LITERATURE Canvas test Basic Chemistry for Conservation and Restoration

Useful information:

When answering questions of the chemistry test, it is essential to have the following items at hand:

- Periodic Table (see pg. 24 of this document)

http://www.sciencegeek.net/tables/WikimediaPeriodic.pdf

- Variation in Electronegativity (6th ed Figure 3.12 (p92), 7th ed Figure 2D.2 (p97) or e.g. (see pg. 23 of this document) http://www.chemhume.co.uk/ASCHEM/Unit%201/Ch3IMF/Images%203/electronegativity_values.jpg
 - Electron-pair geometries (only: linear, trigonal planar and tetrahedral) and molecular shapes derived from them, e.g. the first three rows in (see pg. 23 of this document) <u>https://ontrack-media.net/gateway/chemistry/g_cm314rs5.html</u>
 - HO1 anion-cation list (see pg. 7-8 of this document)

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Chemistry for Conservation 2019-2020

Fundamental (A, B, etc) and Chapter/ paragraph numbering:

Peter Atkins, Loretta Jones, Leroy Laverman - Chemical principles. The quest for insight

6th edition (W.H. Freeman and Company,New York)

Elements and atoms, Matter, energy, radiation and the quantum-mechanic model of atoms

A.3 Energy B.1 Atoms B.2 The Nuclear Model B3 Isotopes B4 The Organization of the Elements 2.1* The principal quantum number 2.2* Atomic Orbitals 2.3 Electron Spin 2.4 The Electronic Structure of Hydrogen Exercises: B3, B5, B9, 2.25, 2.31

* See Summary of Basic Chemistry concepts 5-9 (pg. 5)

Electronic structure of many-electron atoms, periodic table

2.5 Orbital Energies 2.6 The Building-Up Principle 2.7 Electronic Structure and the Periodic Table Exercises: 2.37abd, 2.38abd, 2.39,2.40, 2.49-2.52

Ionic compounds, molecular compounds, covalent bonds

C.1 What are Compounds? C.2 Molecules and Molecular Compounds C.3 Ions and Ionic Compounds Exercises: C7-C9, C13-C14

Covalent bonds, valence bond theory

3.5 Lewis Structures 3.6 Lewis Structures of Polyatomic Species 3.7 Resonance 3.8 Formal Charge
3.9 Radicals and Biradicals 3.10 Expanded Valence Shells
4.4 Sigma and pi bonds 4.5 Electron promotion and hybridization of orbitals 4.6 Other common types of hybridization 4.7 Characteristics of double bonds
Exercises see: Small molecules and polyatomic ions (pg. 4)

Molecular shape, electronegativity and polarity of molecules,

3.12 Correcting the Covalent Model: Electronegativity

4.1 The Basic VSEPR Model 4.2 Molecules with Lone Pairs on the Central atom 4.3 Polar molecules Exercises see: Small molecules and polyatomic ions (pg. 4)

Note: only the electron pair arrangements: linear, trigonal planar and tetrahedral

Note: only the molecular shapes: linear, bent (=angular), trigonal planar, trigonal pyramidal and tetrahedral

Intermolecular forces

6.1 The origin of intermolecular forces 6.2 Ion-Dipole Forces 6.3 Dipole-Dipole Forces 6.4 London Forces 6.5 Hydrogen Bonding 10.9 The Like-Dissolves-Like Rule Exercises see: Small molecules and polyatomic ions (pg. 4)

Acids and bases

J.1 Acids and Bases in Aqueous Solution J.2 Strong and Weak Acids and Bases J.3 Neutralization 12.1 Brønsted-Lowry Acids and Bases 12.4 Proton Exchange Between Water Molecules 12.5 The pH Scale 12.6 The pOH of Solutions 12.7 Acidity and Basicity Constants 12.8 The Conjugate Seesaw 12.10 The Strengths of Oxoacids and Carboxylic Acids 12.13 The pH of salt solutions (till Example 12.10, no calculations) Exercises: 12.3acd, 12.4acd, 12.21, 12.35, 12.36, 12.43, 12.44, 12.45, 1247, 12.48

Organic compounds and functional groups

20.1 Haloalkanes 20.2 Alcohols 20.3 Ethers 20.4 Phenols 20.5 Aldehydes and Ketones 20.6 Carboxylic Acids 20.7 Esters 20.8 Amines, Amino Acids, and Amides In 20.1 NOT the nucleophilic substitution In 20.3 NOT the crown ethers Exercises: 20.61a, 20.62a, 20.67, 20.68

Chemistry for Conservation 2019-2020

Fundamental (A, B, etc) and Chapter/ paragraph numbering: Peter Atkins, Loretta Jones, Leroy Laverman – Chemical principles. The quest for insight **7th** edition (W.H. Freeman and Company,New York)

Elements and atoms, Matter, energy, radiation and the quantum-mechanic model of atoms A.4 Energy

B.1 Atoms, B.2 The Nuclear Model, B.3 Isotopes, B.4 The Organization of the Elements
1D.3 *Quantum numbers, shells and subshells, 1D.4 *The shapes of orbitals, 1D.5 Electron Spin,
1D.6 The Electronic Structure of Hydrogen
*See Summary of Basic Chemistry concepts 5-9 (pg. 5)
Exercises: B.3, B.5, B.9, 1D.19, 1D.25

Electronic structure of many-electron atoms, periodic table

1E.1 Orbital Energies, 1E.2 The Building-Up Principle, 1F.1 The general structure of the Periodic Table Exercises: 1E.5abd, 1E.6abd, 1E.7, 1E.8, 1E.19, 1E.21, 1E.22

Ionic compounds, molecular compounds, covalent bonds

C.1What are Compounds? C.2 Molecules and Molecular Compounds, C.3 Ions and Ionic Compounds 2A.1 The ions that elements form Exercises: C.7, C.9, C.13

Covalent bonds, valence bond theory

2A.2 Lewis symbols, 2B.1 Lewis Structures, 2B.2 Resonance, 2B.3 Formal Charge, 2C.1 Radicals,
2C.2 Expanded Valence Shells
2F.1 Sigma and pi bonds, 2F.2 Electron promotion and hybridization of orbitals, 2F.3 Other common types of hybridization, 2F.4 Characteristics of double bonds
Exercises see: Small molecules and polyatomic ions (see pg. 4)

Molecular shape, electronegativity and polarity of molecules,

2D.1 Correcting the Covalent Model: Electronegativity 2E.1 The Basic VSEPR Model, 2E.2 Molecules with Lone Pairs on the Central atom 2E.3 Polar molecules Exercises see: Small molecules and polyatomic ions (see pg. 4)

Note: only the electron pair arrangements: linear, trigonal planar and tetrahedral

Note: only the molecular shapes: linear, bent (=angular), trigonal planar, trigonal pyramidal and tetrahedral

Intermolecular forces

3F.1 The origin of intermolecular forces, 3F.2 Ion-Dipole Forces, 3F.3 Dipole-Dipole Forces,
3F.4 London Forces, 3F.5 Hydrogen Bonding
5D.2The Like-Dissolves-Like Rule
Exercises see: Small molecules and polyatomic ions (see pg. 4)

Acids and bases

J.1 Acids and Bases in Aqueous Solution, J.2 Strong and Weak Acids and Bases, J.3 Neutralization
6A.1 Brønsted-Lowry Acids and Bases, 6A.4 Proton Exchange Between Water Molecules,
6B.1 The interpretation of pH, 6B.2 The pOH of Solutions, 6C.1 Acidity and Basicity Constants ,
6C.2 The Conjugate Seesaw, 6C.4 The Strengths of Oxoacids and carboxylic acids
6D.3 The pH of salt solutions (till Example 6D.4, no calculations)
Exercises: 6A.3acd, 6A.4acd, 6A.19, 6C.3, 6C.4, 6C.11, 6C.12, 6C.13, 6C.15, 6C.16

Organic compounds and functional groups

11A.1 Types of aliphatic hydrocarbons, 11A.2 Isomers (till p785 optical isomers), 11A.3 Physical properties of alkanes and alkenes, 11C.1 Aromatic compounds. Nomenclature
11D.1 Haloalkanes, 11D.2 Alcohols, 11D.3 Ethers, 11D.4 Phenols, 11D.5 Aldehydes and Ketones , 11D.6 Carboxylic Acids, 11D.7 Esters, 11D.8 Amines, Amino Acids, and Amides 11D.1 NOT: nucleophilic substitution

Exercises: 11E.25a, 11E.26a, 11.25, 11.26

Exercises small molecules and polyatomic ions

- a) Draw for each particle its Lewis structure, or its Lewis structures if equivalent resonance structures exist
- b) Determine for each of the particles the electron-pair geometry and molecular shape at the central atom. Consider in particles 5-12 all non-hydrogen atoms as central atoms.
- c) Argue for each neutral particle whether it is expected to be polar or apolar (= non-polar)
- d) For the neutral particles, indicate the intermolecular forces that are present when the particles are in the liquid state
- 1) HClO hypochlorous acid
- 2) CO_2 carbon dioxide
- 3) HCN hydrocyanic acid
- 4) HNO₂ nitrous acid
- 5) CH₃CH₂OH ethanol
- 6) CH_3CHO ethanal (= acetaldehyde)
- 7) CH₃COOH acetic acid (= ethanoic acid)
- 8) CH₃COCH₃ acetone (= dimethylketone)
- 9) CH₃CH₂OCH₂CH₃ diethylether
- 10) CH₃COOCH₃ methylacetate
- 11) CH₃CH₂NHCH₂CH₃ diethylamine
- 12) HCONH₂ formamide (= methanamide)
- 13) HNO₃ nitric acid
- $14)O_3$ ozone
- $15) \text{CO}_3^2$ carbonate anion
- 16) SO_2 sulfur dioxide
- 17) H₃PO₄ phosphoric acid
- 18) HClO₂ chlorous acid
- 19) ClO_2^- chlorite anion
- 20) NO₂ nitrogen dioxide

Summary of Basic chemistry concepts (except acids and bases)

Ideally, you should (still) know that, know how to, and be familiar with :

- 1 The amount of protons, neutrons and electrons of atoms and ions of the elements with Z = 1-57 and 72-89 using the Periodic Table (1A4 sheet, will be supplied)
- 2 Calculation of the total amount of valence electrons of the atoms and ions of the elements with Z = 1-57and 72-89 using the supplied Periodic Table
- 3 A radical is a particle (molecule, ion) that has an odd amount of valence electrons
- 4 Common anions and cations (listed on a 2A4 sheet, will be supplied) in structural formulas
- 5 The concept of atomic orbitals (regions in space around the nucleus that have a high probability for an electron to be present)
- 6 The principal quantum number n (= 1, 2, 3...) refers to an energy level (shell) relative to the nucleus and the average volume of the orbital(s) at this level
- 7 The existence of various types (s, p, d, f) of atomic orbitals, and that s-orbitals have a spherical shape while p-orbitals are dumb-bell shaped
- 8 The notation of the orbitals: the *n* followed by the type of orbital (s,p,d,f), e.g.1s,2p, 3p.
- 9 In each shell (each n) there is only one s orbital (1s, 2s, 3s, 4s, 5s); for n = 2,3, 4,5, ... there are three p orbitals (2p_x, 2p_y, 2p_z, 3p_x, 3p_y, 3p_z, etc); for n = 3,4,5,... there are five d orbitals; for n = 4, 5, ... there are seven f orbitals.
- 10 Each orbital can contain at most two electrons (with paired spin)
- 11 Only valence (=outer-shell) electrons are involved in chemical bonds
- 12 Two important types of chemical bonds, the ionic bond and the covalent bond
- 13 A single covalent bond (σ bond, sigma bond) is formed by an end-to-end overlap of (atomic) orbitals
- 14 Some elements (esp C, N, O) can form double and triple bonds, involving one and two pi (π) bonds respectively
- 15 A pi bond is formed by side-side overlap of parallel p-orbitals
- 16 Valence electrons occur in pairs, either as bonding pair (sigma bond, pi bond) between two atoms, or as lone pair at an atom
- 17 The Lewis structure of a covalently bonded molecule or a polyatomic ion depicts all the elements and their valence electrons (in pairs)
- 18 The construction of a Lewis structure with the octet rule (max. eight valence electrons near a nucleus) strictly applying to the elements C, N, O and F
- 19 Elements in periods 3-5 can accommodate more than eight valence electrons near the nucleus
- 20 For some molecules and polyatomic ions several (equivalent) resonance structures are needed that together describe the Lewis structure
- 21 The occurrence of resonance structures implies delocalization of pi-bond electrons and lone-pair electrons
- 22 The electron-pair geometry (=electron-pair arrangement, EPG) is the spatial arrangement of all sigma bonds and lone pairs around a chosen or central atom in a molecule or polyatomic ion (two pairs: linear EPG, three pairs : trigonal planar EPG, four pairs: tetrahedral EPG)
- 23 No lone pairs at a central atom: molecular shape (MS) equals the EPG. In trigonal planar EPG one lone pair: bent (=angular) MS. In tetrahedral EPG one lone pair: trigonal pyramid MS. In tetrahedral EPG two lone pairs: bent MS.
- 24 The absolute difference (so leaving out any minus sign) in Pauling electronegativity ($\Delta \chi$) between two bonded atoms is a measure for the type of bond. For $0 < \Delta \chi < 0.5$ the bond is non-polar covalent. For increasing $\Delta \chi$ (> 0.5 till 1.5) the covalent bond becomes increasingly polar, and eventually if $\Delta \chi > 2.0$ the bond is ionic (= no common bonding pair)
- 25 To establish whether a part of a molecule at a chosen central atom is polar or non-polar (= apolar) using the MS at this central atom and the (absolute) difference in Pauling electronegativity between the central atom and each of the atoms bonded to this central atom.

- 26 (Parts of) molecules with less than six C atoms that also contain electronegative atoms like O, N, F or Cl are usually polar, unless the arrangement of the O, N, F or Cl atoms is completely symmetric
- 27 (Parts of) molecules that only contain C atoms with sigma bonds and H are apolar
- 28 In the liquid and/or solid state three types of intermolecular interactions can be present: London (dispersion) forces (LF), dipole-dipole interactions (DP) and hydrogen bonds (HB)
- In 29-32 the liquid and/or solid state is considered
 - 29 LF are always present between molecules. LF become larger when the molecular contact area increases
 - 30 DP occur only between polar (parts of) molecules
 - 31 HB occur between two electronegative atoms (O, N, F) provided a hydrogen atom is bonded to one of them, and the other has at least one lone pair
 - 32 Stronger intermolecular forces imply, amongst others, higher boiling points
 - 33 Like-dissolves-like: the more similar the intermolecular forces of two compounds are, the better they are miscible.
 - 34 Interpretation of a condensed structural formula of a small organic molecule in terms of the complete Lewis structure
 - 35 Interpretation of a line structure of an organic molecule that contains any of the following functional groups: alcohol, aldehyde, ketone, ether, carboxylic acid, ester, amine, amide
 - 36 A primary alcohol can be oxidized to an aldehyde, and an aldehyde to a carboxylic acid
 - 37 A secondary alcohol can be oxidized to a ketone
 - 38 An ester can be hydrolyzed (with water) into an alcohol and a carboxylic acid and, vice versa, a condensation reaction of the latter two compounds gives an ester and water
 - 39 An amide can be hydrolyzed into an amine and a carboxylic acid and, vice versa, a condensation reaction of the latter two compounds gives an amide and water
 - 40 Structural isomers
 - 41 Aliphatic (straight, branched, cyclic) and aromatic hydrocarbons
 - 42 Saturated (single bonds only) and unsaturated (contains one or more C=C and/or C=C bond) hydrocarbons
 - 43 Conjugated systems
 - 44 Cis- and -trans isomers occur in hydrocarbons that are cyclic or contain C=C bonds

No questions will be asked about the following subjects:

The elements with Z = 58-71 and Z = 90-111

f-orbitals

d-orbitals, except for the total amount of valence electrons present (can be read off the supplied Periodic Table) diradicals

mathematical and/or physical formulas

excited states

The EG's : trigonal bipyramidal, octahedral

The MS's : T-shape, See-saw, trigonal bipyramidal, Square planar, Square pyramidal, Octahedral

The concept of hybridization

Specific names of compounds (only the functional group classes alcohol, aldehyde, ketone, ether, carboxylic acid, phenol, ester, amine, amide)

The list below is a slightly modified, and at some points extended version, of:
http://www.chemteam.info/Nomenclature/HO1-Anion-Cation-List.pdf

Symbols and Charges of Monoatomic Ions					
Symbol and N	•	mbol and Name		ymbol and Name (ar	nion) Symbol and Name (anion)
H ⁺ hydrogen	· / ·	silver	•	H [–] hydride	N ³⁻ nitride
Li ⁺ lithium	Ni ²	nickel		F^{-} fluoride	P ³⁻ phosphide
Na ⁺ sodium	Al	aluminum		Cl ⁻ chloride	As ^{3[±]} arsenide
K ⁺ potassium				Br ⁻ bromide	
Rb ⁺ rubidium				I ⁻ iodide	
Cs ⁺ cesium			(O ²⁻ oxide	
Be ²⁺ beryllium	1			$S^{2^{-}}$ sulfide	
Mg ²⁺ magnesi	um		C	Se ^{2–} selenide	
Ca ²⁺ calcium			r	$\Gamma e^{2^{-}}$ telluride	
Sr ²⁺ strontium					
Ba ²⁺ barium					
Ra ²⁺ radium					
Zn ²⁺ zinc					
<u>c</u>	Systematic name	Common		Systematic name	Common
Symbol_+	(Stock system)	name	$\operatorname{Symbol}_{2^+}$	(Stock system)	name
Cu ₂₊	copper(I)	cuprous	$Hg_{2^{+}}$	mercury(I)	mercurous
Cu ₂₊	copper(II)	cupric	Hg_{2+}	mercury(II)	mercuric
Fe ⁻ ₃₊	iron(II)	ferrous	Pb	lead(II)	plumbous
Fe ₂₊	iron(III)	ferric	Pb^{4+}_{2+}	lead(IV)	plumbic
Sn_{4^+}	tin(II)	stannous	Co ₃₊	cobalt(II)	cobaltous
Sn 2+	tin(IV)	stannic	Co_+	cobalt(III)	cobaltic
Cr ₃₊	chromium(II)	chromous	Au 3+	gold(I)	aurous
Cr 2+	chromium(III)	chromic	Au ³⁺	gold(III)	auric
Mn	manganese(II)	manganous Symbols an	Mn [°]	manganese(III) f Polyatomic Ions	manganic
Formula Name	e Formula N	v	la Name	Formula Name	
NO ₃ nitrate				IO ₄ periodate	
NO_2^- nitrite	_	rate BrO_3^{-}	-	-	
$\operatorname{CrO_4}^{2^-}$ chroma		rite BrO_2^-			
γ_				IO ⁻ hypoiodite	
		•		O_2^- superoxide	
MnO_4 perma	nganate NH_2^- ar	nide CO_3^{2-}	carbonate	HCO_3 hydrogen ca	arbonate (bicarbonate)
SO_4^{2-} sulfate	HSO ₄ hy	drogen sulfate (l	bisulfate) SO	3^{2-} sulfite HSO ₃ ⁻¹	nydrogen sulfite (bisulfite)
$C_2O_4^{2-}$ oxalate	HC_2O_4 h	ydrogen oxalate	(binoxalate)	HCOO ⁻ formate Cl	H ₃ COO ⁻ acetate
PO_4^{3-} phospha				ihydrogen phosphate	
HPO_3^{2-} phosp	honate (phosphite) $H_2PO_3^-$ hydro	ogen phospho	onate	
			7		

More Symbols and Charges of Polyatomic ions

$S_2O_3^{2-}$ thiosulfate	HS_hydrogen sulfide	CrO ₄ ²⁻ chromate
AsO_4^{3-} arsenate	BO_3^{3-} borate	MnO ₄ ²⁻ manganate
$SeO_4^{2^-}$ selenate	$B_4O_7^{2-}$ tetraborate	MnO ₄ ⁻ permanganate
${\rm SiO_3}^{2-}$ silicate	${\rm SiF_6}^{2-}$ hexafluorosilicate	
$C_4H_4O_6^{2-}$ tartrate	SCN ⁻ thiocyanate	

The most common positively charged polyatomic ion is NH_4^+ , the ammonium ion.

Prefixes Used to Indicate Number in a Name Involving Two Non-Metals

mono-	1	hexa–	6
di–	2	hepta-	7
tri–	3	octa-	8
tetra-	4	nona–	9
penta-	5	deca-	10

These prefixes are used in naming binary compounds involving two non-metals, e.g. P₂O₅, Cl₂O, NO, N₂O, NO₂, N₂O₅, PCl₃, PCl₅, SO₂, SO₃, SiO₂. Sometimes metal ions are involved in a Greek prefix name, but these are less common. Examples include UF₆, SbCl₃, SbCl₅, OsO₄, BiCl₃.

There is a preferred order of the non-metals when writing them in a formula. It is: Rn, Xe, Kr, B, Si, C, Sb, As, P, N, H, Te, Se, S, I, Br, Cl, O, F.

CO is carbon monoxide, NOT carbon monooxide. As_4O_6 is tetrarsenic hexoxide, NOT tetraarsenic hexaoxide.

Acid Names – add the word acid to each name when saying or writing. Non–oxygen containing acids

Non-oxygen co	maming actus		Oxygen	i containing actus
	Name when dis-	Name when a pure		
Formula	solved in water	compound	Formula	Name
HF	hydrofluoric acid	hydrogen fluoride	HNO ₃	nitric acid
HC1	hydrochloric acid	hydrogen chloride	HNO_2	nitrous acid
HBr	hydrobromic acid	hydrogen bromide	$\mathrm{H}_2\mathrm{SO}_4$	sulfuric acid
HI	hydroiodic acid	hydrogen iodide	H_2SO_3	sulfurous acid
HCN	hydrocyanic acid	hydrogen cyanide	H_3PO_4	phosphoric acid
H_2S	hydrosulfuric acid	hydrogen sulfide	H_3PO_3	phosphorous acid
			H_2CO_3	carbonic acid
			$HC_2H_3O_2$	acetic acid (also written CH ₃ COOH)
			НСООН	formic acid
			$H_2C_2O_4$	oxalic acid
Halogen and o	xygen containing ac	ids		
HOF hypofluor	ous acid *	*		*
HClO hypochle	orous acid HClO ₂ chl	orous acid HClO ₃ ch	loric acid H	HClO ₄ perchloric acid
HBrO hypobromic acid HBrO ₂ bromous acid* HBrO ₃ bromic acid HBrO ₄ perbromic acid				

HIO hypoiodic acid * HIO₃ iodic acid HIO₄ periodic acid

* does not exist or instable

Chemistry for Conservation Answers to the exercises

Atkins, Jones and Laverman (6th and 7th edition)

Answers (very short) to odd-numbered exercises can be found in the back of the book, but some cases a more comprehensive answer is in order.

 $2.38abd(6^{th}) = 1E.6abd(7^{th})$

- 2.38a False. On average an electron in an 1s orbital is closer to the nucleus than an electron in a 2s orbital so the 1s-electron is better in shielding off the nucleus. As a result, the Z_{eff} experienced by a 2s-electron is lower than the Z_{eff} experienced by a 1s-electron.
- 2.38b False. Same type of argumentation as above: a 2s- electron is on average closer to the nucleus than a 2p-electron, so a 2s-electron shields off the nucleus better, thus a 2p-electron experiences a lower Z_{eff}
- 2.38d False. A 2s- electron is on average closer to the nucleus than a 2p-electron and this implies that the 2s-electron energy is lower

 $2.39(6^{\text{th}}) = 1E.7(7^{\text{th}})$

- (a) Is an excited state: the 2p electrons do not need to pair because there are empty 2p orbitals
- (b) Is an excited state: in the ground state the electron spins are as parallel as possible
- (c) Is an excited state: the ground state has two paired electrons in the 2s
- (d) Ground state

 $2.40(6^{\text{th}}) = 1E.8(7^{\text{th}})$

Germanium. Configuration (d) represents the ground state

 $2.49(6^{\text{th}}) = 1E.19(7^{\text{th}})$

Predict the number of valence electrons present in each of the following atoms, excluding (and including) the outermost d-electrons and/or f-electrons: (a) N; (b) Ag; (c) Nb; (d) W

(a) 3; (b) 1 (11); (c) 5; 6 (20)

2.50 (6th)

Predict the number of valence electons present in each of the following atoms, excluding (and including) the outermost d-electrons and/or f-electrons: (a) Bi; (b) Ba ; (c) Mn ; (d) Zn

(a) 6(30); (b) 2; (c) 7; 2(12)

 $2.52 (6^{\text{th}}) = 1E.22 (7^{\text{th}})$

(a) 2; (b) 3; (c) 1; (d) 0

C.8 (6th)

State whether each of the following elements is more likely to form a cation or an anion, and write the formula for the ion most likely to be formed: (a) tellurium; (b) barium ; (c) rubidium ; (d) bromine

(a) anion Te^{2-} ; (b) cation Ba^{2+} ; (c) cation Rb^+ ; (d) anion Br^-

 $C.10(6^{th})$

How many protons, neutrons and electrons are present in

- (a) ${}^{66}Zn^{2+}$; (b) ${}^{150}Sm^{3+}$; (c) ${}^{133}Cs^{+}$; (d) ${}^{127}I^{-}$
 - (a) 30p 36n 28e ; (b) 62p 88n 59e ; (c) 55p 78n 54e ; (d) 53p 74n 54e

 $C.14(6^{th})$

Write the formula of a compound formed by combining the most common ions of (a) Mg and N ; (b) Ga and S ; (c) Ba and Cl ; (d) K and Se

(a) Mg_3N_2 ; (b) Ga_2S_3 ; (c) $BaCl_2$; (d) K_2Se

 $12.3acd(6^{th}) = 6A.3acd(7^{th})$

(a) $H_2SO_4(aq) + H_2O(\ell) \rightleftharpoons HSO_4(aq) + H_3O^+(aq)$

H₂SO₄ acid, HSO₄⁻ conjugated base

 H_2O base, H_3O^+ conjugated acid

(c) $H_2PO_4^-(aq) + H_2O(\ell) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

 $H_2PO_4^-$ acid, HPO_4^{2-} conjugated base

 H_2O base, H_3O^+ conjugated acid

(d) HCOOH(aq) +H₂O(
$$\ell$$
) \rightleftharpoons HCOO⁻(aq) + H₃O⁺(aq)

HCOOH acid, HCOO⁻ conjugated base

 H_2O base, H_3O^+ conjugated acid

 $12.4acd(6^{th}) = 6A.4acd(7^{th})$

(a)
$$CN^{-}(aq) + H_2O(\ell) \rightleftharpoons HCN(aq) + OH^{-}(aq)$$

CN⁻ base, HCN conjugated acid

H₂O acid, OH⁻ conjugated base

(c)
$$CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq)$$

 CO_3^{2-} base, HCO_3^{-} conjugated acid

 H_2O acid, OH^- conjugated base

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(d) HPO_4^{2-}(aq) + H_2O(\ell) \rightleftharpoons H_2PO_4^{-}(aq) + OH^{-}(aq)
HPO_4^{2-} base, H_2PO_4^{-} conjugated acid
H_2O acid, OH^{-} conjugated base
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 $12.21 (6^{\text{th}}) = 6A.19 (7^{\text{th}})$

Note: Question 12.21 (c) is correct, but question 6A.19 (7th) (c) is incorrect, it should be: 3.1 mmol.L⁻¹

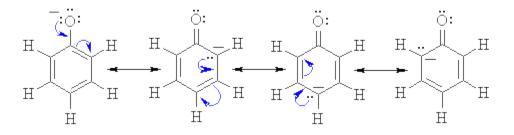
 $12.36(6^{\text{th}}) = 6\text{C.4}(7^{\text{th}})$

- (a) $pK_b = 5 \log(1.8) = 4.74$
- (b) $pK_b = 5 log(1.1) = 4.96$
- (c) $pK_b = 6 \log(1.7) = 5.77$
- (d) $pK_b = 8 log(1.1) = 7.96$
- (e) hydroxylamine < hydrazine < deuterated ammonia < ammonia

 $12.43 (6^{\text{th}}) = 6\text{C}.11 (7^{\text{th}})$

2,4,6-trichlorophenol is the stronger acid because its K_a is larger

The electronegative chlorines pull away the lone pairs that are localized on the carbons in the resonance structures of the phenolate anion shown below.



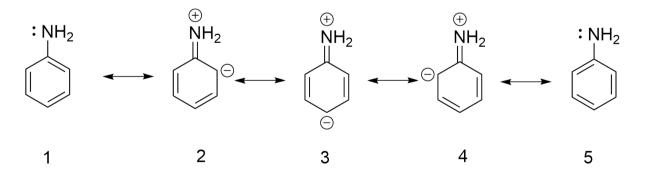
Source: http://www.chem.ucalgary.ca/courses/350/Carey5th/Ch24/ch24-1.html

This means that the - charge on the oxygen is delocalized further, making the 2,4,6-trichlorophenolate anion a weaker base than the phenolate anion, thus (the conjugated acid) 2,4,6-trichlorophenol is a stronger acid than (the conjugated acid) phenol.

 $12.44~(6^{\text{th}}) = 6\text{C}.12~(7^{\text{th}})$

Aniline is the stronger base, it has a lower pK_b value.

The electronegative chlorine in 4-chloroaniline pulls away the lone pair that is localized on the carbon in the resonance structure 3 of (4-chloro)aniline (see below). This means that the lone pair of the N in 4-chloroaniline is delocalized further (so less available to bind a H^+) than in aniline, so 4-chloroaniline is a weaker base than aniline.



Source: <u>https://chemistry.stackexchange.com/questions/83004/does-the-amine-group-participate-in-resonance-in-aniline</u>

 $12.45~(6^{\text{th}}) = 6\text{C}.13~(7^{\text{th}})$

Ammonia $pK_b = 14-9.26 = 4.74$; Methylamine $pK_b = 14-10.56 = 3.44$ Ethylamine $pK_b = 14-10.81 = 3.19$; Aniline $pK_b = 14-4.63 = 9.37$

Aniline is a much weaker base than ammonia because the lone pair at the N of aniline is less available to bind a H^+ (see resonance structures in the previous exercise 12.44 / 6C.12)

Methylamine is a stronger base than ammonia because the pK_b of methylamine is lower, similarly ethylamine a stronger base than methylamine. Apparently, a methyl group has the capacity to push electrons towards the N, and an ethyl group an even stronger capacity.

 $12.47 (6^{\text{th}}) = 6C.15 (7^{\text{th}})$

 HIO_3 is a stronger acid (much lower pK_a). IO⁻ has only one Lewis structure so the – charge remains localized on the O. However, IO_3^- has three equivalent resonance structures, so the – charge is delocalized (spread over the three oxygens) so less available to (re-)bind a H⁺.

Thus, IO_3^- is a weaker base than IO^- so (the conjugated acid) HIO_3 is a stronger acid than (the conjugated acid) HIO_3 .

 $12.48(6^{\text{th}}) = 6\text{C}.16(7^{\text{th}})$

Chlorine is more electronegative than bromine, so in ClO⁻ the negative charge is pulled away more from the O than in BrO⁻. As a result, ClO⁻ is a weaker base than BrO⁻, so (the conjugated acid) HClO is a stronger acid than (the conjugated acid) HBrO.

 $20.61a(6^{\text{th}}) = 11E.25a(7^{\text{th}})$

(a) from left to right: aldehyde, (4x) secondary alcohol, primary alcohol

 $20.62a(6^{\text{th}}) = 11\text{E}.26a(7^{\text{th}})$

(a) From left to right: in the 5-ring: 2x secondary amine, 2x alkene, primary amine, carboxylic acid

 $20.67 (6^{\text{th}}) = 11.25 (7^{\text{th}})$

- (a) from left to right: phenol, ether, aldehyde
- (b) from left to right: alkene, ketone, alkene
- (c) from left to right: tertiary amides , alkene, tertiary amides

 $20.68~(6^{\text{th}}) = 11.26~(7^{\text{th}})$

- (a) from left to right: ether, phenol, ketone
- (b) from left to right: secondary amide, phenol
- (c) at the left (top to down) primary amine, aromatic ring, ester; at the right tertiary amide

Answers to Exercises small molecules (in liquid state) and polyatomic ions

Abbreviations:

- EPG = Electron-pair geometry (at a central atom) MS = Molecular shape (at a central atom) FC = Formal charge ; EP = Electron pairs VE = amount of valence electrons LF = London (dispersion) forces
- DP = Dipole-dipole interactions
- HB = Hydrogen bonds

In the $\Delta \chi$ calculation the most electronegative element is given first. In the drawings of the local dipoles in the MS (in c) the local dipole arrows point in the direction of the more electronegative element. The electronegativity data were taken from,

http://www.chemhume.co.uk/ASCHEM/Unit%201/Ch3IMF/Images%203/electronegativity_values.jpg

1 HClO hypochlorous acid All FC = 0 a VE: H 1 Cl 7 O 6 total 14 VE => 7 EP

b EPG at O: Tetrahedral MS at O: Angular (= bent)

c polar The two local dipoles with an interangle (somewhat smaller than) 109.5 ° (angular, derived from tetrahedral with two lone pairs) add up to a total dipole that is larger than 0.5

 $\Delta \chi$ (O-Cl)= 3.44-3.16 = 0.28 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24

d LF, DP, HB

2 CO₂ carbon dioxide All FC = 0 a VE: C 4 2xO = 2x6 = 12Total 16 VE => 8 EP

b EPG at C: linear MS at C: linear

c apolar. The two local O-C dipoles are equally large but in opposite direction (interangle 180°) so they cancel each other

$\Delta \chi$ (O-C) = 3.44-2.55 = 0.89	0.89 0.89
d LF	

U.20 0 1.24 H

(0= c = 0)

HCN hydrocyanic acid 3 All FC = 0a VE: H 1 С 4 N 5 10 VE => 5 EP Total

b EPG at C: linear MS at C: linear

c polar. The two local dipoles are parallel and add up to a total that is larger than 0.5

 $\Delta \chi$ (C-H) = 2.55-2.20 = 0.35 $\Delta \chi$ (N-C) = 3.04-2.55 = 0.49

C	2.3	,	О,	Jg
	\rightarrow			
H		C	- 1	N

(0= N-0-H

d LF, DP

HNO₂ nitrous acid 4

> All FC = 0a VE: H 1 5 Ν 2xO = 2x6 = 1218 VE => 9 EP Total

b EPG at N: trigonal planar MS at N: angular (= bent)

c polar. The three local dipoles add up to a total that is larger than 0.5 The O-N and O-H dipoles point towards the (common) O and because of their of interangle (angular, derived from trigonal planar with a lone pair, so smaller than 120°) they add up to a total larger than 1.2. The remainder O-N dipole (0.40) is much smaller.

 $\Delta \chi$ (O-N) = 3.44-3.04 = 0.40 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24 140 0.40 IN V 0 - H 1.24

0,40

d LF, DP, HB

5 CH₃CH₂OH ethanol 1 2 3 a All FC = 0

- b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: tetrahedral MS at C2: tetrahedral EPG at O3: tetrahedral MS at O3: angular (= bent)
- c polar. The O-C and O-H local dipoles point towards the (common) O and because of their of interangle (smaller than 109.5°; MS is angular, derived from tetrahedral with two lone pairs) they add up to a total larger than 0.5. The apolar part (C, H) is small.

 $\Delta \chi$ (O-C) = 3.44-2.55 = 0.89 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24



d LF, DP, HB

a All FC = 0

6 CH₃CHO ethanal (= acetaldehyde) l 2

- b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: trigonal planar MS at C2: trigonal planar
- c polar. The O-C dipole is dominating, while the four local C-H dipoles (approximately tetrahedral) will cancel each other.

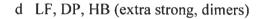
 $\Delta \chi$ (O-C) = 3.44-2.55 = 0.89 $\Delta \chi$ (C-H) = 2.55-2.20 = 0.35

7 CH₃COOH acetic acid (= ethanoic acid) 1 2 3

a All FC = 0

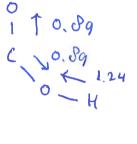
- b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: trigonal planar MS at C2: trigonal planar EPG at O3: tetrahedral MS at O3: angular (= bent)
- c polar. The three local dipoles add up to a total that is larger than 0.5
 The two C-O dipoles have an interangle of ~120 ° (trigonal planar) so they add up to a sum dipole of 0.89. This sum dipole (0.89) has an interangle with the large O-H dipole (1.24) (smaller than 109.5°, MS is angular, derived from tetrahedral with two lone pairs) but their sum is certainly larger than 0.5

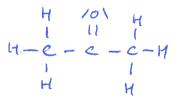
 $\Delta \chi$ (O-C) = 3.44-2.55 = 0.89 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24



- 8 CH₃COCH₃ acetone (= dimethylketone) 1 2 3
 - a All FC = 0
 - b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: trigonal planar MS at C2: trigonal planar EPG at C3: tetrahedral MS at C3: tetrahedral
 - c polar. Only one local dipole.

$$\Delta \chi$$
 (O-C) = 3.44-2.55 = 0.89





CH₃CH₂OCH₂CH₃ diethylether 9 2 34 1

a All FC = 0

b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: tetrahedral MS at C2: tetrahedral EPG at O3: tetrahedral MS at O3: angular EPG at C4: tetrahedral MS at C4: tetrahedral EPG at C5: tetrahedral MS at C5: tetrahedral

polar. The two local O-C dipoles point towards the (common) O and because of С their of interangle (smaller than 109.5°, MS is angular, derived from tetrahedral with two lone pairs) they add up to a total larger than 0.5. The apolar part (four C,H) is still small compared to the polar part 0 K 0,89

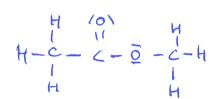
 $\Delta \chi$ (O-C) = 3.44-2.55 = 0.89

d LF, DP

10 CH₃COOCH₃ methylacetate 2 3 4 1

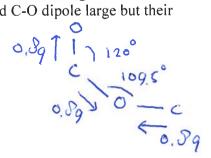
a All FC = 0

b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: trigonal planar MS at C2: trigonal planar EPG at O3: tetrahedral MS at O3: angular EPG at C4: tetrahedral MS at C4: tetrahedral



polar. The three local C-O dipoles add up to a total that is larger than 0.5 С The two C-O dipoles at C2 have an interangle of ~120 ° (trigonal planar) so they add up to a sum dipole of 0.89. This sum dipole has an interangle of ~109.5 $^{\circ}$ (angular, derived from tetrahedral so ~109.5) with the third C-O dipole large but their sum is certainly larger than 0.5

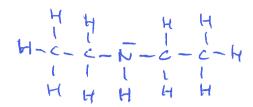
$$\Delta \chi (\text{O-C}) = 3.44-2.55 = 0.89$$



CH₃CH₂NHCH₂CH₃ diethylamine 11 1 2 3 4 5

a All FC = 0

b EPG at C1: tetrahedral MS at C1: tetrahedral EPG at C2: tetrahedral MS at C2: tetrahedral EPG at N3: tetrahedral MS at N3: trigonal pyramid EPG at C4: tetrahedral MS at C4: tetrahedral EPG at C5: tetrahedral MS at C5: tetrahedral

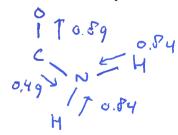


Polar. All three dipoles point towards the N, their sum is larger than 0.5. С 0,497. N ~ H ~ N ~ H ~ 0.40 The apolar part (four C,H) is still small compared to the polar part

 $\Delta \chi$ (N-C) = 3.04-2.55 = 0.49 $\Delta \chi$ (N-H) = 3.04-2.20 = 0.84

- LF, DP, HB d
- $HCONH_2$ formamide (= methanamide) 12 1 2
 - All FC = 0a
 - EPG at C1: trigonal planar b MS at C1: trigonal planar EPG at N2: tetrahedral MS at N2: trigonal pyramid
 - c polar. The O-C local dipole is not cancelled by the two N-H dipoles and the N-C dipole
 - $\Delta \chi$ (O-C) = 3.44-2.55 = 0.89 $\Delta \chi$ (N-C) = 3.04-2.55 = 0.49 $\Delta \chi$ (N-H) = 3.04-2.20 = 0.84





101 H-C-N-H

13 HNO₃ nitric acid а

VE: H 1
N 5
$$3xO = 3x6 = 12$$

Total 24 VE => 12 EP

b EPG at N: trigonal planar MS at N: trigonal planar

c polar. There is a permanent charge separation: a positive formal charge (+1) on the N, and a negative charge (-1) spread over two oxygens. In addition, the three local dipoles add up to a total that is larger than 0.5 The O-N and O-H dipoles point towards the (common) O and because of their of interangle (angular, derived from trigonal planar so $\sim 120^{\circ}$) they add up to a total larger than 1.2. The remainder O-N dipole (0.4) is much smaller

 $\Delta \chi$ (O-N) = 3.44-3.04 = 0.40 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24 1.24

d LF, DP, HB

14 O₃ ozone

a

3xO = 3x6 = 18VE: Total 18 VE => 9 EP

- b EPG at central O: trigonal planar MS at central O: angular (= bent)
- c polar. There is a permanent charge separation: a positive formal charge (on the central O, and a negative charge spread over the two other oxygens.

d LF, DP



 $(\overline{0} = \overline{0} - \overline{0}] \xrightarrow{\Theta} (\overline{0} - \overline{0} = \overline{0})$

15 CO_3^{2-} carbonate anion a VE: C 4 3xO = 3x6 = 18Charge -2 => 2 (2 extra VE) Total 24 VE => 12 EP

- b EPG at (central) C: trigonal planar MS at (central) C: trigonal planar
- 16 SO_2 sulfur dioxide a All FC = 0

VE: S 6 2xO = 2x6 = 12Total 18 VE => 9 EP

- b EPG at (central) S: trigonal planar MS at (central) S: angular (= bent)
- c polar. The two local S-O dipoles add up to a total that is larger than 0.5 because of their of interangle (smaller than 120°, derived from trigonal planar with a lone pair)

$$\Delta \chi$$
 (O-S) = 3.44-2.58 = 0.89

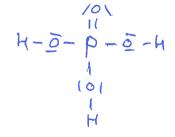
d LF, DP

- 17 H₃PO₄ phosphoric acid a All FC = 0 VE: 3xH = 3x1 = 3N 5 4xO = 4x6 = 24Total 32 VE => 16 EP
 - b EPG at (central) P: tetrahedral MS at (central) P: tetrahedral.
 - c polar. Asymmetric tetrahedral at the central P with many electronegative O but too difficult to argue using local dipoles

 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24 $\Delta \chi$ (O-P) = 3.44-2.19 = 1.25

d LF, DP, HB





(0= J = 0)

 $(\overline{0} = \overline{0} = \overline{0})$ $(\overline{0} = \overline{0} = \overline{0} = \overline{0})$ $(\overline{0} = \overline{0} = \overline{0} = \overline{0})$ $(\overline{0} = \overline{0} = \overline{0} = \overline{0})$

21

18 HClO₂ chlorous acid a All FC = 0

> VE: H 1 Cl 7 2xO = 2x6 = 12Total 20 VE => 10 EP

- b EPG at (central) Cl: tetrahedral MS at (central) Cl: angular (= bent)
- c polar. At the common O, the small O-Cl dipole and the large O-H dipole add up to a total that is much larger than 0.5. The small second O-Cl dipole does not change this much.

 $\Delta \chi$ (O-Cl) = 3.44-3.16 = 0.28 $\Delta \chi$ (O-H) = 3.44-2.20 = 1.24

d LF, DP, HB

19 ClO_2^- chlorite anion a VE: Cl 7 2xO = 2x6 = 12Charge -1 => 1 (1 extra VE) Total 20 VE => 10 EP

b EPG at (central) Cl: tetrahedral MS at (central) Cl: angular (=bent)

20 NO₂ (g) nitrogen dioxide

a VE: N 5 2xO = 2x6 = 12Total 17 VE => 8 EP + 1 single electron (radical!)

ũ-01 ↔ 10- ℓ=0)

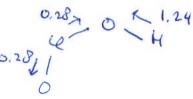
$$(0=N-\overline{0}) \longleftrightarrow (\overline{0}-N=0)$$

- b EPG at (central) N: trigonal planar (the single electron at the N takes up space, so treat it similar to a lone pair in determining the EPG)MS at (central) N: angular (=bent)
- c polar. There is a permanent charge separation: a positive formal charge (+1) on the N, and a negative charge (-1) spread over two oxygens.
 In addition, the two local O-N dipoles add to this, being in the same direction as the positive-negative charge dipoles

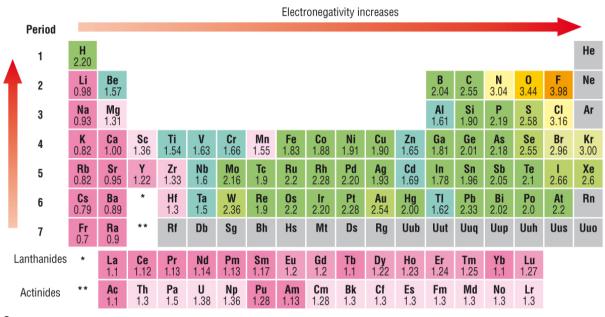
$$\Delta \chi (\text{O-N}) = 3.44 - 3.04 = 0.40$$



6= U - 0-H



Variation in Electronegativity



Source:

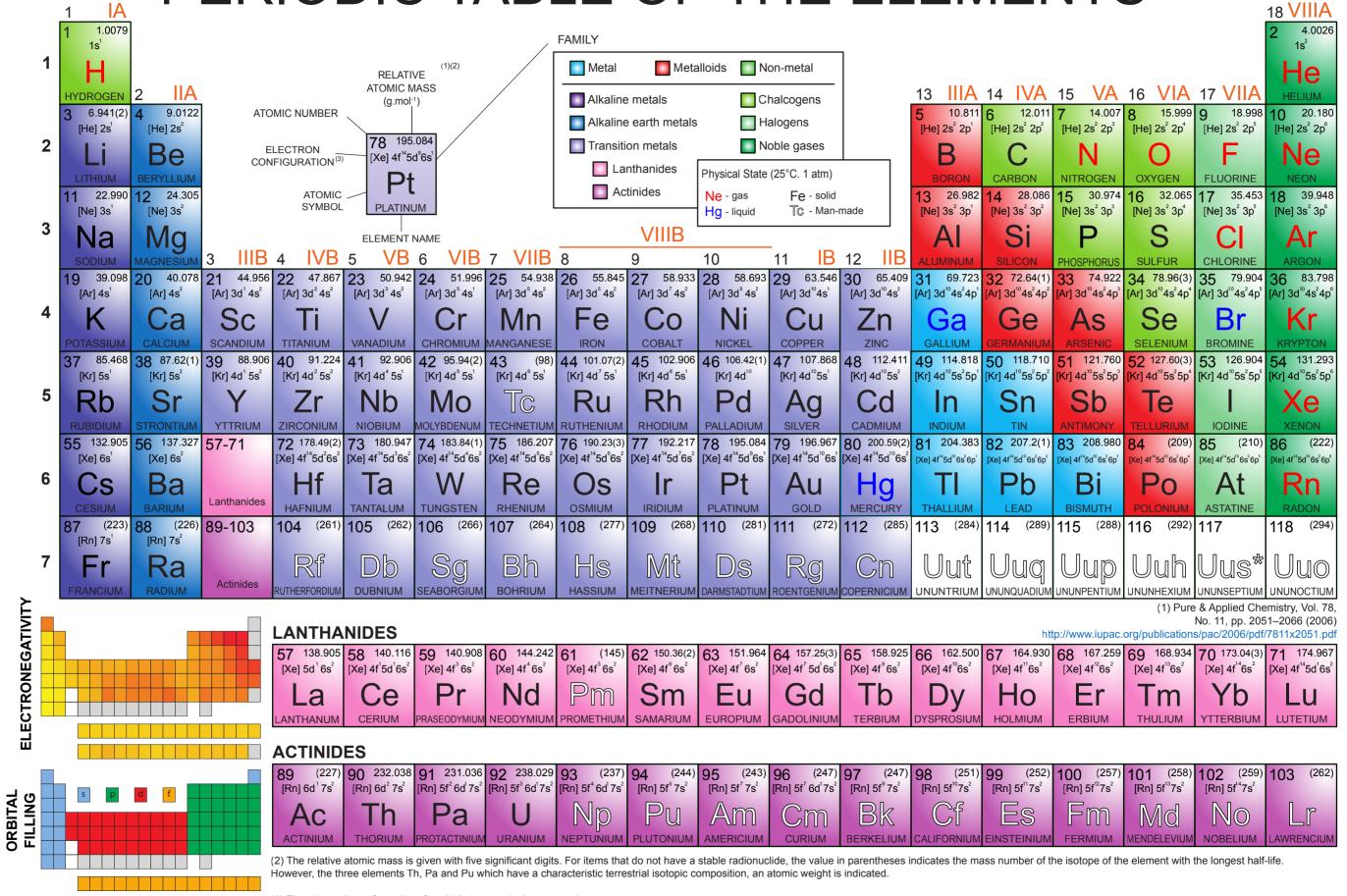
http://www.chemhume.co.uk/ASCHEM/Unit%201/Ch3IMF/Images%203/electronegativity_values.jpg

Electron-pair geometries and molecular shapes

Number of Electron- Molecular Geometry					etry	
Electron Dense Areas	Pair Geometry	No Lone Pairs	1 Ione Pair	2 Ione Pairs	3 Ione Pairs	4 Ione Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

Source: https://ontrack-media.net/gateway/chemistry/g_cm3l4rs5.html

PERIODIC TABLE OF THE ELEMENTS



(3) The electronic configurations for which there is doubt are not given.

GROUP