2214(a)

THE UNIVERSITY OF SYDNEY

CHEM1405 - CHEMISTRY (VETERINARY SCIENCE)

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

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.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	31	

Short answer section

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

Marks

- Explain what is meant by hybridisation of atomic orbitals. **1**

- Carbon has atomic number $Z = 6$. What is the ground state electron configuration for an atom of carbon? **5**

What compound would you expect to form between a carbon atom with that electron configuration and hydrogen, *i.e.* what is the value of x in the formula CH_x? Explain.

What shape would that molecule have? Explain.

What molecule forms instead? Explain.

Marks
5

- Stearic acid, $C_{18}H_{36}O_2$, is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:

$$C_{18}H_{36}O_2(s) + 26O_2(g) \rightarrow 18CO_2(g) + 18H_2O(l)$$

Calculate $\Delta H°$ for this reaction given the following heats of formation.

Compound	$C_{18}H_{36}O_2(s)$	$CO_2(g)$	$H_2O(l)$
$\Delta_f H°$ / kJ mol^{-1}	–948	–393	–285

$\Delta H°$ =

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the $\Delta H°$ for the combustion of stearic acid in air given that:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H° = +44 \text{ kJ mol}^{-1}$$

$\Delta H°$ =

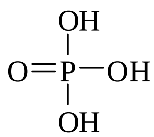
Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

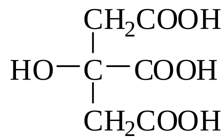
Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

Answer:

Marks
3

- Consider the two triprotic acids, phosphoric acid and citric acid.





Acid	Formula	K_{a1}	K_{a2}	K_{a3}
phosphoric	H_3PO_4	7.1×10^{-3}	6.3×10^{-8}	4.5×10^{-13}
citric	$C_6H_8O_7$	7.1×10^{-4}	1.7×10^{-5}	6.4×10^{-6}

Explain why $K_{a1} > K_{a2} > K_{a3}$ for both acids.

For phosphoric acid, the K_a values differ by about 5 orders of magnitude while for citric acid there is a much smaller difference. Explain.

Marks
4

- Henry's law relates the solubility of a gas to its pressure. *i.e.* c = *k*p

  The Henry's law constant for $N_2(g)$ at 298 K is 6.8×10^{-4} mol L^{-1} atm^{-1}. A diver descends to a depth where the pressure is 5 atm. If the diver's body contains about 5 L of blood, calculate the maximum amount of nitrogen gas dissolved in the diver's blood at 1 atm and at 5 atm. (Assume solubility of nitrogen in water and blood to be the same.)

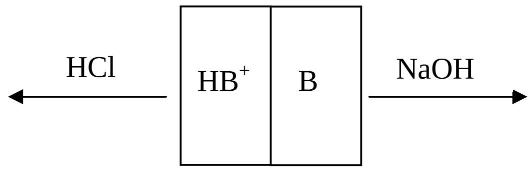
1 atm:	5 atm:

  If all the gas dissolved at 5 atm were suddenly released, what volume would it occupy at 1 atm and 298 K?

Answer:

Marks
7

- A buffer system with a weak base B and its conjugate acid HB^+ is shown in the diagram below with equal concentrations. Complete the diagram by showing the relative concentrations after the addition of some HCl or NaOH.



Write down the balanced net ionic equations for both these reactions.

Calculate the pH of a buffer if it contains 0.200 mol of $NaNO_2$ and 0.300 mol of HNO_2 in 1.00 L of water. The pK_a of HNO_2 is 3.15.

pH =

What is the pH if (a) 0.05 mol of HCl(g) and (b) 0.25 mol of HCl(g) is added?

(a) pH = (b) pH =

Marks

- The radioactive isotope ^{99m}Tc has a half life of 6.0 hours. How much time after production of the ^{99m}Tc isotope do radiologists have to examine a patient if at least 35 % of the original activity is required to get useful exposures? **2**

Answer:

- Consider the following *unbalanced* reaction at 25 °C: **3**

$$Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn^{4+}(aq)$$

Calculate the standard cell potential.

Answer:

Calculate the equilibrium constant, K, for the reaction at 25 °C.

Answer:

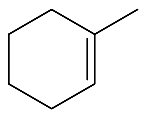
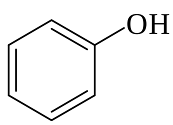
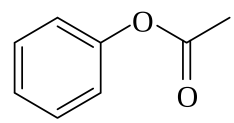
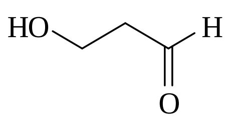
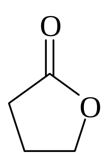
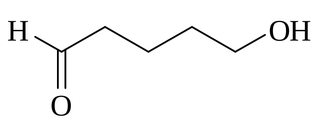
Page Total:

	Marks
• The observed geometry of the N atom in H_2NCOCH_3 is trigonal planar. Draw a Lewis structure consistent with this observation and explain this observation.	**2**
• The reaction $2A + B \rightarrow C + 3D$ has reached equilibrium. What is the expression for the equilibrium constant, K_c?	**2**
Explain how the equilibrium constant, K_c, changes when more C is added to the reaction mixture.	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

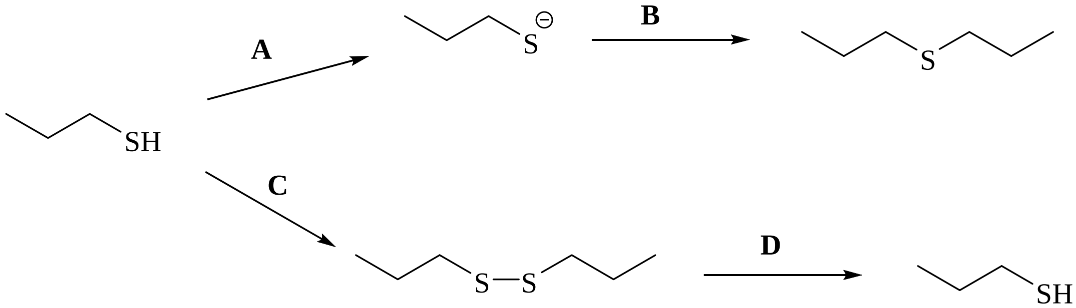
Marks
6

- Complete the following table.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	HCl / CCl_4 solvent	
		
$CH_3CH_2CHCH_2CH_3$ Br		$CH_3CH_2CHCH_2CH_3$ $Br^{\ominus}$ $^{\oplus}N(CH_3)_3$
	$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
	3 M NaOH / heat	
	catalytic $H^{\oplus}$	

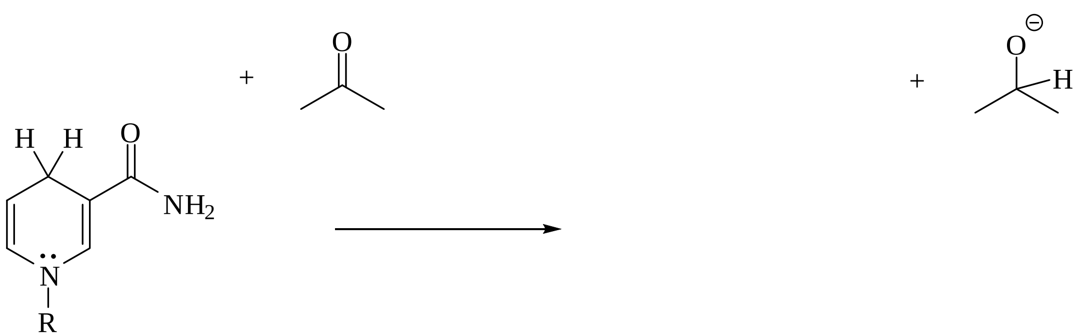
Marks

- Indicate the reagents used in the laboratory to undertake the following transformations. **4**



A:	
B:	
C:	
D:	

- NADH is the most important reducing agent in Nature. It is itself oxidised to NAD^+. Complete the scheme below by: **3**
  (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

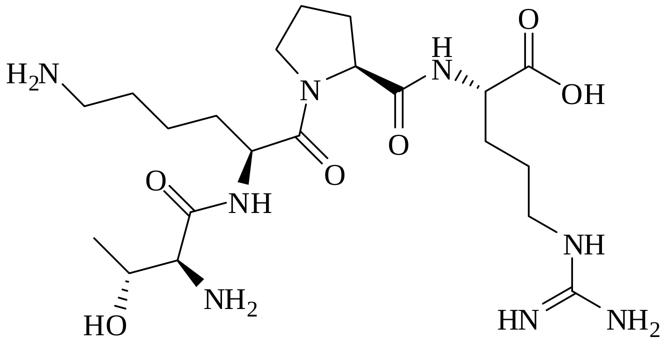
NAD^+

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Page Total:

Marks
6

- Tuftsin is a tetrapeptide (Thr-Lys-Pro-Arg) produced by enzymatic cleavage of the Fc-domain of the heavy chain of immunoglobulin G. It is mainly produced in the spleen and its activity is related primarily to immune system function.



tuftsin

Draw the Fischer projections of the four L-amino acids that result from the acid hydrolysis of tuftsin.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks

4

What is the major species present when lysine (Lys) is dissolved in water at pH 12 and pH 5.6. The pK_a values of lysine are 1.82 (α-COOH), 8.95 (α-$NH_3^{\oplus}$) and 10.53 (side chain).

pH 12	pH 5.6

Give the constitutional formulas for the following dipeptides in their zwitterionic states. The pK_a values of proline are 1.95 and 10.64.

Lys-Thr

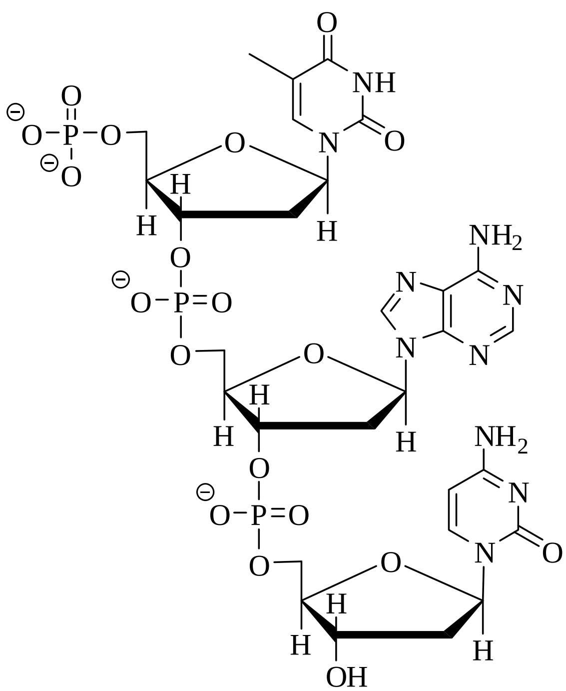
Pro-Lys

2

- Glycine, NH_2CH_2COOH, is the simplest of the naturally occurring amino acids. It has a melting point of 238 ^{o}C, while CH_3CH_2COOH has a melting point of –21 ^{o}C. Give one reason for this difference.

Marks
5

- Is the following structure a fragment of DNA or RNA? Give two reasons.



Clearly identify on the above structure one example of each of the following subunits.

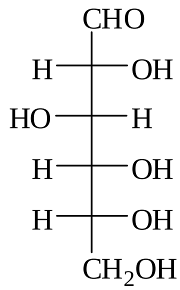
nucleic base

nucleoside

nucleotide

Marks
5

- The open chain form of D-glucose has the structure shown.



Draw the Haworth projection of β-D-glucopyranose.

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

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

Would you expect D-glucose to be water soluble? Why?

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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
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+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

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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** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = ½mv^2$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = $8033 \ln(A_0/A_t)$ years	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative Properties & Solutions $\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	**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 = πr^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]