22/04(a)

The University of Sydney

CHEMISTRY 1A - CHEM1101

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2003 **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 •.
- 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 sheets.
- Pages 7, 18 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-6	18	

Short answer section

Page	Marks			Marker
	Max	Gained		
8	8			
9	11			
10	6			
11	4			
12	6			
13	6			
14	5			
15	5			
16	4			
17	6			
19	4			
20	6			
21	3			
22	3			
23	5			
Total	82			

Marks
8

- In the spaces provided, explain the meaning of the following terms.

(a) cathode ray

(b) a node on a wave or wavefunction

(c) an n-type semiconductor

(d) aufbau principle

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- Balance the following nuclear reactions by identifying the missing nuclear particle. **4**

$$^{77}_{33}\text{As} \rightarrow ^{77}_{34}\text{Se} + \square$$

$$^{2}_{1}\text{H} + ^{1}_{1}\text{H} \rightarrow ^{3}_{2}\text{He} + \square$$

$$^{16}_{8}\text{O} + ^{1}_{1}\text{p} \rightarrow ^{13}_{7}\text{N} + \square$$

Which of the particles emitted above is the most penetrating and therefore causes the greatest biological damage as an external radiation source?

- Calculate the radiocarbon age of a sample whose ^{14}C activity is 0.344 of a modern standard. **3**

Answer:

- The only stable isotope of fluorine is ^{19}F. Calculate the specific activity of ^{17}F (in Curie), given its half-life of 66 s. **4**

Answer:

Predict the nuclear decay mode of ^{17}F, and briefly discuss its suitability for use in positron emission tomography for medical diagnostics.

Marks

- State one piece of experimental evidence that led to the development of quantum mechanics. **2**

- Sketch the following wave functions as lobe representations. **2**

(a) a 2*p* atomic orbital	(b) a σ* molecular orbital

- Consider a metal target being struck by 30 keV electrons. Calculate the shortest wavelength radiation emitted from the metal target in the continuous (bremsstrahlung) X-ray spectrum. **2**

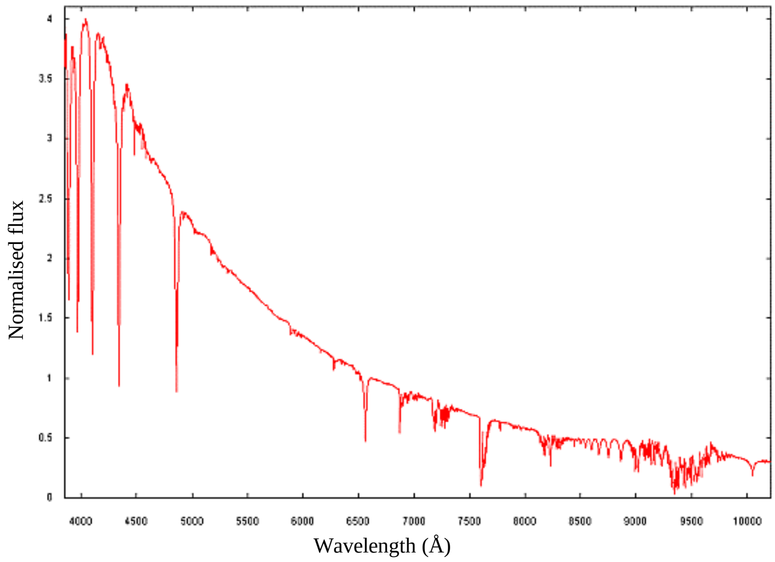
Answer:

Marks

- Write the ground state electron configurations for the following elements. Aluminium is done as an example. **2**

Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
O	
Ge	

- The emission spectrum of the star Vega is shown below. Estimate its temperature from its maximum emission at around 4100 Å. **2**



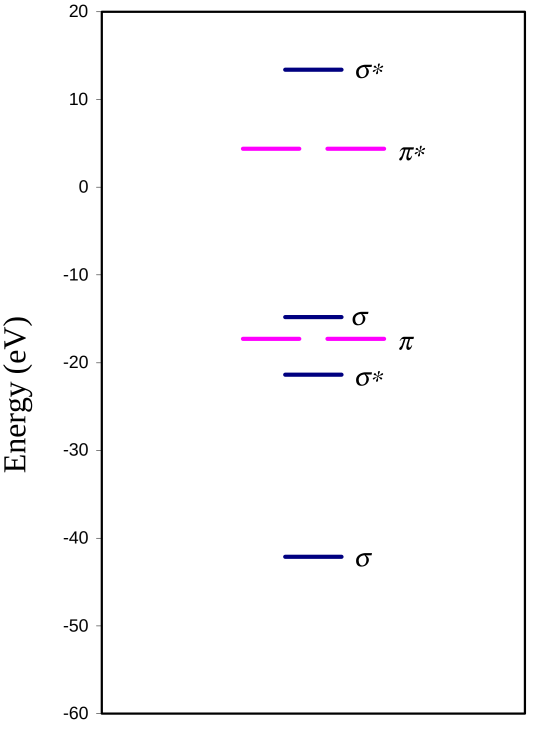
Answer:

Marks
6

- Carbon monoxide, CO, is a toxic gas emitted as a pollutant from car engines.

How many valence electrons are there in CO?

Complete the MO diagram for the ground state of carbon monoxide by inserting the appropriate number of electrons into the appropriate orbitals.



What is the bond order of CO?

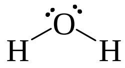
Estimate the absorbance wavelength (in nm) corresponding to the HOMO to LUMO transition.

Answer:

Do you expect CO to be paramagnetic? Explain your answer.

Marks

- Complete the table below showing the number of valence electrons, the Lewis structures and the predicted shapes of the following species. **4**

Formula	Number of valence electrons	Lewis structure	Name of molecular shape
e.g. H_2O	8		Bent (angular)
SF_6			
CH_3^-			

- Briefly explain why the atomic radius increases abruptly from neon to sodium. **2**

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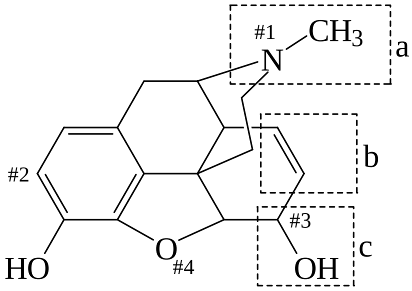
Marks 5

- The structure of morphine is given below.



Name the functional groups in morphine that have been highlighted by the boxes.

a =	
b =	
c =	

What are the approximate bond angles at the labelled atoms?

Atom	Bond angles
#1 N	
#2 C	
#3 C	
#4 O	

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Marks

- In the chlor-alkali process, three useful products are formed, including two of the "top ten" chemicals. Write the overall reaction, identify the two "top ten" chemicals, and propose why the third useful product is not usually harnessed in this process. **3**

Explain why the Na^{+}(aq) is not reduced to Na(s) in this process.

- How does nitric oxide, NO(g), form in a car engine? What happens to the NO once emitted from the tailpipe? Make sure you include the appropriate chemical reactions in your answer. **2**

Marks
4

- A 50.0 mL solution contained 10.00 g of NaOH in water at 25.00 °C. When it was added to a 250.0 mL solution of 0.200 M HCl at 25.00 °C in a "coffee cup" calorimeter, the temperature of the solution rose to 33.95 °C. Assuming the specific heat of the solution is 4.18 J K^{-1} g^{-1}, that the calorimeter absorbs a negligible amount of heat, and that the density of the solution is 1.00 g mL^{-1}, calculate ΔH_r (in kJ mol^{-1}) for the following reaction. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

When the experiment was repeated using 12.00 g of NaOH in water, the temperature increase was the same. Explain.

Marks

- You are a member of a research team of industrial chemists who are discussing the operation of an ammonia plant. Ammonia is formed from nitrogen and hydrogen according to the following equilibrium reaction. **3**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The plant operates close to 700 K, at which K_p is 1.00×10^{-4} atm^{-2} and employs the stoichiometric ratio 1:3 of N_2:H_2. At equilibrium the partial pressure of NH_3 is 50 atm. Calculate the partial pressures of each reactant and hence the total pressure under these conditions.

p(N_2) =	p(H_2) =	p(total) =

- Ammonium carbamate (NH_2COONH_4) is a salt of carbamic acid that is found in the blood and urine of mammals. At 250 ºC, $K_c = 1.58 \times 10^{-8}$ M^3 for the following equilibrium: **3**

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

If 7.81 g of NH_2COONH_4 is introduced into a 0.500 L evacuated container, what is the total pressure inside the container at equilibrium at 250 ºC?

Answer:

Marks

- Diborane (B_2H_6) is a highly reactive compound, which was once considered as a possible rocket fuel for the US space program. Calculate the heat of formation of diborane at 298 K from the following reactions. **2**

Reaction	ΔH_r (kJ mol^{-1})
$2B(s) + {}^{3}/_{2}O_2(g) \rightarrow B_2O_3(s)$	–1273
$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$	–2035
$H_2(g) + {}^{1}/_{2}O_2(g) \rightarrow H_2O(l)$	–286
$H_2O(l) \rightarrow H_2O(g)$	+44

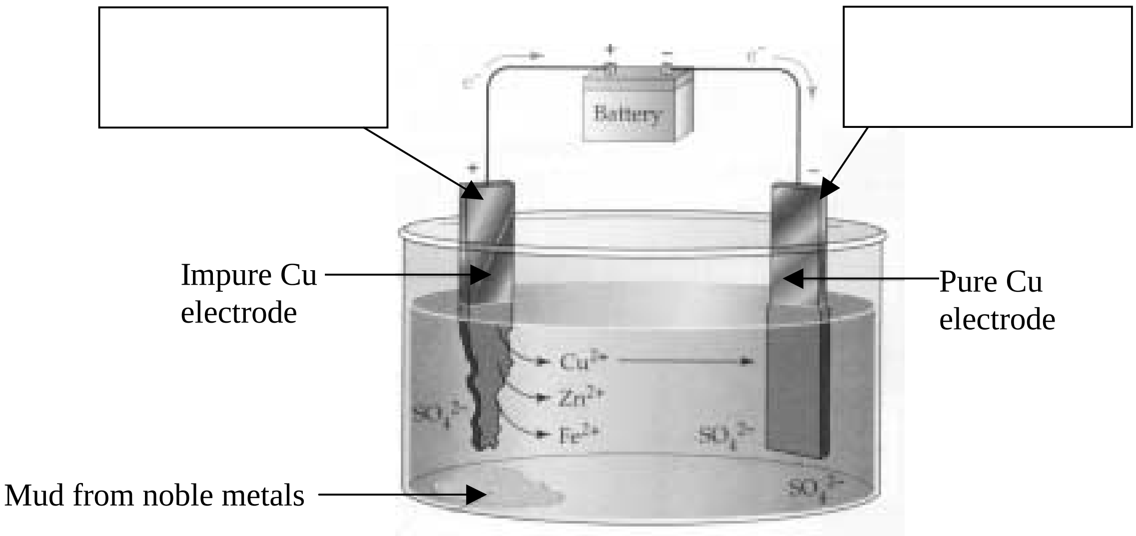
Answer:

- What is meant by "cathodic protection"? Which of the following metals can provide cathodic protection to iron and why? **2**

Zn, Ni, Al, Sn

Marks
6

- In the refining of copper, impure copper electrodes are electrolysed in a manner such as described in the following figure. Indicate in the boxes on the figure, which electrode is the anode and which is the cathode.



Why are noble metals left as a mud on the bottom of the reaction cell?

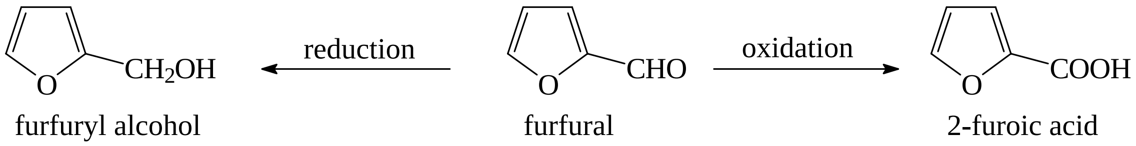
Explain why Zn^{2+} and Fe^{2+} are not deposited from solution during this reaction.

How many kilograms of pure copper will be obtained when the electrolytic cell is operated for 24.0 hours at a constant current of 100.0 A?

Answer:

Marks
3

- Corn is a valuable source of industrial chemicals. For example, furfural is prepared from corncobs. It is an important reactant in plastics manufacture and a key solvent in the production of cellulose acetate, which is used to make products such as videotape and waterproof fabric. Furfural can be reduced to furfuryl alcohol or oxidised to 2-furoic acid. The structures of these three compounds are shown below.



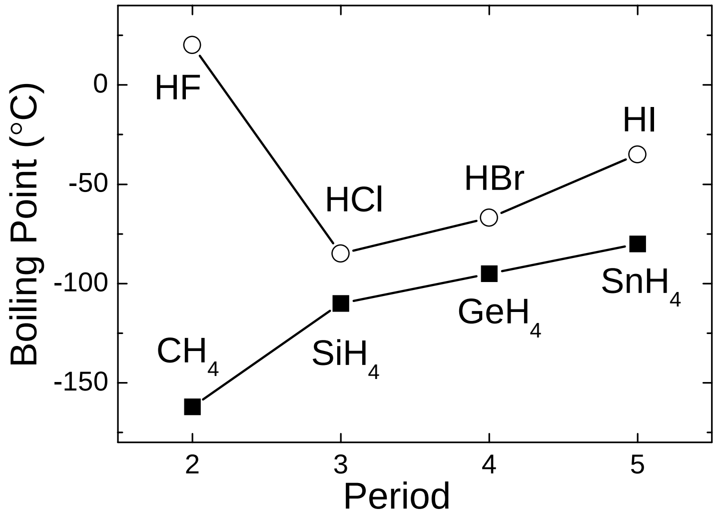
Explain, in terms of oxidation numbers, why we say that furfural is *oxidised* to 2-furoic acid and *reduced* to furfuryl alcohol.

Which of these three compounds can form hydrogen bonds? Draw the structure in each case.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
3

- The figure below shows the boiling points of Group 14 and 17 hydrides as a function of the period (row) of the periodic table.

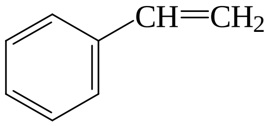


A number of trends are apparent from this figure, including:
- the tetrahydrides have lower boiling points than the monohydrides,
- the boiling point increases with period, with the exception of HF.

Explain these two trends, and the reason that HF is exceptional.

Marks
5

- Styrene is the monomer from which the important polymer, polystyrene, is manufactured. The formula of styrene is shown below.



Draw the repeating unit for polystyrene.

The average C–C bond length in the backbone of polystyrene is 0.154 nm and the C–C–C bond angle is 109.5°. Calculate the total extended end-to-end distance of the polymer chain, and the average radius of gyration in a sample of polystyrene that has a molar mass of 100,000 g mol^{-1}.

Unlike polystyrene, which exhibits free rotation about the C-C single bonds, a polypeptide exhibits restricted rotation in its backbone because of the partial double bond character of the peptide bond. Explain this feature of polypeptides using resonance structures of the peptide bond.

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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}

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}

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

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

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

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Standard Reduction Potentials, $E°$

Reaction	$E°$ / V
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+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
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-(aq)$	–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

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Useful formulas

Quantum Chemistry

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

$\lambda = h/mu$

$4.5k_BT = hc/\lambda$

Gas Laws

$PV = nRT$

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

Kinetics

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

$t_{½} = \ln 2/k$

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

Radioactivity

$A = \lambda N$

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

$t = 8033 \ln(A_0/A_t)$

Colligative properties

$\pi = cRT$

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Electrochemistry

$\Delta G° = -nFE°$

$E = E° - (RT/nF) \ln Q$

$E° = (RT/nF) \ln K$

Moles of e^- $= It/F$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

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

Polymers

$R_g = \sqrt{\frac{nl_0^2}{6}}$

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]									

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]