2208(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2010 **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 •.
- 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 22 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	30	

Short answer section

Page	Marks			Marker
	Max	Gained		
11	8			
12	5			
13	5			
14	8			
15	3			
16	6			
17	6			
18	7			
19	5			
20	3			
22	8			
23	5			
Total	70			
Check Total				

Marks

- Explain why HOCl is a stronger Brønsted acid than HOBr but HCl is a weaker acid than HBr. **2**

- Titanium has three common oxidation states, +II, +III and +IV. Using the box notation to represent atomic orbitals, predict whether compounds of Ti^{2+}, Ti^{3+} and Ti^{4+} would be paramagnetic or diamagnetic. **2**

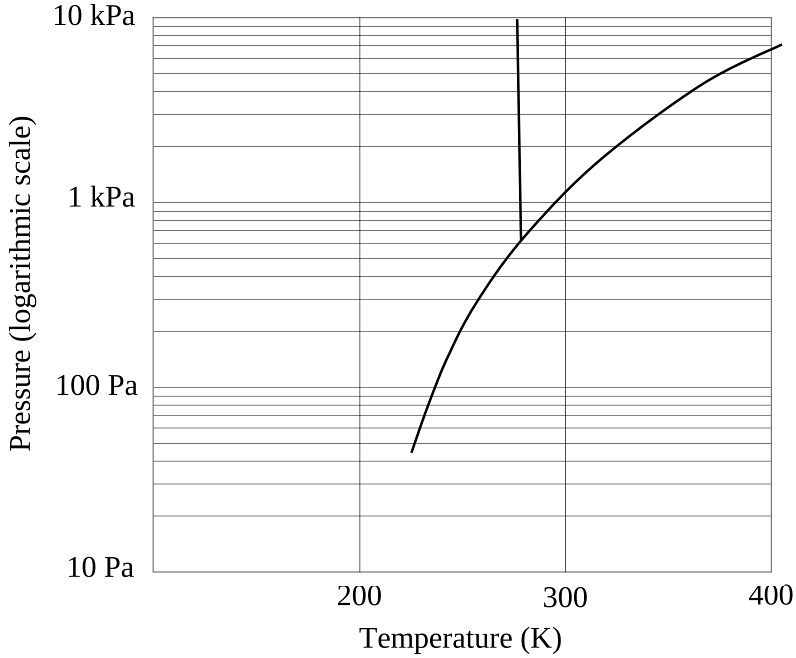
- Provide a systematic name for the complex *trans*-$[NiBr_2(en)_2]$ and draw its structure. Is this complex chiral? Explain your reasoning. **4**

  en = ethylenediamine = ethane-1,2-diamine

Page Total:

Marks
5

- The diagram below shows part of the phase diagram of water.



The average pressure on the surface of Mars is around 0.6 kPa. If the night time temperature is –60 °C and a summer day temperature is 20 °C, describe what happens to any water on the surface of Mars as the sun rises.

The highest surface pressure on Mars is thought to occur at the Hellas Basin, a low-lying area created by the impact of a large asteroid. If the pressure in this region is 1.2 kPa, use the phase diagram to estimate the temperature range in which liquid water will occur. Show your working on the phase diagram.

Marks
5

- Complete the following table. (EDTA = ethylenediaminetetraacetate)

Formula	$[Ni(NH_3)_6](NO_3)_2$	*trans*-$[PtCl_2(NH_3)_2]$	Na[Fe(EDTA)]
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Coordination geometry of the complex ion			
List all the ligand donor atoms			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
8

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[Co(NH_3)_5(OH_2)]^{3+}$ as an example.

Solution A consists of a 0.10 M aqueous solution of $[Co(NH_3)_5(OH_2)](NO_3)_3$ at 25 °C. Calculate the pH of Solution A. The pK_a of $[Co(NH_3)_5(OH_2)]^{3+}$ = 5.69.

pH =

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[Co(NH_3)_5(OH)](NO_3)_2$ dissolved in water. Calculate the pH of Solution B.

pH =

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a pH = 7.00.

Marks

- Calculate the molar solubility of lead bromide given that its solubility product constant, K_{sp}, is 2.1×10^{-6}. **2**

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 6

- The following reaction is run from 4 different starting positions.

$$H_2SeO_3 + 6I^- + 4H^+ \rightarrow Se + 2I_3^- + 3H_2O$$

Experiment Number	Initial $[H_2SeO_3]$ (mol L^{-1})	Initial $[I^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Initial rate of increase of $[I_3^-]$ (mol L^{-1} s^{-1})
1	0.100	0.100	0.100	1.000
2	0.100	0.075	0.100	0.422
3	0.075	0.100	0.100	0.750
4	0.100	0.075	0.075	0.237

Determine the rate law for the reaction.

Rate law:

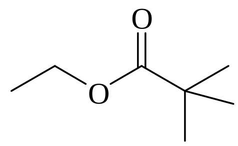
Calculate the value of the rate constant.

Answer:

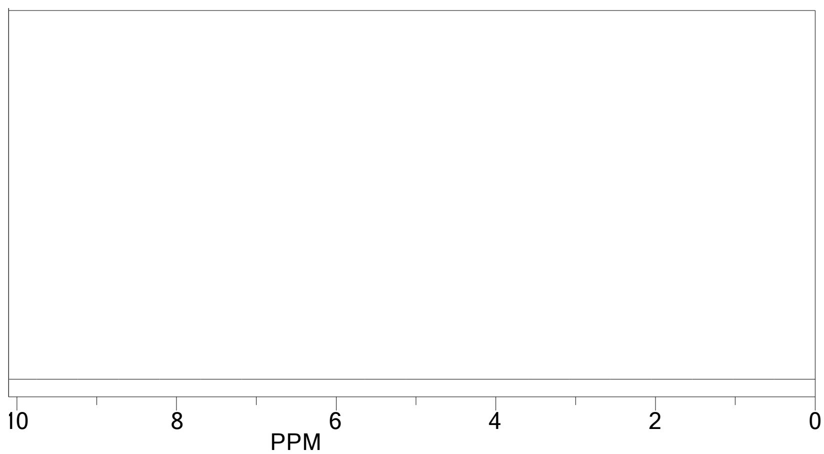
Page Total:

Marks
6

- Below is the structure of an ester.



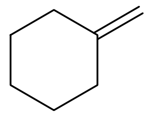
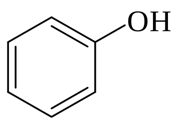
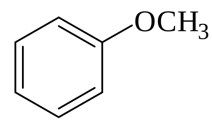
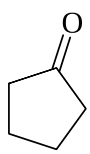
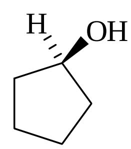
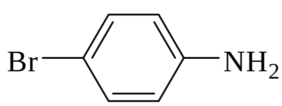
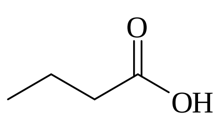
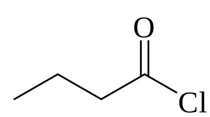
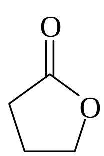
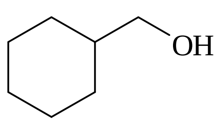
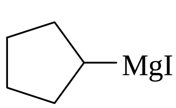
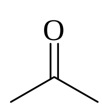
Using the blank scale below, sketch the ^{1}H NMR spectrum that you would expect to see for this molecule. You will need to indicate the approximate chemical shift of each signal (by drawing it in the appropriate place on the blank spectrum and labelling the molecule to show which peak is which) as well as the integral associated with each peak and the splitting (multiplicity).



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 8

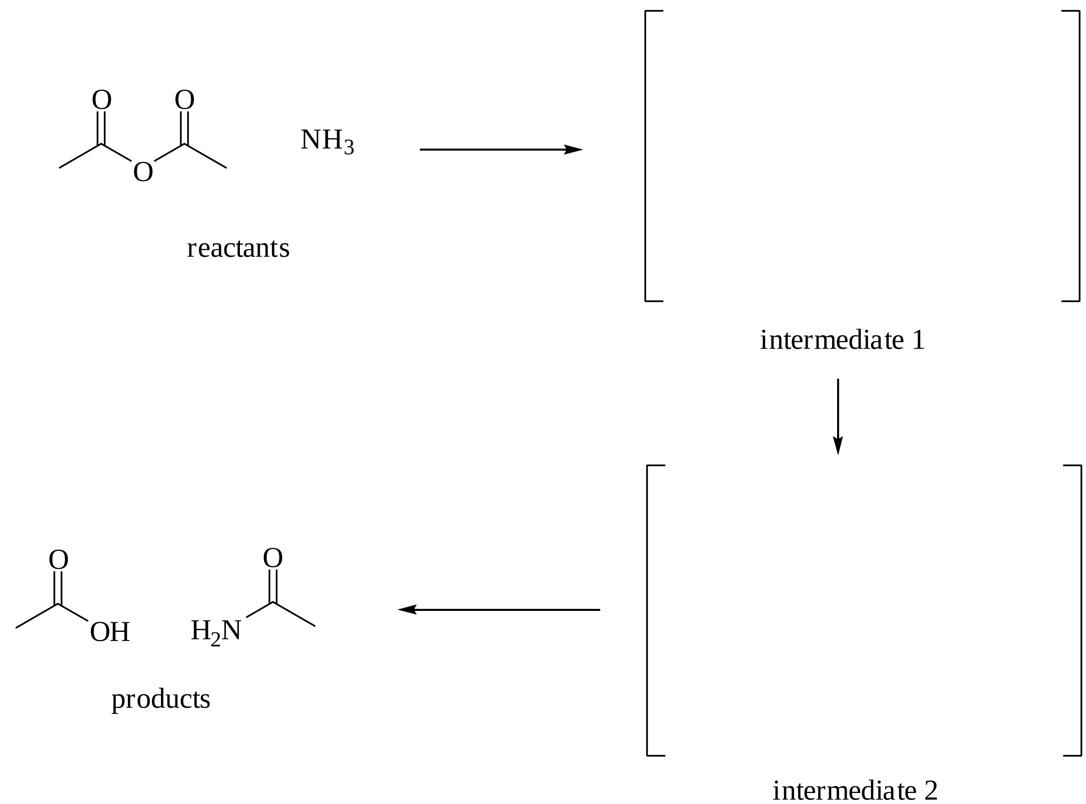
- Complete the following table.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	HBr	
		
		
	2 M HCl	
		
	$H^{\oplus}$ / H_2O / heat	
	$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
		

Page Total:

Marks
5

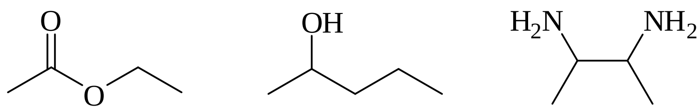
- The following is a nucleophilic addition-elimination reaction between ammonia and an acid anhydride. Provide curly arrows needed for the mechanism, and draw the structures of the two intermediates on this pathway.



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
3

- Suppose a molecule has been isolated from a natural source. When a sample of the molecule is analysed by low resolution mass spectrometry, it shows a molecular ion peak that implies the molecule has a molecular weight of 88. You determine that the molecule might be one of the following three possibilities, all of which have a molecular weight of 88.



A **B** **C**

Further data are acquired for the compound as follows:

- Elemental analysis data: C, 68.13%; H, 13.72% (another element is also present)
- High resolution mass spectrum suggests the molecular weight is actually 88.0888.

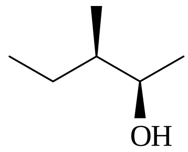
Explain how ***either*** high resolution mass spectrometry ***or*** the elemental analysis data allows you to distinguish between these three possibilities and hence identify which of **A**, **B** or **C** is in the sample.

Information you may need:

Average atomic masses: C: 12.0107, H: 1.0079, O: 15.9994, N: 14.0067
Exact isotopic masses: ^{12}C: 12.0000, ^{1}H: 1.0078, ^{16}O: 15.9949, ^{14}N: 14.0031

Marks
8

- The structure of a chiral molecule, **P**, is shown below. **P** has a specific optical rotation of +26˚.



P

Assign the stereochemistry at the two stereogenic centres, showing your working.

Draw the structure of a molecule that will have a specific optical rotation of –26˚.

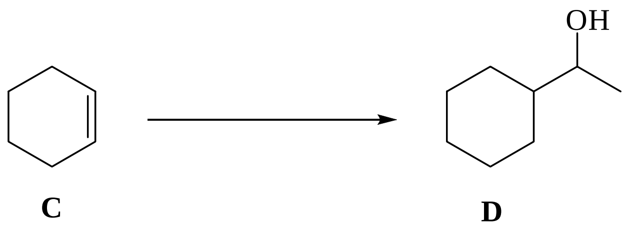
Draw a diastereoisomer of **P**.

The addition of hot concentrated sulfuric acid causes **P** to transform into another molecule, **Q** (C_6H_{12}) that is optically inactive. What is the structure of molecule **Q** and why is it optically inactive?

Name molecule **Q**.

Marks
5

- Devise a synthesis of 1-cyclohexylethanol (**D**) from cyclohexene (**C**). Provide reagents for each step, as well as the structures of any intermediate compounds generated as part of the route. You do not need to show any mechanisms.
  Hint: a number of steps is required.



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	1 Ci = 3.70×10^{10} Bq
0 °C = 273 K	1 Hz = 1 s^{-1}
1 L = 10^{-3} m^3	1 tonne = 10^3 kg
1 Å = 10^{-10} m	1 W = 1 J s^{-1}
1 eV = 1.602×10^{-19} J	

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

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
$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(g) + 7H_2O$	+1.36
$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$	+1.36
$O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O$	+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
$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$	+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 $pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	**Gas Laws** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = ½mv^2$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = $8033 \ln(A_0/A_t)$ years	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
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** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $\ln\frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
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]	112 COPERNICIUM **Cn** [283]						

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]