planar, its bond angles are about 120°, and it is sp^2 hybridized. (c) The C=O double bond contains 1 sigma bond and 1 pi bond.

C1. (a) The carbon in HCN has two bonding domains, the C-H single bond and the C≡N triple bond counted once, and no lone pair: 2 electron domains. Its electron geometry is linear, the molecular geometry is linear, the H-C-N bond angle is 180°, and carbon is sp hybridized. (b) Each nitrogen in N_2 has two electron domains, the triple bond counted once plus one lone pair. Two domains mean sp hybridization, with the bond domain and the lone pair arranged 180° apart. A diatomic molecule has no bond angle, because a bond angle needs three atoms; the 180° figure describes the arrangement of the two domains on each nitrogen, not an angle inside the molecule. (c) Each triple bond contains 1 sigma bond and 2 pi bonds. The two pi bonds are formed by side to side overlap of two pairs of unhybridized p orbitals. Rotation about the bond would break that side to side overlap, so the pi bonds restrict rotation; only the sigma bond, symmetrical about the internuclear axis, is compatible with turning.

C2. (a) All three have 6 electron domains, so all three share an octahedral electron geometry. (b) SF_6 has six bonding domains and no lone pair, so its molecular geometry is also octahedral. BrF_5 has five bonding domains and one lone pair; the lone pair occupies one octahedral position, leaving five fluorine atoms in a square pyramidal molecular geometry. XeF_4 has four bonding domains and two lone pairs; the lone pairs sit opposite each other, 180° apart, leaving four fluorine atoms in one plane, a square planar molecular geometry. (c) In SF_6 the ideal bond angles are 90° between adjacent bonds and 180° between opposite bonds. In BrF_5 the lone pair pushes the four basal fluorine atoms away from itself, so the angles between the axial bond and the basal bonds fall below the ideal 90°. In XeF_4 the two lone pairs are opposite and their effects on the plane cancel symmetrically, so the square planar angles stay at the ideal 90° and 180°. (d) The sp^3d^2 label should not be used. In AP Chemistry CED terms, hybridization labels run from sp for two domains to sp^2 for three and sp^3 for four; five and six domain structures are explained by electron domain repulsion and lone pair placement within the octahedral or trigonal bipyramidal electron geometry, without assigning d orbital hybridization.

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C3. (a) Claim (1) is correct. CH_4: carbon has four bonding domains and no lone pair, 4 electron domains, tetrahedral electron geometry, sp^3. NH_3: nitrogen has three bonding domains and one lone pair, 4 electron domains, tetrahedral electron geometry, sp^3. H_2O: oxygen has two bonding domains and two lone pairs, 4 electron domains, tetrahedral electron geometry, sp^3. The hybridization follows the total domain count in all three. (b) Claim (2) is wrong. CH_4 is tetrahedral, because all four domains are bonds. NH_3 is trigonal pyramidal, because one of its four domains is a lone pair and only three atoms are counted. H_2O is bent, because two of its four domains are lone pairs and only two atoms are counted. (c) Claim (3) is wrong. CH_4 has no lone pair, so its angle stays at the ideal 109.5°. NH_3 has one lone pair, whose repulsion exceeds bonding pair repulsion, compressing the H-N-H angle to about 107°. H_2O has two lone pairs, and lone pair-lone pair repulsion is the strongest of all, compressing the H-O-H angle furthest, to about 104.5°. The angle order is CH_4 > NH_3 > H_2O. (d) CH_4 is nonpolar: its four bonds are arranged symmetrically in a tetrahedron, so any small bond dipoles cancel. NH_3 is polar: its trigonal pyramidal geometry points the three N-H bond dipoles to the same side of the molecule, so they add to a net dipole. H_2O is polar: its bent geometry means the two O-H bond dipoles cannot cancel, so they add to a net dipole.

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