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CHEMISTRY
PHYSICAL CHEMISTRY

Level & Board	CIE (A-LEVEL)
TOPIC:	ELECTROCHEMISTRY
PAPER TYPE:	SOLUTION - 1
TOTAL QUESTIONS	13
TOTAL MARKS	166

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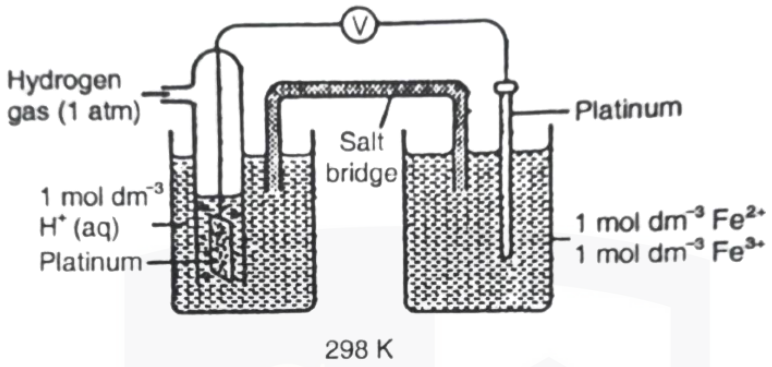
Electrochemistry

1)

(a)



The reading on the voltmeter gives the electrode potential of Fe^{3+} / Fe^{2+}

(b) (i) Sn : Increases from +2 to +4 by units.

O : decreases from -1 to -2 by 1 unit.

(ii) $E^{\ominus}_{cell}$ =177 – 0.15 = +1.62 V > 0

The reaction is energetically feasible under standard conditions.

(c) (i) Ag^+ (aq) + Fe^{2+}(aq) ⟶ Ag(s) + Fe^{3+}(aq)

$E^{\ominus}_{cell}$ = 0.80 – 0.77 = + 0.03 V = 0

Ag^+ will oxidise Fe^{2+} while itself is reduced to metallic Ag.

(ii) $2V^{3+}(aq) + Cu^{2+}(aq) + 2H_2O(l) \longrightarrow 2VO^{2+}(aq) + Cu(s) + 4H^+(aq)$

$E^{\ominus}_{cell}$ = 0 V, no reaction takes place when V^{3+} and Cu^{2+} are mixed.

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2)

(a)

	NaBr(l)	NaBr(aq)	CuF_2(aq)
Cathode	Na	H_2	Cu
Anode	Br_2	O_2	O_2

(i) In NaBr(l), the ions present are Na^+ and Br^-. Hence,

$Na^+ + e^- \longrightarrow Na$

$Br^- \longrightarrow \frac{1}{2}Br_2 + e^-$

(ii) In NaBr(aq), the ions present are Na^+, Br, H^+ and OH^-

H^+ is discharged due to its higher $E^{\ominus}$(0 V) compared to Na^+ (-2.71V).

$H^+ + e^- \longrightarrow \frac{1}{2}H_2$

OH^- ion is discharged preferentially over Br^- due to its lower $E^{\ominus}$ value

(OH^- : + 0.40 V, Br^- : + 1.07 V).

$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

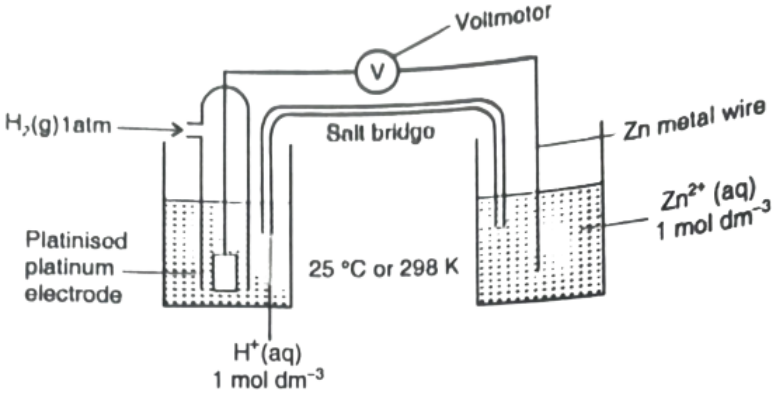
(iii) In CuF_2(aq), the ions present and Cu^{2+} , F- and OH^-

Cu^{2+} is discharged since it has a more positive $E^{\ominus}$(+0.34 V) compared to H^- (0 V).

$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

3)

(a)



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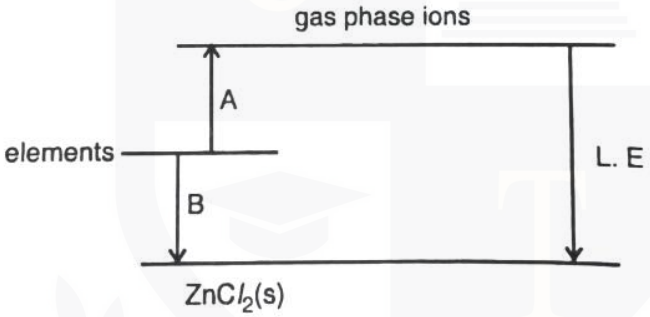
(b)

Conditions	product at anode	product at cathode
$ZnCl_2(1)$	Chlorine	Zinc
$ZnCl_2$ (concentrated aqueous)	Chlorine	hydrogen
$ZnCl_2$ (dilute aqueous)	oxygen	hydrogen

(a)



A + LE = B

LE = B – A

= (- 415) – (131 + 1730) – {244 + 2(- 349)}

∴ Lattice Energy = 2730 KJ mol^{-1}

4)

(a (i) **A:** Cl_2 (chlorine)

B: NaCl or HCl or $Cl^-(aq)$

C: Salt bridge or KNO_3 (aq)

D: Platinum / Pt

E: Mixture of Fe^{2+} Fe^{3+} salts. 1 mol dm^{-3} concentration.

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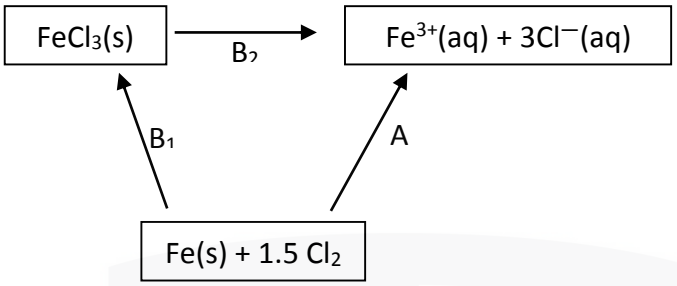
(ii) $E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$ = 0.77 – 1.36 = - 0.59 V.

Direction of electron flow: from right to left

(b) (i)



Apply Hess' law

$\Delta H^{\ominus}_{A} = \Delta H^{\ominus}_{B_1} + \Delta H^{\ominus}_{B_2}$

$\Delta H^{\ominus}_{B_2} = \Delta H^{\ominus}_{A} - \Delta H^{\ominus}_{B_1}$

= [(-48.5) + 3(-167.2)] – (-399.5)

= -550.1 + 399.5 = 150.6 $KJmol^{-1}$

(ii) $2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$

$E^{\ominus}$ = 0.77 – 0.34 = + 0.43V

5)

(a) anode $Cl^-(aq) \rightarrow \frac{1}{2} Cl_{2(g)} + e^-$

cathode: $H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_{2(g)}$

(b) Because the iron in steel will react with chlorine.

(c) (i) Sodium hydroxide (NaOH)

(ii) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Leaving OH^- in solution as NaOH

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(d) sodium: sodium burns with a yellow flame and forms a white solid.

$2Na + Cl_2 \rightarrow SNaCl$

Phosphorus: Phosphorus burns with a white flame and forms a colorless liquid (PCl_3)

OR a white solid PCl_5.

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

$PCl_3 + Cl_2 \rightarrow PCl_5$

(e) MgCl2: 6.5 SiCl4:2

MgCl2 dissolves without reaction SiCl4 reacts with water (Hydrolyse)

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

6)

(a) NaCl(s): observation: Dense white fumes

Equation: $2NaCl + H_2SO_4 \rightarrow NaSO_4 + 2HCl$

NaBr(s): observation: Brown fumes

Equation: $2NaBr + 3H_2SO_4 \rightarrow 2NaHSO_4 + 2H_2O + SO_2 + Br_2$

(b) $E^{\ominus}$ values: Cl_2 / Cl^- = 1.36, Br_2 = 1.07

$E^{\ominus}$ of Cl_2 is more positive, and stronger oxidizing agent therefore HCl will not be oxidized to chlorine

(c) Suitable reductant: Sn^{4+} / Sn^{2+}, $E^{\ominus}$ = 0.15 V

Equation $Sn^{2+} + Br_2 \rightarrow Sn^{4+} + 2Br^-$

$E^{\ominus}$ = reduction – oxidation

= 1.07 – 0.15 = 0.92 V

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7)

(a) (i) variable oxidation status

(ii) able to form complex ions

(b) equation: $MnO^-_4 + 8H + 5Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+} + 4H_2O$

Method: Measure a known volume of Fe2+ (aq) with the help of a pipette and

place in conical flask. Add an excess of dilute H_2SO_4. Titrate the mixture against MnO_4^-

solution of known concentration till permanent pink colour appears. Note the volume of MnO_4^- (aq) Repeat the titration and take average of consistent readings.

(c) (i) $2\ Mn^-_4 + 5\ SO_2\ \ 2\ H_2O \rightarrow 2\ Mn^{2+} + 5\ SO^{2-}_4 + 4\ H^+$

Oxidation numbers: +7 +4 +2 +6

(ii) $1\ Cr_2O^{2-}_7 + 6\ NO_2 + 2\ H^+ \rightarrow 2\ Cr^{3+} + 6\ NO_3^- + 1\ H_2O$

Oxidation numbers: +6 +4 +3 +5

(d) Fe^{3+} is a homogeneous catalyst

Fe^{3+} oxidises I^- to I_2 and reduces itself to Fe^{2+}

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

Fe^{2+} reduces $S_2O^{2-}_8$ to SO^{2-}_4 and oxidises itself to Fe^{3+}

$2Fe^{2+} + S_2O^{2-}_8 \rightarrow 2Fe^{3+} + 2SO^{2-}_4$

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8)

(a) (i) $Cu(s) \rightarrow Cu^{2+} + 2e^-$

(ii) $E^{\ominus}$ for Ag+ / Ag is 0.80V more positive than 0.34V for Cu2+ /Cu(s). Hence silver is less reactive than copper and will not oxidise.

(iii) $E^{\ominus}$ for Ni^{2+} /Ni is -0.25V. Nickel will readily oxidise and terms solutions of nickel ions.

(iv) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (Pure copper)

(v) $E^{\ominus}$ for Zn^{2+} / Zn is -0.76V. Hence Zn^{2+} will not reduce at cathode.

(vi) $Cu^{2+}(aq)$ are reduced at cathode to copper solid. Thus blue solution fades away leaving Zn^{2+} and Ni^{2+} in solution.

(b) (i) Amount of copper $=\frac{225}{63.5}$ = 3.5433 ≈3.54 mol

Number of electrons needed = 2 ×3.5433 = 7.087 ≈ 7.09 mol

No. of coulombs = 1× t = 20 ×10 × 60 × 60 = 720000 C

96500 C of charge is carried by 1 moles of electrons.

720000 C of charge is carried by $\frac{720000}{96500}$ = 7.461 moles of electrons.

∴ 7.46 moles of electrons passed through the cell.

(c) for Ni^{2+} / Ni = - 0.25V

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

iron in the alloy will dissolve because iron is more reactive than Nickel.

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9)

(i) The diaphragm cell consists of a titarium anode and a steel cathode. An asbestos diaphragm is placed between the electrodes.

Purified brine solution, consisting of Na^+ , H^+ , Cl^- and OH^- ions, is pumped into the anode

compartment and the level is kept above that of the cathode compartment.

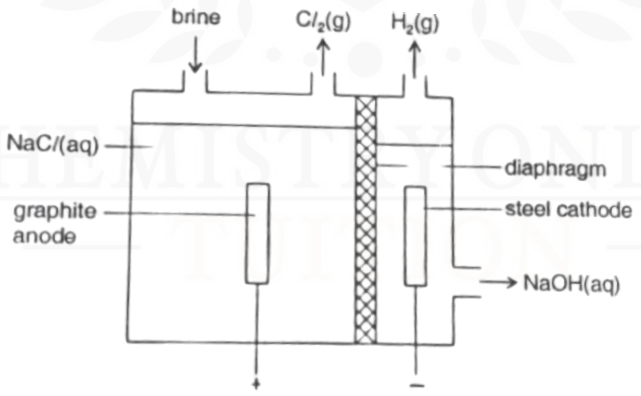
This allows brine solution to seep through the porous asbestos diaphragm into cathode side, and also prevents hydroxide ions migrating to the anode.

This sodium hydroxide solution is formed in the cathode compartment.

The Cl- ions are oxidized at the anode and the H+

ions are reduced at the cathode to form chlorine and hydrogen gas respectively.

The asbestos diaphragm also prevents sodium hydroxide from making contact with the chlorine, therapy preventing the formation of sodium chlorate (I).



(ii) anode: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

cathode: $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

(iii) Sodium Hydroxide.

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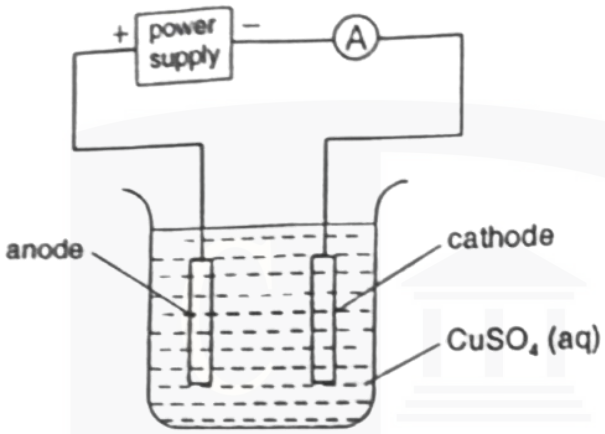
10)

(a) F = Le

(b) (i)



(ii) Moles of copper deposited = $\frac{final\ mass - initial\ mass}{A_r of\ Cu}$

= $\frac{52.542-52.243}{63.5}$ = 0.0047087 ≈ 4.71 × 10^{-3} mol

Since, Cu^{2+} +2e^- → Cu

∴ moles of electrons required = 4.71× 10^{-3} × 2 = 9.42 × 10^{-3}

Amount of charge passed, Q = it

= 0.5 × (30×60) = 900 C

Number of electrons passed = $\frac{Q}{e}$ = $\frac{900}{1.6\times10^{-19}}$ = 5.625 × 10^{21}

∴ $L\ \frac{number\ of\ electrons\ passed}{moles\ of\ electrons\ required}$

= $\frac{5.625\times10^{21}}{9.42\times10^{-3}}$ = 5.97 × 10^{23} mol^{-1}

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(c)

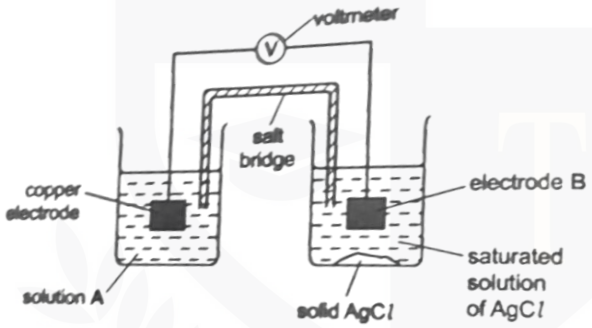
Compound	Product at anode	Product at cathode
AgF	O_2	Ag
$FeSO_4$	O_2	H_2
$MgBr_2$	Br_2	H_2

11)

(a) (i) Solution: A: CuSO4

Electrode B: silver

(ii)



(b) (i) Ag+ + e- ⇌ Ag $E^{\ominus}$= + 0.80V

Cu2+ + 2e- ⇌ Cu $E^{\ominus}$ = + 0.34V

$E^{\ominus}_{cell}$ = 0.80 – 0.34 = + 0.46V

(ii) E_{cell} = 0.17V, standard $E^{\ominus}_{cell}$ = 0.46V

$E^{\ominus}_{cell}$ - E_{cell} = 0.46 – 0.17 = 0.29V

∴ $E_{Ag\ electrode}$ = 0.80 – 0.29 = 0.51V

(iii) $E_{electrode}$ = $E^{\ominus}_{electrode}$ + 0.06 log[Ag^+]

0.51= 0.80 + 0.06 log[Ag^+]

log[Ag^+] = $\frac{0.51-0.80}{0.06}$

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$\log[Ag^+] = -4.8333$

$[Ag^+] = 10^{-4.8333}$

$= 1.47\times10^{-5}$ mol/dm^3

(c) (i) $K_{sp} = [Ag^+]^2[SO^{2-}_4]$, units: mol^3/dm^9

(ii) $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO^{-2}_4$

$[SO_4^{-2}] : [Ag^+] = 1 : 2$

$\Longrightarrow [SO_4^{-2}] = \frac{[Ag^+]}{2}$

$\therefore K_{sp} = (1.6\times10^{-2})^2 \times \left(\frac{1.6\times10^{-2}}{2}\right)$

$= 2.048 \times 10^{-6} \approx 2.05 \times 10^{-6}$ mol^3/dm^9

(d) Solubility of silver Halides in NH_3(aq) decreases down the group/ also, AgCl is white, AgBr has a cream colour, and AgI is yellow in colour. This information can be used to distinguish between solutions of the halide ions Cl^- , br^- and I^-

(e) Solubility decreases down the group, as the cationic size increases and lattice energy decreases. The hydration energy of the cation also decreases. The decrease in hydration energy is more than the lattice energy therefore H $\Delta H_{solution}$ becomes more endothermic.

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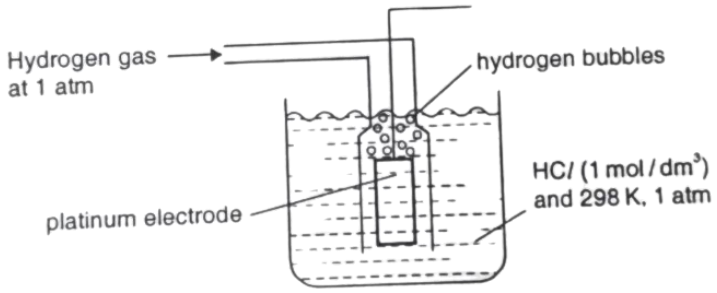
12)

(a) (i)



(ii) $Cr^{3+} + e^- \rightleftharpoons Cr2+$ ($E^{\ominus}$ = - 0.41V)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ ($E^{\ominus}$ = + 1.33)

$\therefore\ E^{\ominus}_{cell}$ = 1.33 – (- 0.41) = 1.74 V

equation: $Cr_2O_7^{2-} + 14H^+ 6Cr^{2+} \rightleftharpoons 8Cr^{3+} + 7H_2O$

(iii) The colour of the solution changes from orange to green.

(b) $pKa = -\log_{10}(K_a(CH_3CO_2H))$

$= -\log_{10}(1.79 \times 1=^{-5}) = 4.75$

$pH = pK_a + \log_{10}\left(\frac{(salt)}{(acid)}\right) \implies \log_{10}\left(\frac{[CH_3CO_2Na]}{[CH_3CO_2H]}\right) = pH - pK_a$

$= 5.5 – 4.75 = 0.753$

$\implies \left(\frac{[CH_3CO_2Na]}{[CH_3CO_2H]}\right) = 10^{0.753} = 5.66$

Let volume of CH_3CO_2H be x and volume of CH_3CO_2Na be y in the 100 cm^3 buffar solution

Thus, $\frac{y}{x} = 5.66 \implies y = 5.66x$

Also, $x + y = 100 \implies x + 5.66x = 100 \implies x = 15.0\ cm^3$

$\therefore y = 100 – x = 100 – 15 = 85\ cm^3$

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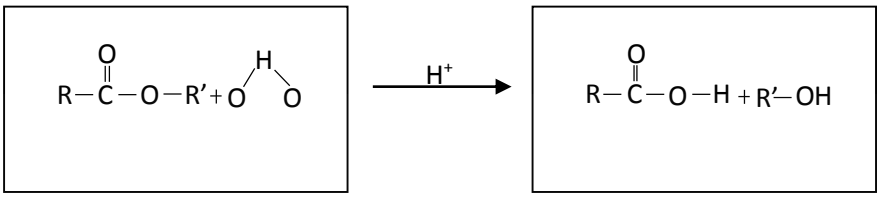
(c) (i) added HCl: $CH_3CO_2Na + HCl \longrightarrow CH_3CO_2H + NaCl$

(ii) added NaOH : $CH_3CO_2H + NaOH \longrightarrow CH_3CO_2Na + H_2O$

(d)



13)

(a) A: Voltmeter

B: Platinum

C: 1 mol / dm^2 HCl

D: Lead

(b) (i)

Electrode potential / V	Place one tick only in this column
- 0.17	√
- 0.13	
- 0.9	
0.00	

Explanation: $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$. As $[Pb^{2+}]$ decreases from 1 mol/dm^3, the equilibrium shifts towards the left hand side and Pb^{2+} is less likely to be reduced.

(ii) $K_{sp} = [Pb^{2+}][Cl^-]^2$

(iii) Given that, $[PbCl_2] = 3.5 \times 10^{-2}$ mol/dm^3

$\therefore [Pb^{2+}] = 3.5 \times 10^{-2}$ mol/dm^3, $[Cl^-] = 7 \times 10^{-2}$ mol/dm^3

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$= (3.5 \times 10^{-2}) (7 \times 10^{-2})^2 = 1.715 \times 10^{-4}$ mol/dm^3.

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(c) (i) $E^{\ominus}$ $Pb^{2+}Pb$ = - 0.13V and $E^{\ominus}(Sn^{2+}/Sn)$ = - 0.14V

Since the two electrode potentials are very close, therefore the behavior of $PbCl_2$ and $SnCl_2$ towards reducing agents is very similar.

However, $E^{\ominus}(Sn^{4+}/Sn^{2+})$ = 0.15V and $E^{\ominus}(Pb^{4+}/Pb^{2+})$ = 1.69V.

This means that Sn^{2+} is easily oxidized to Sn^{4+} but Pb^{2+} is not easily oxidized to Pb^{4+}.

(ii) the reduction of $PbCl_2$: $PbCl_2 + Zn \longrightarrow Pb + ZnCl_2$.

The oxidation of $SnCl_2$: $Sn^{2+} + Br_2 \longrightarrow Sn^{4+} + 2Br^-$.

(d) (i) $Pb^{2+}(g) + 2Cl^-(g) \longrightarrow PbCl_2(s)$

(ii) $\Delta H_f = \Delta H_{at} + E(Cl - Cl) + 1^{st}$ IE(Pb) + 2^{nd} IE(Pb) + $2 \times E_A$ (Cl) + LE

- 359 = 195 + 242 + 716 + 1450 + (2×- 349) + LE

LE = - 2264 KJ/mol

(iii) Lattice energy of PbCl2 would be greater than the lattice energy of PbBr2 as the chloride ion has a smaller ionic radius than the bromide ion.

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