2206(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1B - CHEM1102

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2013 **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	28	

Short answer section

Page	Marks Max	Gained		Marker
11	8			
12	4			
13	4			
14	6			
15	2			
16	7			
17	6			
18	9			
19	3			
20	7			
21	5			
22	5			
23	6			
Total	72			
Check Total				

Marks 8

- Use the information already provided to complete the following table.
  (ox = oxalate = $C_2O_4^{2-}$)

Formula	$[CrCl_2(NH_3)_4]^n$	$[Fe(ox)_3]^n$	$[ZnCl_2(NH_3)_2]^n$
Oxidation state of transition metal ion		+III	
Number of *d*-electrons in the transition metal ion			10
Number of unpaired *d*-electrons in the transition metal ion			
Charge of complex (*i.e.* n)	1+		
Is the metal atom paramagnetic?			

The complex $[PtCl_2(NH_3)_2]$ has two isomers, while its zinc analogue (in the table) exists in only one form. Using diagrams where appropriate, explain why this is so.

- What is the pH of a 0.1 M solution of ammonium chloride, given the K_b for ammonia is 1.8×10^{-5}.

Marks 4

pH =

What is the ratio of ammonia to ammonium ion in this solution?

Answer:

	Marks
Describe the periodic trends exhibited by atomic radii. Justify these trends in terms of principal quantum number, n, and effective nuclear charge, Z_{eff}.	**2**
Giving reasons, order either the set of oxyacids or the binary acids in terms of increasing acidity. $HClO$, $HClO_2$, $HClO_3$, $HClO_4$ or H_2O, H_2S, H_2Se, H_2Te	**2**

- What is the pH of a solution which is 0.10 M in both acetic acid and sodium acetate? The K_a for acetic acid is 1.8×10^{-5}.

Marks 4

Answer:

What is the final pH if 0.010 mol of HCl is added to 1.0 L of the above solution?

Answer:

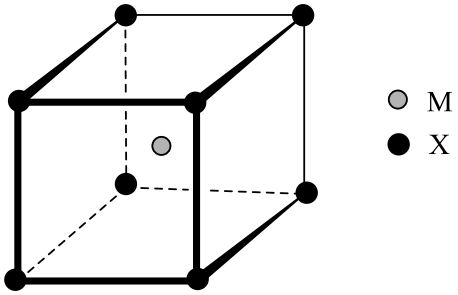
- The K_{sp} for $Fe(OH)_3$ is 2.64×10^{-39}. What is its molar solubility in water?

2

Answer:

Marks 2

- The unit cell below has a cation (M) at the centre of the cell and anions (X) at the corners.



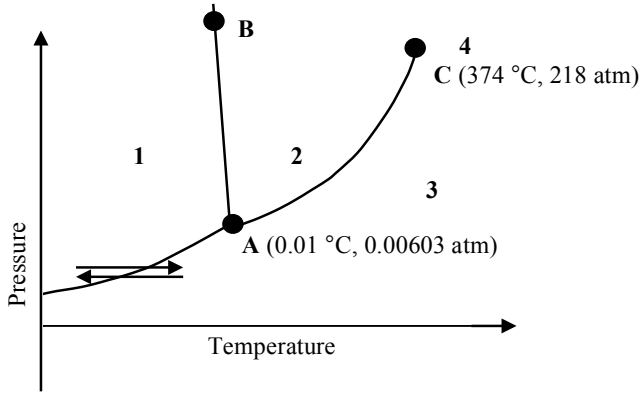
What is the formula of the compound?

What is the coordination number of each type of ion?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 7

- A phase diagram of water is shown below.



Identify the four phases shown as 1-4 in the phase diagram.

1:	2:
3:	4:

What are the phase changes highlighted by the forward and reverse arrows called?

Forward:	Reverse:

What names are given to the points A and C?

A:	C:

The boundary line A-B is slightly tilted to the left. What are the physical and biological significances of this?

What are the physical characteristics of water in phase 4?

Marks

- Given the following experimental data, find the rate law and the rate constant for the following reaction: **3**

$$NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$$

Run	[NO(g)] / M	[NO_2(g)] / M	[O_2(g)] / M	Rate / M s^{-1}
1	0.10	0.10	0.10	2.1×10^{-2}
2	0.20	0.10	0.10	4.2×10^{-2}
3	0.20	0.30	0.20	1.26×10^{-1}
4	0.10	0.10	0.20	2.1×10^{-2}

Rate = | k =

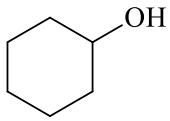
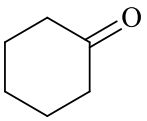
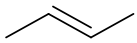
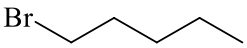
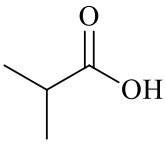
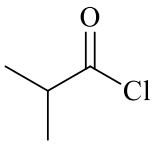
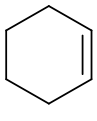
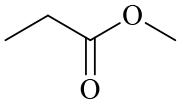
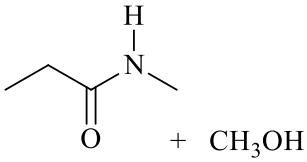
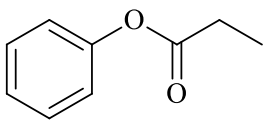
- The rate constant for a reaction is 5.0×10^{-3} s^{-1} at 215 °C and 1.2×10^{-1} s^{-1} at 452 °C. What is the activation energy of the reaction in kJ mol^{-1}? **3**

Answer:

What is the rate constant for this reaction at 100 °C?

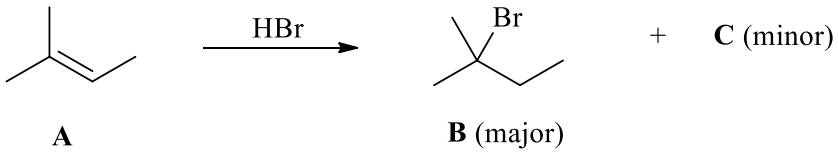
Answer:

• Complete the following table. **Marks 9**

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
		
	dilute H_2SO_4	
	hot conc. KOH in ethanol solvent	
		
	H_2, Pd/C	
	1. CO_2 2. $H^{\oplus}$ / H_2O	
		
	$OH^{\ominus}$ / H_2O / heat	

Marks
3

- When alkene **A** is reacted with HBr, the major reaction product is **B**. However, a minor product, **C**, is also formed that is isomeric with **B**.



A **B** (major)

What is the structure of product **C**?

By describing an intermediate formed in this reaction, explain why less of **C** is formed than **B**.

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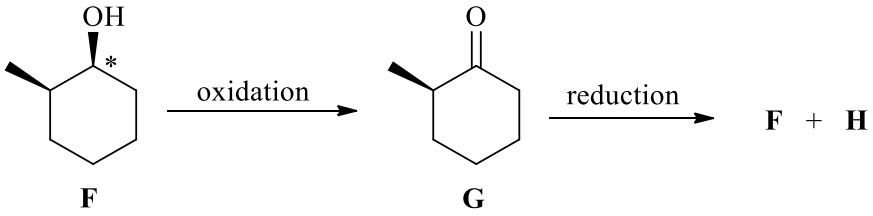
Marks 7

- Shown below is a reaction sequence beginning with the chiral alcohol, **F**.



F **G**

Draw the enantiomer of **F**.

The specific optical rotation of **F** is +24°. What is the optical rotation of a mixture consisting of equal amounts of **F** and its enantiomer?

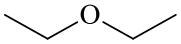
Assign the stereochemistry of the atom in alcohol **F** indicated by the asterisk (*), showing how you arrived at your answer.

Alcohol **F** is oxidised to give the corresponding ketone, **G**. Is this molecule still chiral? Why/why not? Explain your answer.

Ketone **G** is reduced with sodium borohydride, to give a mixture of two alcohols, **F** and **H.** **H** is a diastereomer of **F**. Draw the diastereomer **H**. What is the expected ratio of alcohols **F** and **H** in this mixture? Why?

Marks 5

- Below is the structure of an ether, **J**.



J

Draw a constitutional isomer of **J**.

Draw a conformational isomer of **J**.

There are no configurational isomers of **J**. Why not?

Below is the structure of an alkene, **K**, which *does* have a configurational isomer.

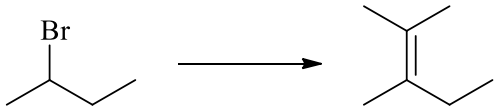
K

Draw this configurational isomer.

Name **K**, making sure your name distinguishes **K** from its isomer.

- Devise a synthesis of the alkene **M** using 2-bromobutane (**L**) and acetone (propanone) as starting materials. Show all relevant intermediates and reagents.

Marks 5



L **M**

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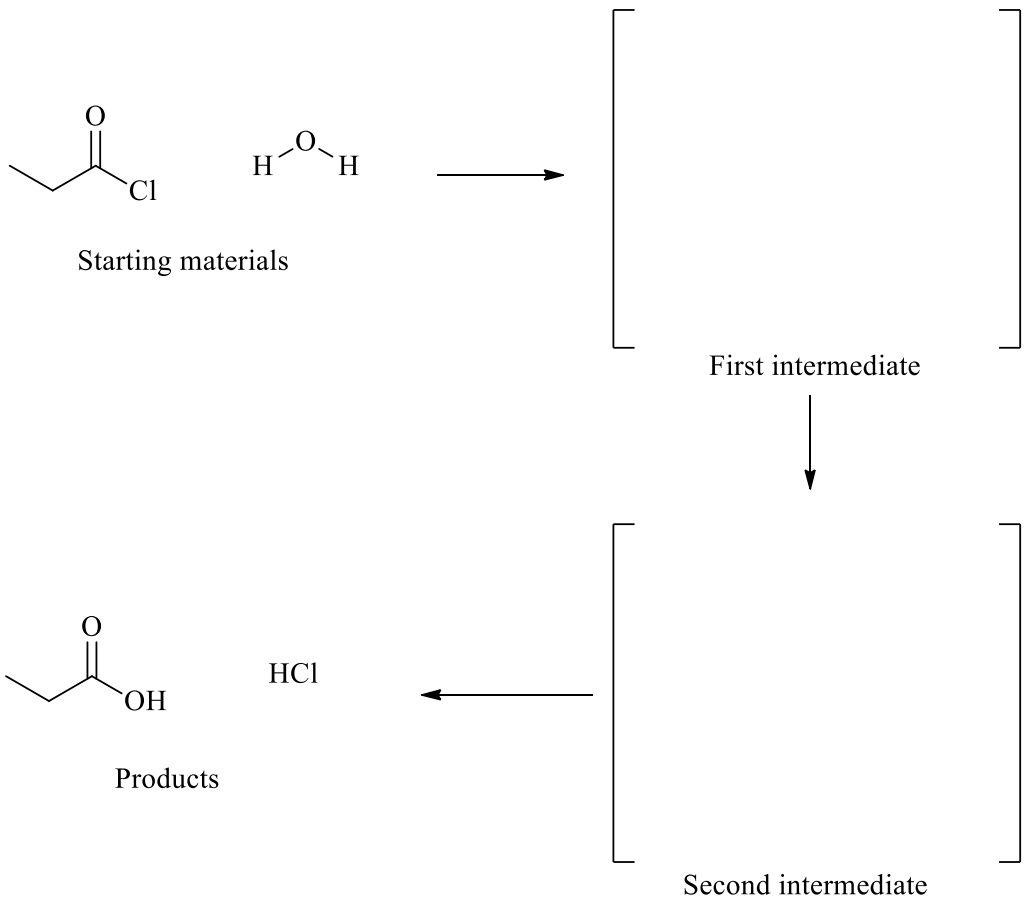
Marks 6

- Below is the reaction between an acid chloride and water to give a carboxylic acid. Provide curly arrows for this mechanism and draw the structures of the two intermediates on the pathway.



Indicate the hybridisation of the two oxygen atoms in the starting materials.

acid chloride:	water:

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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 = 1.013 bar
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
10^{12}	tera	T

CHEM1102 - CHEMISTRY 1B

Useful formulas

Quantum Chemistry

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

$\lambda = h/mv$

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

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

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

$T\lambda = 2.898 \times 10^6$ K nm

Electrochemistry

$\Delta G^\circ = -nFE^\circ$

Moles of $e^- = It/F$

$E = E^\circ - (RT/nF) \times \ln Q$

$E^\circ = (RT/nF) \times \ln K$

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

Acids and Bases

$pH = -\log[H^+]$

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

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

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

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

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

$\ln[A] = \ln[A]_0 - kt$

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

Colligative Properties & Solutions

$\Pi = cRT$

$P_{solution} = X_{solvent} \times P^\circ_{solvent}$

$c = kp$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Thermodynamics & Equilibrium

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G = \Delta G^\circ + RT \ln Q$

$\Delta G^\circ = -RT \ln K$

$\Delta_{univ} S^\circ = R \ln K$

$K_p = K_c \left(\frac{RT}{100}\right)^{\Delta n}$

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 = $4\pi r^2$

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
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+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
$NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow NH_4^+(aq) + 3H_2O$	+0.88
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+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
$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O$	+0.32
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.126
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.136
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.28
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–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

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** [263]	105 DUBNIUM **Db** [268]	106 SEABORGIUM **Sg** [271]	107 BOHRIUM **Bh** [274]	108 HASSIUM **Hs** [270]	109 MEITNERIUM **Mt** [278]	110 DARMSTADTIUM **Ds** [281]	111 ROENTGENIUM **Rg** [281]	112 COPERNICIUM **Cn** [285]		114 FLEROVIUM **Fl** [289]		116 LIVERMORIUM **Lv** [293]		

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]