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5.111 Principles of Chemical Science
Fall 2008

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Second Hour Exam- Answer Key

5.111

Write your name below. **Do not open the exam until the start of the exam is announced.** The exam is closed notes and closed book.

1. Read each part of each problem carefully and thoroughly.
 2. Read all parts of each problem. **MANY OF THE LATTER PARTS OF A PROBLEM CAN BE SOLVED WITHOUT HAVING SOLVED EARLIER PARTS.** However, if you need a numerical result that you were not successful in obtaining for the computation of a latter part, make a physically reasonable approximation for that quantity (and indicate it as such) and use it to solve the latter parts.
 3. A problem that requests you to “calculate” implies that several calculational steps may be necessary for the problem’s solution. You must show these steps clearly and indicate all values, including physical constants used to obtain your quantitative result. Significant figure usage must be correct.
 4. If you don’t understand what the problem is requesting, raise your hand and a proctor will come to your desk.
 5. Physical constants, formulas and a periodic table are given on the last page. You may detach this page **once the exam has started.**
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Suggested time

1. 14 minutes (30 points) _____
2. 8 minutes (12 points) _____
3. 8 minutes (20 points) _____
4. 12 minutes (27 points) _____
5. 8 minutes (11 points) _____

Total (100 points) _____

Name _____

1. (30 points) Lewis structures and VSEPR theory

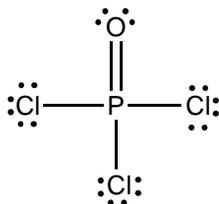
Draw the **most stable** Lewis structure for each of the following molecules, subject to the information given for each. Be sure to **include the lone pairs** and, if applicable, draw any **resonance forms** that are equal in energy. **Indicate any nonzero formal charges.**

(a) (i) (6 points) Draw the Lewis structure of POCl_3 . Include any relevant resonance forms, and indicate any nonzero formal charges.

32 valence electrons

40 electrons needed to fill valence shells

8 bonding electrons } after valence shell expansion, 10 bonding electrons and 22 lone pair electrons
24 lone-pair electrons } (eliminating all formal charges)



(ii) (2 points) Name the geometry around the phosphorus atom.

tetrahedral

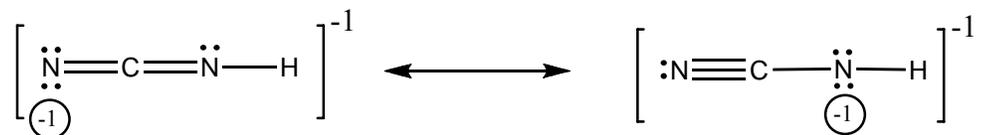
(b) (8 points) Draw the Lewis structure of $(\text{NCNH})^{-1}$ (atom order as indicated). Include any relevant resonance forms, and indicate any nonzero formal charges.

16 valence electrons

26 electrons needed to fill valence shells

10 bonding electrons

6 lone-pair electrons



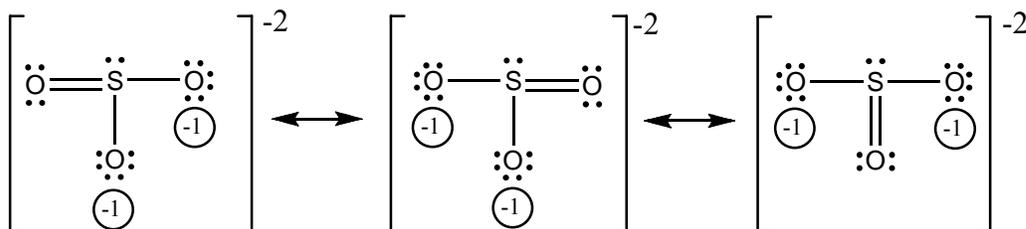
Formal charges are circled on atoms where the FC is not zero.

(c) (i) (6 points) Draw the Lewis structure of $(\text{SO}_3)^{2-}$. Include any relevant resonance forms, and indicate any nonzero formal charges.

26 valence electrons

32 electrons needed to fill valence shells

6 bonding electrons } after valence shell expansion, 8 bonding electrons and 18 lone pair electrons
 20 lone-pair electrons } (eliminating all formal charges)



(ii) (2 points) Name the geometry around the sulfur atom.

trigonal pyramidal

(iii) (2 points) Circle the one value that best describes the O-S-O bond angle in $(\text{SO}_3)^{2-}$.

< 90°; 90°; > 90°; **< 109.5°;** 109.5°; > 109.5°; < 120°; 120°; > 120°; < 180°; 180°; > 180°

(iv) (2 points) Is $(\text{SO}_3)^{2-}$ a **polar** or a **non-polar** molecule?

polar

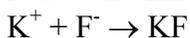
2. (12 points) Ionic bonds

KF has an ionic bond with a bond length of 0.217 nm. Calculate the ΔE , in kJ/mol, for the **formation** of a KF bond from the neutral atoms K and F. For this calculation, assume that the potassium and fluorine ions are point charges. IE and EA information for K and F is provided in the table below.

	Ionization energy (kJ/mol)	Electron affinity (kJ/mol)
potassium (K)	418	48
fluorine (F)	1680	328



First calculate the ΔE for the formation of an ionic bond from the two ions:



$$U(r) = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 r} = \frac{(-1)(1)(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1})(0.217 \times 10^{-9} \text{ m})}$$

$$U(r) = -1.063 \times 10^{-18} \text{ J}$$

$$U(r) = -1.063 \times 10^{-18} \text{ J} \times \frac{\text{kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{\text{mol}} = -640.1 \text{ kJ/mol}$$

$$U(r) = -640.1 \text{ kJ/mol}$$

$$\Delta E_{\text{total}} = IE_K - EA_F + U(r)$$

$$K \rightarrow K^+ + e^- \equiv IE_K \quad 418 \text{ kJ/mol}$$

$$F + e^- \rightarrow F^- \equiv -EA_F \quad -328 \text{ kJ/mol}$$

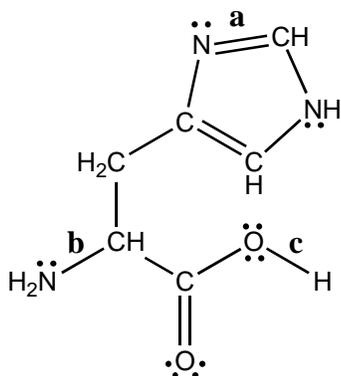
$$K^+ + F^- \rightarrow KF \equiv U(r) \quad -640.1 \text{ kJ/mol}$$

$$K + F \rightarrow KF \quad -550.1 \text{ kJ/mol}$$

$$\mathbf{-550. \text{ kJ/mol} \quad \text{or} \quad -5.50 \times 10^2 \text{ kJ/mol}}$$

3. (20 points) **Hybridization**

(a) (12 points) The structure of the amino acid histidine is provided below. For the indicated bonds, a-c, write the symmetry of each bond, and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form each of the bonds. Where appropriate, include the x, y, or z designations with the orbitals.



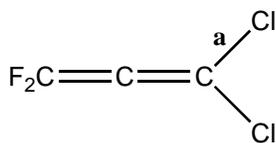
N-C bond a: $\sigma(\text{N}2\text{sp}^2, \text{C}2\text{sp}^2)$
 $\pi(\text{N}2\text{p}_y, \text{C}2\text{p}_y)$ or $\pi(\text{N}2\text{p}_x, \text{C}2\text{p}_x)$

N-C bond b: $\sigma(\text{N}2\text{sp}^3, \text{C}2\text{sp}^3)$

O-H bond c: $\sigma(\text{O}2\text{sp}^3, \text{H}1\text{s})$

(b) (8 points)

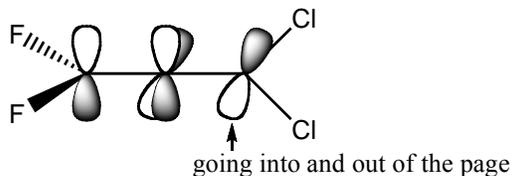
(i) For the molecule below, indicate the symmetry in the C-Cl bond (labeled a), and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form the bond. If appropriate, include the x, y, or z designations with the orbitals.



C-Cl bond a: $\sigma(\text{C}2\text{sp}^2, \text{Cl}3\text{p}_z)$

(ii) Do the chlorine atoms in the $\text{F}_2\text{C}=\text{C}=\text{CCl}_2$ molecule above lie in the **same plane** as the fluorine atoms or in a **perpendicular plane** to the fluorine atoms? Briefly explain your answer (with words or a picture).

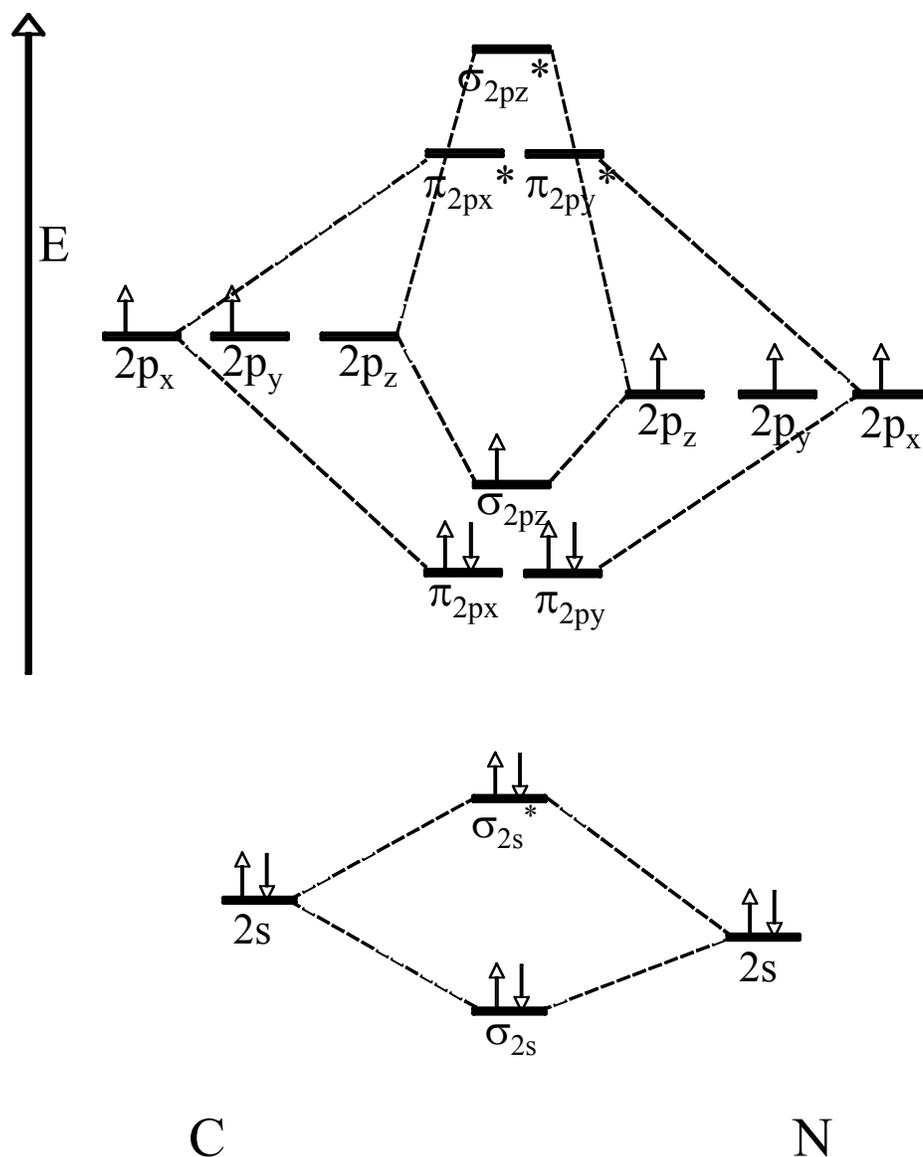
perpendicular plane. The p-orbitals in the two sp^2 -hybridized carbon atoms are perpendicular to each other (p_y and p_x), meaning the F-C-F bonds and the Cl-C-Cl bonds also lie in perpendicular planes.



4. (27 points) **Molecular orbital theory**

(a) (21 points)

(i) (9 points) Draw an energy correlation diagram for the molecular orbitals of the **valence electrons** in CN. Label the atomic and molecular orbitals, including the x, y and z designations where appropriate. The relative ordering of the energies of the states must be correct. **Use the full space available** to spread out your energy levels so that the labels for the orbitals fit easily.



(ii) (2 points) Of the CN molecular orbitals **occupied by valence electrons**, name the orbitals that have a nodal plane along the internuclear (bond) axis.

$\pi 2p_x$ and $\pi 2p_y$

(iii) (4 points) Determine the bond order of the cyanide molecule, CN, and the cyanide ion, CN⁻¹.

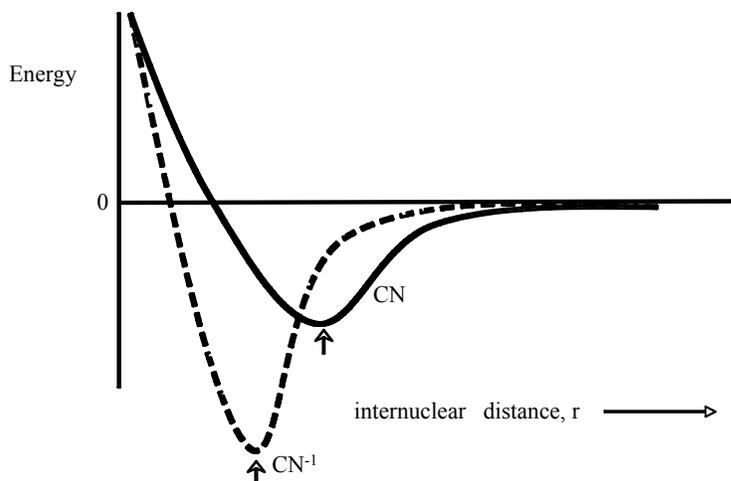
$$\frac{1}{2}(\# \text{ of bonding electrons} - \# \text{ of anti-bonding electrons})$$

$$\text{BO of CN: } \frac{1}{2}(7-2) = \mathbf{2.5}$$

$$\text{BO of CN}^{-1}: \frac{1}{2}(8-2) = \mathbf{3}$$

(iv) (4 points) Below is an energy diagram of the CN covalent bond in a neutral CN molecule. On the same graph, plot the energy vs. internuclear distance, r , of the CN covalent bond in a CN⁻¹ ion. Indicate the equilibrium bond distances with arrows. The **relative** values of the bond distances and energies must be correct, but no numbers are needed.

Note: this question is graded based on your answer to part (iii), since it depends on bond order.



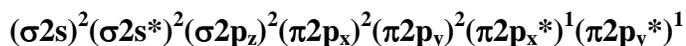
(v) (2 points) Which of the following are radical species: CN, CN⁻¹, both, or neither?

CN is the only radical species.

(b) (6 points)

Write the **valence** electron configuration for O₂.

(12 valence electrons)



5. (11 points) **Thermochemistry**

(a) (7 points) Consider the reaction below for the conversion nitrogen dioxide to nitric oxide and O₂.



	ΔH_f° (kJ/mol)
NO ₂ (g)	+33.18
NO(g)	+90.25

Calculate ΔH° (per mol of O₂ formed) for the reaction at 298 K.

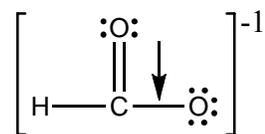
$$\Delta H_r^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$\Delta H_r^\circ = [2\Delta H_f^\circ(\text{NO}) + \Delta H_f^\circ(\text{O}_2)] - [2\Delta H_f^\circ(\text{NO}_2)]$$

$$\Delta H_r^\circ = [2(90.25 \text{ kJ/mol}) + (0)] - [2(33.18 \text{ kJ/mol})]$$

$$\Delta H_r^\circ = \mathbf{114.1 \text{ kJ}} \quad \text{or} \quad \mathbf{114.14 \text{ kJ}} \quad (\text{also ok to have kJ/mol, since the questions says per mol of O}_2)$$

(b) (4 points) Using the table of mean bond enthalpies provided, predict the bond enthalpy (in kJ/mol) for the CO bond marked with an arrow in the molecule below.



Note: the C-O bond is a 1½ bond (not a single bond) due to resonance.

$$360 \text{ kJ/mol} < \text{bond enthalpy} < 743 \text{ kJ/mol}$$

It is also fine if a student calculated a number, as long as it is above 400 and less than 700 kJ/mol (ie. 552 kJ/mol).

Bond	Mean Bond Enthalpy (in kJ/mol)
C-H	412
C-C	348
C=C	612
C-O	360
C=O	743

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 ^a																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
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<table border="1"> <thead> <tr> <th colspan="2">The Active Metals</th> <th colspan="16">The Nonmetals</th> <th colspan="2">Noble Gases</th> </tr> </thead> <tbody> <tr> <td>1</td><td>H</td><td colspan="16"></td><td>2</td><td>He</td> </tr> <tr> <td></td><td>1.008</td><td colspan="16"></td><td></td><td>4.003</td> </tr> <tr> <td>3</td><td>Li</td><td>4</td><td>Be</td><td colspan="16"></td><td>9</td><td>F</td><td>10</td><td>Ne</td> </tr> <tr> <td></td><td>6.941</td><td></td><td>9.012</td><td colspan="16"></td><td></td><td>18.998</td><td></td><td>20.179</td> </tr> <tr> <td>11</td><td>Na</td><td>Mg</td><td colspan="16"></td><td>16</td><td>S</td><td>17</td><td>Cl</td><td>18</td><td>Ar</td> </tr> <tr> <td></td><td>22.990</td><td>24.305</td><td colspan="16"></td><td></td><td>32.06</td><td></td><td>35.453</td><td></td><td>39.948</td> </tr> <tr> <td>19</td><td>K</td><td>Ca</td><td>20</td><td>Sc</td><td>21</td><td>Ti</td><td>22</td><td>V</td><td>23</td><td>Cr</td><td>24</td><td>Mn</td><td>25</td><td>Fe</td><td>26</td><td>Cu</td><td>27</td><td>Ni</td><td>28</td><td>Zn</td><td>29</td><td>Ga</td><td>30</td><td>Ge</td><td>31</td><td>As</td><td>32</td><td>Se</td><td>33</td><td>Br</td><td>34</td><td>Kr</td> </tr> <tr> <td></td><td>39.098</td><td>40.08</td><td>44.956</td><td>47.88</td><td>50.942</td><td>51.996</td><td>54.938</td><td>55.847</td><td>58.933</td><td>58.69</td><td>63.546</td><td>65.38</td><td>69.72</td><td>72.59</td><td>74.922</td><td>78.96</td><td>79.904</td><td>83.80</td><td>85</td><td>86</td> </tr> <tr> <td>37</td><td>Rb</td><td>Sr</td><td>38</td><td>Y</td><td>Zr</td><td>39</td><td>Nb</td><td>40</td><td>41</td><td>42</td><td>Mo</td><td>43</td><td>Tc</td><td>44</td><td>Ru</td><td>45</td><td>Rh</td><td>46</td><td>Pd</td><td>47</td><td>Cd</td><td>48</td><td>In</td><td>49</td><td>Sn</td><td>50</td><td>Sb</td><td>51</td><td>Te</td><td>52</td><td>I</td><td>53</td><td>Xe</td> </tr> <tr> <td></td><td>85.468</td><td>87.62</td><td>88.906</td><td>91.224</td><td>92.906</td><td>95.94</td><td>(98)</td><td>101.07</td><td>102.906</td><td>106.42</td><td>107.868</td><td>112.41</td><td>114.82</td><td>118.69</td><td>121.75</td><td>127.60</td><td>126.904</td><td>131.29</td><td>81</td><td>82</td><td>83</td><td>84</td><td>85</td><td>86</td> </tr> <tr> <td>55</td><td>Cs</td><td>Ba</td><td>56</td><td>La</td><td>57</td><td>Hf</td><td>72</td><td>Ta</td><td>73</td><td>74</td><td>W</td><td>75</td><td>Re</td><td>76</td><td>Os</td><td>77</td><td>Ir</td><td>78</td><td>Pt</td><td>79</td><td>Au</td><td>80</td><td>Hg</td><td>81</td><td>Tl</td><td>82</td><td>Pb</td><td>83</td><td>Bi</td><td>84</td><td>Po</td><td>85</td><td>At</td> </tr> <tr> <td></td><td>132.905</td><td>137.33</td><td>138.905</td><td>178.49</td><td>180.948</td><td>183.85</td><td>186.21</td><td>190.2</td><td>192.22</td><td>195.08</td><td>196.966</td><td>200.59</td><td>204.38</td><td>207.2</td><td>208.98</td><td>209</td><td>210</td><td>211</td><td>212</td><td>213</td><td>214</td><td>215</td><td>216</td><td>217</td><td>218</td><td>219</td><td>220</td><td>221</td><td>222</td> </tr> <tr> <td>87</td><td>Fr</td><td>Ra</td><td>88</td><td>Ac</td><td>89</td><td>Unq</td><td>104</td><td>Unp</td><td>105</td><td>Unh</td><td>106</td><td>U</td><td>91</td><td>92</td><td>93</td><td>94</td><td>95</td><td>96</td><td>97</td><td>98</td><td>99</td><td>100</td><td>101</td><td>102</td><td>103</td><td>104</td><td>105</td><td>106</td><td>107</td><td>108</td><td>109</td><td>110</td><td>111</td><td>112</td><td>113</td><td>114</td><td>115</td><td>116</td><td>117</td><td>118</td><td>119</td><td>120</td><td>121</td><td>122</td> </tr> <tr> <td></td><td>(223)</td><td>226.025</td><td>227.028</td><td>(261)</td><td>(262)</td><td>(263)</td><td>(264)</td><td>(265)</td><td>(266)</td><td>(267)</td><td>(268)</td><td>(269)</td><td>(270)</td><td>(271)</td><td>(272)</td><td>(273)</td><td>(274)</td><td>(275)</td><td>(276)</td><td>(277)</td><td>(278)</td><td>(279)</td><td>(280)</td><td>(281)</td><td>(282)</td><td>(283)</td><td>(284)</td><td>(285)</td><td>(286)</td><td>(287)</td><td>(288)</td><td>(289)</td><td>(290)</td><td>(291)</td><td>(292)</td><td>(293)</td><td>(294)</td><td>(295)</td><td>(296)</td><td>(297)</td><td>(298)</td><td>(299)</td><td>(300)</td><td>(301)</td><td>(302)</td><td>(303)</td><td>(304)</td><td>(305)</td><td>(306)</td><td>(307)</td><td>(308)</td><td>(309)</td><td>(310)</td><td>(311)</td><td>(312)</td><td>(313)</td><td>(314)</td><td>(315)</td><td>(316)</td><td>(317)</td><td>(318)</td><td>(319)</td><td>(320)</td><td>(321)</td><td>(322)</td><td>(323)</td><td>(324)</td><td>(325)</td><td>(326)</td><td>(327)</td><td>(328)</td><td>(329)</td><td>(330)</td><td>(331)</td><td>(332)</td><td>(333)</td><td>(334)</td><td>(335)</td><td>(336)</td><td>(337)</td><td>(338)</td><td>(339)</td><td>(340)</td><td>(341)</td><td>(342)</td><td>(343)</td><td>(344)</td><td>(345)</td><td>(346)</td><td>(347)</td><td>(348)</td><td>(349)</td><td>(350)</td><td>(351)</td><td>(352)</td><td>(353)</td><td>(354)</td><td>(355)</td><td>(356)</td><td>(357)</td><td>(358)</td><td>(359)</td><td>(360)</td> 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	22.990	24.305																		32.06		35.453		39.948																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
19	K	Ca	20	Sc	21	Ti	22	V	23	Cr	24	Mn	25	Fe	26	Cu	27	Ni	28	Zn	29	Ga	30	Ge	31	As	32	Se	33	Br	34	Kr																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
	39.098	40.08	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.38	69.72	72.59	74.922	78.96	79.904	83.80	85	86																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	
37	Rb	Sr	38	Y	Zr	39	Nb	40	41	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Cd	48	In	49	Sn	50	Sb	51	Te	52	I	53	Xe																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
	85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.906	106.42	107.868	112.41	114.82	118.69	121.75	127.60	126.904	131.29	81	82	83	84	85	86																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
55	Cs	Ba	56	La	57	Hf	72	Ta	73	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
	132.905	137.33	138.905	178.49	180.948	183.85	186.21	190.2	192.22	195.08	196.966	200.59	204.38	207.2	208.98	209	210	211	212	213	214	215	216	217	218	219	220	221	222																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
87	Fr	Ra	88	Ac	89	Unq	104	Unp	105	Unh	106	U	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
	(223)	226.025	227.028	(261)	(262)	(263)	(264)	(265)	(266)	(267)	(268)	(269)	(270)	(271)	(272)	(273)	(274)	(275)	(276)	(277)	(278)	(279)	(280)	(281)	(282)	(283)	(284)	(285)	(286)	(287)	(288)	(289)	(290)	(291)	(292)	(293)	(294)	(295)	(296)	(297)	(298)	(299)	(300)	(301)	(302)	(303)	(304)	(305)	(306)	(307)	(308)	(309)	(310)	(311)	(312)	(313)	(314)	(315)	(316)	(317)	(318)	(319)	(320)	(321)	(322)	(323)	(324)	(325)	(326)	(327)	(328)	(329)	(330)	(331)	(332)	(333)	(334)	(335)	(336)	(337)	(338)	(339)	(340)	(341)	(342)	(343)	(344)	(345)	(346)	(347)	(348)	(349)	(350)	(351)	(352)	(353)	(354)	(355)	(356)	(357)	(358)	(359)	(360)																																																																																																																																																																																																																																																																																																																																																																																																														

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$$c = 2.99792 \times 10^8 \text{ m/s}$$

$$h = 6.62608 \times 10^{-34} \text{ J s}$$

$$N_a = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$$

$$m_e = 9.10939 \times 10^{-31} \text{ kg}$$

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

$$U(r) = (z_1 z_2 e^2) / (4\pi\epsilon_0 r)$$

$$\epsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2 / (\text{Jm})$$

$$\text{Electronegativity} = (IE + EA) / 2$$

$$\Delta G = \Delta H - T\Delta S$$

Inner Transition Metals																											
58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu
	140.12	140.908	144.24	(145)	150.36	151.96	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967													
90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr
	232.038	231.036	238.029	237.048	(244)	(243)	(247)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)												

* Lanthanides

† Actinides