Topics in the November 2008 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2008-N-2:

- Periodic Trends in Aqueous Oxide
- Crystal Structures

2008-N-3:

- Solubility Equilibrium
- Hydrolysis of Metal Ions
- Coordination Chemistry

2008-N-4:

- Hydrolysis of Metal Ions
- Coordination Chemistry

2008-N-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2008-N-6:

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

2008-N-7:

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

2008-N-8:

- Kinetics

2008-N-9:

- Kinetics
- Kinetics - Influences

2008-N-10:

- Representations of Molecular Structure
- Carboxylic Acids and Derivatives

2008-N-11:

- Stereochemistry

2008-N-12:

- Alkenes
- Stereochemistry

2008-N-13:

- Alkenes
- Aromatic Compounds

2008-N-14:

- Structural Determination

2008-N-15:

- Synthetic Strategies

22/08(a) **The University of Sydney**

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2008 **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 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	
Pages	Max	Gained
2-10	30	

Short answer section

	Marks			
Page	Max	Gained		Marker
10	5			
11	7			
12	8			
13	5			
14	3			
15	3			
16	2			
17	4			
18	5			
19	8			
20	5			
21	5			
22	5			
23	5			
Total	70			

Marks

- Briefly explain how the concept of electronegativity can rationalise the existence of acidic, basic and amphoteric oxides. **3**

Draw the face-centred cubic unit cell. **2**

Marks

4

A solution is prepared that is 0.10 M in potassium bromide and 0.10 M in potassium chromate. A concentrated aqueous solution of silver nitrate is added with stirring. What is the concentration of Ag^+(aq) ions when silver bromide first appears?
K_{sp} of AgBr = 5.0×10^{-13}

Answer:

What is the concentration of Ag^+(aq) ions when silver chromate first appears?
K_{sp} of Ag_2CrO_4 = 2.6×10^{-12}

Answer:

What is the concentration of Br^-(aq) ions when silver chromate first appears?

Answer:

3

- Calculate the equilibrium constant for the following reaction.

$$AgI(s) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) + I^-(aq)$$

Data: K_{stab} of $[Ag(CN)_2]^-$ = 3×10^{20}; K_{sp} of AgI = 8.3×10^{-17}

Answer:

Marks

- Which of the cations, $[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{2+}$, has the larger pK_a? Briefly explain why. **2**

- Consider the compound $[CrCl(OH_2)_4(NCS)]Cl\cdot 2H_2O$. **3**

  What is the oxidation state of the transition metal ion?

  What is the coordination number of the transition metal ion?

  How many *d*-electrons in the transition metal ion?

  List all the ligand donor atoms.

- Consider the complexes *cis*-$[PtCl_2(NH_3)_2]$ and *trans*-$[PtCl_2(NH_3)_2]$. Draw the structures of the two isomers, clearly illustrating the stereochemistry. **3**

  Briefly suggest why *cis*-$[PtCl_2(NH_3)_2]$ is an effective anti-cancer drug, but *trans*-$[PtCl_2(NH_3)_2]$ is not.

Marks
5

- Buffers made of mixtures of $H_2PO_4^-$ and HPO_4^{2-} are used to control the pH of soft drinks. What is the pH of a 350 mL drink containing 6.0 g of NaH_2PO_4 and 4.0 g of Na_2HPO_4?

  For phosphoric acid, H_3PO_4, pK_{a1} = 2.15, pK_{a2} = 7.20 and pK_{a3} = 12.38.

  Briefly describe how this buffer system functions. Use equations where appropriate.

  Is this buffer better able to resist changes in pH following the addition of acid or of base? Explain your answer.

Marks
3

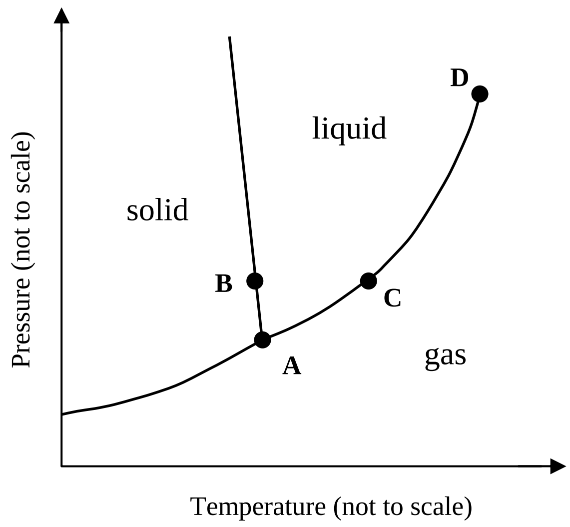
- The figure below illustrates the phase diagram for water. The points on the diagram correspond to:

  A: Triple point (0.0098 °C, 0.610 kPa)

  B: Normal melting point (0 °C, 1.01×10^2 kPa)

  C: Normal boiling point (100 °C, 1.01×10^2 kPa)

  D: Critical point (374.4 °C, 2.18×10^4 kPa)



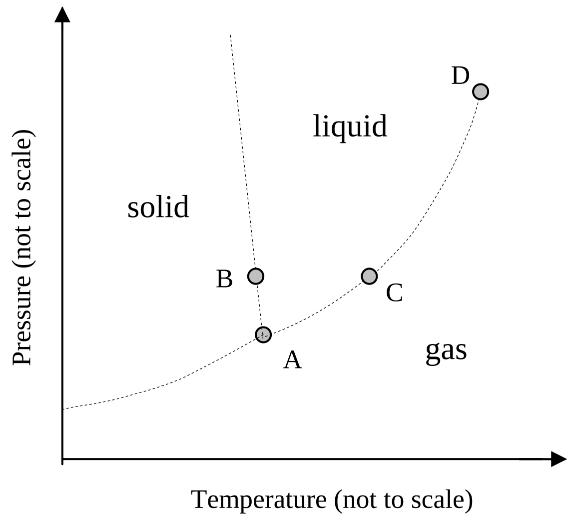
Describe all of the phase changes that occur when water at 1.01×10^2 kPa is slowly warmed from –20 °C to 200 °C.

Describe all of the phase changes that occur when water at 0 °C is slowly compressed from 0.500 kPa to 1000 kPa.

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks
3

Addition of salt to water raises its boiling point and lowers its melting point. Sketch the phase diagram for water containing salt, showing how it relates to the phase diagram for water (shown as dotted lines below).



In terms of the relative entropies of all relevant species, explain why the boiling point of salt water is higher than that of pure water.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
2

- The following data were obtained for the reaction between gaseous nitric oxide and chlorine at –10 °C:

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

Experiment Number	Initial P_{NO} (atm)	Initial P_{Cl_2} (atm)	Initial Reaction Rate (atm s^{-1})
1	2.16	2.16	0.065
2	2.16	4.32	0.130
3	4.32	4.32	0.518

Derive an expression for the rate law for this reaction and calculate the value of the rate constant.

Rate law:

Rate constant:

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks
4

The mechanism for this reaction has been postulated to be that below.

$$2NO(g) \rightleftharpoons N_2O_2(g) \quad \text{fast}$$

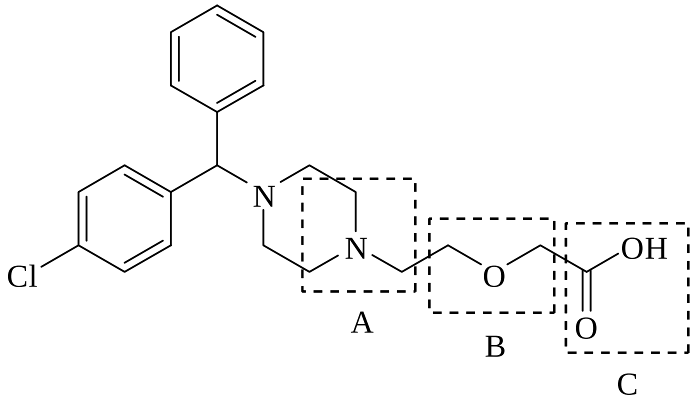
$$N_2O_2(g) + Cl_2 \rightarrow 2NOCl(g) \quad \text{slow}$$

Work out the rate law expected for this mechanism and hence show that it is consistent with the experimental rate law and the chemical equation.

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

Marks
5

- The structure of the antihistamine, Zyrtec™, is given below.



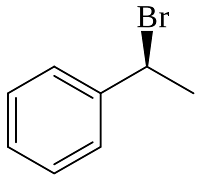
What is the name of the functional group in Box A?	
What is the name of the functional group in Box B?	
What is the name of the functional group in Box C?	

By drawing an arrow on the structure above, clearly indicate the stereocentre in the structure of Zyrtec.

Draw the product of the reaction when Zyrtec is treated with $LiAlH_4$ followed by dilute acid.

Marks
8

- Consider compound **F** shown below.


F

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

Draw the enantiomer of compound **F**.

When compound **F** is reacted with hot KOH solution, a product (**G**) is formed that shows three peaks in the ^{1}H NMR spectrum in the region 7-8 ppm and three peaks in the region 5-6 ppm. Draw the structure of this product.

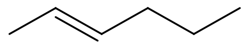
When **G** is reacted with dilute sulfuric acid, a further product, **H**, is formed. **H** has a peak at 3300 cm^{-1} in its IR spectrum. Draw the structure of product **H**.

Is **H** formed as a single enantiomer, as a racemate, or is **H** achiral?

Assuming an S_N2 mechanism, draw the product of the substitution reaction between **F** and $(CH_3)_2NH$, indicating stereochemistry where appropriate.

Marks
5

- Consider the compound **J** below.



J

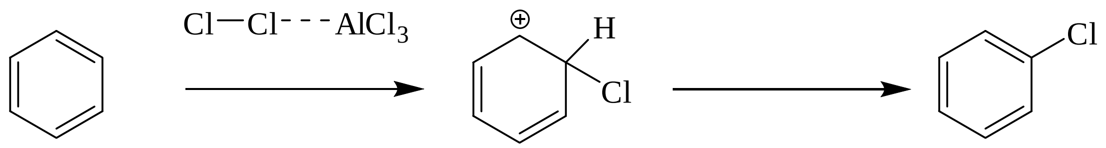
What is the systematic name for compound **J**.

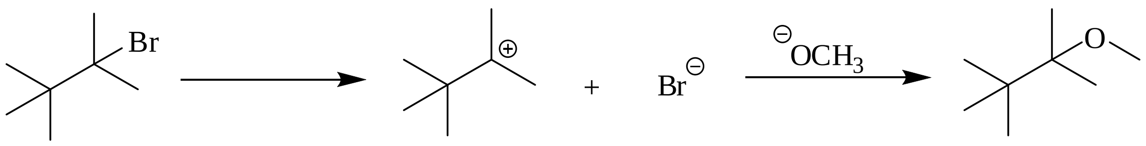
Draw a constitutional isomer of **J**.

Draw a configurational isomer of **J**.

Draw the structure of the product formed when compound **J** is reacted with hydrogen gas (H_2) and a palladium on carbon (Pd/C) catalyst.

	Marks
• Complete the following mechanism by adding curly arrows to illustrate the bonding changes that take place.	**5**





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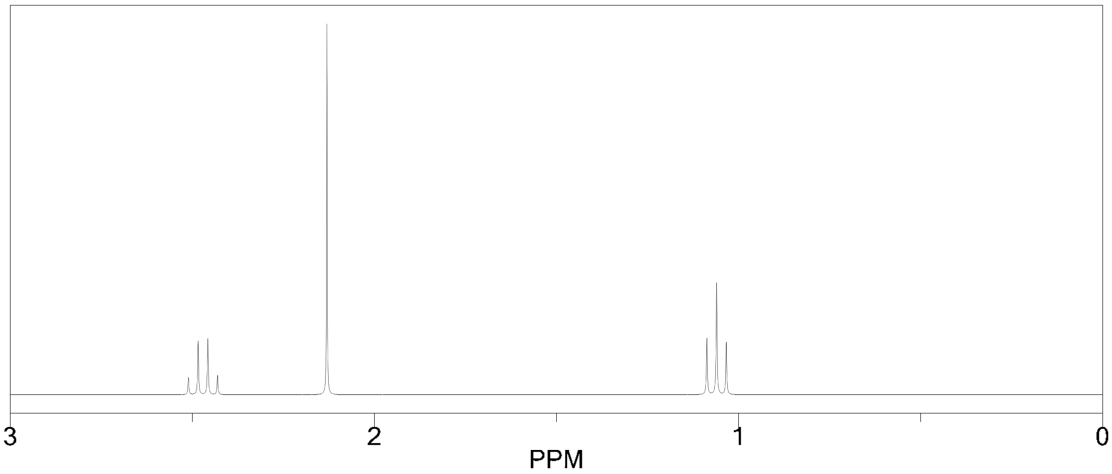
Marks
5

- An unknown compound **K** with the molecular formula C_4H_8O gives the following spectroscopic data.

  ^{1}H NMR: 1.06 ppm, triplet, integration = 3H
  2.13 ppm, singlet, integration = 3H
  2.47 ppm, quartet, integration = 2H

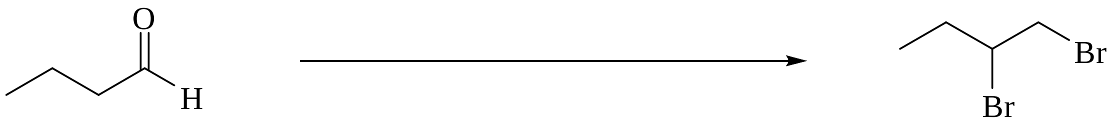


IR spectroscopy: stretch at 1715 cm^{-1}.

Use the information above to deduce the structure of compound **K**. Give reasoning for the structure chosen.

Marks
5

- Devise a synthesis of 1,2-dibromobutane from butanal. Provide any intermediate structures and reagents. (Hint: More than one step is required.)



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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
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+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

CHEM1102 - CHEMISTRY 1B

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]