Topics in the June 2008 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2008-J-2:

- Nuclear and Radiation Chemistry
- Atomic Electronic Spectroscopy
- Bonding in H_2 - MO theory
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O
- Band Theory - MO in Solids
- Types of Intermolecular Forces

2008-J-3:

- Nuclear and Radiation Chemistry

2008-J-4:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O
- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen

2008-J-5:

- Lewis Structures
- VSEPR

2008-J-6:

- Wave Theory of Electrons and Resulting Atomic Energy Levels

2008-J-7:

- Polar Bonds
- Types of Intermolecular Forces
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2008-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2008-J-9:

- Nitrogen in the Atmosphere

2008-J-10:

- Thermochemistry
- First and Second Law of Thermodynamics

2008-J-11:

- Thermochemistry
- First and Second Law of Thermodynamics

2008-J-13:

- Electrochemistry

2008-J-14:

- Electrochemistry
- First and Second Law of Thermodynamics

22/45(a) **The University of Sydney**

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

JUNE 2008 **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 23 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 14, 21, 23 and 28 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-11	33	

Short answer section

Page	Marks Max	Gained		Marker
12	6			
13	7			
15	7			
16	3			
17	4			
18	6			
19	6			
20	3			
22	6			
24	4			
25	5			
26	4			
27	6			
Total	67			

Marks
6

- In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.

(a) antibonding molecular orbital

(b) emission spectroscopy

(c) half-life

(d) band gap

(e) dispersion interaction

(f) a triple bond

Marks

- Explain why a sustained fission chain reaction can only occur when a critical mass is prepared. **2**

- The half life of ^{3}H is 12 years. Calculate how long it takes (rounded to the nearest year) for the activity of a sample of tritium to have dropped to 0.1% of its original value. **2**

Answer:

- Consider the following list of unstable isotopes and their decay mechanisms. **3**

$^{33}_{17}Cl \rightarrow\ ^{0}_{+1}e +\ ^{33}_{16}S$ half-life = 2.5 s

$^{32}_{15}P \rightarrow\ ^{0}_{-1}e +\ ^{32}_{16}S$ half-life = 14.3 days

$^{199}_{82}Pb \rightarrow\ ^{0}_{+1}e +\ ^{199}_{81}Tl$ half-life = 90 minutes

$^{13}_{7}N \rightarrow\ ^{0}_{+1}e +\ ^{13}_{6}C$ half-life = 10 minutes

From this list, select the isotope that best satisfies the following requirements. Provide a reason for your choice in each case.

Requirement	Isotope	Reason for choice
Isotope used in medical imaging		
Decay represents the transformation of a neutron into a proton		
The isotope with the highest molar activity		

Marks

3

- The electronic energies of the molecular orbitals of homonuclear diatomics from the period starting with Li can be ordered as follows (with energy increasing from left to right):

  σ σ* σ σ* π σ π* σ*

  Using this ordering by energy of the molecular orbitals, how many unpaired spins do you expect in the ground state configurations of each of B_2, C_2, N_2, O_2 and F_2?

B_2	C_2	N_2	O_2	F_2

Consider the 15 species X_2^-, X_2 and X_2^+ where X is B, C, N, O or F. What is the maximum bond order found among these 15 species and which molecules or ions exhibit this bond order?

What is the minimum bond order found among these 15 species and which molecules or ions exhibit this bond order?

4

- Imagine a Universe X in which electrons had *three* possible spin states (*i.e.* with electron spin quantum numbers –1, 0 and +1) instead of the two they have in our universe. Assume that all other properties of electrons and nuclei in Universe X are identical to those in our universe.

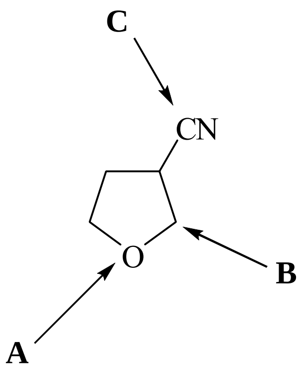
  What are the atomic numbers of the first two noble gases in Universe X?

  Write down the ground state electron configuration of the atom with atomic number 14 in Universe X.

  How would the energy difference between the 2*s* and 2*p* orbitals in multi-electron atoms compare between our universe and Universe X? Give a brief explanation of your answer.

Marks
3

- Consider the molecule whose structure is shown below. Complete the table concerning the atoms **A**, **B** and **C** indicated by the arrows.



Selected atom	Number of lone pairs about the selected atom	Number of σ-bonds associated with the selected atom	Geometry of σ-bonds about the selected atom
A			
B			
C			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- Moseley discovered experimentally in 1913 that the atomic number, *Z*, of an element is inversely proportional to the square root of the wavelength, λ, of fluorescent X-rays emitted when an electron drops from the $n = 2$ to the $n = 1$ shell.

  i.e. $$\frac{1}{\sqrt{\lambda}} = kZ$$

  Derive an expression for the constant of proportionality, *k*, for a hydrogen-like atom which would allow the value of *k* to be theoretically calculated.

Marks

- Describe two physical properties of liquid or solid N_2 that distinguish it from liquid or solid H_2O. **2**

- One problem with the Rutherford model of the atom was that there was nothing to stop the electrons from spiralling into the nucleus. Briefly explain how the quantum theory of the electrons resolved this problem. **2**

- From the list of molecules below, select all the polar molecules and list them from left to right in order of increasing molecular dipole moment. **2**

BF_3, CH_3Cl, CH_3F, CO_2, CF_4, NF_3

Marks
6

- Write a balanced equation for (i) the explosive decomposition, and (ii) the combustion in air, of TNT, $C_7H_5N_3O_6(s)$.

(i)

(ii)

What is the essential difference between these two processes?

What is the increase in the number of moles of gas (per mole of TNT consumed) for each of these two processes?

(i)

Answer:

(ii)

Answer:

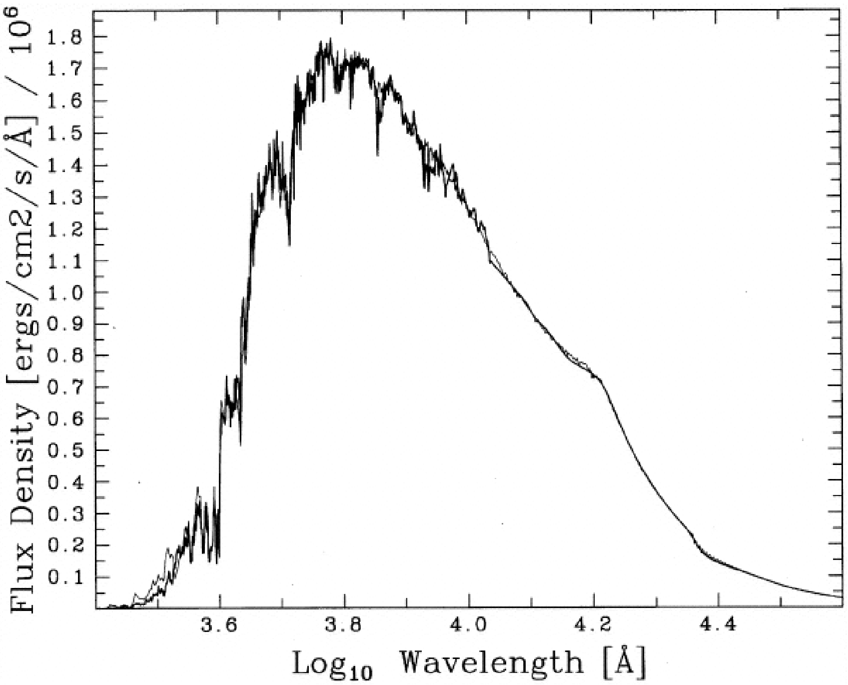
Which of these two processes releases more energy into the surroundings?

Data: $\Delta_f H°(TNT) = 6.9$ kJ mol^{-1} $\Delta_f H°(CO(g)) = -111$ kJ mol^{-1}
$\Delta_f H°(CO_2(g)) = -393$ kJ mol^{-1} $\Delta_f H°(H_2O(g)) = -242$ kJ mol^{-1}

Answer:

Estimate the surface temperature of the star Arcturus from its emission spectrum shown in the figure below.

Marks
3



Answer:

On the figure above, sketch the broad emission spectrum of a red giant, clearly showing the emission maximum and the overall intensity.

Marks
6

- A calorimeter containing 300.0 mL of water at 25 °C was calibrated as follows. A 1000.0 W heating coil was run for 10.0 s, after which time the temperature had increased by 7.5 °C. Calculate the heat capacity of the empty calorimeter. The specific heat of water is 4.184 J K^{-1} g^{-1}.

Answer:

A solution containing 0.040 mol Ag^{+}(aq) was mixed with a second solution containing 0.050 mole Br^{-}(aq) in this calorimeter, causing AgBr(s) to precipitate. The temperature increased by 2.4 °C. Given the solubility product constant is K_{sp}(AgBr) = 5 × 10^{-13} M^{2} , calculate the equilibrium concentrations of Ag^{+}(aq) and Br^{-}(aq) present in the final solution of volume 320 mL.

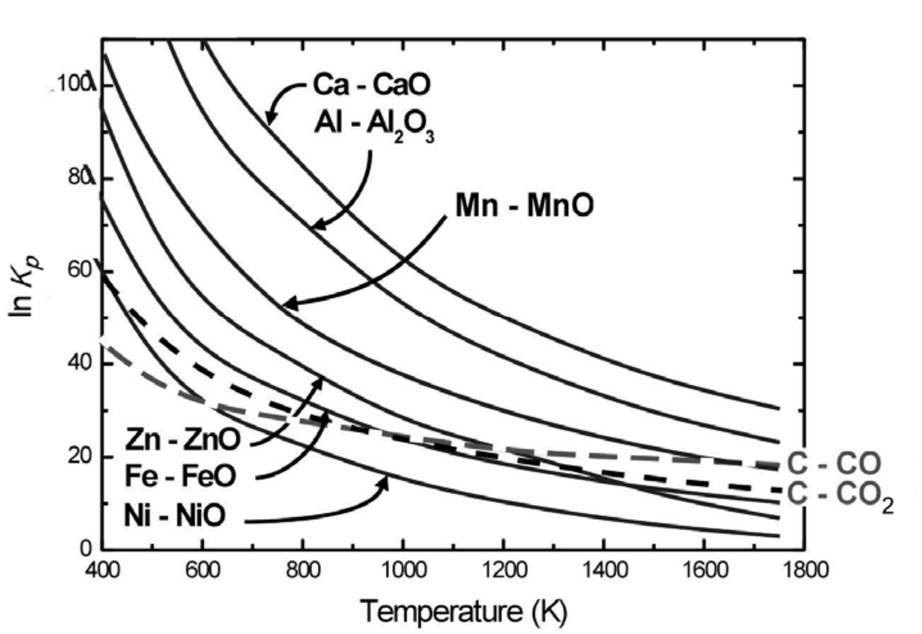
[Ag^{+}(aq)]:	[Br^{-}(aq)]:

Calculate the enthalpy of solution of AgBr(s).

Answer:

Marks
4

- Use the figure below to help answer the following.



Write a balanced equation for the smelting of one of these metal oxides with coke in which a major product is CO_2. Give the approximate temperature range over which this reaction is spontaneous and state what happens outside this temperature range.

Over what temperature range can ZnO be reduced by Fe? What other metal could be used instead to increase the temperature range in which metallic Zn was produced?

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
5

Estimate the partial pressure of CO that would be expected at equilibrium in the smelting of ZnO by coke at 1500 K.

Metallic copper is produced by smelting chalcopyrite, $CuFeS_2(s)$, directly in oxygen to produce iron oxides and SO_2. Write a balanced equation for this reaction, and sketch the $\ln K_p$ *versus* temperature curve for Cu-CuO on the diagram on page 24. Clearly label the curve you have drawn.

Marks
4

- A voltaic cell consists of Zn^{2+}/Zn and Cu^{2+}/Cu half cells with initial concentrations of $[Zn^{2+}]$ = 1.00 M and $[Cu^{2+}]$ = 0.50 M. Each half cell contains 1.00 L of solution.

  What is the voltage of the cell at 20 °C after equilibrium has been reached?

  What are the concentrations of the Zn^{2+}(aq) and the Cu^{2+}(aq) ions at 20 °C after equilibrium has been reached?

$[Zn^{2+}]_{eq}$ =	$[Cu^{2+}]_{eq}$ =

Marks

- Judging by the electrochemical series of standard reduction potentials, $H^+(aq)$ should be reduced to $H_2(g)$ by exposure to metallic Fe, which is oxidised to $Fe^{2+}(aq)$. Why do we not see water on iron spontaneously generating hydrogen gas? **2**

- State the Second Law of Thermodynamics, and explain how an exothermic process in a closed system changes the entropy of the surroundings. **4**

The standard enthalpy and entropy of solution of poly(oxyethylene) in water are $\Delta H° = –7.8$ kJ mol$^{–1}$ and $\Delta S° = –31$ J K$^{–1}$ mol$^{–1}$. Use these data to predict whether the solubility of poly(oxyethylene) in water increases or decreases when the solution is warmed.

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	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	**Electrochemistry**
$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $4.5k_BT = hc/\lambda$ $T = 2.898 \times 10^6/\lambda(\text{nm})$	$\Delta G° = -nFE°$ $Moles\ of\ e^- = It/F$ $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)
Acids and Bases	**Gas Laws**
$pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$
Colligative properties	**Kinetics**
$\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	$t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Radioactivity	**Thermodynamics & Equilibrium**
$t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age $= 8033 \ln(A_0/A_t)$ years	$\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $K_p = K_c (RT)^{\Delta n}$
Miscellaneous	**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 $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

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]