Topics in the November 2009 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2009-N-2:

- Physical States and Phase Diagrams

2009-N-3:

- Periodic Trends
- Weak Acids and Bases

2009-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2009-N-5:

- Coordination Chemistry

2009-N-6:

- Kinetics

2009-N-7:

- Solubility Equilibrium

2009-N-8:

- Alkenes
- Alcohols
- Amines
- Organic Halogen Compounds

2009-N-9:

- Alcohols
- Amines
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2009-N-10:

- Alkenes
- Stereochemistry
- Carboxylic Acids and Derivatives

2009-N-11:

- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2009-N-12:

- Structural Determination
- Synthetic Strategies

22/02(a)

The University of Sydney

FUNDAMENTALS OF CHEMISTRY 1B - CHEM1002

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2009 **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 13, 19, 21 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

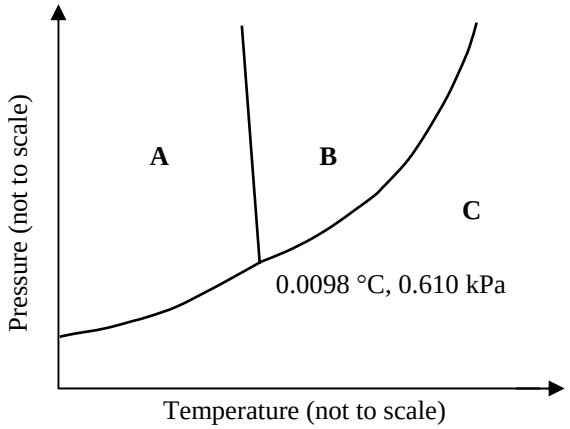
	Marks	
Pages	Max	Gained
2-9	32	

Short answer section

Page	Marks Max	Gained		Marker
10	6			
11	7			
12	6			
14	6			
15	2			
16	6			
17	8			
18	6			
20	7			
22	6			
23	8			
Total	68			

Marks 6

- Consider the pressure/temperature phase diagram of H_2O shown below.



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

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

What are the temperature and pressure for the normal boiling point of water?

Use the phase diagram to explain why it takes longer to hard boil eggs on the top of a 6000 m high mountain rather than at sea level.

The unusual property of water, with the solid being less dense than the liquid, can be deduced from the phase diagram. How?

	Marks
• The periodic table lists elements in a systematic fashion. Briefly explain why the atomic radii decrease in period 3 (Na $\rightarrow$ Cl) from left to right.	**3**
What consequence does the shrinking atomic size have for the nature and reactivity of these elements?	
• Conjugate acid/base pairs exist in aqueous solutions of weak acids. What is the difference between a weak acid and its conjugate base?	**4**
How are the strength of a weak acid and its conjugate base related?	
From the following list select 2 conjugate acid/base pairs. Identify acid and base in both pairs. $H_2PO_4^+$ H_2CO_3 $H_2PO_4^-$ H_2SO_4 HPO_4 SO_4^{2-} H_3PO_4 HCO_3^- HPO_4^{2-}	

Marks 6

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

How do you determine the concentration of a weak acid through titration with a strong base? Include all necessary steps in your explanation.

How do you determine the pK_a of a weak acid through titration with a strong base? Include all necessary steps in your explanation.

Marks 6

- Dissolution of iron(II) chloride in water leads to formation of $Fe^{2+}(aq)$ and $Cl^{-}(aq)$ ions. Draw a picture of the complex ion present, clearly showing the stereochemistry and which atoms are bonded to the Fe(II) ion.

This complex is paramagnetic. Using the box notation to represent atomic orbitals, account for this property.

Solutions containing the $Fe^{2+}(aq)$ ion are acidic. Account for this property and write the chemical equation for the reaction that leads to this acidity.

	Marks
• Assuming aspirin has a half life of around 3 hours in the body, how much of an 80 mg dose will still be in the body after 1 day?	**2**
Answer:	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

- The pH of the ocean before the industrial revolution was around 8.22. Show that this pH corresponds to a concentration of $[OH^-(aq)] = 1.7 \times 10^{-6}$ M.

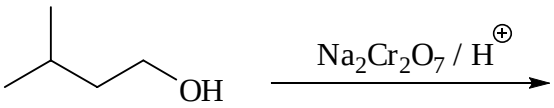
All forms of life depend on iron and the concentration of iron in the oceans and elsewhere is one of the primary factors limiting the growth rates of the most basic life forms. One reason for the low availability of iron(III) is the insolubility of the hydroxide, $Fe(OH)_3$, which has a K_{sp} of only 1×10^{-39}. What was the maximum concentration of $Fe^{3+}(aq)$ at a pH of 8.22?

Answer:

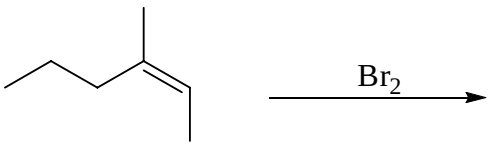
Industrialisation has led to an increase in atmospheric CO_2. What effect has this had on the amount of $Fe^{3+}(aq)$ in sea water?

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.



Name:



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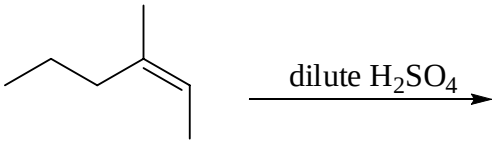
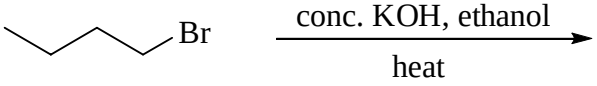
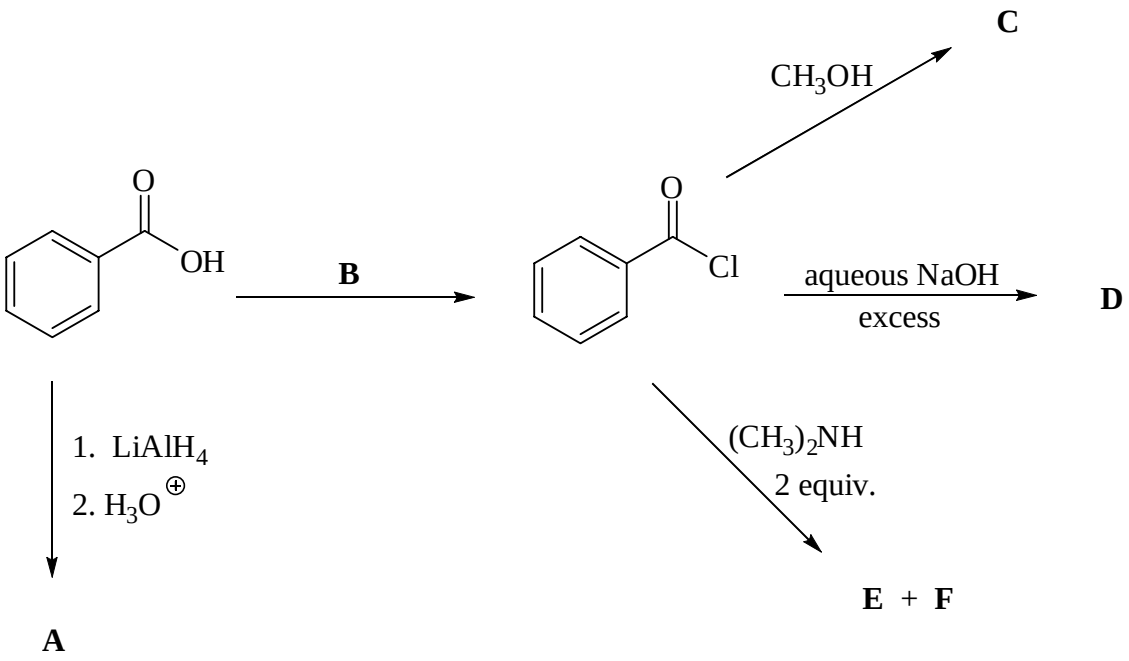




Name:

Marks
6

- Consider the following reaction sequence.

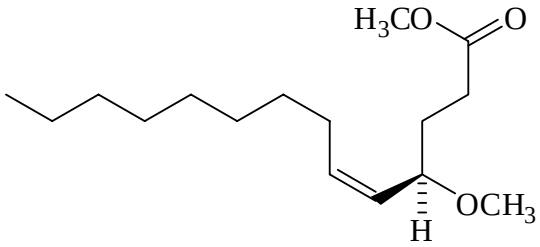


Give the reagent **B** and draw the constitutional formulas of the major organic products, **A**, **C**, **D**, **E** and **F**, formed in these reactions.

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

Marks 7

- Compound (**X**) is a derivative of a naturally occurring Japanese beetle pheromone.



(**X**)

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

What is the stereochemistry of the C–C double bond in (**X**)?

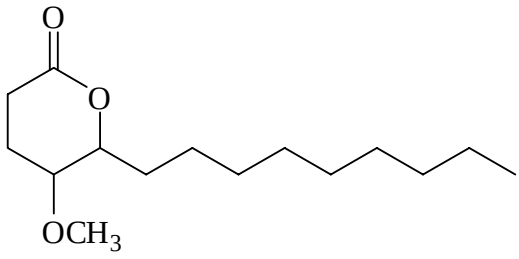
List the substituents attached to the stereogenic centre in descending order of priority according to the sequence rule.

highest priority			lowest priority

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

On heating with 4 M H_2SO_4, one of the products obtained is compound (**Y**), whose structure is shown on the right. Explain the formation of this product.

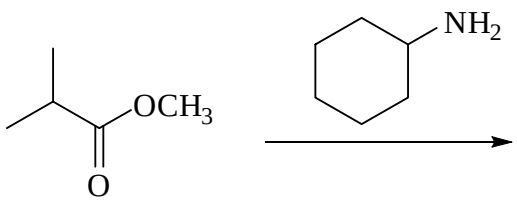
(**Y**)

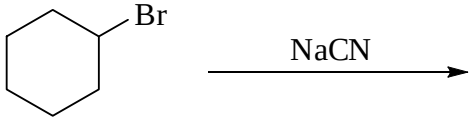


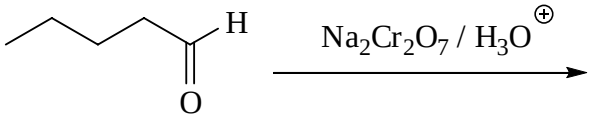
How many different stereoisomers are possible for compound (**Y**)?

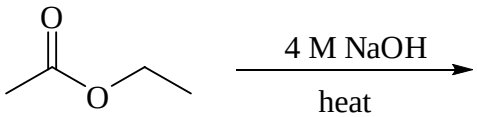
Marks 6

- Give the constitutional formula(s) of the organic products formed in each of the following reactions.



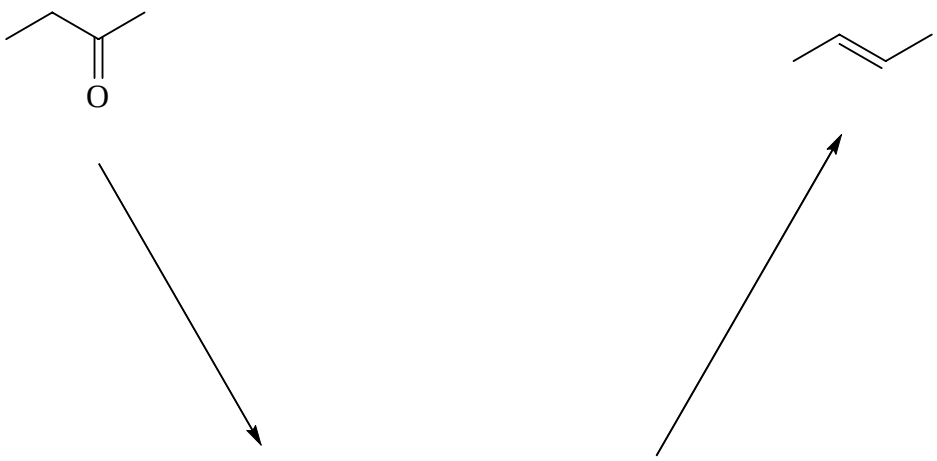






Marks 8

- 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 can IR spectroscopy distinguish between the starting material, the intermediate and the product?

How can ^{13}C NMR spectroscopy distinguish between the starting material, the intermediate and the product?

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 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2}

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
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.01
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-(aq)$	+1.10
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+}(aq) + 2H_2O$	+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
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$	+0.62
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+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

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 $e^- = It/F$

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

$= E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

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

$E = E° - \frac{0.0592}{n} \log Q$ (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

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

$E_k = \frac{1}{2}mv^2$

Radioactivity

$t_{1/2} = \ln 2/\lambda$

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age $= 8033 \ln(A_0/A_t)$ years

Kinetics

$t_{1/2} = \ln 2/k$

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

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

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

Colligative Properties and 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 and Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta_{univ} S° = R \ln K$

$K_p = K_c (RT)^{\Delta n}$

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 $= \pi r^2$

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]							

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]