22/14(a)

The University of Sydney

CHEM1108 - CHEMISTRY 1A LIFE SCIENCES

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2008 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 21 pages of examinable material.
- Complete the examination paper in **INK.**
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.
- Each new short answer question begins with a •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution. Logarithms may also be used.
- Numerical values required for any question as well as a Periodic Table are printed on a separate data sheet.
- Pages 21 and 24 are for rough work only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	29	

Short answer section

Page	Marks Max	Gained		Marker
11	9			
12	8			
13	4			
14	7			
15	5			
16	5			
17	7			
18	2			
19	5			
20	6			
22	7			
23	6			
Total	71			
Check Total				

Marks

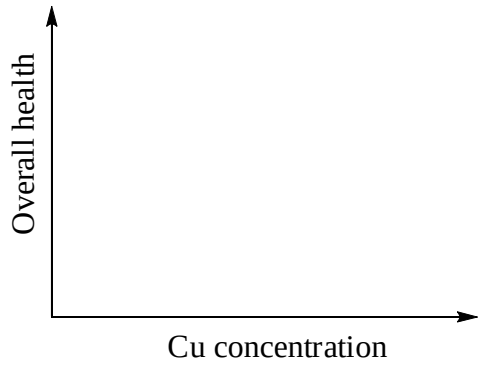
- Complete the following table, giving either the systematic name or the molecular formula as required. **2**

Formula	Systematic name
SO_2	
$CoCl_2 \cdot 6H_2O$	
	silver chromate
	potassium hydrogencarbonate

- Complete the following table, providing the ground state electron configuration for each of the following species. **3**

Species	Ground state electron configuration
nitrogen atom	
chloride ion	
manganese(II) ion	

- Copper is an essential element in human biology, deficiencies leading to blood disorders. Excess copper can occur in cases of poisoning or in Wilson's disease. Draw a graph showing the relationship between overall health and the level of copper in the body and identify the 'healthy' range. **4**

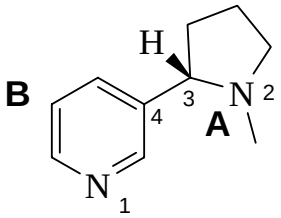


Describe one biological function of copper.

Suggest one approach for treating an excess level of copper.

Marks 8

- The molecular structure of nicotine, the addictive component of tobacco, is shown below.



List the types of intermolecular interactions that each of the following sites on nicotine would be involved in when it is dissolved in water.

A
B

Provide the requested information for each of the indicated atoms in nicotine.

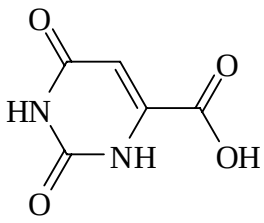
Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry around the atom
N-1			
N-2			
C-3			
C-4			

The pK_b of N-1 is 10.88 and the pK_b of N-2 is 5.98. Draw the structure of the predominant form of nicotine that exists in the human body at pH 7.4.

Marks 4

- Lithium salts, especially lithium carbonate, are commonly used in the treatment of bipolar disorder. Write the net ionic equation for the reaction which occurs between lithium carbonate and hydrochloric acid in the stomach.

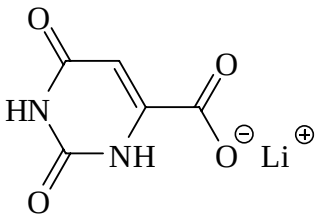
Lithium orotate (as a monohydrate salt, $LiC_5H_3N_2O_4 \cdot H_2O$) is a controversial alternative formulation sold in some health food stores. The orotate ion is the conjugate base of orotic acid, whose structure is shown below.



orotic acid

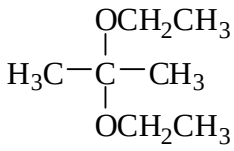
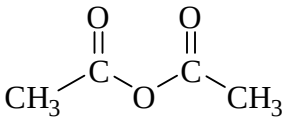
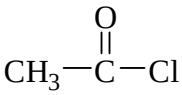
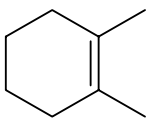
Like the carbonate, lithium orotate is taken orally. Using an equation, comment on any differences between the form in which lithium is bioavailable from these two lithium salts.

Like three of the bases found in DNA and RNA, orotic acid is a derivative of pyrimidine. Also like those bases, orotic acid and its salts have tautomers. Draw the structural formula of a tautomer of lithium orotate.

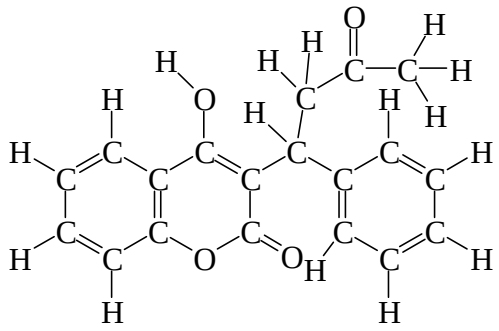
lithium orotate	tautomer of lithium orotate
	

- Complete the following table. Make sure you indicate any relevant stereochemistry.

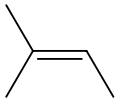
Marks 7

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
CH_3CH_2COOH	1. $SOCl_2$ 2. CH_3CH_2OH	
	dilute $H^{\oplus}$	
$H-C\equiv C-CH_3$	excess Br_2 in diethyl ether solvent	
$CH_3CH_2CH_2CH_2CH_2OH$	 conc. H_2SO_4 catalyst	
	H_2O	
	H_2 / Pd / C ethanol solvent	

	Marks
• A structural formula for Warfarin, an anticoagulant, showing all atoms and bonds is shown below. Draw a stick representation of the formula in the adjacent box.	**1**



• Consider the alkene, 2-methyl-2-butene (**B**).	**4**



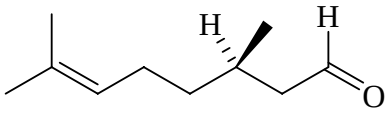
(**B**)

When (**B**) is treated with hydrogen chloride in methanol, two carbocations can be formed. The major carbocation reacts with nucleophiles that are present in the reaction to give an alkyl halide and an ether. Provide constitutional formulas of these intermediates and products in the appropriate boxes below.

major carbocation	minor carbocation
alkyl halide product	ether product

Marks 5

- (+)-Citronellal is a widely occurring natural product present in citronella oil, lemon and lemon grass. It is used as a soap perfume and in insect repellents.



citronellal

Give the molecular formula of citronellal.

Identify the functional groups present in citronellal.

Draw the constitutional formula of the product(s) formed when citronellal is treated with each of the following reagents.

$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
3 M H_2SO_4	
excess CH_3OH / catalytic amount H_2SO_4	

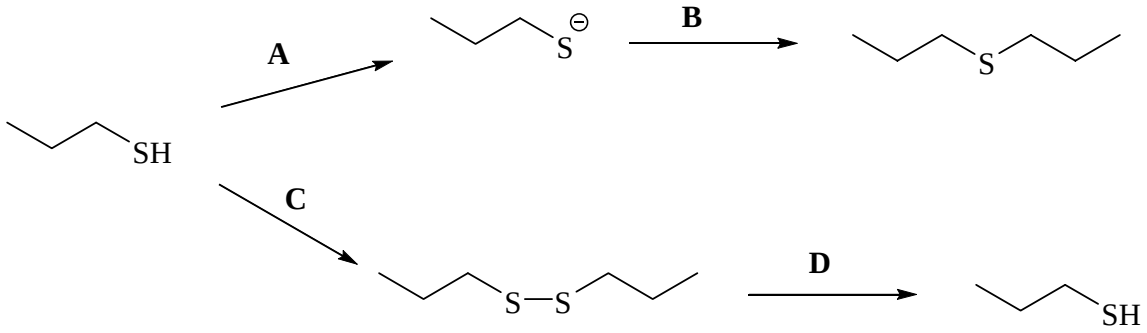
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Devise a synthesis of 1,2-dibromocyclohexane from cyclohexanone. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

Marks
3

- Indicate the reagents used in the laboratory to undertake the following transformations.

4



A:

B:

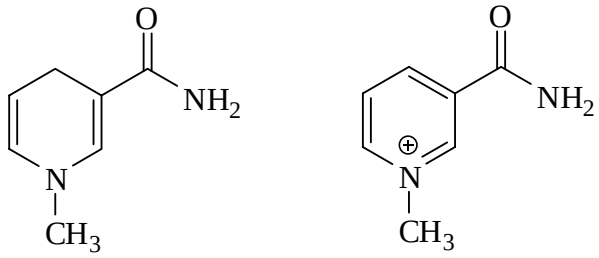
C:

Provide a description for transformation **B**.

Provide a description for transformation **D**.

- Using a spectroscopic technique, how would you distinguish between the following pairs of compounds? Indicate the observations you would make.

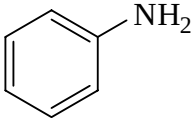
Marks 2

Compounds	Technique and observation
	
	

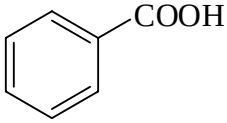
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

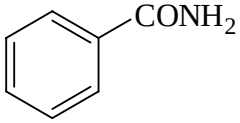
- Aniline, benzoic acid and benzamide are all insoluble in water, but soluble in ether. Explain how, by using simple laboratory reagents and equipment, each compound could be separated and recovered from a mixture of all three.



aniline



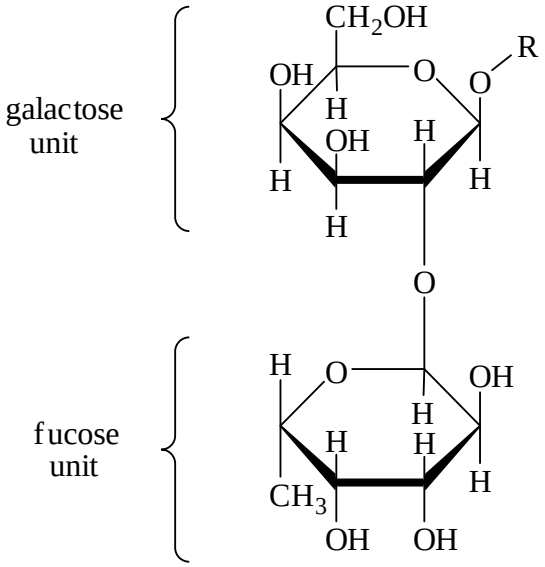
benzoic acid



benzamide

Marks 6

- An important group of oligosaccharides is the blood group antigens. The blood group antigen of humans with blood group O can be represented by the partial structure below, in which R is a glycoprotein.



Specify the fucose unit as a furanose or a pyranose.

Specify fucose as a hexose, a pentose or a tetrose.

The type O blood group antigen can be hydrolysed to galactose, fucose and a glycoprotein unit. Give the Fischer projections of the open chain form of galactose and fucose.

Fischer projection of galactose	Fischer projection of fucose

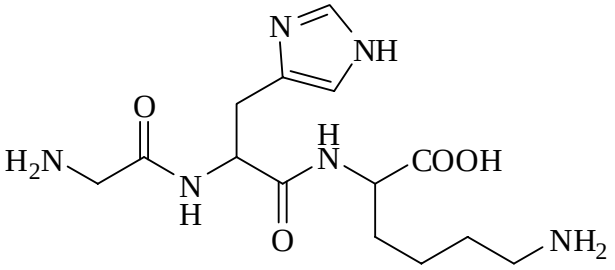
On your Fischer projection of galactose indicate with an asterisk (*) the carbon atom used in the D/L convention.

Specify the galactose from blood antigen as D-galactose or L-galactose.

Specify the fucose from blood antigen as D-fucose or L-fucose.

Marks 7

- The tripeptide glycyl-L-histidyl-L-lysine (**M**) is a liver growth factor.



(**M**)

At pH 4 this tripeptide exists mainly as a species (**N**) with three positive charges. Give the constitutional formula for (**N**).

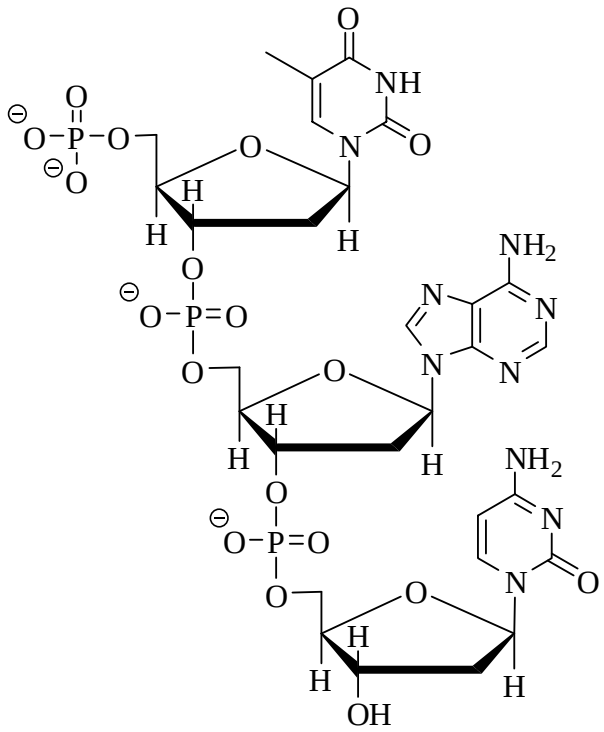
Vigorous acid hydrolysis of tripeptide (**M**) gives three amino acids: glycine, L-histidine and L-lysine. Give constitutional formulas of these amino acids obtained after hydrolysis of (**M**) with 6 M HCl. Make sure you show the products in the appropriate ionic states and with the correct stereochemistry.

glycine	L-histidine	L-lysine

Why does histidine have an "L" descriptor, but glycine does not?

- Is the following structure a fragment of DNA or RNA? Give two reasons.

Marks 6



Clearly identify on the above structure one example of each of the following subunits.

phosphate ester

nucleic base

nucleoside

nucleotide

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DATA SHEET

Physical constants

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Faraday constant, $F = 96485$ C mol^{-1}

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

Speed of light in vacuum, $c = 2.998 \times 10^{8}$ m s^{-1}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

Boltzmann constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1}

Gas constant, $R = 8.314$ J K^{-1} mol^{-1}

$= 0.08206$ L atm K^{-1} mol^{-1}

Charge of electron, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg

Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg

Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ kg

Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L

Density of water at 298 K = 0.997 g cm^{-3}

Conversion factors

1 atm = 760 mmHg = 101.3 kPa

0 °C = 273 K

1 L = 10^{-3} m^3

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J

1 Ci = 3.70×10^{10} Bq

1 Hz = 1 s^{-1}

1 tonne = 10^3 kg

1 W = 1 J s^{-1}

Decimal fractions

Fraction	Prefix	Symbol
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Decimal multiples

Multiple	Prefix	Symbol
10^3	kilo	k
10^6	mega	M
10^9	giga	G

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Standard Reduction Potentials, E°

Reaction	$E°$ / V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.18
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.89
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

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Useful formulas

Quantum Chemistry

$E = h\nu = hc/\lambda$

$\lambda = h/mv$

$E = -Z^2E_R(1/n^2)$

$\Delta x \cdot \Delta(mv) \geq h/4\pi$

$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$

$4.5k_BT = hc/\lambda$

$T = 2.898 \times 10^6/\lambda(\text{nm})$

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

$E = E° - (RT/nF) \times 2.303 \log Q$

$= E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

$= (RT/nF) \times \ln K$

$E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Gas Laws

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

Colligative properties

$\pi = cRT$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Kinetics

$t_{½} = \ln 2/k$

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

$\ln[A] = \ln[A]_o - kt$

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

Radioactivity

$t_{½} = \ln 2/\lambda$

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age $= 8033 \ln(A_0/A_t)$ years

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$K_p = K_c (RT)^{\Delta n}$

Miscellaneous

$A = -\log \frac{I}{I_0}$

$A = \varepsilon cl$

$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_A$

Mathematics

If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [266]	107 BOHRIUM **Bh** [262]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [266]	110 DARMSTADTIUM **Ds** [271]	111 ROENTGENIUM **Rg** [272]							

LANTHANIDES	57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97
ACTINIDES	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]