Carleton UNIVERSITY

CHEM 1006 A
Winter 2018

Midterm #2: Thursday, March 8th, 2018

Test duration: 80 minutes
Instructor: Alyssa Nause

Student Name: Solutions

Student Number: _____

Answer the questions on the exam paper.

If more space is needed, use reverse of exam pages.

Part A: Short Answer (5 marks each)

/5

1. For each acid-base reaction below, identify the conjugate pairs:

   a. $H_2S_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-_{(aq)} + H_3O^+_{(aq)}$

   b. $HNO_{2(aq)} + NH_{3(aq)} \rightleftharpoons NO_2^-{}_{(aq)} + NH_4^+{}_{(aq)}$

1.25

a) $H_2S_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-_{(aq)} + H_3O^+_{(aq)}$

Base — conjugate acid

Acid — conjugate base

1.25

1.25

b) $HNO_{2(aq)} + NH_{3(aq)} \rightleftharpoons NO_2^-{}_{(aq)} + NH_4^+{}_{(aq)}$

Base — conjugate acid

Acid — conjugate base

1.25

(each pair = 1.25)

/5

2. a) Define the relation between the rate of a reaction and the temperature of the reaction.
   b) Describe what impact temperature has on the activation energy of the reaction and the progress of the reaction.

a) Rate of reaction $\propto$ Temperature

2.5

(increasing the temperature usually increases the rate of reaction; they are proportional)

b) Temperature has (1) no impact on activation energy. The rate increase with increased temperature will allow the reaction to progress more quickly.

1.5

/5

3. The following overall reaction has part of a potential mechanism listed below. Predict the unknown step of the mechanism.

Overall: $NH_4^+{}_{(aq)} + HNO_{2\,(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)} + H^+{}_{(aq)}$

Mechanism: Step 1: $HNO_{2\,(aq)} + \cancel{H^+_{(aq)}} \rightarrow H_2O_{(l)} + NO^+{}_{(aq)}$
Step 2: $NH_4^+{}_{(aq)} \rightarrow NH_{3(aq)} + \cancel{H^+_{(aq)}}$
Step 3: unknown
Step 4: $NH_3NO^+{}_{(aq)} \rightarrow H_2O_{(l)} + H^+{}_{(aq)} + N_{2(g)}$

Sum of Mechanism so far:

$HNO_{2(aq)} + NH_4^+{}_{(aq)} + NH_3NO^+{}_{(aq)} \rightarrow 2H_2O_{(l)} + NH_{3(aq)} + NO^+_{(g)} + H^+{}_{(aq)} + N_{2(g)}$

Overall reaction: $NH_4^+{}_{(aq)} + HNO_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)} + H^+{}_{(aq)}$

(Circled differences)

Step 3 (proposed): $NH_{3\,(aq)} + NO^+{}_{(aq)} \rightarrow NH_3NO^+{}_{(aq)}$

(1) present (1) present (1) present

(1) phases

(1) correct order/placement

/5

4. Define an amphiprotic acid or base, and give an example of a compound that is amphiprotic.

(2.5) An amphiprotic species is a compound that can act either as an acid (donating a proton) or as a base (accepting a proton).

(2.5) Ex: H_2O as acid or base

correct example (reaction not needed, just valid compound)

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$

Acid: $H_2O_{(l)}$ → C.B. $OH^-{}_{(aq)}$

Base: $H_2O_{(l)}$ → C.A. $H_3O^+{}_{(aq)}$

Part B: Long Answer Problems (10 marks each)

10

5. MnO_2 is often used to improve the efficiency of the decomposition of hydrogen peroxide to water and oxygen gas. The overall reaction has an energy change of -108 kJ/mol.

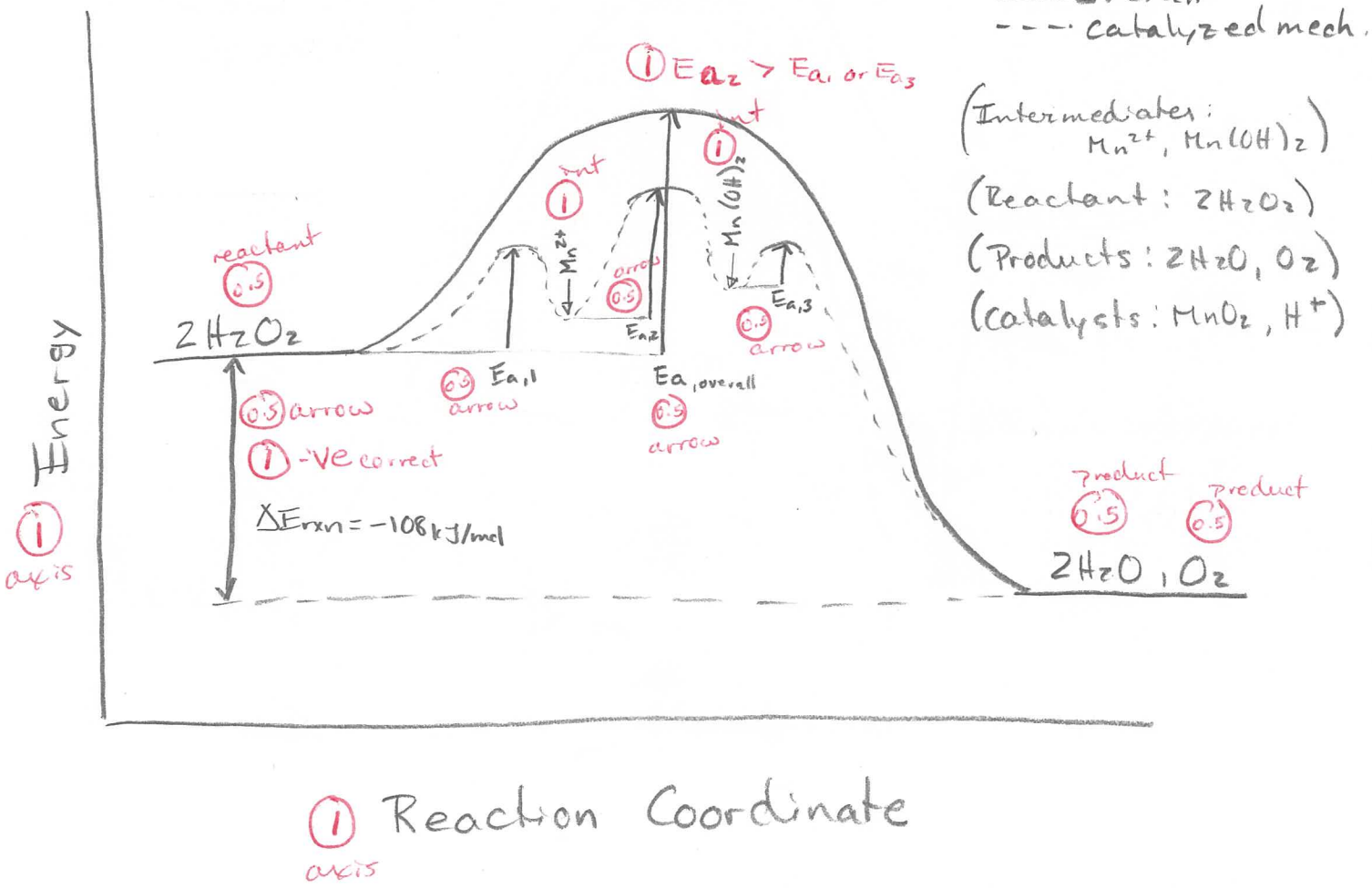
   a. Sketch an energy profile for the overall reaction and its catalyzed mechanism (sketch both on the same plot).
   b. On your sketched energy profile, include arrows to indicate each activation energy and the energy change of the reaction.
   c. Note each non-catalyst species in the catalyzed mechanism in its appropriate location on the energy profile.

Overall: $E_{a,overall}$ = 275 kJ/mol

$$2H_2O_2\,(l) \xrightarrow{MnO_2\,(s),\,H^+\,(aq)} 2H_2O\,(l) + O_2\,(g)$$

Catalyzed Mechanism:

1) $MNO_2\,(s) + H_2O_2\,(l) + 2H^+\,(aq) \rightarrow Mn^{2+}\,(aq) + 2H_2O\,(l) + O_2\,(g)$ $E_{a,1}$ = 55 kJ/mol
2) $Mn^{2+}\,(aq) + 2H_2O\,(l) \rightarrow Mn(OH)_2\,(aq) + 2H^+\,(aq)$ $E_{a,2}$ = 95 kJ/mol
3) $Mn(OH)_2\,(aq) + H_2O_2\,(l) \rightarrow MnO_2\,(s) + 2H_2O\,(l)$ $E_{a,3}$ = 35 kJ/mol



/10

6. The reaction of nitric oxide with hydrogen at 1280°C. For the following reaction and experimental data:
   a. determine the rate law and overall reaction order.
   b. determine the rate constant.

$$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

Run	$[NO]_o$ (M)	$[H_2]_o$ (M)	Initial Rate (M/min)
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120

a) Rate law: $\text{Rate} = k[NO_{(g)}]^x[H_{2(g)}]^y$ (0.5) starting point

Use Run #1, 3 to Find y:

$$\frac{(\text{Initial Rate})_1}{(\text{Initial Rate})_3} = \frac{k([NO]_1)^x([H_2]_1)^y}{k([NO]_3)^x([H_2]_3)^y}$$ (0.5) ratio for y

$$\frac{0.00600\ M/min}{0.0120\ M/min} = \frac{(0.0100M)^x(0.0100M)^y}{(0.0100M)^x(0.0200M)^y}$$

$$0.5 = \left(\frac{0.0100\ M}{0.0200\ M}\right)^y$$

$$0.5 = (0.5)^y$$

$$\ln(0.5) = y(\ln(0.5))$$ (0.5) calc

$$y = \frac{\ln(0.5)}{\ln(0.5)}$$

$$y = 1$$

(0.5) calc, no errors (result)
(0.5) round (to integer)

(cont'd on page 8)

(6.a))

Use Run # 1, 2 to find x: (any pair of runs ok to use)

$$\frac{(I.R.)_1}{(I.R.)_2} = \frac{k([NO]_1)^x([H_2]_1)^y}{k([NO]_2)^x([H_2]_2)^y}$$

(0.5) ratio for x

$$\frac{0.00600\ M/min}{0.144\ M/min} = \frac{(0.0100M)^x(0.0100M)^y}{(0.0200M)^x(0.0300M)^y}$$

($y=1$, found previously)

$$0.041667 = \frac{(0.0100M)^x(0.0100M)^1}{(0.0200M)^x(0.0300M)^1}$$

$$\left(\frac{0.0100M}{0.0200M}\right)^x = (0.041667)\frac{(0.0300M)^1}{(0.0100M)^1}$$

$$(0.5)^x = 0.124999$$

$$x(\ln(0.5)) = \ln(0.124999)$$

(0.5) calc

$$x = \frac{\ln(0.124999)}{\ln(0.5)}$$

$$x = 3.00000023$$

$$\underline{x = 3}$$

(0.5) result (no errors)
(0.5) round (to integer)

∴ Rate law: $\underline{\text{Rate} = k[NO_{2(g)}]^3[H_{2(g)}]}$

(0.5) rate law w/ order
(1) rate law correct
(1) correct total
(0.5) sum orders found

∴ overall Reaction order $= x + y = 3 + 1 = \underline{4}$

(cont'd on pg 6)

(6.)

b) $\text{Rate} = k[NO_{2(g)}]^3[H_{2(g)}]$

(Use any trial to find k:)

$$k = \frac{(\text{Initial Rate})_1}{([NO_{2(g)}]_1)^3([H_{2(g)}]_1)^1}$$

(0.5) values from same trial (any trial)

$$k = \frac{(0.00600\ M/min)}{(0.0100M)^3(0.0100\ M)^1}$$

(0.5) calc, no further errors

$$k = 6.00 \times 10^5\ \ M^{-3}\ min^{-1}$$

(0.5) result

(0.5) unit

(0.5) 3 sig. figs

(units: $\frac{M/min}{(M^3)(M)} = M^{-3}\ min^{-1}$)

/10

7. Determine the overall reaction and the rate law for the following mechanism. If possible, substitute any invalid compounds in the predicted rate law to determine the corrected predicted rate law.

1) $Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$ (fast, reversible)

2) $Cl_{(g)} + H_{2(g)} \rightarrow HCl_{(g)} + H_{(g)}$ (slow)

3) $H_{(g)} + Cl_{(g)} \rightarrow HCl_{(g)}$ (fast)

Alt ①

① forward: ~~$Cl_{2(g)}$~~ $\rightarrow$ ~~$2Cl_{(g)}$~~

① backward: ~~$2Cl_{(g)}$~~ $\rightarrow$ ~~$Cl_{2(g)}$~~

② $Cl_{(g)} + H_{2(g)} \rightarrow HCl_{(g)} +$ ~~$H_{(g)}$~~

③ ~~$H_{(g)}$~~ $+ Cl_{(g)} \rightarrow HCl_{(g)}$

overall: $2Cl_{(g)} + H_{2(g)} \rightarrow 2HCl_{(g)}$

not stable on its own (not std state of Cl)

② using Alt ① or Alt ②

correct, no errors

Alt ②

① $Cl_{2(g)} \rightarrow$ ~~$2Cl_{(g)}$~~

② ~~$Cl_{(g)}$~~ $+ H_{2(g)} \rightarrow HCl_{(g)} +$ ~~$H_{(g)}$~~

③ ~~$H_{(g)}$~~ $+$ ~~$Cl_{(g)}$~~ $\rightarrow HCl_{(g)}$

① phases in overall

overall: $Cl_{2(g)} + H_{2(g)} \rightarrow 2HCl_{(g)}$

more likely b/c Cl is Cl_2 in std. state

Rate law: $Rate = k_2[Cl_{(g)}][H_{2(g)}]$

(int in Alt ②)

(not std state, cannot be measured in Alt ①)

② decide to replace $[Cl_{(g)}]$

Use Reversible reaction and Equality of rates to replace $[Cl_{(g)}]$

(cont'd on p. 10)

Rate ① forward = Rate ① backward

$k_1[Cl_{2(g)}] = k_{-1}[Cl_{(g)}]^2$ ① correct

$[Cl_{(g)}]^2 = \frac{k_1}{k_{-1}}[Cl_{2(g)}]$

$[Cl_{(g)}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_{2(g)}]^{1/2}$ (or square roots)

① correct rearrangement

∴ Rate law: $\text{Rate} = k_2[Cl_{(g)}][H_{2(g)}]$

$\text{Rate} = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_{2(g)}]^{1/2}[H_{2(g)}]$

① substitution mark

① phases

① no errors

(OR $\text{Rate} = k[Cl_{2(g)}]^{1/2}[H_{2(g)}]$, where $k = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}$)

Equations and Constants:

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

$N_{Av} = 6.022 \times 10^{23}\ mol^{-1}$

$n = m/M$

$c = n/V$

$\rho = m/V$

$b = n/m$

$X_C = n_C/n_{total}$

$t_{1/2} = \ln 2 / ak$

$t_{1/2} = 1 / 2k[A]_o$

$\ln[A] = -akt + \ln[A]_o$

$1/[A] = 2kt + 1/[A]_o$

$Rate = k[A]^x[B]^y$

$k_1[A_2] = k_{-1}[A]^2$

$k = Ae^{-Ea/RT}$

$\ln(k) = \ln(A) - E_a/RT$

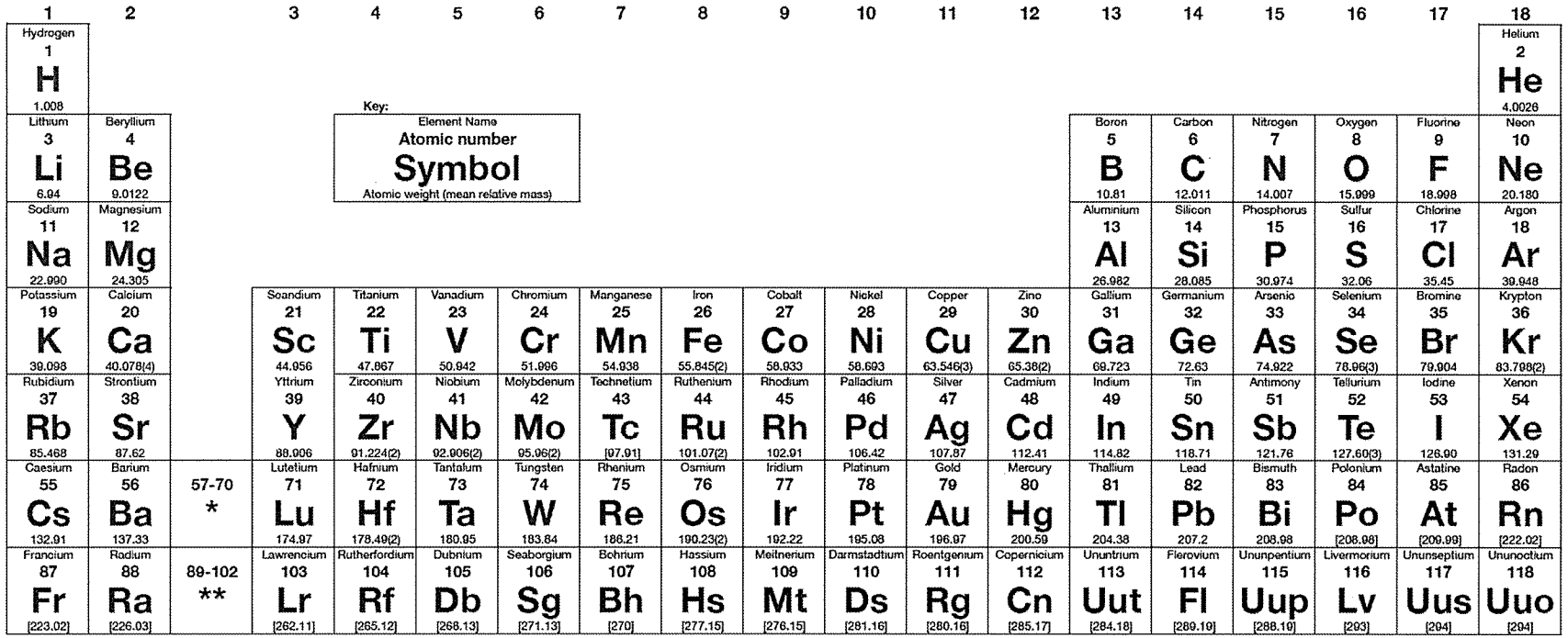
$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$0 = ax^2 + bx + c$

$1\ atm = 1.01325 \times 10^5\ Pa = 760\ Torr = 1.01325\ bar$

$T(K) = T(^oC) + 273.15$


1
2
3
4
5
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7
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11
12
13
14
15
16
17
18
Hydrogen 1 H 1.008
Helium 2 He 4.0026
Key:
Element Name
Atomic number
Symbol
Atomic weight (mean relative mass)
Lithium 3 Li 6.94
Beryllium 4 Be 9.0122
Boron 5 B 10.81
Carbon 6 C 12.011
Nitrogen 7 N 14.007
Oxygen 8 O 15.999
Fluorine 9 F 18.998
Neon 10 Ne 20.180
Sodium 11 Na 22.990
Magnesium 12 Mg 24.305
Aluminium 13 Al 26.982
Silicon 14 Si 28.085
Phosphorus 15 P 30.974
Sulfur 16 S 32.06
Chlorine 17 Cl 35.45
Argon 18 Ar 39.948
Potassium 19 K 39.098
Calcium 20 Ca 40.078(4)
Scandium 21 Sc 44.956
Titanium 22 Ti 47.867
Vanadium 23 V 50.942
Chromium 24 Cr 51.996
Manganese 25 Mn 54.938
Iron 26 Fe 55.845(2)
Cobalt 27 Co 58.933
Nickel 28 Ni 58.693
Copper 29 Cu 63.546(3)
Zinc 30 Zn 65.38(2)
Gallium 31 Ga 69.723
Germanium 32 Ge 72.63
Arsenic 33 As 74.922
Selenium 34 Se 78.96(3)
Bromine 35 Br 79.904
Krypton 36 Kr 83.798(2)
Rubidium 37 Rb 85.468
Strontium 38 Sr 87.62
Yttrium 39 Y 88.906
Zirconium 40 Zr 91.224(2)
Niobium 41 Nb 92.906(2)
Molybdenum 42 Mo 95.96(2)
Technetium 43 Tc [97.91]
Ruthenium 44 Ru 101.07(2)
Rhodium 45 Rh 102.91
Palladium 46 Pd 106.42
Silver 47 Ag 107.87
Cadmium 48 Cd 112.41
Indium 49 In 114.82
Tin 50 Sn 118.71
Antimony 51 Sb 121.76
Tellurium 52 Te 127.60(3)
Iodine 53 I 126.90
Xenon 54 Xe 131.29
Caesium 55 Cs 132.91
Barium 56 Ba 137.33
57-70 *
Lutetium 71 Lu 174.97
Hafnium 72 Hf 178.49(2)
Tantalum 73 Ta 180.95
Tungsten 74 W 183.84
Rhenium 75 Re 186.21
Osmium 76 Os 190.23(2)
Iridium 77 Ir 192.22
Platinum 78 Pt 195.08
Gold 79 Au 196.97
Mercury 80 Hg 200.59
Thallium 81 Tl 204.38
Lead 82 Pb 207.2
Bismuth 83 Bi 208.98
Polonium 84 Po [208.98]
Astatine 85 At [209.99]
Radon 86 Rn [222.02]
Francium 87 Fr [223.02]
Radium 88 Ra [226.03]
89-102 **
Lawrencium 103 Lr [262.11]
Rutherfordium 104 Rf [265.12]
Dubnium 105 Db [268.13]
Seaborgium 106 Sg [271.13]
Bohrium 107 Bh [270]
Hassium 108 Hs [277.15]
Meitnerium 109 Mt [276.15]
Darmstadtium 110 Ds [281.16]
Roentgenium 111 Rg [280.16]
Copernicium 112 Cn [285.17]
Ununtrium 113 Uut [284.18]
Flerovium 114 Fl [289.19]
Ununpentium 115 Uup [288.19]
Livermorium 116 Lv [293]
Ununseptium 117 Uus [294]
Ununoctium 118 Uuo [294]
*lanthanoids
Lanthanum 57 La 138.91
Cerium 58 Ce 140.12
Praseodymium 59 Pr 140.91
Neodymium 60 Nd 144.24
Promethium 61 Pm [144.91]
Samarium 62 Sm 150.36(2)
Europium 63 Eu 151.96
Gadolinium 64 Gd 157.25(3)
Terbium 65 Tb 158.93
Dysprosium 66 Dy 162.50
Holmium 67 Ho 164.93
Erbium 68 Er 167.26
Thulium 69 Tm 168.93
Ytterbium 70 Yb 173.05
**actinoids
Actinium 89 Ac [227.03]
Thorium 90 Th 232.04
Protactinium 91 Pa 231.04
Uranium 92 U 238.03
Neptunium 93 Np [237.05]
Plutonium 94 Pu [244.06]
Americium 95 Am [243.06]
Curium 96 Cm [247.07]
Berkelium 97 Bk [247.07]
Californium 98 Cf [251.08]
Einsteinium 99 Es [252.08]
Fermium 100 Fm [257.10]
Mendelevium 101 Md [258.10]
Nobelium 102 No [259.10]