UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2008/2009

TITLE OF PAPER: **INORGANIC CHEMISTRY I**

COURSE NUMBER: **C301**

TIME ALLOWED: **THREE (3) HOURS**

INSTRUCTIONS: **THERE ARE SIX (6) QUESTIONS.
ANSWER ANY FOUR (4) QUESTIONS.
EACH QUESTION IS WORTH 25 MARKS.**

A PERIODIC TABLE AND A TABLE OF CONSTANTS HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

"Marks will be awarded for method, clearly labelled diagrams, organization and presentation of thoughts in clear and concise language"

Question One

a) Give the IUPAC name for each of the following:

i) $K_5[Mo(CN)_7]$
ii) $[Cr(NH_3)_6][Cr(CN)_6$
iii) $[Co(DMSO)_6](ClO_4)_3$
iv) $Ti(OCH_2CH_3)_4$

[6 mks]

b) Give the formula and draw the structure of each of the following:

i) Tetraoxomanganate(VII)
ii) Bis(acetyacetonato)oxovanadium(IV)
iii) Tri-μ-chlorobis(trichlorotungstate(III))

[6 mks]

c) State the type of isomerism that may be exhibited by the following six-coordinate complexes, and draw structures of the isomers:

i) $Ru(py)_3Cl_3$
ii) $Ru(bpy)_2Cl_2$
iii) $Ru(dien)Br_3$

[13 mks]

Question Two

a) The first charge transfer band for $[MnO_4]^-$ occurs at 18320 cm^{-1} and that for $[MnO_4]^{-2}$ at 22940 cm^{-1}. Explain the origin of these absorption bands, and comment on the trend in relative energies on going from $[MnO_4]^-$ to $[MnO_4]^{2-}$

[3 mks]

b) Dissolution of vanadium metal in aqueous HBr solution leads to formation of a complex corresponding to formula "$VBr_3.6H_2O$". X-ray diffraction data reveal that the compound contains a complex cation containing a center of symmetry. Suggest the possible formula(s) and structure(s) for the complex cation.

[6 mks]

c) Give an explanation for the fact that the complex $[Co(en)_2Cl_2]_2[CoCl_4]$ has a room temperature magnetic moment of 3.71 BM

[6 mks]

d) The treatment of an aqueous solution of $NiCl_2$ with $H_2NCH(Ph)CH(Ph)NH_2$ gives a blue complex (μ_{eff} = 3.30 BM) which, upon heating, forms a yellow diamagnetic compound. Suggest explanations for these observations.

[10 mks]

Question Three

a) Comment on the following statements concerning electronic spectra

i) $[OsCl_6]^{3-}$ and $[RuCl_6]^{3-}$ exhibit LMCT bands at 282 and 348 nm respectively **[6 mks]**

ii) $[Fe(bpy)_3]^{2+}$ is expected to exhibit an MLCT band rather than an LMCT band

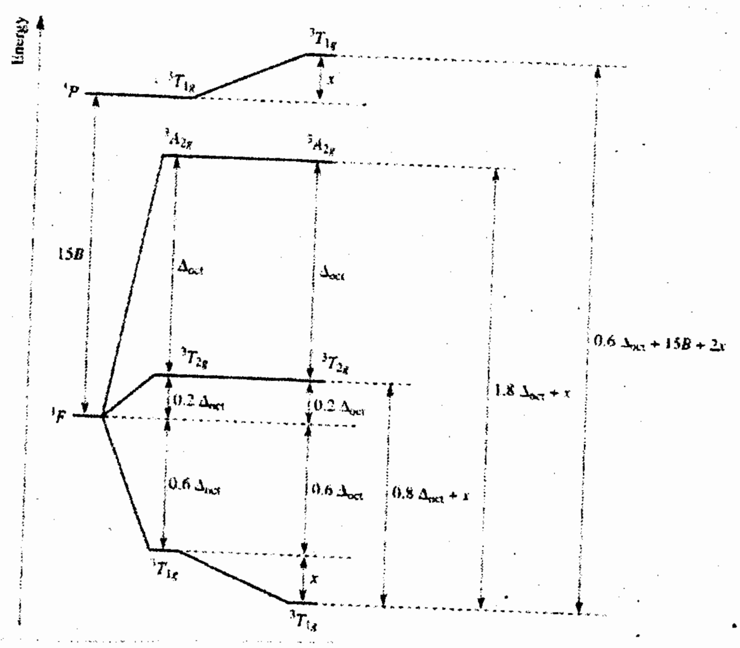
[4 mks]

b) Values of Racah parameters B for free gaseous Cr^{3+}, Mn^{2+} and Ni^{2+} ions are 918, 960 and 1041 cm^{-1} respectively. For the corresponding hexaqua ions, values of B are 725, 835 and 940 cm^{-1} respectively. Suggest a reason for the reduction in B upon forming each complex ion.

[5 mks]

c) The electronic spectrum of $[V(H_2O)_6]^{3+}$ shows peaks at 17400, 25200 and 34500 cm^{-1}. Use the diagram below to assign the peaks and calculate the values of x, Δ_o and the Racah parameter B.

[10 mks]



The **Orgel diagram for Question 3 c)**

Question Four

a) Complete and balance the following reactions:

i) $[Cr(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftarrows$

ii) $[CrO_4]^{2-}(aq) + H^+(aq) \rightleftarrows$

iii) $TiCl_4 + ROH + R'NH_2 \longrightarrow$

iv) $V + O_2 \xrightarrow{\Delta}$

v) $Mn + O_2 \xrightarrow{\Delta}$

[8 mks]

b) Draw the structures of the following:

i) $[TiO(DMSO)_5]Cl_2$, DMSO = $CH_3S(O)CH_3$

ii) $[MoS_4]^{2-}$

iii) $[CuO_2]^{2-}$, coordination no. =4

iv) $VF_5(s)$, coordination no. =6

[8 mks]

c) Gold does not dissolve in hydrochloric acid, but does dissolve in aqua regia, which is a mixture of hydrochloric acid and nitric acid. On the other hand, nickel easily dissolves in hydrochloric acid as well as in aqua regia. Explain the observed difference in the properties of the two metals. Where necessary, your answer should be accompanied by reaction equations.

[7 mks]

d) Explain why Zn(II) compounds are diamagnetic irrespective of the coordination environment of the zinc(II) ion.

[2 mks]

Question Five

a) Define and give one example or illustration of each of the following

i) Kinetically inert complex
ii) Anation reaction
iii) Mixed-order reaction
iv) Self-exchange electron transfer

[8 mks]

b) Consider the reaction

$$ML_xX + Y \longrightarrow ML_xY + X$$

where X is the leaving group and Y is the entering group. Use appropriate reaction equations to illustrate the two possible limiting mechanisms and sketch reaction profiles for each of the reaction pathways. The diagrams should be labeled, indicating reactants, intermediates (if any), etc. **[11 mks]**

c) Using a sequence of reaction equations, give an outline how you would prepare

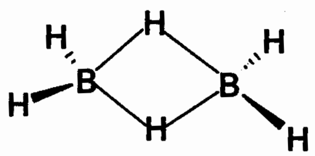
i) cis-$[PtCl_2(NH_3)(NO_2)]$
ii) trans-$[PtCl_2(NH_3)(NO_2)]$

[6 mks]

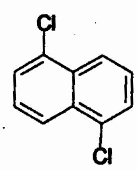
Question Six

a) With the help of the flow-chart which is provided, determine the point group for each of the following:

i) B_2H_6

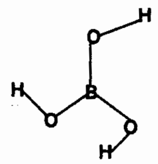


ii) 1,5-dichloronaphthalene



iii) O=C=S

iv) Boric acid, $B(OH)_3$

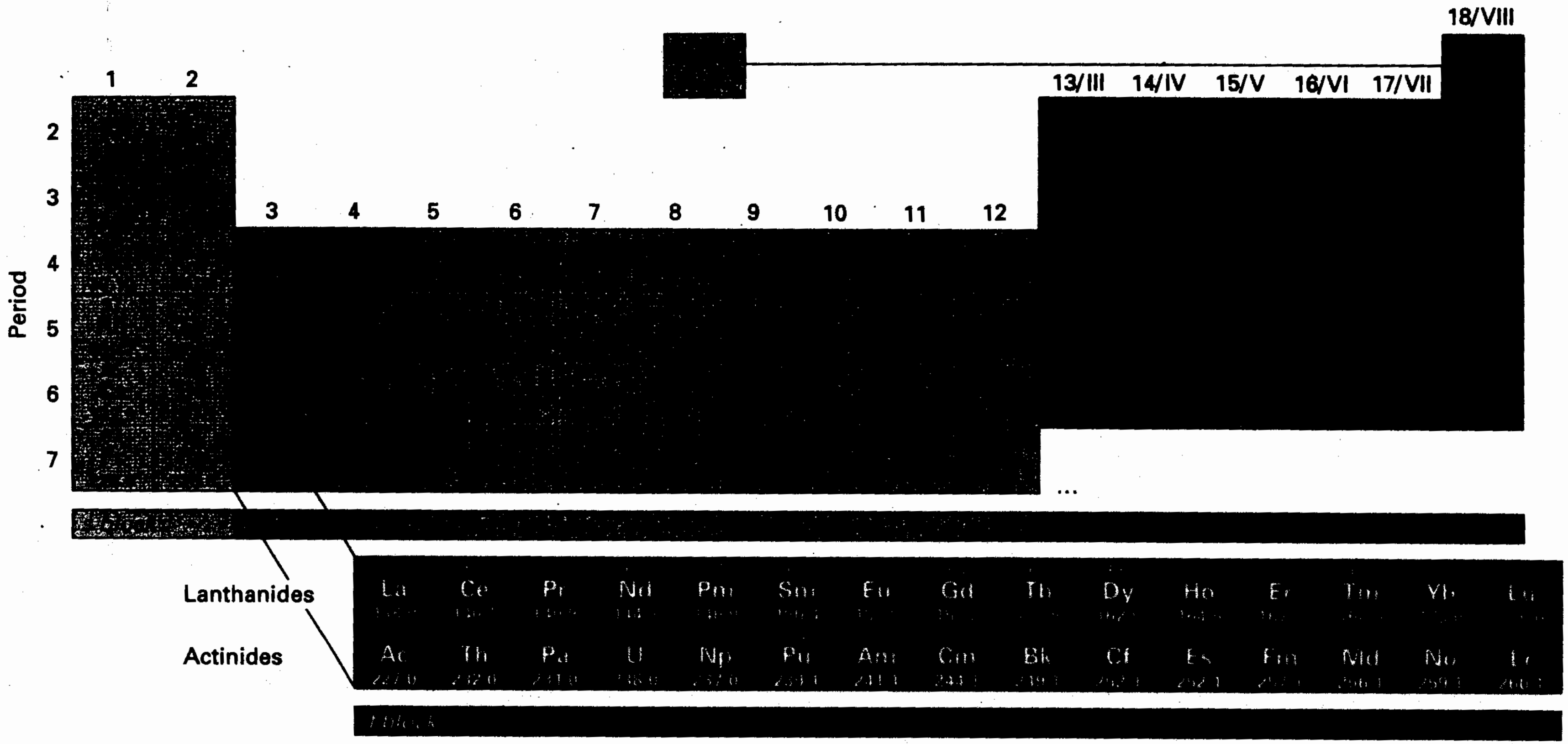


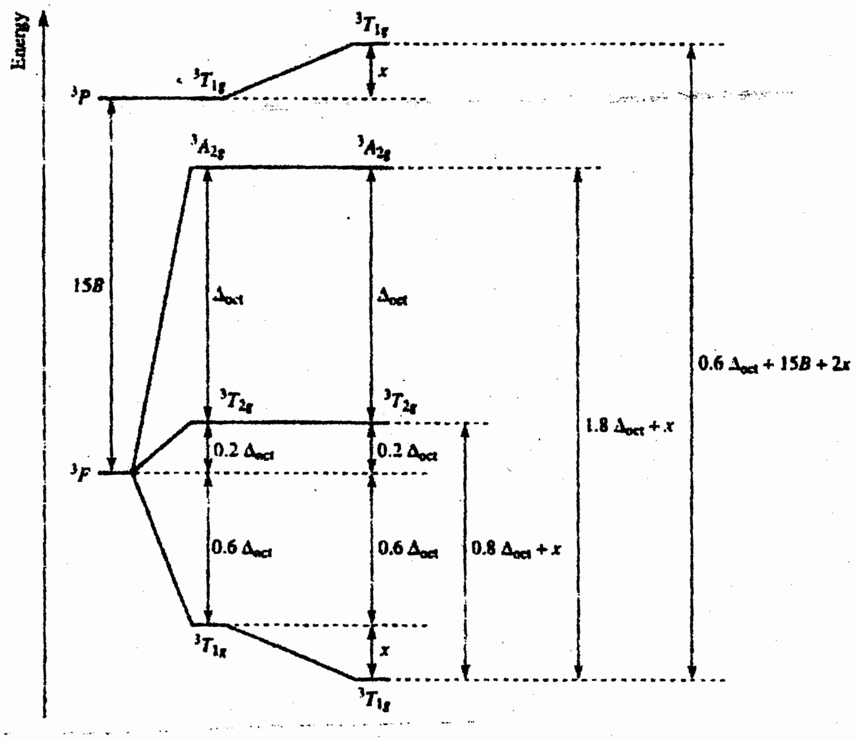
[12 mks]

b) The complex ion, $[Pt(CO)_4]^{2+}$, has one strong peak at 2235 cm^{-1}, which is assigned to a C-O stretching vibration mode, in its IR spectrum and this peak is absent in the Raman spectrum. In the Raman spectrum, two absorption bands (which are absent in the IR spectrum) due to C-O stretching are observed at 2257 and 2281 cm^{-1}. Show that these data are consistent with the structure of $[Pt(CO)_4]^{2+}$ having D_{4h} symmetry.

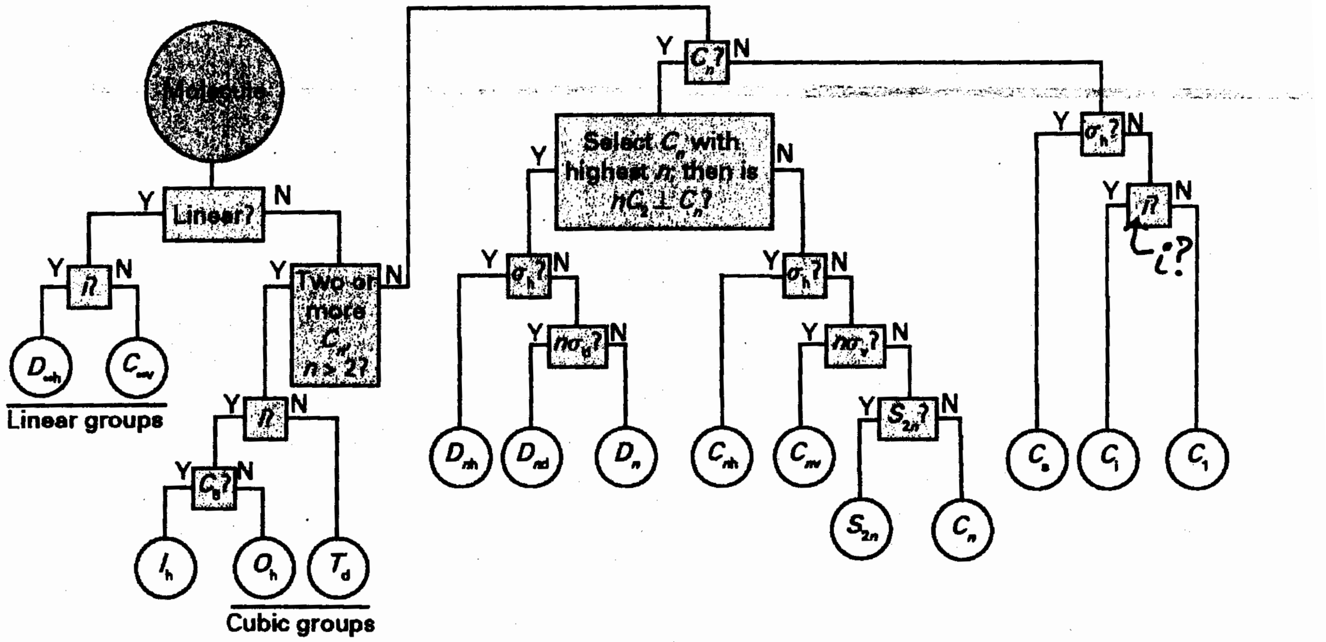
[13 mks]

The Periodic Table





The Orgel diagram for Question 3 c)



The flow-chart (Decision tree) used for assigning point groups

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Elementary charge	e	$1.602\,177 \times 10^{-19}\ \mathrm{C}$
Faraday constant	$F = eN_A$	$9.6485 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
Gas constant	$R = kN_A$	$8.314\,51\ \mathrm{J\ K^{-1}\ mol^{-1}}$
		$8.205\,78 \times 10^{-2}\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}}$
		$62.364\ \mathrm{L\ Torr\ K^{-1}\ mol^{-1}}$
Planck constant	h	$6.626\,08 \times 10^{-34}\ \mathrm{J\ s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}\ \mathrm{J\ s}$
Avogadro constant	N_A	$6.022\,14 \times 10^{23}\ \mathrm{mol^{-1}}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27}\ \mathrm{kg}$
Mass of		
electron	m_e	$9.109\,39 \times 10^{-31}\ \mathrm{kg}$
proton	m_p	$1.672\,62 \times 10^{-27}\ \mathrm{kg}$
neutron	m_n	$1.674\,93 \times 10^{-27}\ \mathrm{kg}$
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}\ \mathrm{J\ s^2\ C^{-2}\ m^{-1}}$
		$4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}$
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}$
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}\ \mathrm{J^{-1}\ C^2\ m^{-1}}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}\ \mathrm{J\ T^{-1}}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}\ \mathrm{J\ T^{-1}}$
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}\ \mathrm{m}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^{5}\ \mathrm{cm^{-1}}$
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}\ \mathrm{N\ m^2\ kg^{-2}}$
Standard acceleration of free fall†	g	$9.806\,65\ \mathrm{m\ s^{-2}}$

† Exact (defined) values

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

APPENDIX C POTENTIALS OF SELECTED HALF-REACTIONS AT 25 °C

A summary of oxidation/reduction half-reactions arranged in order of decreasing oxidation strength and useful for selecting reagent systems.

Half-reaction		E°, V
$F_2(g) + 2H^+ + 2e^-$	$= 2HF$	3.06
$O_3 + 2H^+ + 2e^-$	$= O_2 + H_2O$	2.07
$S_2O_8^{2-} + 2e^-$	$= 2SO_4^{2-}$	2.01
$Ag^{2+} + e^-$	$= Ag^+$	2.00
$H_2O_2 + 2H^+ + 2e^-$	$= 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^-$	$= MnO_2(s) + 2H_2O$	1.70
$Ce(IV) + e^-$	$= Ce(III)$ (in 1*M* $HClO_4$)	1.61
$H_5IO_6 + H^+ + 2e^-$	$= IO_3^- + 3H_2O$	1.6
Bi_2O_4 (bismuthate) $+ 4H^+ + 2e^-$	$= 2BiO^+ + 2H_2O$	1.59
$BrO_3^- + 6H^+ + 5e^-$	$= \frac{1}{2}Br_2 + 3H_2O$	1.52
$MnO_4^- + 8H^+ + 5e^-$	$= Mn^{2+} + 4H_2O$	1.51
$PbO_2 + 4H^+ + 2e^-$	$= Pb^{2+} + 2H_2O$	1.455
$Cl_2 + 2e^-$	$= 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$= 2Cr^{3+} + 7H_2O$	1.33
$MnO_2(s) + 4H^+ + 2e^-$	$= Mn^{2+} + 2H_2O$	1.23
$O_2(g) + 4H^+ + 4e^-$	$= 2H_2O$	1.229
$IO_3^- + 6H^+ + 5e^-$	$= \frac{1}{2}I_2 + 3H_2O$	1.20
$Br_2(l) + 2e^-$	$= 2Br^-$	1.065
$ICl_2^- + e^-$	$= \frac{1}{2}I_2 + 2Cl^-$	1.06
$VO_2^+ + 2H^+ + e^-$	$= VO^{2+} + H_2O$	1.00
$HNO_2 + H^+ + e^-$	$= NO(g) + H_2O$	1.00
$NO_3^- + 3H^+ + 2e^-$	$= HNO_2 + H_2O$	0.94
$2Hg^{2+} + 2e^-$	$= Hg_2^{2+}$	0.92
$Cu^{2+} + I^- + e^-$	$= CuI(s)$	0.86
$Ag^+ + e^-$	$= Ag$	0.799
$Hg_2^{2+} + 2e^-$	$= 2Hg$	0.79
$Fe^{3+} + e^-$	$= Fe^{2+}$	0.771
$O_2(g) + 2H^+ + 2e^-$	$= H_2O_2$	0.682
$2HgCl_2 + 2e^-$	$= Hg_2Cl_2(s) + 2Cl^-$	0.63
$Hg_2SO_4(s) + 2e^-$	$= 2Hg + SO_4^{2-}$	0.615
$Sb_2O_5 + 6H^+ + 4e^-$	$= 2SbO^+ + 3H_2O$	0.581
$H_3AsO_4 + 2H^+ + 2e^-$	$= HAsO_2 + 2H_2O$	0.559
$I_3^- + 2e^-$	$= 3I^-$	0.545
$Cu^+ + e^-$	$= Cu$	0.52
$VO^{2+} + 2H^+ + e^-$	$= V^{3+} + H_2O$	0.337
$Fe(CN)_6^{3-} + e^-$	$= Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^-$	$= Cu$	0.337
$UO_2^{2+} + 4H^+ + 2e^-$	$= U^{4+} + 2H_2O$	0.334

(*continued*)

APPENDIX C (continued)

Half-reaction		E° (V)
$Hg_2Cl_2(s) + 2e^-$	$= 2Hg + 2Cl^-$	0.2676
$BiO^+ + 2H^+ + 3e^-$	$= Bi + H_2O$	0.32
$AgCl(s) + e^-$	$= Ag + Cl^-$	0.2222
$SbO^+ + 2H^+ + 3e^-$	$= Sb + H_2O$	0.212
$CuCl_3^{2-} + e^-$	$= Cu + 3Cl^-$	0.178
$SO_4^{2-} + 4H^+ + 2e^-$	$= SO_2(aq) + 2H_2O$	0.17
$Sn^{4+} + 2e^-$	$= Sn^{2+}$	0.15
$S + 2H^+ + 2e^-$	$= H_2S(g)$	0.14
$TiO^{2+} + 2H^+ + e^-$	$= Ti^{3+} + H_2O$	0.10
$S_4O_6^{2-} + 2e^-$	$= 2S_2O_3^{2-}$	0.08
$AgBr(s) + e^-$	$= Ag + Br^-$	0.071
$2H^+ + 2e^-$	$= H_2$	0.0000
$Pb^{2+} + 2e^-$	$= Pb$	−0.126
$Sn^{2+} + 2e^-$	$= Sn$	−0.136
$AgI(s) + e^-$	$= Ag + I^-$	−0.152
$Mo^{3+} + 3e^-$	$= Mo$	*approx.* −0.2
$N_2 + 5H^+ + 4e^-$	$= H_2NNH_3^+$	−0.23
$Ni^{2+} + 2e^-$	$= Ni$	−0.246
$V^{3+} + e^-$	$= V^{2+}$	−0.255
$Co^{2+} + 2e^-$	$= Co$	−0.277
$Ag(CN)_2^- + e^-$	$= Ag + 2CN^-$	−0.31
$Cd^{2+} + 2e^-$	$= Cd$	−0.403
$Cr^{3+} + e^-$	$= Cr^{2+}$	−0.41
$Fe^{2+} + 2e^-$	$= Fe$	−0.440
$2CO_2 + 2H^+ + 2e^-$	$= H_2C_2O_4$	−0.49
$H_3PO_3 + 2H^+ + 2e^-$	$= HPH_2O_2 + H_2O$	−0.50
$U^{4+} + e^-$	$= U^{3+}$	−0.61
$Zn^{2+} + 2e^-$	$= Zn$	−0.763
$Cr^{2+} + 2e^-$	$= Cr$	−0.91
$Mn^{2+} + 2e^-$	$= Mn$	−1.18
$Zr^{4+} + 4e^-$	$= Zr$	−1.53
$Ti^{3+} + 3e^-$	$= Ti$	−1.63
$Al^{3+} + 3e^-$	$= Al$	−1.66
$Th^{4+} + 4e^-$	$= Th$	−1.90
$Mg^{2+} + 2e^-$	$= Mg$	−2.37
$La^{3+} + 3e^-$	$= La$	−2.52
$Na^+ + e^-$	$= Na$	−2.714
$Ca^{2+} + 2e^-$	$= Ca$	−2.87
$Sr^{2+} + 2e^-$	$= Sr$	−2.89
$K^+ + e^-$	$= K$	−2.925
$Li^+ + e^-$	$= Li$	−3.045

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

TRANSITION ELEMENTS

Atomic mass → Symbol → Atomic No. →

Series														
*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.