

Periodic Table



Alkalia Alkaline Transition Basic Semimetal Nonmetal Halogen Case Lanthanide Actinide

PRINCIPLE

Aufbau 1

an electron occupies orbitals in order from lowest energy to highest

Pauli

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in a single atom, no two electrons will have an identical set or the same quantum numbers

= opposite spin

Hund

Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin).





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Elements of First Transition Series

d - block elements







https://www.careers360.com/spdf-full-form



https://madoverchemistry.com/2017/03/14/41-the-periodic-table-spdf-blocks/





The elements lying between s-block and p-block elements of the periodic table and their properties represent a change from the electropositive s-block element to electronegative p-block elements. Such elements are often called "Transition Elements".

Syllabus

- Introduction, definition, electronic configuration, reversal of energies of 3d and 4s orbitals,
- Physical properties such as atomic properties (atomic radii, Ionic radii, and ionization potential), metallic conductivity, reducing properties, tendency of formation of alloys, catalytic properties and magnetic properties.
 Calculation of spin only magnetic momentum of inner orbital and outer orbital complexes [NiCl₄]⁻², [Ni(CN)₄]⁻², [FeF₆]⁻⁴, [Fe(CN)₆]⁻⁴

01.



Electronic configuration

(n-1)d¹⁻¹⁰ ns¹⁻² or (0,1,2)

Element	z	Electron configuration	Noble gas configuration	Electron in box diagram
Scandium	21	1s² 2s² 2p ⁶ 3s² 3p ⁶ 4s² 3d ¹	[Ar] 4s ² 3d ¹	
Titanium	22	1s² 2s² 2p ⁰ 3s² 3p ⁰ 4s² 3d²	[Ar] 4s ² 3d ²	
Vanadium	23	1s² 2s² 2p ⁶ 3s² 3p ⁶ 4s² 3d³	[Ar] 4s² 3d²	
Chromium	24	1s² 2s² 2p ⁶ 3s² 3p ⁶ 4s ¹ 3d²	[Ar] <mark>4s' 3d</mark> 9	
Manganese	25	1s² 2s² 2p# 3s² 3p# 4s² 3d#	[Ar] 4s ² 3d ⁵	
Iron	26	1s² 2s² 2pº 3s² 3pº 4s² 3d°	[Ar] 4s ² 3d ⁶	
Cobalt	27	1s² 2s² 2p ⁶ 3s² 3p ⁶ 4s² 3d²	[Ar] 4s ² 3d ⁷	
Nickel	28	1s² 2s² 2p ^e 3s² 3p ^e 4s² 3d ^s	[Ar] 4s ² 3d ³	
Copper	29	1s² 2s² 2p ⁶ 3s² 3p ⁶ 4s ¹ 3d ¹⁰	[Ar] 4s' 3d**	
Zinc	30	1s² 2s² 2p ⁶ 3s² 3p ⁶ 4s² 3d ¹⁰	[Ar] 4s ² 3d ¹⁰	

The transition elements are those elements which have incompletely (Partly) filled d-sub-shells in their ground state or in any one of their oxidation states"

 $(n-1)d^{1-10} ns^{1-2 or(0,1.2)}$

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration
Scandium (Sc)	21	+3	Sc: [Ar] $4s^23d^1$ Sc: [Ar] $\frac{1}{4s}$ $\frac{1}{3d}$
Titanium (Ti)	22	+4	Ti: [Ar] $4s^23d^2$ Ti: [Ar] $\frac{1}{4s}$ 1 $\frac{1}{3d}$
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^23d^3$ V: [Ar] $\frac{1}{4s}$ 1 1 1 $\frac{1}{3d}$
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] 4s ¹ 3d ⁵ Cr: [Ar] $\frac{1}{4s}$ $\frac{1}{4s}$ 1 1 $\frac{1}{3d}$
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^23d^5$ Mn: [Ar] $\frac{1}{4s}$ 1 1 1 1 1 1 $3d$
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$ Fe: [Ar] $\frac{1}{4s}$ $\frac{1}{4s}$ $\frac{1}{3d}$
Cobalt (Co)	27	+2,+3	Co: [Ar] $4s^23d^7$ Co: [Ar] $\frac{1}{4s}$ $\frac{1}{4s}$ $\frac{1}{3d}$
Nickel (Ni)	28	+2	Ni: [Ar] $4s^23d^8$ Ni: [Ar] $\frac{1}{4s}$ $\frac{1}{4s}$ $\frac{1}{3d}$
Copper (Cu)	29	+1,+2	Cu: [Ar] $4s^{1}3d^{10}$ Cu: [Ar] $\frac{1}{4s}$ $\frac{1}{4s}$ $\frac{1}{3d}$
Zinc (Zn)	30	+2	Zn: [Ar] $4s^23d^{10}$ Zn: [Ar] $1l$ $1l$ $1l$ $1l$ $1l$ $1l$ $1l$ $1l$



REVERSAL OF ENERGIES OF 3d AND 4s ORBITALS

Electronic energies orbitals



d-Block 2 Н He 6 3 5 7 8 10 9 4 Ċ Li В Ν \mathbf{O} Be F Ne 11 12 13 14 15 16 17 18 Si S Na Mg AL P CL Ar 21 22 23 25 26 27 28 29 31 32 33 34 35 19 20 24 30 36 К Ċа Sc Ti Y Cr Mn. Fe Co Ni Cu Zn Ga Ge Ås. Se Br Kr

s block 4s orbital filling **d block** 3d orbitals filling **p block** 4p orbitals filling

Elements	Symbol	At. No.	Expected Electronic Configuration	Observed Electronic Configuration
Scandium	Sc	21	[Ar] 3d ¹ 4s ²	[Ar] 3d ¹ 4s ²
Titanium	Ti	22	[Ar] $3d^2 4s^2$	[Ar] 3d ² 4s ²
Vanadium	v	23	[Ar] 3d ³ 4s ²	[Ar] 3d ³ 4s ²
Chromium	Cr	24	[Ar] 3d ⁴ 4s ²	[Ar] 3d ⁵ 4s ¹
Manganese	Mn	25	[Ar] 3d ⁵ 4s ²	[Ar] 3d ⁵ 4s ²
Iron	Fe	26	[Ar] 3d ⁶ 4s ²	[Ar] 3d ⁶ 4s ²
Cobalt	Co	27	[Ar] 3d ⁷ 4s ²	[Ar] 3d ⁷ 4s ²
Nickel	Ni	28	[Ar] 3d8 4s2	[Ar] 3d ⁸ 4s ²
Copper	Cu	29	[Ar] 3d ⁹ 4s ²	[Ar] 3d ¹⁰ 4s ¹
Zinc	Zn	30	[Ar] 3d ¹⁰ 4s ²	[Ar] 3d ¹⁰ 4s ²

Electronic Structure of Fe & Fe(III)

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ Fe³⁺: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

The 4s electrons are lost first followed by one of the 3d electrons.

1.We say that the 4s orbitals have a lower energy than the 3d, and so the 4s orbitals are filled **first**.

2.We know that the 4s electrons are lost first during ionization. The electrons lost first will come from the highest energy level, furthest from the influence of the nucleus. So the **4s orbital must have a higher energy** than the 3d orbitals.

Outer 4s Electrons are shielded by inner 3d electrons



The elements up to argon: There is no problem with these. The general pattern that we drew in the diagram above works well.

Potassium and calcium: The pattern is still working here. The 4s orbital has a lower energy than the 3d, and so fills next. That entirely fits with the chemistry of potassium and calcium.

The d-block elements: For reasons which are too complicated to go into at this level, once you get to scandium, the energy of the 3d orbitals becomes slightly less than that of the 4s, and that remains true across the rest of the transition series

> So, when transition metal atoms form ions, they loss electrons from .. 4s-orbital before the 3d-orbitals.

why is not the electronic configuration of scandium [Ar] 3d³ rather than [Ar] 3d¹ 4S²?

Making Sc³⁺

Imagine you are building a scandium atom from boxes of protons, neutrons and electrons. You have built the nucleus from 21 protons and 24 neutrons, and are now adding electrons around the outside. So far you have added 18 electrons to fill all the levels up as far as 3p. Essentially you have made the ion Sc³⁺.

Making Sc²⁺

Now you are going to add the next electron to make Sc2+. Where will the electron go? The 3d orbitals at scandium have a lower energy than the 4s, and so the next electron will go into a 3d orbital. The structure is [Ar] 3d¹.

Making Sc⁺

You might expect the next electron to go into a lower energy 3d orbital as well, to give [Ar] $3d^2$. But it doesn't. The energetically most stable structure for Sc+ is therefore [Ar] $3d^14s^1$.

Making Sc:

Putting the final electron in, to make a neutral scandium atom, needs the same sort of discussion. In this case, the lowest energy solution is the one where the last electron also goes into the 4s level, to give the familiar [Ar] $3d^{4}4s^{2}$ structure.

Electronic Configuration anamalous

Chromium



 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$

1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹

A half - filled or full d - sub shell offers more stability than a full s - sub shell. Copper



1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹ 4s²

1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹

Because that is the structure in which the balance of repulsions and the size of the energy gap between the 3d and 4s orbitals happens to produce the lowest energy for the system.

Properties of Transition elements



Physical Properties

- Atomic Properties
- Metallic Properties
- Reducing Properties
- Catalytic Properties
- Magnetic Properties



Atomic Properties

The properties related to the atomic structure are known as atomic properties.

- Atomic Radii
- Ionic Radii
- Ionization Potential or Ionization energy







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Atomic Radii

Sc to Mn

decrease is due to the gradual increase in nuclear charge with consequent contraction in size.

Screening

the electrons added to 3dorbital screen the 4s-orbital electrons, the attraction between the nucleus and the 4s electrons decreases due to screening effect.

Atomic Properties



Because of screening effect, the actual nuclear charge is decreased by the quantity σ,the Screening constant

> Slater rule $Z_{eff} = Z - \sigma$

Number of intervening electrons

Size of the atom

Slater rule

- $\sigma = 0.35$ (e in nth shell) + 0.85 (e in n-1 shell) + 1.0 (e in next inner shell)
 - $K(Z = 19) = 18^2 28^2 2p^6 38^2 3p^6 48^1$
- $\sigma = 0.35(0) + 0.85(8) + 1.0(10)$ =16.80

Z $_{\rm eff}$ for 4s1 electron is 2.20

 $Z_{eff} = Z - \sigma$ Z _{eff} = 19 - 16.80 =2.20

Let us now calculate o for 3d¹ electron in K(19)

 $\sigma = 0.35$ (remaining electrons from (n-1)d orbitals) + 1.0 (electron present in (n-1)s & (n-1)p and inner shell)

Thus [Ar] 3d⁰ 4s¹ electronic configuration would be more stable and hence the 4s orbital is filled earlier than the 3d orbital

Removal of electron from 4s orbital

Mn (Z= 25) [Ar] $3d^5 4s^2$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

 $\sigma \text{ for } 4s^1 = 0.35(\text{no. of e remaining in } 4s)$ + 0.85 (no. of e in n-1 shell)+ 1.0 (no of e in inner shells)

 σ for 4s¹ = 0.35(1) + 0.85 (13) + 1.0 (10) = 21.40

Z _{eff}= 25 - 21.40 =3.60

=5.60

 σ for 3d¹ = 0.35(e remaining in n-1 d shell) + 1.0 (no of in inner shells) = 0.35 x 4 + 1.0 x 18 = 19.40 Z_{eff}= 25 - 19.40

Ionic Radii of cations of 3d

Elements	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
Ionic Radii	+2=81	+2=91	+2=88	+2=84	+2=80	+2=76	+2=76	+2=72	+1=91	+2=74
(pm)	+3=88.5	+3=76	+3=74	+3=69	+3=66	+3=64	+3=63		+2=61	
		+4=74.	+4=72	+4=68	+7=60					
		5	+5=68	+5=63						
				+6=58						

- ionic radii for various oxidation states are also different
- ionic radii of the same element in different oxidation state decreases with increase in oxidation number e.g. Cr

Atomic Properties

Ionization Potential or Ionization energy increase with increasing atomic number

> Increased nuclear charge pull the electron cloud toward to nucleus more energy is needed to remove electron

> The ionic potential of the d-block element of a first transition series is intermediate between S and P blocks elements. It means that these have been less electropositive than the S-block elements



Both atoms have the same number of shielding core electrons (2), but fluorine has a greater nuclear charge (9+ vs 2+), and therefore a greater effective nuclear charge (7+ vs 1+).

Atomic Properties

IONIZATION POTENTIAL



Ionization Potential or Ionization energy

Very close to each other Because of Screening effect produced by addition of e- in d orbital

Metallic Conductivity

good conductors of electricity and heat presence of free mobile electrons (vacant orbitals) in metallic bonding

Conductivity of oxides

- TiO, VO, CrO2 etc.. possess conductivity like metal
- TiO2, V203 etc.. are semi conductor
- V205, Cr203, Fe203 etc.. are insulator



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Po





Reducing Property

-ve std potential

d-block elements Std Hydrogen electrode (Zero)

Reducing property

Depend on formation of aquatic ions Easy oxidation

 $M \rightarrow M^{+2}_{(aq)} + 2e^{-}$

No reductant

High heat of vaporization High ionization energies Low heat of hydration

Reductant

Not good reducing agents as group 1,2 & 13

Exemption

Cu Positive electrode potential and negative E⁰ (oxidation)

Tendency of formation of alloys

Tendency of formation of alloys

- 1. Homogeneous mixture of one or more metals
- 2. Atomic volume of 15% or more can form alloy.
- 3. Transition metals are almost of same size, replacement of atoms give alloy.
- 4. Hard, High MP, corrosion resistant
- 5. Cr-Ni, Cr-Ni-Fe, Cr-V-Fe, Mn-Fe etc
- 6. Transition Non Transition alloy
 - a. Brass (Cu-Zn)
 - b. Bronze (Cu-Ti)
 - c. Pure Gold with Cu/Cd
- 7. Steel with Fe along with Cr, Mn, W etc

Catalytic Properties



Pa

90 Th



A number of transition elements and their compounds are used as a catalyst in various chemical reaction. Lower Activation energy intermediate are produced

CATALYIC ACTIVITY

Transition metals and their compounds are well known for their catalytic activities.

Nickel is used as catalyst for the hydrogenation of unsaturated compounds

Iron-Molybdenum is used as a catalyst in the synthesis of ammonia by Haber's process.

Platinum is used in the contact process for the combination of SO_2 with O_2 to generate SO_3

Vanadium petaoxide is used for the oxidation of SO₂ with O₂ to prepare SO₃

Manganese dioxide is used to catalyze the decomposition of H_2O_2 .

The catalytic activity of the transition elements is due to the availability of d-orbitals. The d-orbitals which are exposed to the surface, participate in the formation of activated complex which serves as a reactive intermediate in the overall reactions. These reactive intermediates provide low energy reaction pathways and accelerates the rate of the reaction

Some Examples

- 1. Ziegler-Natta (TiCl4) catalyst for manufacturing of Polythene
- 2. Fenten's reagent (FeSO4 + H2O2) for oxidation of alcohol to aldehydes.
- 3. MnO2 for oxygen preparation in Laboratory.
- 4. CuCl2 in the manufacturing of chloride.
- 5. Pt-Black in preparation of HCHO
- 6. REACTANTS + CATALYST → Unstable intermediate compound →Decomposition gives products + Catalyst

The transition metals and their compound provide a large surface are on which the reactants may be absorbed and there for come closer for the reaction. This can be explained by adsorption theory.

Magnetic Properties



Magnetic Properties

Measurement of number of unpaired electrons

External Magnetic Field

Most of the compounds of transition metals are paramagnetic in nature.



Origin of Paramagnetism



Paramagnetic Substance

The resultant or total moment in them is sufficiently high to overcome the magnetic moment induced by an approaching magnetic field. Hence, such substances instead of experiencing repulsion, are attracted in a magnetic field and are called paramagnetic substances



Bohr Magneton

- Magnetic Moment increase with increase of the unpaired electrons in 3d-series
- Magnetic Moment µ and number of unpaired n electrons are related

•
$$\mu = \sqrt{n(n+2)}$$
 B.M.

The calculated magnetic moments corresponding to 1, 2, 3, 4 and 5 unpaired electrons will be $\sqrt{3} = 1.73$ • $\sqrt{8} = 2.83BM$ • $\sqrt{15} = 3.87BM$ $\sqrt{24} = 4.90BM$ $\sqrt{35} = 5.92BM$

Ferromagnetic substances

Highly Magnetic properties Iron Oxide, Iron Metal 1000 times more magnetic than metal

Ion	Configuration	Unpaired	Magnetic moment				
		electron(s)	Calculated	Observed			
Sc ³⁺	3 <i>d</i> °	0	0	0			
Ti ³⁺	$3d^1$	1	1.73	1.75			
T1 ²⁺	3 <i>d</i> ²	2	2.84	2.76			
V ²⁺	$3d^3$	3	3.87	3.86			
Cr ²⁺	$3d^4$	4	4.90	4.80			
Mn ²⁺	3ď	5	5.92	5.96			
Fe ²⁺	$3d^6$	4	4.90	5.3 - 5.5			
Co ²⁺	3ď	3	3.87	4.4 - 5.2			
Ni ²⁺	3d ⁸	2	2.84	2.9 - 3, 4			
Cu ²⁺	3 <i>d</i> °	1	1.73	1.8 - 2.2			
Zn ²⁺	3d ¹⁰	0	0				



Spin Only Magnetic Moment

104	88	
Rf	Ra	

85	90
At	Th

Spin only Magnetic Moment

Inner orbital Complexes

26

Fe

- Strong Field or low spin ligand
- Hybridization (dsp2, d2sp3)
- Square Planner ,Octahedral
- Ligand CN⁻

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Outer Orbital complexes

- Weak Field or high spin ligand
- Hybridization (sp3, sp3d2)
- Tetrahedral , octahedral
- Ligand Cl⁻, F⁻



Spin Only Magnetic Moment of Complexes



Inner Orbital Complexes

 $[Ni(CN)_4]^{-2}$ $[Fe(CN)_6]^{-4}$

Outer Orbital Complexes

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 $[FeF_6]^{-4}$ [NiCl₄] -2

Inner Orbital Complexes





Inner Orbital Complexes





Outer Orbital Complexes



Octahedral, paramagnetic complex

USES of 3d-elements

	Element
Electronic Devices, High Intensity Lamps	Scandium
Aircraft Industries,catalyst,paper paint plastic cosmetics manufacture, alloy with Al	Titanium
As catalyst, alloy with Fe in cutting tools	Vanadium
Alloy in SS,Electroplated coating, Cr203 as pigment	Chromium

USES of 3d-elements

	Element
KMnO4 oxidizing agent, disinfectant	Manganese
Steel manufacturing, inorganic drug, catalyst	Iron
Various salts as colouring agents in porcelain glass pottery tiles etc, alloy in cutting tools	Cobalt
food processes and pharmaceutical plants	Nickel

USES of 3d-elements

	Element
Electrical conductor, coins, pipes, mixed oxides as superconductors, CuSO4+Cu(OH)2 in agriculture against fungal attack	Copper
Coating, alloy (brass), battery, ZnO in paints rubbber cosmetic etc, ZnS in Luminous dials, X-ray TV screen fluroscent lights	Zinc

Thank You

1 H			8								,C	1					2 He
3	4	4										5	6	7	8	9	10
Li	Be	Be										B	C	N	O	F	Ne
11	12	12								13	14	15	16	17	18		
Na	Mg	Mg								Al	Si	P	S	Ci	Ar		
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	C0	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51 Sb	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn		Te	I	Xe
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85 At	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po		Rn
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Lr	Rf	Db	Sg	Bh	HS	Mt	Ds	Rg	Cn	Nh	Fi	Mc	Lv	Ts	Og
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		