Name: _____ **Seat Number:** _____

Student Number: _____

CHM 2311
Midterm 2
March 26, 2009

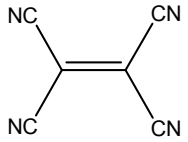
You have 80 minutes to complete this exam.
Please read the questions carefully.
There some useful data and a periodic table on the last 2 pages of the exam.

Please write legibly and show your work to receive credit for your answers.
Partial marks *may in some cases* **be awarded for partially correct work.**

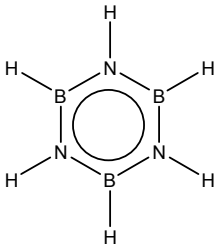
Question	Mark
1	**/10**
2	**/ 7**
3	**/ 3**
4	**/3**
5	**/ 4**
6	**/ 11**
7	**/2**
8	**/10**
Total	**/50**

1. (**10 points)** Determine the point group for each of the following molecules/shapes.

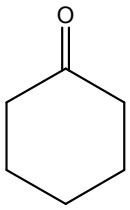
A.



B.

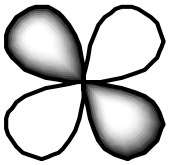


C.

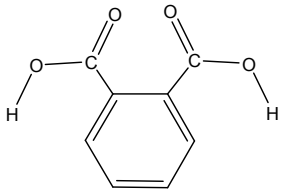


Point Group: A.____D2h_____ B.___D3h_____ C.___C2v_____

D.



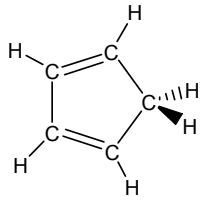
E.



F. SF_5Cl

Point Group: D.___D2h_____ E.___C2v_____ F.___C4v____

G.



H. NO_3^-

I. H_3O^+

Point Group: G. ___C2v____ H. __D3h___ I. ____C3v_____

J. PO_4^{3-}

Point Group: J. ___Td____

2. **(6 points; ½ point per blank)** Determine the irreducible representations (i.e. set of characters) corresponding to the p_y, the d_{xy}, and the d_z^2 orbitals on the central atom of a molecule in the D_2 point group. Please write your answers in the character table below. (It is not necessary to show your derivations. You may use the back of one of the exam pages for your scratch work.) It is ***not necessary to determine the symmetry labels.***

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	
	1	1	1	1	z^2
	1	1	-1	-1	Xy
	1	-1	1	-1	Y

(1 points; no partial marks) Which of the irreducible representations above also corresponds to an s orbital on the central atom?

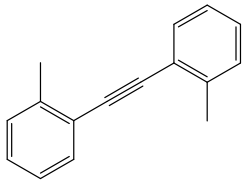
D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	
	1	1	1	1	

3. **(3 points; ½ point per blank)** In the left column of the character tables below, write the symmetry labels corresponding to each of the irreducible representations.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

4. **(3 points)** The molecule 1,2-di(o-tolyl)ethyne has C_{2h} symmetry. List all of the symmetry operations for this molecule.



Answer: E, C_2, σ_h, i (1 for E, 1 for C2 and σh, 1 for i)

5. **(4 points; no partial marks)**
(a) Which of the following diatomics has the highest bond order? Which has the lowest bond order?

CN^-, CO^-, NO, O_2, O_2^{2-}

Answer:

Molecule	number of valence electrons
CN^-	10
CO^-	11
NO	11
O_2	12
O_{2-}^{2-}	14

Regardless of the level of secondary orbital mixing, CN^- will have the highest bond order.
Regardless of the level of secondary orbital mixing, O_2^{2-} will have the lowest bond order.

Highest bond order: _____

Lowest bond order: _____

(b) Which of the species in part (a) should be diamagnetic.

Answer
CN^-, O_2^{2-}

6. In some cases, compounds of Group 18 can be isolated or observed. The diatomic cation, KrO^+ was reported in *Chem. Phys. Lett.* **1997**, *278*, 202. We will examine the molecular orbitals of KrO^+.

(a) (**9 points**) Using only the valence s and p-orbitals and neglecting secondary orbital mixing, propose a molecular orbital energy diagram for KrO^+.

Atomic Orbital Energies

	2s (eV)	2p(eV)			4s (eV)	4p (eV)
O	-32.4	-15.9		Kr	-27.5	-14.3

Include the following in your diagram:

(i) Energy axis

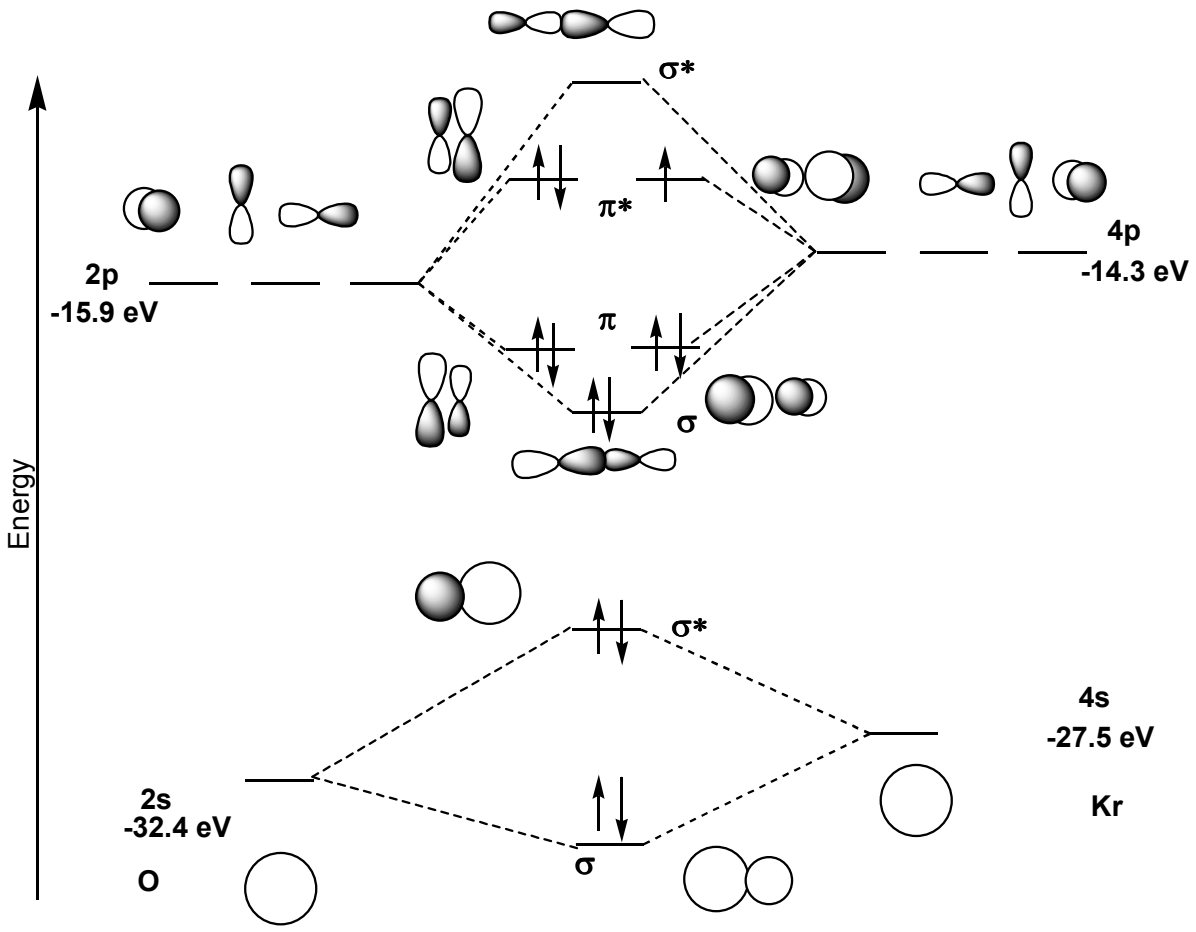
(ii) Atomic orbitals at the appropriate energies (include a sketch of each orbital) **(2)**

(iii) Molecular orbitals at the appropriate energies (include a sketch of each orbital) **(4)**

(iv) Labels for all atomic orbitals (e.g. 2s, 3p, etc...) **(1)**

(v) Labels for all molecular orbitals (e.g. σ^*, σ_g, π_u, etc...) **(1)**

(vi) Electrons in appropriate orbitals **(1)**



6+8-1 = 13 electrons

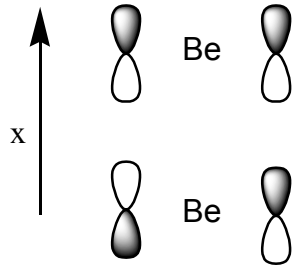
(b) (**1 point**) Predict the bond order in KrO^+

Bond order = 1.5

(c) (**1 points**) Identify the Highest Occupied Molecular Orbital (HOMO). Toward which atom would the HOMO be polarized and why?

Answer
The highest occupied MO are the π^* pair that are occupied by 3 electrons.
These MO's should be polarized toward the Kr center.

7. (**2 points**) For the molecule BeF_2, the following is a valid group orbital (SALC). Following the procedures from lecture and with the orientation shown in figure, assign the symmetry labels for these orbitals.



Label: B3u

Label: B2g

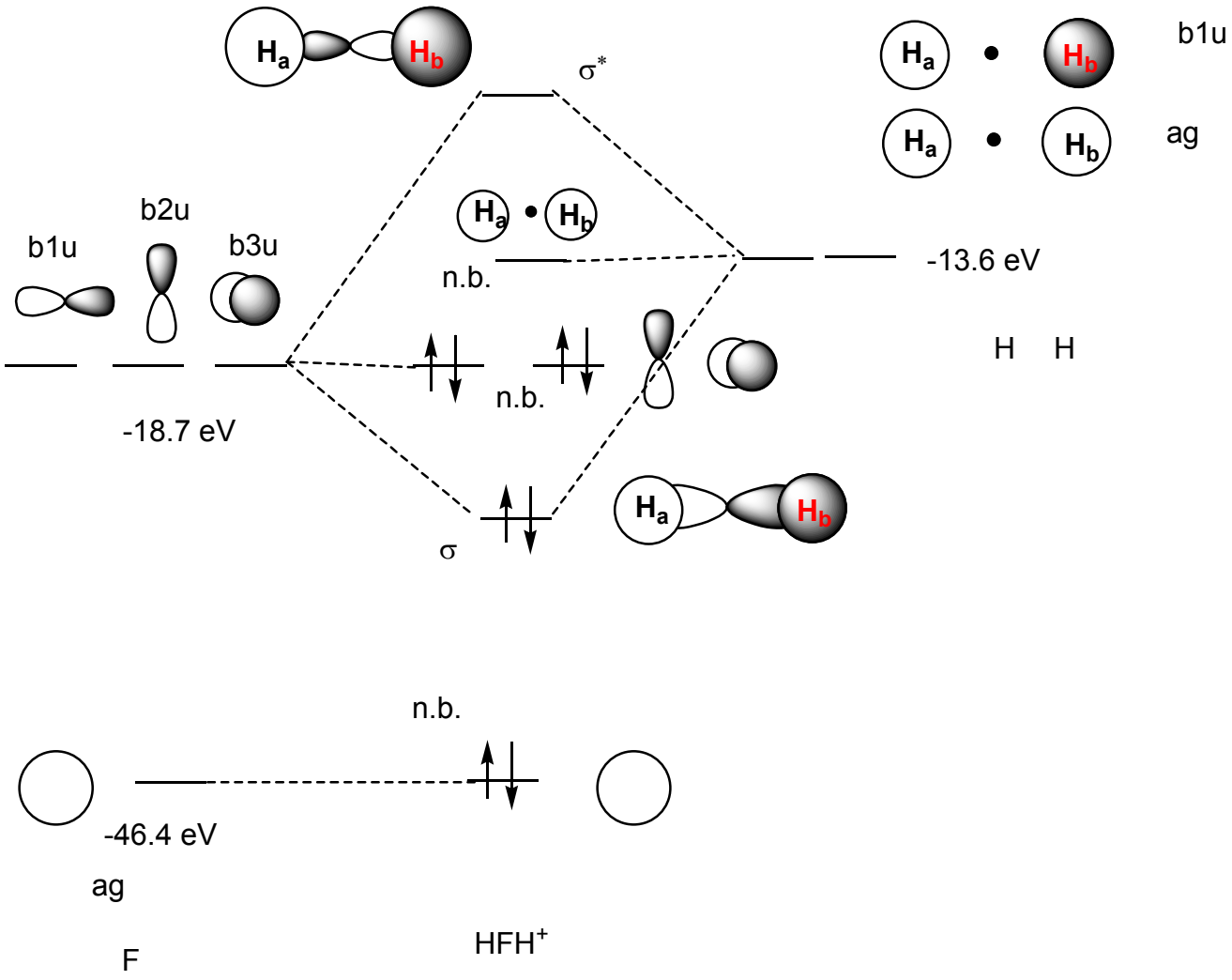
7. (**10 points**) In this problem you will prepare and analyze the MO diagram of a proposed ***linear HFH^+ cation***. NOTE: Please use the back of the page for your rough work. Neatness of the diagram will be important for receiving full marks.

(a) Sketch the group orbitals that you will use in this diagram. **(1)**

(b) Sketch the MO energy diagram and put in the appropriate number of electrons. Make sure to include sketches of each molecular orbital and label them. **(4+1+3)**

(c) How does the bond order change on going from linear HFH^+ to linear HFH^-? Explain your answer. **(1)**

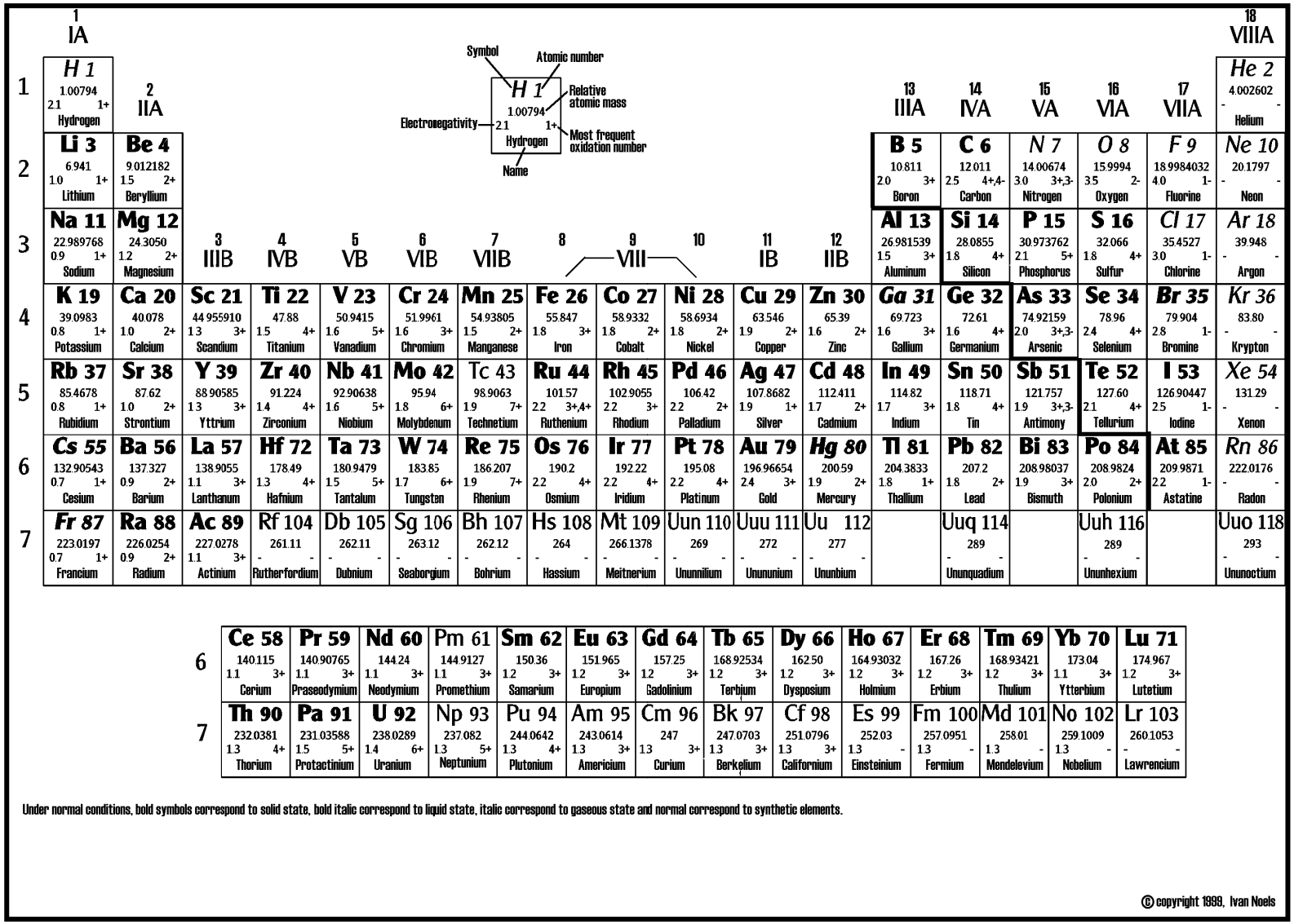
Orbital energies
H 1s -13.6 eV
F 2s -46.4 eV
F 2p -18.7 eV



Adding 2 electrons will add to the non-bonding orbital and not change the bond order.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z, xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y, xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x, yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x


Symbol
Atomic number
H 1
1.00794
Relative atomic mass
Electronegativity
2.1
1+
Most frequent oxidation number
Hydrogen
Name
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIII
10
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 H 1.00794 2.1 1+ Hydrogen
2 He 4.002602 - - Helium
2 Li 6.941 1.0 1+ Lithium
2 Be 9.012182 1.5 2+ Beryllium
2 B 5 10.811 2.0 3+ Boron
2 C 6 12.011 2.5 4+,4- Carbon
2 N 7 14.00674 3.0 3+,3- Nitrogen
2 O 8 15.9994 3.5 2- Oxygen
2 F 9 18.9984032 4.0 1- Fluorine
2 Ne 10 20.1797 - - Neon
3 Na 11 22.989768 0.9 1+ Sodium
3 Mg 12 24.3050 1.2 2+ Magnesium
3 Al 13 26.981539 1.5 3+ Aluminum
3 Si 14 28.0855 1.8 4+ Silicon
3 P 15 30.973762 2.1 5+ Phosphorus
3 S 16 32.066 1.8 4+ Sulfur
3 Cl 17 35.4527 3.0 1- Chlorine
3 Ar 18 39.948 - - Argon
4 K 19 39.0983 0.8 1+ Potassium
4 Ca 20 40.078 1.0 2+ Calcium
4 Sc 21 44.955910 1.3 3+ Scandium
4 Ti 22 47.88 1.5 4+ Titanium
4 V 23 50.9415 1.6 5+ Vanadium
4 Cr 24 51.9961 1.6 3+ Chromium
4 Mn 25 54.93805 1.5 2+ Manganese
4 Fe 26 55.847 1.8 3+ Iron
4 Co 27 58.9332 1.8 2+ Cobalt
4 Ni 28 58.6934 1.8 2+ Nickel
4 Cu 29 63.546 1.9 2+ Copper
4 Zn 30 65.39 1.6 2+ Zinc
4 Ga 31 69.723 1.6 3+ Gallium
4 Ge 32 72.61 1.6 4+ Germanium
4 As 33 74.92159 2.0 3+,3- Arsenic
4 Se 34 78.96 2.4 4+ Selenium
4 Br 35 79.904 2.8 1- Bromine
4 Kr 36 83.80 - - Krypton
5 Rb 37 85.4678 0.8 1+ Rubidium
5 Sr 38 87.62 1.0 2+ Strontium
5 Y 39 88.90585 1.3 3+ Yttrium
5 Zr 40 91.224 1.4 4+ Zirconium
5 Nb 41 92.90638 1.6 5+ Niobium
5 Mo 42 95.94 1.8 6+ Molybdenum
5 Tc 43 98.9063 1.9 7+ Technetium
5 Ru 44 101.57 2.2 3+,4+ Ruthenium
5 Rh 45 102.9055 2.2 3+ Rhodium
5 Pd 46 106.42 2.2 2+ Palladium
5 Ag 47 107.8682 1.9 1+ Silver
5 Cd 48 112.411 1.7 2+ Cadmium
5 In 49 114.82 1.7 3+ Indium
5 Sn 50 118.71 1.8 4+ Tin
5 Sb 51 121.757 1.9 3+,3- Antimony
5 Te 52 127.60 2.1 4+ Tellurium
5 I 53 126.90447 2.5 1- Iodine
5 Xe 54 131.29 - - Xenon
6 Cs 55 132.90543 0.7 1+ Cesium
6 Ba 56 137.327 0.9 2+ Barium
6 La 57 138.9055 1.1 3+ Lanthanum
6 Hf 72 178.49 1.3 4+ Hafnium
6 Ta 73 180.9479 1.5 5+ Tantalum
6 W 74 183.85 1.7 6+ Tungsten
6 Re 75 186.207 1.9 7+ Rhenium
6 Os 76 190.2 2.2 4+ Osmium
6 Ir 77 192.22 2.2 4+ Iridium
6 Pt 78 195.08 2.2 4+ Platinum
6 Au 79 196.96654 2.4 3+ Gold
6 Hg 80 200.59 1.9 2+ Mercury
6 Tl 81 204.3833 1.8 1+ Thallium
6 Pb 82 207.2 1.8 2+ Lead
6 Bi 83 208.98037 1.9 3+ Bismuth
6 Po 84 208.9824 2.0 2+ Polonium
6 At 85 209.9871 2.2 1- Astatine
6 Rn 86 222.0176 - - Radon
7 Fr 87 223.0197 0.7 1+ Francium
7 Ra 88 226.0254 0.9 2+ Radium
7 Ac 89 227.0278 1.1 3+ Actinium
7 Rf 104 261.11 - - Rutherfordium
7 Db 105 262.11 - - Dubnium
7 Sg 106 263.12 - - Seaborgium
7 Bh 107 262.12 - - Bohrium
7 Hs 108 264 - - Hassium
7 Mt 109 266.1378 - - Meitnerium
7 Uun 110 269 - - Ununnilium
7 Uuu 111 272 - - Ununnium
7 Uu 112 277 - - Ununbium
7 Uuq 114 289 - - Ununquadium
7 Uuh 116 289 - - Ununhexium
7 Uuo 118 293 - - Ununoctium
6 Ce 58 140.115 1.1 3+ Cerium
6 Pr 59 140.90765 1.1 3+ Praseodymium
6 Nd 60 144.24 1.1 3+ Neodymium
6 Pm 61 144.9127 1.1 3+ Promethium
6 Sm 62 150.36 1.2 3+ Samarium
6 Eu 63 151.965 1.2 3+ Europium
6 Gd 64 157.25 1.2 3+ Gadolinium
6 Tb 65 168.92534 1.2 3+ Terbium
6 Dy 66 162.50 1.2 3+ Dysposium
6 Ho 67 164.93032 1.2 3+ Holmium
6 Er 68 167.26 1.2 3+ Erbium
6 Tm 69 168.93421 1.2 3+ Thulium
6 Yb 70 173.04 1.1 3+ Ytterbium
6 Lu 71 174.967 1.2 3+ Lutetium
7 Th 90 232.0381 1.3 4+ Thorium
7 Pa 91 231.03588 1.5 5+ Protactinium
7 U 92 238.0289 1.4 6+ Uranium
7 Np 93 237.082 1.3 5+ Neptunium
7 Pu 94 244.0642 1.3 4+ Plutonium
7 Am 95 243.0614 1.3 3+ Americium
7 Cm 96 247 1.3 3+ Curium
7 Bk 97 247.0703 1.3 3+ Berkelium
7 Cf 98 251.0796 1.3 3+ Californium
7 Es 99 252.03 1.3 - Einsteinium
7 Fm 100 257.0951 1.3 - Fermium
7 Md 101 258.01 1.3 - Mendelevium
7 No 102 259.1009 1.3 - Nobelium
7 Lr 103 260.1053 - - Lawrencium
Under normal conditions, bold symbols correspond to solid state, bold italic correspond to liquid state, italic correspond to gaseous state and normal correspond to synthetic elements.
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