Topics in the November 2014 Exam Paper for CHEM1904

Click on the links for resources on each topic.

2014-N-2:

- Crystal Structures

2014-N-3:

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

2014-N-4:

- Metal Complexes
- Coordination Chemistry

2014-N-5:

- Metal Complexes
- Coordination Chemistry

2014-N-6:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-7:

- Kinetics

2014-N-8:

- Carboxylic Acids and Derivatives

2014-N-9:

- Alkenes
- Stereochemistry

2014-N-10:

- Alkenes
- Stereochemistry

2014-N-11:

- Amines
- Aromatic Compounds

2014-N-12:

- Aromatic Compounds

2014-N-13:

- Carboxylic Acids and Derivatives

Confidential

THE UNIVERSITY OF SYDNEY

SEAT NUMBER: ....

STUDENT ID: ....

SURNAME: ....

GIVEN NAMES: ……………………………………..

CHEM1902 and CHEM1904
Chemistry 1B (Advanced) and Chemistry 1B (SSP)

Final Examination
Semester 2, 2014

Time Allowed: Three hours + 10 minutes reading time

This examination paper consists of 24 pages

INSTRUCTIONS TO CANDIDATES

1. This is a closed book exam.
2. A simple calculator (programmable versions and PDA's not allowed) may be taken into the exam room.

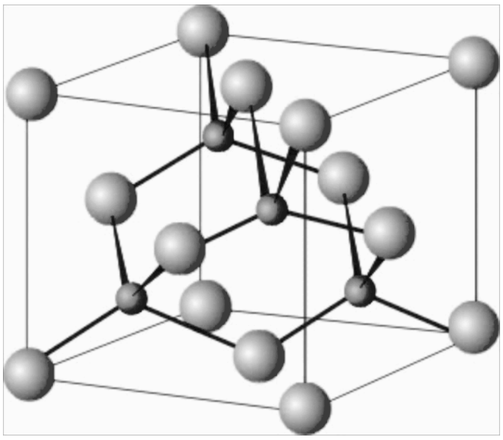
Make	Model

3. The total score for this paper is 100. The possible score per page is shown in the adjacent table.
4. The paper comprises 30 multiple choice questions and 12 pages of short answer questions. ANSWER ALL QUESTIONS.
5. Follow the instructions on page 2 to record your answers to the multiple choice questions. Use a dark lead pencil so that you can erase errors made on the computer sheet.
6. Answer all short answer questions in the spaces provided on this question paper. Credit may not be given where there is insufficient evidence of the working required to obtain the solution.
7. Take care to write legibly. Write your final answers in ink, not pencil.
8. 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.

	Marks			
Page(s)	Max	Gained		Marker
~~2-9~~	~~30~~			~~MCQ~~
10	5			
11	5			
12	6			
13	2			
14	8			
16	4			
17	6			
18	7			
19	7			
20	6			
21	9			
23	5			
Total	100			
Check Total				

Marks
5

- The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent nitrogen atoms and the smaller spheres represent boron atoms.



From the unit cell shown above, determine the empirical formula of boron nitride.

Answer:

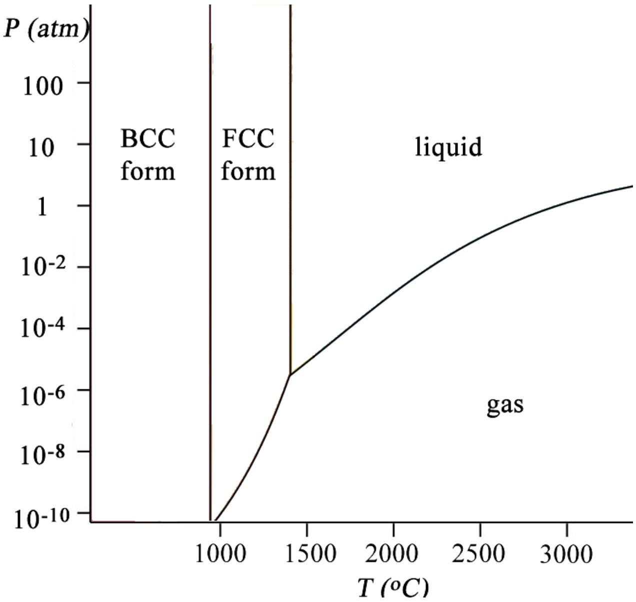
Determine the oxidation state of the boron atoms.

Answer:

The cubic form of boron nitride is more thermally stable in air than diamond. Provide a reasonable explanation for this observation.

Marks
5

- A simplified phase diagram for iron is shown below, with the solid part divided into the body-centred cubic (BCC) and face-centred cubic (FCC) phases.



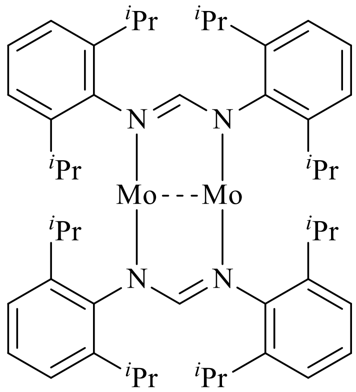
Which form of iron is stable at room temperature and pressure?

If molten iron is cooled slowly to around 1200 °C and then cooled rapidly to room temperature, the FCC form is obtained. Draw arrows on the phase diagram to indicate this process and explain why it leads to the FCC form as a metastable phase.

The line dividing the BCC and FCC forms is almost, but not quite vertical. Predict which way this line slopes and explain your answer.

Marks
6

- In 2009, great excitement was generated amongst chemists worldwide with the report of a neutral Mo complex containing two bridging, anionic *N*-donor ligands. The structure of the complex is shown below. ^{i}Pr = isopropyl = $–CH(CH_3)_2$

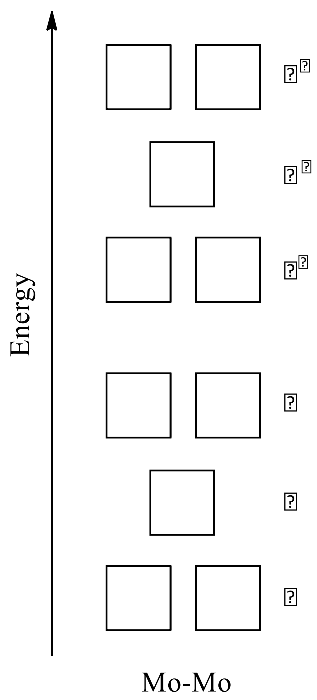


Name the complex by using standard IUPAC nomenclature. For simplicity, the name of the *N*-donor ligand (in its neutral form) can be shortened to "aminidate".

The Mo complex above possesses an extremely short Mo–Mo bond (202 pm), much shorter than the bonding distance between Mo atoms in Mo metal (273 pm)!

(a) Propose a reasonable explanation for the very short Mo–Mo bond length in the complex by adding *d*-electrons into the (*partial*) MO scheme shown below.

(b) Determine the bond order for the metal-metal bond and re-draw the structure of the complex shown above indicating the actual bonding between the two Mo atoms.



THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

Marks
2

Oxidation of the Mo complex by **two** electrons gives rise to a paramagnetic species in which the Mo–Mo distance increases significantly. Give a reasonable hypothesis for the bond-lengthening phenomenon.

Determine the number of unpaired electrons in the oxidised Mo complex.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
8

- Boric acid, $B(OH)_3$, is a weak acid (pK_a = 9.24) that is used as a mild antiseptic and eye wash. Unusually, the Lewis acidity of the compound accounts for its Brønsted acidity. By using an appropriate chemical equation, show how this compound acts as a Brønsted acid in aqueous solution.

Solution A consists of a 0.60 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

pH =

At 25 °C, 1.00 L of Solution B consists of 112 g of $NaB(OH)_4$ dissolved in water. Calculate the pH of Solution B.

pH =

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 9.24.

Answer:

THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- At a certain temperature the following data were collected for the decomposition of HI.

$$2HI \rightarrow H_2 + I_2$$

Experiment	Initial [HI] (mol L^{-1})	Initial rate of reaction (mol L^{-1} s^{-1})
1	1.0×10^{-2}	4.0×10^{-6}
2	2.0×10^{-2}	1.6×10^{-5}
3	3.0×10^{-2}	3.6×10^{-5}

Determine the rate law for the reaction.

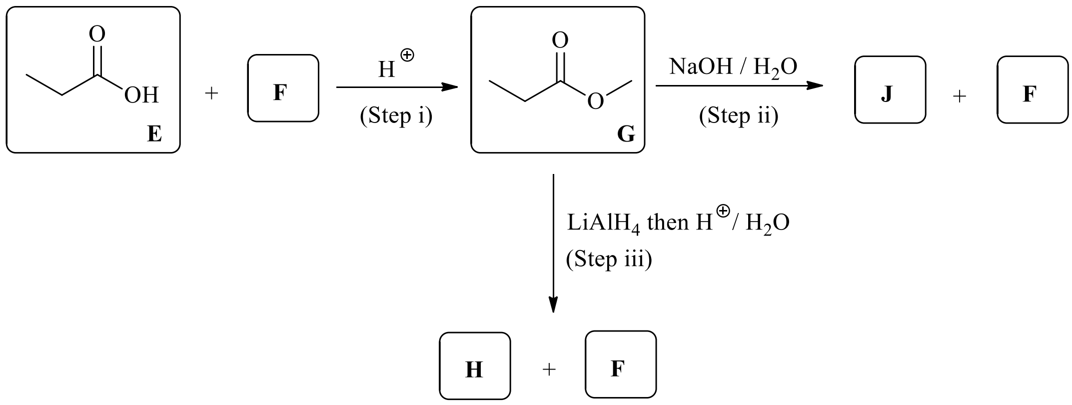
What is the value of the rate constant for the decomposition of HI?

Answer:

Page Total:

Marks
6

- Consider the following reaction sequences beginning with the carboxylic acid, **E**.



Name compounds **E** and **G**.

E:
G:

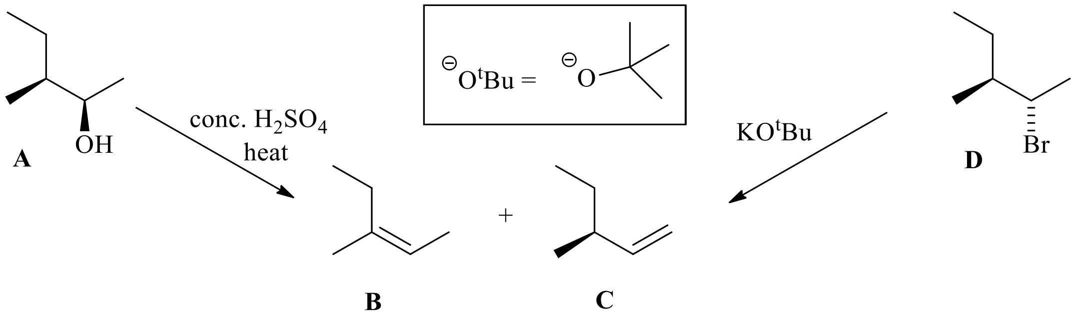
Propose structures for compounds **F**, **H** and **J**.

F	**H**	**J**

Propose a mechanism for step (ii).

Marks
7

- The elimination of H_2O from alcohol **A** can form the isomeric alkenes **B** and **C**. Elimination of HBr from the alkyl halide **D** can generate the same alkenes.



Assign the absolute configuration of alcohol **A**. Show your working.

Name compound **B** fully.

Draw the enantiomer of **A** and a diastereoisomer of **D**.

enantiomer of **A**	diastereoisomer of **D**

Propose a mechanism for the formation of **B** from **A** under the conditions shown.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
7

Explain why **C** is the minor product of this reaction.

A diastereoisomer of **B** is also formed in these reactions. Draw its structure. Do you expect **B** or its diastereoisomer to be the major product formed when **A** undergoes the above elimination reaction? Explain your reasoning.

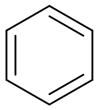
Propose a mechanism for the formation of **C** from **D** under the conditions shown.

Explain why **C** is the major product of this reaction.

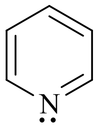
What would be the major product if the enantiomer of **D** were exposed to the same reaction conditions?

Marks
6

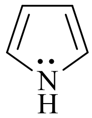
- Benzene, pyridine and pyrrole are all aromatic.



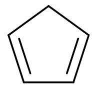
benzene



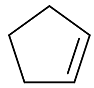
pyridine



pyrrole



cyclopentadiene
pK_a = 15



cyclopentene
pK_a = 45

What three criteria must be met for a compound to be aromatic?

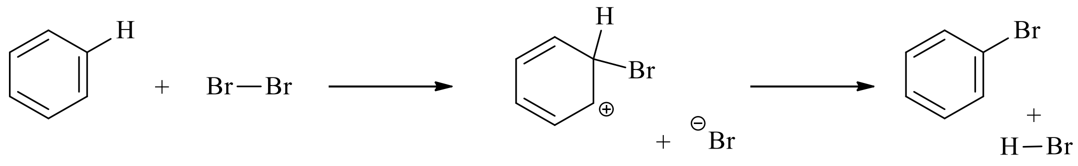
Apply your previous answer to explain the following.

Pyridine is basic but pyrrole is not.

The pK_a of cyclopentadiene is much lower than that of cyclopentene.

Marks
9

- Benzene can undergo an S_EAr reaction with bromine, Br_2, as shown below. Demonstrate your understanding of this reaction by adding curly arrows to complete the mechanism.



Explain what each part of the abbreviation S_EAr means.

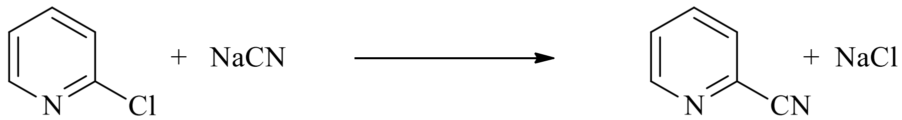
S =	
E =	
Ar =	

Identify one nucleophile and one electrophile in the scheme above.

nucleophile	electrophile

Iron(III) bromide, $FeBr_3$, is often added to the reaction shown above. Why?

2-Chloropyridine can undergo the following reaction with sodium cyanide.



This reaction also proceeds via a two-step mechanism and an ionic *(i.e.* charged) intermediate. Apply your understanding of organic reactions to propose a mechanism for this reaction.

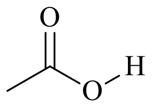
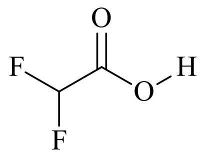
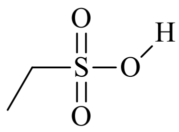
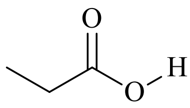
If the reaction of benzene shown above is S_EAr, how would you classify this reaction of chloropyridine?

Page Total:

THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- Draw the conjugate bases for the following acids.

S	**T**	**U**	**V**
			
Conjugate base of **S**	Conjugate base of **T**	Conjugate base of **U**	Conjugate base of **V**

Which of **S** and **T** is the stronger acid? Give a reason for your answer.

Which of **U** and **V** is the stronger acid? Give a reason for your answer.

THIS PAGE IS FOR ROUGH WORKING ONLY.

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

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	(+0.82 at pH = 7)
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+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	
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$	+0.62	
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53	
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34	
$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O$	+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	(–0.41 at pH = 7)
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–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	

Useful formulas

Thermodynamics & Equilibrium	Electrochemistry
$\Delta U = q + w = q - p\Delta V$ $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $\ln\frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$	$\Delta G° = -nFE°$ $\text{Moles of } e^- = It/F$ $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n}\log Q$ (at 25 °C)
Acids and Bases	**Gas Laws**
$pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = ½mv^2$
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	$t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Mathematics	**Quantum Chemistry**
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 = $4\pi r^2$ Volume of sphere = $^4/_3\ \pi r^3$	$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm
Miscellaneous	**Colligative Properties & Solutions**
$A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	$\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$

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]