22/46(a) The University of Sydney

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

CONFIDENTIAL **TIME ALLOWED: THREE HOURS**

NOVEMBER 2008 **SECOND SEMESTER EXAMINATION**

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 22 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.
- Page 24 is for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Page	Max	Gained
2-9	30	

Short answer section

	Marks			
Page	Max	Gained		Marker
10	4			
11	4			
12	4			
13	5			
14	5			
15	6			
16	5			
17	10			
18	5			
19	3			
20	3			
21	9			
22	4			
23	3			
Total	70			

Marks
4

- The ocean contains a variety of forms of CO_3^{2-} and CO_2 with a variety of acid-base and solubility equilibria determining their concentrations. There is concern that increasing levels of CO_2 will lead to increased dissolution of $CaCO_3$ and critically affect the survival of life forms that rely on a carbonaceous skeleton.

  Calculate the concentrations of Ca^{2+} and CO_3^{2-} in a saturated solution of $CaCO_3$. (The K_{sp} of $CaCO_3$ is 3.3×10^{-9}.)

$[Ca^{2+}]$ =	$[CO_3^{2-}]$ =

  Calculate the pH of such a solution. (The pK_a of HCO_3^- is 10.33).

pH =

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks
4

The pH of surface ocean water is currently 8.10 (having fallen from a pre-industrial era level of 8.16), the concentration of HCO_3^- is 2.5×10^{-3} M, and it is saturated with $CaCO_3$. Calculate the concentration of Ca^{2+} in these conditions.

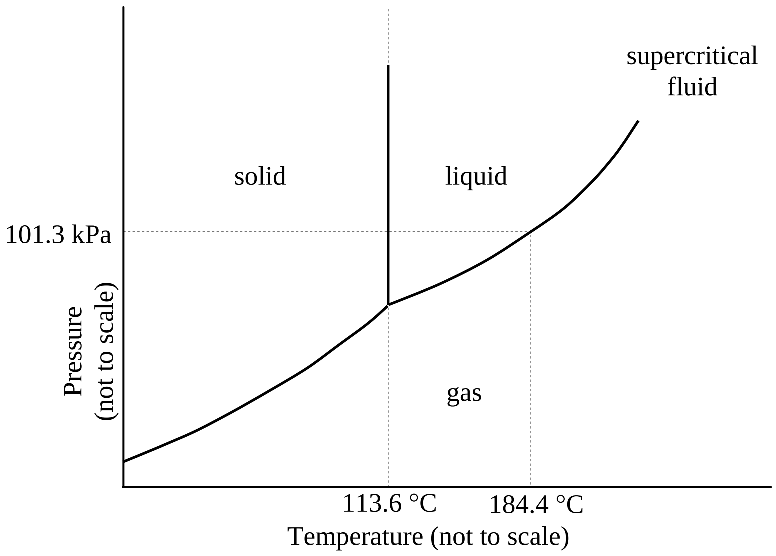
$[Ca^{2+}]$ =

The pH is expected to drop to about 7.8 by the end of the century as CO_2 levels increase further. What effect will this have on the solubility of $CaCO_3$ in sea water? Use chemical equations to assist with explaining your answer.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- F_2 and Cl_2 are gases at room temperature, Br_2 is a liquid, and I_2 is a solid. Explain why the melting points and boiling points of the halogens increase going down the group.



Shown above is the phase diagram for iodine. What are the melting and boiling points of iodine at atmospheric pressure?

In what way would you need to change the conditions to make iodine, initially at room temperature and pressure, sublime?

Describe what will happen if pressure is applied to a sample of solid iodine.

Marks
5

- Alfred Werner, one of the founders of the field of coordination chemistry, prepared a series of platinum complexes that contained ammonia and chloride ions. One of these had the empirical formula $PtCl_4.4NH_3$ and when reacted with silver nitrate released two chloride ions per formula unit. Write the structural formula of this compound and write the name of this compound.

Draw the possible structures of the metal complex.

What types of isomers can be formed by a compound with this empirical formula?

What is the *d* electron configuration of the Pt in this complex?

Marks
5

- 2-Bromo-2-methylpropane reacts with hydroxide ions to give 2-methyl-2-propanol.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

The following rate data were collected at 55 °C.

Experiment	$[(CH_3)_3CBr]_0$ (M)	$[OH^-]_0$ (M)	Initial rate ($d[(CH_3)_3COH]/dt$, M s^{-1})
1	0.050	0.10	5.0×10^{-4}
2	0.20	0.10	2.0×10^{-3}
3	0.20	0.30	2.0×10^{-3}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 55 °C.

Answer:

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

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks

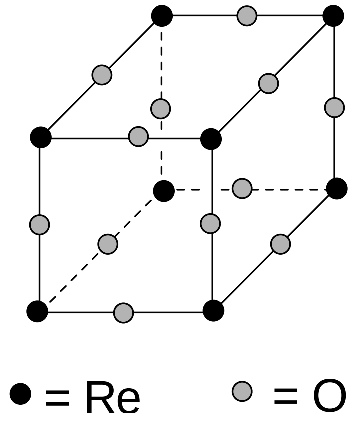
The reaction is exothermic. Draw the potential energy *vs* reaction coordinate diagram for this mechanism, labelling all species that can be isolated. **2**

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO_3, is 0.79, how many moles of sodium iodate, $NaIO_3$, would need to be added to this solution to raise its pH to 2.00? **4**

Answer:

Marks
5

- The diagram below shows the structure of an oxide of rhenium. The unit cell is cubic with rhenium at each of the corners and oxygen in the centre of each of the edges.



What is the chemical formula of this oxide?

Answer:

What are the coordination numbers of rhenium and oxygen in this compound?

Re:	O:

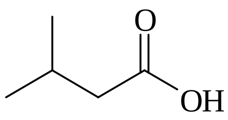
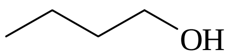
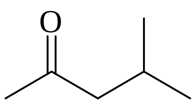
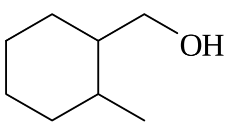
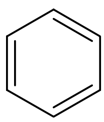
There is a large hole at the centre of the cell that in some compounds is occupied by a cation. What is the coordination number of a cation occupying this site?

Given that the density of this oxide is 7.1 g cm^{-3}, calculate the length of the cell edge. (The structure is cubic.)

Answer:

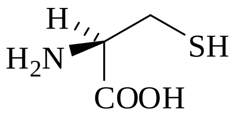
Marks
10

- Complete the following table by drawing the structures of the intermediate and final organic product(s) as required. The intermediate product is formed when the starting material is treated with Reagent 1. The final product is formed when the intermediate product is treated with Reagent 2.

Starting material	Intermediate product	Final product
	Reagent 1: $SOCl_2$	Reagent 2: CH_3NH_2
	Reagent 1: $K_2Cr_2O_7$ / $H^{\oplus}$	Reagent 2: CH_3OH / $H^{\oplus}$
	Reagent 1: $NaBH_4$ then H_2O	Reagent 2: conc. H_2SO_4
	Reagent 1: CH_3MgBr	Reagent 2: CH_3I
	Reagent 1: Br_2 / $FeBr_3$ (cat.)	Reagent 2: Mg / dry ether

Marks
5

- Consider the amino acid L-cysteine shown below.



Draw the zwitterionic form of L-cysteine.

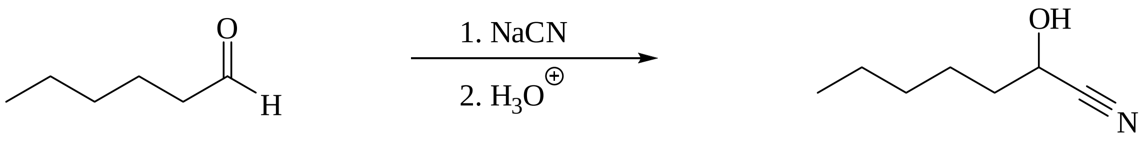
Draw the dipeptide L-cysteinyl-L-cysteine.

Assign the absolute configuration (*R* or *S*) of L-cysteine. Show your working.

Draw the enantiomer of L-cysteine.

Marks 3

- Apply your understanding of curly arrows to propose a mechanism for the following reaction.



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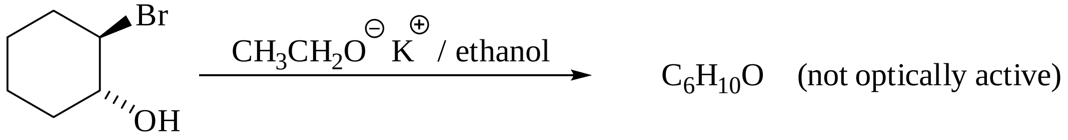
Marks
3

- Propose a structure for the product of the following reaction. Outline a mechanism for its formation, showing all curly arrows and intermediates.



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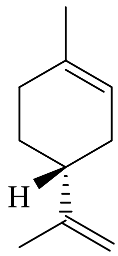
Marks
9

- Consider the isomer of limonene shown below.



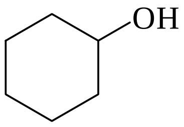
Show the major organic products formed when limonene is treated with excess H_2 in the presence of a Pd/C catalyst. Pay particular attention to any relevant stereochemistry. Identify which would be the major product and explain why it forms preferentially.

Use Markovnikov's rule to predict the two major products of the reaction between limonene and excess HBr. Draw these isomers and identify the isomeric relationship between them. Specify the optical activity (active or inactive) of each isomer.

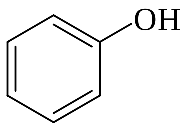
At what *m*/*z* would the molecular ion of one of these isomers appear in its mass spectrum? Explain your answer.

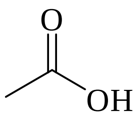
Marks
4

- For each of the following pairs of compounds, identify which is the stronger acid and give reasons for your choice.

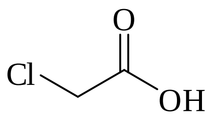


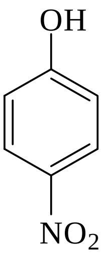
and





and





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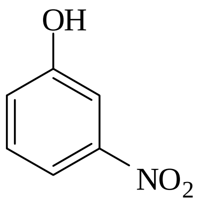
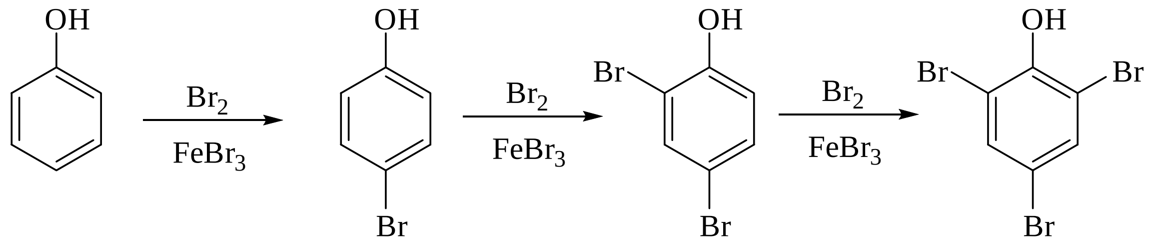


Marks
3

- The bromination of phenol proceeds as follows.



Show the Wheland intermediate for one of these steps and explain why bromination occurs at positions 2, 4 and 6, but not at positions 3 and 5.

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CHEM1902 - CHEMISTRY 1B (ADVANCED)
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}

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

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

Standard Reduction Potentials, *E*°

Reaction	*E*° / V
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.01
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-(aq)$	+1.10
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+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
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.28
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–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

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

Useful formulas

Thermodynamics & Equilibrium	**Electrochemistry**
$\Delta U = q + w = q - p\Delta V$ $\Delta_{universe}S = \Delta_{sys}S - \dfrac{\Delta_{sys}H}{T_{sys}}$ $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT\ln Q$ $\Delta G° = -RT\ln K$ $K_p = K_c (RT)^{\Delta n}$	$\Delta G° = -nFE°$ $Moles\ of\ e^- = It/F$ $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \dfrac{0.0592}{n}\log Q$ (at 25 °C)
Colligative properties	**Quantum Chemistry**
$\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$
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 = $8033 \ln(A_0/A_t)$	$t_{½} = \ln 2/k$ $k = Ae^{-E_a/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$
Miscellaneous	**Mathematics**
$A = -\log_{10}\dfrac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\dfrac{e^2}{4\pi\varepsilon_0 r}N_A$	If $ax^2 + bx + c = 0$, then $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

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]							

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]