22/08(a)

The University of Sydney

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 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 19 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 12, 15, 23 & 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-9	33	

Short answer section

Page	Marks Max	Gained		Marker
10	7			
11	7			
13	8			
14	6			
16	6			
17	8			
18	5			
19	6			
20	3			
21	6			
22	5			
Total	67			

	Marks
• Explain why H_2SO_4 is a stronger acid than H_2SO_3.	**2**
• Explain why compounds of *d*-block elements are frequently paramagnetic. Use examples in your answer.	**2**
• Provide a systematic name for *cis*-$[Co(en)_2Cl_2]Cl$. Is this complex chiral? Explain your reasoning by drawing the structure of the complex. en = $NH_2CH_2CH_2NH_2$ = ethane-1,2-diamine = ethylenediamine	**3**

Marks 7

- Solution A consists of a 0.020 M aqueous solution of aspirin (acetylsalicylic acid, $C_9H_8O_4$) at 25 °C. Calculate the pH of Solution A. The pK_a of aspirin is 3.52.

Answer:

At 25 °C, 1.00 L of Solution B consists of 4.04 g of sodium acetylsalicylate ($NaC_9H_7O_4$) dissolved in water. Calculate the pH of Solution B.

Answer:

Solution B (200.0 mL) is mixed with Solution A (400.0 mL) and water (200.0 mL) to give Solution C. Calculate the pH of Solution C after equilibration at 25 °C.

Answer:

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

Marks

- Write a balanced chemical equation representing the dissolution of $FeCO_3$ in water at pH 7. **4**

Ignoring any hydrolysis of the ions, calculate the solubility (in g L^{-1}) of $FeCO_3$ in water at pH 7. The solubility product constant, K_{sp}, for $FeCO_3$ is 2.1×10^{-11}.

Answer:

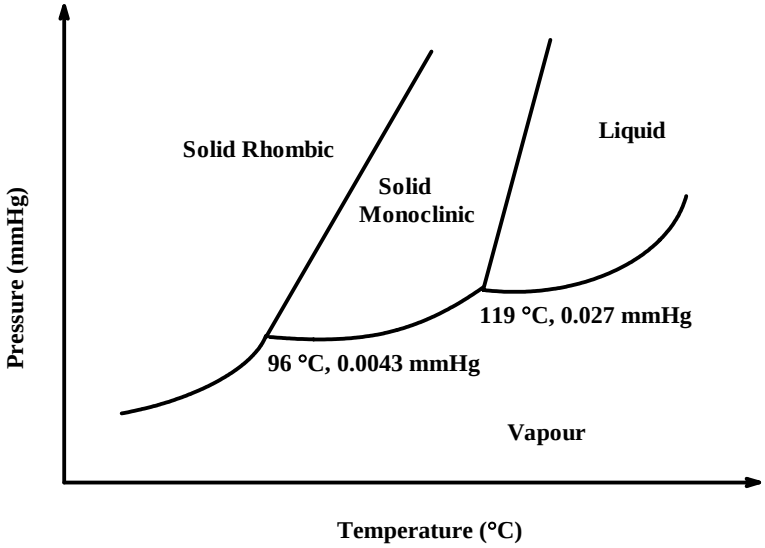
- The concentration of iron in the ocean is one of the primary factors limiting the growth rates of some basic life forms. The pH of the oceans before the Industrial Revolution was around 8.22. What was the maximum concentration of $Fe^{3+}(aq)$ in the ocean at this pH? The K_{sp} of $Fe(OH)_3$ is 1×10^{-39}. **4**

Answer:

Industrialisation has led to an increase in atmospheric CO_2. What effect has this had on the amount of $Fe^{3+}(aq)$ in sea water?

Marks 6

- Solid sulfur can exist in both rhombic and monoclinic forms. A portion of the phase diagram for sulfur is reproduced schematically below.



How many triple points are there in the phase diagram?

What phases are in equilibrium at each of the triple points?

What phase is stable at room temperature and 760 mmHg pressure?

Can monoclinic sulfur exist in equilibrium with sulfur vapour at 1.0 atm pressure?

Which solid form of sulfur is more dense? Explain your reasoning.

Describe the phase changes that occur when sulfur at 0.01 mmHg is slowly warmed from 90 °C to 130 °C.

- An alloy is formed by combining elements A and B. The alloy has a face-centred cubic structure, with atoms of A at the corners and atoms of B in the faces. What is the formula of the alloy? Explain your reasoning.

Marks 3

Answer:

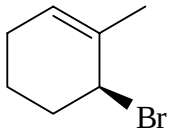
- Derive expressions for the equilibrium constants for the complexation of Pb^{2+} (K_1) and of Ca^{2+} (K_2) by $EDTA^{4-}$.

3

Briefly explain why the chelating agent, EDTA, is administered as $[Ca(EDTA)]^{2-}$ to treat lead poisoning and determine which of K_1 or K_2 must be greater for the therapy to be effective.

Marks 8

- Consider compound **F** shown below.



F

Assign the stereocentre in compound **F** as (*R*) or (*S*), explaining your reasoning.

Assign the double bond stereochemistry in compound **F**, explaining your reasoning.

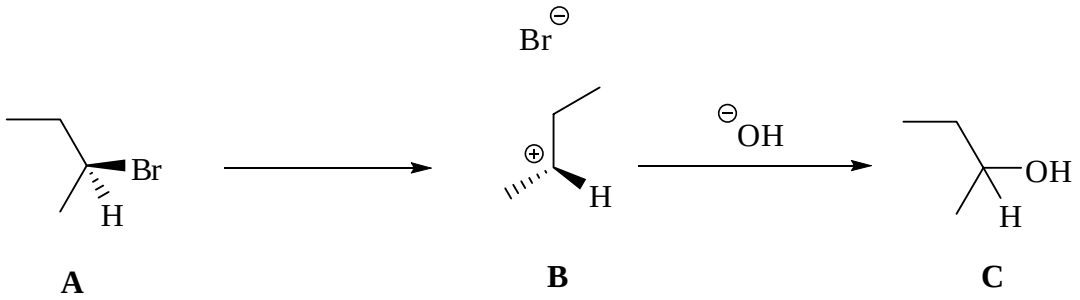
Draw the enantiomer of compound **F**.

When compound **F** is reacted with hydrogen gas in the presence of a palladium catalyst, two stereoisomeric products, **G** and **H**, are formed. Draw these products.

What word is used to describe the stereochemical relationship between **G** and **H**?

Marks 5

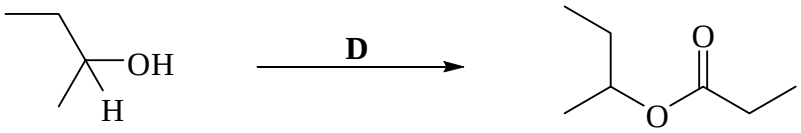
- Bromide **A** undergoes a reaction with hydroxide ions (OH^-) to produce alcohol **C**. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place in the conversion of **A** to **B** and from **B** to **C**.



A **B** **C**

What is the name of the reaction taking place when **A** is converted to **C** via carbocation intermediate **B**?

What is the stereochemical outcome of this reaction? Give reasons for your answer.

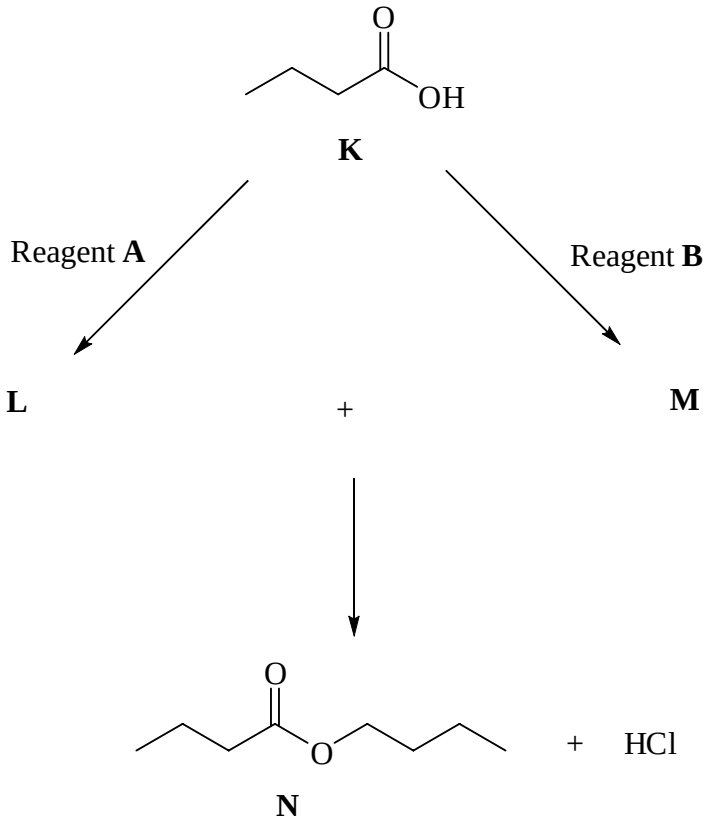


C **E**

Alcohol **C** can be further reacted with reagent **D** to generate ester **E**. Provide a structure of a suitable reagent **D** for the synthesis of ester **E** from alcohol **C**.

Marks
6

- Consider the following reaction sequence.

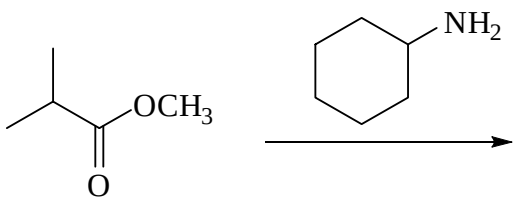


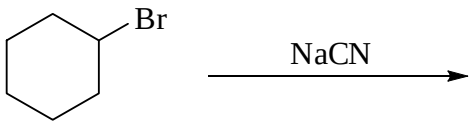
Compound **K** below can be converted into two different intermediates, **L** and **M**, which can react together to give compound **N** and the inorganic byproduct HCl. Give the reagents **A** and **B** and draw the structure of the intermediates **L** and **M**.

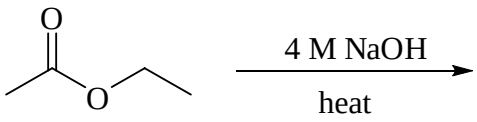
A	**B**
L	**M**

Marks 3

- Give the constitutional formula(s) of the organic products formed in each of the following reactions





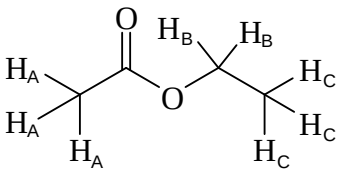


THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

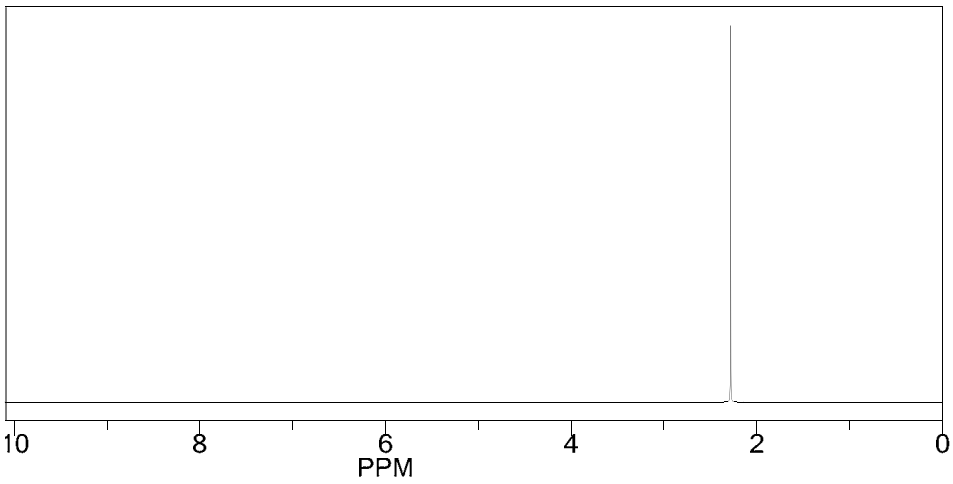
Marks 6

- Sketch the resonances you would expect to observe for protons H_B and H_C in the ^1H NMR spectrum of compound **X**. Ensure that the approximate chemical shifts, as well as peak splittings and signal integrations are incorporated in your answer. (The resonance for H_A is provided as a guide.)

X



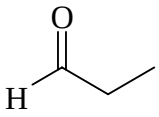
H_A, singlet,
Integration = 3



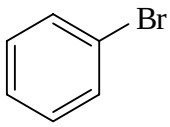
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

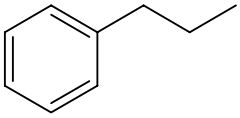
- Devise a synthesis of propylbenzene (**V**) using propanal (**T**) and bromobenzene (**U**) as starting materials. Provide any intermediate structures and reagents.
  (Hint: More than one step is required.)



T



U



V

CHEM1102 - CHEMISTRY 1B

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 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2}

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

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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
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-(aq)$	+1.10
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+}(aq) + 2H_2O$	+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
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+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

CHEM1102 - CHEMISTRY 1B

Useful formulas

Quantum Chemistry

$E = h\nu = hc/\lambda$

$\lambda = h/mv$

$E = -Z^2 E_R(1/n^2)$

$\Delta x \cdot \Delta(mv) \geq h/4\pi$

$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$

$T\lambda = 2.898 \times 10^6$ K nm

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

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

$E_k = \frac{1}{2}mv^2$

Radioactivity

$t_{1/2} = \ln 2/\lambda$

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age = $8033 \ln(A_0/A_t)$ years

Kinetics

$t_{1/2} = \ln 2/k$

$k = Ae^{-Ea/RT}$

$\ln[A] = \ln[A]_o - kt$

$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Colligative Properties and Solutions

$\Pi = cRT$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$c = kp$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Thermodynamics and Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta_{univ} S° = R \ln K$

$K_p = K_c (RT)^{\Delta n}$

Miscellaneous

$A = -\log \frac{I}{I_0}$

$A = \varepsilon cl$

$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_A$

Mathematics

If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

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]