Topics in the November 2013 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2013-N-2:

- Weak Acids and Bases
- Calculations Involving pK_a

2013-N-3:

- Solubility Equilibrium
- Coordination Chemistry

2013-N-4:

- Physical States and Phase Diagrams
- Intermolecular Forces and Phase Behaviour

2013-N-5:

- Coordination Chemistry

2013-N-6:

- Solubility Equilibrium
- Hydrolysis of Metal Ions
- Coordination Chemistry

2013-N-7:

- Kinetics
- Kinetics - Influences

2013-N-8:

- Alcohols
- Aldehydes and Ketones
- Alkenes
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2013-N-9:

- Synthetic Strategies

2013-N-10:

- Stereochemistry

2013-N-11:

- Alkenes
- Synthetic Strategies

2013-N-12:

- Carboxylic Acids and Derivatives
- Alcohols

2013-N-13:

- Carboxylic Acids and Derivatives

2013-N-14:

- Alkenes
- Aldehydes and Ketones

2208(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2013 **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 attemp ted. 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 •.
- 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 11 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-9	29	

Short answer section

Page	Marks Max	Gained		Marker
10	7			
12	8			
13	7			
14	3			
15	7			
16	5			
17	6			
18	7			
19	7			
20	4			
21	5			
22	3			
23	2			
Total	71			

Marks 7

- The pK_a of formic acid, HCO_2H, is 3.77. What is the pH of a 0.20 M solution of formic acid?

pH =

Give the equation for the reaction of formic acid with solid sodium hydroxide.

Calculate the ratio of formate ion / formic acid required to give a buffer of pH 4.00.

Answer:

What amount (in mol) of sodium hydroxide must be added to 100.0 mL of 0.20 M HCO_2H to prepare a solution buffered at pH 4.00?

Answer:

Page Total:

Marks

- Give the equation for the dissolution of hydroxyapatite, $Ca_5(PO_4)_3(OH)$, in water. **2**

What is the formula for the solubility product constant for hydroxyapatite?

- Complete the following table. **6**

Formula	Geometry of complex	Ligand donor atom(s)
$[Zn(OH)_4]^{2-}$		
$[CoCl(NH_3)_5]SO_4$		
$K_4[Fe(CN)_6]$		
$[Ag(CN)_2]^-$		

Select any complex ion from the above table and state whether it is paramagnetic, diamagnetic or neither. Explain your reasoning.

Page Total:

Marks 7

- A phase diagram of a pure compound has a triple point at 13 °C and 205 mmHg, a normal melting point at 17 °C, and a normal boiling point at 87 °C. Draw a phase diagram for this compound. Label all the different regions of the phase diagram.

Indicate whether each of the following statements regarding this compound is true or false.

The density of the solid is greater than that of the liquid.	True / False
If the pressure is reduced from 835 mmHg to 85 mmHg at a constant temperature of 11 °C, sublimation occurs.	True / False
At a constant pressure of 835 mmHg, evaporation occurs if the temperature is raised from 13 °C to 81 °C.	True / False

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

- Which of the following complexes is/are chiral? Explain your reasoning. Use diagrams where necessary.

  acetylacetonate ion = $CH_3COCHCOCH_3^-$

  ethylenediamine = $NH_2CH_2CH_2NH_2$

Marks 3

tris(acetylacetonato)chromium(III)

trans-bis(ethylenediamine)difluoridochromium(III) chloride

acetylacetonatobis(ethylenediamine)chromium(III) iodide

Page Total:

Marks 7

- What is the solubility of $Cu(OH)_2$ in mol L^{-1}? K_{sp} $(Cu(OH)_2)$ is 1.6×10^{-19} at 25 °C.

Answer:

The overall formation constant for $[Cu(NH_3)_4]^{2+}$ is 1.0×10^{13}. Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.

Calculate the value of the equilibrium constant for the following reaction.

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

Answer:

Would you expect $Cu(OH)_2(s)$ to dissolve in 1 M NH_3 solution? Briefly explain your answer.

Page Total:

Marks 5

- The following data were obtained for the iodide-catalysed decomposition of hydrogen peroxide, H_2O_2.

Experiment	$[I^-]$(M)	$[H_2O_2]$ (M)	Initial rate(M s^{-1})
1	0.375	0	0
2	0.375	0.235	0.000324
3	0.375	0.470	0.000657
4	0.375	0.705	0.001024
5	0.375	0.940	0.001487
6	0	0.948	0
7	0.050	0.948	0.00045
8	0.100	0.948	0.00095
9	0.150	0.948	0.00140
10	0.200	0.948	0.00193

Determine the rate law from these data.

Use the data from Experiment 10 to calculate the rate constant for this reaction.

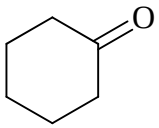
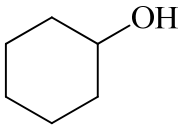
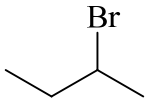
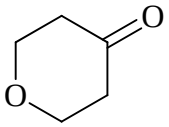
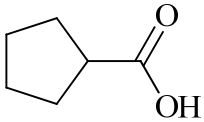
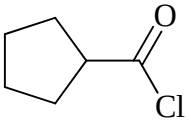
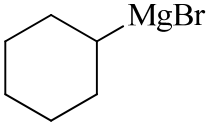
k =

Iodide ion is used as a catalyst in this reaction. What is the role of a catalyst in a chemical reaction?

Page Total:

Marks 6

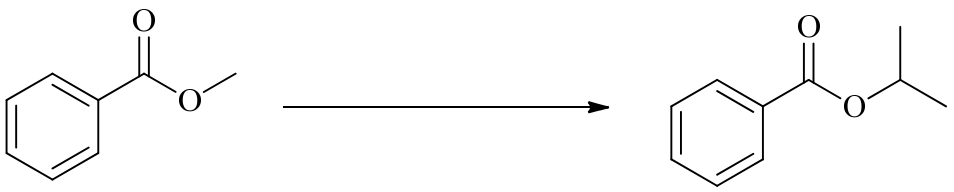
- Complete the following table.

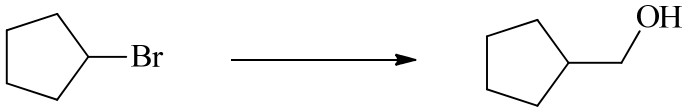
STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
		
	HI	
	hot conc. KOH in ethanol	
	$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
		
	1. CO_2 2. $H^{\oplus}$ / H_2O	

Page Total:

Marks 7

- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structures of any intermediate compounds formed.





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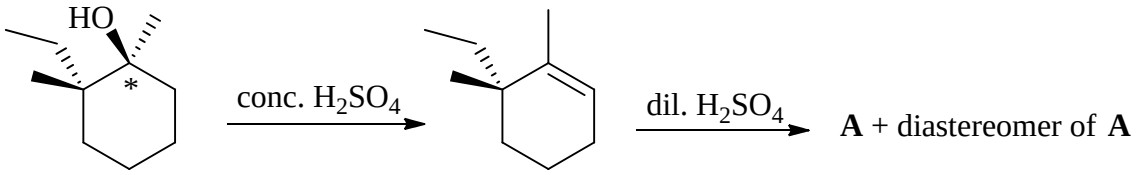
Marks 7

- Shown below is a reaction sequence beginning with the chiral alcohol, **A**.



A **B**

Draw the enantiomer of **A**.

The specific optical rotation of **A** is +30. If equal amounts of **A** and its enantiomer are mixed, what is the optical rotation of the mixture?

Assign the stereochemistry of the atom in alcohol **A** indicated by the asterisk (*), showing how you arrived at your answer.

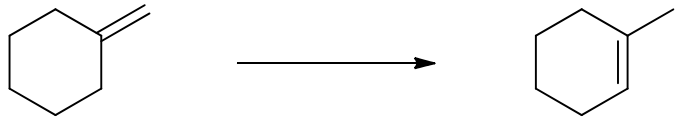
Alcohol **A** is dehydrated to give the alkene **B**. Is alkene **B** chiral? Why/why not?

Alkene **B** is hydrated with dilute sulfuric acid, to give a sample that contains **A** and a diastereomer of **A**. Draw this diastereomer. In this sample, what do you expect to be the ratio of **A** and its diastereomer? Why?

Page Total:

Marks 4

- Devise a way to convert alkene **C** to alkene **D** using hydrogen bromide (HBr) as one of the reagents. Provide any other reagents you might need. If any of the steps you use could form two products, explain whether there is any selectivity and why.

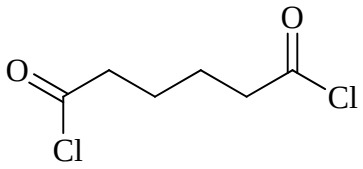


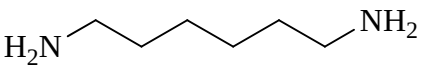
C **D**

Page Total:

Marks

- The polymer Nylon 66 can be made by mixing the following two reagents.

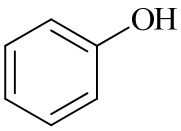


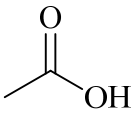


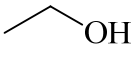
Draw the structure of Nylon 66.

2

- Consider the three compounds shown below.







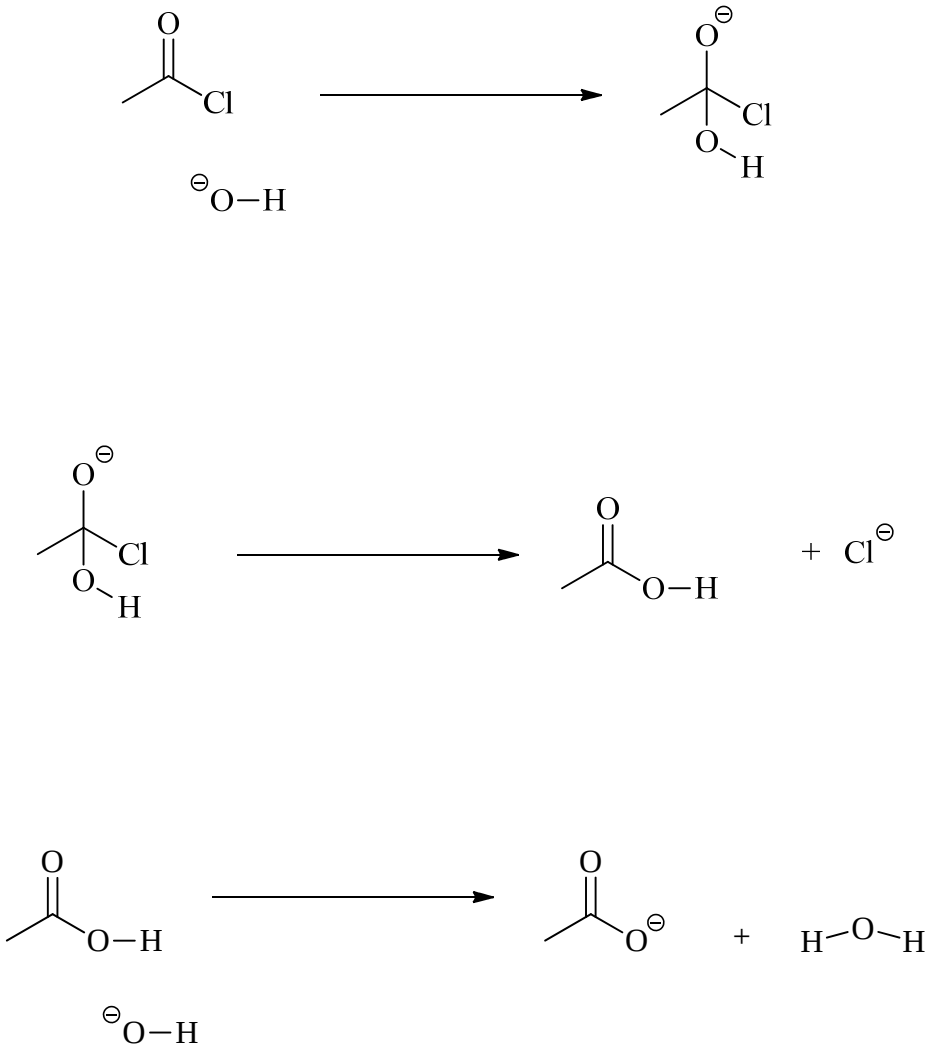
Arrange these compounds in order of increasing acidity. Explain your reasoning.

3

Page Total:

Marks 3

- The incomplete mechanism for the reaction of acetyl chloride with hydroxide ions is shown below. The reaction occurs in three steps. In each step complete the mechanism by adding curly arrows to indicate the bond changes taking place.



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

- Hydrogen chloride, HCl, reacts with the compound $CH_3CH=C=O$ in an electrophilic addition reaction. Use your knowledge of the mechanism of electrophilic addition to a C=C double bond to predict the major product of this reaction. Explain your reasoning.

Marks 2

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

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 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

CHEM1102 - CHEMISTRY 1B

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
$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O$	+0.32
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+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

CHEM1102 - CHEMISTRY 1B

Useful formulas

Quantum Chemistry

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

$\lambda = h/mv$

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

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

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

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

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

$pH = -\log[H^+]$

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

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 & 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 & 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 $= \pi r^2$

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]	112 COPERNICIUM **Cn** [283]		114 FLEROVIUM **Fl** [289]		116 LIVERMORIUM **Lv** [293]		

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]

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