22/05(a)

The University of Sydney

CHEMISTRY 1A (PHARMACY) — CHEM1611

<u>CHEM1611 - CHEMISTRY 1A (PHARMACY)</u>

<u>FIRST SEMESTER EXAMINATION</u>

CONFIDENTIAL

JUNE 2005 **<u>TIME ALLOWED: THREE HOURS</u>**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

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

<u>INSTRUCTIONS TO CANDIDATES</u>

- All questions are to be attempted. There are 15 pages of examinable material.
- Complete the written section of the examination paper in **<u>INK</u>.**
- 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.
- Pages 10, 13, 18 & 20 are for rough working only.

<u>OFFICIAL USE ONLY</u>

Multiple choice section

	Marks	
Pages	Max	Gained
2-6	28	

Short answer section

Page	Marks			Marker
	Max	Gained		
7	11			
8	4			
9	8			
11	7			
12	9			
14	6			
15	8			
16	6			
17	6			
19	7			
Total	72			

Marks

5

- Complete the following table. Give, as required, the formula, the systematic name, the oxidation number of the underlined atom and, where indicated, the number of *d* electrons for the element in this oxidation state.

FORMULA	SYSTEMATIC NAME	OXIDATION NUMBER	NUMBER OF *d* ELECTRONS
$\underline{S}O_3$			
$K\underline{Mn}O_4$			
$\underline{Co}Cl_2{\cdot}6H_2O$			
	ammonium sulfate		

4

- Draw the Lewis structures, showing all valence electrons for the following species. Indicate which of the species have contributing resonance structures.

NO_3^-	CO_2	N_2H_2
Resonance: YES / NO	Resonance: YES / NO	Resonance: YES / NO

2

- A sample of carboxypeptidase (an enzyme) was purified and found on analysis to contain 0.191% by weight of zinc. What is the *minimum* molecular weight of the enzyme if we assume it is a monomer?

Answer:

Marks
4

- Solutions of lead(II) nitrate (0.080 M, 60 mL) and potassium iodide (0.080 M, 40 mL) are mixed. What amount (in mol) of PbI_2(s) precipitates?

Answer:

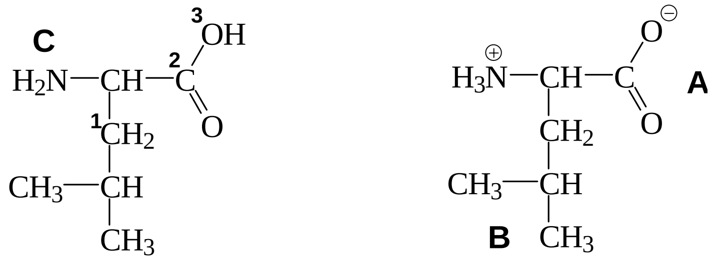
What is the final concentration of K^+(aq) ions remaining in solution after the reaction?

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
8

- Shown here are the classical and the zwitterionic forms of the amino acid leucine.



List the types of intermolecular interactions in which each of the indicated sites (**A**, **B** and **C**) in leucine could be involved.

A	
B	
C	

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

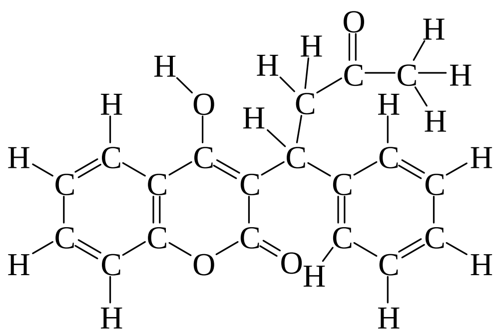
Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry/shape of σ-bonding electron pairs around the atom
[1]C			
[2]C			
[3]O			

Given that the pK_a of the carboxylic acid group of leucine is 2.32 and the pK_b of the amine group is 4.24, do you expect the classical or the zwitterionic form to predominate when leucine is dissolved in water? In other words, does the following equilibrium lie to the right or left? Show your reasoning.

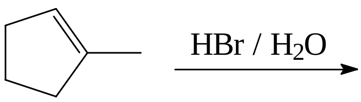
$$H_2N{-}CH(CH_2CH(CH_3)_2){-}COOH \rightleftharpoons H_3\overset{\oplus}{N}{-}CH(CH_2CH(CH_3)_2){-}CO_2^{\ominus}$$

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**



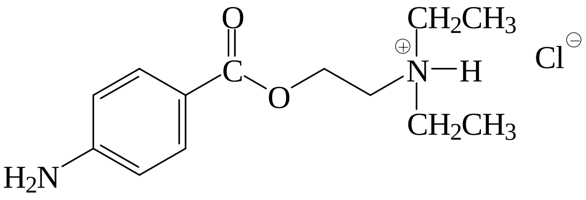
- When 1-methylcyclopentene is treated with hydrogen bromide in water, two carbocations can be formed. Give the structures of these carbocations in the spaces below, indicating which is the more stable species. **4**



More stable carbocation	Less stable carbocation

Give the constitutional formula(s) of the product(s) arising from the more stable carbocation in the above reaction.

- When procaine hydrochloride (**F**), an anaesthetic, is heated with 4 M aqueous NaOH, two products, (**G**) and (**H**), are obtained. Give the constitutional formulas of (**G**) and (**H**). **2**

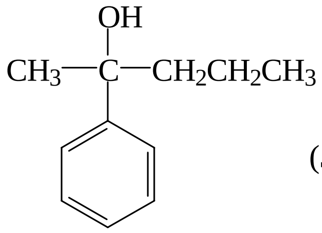


(**F**)

(**G**)	(**H**)

Marks
9

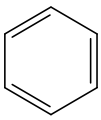
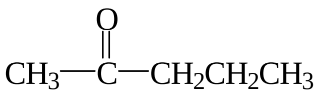
- 2-Phenyl-2-pentanol (**J**) is treated with concentrated sulfuric acid to give a mixture of three alkenes (**K**), (**L**) and (**M**). Alkenes (**K**) and (**L**) are diastereomers while (**K**) and (**M**) [and (**L**) and (**M**)] are constitutional isomers. Give the structures and systematic names for (**K**), (**L**) and (**M**).



(**J**)

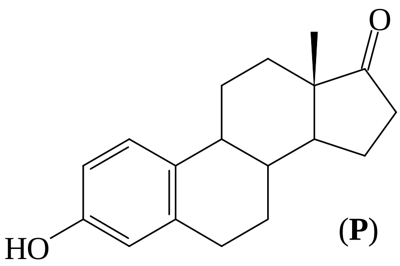
(**K**)	(**L**)	(**M**)
Name	Name	Name

Outline a reaction sequence that converts benzene into 2-phenyl-2-pentanol (**J**) and that also uses 2-pentanone as a reactant somewhere in the sequence. Any solvents and inorganic reagents may be used. More than one step is required. Show clearly the reagents you would use and draw constitutional formulas for any intermediate compounds.

benzene  2-pentanone 

Marks
6

- The structure of estrone (**P**), an important female hormone, is shown on the right.



(**P**)

Give the molecular formula of estrone (**P**).

Identify the functional groups present in estrone (**P**).

How many stereogenic (chiral) centres are there in estrone (**P**)?

Treatment of estrone (**P**) with $LiAlH_4$ in dry ether (solvent) followed by aqueous acid gives alcohols (**Q**) and (**R**), which are diastereomers. Draw the structures of (**Q**) and (**R**).

(**Q**)	(**R**)

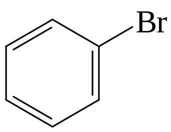
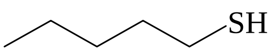
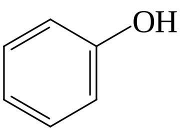
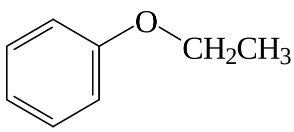
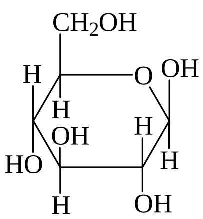
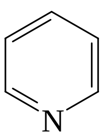
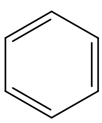
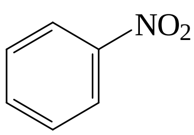
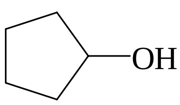
Reaction of estrone (**P**) with excess methanol and HCl gives an acetal (**S**). Give the constitutional formula of (**S**).

(**S**)

What are the reagents and reaction conditions that will convert the acetal (**S**) back to estrone and methanol?

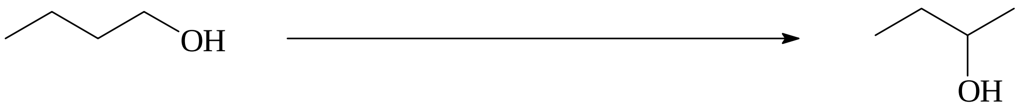
- Complete the following table.

Marks
8

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
$CH_3CH_2CHCH_2CH_3$ (Br on C-3)		$CH_3CH_2CHCH_2CH_3$ (on C-3: $Br^{\ominus}$ $^{\oplus}N(CH_3)_3$)
	1. Mg / dry ether 2. CO_2 3. $H^{\oplus}$ / H_2O	
	I_2 / air	
		
	CH_3OH / $H^{\oplus}$ catalyst	
	HCl	
		
	$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	

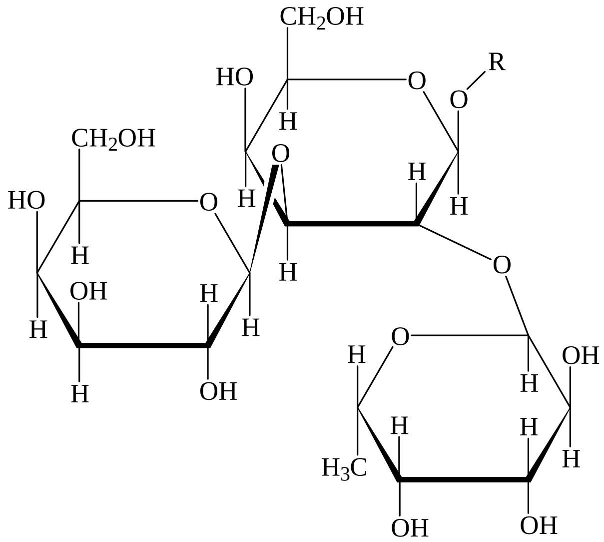
Marks
6

- 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 6

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



The type B blood group antigen can be hydrolysed to galactose (2 mole equiv.), fucose (1 mole equiv.) and a glycoprotein unit.

Specify the fucose unit in the type B blood group antigen as a furanose or a pyranose.	
Specify fucose as a hexose, a pentose or a tetrose.	

Give the Fischer projections of the open chain form of galactose and fucose.

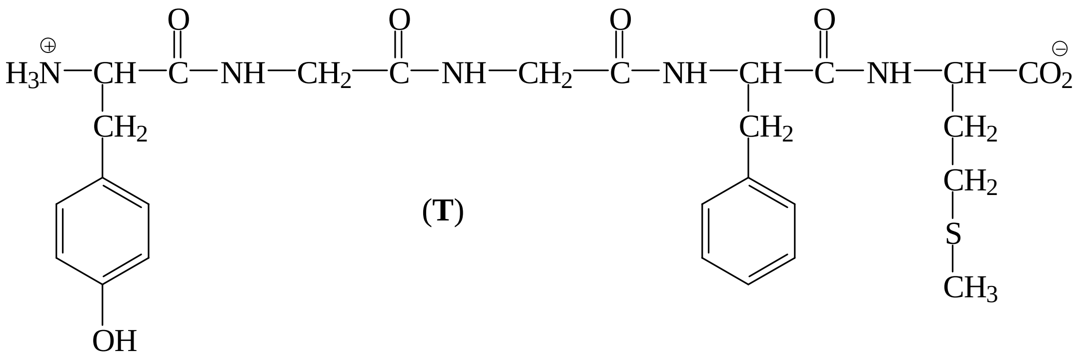
Fischer projection of galactose	Fischer projection of fucose

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

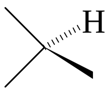
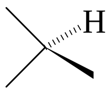
- The neurohormone Tyr-Gly-Gly-Phe-Met (**T**) known as methionine enkephalin is a naturally occurring peptide which controls pain perception in vertebrates.



(**T**)

Name the functional groups in (**T**).

Four amino acids (tyrosine, glycine, phenylalanine and methionine) are obtained on complete acid hydrolysis of (**T**). Draw the stereoformulas of L-tyrosine and L-methionine in the boxes below. Indicate their absolute configurations using the (*R*)- and (*S*)- convention.

L-tyrosine	L-methionine
	
Absolute configuration	Absolute configuration

Give the constitutional formula for the product obtained when tyrosine, the *N*-terminal amino acid in peptide (**T**), is dissolved in 1 M NaOH solution.

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}

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}

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
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+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
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.28
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–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

CHEM1611 - CHEMISTRY 1A (PHARMACY)

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = Z^2E_R(1/n^2)$	**Radioactivity** $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$
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 $\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_fm$ $\Delta T_b = K_bm$	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
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)	**Thermodynamics & Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $K_p = K_c (RT)^{\Delta n}$
Polymers $R_g = \sqrt{\frac{nl_0^2}{6}}$	**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]									

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]