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JEE Main, JEE Advanced and NEET

Inorganic Chemistry Exceptions for JEE and NEET

The trends of the periodic table have a small number of exceptions, and the exam asks the exceptions. Here are 53 of them in one place: what the trend predicts, what really happens, and the reason, with the data values. A quiz of 18 questions follows.

Electronic configuration

The filling order 4s before 3d fails where a half-filled or full d subshell is within reach.

Expected Orbitals fill in the order 4s, then 3d.

Exception Cr is $[\mathrm{Ar}]\ 3d^5\ 4s^1$ and Cu is $[\mathrm{Ar}]\ 3d^{10}\ 4s^1$.

Why Half-filled and fully filled d subshells are extra stable (more exchange energy), and 3d and 4s lie close in energy.

Expected The 4d and 5d metals copy Cr and Cu.

Exception Mo is $4d^5\ 5s^1$ and Ag is $4d^{10}\ 5s^1$, but W is $5d^4\ 6s^2$. Pd is $4d^{10}\ 5s^0$, the only d-block atom with an empty s orbital.

Why The gap between ns and (n-1)d changes from row to row, so these are learnt, not derived. Others: Nb $4d^4\ 5s^1$, Ru $4d^7\ 5s^1$, Rh $4d^8\ 5s^1$, Pt $5d^9\ 6s^1$, Au $5d^{10}\ 6s^1$.

Expected The electron that entered last leaves first.

Exception Transition metal ions lose the ns electrons first: Fe^{2+} is $3d^6$, not $3d^4\ 4s^2$.

Why Once the 3d orbitals are occupied they lie below 4s in energy.

Expected Lanthanoids fill 4f from the first element on.

Exception La is $5d^1\ 6s^2$ with no 4f electron. Ce is $4f^1\ 5d^1\ 6s^2$, Gd is $4f^7\ 5d^1\ 6s^2$ and Lu is $4f^{14}\ 5d^1\ 6s^2$.

Why An empty, half-filled or full 4f subshell is favoured, so one electron stays in 5d.

Atomic and ionic radius

Radii are in pm.

Expected Atomic radius increases down a group.

Exception Ga (135) is smaller than Al (143). Group 13 order: B < Ga < Al < In < Tl.

Why The ten 3d electrons of Ga shield the nucleus poorly, so the outer electrons are pulled in.

Expected A 5d atom is larger than the 4d atom above it.

Exception Zr (160) and Hf (159) are almost the same size. So are Nb and Ta, and Mo and W.

Why Lanthanoid contraction: the fourteen 4f electrons shield poorly.

Expected Radius decreases across a period.

Exception Each noble gas appears larger than the halogen before it: Ne 160, F 64.

Why Noble gas values are van der Waals radii of atoms that are not bonded. The other values are covalent radii.

Expected Radius decreases steadily across the 3d series.

Exception It falls from Sc (164) to Cr (129), is almost constant from Fe to Ni (126, 125, 125), and rises again at Cu (128) and Zn (137).

Why Each added 3d electron shields the 4s electrons and cancels most of the extra nuclear charge. In the full d^{10} shell, repulsion between electrons wins.

Ionisation enthalpy

First ionisation enthalpy in kJ/mol, unless a line says second or third.

Expected Ionisation enthalpy rises across a period.

Exception Period 2: B (801) is below Be (899), and O (1314) is below N (1402). Order: Li < B < Be < C < O < N < F < Ne.

Why B loses a 2p electron, which is held less firmly than the 2s electrons of Be. O loses a paired 2p electron, while N has a half-filled $2p^3$ set.

Expected Ionisation enthalpy rises across a period.

Exception Period 3: Al (577) is below Mg (737), and S (1000) is below P (1012). Order: Na < Al < Mg < Si < S < P < Cl < Ar.

Why The same two reasons: 3p against 3s, and a paired electron against a half-filled set.

Expected Ionisation enthalpy falls down a group.

Exception Group 13: B (801) > Tl (589) > Ga (579) > Al (577) > In (558).

Why The d electrons of Ga and the d and f electrons of Tl shield poorly, so their outer electrons are held more firmly than expected.

Expected Ionisation enthalpy falls down a group.

Exception Group 14: C (1086) > Si (786) > Ge (761) > Pb (715) > Sn (708).

Why Poor shielding by the 4f and 5d electrons of Pb.

Expected Ionisation enthalpy falls down a group.

Exception Group 11: Au (890) > Cu (745) > Ag (731). In general the 5d metals have higher values than the 4d metals.

Why Lanthanoid contraction makes the 5d atoms small for their nuclear charge.

Expected The second and third ionisation enthalpies rise smoothly across the 3d series.

Exception Second: Cr (1592) is above Mn (1509), and Cu (1958) is above Zn (1734). Third: Mn (3260) is above Fe (2962).

Why The electron has to leave a stable set: Cr^+ is $3d^5$, Cu^+ is $3d^{10}$ and Mn^{2+} is $3d^5$.

Electron gain enthalpy and electronegativity

Electron gain enthalpy in kJ/mol; electronegativity on the Pauling scale.

Expected Electron gain enthalpy becomes less negative down a group.

Exception Cl (-349) is more negative than F (-328), and S (-200) is more negative than O (-141). Orders: Cl > F > Br > I and S > Se > Te > Po > O.

Why The second period atom is very small, so the incoming electron is repelled strongly by the crowded 2p electrons.

Expected An atom releases energy when it gains an electron.

Exception Noble gases, Be and Mg have positive values, and N is close to zero.

Why The electron must start a new subshell (noble gases, Be, Mg) or pair up in a half-filled set (N).

Expected Gaining an electron releases energy.

Exception The second electron gain enthalpy is always positive: $\mathrm{O^- + e^- \longrightarrow O^{2-}}$ needs 780 kJ/mol.

Why An electron is being pushed on to an ion that is already negative.

Expected The element with the most negative electron gain enthalpy is the strongest oxidising agent.

Exception $\mathrm{F_2}$, not $\mathrm{Cl_2}$, is the strongest oxidising agent.

Why The F-F bond is weak (158.8 kJ/mol) and $\mathrm{F^-}$ has a very high hydration enthalpy (515 kJ/mol, against 381 for $\mathrm{Cl^-}$).

Expected Electronegativity falls down a group.

Exception Group 13: B (2.0) > Tl (1.8) > In (1.7) > Ga (1.6) > Al (1.5). In group 14, Pb (1.9) is above Si, Ge and Sn (1.8 each).

Why Poor shielding by d and f electrons raises the pull of the heavier atoms on bonding electrons.

Melting point, boiling point and density

Expected Density rises down a group.

Exception K (0.86 g/cm^3) is lighter than Na (0.97). In group 2 the order is Ca (1.55) < Mg (1.74) < Be (1.84) < Sr < Ba.

Why From Na to K, and from Mg to Ca, the atomic volume jumps by more than the mass does.

Expected Melting point falls down group 13.

Exception Ga melts at 303 K, far below Al (933 K), In (430 K) and Tl (576 K).

Why Solid gallium is built of $\mathrm{Ga_2}$ units that hold one another weakly.

Expected Melting point falls down group 14.

Exception Pb (600 K) melts above Sn (505 K). Order: C > Si > Ge > Pb > Sn.

Why No simple rule gives this one. Learn the order.

Expected Boiling point of the hydrides rises down a group with molar mass.

Exception Group 15: $\mathrm{PH_3}$ (185.5 K) < $\mathrm{AsH_3}$ (210.6) < $\mathrm{NH_3}$ (238.5) < $\mathrm{SbH_3}$ (254.6) < $\mathrm{BiH_3}$ (290).

Why Hydrogen bonding lifts $\mathrm{NH_3}$ above $\mathrm{PH_3}$ and $\mathrm{AsH_3}$, but not above the much heavier $\mathrm{SbH_3}$.

Expected Boiling point of the hydrides rises down a group with molar mass.

Exception Group 16: $\mathrm{H_2S}$ (213 K) < $\mathrm{H_2Se}$ (232) < $\mathrm{H_2Te}$ (269) < $\mathrm{H_2O}$ (373). Group 17: HCl (189 K) < HBr (206) < HI (238) < HF (293).

Why Hydrogen bonding in $\mathrm{H_2O}$ and HF is strong enough to put them at the top of their groups.

Expected Melting point of the transition metals rises to the middle of a series and then falls.

Exception Mn melts lower than its neighbours Cr and Fe. Zn, Cd and Hg are the lowest of their series, and Hg is a liquid.

Why Mn ($3d^5\ 4s^2$) holds its electrons firmly, so fewer take part in metallic bonding. Zn, Cd and Hg have a full d^{10} shell and no unpaired d electrons.

Expected Transition metals have a high enthalpy of atomisation.

Exception Zn has the lowest value of the 3d series, 126 kJ/mol.

Why With no unpaired d electrons, its metallic bonding is weak.

Bond strength, acidity and polarity

Expected Bond enthalpy of the halogen molecules falls down the group.

Exception $\mathrm{Cl_2}$ (242.6) > $\mathrm{Br_2}$ (192.8) > $\mathrm{F_2}$ (158.8) > $\mathrm{I_2}$ (151.1 kJ/mol).

Why The lone pairs on the two small F atoms repel strongly at the short F-F distance.

Expected Single bonds between second period atoms are the strongest of their group.

Exception N-N is weaker than P-P, and O-O is weaker than S-S.

Why Lone pair repulsion at a short bond length. So nitrogen and oxygen show little catenation, while sulphur forms $\mathrm{S_8}$ rings and phosphorus forms $\mathrm{P_4}$.

Expected The more electronegative halogen gives the stronger acid HX.

Exception Acid strength: HF < HCl < HBr < HI. HF is a weak acid (pK_a 3.2).

Why Acid strength follows the H-X bond enthalpy (574 kJ/mol for HF, 295 for HI), not the electronegativity.

Expected The more electronegative halogen makes boron a stronger Lewis acid.

Exception $\mathrm{BF_3} < \mathrm{BCl_3} < \mathrm{BBr_3} < \mathrm{BI_3}$.

Why Back bonding from a filled 2p orbital of F into the empty 2p orbital of B is strongest in $\mathrm{BF_3}$ and makes boron less electron deficient.

Expected More electronegative atoms give a larger dipole moment.

Exception $\mathrm{NH_3}$ (1.47 D) is far more polar than $\mathrm{NF_3}$ (0.23 D).

Why In $\mathrm{NH_3}$ the lone pair moment adds to the N-H bond moments. In $\mathrm{NF_3}$ it opposes the N-F bond moments.

Expected An acid with three hydrogen atoms is tribasic.

Exception $\mathrm{H_3PO_3}$ is dibasic, $\mathrm{H_3PO_2}$ is monobasic, and $\mathrm{H_3BO_3}$ is a monobasic Lewis acid.

Why Only hydrogen on oxygen ionises: $\mathrm{H_3PO_3}$ has two P-OH groups and $\mathrm{H_3PO_2}$ has one. $\mathrm{B(OH)_3}$ gives no proton of its own; it takes $\mathrm{OH^-}$ from water.

Oxidation states and compounds that do not exist

Expected The group oxidation state is the most stable one.

Exception $\mathrm{Tl^+}$, $\mathrm{Pb^{2+}}$ and $\mathrm{Bi^{3+}}$ are more stable than $\mathrm{Tl^{3+}}$, $\mathrm{Pb^{4+}}$ and $\mathrm{Bi^{5+}}$.

Why Inert pair effect: the ns^2 pair of the heavy elements stays out of bonding. So $\mathrm{PbO_2}$ and $\mathrm{Tl^{3+}}$ are oxidising agents, while $\mathrm{SnCl_2}$ is a reducing agent.

Expected Thallium triiodide contains thallium(III).

Exception $\mathrm{TlI_3}$ is TlI with the triiodide ion, $\mathrm{I_3^-}$.

Why Thallium(III) would oxidise iodide.

Expected A metal ion forms a halide with every halogen.

Exception $\mathrm{PbI_4}$, $\mathrm{FeI_3}$ and $\mathrm{CuI_2}$ do not exist.

Why $\mathrm{Pb^{4+}}$, $\mathrm{Fe^{3+}}$ and $\mathrm{Cu^{2+}}$ oxidise $\mathrm{I^-}$ to $\mathrm{I_2}$. Copper(II) with KI gives white $\mathrm{Cu_2I_2}$ and iodine.

Expected Group 15 elements form pentahalides.

Exception $\mathrm{NCl_5}$ and $\mathrm{NF_5}$ do not exist, but $\mathrm{PCl_5}$ does. For bismuth only $\mathrm{BiF_5}$ is known.

Why Nitrogen has no d orbitals in its valence shell, so its covalency cannot go beyond 4. Bismuth(V) is too strongly oxidising for the other halides.

Expected The maximum covalency is the same down a group.

Exception Boron stops at $\mathrm{[BF_4]^-}$ but aluminium forms $\mathrm{[AlF_6]^{3-}}$. $\mathrm{[SiF_6]^{2-}}$ exists but $\mathrm{[CF_6]^{2-}}$ does not.

Why Second period atoms have only four valence orbitals, 2s and 2p.

Expected Covalent halides of non-metals are hydrolysed by water.

Exception $\mathrm{CCl_4}$ and $\mathrm{NF_3}$ are not hydrolysed, though $\mathrm{SiCl_4}$ and $\mathrm{NCl_3}$ are. $\mathrm{SF_6}$ is inert.

Why Carbon has no vacant d orbital to accept a lone pair from water; in $\mathrm{NF_3}$ neither nitrogen nor fluorine has one, while in $\mathrm{NCl_3}$ chlorine does. In $\mathrm{SF_6}$ six fluorine atoms block the sulphur atom.

Expected Oxygen is negative in all its compounds.

Exception Oxygen is $+2$ in $\mathrm{OF_2}$ and $+1$ in $\mathrm{O_2F_2}$. Fluorine is -1 in every compound.

Why Only fluorine is more electronegative than oxygen.

Expected Oxides of non-metals are acidic.

Exception CO, NO and $\mathrm{N_2O}$ are neutral oxides.

Why They form no salt with acids or with bases.

d- and f-block elements

Electrode potentials are standard values in volts.

Expected Every d-block element is a transition element.

Exception Zn, Cd and Hg are not transition elements. Sc is one.

Why A transition element has an incomplete d subshell in the atom or in a common ion. Zn, Cd and Hg are d^{10} in both. Sc is $3d^1$ as an atom.

Expected The highest oxidation state keeps rising across the 3d series.

Exception It rises from $+3$ at Sc to $+7$ at Mn and then falls. Zn shows only $+2$.

Why After Mn the 3d electrons are held too firmly to be used in bonding.

Expected Fluorine brings out the highest oxidation state of a metal.

Exception The highest fluoride of manganese is $\mathrm{MnF_4}$, but its highest oxide is $\mathrm{Mn_2O_7}$.

Why Oxygen can form multiple bonds to the metal, so it stabilises higher oxidation states than fluorine does.

Expected $E^\circ(\mathrm{M^{2+}/M})$ becomes steadily less negative across the 3d series.

Exception Mn (-1.18), Ni (-0.25) and Zn (-0.76) are more negative than the trend, and Cu is positive ($+0.34$).

Why $\mathrm{Mn^{2+}}$ is d^5 and $\mathrm{Zn^{2+}}$ is d^{10}; $\mathrm{Ni^{2+}}$ has a very high hydration enthalpy. For copper, hydration does not pay back the atomisation and ionisation enthalpies, so Cu does not release $\mathrm{H_2}$ from acids.

Expected Ions with the same number of d electrons behave alike.

Exception $\mathrm{Cr^{2+}}$ is a reducing agent but $\mathrm{Mn^{3+}}$ is an oxidising agent, though both are d^4.

Why $\mathrm{Cr^{2+}}$ goes to $\mathrm{Cr^{3+}}$, which has a half-filled t_{2g} set. $\mathrm{Mn^{3+}}$ goes to $\mathrm{Mn^{2+}}$, which is d^5. E°: $\mathrm{Cr^{3+}/Cr^{2+}}$ is -0.41, $\mathrm{Mn^{3+}/Mn^{2+}}$ is $+1.57$.

Expected An ion with a full d^{10} shell is stable.

Exception $\mathrm{Cu^+}$ is not stable in water: $\mathrm{2\,Cu^+ \longrightarrow Cu^{2+} + Cu}$.

Why The much higher hydration enthalpy of $\mathrm{Cu^{2+}}$ more than pays for the second ionisation enthalpy.

Expected Lanthanoids show only the $+3$ state.

Exception $\mathrm{Ce^{4+}}$ is a strong oxidising agent. $\mathrm{Eu^{2+}}$ and $\mathrm{Yb^{2+}}$ are reducing agents.

Why $\mathrm{Ce^{4+}}$ is $4f^0$, $\mathrm{Eu^{2+}}$ is $4f^7$ and $\mathrm{Yb^{2+}}$ is $4f^{14}$, yet each returns to $+3$ in its reactions.

Expected Species with d^0 or d^{10} metal ions are colourless.

Exception $\mathrm{MnO_4^-}$ (purple), $\mathrm{Cr_2O_7^{2-}}$ (orange) and $\mathrm{CrO_4^{2-}}$ (yellow) are d^0 and coloured.

Why Their colour comes from charge transfer from oxygen to the metal, not from a d-d transition. $\mathrm{Sc^{3+}}$, $\mathrm{Ti^{4+}}$, $\mathrm{Zn^{2+}}$ and $\mathrm{Cu^+}$ are colourless as expected.

Coordination compounds

Expected Weak field ligands give high spin complexes.

Exception $\mathrm{[Co(H_2O)_6]^{3+}}$ is low spin and diamagnetic, though water is a weak field ligand. $\mathrm{[CoF_6]^{3-}}$ is the high spin complex of cobalt(III), with 4 unpaired electrons.

Why The $+3$ charge of cobalt makes Δ_o large enough to pair the six d electrons with almost every ligand.

Expected Strong field ligands give inner orbital complexes.

Exception $\mathrm{[Ni(NH_3)_6]^{2+}}$ is an outer orbital complex (sp^3d^2) with 2 unpaired electrons.

Why A d^8 ion cannot empty two of its 3d orbitals, whatever the ligand.

Expected A complex with four ligands is tetrahedral.

Exception $\mathrm{[Ni(CN)_4]^{2-}}$ and $\mathrm{[PtCl_4]^{2-}}$ are square planar (dsp^2) and diamagnetic. $\mathrm{[NiCl_4]^{2-}}$ is tetrahedral with 2 unpaired electrons. $\mathrm{[Ni(CO)_4]}$ is tetrahedral and diamagnetic.

Why A d^8 ion goes square planar with a strong field ligand, or when the metal is from the 4d or 5d series. In $\mathrm{[Ni(CO)_4]}$ nickel is $3d^{10}$.

Expected Strong field ligands give low spin tetrahedral complexes.

Exception Tetrahedral complexes are almost always high spin.

Why $\Delta_t = \frac{4}{9}\Delta_o$, which is smaller than the pairing energy.

Expected NO is a neutral ligand.

Exception In the brown ring complex $[Fe(H_2O)_5(NO)]^{2+}$ iron is $+1$ and the ligand is NO^+. The complex has 3 unpaired electrons.

Why NO gives one electron to Fe^{2+} before it bonds.

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