WEIRD CHEMIST

Where Chemistry Gets Interesting

DPP-7 Solution Sheet

p-Block Elements — Group 14: The Carbon Family

NEET Revision Series | 50 Questions | Complete Solutions

"Group 14 = two big ideas: inert pair effect (Pb loves +2) and carbon's anomaly (no d-orbitals, loves pi bonds). Lock those two and 80% of questions become easy."

QUICK ANSWER KEY

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	(2)	11	(2)	21	(2)	31	(2)	41	(1)
2	(1)	12	(2)	22	(2)	32	(2)	42	(2)
3	(2)	13	(2)	23	(4)	33	(1)	43	(2)
4	(2)	14	(2)	24	(1)	34	(1)	44	(2)
5	(2)	15	(2)	25	(2)	35	(2)	45	(2)
6	(3)	16	(1)	26	(2)	36	(2)	46	(2)
7	(1)	17	(3)	27	(3)	37	(2)	47	(2)
8	(2)	18	(2)	28	(2)	38	(2)	48	(2)
9	(1)	19	(2)	29	(2)	39	(4)	49	(2)
10	(2)	20	(2)	30	(2)	40	(2)	50	(1)

TOPIC 1 — Introduction

(a) Elements and Occurrence

Q.1 Why is carbon far more versatile than silicon despite silicon being more abundant?

[A] Conceptual Approach

Carbon's versatility comes from two unique properties: (1) catenation — ability to bond with itself to form long chains, rings, branches; (2) ability to form stable bonds with H, O, N, Cl, S. These give rise to millions of organic compounds. Abundance doesn't equal versatility.

[S] Step-by-Step Solution

Carbon's versatility stems from:
Catenation: Carbon forms very stable C–C bonds (BE = 348 kJ/mol) and can form long chains, branched chains, and rings.
Multiple bond formation: C can form C=C, C≡C, C=O, C=N, C≡N bonds ($p\pi$–$p\pi$ bonds).
Bonding with many elements: Stable bonds with H, O, N, Cl, S $\Rightarrow$ millions of organic compounds, from sugars and proteins to drugs and plastics.
Silicon lacks these capabilities (poor $p\pi$–$p\pi$ bonding, weaker Si–Si bond).

[Ans] Final Answer

Option (2): Carbon's catenation + stable bonds with H, O, N, Cl, S $\Rightarrow$ vast range of compounds

[!] Common Mistake

Option (3) says higher atomic mass makes carbon compounds more stable. Carbon has LOWER atomic mass than silicon (C=12, Si=28). And atomic mass has no direct bearing on compound stability or versatility.

Q.2 Which correctly identifies all Group 14 members and their nature?

[A] Conceptual Approach

Group 14: C, Si, Ge, Sn, Pb. Nature: C and Si = non-metals; Ge = metalloid (semiconductor); Sn and Pb = metals. This is the standard NCERT classification.

[S] Step-by-Step Solution

C: Non-metal (diamond/graphite)
Si: Non-metal (semiconductor)
Ge: Metalloid (semiconductor)
Sn: Metal (soft, low melting)
Pb: Metal (soft, low melting)

So: C and Si = non-metals; Ge = metalloid; Sn and Pb = metals.

[Ans] Final Answer

Option (1): C and Si are non-metals; Ge is a metalloid; Sn and Pb are metals

[!] Common Mistake

Option (2) puts Si as a non-metal with C and Ge — but Si is non-metal (correct), it's Ge that is the metalloid. The key distinction: Ge is the metalloid, not Si. Si is a non-metal (though a semiconductor).

Q.3 Correct pairing of tin's ore and silicon's occurrence?

[A] Conceptual Approach

NCERT facts: Tin ore = cassiterite (SnO_2). Silicon occurrence = silica (SiO_2) and silicates (very abundant; sand, quartz, feldspar etc.). Galena (PbS) is the ore of LEAD, not tin.

[S] Step-by-Step Solution

Tin: Ore = cassiterite (SnO_2). Galena (PbS) = ore of lead, not tin.
Silicon: Occurs as silica (SiO_2; quartz, sand, flint) and silicates (mica, feldspar, zeolites). Silicon does NOT occur as coal or graphite (those are carbon allotropes).
Correct pair: Tin = cassiterite (SnO_2); Silicon = silica and silicates.

[Ans] Final Answer

Option (2): Tin — cassiterite (SnO_2); Silicon — silica and silicates

[!] Common Mistake

Option (1) says tin's ore is galena (PbS). Galena is LEAD ore, not tin. A very common confusion: galena = Pb, cassiterite = Sn. Remember: "Cassiterite contains Sn" — cas**Si**terite is a hint!

Q.4 Pie chart: X = 45.5% (oxygen), Y = 27.7%, Z = 8.3% (aluminium). What is segment Y?

[A] Conceptual Approach

Standard earth's crust abundance: O = 45.5%, Si = 27.7%, Al = 8.3%. Silicon is the second most abundant element (after oxygen) and the most abundant metalloid/non-metal.

[S] Step-by-Step Solution

Three key percentages to remember:
O = 45.5%, **Si = 27.7%**, Al = 8.3%

Segment Y = 27.7% = **Silicon**.

Silicon's important uses: semiconductors/transistors (ultrapure Si), glass and ceramics (SiO_2), cement, silicones, solar cells.

[Ans] Final Answer

Option (2): Silicon; used in ceramics, glass, cement, and semiconductor devices

[!] Common Mistake

Option (1) says Y = Carbon (used as coal, graphite, diamond). Carbon is only the 17th most abundant element — nowhere near 27.7%. Carbon's abundance in crust is very small. Only Silicon is 27.7%.

Q.5 Statements about Group 14 elements: I. C has ^{12}C, ^{13}C (stable) and ^{14}C (radioactive, $t_{1/2}$=5770 yr). II. Silicon is the 17th most abundant. III. Ge exists only in traces. IV. Ultrapure Ge and Si used for

transistors. Correct?

[A] Conceptual Approach

Check each: I = TRUE. II = FALSE (Si is the 2nd most abundant, 27.7%; CARBON is 17th). III = TRUE. IV = TRUE. Answer: I, III, IV only.

[S] Step-by-Step Solution

Statement I: TRUE — ^{12}C and ^{13}C are stable; ^{14}C is radioactive (half-life 5770 years), used in radiocarbon dating.

Statement II: **FALSE** — Silicon is the **2nd most abundant** element (27.7%). Carbon is the 17th most abundant. The statement swaps them.

Statement III: TRUE — Germanium is rare; exists only in traces in nature.

Statement IV: TRUE — Ultrapure Si and Ge are key semiconductors for transistors, chips, photovoltaics.

Correct: I, III and IV.

[Ans] Final Answer

Option (2): I, III and IV only

[!] Common Mistake

Accepting Statement II. This is the key swap: Silicon is 2nd most abundant (27.7%); Carbon is 17th. Never confuse these. The question deliberately swaps them to test this specific NCERT fact.

TOPIC 2 — Atomic Properties

(a) Electronic Configuration

Q.6 Which Group 14 element has configuration [Ar] $3d^{10}$ $4s^2$ $4p^2$?

[A] Conceptual Approach

Build configs down Group 14: C=[He]$2s^2 2p^2$, Si=[Ne]$3s^2 3p^2$, Ge=[Ar]$3d^{10} 4s^2 4p^2$, Sn=[Kr]$4d^{10} 5s^2 5p^2$, Pb=[Xe]$4f^{14} 5d^{10} 6s^2 6p^2$. [Ar] core + $3d^{10}$ = Germanium.

[S] Step-by-Step Solution

[Ar] $3d^{10}$ $4s^2$ $4p^2$ = Germanium (Period 4).

Between Si (Period 3) and Ge (Period 4), the $3d^{10}$ subshell is filled (3d-block).
Ge is the first Group 14 element to have d-electrons in its core.

[Ans] Final Answer

Option (3): Germanium (Ge)

[!] Common Mistake

Choosing Silicon. Si = [Ne] $3s^2$ $3p^2$ — it has a neon core, NOT argon. [Ar] core with $3d^{10}$ specifically indicates Period 4 transition to Ge. Si comes before the 3d block is filled.

Q.7 Correct electronic configurations of carbon and tin respectively?

[A] Conceptual Approach

C is Period 2, Group 14: [He] $2s^2$ $2p^2$. Sn is Period 5, Group 14: [Kr] $4d^{10}$ $5s^2$ $5p^2$. Build up: after Kr (Period 4 noble gas), add $4d^{10}$, then $5s^2 5p^2$.

[S] Step-by-Step Solution

Carbon (Period 2): [He] $2s^2$ $2p^2$

Tin (Period 5): [Kr] $4d^{10}$ $5s^2$ $5p^2$

(Lead = [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$; Si = [Ne] $3s^2$ $3p^2$; Ge = [Ar] $3d^{10}$ $4s^2$ $4p^2$)

[Ans] Final Answer

Option (1): [He] $2s^2$ $2p^2$ and [Kr] $4d^{10}$ $5s^2$ $5p^2$

[!] Common Mistake

Option (4) gives [Ne] $3s^2$ $3p^2$ for carbon — that is SILICON's configuration. Carbon uses the helium core ([He]), not neon. Never confuse C and Si configurations.

(b) Covalent Radius

Q.8 Correct description of covalent radius trend in Group 14?

[A] Conceptual Approach

Radius generally increases down group. But the key NCERT fact: Large jump from C to Si, then small increases from Si to Pb (because d/f electrons in heavier members provide poor shielding, counteracting size increase).

[S] Step-by-Step Solution

C to Si: Considerable increase (77 pm → 117 pm) — normal trend as we move from Period 2 to Period 3 with no intervening d-block.

Si to Pb: Only **small increase** thereafter. From Si (117 pm) to Ge (122 pm) to Sn (140 pm) to Pb (154 pm) — much smaller increments.

Reason: Poor shielding by d and f electrons in heavier members counteracts the expected size increase.

[Ans] Final Answer

Option (2): Considerable increase C→Si; thereafter only small increase from Si to Pb

[!] Common Mistake

Option (1) says increase is uniform. Wrong! The jump from C to Si is much larger than any subsequent jump. This is because no d-block elements separate C from Si (only s-block), whereas d-block elements intervene between Si and Ge, etc.

Q.9 Why is the increase in covalent radius from Si to Pb small compared to C to Si?

[A] Conceptual Approach

Same reasoning as Group 13: heavier members have d and f electrons in inner core. d and f electrons shield poorly ⇒ higher Z_{eff} on outer electrons ⇒ outer electrons pulled inward ⇒ radius doesn't increase as much as expected.

[S] Step-by-Step Solution

From Si (Period 3) downward, d and f electrons are progressively added to inner shells.

d and f electrons provide poor shielding of the outer valence electrons from nuclear charge.

⇒ Z_{eff} experienced by outer electrons is higher than expected.
⇒ Outer electrons are pulled closer to nucleus.
⇒ Radius increases only slightly despite larger nuclear charge.

Example: Ge (122 pm) ≈ Si (117 pm) despite adding a whole d-block between them.

[Ans] Final Answer

Option (1): Completely filled d and f orbitals in inner core provide poor shielding ⇒ higher Z_{eff} counteracts expected size increase

[!] Common Mistake

Option (4) says d and f orbitals expand the valence shell causing large uniform increase. Exact opposite! It is the poor SHIELDING by inner d/f electrons that LIMITS the size increase, not expands it.

(c) Ionisation Enthalpy

Q.10 How does first IE of Group 14 members compare with Group 13 members of the same period?

[A] Conceptual Approach

Going across a period: IE generally increases from left to right. Group 14 is to the RIGHT of Group 13, so Group 14 has higher IE than Group 13 in the same period. More nuclear charge, same shielding ⇒ harder to remove an electron.

[S] Step-by-Step Solution

Same period: Group 14 is to the right of Group 13 ⇒ higher nuclear charge + similar shielding ⇒ higher IE.

Example: C (1086 kJ/mol) > B (800 kJ/mol); Si (786) > Al (577); Ge (762) > Ga (579).

Also: Group 14 has ns^2np^2 configuration — the half-filled p subshell is more stable, contributing to slightly higher IE.

[Ans] Final Answer

Option (2): First IE of Group 14 is higher than corresponding Group 13 members due to higher nuclear charge

[!] Common Mistake

Option (1) says Group 14 IE is LOWER. Wrong! Moving right across a period increases IE (more protons, same core electrons). Group 14 is to the right of Group 13, so Group 14 always has higher IE within the same period.

Q.11 IE decreases from Si→Ge→Sn, but shows a slight INCREASE from Sn to Pb. Correct explanation?

[A] Conceptual Approach

Between Sn (Period 5) and Pb (Period 6), the entire lanthanide series ($4f^{14}$) is added. f-electrons shield very poorly ⇒ Z_{eff} on Pb's outer electrons is significantly higher than expected ⇒ IE increases slightly despite larger atomic size.

[S] Step-by-Step Solution

Between Sn and Pb: 14 f-electrons (lanthanide series, $4f^{14}$) are added to the inner core.

f-electrons provide extremely poor shielding (even worse than d-electrons).

⇒ Z_{eff} on Pb's outer 6p electrons is **higher than expected**.
⇒ Outer electrons are harder to remove ⇒ IE increases from Sn to Pb despite larger size.

(This is the same principle as lanthanide contraction and the Group 13 IE discontinuity.)

[Ans] Final Answer

Option (2): Poor shielding by intervening d and f orbitals in Pb raises Z_{eff} ⇒ slight increase in IE from Sn to Pb

[!] Common Mistake

Option (1) says Pb has smaller size than Sn. Wrong! Pb (154 pm) is LARGER than Sn (140 pm). The correct reason is not size — it is poor shielding by f-electrons that increases Z_{eff} on the outer electrons of Pb.

(d) Electronegativity

Q.12 How does electronegativity of Group 14 compare with Group 13?

[A] Conceptual Approach

Going right across a period: EN increases. Group 14 is to the right of Group 13. Also, Group 14 has a smaller atomic size compared to Group 13 of the same period (more nuclear charge, same period). Smaller size = higher EN.

[S] Step-by-Step Solution

Group 14 vs Group 13 (same period):
- Higher nuclear charge in Group 14 ⇒ more attraction for electrons.
- Smaller atomic size in Group 14 ⇒ bonding electrons held closer.

⇒ Group 14 elements are **slightly more electronegative** than Group 13 elements of the same period.

Example: C (2.5) > B (2.0); Si (1.8) > Al (1.5).

[Ans] Final Answer

Option (2): Group 14 elements are slightly more electronegative than Group 13 due to smaller atomic size

[!] Common Mistake

Option (1) says Group 14 is LESS electronegative. Wrong! More protons (higher Z) and smaller size in Group 14 both increase EN. Group 14 is always to the RIGHT, always more electronegative than Group 13 in the same period.

Q.13 EN values: C=2.5, Si=1.8, Ge=1.8, Sn=1.8, Pb=1.9. Correct conclusion?

[A] Conceptual Approach

The data shows: big drop from C to Si, then essentially flat from Si to Pb (all 1.8), with a tiny increase at Pb (1.9). Carbon is uniquely high in EN among Group 14.

[S] Step-by-Step Solution

From the data:
- **C (2.5) is significantly higher** than the rest.
- **Si = Ge = Sn = 1.8** — virtually identical.
- Pb = 1.9 — very slight increase.

Conclusion: Carbon has a significantly higher EN; from Si to Pb values are almost constant, with a very slight increase at Pb.

This irregularity is due to d and f orbital effects (poor shielding) making Pb slightly more electronegative than simple trends would predict.

[Ans] Final Answer

Option (2): C has significantly higher EN than the rest; Si to Pb values almost the same, slight increase at Pb

[!] Common Mistake

Option (1) says EN decreases uniformly C to Pb. The data shows it is NOT uniform — the drop from C (2.5) to Si (1.8) is huge, but then Si, Ge, Sn are all equal at 1.8. It's definitely not a uniform/smooth decrease.

TOPIC 3 — Physical Properties

(a) Physical State at Room Temperature

Q.14 Correct description of physical state and nature of all Group 14 elements at RT?

[A] Conceptual Approach

All Group 14 elements are SOLIDS at room temperature. C = non-metal; Si = non-metal; Ge = metalloid; Sn and Pb = soft metals with LOW melting points (Sn mp=505 K, Pb mp=600 K).

[S] Step-by-Step Solution

All Group 14 elements are **solids** at 298 K.

Nature:
C — Non-metal (graphite, diamond, fullerenes)
Si — Non-metal (semiconductor)
Ge — Metalloid (semiconductor)
Sn — Metal (soft, mp = 505 K)
Pb — Metal (soft, mp = 600 K)

Sn and Pb are soft metals with comparatively low melting points.

[Ans] Final Answer

Option (2): All solids; C and Si = non-metals; Ge = metalloid; Sn and Pb = soft metals with low melting points

[!] Common Mistake

Option (4) says all are metals with high melting points. Carbon and silicon are non-metals and Ge is a metalloid. Also, Sn (505 K) and Pb (600 K) have relatively LOW melting points compared to C (4373 K) or Si (1693 K).

(b) Boiling Point Order

Q.15 Data: Si=3550 K, Ge=3123 K, Sn=2896 K, Pb=2024 K. Carbon's bp not listed. Correct conclusion?

[A] Conceptual Approach

From data: boiling points clearly decrease Si $>$ Ge $>$ Sn $>$ Pb. Carbon has the highest MELTING point (4373 K) in the group; by analogy, it should also have the highest boiling point (around 4827 K). So overall order: C $>$ Si $>$ Ge $>$ Sn $>$ Pb.

[S] Step-by-Step Solution

From the given data: Si (3550) $>$ Ge (3123) $>$ Sn (2896) $>$ Pb (2024) K.

Boiling point **decreases** from Si to Pb.

Carbon has the highest melting point (4373 K) in Group 14 $\Rightarrow$ it is expected to have the highest boiling point as well (carbon boils around 4827 K as sublimation point).

Overall bp order: **C** $>$ **Si** $>$ **Ge** $>$ **Sn** $>$ **Pb** (decreasing down the group).

[Ans] Final Answer

Option (2): BP decreases from Si to Pb; carbon (highest MP = 4373 K) expected to have the highest BP

[!] Common Mistake

Option (1) says BP increases smoothly from Si to Pb. The data clearly shows DECREASING values (3550 $>$ 3123 $>$ 2896 $>$ 2024). Never say boiling point increases when the numbers decrease!

(c) Melting Point Order

Q.16 Melting/boiling points of Group 14 are much higher than Group 13. Which data best supports stronger interatomic bonds in Group 14?

[A] Conceptual Approach

Comparing Group 14 vs Group 13 in the same period: the melting point of the Group 14 element should be higher, supporting stronger bonding. C (4373 K) vs B (2450 K) is the clearest comparison.

[S] Step-by-Step Solution

Carbon (Group 14) mp = 4373 K vs **Boron (Group 13) mp = 2450 K**.

Carbon's melting point is nearly *double* that of boron — both in Period 2.

This strongly supports the argument that Group 14 elements form **stronger interatomic bonds** than Group 13 elements of the same period, explaining their higher melting/boiling points.

[Ans] Final Answer

Option (1): Carbon mp (4373 K) vs boron mp (2450 K) — higher value for C supports stronger bonding in Group 14

[!] Common Mistake

Option (2) mentions Pb mp (600 K) $<$ Al mp (933 K). This contradicts the general trend and should NOT be used to support the claim. Choose the comparison that BEST supports the argument — which is C vs B at the top of each group.

Q.17 Statements about physical properties: I. All Group 14 = solids at RT. II. C and Si = non-metals; Ge = metalloid; Sn and Pb = soft metals with low mp. III. MP and BP of Group 14 $\gg$ Group 13. IV. Sn has higher mp than Pb. All correct?

[A] Conceptual Approach

Check each: I = TRUE. II = TRUE. III = TRUE (C=4373 K vs B=2450 K etc.). IV = TRUE (Sn=505 K vs Pb=600 K — wait: Sn=505 $<$ Pb=600, so Sn has LOWER mp than Pb!). Statement IV is FALSE.

[S] Step-by-Step Solution

Statement I: TRUE — all five are solids at 298 K.

Statement II: TRUE — correct classification (NCERT).

Statement III: TRUE — Group 14 MP/BP are generally much higher than Group 13 (compare C vs B, Si

vs Al).

Statement IV: **TRUE** — Sn mp = 505 K, Pb mp = 600 K. Sn (505) < Pb (600), so Sn has **lower** mp than Pb... but the question says "Sn has HIGHER mp than Pb" which would be FALSE.
Wait: 505 < 600, so Sn melts at lower temperature than Pb. Statement IV ("Sn has higher mp than Pb") is FALSE.

Correct statements: I, II, and III only.

[Ans] Final Answer

Option (3): I, II, III and IV only — Actually: IV is FALSE (Sn mp=505 K < Pb mp=600 K). Correct answer is option (2): I, II and III only

[!] Common Mistake

Accepting Statement IV as true. Sn has mp = 505 K which is LOWER than Pb's 600 K. So the statement "Sn has higher mp than Pb" is FALSE. The correct option should be (2): I, II and III only. If the key says (3), verify with the data table.

(d) Density

Q.18 From the data table, which element has the lowest MP and which has the highest density?

[A] Conceptual Approach

Scan the table: MP values: C=4373, Si=1693, Ge=1218, Sn=505, Pb=600. Lowest MP = Sn (505 K). Density: C=3.51, Si=2.34, Ge=5.32, Sn=7.26, Pb=11.34. Highest density = Pb (11.34 g/cm^3).

[S] Step-by-Step Solution

Lowest melting point: Sn = 505 K (lowest in the table; even lower than Pb's 600 K).

Highest density: Pb = 11.34 g/cm^3 (heaviest, densest Group 14 element).

Note: Pb's density (11.34) is much higher than Sn (7.26), Ge (5.32), Si (2.34), C (3.51).

[Ans] Final Answer

Option (2): Lowest MP = Sn (505 K); Highest density = Pb (11.34 g/cm^3)

[!] Common Mistake

Confusing Sn and Pb for lowest MP. Pb (600 K) melts higher than Sn (505 K). Sn has the lowest melting point in Group 14. This is a direct data-reading question — always double-check the numbers before answering.

TOPIC 4 — Chemical Properties

(a) Oxidation States

Q.19 Stability of +2 state increases Ge<Sn<Pb. Student claims Pb(IV) compounds are strong

oxidising agents. Correct support?

[A] Conceptual Approach

Inert pair effect in Pb: $6s^2$ electrons are reluctant to participate (poor shielding by $5d^{10}$ and $4f^{14}$). Pb^{4+} is unstable — it readily accepts electrons back to become Pb^{2+}. Accepting electrons = oxidising agent.

[S] Step-by-Step Solution

Inert pair effect in lead: The $6s^2$ electrons of Pb are held tightly (poor shielding by inner d and f electrons).

Pb^{4+} is **thermodynamically unstable** — it has a strong tendency to revert to Pb^{2+} by accepting 2 electrons.

Accepting electrons = **oxidising agent**!

Example: PbO_2 is a strong oxidant — it oxidises Mn^{2+} to MnO_4^-, HCl to Cl_2, etc.

[Ans] Final Answer

Option (2): Inert pair effect makes Pb^{4+} unstable; readily accepts electrons to revert to Pb^{2+} $\Rightarrow$ Pb(IV) compounds are strong oxidising agents

[!] Common Mistake

Option (1) says Pb prefers +4 and it is stable/non-oxidising. Exact opposite! Due to inert pair effect, Pb prefers +2. The +4 state is unstable and wants to GAIN electrons (be reduced) — that's why it is an oxidising agent.

Q.20 Which statement about +4 and +2 oxidation states of Group 14 is correct?

[A] Conceptual Approach

+4 compounds are covalent (not ionic) because the sum of first 4 IEs is very high — no lattice energy can compensate. In heavier members: inert pair effect makes +2 more stable. For C and Si: +4 is the dominant state.

[S] Step-by-Step Solution

+4 compounds are covalent: Sum of $IE_1 + IE_2 + IE_3 + IE_4$ is enormous for Group 14 elements. No ionic compound could be stable. So EX_4 compounds are all covalent (e.g., CCl_4, $SiCl_4$).

+2 stability increases down the group: Inert pair effect stabilises E^{2+} in heavier elements (Sn, Pb). Ge, Sn, Pb all form stable +2 compounds; Pb predominantly +2.

[Ans] Final Answer

Option (2): +4 compounds are generally covalent (very high total IE); in heavier members +2 state more stable due to inert pair effect

[!] Common Mistake

Option (1) says +4 compounds are ionic because IE is LOW. Completely wrong! The total IE for removing 4 electrons is astronomically HIGH (6000–8000 kJ/mol) — that's precisely why +4 compounds must be COVALENT (can't form E^{4+} ions).

Q.21 CCl_4 has 8 electrons around C (electron precise). Why can't C form $[CF_6]^{2-}$ like Si forms $[SiF_6]^{2-}$?

[A] Conceptual Approach

$[EF_6]^{2-}$ requires coordination number 6 (6 F atoms around E). This needs the central atom to accommodate 12 electrons = expand octet using d-orbitals. Carbon (Period 2) has NO d-orbitals. Maximum covalence of C = 4.

[S] Step-by-Step Solution

CCl_4: C has 4 bonds = 8 electrons = complete octet. Carbon **cannot** go beyond 8 electrons because it has NO vacant d-orbitals.

$[SiF_6]^{2-}$, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$: Si, Ge, Sn have accessible 3d/4d/5d orbitals.
These allow expansion of covalence beyond 4 (up to 6, giving octahedral complexes).

$\therefore$ Carbon cannot form $[CF_6]^{2-}$ — no d-orbitals, max covalence = 4.

[Ans] Final Answer

Option (2): Carbon lacks d-orbitals; max covalence = 4; cannot expand coordination sphere to 6 like Si, Ge, Sn

[!] Common Mistake

Option (1) says carbon has too many electrons and can't accept more. Wrong! Carbon doesn't have "too many" electrons. It has a full octet in CCl_4, yes — but the reason it can't go beyond is absence of d-orbitals, not excess electrons.

Q.22 $[SiF_6]^{2-}$, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ have sp^3d^2 hybridisation. What is their geometry? Why is C excluded?

[A] Conceptual Approach

sp^3d^2 hybridisation = 6 orbitals = 6 bond pairs = octahedral geometry. C excluded because it lacks d-orbitals (no sp^3d^2 possible for C).

[S] Step-by-Step Solution

sp^3d^2 hybridisation: uses 1s + 3p + 2d = 6 orbitals.
Geometry: **Octahedral** (all 6 ligands at equal angles, 90°).

Carbon excluded: Period 2 element — no d-orbitals available for sp^3d^2 hybridisation.
Max covalence of C = 4 (only s and p orbitals: sp^3 max).

Si, Ge, Sn (Period 3, 4, 5): have 3d, 4d, 5d orbitals $\Rightarrow$ can form sp^3d^2 $\Rightarrow$ octahedral complexes.

[Ans] Final Answer

Option (2): Complexes are octahedral (sp^3d^2); C excluded because it lacks d-orbitals and cannot expand covalence beyond 4

[!] Common Mistake

Option (1) says complexes are tetrahedral (sp^3). Tetrahedral = 4-coordinate, sp^3. But the question states these complexes have sp^3d^2 hybridisation, which is 6-coordinate = OCTAHEDRAL, not tetrahedral.

Q.23 Statements: I. Carbon also shows negative oxidation states. II. Sn in +2 is a reducing agent. III. Pb(+2) stable; Pb(+4) is strong oxidising agent. IV. Ge forms stable +4; few +2 compounds. All

correct?

[A] Conceptual Approach

I: TRUE (C in CH_4 is -4; in CO is -2). II: TRUE (Sn^{2+} is a reducing agent, converts to Sn^{4+}). III: TRUE (inert pair effect). IV: TRUE (Ge is early in group; inert pair effect mild). All four are correct.

[S] Step-by-Step Solution

Statement I: TRUE — Carbon shows -4 (CH_4), -2 (in alcohols), 0 (diamond), $+2$ (CO), $+4$ (CO_2). Negative states exist.

Statement II: TRUE — Sn^{2+} is a reducing agent (it gets oxidised to Sn^{4+}). $SnCl_2$ is a common reducing agent in analytical chemistry.

Statement III: TRUE — Inert pair effect: Pb^{2+} is stable; Pb^{4+} (e.g., PbO_2) is a strong oxidant.

Statement IV: TRUE — Ge shows predominantly +4; +2 compounds of Ge are few and less stable.

All four statements are correct.

[Ans] Final Answer

Option (4): All four statements are correct

[!] Common Mistake

Rejecting Statement I thinking C only shows +2 and +4. Carbon's oxidation states span from -4 to $+4$: -4 (CH_4), -3 (ethane per carbon), 0 (graphite), $+2$ (CO), $+4$ (CO_2). Negative states are very real for carbon.

(b) Reactivity Towards Oxygen (Air)

Q.24 CO_2, SiO_2, GeO_2 are acidic; SnO_2, PbO_2 are amphoteric. CO is neutral; GeO is acidic; SnO, PbO are amphoteric. Which observation best supports: "acidic character of oxides decreases down Group 14"?

[A] Conceptual Approach

To show acidic character DECREASING: need to compare a clearly acidic oxide (top of group) with a less acidic/amphoteric oxide (bottom). CO_2 (acidic) vs SnO_2/PbO_2 (amphoteric) shows this clearly.

[S] Step-by-Step Solution

Evidence for decreasing acidic character in dioxides:
CO_2 (acidic) $\rightarrow$ SiO_2 (acidic) $\rightarrow$ GeO_2 (acidic) $\rightarrow$ SnO_2 (amphoteric) $\rightarrow$ PbO_2 (amphoteric).

Best support: CO_2 is acidic while SnO_2 and PbO_2 are amphoteric.
As we go down Group 14, oxides become less acidic and more amphoteric (more basic character develops with increasing metallic nature).

[Ans] Final Answer

Option (1): CO_2 is acidic while SnO_2 and PbO_2 are amphoteric — shows oxides become less acidic going down

[!] Common Mistake

Option (2) says CO neutral and SnO amphoteric shows INCREASING acidic character. Wrong! If CO (neutral) → SnO (amphoteric), that shows SnO has both acidic AND basic character — which means it has MORE acidic character than CO (neutral). This would support INCREASING, not decreasing. The question asks for DECREASING, so use option (1).

Q.25 Higher oxidation state oxides are more acidic than lower. Apply this to germanium oxides.

[A] Conceptual Approach

Ge higher OS oxide = GeO_2 (+4). Ge lower OS oxide = GeO (+2). Rule: higher OS = more acidic. So GeO_2 is more acidic than GeO. NCERT says GeO is "distinctly acidic" but GeO_2 is also acidic.

[S] Step-by-Step Solution

NCERT data on germanium oxides:
GeO_2: acidic (higher OS = +4, more acidic).
GeO: distinctly acidic but LESS acidic than GeO_2 (lower OS = +2).

Principle: Higher oxidation state ⇒ more acidic oxide.
GeO_2 (+4) > GeO (+2) in acidic character.

[Ans] Final Answer

Option (2): GeO_2 is acidic; GeO is distinctly acidic but less so than GeO_2

[!] Common Mistake

Option (1) says GeO_2 is neutral and GeO is acidic. Wrong! GeO_2 is acidic (reacts with bases to form germanates). The higher OS oxide (GeO_2) is always MORE acidic than the lower OS oxide (GeO).

Q.26 Which oxides react with both NaOH and HCl, confirming amphoteric nature?

[A] Conceptual Approach

Amphoteric = reacts with BOTH acid AND base. From NCERT: SnO_2, PbO_2 (dioxides) and SnO, PbO (monoxides) are amphoteric. CO_2 and SiO_2 are only acidic (react with bases only).

[S] Step-by-Step Solution

Amphoteric oxides react with both dilute HCl and dilute NaOH:

SnO_2: acidic with NaOH (→ stannate), basic with HCl (→ $SnCl_4$).
PbO_2: acidic with NaOH (→ plumbate), basic with HCl (→ $PbCl_4$).

(CO_2 and SiO_2 are purely acidic; CO is neutral; GeO is purely acidic.)

[Ans] Final Answer

Option (2): SnO_2 and PbO_2

[!] Common Mistake

Option (1) CO_2 and SiO_2 — these are purely ACIDIC (react with base only, not acid). They are NOT amphoteric. Only SnO_2, PbO_2, SnO, and PbO are amphoteric in Group 14.

Q.27 From the oxide classification chart, which conclusion is INCORRECT?

[A] Conceptual Approach

Check each option against the chart. Option (3) says "all monoxides and dioxides are acidic" — clearly wrong since CO is neutral and SnO, PbO, SnO_2, PbO_2 are amphoteric.

[S] Step-by-Step Solution

From the chart:

(1) Acidic character of dioxides decreases (CO_2/SiO_2/GeO_2=acidic → SnO_2/PbO_2=amphoteric) → TRUE.

(2) CO=neutral, GeO=acidic, SnO/PbO=amphoteric → TRUE (matches chart).

(3) "All monoxides and dioxides are acidic" → **FALSE/INCORRECT** — CO is neutral; SnO, PbO, SnO_2, PbO_2 are amphoteric, not acidic.

(4) Higher OS oxides more acidic than lower OS (GeO_2 more acidic than GeO, etc.) → TRUE.

[Ans] Final Answer

Option (3): Incorrect conclusion — NOT all oxides are acidic; CO is neutral, SnO/PbO/SnO_2/PbO_2 are amphoteric

[!] Common Mistake

Choosing option (1) as incorrect. Decreasing acidic character from CO_2 to PbO_2 is CORRECT (shown in chart). The incorrect statement is (3) which overgeneralises and claims all oxides are acidic — ignoring neutral CO and amphoteric Sn/Pb oxides.

Q.28 Statements: I. All Group 14 form MO and MO_2 when heated in O_2. II. SiO exists only at high T. III. CO_2/SiO_2/GeO_2 acidic; SnO_2/PbO_2 amphoteric. IV. CO=amphoteric, GeO=neutral, SnO/PbO=acidic. Which are correct?

[A] Conceptual Approach

I=TRUE. II=TRUE (SiO is unstable at RT). III=TRUE (NCERT). IV=FALSE (CO=neutral, GeO=acidic, SnO/PbO=amphoteric — exactly reversed in the question).

[S] Step-by-Step Solution

Statement I: TRUE — Group 14 elements form both MO (monoxide) and MO_2 (dioxide).

Statement II: TRUE — SiO is not stable at RT; exists only at very high temperatures.

Statement III: TRUE (NCERT data).

Statement IV: **FALSE** — The correct facts are: CO is **neutral**; GeO is **acidic**; SnO and PbO are **amphoteric**. Statement IV reverses all three: it says CO=amphoteric, GeO=neutral, SnO/PbO=acidic. All three assignments are wrong.

Correct statements: I, II, and III.

[Ans] Final Answer

Option (2): I, II and III only

[!] Common Mistake

Accepting Statement IV. This is a classic trap: all three nature labels are swapped. Remember: CO = neutral (it's a weird neutral gas), GeO = acidic (Ge is still relatively non-metallic), SnO/PbO = amphoteric (Sn and Pb are metals with some non-metallic character).

(c) Reactivity Towards Water

Q.29 Correct summary of Group 14 reactivity towards water?

[A] Conceptual Approach

NCERT: C, Si, Ge = unaffected by water (they are non-metals/metalloid, kinetically inert). Sn = reacts with steam to form SnO_2 + H_2. Pb = unaffected (protective oxide film).

[S] Step-by-Step Solution

C, Si, Ge: Unaffected by water (even hot water or steam) under normal conditions.

Sn: Reacts with **steam** (not cold water):

$$Sn + 2H_2O(\text{steam}) \rightarrow SnO_2 + 2H_2 \uparrow$$

Pb: Unaffected by water — a **protective PbO film** forms on the surface, preventing further reaction (similar to Al passivation).

[Ans] Final Answer

Option (2): C, Si, Ge unaffected; Sn decomposes steam to SnO_2 + H_2; Pb unaffected due to protective oxide film

[!] Common Mistake

Option (1) says all Group 14 react vigorously with water. Very wrong! C, Si, Ge are quite inert towards water. Only Sn reacts (with steam), and Pb is passive. Option (3) says carbon reacts with cold water — carbon does NOT react with cold or hot water.

Q.30 Lead is unaffected by water despite being reactive. Correct explanation?

[A] Conceptual Approach

Same as Al passivation — Pb reacts with water initially forming a thin PbO (or $Pb(OH)_2$ or $PbCO_3$) layer that adheres firmly to the surface, blocking further reaction.

[S] Step-by-Step Solution

When Pb is exposed to water: a thin, dense **protective oxide/hydroxide film** forms on the surface (PbO or $Pb(OH)_2$).

This film:

- Adheres tightly to the Pb surface
- Is impermeable to water
- Prevents further reaction

This is why Pb was historically used for water pipes (though harmful due to Pb^{2+} leaching over time).

[Ans] Final Answer

Option (2): A protective oxide film forms on lead's surface, preventing further reaction with water

[!] Common Mistake

Option (3) says Pb is a noble metal. Lead is definitely NOT a noble metal. Noble metals = Pt, Au, Ag, Pd. Pb is a reactive metal that is passivated by its oxide layer — similar to Al, not because it is noble.

(d) Reactivity Towards Halogens

Q.31 Except CCl_4, other Group 14 tetrachlorides are easily hydrolysed. $SiCl_4$ accepts lone pair from water into Si's d orbital. Why does CCl_4 resist hydrolysis?

[A] Conceptual Approach

Hydrolysis mechanism: water's O donates lone pair to the central atom's empty orbital (in the first step). Carbon has NO vacant d-orbital. The lone pair from water has nowhere to go on C. First step cannot happen $\Rightarrow$ CCl_4 resists hydrolysis.

[S] Step-by-Step Solution

$SiCl_4$ hydrolysis mechanism:
Step 1: O of H_2O donates lone pair into **vacant 3d orbital of Si** $\Rightarrow$ forms Si–O coordinate bond.
Step 2: Cl leaves as HCl. Continue until $Si(OH)_4$ formed.

Why CCl_4 resists:
Carbon **has no vacant d-orbital**. The oxygen of water has no orbital on C to donate into.
The first step of hydrolysis mechanism **cannot occur**.

$\therefore$ CCl_4 is kinetically inert towards hydrolysis despite thermodynamics being favourable.

[Ans] Final Answer

Option (2): Carbon has no vacant d-orbitals to accept lone pair from water; first step of hydrolysis cannot occur

[!] Common Mistake

Option (1) says C–Cl bond is stronger (C more electronegative). While C–Cl bond is polar, this is NOT the reason CCl_4 resists hydrolysis. $SiCl_4$ also has Si–Cl bonds but hydrolyses easily. The key difference is the d-orbital availability for the first mechanistic step.

Q.32 PbI_4 does not exist. $PbCl_4$ and $PbBr_4$ exist but are unstable. Correct explanation for PbI_4's non-existence?

[A] Conceptual Approach

For PbX_4 to form: Pb must provide 4 unpaired electrons (from $6s^26p^2$ $\rightarrow$ excite one 6s electron to higher orbital). The energy to do this must be recovered by forming 4 Pb–X bonds. The Pb–I bond is weak (iodine is large, bond energy low). The bond formation energy is insufficient to compensate the energy needed to promote the 6s electrons.

[S] Step-by-Step Solution

For PbX_4 formation, the $6s^2$ electrons of Pb must be uncoupled and promoted.

Energy required to unpair $6s^2$ electrons + promote one to a higher orbital must be compensated by energy released in forming 4 Pb–X bonds.

Pb–I bond: I is a large atom; Pb–I bond energy is very low (weak bond).
The energy released by forming 4 Pb–I bonds is **insufficient** to compensate the promotion energy.

$\therefore$ PbI_4 cannot form — thermodynamically unfavourable.

Pb–Cl bond is stronger (Cl is smaller), so $PbCl_4$ can form (barely), but Pb–I is too weak.

[Ans] Final Answer

Option (2): Pb–I bond energy is insufficient to unpair $6s^2$ electrons and promote one to higher orbital for 4-bond formation

[!] Common Mistake

Option (3) says iodine is too LARGE for steric reasons. While I is large, the real reason is energetic — the Pb–I bond is too weak to provide the energy needed to promote 6s electrons. $PbCl_4$ exists (though unstable), so steric reasons alone don't explain PbI_4's non-existence.

Q.33 Group 14 MX_4 halides: geometry? Which are ionic exceptions?

[A] Conceptual Approach

MX_4 with sp^3 hybridisation = tetrahedral. Most are covalent, but SnF_4 and PbF_4 are exceptions (ionic) because F^- is small and has high lattice energy that can compensate the high IE for +4.

[S] Step-by-Step Solution

Geometry of MX_4: sp^3 hybridisation $\Rightarrow$ **Tetrahedral geometry**.

Most MX_4 are covalent (e.g., CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$).

Ionic exceptions: **SnF_4 and PbF_4**.
Fluorine is small with very high lattice energy $\Rightarrow$ can compensate the large sum of 4 IEs $\Rightarrow$ forms ionic lattice.

[Ans] Final Answer

Option (1): Tetrahedral geometry; SnF_4 and PbF_4 are ionic exceptions

[!] Common Mistake

Option (4) says ALL MX_4 are covalent without exception. Wrong! SnF_4 and PbF_4 are ionic. The small size and high electronegativity of F^- makes the lattice energy large enough to make ionic structures energetically viable for Sn and Pb.

Q.34 Correct comparison: GeX_4 vs GeX_2, and PbX_2 vs PbX_4?

[A] Conceptual Approach

Inert pair effect increases down the group. Ge: inert pair effect mild $\Rightarrow$ GeX_4 more stable than GeX_2. Pb: strong inert pair effect $\Rightarrow$ PbX_2 more stable than PbX_4.

[S] Step-by-Step Solution

Germanium: Inert pair effect relatively mild.
$\Rightarrow$ GeX_4 is more thermally and chemically stable than GeX_2.

Lead: Inert pair effect is strong.
$\Rightarrow$ PbX_2 is more stable than PbX_4 (which is a strong oxidant, thermally unstable).

Summary: $GeX_4 > GeX_2$ (stability); $PbX_2 > PbX_4$ (stability).

[Ans] Final Answer

Option (1): GeX_4 more stable than GeX_2; PbX_2 more stable than PbX_4

[!] Common Mistake

Option (3) says both EX_4 are always more stable. Wrong for Pb! Lead's inert pair effect reverses the stability: $PbX_2 > PbX_4$. This is the key trend: +4 stable at top (C, Si, Ge) but +2 stable at bottom (Sn, Pb).

Q.35 Final product of complete hydrolysis of $SiCl_4$?

[A] Conceptual Approach

$SiCl_4$ + H_2O step by step: each Cl is replaced by OH. After complete hydrolysis (4 steps), all four Cl atoms are replaced by OH groups $\Rightarrow$ $Si(OH)_4$ (silicic acid). HCl is released (4 HCl per $SiCl_4$).

[S] Step-by-Step Solution

Complete hydrolysis:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$

Products: **$Si(OH)_4$** (silicic acid) + **HCl** (hydrochloric acid).

$Si(OH)_4$ = silicic acid (weak acid; can further condense to form silicates).

[Ans] Final Answer

Option (2): $Si(OH)_4$ (silicic acid) and HCl

[!] Common Mistake

Option (1) says products are SiO_2 and HCl. SiO_2 is NOT the direct hydrolysis product — it would require dehydration of $Si(OH)_4$ at high temperature. The direct product in aqueous conditions is $Si(OH)_4$ (silicic acid), not SiO_2.

Q.36 Student wants to prepare SnF_4 and PbF_4. Are they ionic or covalent?

[A] Conceptual Approach

SnF_4 and PbF_4 are the IONIC exceptions among MX_4 halides. Unlike most MX_4 (covalent, tetrahedral), SnF_4 and PbF_4 have high enough lattice energy from F^- to form ionic structures.

[S] Step-by-Step Solution

SnF_4 and **PbF_4** are **ionic** in nature.

Reason: F^- is the smallest, most electronegative halide. It has very high lattice energy when combined with Sn^{4+} and Pb^{4+}, making ionic structures energetically favourable.

All other MX_4 (where X = Cl, Br, I) are covalent. SnF_4 and PbF_4 are the two ionic exceptions.

[Ans] Final Answer

Option (2): SnF_4 and PbF_4 are ionic exceptions among MX_4 halides

[!] Common Mistake

Option (1) says both are covalent tetrahedral like most MX_4. Wrong! SnF_4 and PbF_4 are specifically IONIC exceptions. This is a standard NCERT fact tested in NEET. Remember: only the fluorides of Sn and Pb are ionic among Group 14 tetrahalides.

Q.37 In Step 1 of $SiCl_4$ hydrolysis, what type of bond forms between Si and oxygen of water?

[A] Conceptual Approach

Hydrolysis mechanism: O of H_2O donates a lone pair into the vacant d-orbital of Si. A lone pair donation from one atom to another's empty orbital = coordinate (dative) bond.

[S] Step-by-Step Solution

Step 1:

$$SiCl_4 + H_2O \rightarrow SiCl_4 \cdot OH_2 \text{ (intermediate)}$$

The oxygen of water donates its lone pair into the **vacant 3d orbital of silicon**.

This is a **coordinate (dative) bond**: both electrons come from oxygen and are donated to the empty Si d-orbital.

It is a Lewis acid–base interaction: Si acts as Lewis acid (accepts lone pair); O acts as Lewis base (donates lone pair).

[Ans] Final Answer

Option (2): Coordinate (dative) bond — O donates lone pair into vacant d-orbital of Si

[!] Common Mistake

Option (1) says ionic bond by complete electron transfer. Wrong! No complete electron transfer occurs here. It is a coordinate bond (partial donation of lone pair from O to Si's d-orbital), which is the first step of a hydrolysis mechanism, not ionisation.

Q.38 Dihalide stability: Ge<Sn<Pb (increasing). Tetrahalide stability: GeX_4 >SnX_4 >PbX_4 (decreasing). Correct conclusion from both trends?

[A] Conceptual Approach

Both trends together = classic inert pair effect picture: as you go down Group 14, +2 becomes more stable (dihalides increase) and +4 becomes less stable (tetrahalides decrease). This is the textbook statement of the inert pair effect.

[S] Step-by-Step Solution

The two trends together tell one story: **inert pair effect increases down the group**.

Going down Group 14:

• **Dihalide (MX_2) stability**: Ge < Sn < Pb — +2 state becomes more stable.
• **Tetrahalide (MX_4) stability**: Ge > Sn > Pb — +4 state becomes less stable.

The ns^2 (inert pair) electrons become progressively more reluctant to participate in bonding as we go down. ⇒ +2 state stabilises; +4 state destabilises.

[Ans] Final Answer

Option (2): +2 state becomes progressively more stable while +4 becomes less stable, consistent with increasing inert pair effect down Group 14

[!] Common Mistake

Option (1) says tetrahalide is always more stable. Wrong for Pb! $PbCl_2$ is more stable than $PbCl_4$. Option (3) says both increase uniformly. Wrong! They go in opposite directions. The key insight: inert pair effect creates opposing trends for the two oxidation states.

Q.39 Statements: I. C does not react with halogens; all others do. II. Most MX_4 covalent tetrahedral; SnF_4/PbF_4 ionic. III. PbI_4 non-existent because Pb–I bond energy insufficient. IV. Except CCl_4, all Group 14 tetrachlorides hydrolysed by water. All correct?

[A] Conceptual Approach

I=TRUE. II=TRUE. III=TRUE. IV=TRUE. All four statements are NCERT facts.

[S] Step-by-Step Solution

Statement I: TRUE — Carbon does not react directly with halogens under normal conditions; Si, Ge, Sn, Pb do.

Statement II: TRUE — Most MX_4 are covalent tetrahedral; SnF_4 and PbF_4 are ionic exceptions.

Statement III: TRUE — Pb–I bond energy is too low to compensate the energy needed to promote $6s^2$ electrons; PbI_4 doesn't form.

Statement IV: TRUE — CCl_4 resists hydrolysis (no d-orbitals in C); $SiCl_4$, $GeCl_4$, $SnCl_4$ are all easily hydrolysed (d-orbitals available).

All four statements are correct.

[Ans] Final Answer

Option (4): All four statements are correct

[!] Common Mistake

Doubting Statement I (thinking C does react with halogens). Carbon does NOT react directly with halogens under normal lab conditions. Unlike Si (reacts with F_2 and Cl_2 on heating), carbon requires extreme conditions or doesn't react at all directly.

Q.40 Statements: I. Heavier Ge–Pb can form MX_2 dihalides. II. Stability of dihalides decreases Ge→Pb. III. GeX_4 more stable than GeX_2. IV. $SiCl_4$ hydrolyses via lone pair donation into Si's d-orbital → silicic acid. Which are correct?

[A] Conceptual Approach

I=TRUE (Ge, Sn, Pb all form MX_2). II=FALSE (stability of dihalides INCREASES Ge<Sn<Pb). III=TRUE (inert pair effect mild for Ge). IV=TRUE (mechanism of $SiCl_4$ hydrolysis).

[S] Step-by-Step Solution

Statement I: TRUE — Ge, Sn, Pb all form dihalides (MX_2).

Statement II: **FALSE** — Dihalide stability **increases** Ge < Sn < Pb (inert pair effect increases, stabilising +2). The statement says "decreases" which is wrong.

Statement III: TRUE — Ge is near the top of the inert pair trend; GeX_4 is thermally more stable than GeX_2.

Statement IV: TRUE — $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$ via d-orbital lone pair acceptance mechanism.

Correct statements: I, III, and IV.

[Ans] Final Answer

Option (2): I, III and IV only

[!] Common Mistake

Accepting Statement II. Classic trap! Dihalide stability INCREASES going down (Ge < Sn < Pb). This is the inert pair effect making +2 more stable as you go down. "Decreasing stability" would be the trend for TETRAHALIDES ($GeX_4 > SnX_4 > PbX_4$), not dihalides.

TOPIC 5 — Anomalous Behaviour of Carbon

Q.41 Bond enthalpies: C–C=348, Si–Si=297, Ge–Ge=260, Sn–Sn=240 kJ/mol. Student concludes catenation decreases down Group 14. Best support?

[A] Conceptual Approach

Catenation strength $\propto$ M–M bond enthalpy. C–C is strongest $\Rightarrow$ highest catenation. As BE decreases down the group, catenation decreases. Order: C $\gg$ Si > Ge > Sn; Pb = essentially no catenation.

[S] Step-by-Step Solution

Bond enthalpies (kJ/mol): C–C (348) > Si–Si (297) > Ge–Ge (260) > Sn–Sn (240)

Higher bond enthalpy = stronger bond = more stable chains = higher catenation tendency.

- **C**: Highest BE (348) $\Rightarrow$ greatest catenation (millions of organic compounds).
- Si, Ge, Sn: Decreasing BE $\Rightarrow$ decreasing catenation.
- **Pb**: No catenation (Pb–Pb bonds too weak + inert pair effect).

Order: C $\gg$ Si > Ge $\approx$ Sn; Pb = no catenation.

[Ans] Final Answer

Option (1): C–C BE (348) is highest $\Rightarrow$ carbon chains most stable; decreasing BE down group explains decreasing catenation: C $\gg$ Si > Ge $\approx$ Sn

[!] Common Mistake

Option (2) says C–C is the WEAKEST bond. Completely wrong! C–C (348 kJ/mol) is the STRONGEST homoatomic bond in Group 14. It decreases going down: C > Si > Ge > Sn. Stronger bond = more catenation, not less.

Q.42 Heavier Group 14 (Si, Ge, Sn, Pb) cannot form pπ–pπ multiple bonds. Correct explanation?

[A] Conceptual Approach

pπ–pπ bonding requires effective sideways overlap of p-orbitals. Carbon's 2p orbitals are small and compact $\Rightarrow$ good overlap. Si, Ge, Sn have 3p, 4p, 5p orbitals that are large and diffuse $\Rightarrow$ poor sideways overlap $\Rightarrow$ cannot form effective π bonds.

[S] Step-by-Step Solution

pπ–pπ bond requires effective sideways overlap of two p-orbitals.

Carbon (2p orbitals): Small, compact $\Rightarrow$ good sideways overlap $\Rightarrow$ effective π bond.

Si, Ge, Sn (3p, 4p, 5p orbitals): Large and **diffuse** orbitals.
Sideways overlap is poor (large orbitals cannot come close enough for effective lateral overlap).

$\Rightarrow$ pπ–pπ multiple bond formation is ineffective in heavier elements.

$\therefore$ C can form C=C, C$\equiv$C, C=O, C=S, C$\equiv$N; but Si, Ge, Sn cannot form analogous multiple bonds.

[Ans] Final Answer

Option (2): Heavier elements have large, diffuse orbitals $\Rightarrow$ poor sideways pπ–pπ overlap $\Rightarrow$ multiple bonds not formed

[!] Common Mistake

Option (4) says electronegativity is too high in heavier elements. Wrong! Actually heavier elements have LOWER electronegativity than carbon. The correct reason is orbital size — large, diffuse orbitals cannot overlap effectively sideways, preventing π bond formation.

Q.43 Carbon has max covalence of 4; other Group 14 can exceed 4. Why?

[A] Conceptual Approach

Expanding covalence beyond 4 requires d-orbitals. Carbon (Period 2): only 2s and 2p orbitals available. No d-orbitals in Period 2 valence shell. Maximum = 4 bonds (sp^3). Si+ (Period 3+): have d-orbitals $\Rightarrow$ can form 5 or 6 bonds.

[S] Step-by-Step Solution

Carbon: Valence shell = 2s, 2p only. No d-orbitals.
Maximum bonds = 4 (using all 4 valence orbitals: 1s + 3p = sp^3).
Cannot form 5th or 6th bond — no orbital available.

Silicon, Germanium, Tin, Lead: Have accessible d-orbitals (3d, 4d, 5d, 6d).
Can use these for bonding $\Rightarrow$ covalence can exceed 4.

Examples: SiF_6^{2-} (CN=6, sp^3d^2), $SnCl_5^-$ (CN=5, sp^3d).

[Ans] Final Answer

Option (2): Only s and p orbitals in C (no d-orbitals) ⇒ max 4 bonds; heavier members have d-orbitals ⇒ can exceed covalence 4

[!] Common Mistake

Option (1) says carbon has MORE electrons than Si, preventing >4 bonds. Carbon has FEWER electrons than Si (C=6e$^-$, Si=14e$^-$). Electron count is not the issue — it's the ABSENCE of d-orbitals in carbon that limits its covalence.

Q.44 Correct order of catenation in Group 14 and reason for Pb's position?

[A] Conceptual Approach

Catenation decreases down the group as M–M bond strength decreases and electronegativity decreases (more metallic character means less tendency for covalent chain formation). Pb = no catenation (Pb–Pb bonds too weak; inert pair effect favours Pb^{2+}, not Pb–Pb chains).

[S] Step-by-Step Solution

Order: C $\gg$ Si $>$ Ge $\approx$ Sn; **Pb = no catenation**.

Why Pb doesn't catenate:
- Pb–Pb bond enthalpy is very low (weaker than Sn–Sn).
- Increasing atomic size ⇒ decreasing electronegativity ⇒ less tendency to form covalent chains.
- Inert pair effect in Pb means Pb prefers to exist as Pb^{2+} rather than forming Pb–Pb bonds.

Carbon is unique: C–C bond (348 kJ/mol) is strong + small size + high EN = ideal for chain formation.

[Ans] Final Answer

Option (2): Order C $\gg$ Si $>$ Ge $\approx$ Sn; Pb does not catenate due to very weak Pb–Pb bonds, low EN, and inert pair effect

[!] Common Mistake

Option (4) says Si > C. Completely wrong! Carbon's C–C bond (348) is stronger than Si–Si (297), and carbon's catenation is by far the greatest in Group 14 — forming millions of chains, rings, and networks in organic chemistry.

Q.45 Which is a direct consequence of carbon's catenation and pπ–pπ bond formation?

[A] Conceptual Approach

Allotropes = different structural forms of the same element. Carbon's allotropes (diamond, graphite, fullerenes) arise directly from its ability to: (a) form C–C chains (catenation) and (b) form C=C or π bonds (pπ–pπ). Diamond = catenation only; graphite = both; fullerenes = both.

[S] Step-by-Step Solution

Catenation: Allows C to link with itself forming long chains and rings.
pπ–pπ bonding: Allows C=C double bonds in graphite layers and fullerenes.

Direct consequence: Formation of **allotropes** —
- Diamond: 3D covalent network (catenation, sp^3).

- Graphite: Layered structure with C=C bonds (catenation + pπ–pπ).
- Fullerenes: Spherical/tubular cages (catenation + pπ–pπ).

Without these two properties, carbon could not form multiple structurally distinct allotropes.

[Ans] Final Answer

Option (2): Formation of allotropes like diamond, graphite, and fullerenes

[!] Common Mistake

Option (3) says CCl_4's resistance to hydrolysis is a consequence. CCl_4's hydrolysis resistance is due to absence of d-orbitals (kinetic reason), NOT due to catenation or pπ–pπ bonding. These are different properties.

Q.46 Researcher wants pπ–pπ multiple bonding between Group 14 element and small, electronegative atom. Which combination is feasible?

[A] Conceptual Approach

pπ–pπ bonding requires BOTH atoms to be small (compact orbitals) and have similar orbital sizes. Carbon (C) is the only Group 14 element that forms effective pπ–pπ bonds. O is also small. C=O is the classic example. Sn, Ge, Pb have large diffuse orbitals — can't form pπ–pπ.

[S] Step-by-Step Solution

Requirements for effective pπ–pπ bonding:
- Both atoms must have small, compact p-orbitals.
- Orbitals must be similar in size for good sideways overlap.

C=O: Carbon (2p) and oxygen (2p) — both Period 2, both small and compact.
$\Rightarrow$ Excellent pπ–pπ overlap $\Rightarrow$ **feasible!**

Sn=O, Pb=S, Ge=N: All involve heavier Group 14 elements with large, diffuse 4p/5p/6p orbitals $\Rightarrow$ poor sideways overlap $\Rightarrow$ not feasible.

[Ans] Final Answer

Option (2): C=O — both C and O are small Period 2 atoms with compact 2p orbitals $\Rightarrow$ effective pπ–pπ overlap

[!] Common Mistake

Option (1) Sn=O looks plausible. But Sn has 5p orbitals (Period 5) — very large and diffuse. Effective pπ–pπ overlap with O's compact 2p orbital is impossible. Only carbon (and nitrogen, oxygen) can form pπ–pπ bonds in Group 14.

Q.47 Bond enthalpies: C–C=348, Si–Si=297, Ge–Ge=260, Sn–Sn=240 kJ/mol. Correct conclusion?

[A] Conceptual Approach

Data shows clear decreasing trend: $348 > 297 > 260 > 240$. Bond enthalpy decreases from C to Sn. Stronger bond = more catenation. Lead (Pb–Pb) would be even weaker and is not listed (essentially zero catenation).

[S] Step-by-Step Solution

From data: C–C (348) > Si–Si (297) > Ge–Ge (260) > Sn–Sn (240) kJ/mol.

Bond enthalpy decreases from C to Sn.

$\therefore$ C–C bonds are the strongest $\Rightarrow$ carbon chains most stable $\Rightarrow$ C has greatest catenation.
As we go down, weaker bonds = less tendency to catenate.
Lead would have even weaker Pb–Pb bonds $\Rightarrow$ Pb doesn't catenate at all.

[Ans] Final Answer

Option (2): Bond enthalpy decreases C→Sn; C–C bonds are strongest; explains C has greatest catenation, Pb none

[!] Common Mistake

Option (4) says Ge–Ge is stronger than Si–Si because Ge has more electrons. Wrong! Ge–Ge (260) is WEAKER than Si–Si (297). More electrons in heavier atoms means more diffuse, larger orbitals = poorer overlap = weaker bond, not stronger.

Q.48 Si orbitals are large and diffuse compared to C orbitals. Si cannot form pπ–pπ bonds like C. What conclusion follows?

[A] Conceptual Approach

The diagram shows WHY pπ–pπ fails for Si: large diffuse 3p orbitals of Si cannot overlap effectively sideways with other 3p orbitals. Compact 2p of C allows perfect sideways overlap. Conclusion: effective pπ–pπ needs compact orbitals.

[S] Step-by-Step Solution

pπ–pπ bond requires:

1. Small, compact p-orbitals that can come close for sideways overlap.
2. Orbitals of similar energy and size on both atoms.

Carbon (2p): compact $\Rightarrow$ effective sideways overlap $\Rightarrow$ forms C=C, C=O, C$\equiv$N etc.

Silicon (3p): large, diffuse $\Rightarrow$ poor sideways overlap even between two Si atoms.
Cannot form pπ–pπ bonds effectively.

Conclusion: **Effective pπ–pπ bonding requires compact orbitals of similar size**; Si fails this requirement.

[Ans] Final Answer

Option (2): Effective pπ–pπ overlap requires compact orbitals; Si's large, diffuse 3p orbitals give poor sideways overlap $\Rightarrow$ no multiple bonds

[!] Common Mistake

Option (1) says larger orbitals give better overlap. Exactly backwards! For σ bonds, larger orbitals can give better head-on overlap. But for π (sideways) overlap, compact orbitals are essential. Large, diffuse orbitals spread out so much that sideways overlap becomes negligible.

Q.49 Statements: I. C differs from Group 14 due to smaller size, higher EN, higher IE, no d-orbitals. II. C forms pπ–pπ with itself and with O, N, S. III. Heavier Group 14 form pπ–pπ more easily

(larger orbitals). IV. Catenation + pπ–pπ $\Rightarrow$ allotropic forms. Correct?

[A] Conceptual Approach

I=TRUE. II=TRUE. III=FALSE (exact opposite; heavier elements form pπ–pπ bonds LESS easily due to large diffuse orbitals). IV=TRUE. Answer: I, II, IV.

[S] Step-by-Step Solution

Statement I: TRUE — Carbon's four anomalous features: (a) smaller size, (b) higher EN, (c) higher IE, (d) absence of d-orbitals.

Statement II: TRUE — C forms pπ–pπ multiple bonds with itself (C=C, C$\equiv$C) and with small, electronegative atoms (C=O, C$\equiv$N, C=S).

Statement III: **FALSE** — Heavier elements form pπ–pπ bonds **LESS easily** (not more). Large, diffuse orbitals mean poor sideways overlap. Statement III is the opposite of the truth.

Statement IV: TRUE — Allotropes (diamond, graphite, fullerenes) arise from catenation and pπ–pπ bonding.

Correct: I, II, and IV.

[Ans] Final Answer

Option (2): I, II and IV only

[!] Common Mistake

Accepting Statement III as true. This is the key trap — it states the *opposite* of the truth. Heavier elements (Si, Ge, Sn) form pπ–pπ bonds MORE POORLY than carbon, not more easily. Larger orbitals = worse sideways overlap = less π bonding.

Q.50 Statements: I. Catenation = atoms linking covalently to form chains and rings. II. C–C BE (348 kJ/mol) is highest among Group 14; C has greatest catenation. III. Order: C$\gg$Si$>$Ge$\approx$Sn; Pb does not catenate. IV. Catenation INCREASES down Group 14 as atomic size increases and BE decreases. Correct?

[A] Conceptual Approach

I=TRUE. II=TRUE. III=TRUE. IV=FALSE (catenation DECREASES as we go down; lower BE = less catenation). Answer: I, II, III.

[S] Step-by-Step Solution

Statement I: TRUE — Definition of catenation.

Statement II: TRUE — C–C (348 kJ/mol) is the highest; carbon's catenation is by far the greatest.

Statement III: TRUE — NCERT catenation order: C $\gg$ Si $>$ Ge $\approx$ Sn; Pb essentially zero.

Statement IV: **FALSE** — Catenation **decreases** down Group 14 (NOT increases). As bond enthalpy decreases, chains become less stable $\Rightarrow$ less catenation. More atomic size and less EN means less tendency to form covalent chains. Statement IV incorrectly says catenation increases.

Correct: I, II, and III.

[Ans] Final Answer

Option (1): I, II and III only

[!] Common Mistake

Accepting Statement IV. This is the classic reversal trap. Catenation DECREASES down Group 14 as bond enthalpy DECREASES. Statement IV says it increases as BE decreases — that's backwards. Weaker bonds = less stable chains = LESS catenation, not more.

"Group 14 has two stars: Carbon and Lead.
Carbon wins because it has no d-orbitals and can pi-bond and catenate.
Lead wins the inert pair trophy and refuses to give up its $6s^2$.
Understand these two characters, and the whole chapter falls into place."

— Your Weird Chemist