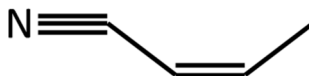


Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

**Part 0: Warmup.**

1. How many sigma bonds are there in the molecule below? (4 points)



- a. 3  
b. 6  
c. 9  
d. 12

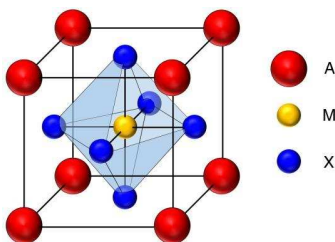
Answer c

2. In order for an ion or molecule to have square planar geometry, valence bond theory would predict that the central atom must be \_\_\_\_\_ hybridized. (4 points)

- a.  $sp^2$   
b.  $sp^3$   
c.  $sp^3d$   
d.  $sp^3d^2$

Answer d

3. The mineral perovskite, consists of calcium, titanium and oxygen. Its unit cell is shown below, with Ti at the corners (A in the diagram), Ca in the center (M in the diagram) and O at each of the faces (X in the diagram). Since the stoichiometry of the unit cell must match that for the compound, what is the formula for perovskite? (4 points)



- a.  $CaTi_8O_4$   
b.  $Ca_2Ti_4O_2$   
c.  $CaTiO_3$   
d.  $CaTiO$

Answer c

4. Complete the following with *increases*, *decreases*, or *does not change*. (6 points)  
a. If the intermolecular forces in a liquid decrease, the normal boiling point of the liquid

decreases

- b. If the intermolecular forces in a liquid decrease, the vapor pressure of the liquid

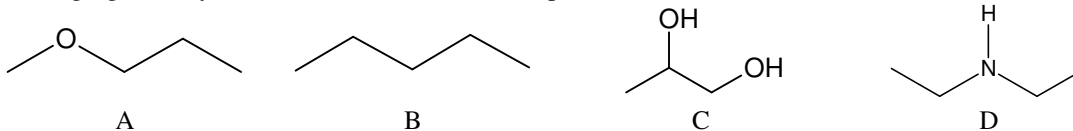
increases

- c. If the temperature of a liquid increases, the equilibrium vapor pressure

increases

**Part I: Complete all of problems 6-8**

5. Consider the compounds below. Arrange the molecules in order of increasing boiling point. Clearly justify your reasoning. Ignore any effects of molecular mass. (12 points)



Your order and justification should be based in the types of intermolecular forces each of the compounds is capable of participating in. For compounds of the same molar mass, boiling point should correlate to intermolecular forces, with the strongest IM forces producing higher boiling point. In order of increasing boiling point:  $B < A < D < C$

B: nonpolar, only dispersion forces

A: somewhat polar, but not capable of participating in H-bonding

D: polar, capable of H-bonding (amine)

C: polar, capable of H-bonding (alcohol). Stronger tendency for H-bonding than D because of more polar O-H bond (compared to N-H)

6. The compound oxygen difluoride is quite unstable, reacting with water to produce oxygen and hydrogen fluoride in an exothermic reaction with  $\Delta H^{\circ}_{\text{rxn}} = -318 \text{ kJ}$ . Use the table of bond energies to calculate the bond dissociation energy of the oxygen-fluorine bond in oxygen difluoride. (12 points)

Bond	H-F	F-F	F=F	H-H	O-H	O-O	O=O
Bond Energy (kJ/mol)	565	159	414	436	464	142	498

Reaction	OF <sub>2</sub>	+	H <sub>2</sub> O	→	2HF	+	O <sub>2</sub>
Lewis Structure	$\text{:}\ddot{\text{F}}\text{--}\ddot{\text{O}}\text{--}\ddot{\text{F}}\text{:}$		$\text{H--}\ddot{\text{O}}\text{--H}$		$\text{H--}\ddot{\text{F}}\text{:}$		$\ddot{\text{O}}\text{=}\ddot{\text{O}}$
Bonds Broken	$2(\text{O-F}) = 2\Delta H_{\text{O-F}}$		$2(\text{O-H}) = 2(464\text{kJ})$				
Bonds Formed					$2(\text{H-F}) = 2(565\text{kJ})$		$1(\text{O=O}) = 498\text{kJ}$

We know the enthalpy change for the reaction, so we can use the relationship below to find the unknown bond energy:

$$\Delta H^{\circ} = \Sigma(\text{Bond Energy for bonds broken}) - \Sigma(\text{Bond energy for bonds formed})$$

$$-318\text{kJ} = (2\Delta H_{\text{O-F}} + 2(464\text{kJ})) - (2(565\text{kJ}) + 498\text{kJ})$$

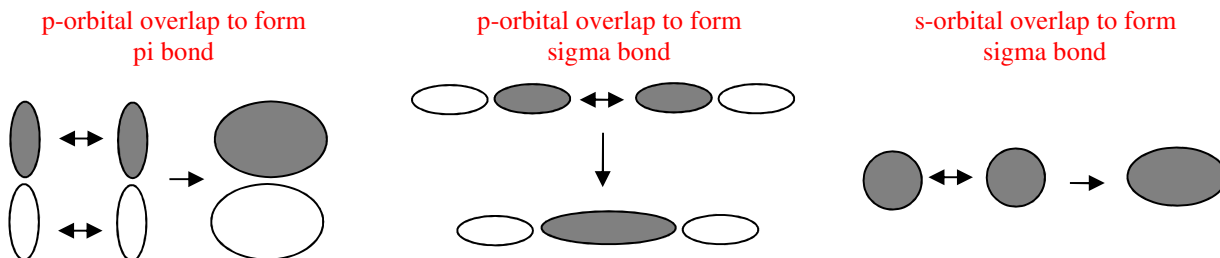
$$2\Delta H_{\text{O-F}} = -318\text{kJ} + (2(565\text{kJ}) + 498\text{kJ}) - 2(464\text{kJ}) = -318\text{kJ} + 1628\text{kJ} - 928\text{kJ} = 382 \text{ kJ}$$

$$\Delta H_{\text{O-F}} = 382\text{kJ}/2 = 191 \text{ kJ per mole of bonds}$$

Answer 191 kJ/mol

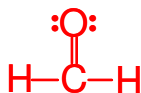
7. In the context of valence bond theory, explain how p-orbitals can form both sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds, but s-orbitals do not. Feel free to use sketches to illustrate your points. (12 points)

The key point here is that in order to form sigma bonds, the orbital must be able to overlap with another orbital in such a way that the electron density is directly between the atoms. To form a pi bond, the overlap must be such that the electron density is off of the axis that connects the atoms. Since s orbitals are spherical, there is no way that they can overlap to form pi bonds, but because of the shape of a p-orbital, there is the possibility of both end-to-end (sigma bond) and side-to-side (pi bond) overlap.



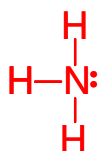
8. Choose two (2) of the compounds below and draw Lewis structure, indicate the hybridization of the underlined atom and estimate all bond angles. Identify the strongest intermolecular interaction the molecule can participate in with another molecule of the same compound. (12 points)

- a. CH<sub>2</sub>O



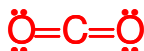
Carbon is **sp<sup>2</sup> hybridized**, all bond angles should be **~120°**. The molecule is polar, but does not have the requirements to undergo hydrogen bonding, so the strongest intermolecular force it could participate in with itself is **dipole-dipole interactions**.

- b. NH<sub>3</sub>



Nitrogen is **sp<sup>3</sup> hybridized**, all bond angles should be **<109.5°** because of the presence of the lone pair on the nitrogen. Ammonia is polar, but also has the necessary characteristics to undergo **hydrogen bonding interactions**, which are the strongest interactions it can undergo.

- c. CO<sub>2</sub>



Carbon is **sp hybridized**, the O-C-O bond angles should be **180°**. While each of the C=O bonds are polar, the geometry is such that the bond dipoles cancel, making the molecule nonpolar. Therefore, **dispersion forces** are the strongest intermolecular interaction.

**Part II. Answer three (3) of problems 9-13. Clearly mark the problems you do not want graded. 12 points each.**

9. A certain liquid has a vapor pressure of 92.0 Torr at 23.0°C and 353.0 Torr at 45.0°C.  
 a. Calculate the enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) for this liquid.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Rearranging (T must be in Kelvin):

$$\Delta H_{\text{vap}} = \frac{\ln\left(\frac{P_2}{P_1}\right) R}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{\ln\left(\frac{353 \text{ Torr}}{92 \text{ Torr}}\right) 8.31441 \frac{\text{J}}{\text{molK}}}{\left(\frac{1}{296 \text{ K}} - \frac{1}{318 \text{ K}}\right)} = 47,835 \frac{\text{J}}{\text{mol}} = 47.8 \frac{\text{kJ}}{\text{mol}}$$

Answer 47.8 kJ/mol

- b. Calculate the normal boiling point of this liquid.

The normal boiling point corresponds to the temperature when the vapor pressure is 1 atm (760 Torr). You can use the enthalpy of vaporization from part a and either of the temperature/pressure values.

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{\ln\left(\frac{P_2}{P_1}\right) R}{\Delta H_{\text{vap}}}$$

$$\frac{1}{T_1} = \frac{\ln\left(\frac{P_2}{P_1}\right) R}{\Delta H_{\text{vap}}} + \frac{1}{T_2} = \frac{\ln\left(\frac{92 \text{ Torr}}{760 \text{ Torr}}\right) 8.31441 \frac{\text{J}}{\text{molK}}}{47,835 \text{ J}} + \frac{1}{296 \text{ K}}$$

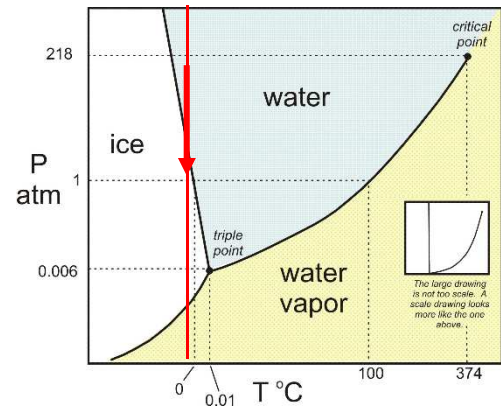
$$\frac{1}{T_1} = -0.000367 \text{K}^{-1} + 0.003378 \text{K}^{-1} = 0.00301 \text{K}^{-1}$$

$$T = (0.00301 \text{K}^{-1})^{-1} = 332 \text{ K or } (332-273) = 59^\circ\text{C}$$

Answer 332 K or 59°C

10. You decide to cool a can of carbonated soda (or pop depending on where you are from) quickly by placing it in the freezer. When you take the can out, the contents are still liquid, but when you open the can, the soda (or pop) immediately freezes. Explain why this happens. You may assume that the soda behaves essentially like water. Use the phase diagram for water, shown below, to support your explanation.

Since the majority of the solution is water, the water phase diagram is a good approximation of the phase behavior of the soda. Consider the red line added to the phase diagram. This line corresponds to  $0^{\circ}\text{C}$ , the temperature at which water freezes at 1 atmosphere. In a freezer, the temperature would be somewhere less than  $0^{\circ}\text{C}$ , so we would be somewhere to the left of this line. Since soda (or pop) is under pressure, yet the contents are still liquid in the unopened can, we must be operating in the “water” region to the left of the red line (we would say that the solution is “supercooled”). When we open the can, we release the pressure (it returns to atmospheric pressure), but the temperature remains unchanged, therefore the system will undergo a phase change corresponding to the red arrow in the diagram (a liquid to solid change), and the solution freezes.



11. The atomic radius of tungsten, W, is 202 pm. If the W has a molar mass of 183.84 g/mol and has a density of 19.3 g/cm<sup>3</sup>, does tungsten form a face-centered cubic lattice? Justify your answer with a calculation.

Let's start by assuming W is fcc. If so, what would its density be? Based on our knowledge of the fcc structure, the length of a diagonal of one face is 4(radius of the atom). Knowing this, we can find the volume of a unit cell.

$a^2 + a^2 = [4(202\text{pm})]^2$ , so  $a = 571$  pm and  $a^3 = \text{volume of unit cell} = (571 \times 10^{-10} \text{ cm})^3$

$$\frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{1 \text{ unit cell}}{1.865 \times 10^{-22} \text{ cm}^3} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} \times \frac{183.84 \text{ g}}{1 \text{ mol}} = \frac{6.55 \text{ g}}{\text{cm}^3}$$

*So, if W were fcc, we'd expect a density of 6.55 g/cm<sup>3</sup>, since the reported density is 19.3 g/cm<sup>3</sup>, W must not form a face-centered cubic lattice.*

**Alternatively**, you could calculate the radius necessary for an element with tungsten's atomic mass and density to have a fcc lattice:

$$\frac{1 \text{ cm}^3}{19.3 \text{ g}} \times \frac{183.84 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} \times \frac{4 \text{ atoms}}{\text{unit cell}} = \frac{6.33 \times 10^{-23} \text{ cm}^3}{\text{unit cell}}$$

So, the volume of a unit cell is  $6.33 \times 10^{-23} \text{ cm}^3$ , which makes the length of one of the edges of the unit cell:  $(6.33 \times 10^{-23} \text{ cm}^3)^{1/3} = 3.985 \times 10^{-8} \text{ cm} = 398.5$  pm

For a fcc lattice, the length of a face diagonal is equal to 4 atomic radii. So, we need to find the length of the diagonal:

$$a^2 + a^2 = c^2$$

$$2a^2 = c^2$$

$$c = (2a^2)^{1/2} = (2 \times 398.5^2 \text{ pm}^2)^{1/2} = 564 \text{ pm}$$

*Therefore the expected atomic radius is  $564 \text{ pm} / 4 = 141$  pm.*

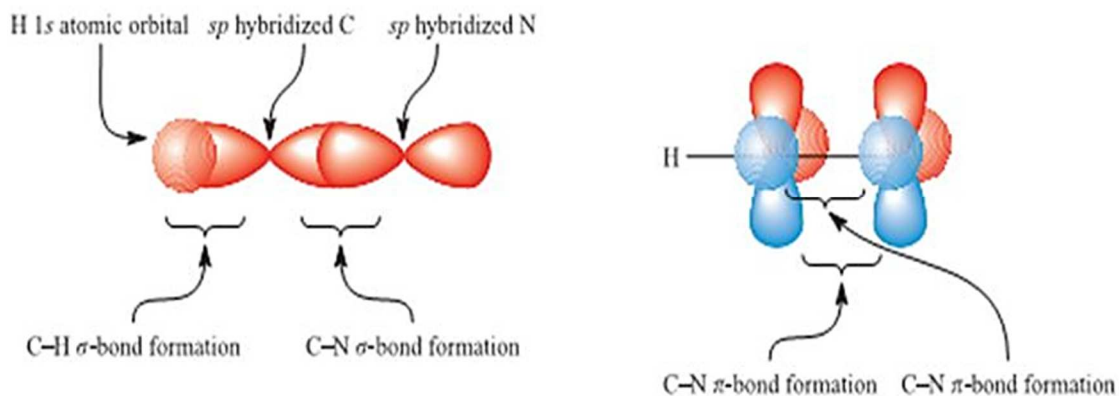
*Since the actual atomic radius of tungsten is 202 pm, it must not form a fcc lattice.*

12. Use valence bond theory to describe the bonding around the carbon atom in HCN. Identify the hybridization on the carbon atom and show how hybridization allows the formation of the necessary sigma and pi bonds in the compound. Drawings may be useful!



We need consider the geometry around the carbon atom in HCN. To do that, we need a Lewis structure, which is shown above. In the structure, we see that carbon has one triple bond to nitrogen (consisting of one sigma and two pi bonds) and one single bond to hydrogen (a sigma bond), with only two atoms around the central atom. This produces linear geometry, which occurs with  $sp$  hybridization. With  $sp$  hybridization, one of the 2p orbitals and the 2s orbital on carbon produces an  $sp$  hybrid orbital, as shown below: The  $sp$  hybrid orbital is able to form sigma bonds with both the H and N.

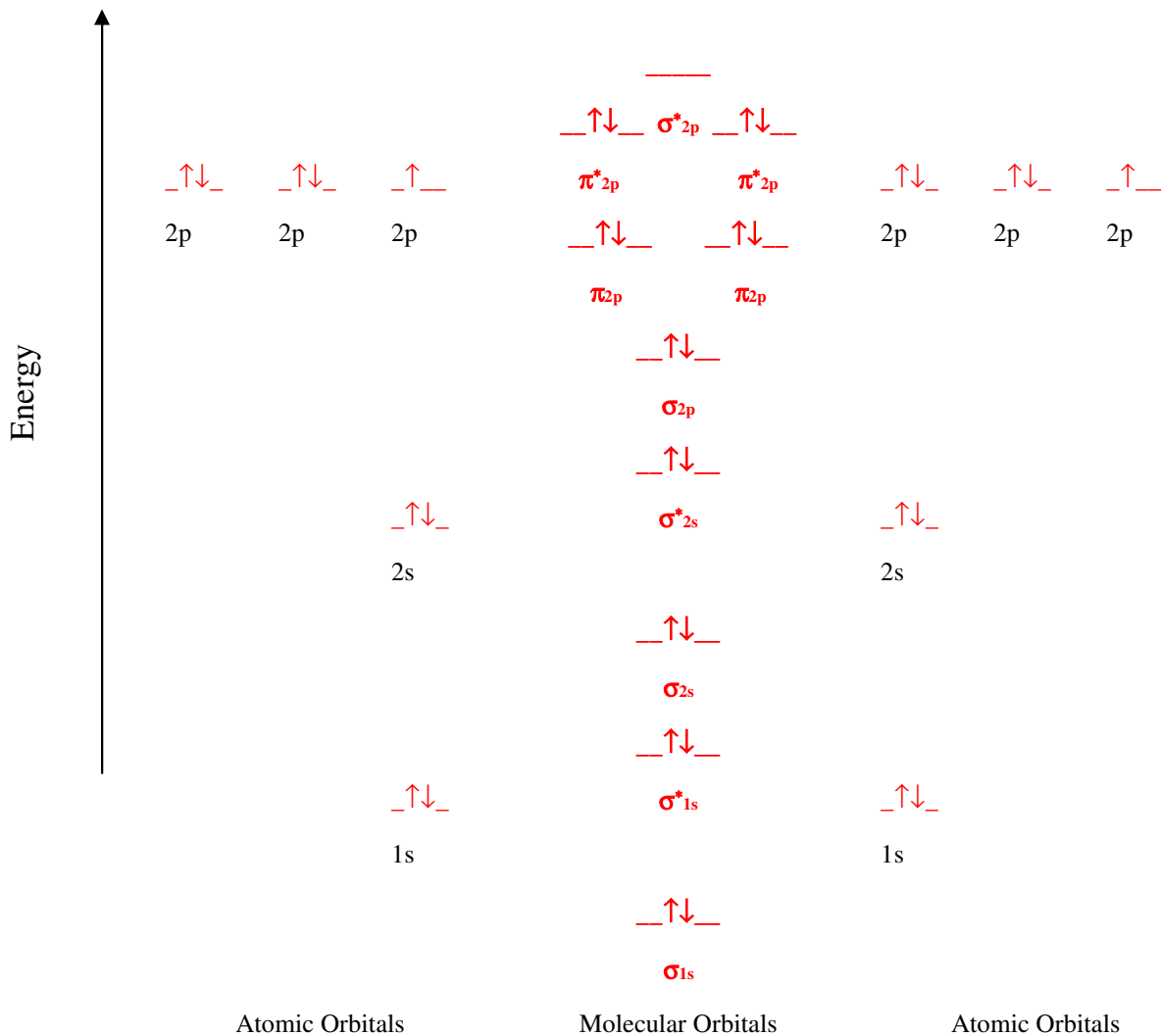
The carbon atom then has two unhybridized 2p orbitals that are able to form pi bonds with the 2p orbitals on the nitrogen. These orbitals are oriented at  $90^\circ$  from one another, which allows the sigma and two pi bonds in the triple bond to coexist.



13. Answer the following questions about peroxide ion ( $\text{O}_2^{2-}$ ).

a. Complete the MO diagram for peroxide below. Account for valence and core electrons. (6 points)

**18 electrons total!!! (O-8, O-8, (-2)-1)**



b. What is the bond order for peroxide? (2 points)

$$\frac{1}{2}(\# \text{bonding electrons} - \# \text{antibonding electrons}) = \frac{1}{2}(10 - 8) = 1$$

c. Is peroxide diamagnetic? Why or why not? (2 points)

Peroxide has no unpaired electrons, so it is diamagnetic.

d. Would you expect the peroxide ion to be more or less stable than molecular oxygen ( $\text{O}_2$ )? Why? (2 points)

$\text{O}_2$  has two fewer electrons, which would lead to the  $\pi^*$  orbital having two fewer electrons. These fewer antibonding electrons would lead to a bond order of 2 for  $\text{O}_2$ , suggesting a more stable molecule.



Possibly Useful Information

$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$	$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$	$1 \text{ atm} = 760 \text{ Torr}$
$a^2 + b^2 = c^2$	$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$	$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
$\Delta H^\circ = \Sigma(\text{Bond Energy for bonds broken}) - \Sigma(\text{Bond energy for bonds formed})$		

Periodic Table of the Elements

1 <b>H</b> Hydrogen 1.008	2 <b>He</b> Helium 4.003																																																																																																																		
3 <b>Li</b> Lithium 6.941	4 <b>Be</b> Beryllium 9.012	5 <b>B</b> Boron 10.811	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998	10 <b>Ne</b> Neon 20.180	11 <b>Na</b> Sodium 22.990	12 <b>Mg</b> Magnesium 24.305	13 <b>Al</b> Aluminum 26.982	14 <b>Si</b> Silicon 28.086	15 <b>P</b> Phosphorus 30.974	16 <b>S</b> Sulfur 32.066	17 <b>Cl</b> Chlorine 35.453	18 <b>Ar</b> Argon 39.948	19 <b>K</b> Potassium 39.098	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.956	22 <b>Ti</b> Titanium 47.867	23 <b>V</b> Vanadium 50.942	24 <b>Cr</b> Chromium 51.996	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933	28 <b>Ni</b> Nickel 58.693	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.631	33 <b>As</b> Arsenic 74.922	34 <b>Se</b> Selenium 78.971	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798	37 <b>Rb</b> Rubidium 85.468	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.906	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.906	42 <b>Mo</b> Molybdenum 95.93	43 <b>Tc</b> Technetium 98.907	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.906	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.868	48 <b>Cd</b> Cadmium 112.414	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.711	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.6	53 <b>I</b> Iodine 126.904	54 <b>Xe</b> Xenon 131.294	55 <b>Cs</b> Cesium 132.905	56 <b>Ba</b> Barium 137.328	57 <b>La</b> Lanthanum 138.905	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodymium 140.908	60 <b>Nd</b> Neodymium 144.243	61 <b>Pm</b> Promethium 144.913	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.925	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.930	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.934	70 <b>Yb</b> Ytterbium 173.053	71 <b>Lu</b> Lutetium 174.967	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.948	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.217	78 <b>Pt</b> Platinum 195.085	79 <b>Au</b> Gold 196.967	80 <b>Hg</b> Mercury 200.592	81 <b>Tl</b> Thallium 204.383	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.980	84 <b>Po</b> Polonium [209]	85 <b>At</b> Astatine [209]	86 <b>Rn</b> Radon [222]	87 <b>Fr</b> Francium [223]	88 <b>Ra</b> Radium [226]	89-103 <b>Lanthanide Series</b>	104 <b>Rf</b> Rutherfordium [261]	105 <b>Db</b> Dubnium [262]	106 <b>Sg</b> Seaborgium [266]	107 <b>Bh</b> Bohrium [264]	108 <b>Hs</b> Hassium [269]	109 <b>Mt</b> Meitnerium [278]	110 <b>Ds</b> Darmstadtium [281]	111 <b>Rg</b> Roentgenium [280]	112 <b>Cn</b> Copernicium [285]	113 <b>Nh</b> Nihonium [286]	114 <b>Fl</b> Flerovium [289]	115 <b>Mc</b> Moscovium [289]	116 <b>Lv</b> Livermorium [293]	117 <b>Ts</b> Tennessine [294]	118 <b>Og</b> Oganesson [294]	119 <b>U</b> Uranium 238.029	120 <b>Th</b> Thorium 232.038	121 <b>Pa</b> Protactinium 231.036	122 <b>Ac</b> Actinium 227.028	123-138 <b>Actinide Series</b>	139 <b>Am</b> Americium 243.061	140 <b>Cm</b> Curium 247.070	141 <b>Bk</b> Berkelium 247.070	142 <b>Cf</b> Californium 251.080	143 <b>Es</b> Einsteinium [254]	144 <b>Fm</b> Fermium 257.095	145 <b>Md</b> Mendelevium 258.1	146 <b>No</b> Nobelium 259.101	147 <b>Lr</b> Lawrencium [262]

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