Name:_____   Section (circle): 1   2   3   4   5

NOT CUMULATIVE Exam 3
December 21, 2005

Good morning!

This exam packet should contain 19 pages, including 2 pages of reference information and a periodic table. Please write your answers in the spaces provided. If you use the backs of pages, please clearly mark the question number by your work. If you wish, you can remove the reference pages since these pages do not need to be handed in.

There are six multi-part questions on this exam. The point values of each question are indicated. Please note that some parts of each question are longer and/or more challenging and thus have greater point values than other parts.

It is recommended that you read through the entire exam before commencing work, and then start with the questions that you find most accessible. Do not waste time frustrating yourself over part of one question at the expense of moving on to another. You should have enough time to return to the parts that you find most challenging.

As always, your reasoning and the process used in arriving at your answer are the most important aspects to be communicated. Be sure to articulate clearly your thinking as you work through each question. Full credit cannot be given unless you show all work or reasoning. Pay attention to significant figures when recording your answers.

Relax! You have prepared well and you have learned a lot this semester. This is an opportunity to show off the results of all your hard work. You will have three hours to complete this exam. If you finish early, leave your completed exam on the front desk.

Remember: it is a violation of the Statement of Intellectual Responsibility at Amherst College to either give or receive help on this exam. The work you turn in must be yours and yours alone.
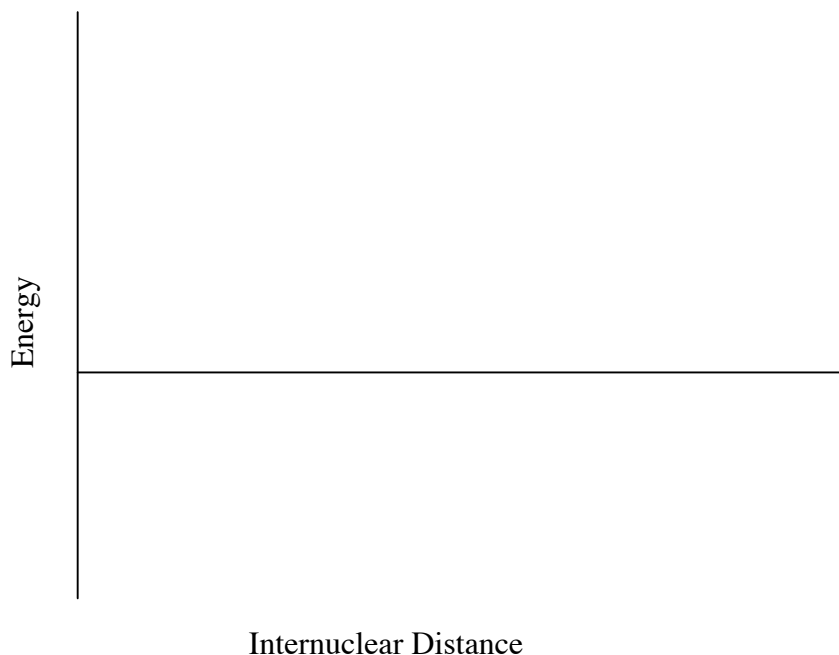
Good luck!

Question	Points	Score
I	20	
II	20	
III	20	
IV	20	
V	25	
VI	30	
Total	135	

Question I. (20 points)

In theory, a diatomic molecule can be formed from one atom of hydrogen and one atom of helium, giving HeH. The ionization energies of hydrogen and helium are 1312 kJ/mol and 2372 kJ/mol, respectively.

1. Draw an energy level diagram for the molecular orbitals in the HeH molecule. Use arrows to show how the electrons will fill the MOs.

2. What is the bond order in this molecule?

3. Are the electrons in the σ-bonding MO of this molecule more likely to be found near the H atom or near the He atom? Explain, in terms of molecular orbital theory, why this is the case. Discuss whether the MO explanation is consistent with a simpler picture of charge distribution based on Coulombic interactions.

4. What charge on HeH, magnitude and sign, would produce the most stable molecule or ion possible? Explain. What would the bond order be in this molecule or ion?

5. Rank the following in order of ionization energy, from lowest to highest: He, HeH$^+$, H$^-$, He$^+$, HeH, H. If there are two or more species that cannot be ordered, indicate as much. Briefly justify your choices.

6. On the axes below, draw potential energy curves, that is, the bond energy of the molecule as a function of distance between the nuclei, for the following molecules and molecular ions: H$_2$, HeH$^+$, HeH, HeH$^-$. Keep in mind how properties such as bond strength and bond length might vary among these species.

Energy

Internuclear Distance

7. Ultimately, all 'orbitals' are wavefunctions (or approximations of wavefunctions), which in turn are solutions to the Schrödinger Equation.

   a. Discuss reasons why we adopt models, such as the localized electron pair model or the molecular orbital model, to describe bonding in molecules, rather than solving the Schrödinger Equation for the molecule.

   b. When solving the Schrödinger Equation for a molecule, one approximation that is often made is that the nuclei are fixed (i.e. don't move) so that only the motion of the electrons must be considered. Assuming this approximation is valid, and drawing on your knowledge of atoms, for what systems would you predict it is possible to solve such a molecular Schrödinger Equation exactly? Explain.

Question II. (20 points)

Three salts (A, B, and C) contain octahedral complexes of chromium and have the molecular formula $CrCl_3 \cdot 6H_2O$.

1. Draw an energy level diagram for the splitting of the d orbitals in an octahedral field, being sure to label the orbitals. Then, distribute the proper number of electrons for the chromium ion in this complex among the energy levels shown in your drawing.

2. Use the following data to determine how many water molecules are bonded directly to the metal in each complex. Heating 0.270 g of each metal salt results in a mass loss of 0.036, 0.018 g and 0.000 g for salts A, B, and C respectively.

3. Use the following data to determine how many chlorides are bonded directly to the metal in each complex. Addition of aqueous silver nitrate to 100.0 ml portions of 0.100 M solutions of each salt results in the formation of different masses of silver chloride. Solution A yields 1430 mg, solution B 2870 mg, and solution C 4300 mg.

4. Draw the three octahedral complexes for salts A, B, and C.

5. Fill in the blank: These three salts are an example of _____ isomerism in transition metal complexes.

6. In the space below, draw any geometrical (G) or linkage (L) isomers of the structures above that may exist; indicate the type with a (G) or (L).

7. When in solution, the solutions have absorptions at 570 nm, 575 nm, and 620 nm. Identify which complex is which in solution and explain how you made this assignment.

Question III. (20 points)

1. Draw an energy level diagram for the molecular orbitals of CO. The diagram should show the energies of the MOs relative to the atomic orbitals and the electron configuration of the molecule.

2. What is the bond order in this molecule?

3. Explain the reasons for following features of the diagram:

    a. The energy of the 2s orbitals of C relative to the 2p orbitals of C

    b. The energy of the valence orbitals of C relative to the valence orbitals of O

4. Would you expect there to be sp-mixing in CO? Explain.

5. Assume the x-axis is the molecule's internuclear axis. For each of the σ-bonding and antibonding MOs in the molecule, rank the contribution of the four orbitals that can form σ-type MOs (C 2s, C $2p_x$, O 2s, O $2p_x$) from the highest to lowest contribution to that MO. If there is no sp-mixing, then indicate 'no contribution' where appropriate.

    a. σ_{2s}

    b. σ^*_{2s}

    c. σ_{2p}

    d. σ^*_{2p}

6. Explain why bonding (or anti-bonding) molecular orbitals cannot be constructed from overlap of the 2s orbital on C and the $2p_y$ orbital on O. A sketch might be helpful here.

7. Draw the Lewis structure for CO, including formal charge, and discuss how the Lewis structure is and is not consistent with the MO model of the molecule.

Question IV. (20 points)

Shown below is the amino acid histidine.

Histidine
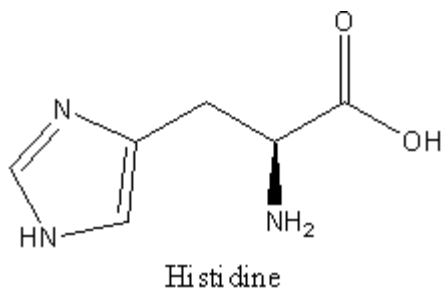
1. First, complete the drawing by inserting all of the implicit H atoms and draw in the lone pairs.

2. Next, indicate on the drawing sp^2 hybridized N and C atoms with a "2" and sp^3 hybridized N and C atoms with a "3".

3. There are four carbon-carbon bonds. Give the bond order for each and indicate whether or not there would be a barrier to rotation about that bond.

4. Why do some bonds have a barrier to rotation?

5. Circle the H atom shown above that is most easily lost when the amino acid becomes deprotonated.

6. The conjugate base formed upon deprotonation of the histidine is stabilized by delocalization of the negative charge. Draw resonance forms that are consistent with this statement.

7. Discuss the hybridization, bond angles, and geometry of the five membered ring that is part of the side group of histidine. Your answer should take into account that the ring is planar and all N-C bonds are equivalent.

8. A proton can be added to the side group of histidine to form an imidazolium cation shown here in all its resonance glory.
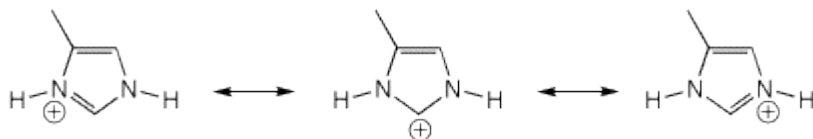
a. Show how the (+) formal charge is calculated for each positively charged atom in the structures above. Don't forget there are implicit H's on some C atoms.

b. What is the N-C bond order (the C between the two N's)?

Question V. (25 points)

1. $[Fe(CN)_6]^{3-}$ is a common complex of iron. Give the oxidation state and electron configuration for Fe in this complex.

2. In the space below, draw a crystal field diagram showing the orbital energies and ground state electron configuration in $[Fe(CN)_6]^{3-}$. (Leave space for $[Fe(NH_3)_6]^{3+}$ blank; it will be used later.)

$$[Fe(CN)_6]^{3-} \qquad\qquad\qquad [Fe(NH_3)_6]^{3+}$$

3. Is this complex paramagnetic or diamagnetic?

4. The complex $[Fe(NH_3)_6]^{3+}$ is observed to be much more strongly affected by a magnetic field than $[Fe(CN)_6]^{3-}$. Next to your diagram in #2 above, draw a crystal field diagram showing the ground state electron configuration in $[Fe(NH_3)_6]^{3+}$. Your diagram should clearly show the relative orbital energies in the two complexes and illustrate the reasons for the magnetic behavior described above.

5. a. Would you expect the wavelength of light absorbed by $[Fe(NH_3)_6]^{3+}$ to be shorter or longer than that absorbed by $[Fe(CN)_6]^{3-}$? Explain.

b. In actuality, $[Fe(NH_3)_6]^{3+}$ only displays a very faint purple color, indicating a very weak absorption. In other words, it is an improbable transition, so while the wavelength is consistent with predictions and lies in the visible range, few photons are actually absorbed. Based on the electron configuration in this complex, explain why one might expect the absorption to be so weak.

6. Now consider the complex *trans*-$[Fe(CN)_2(NH_3)_4]^+$. Because CN^- produces a <u>much</u> stronger crystal field than does NH_3, the usual octahedral field splitting is further distorted in this complex. Using your knowledge of the causes of crystal field splitting and the d-orbital geometries, and assuming the CN^- ligands lie along the z-axis, draw a crystal field diagram showing the orbital energies and electron configuration in *trans*-$[Fe(CN)_2(NH_3)_4]^+$. Label each energy level with the name of the d-orbital to which it corresponds (d_{xy}, d_{z^2}, etc.). Justify the energy ordering you choose.

7. a. Sketch the radial probability distribution $(4\pi r^2 R(r)^2)$ vs. r for the 3, 4, and 5d orbitals on the axes below. Indicate the most probable distance for each, and be sure to label the axes.

   b. Explain how these distribution functions are reflected in expected trends in atomic radius.

   c. The atomic radii of Fe, Ru, and Os are 124, 134, and 135 picometers, respectively. Explain this trend (or lack thereof), especially in light of your response to part 7a.

   d. It is generally observed that as atomic radius increases, ligands in a complex are able to get 'closer' to the central metal atom, resulting in more overlap between the ligand electrons and the metal orbitals. Based on this observation, would you expect the d-d transitions in the hexaammine complexes of Ru(III) to occur at shorter or longer wavelength than in $[Fe(NH_3)_6]^{3+}$? What would you expect the magnetic properties of the hexaammine Ru(III) complex to be?

Question VI. Iron Binding to Heme in Hemoglobin (30 points)
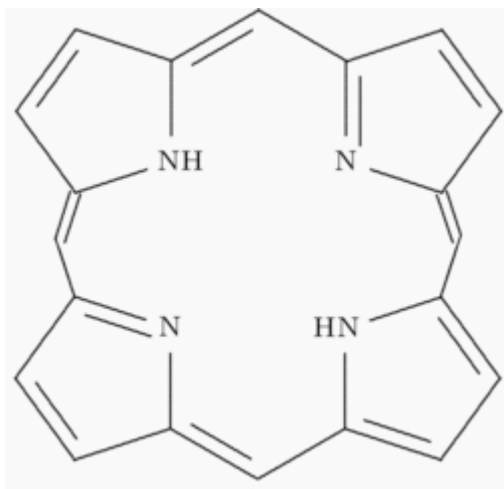
Shown at left is the porphyrin ligand that is similar to the one that binds to Fe(II) in hemoglobin. The questions below seek to understand the properties of this system in terms of the concepts introduced in Chemistry 11. *Restrict your answers to the space provided.*

1. Only two hydrogen atoms are shown explicitly in the drawing. Draw in the remaining <u>H atoms</u> and <u>lone pairs</u> on the picture, and determine the total number of σ _____ and π _____bonds in porphyrin.

2. Question about the single bonds to H
   a. In general (not just in this molecule), are single bonds between carbon and hydrogen atoms ALWAYS the same length? Explain.

   b. Compare the bond lengths in water (H_2O), ammonia (NH_3), and methane (CH_4). Explain.

3. Consider the two nitrogen atoms shown above with one single and one double bond to carbon. Sketch the orbitals that contribute to σ and π bonding and show their overlap. Use a localized electron pair model to completely describe the orbitals used to make the bonds between the N and C atoms as well as to contain any left over electrons on N.

4. Predict the geometry and bond angles about the N for the two C-N-C systems in #3.

5. In fact, all 8 N-C bonds in the entire molecule are identical in length and strength and the molecule is planar. How can we understand this? (words or pictures)

6. Iron binding occurs with the simultaneous loss of two protons. Circle the protons lost and put a square around the atoms that bind to the iron. How many porphyrin lone pairs are involved in metal bonding? _____

7. Some metals can form square planar complexes with ligands like porphyrin.
    a. What orbitals does the metal provide for the ligands' electrons in square planar complexes? Include n and l orbital designations in your answer.

    b. What happens to the energy of the metal's d orbitals in square planar complexes? Be specific and include d orbital labels.

8. In fact, when Fe(II) binds to the porphyrin in hemoglobin, it is octahedral. The fifth coordination site is occupied by a histidine ligand. The histidine free amino acid is shown below, though the only important part for metal bonding is the five-membered ring. Which atom *in the ring* would most likely bond to the metal and why?

Histidine
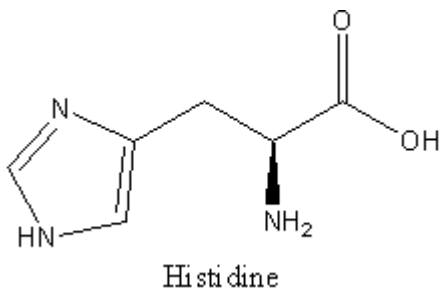
9. It has been mentioned in class and in your text that O_2 bonds to the protein hemoglobin reversibly without oxidation, whereas O_2 binding to just the porphyrin by itself in solution without the protein is accompanied by an irreversible oxidation of the metal and reduction of the O_2. The presence of the protein around the metal-porphyrin complex is said to prevent oxidation by preventing the O_2 from bonding perpendicular to the porphyrin plane. When O_2 binds to the Fe(II) in solution, it binds perpendicular. How can you understand this observation?
   HINT: You might consider which empty molecular orbitals on the O_2 might (in the perpendicular arrangement in solution) overlap with filled atomic orbitals on the Fe(II) in porphyrin to allow the electron to be transferred from one to the other.

10. You have learned that both CN^- and CO can substitute for O_2 in hemoglobin. By considering bond and molecular dipoles of CO and O_2, describe how they might behave differently in the aqueous environment of the blood.

11. When CO binds to hemoglobin, it is possible to excite the complex with 488 nm light from a laser that is strong enough to break the bond between the C and the Fe. What is the energy of the Fe-C bond in kJ/mole?

Equations, Constants, Conversion Factors, and Miscellaneous Information

pH: $pH = -\log[H^+]$

Ideal gas law: $PV = nRT$

van der Waals equation: $\left(P + a\left(\dfrac{n}{V}\right)^2\right)(V - nb) = nRT$

Dalton's law: $P_{total} = \displaystyle\sum_i P_i$

Mole fraction: $\chi_i = \dfrac{n_i}{n_{total}} = \dfrac{P_i}{P_{total}}$

Kinetic molecular theory of gases: $PV = \dfrac{2}{3} n \overline{KE}$

Average kinetic energy: $\overline{KE} = \dfrac{3}{2} RT = \dfrac{1}{2} M \overline{u^2}$

Most probable speed (Boltzmann distribution): $u_{mp} = \sqrt{\dfrac{2RT}{M}}$

Average speed (Boltzmann distribution): $\overline{u} = \sqrt{\dfrac{8RT}{\pi M}}$

Root mean squared speed (Boltzmann distribution): $u_{rms} = \sqrt{\dfrac{3RT}{M}}$

Graham's law of effusion: $\dfrac{\text{Rate of effusion of gas 1}}{\text{Rate of effusion of gas 2}} = \sqrt{\dfrac{M_2}{M_1}}$

Mean free path: $\lambda = \dfrac{1}{\sqrt{2}(N/V)(\pi d^2)}$

Collision rate with container wall (collisions per second): $Z_A = A \dfrac{N}{V} \sqrt{\dfrac{8RT}{2\pi M}}$

Collision rate between gas particles (collisions per second): $Z = 4 \dfrac{N}{V} d^2 \sqrt{\dfrac{\pi RT}{M}}$

Wavelength, frequency, speed relation for waves: $\lambda \nu = c$

Photon energy: $E_{photon} = h\nu = \dfrac{hc}{\lambda}$

Photoelectric effect: $E_{kinetic\ (ejected\ e^-)} = E_{photon} - \Phi = h\nu - h\nu_o$

continued on next page

Equations, Constants, Conversion Factors, and Miscellaneous Information

Kinetic energy: $E_{kinetic} = \dfrac{1}{2} mv^2$

deBroglie wavelength: $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

Heisenberg's uncertainty principle: $\Delta p \times \Delta x \geq \dfrac{h}{4\pi}$ or $m\Delta v \times \Delta x \geq \dfrac{h}{4\pi}$

Energy levels of a one-electron atom: $E_n = \left(-2.178 \times 10^{-18} \text{ J}\right) \left(\dfrac{Z^2}{n^2}\right)$

$$\Delta E = \left(-2.178 \times 10^{-18} \text{ J}\right) \left(Z^2\right) \left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2}\right)$$

XPS: $E_{x-ray} = E_{remove\ e^-} + E_{kinetic\ (ejected\ e^-)} = \left(E_{n=\infty} - E_{orbital}\right) + E_{kinetic\ (ejected\ e^-)} = E_{kinetic\ (ejected\ e^-)} - E_{orbital}$

Avogadro's number: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Ideal gas constant: $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Fundamental charge: $e = 1.60218 \times 10^{-19} \text{ C}$

Proton mass: $m_p = 1.673 \times 10^{-27} \text{ kg}$

Neutron mass: $m_n = 1.675 \times 10^{-27} \text{ kg}$

Electron mass: $m_e = 9.109 \times 10^{-31} \text{ kg}$

Speed of light: $c = 2.9979 \times 10^8 \text{ m s}^{-1}$

Planck's constant: $h = 6.626 \times 10^{-34} \text{ J s}$

1 atm = 760 torr = 101.325 kPa = 101325 Pa

1 L = 10^3 mL = 10^3 cm^3 1 M = 1 mol L^{-1}

1 nm = 10^{-9} m   1 Å = 0.1 nm = 10^{-10} m

1 kg = 10^3 g   1 mg = 10^{-3} g

$T_K = T_{°C} + 273$ STP $\equiv$ 1.000 atm, 273.15 K

1 J = 1 N m = 1 kg m^2 s^{-2} 1 kJ = 10^3 J

Spectrochemical series: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < CN^- < CO$

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																	1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

http://chemlab.pc.maricopa.edu/periodic/printable.gif

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

✱ Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

‡ Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)

Actinium	Ac	Erbium	Er	Mercury	Hg	Scandium	Sc
Aluminum	Al	Europium	Eu	Molybdenum	Mo	Seaborgium	Sg
Americium	Am	Fermium	Fm	Neodymium	Nd	Selenium	Se
Antimony	Sb	Fluorine	F	Neon	Ne	Silicon	Si
Argon	Ar	Francium	Fr	Neptunium	Np	Silver	Ag
Arsenic	As	Gadolinium	Gd	Nickel	Ni	Sodium	Na
Astatine	At	Gallium	Ga	Niobium	Nb	Strontium	Sr
Barium	Ba	Germanium	Ge	Nitrogen	N	Sulfur	S
Berkelium	Bk	Gold	Au	Nobelium	No	Tantalum	Ta
Beryllium	Be	Hafnium	Hf	Osmium	Os	Technetium	Tc
Bismuth	Bi	Hassium	Hs	Oxygen	O	Tellurium	Te
Bohrium	Bh	Helium	He	Palladium	Pd	Terbium	Tb
Boron	B	Holmium	Ho	Phosphorus	P	Thallium	Tl
Bromine	Br	Hydrogen	H	Platinum	Pt	Thorium	Th
Cadmium	Cd	Indium	In	Plutonium	Pu	Thulium	Tm
Calcium	Ca	Iodine	I	Polonium	Po	Tin	Sn
Californium	Cf	Iridium	Ir	Potassium	K	Titanium	Ti
Carbon	C	Iron	Fe	Praesodymium	Pr	Tungsten	W
Cerium	Ce	Krypton	Kr	Promethium	Pm	Uranium	U
Cesium	Cs	Lanthanum	La	Protactinium	Pa	Vanadium	V
Chlorine	Cl	Lawrencium	Lr	Radium	Ra	Xenon	Xe
Chromium	Cr	Lead	Pb	Radon	Rn	Ytterbium	Yb
Cobalt	Co	Lithium	Li	Rhenium	Re	Yttrium	Y
Copper	Cu	Lutetium	Lu	Rhodium	Rh	Zinc	Zn
Curium	Cm	Magnesium	Mg	Rubidium	Rb	Zirconium	Zr
Dubnium	Db	Manganese	Mn	Ruthenium	Ru		
Dysprosium	Dy	Meitnerium	Mt	Rutherfordium	Rf		
Einsteinium	Es	Mendelevium	Md	Samarium	Sm		