

d and f –block elements in Nutshell

1. The elements lying in the middle of periodic table belong to group 3 to 12 are known as d-block element. d block elements are also called as transition elements

2. General electronic configuration of d-block elements: The d-block elements are characterized by the $(n-1)d^{1-10} ns^{1-2}$ valence shell electronic configuration.

3. Some exceptional electronic configurations of transition elements

i) Cr = $3d^5, 4s^1$, Cu = $3d^{10}4s^1$

ii) Nb = $4d^45s^1$, Mo = $4d^5, 5s^1$ Ru = $4d^7 5s^1$, Rh = $4d^85s^1$, Pd = $4d^{10}5s^0$

iii) Pt = $5d^9 6s^1$, Au = $5d^{10} 6s^1$

These irregularities due to

- (i) Nuclear electron attraction
- (ii) Shielding of one electron by several other electrons
- (iii) Inter electron repulsion
- (iv) Exchange energy force

4. d- block elements have wide range of oxidation states

They exhibit a wide range of oxidation states or positively charged forms.

The positive oxidation states allow transition elements to form many different ionic and partially ionic compounds. Oxidation states of first period of d block elements are stated below

Scandium	+3
Titanium	+2, +3, +4
Vanadium	+2, +3, +4, +5
Chromium	+2, +3, +6
Manganese	+2, (+3), +4, (+6), +7
Iron	+2, +3, (+4), (+6)
Cobalt	+2, +3, (+4)
Nickel	(+1), +2, (+3), (+4)
Copper	+1, +2, (+3)
Zinc	+2

5. Atomic and ionic radii:

In a series, the atomic radii first decreases with increase in atomic number upto the middle of the series then become constant and at the end of the series show slight increase

This is because nuclear charge goes on increasing when going from left to right causes contraction but due to shielding effect increases in middle of element counterbalance contraction due to increased nuclear charge

6. Metallic character:

All transition element are having hcp, ccp or bcc lattice. This is because of presence of one or two electrons in ns subshell and also unpaired d-electrons. Greater the number of unpaired d-electron stronger is the metallic character and metals are hard and have higher melting points

On the other hand Zn , Cd and Hg are soft and low melting point because of absence of unpaired d-electrons

Also because of strong metallic bond transition elements have higher density

7. Low ionization energies

First ionization enenthalpies of d-block elements are higher than those of s-block elements and are less than p-block lements. There is slightly and irregular variation in ionization energies of transition metals due to irregular variation of atomic size

8. Higher enthalpy of atomization

Because of large number of unpaired electrons in their atoms, they have strong inter-atomic interactions and hence stronger bonds between atoms resulting in higher enthalpies of atomization

9. Electrode potential and reducing character:

Lower the electrode potential (i.e more negative the standard reduction potential) of the electrode, more stable is the oxidation state of the transition metal ion in aqueous solution

ELEMENT	$E^{\circ} (M^{2+}/M)$ in Volts	M^{3+}/M^{2+}
V	-1.18	-0.26
Cr	-0.90	-0.41
Mn	-1.18	+1.57
Fe	-0.44	+0.77
Co	-0.28	+1.97
Ni	-0.25	---
Cu	+0.34	---
Zn	-0.76	----

10. Catalytic properties:

Many transition elements (like Co, Ni, Pt, Fe, Mo etc) and their compounds are used as catalysts because

- (i) they have variable oxidation states, they easily absorb and reemit wide range of energies to provide the necessary activation energy
- (ii) Because of variable oxidation states, they easily combine with one of the reactants to form, an intermediate which reacts with second reactant to form the final products.
- (iii) Because of presence of free valencies on the surface, they can adsorb the reacting molecules, thereby increasing the concentration of the reactants on the surface and hence the rate of reaction.

11. Coloured ions

Most of the transition metal compounds are coloured both in the solid state and in aqueous solution. This is because of the presence of incompletely filled d-orbitals. When a transition metal compound is formed the degenerate s-orbitals of the metal split into two sets, one having three orbitals d_{xy} , d_{yz} and d_{xz} called t_{2g} orbitals with lower energy and the other having two orbitals $d_{x^2-y^2}$ and d_{z^2} called e_g orbitals with slightly higher energy in an octahedral field. This is called crystal field splitting. When white light falls on these compounds, some wavelength is absorbed for promotion of electrons from one set of lower energy orbitals to another set of slightly higher energy within the same d-subshell. This is called d-d transition. The remainder light is reflected which has a particular colour. The colours of some 3d metal ions

$Ti^{3+} (3d^1)$	Purple	$V^{4+} (3d^1)$	Blue	$V^{3+} (3d^2)$	Green
$Cr^{3+} (3d^3)$	Violet green	$Mn^{3+} (3d^4)$	Violet	$Cr^{2+} (3d^4)$	Blue
$Mn^{2+} (3d^5)$	Pink	$Fe^{3+} (3d^5)$	Yellow	$Fe^{2+} (3d^6)$	Green
$Co^{2+} (3d^6)$	Green	$Ni^{2+} (3d^8)$	Green	$Cu^{2+} (3d^9)$	Blue

Colours of $Cr_2O_7^{2-}$, CrO_4^{2-} , MnO_4^- , Cu_2O are due to charge transfer transition

12. Magnetic properties

Due to presence of unpaired electrons in (n-1) d orbitals, the most of the transition metal ions and their compounds are paramagnetic. The magnetic moment is expressed in Bohr magnetons (B.M.)

A paramagnetic substance is characterized by its effective magnetic moment (μ_{eff}) which is given by the expression

$$\mu_{eff} = \sqrt{n(n+2)} \text{ B.M.}$$

Where n is the number of unpaired electrons and B.M stands for Bohr magneton.

Note mercurous ion is diamagnetic in nature which explains that it exists as dimer, Hg_2^{2+} and not monomer Hg^+

13. Complex formation

Transition metal ions form a large number of complex in which the central metal ion is linked to a number of ligands. This is because

- (i) They have higher nuclear charge and small size . i.e. charge/size ration (charge density) is large
- (ii) They have empty d-orbitals to accept the lone pairs of electrons donated by ligands

Thus in complexes metal ions behave as Lewis acids and ligands behave as Lewis bases.

14. Interstitial compounds

Transition metals form a number of interstitial compounds in which small non-metal atoms such as H, C, B, N and He occupy the empty spaces (interstitial sites) in their lattices and also form bonds with them. These new compounds known as hydrides, carbides, borides, nitrides and halides respectively have higher melting points than respective pure metals, are chemically inert, hard and rigid.

15. Ally formation:

Due to similarity in atomic size, atoms of one transition metal can easily take up positions in the crystal lattice of the other in molten state and are miscible with each other forming solid solutions

16. Preparation of potassium dichloride from iron chromite ore

$K_2Cr_2O_7$ is prepared from Chromite ore ($FeCr_2O_4$).

The finely powdered ore is fused with Na_2CO_3 in free access of air.



The yellow solution of Na_2CrO_4 is filtered and acidified with H_2SO_4 to give a solution from which orange sodium dichromate $Na_2Cr_2O_7 \cdot H_2O$ can be crystallized



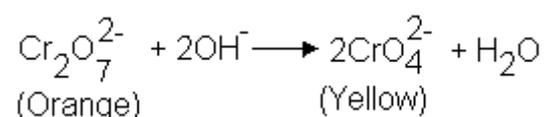
$K_2Cr_2O_7$ is prepared by treating the solution of $Na_2Cr_2O_7$ with potassium chloride



$K_2Cr_2O_7$ being less soluble than $Na_2Cr_2O_7$ Crystallizes out on cooling as Orange crystal

Effect of pH

On increasing pH, the orange colour solution of dichromate, a yellow coloured solution of chromate is formed



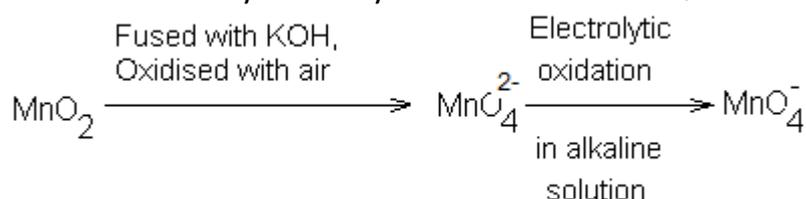
17. Preparation of potassium permanganate.

KMnO₄ is prepared from the mineral, pyrolusite, MnO₂

- (a) The finely powdered pyrolusite mineral is fused with KOH and an oxidizing agent like KNO₃. This produces the dark green K₂MnO₄ which disproportionate in a neutral acidic solution to give permanganate



- (b) Commercially KMnO₄ is prepared by alkaline oxidative fusion of MnO₂ followed by electrolytic oxidation of MnO₄²⁻



18. Lanthanoid contraction:

The regular decrease in the size of lanthanoid ions from La³⁺ to Lu³⁺ is known as lanthanoid contraction. It is due to greater effect of increased nuclear charge than that of the screening effect.

19. Consequences of Lanthanoid contraction

- It results in slight variation in their chemical properties which helps in their separation by ion exchange method
- Each element beyond lanthanum has same atomic radius as that of element lying above it in the same group
- The covalent character of hydroxides of lanthanoids increases as the size decreases from La³⁺ to Lu³⁺. Hence the basic strength decreases.
- Tendency to form stable complexes from La³⁺ to Lu³⁺ increases as the size decreases in that order
- There is a slight increase in electronegativity of the trivalent ions from La to Lu
- Since the radius of Yb³⁺ ion is comparable to the heavier lanthanoid, therefore, they occur together in natural minerals

20. Colour of lanthanoid

Most of the trivalent lanthanoid ions are coloured both in the solid state and in aqueous solution. This is due to the partly filled f-orbitals which permit f-f transition.

21. Magnetic properties of lanthanoid

All lanthanoid ions except Lu³⁺, Yb³⁺ and Ce⁴⁺ are paramagnetic because they contain unpaired electrons in the 4f orbitals. They do not follow simple formula as for transition elements.

Magnetic moments of lanthanoids are calculated by taking into consideration spin as well as orbital contributions and more complex formula

$$\mu_{eff} = \sqrt{4S(S + 1) + L(L + 1)}$$

Which involves the orbital quantum number L and spin quantum number S

22. Actinoid contraction:

There is a regular decrease in ionic radii with increase in atomic number. It is caused due to imperfect shielding of one 5f electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

23. Colour of Actinoid:

Ions of actinoids are generally coloured which is due to f-f transitions. It depends upon the number of electrons in 5f orbitals.

24. Magnetic properties of Actinoid

Like Lanthanoids, actinoids elements are strongly paramagnetic. The magnetic moment is less than the theoretically predicted values. This is due to the fact that 5f electrons of Actinoids are less effectively shielded which results in quenching of orbital contribution

25. Complex formation of Actinoid

Actinoids have greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms. They form complexes even with π -bonding ligands such as alkyl phosphines, thioethers etc.

26. Comparison of Lanthanoides and Actinoides

(i) Electron configuration: In Lanthanoids, 4f orbitals are progressively filled whereas in , 5f orbitals are progressively filled. The general electronic configuration of Lanthanoids is $[Xe]4f^{1-14} 5d^{0-1}6s^2$ where as the general electronic configuration of actinoids is $[Rn]5f^{1-14} 6d^{0-1}7s^2$

(ii) Oxidation States: Lanthanoids shows limited oxidation states (+2, +3, +4) out of which +3 is most common. This is because of large energy gap between 4f, 5d, and 6s subshells. On the other hand, Actinoids show a large number of oxidation states (+3,+4,+5,+6,+7) out of which +3 is most common. This is due to large small energy gap between 5f, 6d and 7s subshells

(iii) Atomic and ionic size: Both show decrease in size of their atoms or M^{3+} ions across the series. In Lanthanoids, the decrease is called lanthanoid contraction, where as in actinoids it is called Actinoid contraction. However, the contraction is greater from element to element in Actinoids due to poor shielding by 5f electrons

(iv) Chemical reactivity: Actinoids are more reactive than Lanthanoids due to bigger atomic size and lower ionization energy. The action of boiling water on actinoids give

mixture of oxide and hydride and combination with most non metals takes place at moderate temperature. HCl attacks all metals but most slightly affected by HNO_3 . The first few members of Lanthanoids are quite reactive, almost like calcium. However with increasing atomic number, their behavior becomes similar to that of Aluminium. They combine with H_2 on gentle heating. When heated with carbon they form carbides. They react with acids to liberate hydrogen gas.

Conceptual questions on d – and f-block elements

Q1) What is meant by transition elements

Ans) A transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states

Q2) What is general electron configuration of transition elements

Ans) $(n-1)d^{1-10} ns^{1-2}$

Q3) Zn, Cd and Hg are not regarded as transition elements why?

Ans) Zinc, Cadmium and Mercury have completely filled d orbitals in their ground state as well as in their oxidized state, hence they are not regarded as transition elements

Q4) On what ground you can say that Scandium ($Z = 21$) is a transition element but Zinc ($Z = 30$) is not?

Ans) On the basis of incompletely filled 3d orbitals in case of Scandium atom in its ground state ($3s^1$), it is regarded as transition element. On the other hand, zinc atom has completely filled d-orbitals ($3d^{10}$) in its ground state as well as in its oxidized state, hence it is not regarded as a transition element

Q5) Silver atom has completely filled d orbitals $4d^{10}$ in its ground state. How can you say that it is a transition element?

Ans) Silver ($Z = 54$) can exhibit +2 oxidation state where it will have incompletely filled d orbitals (d^9), hence a transition element.

Q6) Why do the transition elements exhibit higher enthalpy of atomization

Ans) Because of large number of unpaired electrons in their atoms, they have strong inter-atomic interactions and hence stronger bonds between atoms resulting in higher enthalpies of atomization

Q7) In the series Sc(Z=21) to Zn (Z=30) , the enthalpy of atomization of zinc is the lowest i.e 126KJ mol⁻¹. Why?

Ans) In the formation of metallic bonds, no electrons from d-orbitals are involved in case of Zinc, while in all other metals of 3d series, electrons from the d-orbitals are always involved in the formation of metallic bonds

Q8) Why are Mn⁺² compounds more stable than F²⁺ towards oxidation to their +3 state?

Ans) Electron configuration of Mn²⁺ is 3d⁵ which is half filled and hence stable. Therefore, third ionization enthalpy is very high. In case of Fe²⁺, electronic configuration is 3d⁶. Hence it can lost one electron easily to give stable configuration 3d⁵

Q9) Name a transition element which does not exhibit variable oxidation states

Ans) Scandium (Z=21) does not exhibit variable oxidation states

Q10) Which of the 3d series of the transition metals exhibits the large number of oxidation states and why?

Ans) Manganese (Z=25), as its atom has maximum number of unpaired electrons

Q11) Why is Cr²⁺ reducing and Mn⁺³ oxidizing whom both have d⁴ configuration?

Ans) Cr²⁺ is reducing as its configuration changes from d⁴ to d³, the latter having a half filled t_{2g} level. On the other hand, the change from Mn³⁺ to Mn²⁺ results in the half filled (d⁵) configuration which has extra stability

Q12) What may be stable oxidation states of the transition element with following 'd' electron configuration in the ground state of their atoms : 3d³, 3d⁵, 3d⁸, 3d⁴?

Ans) (1) 3d³ (Vanadium) : = +2, +3, +4 and +5

(2) 3d⁵ (chromium) = +3, +4, and +6

(3) 3d⁵ (Manganese) : +2, +4, +6 and +7

(4) 3d⁸ (Nickel) : +2, +3, +4

(5) 3d⁴ – There is no d⁴ configuration in the ground state

Q13) To what extent do the electronic configuration decides the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples

Ans) In a transition series, the oxidation states which lead to exactly half-filled or completely filled d-orbitals are most stable. For example, in the first transition series, electronic configuration of Mn(Z=25) is $[\text{Ar}]3d^54s^2$. It shows oxidation states +2 to +7 but +2 is more stable than Mn^{3+} because Mn^{2+} has half filled d orbitals. Similarly Fe^{3+} is more stable than Fe^{2+} due to half filled d-orbitals

Q14) Name oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group member

(i) $\text{Cr}_2\text{O}_7^{2-}$ and Cr_4^{2-} , oxidation states of Cr is +6 which is equal to its group numbers

(ii) Mn_4^- , Oxidation state of Mn is +7 which is equal to its group number

Q15) What is lanthanoid contraction? What are the consequences of Lanthanoid contraction

Ans) The decrease in atomic and ionic size with increase in atomic number in lanthanoids is called lanthanoid contraction

Consequences

(i) The ionic radii of the second (4d) and the third (5d) series of transition elements are similar

(ii) Lanthanoids have similar chemical and physical properties

Q16) In what way is the electronic configuration of the transition elements differ from that of the non transition elements

Ans) In transition elements penultimate d-orbitals [(n-1) orbitals] are progressively filled and their electronic configuration is $(n-1)d^{1-10} ns^{1-2}$ whereas in non transition elements outermost s or p orbitals are progressively filled and their electronic configuration is ns^{1-2} or $ns^2 np^{1-6}$

Q17) Transition metals and many of their compounds show paramagnetic behavior. Why?

Ans) This is due to the presence of unpaired electrons in the (n-1)d orbitals

Q18) The transition elements generally form coloured compounds

Ans) It is due to presence of unpaired electrons, they undergo d-d transitions by absorbing light from visible region and radiate complementary colour

Q19) transition metals and their many compounds act as good catalyst

Ans) It is because of their ability to adopt multiple oxidation states and to form complexes. They have large surface area and can form intermediate with reactants which readily change into products.

Q20) What are interstitial compounds? Why are such compounds well known for transition metals?

Ans) Interstitial compounds are those which are formed when small atoms like H, C, or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent

The transition metals have voids between atoms in their crystal lattice. Therefore they are known to form interstitial compounds

Q21) How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples

Ans) In transition elements the oxidation states vary from +1 to any highest oxidation state by one. For example, for manganese it may vary as +2,+3,+4,+5,+6,+7. In the non transition elements the variation is selective, always differing by 2; +2, +4, or +3, +5 etc

Q22) Predict which of the following will be coloured in aqueous solution of

MnO_4^- , Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{2+} and Co^{2+} . Give reason for each

Ans) Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{2+} and Co^{2+} are coloured due to presence of unpaired electrons, they undergo d-d transition by absorbing light from visible region and radiate complementary colour.

MnO_4^- is coloured ion due to charge transfer from oxygen to manganese, it absorbs light from visible region and radiate complementary colour

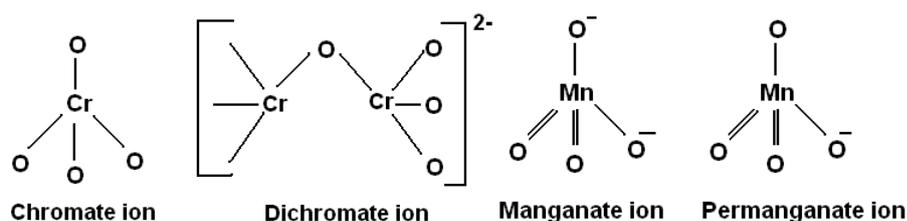
Cu^+ , Sc^{3+} are colourless due to absence of unpaired electrons

Q23) Why d^1 configuration is very unstable ions?

Ans) The ions with d^{1+} configuration have the tendency to lose the only electron present in d-subshell to acquire stable d^0 configuration. Hence they are unstable and undergo oxidation.

Q24) Draw the structure of (i) Chromate ion (ii) Dichromate ion (iii) Manganate ion (4) Permanganate ion

Ans)



Q25) For M^{2+}/M and M^{3+}/M^{2+} systems the E^\ominus values for some metals are follows

$$Cr^{2+}/Cr = -0.9V, Cr^{3+}/Cr^{2+} = -0.4V$$

$$Mn^{2+}/Mn = -1.2V, Mn^{3+}/Mn^{2+} = +1.5V$$

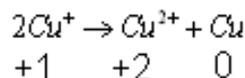
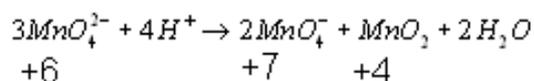
$$Fe^{2+}/Fe = -0.4V, Fe^{3+}/Fe^{2+} = 0.8V$$

Using this data to comment upon (i) the stability of Fe^{3+} in acidic solution as compared to that of Cr^{3+} or Mn^{3+} and (2) the ease with which ion can be oxidized as compared to similar process of either chromium or manganese metal

- (i) Cr^{3+}/Cr^{2+} has a negative reduction potential. Hence Cr^{3+} cannot be reduced to Cr^{2+} i.e Cr^{3+} is most stable,
 Mn^{3+}/Mn^{2+} has large positive E^\ominus value. Hence Mn^{3+} can be easily reduced to Mn^{2+} i.e Mn^{3+} is least stable
 E^\ominus value for Fe^{3+}/Fe^{2+} is positive but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+}
- (ii) Oxidation potential for the given pairs will be +0.9V, +1.2V and +0.4V. thus the order of their getting oxidized will be in the order $Mn > Cr > Fe$

Q26) What is meant by disproportionation? Give two examples of disproportionate reaction in aqueous solution

Ans) When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation



Q27) Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Ans) Copper exhibits +1 oxidation state frequently due to stable electronic configuration ($3d^{10}$)

Q28) Why the lowest oxide of transition metals is basic, the highest is amphoteric/acidic.

Ans) The lower oxide of transition metals is basic because the metal atom has low oxidation state, whereas the highest is acidic due to higher oxidation state. In lower oxidation state, ionic bonds are formed whereas in highest oxidation state covalent bonds are formed. MnO is basic while Mn_2O_7 is acidic

Q29) Why transition metals exhibit highest oxidation state in oxides and fluorides

Ans) It is because oxygen and fluorine are highly electronegative and strong oxidizing agents.

Q30) Comment on the statement that the elements of the first transition series possess many properties different from those of heavier transition elements

Ans) Melting and boiling point of heavier transition elements are greater than those of the lower transition series due to strong intermetallic bonding

The ionization enthalpy of 5d transition series is higher than 4s and 3d transition series

The elements of first transition series do not form complexes with higher coordination number of 7 and 8

Atomic radii of the heavier transition elements (4d and 5d) are larger than of the corresponding elements of the first transition series

The elements of the first series can form high spin or low spin complexes depending upon strength of ligand's but elements of other series form low spin complex irrespective of strength of ligand's

Q31) Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Ans) The 5f electrons are more effectively shielded from nuclear charge. In other words the 5f electrons themselves provide poor shielding. From element to element

Q32) Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

Ans) It is due to increase in effective nuclear charge after losing 2 electrons from s-orbitals, ionic size decreases, stability increases

Q33) Transition elements form large number of complex compounds why?

Ans) This is due to the comparatively small size of the metal ions, high ionic charge and the availability of d orbitals for bond formation

Q34) Transition elements show variable oxidation states. Why?

Ans) In the transition elements, the energies of (n-1)d orbitals and ns orbitals are very close. Hence, electrons from both can participate in bonding

Q35) Why Zr(Zirconium) and Hf(Hafnium) have similar chemical properties?

Ans) Due to lanthanoid contraction, Hf has size similar to that of Zr (i.e. almost identical radii). Hence their properties are similar

Q36) Why Nb and Ta have similar properties?

Ans) Due to lanthanoid contraction Nb has same size to that of Ta. Hence they have similar properties

Q37) What is the separation of Lanthanide elements difficult

Ans) Due to Lanthanoid contraction, the change in the atomic or ionic radii of these elements is very small. Hence their chemical properties are similar

Q38) Why Zn, Cd and Hg are soft and have low melting and boiling points

Ans) In Zn, Cd and Hg all the electrons in d-shell are paired. Hence the metallic bond present in them are weak. Therefore they are soft.

Q39) Why Transition Metals Are Good Catalysts

The most important reason transition metals are good catalysts is that they can lend electrons or withdraw electrons from the reagent, depending on the nature of the

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reaction. The ability of transition metals to be in a variety of oxidation states, the ability to interchange between the oxidation states and the ability to form complexes with the reagents and be a good source for electrons make transition metals good catalysts.



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