UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL I (SEMESTER II) EXAMINATIONS – JULY 2016

SUBJECT: Chemistry

COURSE UNIT: CHE 2114 **TIME: Three (03) hours**

Answer **six (06)** questions only by selecting **two (02)** from each **sections A, B, and C.**

Physical Constants

Quantity	Symbol	Value
Boltzmann constant	k_B	1.3807×10^{-23} J K^{-1}
Proton charge	e	1.6022×10^{-19} C
Gas constant	R	8.314 J K^{-1} mol^{-1}
		0.0821 dm^{3}atm K^{-1} mol^{-1}
Faraday constant	F	9.6485×10^4 C mol^{-1}
Planck constant	h	6.626×10^{-34} J s
Atomic mass unit (amu)	m_u	1.6606×10^{-27} kg
Velocity of light	c	2.998×10^8 m s^{-1}
Electron mass	m_e	9.109×10^{-31} kg
Proton mass	m_p	1.673×10^{-27} kg
Avogadro constant	N_A	6.022×10^{23} mol^{-1}
Vacuum permittivity	ε_o	8.854×10^{-12} J^{-1} C^2 m^{-1}
Standard pressure	atm	101325 Pa (N m^{-2})

Useful Conversion Factors

1 atm = 760 mmHg = 1.01325 bar = 101325 Pa

2.303 (RT/F) = 59.15 mV at 298.15 K

1 eV = 1.6022×10^{-19} J

NOTE: A copy of the Periodic Table is provided at the end of thisquestion paper.

SECTION - A

01. Answer **all** parts.

(a) Draw the following.

(i) A labeled diagram for splitting of d-orbitals in an octahedral field

(ii) *cis*-$[CoCl_2(NH_3)_4]^+$

(ii) optically inactive $[PtCl_2(en)_2]$

[Note: en : bidentate ligand $H_2NCH_2CH_2NH_2$]

[30 marks]

(b) (i) Explain the following very briefly.

(I) Spectrochemical series

(II) Chelate effect

[10 marks]

(ii) The coordination complex ion $[Fe(CN)_6]^{3-}$ is present in Prussian blue. Using the Crystal Field Theory, deduce the number of unpaired electrons present in this complex ion.

[15 marks]

(iii) Calculate the crystal field stabilization energy (CFSE) of $[Fe(CN)_6]^{3-}$.

[10 marks]

(c) (i) State **three** factors affecting the magnitude of the crystal field splitting energy.

[15 marks]

(ii) Using the Valence Bond Theory, determine whether diamagnetic $[Co(NH_3)_6]^{3+}$ is an outer orbital or inner orbital complex.

[15 marks]

(iii) The stepwise formation constants for formation of $[Ni(en)_3]^{2+}$ from $[Ni(H_2O)_6]^{2+}$ and ethylenediamine (en) are log K_1, log K_2 and log K_3. If the values of log K_1, log K_2 and log K_3 are 7.2, 6.28 and 4.26 respectively, calculate the overall formation constant (log β_3) for the above reaction.

[05 marks]

02. Answer **all** parts.

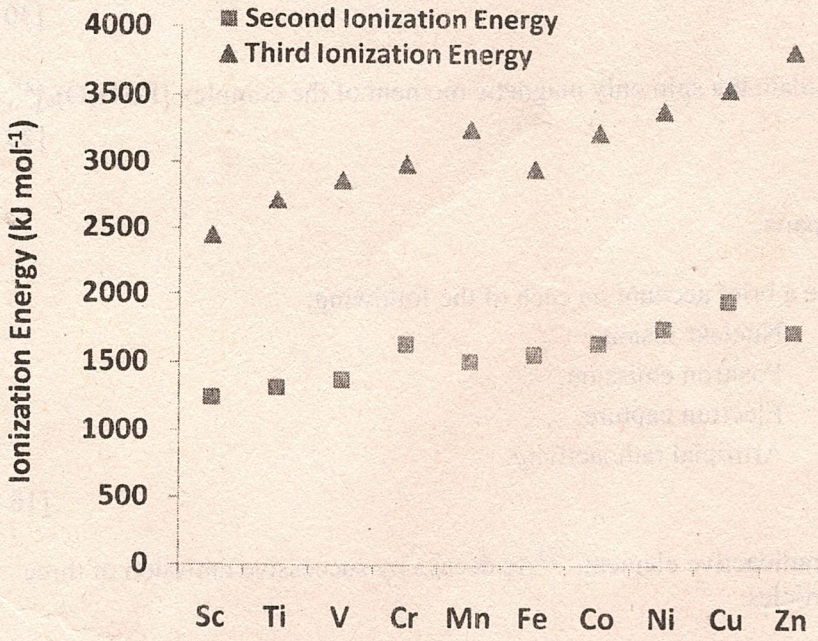
(a) Explain the following statements.

(i) Metals in the second and third transition element series have greater enthalpies of atomization than those of the metals in the first transition series.

(ii) The terms "d-block metals" and "transition metals" are not interchangeable.

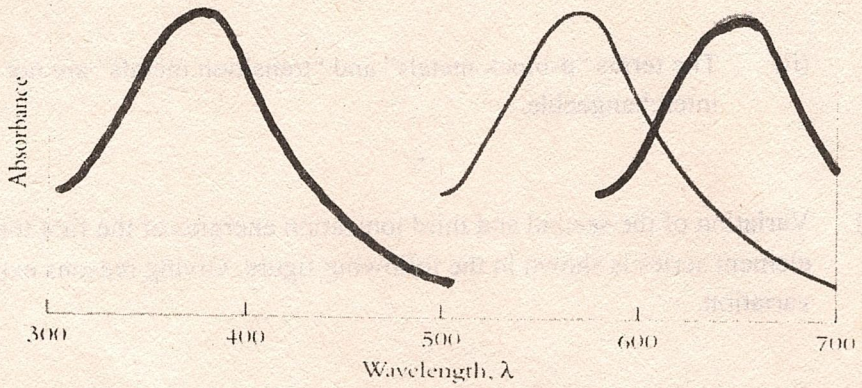
[15 marks]

(b) Variation of the second and third ionization energies of the first transition element series is shown in the following figure. Giving reasons explain this variation.



[35 marks]

(c) The UV-visible spectra of three transition metal complexes $[Cr(H_2O)_6]^{3+}$, $[Cr(CN)_6]^{3-}$ and $[CrF_6]^{3-}$ are shown below. Giving reasons assign each spectrum to the relevant metal complex.



[30 marks]

(d) Calculate the spin only magnetic moment of the complex $[Fe(H_2O)_6]^{2+}$.

[20 marks]

03. Answer **all** parts.

(a) Write a brief account on each of the following:

(i) Nuclear fusion.

(ii) Positron emission.

(iii) Electron capture.

(iv) Artificial radioactivity.

[16 marks]

(b) The radioactive element, ^{225}Ac decays by successive emission of three α-particles.

(i) Write balanced nuclear equations for the above three decay processes.

[06 marks]

(ii) When comparing ^{225}Ac with its final daughter product, which one is closer to the belt of stability in the plot of number of neutrons vs. number of protons?

[06 marks]

(c) Radioactive decay is a first order process and the rate can be expressed by $\frac{-dN}{dt}=\lambda N$. Here, N is the number of nuclei remaining at time t and λ is the decay constant.

(i) Show that, $t_{1/2} = \frac{\ln 2}{\lambda}$ using the above equation. (where $t_{1/2}$ is the half life).

[10 marks]

(ii) Calculate the amount of disintegrations produced from 2.26 g sample of ^{226}Ra, which has a half life of 1600 years.

[12 marks]

(d) (i) Write the ground state electronic configuration of each of the following lanthanide atoms/ions:

Ce Pm Gd^{2+} Lu^{3+}

[12 marks]

(ii) Which ion is more stable, Sm^{3+} or Eu^{2+}? Give reasons for your answer.

[08 marks]

(iii) Assuming that the breakdown of Russell-Saunders coupling is applicable for Dy^{3+} and Ce^{3+}, calculate the magnetic movements of these two ions.
[Note: Σm values of Dy^{3+} and Ce^{3+} are 5 and 1 are respectively. Number of unpaired electrons of Dy^{3+} and Ce^{3+} are 5 and 1 respectively].

[10 marks]

(iv) Monazite deposits are found in the Induruwa and Polkatuwa area near Beruwala. Suggest a suitable procedure to obtain a crude basic salt of Th from monazite using the "acid opening" separation method.

[10 marks]

(v) Write the balanced chemical equation for the disproportionation of Pu^{4+} in aqueous solution.

[10 marks]

SECTION - B

04. Answer **all** parts.

(a) Complexometric titrations are widely used in analytical chemistry in order to determine various metal ion concentrations. Answer the following questions based on this.

(i) Give the name and its chemical structure of the most widely used titrant.

[05 marks]

(ii) List the five types of titration methods that can be used in this field.

[05 marks]

(iii) Discuss briefly the importance of maintaining the pH of the medium. Use suitable diagrams to illustrate your answer.

[15 marks]

(iv) Give reasons for the use of auxiliary complexing agents in the analysis of certain metal ions.

[10 Marks]

(b) Ni^{2+} can be analyzed by a back titration using standard Zn^{2+} solution at pH 5.5 with *xylenol orange* indicator. A solution containing 25.00 mL of Ni^{2+} in dilute HCl was treated with 25.00 mL of 0.0528 mol L^{-1} EDTA solution. The solution was neutralized with NaOH, and the pH was adjusted to 5.5 with acetate buffer. When the solution turned yellow, a few drops of indicator was added. Then titration with 0.0229 mol L^{-1} Zn^{2+} solution required 17.61 mL to reach the red end point.

(i) Calculate the concentration of Ni^{2+} in the unknown solution.

[10 marks]

(ii) What is the reason for carrying out a back titration in this titration?

[05 marks]

(iii) Suggest a quantitative method to analyze ions separately in a mixture of Fe^{3+}/Ca^{2+} solution. Give reasons to your answer.

[10 marks]

(c) Answer the following.

(i) Explain briefly the two analytical methods that can be used to determine the end points in argentometric titrations.

[10 marks]

(ii) List the desired properties of a precipitate that could be used in gravimetric analysis.

[05 marks]

(d) Explain briefly the function of the *nebulizer* as it is an essential component of an atomic absorption spectrophotometer.

[09 marks]

(e) List four (04) sample atomization techniques used in atomic absorption spectrophotometry.

[08 marks]

(f) Discuss the advantages of the *graphite furnace technique*.

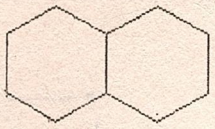
[08 marks]

05. Answer **all** parts.

(a) A cyclic carbonyl compound **A** with molecular formula of C_5H_6O shows a strong absorption at 214 nm. If a hydrogen is replaced by a CH_3 group, the λ_{max} shifted to 226 nm. Provide the exact molecular structure of the compound **A**, and the compound with λ_{max} of 226 nm. Justify your answer.

[20 marks]

(c) An alkene $C_{11}H_{14}$and an unsaturated ketone $C_{10}H_{12}O$, both almost identical in structure having the basic skeleton shown below, show UV absorptions at 269 and 280 nm, respectively.

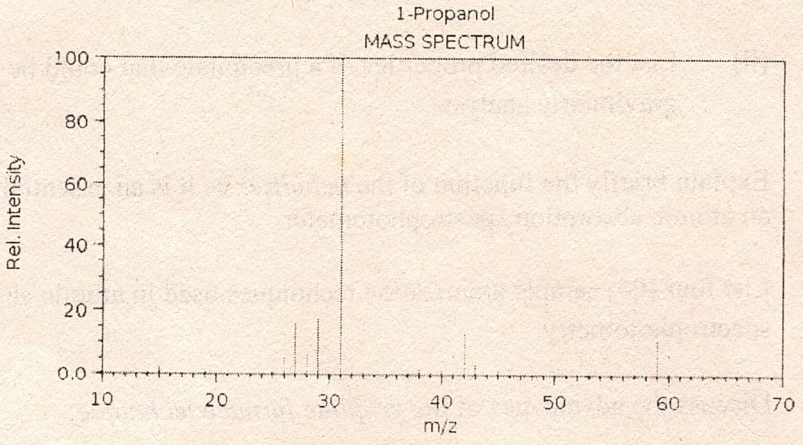


(i) Give their structures.

(ii) Using Woodward-Fieser's rule, calculate the λ_{max} values in order to justify the proposed structures.

[30 marks]

(c) Using the mass spectrum of 1-propanol shown below, answer the following questions.



(i) Draw the structure of the most likely molecular ion formed and give its m/z value.

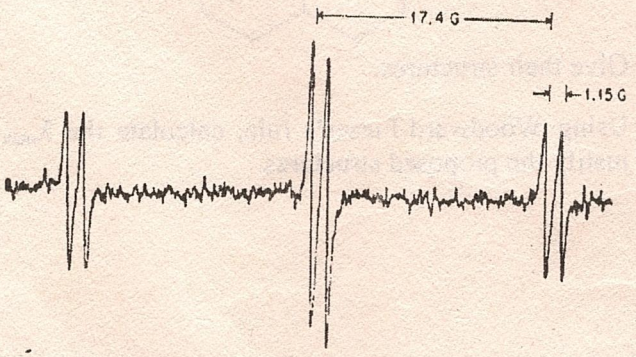
(ii) Draw the structure of the ion responsible for the base peak at m/z = 31 and give a fragmentation mechanism for it's formation.

(iii) Likewise, draw likely structures for the ions that produce the next most intense signals at m/z = 59 and 42.

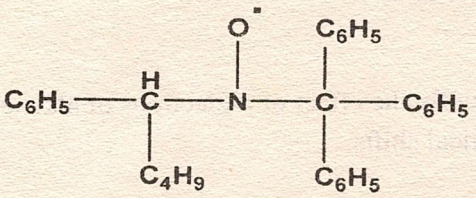
(iv) Why does the peak at m/z = 15 have such a low relative intensity?

[26 marks]

(d) (i) The ESR spectrum of the hydroxyl methyl radical ($\dot{C}H_2OH$) is given below. Briefly explain this observed spectrum.



(ii) Draw expected ESR spectrum for the following N-oxide radical. Clearly indicate the intensity ratio of each peak in your spectrum. (I values of N and H are 1 and ½ respectively).



[24 marks]

06. Answer **all** parts.

(a) Titan is Saturn's largest moon. Using infrared spectroscopy and other methods, the atmosphere of Titan was found to contain traces (1.5 ppb) of cyanoacetylene (C_3HN). Its IR spectrum contains two distinct bands between 2250 and 2150 cm^{-1} and a sharp band above 3000 cm^{-1}.

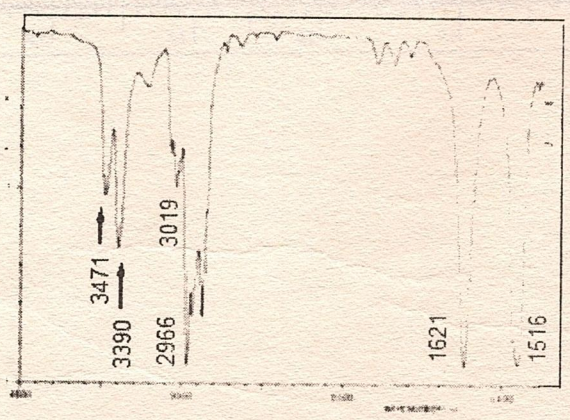
(i) Draw the structure for this molecule and assign approximate peak values (wavenumbers) to the appropriate bonds

[15 marks]

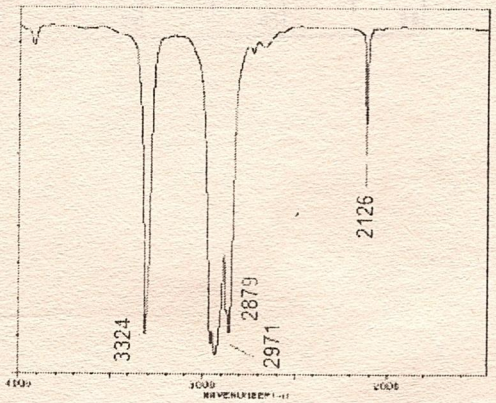
(ii) Which of the two indicated bonds between 2250 and 2150 cm^{-1} has a higher intensity? Explain

[10 marks]

(b) Two molecules with molecular formulae $C_8H_{11}N$ and C_4H_6give following IR spectra. Propose at least one reasonable molecular structure for each molecule.



(i) $C_8H_{11}N$



(ii) C_4H_6

[25 marks]

(c) Explain briefly the following statements pertaining to NMR spectroscopy.

(i) "Nuclear spin plays an important role in NMR spectroscopy"
(ii) "Spin spin coupling helps in structure elucidation of organic compounds"

[10 marks]

(d) Describe briefly the effect of π-electrons of alkenes and alkynes on their ^1H NMR chemical shifts.

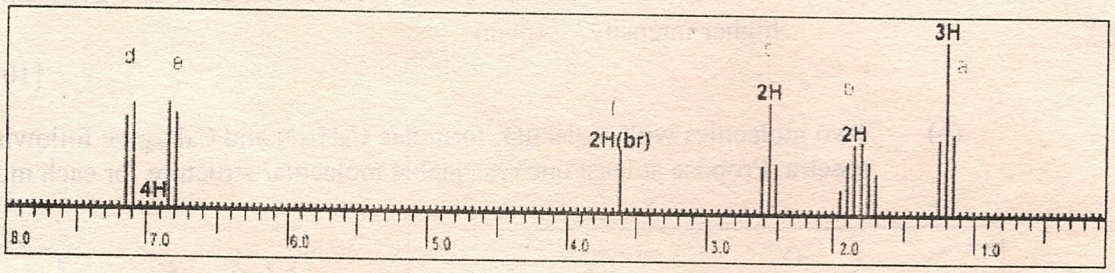
[10 marks]

(e) Suggest a method to distinguish cyclopropane and chlorocyclopropane using ^1H NMR spectroscopy. Give reasons to justify your answer.

[10 marks]

(f) The ^1H NMR spectrum of $C_9H_{13}N$ is given below. Using the given spectrum deduce the chemical structure of this molecule. Assign each peak to the specific group in the structure.

[20 marks]



SECTION - C

07. Answer **all** parts.

(a) (i) List the basic symmetry elements.

(ii) Using appropriate molecule(s) describe the relevant symmetry operations associated with the above symmetry elements listed in (i)

[30 marks]

(b) Using $PtCl_4^{2-}$ as an example explain the following terms pertaining to molecular symmetry.

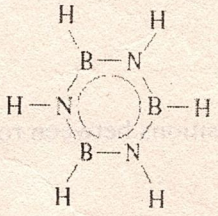
(i) Principal rotational axis.
(ii) Horizontal mirror plane.
(iii) Vertical mirror plane.
(iv) Dihedral mirror plane.

[30 marks]

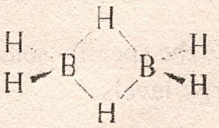
(c) Giving major symmetry elements assign the following molecules into their point groups.

(i) BCl_3

(ii) NH_3



(iii)



(iv)

[30 marks]

(d) Using the answer to the Part (c) above, predict the polarity of the molecules given in part (c).

[10 marks]

8. Answer **all** parts.

(a) Explain what do you understand by the dipole moment of a molecule? What are the conditions that should be satisfied by the dipole moment of a molecule in order for it to be?

(i) Microwave (rotationally) active.

(ii) Infra – red (vibrationally) active.

Explain briefly giving an example in each case.

[25 marks]

(b) Consider the following molecules:

C_6H_6, H_2, HCl, CO_2, CO.

(i) Which of the above molecules are microwave active? Give your reasons briefly.

(ii) Which of the above molecules are infra - red active? Give your reasons briefly.

[25 marks]

(c) The rotation of a diatomic molecule, such as $^1H^{35}Cl$, in the gas phase has been represented using the rigid rotor approximation and rotational energy levels are given by

$$\varepsilon_{rot} = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1) \text{ in } cm^{-1}$$

where $I = \mu r_e^2$.

(i) Identify the symbols B, J, I, μ, and r_e.

[10 marks]

(ii) State the specific selection rule for transitions between rotational energy levels.

[10 marks]

(iii) Five consecutive rotational absorption lines were observed for $^1H^{35}Cl$ at

104.13, 124.73, 145.37, 165.89, 186.23 cm^{-1}.

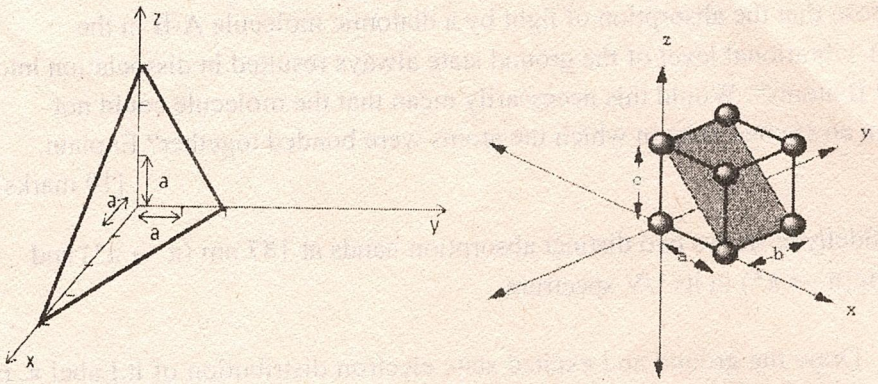
Calculate the moment of inertia and the bond length of the molecule. Qualitatively explain where you would expect the rotational lines for $^2H^{35}Cl$.

[Relative atomic masses: ^1H = 1.0078; ^{35}Cl = 34.969; Atomic mass unit (amu) = 1.6606×10^{-27} kg.]

[30 marks]

09. Answer **all** parts.

(a) (i) Find the Miller indices (hkl) of the planes in the figure given below.



[10 marks]

(ii) Showing the lattice positions of the atoms, draw the following crystallographic planes of the given crystal lattices. Assume that the length of the unit cell of both the lattices is equal to 'a'.

(I) (100), (110) for a bcc crystal

(II) (100), (110) and (111) for an fcc crystal

[20 marks]

(iii) Niobium has an fcc crystal structure with a relative atomic weight of 92.9. When monochromatic x-radiation ($\lambda = 0.1028\ nm$) is focused on the Niobium crystal, the angle of diffraction (2θ) for the first order reflection of (311) set of planes occurs at 71.2^0. Calculate the

(I) separation of the planes

[05 marks]

(II) length of the side of the unit cell

[05 marks]

(III) density of Niobium

[10 marks]

(b) Differentiate between thermally induced reactions and photochemically induced reactions.

[10 marks]

(c) "Suppose that the absorption of light by a diatomic molecule A-B in the lowest vibrational level of the ground state always resulted in dissociation into A and B atoms". Would this necessarily mean that the molecule could not exist in an excited state in which the atoms were bonded together? Explain.

[10 marks]

(d) Formaldehyde shows two distinct absorption bands at 187 nm ($\pi \rightarrow \pi^*$) and 285 nm ($n \rightarrow \pi^*$) in its UV spectrum.

(i) Draw the ground and excited state electron distribution of it.Label π, n and π^* energy levels.

(ii) Show the electron configurations for the two singlet states and two triplet states.

[10 marks]

(e) When a molecule interacts with radiation, a number of processes can occur. List them.

[10 marks]

(f) State the *possible changes* that may happen when a molecule absorbs a photon and gets into one of its excited states.

[10 marks]

@@@@@@@@@@@@@@@@@@@

IUPAC Periodic Table of the Elements

1																	18
1 H hydrogen [1.007, 1.009]	2											13	14	15	16	17	2 He helium 4.003
3 Li lithium [6.938, 6.997]	4 Be beryllium 9.012											5 B boron [10.80, 10.83]	6 C carbon [12.00, 12.02]	7 N nitrogen [14.00, 14.01]	8 O oxygen [15.99, 16.00]	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium [24.30, 24.31]	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.98	14 Si silicon [28.08, 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05, 32.08]	17 Cl chlorine [35.44, 35.46]	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38(2)	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.97	35 Br bromine [79.90, 79.91]	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57-71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium [204.3, 204.4]	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Uut ununtrium	114 Fl flerovium	115 Uup ununpentium	116 Lv livermorium	117 Uus ununseptium	118 Uuo ununoctium

Key:

atomic number
Symbol
name
standard atomic weight

57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0
89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium