NAME: ________SOLUTIONS

Exam I
October 12, 2006

Good evening! While everyone is getting their exams and as you get settled, it might be a good idea for you to work on relaxing. Know that you can do your best work when you believe you can. I know you have studied hard to get to tonight, and I am really interested to see how you do with these questions. I am not just looking for the right answer, but a thought and thought process that leads you to that answer. NEVER EVER LEAVE A QUESTION BLANK

As always, the Amherst College honor code, which you all signed onto during your first days at the college, is in effect. For tonight, this means that "neither a borrower nor a lender be" in turns of information, answers, any exchange. In the spirit of the honor code, I will not proctor the exam, but will sit down front so that you can ask questions if you need to. Should you need to take a break to use the restroom or get some fresh air or take five, do so with as little bother to the others as you can.

This exam contains four questions on the exam, I, II, III, and IV on 11 pages. You should divide your time evenly between the four questions. That means, for the first time through the exam, don't take more than 30 minutes per Roman numeral. Formula sheet and periodic table are on the back, you may tear off the back sheet and have it available for ready reference. Use average atomic weights to four decimal points as provided in that table.

When we start the exam, I will ask you to put all your books, notes, peripherals away. You should have a calculator and an assortment of pens and pencils. Write ONLY on the white spaces underneath the questions unless otherwise instructed to do so.

Extra credit (2 points)

What substance was the focus of research by father and son Arthur and Roger Kornberg over the past 50 years. Arthur won a Nobel in Physiology or Medicine for his work on the basic chemistry of this structure in 1955 and Roger was awarded the Nobel Prize in Chemistry announced just last week for his work on its more complex structures.

a) cholesterol
b) estrogen
c) testosterone
[✓ d) RNA]

I. Stoichiometry, Mass Relationships, (25 points)

Last Monday, the 2006 Nobel Prize in Selection Committee announced that the Nobel Prize in Chemistry (and $1.3 million dollars) was awarded to Roger Kornberg of Stanford University. The biological material Dr. Kornberg worked with is in fact a family of compounds under one general heading. The questions below refer to one member of that family.

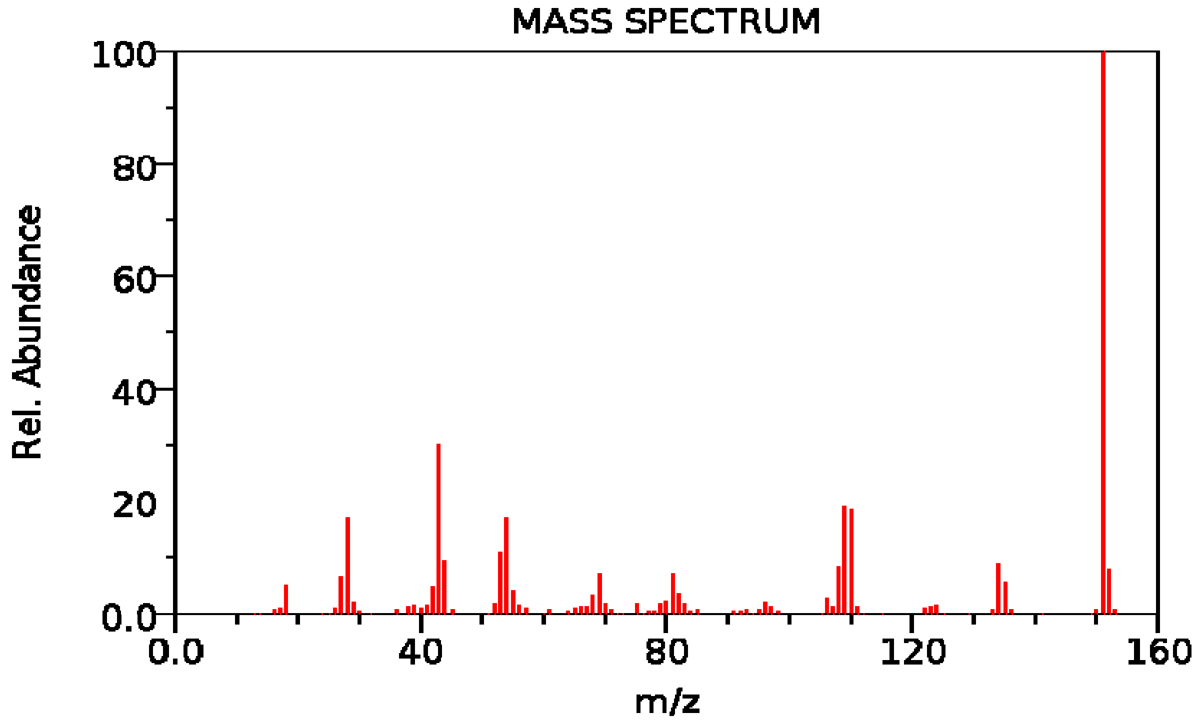
1. The purified substance is found to contain four elements: carbon, nitrogen, oxygen, and hydrogen. Combustion of a 4.2456 mg sample of this material produces 6.5968 mg of carbon dioxide and 1.3498 mg of water. By another method, the substance was determined to contain 24.726 % by mass nitrogen. What is the empirical formula of the compound?
   C_2H_2NO compound is related to the RNA base guanosine

2. The average molar mass for this compound 283.24 g/mole. What is the molecular formula?
   5 x empirical formula: $C_{10}H_{10}N_5O_5$

3. Many people believe that consumption of this compound provides health benefits. It is possible to buy either a bottle of one hundred 500.0 mg capsules 5.000% (by mass) or a bottle containing 250.00 mL of 24.00 mM (1 mM = 0.001 M). The two bottles are the same price. Which formulation is the better buy (i.e. which bottle contains more moles of compound?)

   0.05 x .500g x 100 /283.24 g/mole = 0.008824 moles
   0.02400 x .250 = 0.006 moles
   Capsules are a slightly better deal

4. Mass spectrum. This compound is not easily monitored in the mass spec because it tends to fall apart. One piece of it is however quite stable, and resists fragmentation. The mass spec of the stable fragment is shown below.



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

a. The x axis is labeled m/z. Define z and explain why it is important in the detection of a molecular ion or fragment in the mass spectrometer.

Z is the charge on the ion, which needs to be charged in order to be deflected in the mass spectrometer

b. Assuming a z of +1, what is the approximate molar mass of this stable fragment? 152amu

c. If this molecular ion or fragment contained chlorine, and knowing that the two isotopes of chlorine are ^{35}Cl 75.77% and ^{37}Cl 24.23%, what would you have seen in the mass spectrum? *(use back of page3 to explain)*two peaks separated by 2 amu with 3/1 heights

Balancing Equations, Redox, Acid/Base (25 points)

1. A potent sterilizing solution poured on open wounds is a solution of potassium permanganate and hydrogen peroxide. These two materials will react in acidic solution according to the following equation (ions such as potassium are not written here AND since this is in acidic solution, H^+ and H_2O are not added here buy you may add them as you need to answer questions below):

UNBALANCED EQUATION $[MnO_4]^{-1} + H_2O_2 \rightarrow Mn^{+2} + O_2$

a. Write down the oxidation states of all of the atoms on both sides of the equation.

$$Mn^{+7}O^{-2} + H^{+1}\ O^{-1} \rightarrow Mn^{+2} + O_2^{o}$$

b. Identify first, the substance being oxidized, the number of electrons produced in that half reaction, and the number of product H^+ needed to balance this half of the reaction. Put all of this together to write a balanced half reaction for the oxidation reaction.

$$H_2O^{-1}{}_2 \rightarrow O_2 + 2e^- + 2H^+$$

c. Next, identify the substance being reduced, the number of electrons needed as a reactant in that half reaction, the number of product water molecules necessary to mass balance the extra oxygen, and the number of reactant H^+ necessary to balance this reaction. Put all of this together to write a balanced half reaction for the reduction reaction.

$$8\ H^+ + [MnO_4]^{-1} + 5\ e^- \rightarrow Mn^{+2} + 4H_2O$$

d. Finally, write a net balanced equation for the reaction.

$$5x[H_2O^{-1}{}_2 \rightarrow O_2 + 2e^- + 2H^+]$$
$$2x[8\ H^+ + [MnO_4]^{-1} + 5\ e^- \rightarrow Mn^{+2} + 4H_2O]$$

$$2\ [MnO_4]^{-1} + 5\ H_20_2 + 6\ H^+ \rightarrow 2\ Mn^{+2} + 5\ O_2 + 8\ H_2O$$

First rewrite above the balanced equation from the previous page (if you did not manage to balance this equation assume the ratio of permanganate ion to peroxide is 1:2 (note this is NOT the correct mole ratio):

$$\mathbf{2\,[MnO_4]^{-1} + 5\,H_20_2 + 6\,H^+ \rightarrow 2\,Mn^{+2} + 5\,O_2 + 8\,H_2O}$$

2. Limiting Reagent: If 5.268 g of $KMnO_4$ is dissolved in an acidified solution of exactly 100 mL 30.00 % hydrogen peroxide (assume 1.000 g/mL) identify the limiting reagent, predict the masses of products formed in acid solution and the mass of left over reactant. (Assume here that you have plenty of acid in the solution so that the acid is NOT the limiting reagent)

1. Identify Limiting Reagent:
KMnO4: 5.268 g /Molar Mass 158.04 g/mol = 0.03333 moles
H2O2: 30.00 g/34.00 g/mole= 0.8824 moles
MnO_4/H_2O_2 = 2/5 = 0.4000 ideally
0.03333/0.8824 < 0.4 so MnO_4 is limiting, H_2O_2 is excess

2. Calculate Mass Products and left over reactants
Product Mn^{2+} is 0.03333 x 54.938 = 1.8311 g Mn
Product O_2 is 0.03333(5/2) x 32.000 = 2.6663 g O_2
Left Over H_2O_2 [0.8824 moles – 0.03333(5/2) moles] x 34.016 = 27.169 g left over

3. The reaction above proceeds with the consumption of three moles of acid for every mole of $KMnO_4$. If the initial pH of the 100.0 mL of acidified peroxide is 0.0000, , predict the final pH (Assume the final volume is 101.8 mL).

$[H^+$ = 1.000 M in 100.0 ml is 0.1000 moles
$KMnO_4$ sucked up 0.099999 moles acid, 0.1000 – 0.0999 = 0.0001 moles
[H] = 0.0001 moles/.1018L = M
pH = -log [H+] = 3.008 (could have been up to pH 7 depending on how many sig figs you were working with. All were accepted.

Empirical Gas Laws (25 points)

You may be somewhat sad to learn that some scientists believe fall foliage may be harmful to your health. That's the focus of studies being done at the National Center for Atmospheric Research in Colorado. Dr. Alex Guenther is an atmospheric chemist at the National Center for Atmospheric Research, and he studies the effects of vegetation and fall foliage on air quality and climate. The emissions of these chemicals play a role in producing ozone and smog. The emissions from the plants are called "volatile organic compounds" or VOC's.

1. Dr. Guenther's graduate student purified a sample of VOC from the air above the forest canopy (the air above the top of the trees). This purified VOCs has a density of 3.0406 g/L at STP. What is the molar mass?

Molar Mass of VOC is 68.11 g/mole (isoprene)

2. She determined the density of the original air mixture (molecular nitrogen, molecular oxygen and the VOC) collected at a pressure of 0.9856 atm and 17.82^{o}C to be 29.01 g/mole, determine the "apparent molar mass" of the gas mixture of air above the forest canopy.

Apparent Molar Mass of mixture is 29.02 g/mole

3. Assume that the air just above the tops of the trees is composed of nitrogen, oxygen, and a single type of VOC with a molar mass calculated above . The nitrogen and oxygen in the air will retain the mole ratio of 2.89/1 seen in normal air. Determine the mole fraction of the contaminating VOC.

Mole fraction of VOC is between 0.002 -0.003 depending on how many sig figs you chose to keep working with.
Mole fraction of O_2 is 0.2566
Mole fraction of N_2 is 0.7416

Calculate the partial pressures of each of the gases.

P_{VOC} = 0.002 atm
P_{O2} = 0.253 atm
P_{N2} = 0.731 atom

4. If diffusion of these three gases is related to the effusion predicted from Graham's Law, predict the relative rate of diffusion for oxygen, nitrogen, and this VOC.

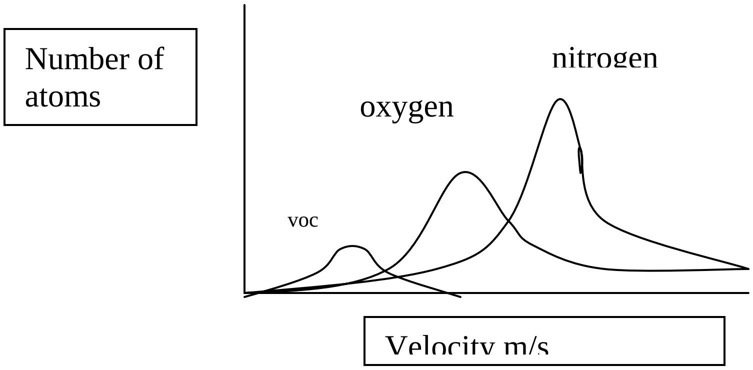
N_2/O_2 = 1.068 VOC/O_2 = 0.685

Kinetic Molecular Theory of Gases (25 points)

1. Calculate the u_{rms} for the Nitrogen, Oxygen, and the VOC components of the gas mixture in problem III at 17.82^{o}C. (If you could not calculate a molar mass for this gas, assume 68.11 g/mole.)

VOC: 326.3 m/s
N_2: 509.0 m/s
O_2: 476.2 m/s

2. Sketch the Boltzmann distribution for the three component gas mixture above. Remember to label your axes and provide as much information as possible.



3. As night falls in the forest, the temperature drops. Describe qualitatively what happens to the velocity distributions of the three gases in this mixture as night falls?

As the temperature drops, the rms velocity decreases and the distributions narrow, causing the entire graph on the previous page to shift to the left and narrow.

4. As sun rises the next day, the temperature rises and more VOC escapes from the trees and joins the mixture of gases above the forest canopy. What prevents this mixture of gases (and any mixture of gas) to separate out into layers of different gas densities with the heaviest gas on the bottom?

The diffusion and the constant random motion of the particles cause the gases to totally mix despite the differences in their masses.

Assorted Equations, Constants, and Conversion Factors

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

Ideal gas law: $PV = nRT$

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

Mole fraction: $\chi_a = n_a/n_{total} = P_a/P_{total}$

Force of collision: $F = \dfrac{\Delta mu}{\Delta t}$

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

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

Average speed: $u_{avg} = \sqrt{\dfrac{8RT}{\pi M}}$

Root mean square speed: $u_{rms} = \sqrt{\dfrac{3RT}{M}}$

Maxwell-Boltzmann distribution: $f(u) = 4\pi\left(\dfrac{m_i}{2\pi k_B T}\right)^{3/2} u^2 e^{-m_i u^2/2k_B T}$

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

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

Collision rate with container wall (collisions per second): $Z_A = \dfrac{1}{4}\dfrac{N}{V}A\sqrt{\dfrac{8RT}{\pi M}}$

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

Van der Waals equation: $\left[P_{obs} + a\left(\dfrac{n}{V}\right)^2\right](V - nb) = nRT$

$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$

$R = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} = 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

1 atm = 760 torr = 1.01325×10^5 Pa

1 L = 1000 mL = 1000 cm^3

T(K) = t(°C) + 273.15

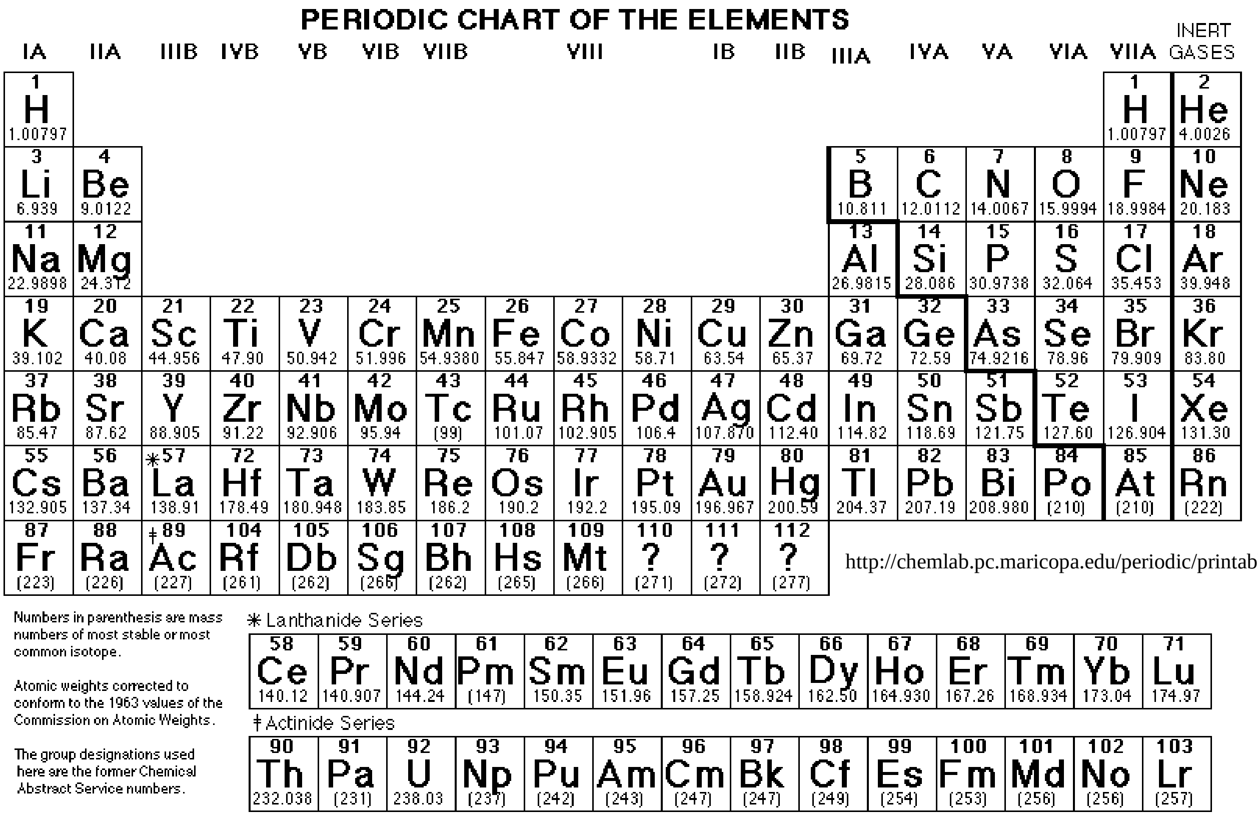
$m_e = 9.10939 \times 10^{-31}$ kg

1 nm = 10^{-9} m

1 Pa = 1 kg $\text{m}^{-1}\ \text{s}^{-2}$

1 J = 1 kg $\text{m}^2\ \text{s}^{-2}$

STP ≡ 1.000 atm, 273.15 K



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)	ǂ89 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

✳ 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

ǂ 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)

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.

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		