Topics in the June 2010 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2010-J-2:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2010-J-3:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2010-J-4:

2010-J-5:

- Nuclear and Radiation Chemistry
- Types of Intermolecular Forces

2010-J-6:

- Lewis Structures
- VSEPR

2010-J-7:

- Thermochemistry

2010-J-8:

- Chemical Equilibrium

2010-J-9:

- Chemical Equilibrium

2010-J-10:

- First and Second Law of Thermodynamics

2010-J-11:

- First and Second Law of Thermodynamics
- Band Theory - MO in Solids
- Polar Bonds
- Ionic Bonding
- Lewis Structures

2010-J-12:

- Electrochemistry
- Electrolytic Cells

2221(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

JUNE 2010 **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 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 24 is for rough working only.

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~~**Multiple choice section**~~

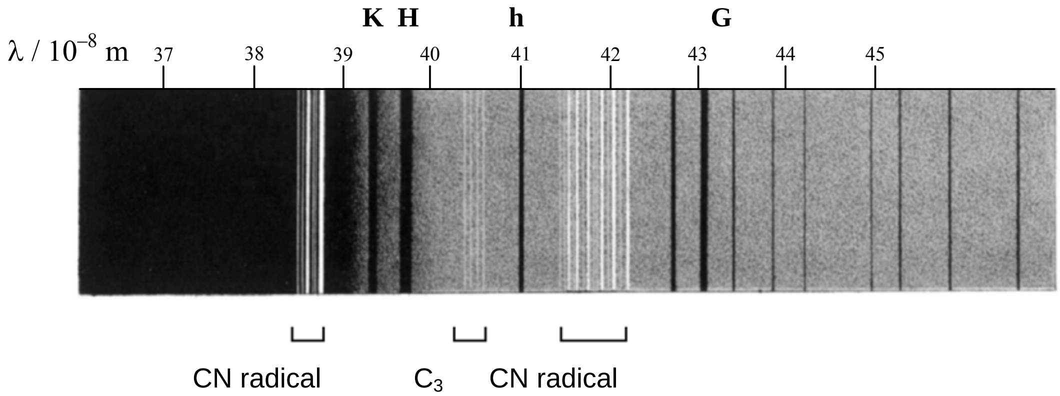
	Marks	
Pages	Max	Gained
2-11	31	

Short answer section

Page	Marks: Max	Marks: Gained		Marker
12	4			
13	7			
14	11			
15	6			
16	6			
17	3			
18	5			
19	7			
20	4			
21	5			
22	7			
23	4			
Total	69			

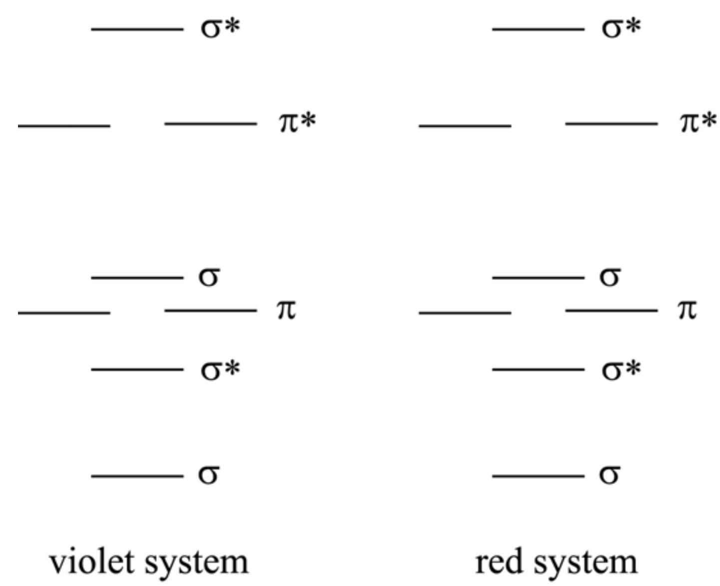
Marks
4

- The "Great Comet of 1881" was discovered by Tebbutt from his observatory at Windsor, NSW. Observations by Huggins of the comet's emission spectrum (pictured) revealed the presence of what was later determined to be the CN radical.



This emission system of CN is known as the "violet system", and results from a radical returning to the ground state as an electron makes a transition from a σ orbital to a σ* orbital. The "red system" of CN results from a radical returning to the ground state as an electron makes a transition from a σ orbital to a π orbital.

On the diagram below, indicate the orbital occupancy, using arrow notation, of the upper electronic states of the "violet" and "red" systems of CN. Also indicate how the excited electron relaxes when the radical emits light (use a curved arrow).



THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

Marks
7

Explain in terms of bond order why the upper state of the violet system exhibits a shorter bond length (1.15Å) than the ground state (1.17Å).

Also indicated in Huggin's spectrum are the Fraunhofer absorption features labelled K, H and G, which arise from calcium. Explain the appearance of these features. (Hint: they would also appear in the spectrum of moonlight.)

The Fraunhofer feature labelled 'h' is due to atomic hydrogen. What is the electronic transition responsible for this absorption feature? (Hint: one of the energy levels involved is n = 2.)

Marks 11

- Thorium is a naturally occurring metal estimated to be about three to four times more abundant than uranium in the Earth's crust. Naturally occurring thorium is composed mainly of one isotope, ^{232}Th, and is an alternative fuel for nuclear energy production.

  ^{232}Th can absorb slow neutrons to produce ^{233}U via the intermediates ^{233}Th and ^{233}Pa. Write balanced nuclear equations to describe this sequential process.

When struck by a neutron, an atom of ^{233}U can undergo α-decay generating 200 MeV of energy. What initial mass of thorium ^{232}Th would be required to provide 6×10^{18} J, Australia's energy needs for one year?

Answer:

^{232}Th also undergoes a (*n*,2*n*) reaction to form ^{231}Th, which subsequently decays to ^{231}Pa. This side reaction is a major contributor to the long term radiotoxicity of spent nuclear fuel. Calculate the activity (in Bq) of 1.0 g of each of these isotopes.

Data:

Isotope	^{232}Th	^{231}Th	^{231}Pa
half life	1.405×10^{10} years	25.5 hours	3.27×10^{4} years

^{232}Th:	^{231}Th:	^{231}Pa:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

How long does it take 1.0 g of ^{231}Th to decay to the same activity as 1.0 g of ^{232}Th? **Marks** **3**

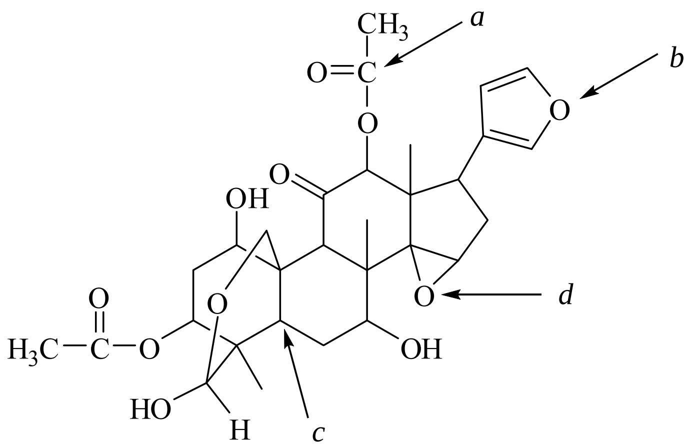
Answer:

- Rationalise the order of the boiling points of the following liquids in terms of their intermolecular forces. **3**

liquid	F_2	HCl	HBr	HI	Cl_2	HF	Br_2	I_2
b.p. (° C)	–188	–85	–67	–35	–34	20	59	184

Marks
6

- Toosendanin (pictured) is an ingredient from traditional Chinese medicine and is effective as an antibotulismic agent both *in vitro* and *in vivo*. The compound can prevent death in animals suffering from botulism and help restore normal activity. It may also help to treat *Botox* overdoses in humans.



Complete the table concerning the atoms *a*, *b* and *c* indicated by the arrows.

Selected atom	Number of σ-bonds associated with the selected atom	Geometry of σ-bonds about the selected atom
a		
b		
c		

Comment on the actual bond angle exhibited by atom *d* as compared to electronically similar atoms elsewhere in the molecule. Is this *epoxide* group likely more or less reactive than an ether? Explain.

Marks
3

- Calcium chloride (1.14 g) is completely dissolved in 100.0 mL of water at 27.00 °C in a 'coffee cup' calorimeter. The temperature of the water after dissolution is 28.97 °C. Calculate the standard enthalpy of solution of $CaCl_2$ (in kJ mol^{-1}). The density of water at 27.0 °C is 0.997 g mL^{-1} and its heat capacity is 4.184 J K^{-1} g^{-1}. Ignore the heat capacity of the $CaCl_2$.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
5

- Ethanol is produced industrially by reacting ethylene with water according to the following equation.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \qquad \Delta H^\circ = -47.8 \text{ kJ mol}^{-1}$$

Equal masses of solid ethylene and water ice are introduced to a 1.00 L flask at 100 K. The flask is evacuated of air, sealed and heated to 600 K. When equilibrium is reached, the flask contains 0.098 mol of ethylene gas and the total pressure is 26.5 atm. What mass of ethylene was introduced to the flask originally?

Answer:

The same experiment is carried out in another flask, but with different initial masses of ethylene and ice. At equilibrium, this flask contains 5.81×10^{-3} mol of H_2O, 1.21×10^{-2} mol of C_2H_4, and 6.33×10^{-1} mol of ethanol. Calculate the concentration equilibrium constant, K_c, at 600 K.

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
7

Calculate the partial pressure equilibrium constant, K_p, at 600 K.

Answer:

What is the standard entropy change $\Delta S°$ (in J K^{-1} mol^{-1}) for the forward reaction at 600 K?

Answer:

How will the yield of ethanol be affected by the following changes?

The volume of the flask is increased.

The temperature is increased.

The walls of the flask are cooled so that only liquid water condenses out.

A catalyst is added.

Marks
4

- Iron oxide that has been exposed to the atmosphere for any length of time will generally contain a mixture of magnetite, Fe_2O_3, and haematite, Fe_3O_4. This mixture can be converted to pure Fe_3O_4 by heating it under an excess of flowing hydrogen gas:

$$3Fe_2O_3(s) + H_2(g) \rightarrow 2Fe_3O_4(s) + H_2O(g) \qquad \Delta H° = -11.0 \text{ kJ mol}^{-1}$$

If 0.0364 kJ of heat is liberated during the conversion of a 7.18 g sample of iron oxide (consisting only of magnetite and haematite) to pure Fe_3O_4, what was the initial mass percentage of haematite in the sample?

Answer:

Fe_3O_4 can be further reduced to FeO under flowing hydrogen.

$$Fe_3O_4(s) + H_2(g) \rightarrow 3FeO(s) + H_2O(g)$$

Based on the following table of thermodynamic data, what is the minimum temperature at which this would be a spontaneous reaction?

	Fe	FeO(s)	Fe_3O_4(s)	H_2(g)	H_2O(g)
$\Delta_f H°$ (kJ mol^{-1})		–272	–1118		–242
$S°$ (J K^{-1} mol^{-1})	27	61	146	131	189

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
5

Would the resulting FeO be stable under those conditions, or would it be reduced further to Fe metal by the following reaction?

$$FeO(s) + H_2(g) \rightarrow Fe(s) + H_2O(g)$$

Explain, with calculations as appropriate.

Describe the nature of the bonding in (i) FeO(s), (ii) H_2(g) and (iii) Fe(s).

Marks

5

- A voltaic cell is set up at 298 K based on the following reaction

$$Cr^{3+}(aq) + Al(s) \rightleftharpoons Cr(s) + Al^{3+}(aq)$$

Express the overall reaction in voltaic cell notation.

Calculate the cell potential at 298 K when the concentration of $Cr^{3+}(aq)$ is 0.213 M and the concentration of $Al^{3+}(aq)$ is 0.078 M.

Answer:

Calculate the equilibrium constant at 298 K.

Answer:

2

- How long (in seconds) would it take for all the gold to be plated out of 55.0 mL of a 2.34×10^{-3} mol L^{-1} solution of $Au^{3+}(aq)$, using a current of 0.75 A?

Answer:

Marks
4

- The aluminium-air battery, in which aluminium metal is oxidised to Al^{3+} and O_2 is reduced to OH^{-}, is being considered as a power source in cars. Briefly compare the relative merits of such a battery with those of a fuel cell for such applications.

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CHEM1901 - CHEMISTRY 1A (ADVANCED)

CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

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

CHEM1901 - CHEMISTRY 1A (ADVANCED)

CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

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
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+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
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–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

CHEM1901 - CHEMISTRY 1A (ADVANCED)

CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ 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** $t_{1/2} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative Properties & Solutions $\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	**Thermodynamics & Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $K_p = K_c (RT)^{\Delta n}$
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]	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]