Inorganic Chemistry with Doc M.

Day 5. Fast-track Symmetry and Point Groups (a quick and pragmatic intro)

Topics:

1. Symmetry operations
   identity, proper rotation, principle rotation axis, reflection planes, inversion center
2. Point groups: The C_{nv} groups, D_{nh} groups
3. Point groups and ABE formulas
4. Point groups with very high or low symmetry

1. Symmetry operations

A. Identity. Everything has an identity symmetry element! The mystery is why I-dentity is abbreviated E!

B. C_n is the proper rotation axis. Consider the rotation of a molecule. If you can rotate it 120^o and get the same appearance to your molecule, the proper rotation is C_n where n = 360/amount of rotation. Build the following molecules using the gumdrops and toothpicks provided. Identify the rotation axes for each of these species.

Our work	Corrected answer (if necessary after discussion)
a. SO_3 (trigonal planar) *one C_3 (2 if counting cw and ccw) and three C_2*	
b. OH_2	
c. NH_3	
d. IF_7 (pentagonal bipyramid)	
e. XeF_4 (square planar)	
f. BrF_5(square pyramid)	
g. HCl	
h. CO_2	

C. The principle rotation axis is the one with the highest n value and is always defined as the z-axis. For SO_3, the principle rotation axis is C_3. Identify the principle rotation axis for each of these.

Our work	Corrected answer (if necessary after discussion)
a. SO_3 *C_3*	
b. OH_2	
c. NH_3	
d. IF_7	
e. XeF_4	
f. BrF_5	
g. HCl	
h. CO_2	

D. Reflection planes

- σ_v This plane contains the principle rotation axis and there are usually ***n*** of them (e.g., SO_3 would have three.)
- σ_h This plane is perpendicular to the principle rotation axis and there are usually zero or one of them, but never more than one.

Using your models, complete the following tables for σ_v and σ_h. When the mirror plane exists, state how many there are.

Molecule:	σ_v	σ_h	σ_d
a. SO_3	*yes, 3*	*yes, 1*	
b. OH_2			
c. NH_3			
d. IF_7			
e. XeF_4			
f. BrF_5			
g. HCl			
h. CO_2			

- σ_d This plane usually occurs between two σ_v planes. It is often not present. Assess the molecules above for σ_d planes.

E. Inversion center. This is an odd duck! Picture your molecule imploding through its center point and coming out completely inverted from whence it started. If you get the same thing back with no atoms seemingly having moved, the beast has an inversion center, ***i***.

Our work	**Corrected answer (if necessary after discussion)**
a. SO_3	
b. OH_2	
c. NH_3	
d. IF_7	
e. XeF_4	
f. BrF_5	
g. HCl	
h. CO_2	

2. Point groups: The C_{nv} groups, D_{nh} groups

In the real world, including the world of polyatomic molecules and ions, objects have one or more symmetry elements. They often occur in groups. For example, the rotation C_2 will always have a mirror plane of some sort. Interestingly, there are only a limited number of combinations of symmetry elements and these combinations are called ***point groups*** and I'm sure there is a reason why...

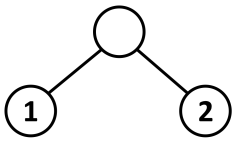
Point groups tend to be of three general types: those with very high symmetry, those with very low symmetry and those in between. A sphere and a circle are examples of very high symmetry and so are the Cartesian coordinate system (octahedron) and the tetrahedron. A clump of dirt or a crumpled up piece of paper are examples of things with very low symmetry. Most of the molecules we've been working with are in between.

Since this guide is a pragmatic approach designed to teach you as much as fast as possible with little regard for nuance and subtleties, here are some of the more common point groups and the symmetry elements they contain:

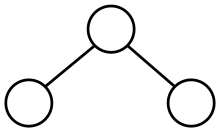
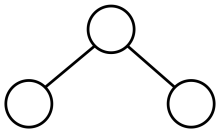
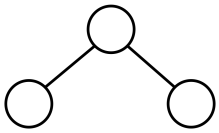
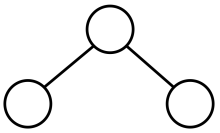
C_{nv} family point groups	**Symmetry elements:**
C_{2v}	E, C_2, σ_v(xz plane), σ_v(yz plane)
C_{3v}	E, two C_3, three σ_v
C_{4v}	E, two C_4, C_2, two σ_v, two σ_d
C_{5v}	E, two C_5, two C_5^2, five σ_v
C_{6v}	
C_{7v}	

D_{nh} family point groups	**Symmetry elements:**
D_{2h}	E, C_2(z), C_2(y), C_2(x), i, σ_v(xy), σ_v(xz), σ_v(yz)
D_{3h}	E, two C_3, three C_2, σ_h two S_3, three σ_v
D_{4h}	E, two C_4, C_2(z-axis), two C_2', two C_2'', i, two S_4, σ_h, two σ_v, and two σ_d
D_{5h}	

Let's first focus on the C_{nv} family. Water is an example of a molecule with C_{2v} symmetry. Here is a picture of water with the two hydrogens numbered so we can refer to one or the other in our discussion. Sketch in the z-axis. For reference, this sheet of paper is the yz plane, so the x-axis is coming out towards us.

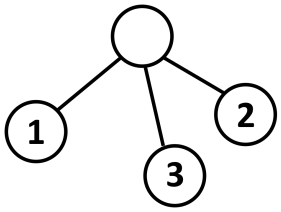


Now, let's see what happens when each of the C_{2v} symmetry *operations* is performed on this molecule. Write the numbers 1 and 2 in each of the hydrogen circles.

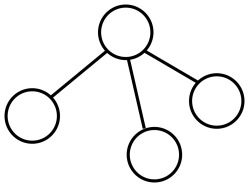
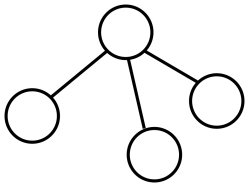
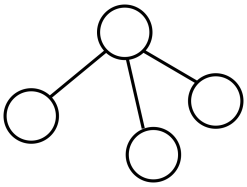
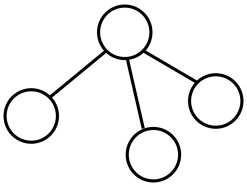
E	C_2	σ_v(xz plane)	σ_v(yz plane)
			

The main point here is that you can perform each of the symmetry operations and still maintain the same arrangement of atoms in space (if the atoms weren't "numbered," we wouldn't see any difference before and after an operation.

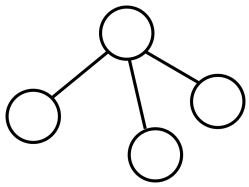
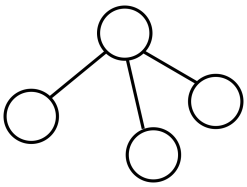
Let's now try a molecule with C_{3v} symmetry such as NH_3. Again, the principle rotation axis, the C_3 axis, is the z-axis. Sketch in the z-axis. For reference, this sheet of paper is the yz plane, so Hydrogen #1 is in the plane, Hydrogen #2 is behind the plane and Hydrogen #3 is in front of the plane. Again, the x-axis is coming out towards us.



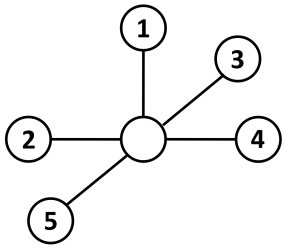
What happens when each of the C_{3v} symmetry operations is performed on ammonia. Write the numbers 1, 2 and 3 in each of the hydrogen circles.

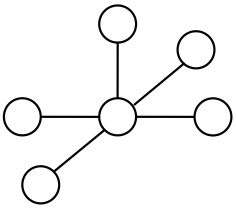
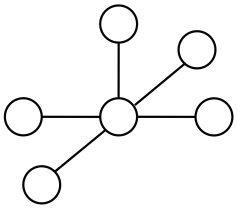
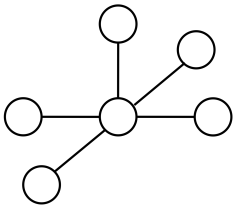
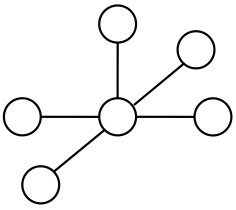
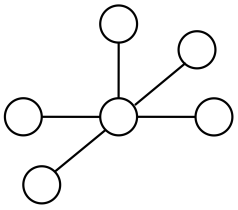
E	C_3 (clockwise rotation)	C_3 (counterclockwise)	σ_v (yz plane)
			

There are two other σ_v reflections. What would each do?

σ_v	σ_v
	

The square pyramid is an example of C_{4v} symmetry. As per the table above, C_{4v} has E, two C_4 rotation axes, a C_2 rotation axis, two σ_v reflection planes, and two σ_d reflection planes.



The E:	One of the two C_4 rotations:	The C_2 rotation:	One of the two σ_v reflection planes:	One of the two σ_d reflection planes:
				

3. Points groups and ABE formulas.

Ok, you are probably wondering, where is the pragmatism promised in the beginning? Here it is: We can relate our ABE formulas to point groups. There are thirteen ABE structural groups all together and six of them are listed of the C_{nv}–type formulas. You will be able to fill in the rest of this table as you work through the rest of this worksheet (in other words, you can go on without filling in anything at the moment.)

The Relationship Between ABE Formulas and Point Groups

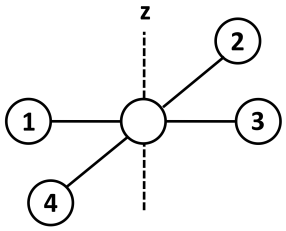
Structural groups	ABE formula	Point Group
2	AB_2	
3	AB_3	
3	AB_2E	C_{2v}
4	AB_4	
4	AB_3E	C_{3v}
4	AB_2E_2	C_{2v}
5	AB_5	
5	AB_4E	C_{2v}
5	AB_3E_2	C_{2v}
5	AB_2E_3	
6	AB_6	
6	AB_5E	C_{4v}
6	AB_4E_2	

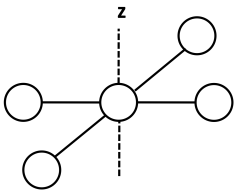
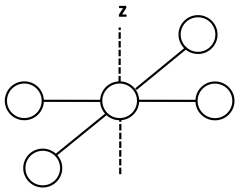
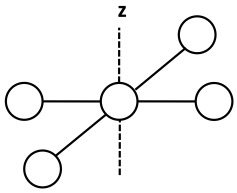
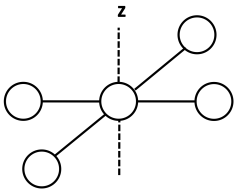
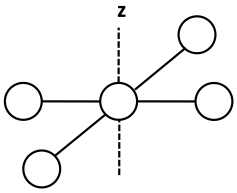
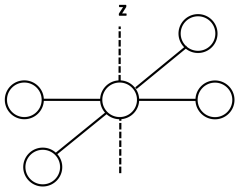
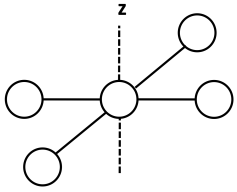
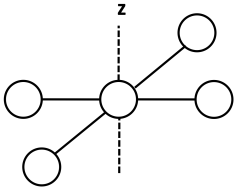
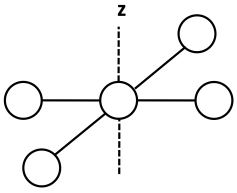
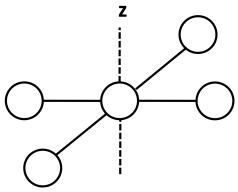
Point groups eventually will make our lives easier! They are used to predict and understand IR and NMR spectra and are used to develop molecular orbital diagrams.

A. The D_{nh} groups.

The C_{nv} point groups covers a lot of ground in terms of the common geometries and ABE formulas! A similarly important family of point groups is the D_{nh} group. The structures AB_3, AB_5, and AB_4E_2 are of this point group family. (Remember that simple molecules of the ABE type (one central element) represent only a small fraction of molecular geometries. For example, benzene is also an example of the D_{nh} group, specifically D_{6h}.)

Square planar molecules of formula AB_4E_2 all belong to the D_{4h} point group and therefore must have all of the symmetry components of the D_{4h} point group. These are: E, two C_4, C_2(z-axis), two C_2' (along x- and y-axes), two C_2'' (between the x- and y-axes), i, two S_4 (we'll discuss), σ_h, two s_v, and two σ_d. Apply these symmetry operations to the following square planar molecule:



E 	Do the clockwise C_4 	C_2 (rotation around z-axis): 	Do the C_2' rotation around the y-axis: 
Do one of the two C_2'' (between the x- and y-axes), 	i 	Do one of the two S_4 (we'll discuss): 	σ_h 
Do either one of the two σ_v: 	Do either one of the two σ_d 	Doodle space	

The most striking difference between the C_{nv} and the D_{nh} point groups is the presence of the horizontal mirror plane, s_h, perpendicular to t he z-axis. ABE structures that have identical tops and

bottoms, that is σ_h mirror planes, belong to the D_{nh} point group. Add the three new D_{nh} point group designations to the table from the previous page:

The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
3	AB_3	
5	AB_5	
6	AB_4E_2	

4. Point groups with very high or low symmetry.

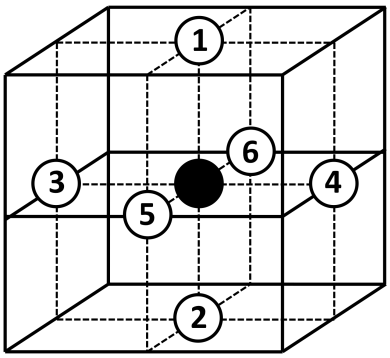
A. Structures with very high symmetry. Molecules and ions with many symmetry elements are easiest just to "spot." There are four of these that we need to be concerned about:

$C_{\infty v}$	linear without σ_h	Example: HCl
$D_{\infty h}$	linear with σ_h	Example: CO_2
T_d	tetrahedron	Example: CH_4
O_h	octahedron	Example: SF_6

Now complete the rest of the table relating ABE formulas to point groups (here and on page 5):

The Relationship Between ABE Formulas and Point Groups

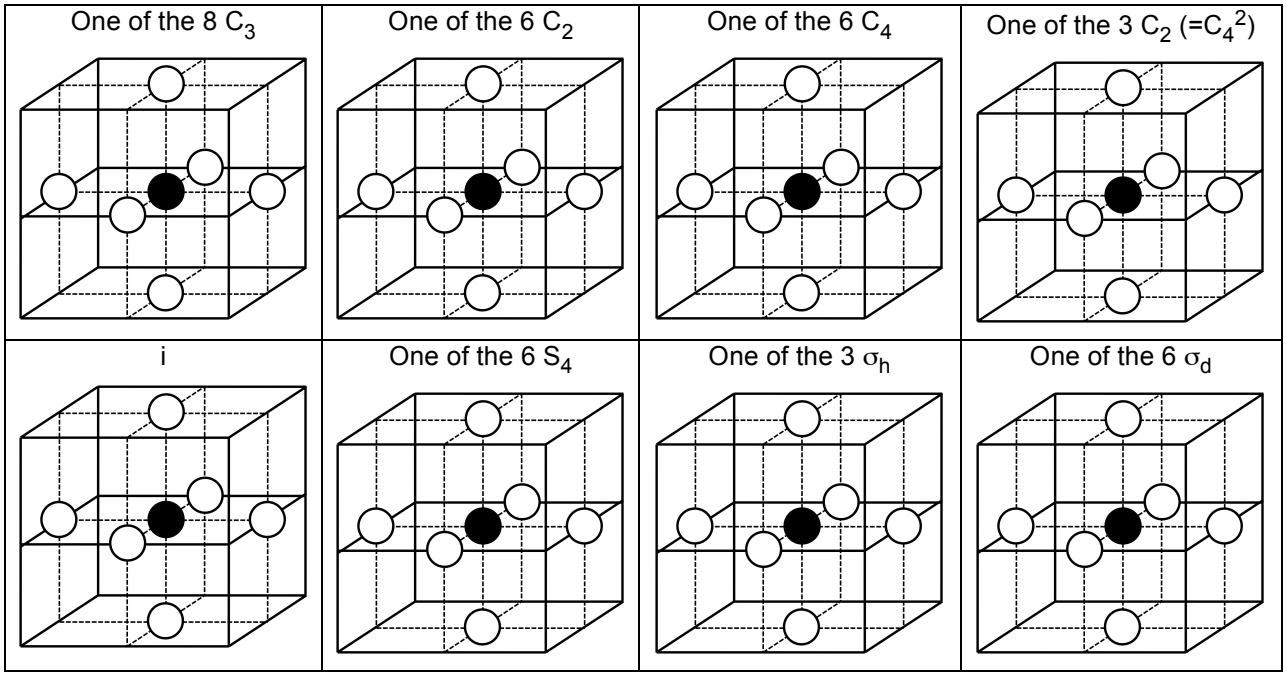
Structural groups	ABE formula	Point Group
2	AB_2	
4	AB_4	
5	AB_2E_3	
6	AB_6	



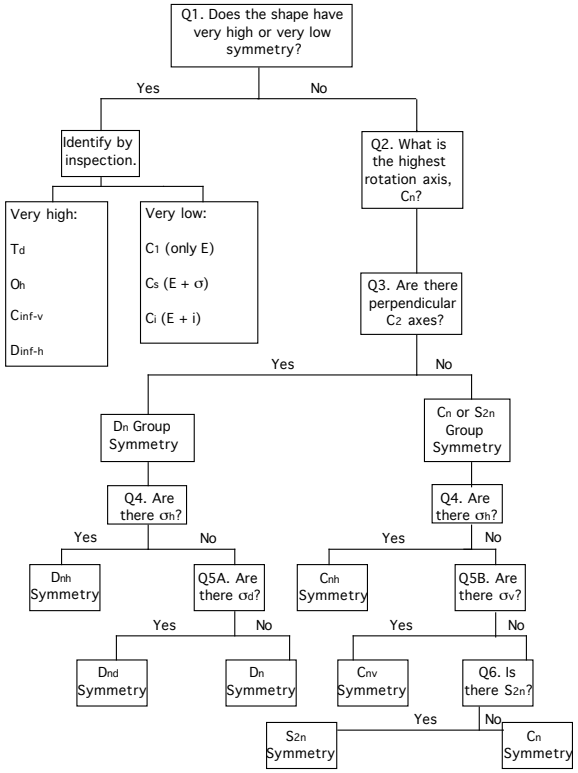
The octahedron. The point group O_h contains 41 symmetry elements (compare to C_{2v} which contained only 4 symmetry elements.) They are E, 8 C_3, 6 C_2, 6 C_4 3 C_2 (=C_4^2), i, 6 S_4, 3 σ_h 6 σ_d. You can find these listed for all point groups as the column headings to the character tables found in Appendix C of our book.

As a "bonus," try to find the various symmetry elements for the

octahedron and (1) sketch the plane or axis being used along with the result. Apply each operation to the octahedral molecule shown at right.



The following flow chart is useful when working with structures other than the straightforward ABE formulas.



Review for ACS Final Exam in Inorganic Chemistry

Symmetry and point groups

1. What is the symmetry point group for cis-$PtBr_2Cl_2^{-2}$? (Hint: square planar)

   (a) D_{2h}

   (b) C_{2v}

   (c) C_{2h}

   (d) D_{4h}

   (e) C_1

2. Which symmetry element is not present in $V(CN)_5(Cl)^{-4}$? (Hint: octahedral)

   (a) C_2

   (b) C_4

   (c) i

   (d) σ_v

   (e) σ_d

3. What is the symmetry point group for BrF_5?

   (a) D_{4h}

   (b) O_h

   (c) D_{3h}

   (d) C_{5v}

   (e) C_{4v}

4. What is the symmetry point group for SF_5Cl?

   (a) D_{4h}

   (b) C_{4v}

   (c) C_{4h}

   (d) D_{4h}

   (e) O_h

Answers: B, C, E, B

Answers to Day 4

2. Intermolecular forces

A. Dipole-dipole forces (3 – 4 kJ/mol)

Molecule	Dipole?	MM (g/mol)	bp (K)
F_2	No	38	85
Cl_2	No	71	239
ClF	Yes	55	172

B. Hydrogen bonding forces (10 - 40 kJ/mol)

Atom	B groups	E-groups	Example
N	3	1	NH_3
O	2	2	H_2O
F	1	3	HF

c. Boiling points of Groups IV, V, VI, and VII hydrides:

Molecule	MM (g/mol)	bp (^oC)	state at 25 ^oC
CH_4	16	-164	gas
SiH_4	32	-112	gas
GeH_4	77	-89	gas

Molecule	MM (g/mol)	bp (^oC)	state at 25 ^oC
NH_3	17	-33	gas
PH_3	34	-87	gas
AsH_3	78	-55	gas
SbH_3	125	-17	gas
BiH_3	212	+22	gas/liquid

Molecule	MM (g/mol)	bp (^oC)	state at 25 ^oC
OH_2	18	100	liquid
SH_2	34	-61	gas
SeH_2	81	-42	gas
TeH_2	130	-2	gas

Molecule	MM (g/mol)	bp (^oC)	state at 25 ^oC
FH	20	+20	gas
ClH	36	-85	gas
BrH	81	-67	gas

C. Instantaneous dipole (London-dispersion) forces (1 – 10 kJ/mol)

Molecule	MM (g/mol)	bp (K)	state at 25 ^oC
F_2	38	85	gas
Cl_2	71	239	gas
Br_2	160	332	liquid
I_2	254	458	solid

Molecule	MM (g/mol)	bp (°C)	state at 25 °C
n-C_5H_{12}	72	36.07	liquid
iso-C_5H_{12}	72	27.85	liquid
neo-C_5H_{12}	72	9.6	gas

3. Predicting physical states at room temperature.

Compound:	Prediction using chart:	Actual mp, bp, phase at room temperature
$AsBr_3$ MM = 315 g/mol	MM > 300 → predict it's a solid	mp = 33 °C bp = 221 °C solid (agrees)
BF_3 MM = 68 g/mol	AB_3 non-polar, MM < 100 → gas	mp = -127 °C bp = -100 °C gas (agrees)
CSe_2 MM = 170 g/mol	AB_2 non-polar, MM: 100 – 200, closer to 200, so → liquid or gas	mp = -46 °C bp = +125 °C liquid (agrees)
CH_3Cl MM = 50.5 g/mol	AB_3B' slightly polar, MM < 100 → gas	mp = -97 °C bp = -24 °C gas (agrees)
NH_4Br MM = 98 g/mol	Ionic → solid	Sublimes 452 °C solid (agrees)
CCl_4 MM = 154 g/mol	AB_4 non-polar, MM: 100 – 200 → predict gas or liquid	mp = -23 °C bp = +77 °C liquid (agrees)
ClO_2 MM = 67.5 g/mol	AB_2E polar, MM < 100 → gas	mp = -60 °C bp = +10 °C gas (agrees)
ClF_3 MM = 92.5 g/mol	AB_3E_2 polar, MM < 100 → gas or liquid	mp = -83 °C bp = +11 °C gas (agrees)
Cl_2O_7 MM = 183 g/mol	Oxygen atom is AB_2E_2 polar, MM: 100 – 200, closer to 200 → liquid or gas	mp = -92 °C bp = +82 °C liquid (agrees)
$(C_2F_4)_n$ MM = 100 g/mol	Polymer → solid	mp = +327 °C bp: none: decomposes solid (agrees)
$PSCl_3$ MM = 169.5 g/mol	AB_3B' slightly polar, MM: 100 - 200 → liquid or gas	mp = -35 °C bp = +125 °C liquid (agrees)
$PSBr_3$ MM = 303 g/mol	MM > 300 → predict it's a solid	mp = +38 °C bp = +212 °C solid (agrees)

Compound:	Prediction using chart:	Actual mp, bp, phase at RT
SCl_2O_2 MM = 135 g/mol	AB_2B_2' slightly polar, MM: 100 - 200 → gas or liquid	mp = -54 °C bp = +69 °C liquid (agrees ?)
$BaCl_2$ MM = 208 g/mol	Ionic → solid	mp = +963 °C bp = +1560 °C solid (agrees)
$GeBr_4$ MM = 392 g/mol	MM > 300 → predict it's a solid	mp = +26 °C bp = +187 °C solid (agrees)
PBr_3 MM = 271 g/mol	AB_3E polar, MM: 200 - 300 → solid or liquid	mp = -40 °C bp = +173 °C liquid (agrees ?)
C_2H_6O, ethanol, C_2H_5OH MM = 46 g/mol	Oxygen atom is AB_2E_2 polar, also hydrogen bonding, MM < 100 → liquid or gas	mp = -117 °C bp = +78 °C liquid (agrees)
C_2H_6O, dimethylether, CH_3OCH_3 MM = 46 g/mol	Oxygen atom is AB_2E_2 polar, no hydrogen bonding, MM < 100 → gas	mp = -141 °C bp = -25 °C gas (agrees)
SiC MM = 43 g/mol	Network covalent → solid	Sublimes at +2700 °C solid (agrees)
PF_3 MM = 88 g/mol	AB_3E polar, MM < 100→ gas or liquid	mp = -102 °C bp = -152 °C gas (agrees)
PF_5 MM = 126 g/mol	AB_5 non-polar, MM: 100 – 200 → gas or liquid	mp = -83 °C bp = -75 °C gas (agrees)
PCl_3 MM = 137.5 g/mol	AB_3E polar, MM: 100 – 200 → gas or liquid	mp = -112 °C bp = +76 °C liquid (agrees ?)
MgO MM = 40.3 g/mol	Ionic → solid	mp = +2800 °C bp = +3600 °C solid (agrees)
Fe MM = 55.9 g/mol	Metallic element → solid	mp = +1535 °C bp = +3000 °C solid (agrees)
$(C_2H_5)_2NH$ MM = 73 g/mol	Nitrogen atom is AB_3E polar, hydrogen bonding, MM < 100 → liquid or gas	mp = -48 °C bp = +56 °C liquid (agrees)
$(CH_3)_2NH$ MM = 45 g/mol	Nitrogen atom is AB_3E polar, hydrogen bonding, MM < 100 → gas or liquid	mp = -93 °C bp = +7.4 °C gas (agrees)
$(CH_3)_3N$ MM = 59 g/mol	Nitrogen atom is AB_3E polar, no hydrogen bonding, MM < 100 → gas or liquid	mp = -117 °C bp = +3 °C gas (agrees)