2206(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1B - CHEM1102

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2010 **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.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	32	

Short answer section

Page	Marks Max	Gained		Marker
11	5			
12	5			
13	5			
14	7			
15	5			
16	4			
17	3			
18	8			
19	4			
20	7			
21	6			
22	3			
23	6			
Total	68			
Check Total				

Marks

- Explain why hydrogen bonding is significant in H_2O (bp 100 °C), but not in H_2Se (bp –41°C) despite both oxygen and selenium being in Group 16 of the Periodic Table. **2**

- Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3}, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9}. **2**

- Which of the following are allotropes? Explain your answer. **1**

^{16}O, ^{18}O, O_2, O_3, O^-, O^{2-}, O_2^-, O_2^{2-}, H_2O, H_2S, H_2O_2.

Page Total:

- The solid-liquid curve in the phase diagram of a particular compound slopes to the left. Can the compound sublime? Explain your answer.

Marks
1

- Following blood donation, a solution of sodium oxalate is added to remove Ca^{2+} ions (as calcium oxalate, $CaC_2O_4 \cdot H_2O$, K_{sp} 2.3×10^{-9}), which cause the blood to clot. If the concentration of Ca^{2+} ions in blood is 9.7×10^{-5} g mL^{-1}, and 100.0 mL of 0.1550 M $Na_2C_2O_4$ is added to a 104 mL sample of blood, what will be the concentration (in mol L^{-1}) of Ca^{2+} ions remaining in the blood?

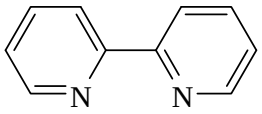
4

Answer:

Page Total:

Marks 5

- Complete the following table. NCS^- = isothiocyanate ion

bipy = 2,2'-bipyridine = $(C_5H_4N)_2$ = 

Formula	$K_2[Zn(CN)_4]$	$[Co(bipy)(NH_3)_4]Cl_3$	$[Co(bipy)_2(NCS)_2]$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Coordination geometry of the complex ion			
List all the ligand donor atoms			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

Marks 7

- A 20.0 mL solution of nitrous acid (HNO_2, $pK_a = 3.15$) was titrated to its equivalence point with 24.8 mL of 0.020 M NaOH. What is the concentration of the HNO_2 solution?

Answer:

What was the pH at the start of the titration?

pH =

What was the pH after (a) 12.4 mL and (b) 24.8 mL of the NaOH had been added?

(a) 12.4 mL: pH =

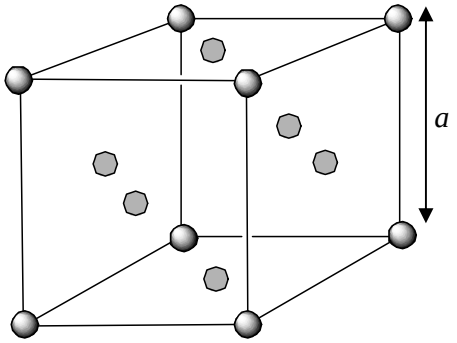
(b) 24.8 mL: pH =

Qualitatively, how would each of these three pH values be affected if 5 mL of water were added to the 20.00 mL of nitrous acid before beginning the titration?

Page Total:

Marks
5

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The unit cell dimension (edge length, *a*) for this alloy is 0.36 nm.



= Au = Cu

What is the chemical formula of the alloy?

Answer:

Pure gold is 24 carat, whilst gold alloys consisting of 75 % gold by weight are termed 18 carat gold. What carat gold is this alloy?

Answer:

What is the volume (in cm^3) of the unit cell?

Answer:

What is the density (in g cm^{-3}) of the alloy?

Answer:

Page Total:

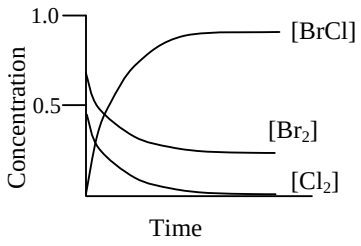
Marks 4

- In the reaction of Cl_2 with Br_2 in CCl_4 solution, BrCl forms according to the equation:

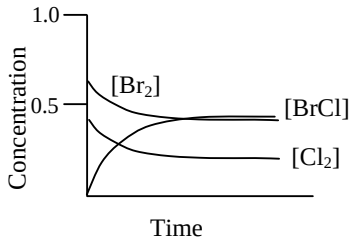
$$Br_2 + Cl_2 \rightarrow 2BrCl \qquad K_c = 2$$

With initial concentrations of $[Br_2] = 0.6$ M, $[Cl_2] = 0.4$ M and $[BrCl] = 0.0$ M, which of the following concentration versus time graphs represents this reaction? Explain qualitatively why you rejected each of the other three graphs.

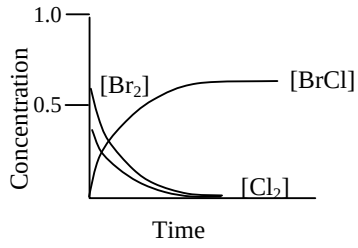
(a)



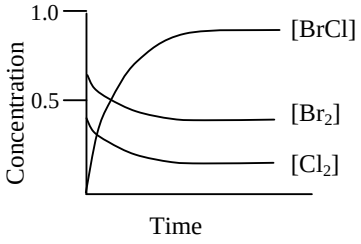
(b)



(c)



(d)



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Marks 3

- Hydrogenation of NO to N_2 and water is a potential means of reducing smog-forming NO_x gases:

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0).

Experiment	P_0 H_2 (kPa)	P_0 NO (kPa)	Rate (kPa s^{-1})
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

What is the order of the reaction? Show all working.

Answer:

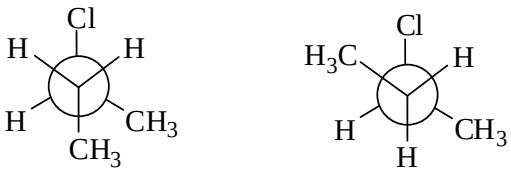
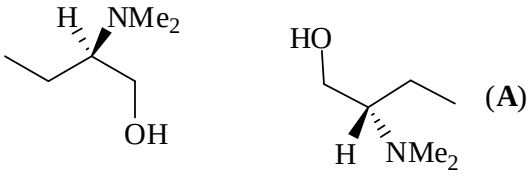
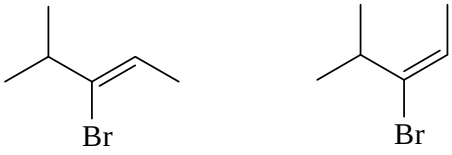
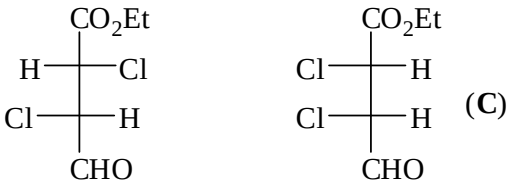
What is the value of the rate constant?

Answer:

Page Total:

Marks 8

- Consider the following pairs of compounds. Indicate the isomeric relationship that exists between the compounds in each set.

	
	
 (**A**)	
(**B**) 	
 (**C**)	

What is the configuration of the stereogenic centre in compound (**A**)?

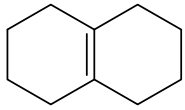
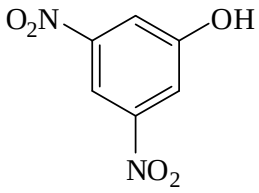
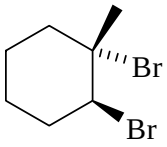
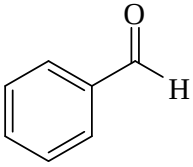
Give the full name of compound (**B**) that unambiguously describes its stereochemistry.

Is compound (**C**) a *meso* isomer? Give a reason for your answer.

Page Total:

Marks 4

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

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	H_2/Pd/C (catalyst)	
	1. NaOH 2. CH_3Br	
	Br_2	
	1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	

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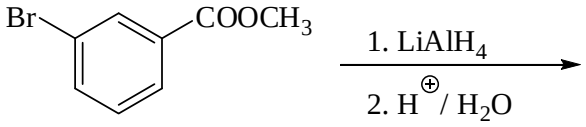
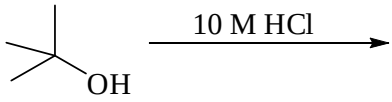
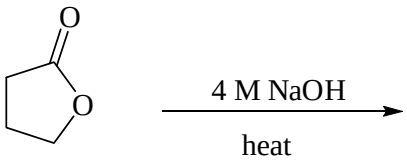
Page Total:

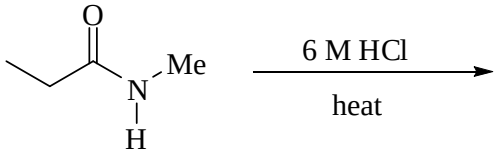
Marks 7

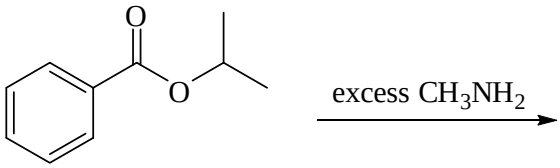
- Give the constitutional formula(s) of the major organic product(s) formed in each of the following reactions.











Page Total:

Marks
6

- Draw the constitutional formulas of all isomers of C_3H_6BrCl.

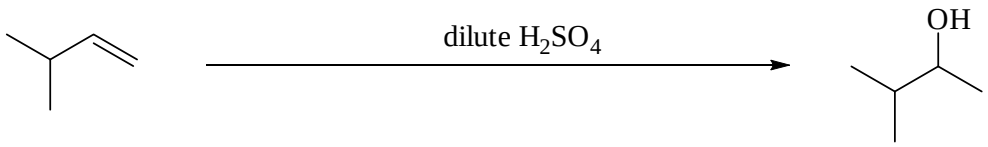
A number of the above isomers are optically active. For all such compounds, draw the two enantiomers.

Select any **one** of the structures you have drawn on this page and write its full systematic name just below it.

Page Total:

Marks 3

- Complete the mechanism for the following reaction. Give the structure of the carbocation intermediate and indicate (using curly arrows) all the bonding changes that occur.



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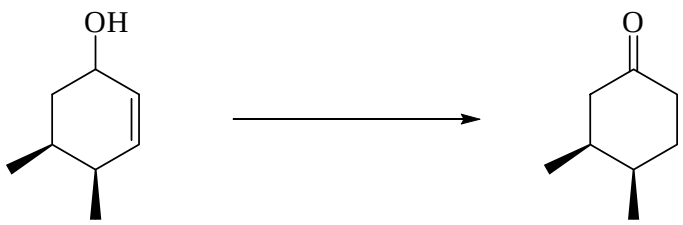
Marks
6

- Devise a synthesis of the following compounds from the starting materials indicated. 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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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

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

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

$\lambda = h/mv$

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

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

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

$T\,\lambda = 2.898 \times 10^6$ 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

$PV = nRT$

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

$E_k = \frac{1}{2}mv^2$

Radioactivity

$t_{1/2} = \ln 2/\lambda$

$A = \lambda N$

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

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

Kinetics

$t_{1/2} = \ln 2/k$

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

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

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

Colligative Properties & Solutions

$\Pi = cRT$

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

$c = kp$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta_{univ} S° = R \ln K$

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

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 $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

Area of circle = πr^2

Surface area of sphere = $4\pi r^2$

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]