Topics in the November 2012 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2012-N-2:

- Weak Acids and Bases
- Calculations Involving pK_a

2012-N-3:

- Weak Acids and Bases
- Calculations Involving pK_a

2012-N-4:

- Crystal Structures

2012-N-5:

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

2012-N-6:

- Solubility Equilibrium

2012-N-7:

- Solubility Equilibrium

2012-N-8:

- Metal Complexes
- Metals in Biology
- Coordination Chemistry

2012-N-9:

- Alcohols
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2012-N-10:

- Alkenes
- Alcohols
- Stereochemistry

2012-N-11:

- Representations of Molecular Structure
- Alkenes
- Stereochemistry
- Aldehydes and Ketones

2012-N-12:

- Alkenes
- Organic Halogen Compounds
- Amines

- Carboxylic Acids and Derivatives

2012-N-13:

- Stereochemistry

2012-N-14:

- Synthetic Strategies
- Stereochemistry

2202(a)

THE UNIVERSITY OF SYDNEY

FUNDAMENTALS OF CHEMISTRY 1B - CHEM1002

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2012 **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 20 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.
- Pages 9, 20 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-8	25	

Short answer section

Page	Marks Max	Gained		Marker
10	6			
11	5			
12	6			
13	5			
14	6			
15	3			
16	5			
17	7			
18	8			
19	8			
21	7			
22	3			
23	6			
Total	75			
Check Total				

Marks
6

- Solution A consists of a 0.050 M aqueous solution of benzoic acid, C_6H_5COOH, at 25 °C. Calculate the pH of Solution A. The pK_a of benzoic acid is 4.20.

pH =

What are the major species present in solution A?

Solution B consists of a 0.050 M aqueous solution of ammonia, NH_3, at 25 °C. Calculate the pH of Solution B. The pK_a of NH_4^+ is 9.24.

pH =

What are the major species present in solution B?

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
5

Write the equation for the reaction that occurs when benzoic acid reacts with ammonia?

Write the expression for the equilibrium constant for the reaction of benzoic acid with ammonia?

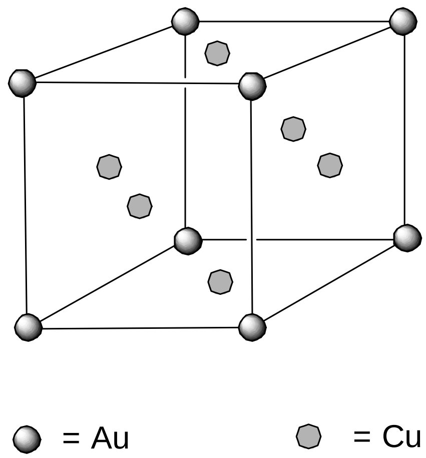
What is the value of the equilibrium constant for the reaction of benzoic acid with ammonia? Hint: multiply the above expression by $[H^+]/[H^+]$.

Answer:

What are the major species in the solution that results from adding together equal amounts of solutions A and B?

Marks
6

- 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. The length of the side of the cubic unit cell is 0.36 nm.



What is the chemical formula of the alloy?

Answer:

Pure gold is 24 carat, whilst gold alloys consisting of 75 % gold by weight are termed 18 carat gold. What carat gold is this alloy?

Answer:

What is the volume (in cm^3) of the unit cell?

Answer:

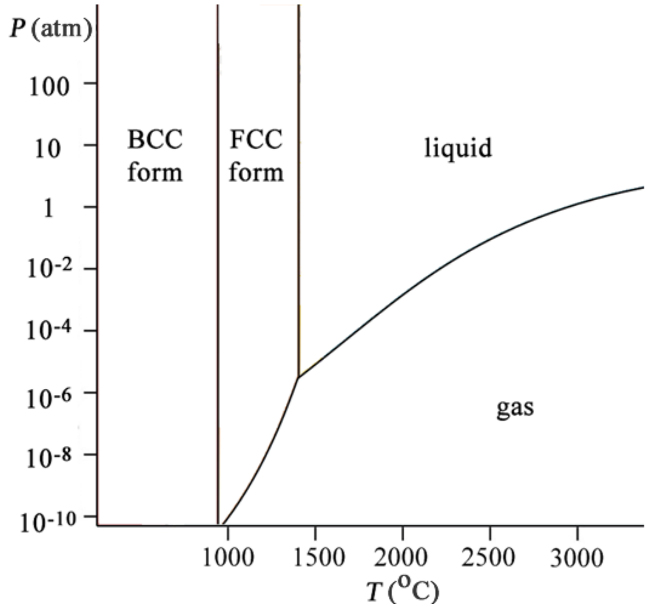
What is the density (in $g\ cm^{-3}$) of the alloy?

Answer:

Page Total:

Marks
5

- A simplified phase diagram for iron is shown below.



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.

The line dividing the BCC and FCC forms is almost, but not quite vertical. Given that the FCC form is more efficiently packed, predict which way this line slopes. Explain your answer.

Marks
6

- Explain what is meant by the "common ion effect".

Magnesium hydroxide is sparingly soluble. Write down the chemical equation for its dissolution in water and the expression for K_{sp}.

What is the molar solubility of magnesium hydroxide in water? $K_{sp} = 7.1 \times 10^{-12}$

Answer:

What is the pH of a saturated solution of magnesium hydroxide in water?

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks

What is the molar solubility of magnesium hydroxide in a buffer solution at pH 9.24? **3**

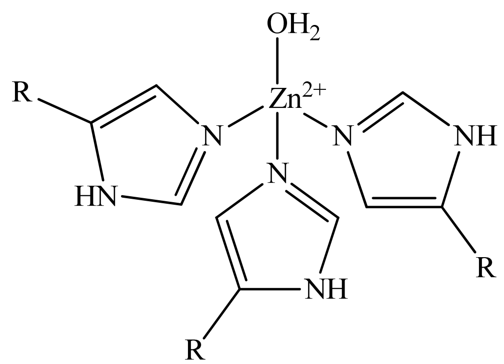
Answer:

Do the relative solubilities of magnesium hydroxide in water and the buffer solution support the concept of the common ion effect? Explain your reasoning.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to three histidine residues and a water molecule.

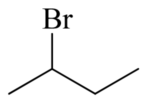
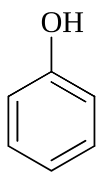
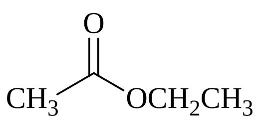
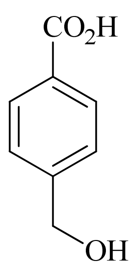
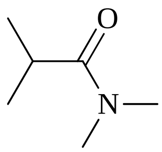


The pK_a of uncoordinated water is 15.7 but the pK_a of the water in carbonic anhydrase is around 7. Suggest an explanation for this large change.

When studying zinc-containing metalloenzymes such as this, chemists often replace Zn^{2+} with Co^{2+} because of their different magnetic properties. Predict which of these species, if either, is attracted by a magnetic field. Explain your reasoning.

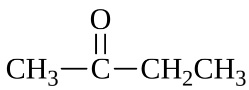
Marks
7

- A number of functional groups react with hydroxide ion. Complete the following table. NB: If there is no reaction, write "no reaction".

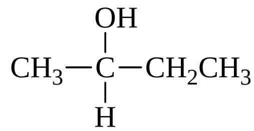
Starting Compound	Reaction Conditions	Organic Product(s)
	1 M aqueous NaOH	
	1 M aqueous NaOH	
	hot 4 M NaOH	
	1 M aqueous NaOH	
	hot 4 M NaOH prolonged heating	

Marks
8

- Butanone is treated first with lithium aluminium hydride, $LiAlH_4$, in dry ether and then with aqueous acid to yield the alcohol, **A**.



butanone



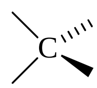
A

State whether **A** is obtained as the (*R*)-enantiomer, the (*S*)-enantiomer or as a racemic mixture. Give a reason for your answer.

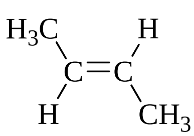
List below the substituents on the stereogenic (chiral) carbon atom in **A**, in descending order as determined by the sequence rule.

Highest priority			Lowest priority

Draw the stereoformula for the (*R*)-enantiomer with the lowest priority substituent at the back.



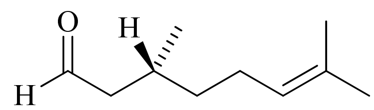
A is treated with concentrated sulfuric acid to give mainly the alkene **B** and two other alkenes **C** and **D**. Alkenes **B** and **C** are diastereomers, **B** and **D** (and **C** and **D**) are constitutional isomers. Give the structures for **C** and **D** and give systematic names for **B**, **C** and **D**.

B	**C**	**D**
		
Name:	Name:	Name:

Page Total:

Marks
8

- The structure of (+)-citronellal, a widely occurring natural product, is shown below.



What is the molecular formula of (+)-citronellal?

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

What functional groups are present in (+)-citronellal?

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

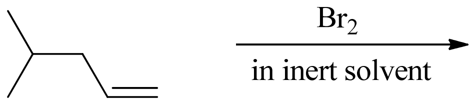
Give the constitutional formula of the organic product formed from (+)-citronellal in each of the following reactions.

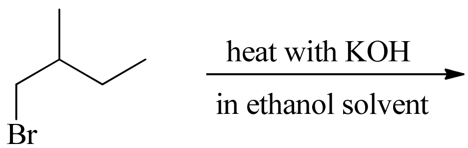
Reagents / Conditions	Constitutional Formula of Product
1. $LiAlH_4$ in dry ether (solvent) 2. H^+ / H_2O	
HBr in CCl_4 (solvent)	
$Na_2Cr_2O_7$ in aqueous acid	
H_2 / Pd-C catalyst	

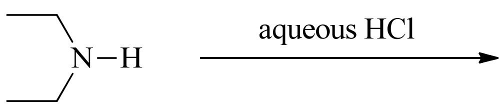
Page Total:

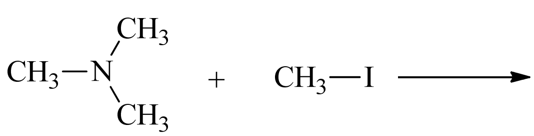
- Give the major organic product(s) from the following reactions. Pay particular attention to the stereochemistry and/or the correct ionic from where relevant.

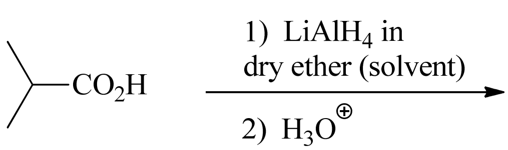
Marks
7

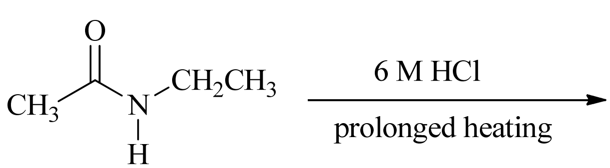






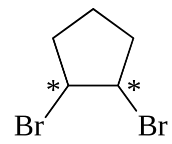






Marks
3

- 1,2-Dibromocyclopentane has two stereogenic carbon atoms, each marked with an asterisk (*) on the structure below.



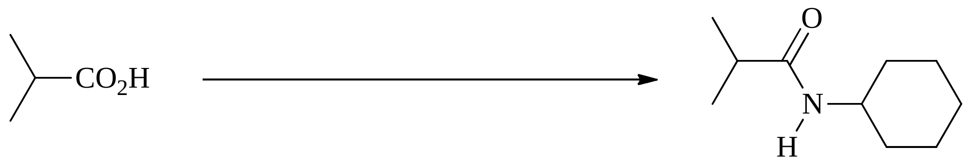
The maximum number of configurational stereoisomers is given by the formula 2^n, where n is the number of stereogenic centres.

1,2-Dibromocyclopentane has only three configurational stereoisomeric forms, not four. Explain briefly why this is the case. Include drawings of the relevant stereoformulas in your answer.

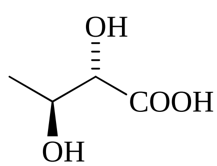
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

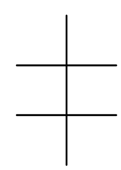
Marks

- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structure of any intermediate compounds formed. You have a supply of cyclohexylamine available. **3**



- Convert the following structure into a Fischer projection. **3**





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Page Total:

CHEM1002 – FUNDAMENTALS OF 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

CHEM1002 – FUNDAMENTALS OF 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

CHEM1002 – FUNDAMENTALS OF CHEMISTRY 1B

Useful formulas

Quantum Chemistry

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

$\lambda = h/mv$

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

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

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

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

Electrochemistry

$\Delta G° = -nFE°$

Moles of e^- = It/F

$E = E° - (RT/nF) \times 2.303 \log Q$

$\quad = E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

$\quad = (RT/nF) \times \ln K$

$E = E° - \frac{0.0592}{n} \log Q$ (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

$t_{½} = \ln 2/k$

$k = Ae^{-Ea/RT}$

$\ln[A] = \ln[A]_0 - kt$

$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

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 = $4\pi r^2$

Volume of sphere = $^4/_3\ \pi r^3$

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

$A = -\log\frac{I}{I_0}$

$A = \varepsilon cl$

$E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$

Colligative Properties & Solutions

$\Pi = cRT$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$c = kp$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

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]