22/08(a)

The University of Sydney

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2007

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	36	

Short answer section

Page	Marks Max	Gained		Marker
11	5			
12	6			
13	4			
14	6			
15	4			
16	3			
17	3			
18	5			
19	5			
20	7			
21	5			
22	5			
23	6			
Total	64			

Marks
5

- Often pH is used to characterise acidic solutions. Give a brief definition of pH.

Describe the difference between a strong acid and a weak acid.

In general, can pH be used to define the strength of an acid? Explain your answer.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Rank $H_2O(l)$, $H_2S(aq)$ and HF(aq) in order of their Brønsted acid strengths. Explain your reasoning.

Marks 2

- Buffer systems are frequently used in chemistry. Briefly describe a buffer system and how it functions? Use equations where appropriate.

4

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 4.00? The K_a of acetic acid is 1.8×10^{-5} M.

Answer:

Marks 4

- Barium sulfate 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 1.167×10^{-8} g will dissolve in 500 mL of water?

Answer:

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

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- What is a chelate ligand?

Marks
4

Draw all possible isomers of $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$

- Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3} M, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9} M.

2

	Marks
• You may recall from a lecture demonstration or your laboratory work that solid CO_2 sublimes under ambient conditions while ice melts. Define the terms sublimation and melting.	**3**
What is a triple point (*e.g.* in the phase diagram of CO_2 or H_2O)?	
What does the different behaviour of ice and solid CO_2 indicate about the relative positions of their respective triple points?	
• Carbon has a number of allotropes, the two major ones being graphite and diamond. The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?	**1**

Marks 3

- Hydrogenation of nitric oxide to nitrogen and water is a potential means of reducing smog-forming NO_x gases:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0).

Run	P_0 (H_2) / kPa	P_0 (NO) / kPa	Rate / kPa s^{-1}
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

Derive an expression for the rate law for this reaction.

Answer:

Calculate the value of the rate constant.

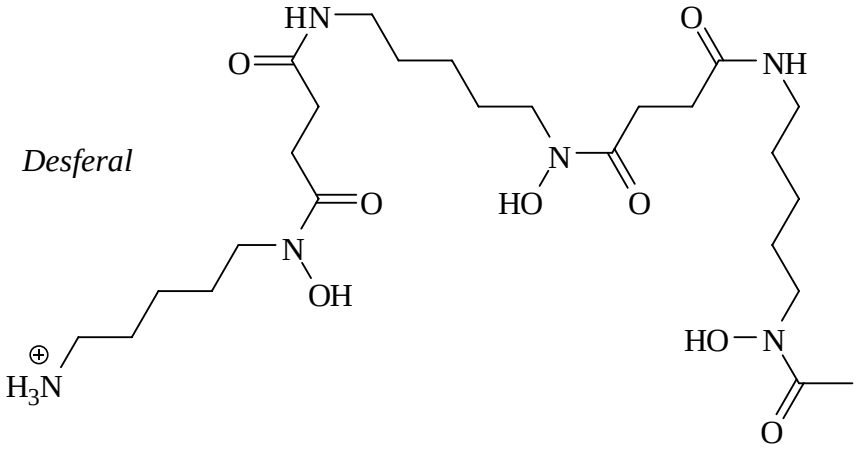
Answer:

What is the order of the reaction?

Marks 3

- Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (*Desferal*), a natural substance isolated from fungi.

Desferal



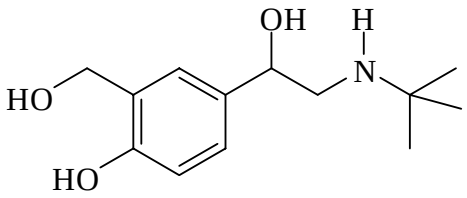
Desferal is taken over 8-12 hour periods up to six times per week. A value of log K = 30.6 is associated with the following equilibrium:

$$Fe^{3+} + LH_3^{+} \rightleftharpoons FeL^{+} + 3H^{+} \quad \text{where } LH_3^{+} = \textit{Desferal}$$

Briefly describe the chemical basis for the use of *Desferal* in iron overload therapy.

Marks 5

- The structure of salbutamol, a drug used to treat bronchospasms, is given below.



Give the molecular formula of salbutamol.

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:

Give the structure(s) of the major organic products formed when salbutamol is treated with the following reagents.

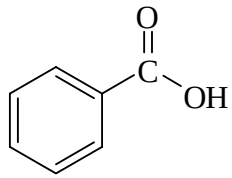
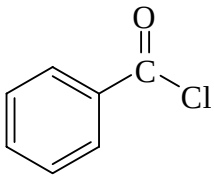
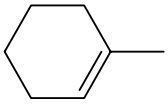
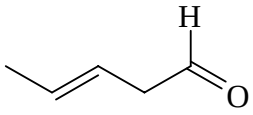
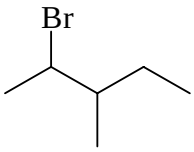
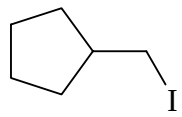
cold HCl (1 M)

NaOH (1 M)

$Cr_2O_7^{2\ominus}$/ $H^{\oplus}$

Marks 5

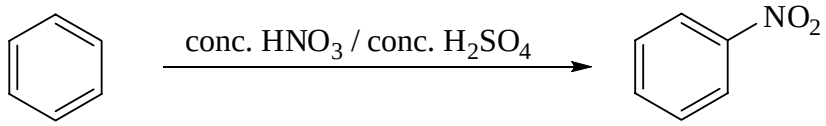
- Complete the following table.

Starting material	Reagents / Conditions	Major organic product(s)
		
	HCl	
	1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	
	hot conc. KOH ethanol (solvent)	
	$CN^{\ominus}$	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

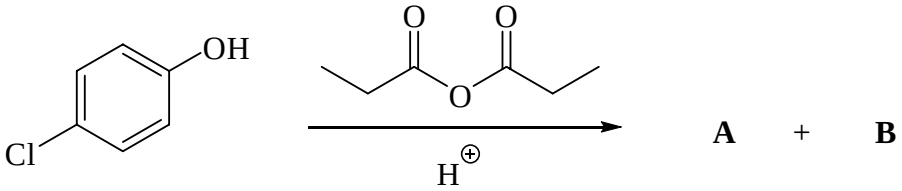
Marks

- A mixture of concentrated nitric and sulfuric acids generates the nitronium ion, NO_2^+. Benzene will react with such a mixture to give nitrobenzene. **2**



What 3-part name is given to the mechanism of this nitration reaction?

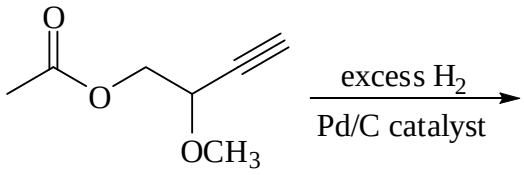
- Consider the reaction sequence below. **2**



Draw the structures of products **A** and **B**.

A	**B**

- Draw the structure of the product, **C,** from the following reaction. **3**

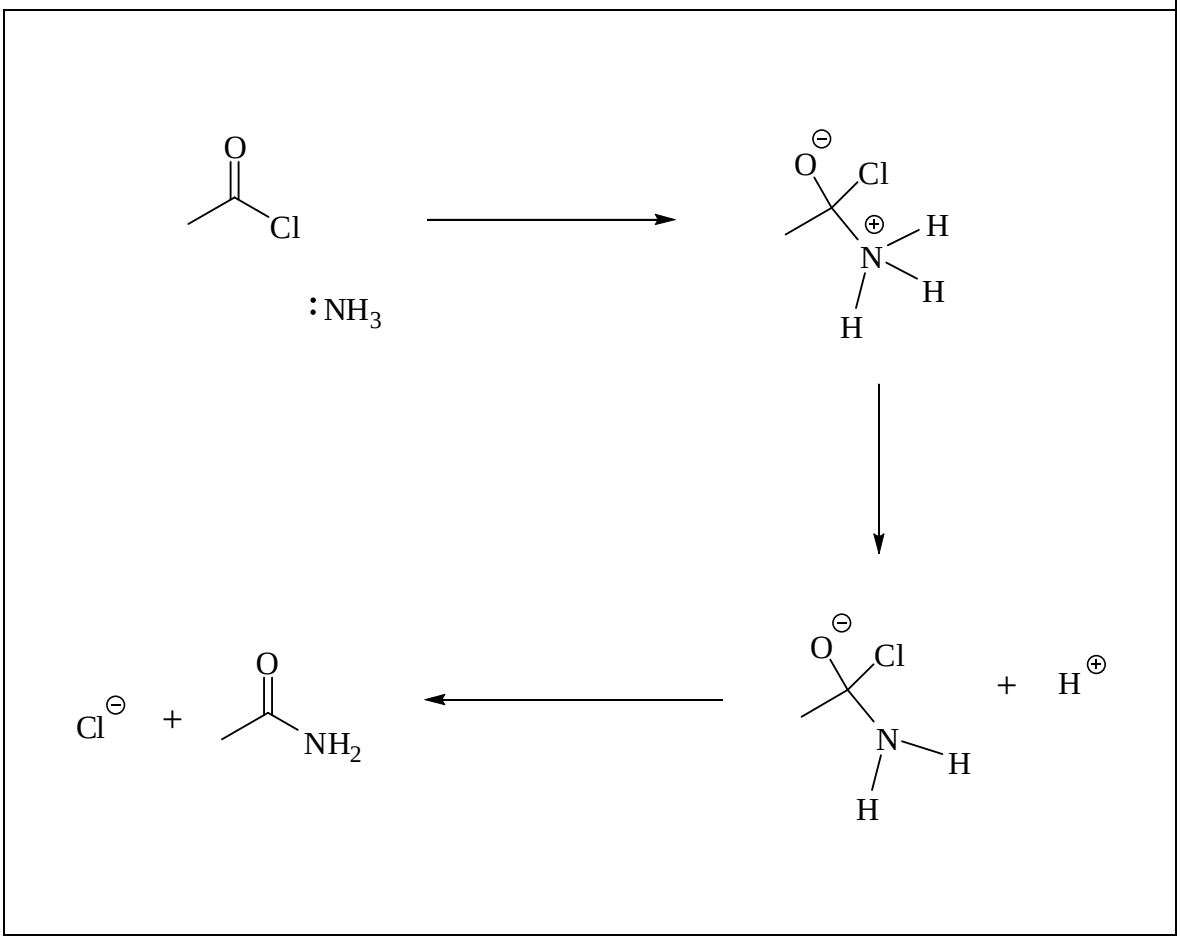


C

Product **C** undergoes hydrolysis when heated with 4 M NaOH. Give the structures of the products (in their correct ionic states) formed in this reaction.

Marks 5

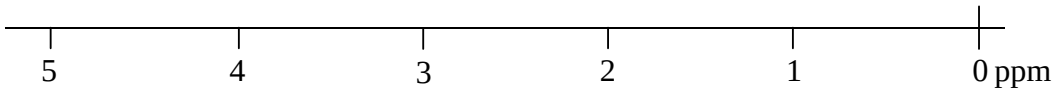
- The incomplete proposed mechanism for the reaction of acetyl chloride with ammonia is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Sketch the ^{1}H NMR spectrum of bromoethane, CH_3CH_2Br. The signals appear at 1.7 and 3.3 ppm. Clearly indicate the splitting patterns of both signals and show their relative intensities.

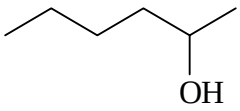
Marks 5



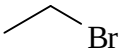
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

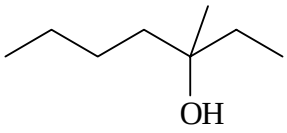
Marks 6

- Devise a synthesis of 3-methylheptan-3-ol using the two starting materials shown. Show the structures of any intermediate products involved, as well as the reagents required for each step. More than one step is required.



and





Would the product be isolated as a racemic mixture or a single enantiomer or is the product achiral?

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}

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}

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

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

Quantum Chemistry

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

$\lambda = h/mv$

$4.5k_BT = hc/\lambda$

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

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

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

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

$PV = nRT$

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

Colligative properties

$\pi = cRT$

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

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Kinetics

$t_{½} = \ln 2/k$

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

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

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

Radioactivity

$t_{½} = \ln 2/\lambda$

$A = \lambda N$

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

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

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

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

Miscellaneous

$A = -\log_{10} \frac{I}{I_0}$

$A = \varepsilon cl$

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

Mathematics

If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

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]							

LANTHANIDES	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
ACTINIDES	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]