Topics in the November 2008 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2008-N-2:

- Metal Complexes
- Strong Acids and Bases
- Weak Acids and Bases

2008-N-3:

- Physical States and Phase Diagrams

2008-N-4:

- Kinetics

2008-N-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2008-N-6:

- Solubility Equilibrium

2008-N-7:

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

2008-N-8:

- Alkenes
- Organic Halogen Compounds

2008-N-9:

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

2008-N-10:

- Alkenes
- Structural Determination
- Alcohols
- Organic Halogen Compounds
- Synthetic Strategies

2008-N-11:

- Structural Determination
- Stereochemistry

2008-N-12:

- Stereochemistry
- Carboxylic Acids and Derivatives

22/02(a)

The University of Sydney

FUNDAMENTALS OF CHEMISTRY 1B - CHEM1002

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 19 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.
- Pages 14, 16, 20 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-9	32	

Short answer section

Page	Marks: Max	Gained		Marker
10	8			
11	6			
12	4			
13	6			
15	8			
17	8			
18	6			
19	6			
21	5			
22	7			
23	4			
Total	68			

Marks

- The nickel(II) ion exists as the $[Ni(OH_2)_6]^{2+}$ complex ion in aqueous solution. Define the term complex. **4**

What is the name of this complex ion?

Why is such a solution acidic?

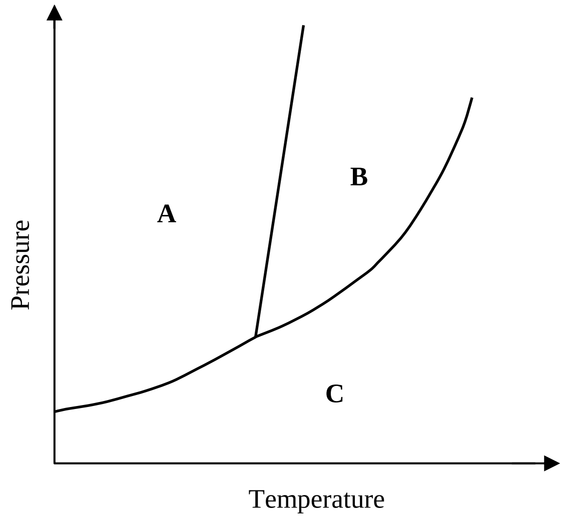
Write a balanced equation for the corresponding reaction.

- You have completed a number of titrations during your laboratory work. What is the difference between the 'end point' and the 'equivalence point' in a titration? **4**

How do you need to consider that distinction when you chose an indicator for a particular titration?

Marks
6

- Examine the following pressure/temperature phase diagram for a one component system.



Which phase exists in the fields labelled **A**, **B** and **C**?

A:	**B**:	**C**:

Explain your assignment of these phases.

What do the lines in the diagram represent?

What happens when you move across a line either by changing temperature or pressure?

For a compound with this phase diagram, would the solid be denser than the liquid or vice versa? Explain your answer.

Marks
4

- The data given in the table below were obtained for the reaction between nitric oxide and chlorine at 1400 K.

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

Experiment number	INITIAL $[Cl_2]$ (mol L^{-1})	INITIAL [NO] (mol L^{-1})	INITIAL REACTION RATE (mol L^{-1} s^{-1})
1	0.10	0.10	0.18
2	0.20	0.10	0.36
3	0.10	0.20	0.72

Deduce the rate law for this reaction and calculate the value of the rate constant.

RATE LAW	RATE CONSTANT
Answer:	Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- Calculate the pH of a 0.020 M solution of $Ba(OH)_2$. **1**

pH =

- Calculate the pH of a 0.150 M solution of HNO_2. The pK_a of HNO_2 is 3.15. **3**

pH =

- Calculate the pH of a solution that is 0.080 M in acetic acid and 0.160 M in sodium acetate. The pK_a of acetic acid is 4.76. **2**

pH =

Marks

- Hydrogen bonding is important for the physical properties of water and consequently the very existence of life on earth. What effect does the formation of hydrogen bonding have on the density of solid water (ice) compared to liquid water. Explain. **4**

Predict the physical form of water under ambient conditions if no hydrogen bonds existed. Explain that prediction.

- $BaSO_4$ is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp}, for $BaSO_4$, given that a maximum of 1.2×10^{-3} g dissolves in 500.0 mL of water. **4**

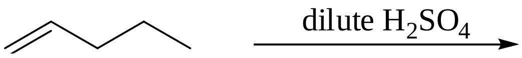
Answer:

Ba^{2+} ions are toxic. Comment on the suitability of $BaSO_4$ as a contrast agent.

What advantage would there be in administering $BaSO_4$ as a slurry which also contains 0.5 M Na_2SO_4?

Marks
8

- Give the name of the starting material where indicated and the constitutional formula of the major organic product formed in each of the following reactions.



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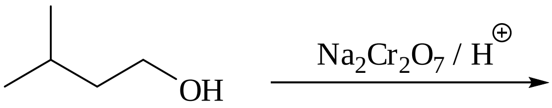

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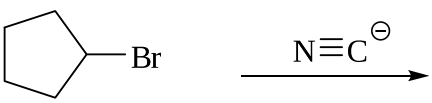
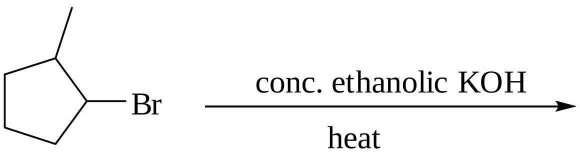
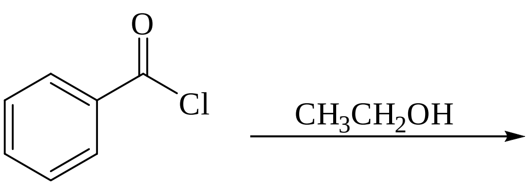


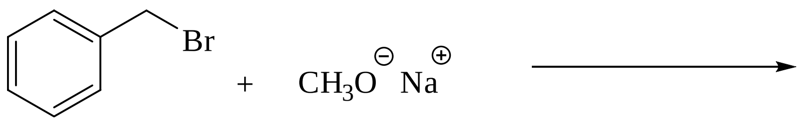
Name:

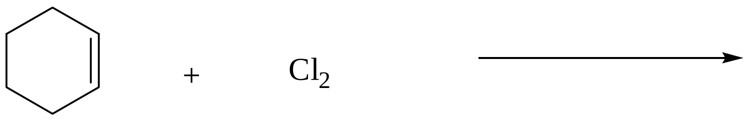




Marks
6

- Classify the starting materials for each of the following reactions as nucleophile and electrophile in the boxes provided and draw the structure of the product.





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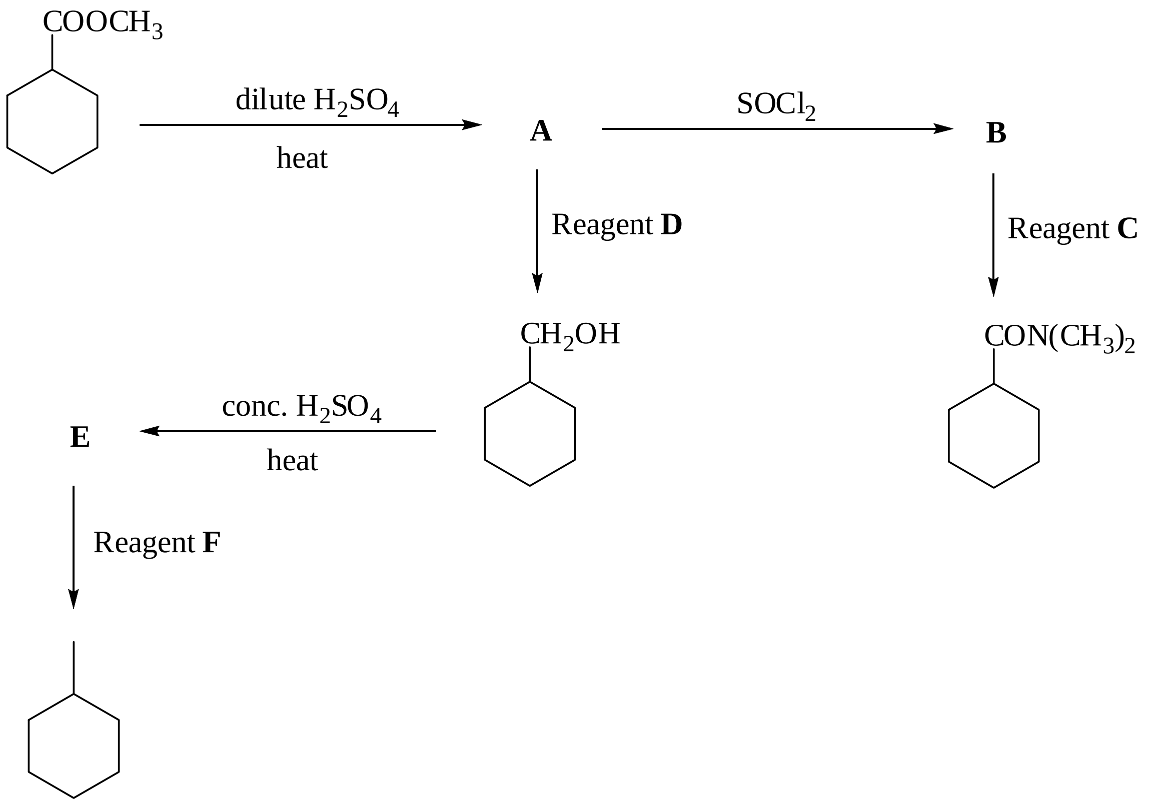
Marks
6

- Consider the following reaction sequence.

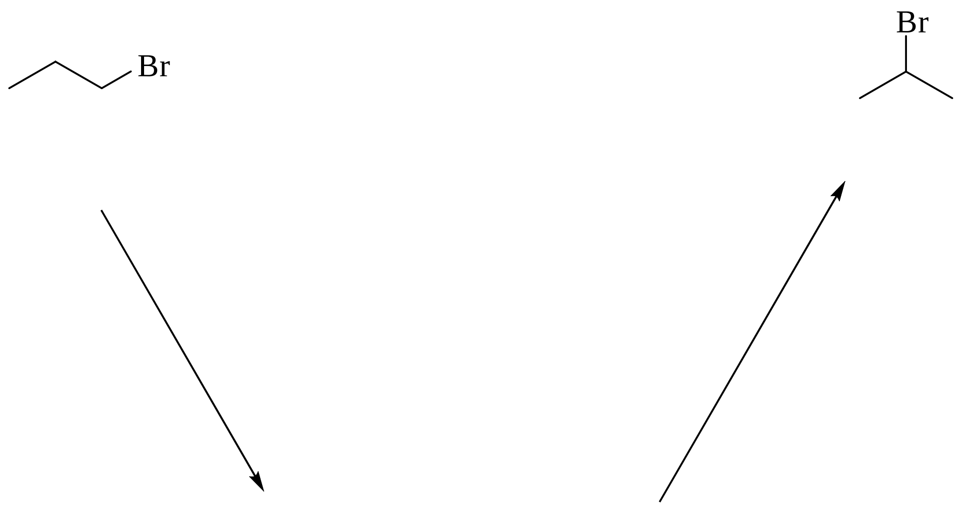


Give the reagents **C**, **D** and **F** and draw the structures of the major organic products, **A**, **B** and **E**, formed in these reactions.

A	**D**
B	**E**
C	**F**

Marks
5

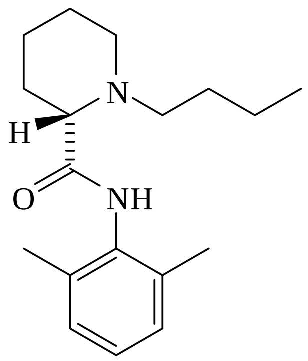
- Show clearly the reagents you would use to carry out the following chemical conversion. Two steps are required. Give the structure of the intermediate compound.



How could you distinguish between the starting material and the product by ^{13}C NMR spectroscopy?

Marks
7

- Bupivacaine is the active molecule in some local anaesthetics. Of the two enantiomers, the one shown below (**X**) is the more effective.



(**X**)

What is the molecular formula of (**X**)?

Calculate the *m*/*z* value for the major peak you would expect to see for the molecular ion in the high resolution mass spectrum.
[Atomic masses: ^{1}H = 1.0078; ^{12}C = 12.0000; ^{16}O = 15.9949; ^{14}N = 14.0031]

Answer:

List the substituents attached to the stereogenic centre in descending order of priority according to the sequence rule.

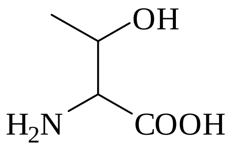
highest priority			lowest priority

What is the absolute stereochemistry of (**X**)? Write (*R*) or (*S*).

Name the functional groups present in (**X**).

Marks
4

- Threonine (**Y**) is an amino acid. On the structure of (**Y**) below, identify all stereocentres in threonine with an asterisk (*).



(**Y**)

How many possible stereoisomers of threonine are there?

Give the structures of the products obtained when threonine is treated with the following reagents.

1 M HCl	1 M NaOH

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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

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

CHEM1002 - FUNDAMENTALS OF CHEMISTRY 1B

Standard Reduction Potentials, *E°*

Reaction	*E°* / V
$S_2O_8^{2-}$ + $2e^-$ → $2SO_4^{2-}$	+2.01
$Co^{3+}(aq)$ + e^- → $Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq)$ + e^- → $Ce^{3+}(aq)$	+1.72
$Au^{3+}(aq)$ + $3e^-$ → $Au(s)$	+1.50
Cl_2 + $2e^-$ → $2Cl^-(aq)$	+1.36
O_2 + $4H^+(aq)$ + $4e^-$ → $2H_2O$	+1.23
Br_2 + $2e^-$ → $2Br^-(aq)$	+1.10
$MnO_2(s)$ + $4H^+(aq)$ + e^- → Mn^{3+} + $2H_2O$	+0.96
$Pd^{2+}(aq)$ + $2e^-$ → $Pd(s)$	+0.92
$Ag^+(aq)$ + e^- → $Ag(s)$	+0.80
$Fe^{3+}(aq)$ + e^- → $Fe^{2+}(aq)$	+0.77
$Cu^+(aq)$ + e^- → $Cu(s)$	+0.53
$Cu^{2+}(aq)$ + $2e^-$ → $Cu(s)$	+0.34
$Sn^{4+}(aq)$ + $2e^-$ → $Sn^{2+}(aq)$	+0.15
$2H^+(aq)$ + $2e^-$ → $H_2(g)$	0 (by definition)
$Fe^{3+}(aq)$ + $3e^-$ → $Fe(s)$	–0.04
$Pb^{2+}(aq)$ + $2e^-$ → $Pb(s)$	–0.13
$Sn^{2+}(aq)$ + $2e^-$ → $Sn(s)$	–0.14
$Ni^{2+}(aq)$ + $2e^-$ → $Ni(s)$	–0.24
$Co^{2+}(aq)$ + $2e^-$ → $Co(s)$	–0.28
$Fe^{2+}(aq)$ + $2e^-$ → $Fe(s)$	–0.44
$Cr^{3+}(aq)$ + $3e^-$ → $Cr(s)$	–0.74
$Zn^{2+}(aq)$ + $2e^-$ → $Zn(s)$	–0.76
$2H_2O$ + $2e^-$ → $H_2(g)$ + $2OH^-(aq)$	–0.83
$Cr^{2+}(aq)$ + $2e^-$ → $Cr(s)$	–0.89
$Al^{3+}(aq)$ + $3e^-$ → $Al(s)$	–1.68
$Mg^{2+}(aq)$ + $2e^-$ → $Mg(s)$	–2.36
$Na^+(aq)$ + e^- → $Na(s)$	–2.71
$Ca^{2+}(aq)$ + $2e^-$ → $Ca(s)$	–2.87
$Li^+(aq)$ + e^- → $Li(s)$	–3.04

CHEM1002 - FUNDAMENTALS OF 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]