22/46(a) **The University of Sydney**

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2007 **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 21 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 •.
- 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 sheet.
- Pages 14 & 24 are for rough working only.

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Multiple choice section

	Marks	
Page	Max	Gained
2-10	36	

Short answer section

	Marks			
Page	Max	Gained		Marker
11	5			
12	5			
13	6			
15	5			
16	5			
17	4			
18	6			
19	6			
20	9			
21	4			
22	5			
23	4			
Total	64			

Marks

2

- In order to reduce the incidence of dental cavities, water is fluoridated to a level of 1 mg L^{-1}. In regions where the water is "hard" the calcium concentration is typically 100 mg L^{-1}. Given that the K_{sp} of calcium fluoride is 3.9×10^{-11} M^3, would it precipitate in these conditions? Show all working.

Answer:

3

- Consider the boiling points of the following monosubstituted benzenes.

	C_6H_6	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5OH	C_6H_5I
b.p.	80 °C	85 °C	132 °C	156 °C	182 °C	188 °C

Explain this order of boiling points.

Marks
5

- The primary buffering system in blood plasma is represented by the following equation:

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad pK_a = 6.1$$

What is the ratio HCO_3^- : H_2CO_3 at the normal plasma pH of 7.4?

Answer:

A typical person has 2 L of blood plasma. If such a person were to drink 1 L of soft drink with a pH of 2.5, what would the plasma pH be if it were not buffered? (Assume all of the H^+ from the soft drink is absorbed by the plasma, but the volume of plasma does not increase.)

Answer:

What is the pH in this typical person with a normal HCO_3^- concentration of 0.020 M? Ignore any other contributions to the buffering.

Answer:

Marks
6

- Alfred Werner, one of the founders of the field of coordination chemistry, made extensive studies of the metal complex $[PtCl_2(NH_3)_2]$. He showed that it existed in two isomeric forms and used this information to predict that the compound had a square-planar molecular geometry. What other molecular geometry would need to be considered for such a complex and on what basis did Werner reject this alternative geometry?

Draw and name the two isomers.

Why does platinum(II) form square-planar complexes?

Which one of the isomers is biologically active? What is its activity? Describe two features of the complex that play important roles in this biological activity.

Marks
5

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

The following rate data were collected at 225 °C.

Experiment	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial rate (d[NO]/dt, M s^{-1})
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	1.3×10^{-2}	2.2×10^{-3}	1.0×10^{-4}
3	6.4×10^{-3}	4.4×10^{-3}	5.1×10^{-5}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 225 °C.

Answer:

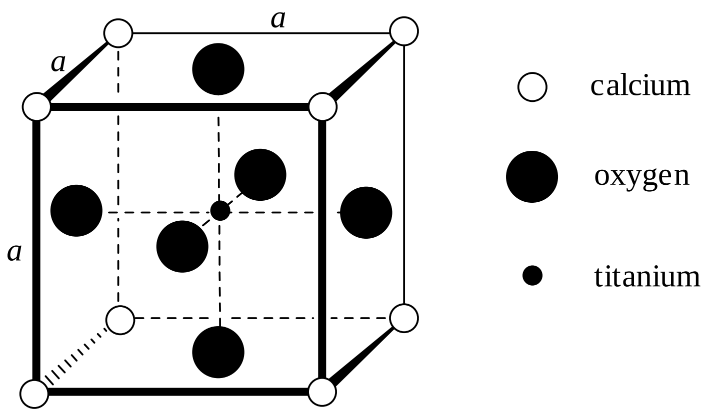
Calculate the rate of appearance of N_2O when $[NO] = [H_2] = 6.6 \times 10^{-3}$ M.

Answer:

Suggest a possible mechanism for the reaction based on the form of the rate law.
Explain your answer.

Marks
5

- The diagram below shows the structure of perovskite, a mineral made up of calcium (at each of the corners), oxygen (in the centre of each of the faces), and titanium (at the centre of the cube). The unit cell dimension (edge length, *a*) for perovskite is 0.38 nm.



What is the chemical formula of perovskite?

Answer:

What is the volume of the unit cell?

Answer:

What is the density of perovskite? Give your answer in g cm^{-3}.

Answer:

Marks
4

- Write balanced ionic equations for the reactions that occur in each of the following. If no reaction occurs, write "NO REACTION".

  Excess 16 M ammonia solution is added to solid silver iodide.

  Excess 4 M ammonia solution is added to a 1 M magnesium sulfate solution.

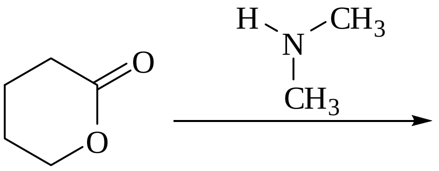
  Excess 4 M hydrochloric acid is added to solid cadmium sulfide.

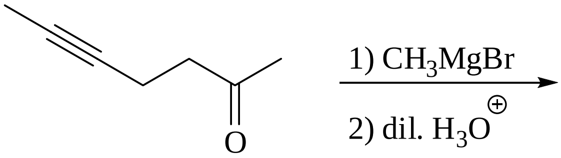
  Excess 4 M sodium hydroxide solution is added to 1 M zinc nitrate solution.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

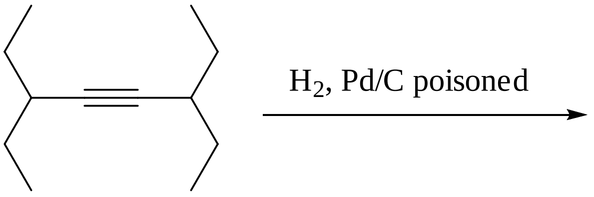
Marks
6

- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.





Name(s):



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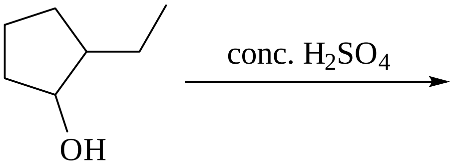

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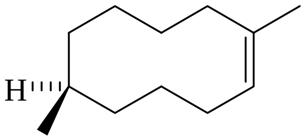
Marks
6

- Compound **X** undergoes an addition reaction on treatment with hydrogen gas in the presence of a palladium on carbon catalyst to form a mixture of cyclic alkanes.



X

Clearly draw all possible products that can form from this reaction, taking care to represent the stereochemistry of the products clearly.

Clearly label each isomer drawn above as either chiral or achiral (not chiral).

Circle one of the isomers and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

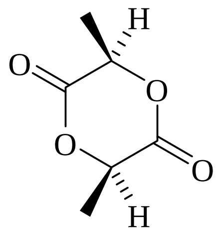
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
9

- Compound **Y** can be readily analysed by ^{1}H NMR spectroscopy.

  On the diagram of **Y**, write the letters **a**, **b**, **c**, *etc*. as necessary to identify each unique hydrogen environment giving rise to a signal in the ^{1}H NMR spectrum.

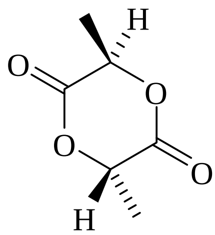
Y



Sketch the ^{1}H NMR spectrum of compound **Y**. Label each signal in the spectrum with **a**, **b**, **c**, *etc.* to correspond with your assignments on the diagram of **Y**. Make sure you show the splitting pattern (number of fine lines) you expect to see for each signal. Also write the relative number of hydrogens you expect above each signal.

Compound **Z** is an isomer of **Y**.

Z

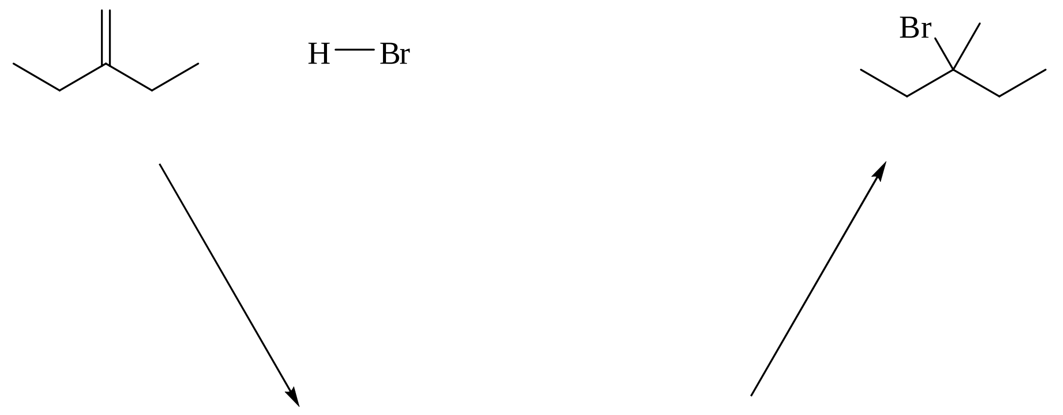


What kind of isomers are they?

How would you distinguish between compounds **Y** and **Z** using chemical reactions, spectroscopic analysis or other means?

Marks
4

- Complete the two-step mechanism for the reaction given below. Draw partial charges, curly arrows and intermediate structures as appropriate to illustrate the bonding changes that take place.



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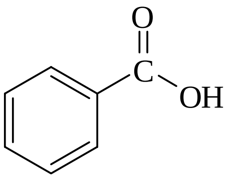
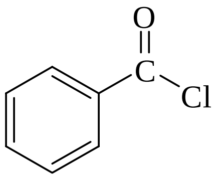
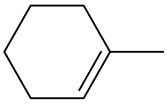
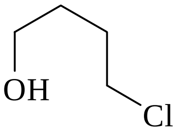
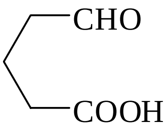
Marks
5

- Complete the following table.

Starting material	Reagents / Conditions	Major organic product(s)
		
	HCl CCl_4 (solvent)	
	Na	
	1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	

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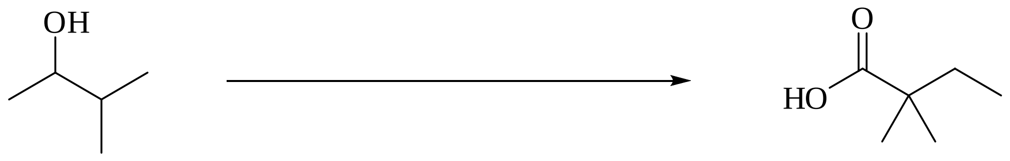
Marks
4

- Show clearly the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds.
  NOTE: More than one step is necessary.



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CHEM1904 - CHEMISTRY 1B (SSP)

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}

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}

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

CHEM1902 - CHEMISTRY 1B (ADVANCED)
CHEM1904 - CHEMISTRY 1B (SSP)

Standard Reduction Potentials, *E*°

Reaction	*E*° / V
$S_2O_8^{2-}$ + $2e^-$ → $2SO_4^{2-}$	+2.01
Co^{3+}(aq) + e^- → Co^{2+}(aq)	+1.82
Ce^{4+}(aq) + e^- → Ce^{3+}(aq)	+1.72
Au^{3+}(aq) + $3e^-$ → Au(s)	+1.50
Cl_2 + $2e^-$ → $2Cl^-$(aq)	+1.36
O_2 + $4H^+$(aq) + $4e^-$ → $2H_2O$	+1.23
Br_2 + $2e^-$ → $2Br^-$(aq)	+1.10
MnO_2(s) + $4H^+$(aq) + e^- → Mn^{3+} + $2H_2O$	+0.96
Pd^{2+}(aq) + $2e^-$ → Pd(s)	+0.92
Ag^+(aq) + e^- → Ag(s)	+0.80
Fe^{3+}(aq) + e^- → Fe^{2+}(aq)	+0.77
Cu^+(aq) + e^- → Cu(s)	+0.53
Cu^{2+}(aq) + $2e^-$ → Cu(s)	+0.34
Sn^{4+}(aq) + $2e^-$ → Sn^{2+}(aq)	+0.15
$2H^+$(aq) + $2e^-$ → H_2(g)	0 (by definition)
Fe^{3+}(aq) + $3e^-$ → Fe(s)	–0.04
Pb^{2+}(aq) + $2e^-$ → Pb(s)	–0.13
Sn^{2+}(aq) + $2e^-$ → Sn(s)	–0.14
Ni^{2+}(aq) + $2e^-$ → Ni(s)	–0.24
Co^{2+}(aq) + $2e^-$ → Co(s)	–0.28
Fe^{2+}(aq) + $2e^-$ → Fe(s)	–0.44
Cr^{3+}(aq) + $3e^-$ → Cr(s)	–0.74
Zn^{2+}(aq) + $2e^-$ → Zn(s)	–0.76
$2H_2O$ + $2e^-$ → H_2(g) + $2OH^-$(aq)	–0.83
Cr^{2+}(aq) + $2e^-$ → Cr(s)	–0.89
Al^{3+}(aq) + $3e^-$ → Al(s)	–1.68
Mg^{2+}(aq) + $2e^-$ → Mg(s)	–2.36
Na^+(aq) + e^- → Na(s)	–2.71
Ca^{2+}(aq) + $2e^-$ → Ca(s)	–2.87
Li^+(aq) + e^- → Li(s)	–3.04

CHEM1902 - CHEMISTRY 1B (ADVANCED)
CHEM1904 - CHEMISTRY 1B (SSP)

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$	**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** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$
Colligative properties $\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-E_a/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age $= 8033 \ln(A_0/A_t)$	**Thermodynamics & Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $K_p = K_c (RT)^{\Delta n}$
Miscellaneous $A = -\log_{10}\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	**Mathematics** If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

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]							

LANTHANIDES	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
ACTINIDES	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]