Topics in the November 2014 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2014-N-2:

- Strong Acids and Bases
- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-3:

- Metal Complexes
- Coordination Chemistry
- Entropy

2014-N-4:

- Metal Complexes
- Coordination Chemistry
- Kinetics

2014-N-5:

- Crystal Structures

2014-N-6:

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

2014-N-7:

- Solubility Equilibrium

2014-N-8:

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

2014-N-9:

- Stereochemistry

2014-N-10:

- Representations of Molecular Structure
- Stereochemistry
- Carboxylic Acids and Derivatives

2014-N-11:

- Carboxylic Acids and Derivatives

2014-N-12:

- Synthetic Strategies
- Stereochemistry

Confidential

THE UNIVERSITY OF SYDNEY

SEAT NUMBER: ....

STUDENT ID: ....

SURNAME: ....

GIVEN NAMES: ....

CHEM1002
Fundamentals of Chemistry 1B

Final Examination
Semester 2, 2014

Time Allowed: Three hours + 10 minutes reading time

This examination paper consists of 20 pages

INSTRUCTIONS TO CANDIDATES

1. This is a closed book exam.
2. A simple calculator (programmable versions and PDA's not allowed) may be taken into the exam room.

Make	Model

3. The total score for this paper is 100. The possible score per page is shown in the adjacent table.
4. The paper comprises 28 multiple choice questions and 11 pages of short answer questions. ANSWER ALL QUESTIONS.
5. Follow the instructions on page 2 to record your answers to the multiple choice questions. Use a dark lead pencil so that you can erase errors made on the computer sheet.
6. Answer all short answer questions in the spaces provided on this question paper. Credit may not be given where there is insufficient evidence of the working required to obtain the solution.
7. Take care to write legibly. Write your final answers in ink, not pencil.
8. Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheet.

	Marks			
Page(s)	Max	Gained		Marker
~~2-8~~	~~28~~			~~MCQ~~
9	8			
10	8			
11	6			
12	2			
13	6			
14	7			
15	10			
16	8			
17	8			
18	3			
19	6			
Total	100			
Check Total				

	Marks
• Above what concentration of H_3O^+ is a solution considered to be acidic at 25 °C?	3

Answer:

At 95 °C the auto ionisation constant of water, K_w, is 45.7×10^{-14}. What is the pH of a neutral solution at 95 °C?

pH =

• Calculate the pH of a 0.020 M solution of lactic acid, $HC_3H_5O_3$, at 25 °C. The pK_a of lactic acid is 3.86.	5

pH =

A 1.0 L solution of 0.020 M lactic acid is added to 1.0 L of 0.020 M sodium hydroxide solution. Write the ionic equation for the reaction that occurs.

Is the resulting solution acidic, basic or neutral? Give a reason for your answer.

Marks
8

- Transition metals are often found in coordination complexes such as $[NiCl_4]^{2-}$. What is a complex?

How does the bonding in the complex $[NiCl_4]^{2-}$ differ from the bonding in CCl_4?

What is a chelate complex?

Why is a chelate complex generally more stable than a comparable complex without chelate ligands?

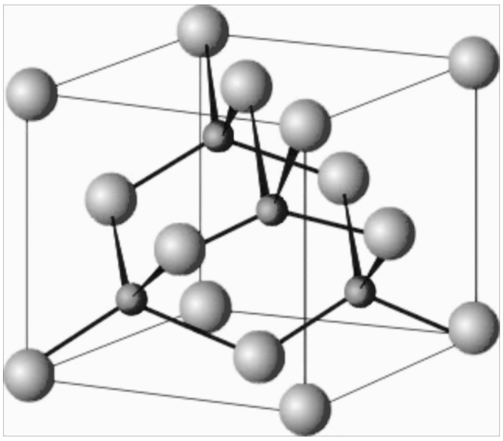
Marks

- An aqueous solution of iron(III) nitrate is pale yellow/brown. Upon addition of three mole equivalents of potassium thiocyanate (KSCN) a bright red colour develops. Draw the metal complex responsible for the red colour, including any stereoisomers. **2**

- The reaction order for a chemical reaction is given by the sum of the powers in the rate law. Why is the reaction order usually given by a small positive integer, *i.e.* 2 or less? **4**

Are zero order reactions possible? Explain your answer using examples if possible.

	Marks
• The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent nitrogen atoms and the smaller spheres represent boron atoms.	2



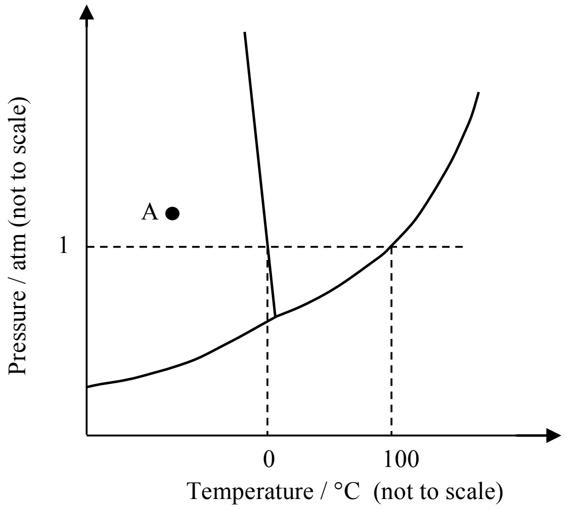
From the unit cell shown above, determine the empirical formula of boron nitride. Show your working.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

- Consider the pressure/temperature phase diagram of H_2O shown below.



Which phase exists at the point labelled A?

What are the temperature and pressure for the normal boiling point of water?

Use the phase diagram to explain why it takes longer to hard boil eggs on the top of a 4000 m high mountain rather than at sea level.

Use the phase diagram to explain why ice cubes float in water.

Marks
7

- Write the equation for the dissolution of lead(II) chloride, $PbCl_2$, in water.

Write the expression for the solubility product constant, K_{sp}, for $PbCl_2$.

What $[Cl^-]$ is needed to reduce the $[Pb^{2+}]$ to the maximum safe level of 0.015 mg L^{-1}?
$K_{sp}(PbCl_2) = 1.6 \times 10^{-6}$

$[Cl^-]$ =

The solubility of sodium chloride is 359 g L^{-1}. If a reservoir of 50,000 L is saturated with lead(II) chloride, can sodium chloride be used to reduce the $[Pb^{2+}]$ to a safe level? If so, what mass of sodium chloride (in kg) would be needed?

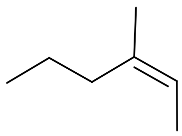
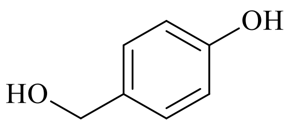
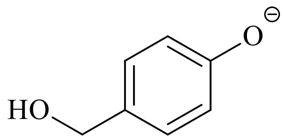
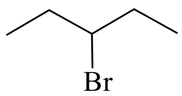
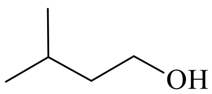
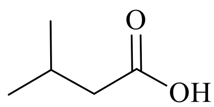
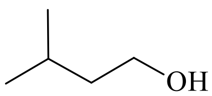
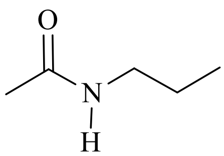
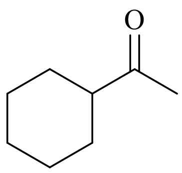
Answer:

Would the water in the reservoir be fit for drinking? Explain your answer.

Page Total:

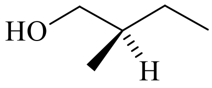
Marks
10

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

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
 **Name:**	dilute H_2SO_4	
		
 **Name:**	$N(CH_3)_3$	
		
	concentrated H_2SO_4	
	$H^{\oplus}$ / H_2O / heat	
	1. $LiAlH_4$ 2. $H^{\oplus}$ / H_2O	

Marks
8

- Consider compound **A**, whose structure is shown below.



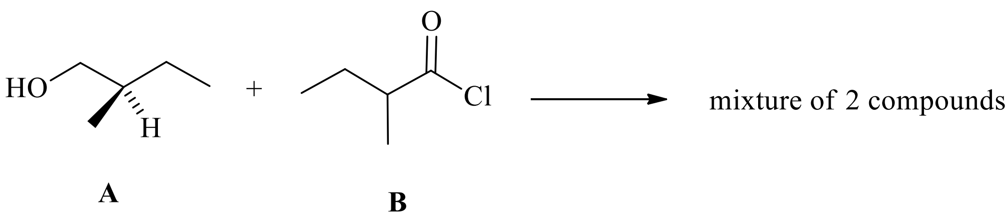
A

List the substituents on the stereogenic (chiral) carbon in compound **A**, in descending order as determined by the sequence rules.

Highest priority | Lowest priority

Give the full name that unambiguously describes the stereochemistry of compound **A**.

When compound **A** is reacted with racemic compound **B**, two compounds are formed as shown below.



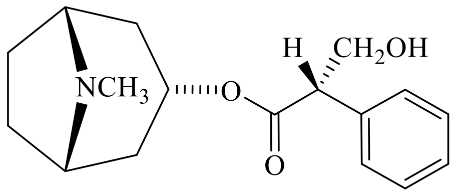
Circle the stereogenic centre in compound B.

Draw the stick structures of the two compounds formed in this reaction. Make sure you clearly show all of the stereochemistry in your structures.

Are the two compounds formed in this reaction enantiomers, constitutional isomers or diastereoisomers?

Marks
8

- The tropane alkaloid (–)-hyoscyamine is found in certain plants of the *Solanaceae* family. It is an anticholinergic agent that works by blocking the action of acetylcholine at parasympathetic sites in smooth muscle, secretory glands and the central nervous system.



Give the molecular formula of (–)-hyoscyamine.

List the functional groups present in (–)-hyoscyamine.

Hydrolysis of (–)-hyoscyamine results in two fragments, tropine and tropic acid. Draw each of these fragments.

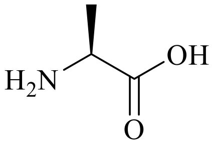
tropine	tropic acid

What is the stereochemistry at the tropic acid stereocentre? Write (*R*) or (*S*).

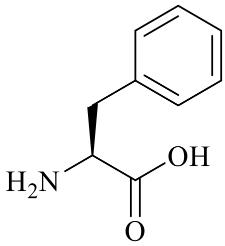
Is tropine optically active? Explain your answer.

Marks
3

- The amino acids alanine and phenylalanine can be reacted together to form two dipeptides. Draw the structures of the two possible dipeptides.



alanine



phenylalanine

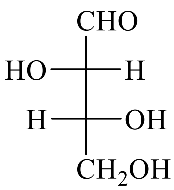
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

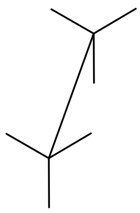
Marks

- 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 sawhorse projection. **3**



D-threose



What does the *D* in the name *D*-threose designate?

THIS PAGE IS FOR ROUGH WORKING ONLY

Page Total:

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

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	(+0.82 at pH = 7)
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+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	
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$	+0.62	
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+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	
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13	
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–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	(–0.41 at pH = 7)
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–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	

Useful formulas

Thermodynamics & Equilibrium $\Delta U = q + w = q - p\Delta V$ $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $\ln \frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$	**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** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
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 = $^4/_3\ \pi r^3$	**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
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]