ADVANCED CHEMISTRY

INORGANIC CHEMISTRY HW #1 - WINTER

Chapter 2

(10) (a) 5d $\quad l=2 \quad m_l = -2, -1, 0, +1, +2$

4f $\quad l=3 \quad m_l = -3, -2, -1, 0, +1, +2, +3$

7g $\quad l=4 \quad m_l = -4, -3, -2, -1, 0, +1, +2, +3, +4$

(b) 3d $\quad n=3 \quad l=2 \quad m_l = -2, -1, 0, +1, +2$

In each case $M_s = \pm \frac{1}{2}$

(12) (a) V (23) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^3$

(b) Br (35) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^5$

(c) Ru (44) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^6\, 5s^2\, 4d^6$

Ru^{3+} $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^6\, 4d^5$

(d) Hg (80) [Xe] $6s^2\, 5d^{10}\, 4f^{14}$

Hg^{2+} [Xe] $4f^{14}\, 5d^{10}$

(e) Sb (51) [Kr] $5s^2\, 4d^{10}\, 5p^3$

(13) Mn^{2+} has five 3d electrons

Ti^{2+} has two 3d electrons

(15) P $(1s^2)(2s^2\,2p^6)(3s^2\,3p^3)$

$S = 4(0.35) + 8(0.85) + 2(1.0) = 10.2$

$Z^* = Z - S = 15 - 10.2 = \underline{\underline{4.8}}$

S $(1s^2)(2s^2\,2p^6)(3s^2\,3p^4)$

$S = 5(0.35) + 8(0.85) + 2(1.0) = 10.55$

$Z^* = Z - S = 16 - 10.55 = \underline{\underline{5.45}}$

Cl $(1s^2)(2s^2\,2p^6)(3s^2\,3p^5)$

$S = 6(0.35) + 8(0.85) + 2(1.0) = 10.90$

$Z^* = Z - S = 17 - 10.90 = \underline{\underline{6.10}}$

Ar $(1s^2)(2s^2\,2p^6)(3s^2\,3p^6)$

$S = 7(0.35) + 8(0.85) + 2(1.0) = 11.25$

$Z^* = Z - S = 18 - 11.25 = \underline{\underline{6.75}}$

P S Cl Ar

———————→ atomic radius decreases

———————→ Z^* increases

Since valence electrons are filling into the same orbital (3p orbital), as Z^* increases the atomic radius must decrease. Indeed this is

(b) O^{2-} $(1s^2)(2s^2 2p^6)$

$S = 7(0.35) + 2(0.85) = 4.15$

$Z^* = Z - S = 8 - 4.15 = \underline{\underline{3.85}}$

F^- $(1s^2)(2s^2\ 2p^6)$

$S = 7(0.35) + 2(0.85) = 4.15$

$Z^* = Z - S = 9 - 4.15 = \underline{\underline{4.85}}$

Na^+ $(1s^2)(2s^2\ 2p^6)$

$S = 7(0.35) + 2(0.85) = 4.15$

$Z^* = Z - S = 11 - 4.15 = \underline{\underline{6.85}}$

Mg^{2+} $(1s^2)\ (2s^2\ 2p^6)$

$S = 7(0.35) + 2(0.85) = 4.15$

$Z^* = Z - S = 12 - 4.15 = \underline{\underline{7.85}}$

all these ions are <u>isoelectronic</u> ions. Therefore as the charge of the nucleus increases, size of the ion must decrease, which means that the effective nuclear charge must increase (this is consistent with the observation).

	O^{2-}	F^-	Na^+	Mg^{2+}
# of p	6	7	8	9
# of $\bar{e}$	8	8	8	8

~~size~~ ⟶ size decreases

⟶ Z^* increases.

(c) Cu $(1s^2)(2s^2\,2p^6)(3s^2\,3p^6)\;(3d^{10})\;(4s^1)$

<u>4s electron</u>

$S = 18(0.85) + 10(1.0) = 25.3$

$Z^* = Z - S = 29 - 25.3 = \underline{\underline{3.7}}$

<u>3d electron</u>

$S = 9(0.35) + 18(1.0) = 21.15$

$Z^* = Z - S = 29 - 21.15 = \underline{\underline{7.85}}$

Z^* for the 4s electron $<<$ Z^* for the 3d electron

∴ 4s electron is likely to be lost compared to the 3d electron.

(d) Ce $1s^2\,2s^2 2p^6\;3s^2 3p^6\;4s^2\,4p^6\,3d^{10}$ ~~4f~~ $5s^2\;4d^{10}\;5p^6$ [~~5d~~ $5d^1$]
$6s^2\;4f^1\;5d^1$

$(1s^2)(2s^2 2p^6)(3s^2 3p^6)(4s^2 4p^6)(3d^{10})(5s^2 5p^6)(4d^{10})$
$(6s^2)(\underline{4f^1})(5d^1)$

~~Sm~~ $(1s^2)\;(2s^2 2p^6)\;(3s^2 3p^6)(3d^{10})\;(4s^2\,4p^6)(4d^{10})\;\underline{\underline{(4f^1)}}$
$(5s^2\,5p^6)\;(5d^1)\;6s^2$

$S = 1.00(46) = 46$ $\qquad Z^* = 58 - 46 = \underline{\underline{12}}$

Pr $(1s^2)(2s^2 2p^6)\;(3s^2\,3p^6)\;(3d^{10})\;(4s^2 4p^6)\;(4d^{10})\;\underline{\underline{(4f^3)}}$
$(5s^2\,5p^6)\;(6s^2)$

$S = 2(0.35) + 46(1.00) = 46.7$ $\qquad Z^* = 59 - 46.7$

$Z^* = \underline{\underline{12.3}}$

Nd $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^2 4p^6)(4d^{10})\underline{\underline{(4f^4)}}$
$(5s^2 5p^6)(6s^2)$

$S = 3(0.35) + 46(1.00) = 47.05$

$Z^* = Z - S = 60 - 47.05 = \underline{\underline{12.95}}$

	Ce		Pr		Nd
atomic #	58	<	59	<	60
Z^*	12	<	12.3	<	12.95 ~~11.1~~

∴ atomic radius must decrease as Z^* increases

~~Ce > Pr~~ Ce > Pr > Nd

⟶ size decreases

This is consistent with lanthanide contraction.

(16) (a) Ga > Ca as you go across the same period atomic size decreases, valence $\bar{e}$ are closer to the nucleus, therefore I.E. increases.

(b) Mg > Ca As you go down a group, atomic radius increases (Ca is larger than Mg). Hence it is easier to remove an $\bar{e}$ from ~~the~~ Ca than from Mg.

(c) P < Si

P [Ne] $3s^2 3p^3$

Si [Ne] $3s^2 3p^2$

Since the 3p orbital is exactly half-filled in P, it is a stable configuration compared with that of Si.

∴ P is less electronegative than Si.

(d) Mn [Ar] $4s^2 3d^5$

Mn^{2+} [Ar] $3d^5$

The 4s electrons experience lower effective nuclear charge (Z^*) than 3d electrons, hence 4s electrons are easier to remove when forming Mn^{2+} ions.

(22) (a) S [Ne] $3s^2 3p^4$

Cl [Ne] $3s^2 3p^5$

Cl needs only one more $\bar{e}$ to achieve the rare gas electron configuration (S needs 2 more $\bar{e}$'s).
Therefore Cl has a higher $\bar{e}$ affinity than S.

(b) I is larger in size than Br since it is lower in Group 7A than Br.

∴ atomic radius of I > atomic radius of Br

and therefore I does not have a higher electron affinity compared with Br.

(c) B $1s^2 2s^2 2p^1$

Be $1s^2 2s^2$

Be's valence orbital (2s) is completely filled. This is a stable configuration.

B has one $\bar{e}$ in its valence orbital (2p), ~~but~~ which can be given up more easily compared with the 2s orbital of Be.

∴ B has a lower I.E. than Be.

(d) P [Ne] $3s^2 3p^3$ ← stable since valence orbital (3p) is exactly half filled.

S [Ne] $3s^2 3p^4$

∴ Easier to remove an $\bar{e}$ from 3p of S than from 3p of P.

∴ S has a lower I.E. than P.

(e) Cl [Ne] $3s^2 3p^5$ ← valence orbital is 3p

F [He] $2s^2 2p^5$ ← valence orbital is 2p

Cl has a larger atomic radius than F.

⇒ easier to remove the valence $\bar{e}$ from Cl compared with that of F.

∴ I.E. of Cl < I.E. of F

(26) (a) $Sr^{2+} < Rb^{+} < Br^{-} < Se^{2-}$

→ size increases

	Sr^{2+}	Rb^{+}	Br^{-}	Se^{2-}	
# of $\bar{e}$	36	36	36	36	← isoelectronic ions.
# of p	38	37	35	~~33~~ 34	

Sr^{2+} ~~Se^{2-}~~ has the <u>highest</u> p: $\bar{e}$ ratio. ⇒ smallest in size

Se^{2-} has the <u>lowest</u> p: $\bar{e}$ ratio ⇒ largest in size.

(b) $Y^{3+} > Zr^{4+} > Nb^{5+}$

	Y^{3+}	Zr^{4+}	Nb^{5+}	
# of $\bar{e}$	36	36	36	isoelectronic ions.
# of p	39	40	41	

p: $\bar{e}$ ratio is highest for Nb^{5+} ⇒ smallest in size

p: $\bar{e}$ ratio is lowest for Y^{3+} ⇒ largest in size.

(c) $Co^{4+} < Co^{3+} < Co^{2+} < Co$

	Co^{4+}	Co^{3+}	Co^{2+}	Co
# of p	27	27	27	27
# of $\bar{e}$	23	24	25	27

highest p: $\bar{e}$ ratio is in Co^{4+} ⇒ smallest in size

lowest p: $\bar{e}$ ratio is in Co ⇒ largest in size.