2214(a)

THE UNIVERSITY OF SYDNEY

CHEM1405 - CHEMISTRY (VETERINARY SCIENCE)

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2012 **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.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	28	

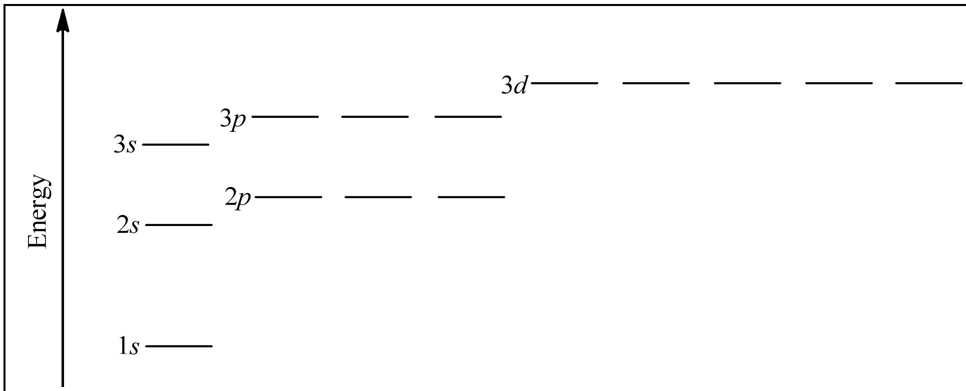
Short answer section

Page	Marks: Max	Marks: Gained		Marker
11	8			
12	7			
13	5			
14	5			
15	5			
16	6			
17	6			
18	7			
19	6			
20	3			
21	4			
22	4			
23	6			
Total	72			

Marks
8

- What is the ground state electron configuration of oxygen?

The following diagram represents the relative energies of the atomic orbitals in the first three shells. Using arrows to represent electrons, show the most stable electron arrangement of the oxygen atom. Label the core electrons and the valence electrons.



Briefly explain how your diagram illustrates the Pauli exclusion principle, Aufbau principle and Hund's rule.

Draw an oxygen molecule showing the shapes of the σ-orbital and the π-orbital present.

Oxygen and sulfur are both Group 16 elements with a valence of two. Oxygen is a diatomic molecule at room temperature, whilst the bonding in solid sulfur consists only of σ-bonds. Suggest reasons why, at room temperature, the O=O molecule is stable and the S=S molecule is not.

Marks
7

- Glycine, NH_2CH_2COOH, the simplest of all naturally occurring amino acids, has a melting point of 292 °C. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. Draw a Lewis structure that indicates the charges on the molecule at the physiological pH of 7.4.

Use your structure to illustrate the concept of resonance.

Describe the hybridisation of the two carbon atoms and the nitrogen atom in glycine and the molecular geometry of the atoms surrounding these three atoms.

Glycine has an unusually high melting point for a small molecule. Suggest a reason for this.

Do you expect glycine to be water soluble? Give a reason for your answer.

Marks
5

- The autoionisation of water conforms to the following balanced equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = 56.3 \text{ kJ mol}^{-1}$$

Is this an exothermic or endothermic reaction?

What will happen to the equilibrium if the temperature is raised?

The equilibrium constant, K, for this reaction is 1.8×10^{-16} at 25 °C. Calculate ΔG.

Answer:

Why is ΔG not equal to ΔH for this reaction?

The pH of pure water is 6.81 at 37 °C. Is water acidic, basic or neutral at this temperature? Explain.

Marks
5

- The radioactive isotopes ^{131}I and ^{137}Cs have been detected in drinking water near the Japanese Fukushima nuclear reactor. They have half lives of 8 days and 30 years, respectively. What is the definition of half-life?

What percentage of both isotopes will still be detectable after 25 years?

^{131}I:	^{137}Cs:

If you were exposed to equal concentrations of both isotopes for 1 hour, which isotope would do more damage? Explain.

Marks
5

- The concentration of a dissolved gas is related to its partial pressure by c = kp. What is the concentration of CO_2 dissolved in blood if the partial pressure of CO_2 in the lungs is 0.053 atm? The k for CO_2 is 0.034 mol L^{-1} atm^{-1}.

Answer:

Calculate the pH of blood if all of this CO_2 reacted to give H_2CO_3.
The K_a of H_2CO_3 is 4.5×10^{-7}.

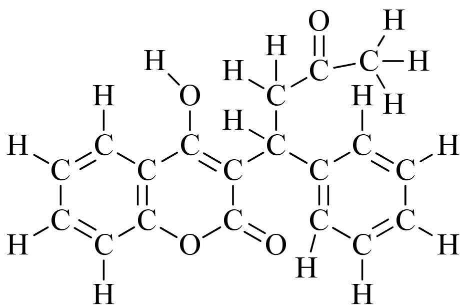
Answer:

Hyperventilation results in a decrease in the partial pressure of CO_2 in the lungs. What effect will this have on the pH of the blood? Use a chemical equation to illustrate your answer.

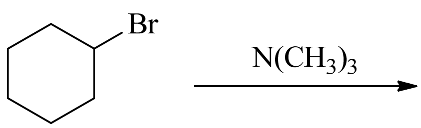
The pH of blood is maintained around 7.4 by the H_2CO_3 / HCO_3^- buffer system. Explain how a buffer works, illustrating your answer with chemical equations.

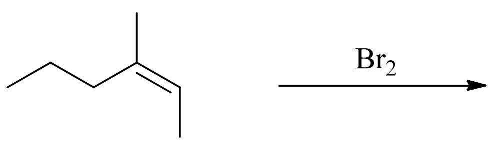
Marks

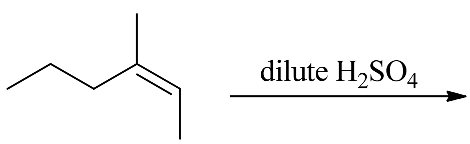
- A structural formula for Warfarin, an anticoagulant, showing all atoms and bonds is shown below. Draw a stick representation of the formula in the box provided. **1**

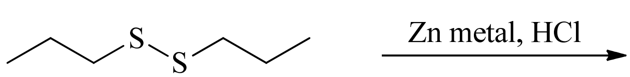


- Give the constitutional formula(s) of the major organic products formed in each of the following reactions: **5**



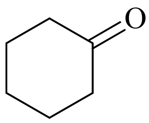
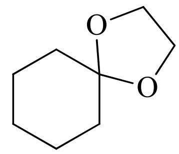
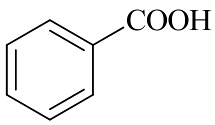
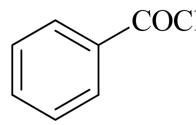
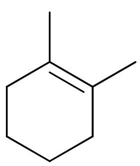
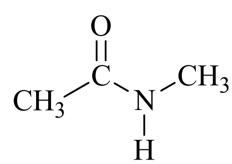






Marks
6

- Complete the following table.

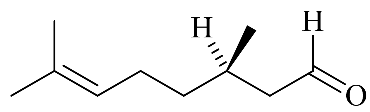
Starting material	Reagent / Conditions	Major organic products(s)
		
		
$CH_3CH_2COOCH_2CH_3$	2 M NaOH heat	
	$H_2(g)$ Pd/C catalyst	
	NH_2CH_3	 + CH_3CH_2OH

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

Marks
4

- (+)-Citronellal is a widely occurring natural product present in citronella oil, lemon and lemon grass. It is used as a soap perfume and in insect repellents.



citronellal

Give the molecular formula of citronellal.

Identify the functional groups present in citronellal.

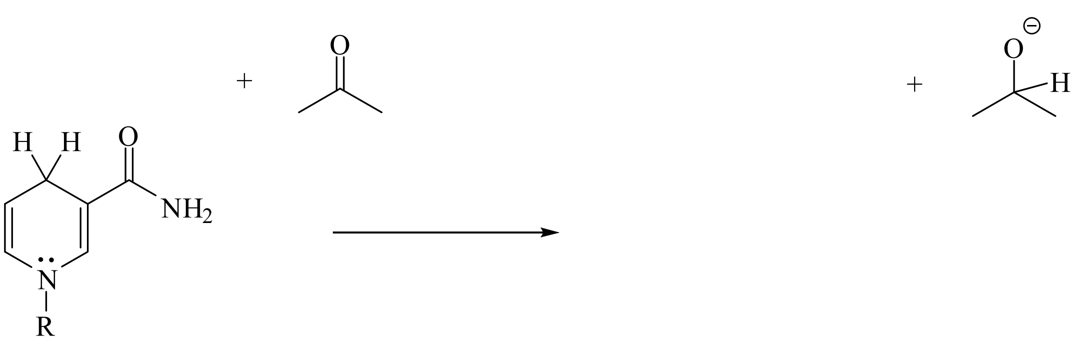
Draw the constitutional formula of the product(s) formed when citronellal is treated with each of the following reagents.

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

excess CH_3OH / catalytic amount H_2SO_4

3

- NADH is the most important reducing agent in Nature. It is itself oxidised to NAD^+. Complete the scheme below by:
(a) drawing in curly arrows to show the movement of electrons during the first step in the reduction of acetone with NADH, and
(b) drawing the structure of NAD^+.

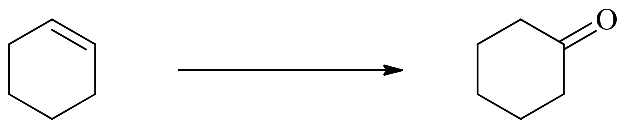


NADH

NAD^+

Marks
6

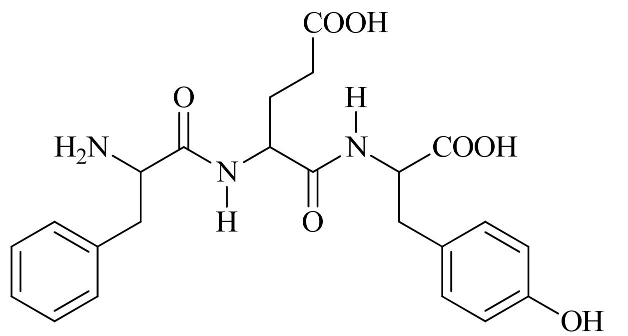
- Show clearly the reagents you would use to carry out the following chemical conversions. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.



Marks **3**

- Consider the tripeptide phenylalanylglutamyltyrosine (Phe-Glu-Tyr) (**F**), whose constitutional formula is shown below.

(F)



Draw the constitutional formula(s) of the product(s) obtained when the tripeptide (**F**) is subjected to the following conditions. Make sure you show the products in the appropriate ionic states.

cold 2 M NaOH
5 M HCl / heat

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
4

The pK_a values of tyrosine are pK_{a1} = 2.20 (α-COOH), pK_{a2} = 9.11 (α-$NH_3^{\oplus}$) and pK_{a3} = 10.07 (-$CH_2C_6H_4OH$). Draw the structure of the zwitterionic form of tyrosine.

At what pH will this be the predominant species in aqueous solution?

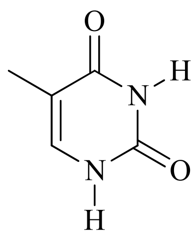
The naturally occurring isomer of phenylalanine is (L)-phenylalanine. Draw the zwitterionic structure of (L)-phenylalanine and indicate the stereogenic centre with an asterisk (*). Determine whether this amino acid has the (*R*) or (*S*) configuration. Show your working.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

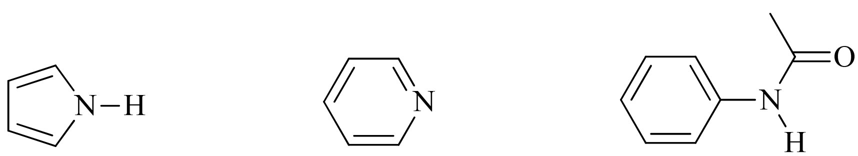
- Draw a tautomer of the structure of thymine, shown below. **1**

thymine



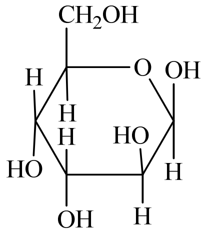
tautomer of thymine

- Rank the following compounds in order of base strength and explain your reasoning. You may use diagrams to assist your explanation. **3**



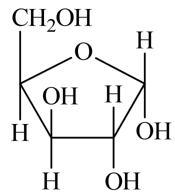
Marks
6

- Consider the following two monosaccharides, (**A**) and (**B**).



(**A**)

β-D-altropyranose



(**B**)

α-D-xylofuranose

Draw Fischer projections of the open chain forms of (**A**) and (**B**).

(**A**)	(**B**)

Draw the major organic product of the reaction of D-altropyranose with the following reagents.

1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	$[Ag(NH_3)_2]^{\oplus}$ / $OH^{\ominus}$

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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}

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	1 Ci = 3.70×10^{10} Bq
0 °C = 273 K	1 Hz = 1 s^{-1}
1 L = 10^{-3} m^3	1 tonne = 10^3 kg
1 Å = 10^{-10} m	1 W = 1 J s^{-1}
1 eV = 1.602×10^{-19} J	

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
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+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
$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O$	+0.32
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+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
$Sc^{3+}(aq) + 3e^- \rightarrow Sc(s)$	–2.09
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–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

CHEM1405 - CHEMISTRY (VETERINARY SCIENCE)

Useful formulas

Quantum Chemistry	**Electrochemistry**
$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm	$\Delta G° = -nFE°$ Moles of $e^- = It/F$ $E = E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)
Acids and Bases	**Gas Laws**
$pH = -\log[H^+]$ $pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = \frac{1}{2}mv^2$
Radioactivity	**Kinetics**
$t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$ years	$t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative Properties & Solutions	**Thermodynamics & Equilibrium**
$\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	$\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ}S° = R \ln K$ $K_p = K_c\left(\frac{RT}{100}\right)^{\Delta n}$
Miscellaneous	**Mathematics**
$A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	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** [263]	107 BOHRIUM **Bh** [264]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [268]	110 DARMSTADTIUM **Ds** [281]	111 ROENTGENIUM **Rg** [272]	112 COPERNICIUM **Cn** [285]						

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]