Topics in the November 2013 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2013-N-2:

- Crystal Structures
- Metal Complexes
- Coordination Chemistry
- Kinetics

2013-N-3:

- Weak Acids and Bases

2013-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2013-N-5:

- Strong Acids and Bases
- Solubility Equilibrium

2013-N-6:

- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

2013-N-7:

- Alkenes
- Alcohols
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2013-N-8:

- Stereochemistry

2013-N-9:

- Representations of Molecular Structure
- Alkenes
- Alcohols

2013-N-10:

- Carboxylic Acids and Derivatives

2013-N-11:

- Synthetic Strategies
- Stereochemistry

2202(a)

THE UNIVERSITY OF SYDNEY

FUNDAMENTALS OF CHEMISTRY 1B - CHEM1002

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 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 17 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 short answer question 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.
- Pages 12 and 20 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

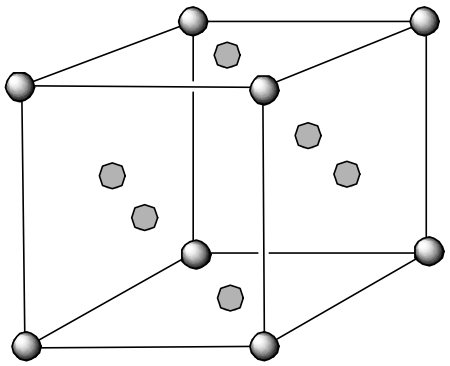
	Marks	
Pages	Max	Gained
2-8	28	

Short answer section

Page	Marks Max	Gained		Marker
9	6			
10	7			
11	7			
13	8			
14	9			
15	11			
16	7			
17	8			
18	3			
19	6			
Total	72			
Check Total				

Marks

- 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.



= Au = Cu

What is the chemical formula of the alloy? **2**

Answer:

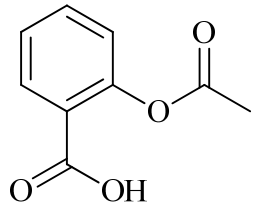
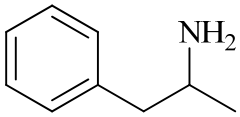
- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Co^{2+}. **2**

- Briefly explain how a catalyst works. **2**

Page Total:

Marks 7

- The structures of the drugs aspirin and amphetamine are shown below.
  (a) Draw the conjugate base of aspirin and the conjugate acid of amphetamine.
  (b) *Circle* the form of each that will be present in a highly acidic environment.

 aspirin	conjugate base of aspirin
 amphetamine	conjugate acid of amphetamine

Ions are less likely to cross cell membranes than uncharged molecules. One of the drugs above is absorbed in the acid environment of the stomach and the other is absorbed in the basic environment of the intestine. Identify which is absorbed in each environment below and *briefly* explain your answers.

Drug absorbed in the stomach:	aspirin / amphetamine
Drug absorbed in the intestine:	aspirin / amphetamine

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

Calculate the pH of a 0.010 M solution of aspirin at 25 °C. The pK_a of aspirin is 3.5 at this temperature.

Marks 7

pH =

Aspirin, $C_9H_8O_4$ is not very soluble. "Soluble aspirin" can be made by reacting aspirin with sodium hydroxide. Write the chemical equation for this reaction.

Is a solution of "soluble aspirin" acidic or basic? Briefly explain your answer.

Marks
8

- The concentration of iron in the ocean is one of the primary factors limiting the growth rates of some basic life forms. Write the chemical equation for the dissolution reaction of $Fe(OH)_3$ in water.

What is the solubility of $Fe(OH)_3$ in mol L^{-1}? K_{sp} ($Fe(OH)_3$) is 2.8×10^{-39} at 25 °C.

Answer:

Before the Industrial Revolution, the concentration of $OH^-(aq)$ in the oceans was about 1.6×10^{-6} M. What pH corresponds to this concentration at 25 °C?

Answer:

What is the solubility of $Fe(OH)_3$ in mol L^{-1} at this pH?

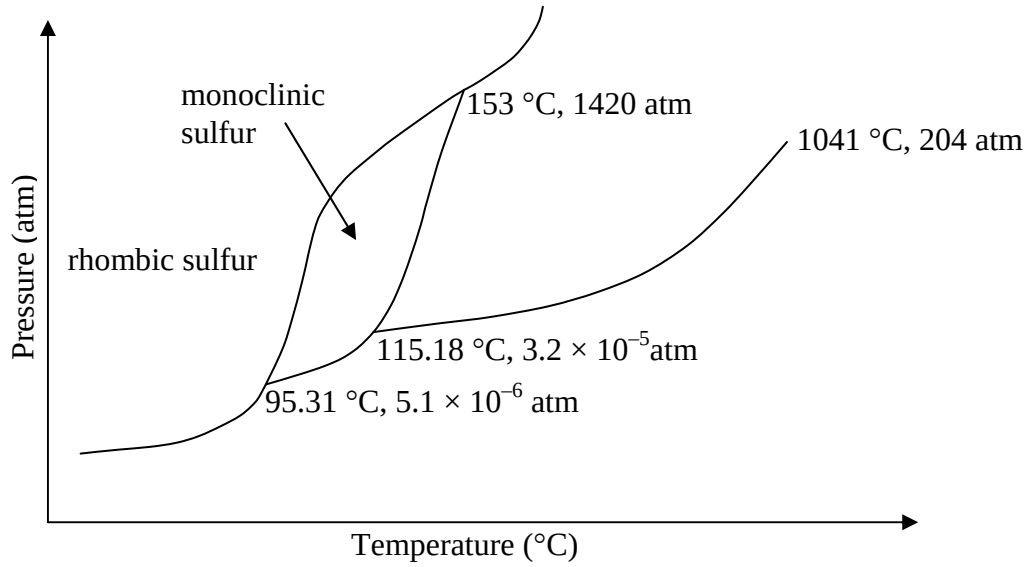
Answer:

Industrialisation has led to an increase in atmospheric CO_2. Predict the effect that this has had on the amount of $Fe^{3+}(aq)$ in sea water and briefly explain your answer.

Page Total:

Marks 9

- Solid sulfur can exist in two forms, rhombic sulfur and monoclinic sulfur. A portion of the phase diagram for sulfur is reproduced schematically below. Complete the diagram by adding the labels "vapour" and "liquid" to the appropriate regions.



Which form of solid sulfur is stable at 25 °C and 1 atm?

Describe what happens when sulfur at 25 °C is slowly heated to 200 °C at a constant pressure of 1 atm.

How many triple points are there in the phase diagram?

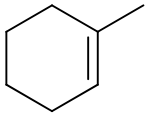
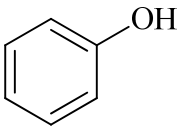
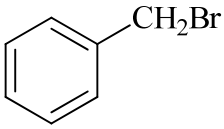
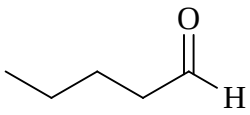
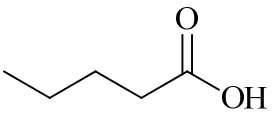
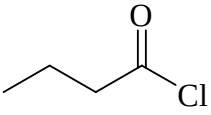
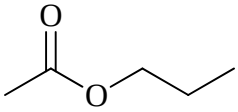
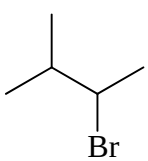
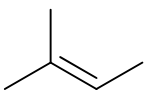
What phases are in equilibrium at each of the triple points?

Which solid form of sulfur is more dense? Explain your reasoning.

Page Total:

- Complete the following table. Make sure you give the name of the starting material where indicated.

Marks 11

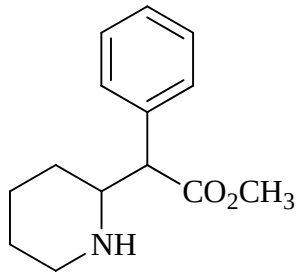
STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
 **Name:**	HBr / CCl_4 (solvent)	
	NaOH	
	KCN / ethanol (solvent)	
 **Name:**		
	excess $(CH_3)_2NH$	
	hot 3 M NaOH	
		

Page Total:

Marks 7

- Methylphenidate, also known as Ritalin, is a psychostimulant drug approved for the treatment of attention-deficit disorder. Identify all stereogenic (chiral) centres in methylphenidate by clearly marking each with an asterisk (*) on the structure below.

methylphenidate



Using a stereogenic centre you have identified, draw the (*R*)-configuration of that centre.

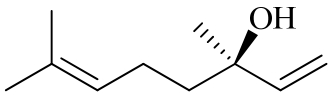
How many stereoisomers are there of methylphenidate? Describe the relationships between these isomers.

Ritalin is generally sold as the hydrochloride salt, formed when methylphenidate is treated with dilute hydrochloric acid. Draw the structure of this salt and suggest why this is the preferred compound for sale.

Page Total:

Marks 8

- The structure of (–)-linalool, a commonly occurring natural product, is shown below.



What is the molecular formula of (–)-linalool?

Which of the following best describes (–)-linalool?
achiral compound, racemic mixture,
(*R*)-enantiomer, or (*S*)-enantiomer

What functional groups are present in (–)-linalool?

Is it possible to obtain (*Z*) and (*E*) isomers of (–)-linalool? Give a reason for your answer.

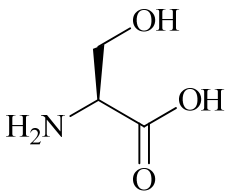
Give the constitutional formula of the organic product formed from (–)-linalool in each of the following reactions. NB: If there is no reaction, write "no reaction".

Reagents / Conditions	Constitutional Formula of Product
Br_2 (in CCl_4 as solvent)	
$Na_2Cr_2O_7$ in aqueous acid	
Na, then CH_3Br	
H_2 / Pd-C catalyst	

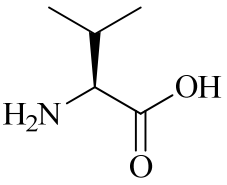
Page Total:

Marks 3

- The amino acids serine and valine can be reacted together to form 2 dipeptides. Draw the structures of the 2 possible dipeptides.



serine



valine

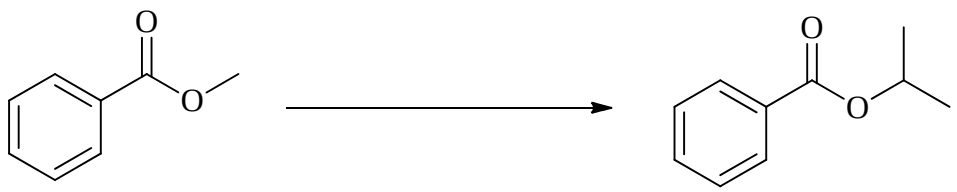
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

Marks

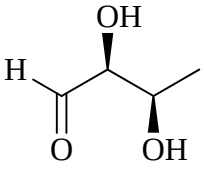
- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structure of any intermediate compounds formed.

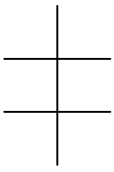
3



- Convert the following structure into a Fischer projection.

3





Page Total:

CHEM1002 – FUNDAMENTALS OF 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
10^{12}	tera	T

CHEM1002 – FUNDAMENTALS OF 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

CHEM1002 – FUNDAMENTALS OF 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

$PV = nRT$

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

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

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

$t_{½} = \ln 2/k$

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

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

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

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** [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]