Important notations:

Determination of Ground state term for d^1 to d^{10} metal ions

What is an energy term of a configuration?

An energy term (also called simply as **term**) is an energy level or a set of energy levels which result from the *electron – electron repulsion* in an electronic arrangement or in a set of electronic arrangements of a configuration of a free metal atom or ion. An energy term contains a set of degenerate energy levels. Since the electron – electron repulsions in all the electronic arrangements of configuration may not be the same, there can be several energy levels in a configuration. Total number of energy levels in a configuration is equal to the total number of possible electronic arrangements for that configuration. In a many – electron system the number of energy levels is calculated though $l-l$ and $s-s$ coupling effects.

An energy term of a configuration is written as $^{2S+1}$ **L** in which the quantity (**2S+1**) is called **spin multiplicity** of the term. Spin multiplicity gives the number of orientations of **S** in space or **spin multiplicity** gives the number of spin energy level. S in the term $^{2S+1}$ **L** is called **resultant spin angular momentum quantum numbers** & **'L'** is called resultant **orbital angular momentum quantum number**, for **L = 0, 1, 2, 3, 4, 5** the symbols used are **S, P, D, F, G, H** respectively. Thus

L	0	1	2	3	4	5
Symbols	S	P	D	F	G	H

Representation of Full spectroscopic term of a given configuration

A term of a given configuration is represented as $^{2S+1}$ **L**. The representation of a full term of a given configuration also contains **J** in addition to **L** & ***2S+1***.

'**J**' is written as a subscript at the right hand of L Thus a full term of a configuration is represented as $^{2S+1}L_J$. Full term is also called ***Russel-Saunders term.***

In this representation:

i. L = *Resultant orbital angular momentum quantum number (also called simply as resultant orbital quantum number).*

ii. S = *Resultant spin angular momentum quantum number (also called simply as resultant orbital quantum number)*

iii. 2S + 1 = *Spin multiplicity of the term. It indicates the number of spin energy levels in a term.*

iv. J = *Resultant (Overall or total or inner) angular momentum quantum number. J is also called simply as resultant (Overall or total or inner quantum number or (Orbital + spin) quantum number.*

Determination of Russel – Saunders symbols or terms for d^n Configurations (n = 1 to 10) of a free metal ion.

Russel – Saunders symbol or term of a given $\mathbf{d}^n$ Configuration is represented as $^{2S+1}\mathbf{L}_J$. The term obtained by removing J from the Russel – Saunders term given above is called **ground state term**. Thus, ground state term is represented as $^{2S+1}\mathbf{L}$.

The determination involves the following steps:

i. Represent d-orbitals by thick bar (**–**) & fill these orbitals with $\mathbf{d}^x$ electrons according to Hund's rule.

ii. Find out the value of *resultant orbital quantum number* (L) with the help of the relation: $L=\sum m_l$.
Where; m_l is the orbital angular momentum for single electron. Values of m_l for $s,p,d\wedge f$ orbitals are as :
$s(l=0)=0;p(l=1)=+1,0,-1;d(l=2)=+2,+1,0,-1,-2;f(l=3)=+3,+2,+1,0,-1,-2,-3.$

L arises due to $l-l$ coupling. The value of L ranges from l_1+l_2 to l_1-l_2 or l_2-l_1 whichever is positive, $i.e.,$

$$L=(l¿¿1+l_2),(l_1+l_2-1),\ldots,(l¿¿1-l_2)¿¿ \textbf{ or } (l_2+l_1)$$

We know that values of $'l$**'** are represented by small letters as shown below:

Values of l = 0 1 2 3 4 5 ....

Small letters = s p d f g h ....

Similarly values of **L** are represented by capital letters:

Values of L = 0 1 2 3 4 5 ....

Capital letters = S P D F G H ....

iii. Find out the value of resultant quantum number (S) with the help of the relation : $S=\sum m_s$.Where m_s is the spin angular momentum for single electron value of **m$_s$** for an electron represented as ↑ is equal to $+1/2$ & that for an electron represented as ↓ is equal to $-1/2$. Resultant spin quantum number (S) arises due to ***S – S coupling***.

iv. Find the value of spin multiplicity, $2S+1$ with the help of the value of S as determined at step (iii) above spin multiplicity is equal to the number of spin energy levels in a term. Spin multiplicity is also equal to $(n+1)$ where 'n' is the number of unpaired electrons.

v. Find out the value of overall quantum number (J). Jarises due to $L-S$ coupling in many electron system.
J can have the values ranging from $(L+S)$ to $(L-S)$ or $(S-L)$ whichever is positive$ie;$

$$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots(L-S)\vee(S-L)$$

If d^x configuration is half – filled or less than half – filled, then the lowest value of J is used for writing the Russel Saunders symbol or term (ground state symbol) ofd^xconfiguration. On the other hand, if d^xconfiguration is more than half- filled, then the highest value of J is used in writing the ground state symbol.

Above procedure can be understood by determining the ground state symbol for $d^1, d^2, \ldots d^9, d^{10}$configurations of a free metal ion. (Note: For all d – orbitals $l=2$)

i. $d^1\, configuration\,(Ti^{+3}\, oxidation\, state)$

$m_l=+2+1\,0-1-2$

$M_s=\frac{+1}{2}$ (↑)

$(n=1)$

$L=\sum ml$

$¿(+2)\times 1$

$¿2$

$L=2$ *indicates D state.*

$S=\sum m_s$

$\therefore S=1\times\left(\frac{+1}{2}\right)$

$¿\frac{1}{2}$

$\therefore$ *Spin multiplicity*, $2S+1=2\times½+1=2$

Since, spin multiplicity $=2$

Ground state term of d^1 *ion* = $^{2S+1}$**L** = ^{2}**D**

$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots\ldots(L-S)$

$¿\left(2+\frac{1}{2}\right),\left(2+\frac{1}{2}-1\right),\ldots\ldots\ldots\left(2-\frac{1}{2}\right)$

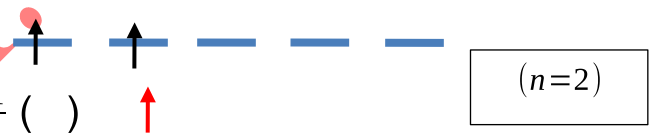
$¿\frac{5}{2},\frac{3}{2}$

Now since d^1 ion is less than half filled, lower value of J will be used; $ie;J=3/2$.
Hence,

Russel — Saunders term of d^1 ion = $^{2S+1}$**L**$_J$ **=** ^{2}**D**$_{3/2}$

ii. d^2 *configuration* $¿$

$m_l=+2+1\,0-1-2$



$M_s=\frac{+1}{2}$ ( )

$L=\sum ml$

$¿(+2)\times1+(+1)\times1$

$¿3$

$L=3$ *indicates F state.*

$S=\sum m_s$

$\therefore S=2\times(\frac{+1}{2})$

¿ 1

$\therefore Spin\,multiplicity, 2S+1=2\times1+1=3$

$Since, spin\,multiplicity=3$

$Ground\ state\ term\ of\ d^2\ ion$ = $^{2S+1}$ **L** = ^{3}**F**

$J=(L+S),(L+S-1),...............(L-S)$

¿ $(3+1),(3+1—1),.........(3-1)$

¿ $4,3,2$

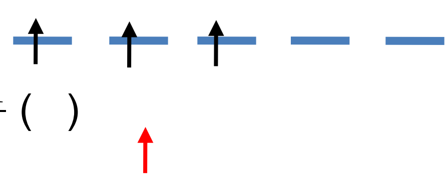
Three values of J(¿ $4,3,2$) show that ^{3}**F** term is split up into three J energy levels which can be designated as ^{3}**F$_4$**, ^{3}**F$_3$**, ^{3}**F$_2$**. Now since d^2 configuration is less than half — filled, the Jenergy level having the lowest value of $J$is the ground state (or term) for d^2 configuration. Thus:

Russel — Saunders term of d^2ion = $^{2S+1}$ **L = ^{3}F$_2$**

Since ^{3}**F$_2$** is the ground state symbol, it has the lowest energy (most stable). The energy of ^{3}**F$_4$**, ^{3}**F$_3$**, ^{3}**F$_2$** state is in the order: ^{3}**F$_2$ < ^{3}F$_3$ < ^{3}F$_4$**

iii. d^3 $configuration$ ¿

$m_l=+2+1\,0-1-2$



$(n=3)$

$M_s=\frac{+1}{2}$ (   )

$L=\sum ml$

$¿(+2)\times 1+(+1)\times 1+(0)\times 1$

$¿3$

$L=3\, indicates\ F\ state.$

$S=\sum m_s$

$\therefore S=3\times(\frac{+1}{2})$

$¿\frac{3}{2}$

$\therefore Spin\ multiplicity, 2S+1=2\times 3/2+1=4$

$Since, spin\ multiplicity=4$

$Ground\ state\ term\ of\ d^3\ ion$ = $^{2S+1}$ **L = ^{4}F**

$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots(L-S)$

$¿\left(3+\frac{3}{2}\right),\left(3+\frac{3}{2}-1\right),\ldots\ldots\ldots\left(3-\frac{3}{2}\right)$

$¿\frac{9}{2},\frac{7}{2}\ldots\frac{3}{2}$

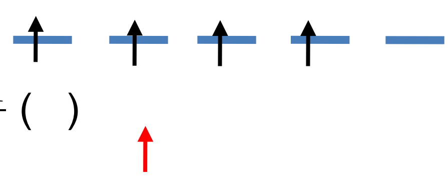
$¿\frac{9}{2},\frac{7}{2},\frac{5}{2},\frac{3}{2}$

Now since d^3 ion is less than half filled, lowest value of J will form the ground state; $ie;J=3/2$. Hence,

Russel — Saunders term of d^1ion = $^{2S+1}$ L $_J$ = $^4F_{3/2}$

iv. $d^4\ configuration¿$

$m_l=+2+1\,0-1-2$



$M_s=\frac{+1}{2}$ ( )

$(n=4)$

$L=\sum ml$

$¿(+2)\times 1+(+1)\times 1+0\times 1+(-1)\times 1$

¿2

$L=2$ *indicates D state*.

$S=\sum m_s$

$\therefore S=4\times(\frac{+1}{2})$

¿2

$\therefore$ *Spin multiplicity*, $2S+1=2\times 2+1=5$

Since, spin multiplicity $=5$

Ground state term of d^4 *ion* = $^{2S+1}$**L** = ^{5}**D**

$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots(L-S)$

¿$(2+2),(2+2-1),\ldots\ldots\ldots\ldots(2-2)$

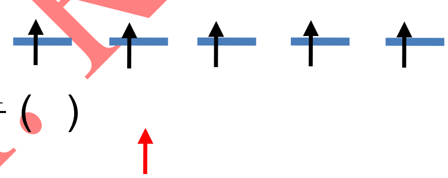
¿$4,3,2,1,0$

Now since d^4 ion is less than half filled, J will have the lowest value; $ie;J=0$.

Russel — Saunders term of d^4**ion =** $^{2S+1}$**L**$_J$ **=** ^{5}**D**$_0$

v. d^5 *configuration*¿

$m_l=+2+1\,0-1-2$



$(n=5)$

$M_s=\frac{+1}{2}$ ( )

$L=\sum ml$

¿$(+2)\times 1+(+1)\times 1+(0)\times 1+(-1)\times 1+(-2)\times 1$

¿0

$L=0$ *indicates S state*.

$S=\sum m_s$

$\therefore S=5\times(\frac{+1}{2})$

¿ $\frac{5}{2}$

$\therefore Spin\,multiplicity, 2S+1=2\times5/2+1=6$

$Since, spin\,multiplicity=6$

$Ground\ state\ term\ of\ d^5\ ion$ = $^{2S+1}$ L = ^{6}F

$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots\ldots(L-S)$

¿ $\left(0+\frac{5}{2}\right),\left(0+\frac{5}{2}-1\right),\ldots\ldots\ldots\left(\frac{5}{2}-0\right)$

¿ $\frac{5}{2},\frac{3}{2},\frac{5}{2}$

¿ $\frac{5}{2}$

Russel — Saunders term of d^5ion = $^{2S+1}$ **L** $_J$ **=** ^{6}**S**$_{5/2}$

vi. $d^6\ configuration$ ¿

$m_l=+2+1\,0-1-2$

$M_s=\frac{+1}{2}$ ( ), $\frac{-1}{2}$ ( ) ↑ ↓

$(n=4)$

$L=\sum ml$

¿ $(+2)\times2+(+1)\times1+0\times1+(-1)\times1+(-2)\times1$

¿ 2

$L=2\ indicates\ D\ state.$

$S=\sum m_s$

$\therefore S=\left(\frac{+1}{2}\right)\times 5+\left(\frac{-1}{2}\right)\times 1$

¿ 2

$\therefore Spin\,multiplicity, 2S+1=2\times 2+1=5$

$Since, spin\,multiplicity=5$

$Ground\ state\ term\ of\ d^4\ ion$ = $^{2S+1}$ **L = ^{5}D**

$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots\ldots(L-S)$

¿ $(2+2),(2+2-1),\ldots\ldots\ldots.(2-2)$

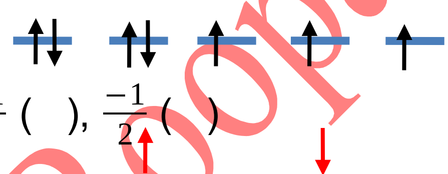
¿ $4,3,2,1,0$

Now since d^6 ion is more than half – filled, the highest value of J forms the ground state, $ie; J=4(highest\ value)$ and hence:

Russel — Saunders term of d^6ion = $^{2S+1}$ **L $_J$ = ^{5}D$_4$**

vii. $d^7\ configuration$

$m_l=+2+1\,0-1-2$



$M_s=\frac{+1}{2}$ ( ), $\frac{-1}{2}$ ( )

$(n=3)$

$L=\sum ml$

¿ $(+2)\times 2+(+1)\times 2+(0)\times 1+(-1)\times 1+(-2)\times 1$

¿ 3

$L=3\ indicates\ F\ state.$

$S=\sum m_s$

$\therefore S=\left(\frac{+1}{2}\right)\times 5+\left(\frac{-1}{2}\right)\times 2$

¿ $\frac{5}{2}-1$

¿ $\frac{3}{2}$

$\therefore Spin\,multiplicity, 2S+1 = 2 \times 3/2 + 1 = 4$

$Since, spin\,multiplicity = 4$

Ground state term of d^7 *ion* = $^{2S+1}$**L** = ^{4}**F**

$$J = (L+S), (L+S-1), \ldots\ldots\ldots\ldots\ldots (L-S)$$

¿ $\left(3+\frac{3}{2}\right), \left(3+\frac{3}{2}-1\right), \ldots\ldots\ldots\ldots \left(3-\frac{3}{2}\right)$

¿ $\frac{9}{2}, \frac{7}{2} \ldots \frac{3}{2}$

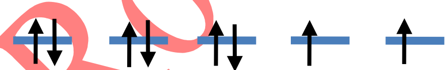
¿ $\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$

Now since d^7 ion is more than half – filled, J will have the highest value. Hence,

Russel — Saunders term of d^7**ion =** $^{2S+1}$**L**$_J$ **=** ^{4}**F**$_{9/2}$

viii. d^8 *configuration*

$m_l = +2\ +1\ 0\ -1\ -2$



$M_s = \frac{+1}{2}(\uparrow), \frac{-1}{2}(\downarrow)$ $(n=2)$

$L = \sum ml$

¿ $(+2) \times 2 + (+1) \times 2 + (0) \times 2 + (-1) \times 1 + (-2) \times 1$

¿ 3

$L = 3$ *indicates F state.*

$S = \sum m_s$

$\therefore S = 5 \times \left(\frac{+1}{2}\right) + 3 \times \left(\frac{-1}{2}\right)$

¿ 1

$\therefore Spin\, multiplicity, 2S+1=2\times 1+1=3$

$Since, spin\, multiplicity=3$

$Ground\ state\ term\ of\ d^2\ ion$ = $^{2S+1}$ L = ^{3}F

$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots(L-S)$
¿ $(3+1),(3+1—1),\ldots\ldots\ldots(3-1)$

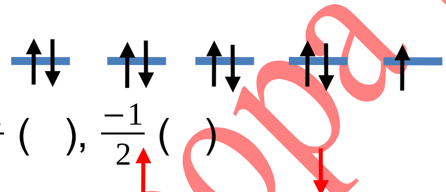
¿ $4,3,2$

Now since d^8 configuration is more than half – filled, the highest value of J is to be used, $ie;\ J=4(highest\ value)$ and hence:

Russel — Saunders term of d^8ion = $^{2S+1}$ L $_J$ = ^{3}F$_4$

ix. $d^9\ configuration$

$m_l=+2+1\,0-1-2$



$M_s=\frac{+1}{2}$ ( ), $\frac{-1}{2}$ ( )

$(n=1)$

$L=\sum ml$
¿ $(+2)\times 2+(+1)\times 2+(0)\times 2+(-1)\times 2+(-2)\times 1$
¿ 2

$L=2\ indicates\ D\ state$

$S=\sum m_s$

$\therefore S=5\times\left(\frac{+1}{2}\right)+4\times\left(\frac{-1}{2}\right)$

¿ $\frac{1}{2}$

$\therefore Spin\, multiplicity, 2S+1=2\times ½+1=2$

$Ground\ state\ term\ of\ d^1\ ion$ = $^{2S+1}$ L = ^{2}D

$$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots\ldots(L-S)$$

¿ $\left(2+\frac{1}{2}\right),\left(2+\frac{1}{2}-1\right),\ldots\ldots\ldots\left(2-\frac{1}{2}\right)$

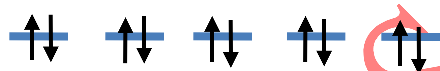
¿ $\frac{5}{2},\frac{3}{2}$

Now since d^9 ion is more than half – filled, J will have higher value, $ie; J=5/2$.
Hence,

Russel — Saunders term of d^1 ion = $^{2S+1}L_J$ = $^2D_{5/2}$

x. d^{10} *configuration*

$m_l=+2+1\,0-1-2$



$M_s=\frac{+1}{2}$ (↑), $\frac{-1}{2}$ (↓)

$(n=0)$

$L=\sum ml$

¿ $(+2)\times 2+(+1)\times 2+(0)\times 2+(-1)\times 2+(-2)\times 2$

¿ 0

$L=0$ *indicates S state*

$S=\sum m_s$

$\therefore S=5\times\left(\frac{+1}{2}\right)+5\times\left(\frac{-1}{2}\right)$

¿ 0

$\therefore$ *Spin multiplicity*, $2S+1=2\times 0+1=1$

Since, spin multiplicity $=1$

Ground state term of d^{10} *ion* **= ^{2S+1}L = ^1S**

$$J=(L+S),(L+S-1),\ldots\ldots\ldots\ldots\ldots(L-S)$$

¿ 0

Russel — Saunders term of d^{10}ion = $^{2S+1}L_J$ = $^1S_0$

d^n configuration (Ion)	$L=\sum$ r state	$S=\sum m_s$ ¿ $\frac{n}{2}$ ¿ of unpaired electrons ¿	Spin multiplicity ¿ $2S+1$ ¿ $n+1$	Ground state term ^{2S+1}L	$J=(L+S),(L+S-1),....(L-S)$	Russel — Saunde term $^{2S+1}L_J$
d^1 ¿	$2(D)$	$1/2$	2	^2D	$3/2$	$^2D_{3/2}$
d^2 ¿	$3(F)$	1	3	^3F	2	$^3F_2$
d^3 ¿	$3(F)$	$3/2$	4	^4F	$3/2$	$^4F_{3/2}$
d^4 ¿	$2(D)$	2	5	^5D	0	$^5D_0$
d^5 ¿	$0(S)$	$5/2$	6	^6S	$5/2$	$^6S_{5/2}$
d^6 ¿	$2(D)$	2	5	^5D	4	$^5D_4$
d^7 ¿	$3(F)$	$3/2$	4	^4F	$9/2$	$^4F_{9/2}$
d^8 ¿	$3(F)$	1	3	^3F	4	$^3F_4$
d^9 ¿	$2(D)$	½	2	^2D	$5/2$	$^2D_{5/2}$
d^{10} ¿	$0(S)$	0	1	^1S	0	$^1S_0$

- The two ions having d^n and d^{10-n} configurations have the same terms with the same value of spin multiplicity but with different value of J.
- For example, the two configurations given in the following four pairs have the same terms given in bracket: $d^1 \wedge d^{10-1} \vee d^9$ – (**^{2}D**), $d^2 \wedge d^{10-2} \vee d^8$ – (**^{3}F**), $d^3 \wedge d^{10-3} \vee d^7$ – (**^{4}F**), $d^4 \wedge d^{10-4} \vee d^6$ – (**^{5}D**), since the two configurations of each pair are hole equivalents to each other.
- The ground state terms of above configuration pairs are given as:

  $d^0, d^{10} \rightarrow$ **^{1}S**

  $d^2, d^8 \rightarrow$ **^{3}F**

  $d^4, d^6 \rightarrow$ **^{5}D**

  $d^1, d^9 \rightarrow$ **^{2}D**

  $d^3, d^7 \rightarrow$ **^{4}F**

  $d^5 \rightarrow$ **^{5}S**
- $d^1, d^9, d^4 \wedge d^6$ ions have the same term symbol which is D (L=2)
- $d^0, d^{10} \wedge d^5$ ions have the same term symbol, S (L=0)
- $d^2, d^8, d^3 \wedge d^7$ ions have the same term symbol, F (L=3)

Question Bank:

1. The ground state term symbol for the free Co^{+2} ion is ………
   a) ^4F

b) ^5F

c) ^4P

d) ^5D

e) ^4D

2. The electronic ground state term for the chromium ion in $[Cr(CN)_6]^{4-}$ is ……..

a) ^3F

b) ^3H

c) ^3G

d) ^5D

3. Find out the ground state term of $3d^5$ configuration of Mn^{+2}.
4. The ground state term symbol for the free ion Fe^{+3} is ……….

a) ^5D

b) ^6S

c) ^6P

d) ^6D

e) ^4F

5. Derive the ground state term symbol for:

i. Ni^{+2}

ii. d^{10} ion

iii. Zn^{+2}

iv. Co^{+3}

v. V^{+2}

6. Find the ground term symbol for $Cr(3d^5\ 4s^1)$.
7. Identify the ground state term giving reasons for the following set **(calculate L): ^{1}S, ^{3}F, ^{3}P, ^{1}G, ^{1}D**
8. Give the ground – state Russell – Saunders terms for $3d^5$ and d^8.

9. Write the Russell – Saunders term symbols for states with the angular momentum quantum numbers (L, S):

a) $\left(0, \frac{5}{2}\right)$

b) $\left(3, \frac{3}{2}\right)$

c) $\left(2, \frac{1}{2}\right)$

d) $(1, 1)$

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