Topics in the November 2012 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2012-N-2:

- Atomic Electronic Spectroscopy

2012-N-3:

- Gas Laws
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2012-N-4:

- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen

2012-N-5:

- Bonding - MO theory (H_2)
- Bonding - MO theory (larger molecules)

2012-N-6:

- Lewis Structures
- VSEPR

2012-N-7:

- Bonding - MO theory (polar bonds)
- Types of Intermolecular Forces

2012-N-8:

- Nuclear and Radiation Chemistry

2012-N-9:

- Thermochemistry
- First and Second Law of Thermodynamics

2012-N-10:

- Thermochemistry

2012-N-11:

- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

2012-N-12:

- First and Second Law of Thermodynamics

2012-N-13:

- Chemical Equilibrium

2012-N-14:

- Electrochemistry

2207(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1A - CHEM1101

CONFIDENTIAL

SECOND SEMESTER EXAMINATION

NOVEMBER 2012 **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 23 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 19, 25, 27 and 28 are for rough working only.

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Multiple choice section

	Marks	
Pages	Max	Gained
2-11	33	

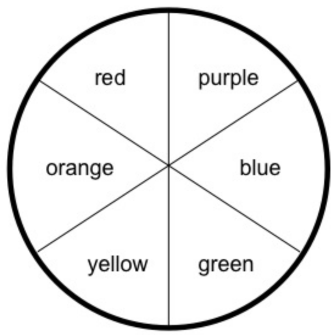
Short answer section

Page	Marks			Marker
	Max	Gained		
12	4			
13	6			
14	5			
15	6			
16	10			
17	2			
18	5			
20	7			
21	6			
22	5			
23	3			
24	5			
26	3			
Total	67			
Check total				

Marks

- Nitrogen dioxide, NO_2, is formed in the atmosphere from industrial processes and automobile exhaust. It is an indicator of poor quality air and is mostly responsible for the brown haze seen in large cities. This question about NO_2 extends over many pages, but each sub-question is essentially independent of the others.

a) NO_2 is a pungent red-orange coloured gas. According to the colour wheel for human vision, reproduced below, what colour light does NO_2 absorb? **1**



Answer:

b) An atmospheric chemist, monitoring pollution in Sydney, measured the absorption of light at 425 nm due to NO_2. Measured over a distance of 100 m, 425 nm light was attenuated by 5 % (*i.e.* 95 % transmission). What is the concentration of NO_2 in the atmosphere? Give your answer in mol L^{-1}. **3**
Data: $\varepsilon(NO_2, 425\ nm) = 300\ M^{-1}\ cm^{-1}$.

Answer:

Marks

c) The Australian air quality guidelines stipulate a concentration of less than 5.0×10^{-9} mol L^{-1}. **4**

Does your answer in part b) exceed Australian air quality guidelines?

YES / NO

What is the partial pressure of NO_2 (in Pa) that corresponds to the Australian guidelines at 25 °C and 100 kPa?

Answer:

d) When NO_2 absorbs UVA light in the atmosphere, at wavelengths shorter than 400 nm, it dissociates into NO + O: **2**

$$NO_2 + h\nu \rightarrow NO + O$$

What is the bond dissociation energy (in kJ mol^{-1}) of the N–O bond in NO_2?

Answer:

Marks
5

e) The oxygen atom in the reaction in part d) is formed in its ground electronic state. What is the ground state electronic configuration for O?

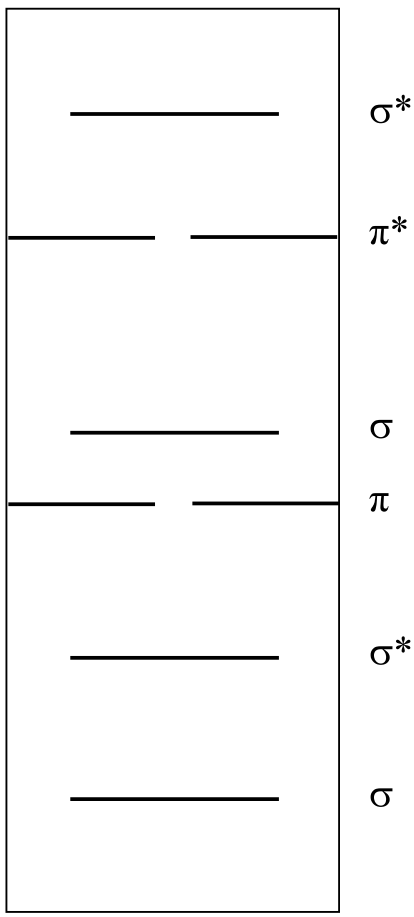
Draw an atomic orbital energy level diagram for the ground state O atom. Name the orbitals and show all electrons.

Name and sketch the atomic orbitals for the highest occupied atomic orbital and the lowest unoccupied atomic orbital in the ground state O atom. Make sure all nodes are clearly identified in your sketch.

sketch of highest occupied orbital	sketch of lowest unoccupied orbital
Name:	Name:

f) The NO molecule formed in the reaction in part d) is also formed in its ground electronic state. Complete the molecular orbital diagram for NO by filling in the valence electrons in the occupied orbitals. Sketch the shape of the π and π* orbitals, clearly showing all nodes. Determine the bond order of NO and whether it is paramagnetic or diamagnetic.

Marks 6

MO orbital energy level diagram for NO	Sketch of the π MO
	
	Sketch of the π* MO

Bond order of NO:

Paramagnetic or diamagnetic?

	Marks
g) In the atmosphere, nitrogen oxides exist in many forms, including NO and NO_2. Two other forms are N_2O and N_2O_4 (the dimer of NO_2). Draw Lewis structures for both N_2O and N_2O_4. Examine your structures closely. If you can draw a second, valid, Lewis structure, draw it underneath.	6

N_2O structure	N_2O_4 structure
Second structure, if appropriate	Second structure, if appropriate

	Marks
h) Use VSEPR theory to determine the shape of N_2O and N_2O_4. Sketch the shape below and indicate the approximate bond angle for all angles in the molecule. Be clear in your sketch as to planar and non-planar structures where appropriate. Hence, or otherwise, indicate whether either molecule has a permanent dipole moment.	4

N_2O	N_2O_4
Dipole moment? YES / NO	Dipole moment? YES / NO

Page Total:

	Marks
i) N_2O is sparingly soluble in water. What does this tell you about the strength of any hydrogen bonding that exists? Rationalise your answer in terms of the structures of the H_2O and N_2O molecules.	2

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 5

- How does the ratio of the number of neutrons to the number of protons in a stable or long-lived radionuclide change as the atomic number increases?

The generation of energy in a nuclear reactor is largely based on the fission of certain long-lived radionuclides (usually ^{235}U or ^{239}Pu). The fission products include every element from zinc through to the *f*-block. Explain why most of the radioactive fission products are β-emitters.

Two of the more common isotopes produced in nuclear reactors are ^{131}I (half-life of 8.02 days) and ^{137}Cs (half-life of 30 years). Both are β-emitters. If you were exposed to equal concentrations of both isotopes for 1 hour, which isotope, ^{137}Cs or ^{131}I, would do more damage? Explain your reasoning.

Marks

4

- Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel that produces no greenhouse gases on combustion. In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the following equation.

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$$

The initial and final states are at 298 K. After combustion with 14.40 g of O_2, some NH_3 remains unreacted. Calculate the enthalpy change during the process, given the following data.

$$\Delta_f H°(NH_3(g)) = –46.11 \text{ kJ mol}^{-1} \text{ and } \Delta_f H°(H_2O(l)) = –285.83 \text{ kJ mol}^{-1}$$

Answer:

3

- ANFO (ammonium nitrate fuel oil) is a powerful explosive used recently in the Oslo bombing. If the fuel oil is replaced by carbon in the form of graphite, calculate what mass of carbon needs to be added to 1.0 kg of ammonium nitrate so that the products of the detonation are N_2, CO_2 and H_2O.

Answer:

Marks
6

- How many 2.0 L casks of wine and/or juices can be cooled on a hot Sydney day from 30 °C to a drinkable 10 °C with one 10.0 kg bag of ice taken from a freezer at –30 °C? Assume the specific heat of the wine and/or juice is the same as that of water, that the cardboard or plastic containers have negligible heat capacity, and that the density of the wine and juices is 1.0 g mL^{-1}.

  $\Delta_{fus}H(H_2O) = 6.0$ kJ mol^{-1}; $C_p°(H_2O(s)) = 2.2$ J K^{-1} g^{-1}; $C_p°(H_2O(l)) = 4.2$ J K^{-1} g^{-1}

Answer:

What other assumption have you made in your calculation?

Marks
5

- The standard Gibbs free energy of formation for ammonia, $NH_3(g)$, is –16.4 kJ mol^{-1}. Consider the following reaction at 298 K.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What is the expression for the equilibrium constant, K_p, for this reaction?

Calculate the value of the equilibrium constant at 298 K.

K_p =

In which direction will this reaction proceed if a mixture of gases is made with:
P_{NH_3} = 1.00 atm; P_{H_2} = 1.00 atm; P_{N_2} = 0.50 atm?

Marks 3

- Consider the process $H_2O(s) \rightleftharpoons H_2O(l)$

  Give the sign of $\Delta H°$ at 273 K and explain your choice.

  Give the sign of $\Delta S°$ at 273 K and explain your choice.

  How does $\Delta G°$ change with an increase in temperature? Explain your answer.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- Consider the following reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

An equilibrium mixture in a 1.00 L vessel was found to contain $[SO_2(g)]$ = 0.800 M, $[NO_2(g)]$ = 0.100 M, $[SO_3(g)]$ = 0.600 M and $[NO(g)]$ = 0.400 M. If the volume and temperature are kept constant, what amount of NO(g) needs to be added to the reaction vessel to give an equilibrium concentration of $NO_2(g)$ of 0.300 M?

Answer:

Marks
3

- The CrO_4^{2-} ion can oxidise the I_3^- ion in acidic solution. The products of the reaction are Cr^{3+} and I_2. Show the separate balanced half-equations for the oxidation and reduction as well as the net balanced redox equation.

Oxidation half-equation	
Reduction half-equation	
Balanced redox equation	

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CHEM1101 - CHEMISTRY 1A

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

CHEM1101 - CHEMISTRY 1A

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

CHEM1101 - CHEMISTRY 1A

Useful formulas

Quantum Chemistry	**Electrochemistry**
$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2 E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm	$\Delta G° = -nFE°$ $Moles\ of\ e^- = It/F$ $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)
Acids and Bases	**Gas Laws**
$pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = \frac{1}{2}mv^2$
Radioactivity	**Kinetics**
$t_{1/2} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$ years	$t_{1/2} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Mathematics	**Thermodynamics & Equilibrium**
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 = $^4/_3\ \pi r^3$	$\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $\ln\frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Miscellaneous	**Colligative Properties & Solutions**
$A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	$\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$

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]