Inorganic Chemistry with Doc M.

Day 4. Intermolecular forces.

Topics:

1. Classes of bonding within substances
   covalent bonding, ionic bonding, metallic forces, network covalents
2. Intermolecular forces
   dipole-dipole forces, hydrogen-bonding, instantaneous dipoles, ion-dipoles
3. Predicting physical states at room temperature

1. Classes of bonding within substances

A. Covalent bonds

C-C	ΔH = 347 kJ/mol
H-H	ΔH = 431 kJ/mol
F-F	ΔH = 155 kJ/mol

B. Ionic forces (E = Z^+Z^-/r)

$LiF \longrightarrow Li^+(g) + F^-(g)$	ΔH = 755 kJ/mol (reverse of lattice energy)
$LiF \longrightarrow Li(g) + F(g)$	ΔH = 567 kJ/mol

C. Metallic forces (metal cations in a “sea of electrons”: M(s) → M(g))

Fe	ΔH = 416 kJ/mol
W	ΔH = 849 kJ/mol
Pb	ΔH = 195 kJ/mol
Hg	ΔH = 61 kJ/mol (Hg(l) → Hg(g))

D. Network covalent forces (endless lattice of covalent bonds)

C	ΔH = 717 kJ/mol (C(s) → C(g))
Si	ΔH = 450 kJ/mol (Si(s) → Si(g))

2. Intermolecular forces

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

For the polar molecule: the dipole forces is given by μ = qr where q = the equal and opposite charges in the molecule (δ^+, δ^-) and r is the distance between δ^+ and δ^-.

For dipole-dipole forces, $E \propto \frac{-\mu_A \mu_B}{r^3}$

Molecule	Dipole?	MM (g/mol)	bp (K)
F_2		38	85
Cl_2		71	
ClF		55	

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

a. Extra-effective dipole-dipole force that occurs when N-H, O-H and F-H bonds exist.

b. For neutral molecules, oxygen has the optimal balance between bonding groups (potentially hydrogen atoms and electron pair groups; both are required for hydrogen bonding:

Atom	B groups	E-groups	Example
N			NH_3
O			H_2O
F			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		
GeH_4	77		

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

Continued…

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

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

d. Hydrogen bonding occurs in solutions even when only one of the members can actually hydrogen bond. For example, aqueous methanal (formaldehyde, HCHO): the aldehyde has no hydrogen-bonding H, but it has two lone pairs on oxygen that can participate in H-bonding with water's O-H hydrogens.

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

A. Strength of the forces: $E \propto \frac{-IE\alpha^2}{r^6}$ where α is the polarizability and IE is the ionization energy

1. The polarizability increases with MM and shape of the molecule

MM factors: All molecules have MM so all molecules have LDF to some extent.

Molecule	MM (g/mol)	bp (K)	state at 25 ^oC
F_2	38		
Cl_2	71		
Br_2	160		
I_2	254		

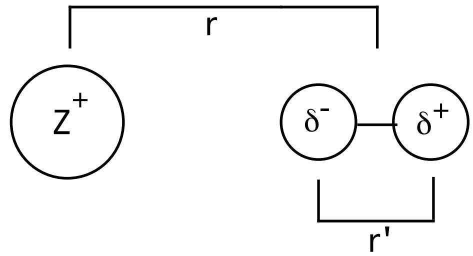
Molecule	MM (g/mol)	bp (^oC)	state at 25 ^oC
n-C_5H_{12}	72		
iso-C_5H_{12}	72		
neo-C_5H_{12}	72		

D. Ion-dipole forces (10 – 50 kJ/mol)

Only applies to solutions, usually aqueous solutions

For polar molecule: the dipole force is given by

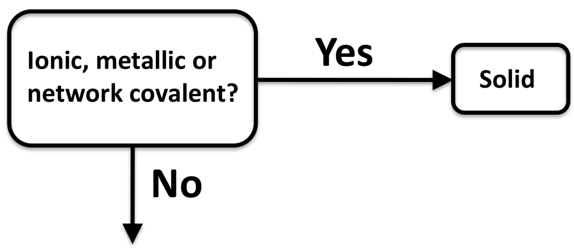
μ = qr' where q = the equal and opposite charges in the molecule (δ^+, δ^-) and r' is the distance between δ^+ and δ^- and ***e*** is the charge on the ion.



For ion-dipole forces, $E \propto \frac{\mu e}{r^2}$

3. Predicting physical states at room temperature.

This chart is overly simplistic, but it shows how LDF can be a very important factor (high MM). In the chart, the MM cut-offs of 100 and 200 g/mol, are rather arbitrary and you can expect to find numerous exceptions.



MM	Non-polar	Polar A little … A lot	H-bonding A little … A lot
< 100	Gas	Gas … liquid	Gas … Liquid
100 – 200	Gas or liquid	Gas … Liquid	Liquid
200 – 300	Liquid or solid	Liquid … Solid	Solid
> 300	Solid	Solid	Solid

1. Use the chart to predict the physical state at room temperature for each of the following. Also, identify which forces led you to your conclusion. In our next class, I will "reveal" the actual melting and boiling points! (Or, if you just can't wait, look them up in a chemistry handbook!)

Compound:	Actual mp, bp, phase at room temperature
$AsBr_3$ MM = 315 g/mol	
BF_3 MM = 68 g/mol	
CSe_2 MM = 170 g/mol	
CH_3Cl MM = 50.5 g/mol	
NH_4Br MM = 98 g/mol	
CCl_4 MM = 154 g/mol	
ClO_2 MM = 67.5 g/mol	
ClF_3 MM = 92.5 g/mol	
Cl_2O_7 MM = 183 g/mol	
$(C_2F_4)_n$ MM = 100 g/mol	
$PSCl_3$ MM = 169.5 g/mol	
$PSBr_3$ MM = 303 g/mol	

SCl_2O_2 MM = 135 g/mol	
$BaCl_2$ MM = 208 g/mol	
$GeBr_4$ MM = 392 g/mol	
PBr_3 MM = 271 g/mol	
C_2H_6O, ethanol, C_2H_5OH MM = 46 g/mol	
C_2H_6O, dimethylether, CH_3OCH_3 MM = 46 g/mol	
SiC MM = 43 g/mol	
PF_3 MM = 88 g/mol	
PF_5 MM = 126 g/mol	
PCl_3 MM = 137.5 g/mol	
MgO MM = 40.3 g/mol	
Fe MM = 55.9 g/mol	
$(C_2H_5)_2NH$ MM = 73 g/mol	
$(CH_3)_2NH$ MM = 45 g/mol	
$(CH_3)_3N$ MM = 59 g/mol	

Review for ACS Final Exam in Inorganic Chemistry

Intermolecular forces

1. Which of these compounds most likely a gas at room temperature?
   (a) BF_3
   (b) PBr_3
   (c) $K_2S_2O_3$
   (d) SnF_2
   (e) SiO_2

2. Which of these compounds exhibits hydrogen bonding?
   (a) B_2H_6
   (b) CH_4
   (c) $CH_3CH_2NCl_2$
   (d) CH_3OCl
   (e) HOBr

3. Lattice energy is greatest for:
   (a) NaCl
   (b) MgO
   (c) $BaCl_2$
   (d) Na_2O
   (e) CsF

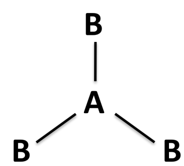
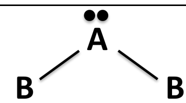
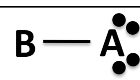
4. Identify the species with the highest melting point.
   (a) $AsCl_3$
   (b) $NH_4C_2H_3O_2$
   (c) SiC
   (d) Mn
   (e) S_8

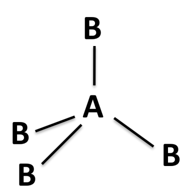
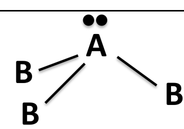
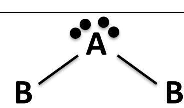
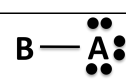
Answers: A, E, B, C

Day 3 answers:

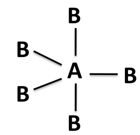
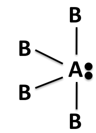
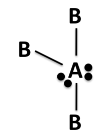
2. Geometries and their name and angles

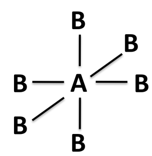
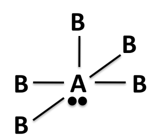
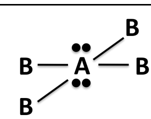
2 groups	name	sketch	angles	example
AB_2	linear		180 º	CO_2 SCN^-
ABE	(none)		not applicable	CN^-

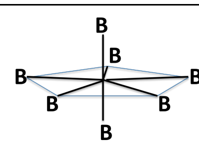
3 groups	name	sketch	angles	example
AB_3	trigonal plane		120 º	BF_3 CO_3^{2-}
AB_2E	bent		~ < 120 º	NO_2^-
ABE_2	(none)		not applicable	NO

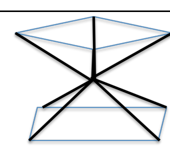
4 groups	name	sketch	angles	example
AB_4	tetrahedral		109.5 º	CH_4 SO_4^{2-}
AB_3E	trigonal pyramid		~ < 109.5 º	NH_3 SO_3^{2-}
AB_2E_2	bent		~ < 109.5 º	OH_2 ClO_2^-
ABE_3	(none)		not applicable	HCl

3. Expanding octets:

5 groups	name	sketch	angles	example
AB_5	trigonal bipyramid		120° 90° 180°	PF_5
AB_4E	see-saw		~ < 120° ~ < 90° ~ < 180°	SF_4 SbF_3^-
AB_3E_2	T-shaped		~ < 90° ~ < 180°	ClF_3 SeF_3^-
AB_2E_3	linear		180°	XeF_2 IF_2^-

6 groups	name	sketch	angles	example
AB_6	octahedron		90° 180°	SF_6 PF_6^-
AB_5E	square pyramid		~ < 90° ~ < 180°	IF_5
AB_4E_2	square plane		90° 180°	XeF_4

7 groups	name	sketch	angles	example
AB_7	pentagonal bioyramid		72° 90° 180°	IF_7

8 groups	name	sketch	angles	example
AB_8	Square antiprism			XeF_8

Step 5:

PCl_6^- AB_6 | PCl_4^+ AB_4 | PCl_5 AB_5
SF_6 AB_6 | SF_4 AB_4E | ClF_3 AB_3E_2

Step 6:

PCl_3O AB_4 | IO_4^- AB_4 | BrO_3^- AB_3E
SO_3 AB_3 | SF_4O AB_5 | ClO_2F_3 AB_5

4. On bulkiness of electrons and bonding groups

(See 2 above: Geometries and their name and angles for details about angles)

PCl_3 AB_3E | SCl_2 AB_2E_2 | OH_3^+ AB_3E
BrF_5 AB_5E | SF_4 AB_4E | CH_3^- AB_3E

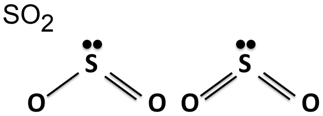
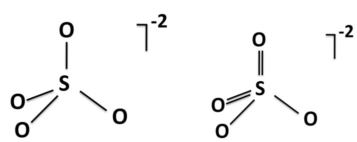
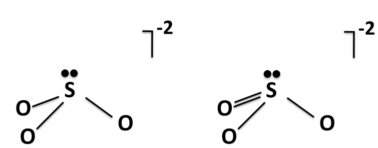
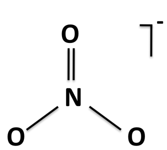
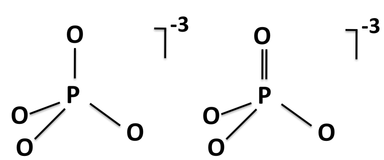
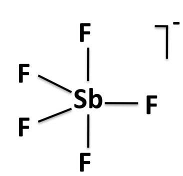
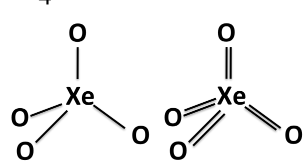
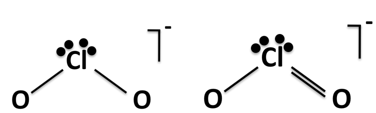
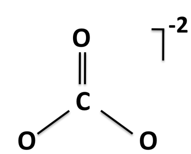
For species with 5 structural groups. (See 2 above: Geometries and their name and angles for details about angles)

SbF_4^- AB_4E | ClF_3 AB_3E_2 | ICl_4^+ AB_4E
PCl_5 AB_5 | SF_4 AB_4E | ICl_2^- AB_2E_3

Similarly, for species with 5 structural groups, oxygen groups prefer the equatorial positions. Oxygen atoms and E-groups always go equatorial! (See 2 above: Geometries and their name and angles for details about angles)

SF_4O AB_5 | ClO_2F_3 AB_5 | SeF_3O^- AB_4E
$SeF_3O_2^-$ AB_5 | $IF_2O_3^-$ AB_5

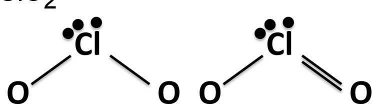
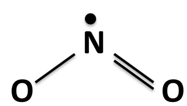
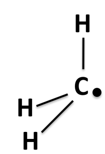
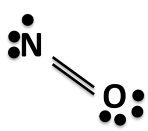
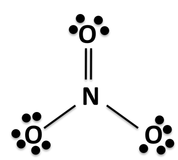
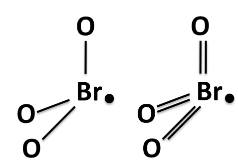
5. On formal charge and bond order (BO)

SO_2 	SO_4^{-2} 	SO_3^{-2} 
NO_3^- 	PO_4^{-3} 	SbF_4^- 
XeO_4 	ClO_2^- 	CO_3^{-2} 

6. On resonance

SO_2 2 resonance forms that obey octet, plus one drawing that minimizes FC, but places 10 electrons around S.	SO_4^{-2} 1 form that obeys octet, plus 6 drawings, each with 2 SO double bonds, that minimize FC, but places 12 electrons around S. No structures should have more than 2 dbl bonds.	SO_3^{-2} 1 form that obeys octet, plus 3 drawings, each with one SO double bond, that minimize FC, but places 10 electrons around S. No structures should have more than 1 dbl bond.
NO_3^- Three resonance forms, all of which obey the octet rule	PO_4^{-3} 1 form that obeys octet, plus 4 drawings, each with one PO double bond, that minimizes FC, but places 10 electrons around P. No structures should have more than 1 dbl bond.	SbF_4^- One Lewis dot structure
XeO_4 1 form that obeys octet, plus 1 drawing with 4 XeO double bonds, that minimizes FC, but places 16 electrons around Xe. The latter is quite unlikely.	ClO_2^- 1 form that obeys octet, plus 2 drawings, each with one ClO double bond, that minimizes FC, but places 10 electrons around Cl. No structures should have more than 1 dbl bond.	CO_3^{-2} Three resonance forms, all of which obey the octet rule

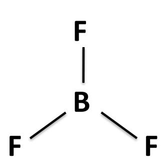
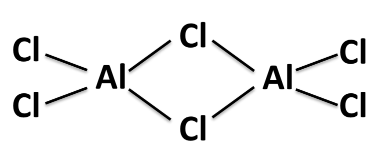
7. On paramagnetic substances.

ClO_2 	NO_2 	CH_3 
NO 	NO_3 	BrO_3 

8. On polarity.

SO_2, polar	SO_3, non-polar	SF_4, polar
SF_6, non-polar	SF_4O, polar	SO_2Cl_2, polar
XeO_4, non-polar	ClO_2, polar	PF_5, non-polar

9. On subvalent central atom species

BF_3 	Al_2Cl_6 	B_2H_6