Inner transition elements – the lanthanides and actinides

In the lanthanides, the *4f* electronic orbitals are being filled (elements 57 to 71, $4f^1$ to $4f^{14}$) while the two outer shell electronic configurations are $5d^0$, $6s^2$. Their properties are therefore extremely similar making chemical separation of individual members very difficult. The **lanthanide contraction** (decrease in size of the individual members as the atomic number increases) produces a slight difference in properties sufficient to separate them using ion-exchange chromatography. A similar series of elements exist in which the *5f* orbitals are being filled and the $6d^0$, $7s^2$ remaining constant. These are the actinides (elements 89 to 103, $5f^1$ to $5f^{14}$). Since elements beyond 92, uranium, are not found in nature, most of the elements in the actinide series are **synthetic elements** of extremely short lifetimes. A list of these elements with their electronic configurations are given below:

Lanthanides			Actinides		
57. Lanthanum	(La)	[Xn] $4f^0, 5d^1, 6s^2$	89. Actinium	(Ac)	[Rn] $5f^0, 6d^1, 7s^2$
58. Cerium	(Ce)	[Xn] $4f^2, 5d^0, 6s^2$	90. Thorium	(Th)	[Rn] $5f^0, 6d^2, 7s^2$
59. Praseodymium	(Pr)	[Xn] $4f^3, 5d^0, 6s^2$	91. Protoactinium	(Pa)	[Rn] $5f^2, 6d^1, 7s^2$
60. Neodymium	(Nd)	[Xn] $4f^4, 5d^0, 6s^2$	92. Uranium	(U)	[Rn] $5f^3, 6d^1, 7s^2$
61. Promethium	(Pm)	[Xn] $4f^5, 5d^0, 6s^2$	93. Neptunium	(Np)	[Rn] $5f^4, 6d^1, 7s^2$
62. Samarium	(Sm)	[Xn] $4f^6, 5d^0, 6s^2$	94. Plutonium	(Pu)	[Rn] $5f^6, 6d^0, 7s^2$
63. Europium	(Eu)	[Xn] $4f^7, 5d^0, 6s^2$	95. Americium	(Am)	[Rn] $5f^7, 6d^0, 7s^2$
64. Gadolinium	(Gd)	[Xn] $4f^7, 5d^1, 6s^2$	96. Curium	(Cm)	[Rn] $5f^7, 6d^1, 7s^2$
65. Terbium	(Tb)	[Xn] $4f^9, 5d^0, 6s^2$	97. Berkelium	(Bk)	[Rn] $5f^9, 6d^0, 7s^2$
66. Dysprosium	(Dy)	[Xn] $4f^{10}, 5d^0, 6s^2$	98. Californium	(Cf)	[Rn] $5f^{10}, 6d^0, 7s^2$
67. Holmium	(Ho)	[Xn] $4f^{11}, 5d^0, 6s^2$	99. Einstenium	(Es)	[Rn] $5f^{11}, 6d^0, 7s^2$
68. Erbium	(Er)	[Xn] $4f^{12}, 5d^0, 6s^2$	100. Fermium	(Fm)	[Rn] $5f^{12}, 6d^0, 7s^2$
69. Thulium	(Tm)	[Xn] $4f^{13}, 5d^0, 6s^2$	101. Mendelevium	(Md)	[Rn] $5f^{13}, 6d^0, 7s^2$
70. Ytterbium	(Yb)	[Xn] $4f^{14}, 5d^0, 6s^2$	102. Nobelium	(No)	[Rn] $5f^{14}, 6d^0, 7s^2$
71. Lutetium	(Lu)	[Xn] $4f^{14}, 5d^1, 6s^2$	103. Lawrencium	(Lr)	[Rn] $5f^{14}, 6d^1, 7s^2$

Oxidation states: The stability associated with empty, half-filled and fully filled orbitals can be observed in La, Eu, Gd, Yb and Lu in the case of lanthanides, and in Ac, Th, Am, Cm, No and Lr in the case of actinides. The main oxidation state shown by all lanthanides in their compounds is +3, obtained by the removal of the two electrons in 6s orbital and one from either *5d* or *4f*. The other oxidation states exhibited by some of the lanthanides can be explained on the basis of the stability of empty, half-filled and fully filled orbitals. For example, Ce exhibits an oxidation state of +4 since it can obtain an empty *4f* orbital by the loss of 4 electrons. Eu prefers an oxidation state of +2, Gd shows an oxidation state of only +3 and Tb shows an oxidation state of +4 since a half-filled $4f^7$ configuration can be retained in all these situations. Yb prefers an oxidation state of +2 since it can retain the full $4f^{14}$ configuration. A similar tendency is expected in the actinides also. These differences in the preferred oxidation states among the lanthanide elements are made use of in their separation by chemical methods.

Colour of salts: Salts of many lanthanide elements are coloured. These colours are seen to depend on the electronic arrangement in the *4f* orbital. When this orbital is empty, half-filled or full, such ions are found to be colourless. Thus La^{3+} ion (f^0), Gd^{3+} (f^7) and Lu^{3+} (f^{14}) are colourless. In the case of other ions, it is seen that configurations with f^n and f^{14-n} have the same colour, because they have the same number of unpaired electrons. Since the f-orbitals are well protected by the 5th and 6th electronic shells, they are split by ligand fields only to a lesser extent compared to the d-orbital splitting in the outer transition elements. The colours are due to low-energy $f \rightarrow f$ electronic transitions.

ions	configuration	colour	ions	configuration	colour
La^{3+}	f^0	colourless	Lu^{3+}	$f^{14} = f^{14-0}$	colourless
Ce^{3+}	f^1	colourless	Yb^{3+}	$f^{13} = f^{14-1}$	colourless
Pr^{3+}	f^2	green	Tm^{3+}	$f^{12} = f^{14-2}$	green
Nd^{3+}	f^3	red	Er^{3+}	$f^{11} = f^{14-3}$	red
Pm^{3+}	f^4	pink	Ho^{3+}	$f^{10} = f^{14-4}$	pink
Sm^{3+}	f^5	yellow	Dy^{3+}	$f^9 = f^{14-5}$	yellow
Eu^{3+}	f^6	colourless	Tb^{3+}	$f^8 = f^{14-6}$	colourless
Gd^{3+}	f^7	colourless	Gd^{3+}	$f^7 = f^{14-7}$	colourless

Relationship of electronic configuration to magnetic and spectroscopic properties of transition elements, lanthanides and actinides – Term symbols.

Magnetic effects in substances arise from unpaired electrons in orbitals. A spinning electron is equivalent to a moving electric field and generates a magnetic moment. In the case of paired electrons with opposite spins in the same orbital, the magnetic fields generated by them oppose each other and cancel. Thus atoms or ions having *only paired electrons* in them do not have any magnetic moment and are called **diamagnetic**. But atoms or ions having *unpaired electrons* in them have a resultant magnetic moment and are said to be **paramagnetic**. In inorganic complexes, the ligands usually contain only paired electrons. Therefore they do not contribute any magnetic moment, and all the magnetism of the compound is due to the central metal ion.

In addition to the spin, motion of electrons in the orbital around the nucleus also generates a magnetic moment. The portion of the total magnetic moment generated by the electron spin is called the "*spin contribution to magnetic moment*" and the portion due to the motion around the nucleus is called the "*orbital contribution to magnetic moment.*" The total magnetic moment of the atom or ion will be the total ***sum of these two contributions for all the unpaired electrons*** in it. For a single electron, its spin contribution depends on its spin quantum number, and its orbital contribution depends on the magnetic quantum numbers available in its orbital. The possible electronic transitions generating the spectrum of the atom or ion also depend on these quantum numbers. If *s* is the spin quantum number of an electron, its spin contribution to magnetic moment, μ_s, is given by:

$$\mu_s = g\sqrt{s(s+1)}$$

where s is the absolute value of the spin (i.e. ½) and 'g' is a constant called the "*gyromagnetic ratio*." The orbital contribution to the magnetic moment for an electron, μ_l, depends on the *l* value of its orbital, and is given by:

$$\mu_l = \sqrt{l(l+1)}$$

These two moments will couple with each other to produce the total magnetic moment due to this electron. The total effect can then be represented by a new quantum number '*j*', where $j = (l + s)$.

Term symbols: When there are more than one unpaired electrons, the resultant magnetic or spectroscopic behaviour of the atom or ion will be the sum total of the spin and orbital contributions of all these electrons. Therefore the resultant behaviour of the atom or ion may be represented using a set of suitable quantum numbers representing the total spin and orbital contributions of all the electrons in it. These are the '*S*' value representing the total spin contribution, the '*L*' value representing the total orbital contribution and 'J' representing the spin-orbit coupling where $J = L + S$. Then, just as the orbital for an electron is given a name *s*, *p*, *d*, or *f* depending on the value of l, spectroscopists have assigned a symbol for the **atom or ion** depending on the value of L. These are correspondingly S, P, D or F depending on whether $L = 0, 1, 2$ or 3.

[Now if we know whether an electron is in the *s*, *p*, *d* or *f* orbital, we can predict the spectral lines that may be obtained from them. But historically the procedure was just the reverse. Spectroscopists observed the spectral lines and assigned names to the orbitals producing them depending on the observed spectral characteristics. *s* = sharp (S → P), *p* = principal (P → S), *d* = diffuse (D → P) and *f* = fundamental (F → D)]

Two schemes have been proposed to make the assigned J values agree with actual experimental observations. These are (1) the **Russel-Saunders coupling** (also known as the ***LS*** **coupling**) and (2) the ***j-j*** **coupling**.

In the Russel-Saunders coupling scheme, all the s values of the individual electrons are first added together to obtain the resultant S value for the atom or ion.

$$S = s_1 + s_2 + s_3 + \ldots = \Sigma s$$

Similarly, the orbital moment values of all individual electrons are summed to obtain the resultant L value for the atom or ion.

$$L = l_1 + l_2 + l_3 + \ldots = \Sigma l = M_L$$

[Actually, it is not the l value, but the magnetic quantum numbers m associated to them that are summed. Therefore L is sometimes written as M_L]. Then

$J = L - S$ (if the orbital is less than half filled) **or** $J = L + S$ (if the orbital is more than half filled).

But in the *j-j* coupling scheme, the j values for all the individual electrons are first determined by adding the l and s values for each electron. These j values are then summed to obtain the resultant J value for the atom or ion.

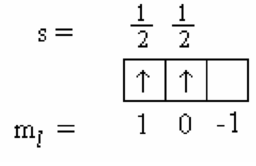
$$j_1 = l_1 + s_1;\ j_2 = l_2 + s_2;\ j_3 = l_3 + s_3;\ \ldots \quad \text{and} \quad J = j_1 + j_2 + j_3 + \ldots = \Sigma j$$

The Russel-Saunders coupling scheme is used for the lighter metals and the j-j coupling scheme is used for heavier atoms such as lanthanides and actinides.

To get the term symbol for the atom or ion in the ground state, it is designated as S, P, D or F depending on the value of L. Then the value $2S+1$, called the **multiplicity** (number of lines into which a spectral line will be split when placed in a magnetic field), is written as a superscript and the J value is written as a subscript. For example, if $S = 1$ and $L = 1$, then the corresponding term symbol is $^3P_0$ (pronounced as "triplet pee". The multiplicities are singlet, doublet, triplet, quartet etc.). If $S = ½$ and $L = 0$, then the term symbol is $^2S_{½}$.

How to obtain the term symbol from the electronic configuration? The actual and correct procedure for determining term symbols is somewhat long and tedious, depending on the number of electrons present. But a fairly easy (but not very accurate) method is discussed here for students exam purpose only. *The trick is to consider only the unpaired electrons.*

Example 1: Term symbol for carbon in the ground state. The electronic configuration is $2p^2$. All the inner electrons are paired and therefore not considered. Following all principles, the arrangement is:

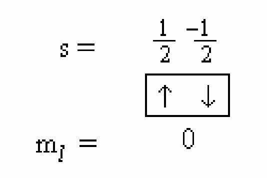


$S = ½ + ½ = 1$; $L = 1 + 0 = 1$; Since L = 1, the symbol is P.

Multiplicity = $2S + 1 = 3$; $J = L - S = 1 - 1 = 0$.

Therefore term symbol for p^2 configuration is **$^3P_0$**

Example 2: For helium, the electronic configuration is $1s^2$. The arrangement is:

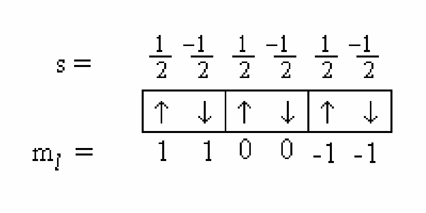


S = ½ - ½ = 0; L = 0; Since L = 0, the symbol is *S*.

Multiplicity = 2S + 1 = 1; J = L – S = 0.

Therefore term symbol for s^2 configuration is **$^1S_0$**

Example 3: For the p^6 configuration in neon,



S = ½ - ½ + ½ - ½ + ½ - ½ = 0; L = 1 + 1 + 0 + 0 – 1 – 1 = 0;

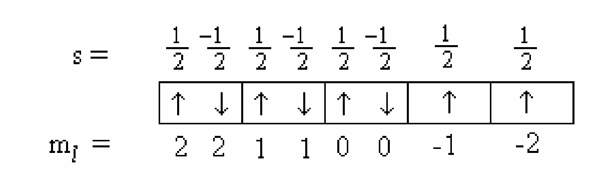
Since L = 0, the symbol is *S*.

Multiplicity = 2S + 1 = 1; J = L – S = 0.

Therefore term symbol for p^6 configuration is **$^1S_0$**

Note: From the above two examples it can be seen that whenever there are only paired electrons, the term symbol is $^1S_0$. The state is a singlet, meaning that there is only one spectral line. That is why we can neglect all paired electrons.

Example 4: For the Ni^{2+} ion, the electronic configuration is $3d^8$. The arrangement is:



S = ½ - ½ + ½ - ½ + ½ - ½ + ½ + ½ = 1;
L = -2 – 1 = -3 (considering only unpaired);

Since L = 3 (take only the absolute value), the symbol is *F*.

Multiplicity = 2S + 1 = 3; J = L + S = 4.

Therefore term symbol for d^8 configuration is **$^3F_4$**

Assignment: Determine the term symbols for the following ions as given in the examples. Verify the correctness of your calculation with the given term symbols.

Ti^{3+}	V^{3+}	Cr^{3+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Mn^{3+}	Fe^{3+}	Co^{3+}
$^2D_{3/2}$	$^3F_2$	$^4F_{3/2}$	$^5D_0$	$^6S_{5/2}$	$^5D_4$	$^4F_{9/2}$	$^3F_4$	$^2D_{5/2}$	$^5D_0$	$^6S_{5/2}$	$^5D_4$

Synthesis and stability of heavier actinides

In 1934-35, Enrico Fermi and coworkers observed that when most elements are bombarded with slow neutrons, they are converted into radioactive products which emit β-rays on decay. Since a β-emission leads to an increase of one unit in the nuclear positive charge, they used uranium as the target for neutrons and produced elements with atomic numbers greater than 92 for the first time. Before this time, only three members of the actinide series were known and the existence of such a series after the lanthanides was not suspected. In 1945, it was G. T. Seaborg of the University of California who suggested the probable existence of such a series of elements. However, the elements within this group show a much wider variation in oxidation states, and therefore greater differences in chemical properties, than the elements in the lanthanide series.

Although more than ten transuranium elements have been discovered, only the first six have been studied extensively for their chemical properties, and only one, plutonium, has been prepared in quantity. The others have been obtained only in very small quantities and studied using tracers or ultramicrochemical techniques.The dangerous level of α-activity in these isotopes makes them unsafe for handling without special equipment.

Neptunium (93): Prepared in 1940 McMillan and Abelson at the University of California by bombarding a layer of uranium oxide with slow neutrons from a cyclotron.

$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239}$ (half life 23 min.)
$_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$ (half life 2.3 days.)

A more stable isotope of neptunium was prepared in weighable quantities by Seaborg and Wahl in 1942 by the action of high-speed neutrons on uranium.

$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{237} + 2\,{}_{0}n^{1}$ (half life 7 days.)
$_{92}U^{237} \rightarrow {}_{93}Np^{237} + {}_{-1}e^{0}$ (half life 2.25×10^{6} years.)

Plutonium (94): Seaborg, McMillan, Wahl and Kennedy synthesized this element in 1940 by bombarding uranium with deuterium.

$_{92}U^{238} + {}_{1}H^{2} \rightarrow {}_{93}Np^{238} + 2\,{}_{0}n^{1}$ (half life 2 days.)
$_{93}Np^{238} \rightarrow {}_{94}Pu^{238} + {}_{-1}e^{0}$ (half life 90 years.)

But another isotope of plutonium with a longer life is produced in large quantities inside nuclear reactors using enriched uranium as fuel. Although the fissionable material in the fuel is U^{235}, some of the neutrons produced are absorbed by the U^{238} present, which then changes into plutonium:

$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239}$ (half life 23 min.)
$_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$ (half life 2.3 days.)
$_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^{0}$ (half life 2.4×10^{4} years.)

The plutonium produced is fissionable and is a much better nuclear fuel than U^{235}. Such reactors which use U^{235} fuel to produce plutonium are therefore called “breeder reactors.” The fuel used in the atom bombs dropped in Hiroshima and Nagasaki was plutonium. It is a strong α-emitter producing about 140 million disintegrations per minute per milligram of material, which can be destructive to living tissues.

Americium (95): Seaborg, James and Morgan synthesized this element in 1944 by bombarding U238 with high-speed (40 Mev) α-particles from a cyclotron.

$_{92}U^{238} + {}_{2}He^{4} \rightarrow {}_{94}Pu^{241} + {}_{0}n^{1}$ (half life 13 years.)
$_{94}Pu^{241} \rightarrow {}_{95}Am^{241} + {}_{-1}e^{0}$ (half life 470 years.)

The α-activity of this species is approximately 70 billion disintegrations per minute per milligram of material. A less dangerous and more stable isotope Am^{243} has been produced with a half life of about 10,000 years.

Curium (96): This was identified by Seaborg, James and Ghiorso in 1944 in products obtained by bombarding plutonium with α-particles from the Berkeley cyclotron.

$_{94}Pu^{239} + {}_{2}He^{4} \rightarrow {}_{96}Cm^{242} + {}_{0}n^{1}$ (half life 162 days.)

The α-activity is approximately 10^{14} disintegrations per minute per milligram, which is not only dangerous to tissues, but also affects the solvents used to study its chemistry. A more stable isotope Cm^{243} with a half life of 100 years has also been reported.

Berkelium (97): This element was discovered in 1949 by Seaborg, Thompson and Ghiorso. It was prepared by bombarding americium with high-speed α-particles from the Berkeley cyclotron.

$_{95}Am^{241} + {}_{2}He^{4} \rightarrow {}_{97}Bk^{243} + 2\,{}_{0}n^{1}$ (half life 4.6 hours.)

This element apparently decays by orbital electron capture. A more stable isotope was also synthesized by the same team:

$_{95}Am^{241} + {}_{2}He^{4} \rightarrow {}_{97}Bk^{245}$ (half life 4.95 days.)

Californium (98): It was discovered in 1950 by Seaborg, Thomson, Ghiorso and Street. It was produced by bombarding microgram amounts of curium-242 with 35-Mev α-particles from the Berkeley cyclotron.

$_{96}Cm^{242} + {}_{2}He^{4} \rightarrow {}_{98}Cf^{244} + 2\,{}_{0}n^{1}$ (half life 45 min.)

Less energetic α-particles produce a more stable isotope.

$_{96}Cm^{242} + {}_{2}He^{4} \rightarrow {}_{98}Cf^{246}$ (half life 35.7 hours.)

As the techniques were developed, heavier nuclei like carbon were tried as bullets to bombard naturally available elements like uranium to produce the very heavy elements in one step:

$_{92}U^{238} + {}_{6}C^{12} \rightarrow {}_{98}Cf^{246} + 4\,{}_{0}n^{1}$

$_{92}U^{238} + {}_{6}C^{12} \rightarrow {}_{98}Cf^{244} + 6\,{}_{0}n^{1}$

Einsteinium (99): This was prepared by bombarding uranium with nitrogen nuclei accelerated in the Berkeley cyclotron.

$_{92}U^{238} + {}_{7}N^{14} \rightarrow {}_{99}En^{247} + 5\,{}_{0}n^{1}$ (half life 7.3 min.)

Fermium (100): The discovery of element 100 was announced simultaneously by a research team at the Argonne National Laboratory and the Seaborg team at the University of California. The first production of an isotope of element 100 took place in an atomic reactor. The synthesis involved transmutation of plutonium in a complicated process. It involved absorption of 15 neutrons by each atom of plutonium and 6 β-particles are emitted in the process.

$$
\begin{aligned}
&{}_{94}Pu^{239} + 2\ {}_{0}n^{1} \rightarrow {}_{94}Pu^{241} \rightarrow {}_{95}Am^{241} + {}_{-1}e^{0} \\
&{}_{95}Am^{241} + {}_{0}n^{1} \rightarrow {}_{95}Am^{242} \rightarrow {}_{96}Cm^{242} + {}_{-1}e^{0} \\
&{}_{96}Cm^{242} + 7\ {}_{0}n^{1} \rightarrow {}_{96}Cm^{249} \rightarrow {}_{97}Bk^{249} + {}_{-1}e^{0} \\
&{}_{97}Bk^{249} + {}_{0}n^{1} \rightarrow {}_{97}Bk^{250} \rightarrow {}_{98}Cf^{250} + {}_{-1}e^{0} \\
&{}_{98}Cf^{250} + 3\ {}_{0}n^{1} \rightarrow {}_{98}Cf^{253} \rightarrow {}_{99}En^{253} + {}_{-1}e^{0} \\
&{}_{99}En^{253} + {}_{0}n^{1} \rightarrow {}_{99}En^{254} \rightarrow {}_{100}Fm^{254} + {}_{-1}e^{0}
\end{aligned}
$$

A Swedish group of scientists at the Nobel Institute of Physics in Stockholm succeeded in making an isotope of element 100 by bombarding uranium with 180-Mev oxygen particles in a cyclotron.

$${}_{92}U^{238} + {}_{8}O^{16} \rightarrow {}_{100}Fm^{252} + 2\ {}_{0}n^{1} \qquad \text{(half life 30 min.)}$$

Mendelevium (101): It was prepared by the Seaborg team by bombarding einsteinium coated on a gold foil with 41-Mev α-particles.

$${}_{99}En^{253} + {}_{2}He^{4} \rightarrow {}_{101}Md^{256} + {}_{0}n^{1} \qquad \text{(half life 30 min.)}$$

It is unusual in that it appears to decay by spontaneous fission.

Nobelium (102): It was synthesized at the Nobel Institute of Physics in Stockholm, Sweden in 1957. It was the combined cooperative effort of research teams from three countries. Scientists from the United States Atomic Energy Commission's Argonne National Laboratory contributed the curium sample which was used as the target. English scientists from Harwell furnished carbon-13, a rare isotope, which was used as the bullet. Swedish scientists at Stockholm provided the specially constructed cyclotron required for such experiments.

$${}_{96}Cm^{242} + {}_{6}C^{13} \rightarrow {}_{102}No^{253} + 2\ {}_{0}n^{1} \qquad \text{(half life 10 min.)}$$

This isotope disintegrated so rapidly that the major problem was to prove that it had been created. Only about 50 atoms of the new element were produced and special techniques were necessary to study its emissions before it disappeared completely.

Higher elements: Only a few atoms have been obtained in these cases because of the non-availability of target materials and the low probability of the desired nuclear reactions. Conclusive studies were not possible. As in 1991, it is claimed that elements up to 109 have been created. Fortunately, the decay properties of the heavier actinides can be predicted. The elements can be separated by ion-exchange chromatography using ammonium 2-hydroxybutyrate as the eluant. Elements of highest atomic number are eluted first. Chemical studies are restricted to rapid tracer experiments. Identification of the heaviest elements are entirely based on their decay properties. The available data suggest that the chemical properties are very similar to the corresponding elements in the lanthanide series. The compounds exist in a variety of different crystal forms (polymorphic) and exhibit a wide variety of colours in solutions.