Chapter 7: Redox Reactions

Exercises — Exercises

Q1 Assign oxidation number to the underlined elements in each of the following species: (a) NaH_2PO_4 (b) $NaHSO_4$ (c) $H_4P_2O_7$ (d) K_2MnO_4 (e) CaO_2 (f) $NaBH_4$ (g) $H_2S_2O_7$ (h) $KAl(SO_4)_2.12H_2O$

SOLUTION

Rules used: Na=+1, K=+1, Ca=+2, Al=+3; H=+1 (except in metal hydrides where H=-1); O=-2 (except peroxides O=-1); algebraic sum = 0 for neutral compound, = ion charge for polyatomic ion.

(a) NaH_2PO_4: Let P = x. Na(+1) + 2H(+1) + x + 4O(-2) = 0 => 1+2+x-8 = 0 => x = +5

(b) $NaHSO_4$: Let S = x. Na(+1) + H(+1) + x + 4O(-2) = 0 => 1+1+x-8 = 0 => x = +6

(c) $H_4P_2O_7$: Let P = x. 4(+1) + 2x + 7(-2) = 0 => 4+2x-14 = 0 => 2x = 10 => x = +5

(d) K_2MnO_4: Let Mn = x. 2(+1) + x + 4(-2) = 0 => 2+x-8 = 0 => x = +6

(e) CaO_2: This is calcium peroxide. In peroxides, O = -1 (O-O bond present). Let O = x. Ca(+2) + 2x = 0 => x = -1

(f) $NaBH_4$: H is bonded to the metal-like B (and Na); H = -1 here (borohydride). Let B = x. Na(+1) + x + 4(-1) = 0 => 1+x-4 = 0 => x = +3

(g) $H_2S_2O_7$: Let S = x. 2(+1) + 2x + 7(-2) = 0 => 2+2x-14 = 0 => 2x = 12 => x = +6

(h) $KAl(SO_4)_2.12H_2O$: K=+1, Al=+3; in SO_4^{2-} let S = x. x + 4(-2) = -2 => x = +6

Answer: (a) P = +5; (b) S = +6; (c) P = +5; (d) Mn = +6; (e) O = -1; (f) B = +3; (g) S = +6; (h) S = +6

Q2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results? (a) KI_3 (b) $H_2S_4O_6$ (c) Fe_3O_4 (d) CH_3CH_2OH (e) CH_3COOH

SOLUTION

(a) KI_3: If all three I atoms had the same oxidation state, then K(+1) + 3x = 0 => x = -1/3 (fractional).

Rationalisation: KI_3 is actually $K^+[I_3]^-$. In the I_3^- ion, the middle I acts as I^+ and bonds to two I^- atoms (or the actual structure has I^+ in centre with two I^- in a linear

arrangement). The average oxidation state is -1/3, which is fractional because the three iodine atoms exist in different environments.

(b) $H_2S_4O_6$ (tetrathionate): 2(+1) + 4x + 6(-2) = 0 => 2+4x-12 = 0 => x = 2.5 (fractional).
Rationalisation: Structure reveals that the two central S atoms are at 0 oxidation state, and the two terminal S atoms (bonded to oxygens) are at +5. The average (0+0+5+5)/4 = 2.5.

(c) Fe_3O_4: 3x + 4(-2) = 0 => x = 8/3 = 2.67 (fractional).
Rationalisation: Fe_3O_4 is a mixed oxide (FeO + Fe_2O_3). It contains one Fe^{2+} and two Fe^{3+} ions. Average = (2+3+3)/3 = 8/3.

(d) CH_3CH_2OH (ethanol): Using the bond-counting approach (C-H bond: C gets -1; C-C: 0; C-O: C gets +1).
C_1 (CH_3): 3 C-H bonds => oxidation number = -3.
C_2 (CH_2OH): 2 C-H bonds (-2) + 1 C-O bond (+1) + 1 C-C (0) => oxidation number = -1.
Verification: (-3) + (-1) + 6(+1) + (-2) = -4+6-2 = 0 ✓

(e) CH_3COOH (acetic acid):
C_1 (CH_3): 3 C-H bonds => oxidation number = -3.
C_2 (COOH): 1 C=O (+2) + 1 C-OH (+1) + 1 C-C (0) => oxidation number = +3.
Verification: (-3) + (+3) + 4(+1) + 2(-2) = 0+4-4 = 0 ✓

Answer: (a) I = -1/3 (average; $KI_3 = K^+I_3^-$); (b) S = 2.5 (average; outer S = +5, inner S = 0); (c) Fe = 8/3 (average; $Fe^{2+} + 2Fe^{3+}$); (d) $C_1(CH_3) = -3$, $C_2(CH_2OH) = -1$; (e) $C_1(CH_3) = -3$, $C_2(COOH) = +3$

Q3 Justify that the following reactions are redox reactions: (a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$ (b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$ (c) $4BCl_3(g) + 3LiAlH_4(s) \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$ (d) $2K(s) + F_2(g) \rightarrow 2K^+F^-(s)$ (e) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

SOLUTION

(a) $CuO + H_2 \rightarrow Cu + H_2O$:
Cu in CuO: +2; Cu product: 0 (Cu reduced, +2 -> 0).
H in H_2: 0; H in H_2O: +1 (H oxidized, 0 -> +1).
Since oxidation and reduction occur simultaneously, this is a redox reaction.

(b) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$:

Fe in Fe_2O_3: +3; Fe product: 0 (Fe reduced, +3 -> 0).
C in CO: +2 (1+x-2=0 => x=+2); C in CO_2: +4 (C oxidized, +2 -> +4).
Both oxidation and reduction occur; this is a redox reaction.

(c) $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$:
B in BCl_3: +3 (B + 3(-1) = 0). B in B_2H_6: 2B + 6(+1) = 0 => B = -3. B is reduced (+3 -> -3).
H in $LiAlH_4$: -1 (hydridic H). H in B_2H_6: +1 (in B_2H_6, B is less electronegative than H; however NCERT assigns H = +1 to be consistent with B = -3 via 2(-3) + 6H = 0 => H = +1). H is oxidised (-1 -> +1).
Al in $LiAlH_4$: +3 (Li(+1)+Al+4(-1)=0 => Al=+3); Al in $AlCl_3$: +3 (no change for Al).
Cl in BCl_3: -1; Cl in LiCl and $AlCl_3$: -1 (no change).
This is a redox reaction: B is reduced from +3 to -3; H is oxidised from -1 to +1. The changes in oxidation state of B and H confirm it.

(d) $2K + F_2 \rightarrow 2K^+F^-$ (2KF):
K: 0 -> +1 (oxidized). F: 0 -> -1 (reduced). Clear redox reaction.

(e) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$:
N in NH_3: -3 (x+3(+1)=0 => x=-3); N in NO: +2 (x-2=0 => x=+2). N oxidized (-3 -> +2).
O in O_2: 0; O in H_2O: -2 and in NO: -2. O reduced (0 -> -2).
Since both oxidation and reduction occur, this is a redox reaction.

Answer: All five reactions are redox reactions: (a) Cu^{2+} reduced to Cu; H_2 oxidized; (b) Fe^{3+} reduced to Fe; C(+2) oxidized to C(+4); (c) B(+3) in BCl_3 reduced to B(-3) in B_2H_6; (d) K oxidized (+1), F reduced (-1); (e) N(-3) in NH_3 oxidized to N(+2) in NO; O_2 reduced to O(-2).

Q4 Fluorine reacts with ice and results in the change: $H_2O(s) + F_2(g) \rightarrow HF(g) + HOF(g)$. Justify that this reaction is a redox reaction.

SOLUTION

Assign oxidation numbers to each element:
In H_2O: H = +1, O = -2.
In F_2: F = 0.
In HF: H = +1, F = -1.
In HOF (hypofluorous acid): H = +1; F = -1 (most electronegative element); let O = x: +1 + x + (-1) = 0 => x = 0.

Changes in oxidation state:
F: 0 (in F_2) -> -1 (in HF and HOF): F is reduced.
O: -2 (in H_2O) -> 0 (in HOF): O is oxidized.
H: +1 throughout (no change).

Electron balance: One O atom loses 2 electrons (oxidized from -2 to 0); two F atoms each gain 1 electron (reduced from 0 to -1). Total gain = $2e^-$ = total loss. ✓

Since oxidation (of O) and reduction (of F) occur simultaneously, this is a redox reaction.

Answer: O in H_2O is oxidized from -2 to 0 (in HOF); F_2 is reduced from 0 to -1 (in HF and HOF). Since both oxidation and reduction occur simultaneously, this is a redox reaction.

Q5 Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these compounds. Count for the fallacy.

SOLUTION

H_2SO_5 (peroxomonosulphuric acid / Caro's acid):
If all O were -2: 2(+1) + x + 5(-2) = 0 => x = +8. But S cannot exceed +6 (maximum oxidation state for a period-3 element). This is the fallacy.
Reality: H_2SO_5 contains one -O-O$^-$ (peroxide) linkage with two O at -1 each, and three normal O at -2.
Correct: 2(+1) + x + 3(-2) + 2(-1) = 0 => 2 + x - 6 - 2 = 0 => x = +6.
Structure: HO-SO_2-O-OH (peroxy acid with one peroxide O-O group).

$Cr_2O_7^{2-}$ (dichromate ion):
2x + 7(-2) = -2 => 2x - 14 = -2 => 2x = 12 => x = +6.
Structure: Two CrO_4 tetrahedra sharing one oxygen vertex (Cr-O-Cr bridge).

NO_3^- (nitrate ion):
x + 3(-2) = -1 => x = +5.
Structure: Planar triangular (trigonal planar) with one N=O and two N-O bonds (or three equivalent N-O bonds by resonance). N is sp^2 hybridised.

Fallacy for H_2SO_5: Assigning -2 to all oxygen atoms gives S = +8 which is impossible for sulphur (maximum is +6). Therefore H_2SO_5 must possess a peroxide (-O-O$^-$) linkage with oxygen in -1 oxidation state to give a chemically valid S = +6.

Answer: S in H_2SO_5 = +6 (has -O-O^- peroxide linkage; assuming all O=-2 gives impossible +8); Cr in $Cr_2O_7^{2-}$ = +6; N in NO_3^- = +5.

Q6 Write formulas for the following compounds: (a) Mercury(II) chloride (b) Nickel(II) sulphate (c) Tin(IV) oxide (d) Thallium(I) sulphate (e) Iron(III) sulphate (f) Chromium(III) oxide

SOLUTION

(a) Mercury(II) chloride: Hg is +2; Cl is -1. Formula: $HgCl_2$

(b) Nickel(II) sulphate: Ni is +2; SO_4^{2-} is -2. Formula: $NiSO_4$

(c) Tin(IV) oxide: Sn is +4; O is -2. Need 2 O to balance: SnO_2

(d) Thallium(I) sulphate: Tl is +1; SO_4^{2-} is -2. Need 2 Tl: Tl_2SO_4

(e) Iron(III) sulphate: Fe is +3; SO_4^{2-} is -2. LCM(3,2)=6; 2 Fe and 3 SO_4: $Fe_2(SO_4)_3$

(f) Chromium(III) oxide: Cr is +3; O is -2. LCM(3,2)=6; 2 Cr and 3 O: Cr_2O_3

Answer: (a) $HgCl_2$; (b) $NiSO_4$; (c) SnO_2; (d) Tl_2SO_4; (e) $Fe_2(SO_4)_3$; (f) Cr_2O_3

Q7 Suggest a list of the substances where carbon can exhibit oxidation states from -4 to +4 and nitrogen from -3 to +5.

SOLUTION

Carbon (oxidation states -4 to +4):
-4: CH_4 (methane); C + 4(+1) = 0 => C = -4
-3: C_2H_6 (ethane); per C atom: x + 3(+1) = 0 => x = -3
-2: CH_3OH (methanol); x + 3(+1) + (-2) + 1 = 0 => x = -2
-1: CH_3CH_2OH (ethanol, CH_2OH carbon); x + 2(+1) + (-2) + 0 = 0 => x = -1 (see Q_2(d))
0: HCHO (formaldehyde); x + 2(+1) + (-2) = 0 => x = 0
+2: HCOOH (formic acid); x + 1 + 2(-2) + 1 = 0 => x = +2
+4: CO_2 (carbon dioxide); x + 2(-2) = 0 => x = +4; also CCl_4

Nitrogen (oxidation states -3 to +5):
-3: NH_3 (ammonia); x + 3(+1) = 0 => x = -3
-2: N_2H_4 (hydrazine); x + 2(+1) = 0 per N => x = -2
-1: NH_2OH (hydroxylamine); x + 2(+1) + (-2) + 1 = 0 => x = -1
0: N_2 (elemental nitrogen)
+1: N_2O (dinitrogen oxide); 2x + (-2) = 0 => x = +1

+2: NO (nitric oxide); x + (-2) = 0 => x = +2
+3: HNO_2 (nitrous acid); +1 + x + 2(-2) = 0 => x = +3
+4: NO_2 (nitrogen dioxide); x + 2(-2) = 0 => x = +4
+5: HNO_3 (nitric acid); +1 + x + 3(-2) = 0 => x = +5

Answer: Carbon: CH_4(-4), C_2H_6(-3), CH_3OH(-2), HCHO(0), HCOOH(+2), CO_2(+4). Nitrogen: NH_3(-3), N_2H_4(-2), NH_2OH(-1), N_2(0), N_2O(+1), NO(+2), HNO_2(+3), NO_2(+4), HNO_3(+5).

Q8 While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why?

SOLUTION

SO_2: Sulphur is in +4 oxidation state (intermediate; range for S is -2 to +6).
Since +4 is intermediate, S can be further oxidised to +6 (SO_3, H_2SO_4) or further reduced to -2 or lower oxidation states. Hence SO_2 acts both as an oxidising and reducing agent.

H_2O_2: Oxygen is in -1 oxidation state (intermediate; range for O is -2 to 0 in most compounds).
O at -1 can be reduced to -2 (H_2O), so H_2O_2 acts as an oxidant. O at -1 can also be oxidised to 0 (O_2), so H_2O_2 also acts as a reductant. Hence H_2O_2 acts both as oxidising and reducing agent.

O_3 (ozone): Oxygen is in 0 oxidation state. Oxygen can only be reduced (to -2); it cannot be oxidised further because 0 is the maximum oxidation state achievable for oxygen under normal conditions (oxygen cannot exhibit positive oxidation state, being the second most electronegative element, except with F). Hence O_3 acts only as an oxidant.

HNO_3 (nitric acid): Nitrogen is in +5 oxidation state, which is the maximum for nitrogen. Since N cannot be oxidised further (cannot go above +5), HNO_3 can only accept electrons (be reduced). Hence HNO_3 acts only as an oxidant.

Answer: SO_2 (S at +4, intermediate) and H_2O_2 (O at -1, intermediate) can both gain and lose electrons, so they act as both oxidant and reductant. O_3 (O at 0, maximum for O) and HNO_3 (N at +5, maximum for N) can only gain electrons; they act only as oxidants.

Q9 Consider the reactions: (a) $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$ (b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + 2O_2(g)$. Why is it more appropriate to write these reactions as: (a) $6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$ (b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + O_2(g) + O_2(g)$. Also suggest a technique to investigate the path of the above redox reactions.

SOLUTION

(a) Photosynthesis: The more detailed equation $6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6H_2O + 6O_2$ explicitly shows that the oxygen evolved comes from water (not from CO_2). The 12 H_2O on the left: 12 O atoms in water are distributed — 6 go into glucose (with C) and 6 come out as O_2. Writing it this way correctly tracks the origin of each oxygen atom.
The simplified version (using only $6H_2O$) obscures which atoms are incorporated into glucose and which form O_2.

(b) $O_3 + H_2O_2 \rightarrow H_2O + O_2 + O_2$: Writing two separate O_2 molecules (one from O_3 and one from H_2O_2) rather than $2O_2$ clarifies that the two oxygen molecules originate from different reactants. One O_2 comes from O_3 (O: 0 -> 0) and one O_2 comes from H_2O_2 (O: -1 -> 0, oxidation).

Technique to investigate the reaction path: Use isotopic labelling (radioactive or stable isotopes).
For reaction (a): Use 18O-labelled water ($H_2{}^{18}O$) and unlabelled CO_2. If the O_2 evolved is $18O_2$, it confirms that O_2 originates from water, not from CO_2.
For reaction (b): Use 18O-labelled H_2O_2. If the O_2 from H_2O_2 is labelled ($^{18}O_2$), it confirms that this molecule's O_2 comes from H_2O_2, while the unlabelled O_2 comes from O_3.

Answer: The more explicit equations track the origin of each oxygen atom. Isotopic labelling (e.g., ^{18}O-labelled H_2O or H_2O_2) is the technique used to trace the path of specific oxygen atoms in these redox reactions.

Q10 The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why?

SOLUTION

In AgF_2, silver is in the +2 oxidation state (Ag^{2+}).
The normal and stable oxidation state of silver is +1 (Ag^+).
Ag^{2+} is a highly unstable oxidation state for silver because it involves a $[Kr]_4d^9$

electronic configuration, which has a strong tendency to gain one electron to achieve the stable $[Kr]_4d^{10}$ configuration of Ag^+.
Therefore, Ag^{2+} in AgF_2 readily accepts an electron (is reduced to Ag^+), oxidising whatever substance donates the electron.
This makes AgF_2 an extremely strong oxidising agent.

The instability of the Ag^{2+} state drives the oxidising action: the compound decomposes or reacts to convert Ag^{2+} -> Ag^+ by oxidising other species.

Answer: AgF_2 contains Ag in the unstable +2 oxidation state. Ag^{2+} has a strong tendency to gain one electron and return to the stable +1 state. This high electron affinity of Ag^{2+} makes AgF_2 a very strong oxidising agent.

Q11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

SOLUTION

When reducing agent is in excess, it keeps reducing the product to lower oxidation states. When oxidising agent is in excess, it keeps oxidising the product to higher oxidation states.

Illustration 1: Carbon (reductant) with oxygen (oxidant):
Excess C (reductant): $2C + O_2$ -> $2CO$ (C in +2, lower state)
Excess O_2 (oxidant): $C + O_2$ -> CO_2 (C in +4, higher state)

Illustration 2: Sulphur (reductant) with oxygen (oxidant):
Excess S: $S + O_2$ -> SO_2 (S in +4, lower state; sulphur excess forms SO_2 then stops)
Excess O_2: $S + 3/2\ O_2$ -> SO_3 or $2SO_2 + O_2$ -> $2SO_3$ (S in +6, higher state)

Illustration 3: P_4 (reductant) with Cl_2 (oxidant):
Excess P_4 (limited Cl_2): $P_4 + 6Cl_2$ -> $4PCl_3$ (P in +3, lower state)
Excess Cl_2: $P_4 + 10Cl_2$ -> $4PCl_5$ (P in +5, higher state)

In each case, the product's oxidation state is lower when the reductant is in excess (available to reduce the product further) and higher when the oxidant is in excess (available to oxidise the product further).

Answer: Three illustrations: (1) C + O_2: excess C gives CO (C = +2); excess O_2 gives CO_2 (C = +4). (2) P_4 + Cl_2: excess P_4 gives PCl_3 (P = +3); excess Cl_2 gives PCl_5 (P = +5). (3) S + O_2: excess S gives SO_2 (S = +4); excess O_2 gives SO_3 (S = +6).

Q12 How do you count for the following observations? (a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why? Write a balanced redox equation for the reaction. (b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why?

SOLUTION

(a) Toluene ($C_6H_5CH_3$) is insoluble in water but soluble in alcohol (a non-aqueous medium). Aqueous $KMnO_4$ (alkaline or acidic) cannot come into contact with toluene efficiently because toluene does not dissolve in water. Alcoholic $KMnO_4$ dissolves in the same medium as toluene, allowing the reaction to occur homogeneously.

The balanced redox equation for oxidation of toluene to benzoic acid (in alkaline medium):
$C_6H_5CH_3 + 2KMnO_4 \rightarrow C_6H_5COOK + 2MnO_2 + KOH + H_2O$
(Full ionic form): $C_6H_5CH_3 + 2MnO_4^- \rightarrow C_6H_5COO^- + 2MnO_2 + OH^- + H_2O$
In this reaction, Mn(+7) is reduced to Mn(+4) and C in CH_3 is oxidised.

(b) Concentrated H_2SO_4 is an oxidising acid.
With Cl^-: H_2SO_4 is not strong enough to oxidise Cl^- (Cl^-/Cl_2 = +1.36 V, higher than SO_4^{2-}/SO_2). The reaction is simply an acid-base displacement: $H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl$ (gas). The product is colourless pungent HCl gas.

With Br^-: Concentrated H_2SO_4 IS strong enough to oxidise Br^- to Br_2 (Br_2/Br^- = +1.09 V, lower than SO_4^{2-}/SO_2 under conc. conditions), producing red-brown bromine vapour:
$H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$
Thus Br^- is oxidised to Br_2 (red vapour) while SO_4^{2-} is reduced to SO_2.

Answer: (a) Toluene is insoluble in water but dissolves in alcohol; alcoholic $KMnO_4$ enables a homogeneous reaction. Equation: $C_6H_5CH_3 + 2KMnO_4 \rightarrow C_6H_5COOK + 2MnO_2 + KOH + H_2O$. (b) H_2SO_4 cannot oxidise Cl^- (too high reduction potential), so only HCl gas forms. H_2SO_4 can oxidise Br^- (lower reduction potential) to Br_2 (red vapour): $H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$.

Q13 Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions: (a) $2AgBr(s) + C_6H_6O_2(aq) \rightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$ (b) $HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$ (c) $HCHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$ (d) $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$ (e) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

SOLUTION

(a) $2AgBr + C_6H_6O_2 \rightarrow 2Ag + 2HBr + C_6H_4O_2$:
Ag in AgBr: +1; Ag product: 0 (AgBr is reduced).
$C_6H_6O_2$ (hydroquinone) -> $C_6H_4O_2$ (benzoquinone): the molecule loses two H atoms, so it is oxidised.
Oxidised substance: $C_6H_6O_2$; Reduced substance: AgBr.
Oxidising agent: AgBr; Reducing agent: $C_6H_6O_2$.

(b) $HCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow 2Ag + HCOO^- + 4NH_3 + 2H_2O$:
C in HCHO: 0 (x+2(+1)+(-2)=0); C in $HCOO^-$: +2 (+1+x+2(-2)=-1 => x=+2). C is oxidised.
Ag in $[Ag(NH_3)_2]^+$: +1; Ag product: 0. Ag^+ is reduced.
Oxidised: HCHO; Reduced: $[Ag(NH_3)_2]^+$.
Oxidising agent: $[Ag(NH_3)_2]^+$; Reducing agent: HCHO.

(c) $HCHO + 2Cu^{2+} + 5OH^- \rightarrow Cu_2O + HCOO^- + 3H_2O$:
C in HCHO: 0 -> C in $HCOO^-$: +2. C is oxidised.
Cu: +2 -> Cu in Cu_2O: +1 (+2*1+(-2)=0? 2(+1)+(-2)=0 ✓). Cu^{2+} is reduced.
Oxidised: HCHO; Reduced: Cu^{2+}.
Oxidising agent: Cu^{2+}; Reducing agent: HCHO.

(d) $N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O$:
N in N_2H_4: -2 (x+2(+1)=0 => x=-2); N in N_2: 0. N is oxidised (-2 -> 0).
O in H_2O_2: -1; O in H_2O: -2. O is reduced (-1 -> -2).
Oxidised: N_2H_4; Reduced: H_2O_2.
Oxidising agent: H_2O_2; Reducing agent: N_2H_4.

(e) $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$ (lead storage battery discharge):
Pb(s): 0 -> +2 in $PbSO_4$ (oxidised).
Pb in PbO_2: +4 -> +2 in $PbSO_4$ (reduced).
Oxidised: Pb(s); Reduced: PbO_2.
Oxidising agent: PbO_2; Reducing agent: Pb(s).

Answer: (a) Oxidised: $C_6H_6O_2$; Reduced: AgBr; OA: AgBr; RA: $C_6H_6O_2$. (b) Oxidised: HCHO; Reduced: $[Ag(NH_3)_2]^+$; OA: $[Ag(NH_3)_2]^+$; RA: HCHO. (c) Oxidised: HCHO; Reduced: Cu^{2+}; OA: Cu^{2+}; RA: HCHO. (d) Oxidised: N_2H_4; Reduced: H_2O_2; OA: H_2O_2; RA: N_2H_4. (e) Oxidised: Pb(s); Reduced: PbO_2; OA: PbO_2; RA: Pb(s).

Q14 Consider the reactions: $2S_2O_3^{2-}(aq) + I_2(s) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ and $S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$. Why does the same reductant, thiosulphate, react differently with iodine and bromine?

SOLUTION

In Reaction 1 (with I_2): S in $S_2O_3^{2-}$ (average oxidation state = +2) is oxidised to S in $S_4O_6^{2-}$ (average = +2.5, i.e., a change of +0.5 per S, or +1 overall for two S atoms).
I_2 is reduced to I^- (0 -> -1). I_2 is a mild oxidising agent ($E(I_2/I^-)$ = +0.54 V).
The mild oxidising power of I_2 can only partially oxidise the thiosulphate ($S_2O_3^{2-}$) to tetrathionate ($S_4O_6^{2-}$).

In Reaction 2 (with Br_2): S in $S_2O_3^{2-}$ (+2) is fully oxidised to S in SO_4^{2-} (+6). Br_2 is a much stronger oxidising agent ($E(Br_2/Br^-)$ = +1.09 V).
The strong oxidising power of Br_2 completely oxidises thiosulphate to sulphate (SO_4^{2-}), a higher oxidation state of S.

Conclusion: The extent of oxidation of thiosulphate depends on the strength of the oxidising agent. I_2 (weaker OA) only oxidises $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (mild oxidation, partial); Br_2 (stronger OA) completely oxidises $S_2O_3^{2-}$ to SO_4^{2-} (full oxidation). This is consistent with the principle that excess or stronger oxidant drives the product to a higher oxidation state.

Answer: I_2 is a weaker oxidising agent (E = +0.54 V) and partially oxidises $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (S: +2 -> +2.5 average). Br_2 is a stronger oxidising agent (E = +1.09 V) and completely oxidises $S_2O_3^{2-}$ to SO_4^{2-} (S: +2 -> +6). The stronger oxidant drives the product to a higher oxidation state.

Q15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

SOLUTION

Fluorine as best oxidant among halogens:

Oxidising power follows: $F_2 > Cl_2 > Br_2 > I_2$ (decreases down the group).

$E(F_2/F^-)$ = +2.87 V (highest in the table) — F_2 has the greatest tendency to gain electrons.

F_2 can oxidise all other halide ions:

$F_2 + 2Cl^- \rightarrow 2F^- + Cl_2$ (F_2 oxidises Cl^-)

$F_2 + 2Br^- \rightarrow 2F^- + Br_2$ (F_2 oxidises Br^-)

$F_2 + 2I^- \rightarrow 2F^- + I_2$ (F_2 oxidises I^-)

F_2 even oxidises water: $2F_2 + 2H_2O \rightarrow 4HF + O_2$

No chemical agent can oxidise F^- to F_2 — F_2 can only be produced by electrolysis.

HI as best reductant among hydrohalic acids:

Reducing power of HX follows: HI > HBr > HCl > HF (increases down the group).

I^- has the largest ionic radius and weakest H-I bond; it gives up electrons most easily.

HI reduces concentrated H_2SO_4: $H_2SO_4 + 8HI \rightarrow H_2S + 4I_2 + 4H_2O$

HBr reduces H_2SO_4 only to SO_2: $H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$

HCl does not reduce H_2SO_4 (only acid-base: $HCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ type).

This shows HI is the strongest reducing agent among hydrohalic acids.

Answer: F_2 has the highest standard electrode potential (+2.87 V) and oxidises all other halide ions and even water — it is the strongest oxidant. HI is the strongest reductant because I^- has the largest size, weakest bond, and highest tendency to donate electrons; it can even reduce concentrated H_2SO_4 to H_2S.

Q16 Why does the following reaction occur? $XeO_6^{4-}(aq) + 2F^-(aq) + 6H^+(aq) \rightarrow XeO_3(g) + F_2(g) + 3H_2O(l)$. What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction?

SOLUTION

Assign oxidation numbers:
Xe in XeO_6^{4-}: x + 6(-2) = -4 => x = +8.
Xe in XeO_3: x + 3(-2) = 0 => x = +6. Xe is reduced (+8 -> +6, gains $2e^-$).
F in F^-: -1; F in F_2: 0. F^- is oxidised (-1 -> 0, loses $1e^-$).
Electron balance: Xe gains $2e^-$, $2F^-$ lose $1e^-$ each ($2e^-$ total). ✓

The reaction occurs because Xe in +8 oxidation state is extremely unstable (the highest known Xe state is +8, far above the most stable +6 or +4). The compound strongly tends to convert Xe(+8) to more stable Xe(+6).

This driving force is so strong that it can even oxidise F^- to F_2, even though F_2 is the strongest known oxidising agent (E = +2.87 V). In other words, XeO_6^{4-} in Na_4XeO_6 is an even more powerful oxidising agent than F_2 itself.

Conclusion: Na_4XeO_6 is an exceptionally strong oxidising agent — it can oxidise F^- to F_2, which no ordinary oxidant can do. This reflects that Xe in +8 oxidation state is so unstable that it drives very unfavourable oxidations.

Answer: Xe in XeO_6^{4-} is at +8 (extremely unstable); it is reduced to +6 in XeO_3. F^- is oxidised to F_2 in the process. Conclusion: Na_4XeO_6 (Xe at +8) is an extraordinarily strong oxidising agent — even stronger than F_2 — because Xe(+8) is so unstable it will oxidise even F^- to F_2.

Q17 Consider the reactions: (a) $H_3PO_2(aq) + 4AgNO_3(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)$ (b) $H_3PO_2(aq) + 2CuSO_4(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)$ (c) $C_6H_5CHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow C_6H_5COO^-(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2O(l)$ (d) $C_6H_5CHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq)$ -> No change observed. What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions?

SOLUTION

In reactions (a) and (b): H_3PO_2 (hypophosphorous acid) reduces both Ag^+ (from $AgNO_3$) and Cu^{2+} (from $CuSO_4$) to their respective metals.
In H_3PO_2: P oxidation state: +1 + x + 2(-2) = 0 => x = +1. It is oxidised to H_3PO_4 (P = +5).

Both Ag^+ and Cu^{2+} are reduced to Ag(s) and Cu(s) respectively.

In reactions (c) and (d): Benzaldehyde (C_6H_5CHO) is the reducing agent.
C in CHO group: x + 1 + (-2) + 0 = ? (partial formula: H-C=O: x+1-2=0 => x=+1).
C_6H_5CHO is oxidised to $C_6H_5COO^-$ (benzoate; C in COOH: +3).

Ag^+ (from $[Ag(NH_3)_2]^+$) IS reduced by C_6H_5CHO — this is the Tollens' test, and benzaldehyde gives a positive result (silver mirror). Reaction (c) occurs.

Cu^{2+} is NOT reduced by C_6H_5CHO — reaction (d) shows no change. This is in contrast to aliphatic aldehydes (HCHO, CH_3CHO) which DO reduce Cu^{2+} to Cu_2O (Fehling's test).

Inference: Ag^+ is a stronger oxidising agent than Cu^{2+} in this context. Ag^+ can be reduced by weaker reducing agents (including aromatic aldehydes like C_6H_5CHO). Cu^{2+} is a weaker oxidising agent and requires a stronger reducing agent (aliphatic aldehydes like HCHO) to be reduced. Aromatic aldehydes are weaker reducing agents than aliphatic aldehydes due to conjugation with the ring, so C_6H_5CHO reduces Ag^+ but not Cu^{2+}.

Answer: Ag^+ is a stronger oxidising agent than Cu^{2+}. Ag^+ is reduced even by weak reducing agents like benzaldehyde (C_6H_5CHO), whereas Cu^{2+} requires a stronger reducing agent (like aliphatic HCHO). Benzaldehyde reduces Ag^+ but not Cu^{2+} because the aromatic ring delocalises electron density, making the aldehyde a weaker reductant.

Q18 Balance the following redox reactions by ion-electron method: (a) $MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$ (in basic medium) (b) $MnO_4^-(aq) + SO_2(g) \rightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ (in acidic solution) (c) $H_2O_2(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + H_2O(l)$ (in acidic solution) (d) $Cr_2O_7^{2-}(aq) + SO_2(g) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (in acidic solution)

SOLUTION

(a) $MnO_4^- + I^- \rightarrow MnO_2 + I_2$ (basic medium):
Oxidation half: $2I^- \rightarrow I_2 + 2e^-$
Reduction half: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$
(Check: Mn:1✓; O:4+2=6=2+4=6✓; H:4=4✓; charge:-1+0-3=-4=-2+0-4? (-1+0-3=-4; right:0-4=-4)✓)
Equalise electrons (LCM=6): oxidation x_3, reduction x_2:
$6I^- \rightarrow 3I_2 + 6e^-$
$2MnO_4^- + 4H_2O + 6e^- \rightarrow 2MnO_2 + 8OH^-$

Net: $2MnO_4^- + 6I^- + 4H_2O \rightarrow 3I_2 + 2MnO_2 + 8OH^-$
(Verify: Mn:2=2✓; I:6=6✓; O:8+4=12=4+8=12✓; H:8=8✓; charge:-2-6+0=-8=0+0-8=-8✓)

(b) $MnO_4^- + SO_2 \rightarrow Mn^{2+} + HSO_4^-$ (acidic):
Oxidation half: $SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+ + 2e^-$
(S: +4->+6; S:1=1✓; O:2+2=4=1+3=4✓; H:4=1+3=4✓; charge left=0; right=-1+3-2=0✓)
Reduction half: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Equalise (LCM=10): oxidation x_5, reduction x_2:
$5SO_2 + 10H_2O \rightarrow 5HSO_4^- + 15H^+ + 10e^-$
$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
Add and cancel: H_2O: 10-8=2 on left; H^+: 16-15=1 on left
Final: $2MnO_4^- + 5SO_2 + 2H_2O + H^+ \rightarrow 2Mn^{2+} + 5HSO_4^-$
(Verify: charge left=-2+0+0+1=-1; right=+4+(-5)=-1✓; O: left=8+10+2=20; right=5*4=20✓; H:left=2*2+1=5; right=5*1=5✓)

(c) $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + H_2O$ (acidic):
Oxidation half: $Fe^{2+} \rightarrow Fe^{3+} + e^-$
Reduction half: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
Equalise: oxidation x_2: $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$
Net: $H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$
(Verify: Fe:2=2✓; O:2=2✓; H:2+2=4=4✓; charge:0+4+2=6=6+0=6✓)

(d) $Cr_2O_7^{2-} + SO_2 \rightarrow Cr^{3+} + SO_4^{2-}$ (acidic):
Oxidation half: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$
(S: +4 -> +6; charge balance: left = 0, right = -2 + 4 - 2 = 0 ✓)
Reduction half: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Equalise (LCM=6): oxidation x_3:
$3SO_2 + 6H_2O \rightarrow 3SO_4^{2-} + 12H^+ + 6e^-$
Add: $Cr_2O_7^{2-} + 3SO_2 + 6H_2O + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3SO_4^{2-} + 12H^+$
Simplify: $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$
(H_2O: 7-6=1 on right; H^+: 14-12=2 on left)
(Verify: Cr:2=2✓; S:3=3✓; O:7+6=13=12+1=13✓; H:2=2✓; charge:-2+0+2=0=+6-6+0=0✓)

Answer: (a) $2MnO_4^- + 6I^- + 4H_2O \rightarrow 3I_2 + 2MnO_2 + 8OH^-$; (b) $2MnO_4^- + 5SO_2 + 2H_2O + H^+ \rightarrow 2Mn^{2+} + 5HSO_4^-$; (c) $H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$; (d) $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$.

Q19 Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent: (a) $P_4(s) + OH^-(aq) \rightarrow PH_3(g) + H_2PO_2^-(aq)$ (b) $N_2H_4(l) + ClO_3^-(aq) \rightarrow NO(g) + Cl^-(g)$ (c) $Cl_2O_7(g) + H_2O_2(aq) \rightarrow ClO_2^-(aq) + O_2(g) + H^+$

SOLUTION

(a) $P_4 + OH^- \rightarrow PH_3 + H_2PO_2^-$ (basic medium):

P in P_4: 0; P in PH_3: -3 (x+3(+1)=0, x=-3, reduced); P in $H_2PO_2^-$: +1 (2(+1)+x+2(-2)=-1, x=+1, oxidised).

For disproportionation of 4 P atoms: let x go to PH_3, (4-x) go to $H_2PO_2^-$: x*3 = (4-x)*1 => 4x=4 => x=1 (1P reduced, 3P oxidised, with 1 P_4 unit).

Half-reactions:

Reduction: $P + 3H_2O + 3e^- \rightarrow PH_3 + 3OH^-$ (charge: -3=-3✓)

Oxidation: $P + 2OH^- \rightarrow H_2PO_2^- + e^-$ (P: 0->+1; charge:-2=-1-1=-2✓; O:2=2✓; H:2=2✓)

Equalise electrons (LCM=3): oxidation x_3, reduction x_1:

$3P + 6OH^- \rightarrow 3H_2PO_2^- + 3e^-$

$P + 3H_2O + 3e^- \rightarrow PH_3 + 3OH^-$

Net: $P_4 + 3H_2O + 3OH^- \rightarrow PH_3 + 3H_2PO_2^-$

(Verify: P:4=1+3=4✓; O:3+3=6=3*2=6✓; H:6+3=9=3+3*2=9✓; charge:-3=-3*1=-3✓)

Oxidising agent: P_4 (the fraction that accepts electrons, i.e., P that goes to PH_3); Reducing agent: P_4 (the fraction that donates electrons, i.e., P that goes to $H_2PO_2^-$).

(Disproportionation: P_4 is both OA and RA.)

(b) $N_2H_4 + ClO_3^- \rightarrow NO + Cl^-$ (basic medium):

N in N_2H_4: -2; N in NO: +2 (oxidised, -2 -> +2, loses $4e^-$ per N, $8e^-$ per N_2H_4).

Cl in ClO_3^-: +5; Cl in Cl^-: -1 (reduced, +5 -> -1, gains $6e^-$).

Oxidation half (basic): $N_2H_4 + 8OH^- \rightarrow 2NO + 6H_2O + 8e^-$

(check: N:2=2✓; O:8=2+6=8✓; H:4+8=12=12✓; charge:-8=-8✓)

Reduction half (basic): $ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^-$

(check: Cl:1=1✓; O:3+3=6=6✓; H:6=6✓; charge:-1+0-6=-7=-1-6=-7✓)

Equalise electrons (LCM=24): oxidation x_3, reduction x_4:

$3N_2H_4 + 24OH^- \rightarrow 6NO + 18H_2O + 24e^-$

$4ClO_3^- + 12H_2O + 24e^- \rightarrow 4Cl^- + 24OH^-$

Net: $3N_2H_4 + 4ClO_3^- \rightarrow 6NO + 4Cl^- + 6H_2O$

(H_2O: 18-12=6 on right; OH^-: 24-24=0; Verify: N:6=6✓; Cl:4=4✓; O:12=6+6=12✓;

H:12=12✓; charge:-4=-4✓)
Oxidising agent: ClO_3^-; Reducing agent: N_2H_4.

(c) $Cl_2O_7 + H_2O_2 \rightarrow ClO_2^- + O_2 + H^+$ (listed as basic medium):
Cl in Cl_2O_7: +7; Cl in ClO_2^-: +3 (reduced, gains $4e^-$ per Cl, $8e^-$ per Cl_2O_7).
O in H_2O_2: -1; O in O_2: 0 (oxidised, loses $1e^-$ per O, $2e^-$ per H_2O_2).
Reduction half (basic): $Cl_2O_7 + 3H_2O + 8e^- \rightarrow 2ClO_2^- + 6OH^-$
(check: Cl:2=2✓; O:7+3=10=4+6=10✓; H:6=6✓; charge:-8=-2-6=-8✓)
Oxidation half (basic): $H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$
(check: O:2+2=4=2+2=4✓; H:2+2=4=4✓; charge:-2=-2✓)
Equalise electrons (LCM=8): oxidation $\times_4$, reduction $\times_1$:
$4H_2O_2 + 8OH^- \rightarrow 4O_2 + 8H_2O + 8e^-$
$Cl_2O_7 + 3H_2O + 8e^- \rightarrow 2ClO_2^- + 6OH^-$
Net: $Cl_2O_7 + 4H_2O_2 + 2OH^- \rightarrow 2ClO_2^- + 4O_2 + 5H_2O$
(OH^-: 8-6=2 on left; H_2O: 8-3=5 on right; Verify: Cl:2=2✓; O:7+8+2=17=4+8+5=17✓; H:8+2=10=10✓; charge:-2=-2✓)
Oxidising agent: Cl_2O_7; Reducing agent: H_2O_2.

Answer: (a) $P_4 + 3H_2O + 3OH^- \rightarrow PH_3 + 3H_2PO_2^-$; OA and RA both: P_4 (disproportionation). (b) $3N_2H_4 + 4ClO_3^- \rightarrow 6NO + 4Cl^- + 6H_2O$; OA: ClO_3^-; RA: N_2H_4. (c) $Cl_2O_7 + 4H_2O_2 + 2OH^- \rightarrow 2ClO_2^- + 4O_2 + 5H_2O$; OA: Cl_2O_7; RA: H_2O_2.

Q20 What sorts of informations can you draw from the following reaction? $(CN)_2(g) + 2OH^-(aq) \rightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$

SOLUTION

Step 1: Assign oxidation states.
In CN^-: assuming N=-3 (standard for cyanide): x+(-3)=-1 => x=+2 for C.
In $(CN)_2$: each CN unit is neutral, so x+(-3)=0 => x=+3 per C.
In CNO^-: N=-3, O=-2: x+(-3)+(-2)=-1 => x=+4.

Step 2: Identify changes:
C in $(CN)_2$: +3; C in CN^-: +2 (reduced, gains $1e^-$); C in CNO^-: +4 (oxidised, loses $1e^-$).

Step 3: Conclusions:
(i) This is a disproportionation reaction: C in $(CN)_2$ is simultaneously reduced (to CN^-) and oxidised (to CNO^-). One CN unit is reduced and the other is oxidised.
(ii) $(CN)_2$ behaves like a halogen (Cl_2, Br_2) in reacting with alkali — the analogy is:

$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$. Cyanogen $(CN)_2$ is therefore called a pseudohalogen and the CN^- ion is a pseudohalide.

(iii) The reaction takes place in basic medium (OH^- is consumed).

(iv) The electron balance is maintained: 1 C loses $1e^-$ and 1 C gains $1e^-$ (within the same molecule, disproportionation).

Answer: $(CN)_2$ undergoes disproportionation in basic medium — one CN unit is reduced to CN^- and the other is oxidised to CNO^-. This is analogous to halogen disproportionation in alkali ($Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$), confirming that $(CN)_2$ is a pseudohalogen and CN^- is a pseudohalide ion.

Q21 The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

SOLUTION

Mn^{3+} undergoes disproportionation: Mn(+3) -> Mn(+2) and Mn(+4).

Reduction half: $Mn^{3+} + e^- \rightarrow Mn^{2+}$ (Mn: +3 -> +2)

Oxidation half: $Mn^{3+} \rightarrow MnO_2 + e^-$ (Mn: +3 -> +4, loses $1e^-$)

Balance O in oxidation half: add $2H_2O$ on right and $4H^+$ on left (acidic medium):

$Mn^{3+} + 2H_2O \rightarrow MnO_2 + 4H^+ + e^-$

(Check: Mn:1✓; O:2=2✓; H:4=4✓; charge:+3=0+4-1=+3✓)

Electrons already equal ($1e^-$ each). Add the two half-reactions:

$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$

(Verify: Mn:2=1+1=2✓; O:2=2✓; H:4=4✓; charge:+6=+2+0+4=+6✓)

Answer: $2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$

Q22 Consider the elements: Cs, Ne, I and F. (a) Identify the element that exhibits only negative oxidation state. (b) Identify the element that exhibits only positive oxidation state. (c) Identify the element that exhibits both positive and negative oxidation states. (d) Identify the element which exhibits neither the negative nor the positive oxidation state.

SOLUTION

(a) Element with only negative oxidation state: F (fluorine).

Fluorine is the most electronegative element and has no d-orbitals available for bonding. It cannot be oxidised to a positive state. F always exhibits -1 (or 0 in F_2 which is elemental). It can only show -1 or 0 (elemental), so among compounds, it

is always -1.

(b) Element with only positive oxidation state: Cs (caesium).
Cs is an alkali metal with very low ionisation energy. It only loses electrons (is oxidised) to form Cs^+. It never gains electrons to form a negative ion (Cs^- is not known under normal chemical conditions). So Cs exhibits only 0 (elemental) or +1 oxidation state.

(c) Element that exhibits both positive and negative oxidation states: I (iodine).
Iodine shows -1 (e.g., HI, KI), 0 (I_2), and positive states (+1 in ICl, +3 in ICl_3, +5 in HIO_3, +7 in HIO_4). The availability of d-orbitals allows positive oxidation states beyond -1.

(d) Element that exhibits neither negative nor positive oxidation state: Ne (neon).
Neon is a noble gas with a complete octet. It has extremely high ionisation energy and no tendency to gain electrons. Ne exists only in the 0 oxidation state (elemental). It forms no chemical compounds under normal conditions.

Answer: (a) F (only -1 in compounds); (b) Cs (only +1 in compounds); (c) I (shows -1, 0, +1, +3, +5, +7); (d) Ne (always 0, no compounds).

Q23 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

SOLUTION

Cl_2 acts as oxidising agent; SO_2 acts as reducing agent.
Cl: 0 -> -1 (in HCl, reduced).
S: +4 (in SO_2) -> +6 (in H_2SO_4, oxidised).
Electron balance: Cl_2 gains $2e^-$ (2 Cl, $1e^-$ each); SO_2 loses $2e^-$. Perfect 1:1 ratio.

Balanced equation:
$Cl_2(g) + SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2HCl(aq)$

Verify: Cl:2=2✓; S:1=1✓; O:2+2=4=4✓; H:4=2+2=4✓

Answer: $Cl_2(g) + SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2HCl(aq)$

Q24 Refer to the periodic table given in your book and now answer the following questions: (a) Select the possible non metals that can show disproportionation reaction. (b) Select three metals that can show disproportionation reaction.

SOLUTION

(a) Non-metals that can show disproportionation:
For disproportionation, an element must be able to exist in at least three oxidation states — the intermediate state disproportionates into higher and lower states.
Suitable non-metals include:
Cl (chlorine): intermediate states 0 (Cl_2), +1 (ClO^-), +3 (ClO_2^-), +5 (ClO_3^-) can disproportionate (e.g., $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$). Cl_2 (0 state) disproportionates.
P (phosphorus): P_4 disproportionates in alkali -> $PH_3 + H_2PO_2^-$.
S (sulphur): S_8 disproportionates in alkali -> $S^{2-} + S_2O_3^{2-}$.
Br (bromine): similar to Cl, Br_2 disproportionates in base.
Also N, I under certain conditions.

(b) Three metals that can show disproportionation:
Cu: $Cu^+ \rightarrow Cu^0 + Cu^{2+}$ (disproportionation of Cu(I) in aqueous solution: $2Cu^+ \rightarrow Cu + Cu^{2+}$)
Mn: $Mn^{3+} \rightarrow Mn^{2+} + MnO_2 + H^+$ (as in Q_{21})
Au: $Au^+ \rightarrow Au^0 + Au^{3+}$ ($2Au^+ \rightarrow Au + Au^{3+}$, Au(I) is unstable in solution)

Answer: (a) Non-metals: Cl, P, S, Br (and others like N, I) — those with three or more accessible oxidation states. (b) Three metals: Cu ($2Cu^+ \rightarrow Cu + Cu^{2+}$), Mn ($2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$), Au ($2Au^+ \rightarrow Au + Au^{3+}$).

Q25 In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g of ammonia and 20.00 g of oxygen?

SOLUTION

Given: mass of NH_3 = 10.00 g, mass of O_2 = 20.00 g.
Molar masses: NH_3 = 14+3 = 17.0 g/mol; O_2 = 32.0 g/mol; NO = 14+16 = 30.0 g/mol.
Reaction: $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Moles of NH_3 = 10.00/17.0 = 0.5882 mol

Moles of O_2 = 20.00/32.0 = 0.6250 mol

Identify limiting reagent (stoichiometric ratio O_2:NH_3 = 5:4 = 1.25):
O_2 needed to react all NH_3 = 0.5882 x (5/4) = 0.7353 mol
Available O_2 = 0.6250 mol < 0.7353 mol => O_2 is the limiting reagent.

Moles of NO produced = moles of O_2 x (4/5) = 0.6250 x 0.8 = 0.5000 mol
Mass of NO = 0.5000 mol x 30.0 g/mol = 15.00 g

Answer: O_2 is the limiting reagent. Maximum mass of NO = 15.00 g

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Q26 Using the standard electrode potentials given in Table 7.1, predict if the reaction between the following is feasible: (a) $Fe^{3+}(aq)$ and $I^-(aq)$ (b) $Ag^+(aq)$ and Cu(s) (c) $Fe^{3+}(aq)$ and Cu(s) (d) Ag(s) and $Fe^{3+}(aq)$ (e) $Br_2(aq)$ and $Fe^{2+}(aq)$.

SOLUTION

A reaction is feasible if E_cell = E_cathode - E_anode > 0.
Standard electrode potentials from Table 7.1 (all as reduction potentials):
Fe^{3+}/Fe^{2+} = +0.77 V; I_2/I^- = +0.54 V; Ag^+/Ag = +0.80 V; Cu^{2+}/Cu = +0.34 V; Br_2/Br^- = +1.09 V.

(a) $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(s)$:
Cathode (reduction): Fe^{3+}/Fe^{2+} = +0.77 V
Anode (oxidation): I_2/I^- = +0.54 V
E_cell = 0.77 - 0.54 = +0.23 V > 0 => Feasible.

(b) $Ag^+(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$:
Cathode: Ag^+/Ag = +0.80 V
Anode: Cu^{2+}/Cu = +0.34 V
E_cell = 0.80 - 0.34 = +0.46 V > 0 => Feasible.

(c) $Fe^{3+}(aq) + Cu(s) \rightarrow Fe^{2+}(aq) + Cu^{2+}(aq)$:
Cathode: Fe^{3+}/Fe^{2+} = +0.77 V
Anode: Cu^{2+}/Cu = +0.34 V
E_cell = 0.77 - 0.34 = +0.43 V > 0 => Feasible.

(d) $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$:
If Ag is oxidised (anode): Ag^+/Ag = +0.80 V
Fe^{3+} reduced (cathode): Fe^{3+}/Fe^{2+} = +0.77 V
E_cell = 0.77 - 0.80 = -0.03 V < 0 => Not feasible.

(e) $Br_2(aq) + Fe^{2+}(aq) \rightarrow Br^-(aq) + Fe^{3+}(aq)$:

Cathode: Br_2/Br^- = +1.09 V
Anode: Fe^{3+}/Fe^{2+} = +0.77 V
E_cell = 1.09 - 0.77 = +0.32 V > 0 => Feasible.

Answer: (a) Feasible (E_cell = +0.23 V); (b) Feasible (E_cell = +0.46 V); (c) Feasible (E_cell = +0.43 V); (d) Not feasible (E_cell = -0.03 V); (e) Feasible (E_cell = +0.32 V).

Q27 Predict the products of electrolysis in each of the following: (i) An aqueous solution of $AgNO_3$ with silver electrodes (ii) An aqueous solution of $AgNO_3$ with platinum electrodes (iii) A dilute solution of H_2SO_4 with platinum electrodes (iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

SOLUTION

(i) $AgNO_3(aq)$ with silver electrodes:
At cathode (reduction): $Ag^+(aq) + e^- \rightarrow Ag(s)$. Silver deposits on cathode.
At anode (oxidation): Silver electrode dissolves: $Ag(s) \rightarrow Ag^+(aq) + e^-$.
Net effect: Silver transfers from anode to cathode. Solution concentration remains constant.

(ii) $AgNO_3(aq)$ with platinum electrodes:
At cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$. Silver deposits.
At anode (Pt, inert): Water is oxidised (Ag^+ won't be oxidised at Pt in preference to water): $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$. Oxygen gas evolves.

(iii) Dilute $H_2SO_4(aq)$ with platinum electrodes:
At cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$. Hydrogen gas evolves.
At anode: $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$. Oxygen gas evolves.
(SO_4^{2-} is not oxidised at Pt in dilute solution; water is preferentially oxidised.)

(iv) $CuCl_2(aq)$ with platinum electrodes:
At cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Copper deposits. ($Cu^{2+}$ reduced in preference to H^+).
At anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$. Chlorine gas evolves. (Cl^- is oxidised in preference to H_2O in $CuCl_2$ solution due to higher Cl^- concentration — overpotential effect and concentration-driven preference.)

Answer: (i) Ag deposits at cathode; Ag anode dissolves. (ii) Ag deposits at cathode; O_2 evolves at Pt anode. (iii) H_2 at cathode; O_2 at anode. (iv) Cu deposits at cathode; Cl_2 evolves at anode.

Q28 Arrange the following metals in the order in which they displace each other from the solution of their salts: Al, Cu, Fe, Mg and Zn.

SOLUTION

A more active metal (lower/more negative electrode potential) displaces a less active metal from its salt solution.

Standard electrode potentials (reduction):

Mg^{2+}/Mg = -2.37 V (most negative, most active)

Al^{3+}/Al = -1.66 V

Zn^{2+}/Zn = -0.76 V

Fe^{2+}/Fe = -0.44 V

Cu^{2+}/Cu = +0.34 V (least negative, least active)

Order of activity (decreasing): Mg > Al > Zn > Fe > Cu

Each metal displaces all those below it in this series.

Mg displaces Al, Zn, Fe, Cu from their salt solutions.

Al displaces Zn, Fe, Cu.

Zn displaces Fe, Cu.

Fe displaces Cu.

Cu displaces none of the above.

Answer: Order of displacement (decreasing activity): Mg > Al > Zn > Fe > Cu. Each metal in the series displaces all those to its right from salt solutions.

Q29 Given the standard electrode potentials: K^+/K = -2.93 V, Ag^+/Ag = 0.80 V, Hg^{2+}/Hg = 0.79 V, Mg^{2+}/Mg = -2.37 V, Cr^{3+}/Cr = -0.74 V. Arrange these metals in their increasing order of reducing power.

SOLUTION

A metal with more negative standard electrode potential has greater tendency to lose electrons and is a stronger reducing agent.

Standard electrode potentials (reduction):

K^+/K = -2.93 V (most negative => strongest reducing agent)

Mg^{2+}/Mg = -2.37 V

Cr^{3+}/Cr = -0.74 V

Hg^{2+}/Hg = +0.79 V

Ag^+/Ag = +0.80 V (most positive => weakest reducing agent)

Increasing order of reducing power (weakest to strongest):

Ag < Hg < Cr < Mg < K

Answer: Increasing order of reducing power: Ag < Hg < Cr < Mg < K

Q30 Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show: (i) which of the electrode is negatively charged, (ii) the carriers of the current in the cell, and (iii) individual reaction at each electrode.

SOLUTION

The galvanic cell is depicted as:

Zn(s)	$Zn^{2+}(aq)$		$Ag^+(aq)$	Ag(s)
(Single vertical bar	= phase boundary; double bar		= salt bridge)	

(i) Which electrode is negatively charged:
Zn electrode is the anode (oxidation occurs). In a galvanic cell, the anode is negatively charged because electrons accumulate there (produced by oxidation) and flow to the external circuit.

(ii) Carriers of current in the cell:
In the external circuit (metallic wire): electrons carry current, flowing from the Zn anode to the Ag cathode.
In the solution/salt bridge: ions carry the current (cations migrate toward the cathode compartment, anions migrate toward the anode compartment).

(iii) Individual electrode reactions:
At anode (Zn electrode, oxidation): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
At cathode (Ag electrode, reduction): $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

Answer: Cell: Zn | $Zn^{2+}(aq)$ || $Ag^+(aq)$ | Ag. (i) Zn electrode (anode) is negatively charged. (ii) Electrons carry current in external circuit; ions carry current in solution/salt bridge. (iii) Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation); Cathode: $2Ag^+ + 2e^- \rightarrow 2Ag$ (reduction).