2208(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2011 **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 tables.
- Each new question of the short answer section begins with a •.
- Only non-programmable, University-approved calculators may be used.
- Students are warned that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.
- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheets.
- Page 24 is for rough working only.

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Multiple choice section

	Marks	
Pages	Max	Gained
2-9	25	

Short answer section

Page	Marks Max	Gained		Marker
10	8			
11	6			
12	8			
13	5			
14	3			
15	4			
16	2			
17	5			
18	7			
19	7			
20	6			
21	3			
22	5			
23	6			
Total	75			
Check Total				

Marks

- Explain why $HClO_4$ is a stronger Brønsted acid than $HBrO_4$, but HCl is a weaker acid than HBr. **2**

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu^{2+}. **2**

- Provide a systematic name for the complex [NiBrCl(en)] and draw both of its possible structures. (en = $NH_2CH_2CH_2NH_2$ = ethylenediamine = ethane-1,2-diamine) **4**

Is either complex chiral? Explain your reasoning.

Marks 6

- Complete the following table. (ox = oxalate = $C_2O_4^{2-}$)

Formula	$Na[FeCl_4]$	$[CrCN(NH_3)_5]Br_2$	$K_3[VO_2(ox)_2]\cdot 3H_2O$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Species formed upon dissolving in water			

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Marks
8

- Solution A consists of a 1.00 M aqueous solution of HOCl at 25 °C. The pK_a of HOCl is 7.54. Calculate the pH of Solution A.

pH =

At 25 °C, 1.00 L of Solution B consists of 74.5 g of NaOCl dissolved in water. Calculate the pH of Solution B.

pH =

Solution B (0.40 L) is poured into Solution A (0.60 L). What amount of NaOH (in mol) must be added to give a solution, after equilibration, with a pH of 8.00?

Answer:

Marks
5

- $BaSO_4$ is used as a contrast agent in medical imaging. It has a K_{sp} of 1.1×10^{-10}. What is the molarity of Ba^{2+} ions in a saturated aqueous solution of $BaSO_4$?

Answer:

What is the molar solubility of $BaSO_4$ in the presence of a 0.1 M solution of Na_2SO_4?

Answer:

The lethal concentration of Ba^{2+} in humans is about 60 mg L^{-1} (4×10^{-4} M). Is there any advantage to administering $BaSO_4$ in the presence of 0.1 M Na_2SO_4 solution? Explain your reasoning.

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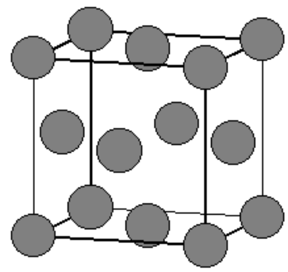
Page Total:

Marks
3

- A face centred cubic (FCC) unit cell has the maximum possible space filling of 74 %. Show the close packed layers, labelling them A, B and C, on the unit cell below.

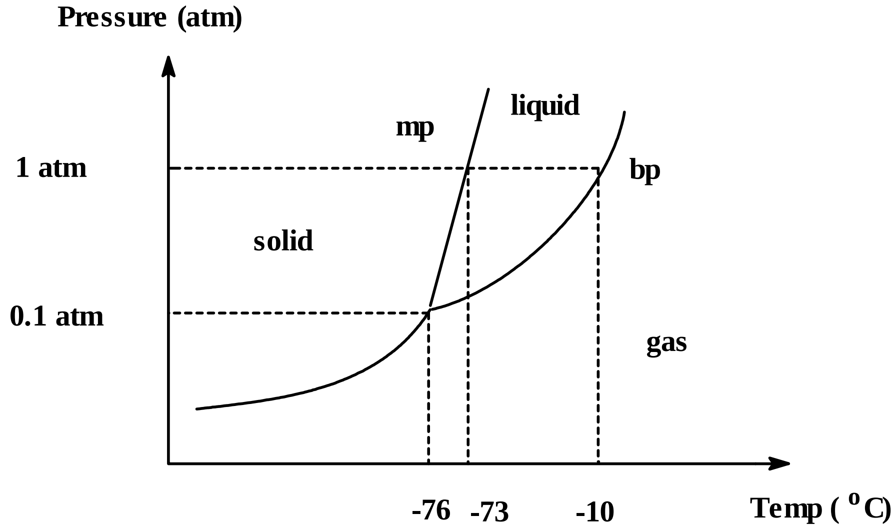


How many atoms are in the unit cell?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- The phase diagram for sulfur dioxide, SO_2, is shown below.



Io, the innermost of the four Galilean moons orbiting Jupiter, is the most geologically active body in the solar system. Its surface is covered with a frost of solid SO_2. The atmospheric pressure on Io is 10^{-7} atm and the surface temperature is between 90 and 110 K (–183 to –163 °C). As the temperature is raised on Io, does the SO_2 melt or sublime?

Io has a hot molten magma core. What is the physical state of SO_2 several hundred metres below the surface of Io, where the temperature is –50 °C and the pressure rises to 1 atm?

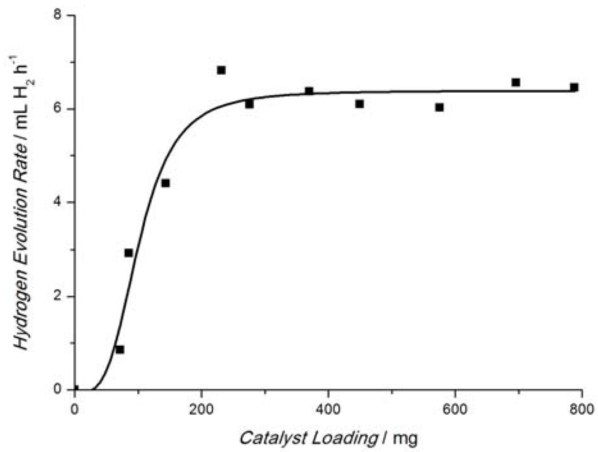
Is it possible to "ice skate" on a surface of solid SO_2? Explain your answer.

Marks
2

- When irradiated with visible light, CdS can catalyse the production of H_2 from water.

$$H_2O + \text{light} \xrightarrow{\text{CdS}} H_2 + \tfrac{1}{2}O_2$$

The rate of H_2 production from 80 mL of water at constant illumination varies with the amount of catalyst present (*i.e.* CdS loading) as shown below.



Why does the rate of H_2 production as a function of catalyst loading plateau?

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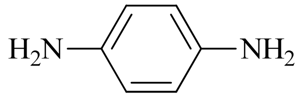
Page Total:

Marks 5

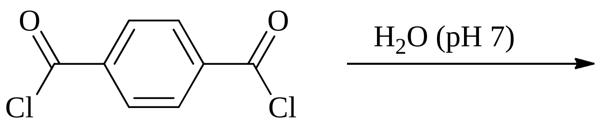
- Indicate the hybridisation of the carbon and nitrogen atoms in the diamine **P**.



P

N atoms:	C atoms:

Draw the product of the reaction when diacyl chloride **Q** reacts with water.



Q

Kevlar (used in bullet-proof vests) is a polyamide polymer which is made from diacyl chloride building block **Q** and diamine building block **P**. Draw the repeating polymer unit formed in the reaction of **P** with **Q**.

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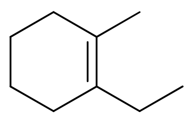
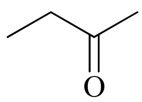
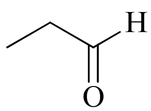
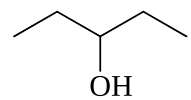
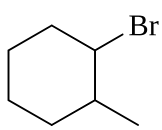
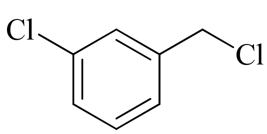
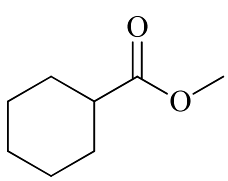
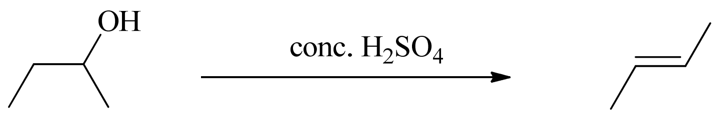
Marks
7

- Complete the following table. If there is no reaction, write "NR". Show any relevant stereochemistry.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	H_2, Pd/C	
	$Cr_2O_7^{2-}$ / H^+	
	(i) (ii) work-up (H_2O/H^+)	
	conc. KOH in ethanol solvent	
	hot aqueous NaOH	
	$(CH_3)_2NH$	

Marks
7

- Consider the following dehydration reaction.



Use curly arrows to show the mechanism of this reaction.

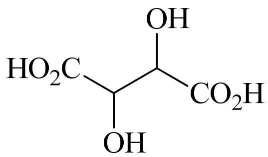
Two minor products are also formed in this reaction. They both have the same molecular formula as the product above. Draw their structures and name them.

Structure	Name

Page Total:

Marks
6

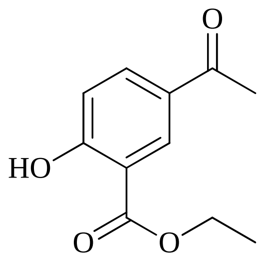
- Consider tartaric acid, whose constitutional formula is shown below.



There are three stereoisomers of tartaric acid - a meso form and a pair of enantiomers. Explain this statement by drawing suitable 3-dimensional structures of tartaric acid and by assigning (*R*) and (*S*) stereocentres where appropriate.

Marks
3

- Compound **T** is a precursor in the synthesis of the asthma drug salbutamol.



T

Give the molecular formula of compound **T**.

Give the structure(s) of all organic products formed when compound **T** is heated with 4 M NaOH.

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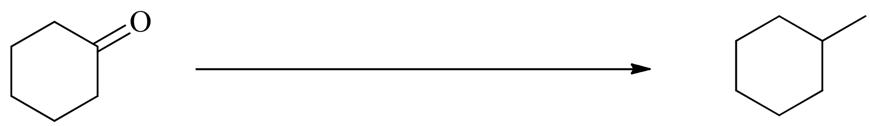
Marks
5

- Devise a synthesis of methylcyclohexane from cyclohexanone. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.



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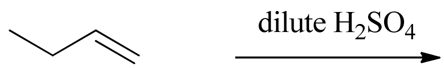
Marks
6

- Give the major product from the following reaction.



Show the mechanism of the reaction. Make sure you show structural formulas for all relevant intermediate species and the final product, as well as using curly arrows to indicate the movement of electrons (*i.e.* the breaking and formation of bonds).

Is the major product formed as the (*R*)-enantiomer, the (*S*)-enantiomer or a racemic mixture, or is it achiral? Give a reason for your answer.

Give the structure of the minor product of this reaction and explain why very little of it forms.

CHEM1102 - CHEMISTRY 1B

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	1 Ci = 3.70×10^{10} Bq
0 °C = 273 K	1 Hz = 1 s^{-1}
1 L = 10^{-3} m^3	1 tonne = 10^3 kg
1 Å = 10^{-10} m	1 W = 1 J s^{-1}
1 eV = 1.602×10^{-19} J	

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

CHEM1102 - CHEMISTRY 1B

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
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(g) + 7H_2O$	+1.36
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+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
$Sc^{3+}(aq) + 3e^- \rightarrow Sc(s)$	–2.09
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–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

CHEM1102 - CHEMISTRY 1B

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K 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** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = ½mv^2$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = $8033 \ln(A_0/A_t)$ years	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Mathematics If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$ Area of circle = πr^2 Surface area of sphere = $4\pi r^2$ Volume of sphere = $^4/_3\ \pi r^3$	**Thermodynamics & Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $\ln\frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Miscellaneous $A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	**Colligative Properties & Solutions** $\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$

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]	112 COPERNICIUM **Cn** [283]						

LANTHANOIDS	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
ACTINOIDS	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]