Topics in the June 2009 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2009-J-2:

- Bonding in H_2 - MO theory
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O
- Band Theory - MO in Solids
- Polar Bonds
- Polymers and the Macromolecular Consequences of Intermolecular Forces

2009-J-3:

- Nuclear and Radiation Chemistry

2009-J-4:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2009-J-5:

- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2009-J-6:

- Lewis Structures
- VSEPR
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2009-J-7:

- Types of Intermolecular Forces

2009-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2009-J-9:

- Nitrogen Chemistry and Compounds

2009-J-10:

- Nitrogen in the Atmosphere

2009-J-11:

- Nitrogen in the Atmosphere

2009-J-12:

- First and Second Law of Thermodynamics
- Chemical Equilibrium

2009-J-14:

- Batteries and Corrosion

22/31(a) **The University of Sydney**

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

JUNE 2009 **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 •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, 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 14, 23, 25 and 28 are for rough working only.

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Multiple choice section

	Marks	
Pages	Max	Gained
2-11	34	

Short answer section

	Marks			
Page	Max	Gained		Marker
12	6			
13	6			
15	6			
16	5			
17	5			
18	4			
19	5			
20	3			
21	5			
22	2			
24	5			
26	6			
27	8			
Total	66			

Marks
6

- In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.

(a) covalent bond

(b) electronegativity

(c) free radical

(d) band gap

(e) hydrogen bond

(f) allotrope

Marks

- The isotope ^{37}Ar has a half-life of 35 days. If each decay event releases an energy of 1.0 MeV, calculate how many days it would take for a 0.10 g sample of ^{37}Ar to release 22.57×10^3 kJ (enough energy to boil 10.0 L of water)? **3**

Answer:

- The isotope ^{222}Rn decays to ^{214}Bi in three steps. Identify all possible decay paths for this process, including all the intermediate isotopes along each path and the identity of the decay process involved in each individual step. **3**

Marks
6

- The electronic energies of the molecular orbitals of diatomics consisting of atoms from H to Ne can be ordered as follows (with energy increasing from left to right):

$$\sigma \ \sigma^{*} \ \sigma \ \sigma^{*} \ 2\times\pi \ \sigma \ 2\times\pi^{*} \ \sigma^{*}$$

(the '2×' denotes a pair of degenerate orbitals)

Use this ordering of the molecular orbitals to identify the following species.

(i) The lowest molecular weight diatomic ion (homo- or heteronuclear) that has **all** of the following characteristics:

a) a single negative charge,
b) a bond order greater than zero *and*
c) is diamagnetic.

(ii) A diatomic species that has the same electronic configuration as O_2.

(iii) All of the atoms with atomic numbers less than or equal to 10 that cannot form stable, neutral, homonuclear diatomic molecules.

Given that there are three degenerate *p* orbitals in an atom, why are there only two degenerate π orbitals in a diatomic molecule?

Marks

- Imagine a Universe X in which electron spin did not exist. *i.e.* An electron has only a single internal state instead of the two spin states it has in our universe. Assume that all other properties of electrons and nuclei in Universe X are identical to those in our universe. **3**

  What are the atomic numbers of the first two alkali metals in Universe X?

  Write down the ground state electron configuration of the atom with atomic number 11 in Universe X.

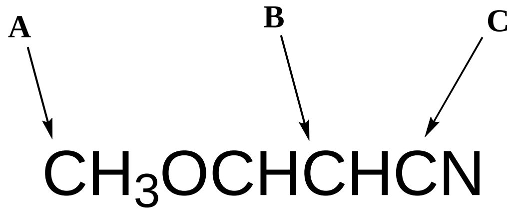
  How would the energy difference between the 2*s* and 2*p* orbitals compare between our universe and Universe X? Provide a brief explanation of your answer.

- In a linear molecule consisting of a carbon chain with alternating double and single bonds, the HOMO and LUMO are often extended over the whole length of the molecule. What will happen to the size of the HOMO-LUMO gap as the length of such a molecule is increased? **2**

  Assuming that the molecule absorbs in the visible range, how will its colour change as the molecule length increases? Give a reason for your answer.

Marks

- Consider the molecule whose structure is shown below. Complete the table concerning the atoms **A**, **B** and **C** indicated by the arrows. **3**



Selected atom	Number of σ-bonds associated with the selected atom	Geometry of σ-bonds about the selected atom
A		
B		
C		

- Determine the value of *n* that corresponds to the lowest excited state of He^{+} from which radiation with a wavelength of 600 nm is able to ionise the electron (*i.e.* excite it to a state of $n = \infty$). Show all working. **2**

Answer:

Marks

- Describe one piece of experimental evidence supporting the conclusion that electrons have wave-like character. **1**

- The boiling points of H_2O and H_2S are 100 °C and –60 °C, respectively. Identify the single property whose difference for oxygen and sulfur is most responsible for this difference in boiling points. **3**

The boiling points of HF and NH_3 are 20 °C and –30 °C, respectively. Explain why these boiling points are lower than that of water *and*, separately, explain why the boiling point of HF is greater than that of NH_3.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- A new process has been developed for converting cellulose from corn waste into the biofuel butanol, C_4H_9OH. A bomb calorimeter with a heat capacity of 3250 J K^{-1} was used to determine the calorific value by burning 5.0 g of butanol in excess oxygen.

  Write a balanced reaction for the combustion of butanol in oxygen.

  Calculate the heat released from this combustion if the temperature of the calorimeter increased from 23.0 to 78.6 °C during the test.

  Answer:

  Use this value to determine the calorific value and molar enthalpy of combustion of butanol.

Marks

- Many explosive compounds contain nitrogen, and form $N_2(g)$ upon decomposition. Briefly explain the significance of the formation of this molecule in terms of both (i) the heat generated and (ii) the spontaneity of such reactions. **3**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
5

The diameter of Saturn's moon, Titan, is 5150 km and it orbits at an average of 1.427×10^9 km from the sun, or 9.54 times farther than the Earth. Its mean surface temperature is 94 K, it has an albedo of 0.09, and it has an atmosphere comprised of methane, nitrogen, ethane, argon and a trace of ammonia.

The temperature of the sun is 5780 K and its radius is 6.96×10^8 m. Determine the magnitude (in K) of the greenhouse effect on Titan's atmosphere.

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 2

Calculate the wavelength of the maximum (black body) emission of Titan.

Answer:

Using the vibrational frequencies provided in the data table below, suggest the gas(es) most likely to be causing Titan's greenhouse effect.

CH_4	3156 cm^{-1};	3026 cm^{-1};	1534 cm^{-1};	1367 cm^{-1}		
C_2H_6	2969 cm^{-1};	1468 cm^{-1};	1388 cm^{-1};	995 cm^{-1};	823 cm^{-1};	289 cm^{-1}
NH_3	3337 cm^{-1};	3444 cm^{-1};	1627 cm^{-1};	950 cm^{-1}		
N_2	2739 cm^{-1}					

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- Write the equations for the combustion of graphite that occur in smelting processes to produce (i) CO(g) and (ii) CO_2(g), *in which one mole of O_2(g) is consumed.*

(i)

(ii)

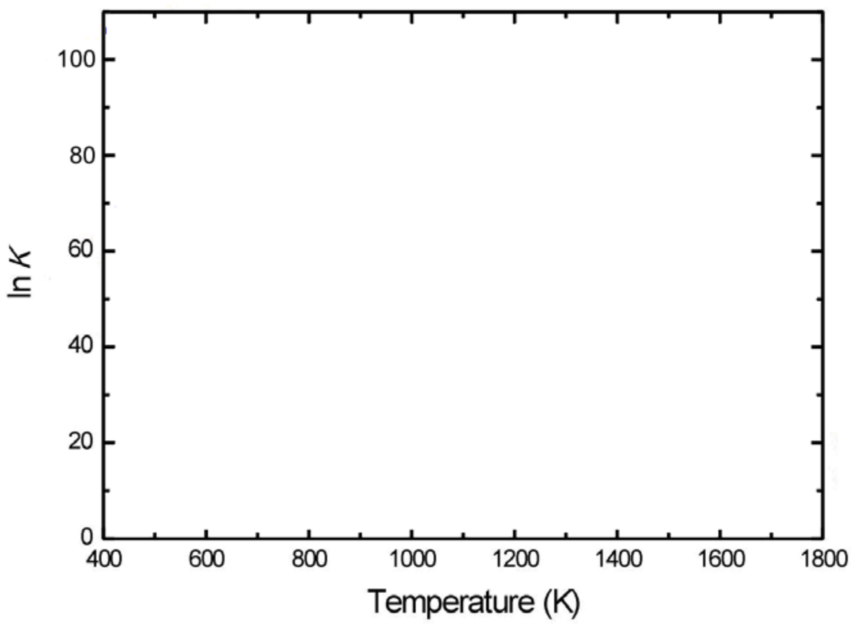
Use the standard enthalpy and entropy data provided to calculate the enthalpy and entropy of these two combustion reactions of graphite.

substance	$\Delta_f H°$ / kJ mol^{-1}	$S°$ / J K^{-1} mol^{-1}	substance	$S°$ / J K^{-1} mol^{-1}
CO(g)	–111	198	C(s)	6
CO_2(g)	–394	214	O_2(g)	205

THIS QUESTION CONTINUES ON THE NEXT PAGE.
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Using calculations where necessary, sketch the temperature-dependence of the equilibrium constant for these two combustion reactions on the graph shown below. (Space for working is included below the graph.)

Marks
6



Over what temperature range is carbon monoxide the favoured product?

Marks
8

- MIT researcher Donald Sadoway has developed a novel kind of battery that uses molten magnesium and antimony electrodes, which react as the cell discharges to form magnesium and antimonide ions dissolved in molten sodium sulfide. The cell potential is 2.76 V. This kind of cell is proposed as a way of storing energy from solar photovoltaic cells to supply electricity at night.

  Write out the spontaneous oxidation and reduction half-cell reactions, and overall (balanced) cell reaction.

  Identify the cathode and the anode.

  Is this a primary or secondary battery, or a fuel cell? Explain your answer briefly.

  A prototype cell provided the extraordinary current of 12,000 A. How long would this discharging cell take to consume 1.0 kg of Mg electrode?

  Answer:

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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	**Electrochemistry**
$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm	$\Delta G° = -nFE°$ *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**
$pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$
Radioactivity	**Kinetics**
$t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$ years	$t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative properties	**Thermodynamics & Equilibrium**
$\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	$\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $K_p = K_c (RT)^{\Delta n}$
Miscellaneous	**Mathematics**
$A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	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]							

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]