Topics in the June 2008 Exam Paper for CHEM1611

Click on the links for resources on each topic.

2008-J-2:

- Assumed Knowledge
- Chemical Bonding
- Atomic Structure
- The Periodic Table

2008-J-3:

- The Shapes of Molecules
- Intermolecular forces
- Acids and Bases

2008-J-4:

- Acids and Bases
- Heterocyclic Compounds

2008-J-5:

- Alkenes
- Alcohols, Phenols, Ethers and Thiols
- Aldehydes and Ketones
- Carbohydrates

2008-J-6:

- Alkenes

2008-J-7:

- Amino Acids, Peptides and Proteins

2008-J-9:

- Alcohols, Phenols, Ethers and Thiols
- Organic Halogen Compounds

2008-J-10:

- Alkenes
- Aromatic Hydrocarbons
- Aldehydes and Ketones

2008-J-11:

- Carboxylic Acids and Derivatives
- Heterocyclic Compounds

2008-J-13:

- Amino Acids, Peptides and Proteins

22/31(a)

The University of Sydney

CHEM1611 - CHEMISTRY 1A (PHARMACY)

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

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 22 pages of examinable material.
- Complete the written section of 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 table.
- Each new question of the short answer section 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.
- A Periodic Table and numerical values required for any question may be found on a separate data sheet.
- Page 24 is for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	28	

Short answer section

Page	Marks Max	Gained		Marker
11	9			
12	8			
13	4			
14	8			
15	6			
16	4			
17	4			
18	7			
19	7			
20	4			
21	3			
22	4			
23	4			
Total	72			

Marks

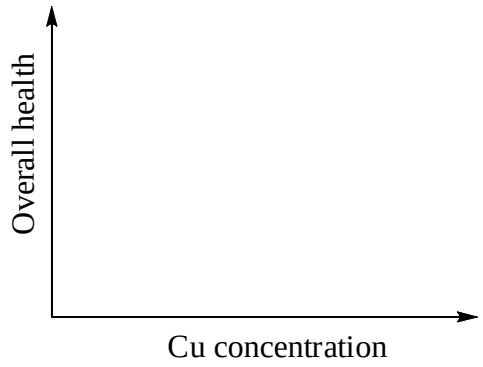
- Complete the following table, giving either the systematic name or the molecular formula as required. **2**

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**

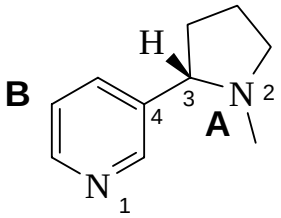


Describe one biological function of copper.

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.

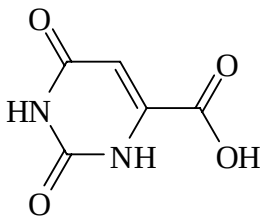
Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry around the atom
N-1			
N-2			
C-3			
C-4			

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.

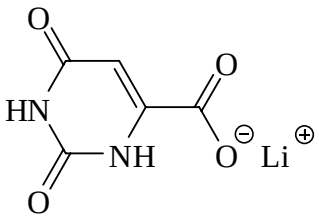
Lithium orotate (as a monohydrate salt, $LiC_5H_3N_2O_4 \cdot H_2O$) is a controversial alternative formulation sold in some health food stores. The orotate ion is the conjugate base of orotic acid, whose structure is shown below.



orotic acid

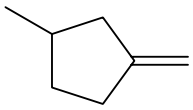
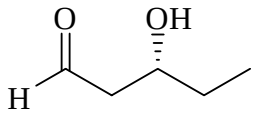
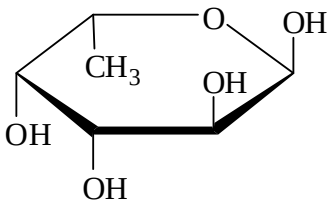
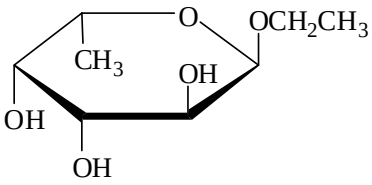
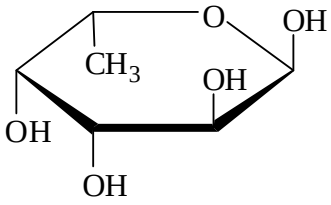
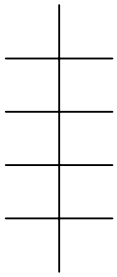
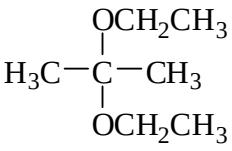
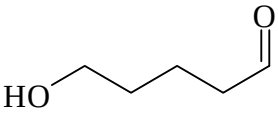
Like the carbonate, lithium orotate is taken orally. Using an equation, comment on any differences between the form in which lithium is bioavailable from these two lithium salts.

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
	

Marks 8

- Complete the following table.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	HBr / CCl_4 (solvent)	
	$H^{\oplus} / Cr_2O_7^{2\ominus}$	
		
	$[Ag(NH_3)_2]^{\oplus} / OH^{\ominus}$	
	dilute $H^{\oplus}$	
	$H^{\oplus}$ catalyst	

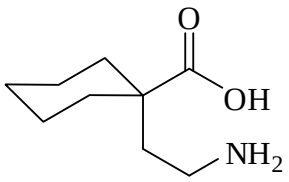
Marks 6

- Cyclohexene undergoes an electrophilic addition reaction with HI in CCl_4 solvent to give iodocyclohexane. Draw the mechanism of this reaction, using curly arrows to indicate the movement of electrons. Include structures for any relevant intermediates.

Draw the two chair conformations of iodocyclohexane and indicate which is likely to be more stable. Briefly explain the reason for your choice.

Marks 4

- Neurontin® is a pharmaceutical now widely used for the treatment of nerve pain. The structure of the active ingredient in Neurontin, gabapentin, is shown below. The pK_a value for the carboxyl group is 3.68, whilst the pK_b value for the amine group is 3.30.



gabapentin

Explain whether gabapentin can reasonably be described as an amino acid.

Orally-delivered pharmaceutical agents that contain amine functional groups are often prepared as hydrochloride salts, rather than as free amines. Suggest a reason why gabapentin is not delivered as a hydrochloride salt, illustrating your answer with a suitable diagram.

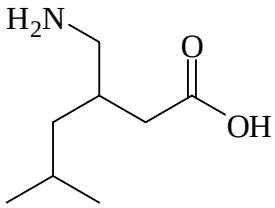
Gabapentin was originally synthesised as it was anticipated that it would bind to the same receptors as the neurotransmitter GABA (4-aminobutanoic acid). Draw the structure of GABA. Suggest a reason why it might have been anticipated that gabapentin would interact with GABA receptors, and what form such interactions might take.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 4

This expectation has proven to be incorrect, as gabapentin does not interact well with GABA receptors. Suggest a reason why this might be the case.

Pregabalin (marketed under the trade name Lyrica) has been developed as a successor to gabapentin as it is more potent. Its structure is shown below.

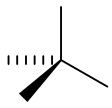


pregabalin

The pharmaceutical formulation contains only the (*S*) enantiomer of pregabalin. Rank the substituents around the stereocentre in decreasing order of priority.

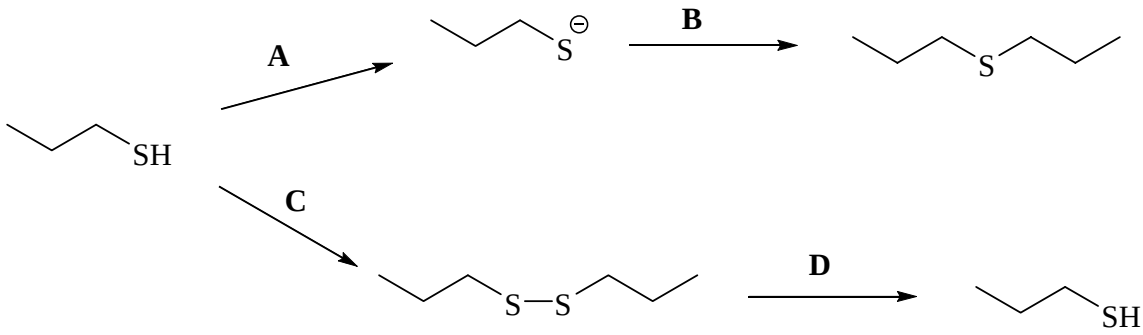
highest priority			lowest priority

Draw the (*S*) enantiomer of pregabalin.



Marks

- Indicate the reagents used in the laboratory to undertake the following transformations. **5**



A:	
B:	
C:	

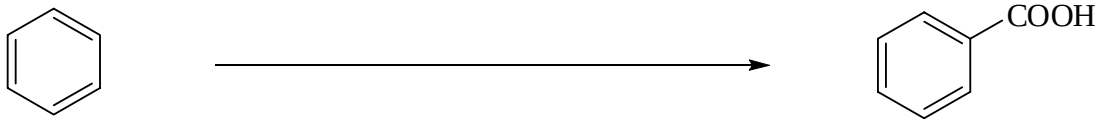
Provide a description for transformation **B**.	
Provide a description for transformation **D**.	

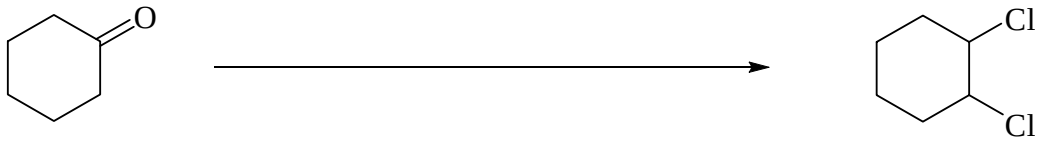
- Define the term "elimination" and illustrate your answer with an equation. **2**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 7

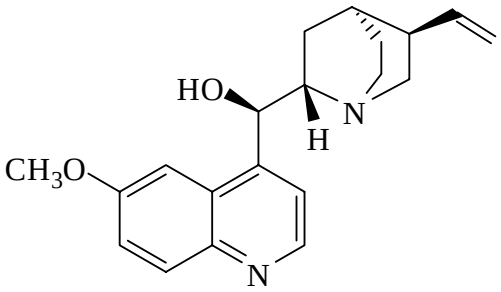
- Show clearly the reagents you would use to carry out the following chemical conversions. Draw constitutional formulas for any intermediate compounds. Note: More than one step is required in both cases.



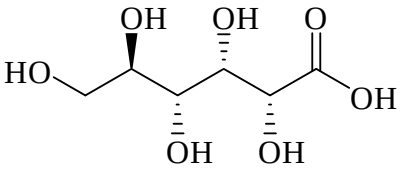


Marks 4

- Quinine has long been used for the treatment of malaria. For an intramuscular injection, quinine is reacted with gluconic acid. Structures and molar masses for these substances are shown below.



quinine
molar mass 324.41 g mol^{-1}



gluconic acid
molar mass 196.16 g mol^{-1}

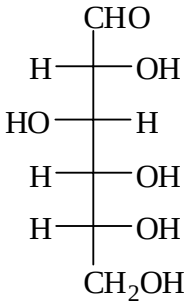
Quinine and gluconic acid can undergo an acid-base reaction to form a salt, or a condensation reaction to form an ester. One molecule of each substance is required for the transformation, and a 160.0 mg dose of quinine gluconate is equivalent to a 100.0 mg dose of quinine. By determining the molar mass of the product formed, or otherwise, determine whether the product formed is an ester or a salt.

Suggest two reasons why it might be important to know whether quinine gluconate is a salt or an ester.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
3

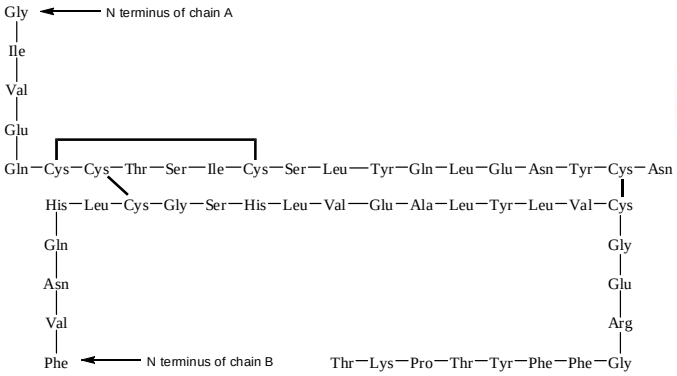
Gluconic acid is formed in biological systems by the oxidation of glucose, which can exist as both an open-chain form and as cyclic forms. The Fischer projection for the open-chain form of D-glucose is shown on the right. Illustrate the formation of the cyclic forms of glucose, and discuss whether gluconic acid can form similar cyclic forms.

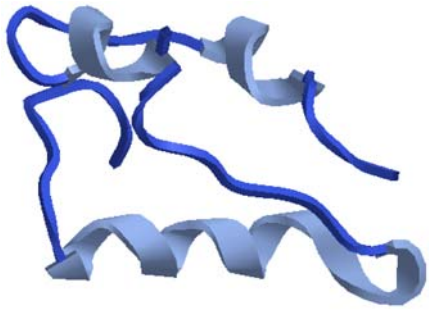


THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 4

- Insulin is an important hormone involved in the regulation of glucose availability in the body. It consists of two peptide chains, one consisting of 21 amino acids (the "A" chain) and one of 30 amino acids (the "B" chain). Below are two representations of insulin, one showing the amino acid sequence and the other a stylised ribbon diagram.





Define the terms *primary structure*, *secondary structure* and *tertiary structure* in relation to proteins. Illustrate your answer with appropriate diagram(s) and by making reference to the representations shown above.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

The peptide links in a protein chain are said to be *resonance stabilised*. Use a diagram to explain what is meant by this term, and indicate one important consequence relating to protein structure and one important consequence relating to the chemistry of proteins.

Marks 4

Modern medicine now uses insulin analogues (where one or more of the amino acid residues has been changed) in the treatment of diabetes. In one such analogue, glargine insulin, the changes have increased the isoelectric point of the enzyme from 5.4 to 6.7, thereby reducing its solubility at physiological pH. Explain how changes in the primary amino acid sequence can alter the pI and solubility of the analogue without altering its interaction with blood-glucose.

CHEM1611 - CHEMISTRY 1A (PHARMACY)

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

CHEM1611 - CHEMISTRY 1A (PHARMACY)

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

CHEM1611 - CHEMISTRY 1A (PHARMACY)

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]