FACULTY OF SCIENCE – DEPARTMENT OF CHEMICAL SCIENCES

CEM01A2/CEM2A10 – JUNE EXAM 2019

29 MAY 2019

INTERMEDIATE INORGANIC CHEMISTRY II

Examiners: Dr Charmaine Arderne **Moderator**: Prof Reinout Meijboom
Exam Total: 100 marks
Duration: 3 hours
Session: 08h30 – 11h30

Instructions: This paper consists of **16** pages including supplementary information
Answer all the questions given below.
All rough work to be done on the opposing open pages
Calculators may be used but NO CELLPHONES are allowed
Unless specified, show all working on how you obtained the final answers
Structures must be drawn using proper stereochemical configurations.
The paper consists of TEN questions worth 10 marks each.

Student Number: ______________________________

ID / Passport Number: ______________________________

Surname and initials (optional): ______________________________

Contact telephone number: ______________________________

Marks:

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10

Percentage:

QUESTION 1 Physical Techniques [10 marks]

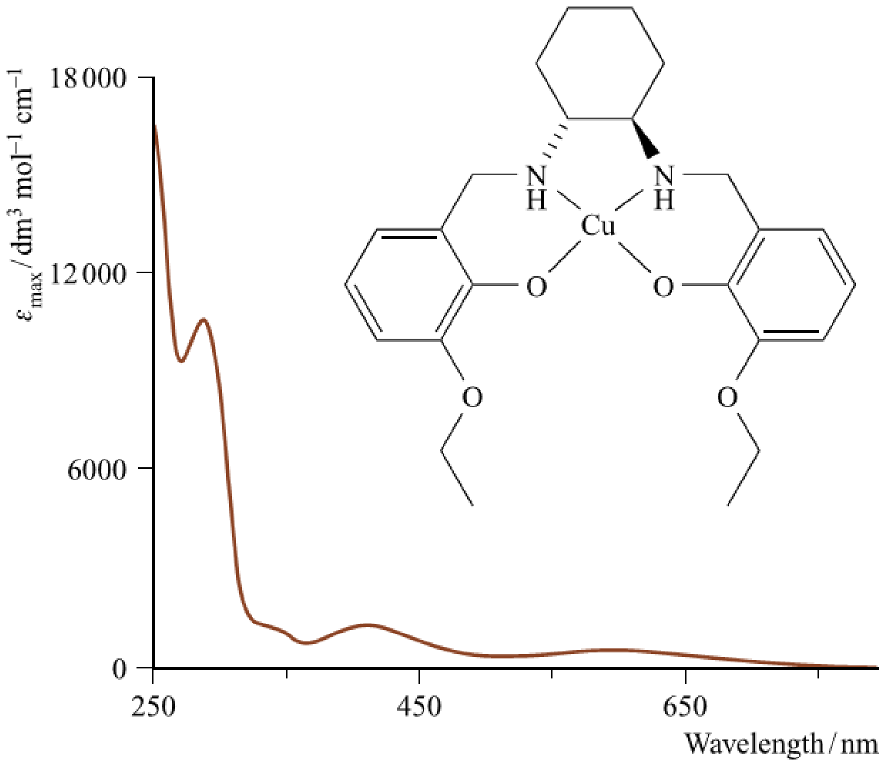
Examine the UV-VIS spectrum given below for a 8.8×10^{-5} M Cu(II) complex in CH_2Cl_2. Solutions of the complex appear brown in colour and the intense bands seen arise from ligand-based $\pi \rightarrow \pi^*$ transitions. A 1 cm cuvette was used for the measurement.

(a) Explain how the $\pi \rightarrow \pi^*$ transitions occur.

(b) What part of the complex gives rise to these transitions (be specific)?

(c) Which absorption peaks are associated with the observed colour of the complex?

(d) Calculate the absorbance that corresponds to the peak at 292 nm.



Answer: Question 1

Answer: Question 1 (continued…)

QUESTION 2 Atomic Structure [10 marks]

Draw pictures of the two *d* orbitals in the *xy*-plane as flat projections in the plane of the paper. Label each drawing with the appropriate mathematical function and include a labelled pair of Cartesian coordinates. Label the orbital lobes correctly with + and – signs.

Answer: Question 2

QUESTION 3 Molecular structure and Bonding [10 marks]

Draw the molecular orbital diagram for lithium fluoride. In doing so, calculate the orbital differences to help you decide which orbitals interact.

Answer: Question 3

QUESTION 4 Structure of simple solids [10 marks]

Calculate the radius of the largest sphere that can be placed in a tetrahedral hole (void) without pushing the spheres apart. (Draw a diagram to help you solve this problem)

Answer: Question 4

QUESTION 5 Acids and Bases [10 marks]

(a) Arrange the following species in order of increasing activity and explain your reasoning.
$[Na(H_2O)_6]^+$; $[Sc(H_2O)_6]^{3+}$; $[Mn(H_2O)_6]^{2+}$; and $[Ni(H_2O)_6]^{2+}$

(b) Using Pauling's rules, predict the pK_a values for the following three species:
H_3PO_4; $H_2PO_4^-$; HPO_4^{2-}

Answer: Question 5

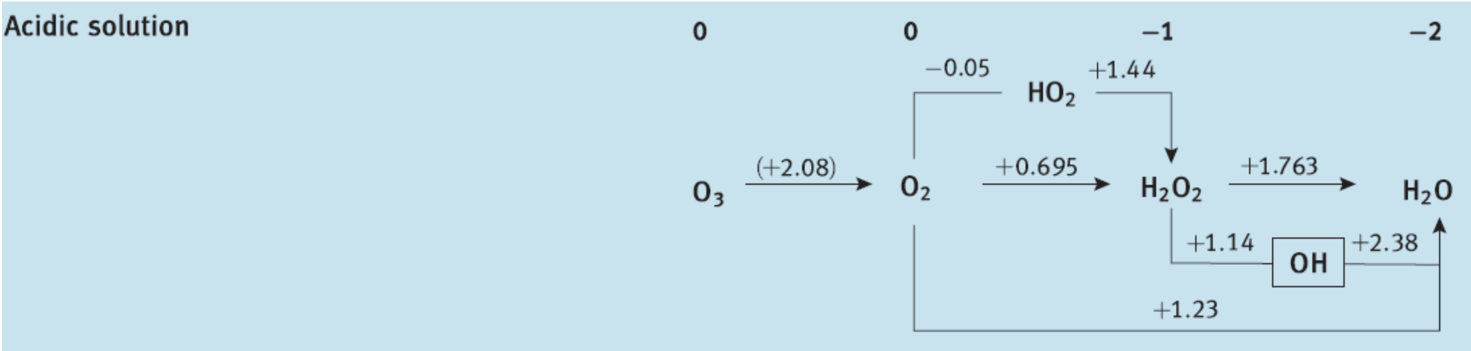
QUESTION 6 Oxidation and Reduction [10 marks]

(a) Use the Latimer diagram below to calculate the value of E^{o} for the ClO_2^- / Cl_2 couple in basic aqueous solution.

$$\underset{+7}{ClO_4^-} \xrightarrow{+0.37} \underset{+5}{ClO_3^-} \xrightarrow{+0.30} \underset{+3}{ClO_2^-} \xrightarrow{+0.68} \underset{+1}{ClO^-} \xrightarrow{+0.42} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

(b) Explain the difference between disproportionation and comproportionation.

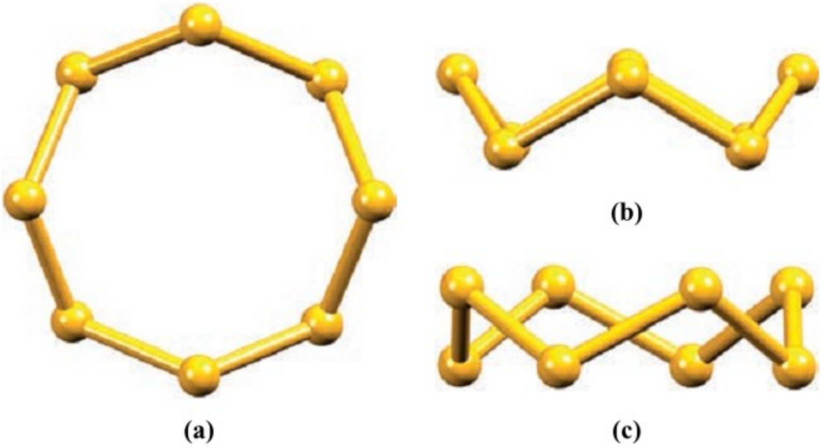
(c) Examine the Latimer diagram for oxygen below. Determine if hydrogen peroxide will disproportionate in acid solution. If so, will the process be spontaneous? (Demonstrate your answer by a short calculation)



Answer: Question 6

QUESTION 7 Molecular Symmetry [10 marks]

Three projections of the cyclic structure of S_8 are given below. All S–S bond distances are the same, as are the S–S–S bond angles. To what point group does S_8 belong?



Answer: Question 7

QUESTION 8 Coordination Chemistry [10 marks]

(a) Name the following complexes

(i) $[Cr(NH_3)_6](CN)_3$

(ii) $[Pt(OH_2)_4][Zn(ox)_2]$

(b) Write the formulas for the following complexes:

(i) diaquadichloridopalladium(II)

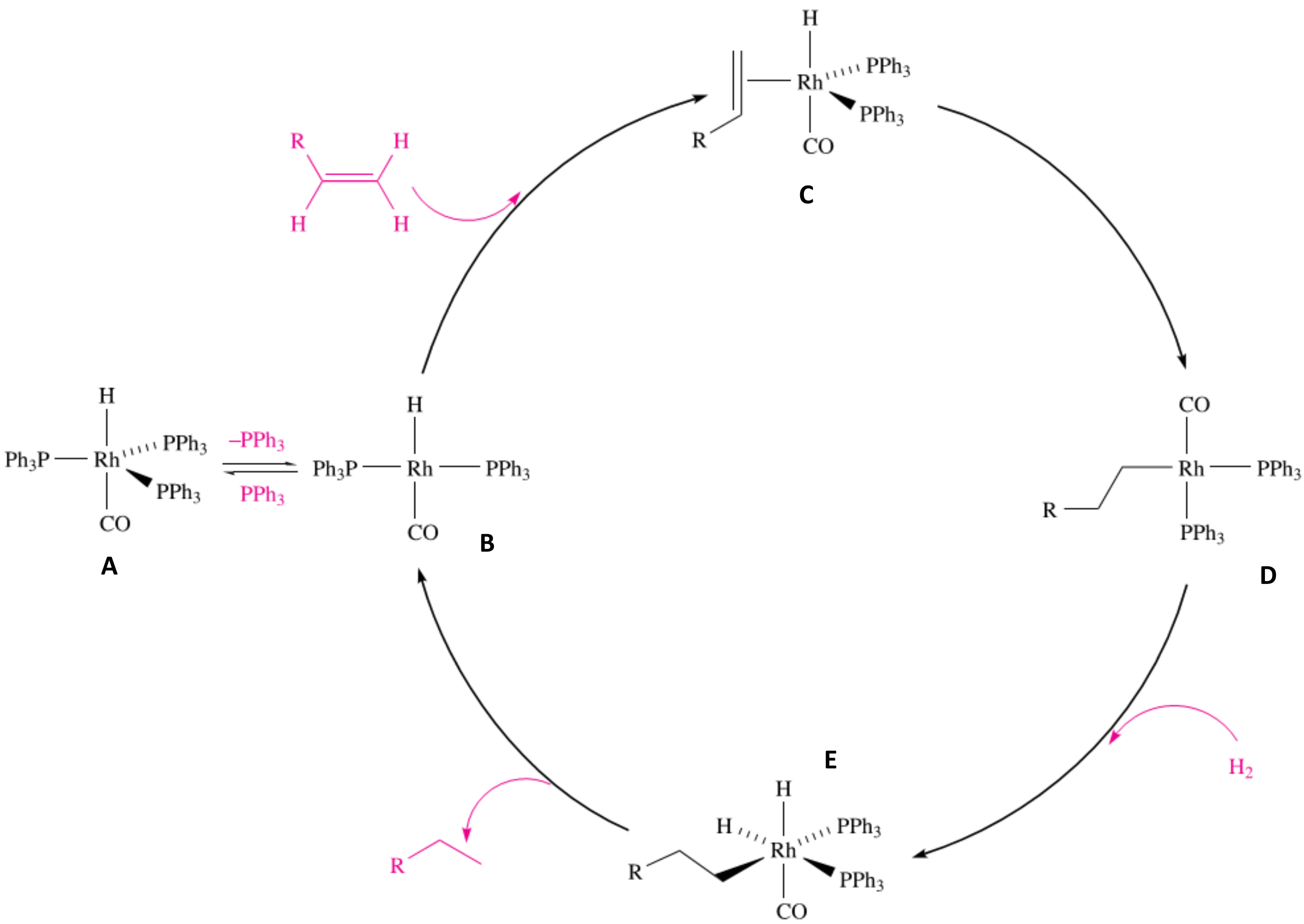
(ii) diamminetetra(thiocyanato-κ*N*)cobaltate(III)

(c) Two types of isomerism are possible for the six-coordinate complex $Cr(NO_2)_2 \bullet 6\ H_2O$. Identify all possible isomers and give one example for each isomer identified .

Answer: Question 8

QUESTION 9 Catalysis [10 marks]

Examine the catalytic process below and answer the questions that follow:



(a) Identify the catalyst in the process by placing a circle around the letter that identifies it.

(b) Draw the full structure for the PPh_3 ligand.

(c) Describe the geometry of the PPh_3 ligand and explain how it can bond to the Rh centre.

(d) Does the Rh metal have a change in oxidation state during this reaction cycle?

(e) Identify the point group of the Rh metal in species **E**.

Answer: Question 9

Answer: Question 9 (continued…)

QUESTION 10 First year concepts [10 marks]

(a) The pH of 0.145 *M* acetic acid is 2.80. Calculate the K_a and the pK_a values for acetic acid.

(b) Calculate the equilibrium concentration of H_3O^+ in a 0.10 *M* solution of butanoic acid (K_a = 1.86×10^{-5}). From this calculate the pH of this solution.

Answer: Question 10

Supplementary Information – Page 1

TABLE 5.2 **Orbital Potential Energies**

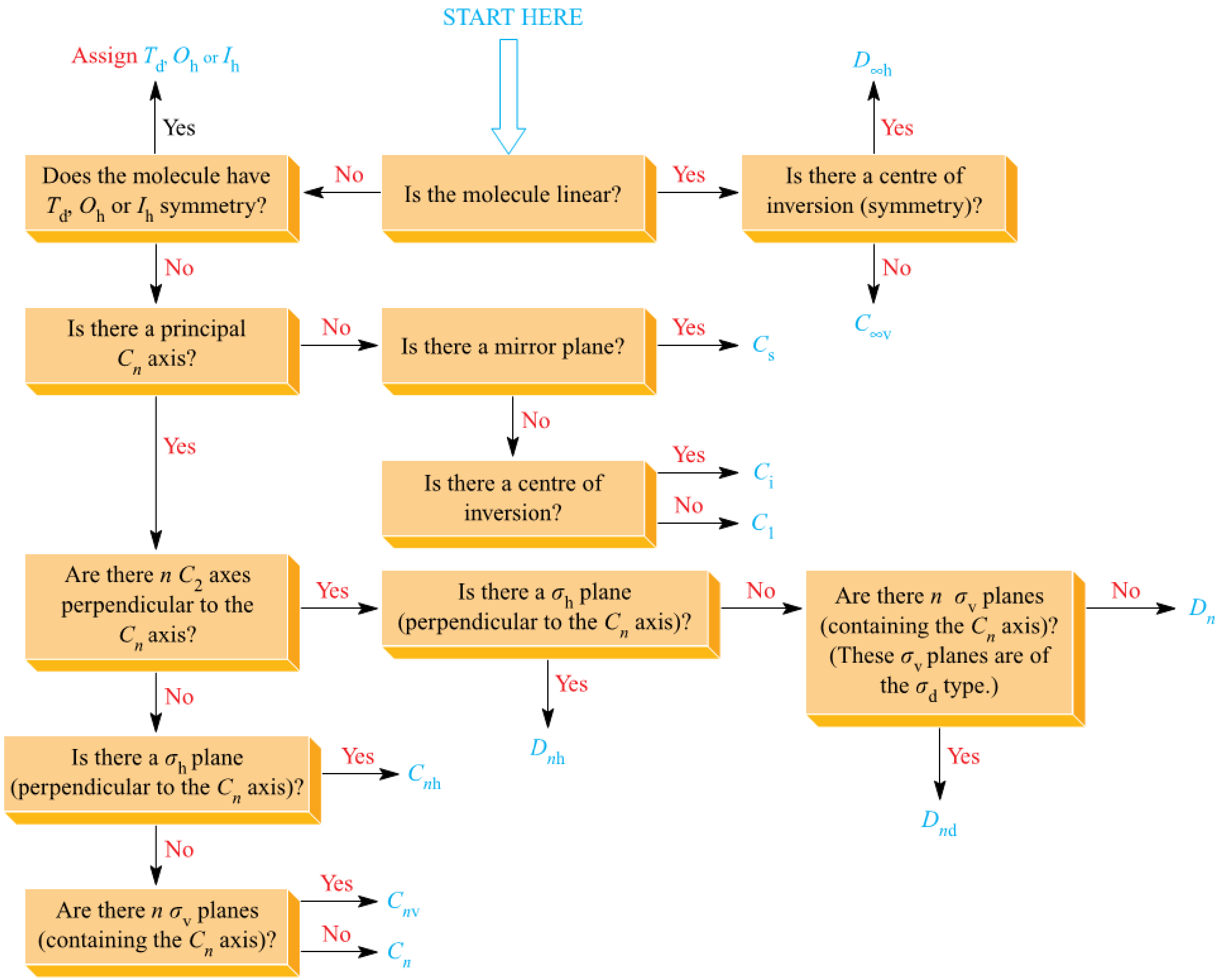
Atomic Number	Element	Orbital Potential Energy (eV) 1s	2s	2p	3s	3p	4s	4p
1	H	−13.61						
2	He	−24.59						
3	Li		−5.39					
4	Be		−9.32					
5	B		−14.05	−8.30				
6	C		−19.43	−10.66				
7	N		−25.56	−13.18				
8	O		−32.38	−15.85				
9	F		−40.17	−18.65				
10	Ne		−48.47	−21.59				
11	Na				−5.14			
12	Mg				−7.65			
13	Al				−11.32	−5.98		
14	Si				−15.89	−7.78		
15	P				−18.84	−9.65		
16	S				−22.71	−11.62		
17	Cl				−25.23	−13.67		
18	Ar				−29.24	−15.82		
19	K						−4.34	
20	Ca						−6.11	
30	Zn						−9.39	
31	Ga						−12.61	−5.93
32	Ge						−16.05	−7.54
33	As						−18.94	−9.17
34	Se						−21.37	−10.82
35	Br						−24.37	−12.49
36	Kr						−27.51	−14.22

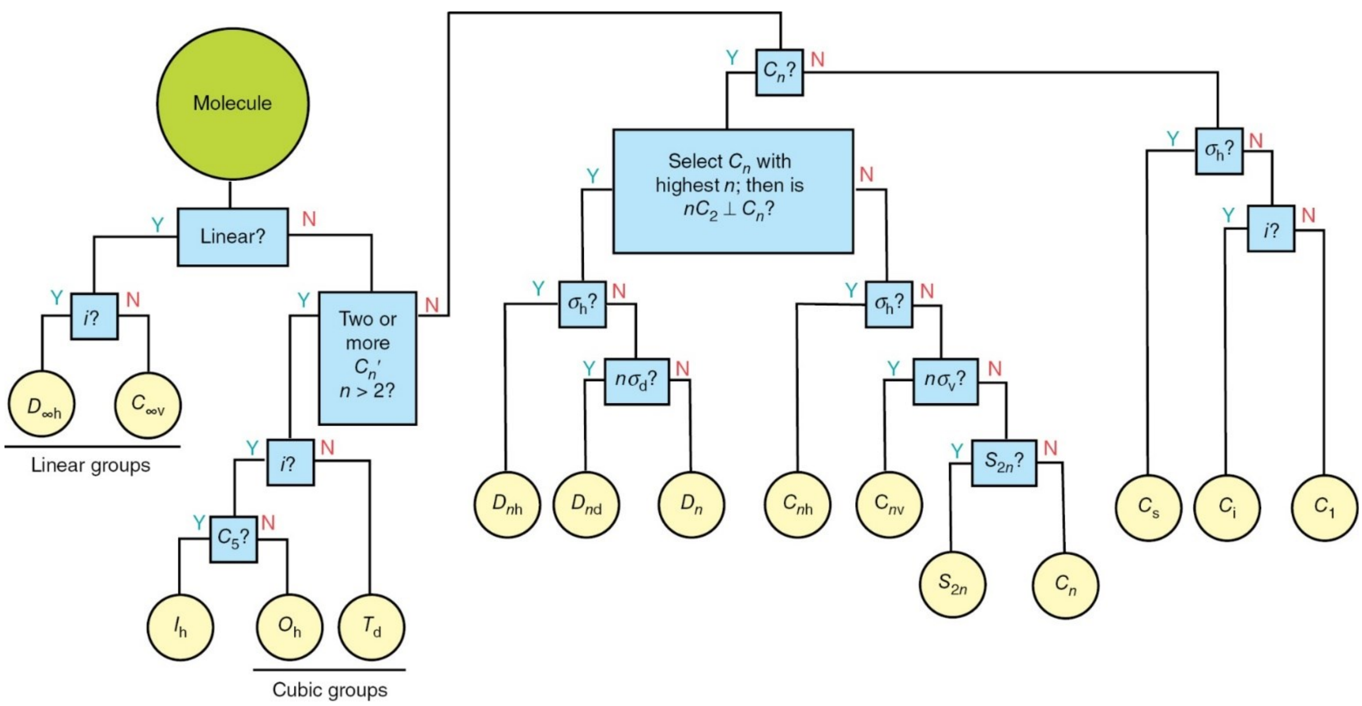
J. B. Mann, T. L. Meek, L. C. Allen, *J. Am. Chem. Soc.*, 2000, *122*, 2780.

All energies are negative, representing average attractive potentials between the electrons and the nucleus for all terms of the specified orbitals.

Additional orbital potential energy values are available in the online Appendix B-9.

Supplementary Information – Page 2





The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	……								
	s block		d block										p block					

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 256.1	102 No 259.1	103 Lr 260.1
	f block														