Topics in the June 2014 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2014-J-2:

- Crystal Structures
- Coordination Chemistry
- Kinetics
- Kinetics - Influences
- Kinetics - Catalysis

2014-J-3:

- Weak Acids and Bases

2014-J-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-J-5:

- Coordination Chemistry

2014-J-6:

- Solubility Equilibrium

2014-J-7:

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

2014-J-8:

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

2014-J-9:

- Stereochemistry
- Carboxylic Acids and Derivatives

2014-J-10:

- Stereochemistry
- Alkenes
- Alcohols

2014-J-11:

- Alcohols
- Organic Halogen Compounds

2014-J-12:

- Carboxylic Acids and Derivatives

- Alcohols
- Aldehydes and Ketones
- Synthetic Strategies

2206(a) # THE UNIVERSITY OF SYDNEY

CHEMISTRY 1B - CHEM1102

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2014 **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 18 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 short answer question 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.
- Page 20 is for rough working only.

OFFICIAL USE ONLY

Multiple choice section

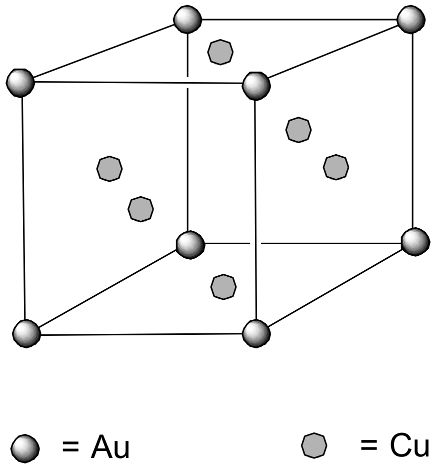
	Marks	
Pages	Max	Gained
2-8	28	

Short answer section

	Marks			
Page	Max	Gained		Marker
9	6			
10	5			
11	7			
12	4			
13	8			
14	6			
15	11			
16	7			
17	8			
18	4			
19	6			
Total	72			
Check Total				

Marks

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. **2**



What is the chemical formula of the alloy?

Answer:

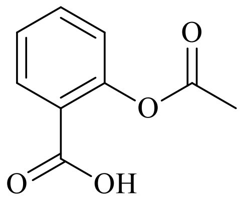
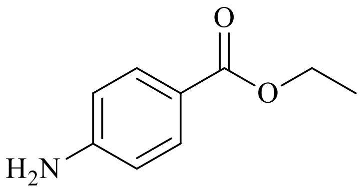
- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Co^{2+}. **2**

- Briefly explain how a catalyst works. **2**

Marks
5

- The structures of the drugs aspirin and benzocaine are shown below.

  (a) Draw the conjugate base of aspirin and the conjugate acid of benzocaine.
  (b) *Circle* the form of each that will be present in a highly acidic environment.

 aspirin	conjugate base of aspirin
 benzocaine	conjugate acid of benzocaine

Ions are less likely to cross cell membranes than uncharged molecules. One of the drugs above is absorbed in the acid environment of the stomach and the other is absorbed in the basic environment of the intestine. Identify which is absorbed in each environment below and *briefly* explain your answers.

Drug absorbed in the stomach:	aspirin / benzocaine
Drug absorbed in the intestine:	aspirin / benzocaine

Aspirin, $C_9H_8O_4$ is not very soluble in water. “Soluble aspirin”, the sodium salt $NaC_9H_7O_4$, is often administered instead. Is a solution of “soluble aspirin” acidic or basic? Briefly explain your answer.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

Marks
7

Calculate the pH of a 0.010 M solution of aspirin at 25 °C. The pK_a of aspirin is 3.5 at this temperature.

pH =

Ammonia, NH_3, is a weak base in water. Write the equation for the acid/base reaction between aspirin and ammonia.

What is the expression for the equilibrium constant, K, for this reaction?

Rewrite this expression in terms of the K_a of aspirin and the K_a of NH_4^+. (Hint: multiply by $[H^+]/[H^+] = 1$) Hence calculate the value of K. The pK_a of NH_4^+ is 9.2.

Answer:

Would aspirin dissolve in a solution of ammonia? Explain your answer.

Page Total:

Marks 4

- Name the complex $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$

Draw all possible isomers of this complex.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
8

- A solution is prepared that contains sodium chloride and sodium chromate (both 0.10 M). When a concentrated solution of silver nitrate is added slowly, white AgCl(s) begins to precipitate. After most of the Cl^-(aq) has been consumed, red Ag_2CrO_4(s) starts to precipitate.

  Ignoring dilution, what is the concentration of silver ions when silver chloride solid first starts to precipitate? K_{sp} (AgCl) is 1.8×10^{-10}.

Answer:

Ignoring dilution, what is the concentration of silver ions when silver chromate solid first starts to precipitate? K_{sp} (Ag_2CrO_4) is 3.6×10^{-12}.

Answer:

What is the concentration of chloride ions when silver chromate solid first starts to precipitate?

Answer:

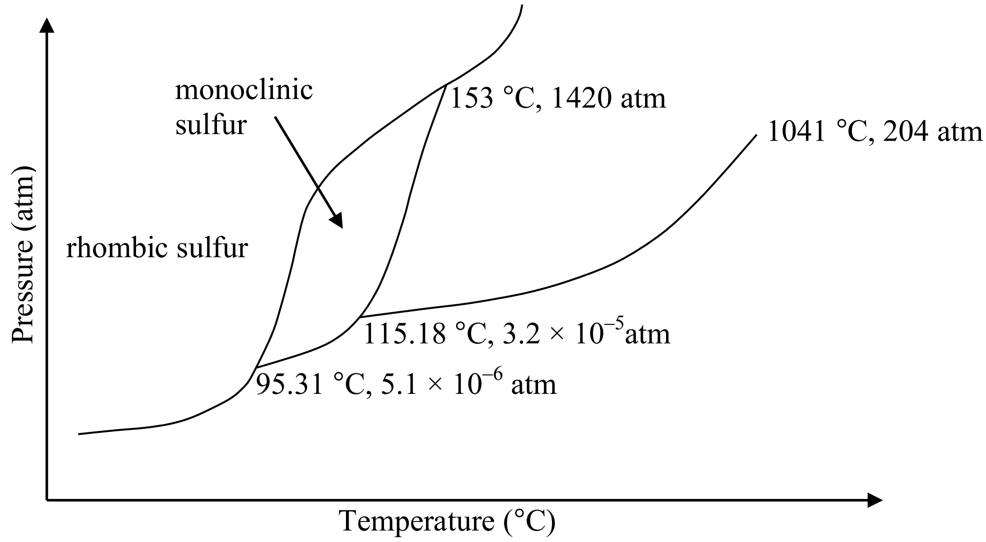
What percentage of the chloride ion is precipitated before any silver chromate is precipitated?

Answer:

Marks 6

- Solid sulfur can exist in two forms, rhombic sulfur and monoclinic sulfur. A portion of the phase diagram for sulfur is reproduced schematically below. The pressure and temperature axes are not drawn to scale.

  Complete the diagram by adding the labels "vapour" and "liquid" to the appropriate regions.



Which form of solid sulfur is stable at 25 °C and 1 atm?

Describe what happens when sulfur at 25 °C is slowly heated to 200 °C at a constant pressure of 1 atm.

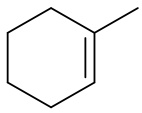
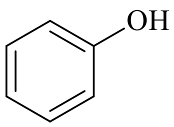
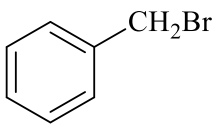
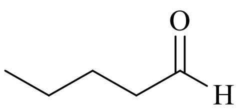
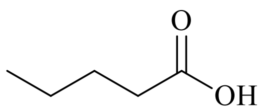
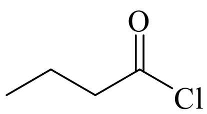
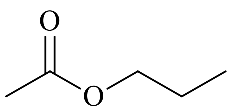
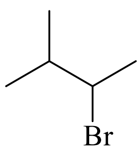
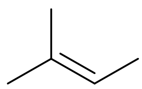
How many triple points are there in the phase diagram?

What phases are in equilibrium at the triple points?

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

Marks
11

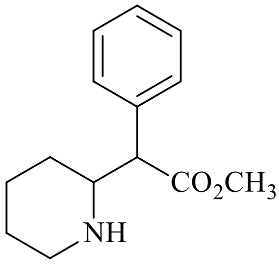
- Complete the following table. Make sure you give the name of the starting material where indicated.

STARTING MATERIAL	REAGENTS/ CONDITIONS	STRUCTURAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
 **Name:**	HBr / CCl_4 (solvent)	
	NaOH	
	KCN / ethanol (solvent)	
 **Name:**		
	$(CH_3)_2NH$	
	hot 3 M NaOH	
		

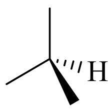
Marks
7

- Methylphenidate, also known as Ritalin, is a psychostimulant drug approved for the treatment of attention-deficit disorder. Identify all stereogenic (chiral) centres in methylphenidate by clearly marking each with an asterisk (*) on the structure below.

methylphenidate



Using one stereogenic centre you have identified, draw the (*R*)-configuration of that centre.

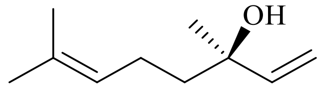


How many stereoisomers are there of methylphenidate? Describe the relationships between these isomers.

Give the products formed when methylphenidate is hydrolysed with 4 M HCl.

Marks
8

- The structure of (–)-linalool, a commonly occurring natural product, is shown below.



What is the molecular formula of (–)-linalool?

Which of the following best describes (–)-linalool?
achiral compound, racemic mixture,
(*R*)-enantiomer, or (*S*)-enantiomer

What functional groups are present in (–)-linalool?

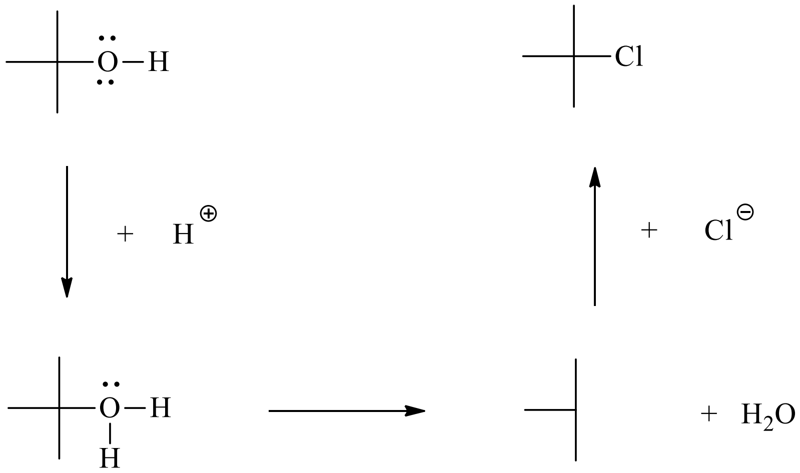
Is it possible to obtain (*Z*) and (*E*) isomers of (–)-linalool? Give a reason for your answer.

Give the structural formula of the organic product formed from (–)-linalool in each of the following reactions. NB: If there is no reaction, write "no reaction".

Reagents / Conditions	Structural Formula of Product
Br_2 (in CCl_4 as solvent)	
$Na_2Cr_2O_7$ in aqueous acid	
Na, then CH_3Br	
H_2 / Pd-C catalyst	

Marks
4

- Concentrated HCl reacts with 2-methyl-2-propanol in an S_N1 reaction to give 2-chloro-2-methylpropane as shown below. Complete the reaction mechanism by adding curly arrows and formal charges on the intermediates as appropriate.



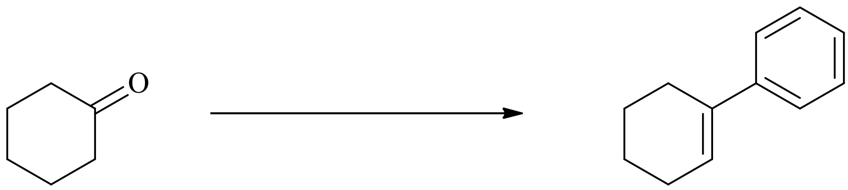
Explain what each part of the abbreviation S_N1 means.

S =
N =
1 =

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

- Show clearly the reagents you would use to carry out the following chemical conversions. More than one step is required in each case. Give the structure of any intermediate compounds formed.



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	1 J = 1 kg m^2 s^{-2}

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
$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(g) + 7H_2O$	+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	Electrochemistry
$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2 E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm	$\Delta G° = -nFE°$ 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	**Gas Laws**
$pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = \frac{1}{2}mv^2$
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	$t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Mathematics	**Thermodynamics & Equilibrium**
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 = $^4/_3\ \pi r^3$	$\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $\ln\frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Miscellaneous	**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** [263]	105 DUBNIUM **Db** [268]	106 SEABORGIUM **Sg** [271]	107 BOHRIUM **Bh** [274]	108 HASSIUM **Hs** [270]	109 MEITNERIUM **Mt** [278]	110 DARMSTADTIUM **Ds** [281]	111 ROENTGENIUM **Rg** [281]	112 COPERNICIUM **Cn** [285]		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]