10/03/19

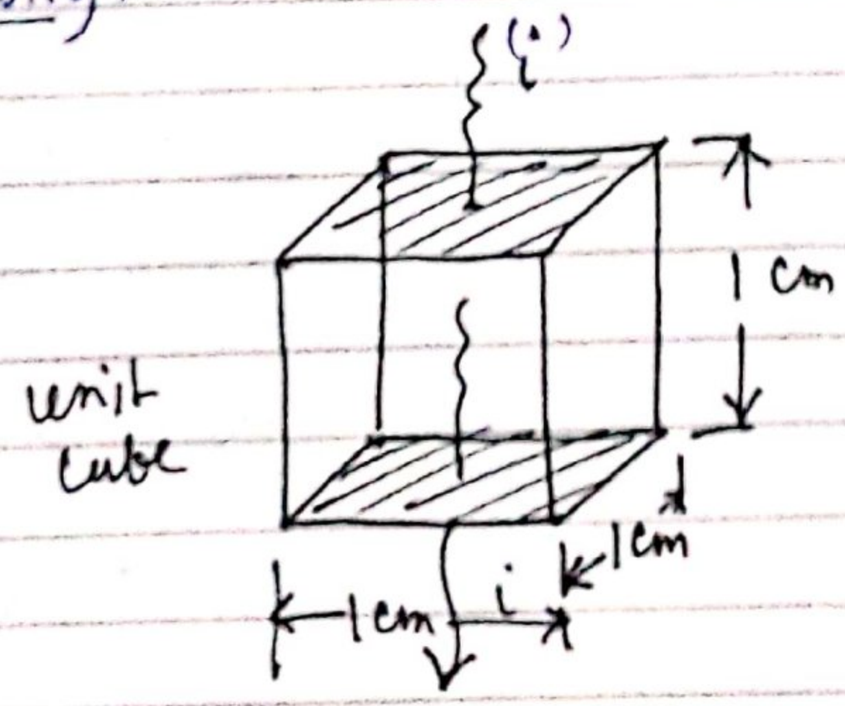
Electro Chemistry

$\therefore$ Resistance, $R \propto \frac{l}{A}$ where l = length of the conductor
A = cross sectional area of the conductor

or $R = \rho \frac{l}{A}$ where The proportionality constant ρ is known as specific resistance or resistivity.

When $l = 1$ cm
& $A = 1$ cm^2 then $R = \rho . 1 \Rightarrow$ from this we can define sp. resistance as – when a current 'i' amp is made to pass ~~through~~ from one face to the opposite one through a unit cube made of the same material with which the conducting wire is made the resistance felt by it is known as specific resistance or resistivity.

$\rho = \frac{R.A}{l}$



Unit of sp. resistance is Ω cm

The reciprocal of ρ is known as specific conductance or conductivity (κ) kappa.

λ

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\frac{l}{A} = C\frac{l}{A}$$

Conductance is the reciprocal of resistance

Cell constant

There are two more conductances well known such as – ① Equivalent Conductance (Λ_{equiv}) and ② Molar Conductance (Λ_M)

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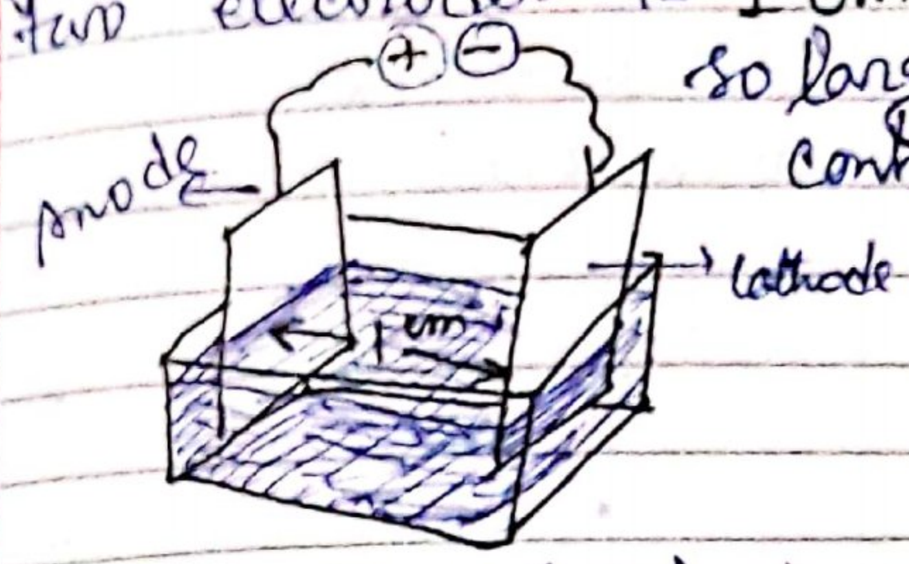
Sp. conductance = Conductance × Cell constant

Unit of specific conductance = Siemens cm^{-1}
or, = $\Omega^{-1} cm^{-1}$ = mho cm^{-1}

Equivalent Conductance (Λ_{equiv}) of a solution at a dilution V may be defined as the conductance of all the ions produced from 1 gm equivalent of the electrolyte dissolved in V cm^3 of the solution when the distance between the two electrodes is 1 cm. and the area of the electrodes is so large that whole of the solution is contained between them.



$$\Lambda_{equiv} = K \times V$$

Suppose the solution has a concentration c gmequiv/litre.
∴ 1000 ml soln contains c gm equiv. of solute

∴ 1 gm equiv. of solute is dissolved in $\frac{1000}{c} = V$

$$\therefore \Lambda_{equiv} = K \times \frac{1000}{C_N}$$

where C_N = concentration of the soln in gm equiv/litre a Normal solution.

$$\boxed{\Lambda_{equiv} = \frac{K \times 1000}{N}}$$

N = Normality

Unit of Equiv. Conductance = S cm^2 (gm equiv/litre)$^{-1}$ (S: siemens)

Molar Conductance (Λ_M) can be defined in similar way as equiv. conductance expressed as

$$\boxed{\Lambda_M = \frac{K \times 1000}{M}}$$

M = molarity

Unit of Molar Conductance = S cm^2 (gmmole/litre)$^{-1}$

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Relation between Equivalent & Molar Conductances

$$\boxed{\Lambda_M = Z \times \Lambda_{equiv.}}$$

where $Z = Z_+ v_+$ or $Z_- v_-$, when $Z_{(+)}$ & $Z_{(-)}$ are the charges of cations and anion and $v_{(+)}$ & $v_{(-)}$ are the absolute valencies of cation & anion respectively.

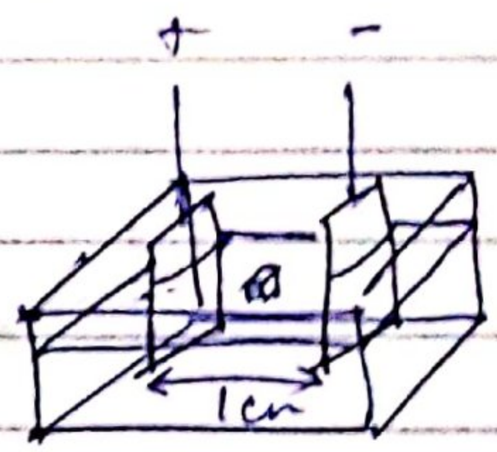
Species	Z
NaCl	$1 \times 1 = 1$
$CaCl_2$	$1 \times 2 = 2$
$AlCl_3$	$1 \times 3 = 3$
Na_2CO_3	$2 \times 1 = 2$

Effect of Dilution on Conductance

$\uparrow \Lambda_M \propto \uparrow$ Dilution

& $\uparrow \Lambda_{equiv.} \propto \uparrow$ Dilution but

$\uparrow R \propto \frac{1}{\text{dilution} \downarrow}$



Both the equivalent and molar conductances of a solution increase with dilution while the specific conductance of a solution decreases with rising dilution. This is because ions present per cm^3 of the solution becomes less and less on dilution while in case of molar and equivalent conductances the number of ion increases as the ~~rat~~ degree of dissociation of electrolyte increases with dilution since increase in no. of ions ~~much~~ on dilution becomes much less

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than increase in the volume of the solution in case of specific conductance kappa.

Variation of Molar Conductance and Equivalent Conductance with Concentration

In the lower concentration range (i.e. in high dilution) the molar conductivity of a strong electrolyte (like - KCl, NaCl etc.) is found to obey the following equation called Debye Hückel Onsagar equation.

$$\Lambda_m = \Lambda_m^{\infty} - \left[A + B\Lambda_m^{\infty}\right]\sqrt{C}$$

where A & B are called Debye Hückel constantants

$$A = \frac{82.4}{(DT)^{1/2}\eta} \qquad B = \frac{8.20\times10^{5}}{(DT)^{3/2}}$$

D and η are the dielectric constant & coefficient of viscosity of the medium respectively at temp. T K and C is the molar concentration. (mole L^{-1})

or $\Lambda_m = \Lambda_m^{\infty} - A\sqrt{C}$

When concentration $C \to 0$ then $\lim_{C\to 0} \Lambda_m = \Lambda_m^{\infty}$ (or Λ_m^{0})

Λ_m^{∞} is the limiting value of the molar conductance at infinite dilution

If 'α' be the degree of ionisation then

$$\alpha = \frac{\Lambda_m^{c}}{\Lambda_m^{0}}$$

Λ_m^{c} → molar conductance at concn C

Λ_m^{0} → molar conductance at infinite or zero dilution

If we plot different values of molar conductances against $\sqrt{C}$ the graph is linear in lower concentration range for strong electrolytes like - KCl and there is slight deviation from linearity in higher concentration. However we can obtain the value of Λ_m^{0} or Λ_m^{∞} by extrapolating the graph to $\sqrt{C} = 0$

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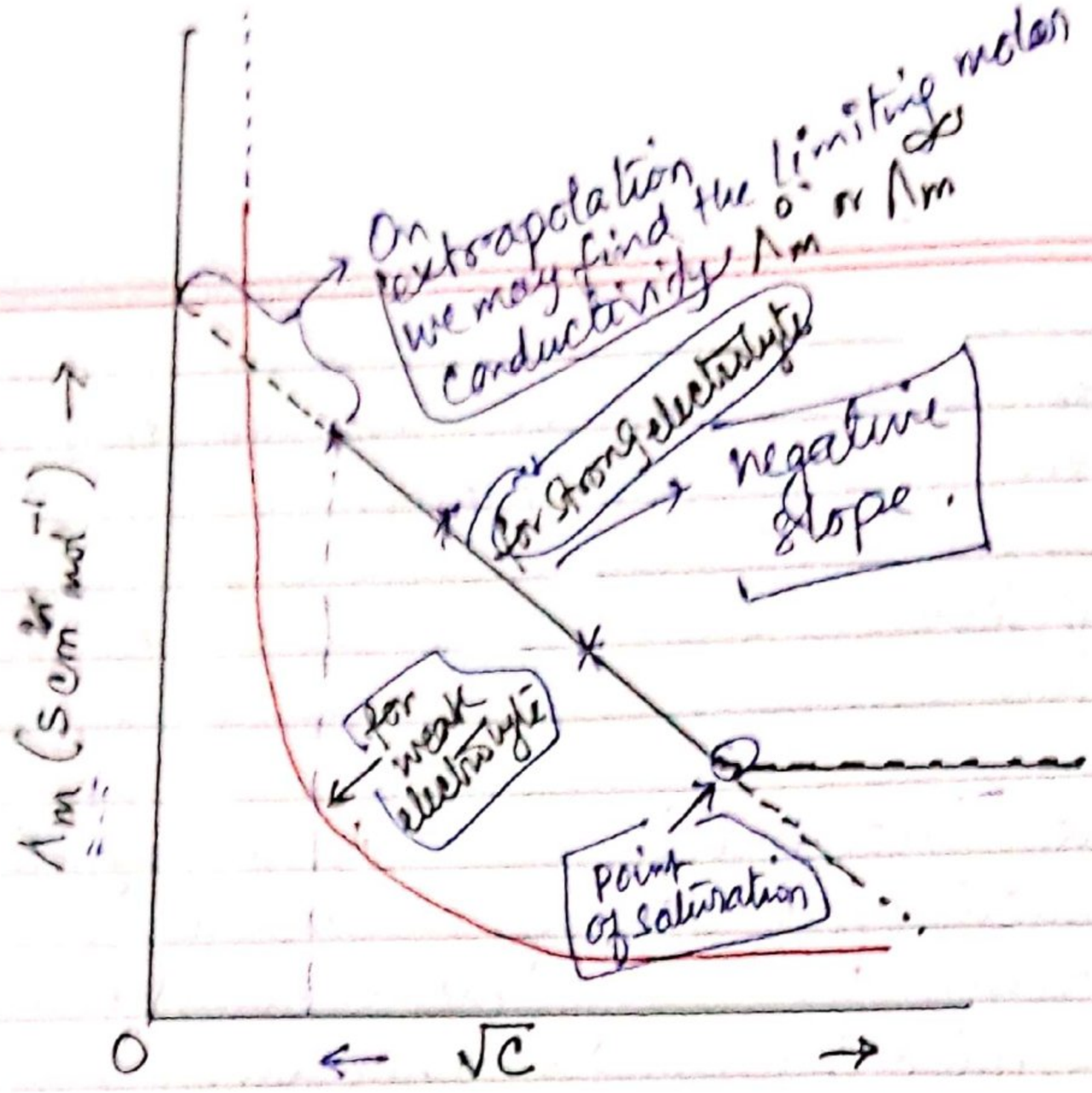

This decrease is not due to a change in the number of ions with concentration but due to change in the interionic attractions. At high concentration there are greater no. of ions per unit volume which increases the attraction between K^+ and Cl^- as a result of which the conducting ability of ions reduces. Hence, Λ_m falls with rise in concentration. When solution is diluted ($\sqrt{C}$ decreases) there is decrease in ionic attraction. Hence, Λ_m increases with decrease in concentration.

Like-Charged

If we plot the same for a weak electrolyte, we will get the same trend of graph and in this case we cannot find the value of limiting molar conductivity only by simple extrapolation.

8. The value of limiting molar conductance (Λ_m^∞) for weak electrolytes is actually obtained by an indirect method based on **Kohlrausch's law of Independent Migration of ions.**

→ see next page →
to next

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3.9 Λ_m = [illegible]

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

initially no. of moles	c	0	0
After ionisation where 'α' is the degree of ionisation then	$c - c\alpha$	$c\alpha$	$c\alpha$

The dissociation constant of HA at definite temp.

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

$$= \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

or

$$K_a = \frac{c\left(\frac{\Lambda_m}{\Lambda_m^0}\right)^2}{\left\{1 - \left(\frac{\Lambda_m}{\Lambda_m^0}\right)\right\}}$$

or

$$\boxed{K_a = \frac{c \times \Lambda_m^2}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m)}}$$

According to Kohlrausch's law of independent migration of ions at infinite dilution —

$$\Lambda^0_{HCOOH} = \Lambda^0_{H^{\oplus}} + \Lambda^0_{COOH^{\ominus}}$$

$$= (349.6 + 54.6)\ S\,cm^2\,mol^{-1}$$

$$= 404.2\ S\,cm^2\,mol^{-1}$$

Degree of dissociation $\alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}} = \frac{46.1}{404.2} = 0.114$

The dissociation constant $K_a = \frac{0.025(46.1)^2}{404.2(404.2 - 46.1)} = \frac{53.13025}{144744.02} = 3.67 \times 10^{-4}$

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21/04/19

Kohlrausch's law of Independent Migration Of Ions

According to this law - "The equivalent conductance of an electrolyte at infinite dilution is the sum of 2 values, one depending upon the cation and the other upon the anion."

$$A_mB_n \rightleftharpoons mA^{n+} + nB^{m-}$$

At infinite dilution or zero th concentration $\Lambda^{\circ}_{m(A_mB_n)} = m\Lambda^{\circ}_{m(A^{n+})} + n\Lambda^{\circ}_{m(B^{m-})}$

Then How can we determine the limiting molar conductance of weak electrolyte like CH_3COOH at its infinite dilution

Ans

$$\Lambda^{\circ}_{m(CH_3COOH)} = ?$$

If we are provided the values of limiting molar conductance of CH_3COONa, HCl, NaCl then

$$\Lambda^{\circ}_{m(CH_3COONa)} + \Lambda^{\circ}_{m(HCl)} - \Lambda^{\circ}_{m(NaCl)} = \Lambda^{\circ}_{m(CH_3COOH)}$$

$$\Lambda^{\circ}_{m(CH_3COOH)} = \Lambda^{\circ}_{m(CH_3COONa)} + \Lambda^{\circ}_{m(HCl)} - \Lambda^{\circ}_{m(NaCl)}$$

$$= \Lambda^{\circ}_{m(CH_3COO^-)} + \cancel{\Lambda^{\circ}_{m(Na^+)}} + \Lambda^{\circ}_{m(H^+)} + \cancel{\Lambda^{\circ}_{m(Cl^-)}}$$

$$- \cancel{\Lambda^{\circ}_{m(Na^+)}} - \cancel{\Lambda^{\circ}_{m(Cl^-)}}$$

$$= \Lambda^{\circ}_{m(CH_3COO^-)} + \Lambda^{\circ}_{m(H^+)}$$

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NCERT Exercise 3

Q.3.9 $R = 1500\ \Omega$ Concentration of KCl soln $= 0.001M$

(Cell constant) $\frac{l}{A} = ?$, $k = 0.146 \times 10^{-3}\ S cm^{-1}$

$$R = \rho \frac{l}{A}$$

$$1500 = \frac{1}{k} \cdot \frac{l}{A}$$

$$\left(\text{cell constant}\right) \frac{l}{A} = 1500 \times 0.146 \times 10^{-3}\ cm^{-1}$$

$$= 0.219\ cm^{-1}$$

Q.3.11 $k = 7.896 \times 10^{-5}\ S cm^{-1}$

Molar Concentration is given as $= 0.00241M$

$$\Lambda_m = \frac{1000 \times k}{M}$$

$$= \frac{10^3 \times 7.896 \times 10^{-5}}{0.00241}$$

$$= 32.76348 5\ S cm^2 (mole/litre)^{-1}$$

if $\Lambda^o_{m(CH_3COOH)} = 390.5\ S cm^2 mol^{-1}$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{32.763485}{390.5}$$

$$= 0.0839$$

$$K_c = \frac{c\alpha^2}{1-\alpha} = \frac{0.00241 \times 0.007}{1 - 0.3090}$$

$$= \frac{0.00001687}{0.9161}$$

$$= 1.84 \times 10^{-5}$$

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For strong electrolytes the values of molar conductivity at infinite dilution are given below

Electrolyte	Λ_m° ($S\ m^2\ mol^{-1}$)
$BaCl_2$	280×10^{-4}
$NaCl$	126.5×10^{-4}
$NaOH$	248×10^{-4}

Calculate $\Lambda_m^\circ [Ba(OH)_2]$

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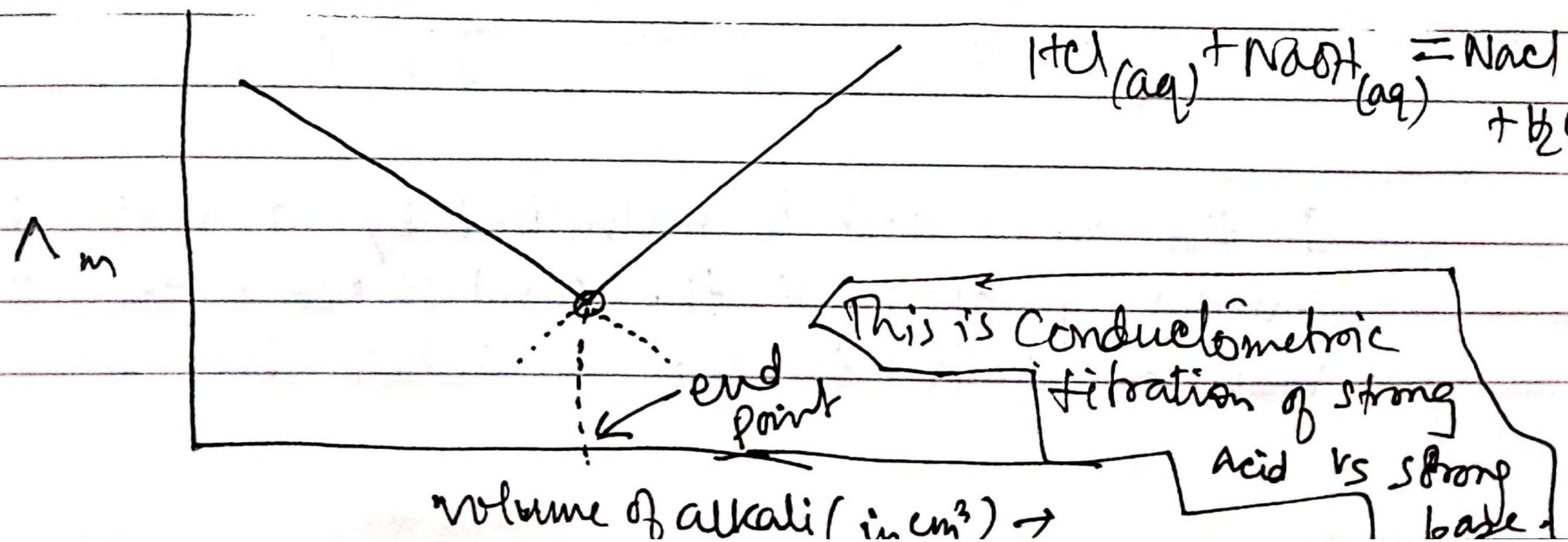
Conductometric titration

A known volume of an acid is taken whose initial conductance is measured. The alkali whose strength should be much higher than that of the acid (in order to avoid dilution error) is added from micro burette in small amounts and the conductance is measured after each addition when the temperature is kept constant. The observed conductances are plotted against the volume of titre added.



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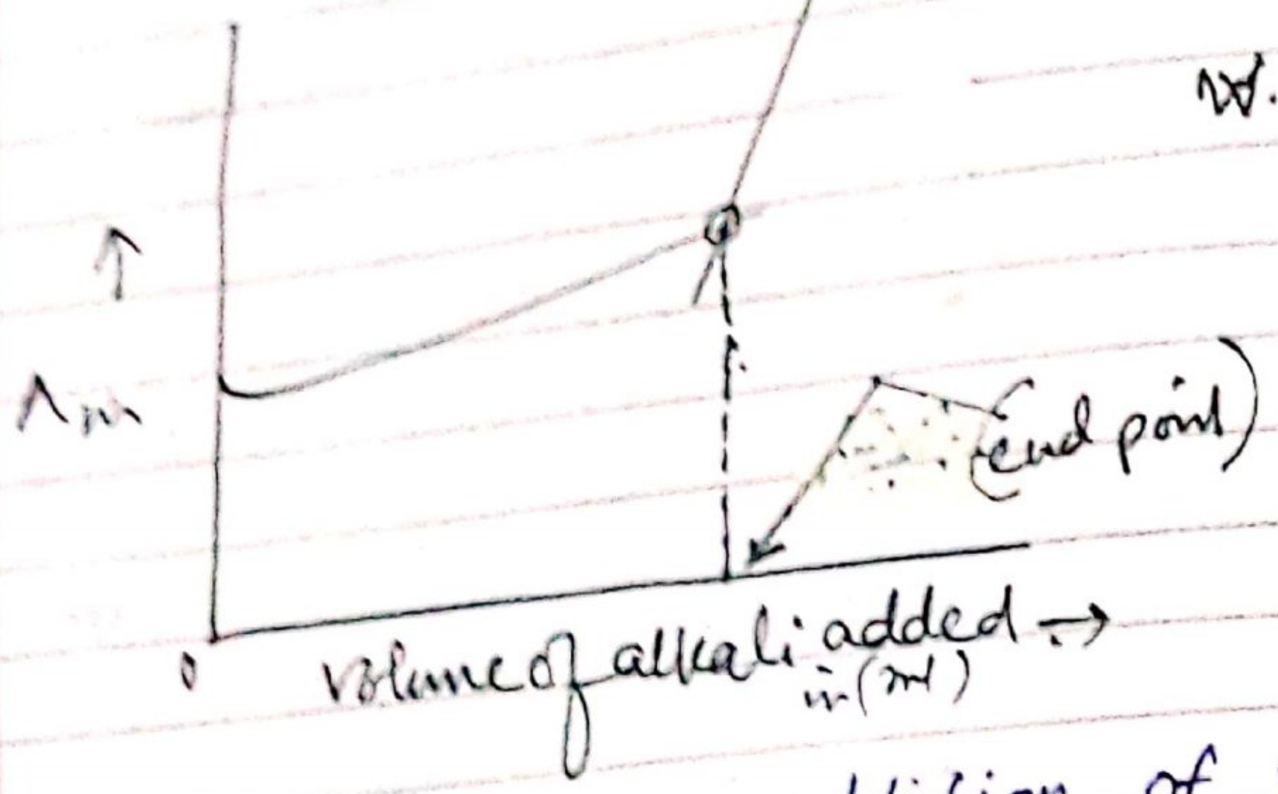
What would be nature of the graph (in conductometric titration) when (i) a weak acid is titrated against a strong base ? (ii) weak acid vs weak base

(i)



$CH_3COOH_{(aq)} + NaOH_{(aq)}$

W. acid (S. base)

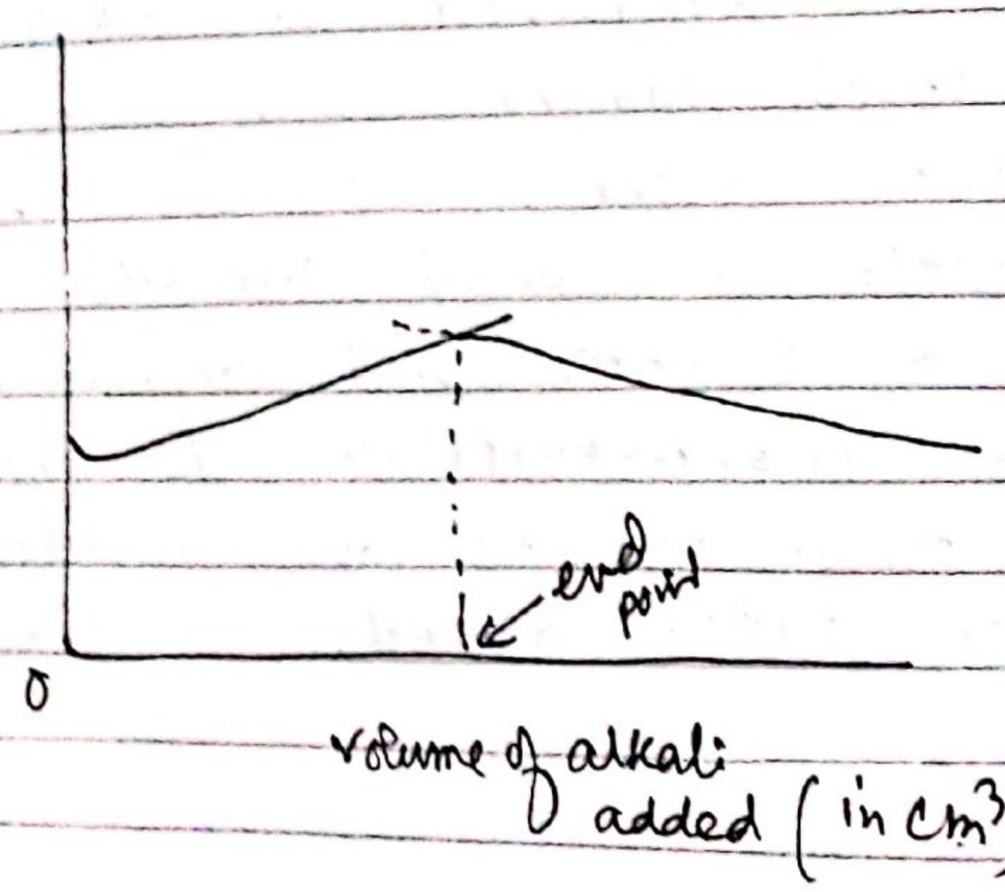
$\downarrow$

$CH_3COO^-Na^+ + H_2O$

(Strong conjugate base)

In this case every addition of OH^- ions from burette into AcOH solution will form more conducting OAc^- ion, thus conductance starts to increase slightly. After complete neutralisation of AcOH, further addition of alkali, (OH^- ion) will rapidly increase in conductance.

(ii)



If the weak acid is neutralised by a weak base, the starting portion of the conductance – titer curve would be similar to that of s. base but when the

$$1e = \frac{1 \text{ Faraday}}{N_A}$$

$$1.602 \times 10^{-19} C \times N_A = 1 \text{ Faraday}$$

∴ Faraday is the charge of 1 mole of e.

end point is reached further addition of base will make very little change in conductance as the base is weak.

Conductometric acid base titrations are very useful in coloured solutions. It is used in :-
(i) following the rate of reaction
(ii) In monitoring the flow process in industries
(iii) In vat dying
(iv) In stream pollution studies
(v) In finding hardness of water

Quantative Aspects of Electrolysis

Michael Faraday showed that the amounts of substance produced at an electrode by electrolysis depends on the quantity of charge passed through the cell. For example, passage of Down's cell yields 1 mol. ie 23g of sodium at the cathode.

$$Na^+_{(g)} + e \longrightarrow Na_{(s)}$$

1 mole 1 mole 1 mole

Quantitative aspects of electrolysis are governed by Faraday's laws of electrolysis :-

First Law of Electrolysis

The amount of chemical change which occurs at any electrode produced is ∝ to the quantity of electric change passing through an electrolytic cell. Greater the no. of moles of electrons transferred the greater the mass of products.

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Coulomb = ampere × second

$Q = (i) \times (t)$

Suppose 'W' gm of a substance is deposited at an electrode when Q coulombs of electricity are passed, then from the 1st law of Faraday we may write

$W \propto Q$.

or $W = ZQ$ where Z, the proportionality constant known as E.C.E (Electrochemical equivalent) which be defined as — "The amount of substance deposited when 1 Coulomb ~~current~~ electric charge is made to pass through the electrolytic solution or mass deposited when 1 ampere current is passed through the soln. for 1 second

when $Q = 1$ Coulomb then $W = Z.1$

$Q = 1$ amp × 1 second

$$Z = \frac{\text{Equivalent mass}}{\text{Faraday}} = \frac{\text{Atomic mass of the substance}}{\text{no. of electrons exchanged during electrolysis} \times \text{Faraday}}$$

2nd law of Faraday's Electricity

If the given quantity of electricity is passed through different electrolytes the different amount of chemical changes produced are all chemically equivalent.

In another way, a given quantity of electricity produces the same number of equivalents of any substance on electrolysis

$$\frac{\text{mass of metal A}}{\text{mass of metal B}} = \frac{\text{equivalent weight of A}}{\text{equivalent weight of B}}$$

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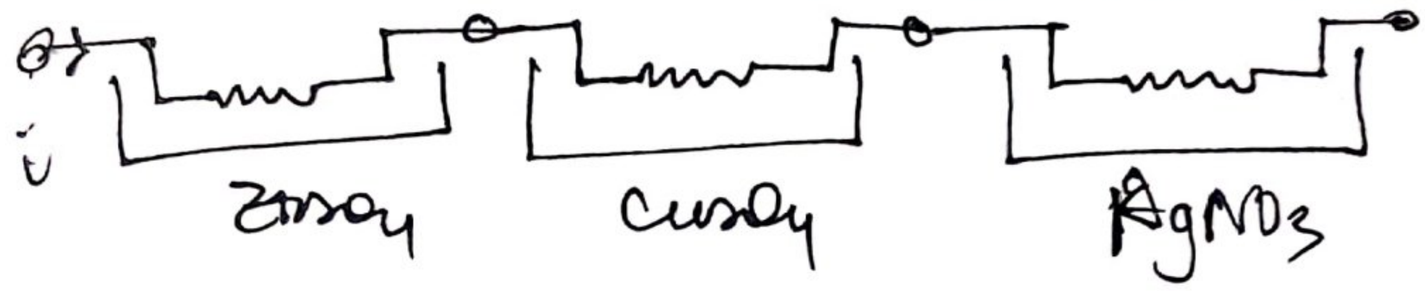

Q.

A B

$W_A \propto Q$ $W_B \propto Q$

or $W_A = Z_A Q$ $W_B = Z_B Q$

$$\frac{W_A}{Z_A} = \frac{W_B}{Z_B} \Rightarrow \frac{W_A}{W_B} = \frac{Z_A}{Z_B} = \frac{\frac{\text{Equiv. mass } A}{F}}{\frac{\text{Equiv. mass } B}{F}} = \frac{E_A}{E_B}$$

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Types of Conductors

	Metallic Conductors	Electrolytic Conductors
(i)	Flow of Electricity undergoes without decomposition of the substance in dry and pure state	(i) Flow of electricity undergoes with decomposition of substance only in aqueous/molten/fused state
(ii)	Electricity produced due to movement of free electrons (no flow of matter takes place)	(ii) Electricity produced due to flow of ions (matter).
(iii)	As temperature increases, conductance decreases due to increase in kernel vibration which causes increase in resistance	(iii) As temperature increases, conductance increase due to increase in dissociation.
(iv)	Resistance caused due to vibration in kernel.	(iv) Resistance caused by inter ionic interactions and viscosity of solvent
(v)	Faraday's Law is not followed.	(v). Faraday's Law is followed
(vi)	They are ohmic conductors.	(vi) They are non-ohmic conductors

(Oxidation) $Zn_{(s)} - 2e \rightarrow Zn^{++}_{(aq)}$

$Cu^{++}_{(aq)} + 2e \rightarrow Cu \downarrow$ red ppt.

net rxn: $Zn_{(s)} + Cu^{++}_{(aq)} \rightarrow Cu\downarrow_{(ppt)} + Zn^{++}_{(aq)}$

Mechanism

This is an example of direct redox rxn → This heat energy arises due to conversion of chemical energy into heat energy as the rxn is spontaneous redox rxn i.e. $\Delta G < 0$

We need to make it as indirect redox rxn just to collect this chemical energy as electrical energy

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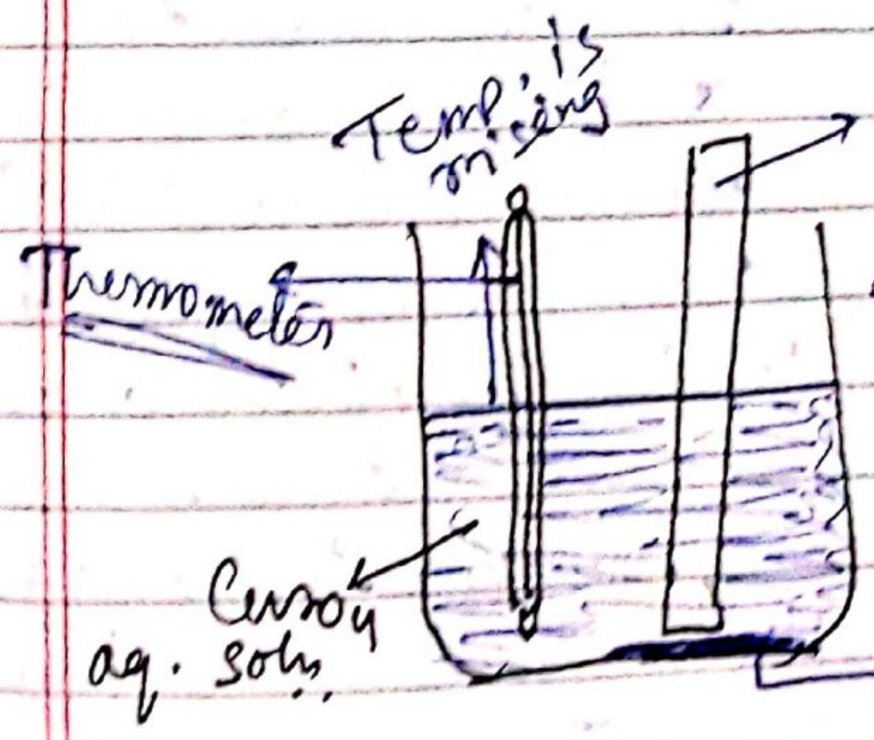
Types of Electrochemical Cells

Electrolytic Cell	Galvanic / Voltaic Cell
(i) It is a device which converts electrical energy to chemical energy i.e electrical energy is supplied to the electrolytic solution to bring out redox reaction.	(i) It is a device which converts chemical energy to electrical energy i.e electrical energy is produced with the help of redox reaction
(ii) Redox reaction is non spontaneous	(ii) Redox reaction is spontaneous
(iii) Both electrodes are fitted in the same beaker filled with electrolyte.	(iii) Both electrodes are fitted in different compart-ments.
(iv) Negative electrode: Cathode Positive electrode: Anode	(iv) Negative electrode: Anode Positive electrode: Cathode
(v) Ions are discharged on both the electrodes	(v) Ions are discharged only on the cathode.
(vi) No salt bridge is used	(vi) No salt bridge or porous pot is used



If a Zn rod is dipped into the deep blue solution $CuSO_{4(aq)}$ solution then what changes will we observe?

Ans: (i) Zn rod is reduced in weight.

(ii) Blue colour of the solution fades away.

(iii) Red ppt under the Zn rod.

(iv) Temp. rises.

$Zn + CuSO_4 = ZnSO_4 + Cu\downarrow$ (red ppt)

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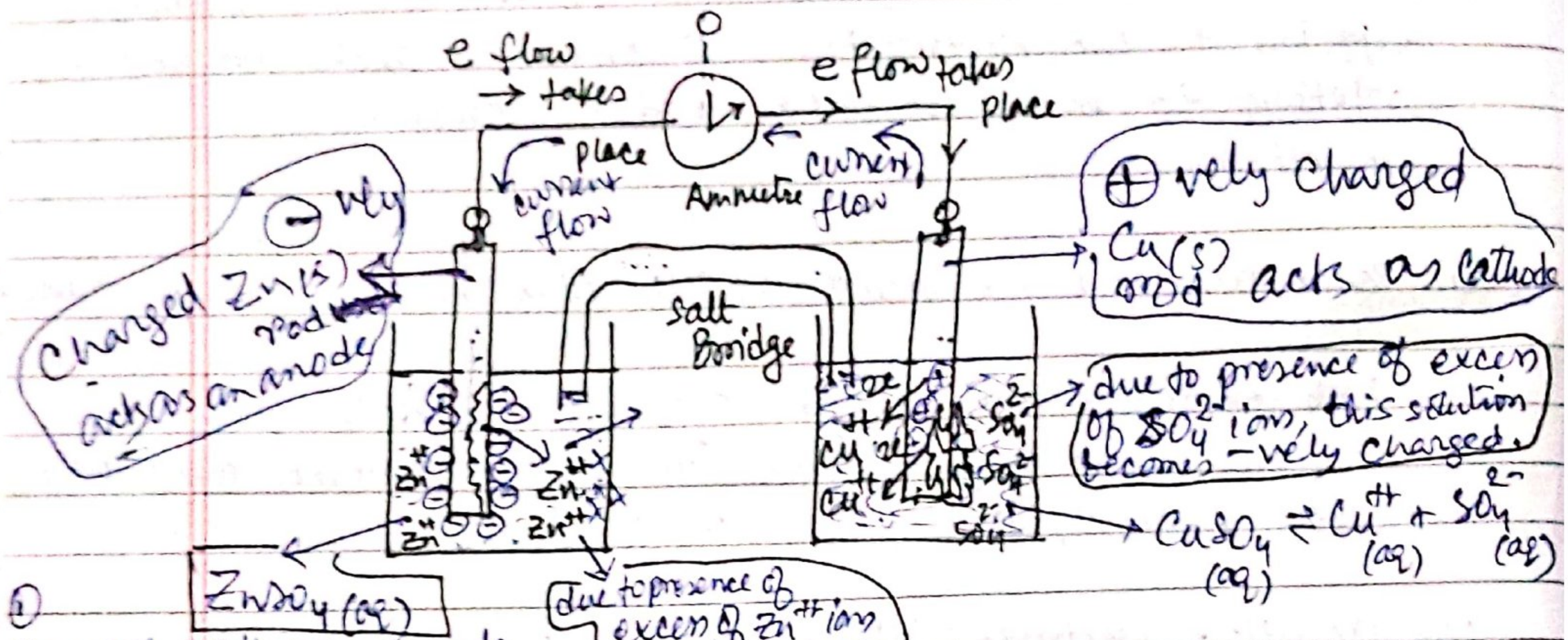
{Ni-Ag Cell
{Cr-Pb Cell etc.

① **Zn-Cu Couple or Daniel Cell** — is an example of Galvanic Cell or Voltaic cell.

② It also is an example of indirect redox rxn in which heat energy is converted into electrical energy.



① As much as the rxn proceeds due to emanation of Zn^{++} ions the total +ve charge of the $ZnSO_4$ soln increases, conc^n of Zn^{++} ion increases & the charge of the dipped Zn rod becomes -ve due to the fact that electroclouds surrounding the Zn rod.

$$Zn_{(s)} - 2e \rightleftharpoons Zn^{++}_{(aq)}$$

Oxidation takes place at Zn rod.

② As long as the rxn proceeds the Zn rod becomes thin to thinner due to degradation.

$$Cu^{2+}_{(aq)} + 2e \rightleftharpoons Cu_{(s)}$$

reduction takes place at Cu rod

① As Cu^{++} ions in $CuSO_4(aq)$ soln swallow electrons coming from Zn rod the overall charge of the Cu rod becomes +ve due to the deficiency of electron or -ve cloud.

② As much as the rxn proceeds the Cu rod becomes thick to thicker due to deposition of Cu, as a result of which the concentration of Cu^{++} decreases which makes the blue colour fades away.

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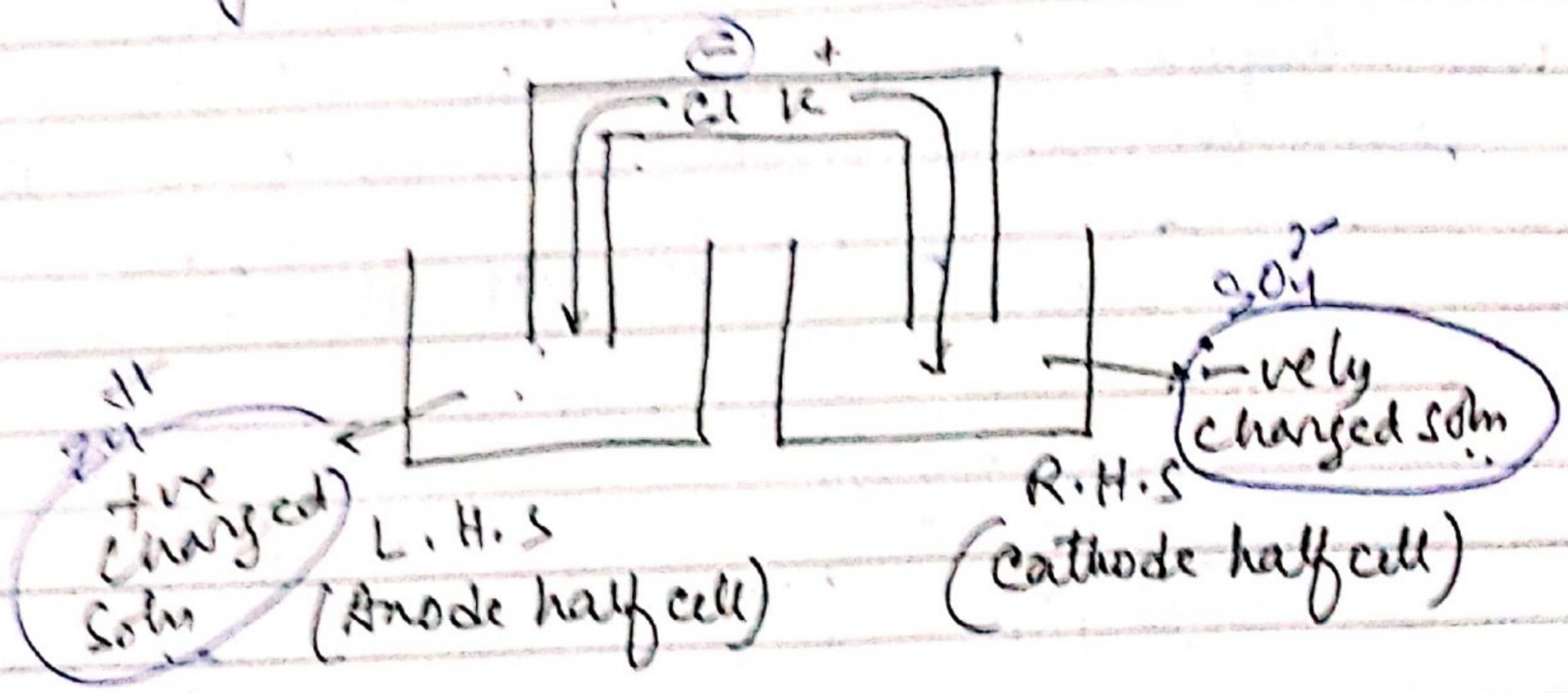
LOAN :

left oxidation Anode negative

In left hand half cell i.e at anode +ve charge in soln prevents the outward flow of electron. and in the right hand half cell, the -ve charge in solution prevents the inward flow of electron.

Salt bridge ▪ an inverted "U" shaped glass tube in which an (inert) electrolyte, like - K_2SO_4, KNO_3, NH_4Cl etc. is introduced.

▪ The two open ends of the salt bridge is closed either with agar-agar powder or jelatin in semi liquid state

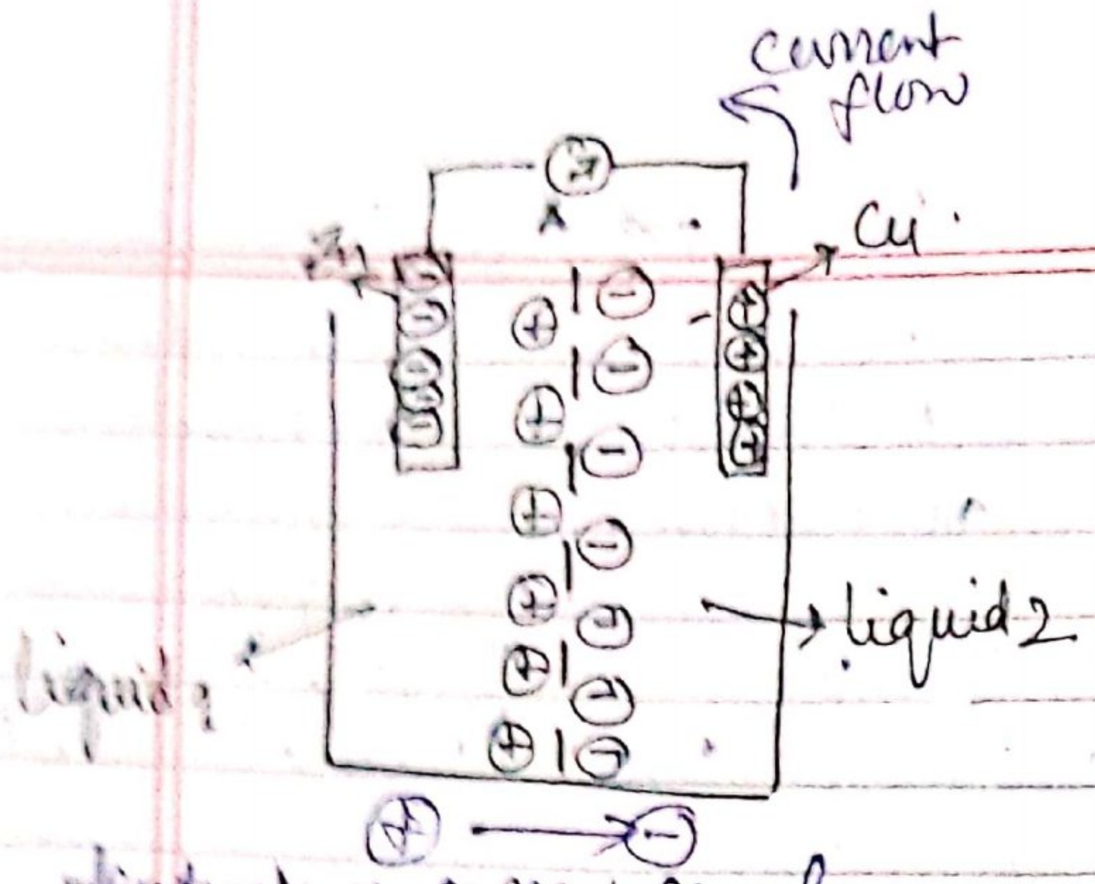


Function of Salt bridge

① It maintains the electrical neutrality of the half cell electrolytes.

② It completes the circuit by allowing the flow of electrons.

③ It maintains the liquid-liquid junction potential (*) V. Imp



tendency of current flow from liquid 1 to liquid 2

At (liquid - liquid junction) a potential difference creates which opposes the potential of the battery.

As an example :- if the potential of the battery be 1.1 volt

i.e. E_{Batter} = 1.1 volt at NTP (i.e. 298 K)

& if $E_{liq\text{-}liq\ junction}$ = 0.1 volt " "

net potential = 1.0 volt.

Conditions for salt bridge

① Nature of electrolytes — Inert electrolyte like —

$KCl \rightleftharpoons K^{\oplus} + Cl^{\ominus}$

$NH_4Cl \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$

$K_2SO_4 \rightleftharpoons 2K^{\oplus} + SO_4^{2-}$

ions don't react with any of ions/rods of half cell.

$Zn^{++} + 2Cl^{-} \Rightarrow ZnCl_2 \rightleftharpoons Zn^{++}_{(aq)} + 2Cl^{\ominus}_{(aq)}$

$ZnCl_2$ → water soluble, unstable

remains as non reactive for a particular situation

Chosing of electrodes

— if we'll use Ag-electrode then we can't use KCl or NH_4Cl as an inert electrolyte in salt bridge because :

$Ag\text{-electrode} + KCl \rightarrow AgCl \downarrow$

white ppt.

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Arrange these species H^+, K^+, CH_3COO^-, OH^- according to their increasing conductance at infinite dilution? Ans

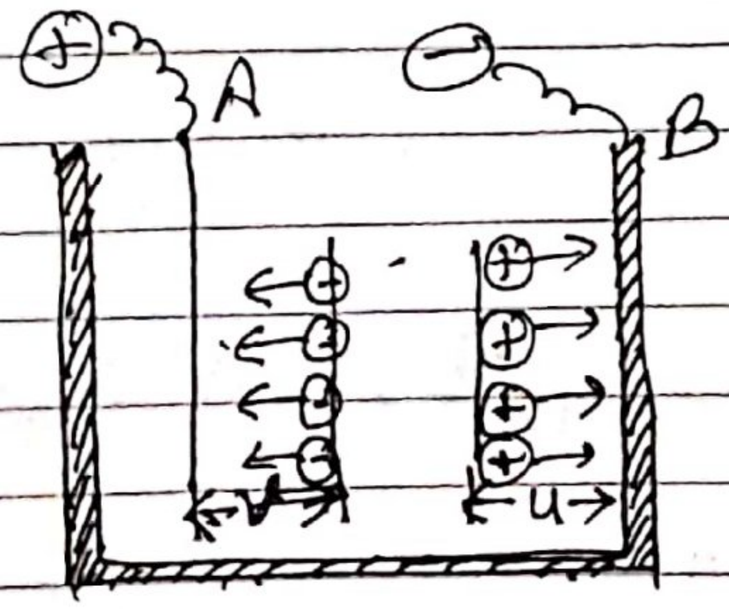
② Good ionic mobility and equal mobility of cations & anions

Both half cells are neutralised simultaneously.

1/05/19

Migration of Ions: Transport Number

Under a potential gradient current is transported by the migration of ions, cation moves to cathode and anion moves to anode. The total charge released at the cathode and anode are of course equal but the fraction of the total current conveyed by the cation & anions are not necessarily equal. The transport of current by ions in a solution depends upon not only the charge and number of the ions but also on the speed of the ions.



It is obvious that having same charge the ions with greater speed will pass a section of the solution in greater number than those with a lower speed. Hence, the former would transport a larger amount of current. Let us take an electrolyte between two electrodes A and B and let the number of cations per cc of the solution be $n_{(+)}$ each carrying a charge $z_{(+)}$. Suppose the current passing through the solution be I under any Potential Difference of E Volts. Further suppose that u and v are the velocities of the cation and anion respectively under this voltage. Now considering

C = the electricity associated with unit cross

only unit cross-section of the two electrodes when the current passes just for 1 second. It is evident that all the anions which are within a distance v from the anode would reach A and during this time all the cations within a distance u from the cathode would reach B. The number of cations to be discharged on B and the number of anions to be discharged on A are respectively n_+u and n_-v respectively.

$\therefore$ the current carried by cations, $I_+ = (n_+u)Z_+e$

$\therefore$ the current carried by anions, $I_- = (n_-v)Z_-e$

$$I = I_{(+)} + I_{(-)}$$

$$\text{or, } I = n_{(+)}u Z_{(+)}e + n_{(-)}v Z_{(-)}e$$

$$I = n_{(+)}Z_{(+)}.e.u + n_{(-)}Z_{(-)}ev$$

The solution being electrically neutral $n_{(+)}Z_{(+)} = n_{(-)}Z_{(-)}$

The fraction of the current carried by cations and anions ~~respectively~~ represented by $t_{(+)}$ and $t_{(-)}$ ~~respectively~~ respectively are called transport or transferance number.

These would be (a) $t_{(+)} = \frac{I_{(+)}}{I} = \frac{n_{(+)}Z_{(+)}eu}{n_{(+)}Z_{(+)}eu + n_{(-)}Z_{(-)}ev} = \frac{u}{u+v}$

(b) $t_{(-)} = \frac{I_{(-)}}{I} = \frac{n_-Z_-ev}{n_+Z_+eu + n_-Z_-ev} = \frac{v}{u+v}$

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$t_+ + t_- = 1$ and $\frac{t_+}{t_-} = \frac{u}{v}$

Q) The equivalent conductance of $AgNO_3$ solution at 250°C for an infinite dilution was found to be 133.3 $\Omega^{-1} cm^2 equiv^{-1}$. The transport no. of Ag^+ ions in very dilute solution of $AgNO_3$ is 0.464. Calculate the equivalent conductance of Ag^+ and NO_3^- at infinite dilution.

Ans: Using, $\lambda^{\infty}_{(Ag^+)}$ = transport number of $Ag^+ \times \Lambda^{\infty}(AgNO_3)$

or $\lambda^{\infty}_{(Ag^+)} = t_{(+)}$ of $Ag^+ \times \Lambda^{\infty}_{(AgNO_3)}$

or $\lambda^{\infty}_{(Ag^+)} = (0.464 \times 133.3) = 61.9\ \Omega^{-1} cm^2 equiv^{-1}$

By Kohlrausch's law, $\lambda^{\infty}_{(AgNO_3)} = \lambda^{\infty}_{(Ag^+)} + \lambda^{\infty}_{(NO_3^-)}$

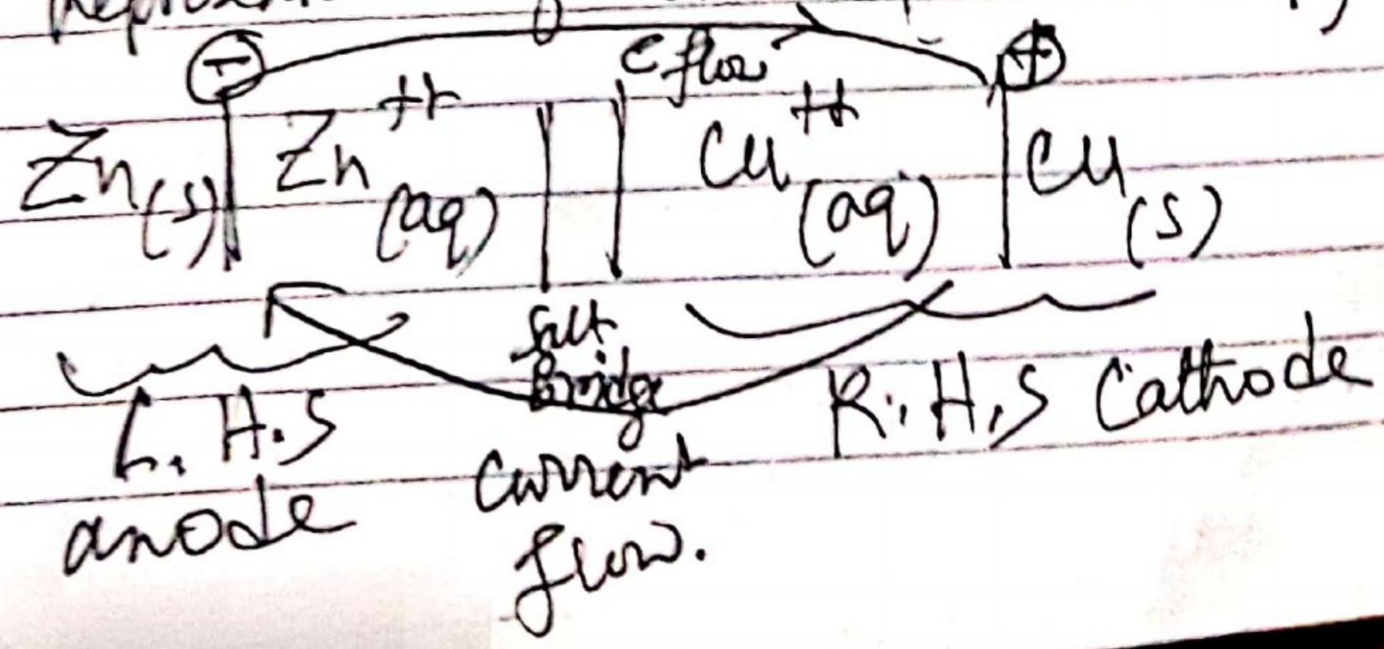
$\lambda_{(NO_3^-)} = \Lambda^{\infty}_{(AgNO_3)} - \lambda^{\infty}_{(Ag^+)}$

$= (133.3 - 61.9)$

$= 71.4\ \Omega^{-1} cm^2 equiv^{-1}$

How to represent a cell?

Representation of Daniel (or Zn-Cu couple) cell :-



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Half cell anodic

cell rxn: oxidn $Zn_{(s)} - 2e \rightleftharpoons Zn^{++}_{(aq)}$

$n = 2$

Half cell cathodic reduction $Cu^{++}_{(aq)} + 2e \rightleftharpoons Cu_{(s)} \downarrow$

Net Redox rxn. $Zn_{(s)} + Cu^{++}_{(aq)} \rightleftharpoons Cu_{(s)} \downarrow + Zn^{++}_{(aq)}$

$$K_{eq} = \frac{[Zn^{++}]}{[Cu^{++}]}$$

$\because$ [Zn] as well as both [Cu] are considered to be 1

② Write the cell rxns for the following cells:

(i) $Cr | Cr^{3+} || Pb^{2+} | Pb$

Cell rxn: Oxidation: $Cr_{(s)} - 3e \rightleftharpoons Cr^{+++}_{(aq)}$]×2

Reduction: $Pb^{++}_{(aq)} + 2e \rightleftharpoons Pb\downarrow_{(s)}$]×3

$n = 6$

Net reaction redox $2Cr_{(s)} + 3Pb^{2+}_{(aq)} \rightleftharpoons 2Cr^{3+}_{(aq)} + 3Pb_{(s)}$

Represent the cell from its cell rxns at 1 chemical change cell.

$Ni_{(s)} - 2e \rightleftharpoons Ni^{2+}_{(aq)}$

$n = 2$

$2Ag^{+}_{(aq)} + 2e \rightleftharpoons 2Ag_{(s)}$

Net rxn: $Ni_{(s)} + Ag^{+}_{(aq)} \rightarrow 2Ag_{(s)} + Ni^{2+}_{(aq)}$

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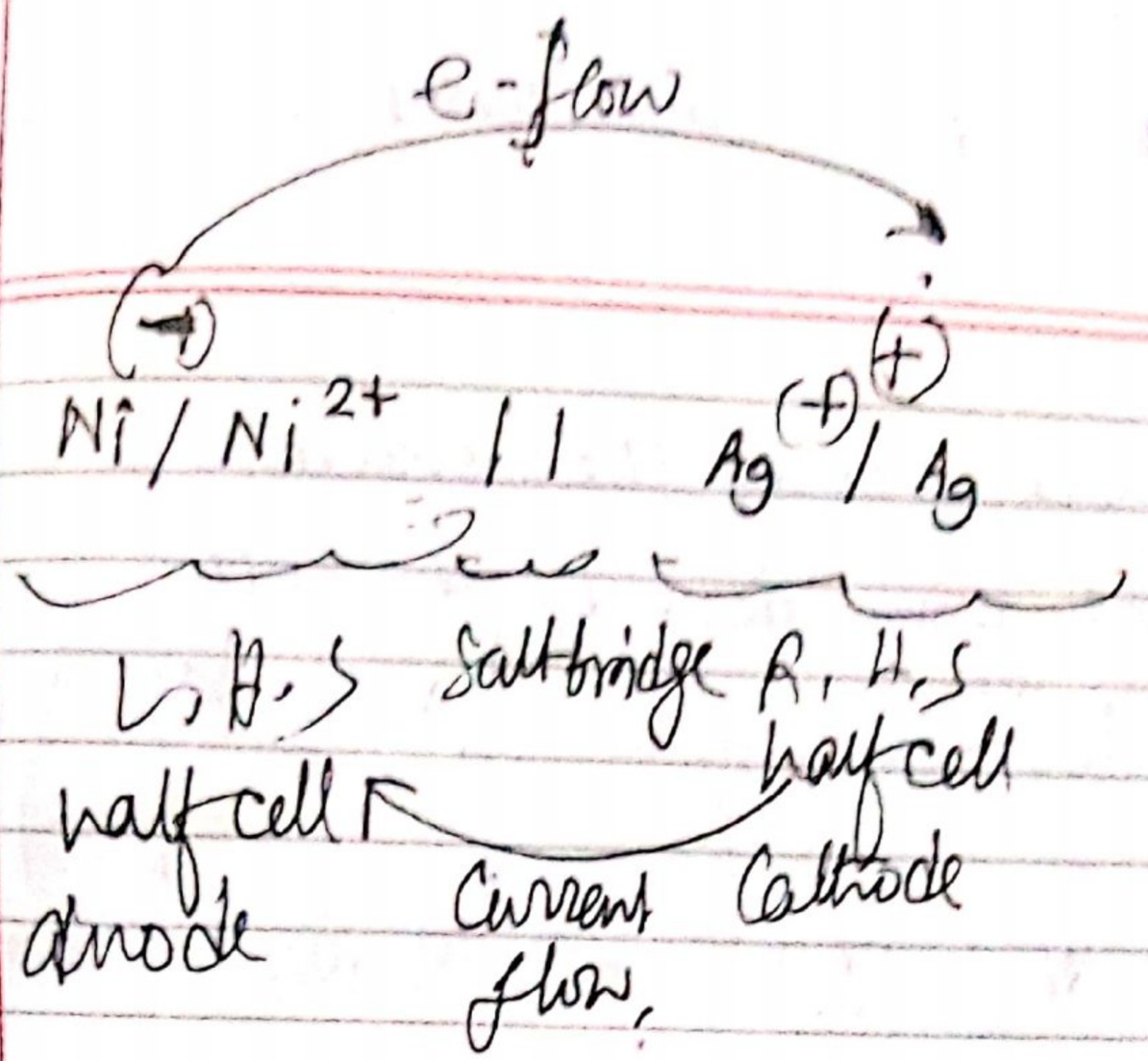

Nernst equation : Reduction Potential-Concen. of Electrolyte

Electrode potential depends upon the concentration of the species in solution so emf of a galvanic cell is controlled by the concentration of the ions. Nernst equation gives a relation between a emf of a galvanic cell and the concentration of ions in solution.

Let us consider a reversible reaction $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant $K_{eq.} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

From thermodynamics the chemical reaction becomes spontaneous due to decrease in free energy (ΔG) which measures the tendency of a chemical reaction to reach at the equilibrium state.

$$\Delta_{rxn} G = -ve$$

$$\Delta_{rxn} G = \sum G_{Products} - \sum G_{Reactants}$$

when $\sum G_{Reactants} > \sum G_{Products}$

$\therefore \Delta_r G < 0$ i.e. -ve, the rxn becomes spontane

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{2-}$$
1 mole 2 mole 3 mole

(*) All electrical work is useful or reversible

$$2Al^{3+} + 6e \rightarrow 2Al$$
$6F$

$\Delta G = (-)$ useful work done by the system

$\Delta G = (-)$ electrical work done by the cell

We know Potential difference $\boxed{\Delta V = \frac{W}{q}}$

where W = work done can be written as

$$W = q \times \Delta V$$

q → charge, ΔV → Potential difference

or, $$\boxed{W = q \times E_{cell}}$$

or, $W_{(electrical\ work)} = nF \times E_{cell}$

$$\therefore \boxed{\Delta G = -nFE_{cell}}$$

when E_{cell} is always +ve

or $E_{cell} > 0$

Under standard condition :- for soln 1M concentration or for gaseous system 1 bar/atm partial pressure at 25°C or 298 K

$$\Delta G^\circ = -nFE^\circ_{cell}$$

ΔG° → Standard Gibb's free energy change

E°_{cell} → Standard EMF of the cell.

The -ve ΔG of a rxn implies its spontaneity. ~~which i~~ ΔG is the measure of the ability of a system to do useful work since we can draw electricity from galvanic cell. It implies that a spontaneous rxn is going on inside the

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cell when ΔG of such rxn must be -ve. Electrical work is the result of the decrease of free energy of the cell rxn. We know that the electrical work obtained from any spontaneous rxn supplying nF coulomb of electricity at a potential E is given by net electrical work = nFe.

(thermochemistry)

From thermodynamics, we know the relation between ΔG & the equilibrium constant of the rxn K_{eq} is

Standard condition

$$\boxed{\Delta G = \Delta G^\circ + RT \ln K_{eq}}$$

$$(-)nFE_{cell} = (-)nFE^\circ_{cell} + RT \ln K_{eq}$$

$[M^{n+}] = 1\,M$
or $P_{gas} = 1$ bar/atm
Temp = 298K

or, $$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln K_{eq}$$

or $$E_{cell} = E^\circ_{cell} - \frac{8.314 \times 298 \times 2.303}{n \times 96500} \log K_{eq}$$

0.0591 is only at 25°C or 298K

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log_{10} K_{eq}}$$ → Rxn Quotient

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}}$$

This is the fundamental form of Nernst equation. This can be applied in both oxidation and reduction process.

Nernst equation helps us to determine the value of emf of either electrode or a cell at any concentration and temperature.

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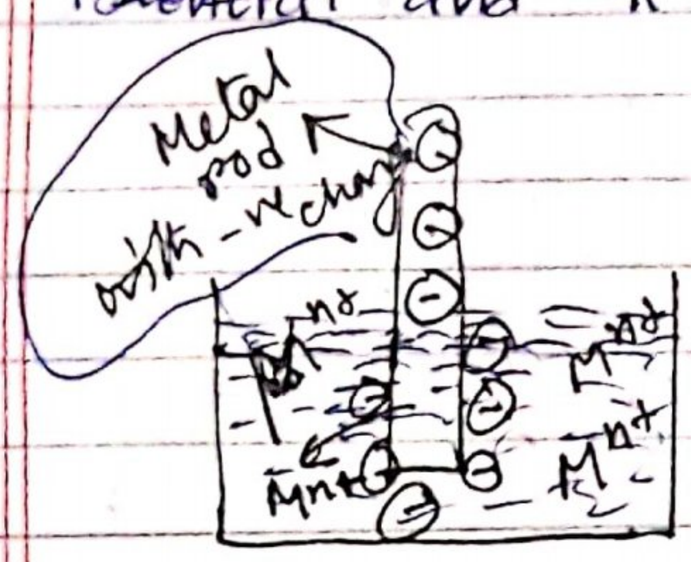
When a metal is brought into contact with its own ions an electrical double layer is formed at the interface between the metal and its salt solution which creates an electric potential at the electrode. There are two types of electrode potential, L.H.S = Oxidation Potential and R.H.S = Reduction Potential.



The potential difference between the electrode (metal) and its electrolytes (under equilibrium) is oxidation potential or the electrode potential

Reductant $- ne \rightleftharpoons$ Oxidant

Oxidn: $M_{(s)} - ne \rightleftharpoons M^{n+}$

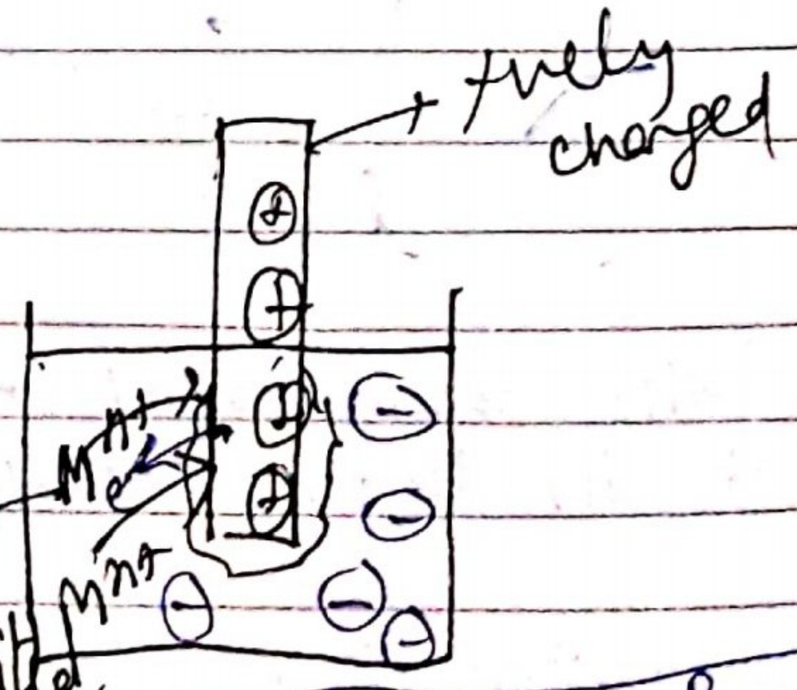
The tendency of an electrode to lose electrons or get oxidised.

$$E_{ox} = E^{o}_{ox} - \frac{0.0591}{n} \log \frac{[ox]}{[Red]}$$

applying Nernst equation $\rightarrow$ $$E_{M/M^{n+}} = E^{o}_{M/M^{n+}} - \frac{2.303RT}{nF} \log [M^{n+}]$$

for oxidation

The potential difference between the electrode or (metal) and its ion (in electrolyte) under equilibrium is known as electrode potential or reduction potential



Metal ions get deposited

Oxidant $+ ne \rightleftharpoons$ Reductant

$$E_{red} = E^{o}_{red} - \frac{0.0591}{n} \log \frac{[Red]}{[ox]}$$

Reduction: $M^{n+}_{(aq)} + ne \rightleftharpoons M_{(s)} \downarrow$

(from solution) (from rod)

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The tendency of an electrode to gain electrons or get reduced.

Applying Nernst equation $E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$

According to IUPAC, the electrode potential is to be considered as reduction potential.

$$\boxed{E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{2.303RT}{nF} \log [M^{n+}]}$$

Under standard conditions:-

(i) whenever we'll take the concentration of ions like $[M^{n+}] = 1M$

(ii) Whenever we'll consider the partial pressure of gas then we'll take 1 atm/bar.

(iii) Temp = 25°C or 298K

Factors Affecting Electrode Potential

(a) Nature of the Metal and its Ion

for oxidation

$M_{(s)} - ne \rightleftharpoons M^{n+}_{(aq)}$

$Mg_{(s)} - 2e \rightleftharpoons Mg^{++}_{(aq)}$ $E^{\circ}_{ox} = 2.37V$

S.H.E $\boxed{H_{2(g)} - 2e \rightleftharpoons 2H^{+}_{(aq)}, E^{\circ}_{ox} = 0.0V}$

$Zn - 2e \rightleftharpoons Zn^{++}$

$Fe - 2e \rightleftharpoons Fe^{++}$ $E^{\circ}_{Fe/Fe^{++}} = x$ volt

$Fe - 3e \rightleftharpoons Fe^{3+}$ $E^{\circ}_{Fe/Fe^{+++}} = y$ volt

for reduction

$M^{n+}_{(aq)} + ne \rightleftharpoons M_{(s)}$

$Ag^{+}_{(aq)} + e \rightarrow Ag_{(s)}$

$E^{\circ}_{Ag^{+}/Ag} = 0.79V$

S.H.E $\boxed{2H^{+}_{(aq)} + 2e \rightarrow H_{2(g)}}$ $E^{\circ}_{H^{+}/\frac{1}{2}H_2} = 0.00$

Red]

Ox]

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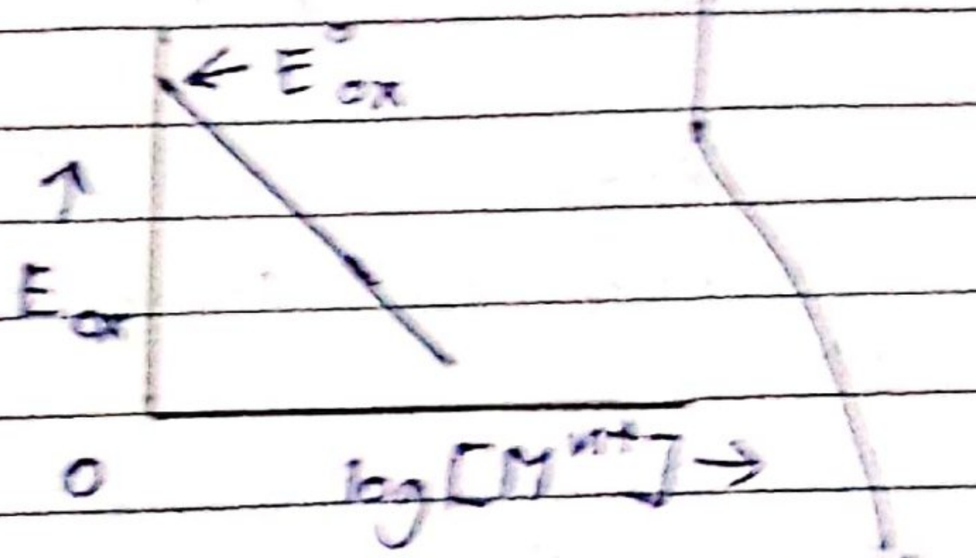
(ii) $[M^{n+}]$, Concentration of ionic species

Oxidation potential of an electrode as $\frac{1}{\text{conc. of ions}}$

Temp. T

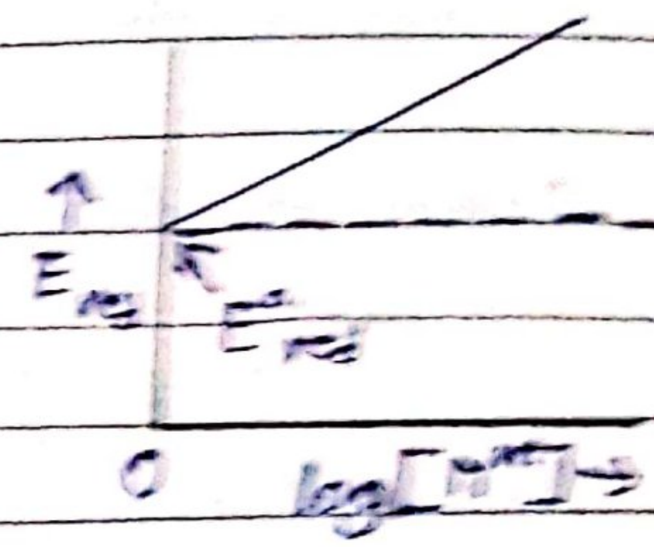
If T increases at constant $[M^{n+}]$ E_{ox} decreases



Reduction potential of an electrode, conc. of ions

Temp. T

If T increases at constant $[M^{n+}]$ E_{red} increases



EMF of the cell is the difference between the electrodes of the cell

$$\therefore E^\circ_{cell} = \overset{\text{Anodic}}{E^\circ_{ox}} + \overset{\text{Cathodic}}{E^\circ_{Red}} = -E^\circ_{Red} + E^\circ_{Red}$$

When $E^\circ_{ox} = -E^\circ_{Red}$ or vice versa $\rightarrow$ $\boxed{OP = -RP}$

$SOP = -SRP$

or, $E^\circ_{cell} = E^\circ_{R.H.S} - E^\circ_{L.H.S}$ when both standard EMF are of reduction potential

or, $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

or, $E^\circ_{cell} = SRP - SOP$

E°

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Calorimetric data

ΔH° — Change in Standard Enthalpy of the rxn

ΔS° — Standard Entropy of the rxn

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Gibb's free energy ΔG°

standard Gibb's free energy change

$\Delta G^\circ = -nFE^\circ_{cell}$

$\Delta G^\circ = -2.303RT\log_{10} K_c$

E°_{cell}

Equilibrium constant K_c

Standard EMF of the cell

$E^\circ_{cell} = \frac{2.303RT}{nF}\log_{10} K_c$

$E^\circ = \frac{0.0591}{n}\log_{10} K_c$

$\Delta G^\circ = -nFE^\circ_{cell}$ and $\Delta G = \Delta G^\circ + 2.303RT\log Q_c$

At equilibrium, $\Delta G = 0$, $Q_c = K_c$

$\therefore \Delta G^\circ = -2.303RT\log Q_c$

$\cancel{-}nFE^\circ_{cell} = \cancel{-}2.303RT\log Q_c$

$\log K_c = \frac{nFE^\circ_{cell}}{2.303RT}$

Putting the values of $F = 96500\,C$, $R = 8.314\,J\,K^{-1}\,mol^{-1}$, $T = 298\,K$

$$\boxed{\log K_c = \frac{nE^\circ_{cell}}{0.0591}}$$

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n = no. of electrons exchanged during redox

$$\Rightarrow K_c = \text{antilog}_{10}\left(\frac{n E^\circ_{cell}}{0.0591}\right)$$

<u>Under standard state conditions :-</u>

Forward rxn (→)	ΔG°	K_c	E°_{cell}
Spontaneous	-ve	>1	+
At equilibrium	0	$=1$	0
Nonspontaneous	+ve	<1	−

- Relationship between the standard potentials of half cells containing a metal in different oxidation states.

If two half cell rxns having potentials E_1° & E_2° are combined to give a 3rd half cell rxn having a potential E_3° then

$$\boxed{\begin{array}{l} Fe \rightarrow Fe^{++} + 2e, \; E^\circ_{Fe^{++}/Fe} = x \\ 2Fe^{++} \rightarrow 2Fe^{+++} + 2e, \; E^\circ_{Fe^{+++}/Fe^{++}} = y \end{array}}$$

Q_c

$$Fe + Fe^{++} \rightarrow 2Fe^{+++}, \; E_3^\circ$$

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-n_3 F E_3^\circ = -n_1 F E_1^\circ - n_2 F E_2^\circ$$

$$n_3 E_3^\circ = n_1 E_1^\circ + n_2 E_2^\circ$$

While using this equation → $E_3^\circ = \dfrac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$

takes values of E° according to rxn. If equal no. of electrons are involved then $E_3^\circ = E_1^\circ + E_2^\circ$

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V. V. Imp

NCERT Text book Pg-64

External potential opposite direction [Galvanic cell → Electrolytic cell]

Determination of ionic product of water (K_w)

$$\Lambda^\circ_{H_2O} = \Lambda^\circ_{H^+} + \Lambda^\circ_{OH^\ominus}$$

$$\Lambda^\circ_{H_2O} = \frac{K \times 1000}{\text{Molarity}}$$ K = specific conductance

$$\text{Molarity} = [H^+][OH^-]$$

$$\Lambda^\circ_{H_2O} = \frac{K \times 1000}{[H^+] \text{ or } [OH^-]}$$

$$[OH^-] = [H^+] = \frac{K \times 1000}{\Lambda^\circ_{H^\oplus} + \Lambda^\circ_{OH^\ominus}}$$

$$= 1.01 \times 10^{-7} \text{ g-ions/litre}$$

∴ Ionic product of water $Q_c = [H^+] \times [OH^-]$

$$= (1.01 \times 10^{-7})^2$$

$$= 1.02 \times 10^{-14} \text{ mol}$$

$$\boxed{pH = \frac{E_{cell} - E^\circ_{cell}}{0.0591}}$$

Determination of solubility product of an electrolyte at infinite dilution

$$K_{sp} = \frac{K \times 1000}{\mu^\infty}$$

Where μ^∞ = Molar conductance at infinite or zero dilution

$$\therefore \boxed{K_{sp} = \frac{K \times 1000}{\mu_c^\infty + \mu_a^\infty}}$$

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When a cell is made by same element and differs in the concentration of the electrolyte in contact with the element, then such cell is called

Concentration Cell

Electro Chemical Cell

(i) A net chemical change occurs inside the cell, example Daniel cell

$Zn | ZnSO_4 || CuSO_4 | Cu$

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

Redox change: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(ii) A decrease in free energy during the redox change brings in an equivalent amount of electrical work done

(iii) The electrode having high standard ~~der~~ oxidation potential works as anode i.e negative electrode

(i) No net chemical change occurs eg, $M | M^+_{(c_1)} || M^+ | M$

$M \rightarrow M^+_{(c_2)} + e^-$

$M^+_{(c_2)} + e^- \rightarrow M$

Net change: $M^+_{(c_1)} \rightarrow M^+_{(c_2)}$

As no electron exchange takes place, $E^\circ_{CELL} = 0$ at $25^\circ C$

(ii) A decrease in free energy during the transfer of concen. from c_1 to c_2 brings in an equivalent amount of electrical work done.

(iii) The electrode having more dilute solution surroundings, works as anode.

- For concentration cell, $Zn | Zn^{++} || Zn^{2+} | Zn$, $E_{CELL} =$ (c_1) (c_2)

$$E_{CELL} = \frac{0.0591}{2} \log \frac{(C_2)}{(C_1)}$$

- For concentration cell, $Pt(H_2) | HCl | Pt(H_2)$ P_1 P_2

$$E_{CELL} = 0.0591 \log \frac{P_1}{P_2}$$

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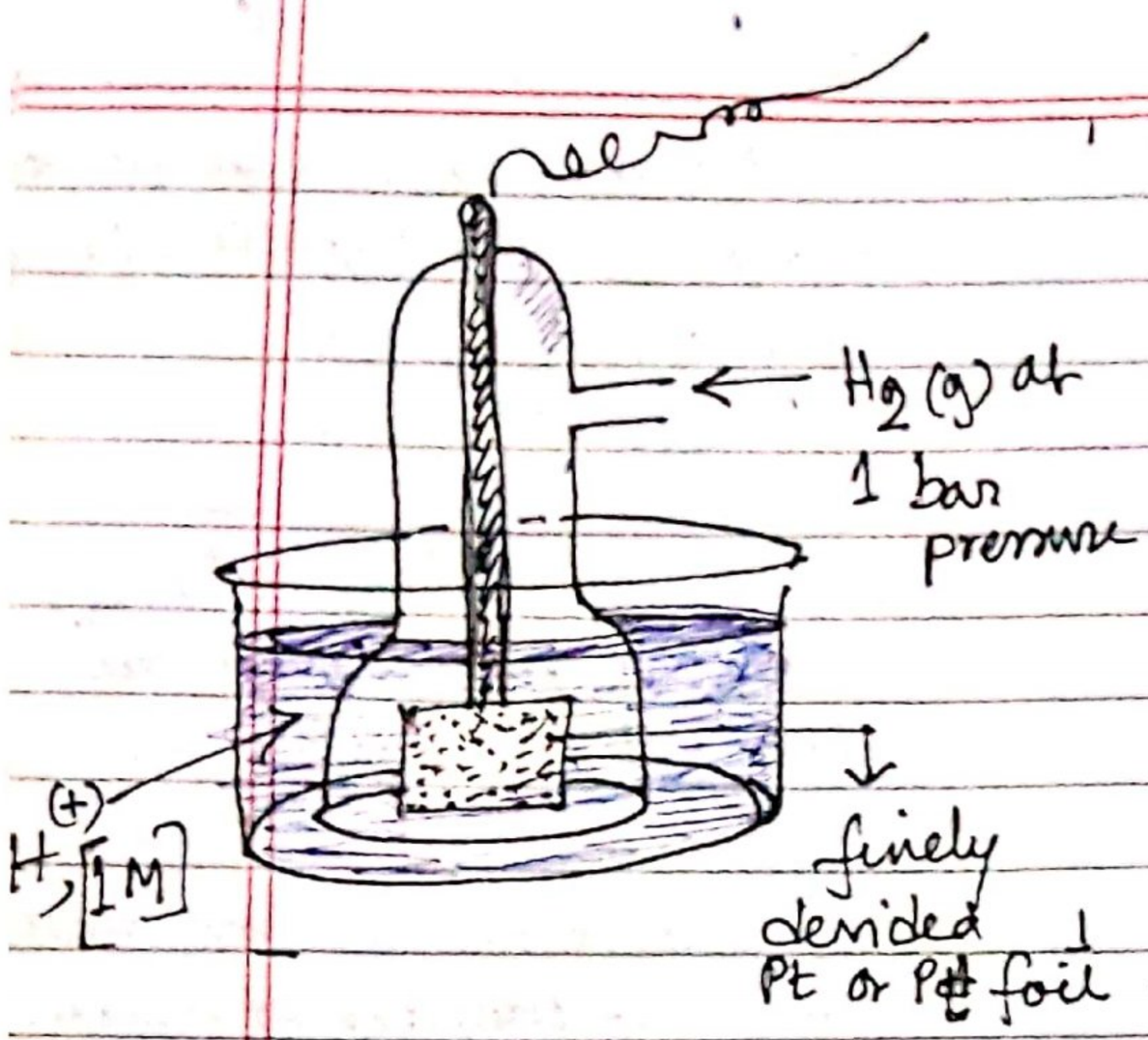

The standard hydrogen electrode or normal hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution of activity 1M and pure hydrogen gas at 1 bar is bubbled through it. The oxidation half cell is represented as –

$Pt, H_2(g) / H^+(aq), 1M$ with rxn

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

and reduction half cell as –

$H^+(aq), 1M / Pt, H_2(g)$ with reaction

$2H^+ + 2e^- \rightarrow H_2(g)$ $\quad E^\circ_{SHE} = 0.00V$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

FUEL CELL Galvanic cells which use energy of combustion of fuels like – H_2, CH_4, CH_3OH etc. as the source to produce electrical energy are called fuel cells.

- Fuel cells are used to convert chemical energy to electrical energy. The fuel cell runs continuously as long as the reactants are supplied, they produce electricity with an efficiency of about 70% such as hydrogen – oxygen fuel cell
- Electrodes are made of porous carbon and electrolyte is a resin containing concen. NaOH(aq) solution. Gases, hydrogen and oxygen diffuse slowly through electrodes

Anode : $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-] \times 2$

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ + heat

Fuel cells are highly efficient and pollution free and used in space crafts.

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Dry cell	Lead storage Battery
(1) Primary cell	Secondary cell
(2) Not rechargable	Rechargable. Used in automobiles
(3) Zn : anode C rod : cathode	Pb : anode PbO_2 : cathode
(4) Reactions:	Reactions:
At anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	At anode: $Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$
At cathode: $2MnO_2(s) + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(s) + H_2O(l)$	At cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Q) A ~~gal~~ galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution and a lead plate in 0.02 M $Pb(NO_3)_2$ solution. Calculate emf of cell at 25°C and write the chemical equations for the electrode rxn.

$E^\circ_{Zn^{2+}/Zn} = -0.76V$

$E^\circ_{Pb^{2+}/Pb} = -0.13V$

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Cell or Battery

A cell or a battery (arrangement of one or more cells connected in series) is basically a galvanic cell where the chemical energy or redox rxn is converted into electrical energy.

Primary Voltaic Cell (The dry Cell)

The primary voltaic cells are those in which the cell rxn occurs only once and the cell becomes dead after use over a period of time and cannot be reused again, eg. dry cells like - Leclanche cell, mercury cell

(i) **Leclanche cell** The electrode rxn for this type of cell is:

At anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$

At cathode: $MnO_2 + NH_4 + e^- \rightarrow MnO(OH) + NH_3$

Ammonia formed in rxn at cathode combines with Zn^{2+} to form the complex like $[Zn(NH_3)_4]^{2+}$. The cell has potential of 1.5V

(ii) **Mercury Cell** It shows the following electrode rxn

$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

The electrode potential of this cell is approximately 1.35V and it remains constant during its life because overall rxn doesn't involve any ion whose concentration can change during process.

Secondary Voltaic Cell The cell in which original reactants are regenerated by passing direct current from external source (recharged) is called secondary cell.

(i) **Lead accumulation** (Lead Storage battery) The most important voltaic cell is lead storage battery commonly used in automobiles and invertors. A 38% solution of H_2SO_4 is used as electrolyte. The rxn takes place while discharging (when cell is in use) is

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Reverse rxn occurs when cell is charged. E_{CELL} is 2.041V

(ii) **Nickel Cadmium Battery** Another important secondary battery is NiCl battery with longer life but more expensive. The overall rxn during discharge is

$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

The reverse rxn occurs when cell is charged.

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Some other Fuel cells

(1) **Phosphonic acid fuel cell** Liquid H_3PO_4 is used as an electrolyte. This is the first fuel cell to be commercialised.

Anode rxn: $2H_2 \rightarrow 4H^+ + 4e^-$

cathode rxn: $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$

(2) **Alkaline Fuel cell** It is one of the most efficient fuel cell, used by NASA since mid 1960s to propagate launching vehicles.

Anode rxn: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

cathode rxn: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(3) **Molten carbonate fuel cell** This can operate at extreme high temperatures of 600°c and above. It is generally used for industrial.

Anode rxn: $H_2 + CO_3^{2-} \rightleftharpoons H_2O + CO_2 + 2e^-$

Cathode rxn: $CO_2 + \frac{1}{2} O_2 + 2e^- \rightleftharpoons CO_3^{2-}$

(4) **Direct Method Fuel cell** Methanol is used as fuel.

Anode rxn: $CH_3OH + H_2O \rightleftharpoons 6H^+ + 6e^- + CO_2$

Cathode rxn: $\frac{3}{2} O_2 + 6H^+ + 6e^- \rightleftharpoons 3H_2O$

Corrosion It is the oxidative deterioration of metal surface with the action of its environment to form unwanted corrosion products like - oxides, sulphides, carbonates, sulphates. It usually affects metallic substances and typically produce oxide(s) or salt(s) of metal, eg., conversion of iron to ~~rust~~ rust $[Fe_2O_3 . xH_2O]$ the tarnishing of silver (due to the formation of Ag_2O) development of a green coating on copper and bronze.

Corrosion of iron or rusting involves the following rxns:-

Oxidation half cell: $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$

$E^0(Fe^{2+}/Fe) = -0.44V$

Reduction half cell: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

$E^0(H^+/O_2/H_2O) = 1.23V$

overall rxn: $2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

$E^0_{CELL} = 1.67V$

Ferrous ions, Fe^{2+} undergo oxidation with O_2 to form rust $[Fe_2O_3 . xH_2O]$

$$2Fe^{2+} + 2H_2O + \frac{1}{2}O_2 \rightarrow Fe_2O_3 + 4H^+ \xrightarrow{H_2O} \underset{(Rust)}{Fe_2O_3 \cdot xH_2O}$$

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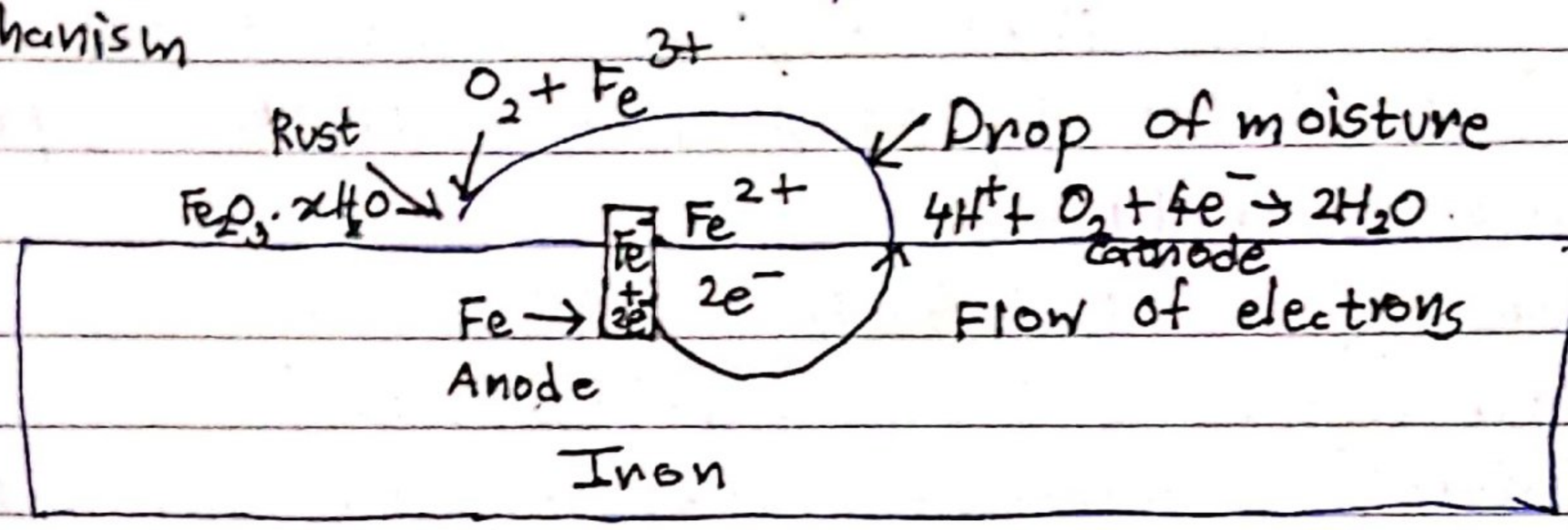
□ Corrosion: Atmospheric gases attacks on surface of metal resulting into formation of compounds such as oxides, sulphides, carbonates, sulphates etc. causing decomposition of metal called corrosion
eg. rusting of iron (rust is hydrated ferric oxide, $Fe_2O_3 \cdot 2H_2O$)

□ Mechanism



Overall rxn: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$
$E^\circ_{CELL} = 1.67V$

$4Fe^{2+}(aq) + O_2(g) + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+(aq)$

$Fe_2O_3 + xH_2O \rightarrow 2Fe_2O_3 \cdot xH_2O$ (rust)

Factors which promote corrosion:

- Reactivity of metal: More active metals are readily corroded
- Presence of air and moisture: Air, moisture and gases like SO_2, CO_2 catalyse the process of corrosion.
- Presence of impurities: Pure metals don't corrode
- Presence of electrolytes: Electrolytes in H_2O increase the ratio of corrosion
- Presence of strains in metals: Corrosion takes place rapidly at bends, scratches, nicks & cuts in the metal

Properties of corrosion:

Barrier protection: Simplest way to prevent corrosion by not allowing metal surface to come in contact with moisture, O_2 and CO_2.
This can be achieved by:-

(i) coating the metal surface with paint or some chemicals (eg. bisphenol)
(ii) applying a thin film of oil or grease on metal surface
(iii) Electroplating with metals like tin, nickel, Zn, Cd, Al etc.

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Sacrificial protection: In this method Fe is covered with a ~~large~~ layer of metal which is more active (electrotve) than Fe and thus prevent the Fe from losing e^-. Example: covering with Sn, Zn, Mg etc. Covering of Fe with layer of Zn is known a galvanization. The layer of metal is decomposed with time so this is known as sacrificial protection.

Electrical protection (cathodic protection): This method is used when Fe articles are in contact with water such as underground water pipes, storage tanks, canals etc. The article of Fe is connected with more active metals like Mg, Zn or Al which acts as anode. Iron pipe acts as cathode in this case.

Using anti rust solution: Solutions of alk phosphate & alkaline chromate are used. The alkalinity prevents availibility of H^+ ions. These solutions are used in car radiations to prevent rusting of Fe in differents parts of engine.

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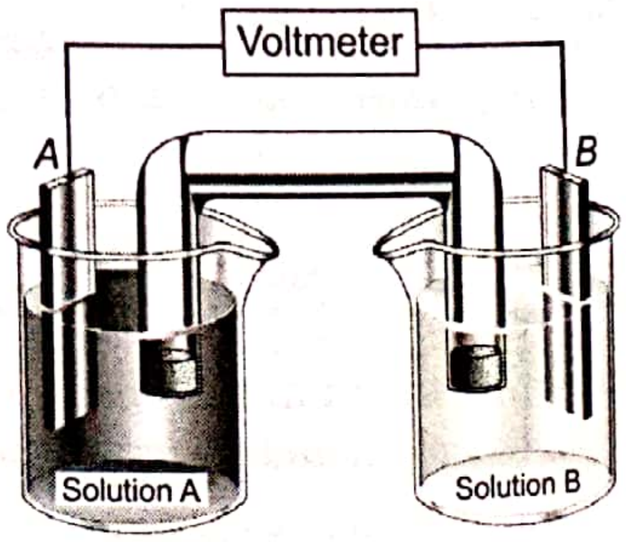
Chapter Drills

Concept Building Preliminaries

1. Write the half-cell reaction for the following cells :
   (a) $Pt(s) | Ti^{3+}, Ti^{4+} || Fe^{3+}, Fe^{2+} | Pt(s)$
   (b) $Pb(s) | PbSO_4(s) | SO_4^{2-} || Zn^{2+} | Zn(s)$
   (c) $Pt(s) | Hg(l), Hg_2Cl_2 | Cl^- || H^+ | H_2, Pt(s)$
   (d) $Pt(s) | QH_2, Q, H^+ || Cl^- | AgCl(s) | Pt(s)$
   QH_2 = Hydroquinone and Q = Quinone
2. Write electrochemical notations for following reactions :
   (a) $H_2(g) + Cu^{2+} \longrightarrow 2H^+ + Cu(s)$
   (b) $Cl_2(g) + 2Fe^{2+} \longrightarrow 2Fe^{3+} + 2Cl^-$
   (c) $Zn(s) + 2AgCl(s) \longrightarrow 2Ag(s) + ZnCl_2$
   (d) $[Fe(CN)_6]^{3-} + \frac{1}{2} H_2(g) \longrightarrow [Fe(CN)_6]^{4-} + H^+$
3. Consider the following half reactions and emf values
   $$Ag(s) \longrightarrow Ag^+(aq) + e^-; \quad E° = -0.80 \text{ V}$$
   $$2I^-(aq) \longrightarrow I_2(g) + 2e^-; \quad E° = -0.53 \text{ V}$$
   Check whether free iodine will react with Ag or not.
4. If emf of the cell
   $Pt(s) | H_2$ (1.0 atm), $HCl || Hg_2Cl_2, Cl^-(1.0M) | Hg(l) | Pt(s)$
   is 0.70 V at 25°C calculate pH of anodic solution. $E°(Hg_2Cl_2/Hg, Cl^-) = 0.20V$.
5. Answer whether the following reactions will occur spontaneously or not, under standard condition.
   (a) will Fe reduces Fe^{3+} to Fe^{2+}? $E°(Fe^{2+}/Fe) = -0.44V$ and $E°(Fe^{3+}/Fe^{2+}) = 0.77V$
   (b) will permanganate ion liberate $O_2(g)$ from water in acidic medium? $E°(MnO_4^-, H^+/Mn^{2+}) = 1.51$ V and $E°(O_2, H_2O/H^+) = 1.22$ V.
   (c) Will $O_2(g)$ oxidizes gold to $Au(CN)_2^-$ in presence of $CN^-(aq)$ and $OH^-(aq)$? $E°[Au(CN)_2^-/Au, CN^-] = -0.60V$ and $E°(O_2/OH^-, H_2O) = 0.40$ V.
   (d) would you use silver spoon to stir a solution of $Cu(NO_3)_2$? $E°(Ag^+/Ag) = 0.80V$ and $E°(Cu^{2+}/Cu) = 0.34V$
   (e) reaction of Pb with $AgNO_3$. $E°(Ag^+/Ag) = 0.80V$ and $E°(Pb^{2+}/Pb) = -0.126V$
   (f) will Sn reduce Fe^{3+} to Fe^{2+}? $E°(Fe^{3+}/Fe^{2+}) = 0.77V$ and $E°(Sn^{2+}/Sn) = 0.15V$
6. Four elements W, X, Y and Z form diatomic molecules and also form singly charged negative ions. The following observations are made in a series of reaction :
   (a) $2X^- + Y_2 \longrightarrow 2Y^- + X_2$
   (b) $2W^- + Y_2 \longrightarrow$ No reaction
   (c) $2Z^- + X_2 \longrightarrow 2X^- + Z_2$
   Arrange W, X, Y and Z in increasing reduction potential series
7. Consider the following half-cells and half-cell reduction potentials :
   $$M^{n+} + ne \longrightarrow M; \quad E_1°$$
   $$M^{m+} + me \longrightarrow M; \quad E_2°$$
   Assuming that $n>m$, show that for the reaction:
   $$M^{n+} + (n-m)e \longrightarrow M^{m+} \text{ that}$$
   the standard state emf is given by
   $$E°_{Cell} = \frac{nE_1° - mE_2°}{n-m}$$
8. What effect, the change in concentration of ions has on the value of electrode potential involving the reaction
   $$M^{n+} + ne \longrightarrow M?$$
9. Show that $E°(Ag^+/Ag)$ is related to $E°(AgX/Ag, X^-)$ by
   $$E°(AgX/Ag, X^-) = E°(Ag^+/Ag) - \frac{2.303RT}{R} pK_{sp}(AgX).$$
10. Show that the emf of the cell
    $M | M_xX_y (M = c_1), A_xX_n(s) || A_xX_n(s),$
    $M_xX_y(M = c_2)/M$, is given by $E = \frac{x+y}{xy}\frac{RT}{F}\ln\frac{c_1}{c_2}$
11. Show that the emf of the following cell
    $A | A_xX_n(s)M_xX_y(M = c_1), || M_xX_y(M = c_2), A_xX_n(s) | A$
    is given by
    $$E = -\frac{x+y}{xy}\frac{RT}{F}\ln\frac{c_2}{c_1}$$
12. The emf of a cell is found to be 0.30 V. What would happen if this cell is connected to a 1.5 V battery with its negative terminal to the (a) negative terminal of battery (b) positive terminal of the battery.
13. The following figure of a galvanic cell has a lead and a zinc electrode:
    $$E°(Zn^{2+}/Zn) = -0.76 \text{ V}$$
    $$E°(Pb^{2+}/Pb) = -0.126 \text{ V}$$



    (a) Label the electrodes A and B as Zn and Pb and identify the ions present in solutions A and B.
    (b) Indicate the direction of current flow in the wire and ion flow in the solution.

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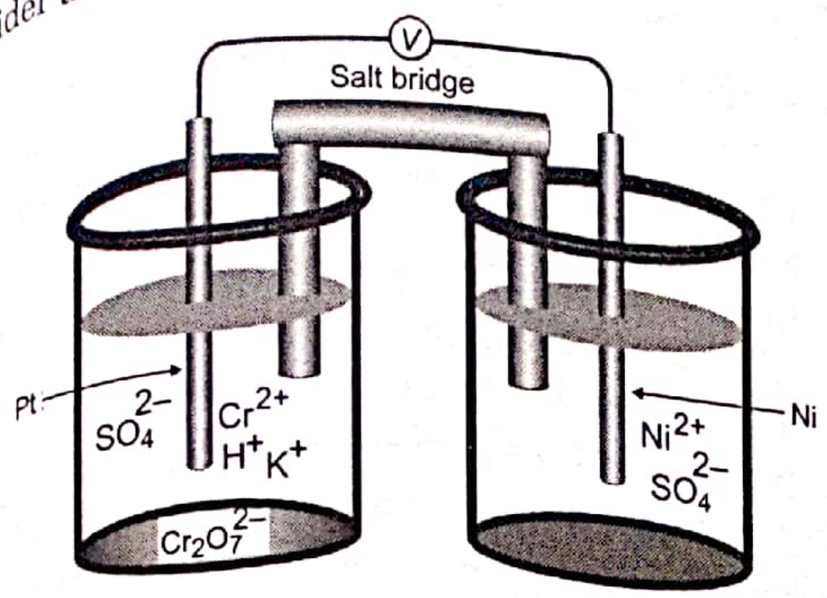
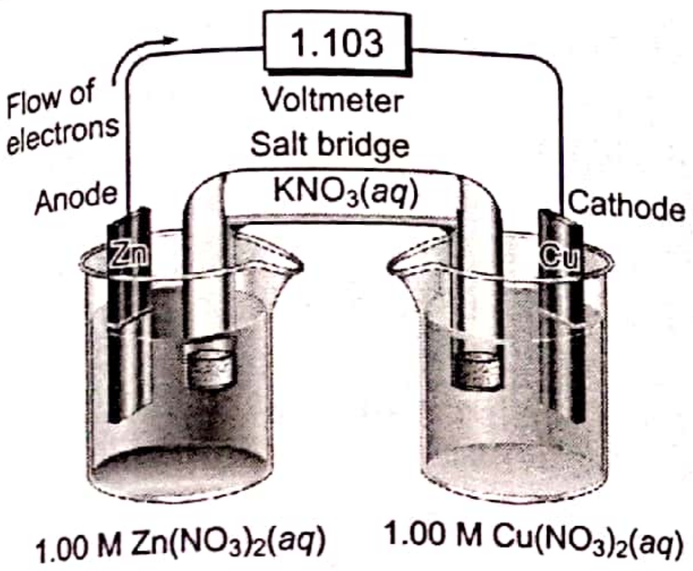
(c) Write the cell reaction and determine the standard state cell potential.

Consider the following galvanic cell :



(a) Identify the anode and the cathode.
(b) Write the balanced equation for the cell reaction.
(c) Write the short hand notation for the cell.

Consider the given galvanic cell.



Does the cell voltage increases, decreases or remains the same when each of the following change is made. Explain your answer.
(a) 5.0 M $CuSO_4$ is added to anode chamber.
(b) 5.00 M H_2SO_4 is added to cathode chamber.
(c) 5.0 M $Zn(NO_3)_2$ is added to anode chamber.
(d) $H_2S(g)$ is passed through cathode chamber. (CuS is a sparingly soluble salt).

16. Explain the following observations :
(a) When molten NaCl is electrolyzed, Na metal is produced at cathode while electrolysis of NaCl(*aq*) results in formation of $H_2(g)$ at cathode.
(b) In an electrolytic cell, cathode is a negative electrode and anode is a positive electrode but the polarity is reversed in galvanic cell.
(c) In absence of a salt bridge, generation of current in galvanic cell is impossible.
(d) Salt bridge is not required for carrying electrolysis using an external source of current.
(e) Electrolysis of water gives hydrogen and oxygen gas but in absence of either acid or a base catalyst, electrolysis of pure water is difficult.

17. Explain the following observations:
(a) Metallic conductivity decreases with temperature but reverse is true for electrolytic conductivity in a solution.
(b) Molar conductivity of both strong and weak electrolyte increases with dilution.
(c) Although Li^+ ion is smaller than K^+ ion, LiCl has smaller electrical conductivity in water than KCl.

Concept Building Numerical Problems *(Base Level)*

Faraday's Laws of Electrolysis

1. An electric heater uses a current of 18 A for 1.0 h. How many electrons passes through it in that time?
2. 1.0 mole of electron passes a given point in a wire every day. What is the current in the wire?
3. Determine the amount of electrons (in mole) required to produce 5.12 g of copper from a copper(II) sulphate solution.
4. A total charge of 96.5 kC is passed through an electrolytic cell containing silver nitrate solution. Determine the quantity of silver deposited.
5. (a) When a current of 150mA is used for 8.0h, what volume of fluorine gas at NTP can be produced from a molten mixture of potassium and hydrogen fluoride?
(b) If the same current is passed for same interval of time, how many litre of oxygen gas could be produced from electrolysis of water?
6. (a) What current is required to produce 4.0 g of chromium metal from Cr(VI)oxide in 24h?
(b) What current is required to produce 4.0 g of sodium metal from molten sodium chloride in the same period?
7. When a titanium chloride solution is electrolysed for 500 s. with a 120mA current, 15mg of titanium is produced. What is the oxidation number of titanium in titanium chloride?
8. A 0.26 g sample of mercury was produced from a mercury nitrate aqueous solution when a current of 210mA was applied for 1200 s. What is the oxidation number of the mercury in the mercury nitrate?
9. An aqueous solution of Na_2SO_4 was electrolysed for 30 min; 25 mL of O_2 was produced at the anode over water at 22°C at a total pressure of 722 torr. Determine the strength of current that was used to produce the oxygen gas. Vapour pressure of water at 22°C is 19.83 torr.
10. A current of 15 A electroplated 50 g of hafnium metal from an aqueous solution in 2.00 h. What was the oxidation number of hafnium in the solution? Molar mass of Hf = 178.5.

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11. A piece of copper metal is to be electroplated on both side with silver to a thickness of 1 micro meter. If the metal strip measures 50 mm × 10 mm × 1 mm, how long must the solution, which consists the $Ag(CN)_2^-$ ion, be electrolysed, using a current of 100mA? The density of silver metal is 10.5 g/cc.

12. In order to plate a copper object with silver, a solution of $AgNO_3$ is electrolysed with the copper object serving as the cathode. A current of 0.50 ampere (0.50 coul/s) flows for 1.0 hour. What mass of silver (atomic weight = 108 g/mol) is plated out?

13. A student wishes to plate a silver coin with copper. The coin is used as the cathode in an electrolysis cell containing aqueous $CuSO_4$. A constant current is applied for 30 minutes. What must the current be in amperes if 1.50 g of copper is plated out? If the thickness of plating be 1.00 mm, what is the radius of coin? (The density of copper is 10.6 g/cm^3).

14. A current of 2amps is used for 60 min. to electrolyze copper from a solution of Cu^{2+} at a potential of 0.337volts.
    (a) How many coulombs are used
    (b) How many moles Cu(s) are plated out?
    (c) What weight Cu(s) in grams is plated out?
    (d) What power in watts was used?

15. Adiponitrile($NC(CH_2)_4CN$), a key intermediate in manufacture of nylon, is made industrially by reduction of acrylo nitrile as

$$2CH_2{=}CH{-}CN + H^+ \longrightarrow NC{-}(CH_2)_4{-}CN$$

How many kilogram of adiponitrile are produced in 10.00 h in a cell that has a constant current of 3.0×10^3 ampere?

16. If you electrolyze a solution of $Ni^{2+}(aq)$ to form Ni(s) for 2.00 h using a current of 2.50 amp, what mass of Ni(s) (AW = 58.69 g/mol) is produced at the cathode?

17. Rechargeable 'nickel-cadmium' or 'ni-cad' batteries are used today in calculators and portable power tools. The half-reactions that occur in a Ni-cad battery are:

$$\text{Anode}: \quad Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$

$$\text{Cathode}: \quad NiO(OH)(s) + H_2O(l) + e^- \longrightarrow Ni(OH)_2(s) + OH^-(aq)$$

Note that the solid products adhere to the surface of the electrodes in this battery. Explain in specific chemical terms what it means to recharge this battery.

18. A metal forms a salt MCl_3. Electrolysis of the molten salt with a current of 0.7 A for 6.63 h produced 3.00 g of metal. What is the molar mass of metal?

19. (a) How many moles of hydronium ions are produced at platinum electrode in the electrolysis of 200 mL of a $CuSO_4$ solution, using a current of 4.00A for 30min.
    (b) If the pH of the solution was initially 7.0, what will be the pH of solution after electrolysis?

20. A current of 2 A is passed for 11 hours through 500 mL of 2M solution of $Ni(NO_3)_2$ using platinum electrodes. What will be the molarity of the solution at the end of the electrolysis?

21. A 100 watt, 100 volt incandescent lamp is connected in series with an electrolytic cell containing $CdSO_4$ solution. What weight of Cd, the current flowing for 10 hrs will produce?

22. In an industrial electrolytic cell with current efficiency of 75%, it is desired to produce 48 kg of Mg metal per hour. Calculate the current required?

23. What volume of hydrogen and oxygen will be produced at 27°C and 740 mm of Hg. By passing a current of 25 amperes through acidulated water for 24 h?

24. 10 g of fairly concentrated solution of $CuSO_4$ is electrolysed by passing 10 A current for 1.5 min.
    (a) What will be the weight of solution after electrolysis?
    (b) What will be the number of equivalent of acid or alkali produced in the solution?

25. In an electrolysis experiment current was passed for 5 hrs through two cells connected in series. The first cell contains a solution of gold and the second cell contains aqueous solution of $CuSO_4$. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of Cu deposited on cathode in the second cell. Also calculate the current strength in ampere.

26. In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidised at anode and O_2 gas is reduced at cathode. If 67.2 litre of H_2 at STP react in 15 min. What is the average current produced? If the entire current is used for electrodeposition of Cu from Cu^{2+}, how many gram of Cu are deposited?

27. A current of 0.195 A is passed through 100 mL of 0.2 M NaCl solution for an hour. Calculate pH of the solution after electrolysis if current efficiency is 90%.

28. 19 g of fused $SnCl_2$ was electrolysed using inert electrode when 0.119 g of Sn was deposited at cathode. If nothing was given out during electrolysis, calculate the ratio of weight of $SnCl_2$ and $SnCl_4$ in fused state after electrolysis.

29. Electrolysis of molten KBr generates bromine gas, which can be used in industrial bromination process. How long will it take to convert a 500 kg batch of phenol to monobromophenol using a current of 20 kA?

30. The cathode reaction in Leclanche cell is given by

$$2MnO_2(s) + Zn^{2+}(aq) + 2e^- \longrightarrow ZnMn_2O_4(s)$$

If Leclanche cell produces a current of 0.005 A, calculate how many hours this current supply will last if there are initially 4.0 g of MnO_2 and excess of Zn^{2+} are present in the cell?

31. A 300 mL solution of NaCl was electrolyzed for 6.0 min. If the pH of the solution was 12.24, calculate the average current used.

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32. Lead storage batteries are rated by ampere hours. The lead anode of a certain lead storage battery have a total mass of 406 g. Calculate the maximum capacity of the battery in ampere hour. Also calculate ΔG° and E° of the lead storage battery? The discharging reactions are:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4 + 2e^-; \quad E^\circ = 0.31\ V$$

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l); \quad E^\circ = 1.7\ V$$

33. The concentration of sulphuric acid in a lead storage battery of an automobile over a period of time has decreased from 38% by mass (density = 1.29 g/mL) to 26% by mass (density = 1.19 g/mL). Assume the volume of solution remains constant at 750 mL. Calculate the total charge in coulombs supplied by the battery. How long will it take to recharge the battery back to the original sulphuric acid concentration using a current of 22.4 A?

34. How long would it take to plate a 0.1 mm coating of Cr on an automobile bumper having a total surface area of 1.0 m^2 from a solution of Cr^{3+} employing a current of strength 100 A? [Density of Cr = 5.8 g/cc]

35. A 0.75 A current passes for 1.0 h through a cell that contains an aqueous solution of sodium sulphate and nickel electrodes. At the cathode, water decomposes to hydrogen gas and at anode; hydronium ions and nickel oxide are produced. Calculate mass of NiO deposited, and volume of hydrogen gas at STP produced.

36. 100 mL 0.1 M solution of $AgNO_3(aq)$ is electrolysed using a current of strength 2.5 A for 1.0 hr. Determine the volume of $H_2(g)$ and $O_2(g)$ at STP produced.

37. A battery was used to supply a constant current of what was believed to be exactly 0.45 A as read on a meter in the external circuit. The cell was based on the electrolysis of a copper sulphate solution. During the 30 min, that current was allowed to flow, a total of 0.3 g of copper metal was deposited at the cathode. Determine the extent to which the meter was inaccurate.

38. A lead storage battery is allowed to discharge until 23.92 g of PbO_2 have been reduced. Determine the mass of $PbSO_4$ formed and time required to recharge the battery to its original state using a current of strength 3.0 A.

39. A balloon is being filled with hydrogen produced by the electrolysis of an aqueous solution of an acid. How long will it take to generate enough hydrogen to lift 1.5 kg by using a current of 8.5 A?

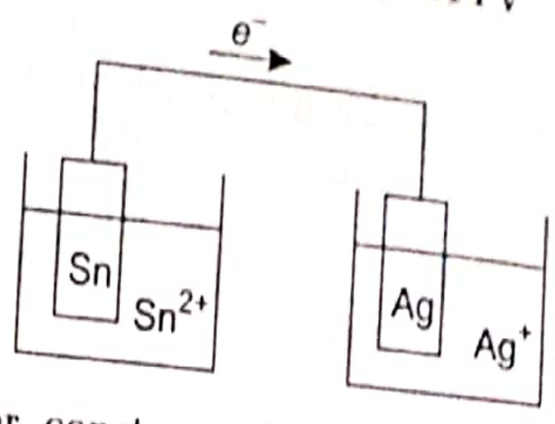
40. A direct current of 1.25 A was passed through 200 mL of 0.25 M $Fe_2(SO_4)_3$ for a period of 1.1 h. The resulting solution in the cathode chamber was analysed by titrating against an acidic permanganate solution and 25 mL of oxidizing agent solution were consumed. Determine molarity of the permanganate solution.

41. A 80 mL sample solution of KI was electrolyzed for 3.0 min using a constant current. The I_2 produced required 37.2 mL of 0.225 M $Na_2S_2O_3$ solution. Also the unreacted KI required 36.3 mL of 0.02 M acidic permanganate solution. Determine current strength and original molarity of KI solution.

Galvanic Cell

42. Write cell reactions for the following cell and determine standard state emf of the cell

$$E^\circ(Ag^+/Ag) = 0.80\ V$$
$$E^\circ(Sn^{2+}/Sn) = -0.14\ V$$



43. A researcher constructs battery based on silver and chromium as: $Cr | Cr^{3+} || Ag^+ | Ag$

$$Cr^{3+} + 3e^- \longrightarrow Cr; \quad E^\circ = -0.74\ V$$
$$Ag^+ + e^- \longrightarrow Ag; \quad E^\circ = +0.80\ V$$

(Atomic weight : Cr = 52; Ag = 108)

(a) What is the overall balanced cell reaction under standard conditions?
(b) Calculate the cell potential, ΔE°
(c) Calculate the equilibrium constant (K_{eq}) at 298 K.
(d) What is ΔE at 298 K when $[Cr^{3+}] = 1.0 \times 10^{-4}$ M and $[Ag^+] = 1.0$ M?
(e) If the battery generates a current of 0.30 amp for 2.0 hrs, what mass of metal is deposited at the cathode?

44. Use the cell indicated to answer the following questions

$Ag | Ag^+ (1\ M) || Ni^{2+} (1\ M) | Ni$: $Ag^+ + e^- \longrightarrow Ag; \quad E^\circ = +0.80\ V;$

$Ni^{2+} + 2e^- \longrightarrow Ni; \quad E^\circ = -0.25\ V$

(a) What is ΔE° for the cell?
(b) Write the balanced overall cell reaction.
(c) Calculate the equilibrium constant for the cell reaction.
(d) Calculate the maximum useful work that can be obtained from this cell.

45. In order to determine the K_{sp} for $Cu(OH)_2$, a chemist constructed the cell shown below. The left half contains a buffer solution (pH=9.0) saturated with $Cu(OH)_2$ while the right half-cell contains Cu^{2+} at 1.0M. The measured cell voltage was 0.265 V.

$Cu | Cu(OH)_2(s)$, Buffer (pH = 9.0) $|| Cu^{2+}$ (1 M) | Cu

(a) Write the overall cell reaction.
(b) Calculate the $[Cu^{2+}]$ in the left half-cell.
(c) Calculate K_{sp} for $Cu(OH)_2$

46. The cell illustrated below was constructed to measure the standard reduction potential of Br_2. Use the data given to calculate $E^\circ(Br_2/Br^-)$. All the reactions are in water.

$$Br_2 | Br^- || Cl^- | Cl_2(g)\ \Delta E^\circ = 0.29\ V$$

and $$Cl_2(g) + 2e^- \longrightarrow 2Cl^- \quad E^\circ = 1.36\ V$$

$\Rightarrow$ $$Br_2 + 2e^- \longrightarrow 2Br^- \quad E^\circ = ?$$

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47. The cell shown below generates a potential of 0.65V at 298K. Calculate K_{sp} for AgBr.

$$Ag \mid AgBr(s), NaBr\ (0.10\ M) \mid\mid AgNO_2\ (0.10\ M) \mid Ag \qquad \Delta E = 0.65\ V$$

48. Calculate the equilibrium constant at 25°C for the reaction occurring in Daniell cell, if the standard emf is 1.1V.

49. Calculate the equilibrium constant for the reaction

$$H_2 + 2Fe^{3+} \longrightarrow 2H^+ + 2Fe^{3+}; \qquad E^\circ(Fe^{3+}/Fe^{2+} = 0.77\ V)$$

50. Calculate E° for the reaction $Cu^+ + e^- \longrightarrow Cu$ making use of the following E° value.

$$E^\circ(Cu^{2+}/Cu^+ = 0.153\ V)$$
$$E^\circ(Cu^{2+}/Cu = 0.337\ V)$$

51. The standard electrode potential at 25°C for

$$\text{Cytochrome } c(Fe^{3+}) + e^- \longrightarrow \text{Cytochrome } c(Fe^{2+})$$

is 0.25 V. Calculate ΔG° for the process,

$$\frac{1}{2}H_2(g) + \text{Cytochrome } c(Fe^{3+}) \longrightarrow H^+ + \text{Cytochrome } c(Fe^{2+})$$

52. Calculate the concentration of I_3^- in a standard solution of iodine in 0.5 M KI, making use of the following standard electrode potentials:

$$E^\circ(I_2/I^- = 0.5355\ V) \quad \text{and} \quad E^\circ(I_3^-/I^- = 0.5365\ V)$$

The molarity of I^- in the standard solution can be assumed to be 0.5M.

53. Calculate emf at 25°C of the cell

$$Pt \mid H_2\ (1.0\ bar) \mid H_2SO_4\ (0.01\ M) \rightleftharpoons CrSO_4(s) \mid Cr$$

Given the following standard electrode potential:

$$CrSO_4(s) + 2e^- \longrightarrow Cr + SO_4^{2-}; E^\circ = -0.4\ V$$

54. Suppose that the cell

$$AgCl(s) \mid HCl\ (0.1\ M) \rightleftharpoons HCl(0.01\ M) \mid AgCl(s) \mid Ag(s)$$

is set up and that the membrane separating the two solution is permeable only to H^+ ions. What is the emf of the cell at 25°C?

55. Show that

$$E^\circ(Fe^{3+}/Fe^{2+}) = 3E^\circ(Fe^{3+}/Fe) - 3E^\circ(Fe^{2+}/Fe).$$

56. For the galvanic cell

$$Ag \mid AgCl(s) \mid KCl\ (0.2\ M) \rightleftharpoons KBr\ (0.001\ M) + AgBr(s) \mid Ag$$

Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking account of the cell reaction at 25°C. Given K_{sp} of AgCl = 2.8×10^{-10} and of AgBr = 3.3×10^{-13}.

57. Zinc granules are added in excess to 750 mL of 1.5 M $Ni(NO_3)_2$ solution at 30°C until the equilibrium is reached. If emf of the cell

$$Zn(s) \mid Zn^{2+}(1\ M) \mid\mid H^+\ (1\ M) \mid H_2(g)\ 1.0\ atm \mid Pt \text{ is } 0.76\ V$$

and that of cell

$$Ni \mid Ni^{2+}\ (1\ M) \mid\mid H^+\ (pH = 0) \mid H_2(g, 1\ atm) \mid Pt \text{ is } 0.24\ V$$

then calculate $[Ni^{2+}]$ at equilibrium. Also find the amount of zinc consumed.

58. Find $E^\circ(MnO_4^-/MnO_2)$ from the following data:

$$E^\circ = (MnO_4^-/Mn^{2+}) = 1.51\ V,$$
and
$$E^\circ = (MnO_2/Mn^{2+}) = 1.23\ V.$$

59. Calculate emf of the following cell

$$Cu(s)/Cu^{2+}\ (0.08\ M) // Cu^{2+}(1.2\ M)/Cu(s)$$

60. The emf of the cell

$$Pt \mid H_2\ (1.0\ atm)\ HCl(x\ M) \mid\mid Hg_2Cl_2, Cl^-\ (1.0\ M) \mid Hg$$

Is 0.79 V at 25°C, calculate the pH of the solution. Given E° for calomal electrode is 0.2 V.

61. For the cell:

$$Pt \mid H_2(g) \mid sol\ X \mid\mid KCl(sat) \mid Hg_2Cl_2(s) \mid Hg \mid Pt$$

the observed emf at 25°C was 612 mV. When solution X was replaced by a standard phosphate buffer whose assigned pH is 6.86, the emf was 741 mV. Find pH of the solution X.

62. The solubility product for AgI in water at 25°C is 8.2×10^{-17}. Determine E° for Ag—AgI electrode if E° for Ag^+/Ag = 0.8V.

63. A galvanic cell is constructed based on the following reactions

$$HAsO_2 \rightleftharpoons As(s); \qquad E^\circ = +0.23\ V$$
and
$$NO_3^- \rightleftharpoons N_2O_4(g); \qquad E^\circ = +0.81\ V.$$

(a) Calculate E° for the spontaneous cell reaction.

(b) Calculate E_{Cell} in the acidic medium assuming concentration of all the species to be 0.1 M and partial pressure of gaseous species to be 1.0 bar.

64. A galvanic cell consists of Co electrode in a 1.0 M Co^{2+} solution and a Pt electrode in a solution containing Fe^{3+} and Fe^{2+}, each at 1.0 M. The two compartments are separated by a salt bridge. Using required data from table 1, determine emf of the cell.

65. A galvanic cell consists of two hydrogen electrodes. One is in a 1.0 M H^+ solution and other in a solution of unknown pH. The cell potential is 0.025 V. Determine unknown pH.

66. A Daniell cell produces a current of 3.5 mA at 1.1 V for 15 min. What is the maximum possible work you can get out of it?

67. Suppose that the potential between a Cu cathode and a $Cu^{2+}(aq)$ solution changes by −15.7 mV. What is the ratio of initial and final concentration of Cu^{2+} ions?

68. A platinum electrode is in contact with a solution containing Fe^{2+} and Fe^{3+} ions. The total concentration of iron ions is 0.033 M. What is the ratio of the concentrations if the potential difference between solution and metal surface is 35mV? $E^\circ(Fe^{3+}/Fe^{2+})$ = 0.77 V.

69. The pH of the solution in the cell $Pt/H_2(g)/HCl(aq)$ $AgCl(s)$, KCl(1.0 M) / Ag is 0.65 . Also $E^\circ(AgCl/Ag, Cl^-)$ = 0.22 V. Calculate emf.

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70. Consider : $Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Ag(s) + Fe^{3+}(aq)$
If equal volumes of 1.0 M solutions of Ag^+ and Fe^{2+} are mixed, what is the equilibrium concentration of Fe^{2+}? Show all work.
(Hint: you need to calculate a K value). Note: $Ag^+|Ag$, $E = +0.80$ V; $Fe^{3+}|Fe^{2+}$, $E = +0.78$ V.

71. Calculate $E°$ for : $Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-}$ given $K_{sp} = 6 \times 10^{-50}$ and $E°(Ag^+/Ag) = 0.80$ V

72. An $I_2(s)/I^-(1.0\ M)$ half-cell is connected to a H^+/H_2 (1.0 atm) half-cell and emf was found to be 0.755 V. If $E°(I_2/I^-)$ is 0.535 V, determine pH of the H^+/H_2 half-cell.

Concept Building Numerical Problems (*Advanced Level*)

74. Explain the following behaviour: In Daniel cell, if Na_2S is added to $Cu\text{-}Cu^{2+}$ side of the cell, the cell potential drops as predicted by Le-Chatelier's principle. However, if a lot of Na_2S is added, the reversal of voltage takes place. Given the following information K_{sp} (CuS) $= 10^{-28}$.

$$Zn^{2+} + 2e^- \longrightarrow Zn(s); \quad E° = -0.76\ V$$
$$Cu^{2+} + 2e^- \longrightarrow Cu(s); \quad E° = 0.34\ V$$
and
$$Cu(s) + S^{2-}(aq) \longrightarrow CuS(s) + 2e^- \quad E° = 0.80\ V$$

75. Consider the following sequence of reactions occurring in the acid medium. All emf (standard) are measured at 25°C and expressed in volt unit:

$$MnO_4^- \xrightarrow{0.564} MnO_4^{2-} \xrightarrow{2.26} MnO_2 \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.51} Mn^{2+} \xrightarrow{-1.18} Mn$$

(a) Determine $E°$ for : $MnO_4^- \longrightarrow Mn^{2+}$
(b) Which will be the better oxidizing agent in acid medium— MnO_4^- or MnO_4^{2-} when the final form of manganese is Mn^{2+}?
(c) Determine the standard emf of following reaction:
$$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2(s) + 2MnO_4^- + 2H_2O$$

76. From the following half-cell potentials

$$Cl^- + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 6e^-; \quad E° = -1.45\ V$$
$$\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-; \quad E° = 1.36\ V$$

Calculate the standard state emf of the half-cell:

$$\frac{1}{2}Cl_2(g) + 3H_2O \longrightarrow ClO_3^-(aq) + 6H^+ + 5e^-$$

77. For the half-cell: $MnO_4^- \longrightarrow Mn^{2+}$ (in acid medium) $E° = 1.51$ V at 25°C. Assuming that $[MnO_4^-] = [Mn^{2+}]$, calculate the redox potentials at pH = 0, 2, 4 and 6. Also explain why the ability of permanganate to oxidize halide ions to free halogen depends upon the acidity of solution.

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-; \quad E° = 1.36\ V$$
$$Br_2(l) + 2e^- \longrightarrow 2Br^-; \quad E° = 1.07\ V$$
$$I_2 + 2e^- \longrightarrow 2I^-; \quad E° = 0.54\ V$$

73. Use the given table of standard half-reaction data to determine $E°$ for the following *unbalanced* reactions:

Half reactions	$E°$ (V, at 25°C)
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	0.955
$NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	0.940
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.229
$Pt^{2+} + 2e^- \longrightarrow Pt(s)$	1.18 V
$V^{3+} + e^- \longrightarrow V^{2+}$	−0.255
$V^{2+} + 2e^- \longrightarrow V(s)$	−1.125

(a) $NO(g) + H_2O + O_2(g) \longrightarrow NO_3^- + H^+$
(b) $V^{3+} + e^- \longrightarrow V(s)$

78. Consider the following half-cell potentials :

$$Cu^{2+} + 2e^- \longrightarrow Cu; \quad E° = 0.34\ V$$
$$Zn^{2+} + 2e^- \longrightarrow Zn; \quad E° = -0.76\ V$$

A solution contains 0.05 M Cu^{2+} and x M Zn^{2+} ions. What would be the value of x such that both Cu^{2+} and Zn^{2+} are deposited simultaneously.

79. The voltage of a certain cell at 37°C and 17°C are 0.36 V and 0.33 V respectively. If the number of electrons transferred in the overall process be two, calculate $\Delta G°$, $\Delta S°$ and $\Delta H°$ at 27°C.

80. Calculate solubility product of $Fe(OH)_3$ given

$$Fe^{3+} + 3e^- \longrightarrow Fe; \quad E° = -0.036\ V$$
$$Fe(OH)_3 + 3e^- \longrightarrow Fe(s) + 3OH^-; \quad E° = -0.77\ V$$

81. Solubility product constant (K_{sp}) of $PbSO_4$ is 10^{-8} at 25°C. Also given the following standard state half-cell potentials:

$$PbSO_4(s) + 2e^- \longrightarrow Pb + SO_4^{2-}; \quad E° = -0.0356\ V$$
$$Pb^{2+} + 2e^- \longrightarrow Pb(s); \quad E° = -0.126\ V$$

Calculate emf of the following cell at 25°C if molarity of H_2SO_4 is 0.02.

$$Pb\,|\,PbSO_4(s)\,||\,0.02\ M\ H_2SO_4\,|\,H_2\ (1.0\ atm)\,|\,Pt$$

82. The following cell

$$Ag(s)\,|\,AgCl(s), HCl\ (0.1\ M)\,|\,glass\,|\,buffer\,||\,saturated\ calomel\ electrode$$

Give an emf of 0.112 V at 25°C when pH of the buffer used is 4.00. When a buffer of unknown pH was used, the potential was 0.038 V. What is the pH of unknown buffer? Also determine the emf when pH of the buffer solution is 2.0.

83. A 2.0 V storage battery is used in electrolysis in which a back emf of 1.45 V is developed. If the resistance of the entire circuit be 10 ohm, determine
(a) the magnitude AC current flowing in the cell.
(b) quantity of heat generated by the current flow per Faraday of electricity.

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84. The cell

$Pt \mid H_2\ (1.0\ bar) \mid H^+ \parallel KCl\ (saturated) \mid Hg_2Cl_2 \mid Hg$

was used to measure the pH of a solution of 0.01M acetic acid in 0.0358 M sodium acetate. Calculate the cell potential expected at 25°C [$K_a = 1.81 \times 10^{-5}$ for acetic acid]

85. The voltage required to electrolyse certain solutions changes as the electrolysis proceeds because the concentration in the solution is changing. In an experiment, 500 dm^3 of a 0.05 M solution of copper(II) bromide was electrolysed until 2.827 g of Cu was deposited. Calculate the theoretical minimum voltage required to sustain the electrolysis reaction at the beginning and at the end of experiment.

86. Write both electrode reaction and overall cell reaction for the cell

$$Tl \mid TlCl(s) \parallel CdCl_2\ (0.01\ M) \mid Cd$$

and calculate emf of the cell if $E^o(Tl^+/Tl = -0.34\ V)$, $E^o(Cd^{2+}/Cd = -0.40V)$ and the solubility product of TlCl is 1.6×10^{-3}.

87. The metal M forms a soluble nitrate and a very slightly soluble chloride. The cell

$M \mid M^+ \mid (0.1\ M), HNO_3\ (0.2\ M) \parallel H_2\ (1.0\ bar), Pt$

has a measured emf = –0.4 V. When sufficient solid KCl is added to make the solution of the cell 0.2 M in K^+, the emf changes to –0.05 V. Calculate the solubility product of MCl.

88. The voltage of the following cell is 0.987 V

$$Pt, H_2\ (1.0\ atm) \mid HOCN\ (1.4 \times 10^{-3}\ M) \parallel Ag^+\ (0.8\ M) \mid Ag(s)$$

Calculate K_a of HOCN, $E^o\ (Ag^+/Ag) = 0.8$ V

89. An electrochemical cell consists of a silver electrode in contact with 346 mL of 0.10 M $AgNO_3$ solution and a magnesium electrode in contact with 288 mL $Mg(NO_3)_2$ solution. (a) Calculate E for the cell at 25°C. (b) A current is drawn from the cell until 1.2 g of silver is deposited at the silver electrode. Calculate E for the cell at this stage of operation. $E^o(Ag^+/Ag) = 0.8$ V and $E^o(Mg^{2+}/Mg) = -2.37$ V.

90. An electrochemical cell is constructed by immersing a piece of copper wire in 25 mL of a 0.2 M $CuSO_4$ solution and a Zinc strip in 25.0 mL of a 0.2 M $ZnSO_4$ solution. (a) Calculate the emf of the cell at 25°C and predict what would happen if a small amount of concentrated NH_3 solution were added to (i) the $CuSO_4$ solution and (ii) to $ZnSO_4$ solution? (b) In a separate experiment 25 mL of 3.0 M NH_3 are added to the $CuSO_4$ solution. If the emf of the cell is 0.68 V, Calculate formation constant of $Cu(NH_3)_4^{2+}$.

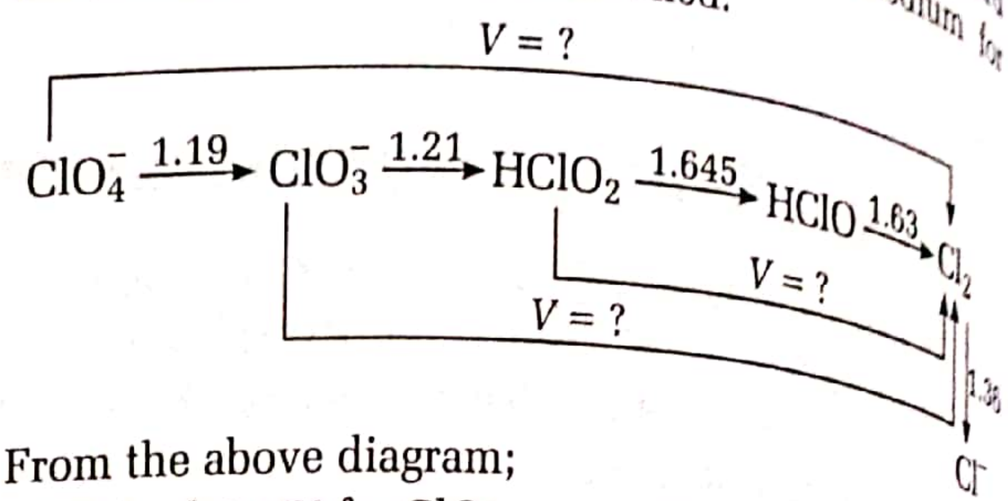
91. The magnitudes (but *not* the signs) of the standard reduction potentials of the two metals X and Y are

$$Y^{2+} + 2e^- \longrightarrow Y; \quad |E°| = 0.34\ V$$
$$X^{2+} + 2e^- \longrightarrow X; \quad |E°| = 0.25\ V$$

When the half-cells of X and Y are connected, electrons flow from X to Y. When X is connected to SHE, electrons flow from X to SHE. (a) Are the E^o values of the half-cell reactions positive or negative? (b) What is the standard emf of a cell made-up of X and Y?

92. The voltage of a certain cell at 25°C and 20°C are 0.3525 V and 0.3533 V respectively. If the number of electrons involved in the overall reactions be two, calculate $\Delta G°$, $\Delta S°$ and $\Delta H°$ at 25°C.

93. In the following sequence of reactions, the standard reduction potentials in volts in acidic medium for individual reactions are mentioned.



From the above diagram;

(a) Calculate $E°$ for $ClO_3^- \longrightarrow Cl_2$

(b) Calculate $E°$ for $ClO_4^- \longrightarrow HClO$

(c) Calculate $\Delta G°$ for the change mentioned in part (a) and (b).

(d) Calculate $E°$ and $\Delta G°$ for the reaction

$$2HClO_2 \longrightarrow HClO + ClO_3^- + H^+$$

(e) Find the other missing values mentioned in the above scheme.

94. In an electrochemical cell, the reduction reaction is $Mg^{2+} + 2e^- \longrightarrow Mg(s)$. The cell operates at 1.531 V and 1.375 g of Mg was deposited during 9 minutes. Calculate the average current during the process.

95. Use the following data to calculate solubility product of PbF_2. A galvanic cell consists of a hydrogen gas electrode ($p(H_2) = 1$ bar, $[H^+] = 1$ M) and a Pb electrode in a 1.0 M KF solution in equilibrium with $PbF_2(s)$. The cell potential is 0.562 V. $E^o(Pb^{2+}/Pb) = -0.13V$.

96. A galvanic cell has Cu electrode in 1.0 M $CuSO_4$ solution and a hydrogen electrode in a solution of unknown pH. The cell potential is 0.72 V. Determine the pH of unknown solution.

97. A concentration cell has Zn electrodes. The electrolyte in each of the half-cells is a solution of $ZnCl_2$ dissolved in water. One has a freezing point of –2.0°C and the other has a freezing point of –0.9°C. What is the potential of the cell at 25°C?

98. A galvanic cell consist of a Zn electrode in a 0.1 M Zn^{2+} solution and a second half-cell with a Pt electrode in a 0.1 M solution of HIO_3. Determine cell potential if K_a of HIO_3 is 0.20. $E^o(Zn^{2+}/Zn) = -0.76$ V

99. A galvanic cell consists of Cu electrode in a 0.5 L 1.0 M $CuSO_4$ solution and a Zn electrode in 0.5 L 1.0 M $ZnCl_2$ solution. A steady current of 1.0 A is drawn for 10 h. Determine concentration of each ions remained at the end of electrolysis.

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100. The chlorate ion ClO_3^- can disproportionate in basic solution according to the reaction:

$$2ClO_3^-(aq) \rightleftharpoons ClO_2^-(aq) + ClO_4^-(aq).$$

What is the equilibrium concentration of the ions resulting from a solution initially at 0.1M in chlorate ion? $E°(ClO_4^-/ClO_3^-) = 1.19$ V, $E°(ClO_3^-/ClO_2^-) = 1.21$ V

101. At 27°C, $\left(\frac{\partial E°}{\partial T}\right)_p = -1.25 \times 10^{-3}$ VK^{-1} and $E° = 1.36$ V for the cell $Pt/H_2(g) \rightleftharpoons HCl(aq)/Cl_2/Pt$ Calculate entropy and enthalpy change in their standard state.

102. Calculate Gibb's free energy change and equilibrium constant for the reaction

$$Ni^{2+} + 2H_2O \longrightarrow Ni(OH)_2 + 2H^+ \text{ given that}$$

$$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O; \quad E° = 1.678 \text{ V}$$

and $$NiO_2 + 2H_2O + 2e \longrightarrow Ni(OH)_2 + 2OH^-; \quad E° = -0.49 \text{ V}$$

103. For the cell at 25°C :

$$Pt \mid Ag \mid AgCl(s) \mid HCl(aq) \mid Hg_2Cl_2(s) \mid Hg \mid Pt$$

$\left(\frac{\partial E°}{\partial t}\right)_p = 0.338$ mV K^{-1}. Find $\Delta G°$, $\Delta H°$ and $\Delta S°$. Use required data from table 1.

104. The standard electromotive force of the cell:

$$Fe/Fe^{2+}(aq) // Cd^{2+}/Cd \text{ is } 0.0372 \text{ V}$$

The temperature coefficient of emf is -0.125 V K^{-1}. Calculate the quantities $\Delta G°, \Delta H°$ and $\Delta S°$.

105. The concentration of Ca^{2+} in sea water is determined using a Ca^{2+} selective electrode. A 10 mL sample of sea water is diluted to 100 mL and its 50 mL aliquot is placed in a beaker with Ca^{2+} ion selective electrode and a reference electrode. The emf was found to be -0.053 V. A 1.0 mL aliquot of 0.05 M Ca^{2+} ion is added and emf was found to be -0.0422 V. What is the concentration of Ca^{2+} in seawater? Ignore volume change due to addition of second aliquot.

106. Use the van der Waals' equation of state to calculate the pressure at 35°C that would result if the chlorine produced from electrolysis of 10 kg molten NaCl is compressed into a tank with a volume of 75 L. Assume 96% efficiency of the electrolysis.

107. A galvanic cell consist of Zn electrode dipped in 1.0 L 0.2 M $Zn(NO_3)_2$ solution and a silver electrode dipped into a 1.0 L 0.1 M $AgNO_3$ solution at 25°C. emf of this cell is 1.52 V. Now KCl(s) is added to cathode chamber resulting in precipitation of AgCl and a change in emf. After addition, emf of the cell was found to be 1.04 V and $[K^+]$ is 0.30 M. Determine K_{sp} of AgCl.

108. To an aqueous solution of weak acid (HA), 20 mL NaOH is added and connected to a reference $Ag/AgCl/Cl^-$ (0.1M) electrode. emf of the cell was found to be 0.47 V. To the test solution, 30 mL of NaOH from same stock was added further and new emf was found to be 0.50 V. Determine acid dissociation constant of the weak acid. $E°(AgCl/Ag, Cl^-) = 0.23$ V.

109. Platinum is a very inert metal, however, it can be dissolved by the acid aqua regia, which is a mixture of concentrated hydrochloric acid and nitric acid. Based on the standard potential data given below show that nitric acid alone is incapable of dissolving platinum, while aqua regia, a mixture of nitric and hydrochloric acids, is capable of dissolving platinum. Hint: The product of the reaction of platinum metal with nitric acid is Pt^{2+} while the product of the reaction of platinum metal with aqua regia is $PtCl_6^{2-}$.

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O(l); \quad E°(V) = 0.955$$

$$Pt^{2+} + 2e^- \longrightarrow Pt(s); \quad E°(V) = 1.18$$

$$PtCl_4^{2-} + 2e^- \longrightarrow Pt(s) + 4Cl^-; \quad E°(V) = 0.755$$

$$PtCl_6^{2-} + 2e^- \longrightarrow PtCl_4^{2-} + 2Cl^-; E°(V) = 0.680$$

110. The residents of a certain town are concerned that the town's drinking water might have a high concentration of lead (Pb^{2+}). They have asked you to investigate whether they should worry about the lead concentration. To measure the concentration of the lead ions, you decided to take a sample of drinking water, acidify it with nitric acid, and use it as one half of the following galvanic cell

$$Pb \mid \text{drinking water} \mid\mid Pb^{2+} (1.00 \times 10^{-3} \text{ M}) \mid Pb$$

The cell potential, E_{Cell}, for this voltaic cell is measured at +0.0725 V. Calculate the Pb^{2+} concentration in the drinking water in units of ppm. (atomic mass Pb = 207.2 g/mole). Given the following $E°$ values at 25°C.

$$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}; \quad E° = 1.69$$

$$Pb^{2+} + 2e^- \longrightarrow Pb(s); \quad E° = -0.126$$

$$PbO_2(s) + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O(l); \quad E° = 1.458$$

111. The following voltaic cell was constructed to determine how well the complexing agent 1,4,8,11-tetraazacyclotetadecane (cyclam) reacts with Zn^{2+} to form the corresponding complex ion, $Zn(cyclam)^{2+}$:

$$Ag/AgCl \mid\mid Zn^{2+}, \text{cyclam}, pH = 10 \mid Zn$$

$$Zn^{2+} + \text{cyclam} \longrightarrow Zn(\text{cyclam})^{2+}$$

Given: $$Zn^{2+} + 2e^- \longrightarrow Zn(s); \quad E° = -0.762 \text{ V}$$

Initially, 1.0 μmole of $ZnSO_4$ is added to the right compartment and diluted with 200 mL of water buffered to pH 10. The voltaic cell potential for this mixture is measured at -1.116 V *vs* Ag/AgCl.

Next, 0.1 mole of cyclam is added to the right compartment of the voltaic cell. The measured cell potential drops to -1.509 V *vs* Ag/AgCl. Based on this data calculate the concentration of Zn^{2+} present in the voltaic cell after cyclam is added. Is cyclam a good sequestering agent for Zn^{2+}?

112. Suppose that 50 mL of a 0.050 M TiO^{2+} solution buffered at pH 0.5 was titrated with a 0.050 M standard Cr^{2+} solution. A Pt electrode (cathode) and an SCE (anode) were used to monitor the progress of the titration.

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(a) Write a balanced chemical equation for this titration reaction and calculate the potential of the voltaic cell after 60.00 mL of the Cr^{2+} solution has been added.
(b) Calculate the potential of the voltaic cell at the equivalence point. Given:

$$Cr^{2+} + 2e^- \longrightarrow Cr(s); \quad E° = -0.89 \text{ V}$$
$$Cr^{3+} + e^- \longrightarrow Cr^{2+}; \quad E° = -0.42 \text{ V}$$
$$TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O; \quad E° = -0.10 \text{ V}$$

113. The following redox reaction occurs in a voltaic cell

$$2Sc(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \longrightarrow 2Sc^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

(a) Calculate the cell potential, E_{Cell}, when $[Cr_2O_7^{2-}] = 6.2 \times 10^{-5}$ M, $[Sc^{3+}] = 0.35$ M, $[Cr^{3+}] = 0.75$ M, and the pH is 1.85. The standard cell potential, $E°_{Cell}$, for this cell is 3.70 V.
(b) What is the effect on the E_{cell} of decreasing the concentration of $Cr_2O_7^{2-}$ in the cathode compartment?
(c) What is the effect on the E_{cell} of adding a solution of $Mg(NO_3)_2$ to the anode compartment, increasing the quantity of Mg^{2+} but not its concentration?

114. An alkaline battery consists of a powdered Zn/gel anode and a C/MnO_2 cathode. At the anode, Zn is oxidized to Zn^{2+} which reacts with the OH^- ion present in the paste to form $Zn(OH)_2(s)$. Suppose that an alkaline battery was manufactured using Fe metal instead of Zn metal, and that the Fe was oxidized to Fe^{2+} at the anode. What effect would this have on the cell potential or emf of the battery? Explain your answer briefly.

Electrolytic Conductivity

115. Molar conductivity of a 0.05M aqueous solution of $MgCl_2$ is 195 S cm^{2}mol^{-1} at 27°C. A cell with electrodes that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.05 M $MgCl_2$ solution. How much current will flow when a potential difference across the electrodes is 5.00 V.

116. A conductivity cell is filled with 0.1M KCl solution at 27°C. The measured resistance of solution is 25Ω. The specific conductivity of the above solution is 0.0116 S cm^{-1}. Determine molar conductivity of 0.10 M KCl solution. If the same cell is filled with 0.01 M acetic acid solution the cell resistance is 1982Ω, determine molar conductivity of acetic acid solution.

117. A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a conductivity cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω. The molar conductivity of 0.02 M KCl solution was found to be 138.3 S cm^2 mol^{-1}. Now 500 g NaCl is dissolved in the swimming pool and stirred thoroughly. A sample of this solution gave a resistance of 7600 Ω. The molar conductivity of present swimming pool water was found to be 126 S cm^2 mol^{-1}. Determine volume of water present in the swimming pool.

118. When a conductivity cell is filled with 0.10 M KCl, resistance was found to be 60 ohm at 25°C. Also molar conductivity of the above 0.10 M KCl solution was measured to be 129 S cm^2 mol^{-1}. When the above conductivity cell is filled with a solution containing 2.85 g of $MgCl_2$ per litre, its resistance was 142 ohm. Determine the (a) cell constant (b) specific conductivity of $MgCl_2$ solution (c) Molar conductivity of $MgCl_2$ solution.

119. Hydrofluoric acid is a weak acid. At 25°C, the molar conductivity of 0.002 M HF solution is 176 S cm^2 mol^{-1}. Also, molar conductivity at infinite dilution Λ^∞ (HF) is 405 S cm^2 mol^{-1}. What is K_a of HF.

120. The molar conductivity of a 0.01 M KCl solution, at 25°C, is 150 S cm^{2}mol^{-1} and resistance of solution is 525 ohms. Resistance of the same cell when filled with 0.1M NH_4OH solution is 2030 ohms. Also ionic conductivities of NH_4^+ and OH^- are 73.4 and 198.6 S cm^2 mol^{-1} respectively. Determine the degree of ionization of NH_4OH.

121. The conductivity of a saturated solution of CaF_2 at 25°C was found to be 4.2×10^{-5} ohm^{-1} cm^{-1}. The conductivity of water used for making this solution was 2.8×10^{-6} ohm cm^{-1}. Also given, at infinite dilution $\Lambda^\infty\left(\frac{1}{2}Ca^{2+}\right) = 52$ and $\Lambda^\infty(F^-) = 48$ S cm^2 mol^{-1}. What is the solubility in g/litre and solubility product of CaF_2 at 25°C.

122. The specific conductivity of a saturated solution of silver oxalate is 3.8×10^{-5} S cm^{-1} at 25°C. Conductivity of water from which the above solution is made is 6.2×10^{-8} S cm^{-1}. Calculate the molar conductivity of oxalate ion, given molar conductivity of Ag^+ ion at infinite dilution is 62 S cm^2 mol^{-1} and solubility product of $Ag_2C_2O_4$ at 25°C is 1.2×10^{-11}.

123. Silver chloride salt is only slightly soluble in water and a saturated solution of AgCl may be regarded as infinitely dilute. At 25°C the conductivity of a saturated solution is 1.8×10^{-6} S cm^{-1} after correction for water. Also, at infinite dilution, molar ionic conductivities are $Ag^+(\Lambda^\infty) = 62$ S cm^2 mol^{-1} $Cl^-(\Lambda^\infty) = 76$ S cm^2 mol^{-1}. Determine the solubility product of AgCl at 25°C.

124. A particular conductivity cell has a resistance of 468 Ω when filled with 0.001 M HCl solution of 1580 Ω when filled with 0.001 M NaCl solution and 1650 Ω when filled with 0.001 M_{NaNO_3} solution. The molar conductivity of $NaNO_3$ is 121 S cm^2 mol^{-1}. Determine?
(a) Specific conductivity of 0.001 M $NaNO_3$ solution.
(b) Cell constant
(c) Resistance of the cell when filled with 0.001 M HNO_3 and molar conductivity of HNO_3.

125. A conductance cell is filled with 0.05 M KCl solution (specific conductivity = 6.67×10^{-3} S cm^{-1}) at 25°C and the measured resistance is 245 Ω when the cell is filled with 0.01 M NaOH, the measured resistance is 680 ohm at 25°C. What is the specific and molar conductivity of 0.01 M NaOH.

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126. Given the following molar conductivities at infinite dilution and 25°C: HCl = 426, KCl = 150, $CaCl_2$ = 272, NaCl = 126.5 and Na_2SO_4 = 260 S cm² mol⁻¹. Calculate Λ^∞ of (a) H_2SO_4 (b) K_2SO_4 and (c) $CaSO_4$.

127. Given the molar conductivities at 25°C : HCl = 426 S cm² mol⁻¹; NaCl = 126 S cm² mol⁻¹, Sodium crotonate (NaC) = 83 S cm² mol⁻¹. Calculate the degree of dissociation and dissociation constant of crotonic acid. The specific conductivity of a 0.001 M solution of crotonic acid were found to be 3.83×10^{-5} S cm⁻¹.

128. The conductivity of water at 25°C is 0.554×10^{-7} S cm⁻¹. Calculate the degree of dissociation and ionic product of water at 25°C. Given : $\lambda(H^+) = 350$ S cm² mol⁻¹ and $\lambda(OH^-) = 198$ S cm² mol⁻¹.

129. The specific conductivity of a 0.001 M Na_2SO_4 solution is 2.6×10^{-4} S cm⁻¹ and increases to 7.0×10^{-4} S cm⁻¹ when the solution is saturated with $CaSO_4$. The molar conductivities of Na^+, and Ca^{2+} ions are 50 and 120 S cm² mol⁻¹ respectively. Calculate
(a) The specific conductivity of only $CaSO_4$ in the solution.
(b) Solubility product of $CaSO_4$ solution.
Specific conductivity of water used is 5×10^{-7} S cm⁻¹.

Multiple Choice Questions (*Base Level*)

These questions have only one correct option

1. If an orange is used to power the fruit clock, which of the following statements is TRUE?
(a) Free electrons flow through the orange to maintain electrical neutrality.
(b) The orange allows the Zn^{2+} and Cu^{2+} ions produced in the reaction to mix thereby maintaining electrical neutrality.
(c) The acids present in the orange are oxidized at the anode to produce hydrogen gas.
(d) The orange functions as the salt bridge by maintaining electrical neutrality.

2. Which of the following metals could be used successfully to galvanize iron?
(a) Ni (b) Cu (c) Sn (d) Mn

Half-cells	$E°$ (at 25°C)
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.23
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.03
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.41

3. A beaker contains a small amount of gold dust (Au(s)). Which of the following aqueous solutions, when added to the beaker, would dissolve the gold dust (*ie*, convert Au(s) to $Au^{3+}(aq)$)?
(a) $Cr_2O_7^{2-}$ (acidic solution) (b) H_2O_2 (acidic solution)
(c) Al^{3+} (d) Zn^{2+}

Half-cells	$E°$ (at 25°C)
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$Al^{3+} + 3e^- \longrightarrow Al$	−1.66
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.73
$Cr_2O_7^{2-} + 6e^- + H^+ \longrightarrow 2Cr^{3+}$	1.23
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.30

4. Which of the following statements best describes what will happen when liquid bromine (Br_2) is poured into a beaker containing aluminium metal?
(a) Br_2 will be reduced; Al will be oxidized.
(b) Br_2 will be oxidized; Al will be reduced.
(c) Br_2 will function as the reducing agent; Al will function as the oxidizing agent.
(d) A reaction will not occur.

5. Consider the following galvanic cell reaction at 25°C,
$$4Cr^{2+}(aq) + O_2(g) + 4H_3O^+(aq) \longrightarrow 4Cr^{3+}(aq) + 6H_2O(l)$$
Which of the following statements best describes what would happen to the cell potential if the concentration of Cr^{2+} is increased?
(a) The cell potential would become less positive.
(b) The cell potential would become more positive.
(c) The cell potential would remain the same.
(d) Insufficient information to answer this question.

6. Which of the following half-reactions is involved in the STANDARD HYDROGEN ELECTRODE?
(a) $Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$
(b) $2H_3O^+(aq) + 2e^- \longrightarrow 2H_2O(l) + H_2(g)$
(c) $H_2O_2(aq) + 2H_3O^+(aq) + 2e^- \longrightarrow 4H_2O(l)$
(d) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

7. Which of the following metal ions will plate out on a piece of galvanized iron which has NOT had the layer of Zn metal removed?
(a) Cu^{2+} (b) Au^{3+}
(c) Ni^{2+} (d) All of these

8. Suppose that gold is being plated onto another metal in a electrolytic cell. The half-cell reaction producing the Au(s) is
$$3e^- + AuCl_4^- = Au(s) + 4Cl^-$$
If a 0.30 amp current runs for 15.00 minutes, what mass of Au(s) will be plated, assuming all the electrons are used in the reduction of $AuCl_4^-$?
The Faraday constant is 96485 coul/mol e^- and molar mass of Au is 197.
(a) 0.184 g Au (b) 0.551 g Au
(c) 1.84 g Au (d) 0.613 g Au

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9. Consider a spontaneously operating electrochemical cell in which the net oxidation-reduction reaction is

$3Zr(s) + 4Fe^{3+} \longrightarrow 3Zr^{4+} + 4Fe(s)$.

Choose the statement which is FALSE.

(a) The anode reaction is $Zr \longrightarrow Zr^{4+} + 4e^-$

(b) The cathode reaction is $Fe^{3+} + 3e^- \longrightarrow Fe$

(c) Electrons flow from the cathode to the anode.

(d) The standard potential for this cell will be > 0.

10. What is the cell potential (standard emf '$E°$') for the reaction below? [$E°(Fe^{2+}(aq)/Fe) = -0.44V$ and $E°(O_2(g)/H_2O/OH^-) = +0.4V$]

$2Fe(s) + O_2(g) + 2H_2O(l) \rightleftharpoons 2Fe^{2+}(aq) + 4OH^-(aq)$

(a) $E°_{Cell} = -0.48$ V (b) $E°_{Cell} = -0.04$ V

(c) $E°_{Cell} = +0.84$ V (d) $E°_{Cell} = +1.28$ V

11. Which of the following statements is (are) true about electrochemistry?

I. The greater the electronegativity value the more the element wants to get rid of electrons.

II. If the cell potential is positive, then the electrochemical reaction is spontaneous.

III. The amount of material plated out in an electrochemical cell is related to the number of electrons that pass through the cell.

(a) I and II (b) Only II

(c) Only III (d) II and III

12. The lead-acid battery in a car has six voltaic cells connected in series. Each cell has a $E° = 2.041$ V. Calculate the $\Delta G°$ for each cell assuming that 2.0 moles of electrons are exchanged per moles of reaction in this redox reaction.

(a) $\Delta G° = -3.93 \times 10^5$ kJ/mol

(b) $\Delta G° = 3.93 \times 10^2$ kJ/mol

(c) $\Delta G° = 9.85 \times 10^4$ kJ/mol

(d) $\Delta G° = -3.93 \times 10^2$ kJ/mol

13. Which of the following best explains why concentration cells must be run under non-standard conditions in order for them to do electrical work?

(a) A concentration cell can only do electrical work when either NH_3 or NaOH is added to one of the half-cells.

(b) A concentration cell cannot do electrical work at 25°C.

(c) The change in free energy for a concentration cell is always negative under standard conditions.

(d) A concentration cell has a cell potential equal to zero under standard conditions.

14. Which of the following statements about a salt bridge in a voltaic cell is TRUE?

(a) Free electrons flow through the salt bridge to maintain electrical neutrality in the two half-cells.

(b) The salt bridge allows the ions present in the two half-cells to mix extensively.

(c) The wire must be connected directly to the salt bridge in order for the salt bridge to be able to maintain electrical neutrality in the two half-cells.

(d) Ions from the electrolyte in the salt bridge flow into each half-cell to maintain electrical neutrality.

15. Which of the following reactions can be used to construct a voltaic cell?

(a) $H_3O(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$

(b) $HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

(c) $Cu^{2+}(aq) + 4F^-(aq) \rightleftharpoons CuF_4^{2-}(aq)$

(d) $O_2(g) + 4H_3O^+(aq) + 4I^-(aq) \rightleftharpoons 2I_2(aq) + 6H_2O(l)$

16. Consider the following standard reduction potentials:

Half reaction	(V)
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	$E° = -0.23$ V
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	$E° = -0.41$ V
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	$E° = -1.03$ V
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	$E° = -0.28$ V
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	$E° = -0.74$ V

Which of the following metals could be used successfully to galvanize steel?

(a) Ni only (b) Ni and Co

(c) Fe only (d) Mn and Cr

17. Which of the following is TRUE for an operating voltaic cell?

(a) $\Delta G > 0; E = 0$ (b) $\Delta G < 0; E < 0$

(c) $\Delta G = 0; E > 0$ (d) $\Delta G < 0; E > 0$

18. You know that silver tarnish [$Ag_2S(s)$] can be converted to silver metal ($Ag(s)$) by placing the tarnished silver piece in a dilute solution of baking soda contained in an aluminium pan. The following half-reactions are thought to be involved,

$$Ag_2S(s) + 2H_3O^+(aq) + 2e^- \rightleftharpoons 2Ag(s) + H_2S(g) + 2H_2O(l)$$

$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$$

Which of the following statements is TRUE?

(a) As the silver piece is being cleaned, H_3O^+ ions are produced and H_2S gas is consumed.

(b) It is necessary that the silver piece and the aluminium pan touch so that electrons can be transferred.

(c) As the silver piece is being cleaned, Al^{3+} ions in the solution are reduced to Al metal.

(d) The silver piece being cleaned functions as the anode.

19. In an electrochemical process called 'electrolysis', H_2 gas and O_2 gas can be obtained by passing an electric current through liquid water,

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

Which species is the OXIDIZING AGENT and which species is the REDUCING AGENT in this reaction, respectively?

(a) $H_2O(l)$; $H_2(g)$ (b) $O_2(g)$; $H_2O(l)$

(c) $H_2O(l)$; $H_2O(l)$ (d) $O_2(g)$; $H_2(g)$

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20. Which of the following statements about porous disks in voltaic cells is TRUE?
(a) Free electrons flow through the porous disk to maintain electrical neutrality in the two half-cells.
(b) Ions present in the two half-cells flow through the porous disk to maintain electrical neutrality in both half-cells.
(c) A porous disk contains a strong electrolyte like potassium chloride (KCl).
(d) The wire must be connected directly to the porous disk in order for the porous disk to be able to maintain electrical neutrality in the two half-cells.

21. In the Standard Hydrogen Electrode, a platinum wire is used as the electrode. Consider the following standard reduction potentials,

$$Zn^{2+} + 2e^- \rightleftharpoons Zn(s); \quad E° = -0.76\ V$$
$$2H_3O^+(aq) + 2e^- \rightleftharpoons 2H_2O(l) + H_2(g); \quad E° = 0.00\ V$$
$$Pt^{2+}(aq) + 2e^- \rightleftharpoons Pt(s); \quad E° = 1.20\ V$$

Which of the following statements best describes what would happen if the platinum wire in the Standard Hydrogen Electrode were replaced with a zinc wire? **Note:** Assume that this is the only change made to the half-cell.
(a) Zinc ion in the solution would be reduced; the mass of the zinc electrode would increase.
(b) The pH of the solution would decrease.
(c) The zinc electrode would be oxidized; the mass of the zinc electrode would decrease.
(d) This change would have no effect - the Standard Hydrogen Electrode would continue to function properly.

22. Consider a diagram of a voltaic cell constructed from zinc and copper in which a tube containing a porous disk and a solution of KCl was placed in each half-cell (the two tubes are not connected). Which of the following statements best describes why this cell has a cell potential of 0.00 V?
(a) The sum of the zinc and copper half-cell potentials is equal to 0.00 V.
(b) Electrical neutrality cannot be maintained in the half-cells and the KCl tubes.
(c) All voltaic cells which use zinc in one of the half-cells have a cell potential of 0.00 V.
(d) The tubes needed to contain a weak electrolyte, like AgCl, in order for the cell to function.

23. Which of the following statements best describes what will happen when magnesium metal is added to an aqueous solution containing 1.0 M ferric ion (Fe^{3+}) at 25°C?

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s); E° = -2.375\ V$$
$$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s); \ E° = -0.036\ V$$

(a) Mg(s) will be oxidized; $Fe^{3+}(aq)$ will be reduced; the standard cell potential will be 2.339 V.
(b) Mg(s) will be oxidized; $Fe^{3+}(aq)$ will be reduced; the standard cell potential will be –2.339 V.
(c) $Fe^{3+}(aq)$ will be oxidized; Mg(s) will be reduced; the standard cell potential will be –2.339 V.
(d) $Fe^{3+}(aq)$ will be oxidized; Mg(s) will be reduced; the standard cell potential will be 2.339 V.

24. Suppose you have been given the task of selecting a metal to be used as the sacrificial anode for the cathodic protection of a buried iron fuel tank. Considering the following standard reduction potentials,

$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pd(s); \quad E° = 0.99\ V$$
$$Ag^+(aq) + e^- \rightleftharpoons Ag(s); \quad E° = 0.80\ V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s); \quad E° = 0.34\ V$$
$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s); \quad E° = -0.23\ V$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s); \quad E° = -0.41\ V$$

Which of the following metals could be used as the sacrificial anode in this application?
(a) Pd (b) Ni
(c) Cu (d) None

25. The cell potential for the electrochemical reaction shown below depends upon the Cl^- and Cu^{2+} concentrations. Calculate the cell potential (in V) at 25°C if $[Cu^{2+}] = 3.5$ M and $[Cl^-] = 1.7$ M.

$$Cu^{2+}(aq) + 2Cl^-(aq) + 2Ag(s) \rightleftharpoons Cu(s) + 2AgCl(s); \quad E° = 0.12\ V$$

(a) 0.15 V (b) –0.15 V
(c) 0.30 V (d) –0.30 V

26. Consider following reaction and standard cell potential

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq) \quad E° = +0.25\ V$$

Which of the following best describes what would happen in a solution that initially contains 1.0 M Ni^{2+}, 0.01 M NH_3 and 6.0 M $Ni(NH_3)_6^{2+}$ at 25°C? (Assume that the number of moles of electrons transported in this reaction is equal to 2.)
(a) The concentrations of both Ni^{2+} and NH_3 would decrease and concentration of $Ni(NH_3)_6^{2+}$ would increase.
(b) The concentrations of both Ni^{2+} and NH_3 would increase and the concentration of $Ni(NH_3)_6^{2+}$ would decrease.
(c) The concentration of $Ni(NH_3)_6^{2+}$ would decrease, the concentration of NH_3 would increase and the concentration of Ni^{2+} would remain the same.
(d) The concentrations of Ni^{2+}, NH_3 and $Ni(NH_3)_6^{2+}$ would all remain the same.

27. Consider the following standard reduction potentials:

$$Ca^{2+} + 2e^- \rightleftharpoons Ca; \quad E° = -2.76\ V$$
$$Pb^{2+} + 2e^- \rightleftharpoons Pb; \quad E° = -0.13\ V$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu; \quad E° = 0.34\ V$$
$$Hg_2^{2+} + 2e^- \rightleftharpoons Hg; \quad E° = 0.80\ V$$
$$Pt^{2+} + 2e^- \rightleftharpoons Pt; \quad E° = 1.20\ V$$

Which of the following metals is the strongest reducing agent?
(a) Ca (b) Pb
(c) Cu (d) Hg

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28. Consider the following standard reduction potentials

$$Fe^{2+} + 2e^- \rightleftharpoons Fe; \quad E° = -0.41 \text{ V}$$
$$Ag^+ + e^- \rightleftharpoons Ag; \quad E° = 0.80 \text{ V}$$
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-; \quad E° = 0.40 \text{ V}$$

Which of the following statements best describes what would happen if a block of silver metal were connected to a buried iron pipe via a wire?

(a) The silver metal would corrode, a current would be produced in the wire, and O_2 would be reduced on the surface of the iron pipe.
(b) The silver metal would corrode, a current would be produced in the wire, and Fe^{2+} would be reduced on the surface of the iron pipe.
(c) The iron pipe would corrode, a current would be produced in the wire, and Ag^+ would be reduced on the surface of the silver metal.
(d) The iron pipe would corrode, no current would be produced in the wire, and O_2 would be reduced on the surface of the iron pipe.

29. Consider the following reduction-oxidation reaction :

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq); \quad E° = +1.10 \text{ V}$$

When the components of the two half-reactions involved in this reaction are correctly separated, this reaction can be used to do electrical work and the change in internal energy of the system decreases. Which of the following statements best describes what will happen if Zn(s) is added to a solution containing $Cu^{2+}(aq)$ at constant volume at 25°C?

(a) The reaction will occur and the temperature of the solution will increase.
(b) The reaction will occur and the temperature of the solution will decrease.
(c) The reaction will occur and the temperature of the solution will remain the same.
(d) The reaction will not occur and the temperature of the solution will remain the same.

Direction for Q. Nos. 30 to 33 : *Use the following information to answer the these questions.*

A galvanic cell is constructed from a half-cell containing a solid copper electrode in 1.0 M $Cu(NO_3)_2$ solution and a half-cell containing a solid aluminium electrode in 1.0 M $Al(NO_3)_3$ solution at standard conditions. The half-cells are linked by an external circuit and by a KCl salt bridge.

$$Cu^{2+} + 2e^- \longrightarrow Cu; \quad E° = 0.34 \text{ V}$$
$$Al^{3+} + 3e^- \longrightarrow Al; \quad E° = -1.66 \text{ V}$$

30. The balanced overall (net) cell reaction for a spontaneous process is

(a) $Cu(s) + Al^{3+}(aq) \rightleftharpoons Cu^{2+}(aq) + Al(s)$
(b) $3Cu(s) + 2Al^{3+}(aq) \rightleftharpoons 3Cu^{2+}(aq) + 2Al(s)$
(c) $3Cu^{2+}(aq) + 2Al(s) \rightleftharpoons 3Cu(s) + 2Al^{3+}(aq)$
(d) $Cu^{2+}(aq) + Al(s) \rightleftharpoons Cu(s) + Al^{3+}(aq)$

31. Which of the following statements is TRUE about this cell?

(a) The aluminium electrode is the anode; the copper electrode is the cathode.
(b) The electrons flow from the copper electrode to the aluminium electrode.
(c) The cell diagram is |Cu solid|Cu^{2+}, 1.0 M |salt bridge |Al solid|Al^{3+}, 1.0 M|
(d) ΔS is the driving force of this reaction.

32. This cell generates a standard potential of

(a) +1.32 V (b) −2.00 V
(c) −1.32 V (d) +2.00 V

33. An expression for the equilibrium constant of this reaction at 25°C is

(a) e^{205} (b) e^{298}
(c) e^{467} (d) e^{831}

34. Copper and zinc electrodes stuck in an apple are used to run a small clock. Which of the following statements must be TRUE?

(a) The zinc strip was the anode.
(b) The apple was the salt bridge.
(c) $E_{Cell} > 0$.
(d) $\Delta G < 0$.

Direction for Q. Nos. 35 to 39 : *Use the following information to answer the these questions.*

A galvanic cell is constructed from a half-cell containing a solid chromium electrode in 1.0 M $Cr(NO_3)_3$ solution and a half-cell containing a solid tin electrode in 1.0 M $Sn(NO_3)_2$ solution. The half-cells are linked by an external circuit and by a KCl salt bridge.

$$Sn^{2+} + 2e^- \longrightarrow Sn; \quad E° = -0.14$$
and
$$Cr^{3+} + 3e^- \longrightarrow Cr; \quad E° = -0.74$$

35. The balanced overall (net) cell reaction is

(a) $Sn(s) + Cr^{3+}(aq) \rightleftharpoons Sn^{2+}(aq) + Cr(s)$
(b) $3Sn(s) + 2Cr^{3+}(aq) \rightleftharpoons 3Sn^{2+}(aq) + 2Cr(s)$
(c) $3Sn^{2+}(aq) + 2Cr(s) \rightleftharpoons 3Sn(s) + 2Cr^{3+}(aq)$
(d) $Sn^{2+}(aq) + Cr(s) \rightleftharpoons Sn(s) + Cr^{3+}(aq)$

36. Which of the following statements is TRUE about this cell?

(a) The chromium electrode is the anode; the Sn electrode is the cathode.
(b) The electrons flow from the tin electrode to the chromium electrode.
(c) The cell diagram is |Sn solid|Sn^{2+}, 1.0 M| salt bridge|Cr solid|Cr^{3+}, 1.0 M|.
(d) ΔH is the driving force of this reaction.

37. This cell generates a potential of ..... volts.

(a) 0.30 V (b) −0.30 V
(c) 0.60 V (d) −0.60 V

38. The value of the equilibrium constant at 25°C for this reaction is closest to

(a) 1.0×10^{-66} (b) 6.7×10^{-43}
(c) 7.4×10^{1} (d) 7.7×10^{61}

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39. The value of ΔG° for this reaction is ? kJ.
(a) −320 (b) −247
(c) 244 (d) −347

40. Which of the following reactions must be carried out in an electrolytic cell rather than a galvanic cell?
(a) $Zn^{2+} + Ca \rightleftharpoons Zn + Ca^{2+}$
(b) $\frac{3}{2} Br_2 + Al \rightleftharpoons Al^{3+} + 3Br^-$
(c) $2Al + 3Fe^{2+} \rightleftharpoons 2Al^{3+} + 3Fe$
(d) $Br_2 + 2Cl^- \rightleftharpoons 2Br^- + Cl_2$

41. A metal bucket is to be galvanized by plating the bucket by an electrolytic procedure using aqueous $ZnCl_2$ as the electrolyte. How many moles of zinc are deposited in 20.0 min by a constant current of 10 A?
(a) 0.01 (b) 0.03
(c) 0.06 (d) 0.10

42. Which statement is TRUE for an operating electrolytic cell?
(a) $\Delta G > 0$ and $E_{Cell} < 0$. (b) $\Delta G = 0$ and $E_{Cell} > 0$.
(c) $\Delta G < 0$ and $E_{Cell} = 0$. (d) $\Delta G < 0$ and $E_{Cell} > 0$.

43. Which of the following statements about the standard hydrogen electrode is TRUE?
(a) Hydrogen gas is bubbled through the electrode at a pressure of 2.0 atm.
(b) The electrode contains a copper wire that serves as a chemically inert surface for reduction-oxidation reactions to occur.
(c) The electrode contains a platinum wire that serves as a chemically inert surface for reduction-oxidation reactions to occur.
(d) The standard hydrogen electrode is assigned a half-cell potential of 1.0 V.

44. $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ are removed from waste solution by first precipitating these ions as the sulphides. Which of the following species could have been added to the waste solution to reduce both $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ to the corresponding metals (*ie*, Cu (*s*) and Zn (*s*))?
(a) Al (*s*) (b) Sn (*s*)
(c) Pb (*s*) (d) Ag (*s*)

45. Some brands of 'iron-fortified' cereals contain elemental iron. Which of the following statements is most likely TRUE?
(a) Elemental iron is reduced by the acid in the stomach.
(b) Elemental iron is oxidized by the acid in the stomach.
(c) Elemental iron is neither oxidized nor reduced by the acid in the stomach.
(d) Elemental iron is a Bronsted acid and reacts with Bronsted bases in the body.

46. Which of the following is NOT a use of a galvanic cell?
(a) Calculate values for standard free energy change.
(b) Determine the order of a half-cell reaction.
(c) Calculate E° of a half-cell reaction.
(d) Determine the value of K_{sp} for a salt.

47. A copper wire placed in a solution of silver nitrate ($AgNO_3$). Over a period of time, you observed a spontaneous reaction in which the solution turned blue and silvery needles formed on the copper wire. Which of the following statements must be TRUE about this process?
(a) $\Delta G > 0$ and $E_{Cell} < 0$ (b) $\Delta G = 0$ and $E_{Cell} > 0$
(c) $\Delta G < 0$ and $E_{Cell} = 0$ (d) $\Delta G < 0$ and $E_{Cell} > 0$

48. Consider a standard state galvanic cell with zinc and silver electrodes immersed in 1.0 M solutions of $Zn(NO_3)_2$ and $AgNO_3$ respectively. The relevant reduction potentials are as follows :

$$Ag^+ + e^- \longrightarrow Ag; \quad E^\circ = 0.80\ V$$

and

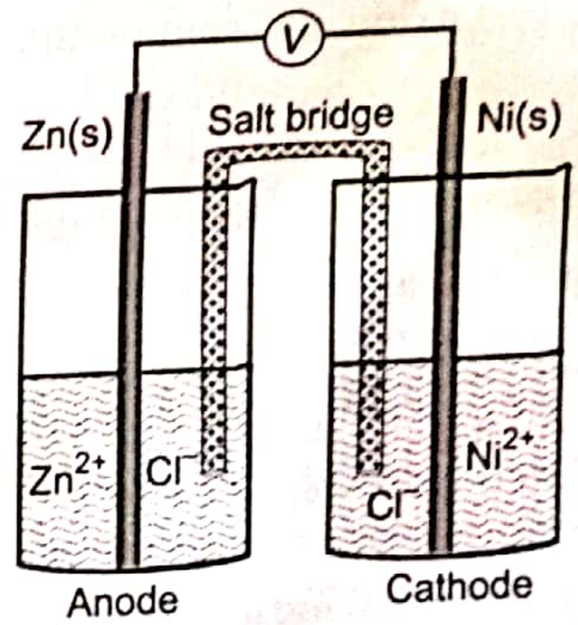
$$Zn^{2+} + 2e^- \longrightarrow Zn; \quad E^\circ = -0.76\ V$$

Which of the following statements is FALSE?
(a) The silver electrode is the cathode.
(b) Increasing the Zn^{2+} concentration will increase the cell voltage.
(c) Electrons in the circuit will flow from the zinc to the silver.
(d) The standard cell potential for this system is 1.56 volts.

49. An electrolysis plant processes sea-water to obtain Mg(s). If the plant operates its electrolytic cells at a total current of 1.0×10^6 A for 2.2 hrs, how many moles of Mg(s) will be produced from sea-water containing Mg^{2+}?
(a) 4.10×10^4 moles (b) 7.92×10^9 moles
(c) 9.64×10^4 moles (d) 8.20×10^4 moles

50. Which of the following is most likely TRUE for a 'dead battery'?
(a) $\Delta G < 0$ and $E_{Cell} = 0$ (b) $\Delta G > 0$ and $E_{Cell} < 0$
(c) $\Delta G = 0$ and $E_{Cell} = 0$ (d) $\Delta G = 0$ and $E_{Cell} < 0$

Direction for Q. Nos. 51 to 53 : *The next three (3) questions are based on the galvanic cell skethed below*



$$Zn^{2+} + 2e^- \longrightarrow Zn; \quad E^\circ = -0.76\ V$$
$$Ni^{2+} + 2e^- \longrightarrow Ni; \quad E^\circ = -0.23\ V$$

51. The spontaneous reaction that takes place in this cell is
(a) $Zn + Ni \longrightarrow Zn^{2+} + Ni^{2+}$
(b) $Zn + Ni^{2+} \longrightarrow Zn^{2+} + Ni$
(c) $Ni + Zn^{2+} \longrightarrow Ni^{2+} + Zn$
(d) $Ni^{2+} + 2K \longrightarrow 2K^+ + Ni$

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52. When the cell is operating
(a) e^- flow through the external circuit to the Zn electrode, while K^+ diffuses into the Zn/Zn^{2+} half-cell and Cl^- diffuses into the Ni/Ni^{2+} half-cell.
(b) e^- flow through the external circuit to the Zn electrode, while K^+ diffuses into the Ni/Ni^{2+} half-cell and Cl^- diffuses into the Zn/Zn^{2+} half-cell.
(c) e^- flow through the external circuit to the Ni electrode, while K^+ diffuses into the Zn/Zn^{2+} half-cell and Cl^- diffuses into the Ni/Ni^{2+} half-cell.
(d) e^- flow through the external circuit to the Ni electrode, while K^+ diffuses into the Ni/Ni^{2+} half-cell and Cl^- diffuses into the Zn/Zn^{2+} half-cell.

53. Pt electrodes are often used in galvanic cells. The above cell could continue to operate if
(a) both the Zn and Ni electrodes were replaced by Pt electrodes.
(b) the Zn electrodes were replaced by Pt; however, the Ni electrode is needed.
(c) the Ni electrode were replaced by Pt; however, the Zn electrode is needed.
(d) either electrode is replaced by Pt and the other electrode remains as before.

Direction for Q. Nos. 54 to 58 : *Use the table of standard reduction potentials at 25°C below to answer the next five questions.*

Half reaction	$E°$, V
$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.87
$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Au^{3+} + 3e^- \longrightarrow Au$	+1.50

54. The strongest oxidising agent on this list is
(a) Ca^{2+} (b) Au^{3+}
(c) Au (d) H^+

55. The strongest reducing agent on this list is
(a) Ca^{2+} (b) Ca
(c) Au^{3+} (d) Au

56. Which of the oxidizing agents in the above list can oxidize Au to Au^{3+} at standard conditions?
(a) NO_3^- in the presence of acid
(b) Ca^{2+}
(c) All of the oxidizing agents with positive half-cell potentials for the reduction half reaction.
(d) None of these oxidising agents

57. What is the cell potential at 25°C for the reaction,
$$3Ag(s) + NO_3^- + 4H^+ \longrightarrow 3Ag^+ + NO(g) + 2H_2O$$
when $[NO_3^-] = 2.0$ M, $[Ag^+] = 0.010$ M, the pH is 1.00, and the pressure of NO is 0.20 atm?
(a) 0.10 V (b) 0.16 V
(c) 0.22 V (d) 0.30 V

58. The equilibrium constant for the reaction,
$$Sn(s) + 2H^+ \longrightarrow Sn^{2+} + H_2(g) \text{ at } 25°C \text{ is}$$
(a) 5.4×10^4 (b) 2.3×10^2
(c) 1.1×10^2 (d) 1.00

59. A concentration cell is made up of the Fe/Fe^{2+} couple, where the Fe^{2+} concentrations are 1.0 M and 0.10 M. Which of the following statements best describes the operation of this cell?
(a) The anode compartment contains a 0.10 M Fe^{2+} solution, which decreases in concentration as the cell operates, and the cathode compartment contains a 1.0 M Fe^{2+} solution which also decreases in concentration as the cell operates.
(b) The anode compartment contains a 0.10 M Fe^{2+} solution, which increases in concentration as the cell operates, and the cathode compartment contains a 1.0 M Fe^{2+} solution which decreases in concentration as the cell operates.
(c) The anode compartment contains a 0.10 M Fe^{2+} solution, which decreases in concentration as the cell operates, and the cathode compartment contains a 1.0 M Fe^{2+} solution which increases in concentration as the cell operates.
(d) The anode compartment contains a 1.0 M Fe^{2+} solution, which decreases in concentration as the cell operates and the cathode compartment contains a 0.10 M Fe^{2+} solution which increases in concentration as the cell operates.

60. Which of the following statements about the lead storage battery is incorrect?
(a) Anode consists of lead and the cathode of lead dioxide.
(b) Electrolyte is an aqueous solution of sulphuric acid.
(c) As the battery runs down, the density of the electrolyte decreases.
(d) As the battery runs down, lead sulphate is formed on the anode and lead sulphite is formed on the cathode.

61. Iron can be protected against corrosion by cathodic protection. In this process
(a) a metal that is a stronger reducing agent than iron serves as the cathode
(b) a metal that is a stronger oxidizing agent than iron serves as the cathode
(c) a metal that is a weaker reducing agent than iron serves as the anode
(d) a metal that is a stronger reducing agent than iron serves as the anode

62. The chief reason that an active metal such as sodium is commercially prepared in the metallic state by electrolysis is that
(a) electricity is cheap, while chemicals are expensive.
(b) chemical preparation is too slow and no good catalysts are available.
(c) there are no convenient reducing agents available that can reduce sodium ions to the metal.
(d) there are no oxidizing agents strong enough to form metallic sodium.

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63. Chromium plating is applied by electrolysis to objects suspended in a dichromate solution, according to the following (unbalanced) half reaction :

$$Cr_2O_7^{2-}(aq) + e^- + H^+(aq) \longrightarrow Cr(s) + H_2O(l)$$

How many hours would it take to apply a chromium plating of thickness 2.0×10^{-2} mm to a car bumper of surface area 0.25 m^2 in an electrolysis cell carrying a current of 75.0 A? [The density of chromium is 7.19 g/cm^3.]

(a) 2.2 h (b) 1.5 h
(c) 3.0 h (d) 0.25 h

64. Calculate the concentration of Cu^+, at 10°C, when the cell potential for the following reaction is 0.06 V and $[Cu^{2+}] = 1.2$ M and $[Cl^-] = 3.5$ M. [$E°(Cu^{2+}/Cu^+) = 0.15$ V and $E°(Cl_2/Cl^-) = 1.36$ V; $E°(Hg_2Cl_2/Hg, Cl^- = 0.27$ V)]

$$Hg_2Cl_2(s) + 2Cu^+(aq) \longrightarrow 2Cu^{2+}(aq) + 2Hg(l) + 2Cl^-(aq)$$

(a) 0.30 M (b) 0.41 M
(c) 0.46 M (d) 1.0 M

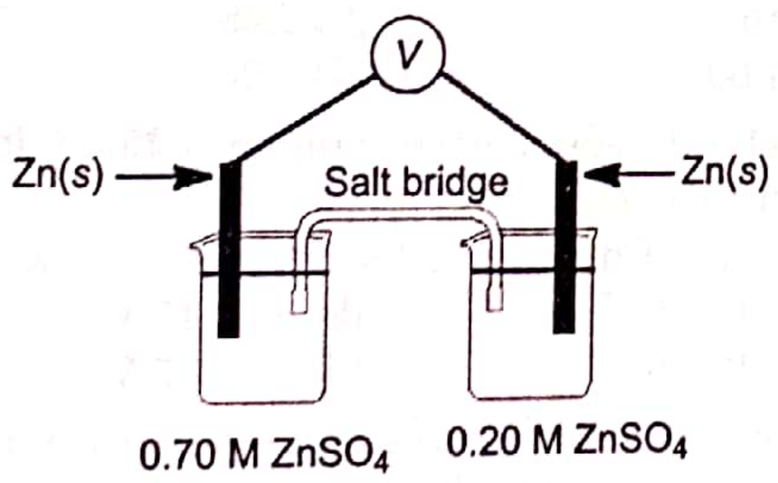
65. Which of the following chemical species could be used to oxidize Hg to Hg^{2+}?

(a) Li^+ (b) Cu^{2+}
(c) Ce^{4+} (d) Fe^{3+}

66. Calculate the standard enthalpy change for a cell reaction which has a standard cell potential of 1.50 V. The cell reaction involves the transfer of 2 moles of electrons and the standard entropy change is 110 J/K.

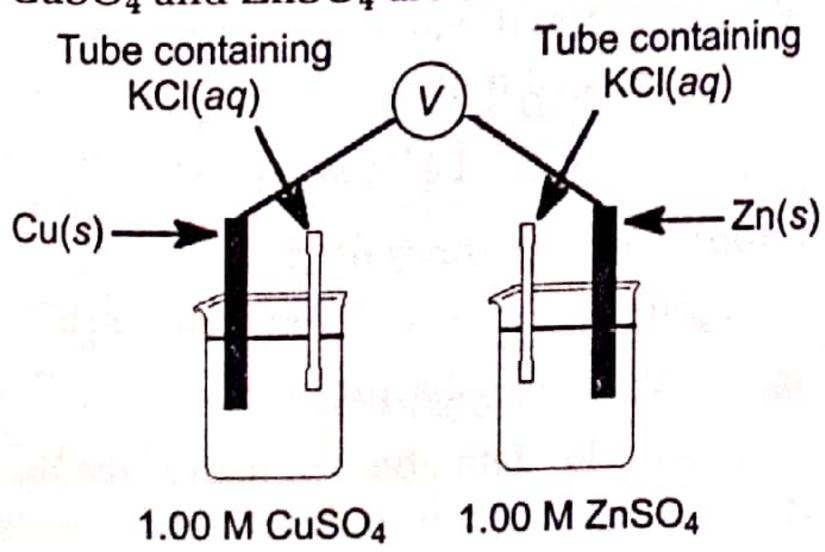
(a) −287 kJ (b) −257 kJ
(c) −144 kJ (d) 123 kJ

67. Calculate the cell potential (in V) at 25°C for the galvanic cell shown in the diagram below.
Note: $ZnSO_4$ *is a soluble salt.*



(a) 1.6×10^{-2} (b) 0.60 V
(c) 0.80 V (d) 1.2 V

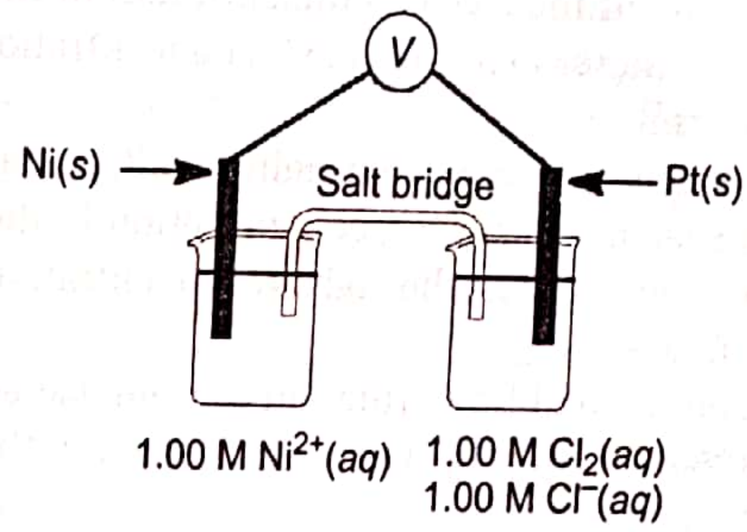
68. Consider the following diagram :
Note: $CuSO_4$ and $ZnSO_4$ are both soluble salts.



$$Zn^{2+} + 2e^- \longrightarrow Zn; \quad E° = -0.76 \text{ V}$$
$$Cu^{2+} + 2e^- \longrightarrow Cu; \quad E° = 0.34 \text{ V}$$

At 25°C, the measured cell potential would be
(a) positive. (b) zero.
(c) negative. (d) It is impossible to tell

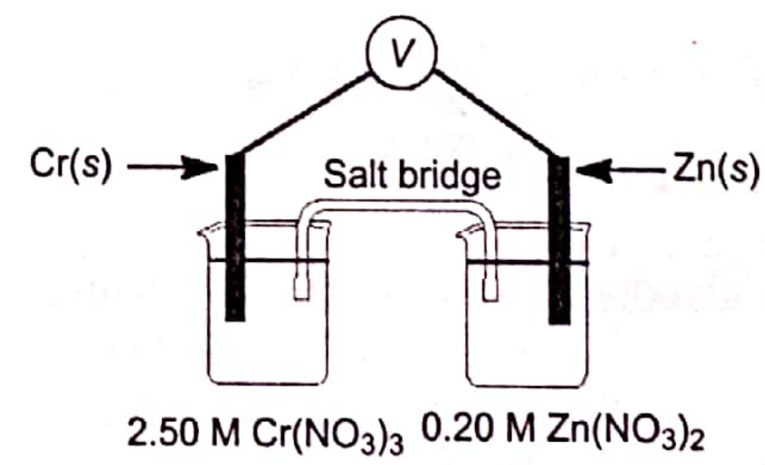
69. Consider the following diagram :



Which of the following describes what happens to the concentrations of Ni^{2+}, Cl_2 and Cl^-, and the masses of the Ni and Pt electrodes as this galvanic cell generates an electrical current spontaneously at 25°C?

	$[Ni^{2+}]$	$[Cl_2]$	$[Cl^-]$	Mass (Ni) electrode	Mass (Pt) electrode
(a)	decreases	increases	decreases	decreases	no change
(b)	decreases	increases	increases	increases	decreases
(c)	increases	decreases	increases	decreases	increases
(d)	increases	decreases	increases	decreases	no change

70. Calculate the cell potential (in V) at 25°C for the galvanic cell shown in the diagram below. *Note:* $Cr(NO_3)_3$ *and* $Zn(NO_3)_2$ *are soluble salts.*



$$Zn^{2+} + 2e^- \longrightarrow Zn; \quad E° = -0.76 \text{ V}$$
$$Cr^{3+} + 3e^- \longrightarrow Cr; \quad E° = -0.74 \text{ V}$$

(a) 0.05 V (b) 0.3 V
(c) 0.6 V (d) 0.8 V

71. Calculate the free energy change per mole of Cu^{2+} formed in the following reaction at 25°C.

$$Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$$
$$Cu^{2+} + 2e^- \longrightarrow Cu; \quad E° = 0.34 \text{ V};$$
$$Ag^+ + e^- \longrightarrow Ag; \quad E° = 0.80 \text{ V}.$$

(a) 0.46 kJ (b) 89 kJ
(c) 44.5 kJ (d) −89 kJ

72. What is K_{eq} for the reaction

$$Mg(s) + Pb^{2+} \longrightarrow Mg^{2+} + Pb?$$
$$Pb^{2+} + 2e^- \longrightarrow Pb; \quad E° = -0.13 \text{ V};$$
$$Mg^{2+} + 2e^- \longrightarrow Mg; \quad E° = -2.37 \text{ V}.$$

(a) 5×10^{75} (b) 3×10^{84}
(c) 2×10^{-75} (d) Insufficient information

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73. What would you observe if you set up the following electrochemical cell:

$$Ag|AgNO_3(0.001\ M)|AgNO_3(1\ M)|Ag?$$

(a) Electrons will flow from left to right, causing a decrease in the $AgNO_3$ concentration in the left cell, and an increase in the $AgNO_3$ concentration in the right cell.
(b) Electrons will flow from right to left, causing an increase in the $AgNO_3$ concentration in the left cell, and a decrease in the $AgNO_3$ concentration in the right cell.
(c) Electrons will flow from left to right, causing an increase in the $AgNO_3$ concentration in the left cell, and a decrease in $AgNO_3$ concentration in the right cell.
(d) Electrons will flow from right to left, causing a decrease in the $AgNO_3$ concentration in the left cell, and an increase in the $AgNO_3$ concentration in the right cell.

74. What is $E°$ for the half reaction given the following?

$$MX_2(s) + 2e^- = M(s) + 2X^-; \quad E° = ?$$
$$M^{2+} + 2e^- = M(s); \quad E° = 0.100\ V$$
$$MX_2(s) = M^{2+} + 2X^-; \quad K_{sp} = e^{-10}$$

(a) $E° = 0.100 - \frac{0.0592}{2} \ln \frac{1}{K_{sp}}$
(b) $E° = 0.100 - \frac{0.0592}{2} \log \frac{1}{K_{sp}}$
(c) $E° = 0.100 - \frac{0.0592}{2} \log K_{sp}$
(d) $E° = 0.100 + \frac{0.0592}{2} \log \frac{1}{K_{sp}}$

75. Consider the following electrode potentials:

$$Mg^{2+} + 2e^- \longrightarrow Mg; \quad E° = -2.37\ V$$
$$V^{2+} + 2e^- \longrightarrow V; \quad E° = -1.18\ V$$
$$Cu^{2+} + e^- \longrightarrow Cu^+; \quad E° = 0.15\ V$$

Which of the following reactions will proceed spontaneously from left to right?
(a) $Mg^{2+} + V \longrightarrow Mg + V^{2+}$
(b) $Mg^{2+} + 2Cu^+ \longrightarrow Mg + 2Cu^{2+}$
(c) $V^{2+} + 2Cu^+ \longrightarrow V + 2Cu^{2+}$
(d) $V + 2Cu^{2+} \longrightarrow V^{2+} + 2Cu^+$

76. Which of the following offers the best explanation for the fact that $E°$ values are independent of the amount of reaction?
(a) As the free-energy change increases, the number of electrons transferred decreases.
(b) The free-energy change of a reaction is independent of the amount of reaction.
(c) The number of electrons transferred in a reaction is independent of the amount of reaction.
(d) As the free-energy change increases, the number of electrons transferred also increases.

77. Which of these statements about a galvanic cell are not true?
(i) The cathode carries a positive sign.
(ii) The anions migrate toward the cathode.
(iii) The electrons are released through the anode.
(iv) Reduction occurs at the anode.
(a) (iii) and (iv) (b) (ii) and (iv)
(c) (ii) and (iii) (d) (i) and (ii)

78. Which of the following is not true regarding the relationship of the free-energy change and the cell potential of a galvanic cell?
(a) The free-energy change and the cell potential of a galvanic cell are quantitative measures of the driving force of a chemical reaction.
(b) Both the free-energy change and the cell potential are dependent on the composition of the reaction mixture.
(c) The free-energy change is directly proportional to the cell potential.
(d) If the free-energy change indicates a spontaneous reaction, then the cell potential has a negative value.

79. Consider the galvanic cell, $Pb(s)\ |\ Pb^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$. How should the concentrations of the species present be changed to make cell potential more positive?
(a) Increase $[Pb^{2+}]$ (b) Increase $[Cu^{2+}]$
(c) Increase the amount of $Pb(s)$
(d) Decrease the amount of $Pb(s)$

80. The potential of the cell below was 1.05 V. What is the pH? $E°(Ag) = 0.799\ V$

$$Pt|\ H_2(1atm)|\ H^+(aq)||\ Ag^+(0.100\ M)|\ Ag$$

(a) 10.50 (b) 5.25
(c) 1.00 (d) 7.00

81. What is the standard cell voltage at 25.0°C for the reverse of the reaction below?

$$Pb^{2+}(aq) + Cd(s) \leftrightarrow Pb(s) + Cd^{2+}(aq); \quad K = 1.356 \times 10^9$$

(a) +0.270 V (b) +0.117 V
(c) −0.270 V (d) −0.117 V

82. Which of the answers below is the correct representation according to the shorthand method of the following galvanic cell?

$$2Fe^{2+}(aq) + 3Ni(s) \longleftrightarrow 2Fe(s) + 3Ni^{2+}(aq)$$

(a) $Fe^{3+}(aq)|\ Fe(s)||\ Ni(s)|\ Ni^{2+}(aq)$
(b) $Fe^{3+}(aq)|\ Ni(s)||\ Fe(s)|\ Ni^{2+}(aq)$
(c) $Ni(s)|\ Ni^{2+}(aq)||\ Fe(s)|\ Fe^{3+}(aq)$
(d) $Ni(s)|\ Ni^{2+}(aq)||\ Fe^{3+}(aq)|\ Fe(s)$

83. $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E° = 0.800\ V$

$$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq); \quad E° = +0.071\ V$$
$$Br_2(l) + 2e^- \longrightarrow Br^-(aq); \quad E° = +1.066\ V$$

Use some of the data above to calculate K_{sp} at 25°C for AgBr.
(a) 6.3×10^{-2} (b) 4.9×10^{-13}
(c) 1.9×10^{-15} (d) 2.4×10^{-34}

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84. How long must a 50.0 A current be passed through an electrolytic cell for refining copper to produce 3.00 mol of copper?
(a) 1.50 hrs (b) 1.61 hrs
(c) 2.50 hrs (d) 3.22 hrs

85. Doubling all the coefficients in the equation for the cell reaction
(a) doubles both $E°$ and $\Delta G°$
(b) doubles $E°$, but does not change $\Delta G°$
(c) doubles $\Delta G°$, but does not change $E°$
(d) does not change $E°$ or $\Delta G°$

86. Given: $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$; $E° = +0.771$ V
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$; $E° = -0.126$ V

Calculate the standard cell potential for the cell based on the reaction below and predict whether the reaction can occur spontaneously under standard conditions.
$$Pb^{2+}(aq) + 2Fe^{2+}(aq) \longrightarrow 2Fe^{3+}(aq) + Pb(s)$$
(a) $E° = -0.897$ V, non-spontaneous
(b) $E° = -0.897$ V, spontaneous
(c) $E° = +0.897$ V, non-spontaneous
(d) $E° = +0.897$ V, spontaneous

87. Given that $E° = +0.897$ V, calculate E at 25°C for
$$Pb(s)|Pb^{2+}(0.040\ M)||Fe^{3+}(0.20\ M), Fe^{2+}(0.010\ M)|Pt(s)$$
(a) +0.779 V (b) +0.935 V
(c) +1.015 V (d) +1.134 V

88. A steel pipe can be protected from corrosion by attaching the pipe to a piece of magnesium because
(a) magnesium forms a tight oxide coating.
(b) magnesium is more easily oxidized than iron.
(c) magnesium is inert.
(d) magnesium and steel form a corrosion resistant alloy.

89. How many grams of chromium can be plated out by passing a current of 8.00 A through an aqueous solution containing Cr^{3+} ions for 40.0 minutes? Molar mass of Cr = 52.
(a) 3.45 g (b) 6.15 g
(c) 10.3 g (d) 31.0 g

90. Calculate the cell potential E at 25°C for the reaction
$$2Al(s) + 3Fe^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Fe(s)$$
given that $[Fe^{2+}] = 0.020$ M, $[Al^{3+}] = 0.10$ M, and the standard reduction potential is −1.66 V for Al^{3+}/Al and −0.45 V for Fe^{2+}/Fe.
(a) +1.03 V (b) +1.17 V
(c) +1.18 V (d) +1.20 V

91. For a particular cell based on the reaction
$$3AgCl(s) + Al(s) \longrightarrow 3Ag(s) + Al^{3+}(aq) + 3Cl^-(aq)$$
$E = +1.750$ V and $E° = +1.884$ V at 25°C. What is the value of the equilibrium constant K, at 25°C for the reaction?
(a) 3.6×10^{29} (b) 6.7×10^{31}
(c) 4.8×10^{88} (d) 3.0×10^{95}

92. The cell reaction for a lead storage battery is:
$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow PbSO_4(s) + 2H_2O(l);\quad E° = +1.92\ V$$
To provide a potential of about 12 V, one could
(a) adjust the pH to 12
(b) adjust the pH to 1
(c) connect six cells in series
(d) greatly increase the surface area of the Pb(s) and $PbO_2(s)$

93. Which of the following statements concerning the rusting of iron is false?
(a) The oxidation site can occur at a different place on the metal surface than the reduction site.
(b) The metal is reduced.
(c) The rusting of iron requires both oxygen and water.
(d) Salt increases the rate of corrosion by providing ions to carry the current.

94. How many grams of nickel can be produced by passing a current of 15.0 A through aqueous $NiCl_2$ for 80.0 minutes?
(a) 14.7 g (b) 21.9 g
(c) 43.8 g (d) 48.4 g

95. Consider the effect of each of the following changes on the cell voltage for a voltaic cell using following reaction:
$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$
(i) The pressure of the H_2 gas is decreased.
(ii) The area of the anode is doubled.
(iii) H^+ concentration is increased by the addition of H_2SO_4 to the anode compartment.
(iv) Sodium nitrate is added to the anode compartment.
In which case(s) does the cell voltage increase?
(a) (i) (b) (iv)
(c) (ii) (d) (i) and (iii)

96. A voltaic cell is set up with copper and lead electrodes in contact with $CuSO_4(aq)$ and $Pb(NO_3)_2(aq)$, respectively, at 25°C. The standard electrode potentials are
$Cu^{2+} + 2e^- \longrightarrow Cu$; $E° = +0.34$ V
$Pb^{2+} + 2e^- \longrightarrow Pb$; $E° = -0.13$ V

If the Pb^{2+} and Cu^{2+} concentrations are each 1 M, and the cell is allowed to run in the spontaneous direction, the cell potential is
(a) 0.94 V (b) 0.58 V
(c) 0.47 V (d) 0.21 V

97. A concentration cell is constructed with copper electrodes and Cu^{2+} in each compartment. In one compartment, the $[Cu^{2+}] = 1.0 \times 10^{-3}$ M and in the other compartment, $[Cu^{2+}] = 2.0$ M. Calculate the potential for this cell at 25°C.
(a) 0.098 V (b) 0.195 V
(c) 0.32 V (d) 0.68 V

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98. If $\Delta G^\circ = -nFE^\circ$, then
(a) E° is between –1.00 and –0.5 V, and the reaction is not spontaneous.
(b) E° is between –0.5 and 0 V, and the reaction is not spontaneous.
(c) E° is between 0 and 0.5 V, and the reaction is spontaneous.
(d) E° is between 0.5 and 1.0 V, and the reaction is spontaneous.

99. $E^\circ = 0.62$ V for the following reaction :

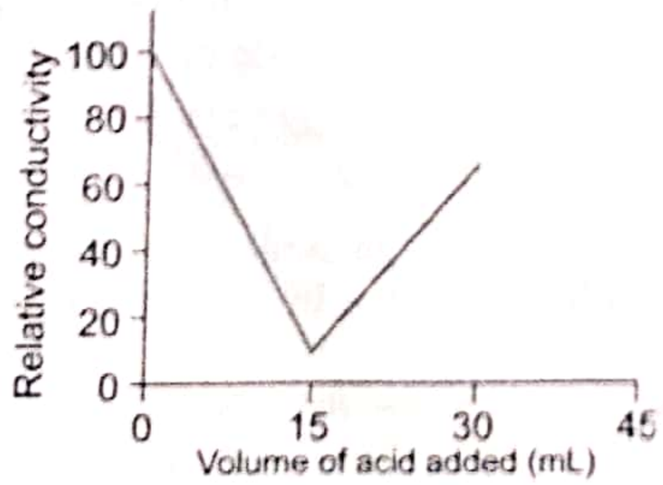
$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

What is ΔG° for this reaction at 25°C?
(a) –119.6 kJ (b) –59.8 kJ
(c) 59.8 kJ (d) 119.6 kJ

100. Which of the following is a true statement about chemical equilibrium in general?
(a) At a given temperature, the value of the equilibrium constant for a given reaction depends on the initial reactant concentrations.
(b) At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction.
(c) At equilibrium, the rate of the forward reaction is zero, and the rate of the reverse reaction is zero, resulting in no subsequent changes in concentrations with time.
(d) The value of the equilibrium constant increases with increased temperature for both endothermic and exothermic reactions.

101. The molar free energy change for transporting a positive molecule from the inside to the outside of a membrane when the concentration of this molecule is greater on the inside and the voltage across the membrane is more positive on the inside is
(a) positive (b) negative
(c) zero (d) Insufficient information.

102. 20 mL of KOH solution was titrated with 0.20 mol L^{-1} H_2SO_4 solution in a conductivity cell. The data obtained were plotted to give the graph shown below :



The concentration of the KOH solution was
(a) 0.30 mol L^{-1} (b) 0.15 mol L^{-1}
(c) 0.12 mol L^{-1} (d) 0.075 mol L^{-1}

103. Fill in the blanks:
In an electrochemical cell, electrons move through the external circuit from the _____ to the _____, and negative charge in the form of ions flow in solution from the _____ compartment to the _____ compartment. The answers in order are
(a) cathode, anode, cathode, anode
(b) anode, cathode, cathode, anode
(c) cathode, anode, anode, cathode
(d) anode, cathode, anode, cathode

104. Given the following information :

Half-reaction	E°_{red}
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.154 V
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	–0.440 V
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(s)$	+0.771 V
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	–0.74 V

Determine the standard potential (in V) of a cell based on the reaction:

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

(a) + 0.46 (b) + 0.62
(c) + 1.39 (d) – 0.46

105. How many minutes will it take to plate out 2.19 g of chromium metal from a solution of Cr^{3+} using a current of 35.2 A?
(a) 5.77 (b) 346
(c) 115 (d) 1.92

106. Given the following standard reduction potentials

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-; \quad E^\circ = +1.36\ V$$

$$IO_3^- + 6H^+ + 5e^- \longrightarrow \frac{1}{2} I_2 + 3H_2O; \quad E^\circ = +1.20\ V$$

What would happen if you made a galvanic cell containing 1M KIO_3, 1 M H^+, and 1M I_2 on one side and the other side had 1 atm Cl_2 and 1M HCl? (Assume appropriate electrodes and salt bridge).
(a) The cell would not work because the oxidizing agents should be all in the same side.
(b) I_2 would turn into IO_3^- and Cl_2 would turn into Cl^-
(c) I_2 would react with IO_3^- and Cl_2 would react with Cl^-
(d) IO_3^- would turn into I_2 and Cl_2 would turn into Cl^-

107. Given the following standard reduction potentials (25°C)

$$Ag(CN)_2^- + e^- \rightleftharpoons Ag + 2CN^-; \quad E^\circ = -0.310\ V$$

$$Ag^+ + e^- \rightleftharpoons Ag; \quad E^\circ = 0.800\ V$$

$$Cu^+ + e^- \rightleftharpoons Cu; \quad E^\circ = +0.520\ V$$

$$Cu(CN)_2^- + e^- \rightleftharpoons Cu + 2CN^-; \quad E^\circ = -0.440\ V$$

Calculate ΔG°_{rxn} (in kJ) for the following reaction at 25°C:

$$Cu(CN)_2^- + Ag^+ \rightleftharpoons Ag(CN)_2^- + Cu^+$$

(a) –14.5 (b) 12.5
(c) 14.5 (d) –12.5

108. For the equilibrium reaction, $Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$, the cell notation when the reactants and products are in standard state is

$$Ag(s) | Ag(CN)_2^-\ (1.00\ M),$$
$$CN^-\ (1.00\ M) || Ag^+(1.00\ M) | Ag^+(s)$$

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If the cell with the new indicated concentrations is now set up, $Ag(s) | Ag(CN)_2^-(2.00\ M)$,

$$CN^-(2.00\ M) || Ag^+(0.50\ M) || Ag(s)$$

Then
(a) the reaction will shift to the right
(b) the reaction will shift to the left
(c) the cell voltage will become more positive
(d) the cell voltage will be unchanged

109. Given the reaction, $2Hg(l) + Cl_2(g) \longrightarrow Hg_2Cl_2(s)$

Assume that the standard E°_{Cell} voltage is related to the Celsius temperature by the following equation and all substances are at standard state. In doing this, you can assume any temperature(s) you desire.

At 298 K (25°C), $E^\circ_{Cell} = +1.058$ volts.

$$E^\circ_{Cell} = 1.058 - 0.00017\,(t - 25°C)$$

The $\Delta H°$ (in kJ) for the reaction (as written) at 298 K is
(a) −321 (b) +107 (c) +214 (d) −214

110. Given the following cell

$$Zn(s) | Zn^{2+}(1\ M) || H^+(?M) | H_2(g)(1\ atm).$$

The measured cell voltage is $E_{Cell} = 0.653$ V. Calculate the pH of the solution in the cathode compartment.

Given: $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$; $E° = -0.771$ V

(a) 1.0 (b) 1.5
(c) 2.0 (d) 3.0

111. What is the voltage of a galvanic cell that does 788 J of work when 255 C of charge is transferred?
(a) 2.01×10^5 V (b) −0.324 V
(c) 3.09 V (d) 0.324 V

112. What is the amount of O_2 produced by electrolysis of water using a current of 0.120 A for 65.0 min. Assume the water contains an electrolyte.
(a) 5.42×10^{-3} mol (b) 6.02×10^{-5} mol
(c) 1.21×10^{-3} mol (d) 3.65×10^{-3} mol

113. Calculate the ΔG for the following cell when 1.50 mol $Cl_2(g)$ is produced at a voltage of 0.560 V

$$2BaCrO_4(s) + 16H_3O^+(aq) + 6Cl^-(aq) \longrightarrow 2Ba^{2+}(aq) + 2Cr^{3+}(aq) + 3Cl_2(g) + 24H_2O$$

(a) -5.42×10^4 J (b) -1.62×10^5 J
(c) -1.89×10^2 J (d) -3.56×10^5 J

114. Consider a galvanic cell having the following reaction:

$$2VO^{2+}(aq) + 4H^+(aq) + Zn(s) \longrightarrow 2VO^{2+}(aq) + 2H_2O(l) + Zn(aq); E^\circ_{Cell} = +1.76\ V$$

Which statement below is false?
(a) If the equation above is multiplied by 2 the E°_{Cell} of the cell will not change.
(b) When equilibrium is established, $E_{Cell} = E^\circ_{Cell}$
(c) VO_2^+ is the oxidising agent.
(d) As the pH is lowered, the reaction becomes more spontaneous.

115. Which one of the following statements is false regarding galvanic and electrolytic cells?
(a) In both cells, redox reactions take place.
(b) In electrolytic cells, a current is forced through a cell to produce a chemical change for which the cell potential is negative.
(c) In both cells, reduction takes place at the cathode.
(d) The ion flow through the salt bridge in galvanic cell is opposite to the flow in electrolytic cell.

116. Consider the following cell at 25°C

$$Zn(s) | Zn^{2+}(aq, 0.20\ M) || Cl_2(g, 1.0\ atm),$$

$$Cl^-(aq, x\ M?) | Pt(s)$$

For this cell, $E° = 2.12$V and $E = 2.1$ V at 25°C
What is the $Cl^-(aq)$ concentration in the cathode compartment?
(a) 0.13 M (b) 0.2 M
(c) 0.33 M (d) 0.47 M

117. The standard reduction potential of Ag^+/Ag electrode is 0.80 V and the standard potential of the cell below is +0.84 V

$$Fe(s) | Fe^{3+}(aq) || Ag^+(aq) | Ag(s)$$

What is the standard reduction potential of Fe^{3+}/Fe electrode?
(a) +1.64 V (b) −1.64 V
(c) −0.12 V (d) −0.04 V

118. Based on the following data, calculate $E°$ for the reaction

$$CH_4(g) + 2O_2 \longrightarrow CO_2(g) + 2H_2O(g)$$

ΔG_f° (kJ/mol)	−50.80	−394.4	−228.6

(a) 1.23 V (b) 1.04 V
(c) 1.75 V (d) 1.92 V

119. A salt bridge is necessary for the operation of galvanic cell because
(a) it allows electrons to flow into the salt solutions.
(b) it allows the two salt solutions to mix.
(c) it allows for the separation of charge.
(d) it allows ions to flow to prevent the build up of charge.

120. Given the half reaction

$$Zn^{2+} + 2e^- \longrightarrow Zn(s); \quad E° = -0.76\ V$$

What is the standard potential of the following half reaction?

$$3Zn(s) \longrightarrow 3Zn^{2+} + 6e^-$$

(a) 0.76 V (b) −0.76 V
(c) 2.28 V (d) −2.28 V

121. Which one of the following statements is false in a concentration cell made of Fe in 0.010 M $Fe^{2+}(aq)$ and Fe in 0.10 M Fe^{2+}?
(a) The $E^\circ_{Cell} = 0$
(b) $\Delta G = 0$
(c) Electron flows from anode to cathode
(d) The cell reaction is:

$$Fe^{2+}(aq, 0.010\ M) \longrightarrow Fe^{2+}(aq, 0.10\ M)$$

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122. Calculate K_{sp} for $PbI_2(s)$ at 25°C

$$PbI_2(s) + 2e^- \longrightarrow Pb(s) + 2I^-(aq); \quad E° = -0.365 \text{ V}$$

$$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s); \quad E° = -0.126 \text{ V}$$

(a) 4.5×10^{-13} (b) 9.1×10^{-5}
(c) 2.5×10^{-17} (d) 8.3×10^{-9}

123. Consider the two reactions below and circle the false statement.

1. $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)\ \Delta G_1°, E^\circ_{Cell_1}$
2. $2Cu(s) + 4Ag^+(aq) \longrightarrow 2Cu^{2+}(aq) + 4Ag(s)\ \Delta G_2°, E^\circ_{Cell_2}$

(a) $E°$ for both reaction is $-\Delta G°/nF$
(b) $\Delta G_2° = 2\Delta G_1°$
(c) n(no. of e^- transferred) in reaction 2 = $2n$ in reaction 1
(d) $E^\circ_{Cell(2)} = 2E^\circ_{Cell(1)}$

124. What is the K_c for the following reaction at 25°C?

$$3Fe^{2+}(aq) \longrightarrow 2Fe^{3+}(q) + Fe(s)$$

Given : $Fe^{3+}(aq) + 1e^- \longrightarrow Fe^{2+}(aq); E° = 0.770$ V

$Fe^{3+}(aq) + 3e^- \longrightarrow Fe(s); \quad E° = -0.0360$ V

(a) 1.68×10^{37} (b) 1.21×10^{-41}
(c) 5.95×10^{-38} (d) 2.37×10^{-14}

125. Calculate $\Delta G°$ for the reaction that occurs in the following galvanic cell:

$$Ag(s) | AgI(s), I^-(aq) || Ag^+(aq) | Ag(s)$$

Given : $Ag^+(aq) + 1e^- \longrightarrow Ag(s) \quad E° = 0.800$ V

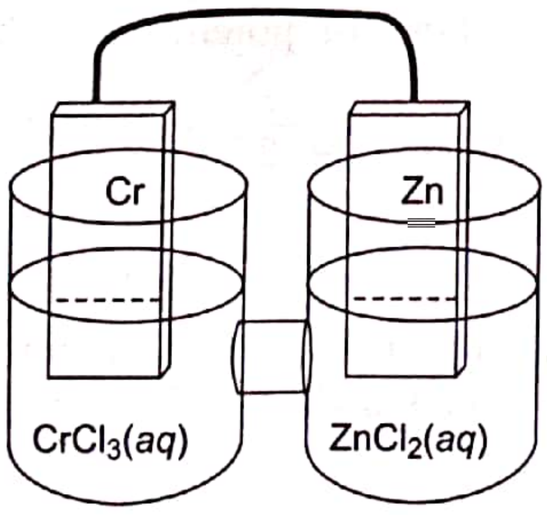
$AgI(s) + 1e^- \longrightarrow Ag(s) + I^-(aq) \quad E° = 0.152$ V

(a) +91.9 kJ (b) –77.2 kJ
(c) –62.5 kJ (d) +62.5 kJ

126. Electrolysis of sea-water produces $Cl_2(g)$ at the anode by the oxidation of $Cl^-(aq)$ ions. What volume of the gas will be produced at STP by a current of 1.50 A applied for 90.0 minutes?

(a) 0.313 L (b) 0.548 L
(c) 0.94 L (d) 0.470 L

127. Which of the following is true for the cell shown below?

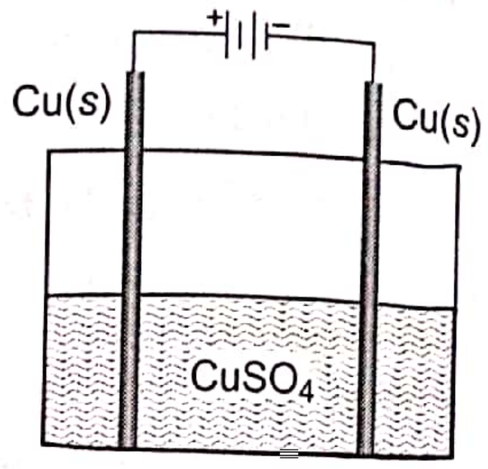


$Zn^{2+} + 2e^- \longrightarrow Zn; \quad E° = -0.76$ V

$Cr^{3+} + 3e^- \longrightarrow Cr; \quad E° = -0.74$ V

(a) The electrons flow from the cathode to the anode.
(b) The electrons flow from the zinc to the chromium.
(c) The electrons flow from the chromium to the zinc.
(d) The chromium is oxidised.

128. The diagram below shows an electrolysis cell, which contains 1L of an aqueous 1M copper (II) sulphate solution.



If 0.4 moles of electrons pass through the cell, the concentration of copper ions after passage of the charge will be,

(a) 0.4 M (b) 0.8 M
(c) 1.0 M (d) 1.2 M

129. The next two questions deal with the following galvanic cell which involves the following reduction potentials:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \quad E° = +0.80 \text{ V}$$

$$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s) \quad E° = -0.74 \text{ V}$$

Calculate E^o for the following galvanic cell:

$$3Ag^+(aq) + Cr(s) \longrightarrow Cr^{3+}(aq) + 3Ag(s)$$

(a) –1.54 V (b) –0.06 V
(c) +0.06 V (d) +1.54V

130. Which of the following describes what happens to the concentrations of Cr^{3+} and Ag^+ and the masses of the electrodes as this galvanic cell generates an electrical current spontaneously at 25°C?

	Concentration of Cr^{3+}	Concentration of Ag^+	Mass of Ag electrode	Mass of Cr electrode
(a)	decreases	decreases	increases	increases
(b)	decreases	increases	decreases	increases
(c)	increases	decreases	increases	decreases
(d)	increases	increases	decreases	decreases

131. Given the following reduction potentials, what is the product at the anode when a current is passed through an aqueous solution of $FeBr_2$? (**Hint** : Remember, which chemicals and ions are really in the solution and subject to the electrolysis.)

$$Br_2 + 2e^- \longrightarrow 2Br^-; \quad E° = 1.08 \text{ V}$$

$$O_2 + 4H^+ \longrightarrow H_2O; \quad E° = 0.82 \text{ V}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe; \quad E° = -0.44 \text{ V}$$

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-; E° = -0.83 \text{ V}$$

(a) Fe (b) Br_2
(c) O_2 (d) H_2

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132. Given the following information, rank the 'activity' of the metals as reducing agents:

Cr reacts with $NiBr_2$ and $CdBr_2$, but not with $ZnBr_2$

Cd reacts with $NiBr_2$, but not with $ZnBr_2$ or $CrBr_3$

(a) Zn > Cr > Cd > Ni
(b) Ni > Cr > Cd > Zn
(c) Zn > Cr > Ni > Cd
(d) Zn > Cd > Cr > Ni

133. Which of the following statements is **true** for a voltaic cell formed by a reaction between Ag^+ and Mg?
(a) The mass of the magnesium electrode increases during discharge.
(b) The concentration of Ag^+ ions increases during discharge.
(c) Electrons leave the Mg electrode to pass through the external circuit towards the Ag electrode during discharge.
(d) Anions from the salt bridge move into the compartment containing Ag.

134. Given these two half reactions and their standard reduction potentials, which equation represents a spontaneous reaction?

$$Zn^{2+} + 2e^- \longrightarrow Zn; \quad -0.763\ V$$
$$Ni^{2+} + 2e^- \longrightarrow Ni; \quad -0.25\ V$$

(a) $Zn^{2+}(aq) + Ni(s) \longrightarrow Zn(s) + Ni^{2+}(aq)$
(b) $Ni^{2+}(aq) + Zn(s) \longrightarrow Ni(s) + Zn^{2+}(aq)$
(c) $Ni^{2+}(aq) + Zn^{2+}(aq) \longrightarrow Ni(s) + Zn(s)$
(d) $Ni(s) + Zn(s) \longrightarrow Ni^{2+}(aq) + Zn^{2+}(aq)$

135. With respect to the electrolysis of molten $AlCl_3$, which of the following statements concerning this electrolysis is false?
(a) For every Faradays passed through the cell, one-half mole of Cl_2 is produced at the anode.
(b) For every Faradays passed through the cell, one-third mole of Al is produced at the anode.
(c) For every three Faradays passed through the cell, one mole of Al is produced at the cathode.
(d) For every two Faradays passed through the cell, one mole of Cl_2 is produced at the anode.

136. A concentration cell is constructed by suspending a silver electrode in 1.00 L of 0.100 M $AgNO_3$. Another silver electrode is suspended in 1.00 L of 0.200 M $AgNO_3$. The two half-cells are connected by a salt bridge. Which silver electrode is the anode ?
(a) The silver electrode suspended in 0.100 M $AgNO_3$
(b) The silver electrode suspended in 0.200 M $AgNO_3$
(c) Either electrode could be the anode
(d) Impossible to tell

137. The equation for one of the half-reactions in a lead storage battery is:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

What happens to the properties of the electrolyte as this cell discharges?

	Density	pH
(a)	Increases	Increases
(b)	Increases	Decreases
(c)	Decreases	Decreases
(d)	Decreases	Increases

138. For the voltaic cell based on this reaction:

$$2Ag^+(aq) + Cu \rightleftharpoons Cu^{2+}(aq) + 2Ag$$

the concentrations of the aqueous ions and sizes of the electrodes can be changed independently. Which statement is correct?
(a) Increasing the $[Cu^{2+}]$ two-fold has the same effect on the cell voltage as increasing the $[Ag^+]$ four-fold.
(b) Decreasing the $[Cu^{2+}]$ ten-fold has the same effect on the cell voltage as decreasing the $[Ag^+]$ by the same ratio.
(c) Decreasing the $[Cu^{2+}]$ ten-fold has less effect on the cell voltage than decreasing the $[Ag^+]$ by the same amount.
(d) Doubling the sizes of the cathode has exactly the same effect on the cell voltage as decreasing the $[Cu^{2+}]$ by a factor of two.

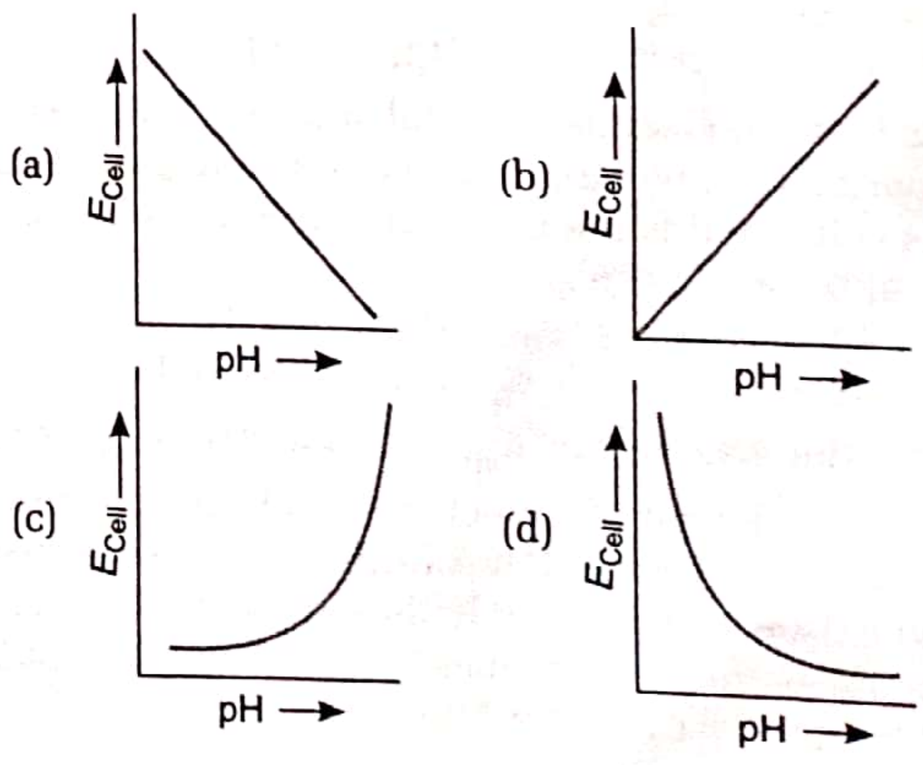
139. A solution containing equimolar amounts of $NiCl_2$ and $SnBr_2$ is electrolyzed using a 9V battery and graphite electrodes. What are the first products formed?
(a) Ni(s) at cathode, $Cl_2(aq)$ at anode
(b) Ni(s) at cathode, $Br_2(aq)$ at anode
(c) Sn(s) at cathode, $Br_2(aq)$ at anode
(d) Sn(s) at cathode, $Cl_2(aq)$ at anode

Half-reaction	Standard Reduction Potential (V)
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$;	−0.236
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$;	−0.141
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$;	1.077
$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq)$;	1.360

140. Which of the following graph correctly illustrates the dependence of the cell voltage, E_{Cell}, on the pH for the reaction,

$$2Ag^+(aq) + H_2(g) \longrightarrow 2Ag(s) + 2H^+(aq)$$

Assume the silver ion remains constant at, $[Ag^+] = 1.0$ M and the H_2 pressure remains constant at 1atm.



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141. E^o of the cell mentioned below is 0.31 V:

$$Zn/Zn^{2+} // Fe^{2+}/Fe$$

And E^o for Zn^{2+}/Zn and Fe^{3+}/Fe^{2+} are –0.76 V and 0.77 V respectively. The E^o for Fe^{3+}/Fe would be

(a) 0.04 V (b) –0.04 V
(c) –0.13 V (d) 0.13 V

142. An aqueous solution containing 1.0 M of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$. The value of their standard reduction potential are :

$Ag^+/Ag = 0.80$ V, $Hg_2^{2+}/Hg = 0.79$ V, $Cu^{2+}/Cu = 0.34$V and $Mg^{2+}/Mg = -2.37$ V. With increasing voltage, the sequence of deposition of metals on the cathode will be:

(a) Ag, Hg, Cu and Mg (b) Mg, Cu, Hg and Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag

143. Given the following Standard EMF: $Mn^{2+}(aq)/Mn(s) = -1.18$ V; $H_2O/H_2(g)$, $OH^-(aq) = -0.83$ V; $I_2(s)/2I^- = +0.53$V; and $O_2(g)$, $H^+(aq)/H_2O = +1.23$ V. We would predict that the electrolysis of an aqueous solution of MnI_2 would probably produce

(a) Mn, I_2 (b) Mn, O_2
(c) H_2, I_2 (d) H_2, O_2

144. Consider the following galvanic cell reaction at 25°C,

$$4Cr^{2+}(aq) + O_2(g) + 4H_3O^+(aq) \longrightarrow 4Cr^{3+}(aq) + 6H_2O(l)$$

Which of the following statements best describes what would happen to the cell potential if the concentration of Cr^{2+} is increased?

(a) The cell potential would become less positive.
(b) The cell potential would become more positive.
(c) The cell potential would remain the same.
(d) It is impossible to tell.

145. Consider the following standard reduction potentials,

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{3+}(aq) \quad E^\circ = 0.77 \text{ V}$$

$$H_2O_2(aq) + 2e^- \rightleftharpoons 2OH^-(aq) \quad E^\circ = 0.88 \text{ V}$$

For the voltaic cell reaction below, calculate the Fe^{2+} concentration (in M) that would be needed to produce a cell potential equal to 0.16 V at 25°C when $(OH^-) = 0.10$ M, $(Fe^{3+}) = 0.50$ M and $(H_2O_2) = 0.35$ M.

$$2Fe^{2+}(aq) + H_2O_2(aq) \rightleftharpoons 2Fe^{3+}(aq) + 2OH^-(aq)$$

(a) 0.3 M (b) 0.4 M
(c) 0.6 M (d) 0.75 M

146. A galvanic cell has a potential of 2.50 V. If in a particular experiment, 2.00 moles of electron were passed through this cell, what is the maximum useful work, w_{max}, that could be obtained?

(a) 4.82×10^5 J (b) 7.80×10^5 J
(c) 2.02×10^4 J (d) 1.00×10^3 J

147. With the knowledge K_{sp} for $Mg(OH)_2$ ($K_{sp} = 1.8 \times 10^{-11}$), a chemist constructed the cell shown below. The left half contains a buffer solution (pH=?) saturated with $Mg(OH)_2$, while the right half-cell contains Cu^{2+} at 1.0M. The measured cell voltage was 2.7 V. $Mg|Mg(OH)_2(s)$, Buffer (pH=?)$||Cu^{2+}(1M)|Cu$

The pH in the left half-cell is $[E^\circ\{Mg(OH)_2\}] = -2.7$ V, $Cu^{2+}/Cu = 0.3$ V] (closest).

(a) 5 (b) 9 (c) 6 (d) 10

148. Consider the following redox reaction occurring in acidic medium :

$$BrO_3^- \xrightarrow{E^\circ = 1.5 \text{ V}} BrO^- \xrightarrow{E^\circ = 1.6 \text{ V}} Br_2$$
$$BrO_3^- \xrightarrow{E^\circ = ?\text{V}} Br_2$$

The unknown standard reduction potential is

(a) –1.6 V (b) 1.6 V
(c) –1.52 V (d) 1.52 V

149. Which of the following statements concerning conductance and molar conductance is true?

(a) Both conductance and molar conductance increase on increasing concentration.
(b) Both conductance and molar conductance decrease on increasing concentration.
(c) Conductance increases but molar conductance decrease on increasing concentration.
(d) Conductance decreases but molar conductance increases on increasing concentration.

150. Which of the following statements concerning concentration dependence of molar conductivity for a strong and a weak electrolyte is true?

(a) Molar conductivity increases linearly on increasing concentration for both types of electrolytes.
(b) Molar conductivity decreases linearly on increasing concentration for both types of electrolytes.
(c) Molar conductivity increases linearly on dilution for strong electrolyte but it is constant for weak electrolyte.
(d) On dilution, molar conductivity increases linearly for strong electrolyte but for weak electrolyte, the increase is gradual in higher concentration range but very rapid in lower concentration range.

151. Which of the following is not an essential requirement for Kohlrausch's law of independent migration of ions to hold true?

(a) The solution must be infinitely dilute.
(b) Electrolyte must be strong.
(c) Electrolyte must be completely ionized.
(d) There should be no inter-ionic interaction.

152. In a conductometric analysis, if temperature is changed slightly, which of the following will not change?

(a) Specific conductance (b) Equivalent conductance
(c) Cell constant (d) Resistance of the solution

153. Given the following molar conductivity at infinite dilution and 25°C,

$$HCl: \Lambda_m^\infty = 426.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$KCl: \Lambda_m^\infty = 271.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$CH_3COOK: \Lambda_m^\infty = 114.42 \text{ S cm}^2 \text{ mol}^{-1}$$

The molar conductance at infinite dilution and 25°C for acetic acid solution is

(a) 583.28 S cm^2 mol^{-1} (b) 269.12 S cm^2 mol^{-1}
(c) 289.63 S cm^2 mol^{-1} (d) 172.94 S cm^2 mol^{-1}

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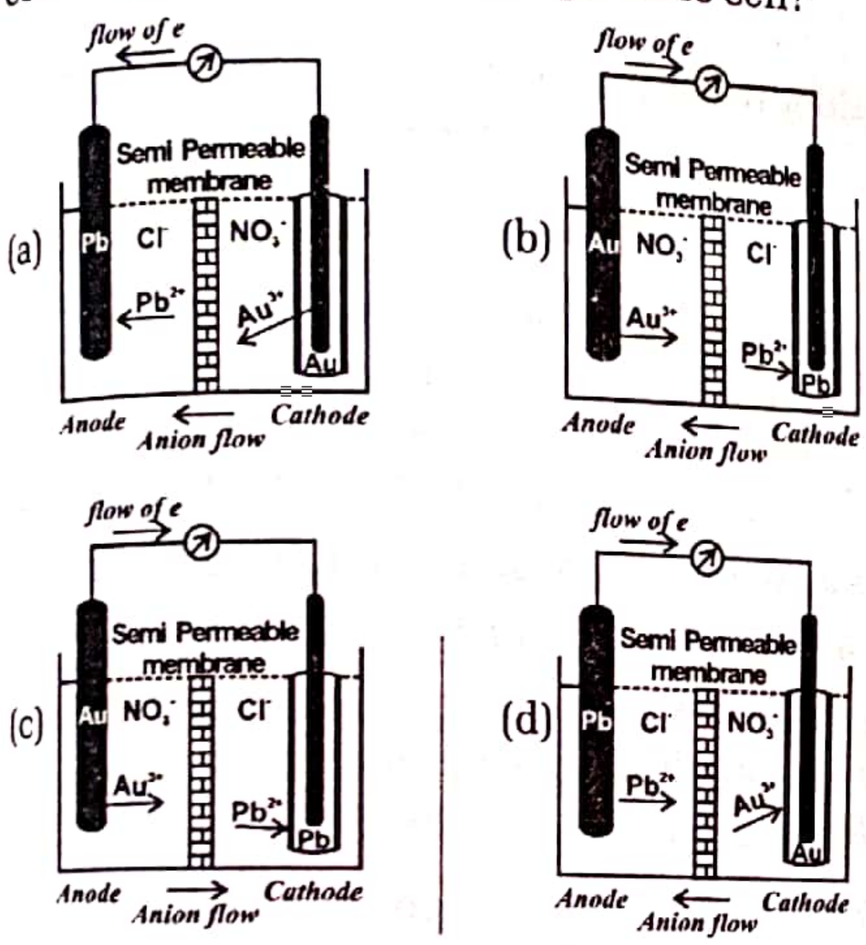
154. An aqueous solution of a weak acid (HA) has a molar conductance of 19 S cm^2 mol^{-1} and it is only 1% ionized in given condition. The limiting value of molar conductance of above acid under similar experimental condition is
(a) 1900 S cm^2 mol^{-1} (b) 950 S cm^2 mol^{-1}
(c) 475 S cm^2 mol^{-1} (d) Infinite

155. For a strong electrolyte, dilution increases the molar conductivity because
(a) It increases the extent of ionization of electrolyte
(b) It increases the extent of ionization of water
(c) It increases the inter-ionic interaction
(d) It weaken the inter-ionic attraction

Multiple Choice Questions *(Advanced Level)*

Nos. 1-9 (These question have only one correct option)

1. An $Au(NO_3)_3$ solution containing a gold electrode is connected by means of a salt bridge to a $PbCl_2$ solution containing lead electrode. Which of the following is the correct representation of this galvanic cell?



2. The cell shown below generates a potential of 0.65 V at 300 K. K_{sp} for AgBr is?

$Ag \mid AgBr(s), NaBr\ (0.10\ M) \parallel AgNO_3\ (0.10\ M) \mid Ag$

$E = 0.65$ V

(a) 1.15×10^{-9} (b) 2.00×10^{-30}
(c) 1.25×10^{-13} (d) 3.5×10^{-11}

3. For the voltaic cell based on this reaction:

$$2Ag^+(aq) + Cu \rightleftharpoons Cu^{2+}(aq) + 2Ag$$

the concentrations of the aqueous ions and sizes of the electrodes can be changed independently. Which statement is correct?
(a) Increasing the $[Cu^{2+}]$ two-fold has the same effect on the cell voltage as increasing the $[Ag^+]$ four-fold.
(b) Decreasing the $[Cu^{2+}]$ ten-fold has the same effect on the cell voltage as decreasing the $[Ag^+]$ by the same ratio.
(c) Decreasing the $[Cu^{2+}]$ ten-fold has less effect on the cell voltage than decreasing the $[Ag^+]$ by the same amount.
(d) Doubling the sizes of the cathode has exactly the same effect on the cell voltage as decreasing the $[Cu^{2+}]$ by a factor of two.

4. Consider the following standard reduction potentials,

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq); \quad E° = 0.77\ V$$
$$H_2O_2(aq) + 2e^- \rightleftharpoons 2OH^-(aq); \quad E° = 0.88\ V$$

For the voltaic cell reaction below, calculate the Fe^{2+} concentration (in M) that would be needed to produce a cell potential equal to 0.16 V at 25°C when $(OH^-) = 0.10$ M, $(Fe^{3+}) = 0.50$ M and $(H_2O_2) = 0.35$ M.

$$2Fe^{2+}(aq) + H_2O_2(aq) \rightleftharpoons 2Fe^{3+}(aq) + 2OH^-(aq)$$

(a) 0.44 M (b) 0.6 M
(c) 0.76 M (d) 1.24 M

5. Consider the following standard reduction potentials,

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s); \quad E° = 0.800\ V$$
$$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-(aq); \quad E° = -0.164\ V$$

Calculate the value of the solubility product K_{sp}, at 25°C for silver iodide (AgI).

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

(a) 5×10^{-17} (b) 6×10^{-15}
(c) 2×10^{-14} (d) 4×10^{-12}

6. Consider the following standard reduction potentials,

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s); \quad E° = 0.34\ V$$
$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq); \quad E° = 0.59\ V$$
$$O_2(g) + 2H_3O^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq) + 2H_2O(l); \quad E° = 0.68\ V$$

and the following redox reactions :

(i) $H_2O_2(aq) + 2H_2O(l) + Cu^{2+}(aq) \rightleftharpoons O_2(g) + 2H_3O^+(aq) + Cu(s)$

(ii) $2MnO_4^-(aq) + 4H_2O(l) + 3Cu(s) \rightleftharpoons 3Cu^{2+}(aq) + 2MnO_2(s) + 8OH^-(aq)$

(iii) $2MnO_4^-(aq) + 10H_2O(l) + 3H_2O_2(aq) \rightleftharpoons 3O_2(g) + 6H_3O^+(aq) + 2MnO_2(s) + 8OH^-(aq)$

Which of the redox reactions above will be spontaneous under standard conditions?
(a) (i) only (b) (ii) only
(c) (i) and (iii) (d) (ii) and (iii)

7. Calculate the cell potential (in V) at 25°C for a copper concentration cell in which the Cu^{2+} concentration in one half-cell is equal to 0.050 M and the Cu^{2+} concentration in the other half-cell is equal to 1.5 M.

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Note : The number of moles of electrons transferred is equal to 2.

(a) 0.40 V (b) 0.80 V (c) 0.044 V (d) 0.34 V

8. Use the Standard Reduction Potentials given below to calculate K_f for $Zn(NH_3)_4^{2+}$ at 25°C.

$$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq), \quad K_f = ?$$

$$Zn(NH_3)_4^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3(aq); \; E^\circ = -1.04 \text{ V}$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s); \quad E^\circ = -0.76 \text{ V}$$

(a) 6×10^{18} (b) 3×10^9 (c) 2×10^6 (d) 3×10^{-9}

9. Consider the following standard reduction potentials :

$$I_3^-(aq) + 2e^- \rightleftharpoons 3I^-(aq); \quad E^\circ = 0.53 \text{ V}$$

$$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq); \quad E^\circ = -0.41 \text{ V}$$

Calculate ΔG° (in kJ) for the following reaction at 25°C.

$$Cr^{2+}(aq) + I_3^-(aq) \rightleftharpoons Cr^{3+}(aq) + I^-(aq)$$

(a) 180 (b) −180
(c) 90 (d) −90

Q.Nos. 10-37 (These question may have more than one correct option)

10. Which one of the following statements is(are) true regarding galvanic and electrolytic cells?
(a) In both cells, redox reactions take place.
(b) In electrolytic cells, a current is forced through a cell to produce a chemical change for which the cell potential is negative.
(c) In both cells, reduction takes place at the cathode.
(d) The ion flow through the salt bridge in galvanic cell is opposite to the flow in electrolytic cell.

11. Which one of the following statements is(are) false in a concentration cell made of Fe in 0.010 M $Fe^{2+}(aq)$ and Fe in 0.10 M Fe^{2+}?
(a) The $E^\circ_{cell} = 0$
(b) $\Delta G = 0$
(c) The cell reaction is: $Fe^{2+}(aq, 0.010 \text{ M}) \rightarrow Fe^{2+}(aq, 0.10 \text{ M})$
(d) At equilibrium, the $[Fe^{2+}]_{anode} = [Fe^{2+}]_{cathode}$

12. The emf of a galvanic cell depends upon
(a) surface area of electrodes
(b) concentration of electrolyte
(c) volume of electrolyte
(d) temperature

13. A chemist found that the standard electrode potential $E^\circ(Zn^{2+}/Zn) = -0.76$ V. Which spontaneous cell(s) will give this value of emf?
(a) $Zn|Zn^{2+}(1 \text{ M})||H^+(1 \text{ M})|H_2(1 \text{ atm})|Pt$
(b) $Zn|Zn^{2+}(4 \text{ M})||H^+(2 \text{ M})|H_2(1 \text{ atm})|Pt$
(c) $Zn|Zn^{2+}(10 \text{ M})||H^+(10 \text{ M})|H_2(1 \text{ atm})|Pt$
(d) $Zn|Zn^{2+}(2 \text{ M})||H^+(2 \text{ M})|H_2(2 \text{ atm})|Pt$

14. Standard reduction potentials of various reactions involving bromine are given as

$$BrO_4^- \xrightarrow{1.74 \text{ V}} BrO_3^- \xrightarrow{+1.47\text{V}} HOBr \xrightarrow{+1.6\text{V}} \frac{1}{2}Br_2(l) \xrightarrow{+1.07} Br^-$$

Given that HOBr undergoes disproportionation, which of the following set of products are possible?
(a) BrO_4^-, Br^- (b) BrO_4^-, Br_2
(c) BrO_3^-, Br_2 (d) BrO_3^-, Br^-

15. Consider the cell :
$Pt|H_2(P_1 \text{ atm})|H^+(x_1 \text{ M})||H^+(x_2 \text{ M})|H_2(P_2 \text{ atm})Pt$.
The cell reaction will be spontaneous if
(a) $p_1 = p_2$ and $x_1 > x_2$ (b) $p_1 = p_2$ and $x_1 < x_2$
(c) $x_1 = x_2$ and $p_1 > p_2$ (d) $x_1 = x_2$ and $p_1 < p_2$

16. Consider the sequence $A^{a+} \xrightarrow{E_1^\circ} A^{b+} \xrightarrow{E_2^\circ} A^{c+}$, $A^{a+} \xrightarrow{E^\circ} A^{c+}$

Given that $E^\circ = \frac{E_1^\circ + E_2^\circ}{2}$, which of the following might represent correct set of values for a, b and c?
(a) $a = 3, b = 2, c = 1$ (b) $a = 5, b = 3, c = 1$
(c) $a = 6, b = 4, c = 4$ (d) $a = 6, b = 4, c = 4$

17. In a standard solution of X^- and Y^- ions, gas Z_2 is passed. X_2 is liberated and Z^- is formed while Y^- remain unaffected. E_x°, E_y° and E_z° represent standard reduction potentials of X_2, Y_2 and Z_2 respectively. Which of the following can be inferred from this equation?
(a) $E_z^\circ > E_x^\circ$ (b) $E_z^\circ > E_y^\circ$
(c) $E_y^\circ > E_x^\circ$ (d) $E_z^\circ > \frac{1}{2}(E_x^\circ + E_y^\circ)$

18. When a lead storage battery discharges
(a) $PbSO_4$ is formed (b) Pb is formed
(c) SO_2 is consumed (d) H_2SO_4 is consumed

19. During electrolysis, $O_2(g)$ is evolved at anode in
(a) dil. H_2SO_4 with Pt electrode
(b) aqueous $AgNO_3$ with Pt electrode
(c) dil. H_2SO_4 with Cu electrode
(d) fused NaOH with a Fe cathode and Ni anode

20. The specific conductivity of a saturated solution of AgCl is 3.4×10^{-4} S cm^{-1} at 25°C. If $\lambda(Ag^+) = 62.3$ S cm^2 mol^{-1}, $\lambda(Cl^-) = 67.7$ S cm^2 mol^{-1}, solubility of AgCl at 25°C is
(a) 2.6×10^{-5} M (b) 3.73×10^{-3} g/L
(c) 3.7×10^{-5} M (d) 2.6×10^{-3} g/L

21. A redox reaction occurs spontaneously if
(a) the free energy change is negative ($\Delta G < 0$)
(b) the $\Delta G > 0$
(c) the standard state cell emf (E°) is negative
(d) the emf of cell (E_{cell}) is positive

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22. Iron metal is allowed to react with 1.0 M HCl solution. E° for the Fe/Fe^{2+} is 0.34 V. The correct deduction regarding this reaction is(are)?
(a) Fe will be oxidized to Fe^{2+} spontaneously.
(b) Fe^{2+} will be spontaneously reduced to Fe.
(c) Since emf is positive, reaction will occur spontaneously.
(d) Since emf is positive, reaction will not occur spontaneously.

23. During electrolysis of aqueous $CuBr_2(aq)$ using Pt electrode,
(a) $Br_2(g)$ is evolved at anode.
(b) $Cu(s)$ is deposited at cathode
(c) $Br_2(g)$ is evolved at anode and $H_2(g)$ at cathode
(d) $H_2(g)$ is evolved at anode.

24. If pressure of $H_2(g)$ is increased from 1.0 to 100 atm, keeping pH of solution constant, the voltage of hydrogen half-cell at 25°C will be
(a) 0.059 V
(b) −0.059 V
(c) 0.295 V
(d) 0.118 V

25. A current of 2.68 A is passed for 1.0 h through an aqueous solution of $CuSO_4$ using copper electrodes. Select the correct statement(s) from the following.
(a) Increase in mass of cathode = 3.174 g
(b) Decrease in mass of anode = 3.174 g
(c) No change in mass of electrodes
(d) The ratio between the change in mass of cathode to anode is 1:2

26. The standard emf of the following cell:
$Cd(s) | CdCl_2(aq)\ (0.10\ M) || AgCl(s) | Ag(s)$
In which the cell reaction is
$$2AgCl(s) + Cd(s) \longrightarrow 2Ag(s) + Cd^{2+}(aq) + 2Cl^-(aq)$$
is 0.6915 V at 0°C and 0.6753 V at 25°C. The ΔH of reaction at 25°C is
(a) −176 kJ
(b) −234.7 kJ
(c) 123.5 kJ
(d) −167.26 kJ

27. When 4.00 A of current is passed through a 1.0 L 0.10 M $Fe^{3+}(aq)$ solution for 1.0 hr, it is partly reduced to Fe(s) and partly to $Fe^{2+}(aq)$. The correct statement(s) is (are)? Assume F = 96000.
(a) 0.10 mole of electrons are required to convert all Fe^{3+} to Fe^{2+}.
(b) 0.025 mole of Fe(s) will be deposited.
(c) 0.075 mole of iron remains as Fe^{2+}.
(d) 0.050 mole of iron remains as Fe^{2+}.

28. When a galvanic cell starts operating, with passage of time,
(a) spontaneous character of the cell decreases, E_{Cell} decreases.
(b) reaction quotient 'Q' decreases, E_{Cell} increases.
(c) useful work obtainable from the cell increases.
(d) as cell stops producing voltage, $Q = K$.

29. Which of the following is/are true statement(s)?
(a) If $E^\circ(M^{n+}/M)$ is negative (< 0), H^+ will be reduced to H_2 by the metal.
(b) If $E^\circ(M^{n+}/M)$ is positive, M^{n+} will be reduced to M by H_2.
(c) In a cell M^{n+}/M is attached to a hydrogen electrode. For a spontaneous cell reaction, M will act as negative electrode if $E^\circ(M^{n+}/M)$ is positive.
(d) Compounds of active metals like Zn, Na, Mg etc. are reducible by H_2 while compounds of noble metals as of Cu, Ag and Au are not reducible.

30. Consider the following half reaction:
$$A(s) \longrightarrow A^{n+}(aq) + ne^- \quad [A^{n+}] > 1.00\ M$$
The correct statement(s) is/are?
(a) Electrode potential $E(A/A^{n+})$ decreases with increase in $[A^{n+}]$
(b) With constant $[A^{n+}]$, $E(A^{n+}/A)$ increases with rise in temperature
(c) At constant temperature $E(A^{n+}/A)$ increases on increasing $[A^{n+}]$
(d) With constant $[A^{n+}]$, $E(A/A^{n+})$ increases with rise in temperature

31. Which of the following is(are) correct thermodynamic relationship?
(a) $\Delta G^\circ = -2.303\ RT \log K$
(b) $\Delta G = \Delta G^\circ + 2.303\ RT \log K$
(c) $E^\circ_{cell} = \dfrac{0.0591}{n} \log K$ at 25°C
(d) $E = E^\circ - \dfrac{0.0591}{n} \log K$ at 25°C

32. The ionic conductivity of Na^+ ion is greater than that of Li^+ in aqueous solution. It is because of the reason
(a) The ionic radius of Na^+ is greater than Li^+.
(b) The speed of Na^+ is greater than that of Li^+.
(c) Li^+ has greater hydrated radius than that of Na^+.
(d) Li^+ has greater polarizing power than polarizing power of Na^+.

33. Consider the following electrochemical cell at 25°C.
$Pb(s) | PbSO_4$ (saturated) $|| PbI_2$ (saturated) $| Pb(s)$
Which of the following expression can be used to determine emf of the cell?
(a) $E = -\dfrac{0.0592}{2} \log \left(\dfrac{[Pb^{2+}]_{anode}}{[Pb^{2+}]_{cathode}} \right)$
(b) $E = \dfrac{0.0592}{2} \log \left(\dfrac{[Pb^{2+}]_{anode}}{[Pb^{2+}]_{cathode}} \right)$
(c) $E = \dfrac{0.0592}{2} \log \left(\dfrac{\left(\dfrac{K_{sp}}{4}\right)^{1/3}_{PbI_2}}{(K_{sp})^{1/2}_{PbSO_4}} \right)$
(d) $E = \dfrac{0.0592}{2} \log \left(\dfrac{(K_{sp})_{PbI_2}}{(K_{sp})_{PbSO_4}} \right)$

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34. Consider the following galvanic cell

$$Cd(s)|Cd^{2+}(1.0\ M)||Cu^{2+}(1.0\ M)|Cu(s)$$

If we wish to make a cell with a more positive value of emf using the same substances, we should
(a) Increase $[Cd^{2+}]$ as well as $[Cu^{2+}]$ to 2.0 M
(b) Reduce only $[Cd^{2+}]$ to 0.1 M
(c) Increase only $[Cu^{2+}]$ to 2.0 M
(d) Decrease $[Cd^{2+}]$ as well as $[Cu^{2+}]$ to 0.10 M

35. The correct statement(s) regarding conductivity of an electrolytic solution is(are)
(a) Specific conductivity increases with dilution.
(b) Molar conductivity increases on dilution.
(c) Equivalent conductivity decreases on dilution.
(d) Conductance of solution increases on heating.

36. In which of the following cell, emf is greater than E°_{cell}?
(a) $Pt(s)|H_2(1.0\ atm)|H^+(pH=5)||H^+(pH=3)|H_2(g)|Pt(s)$
(b) $Zn(s)|Zn^{2+}(0.2\ M)||Cu^{2+}(0.1\ M)|Cu(s)$
(c) $Cr(s)|Cr^{3+}(0.1\ M)||Cu^{2+}(0.2\ M)|Cu(s)$
(d) $Pt(s)|H_2(1.0\ atm)|H^+(pH=4)||H^+(pH=6)|H_2(g)|Pt(s)$

37. For a strong electrolyte, equivalent conductance increases slowly with dilution and can be expressed by the relationship $\Lambda_m = \Lambda_m^0 - A\sqrt{C}$
Where A is a constant.
Which electrolyte(s) have same value of the constant A?
(a) NaCl (b) $CaCl_2$
(c) $ZnCl_2$ (d) $MgSO_4$

Q. Nos. 38-59 (Statement I and II Type Questions)

Answer the following questions according to the following four responses.
(a) Both Statement I and Statement II factually are true and Statement II is the correct explanation of Statement I.
(b) BothStatement I and Statement II factually are true but Statement II is not the correct explanation of Statement I.
(c) Statement I is true but Statement II is incorrect.
(d) Statement I is wrong but Statement II is true.

38. **Statement I** Decreasing concentration by dilution increases the equivalence conductance of aqueous solution NaCl.
Reason With dilution, degree of ionization of NaCl increases.

39. **Statement I** Rusting of iron is prevented by galvanization using Zn metal.
Statement II Zn has lower standard reduction potential than iron.

40. **Statement I** In a Galvanic cell, electrons flow through external circuit, not through internal circuit, *i.e.*, salt bridge.
Statement II There is greater potential difference between electrodes of cell than potential difference between an electrode and an ion from the salt bridge.

41. **Statement I** The electrode potential of standard hydrogen electrode is zero only at 0°C.
Statement II Standard hydrogen electrode is a standard reference electrode.

42. **Statement I** Absolute value of $E°$(red) of a half-cell can't be determined.
Statement II Oxidation or reduction cannot be carried out in isolation.

43. **Statement I** Lead storage battery does not require a salt bridge.
Statement II The solid state nature of both oxidizing and reducing agent prevent their direct contact.

44. **Statement I** Lead Storage battery has almost constant cell potential.
Statement II Most of the reagents used are either solids or highly concentrated solutions.

45. **Statement I** Salt bridge is usually used in an electrochemical cells.
Statement II The ions of the electrolyte used in salt bridge should have nearly same transport numbers.

46. **Statement I** The molar conductivity of strong electrolyte solution does not changes on dilution.
Statement II At high concentration of electrolytes, the ions of opposite charges influence the speeds of each other besides the viscosity of solution.

47. **Statement I** In electrolytic reduction method used for the extraction of aluminium from alumina, some cryolite is added.
Statement II Cryolite dissolves the alumina readily.

48. **Statement I** Blocks of magnesium metals are often stapled to steel hulls of ship going to ocean.
Statement II Magnesium provide cathodic protection to iron.

49. **Statement I** Electrolysis of molten CaH_2 produces $H_2(g)$ at anode.
Statement II In CaH_2, hydrogen is present in the form of hydride (H^-).

50. **Statement I** Electrolysis of aqueous solution of NaCl increases the pH of solution being electrolyzed.
Statement II During electrolysis NaOH is produced.

51. **Statement I** One Faraday of electricity deposit one-gram equivalent of Ag or Cu or Al.
Statement II One mole of electrons are required to reduce one mole of each Ag^+, Cu^{2+} or Al^{3+}.

52. **Statement I** When acidified $ZnSO_4$ solution is electrolyzed between Zn electrodes, it is Zn that is deposited at the cathode and $H_2(g)$ is not evolved.
Statement II The electrode potential of Zn is more negative than hydrogen as the overpotential for hydrogen evolution on Zn is quite large.

53. **Statement I** At the end of electrolysis using Pt electrodes, an aqueous solution of $CuSO_4$ becomes colourless.
Statement II $CuSO_4$ changes to $Cu(OH)_2$ during electrolysis.

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54. **Statement I** Equivalent conductance of an electrolytic solution increases with dilution.
Statement II The number of ions in one litre of solution increases with dilution.

55. **Statement I** For the following galvanic cell:
$Zn(s)|Zn^{2+}(C_1)||Zn^{2+}(C_2)|Zn(s)$ C_1 must be smaller than C_2.
Statement II For concentration cell, E°_{cell} is zero.

56. **Statement I** A saturated solution of KCl is used for making salt bridge.
Statement II Ionic mobility of K^+ and Cl^- are comparable.

57. **Statement I** In a Daniel cell, if concentration of both Cu^{2+} and Zn^{2+} ions are doubled, the emf of the cell will also be doubled.
Statement II If concentrations of ions in contact with metal are doubled, the electrode potential is also doubled.

58. **Statement I** The cell constant of a cell depends upon the nature of the materials of electrodes.
Statement II The observed conductance of a solution depends upon the nature of the materials of electrodes.

59. **Statement I** If both oxidizing and reducing agents are taken in the same electrolyte solution, no current flows through the external circuit.
Statement II Electron transfer preferably occurs through internal circuit.

MCQs Based on Understanding of a Passage (*Comprehension Skills' Testing*)

Reading 1 (For Questions 60-63)

The magnitude (but not the sign) of the standard reduction potentials of two metals X and Y are:

$$Y^{2+} + 2e^- \longrightarrow Y \quad |E_1^\circ| = 0.34\,V$$
$$X^{2+} + 2e^- \longrightarrow X \quad |E_2^\circ| = 0.25\,V$$

When the two half-cells of X and Y are connected to construct a cell, electrons flow from X to Y. When X is connected to a standard hydrogen electrode (SHE), electrons flow from X to SHE.

60. Which of the following sign of E_1° and E_2° are true?
(a) Both are negative
(b) Both are positive
(c) E_1° is negative and E_2° is positive
(d) E_1° is positive and E_2° is negative

61. If a half-cell X/X^{2+}(0.1 M) is connected to another half-cell Y/Y^{2+}(1.0 M) by means of a salt bridge and an external circuit at 25°C, the cell voltage would be
(a) 0.06 V (b) 0.12 V
(c) 0.62V (d) 0.72 V

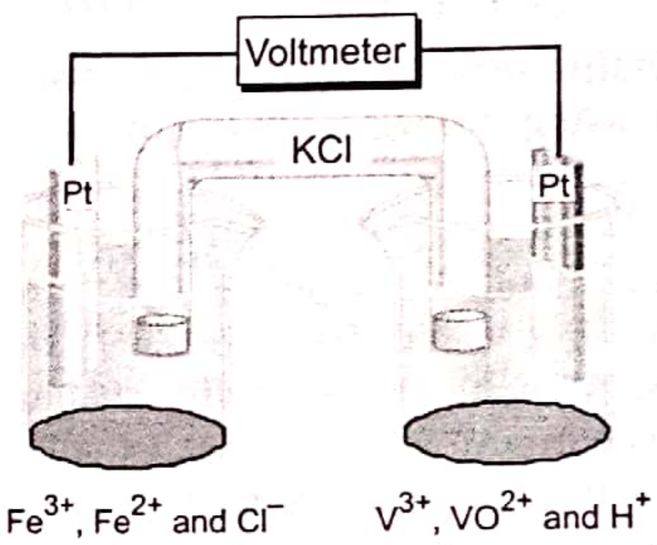
62. If standard emf (E°) of a half-cell Y^{2+}/Y^+ is 0.15 V, the standard emf of the half-cell Y^+/Y will be?
(a) 0.19 V (b) 0.53 V (c) 0.49 V (d) 0.64 V

63. Given the following half-cell: $YI + e^- \longrightarrow Y + I^-$; $E^\circ = -0.27$ V
Solubility product of the iodide salt YI is
(a) 2×10^{-3} (b) 2×10^{-12}
(c) 2×10^{-14} (d) 6.8×10^{-16}

Reading 2 (For Questions 64-66)

An electrochemical cell with inert platinum electrodes is shown below. The half cell reactions are:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \quad E^\circ = +0.77\,V$$
$$VO^{2+} + 2H^+ + e^- \longrightarrow V^{3+} + H_2O; \quad E^\circ = +0.34\,V$$



64. The statement which is incorrect about this cell is
(a) E°_{Cell} is 0.43 V.
(b) Electrons flow from left to right electrode.
(c) If some Fe^{3+} is added to left half-cell, E_{Cell} increases.
(d) If some VCl_3 is added to right half-cell, E_{Cell} increases.

65. Emf of the cell when all the species are at 1.0 M except H^+ which is at 0.01 M is
(a) 1.35 V (b) 0.55 V (c) 0.67 V (d) 0.194 V

66. The maximum useful work that can be obtained from this cell under standard condition is
(a) 32.8 kJ (b) 41.5 kJ (c) 74.3 kJ (d) 107 kJ

Reading 3 (For Questions 67-68)

For the next two questions use the following information:

$$Ni^{2+} + 2e^- \longrightarrow Ni; \quad E^\circ = -0.26\,V \text{ at } 25°C$$
$$Cu^{2+} + 2e^- \longrightarrow Cu; \quad E^\circ = +0.34\,V \text{ at } 25°C$$

67. Which of the following statements apply appropriately if a galvanic cell is constructed using Ni/Cu electrodes?
(a) Ni is produced at cathode and electric current flow through salt bridge.
(b) Cu is produced at cathode and electrons flow from anode to cathode chamber via salt bridge.
(c) $Ni^{2+}(aq)$ is produced at anode and electrons flow from anode to cathode chamber via external circuit.
(d) $Ni^{2+}(aq)$ is produced at anode and migrates to cathode chamber via salt bridge.

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68. The internal flow of current in the above galvanic cell is
(a) Only a movement of positive ions towards Cu-electrode.
(b) a movement of positive ions towards Ni-electrode and of negative ions towards Cu-electrode.
(c) a movement of negative ion towards Ni-electrode and of positive ions towards Cu-electrode.
(d) a movement of hydrogen ions towards Cu-electrode.

Reading 4 (For Questions 69-70)

The next two questions deal with an experiment. An unknown metal 'X' is found to react spontaneously with 1.0M solution of $CuSO_4$, plating out Cu(s). X does not react with a solution of 1.0 M Zn $(NO_3)_2$. The half-reactions for these metals are:

$$X^{2+}(aq) + 2e^- \longrightarrow X(s)$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu$$
$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn$$

69. What is the correct order for listing the metals according to decreasing strength as reducing agent?
(a) X, Cu, Zn (b) Cu, Zn, X
(c) Cu, X, Zn (d) Zn, X, Cu

70. Another metal Y displaces Cu^{2+} from its aqueous solution but can't displace Zn^{2+} from its aqueous solution. Which of the following statements regarding X and Y is correct?
(a) X is stronger reducing agent than Y
(b) X is weaker reducing agent than Y
(c) Both X and Y are weaker reducing agents than Cu
(d) X can be either stronger or weaker reducing agent than Y.

Reading 5 (For Questions 71-72)

For the next two questions, consider the following situations: There are four solutions available. 1.0 M solutions of Ga^{3+}, Cd^{2+}, In^{3+} *and* Ti^{2+}. Al *reacts with all these solutions except* Ti^{2+}. *The* Cd^{2+} *solution reacts with Gallium metal but not with Indium. All the metals react with* HCl *liberating* H_2 *gas.*

71. What is the correct order for metal ion half-cells starting with best electron donor?
(a) In, Cd, Al, Ga, Ti (b) Ti, Al, Ga, Cd, In
(c) Cd, Ti, In, Ga, Al (d) Ga, In, Ti, Al, Cd

72. In the reaction between Cd and Ga half-cells, 0.06 mol of Ga dissolves. Cd would be plated out to the extent of
(a) 0.09 mol (b) 0.06 mol
(c) 0.03 mol (d) 0.02 mol

Reading 6 (For Questions 73-75)

For the next three questions, consider these half reactions and corresponding E° values at 25°C.

(A) $MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons 2H_2O + Mn^{2+}(aq);\ E° = +1.23\ V$

(B) $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s); E° = +0.34\ V$

(C) $Ag^+(aq) + e^- \rightleftharpoons Ag(s); E° = +0.80\ V$

(D) $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s); E° = -0.13\ V$

(E) $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s); E° = -2.34\ V$

73. Which half-reaction(s) would oxidize $H_2(g)$ to $H^+(aq)$?
(a) A-only (b) B and E only
(c) D and E only (d) A, B and C

74. If a current is passed through an aqueous solution containing $Cu(NO_3)_2$, $AgNO_3$ and $Mg(NO_3)_2$, the order in which metals are deposited at cathode is (first metal is one that is deposited first):
(a) Ag, Cu, Mg (b) Mg, Cu, Ag
(c) Cu, Ag (d) Ag, Cu

75. Note these additional half-reactions and E° values:

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq);\quad E° = +1.36\ V$$
$$I_2(g) + 2e^- \rightleftharpoons 2I^-(aq);\quad E° = +0.54\ V$$

Which of the lettered half-reactions will oxidize I^- but not Cl^-?
(a) B only (b) A and C only
(c) D and E only (d) B and D only

Reading 7 (For Questions 76-79)

For the next four questions use the following information:

A voltaic cell consists of an electrode of solid silver immersed in a 0.10M $AgNO_3$ *solution and an electrode of unknown metal 'X' immersed in a 0.10 M solution of* X $(NO_3)_2$. *A porous barrier separates the two half of the cell. Also given:*

$$E°\ (Ag^+/Ag) = 0.80\ V \text{ and } E°_{Cell} = 1.05\ V \text{ at } 25°C$$

76. Which of the following statements regarding the cell and X is incorrect?
(a) Standard Emf ($E°$) of X^{2+}/X is –0.25V at 25°C.
(b) X is a stronger reducing agent than $H_2(g)$
(c) As cell operate, concentrations of both X^{2+} and Ag^+ increases in their respective half-cells.
(d) As cell operate, concentration of X^{2+} increases in anode chamber while concentration of Ag^+ decreases in cathode chamber.

77. Within the cell
(a) X^{2+} ions will migrate towards X-electrode
(b) Electrons will migrate from anode to cathode through porous barrier.
(c) NO_3^- ions will migrate from anode to cathode chamber
(d) Ag^+ ions will migrate towards Ag electrode.

78. If Ag^+/Ag half-cell in the above voltaic cell is replaced by Zn^{2+}/Zn half/cell ($E°_{Zn^{2+}/Zn} = -0.76$ V)
(a) The direction of current flow will remain unchanged.
(b) Polarity of the electrodes will be reversed.
(c) Cell will stop working
(d) Emf of cell will increase

79. The voltage generated by the original voltaic cell at 25°C is:
(a) 1.07 V (b) 1.35 V
(c) 1.02 V (d) 0.75 V

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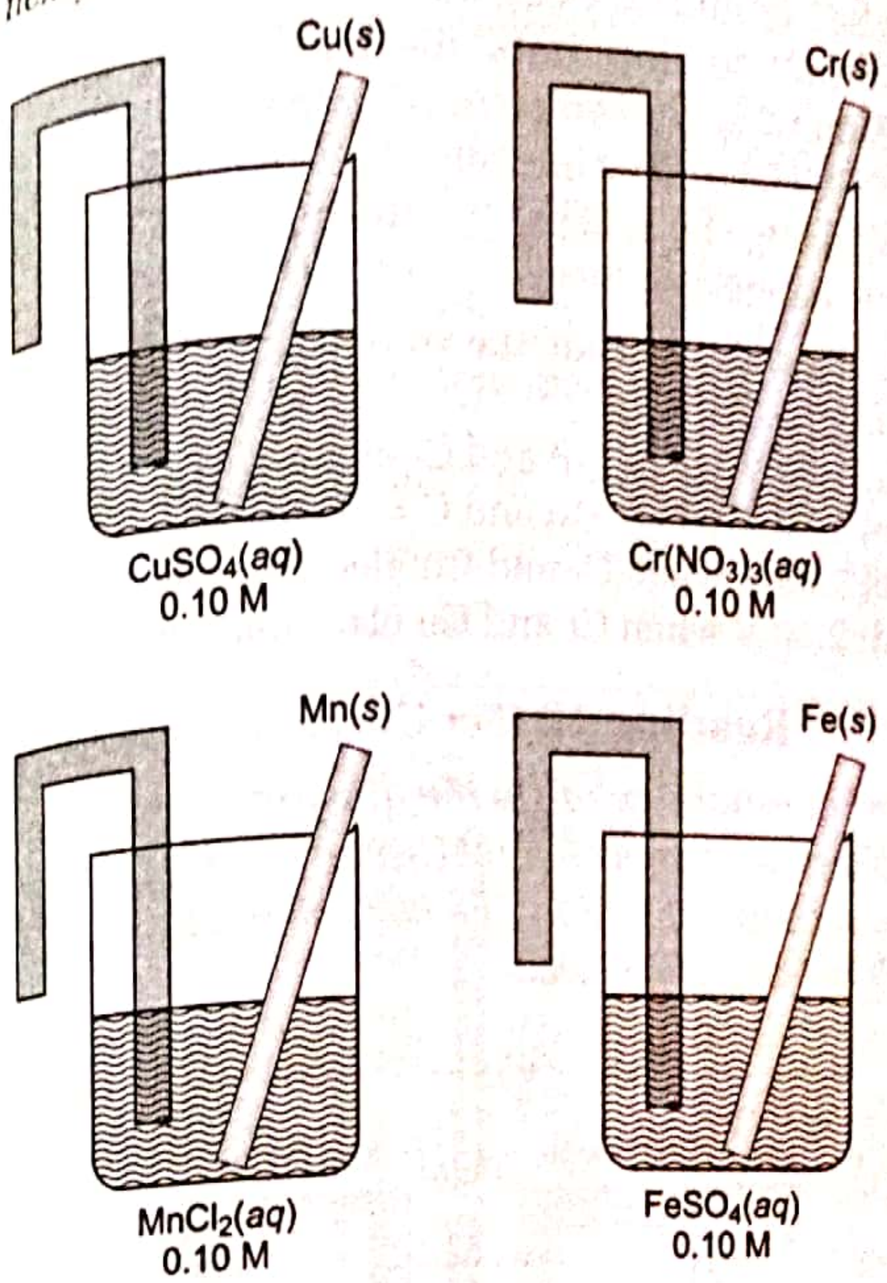
Reading 8 (For Questions 80-83)

For the next four questions, consider these half-cell systems.



$E°$ (at 25°C)	Half-cell	Molar Masses
+0.34 V	$Cu^{2+} + 2e^- \longrightarrow Cu$	Cu = 63.5
-0.74V	$Cr^{3+} + 3e^- \longrightarrow Cr$	Cr = 52
-1.18 V	$Mn^{2+} + 2e^- \longrightarrow Mn$	Mn = 55
-0.45 V	$Fe^{2+} + 2e^- \longrightarrow Fe$	Fe = 56

80. What is the voltmeter reading when Fe and Mn half-cells are connected
(a) 0.72 V (b) 0.73 V
(c) 0.74 V (d) 0.76 V

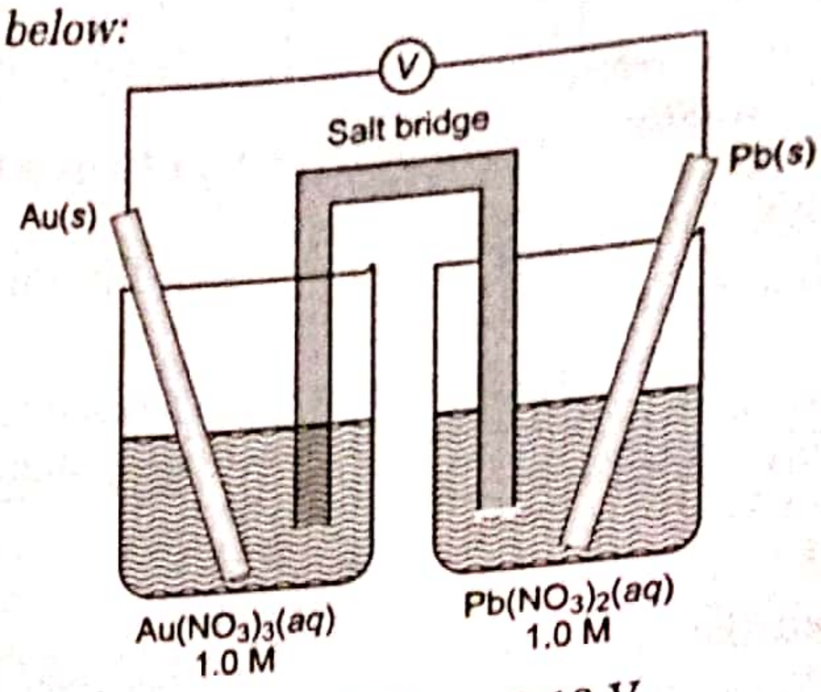
81. If the iron and copper half-cells are connected
(a) the voltmeter reads 0.10 V.
(b) oxidation occurs at iron electrode.
(c) electrons are transferred from copper to the iron electrode.
(d) the copper electrode decreases in mass.

82. If the copper and chromium half-cells are connected and a current is allowed to flow until the Cu-electrode changes in mass by 0.95 g, the Cr-electrode mass:
(a) decreases by 0.34 g
(b) decreases by 0.52 g
(c) increases by 0.63 g
(d) increases by 0.95 g

83. Which of the following combination of half-cells will produce minimum, voltmeter readings
(a) Cu—Cr (b) Cu—Fe
(c) Cr—Mn (d) Cr—Fe

Reading 9 (For Questions 84-86)

For the next three questions, consider the apparatus illustrated below:



$E°(Pb^{2+}/Pb) = -0.13$ V

$E°(Au^{3+}/Au) = +1.50$ V

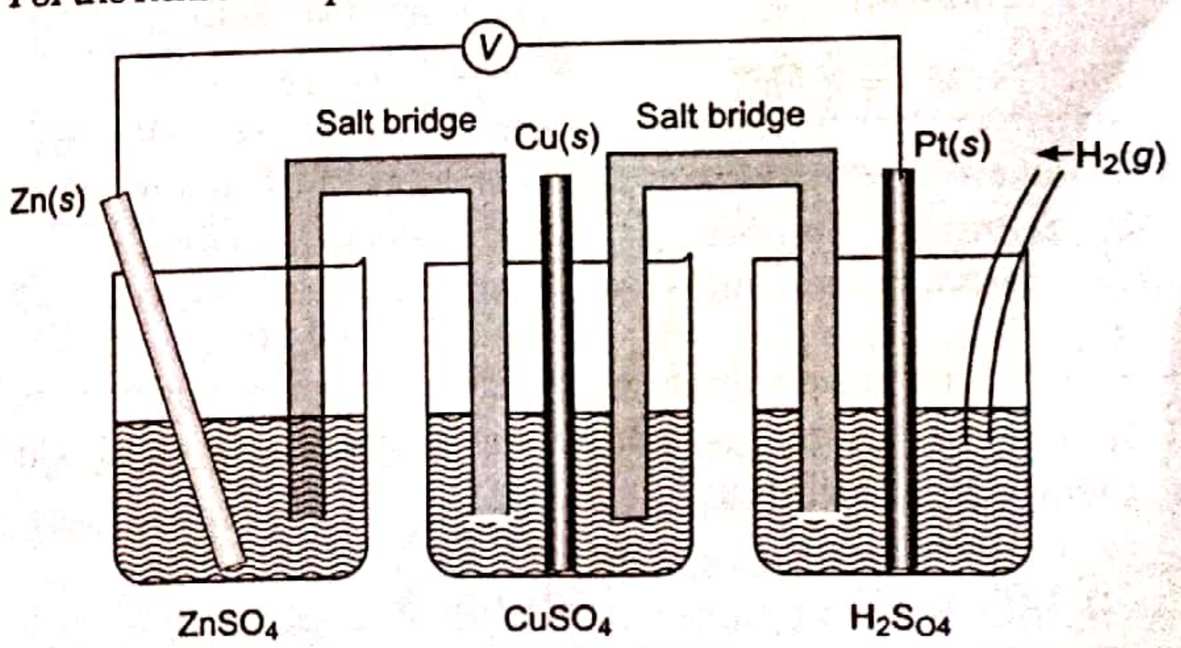
84. The correct net equation for the spontaneous reaction is
(a) $2Pb^{2+} + 3Au^{3+} \rightleftharpoons 2Pb + 3Au$
(b) $2Pb^{2+} + 3Au \rightleftharpoons 2Pb + 3Au^{3+} + 3e^-$
(c) $2Au^{3+} + 3Pb \rightleftharpoons 2Au + 3Pb^{2+}$
(d) $3Au + 2Pb^{2+} \rightleftharpoons 3Au^{3+} + 2Pb$

85. Which of the following statement is incorrect?
(a) NO_3^- will migrate through salt bridge to Pb half-cell.
(b) The voltmeter reading is 1.63V.
(c) The total number of positive ions in system will decrease.
(d) The concentration of $Au^{3+}(aq)$ in left-beaker will decrease.

86. Which of the following statement regarding the above cell is incorrect?
(a) Electrons flow from Pb electrode through external circuit to Au electrode.
(b) Cations remove electrons from Au-electrode.
(c) Electrons are conserved in the system.
(d) Electrons flow through salt bridge towards Au half-cell.

Reading 10 (For Questions 87-89)

For the next three questions use the data and diagram shows below:



$Zn^{2+} + 2e^- \rightleftharpoons Zn(s); \quad E° = -0.76$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu(s); \quad E° = +0.34$ V

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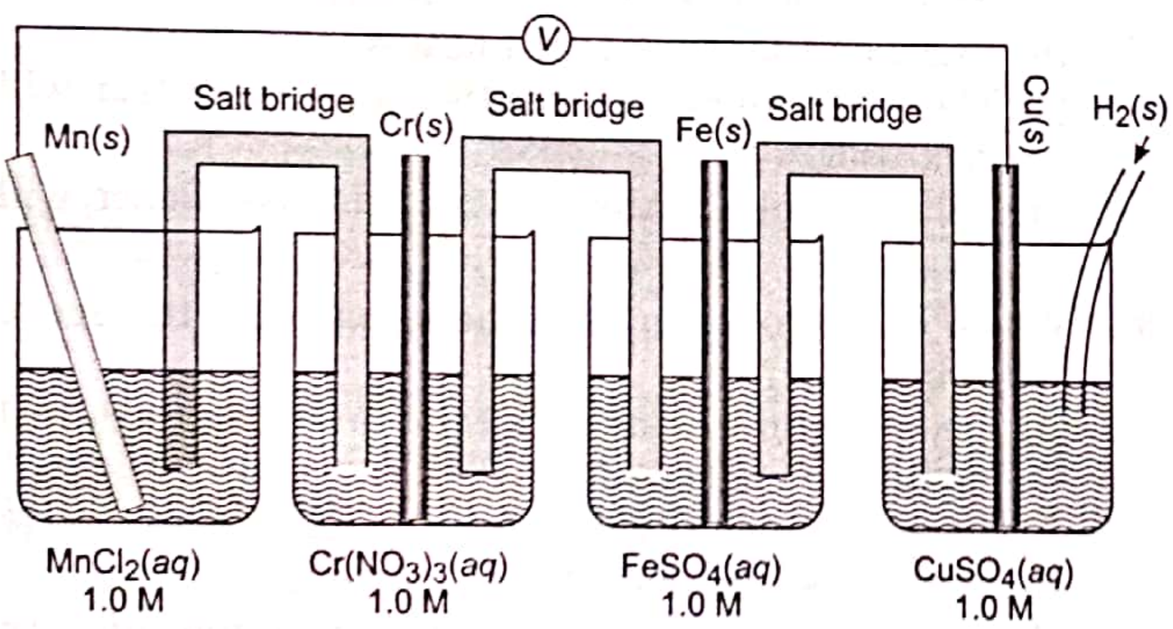
87. When the voltmeter is connected between H_2 and Cu electrode, which of the following statements is false?
(a) The Cu-electrode decreases in mass.
(b) Electrons flow through the voltmeter from H_2 to Cu-electrode.
(c) Changing Cu^{2+} concentration will change the voltage.
(d) SO_4^{2-} ions migrate slowly from the Cu to the H_2 half-cells.

88. What will be the voltmeter reading when it is connected between the Zn and the Cu electrode assuming all ions are present at unit concentrations
(a) −0.34 V (b) 0.42 V
(c) 0.76 V (d) 1.10 V

89. When the voltmeter is connected between Zn and Cu electrodes, the current is allowed to flow through the cell until the mass of Zn electrode has changed by 5.64 gram. During this time, the mass of Cu electrode has
(Molar mass of Cu = 63.5, Zn = 65)
(a) increased by 12.7 g (b) increased by 5.47 g
(c) decreased by 5.47 g (d) decreased by 12. 7 g

Reading 11 (For Questions 90-93)

For the next four questions, refer to the cell system described below:



The voltmeter may be connected to any pair of electrodes. Assuming that no half-reactions other than the following take place answer the following four questions:

Half-cell	E° (V at 25°C)
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1.18
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0.74
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.45
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34

90. If the voltmeter is connected between Cr and Cu electrode, it will read
(a) 0.40 V (b) 0.84 V
(c) 1.08 V (d) 1.52 V

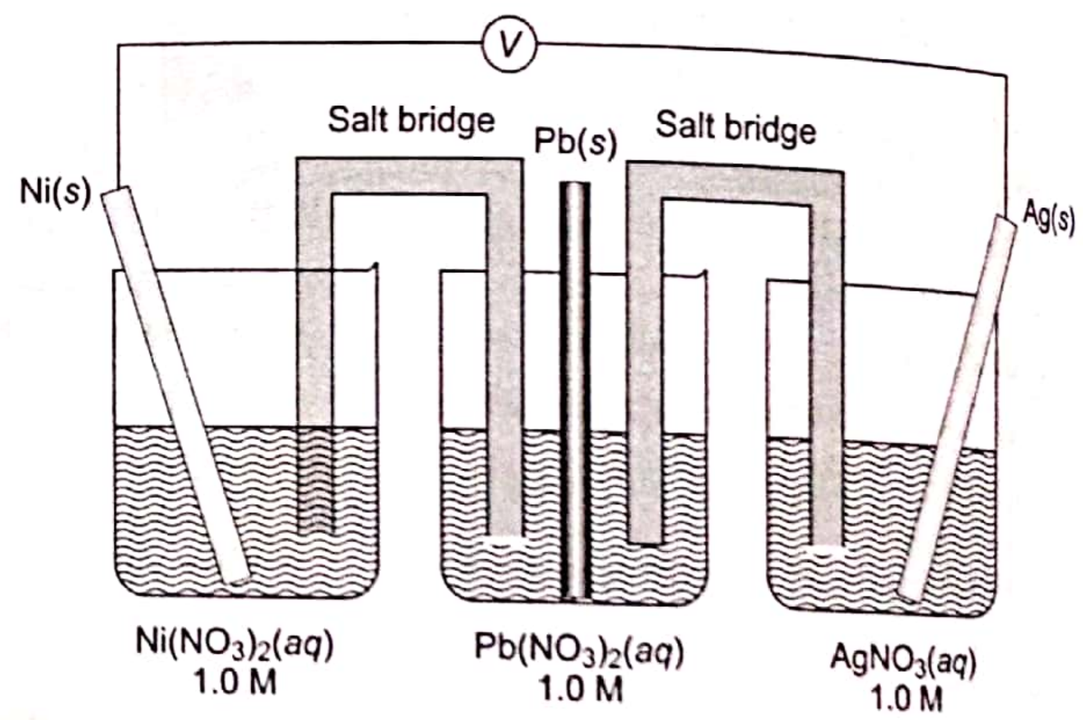
91. The electrodes are removed and each is tested in each of the solutions. Spontaneous reactions occur with all except
(a) Mn with $CuSO_4$ (b) Cr with $FeSO_4$
(c) Cu with $Cr(NO_3)_3$ (d) Fe with $CuSO_4$

92. When Fe and Cu electrodes are connected and current is allowed to flow until the mass of Fe electrode has changed by 5.58 grams, during the same period the mass of Cu-electrode will
(a) change by 5.58 g (b) change by 3.18 g
(c) change by 1.28 g (d) change by 6.36 g

93. In the above system, the voltmeter will read a maximum of
(a) 1.92 V when Mn and Cr electrodes are connected
(b) 1.52 V when Mn and Cu electrodes are connected
(c) 1.08 V when Cr and Cu electrodes are connected
(d) 2.50 V when Cr and Cu electrodes are connected

Reading 12 (For Questions 94-97)

Next four questions relate to the illustrated apparatus below. The beakers are connected by U-tube salt bridges containing a dilute solution of KNO_3. The half-cell reactions and E° values (at 25°C) are also given below:



$$Ni(s) \rightleftharpoons Ni^{2+} + 2e^-; \quad E° = +0.25\,V$$
$$Pb(s) \rightleftharpoons Pb^{2+} + 2e^-; \quad E° = +0.13\,V$$
$$Ag(s) \rightleftharpoons Ag^+ + e^-; \quad E° = -0.80\,V$$

Molar masses : Ag = 108, Pb = 207, Ni = 61

94. If the voltmeter is connected between Pb and Ag electrodes, it will read
(a) 0.93 V (b) 0.80 V
(c) 0.67 V (d) 1.73 V

95. With the voltmeter connected between Pb and Ag electrodes, current is allowed to flow through the cell until the mass of Pb electrode has changed by 2.07 grams. After this time, the mass of Ag electrode will be
(a) 2.16 g less (b) 0.59 g less
(c) 2.16 g greater (d) 1.08 g greater

96. If voltmeter is connected to Ni and Pb electrodes, which of the following statements will apply most appropriately?
(a) Voltage will be 0.12V and it will decrease on increasing the concentrations of Ni^{2+} in solution.
(b) Voltage will be 0.12V and it will decrease on adding some $Pb(NO_3)_2$ to Pb-half-cell.

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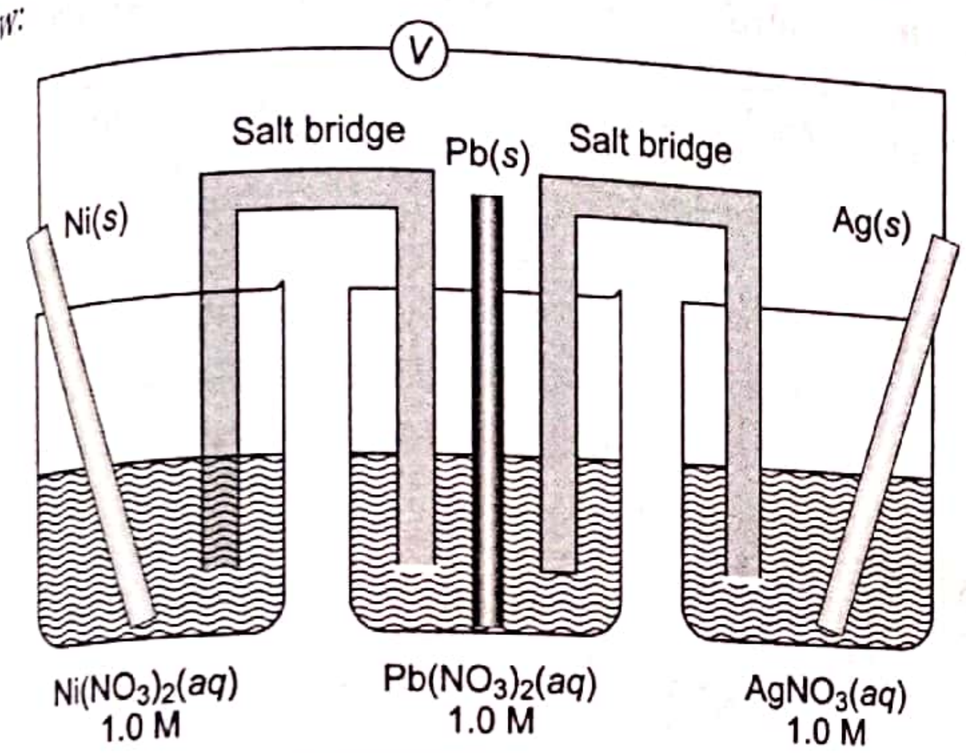
(c) Voltage will be 0.38 V and it will decrease on adding some $Ni(NO_3)_2$ to Ni half-cell.
(d) Voltage will be 0.38V and it will decrease on adding some $Pb(NO_3)_2$ is Pb-half-cell.

97. If the electrodes are removed and tested by immersing e^- in each solutions, spontaneous reactions occur with all except
(a) Pb–$AgNO_3$ (b) Pb–$NI(NO_3)_2$
(c) Ni–$AgNO_3$
(d) Both (b) and (c) are non-spontaneous.

Reading 13 (For Questions 98-100)

The next three questions relate to the illustrated apparatus below:



Half-cells	E°(V at 25°C)	Molar masses
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25 V	Ni = 60
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13 V	Pb = 207
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80 V	Ag = 108

98. When the voltmeter is connected between Ni and Pb electrodes, it reads 0.12 V. After 0.10 mol of electrons have passed through the voltmeter, the mass of Ni electrodes will be
(a) 6 grams greater (b) 3 grams greater
(c) 6 grams less (d) 3 grams less

99. Based on the information above, in which cases would a spontaneous reaction be expected to take place between the metal and the solution paired with it?
(I) Pb(s)—$Ag^+(aq)$ (II) Ag(s)—$Ni^{2+}(aq)$
(III) Pb(s)—$Ni^{2+}(aq)$ (IV) Ag(s)—$Pb^{2+}(aq)$
(V) Ni(s)—$Pb^{2+}(aq)$
(a) Only I and II (b) Only I and V
(c) Only II and V (d) I, III and IV

100. If $Ni/Ni(NO_3)_2$ and $Ag/AgNO_3$ half-cells are connected to a battery, what minimum voltage would be required to reverse the cell reaction
Also given : At 25°C

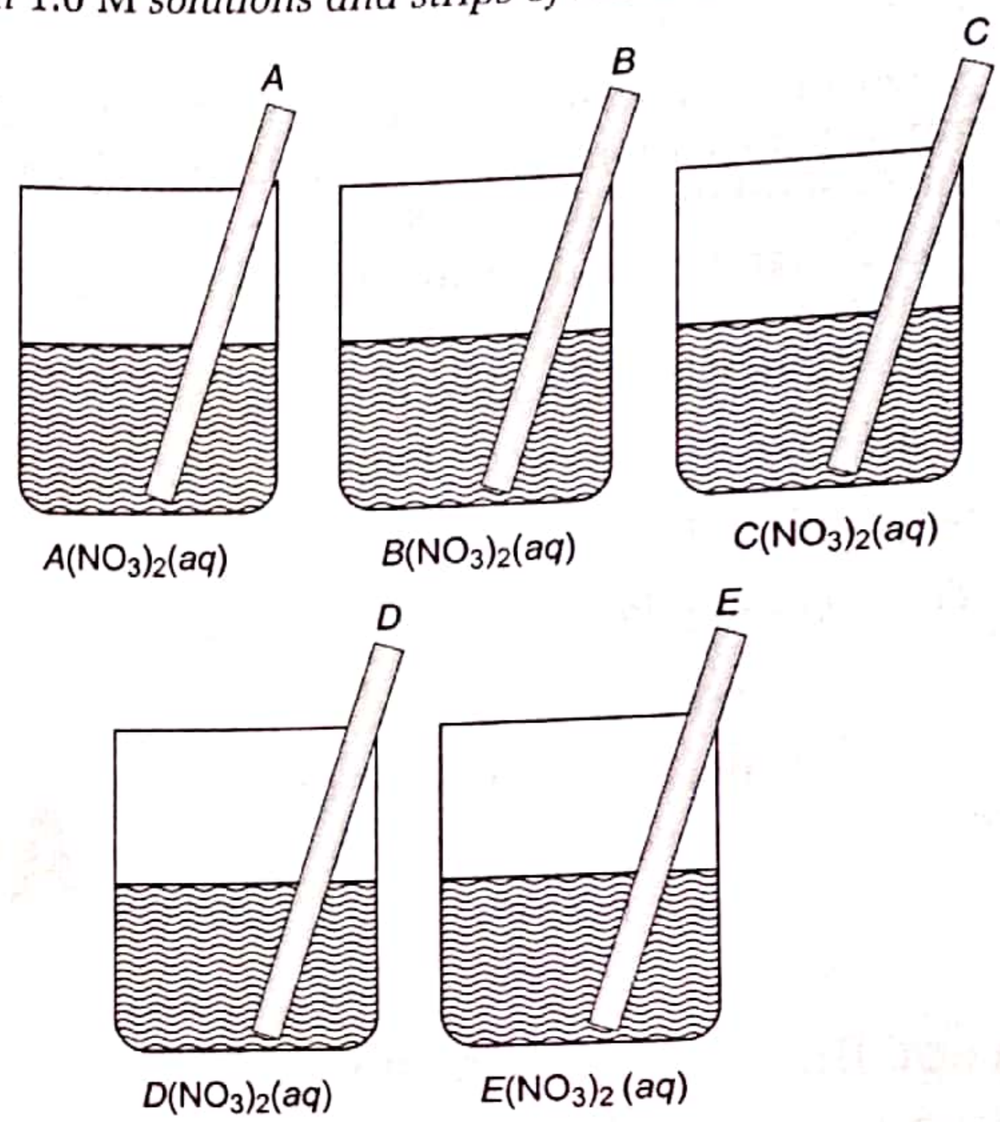
$$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-; \quad E° = -0.828 \text{ V}$$

$$4OH^- \rightleftharpoons O_2 + 2H_2O + 4e^-; \quad E° = -0.40 \text{ V}$$

(a) 1.05 V (b) less than 1.05 V
(c) greater than 1.05 V
(d) the cell is not reversible i.e. water oxidizes before Ag start oxidizing

Reading 14 (For Questions 101-104)

For the next four questions refer to the following illustrations in which 1.0 M solutions and strips of metal shown below:



(I) A strip of metal D was inserted into each solution. Reactions occurred in solutions containing A^{2+} and C^{2+} ions.
(II) Metal B reacted with solutions containing D^{2+} and E^{3+} ions. It was not tested in other solutions.
(III) Metal C does not react with any of the solutions.

101. If metal A were placed in each solution, a reaction would be expected in
(a) solutions containing C^{2+} ions only
(b) solutions containing B^+, C^{2+} and D^{2+} only
(c) solutions containing C^{2+}, D^{2+} and E^{3+} only
(d) solutions containing B^+, D^{2+} and E^{3+} ions only

102. For the metals A to E, a possible decreasing order of their oxidizing strength is
(a) $A > B > C > D > E$ (b) $C > A > E > D > B$
(c) $E > D > C > B > A$ (d) $B > E > D > A > C$

103. If the answer of the above question is assumed to be perfectly correct, all of the following combinations of metal-metal-ion solution represents non-spontaneous conditions except
(a) E—$D(NO_3)_2$ (b) A—$E(NO_3)_3$
(c) A—$C(NO_3)_2$ (d) C—$E(NO_3)_2$

104. Assuming that none of the metals A—E produces $H_2(g)$ when dissolved in HCl, if the above mentioned beakers are connected in series, molar ratio in which metals A—E deposited respectively
(a) 1 : 1 : 1 : 1 : 3 (b) 2 : 2 : 2 : 2 : 3
(c) 3 : 3 : 3 : 2 (d) 3 : 3 : 3 : 3 : 1

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Q.Nos. 105-112
(Single Integer Answer Type Questions)

105. Equivalent conductance of 0.2 M aqueous solution of a weak monobasic acid (*HA*) is 10 S cm^2 equiv^{-1} and that at infinite dilution is 200 S cm^2 equiv^{-1}. Hence, pH of this solution is

106. How many Faradays of electricity is required for electrolysis of 72 g of acidified water?

107. A 500 mL of aqueous NaCl solution is electrolysed for 1.0 min using a current of 8 mA at 25°C. What is the pH of the final solution? (F = 96000 C)

108. The charge required for discharging 115 g of Na from molten NaCl is ..... faradays.

109. Emf of a cell corresponding to the reaction :

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq)[0.10\ M] + H_2(g)[1.0\ atm]$$

is 0.3175 V at 25°C. Also, at 25°C, $E^\circ_{Zn^{2+}/Zn} = -0.76$ V. The pH of solution in cathode chamber is

110. 2.0 L of a buffer solution is prepared, that is 1.0 NaH_2PO_4 and 1.0 M Na_2HPO_4. The solution is divid into two halves between two compartments of electrolyte cell using Pt-electrodes. Assume that the on reaction is the electrolysis of water. If electrolysis carried out for 212 min with a current of 1.25 A; pH of t anode compartment is approximately [$pK_a(H_2PO_4^-) = 7.1$].

111. A current of 0.01 A is passed through a solution iridium bromide. The only reaction at the cathode is th deposition of iridium metal. After 3.0 hrs, 0.072 g of Ir deposited. The oxidation state of iridium ion (atomi weight = 192) is

112. If an aqueous NaCl solution is electrolysed using current of 5 A for 200 min, Volume of $Cl_2(g)$ in litres produced under STP condition is (F = 96000 C).

Answers

Concept Building Priliminaries

5. (a) Spontaneous (b) Spontaneous (c) Spontaneous (d) Yes, reaction is non-spontaneous (e) Spontaneous (f) Spontaneous

6. $E(Z_2/Z^-) < E(X_2/X) < E(Y_2/Y^-) < E(W_2/W^-)$

Concept Building Numerical Problems (*Base Level*)

1. 0.6715 mol **2.** 1.12 A **3.** 0.161 mole **4.** 108 g
5. (a) 0.5031 L (b) 0.2506 L **6.** (a) 0.515 A (b) 0.194 A
7. +2 **8.** +2 **9.** 0.205 A **10.** +4 **11.** 14.18 min
12. 2.014 g **13.** 2.53 A, 0.47 cm
14. (a) 2 A × 60 min × 60 min/s = 7200C
(b) (7200/2) × (1/96500) = 0.0373 moles
(c) 0.0373 × 63.5 = 2.35 g
(d) 0.337 V × 2 A = 0.67 W
15. 60.44 kg **16.** 5.47 g
17. Recharging a battery simply refers to using an external source of electrical energy to force the half-reactions at each electrode to go in the reverse, nonspontaneous direction. This results in the regeneration of the energetic reactants at each electrode so that the spontaneous redox reaction can again take place. For the NiCad battery, recharging the battery forces the following half-reactions to occur :

$$Cd(OH)_2(s) + 2e^- \longrightarrow Cd(s) + 2OH^-(aq)$$

$$Ni(OH)_2(s) + OH^-(aq) \longrightarrow NiO(OH)(s) + H_2O(l) + e^-$$

18. 52 g **19.** (a) 72/965, (b) 0.42
20. 1.18 M **21.** 20.96 **22.** 143 kA **23.** 282.71 L
24. (a) 9.63 g (b) 9.326×10^{-3} equivalent of H_2SO_4
25. 4.7625 g $CuSO_4$, 0.804 A **26.** 643.33 A, 190.5 g Cu
27. 12.82 **28.** 71.34 hrs **29.** 14.26 hrs **30.** 246.5 hrs
31. 1.4 A **32.** 105.66 A, hr, 2.01 V, -3.88×10^5 J
33. 133.52 kC, 1.65 hrs **34.** 16 min **35.** 0.313 L, 1.32 g
36. O_2 = 522 mL, H_2 = 932 mL **37.** 11% **38.** 60.65 g, 1.8 hrs
39. 353 hrs **40.** 0.41 M **41.** I = 4.487 A and *M* = 0.15 M
42. 0.94 V
43. (b) 1.54 V (c) 1.4×10^{78} (d) 1.618 V (e) 2.42 g
44. (a) $E^\circ_{cell} = -1.05$ V (b) $2Ag + Ni^{2+} \longrightarrow 2Ag^+ + Ni$ (c) $K = 3 \times 10^{-36}$ (d) 202.65 kJ
45. (b) 1.04×10^{-9} M (c) 1.04×10^{-19} **46.** 1.07 V
47. 9.6×10^{-14} **48.** 1.63×10^{37} **49.** 1.12×10^{26} mol^2 dm^{-6}
50. 0.521 V **51.** −24.1 kJ//mol **52.** 0.4625 M
53. −0.24 V **54.** 0.059 V **56.** −0.037 V **57.** 1.125 mol
58. 1.696 V **59.** 0.0348 V **60.** pH = 4.23 **61.** 4.68
62. −0.15 V **63.** 0.58 V, 0.48 V **64.** 1.05 V **65.** 0.42
66. 3.5 J **67.** 0.294 **68.** $[Fe^{2+}]/[Fe^{3+}] = 2.7 \times 10^{12}$
69. 0.23 V **70.** 0.306 M **71.** −0.65 V **72.** pH = 3.67
73. (a) 0.274 V (b) −0.835 V

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Concept Building Numerical Problems (*Advanced Level*)

75. (a) 1.508 V, (b) MnO_4^{2-} (c) 0.566 V 76. −1.468 V
77. 1.51, 1.32, 1.132 and 0.943 78. 9.7×10^{15}, Impossible
79. $\Delta G^\circ = -66.585$ kJ, $\Delta S^\circ = 289.5\ JK^{-1}$, $\Delta H^\circ = 20.265$ kJ
80. 5.73×10^{-38} 81. 0.156 V 82. 2.7, −0.006
83. (a) 0.055 A (b) 53.2 kJ 84. 0.5549 V
85. 0.934 V 86. 0.105 V 87. 1.16×10^{-8}
88. 3.26×10^{-4} 89. (a) 3.14 V (b) 3.128 V
90. (a) (i) emf decreases (ii) emf increases (b) $K_f = 5.94 \times 10^{13}$
91. 0.59 V
92. $\Delta G^\circ = -68036$ J, $\Delta G^\circ = -31.266\ JK^{-1}$ and $\Delta H^\circ = -77.35$ kJ
93. (a) 1.468 V (b) 1.384 V (c) $\Delta G^\circ = -1416.62$ kJ, −780.5 kJ (d) $\Delta G^\circ = -83.955$ kJ
94. 19.95 A 95. 4.1×10^{-8} 96. pH = 7.11 97. 0.0102 V
98. 0.722 V 99. $[Cu^{2+}] = 0.963$ M, $[Zn^{2+}] = 1.037$ M
100. $[ClO_2^-] = 0.04$ M, $[ClO_3^-] = 0.92$ M
101. $\Delta H^\circ = -334.85$ kJ, $\Delta S^\circ = -241.85\ JK^{-1}$ 102. 418.36 kJ
103. $\Delta G^\circ = 57.9$ kJ, $\Delta S^\circ = 32.62\ JK^{-1}$, and $\Delta H^\circ = 67.62$ kJ
104. $\Delta H^\circ = -7195$ kJ, $\Delta S^\circ = -24.12$ kJ/mol
105. 5.55×10^{-2} M 106. 22.4 atm 107. 1.46×10^{-10}
108. $K_a = 3.9 \times 10^{-4}$
109. E° with nitric acid = −0.225 V (non-spontaneous) E° with aqua-regia = 0.237 V (spontaneous)
110. 0.73 ppm 111. 2.5×10^{-13} M
112. (a) −0.620 V (b) −0.431 V
113. (a) 3.14 V. (b) E_{Cell} would decrease since $Cr_2O_7^{2-}$ is a reactant. (c) No effect would be observed
114. E_{Cell} would decrease since Fe/Fe^{2+} has a more positive standard reduction potential than Zn/Zn^{2+}. In other words, Fe is a weaker reducing agent than Zn.
115. 0.15 A 116. 14.60 S cm^2 mol^{-1} 117. 199.43×10^3 L
118. (a) 0.774 cm^{-1} (b) 5.45×10^4 S cm^{-1} (c) 181.67 cm^2 mol^{-1}
119. 6.48×10^{-4} 120. 1.43×10^{-2}
121. 1.6×10^{-2} gL^{-1}, 3×10^{-11} M^3 122. 139 S cm^2 mol^{-1}
123. 1.7×10^{-10} M^2
124. (a) 1.21×10^{-4} S cm^{-1} (b) 0.199 cm^{-1} (c) 420 S cm^2 mol^{-1}
125. 240 S cm^2 mol^{-1}
126. (a) 859 S cm^2 mol^{-1} (b) 307 S cm^2 mol^{-1} (c) 279 S cm^2 mol^{-1}
127. $\alpha = 0.1$, $K_a = 1.11 \times 10^{-5}$ 128. $K_w = 10^{-14}$
129. (a) 2.595×10^{-4} S cm^{-1} (b) $K_{sp} = 4.03 \times 10^{-6}$

Multiple Choice Questions (*Base Level*)

1. (d)	2. (d)	3. (b)	4. (a)	5. (b)	6. (b)	7. (d)	8. (a)	9. (c)	10. (c)
11. (d)	12. (d)	13. (d)	14. (d)	15. (d)	16. (d)	17. (d)	18. (b)	19. (c)	20. (b)
21. (c)	22. (b)	23. (a)	24. (d)	25. (a)	26. (b)	27. (a)	28. (d)	29. (a)	30. (c)
31. (a)	32. (d)	33. (c)	34. (d)	35. (c)	36. (a)	37. (c)	38. (d)	39. (d)	40. (d)
41. (c)	42. (a)	43. (c)	44. (a)	45. (b)	46. (b)	47. (d)	48. (b)	49. (a)	50. (c)
51. (b)	52. (d)	53. (c)	54. (c)	55. (b)	56. (d)	57. (c)	58. (a)	59. (b)	60. (d)
61. (d)	62. (c)	63. (b)	64. (b)	65. (c)	66. (b)	67. (a)	68. (b)	69. (d)	70. (a)
71. (d)	72. (a)	73. (a)	74. (b)	75. (d)	76. (c)	77. (c)	78. (b)	79. (b)	80. (b)
81. (c)	82. (d)	83. (b)	84. (d)	85. (c)	86. (a)	87. (c)	88. (b)	89. (a)	90. (c)
91. (d)	92. (c)	93. (b)	94. (b)	95. (d)	96. (c)	97. (a)	98. (c)	99. (a)	100. (b)
101. (b)	102. (a)	103. (d)	104. (b)	105. (a)	106. (b)	107. (a)	108. (d)	109. (d)	110. (c)
111. (c)	112. (c)	113. (b)	114. (b)	115. (d)	116. (b)	117. (d)	118. (b)	119. (d)	120. (a)
121. (b)	122. (d)	123. (d)	124. (b)	125. (c)	126. (c)	127. (b)	128. (c)	129. (d)	130. (c)
131. (c)	132. (a)	133. (c)	134. (b)	135. (b)	136. (a)	137. (d)	138. (c)	139. (c)	
140. (b)	141. (b)	142. (c)	143. (c)	144. (b)	145. (c)	146. (a)	147. (b)	148. (d)	149. (c)
150. (d)	151. (b)	152. (c)	153. (b)	154. (a)	155. (d)				

Multiple Choice Questions (*Advanced Level*)

1. (d)	2. (c)	3. (c)	4. (b)	5. (a)	6. (b)	7. (c)	8. (b)	9. (b)	10. (a,b,c)
11. (b,c)	12. (b,d)	13. (a,b,d)	14. (b,c)	15. (b,c)	16. (a,b,c)	17. (a,c)	18. (a,d)	19. (a,b,d)	20. (a,b)
21. (a,d)	22. (a,c)	23. (a,b)	24. (b)	25. (a,b)	26. (d)	27. (a,b,c)	28. (a,d)	29. (a,b)	30. (a,b,c)
31. (a,c)	32. (b,c,d)	33. (a,c)	34. (b,c)	35. (b,d)	36. (a,c)	37. (b,c)	38. (c)	39. (a)	40. (a)
41. (d)	42. (a)	43. (a)	44. (a)	45. (d)	46. (d)	47. (c)	48. (a)	49. (a)	50. (a)
51. (c)	52. (d)	53. (c)	54. (c)	55. (a)	56. (a)	57. (d)	58. (d)	59. (a)	60. (d)
61. (c)	62. (b)	63. (c)	64. (b)	65. (c)	66. (b)	67. (c)	68. (c)	69. (d)	70. (d)
71. (b)	72. (a)	73. (d)	74. (d)	75. (b)	76. (c)	77. (d)	78. (b)	79. (c)	80. (b)
81. (b)	82. (b)	83. (d)	84. (c)	85. (c)	86. (d)	87. (a)	88. (d)	89. (b)	90. (c)
91. (c)	92. (d)	93. (b)	94. (a)	95. (c)	96. (a)	97. (b)	98. (d)	99. (b)	100. (d)
101. (a)	102. (b)	103. (c)	104. (c)						
105. 2	106. 8	107. 9	108. 5	109. 8	110. 7	111. 3	112. 7		

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Hints & Solutions

Concept Building Numerical Problems (*Base Level*)

1. $Q = i \cdot t = 18 \times 60 \times 60\,C = 64800\,C$

$\because$ 96500 C (1.0 Faraday) of electricity is possessed by 1.0 mol of electrons.

$\Rightarrow$ Moles of electrons passed through

$$= \frac{64800}{96500} = 0.6715 \text{ mol}$$

2. $I = \frac{Q}{t} = \frac{96500}{24 \times 60 \times 60} = 1.12\text{ A}$

3. No. of gram equivalents of Cu to be deposited

$$= \frac{5.12}{63.5} \times 2 = 0.161$$

$\because$ 1.0 mol of electrons deposits 1.0 g equivalent of electrolyte.

$\therefore$ Moles of electrons required = 0.161

4. No. of faraday passed $= \frac{96.5 \times 10^3}{96500} = 1.0$

$\Rightarrow$ No. of gram equivalent of Ag deposited = 1.0

$\Rightarrow$ Mass of Ag deposited = $1.0 \times 108 = 108$ g

5. (a) No. of faradays passed $= \frac{150 \times 10^{-3} \times 8 \times 60 \times 60}{96500}$

$$= 4.476 \times 10^{-2}$$

At NTP, 1.0 g equivalent of $F_2(g) = 11.2$ L

$\Rightarrow$ Volume of $F_2(g)$ produced $= 4.476 \times 10^{-2} \times 11.2$

$$= 0.5013 \text{ L}$$

(b) At NTP, 1.0 g equivalent of $O_2(g) = 5.60$ L

$\Rightarrow$ Volume of $O_2(g)$ produced $= 4.476 \times 10^{-2} \times 5.60$

$$= 0.2506 \text{ L}$$

6. (a) Gram equivalents of Cr $= \frac{4 \times 6}{52} = 0.461$

Quantity of electricity required $= 0.461 \times 96500$

$$= 44486.5\text{C}$$

$\Rightarrow$ $I = \frac{Q}{t} = \frac{44486.5}{24 \times 3600} = 0.515$ A

(b) Gram equivalents of Na $= \frac{4}{23}$

$\Rightarrow$ $Q = \frac{4 \times 96500}{23}$

$\Rightarrow$ $I = \frac{Q}{t} = \frac{4 \times 96500}{23 \times 24 \times 3600} = 0.194$ A

7. No. of faradays passed $= \frac{120 \times 10^{-3} \times 500}{96500}$

$\Rightarrow$ Equivalent weight $= \frac{\text{Weight of element}}{\text{No. of F passed}}$

$$= \frac{15 \times 10^{-3} \times 96500}{120 \times 10^{-3} \times 500} = 24.125$$

$\Rightarrow$ Valency $= \frac{\text{Molar mass}}{\text{Equivalent weight}}$

$$= \frac{48}{24.125} = 2$$

8. As in the previous problem,

Equivalent weight of mercury $= \frac{0.26 \times 96500}{210 \times 10^{-3} \times 1200} = 99.56$

$\Rightarrow$ Valency $= \frac{\text{Molar mass}}{\text{Equivalent weight}} = \frac{200}{99.56} = +2$

9. Partial pressure of $O_2(g) = 722 - 19.83 = 702.17$ torr.

$\Rightarrow$ Mol of $O_2(g) = \frac{pV}{RT} = \frac{702.17}{760} \times \frac{25 \times 10^{-3}}{0.082 \times 295} = 9.55 \times 10^{-4}$

$\Rightarrow$ Gram equivalents of $O_2(g) = 9.55 \times 10^{-4} \times 4 = 3.82 \times 10^{-3}$

$\Rightarrow$ $I = \frac{Q}{t} = \frac{3.82 \times 10^{-3} \times 96500}{30 \times 60} = 0.205$ A

10. Equivalent weight $= \frac{50 \times 96500}{15 \times 2 \times 60 \times 60} = 44.67$

$\Rightarrow$ Valency $= \frac{\text{Molar mass}}{\text{Equivalent weight}} = \frac{178.5}{44.67} = 4$

11. Volume of Ag required $= 5 \times 1 \times 0.1 \times 2 = 1.00\text{ cm}^3$

Mass of Ag required $= \frac{1}{10.5} = 0.0952$ g

Gram-equivalent of Ag $= \frac{0.0952}{108}$

$\Rightarrow$ $t = \frac{Q}{I} = \frac{0.0952 \times 96500}{108 \times 0.10 \times 60} = 14.18$ min.

12. No. of F passed $= \frac{0.50 \times 60 \times 60}{96500} = \frac{18}{965}$

Mass of Ag plated $= \frac{18}{965} \times 108 = 2.014$ g

13. No. of F required $= \frac{15 \times 2}{63.5}$

$\Rightarrow$ $I = \frac{Q}{t} = \frac{3 \times 96500}{63.5 \times 30 \times 60} = 2.53$ A

Also volume of plating $= 2\pi r^2 h = \frac{1.5}{10.6}\text{ cm}^3$

$$r^2 = \frac{1.5}{10.6 \times 2 \times 3.14 \times 0.1} = 0.22\text{ cm}^2$$

$\Rightarrow$ $r = 0.47$ cm

14. (a) $2\text{ A} \times 60 \times 60 = 7200$ C (b) $\frac{7200}{2} \times \frac{1}{96500} = 0.0373$ mole

(c) $0.0373 \times 63.5 = 2.35$ g (d) $0.337 \times 2 = 0.674$ W.

15. The balanced reaction for reduction of acrylonitrile is

$$2CH_2{=}CH{-}CN + 2H^+ + 2e^- \longrightarrow NC{-}(CH_2)_4{-}CN$$

No. of faraday passed $= \frac{3 \times 10^3 \times 10 \times 3600}{96500} = 1119.17$

$\because$ 2.0 F of electricity produces 1.0 mol adiponitrile

16. $Q = It = 2 \times 60 \times 60 \times 2.5\text{C} = \frac{5 \times 3600}{96500}$ F

$\Rightarrow$ mass of Ni deposited $= \frac{5 \times 36}{965} \times \frac{58.69}{2} = 5.47$ g

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18. Equivalent weight of metal $= \dfrac{\text{Weight}}{\text{No. of equivalents}}$

$= \dfrac{3.00 \times 96500}{0.7 \times 6.63 \times 60 \times 60} = 17.32$

$\Rightarrow$ Molar mass = Equivalent weight × Valency

$= 17.32 \times 3$

$= 51.96 \approx 52$ g.

19. (a) Number of Faradays passed $= \dfrac{4 \times 30 \times 60}{96500} = \dfrac{72}{965}$

= moles of H^+ produced

(b) $pH = -\log\left(\dfrac{72}{965} \times 5\right) = 0.42$

20. No. of Faraday passed $= \dfrac{2 \times 11 \times 60 \times 60}{96500} = 0.82$

$\Rightarrow$ No. of gram equivalent of Ni^{2+} deposited = 0.82

$\Rightarrow$ moles of Ni^{2+} deposited $= \dfrac{0.82}{2} = 0.41$

moles of Ni^{2+} present in solution at the end of electrolysis

$= 1 - 0.41 = 0.59$

$\Rightarrow \quad [Ni^{2+}] = \dfrac{0.59}{0.5} = 1.18$ M.

21. Strength of current $(I) = \dfrac{100\ Js^{-1}}{100\ V} = 1\ Cs^{-1} = 1.0$ A

$\Rightarrow$ No. of Faraday passed $= \dfrac{1.0 \times 10 \times 60 \times 60}{96500} = \dfrac{360}{965}$

$\Rightarrow$ Mass of Cd deposited $= \dfrac{360}{965} \times \dfrac{112.4}{2} = 20.96$ g

22. Gram equivalents of Mg required to be produced

$= \dfrac{48000}{12} = 4000$

$\Rightarrow$ Theoretical requirement of electricity = 4000 × 96500 C

$\Rightarrow$ Actual electricity requirement $= 4000 \times 96500 \times \dfrac{100}{75}$ C

$\Rightarrow \quad I = \dfrac{Q}{t} = \dfrac{4}{3} \times \dfrac{4000 \times 96500}{3600} = 142.963 \times 10^3$ A

$\simeq 143$ kA

23. Number of F passed $= \dfrac{25 \times 24 \times 60 \times 60}{96500} = 22.38$

$\Rightarrow$ Moles of $H_2(g)$ produced = 11.19

$\Rightarrow$ Volume of $H_2(g) = \dfrac{nRT}{p} = \dfrac{11.9 \times 0.082 \times 300 \times 760}{740}$

$= 282.71$ L

24. (a) No. of F passed $= \dfrac{10 \times 1.5 \times 60}{96500} = 9.326 \times 10^{-3}$

$\Rightarrow$ Weight of Cu^{2+} discharged $= 9.326 \times 10^{-3} \times \dfrac{63.5}{2}$

$= 0.296$ g

$\Rightarrow$ Weight of $O_2(g)$ produced at anode $= 9.326 \times 10^{-3} \times 8$

$= 0.0746$ g

$\Rightarrow$ Weight of solution left-behind $= 10 - (0.296 + 0.0746)$

$= 9.6294$ g

(b) No. of g equivalent of H_2SO_4 produced $= 9.326 \times 10^{-3}$

25. Gram equivalent of Au $= \dfrac{9.85 \times 3}{197}$ = g eq of Cu

$\Rightarrow$ Weight of Cu deposited $= \dfrac{9.85 \times 3}{197} \times \dfrac{63.5}{2} = 4.7625$ g

Also, $\quad I = \dfrac{Q}{t} = \dfrac{9.85 \times 3 \times 96500}{197 \times 5 \times 60 \times 60}$

$= 0.804$ A

26. No. of g equivalents of H_2 oxidized $= \dfrac{67.2}{11.2} = 6$

$I = \dfrac{Q}{t} = \dfrac{6 \times 96500}{15 \times 60} = 643.33$ A

Weight of Cu deposited $= 6 \times \dfrac{63.5}{2} = 190.5$ g

27. No. of F passed $= \dfrac{0.195 \times 60 \times 60}{96500} = 7.27 \times 10^{-3}$

$\Rightarrow$ $[OH^-]$ in solution $= 7.27 \times 10^{-2} \times 0.9$

$\Rightarrow$ pOH = 1.18 $\Rightarrow$ pH = 12.82

28. Here, Sn^{2+} is oxidised as well as reduced.

geq of Sn^{2+} reduced to Sn $= \dfrac{0.119}{119} \times 2 = 0.002$

geq of Sn^{2+} oxidised to Sn^{4+} = 0.002

$\Rightarrow$ Total loss of Sn^{2+} = 0.002 × 2 = 0.004 equivalent

= 0.002 mole

$\Rightarrow$ $SnCl_2$ left behind = 19 − 0.002 × 190 = 18.62 g

$SnCl_4$ produced = 0.001 mol = 0.001 × 261 = 0.261 g

$\Rightarrow \quad \dfrac{\text{Weight of } SnCl_2}{\text{Weight of } SnCl_4} = \dfrac{18.62}{0.261} = 71.34$

29. $C_6H_5OH + Br_2 \longrightarrow C_6H_4Br(OH) + HBr$

Moles of Br_2 required $= \dfrac{500 \times 1000}{94} = 5319.15$

$\Rightarrow$ g equivalent of Br_2 = 5319.15 × 2

$\Rightarrow \quad t = \dfrac{Q}{I} = \dfrac{5319.15 \times 2 \times 96500}{20000} = 51329.8$ s

$= 14.26$ hr

30. 4.0 g $MnO_2 = \dfrac{4}{87}$ mol = no. of moles of electron transfer taking place.

$\Rightarrow \quad t = \dfrac{Q}{I} = \dfrac{4 \times 96500}{87 \times 0.005} \times \dfrac{1}{3600}$ hr = 246.5 hr

31. pH = 12.24 $\Rightarrow$ pOH = 1.76

$\Rightarrow \quad [OH^-] = 1.738 \times 10^{-2}$ M

$\Rightarrow$ g equivalent of OH^- produced $= 1.738 \times 10^{-2} \times 0.3$

$= 5.2 \times 10^{-3}$

$\Rightarrow \quad I = \dfrac{Q}{t} = \dfrac{5.2 \times 10^{-3} \times 96500}{6 \times 60} = 1.4$ A

32. Equivalent of available Pb $= \dfrac{406}{103} = 3.94$

$\Rightarrow$ No. of ampere-hour (maximum) $= \dfrac{3.94 \times 96500}{3600} = 105.66$

$E° = 1.7 + 0.31 = 2.01$ V

$\Delta G° = -nE°F = -2 \times 2.01 \times 96500$

$= -388$ kJ

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33. Initial mass of $H_2SO_4 = 750 \times 1.29 \times 0.38 = 367.65\,g$

Final mass of $H_2SO_4 = 750 \times 1.19 \times 0.26 = 235.05\,g$

$\Rightarrow$ H_2SO_4 consumed during uses of battery = 135.60 g

$\because$ 1.0 mol of electron are transferred per mol of H_2SO_4 consumed.

$$\therefore \quad Q = \frac{135.60}{98} \times 96500 = 133.52 \text{ kC.}$$

$$\text{Time required for recharging} = \frac{133.52 \times 10^3}{22.4} = 5961 \text{ s}$$
$$= 1.65 \text{ hrs}$$

34. Volume of Cr = 0.01×10^4 cm^3 = 100 cm^3.

$$\text{Mass of Cr} = \frac{100}{5.8} = 17.24 \text{ g}$$

$$\text{g equivalents of Cr} = \frac{17.24 \times 3}{52} = 1.0$$

$$\Rightarrow \quad t = \frac{Q}{I} = \frac{96500}{100} = 965 \text{ s} = 16 \text{ min}$$

35. $$\text{No. of F passed} = \frac{0.75 \times 3600}{96500} = \frac{75 \times 36}{96500}$$

$$\text{Volume of } H_2 \text{ at NTP} = \frac{75 \times 36 \times 11.2}{96500} = 0.313 \text{ L}$$

$$\text{Mass of NiO produced} = \frac{76 \times 36}{96500} \times \frac{93}{2} = 1.32 \text{ g}$$

36. $$\text{No. of F passed} = \frac{2.5 \times 3600}{96500} = \frac{90}{965} = 0.0932$$

Initially Ag^+ will be reduced at cathode.

No. of F consumed for Ag^+ = 0.01

$\Rightarrow$ No. of F consumed for producing

$H_2(g) = 0.0932 - 0.01 = 0.0832$

$\Rightarrow$ Volume of H_2 produced = $0.0832 \times 11200 = 932$ mL.

Since O_2 is produced from beginning;

Volume of $O_2 = 0.0932 \times 5600$
$= 522$ mL

37. $$\text{Equivalent of Cu} = \frac{0.30}{63.5} \times 2 = 9.45 \times 10^{-3}$$

$$\Rightarrow \quad I = \frac{Q}{t} = \frac{9.45 \times 10^{-3} \times 96500}{30 \times 60} = 0.506 \text{ A}$$

$$\text{\% error in current} = \frac{0.506 - 0.45}{0.506} \times 100 = 11\%$$

38. Redox reaction occurring in lead storage battery :

$$Pb(s) + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

$$\text{Moles of } PbO_2 \text{ reduced} = \frac{23.92}{239.2} = 0.10$$

$\Rightarrow$ Mass of $PbSO_4$ formed = $0.20 \times 303.2 = 60.64$ g.

g equivalent of PbO_2 reduced = $0.10 \times 2 = 0.20$

$$\Rightarrow \quad t = \frac{0.2 \times 96500}{3 \times 60 \times 60} \text{ hr} = 1.78 \text{ hr}$$

39. $$\text{Moles of } H_2(g) \text{ required} = \frac{1500}{M(\text{air}) - M(H_2)}$$
$$= \frac{1500}{28.8 - 2} = 55.97$$

No. of F required = 55.97×2

$$\Rightarrow \quad t = \frac{Q}{I} = \frac{55.97 \times 2 \times 96500}{8.5 \times 3600} = 353 \text{ hr}$$

40. $Q = It = 1.25 \times 1.1 \times 3600 = 4950$ C

Cathode reaction is : $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$$\Rightarrow \quad \text{Moles of } Fe^{2+} \text{ produced} = \frac{4950}{96500} = \frac{495}{9650}$$

$$\Rightarrow \quad \frac{495}{9650} = \text{Normality} \times 0.025$$

$$\Rightarrow \quad N = 2.05 \Rightarrow \text{Molarity} = \frac{2.05}{5} = 0.41 \text{ M}$$

41. Equivalent of $Na_2S_2O_3 = 37.2 \times 0.225 \times 10^{-3}$
= Equivalent of I_2

$$\Rightarrow \quad I = \frac{Q}{t} = \frac{37.2 \times 0.225 \times 10^{-3} \times 96500}{3 \times 60} = 4.487 \text{ A.}$$

Equivalent of $KMnO_4 = 36.3 \times 0.1 \times 10^{-3} = 3.63 \times 10^{-3}$

$\Rightarrow$ Total equivalent of KI present initially = 12×10^{-3}

$$\Rightarrow \quad KI = \frac{12 \times 10^{-3}}{0.08} = 0.15 \text{ M}$$

42. At anode : $Sn \longrightarrow Sn^{2+} + 2e^-$; $E° = 0.14$ V

At cathode : $2Ag^+ + 2e^- \longrightarrow 2Ag$; $E° = 0.80$ V

Net cell reaction : $Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$;

$E°_{cell} = 0.94$ V

43. (a) $Cr + 3Ag^+ \longrightarrow Cr^{3+} + 3Ag$

(b) $E° = E°_{cathode} - E°_{anode} = 0.80 - (-0.74) = +1.54$ V

(c) $$RT \ln K = nE°F \Rightarrow \ln K = \frac{3 \times 1.54 \times 96500}{8.314 \times 298}$$

$$\Rightarrow \quad K = 1.4 \times 10^{78}$$

(d) $$E = E° - \frac{0.059}{n} \log \frac{[Cr^{3+}]}{[Ag^+]^3} = 1.54 - \frac{0.059}{3} \log \frac{10^{-4}}{1.0}$$
$$= 1.618 \text{ V}$$

(e) $$\text{No. of faradays passed} = \frac{0.3 \times 2 \times 3600}{96500} = 2.238 \times 10^{-2}$$

$\Rightarrow$ Weight of Ag deposited = $2.238 \times 10^{-2} \times 108 = 2.42$ g

44. (a) $E°_{cell} = -0.25 - 0.80 = -1.05$ V

(b) $2Ag + Ni^{2+} \longrightarrow 2Ag^+ + Ni$

(c) $$RT \ln K = nE°F \Rightarrow \ln K = \frac{2 \times (-1.05) \times 96500}{8.314 \times 298}$$

$$K = 3 \times 10^{-36}$$

(d) $\Delta G° = -nE°F = -2(1.05) \times 96500 = 202.65$ kJ

45. (a) At anode : $Cu + 2OH^- \longrightarrow Cu(OH)_2 + 2e^-$

At cathode : $Cu^{2+} + 2e^- \xrightarrow{\Delta} Cu$

Net : $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$

(b) $$E = 0.265 = -\frac{0.059}{2} \log \frac{[Cu^{2+}]_2}{[Cu^{2+}]_R} = -\frac{0.059}{2} \log \frac{[Cu^{2+}]_2}{1.0}$$

$$\Rightarrow \quad [Cu^{2+}]_2 = 1.04 \times 10^{-9} \text{ M}$$

(c) $K_{sp} = [Cu^{2+}][OH^-]^2 = 1.04 \times 10^{-9} \times 10^{-10} = 1.04 \times 10^{-19}$

46. $\Delta E°_{cell} = E°_{cathode} - E°_{anode}$

$\Rightarrow$ $E°_{anode} = 1.36 - 0.29 = 1.07$ V

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$$0.65 = -\frac{0.059}{1}\log\frac{[Ag^+]_{anode}}{0.10}$$

$$[Ag^+]_{anode} = 9.6 \times 10^{-13}$$

$\Rightarrow$ $K_{sp} = [Ag^+][Br^-] = 9.6 \times 10^{-13} \times 0.10 = 9.6 \times 10^{-14}$

$\Delta G^\circ = -nF^\circ E = -RT \ln K$

$\Rightarrow$ $$\ln K = \frac{nE^\circ F}{RT} = \frac{2 \times 1.1 \times 96500}{8.314 \times 298} = 85.68$$

$$K = 1.63 \times 10^{37}$$

$\Rightarrow$ As in case of 48, $\ln K = \dfrac{2 \times 0.77 \times 96500}{8.314 \times 298} = 59.98$

$\Rightarrow$ $$K = 1.12 \times 10^{26}$$

	E°	$\Delta G^\circ = -nE^\circ F$
$Cu^+ \longrightarrow Cu^{2+} + e^-$	−0.153	0.153 F
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.337	−0.674 F
Adding : $Cu^+ + e^- \longrightarrow Cu$		$\Delta G^\circ = -0.521\ F = -E^\circ F$

$\Rightarrow$ $$E^\circ = 0.521\ V$$

$E^\circ_{cell} = 0.25$

$\Rightarrow$ $\Delta G^\circ = -E^\circ F = -0.25 \times 96500\ J = -24.125\ kJ$

Half-cell reactions can be manipulated as :

$$I_2 + 2e^- \longrightarrow 2I^-; \quad E^\circ = 0.5355\ V$$

$$3I^- \longrightarrow I_3^- + 2e^-; \quad E^\circ = -0.5365\ V$$

Adding : $$I_2 + I^- \rightleftharpoons I_3^-; \quad E^\circ = -0.001\ V$$

$\Rightarrow$ $$\ln K = \frac{-0.001 \times 2 \times 96500}{8.314 \times 298} \Rightarrow K = 0.925$$

Also; $K = \dfrac{[I_3^-]}{0.5} \Rightarrow [I_3^-] = 0.925 \times 0.5 = 0.4625\ M$

$E^\circ = -0.4$ V for the cell :

$$H_2 + CrSO_4 \rightleftharpoons Cr + SO_4^{2-} + 2H^+$$

$$E = -0.4 - \frac{0.059}{2}\log\frac{[H^+]^2[SO_4^{2-}]}{1}$$

$$= -0.4 - \frac{0.059}{2}\log(0.02)^2(0.01) = -0.24\ V$$

At anode : $Ag + Cl^-(0.1\ M) \rightleftharpoons AgCl + e^-$

At cathode : $AgCl + e^- \rightleftharpoons Ag + Cl^-(0.01\ M)$

Net : $Cl^-(0.1\ M) \rightleftharpoons Cl^-(0.01\ M)$; $E^\circ = 0$

$$E = \frac{-0.059}{1}\log\frac{0.01}{0.10} = 0.059\ V$$

$$[Ag^+]_{anode} = \frac{2.8 \times 10^{-10}}{0.2} = 1.4 \times 10^{-9}\ M$$

$$[Ag^+]_{cathode} = \frac{3.3 \times 10^{-13}}{10^{-3}} = 3.3 \times 10^{-10}\ M$$

$$E = 0 - \frac{0.059}{1}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$= -0.059\log\frac{1.4 \times 10^{-9}}{3.3 \times 10^{-10}} = -0.037\ V$$

57. Since both the given half-cells are in standard-state condition,

$$Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni$$

$$E^\circ = -0.24 - (-0.76) = 0.52\ V$$

$\Rightarrow$ $$\ln K = \frac{nE^\circ F}{RT} = \frac{2 \times 0.52 \times 96500}{8.314 \times 303} = 39.83$$

$\Rightarrow$ $$K = 2 \times 10^{17}.$$

Such a large value of K indicate that almost all Ni^{2+} would be reduced.

$\Rightarrow$ Moles of Zn consumed $= 1.5 \times 0.75 = 1.125$ mol.

62. For the reaction

$$AgI \rightleftharpoons Ag^+ + I^-$$

$$\ln K_{sp} = \frac{nE^\circ F}{RT}$$

$\Rightarrow$ $$E^\circ = \frac{RT \ln K_{sp}}{nF} = -0.95\ V$$

The above reaction is combination of :

$$Ag \rightleftharpoons Ag^+ + e^- \quad E^\circ = -0.80\ V$$

$$AgI + e^- \rightleftharpoons Ag + I^- \quad E^\circ = ?$$

Adding : $$AgI + e^- \rightleftharpoons Ag^+ + I^-$$

$$E^\circ = -0.95 = -0.80 + E^\circ(AgI/Ag, I^-)$$

$\Rightarrow$ $$E^\circ(AgIAg, I^-) = -0.15\ V$$

65. For galvanic cell E_{cell} must be positive.

$\Rightarrow$ $$Pt, H_2 \mid H^+(?) \mid\mid H^+(1\ M) \mid H_2, Pt$$

$$E = 0.025 = -0.059\log\frac{[H^+]}{1} = 0.059\ pH$$

$\Rightarrow$ $$pH = 0.42$$

68. For the cell $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$E = 0.035\ V = 0.77 - \frac{0.059}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$\Rightarrow$ $$\frac{[Fe^{2+}]}{[Fe^{3+}]} = 2.7 \times 10^{12}$$

70. The balanced redox reaction is

$$Ag^+ + Fe^{2+} \rightleftharpoons Ag + Fe^{3+}$$

$$E^\circ = 0.80 - 0.78 = 0.02\ V$$

$$\ln K = \frac{nE^\circ F}{RT} = \frac{0.02 \times 96500}{8.314 \times 298}$$

$$= 0.7789 \approx 0.78$$

$\Rightarrow$ $K = 2.18$ Also, initial concentrations are 0.5 M each Ag^+ and Fe^{2+} ions.

Now, $$\underset{0.5-x}{Ag^+} + \underset{0.5-x}{Fe^{2+}} \rightleftharpoons Ag + \underset{x}{Fe^{3+}}$$

$$2.18 = \frac{x}{(0.5-x)^2}$$

or $$2.18x^2 - 3.18x + 0.545 = 0$$

Solving $x = 0.194$ M

$\Rightarrow$ $$Fe^{2+}(eqbm) = 0.5 - 0.194 = 0.306\ M$$

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Concept Building Numerical Problems (*Advanced Level*)

74. The cell reaction for the Daniel cell is :

$$Cu^{2+} + Zn \rightleftharpoons Zn^{2+} + Cu \qquad E^\circ = 1.10\ V$$

and cell-potential is : $E = 1.10 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$

As Na_2S is added, in the beginning, Cu^{2+} decreases due to precipitation of CuS and this results in decrease of E. When a lot of Na_2S is added, the entire Cu^{2+} is precipitated and the cell reaction becomes :

$$CuS + Zn \rightleftharpoons Cu^{2+} + Zn^{2+} + S^{2-} \qquad E^\circ = 1.56\ V$$

Due to large increase in E° value, E_{cell} increases.

75.

Half-reaction	E°	ΔG°
(a) $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	0.564 V	−0.564 F
$MnO_4^{2-} + 2e^- \rightleftharpoons MnO_2$	2.26 V	−4.52 F
$MnO_2 + e^- \rightleftharpoons Mn^{3+}$	0.950 V	−0.95 F
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.51 V	−1.51 F

Adding : $MnO_4^- + 5e^- \rightleftharpoons Mn^{2+}$ $\Delta G^\circ = -7.544\ F = -5E^\circ F$

$\Rightarrow$ $E^\circ = -1.508\ V$

(b) For $MnO_4^{2-} + 4e^- \rightleftharpoons Mn^{2+}$ $E^\circ = 1.745\ V$

$\because$ $E^\circ(MnO_4^{2-}/Mn^{2+}) > E^\circ(MnO_4^-/Mn^{2+})$

$\therefore$ MnO_4^{2-} is a better oxidizing agent.

(c) $MnO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons MnO_2 + 2H_2O$

$E^\circ = 2.260\ V$ ...(i)

$MnO_2 + 2H_2O \rightleftharpoons MnO_4^- + 4H^+ + 3e^-$

$E^\circ = -1.694$ ...(ii)

Multiplying Eq. (i) by 3 and Eq. (ii) by 2 and finally adding them gives :

$$3MnO_4^{2-} + 4H^+ \rightleftharpoons MnO_2(s) + 2MnO_4^- + 2H_2O$$

$E^\circ = 0.566\ V$

77. The balanced half reaction is :

$$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$$

$$E = 1.51 - \frac{0.059}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= 1.51 - \frac{0.059 \times 8}{5}\ pH$$

At pH = 0; E = 1.51 V At pH = 4; E = 1.132 V

At pH = 2; E = 1.32 V At pH = 6; E = 0.943 V

At pH = 0; MnO_4^- will oxidize to all halides.

At pH = 2, MnO_4^- can oxidize only Br^- and I^- but not Cl^-

At pH = 4, MnO_4^- can still oxidize only to Br^- and I^- but not Cl^-.

At pH = 6, MnO_4^- can oxidize only I^- but cannot oxidize Cl^- and Br^-

Conclusion : Oxidising strength of MnO_4^- decreases on increasing pH.

79. Corresponding ΔG° values are

$$\Delta G^\circ(37°C) = -2 \times 0.36 \times 96500\ J$$
$$= -69.48\ kJ$$

$$\Delta G^\circ(37°C) = -2 \times 0.33 \times 96500 = -63.69\ kJ$$

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow$ $-69480 = \Delta H^\circ - 310\Delta S^\circ$

and $-63690 = \Delta H^\circ - 290\Delta S^\circ$ ...(i)

$\Rightarrow$ $20\Delta S^\circ = 5790$ ...(ii)

$\Rightarrow$ $\Delta S^\circ = 289.5\ JK^{-1}$

$\Rightarrow$ $\Delta H^\circ = 20.265\ kJ$

$\Rightarrow$ $\Delta G^\circ(27°C) = 20265 - 300 \times 289.5$

$= -66.586\ kJ.$

80. E° for $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$ is −0.734 V.

$$\Rightarrow \log K_{sp} = \frac{nE^\circ F}{2.303RT} = \frac{-3 \times 0.734 \times 96500}{2.303 \times 8.314 \times 298} = -37.24$$

$$K_{sp} = 5.73 \times 10^{-38}$$

81. $Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$; $E^\circ = 0.356\ V$

$2H^+ + 2e^- \rightleftharpoons H_2$; $E^\circ = 0$

Adding : $Pb + SO_4^{2-} + 2H^+ \rightleftharpoons PbSO_4 + H_2$ $E^\circ = 0.356$

Also, in anode chamber $[SO_4^{2-}] = \sqrt{K_{sp}} = 10^{-4}\ M$

$$E = E^\circ - \frac{0.059}{2}\log\frac{1}{10^{-4} \times (0.04)^2} = 0.356 - 0.20 = 0.156\ V$$

87. The balanced redox reaction is :

$$M + H^+ \rightleftharpoons M^+ + \frac{1}{2}H_2$$

$\Rightarrow$ $-0.40 = E^\circ - 0.059\log\frac{0.1}{0.2} = E^\circ + 0.0177$ ...(i)

After adding KCl, left concentration of $M^+ = x$

$\Rightarrow$ $-0.05 = E^\circ - 0.059\log\frac{x}{0.2}$ ...(ii)

Solving for x : $x = 1.16 \times 10^{-7}$

$\Rightarrow$ $K_{sp} = [M^+][Cl^-] = 1.16 \times 10^{-7} \times 0.1 = 1.16 \times 10^{-8}$

[$\because$ out of 0.2 M Cl^-, 0.1 M has gone in precipitation]

88. $E = 0.8 - 0.059\log\frac{[H^+]}{[Ag^+]}$

$\Rightarrow$ $0.987 = 0.8 - 0.059\log\frac{[H^+]}{0.80}$

$\Rightarrow$ $[H^+] = 5.4 \times 10^{-4} = C\alpha$

$\Rightarrow$ $\alpha = \frac{5.4 \times 10^{-4}}{1.4 \times 10^{-3}} = 0.38$

$\Rightarrow$ $K_a = \frac{C\alpha^2}{1-\alpha} = \frac{1.4 \times 10^{-3}(0.38)^2}{0.62} = 3.26 \times 10^{-4}.$

90. The cell reaction is : $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E = E^\circ - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

(a) $E = E^\circ = 0.34 - (-0.76) = 1.10\ V$

$\because$ $[Cu^{2+}] = [Zn^{2+}]$

(i) Emf will decrease (ii) Emf will increase

(b) After adding NH_3, let x be the molarity of Cu^{2+} in cathode chamber.

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$$E = 0.68 = 1.1 - \frac{0.059}{2}\log\frac{0.2}{x}$$

Solving : $\Rightarrow$ $x = 1.15 \times 0^{-15}$.

Such a low value of x indicate that almost all Cu^{2+} has gone into complex.

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

Initial : 0.1 1.5 0

Eqm : 1.15×10^{-15} M 1.1 M 0.1 M

$$\Rightarrow \quad K_f = \frac{0.1}{(1.1)^4(1.15 \times 10^{-15})}$$

$$= 5.94 \times 10^{13}$$

85. The balanced cell reaction is : $Pb + 2H^+ \rightleftharpoons Pb^{2+} + H_2$

$E° = 0.13$ V

$$\Rightarrow \quad 0.562 = 0.13 - \frac{0.059}{2}\log[Pb^{2+}] \quad (\because [H^+] = 1.0 \text{ M})$$

$$\Rightarrow \quad [Pb^{2+}] = 2.27 \times 10^{-15}$$

86. The spontaneous cell reaction is :

$$H_2 + Cu^{2+} \rightleftharpoons Cu + 2H^+$$

$$0.72 = 0.34 - \frac{0.059}{2}\log\frac{[H^+]^2}{1.0}$$

$$\Rightarrow \quad [H^+] = 7.6 \times 10^{-8}$$

$$\Rightarrow \quad pH = 7.11$$

87. $\because -\Delta T_f = iK_f \cdot m$; i and K_f are same in both electrode chambers.

$$\Rightarrow \quad \frac{M_1}{M_2} = \frac{0.9}{2.0} = \frac{9}{20}$$

$$\Rightarrow \quad E = 0 - \frac{0.059}{2}\log\frac{9}{20} = +0.0102 \text{ V}$$

88. Cell reaction is : $Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2$, $E° = +0.76$ V

Also $\underset{0.1-x}{HIO_3} \rightleftharpoons \underset{x}{H^+} + \underset{x}{IO_3^-}$

$$\Rightarrow \quad 0.2 = \frac{x^2}{0.1 - x}$$

or $x^2 + 0.2x - 0.02 = 0$

$$x = \frac{-0.2 + \sqrt{0.04 + 0.08}}{2} = 0.073 \text{ M}$$

$$\Rightarrow \quad E = 0.76 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[H^+]^2}$$

$$= 0.76 - \frac{0.059}{2}\log\frac{0.1}{(0.073)^2}$$

$$= 0.722 \text{ V}$$

89. No. of Faraday drawn $= \frac{60 \times 60 \times 10}{96500} = \frac{36}{965}$

$\Rightarrow$ g eq of Cu^{2+} deposited = 0.037 = g eq of Zn^{2+} produced.

$\Rightarrow$ moles of Cu^{2+} present in solution $= 0.5 - \frac{0.037}{2} = 0.4815$

$$\Rightarrow \quad [Cu^{2+}] = 0.4815 \times 2 = 0.963 \text{ M}$$

$$\Rightarrow \quad [Zn^{2+}] = (0.5 + 0.0185) \times 2 = 1.037 \text{ M}$$

90. $ClO_3^- \longrightarrow ClO_4^- + 2e^-$; $E° = -1.19$ V

$ClO_3^- + 2e^- \longrightarrow ClO_2^-$; $E° = 1.21$ V

Adding : $2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$. $E° = -0.02$ V

$$\log K = \frac{2 \times 0.02 \times 96500}{2.303 \times 8.314 \times 298} = 0.676$$

$$\Rightarrow \quad K = 4.75$$

Now, $\underset{0.1-2x}{2ClO_3^-} \rightleftharpoons \underset{x}{ClO_2^-} + \underset{x}{ClO_4^-}$

$$K = 4.75 = \frac{x^2}{(0.1 - 2x)^2}$$

$$\Rightarrow \quad 2.18 = \frac{x}{0.1 - 2x}$$

$$\Rightarrow \quad x = 0.04 \text{ M}, [ClO_3^-] = 0.92 \text{ M}$$

101. $nF\left(\frac{\partial E°}{\partial T}\right) = \Delta S° = -2 \times 96500 \times 1.25 \times 10^{-3}$

$$= -241.25 \text{ JK}^{-1}$$

Also, $\Delta G° = -nE°F = -2 \times 1.36 \times 96500$

$$= -262.48 \text{ kJ}$$

$$\Rightarrow \quad \Delta H° = \Delta G° + T\Delta S°$$

$$= -262.48 \times 10^3 - 300 \times 241.25$$

$$= -334.85 \text{ kJ}$$

103. For the reaction :

$$Ag + \frac{1}{2}Hg_2Cl_2 \longrightarrow Ag^+ + Hg + Cl^-; \quad E° = -0.60 \text{ V}$$

$$\Delta S° = nF\left(\frac{\partial E°}{\partial T}\right)$$

$$= 96500 \times 0.338 \times 10^{-3} = 32.62 \text{ JK}^{-1}$$

$$\Delta G° = -nE°F = 0.60 \times 96500 = 57.9 \text{ kJ}$$

$$\Delta H° = \Delta G° + T\Delta S° = 57.9 \times 10^3 + 298 \times 32.62$$

$$= 67.62 \text{ kJ}$$

105. For the half-cell : $Ca^{2+} + 2e^- \rightleftharpoons Ca$

$$E = E° - \frac{0.059}{2}\log\frac{1}{[Ca^{2+}]} = E° + \frac{0.059}{2}\log[Ca^{2+}]$$

Let the concentration of Ca^{2+} in first analysis be x M.

$$\Rightarrow \quad -0.053 = E° + \frac{0.059}{2}\log x \quad \text{...(i)}$$

When 1.0 mL 0.05 M Ca^{2+} is added to 50 mL it would add 10^{-3} M to x.

$$\Rightarrow \quad -0.0422 = E° + \frac{0.059}{2}\log(x + 10^{-3}) \quad \text{...(ii)}$$

Solving Eqs. (i) and (ii) gives $x = 7.55 \times 10^{-3}$

$\Rightarrow$ Original concentration of Ca^{2+} in sea water

$$= 10x = 7.55 \times 10^{-2} \text{ M}$$

108. The cell is : Pt, H_2 | HA || AgCl, Cl^- | Ag

and the cell reaction is $\frac{1}{2}H_2 + AgCl \longrightarrow H^+ + Cl^- + Ag$

$$E = E° - 0.059\log[H^+][Cl^-]$$

$$= 0.23 - 0.059\log[Cl^-] + 0.059 \text{ pH}$$

$$= 0.289 + 0.059 \text{ pH}$$

when emf is 0.47 : $0.47 = 0.289 + 0.059 \text{ pH}_1$

$$\Rightarrow \quad pH_1 = 3.067$$

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Similarly : $0.50 = 0.289 + 0.059\ pH_2$

$\Rightarrow$ $pH_2 = 3.57$

Now, let there be initially x mol HA present and 20 mL NaOH contain y mol of NaOH.

$$\Rightarrow \quad pH_1 = 3.067 = pK_a + \log \frac{y}{x-y} \quad ...(i)$$

$$pH_2 = 3.57 = pK_a + \log \frac{2.5y}{x-2.5y} \quad ...(ii)$$

Solving Eqs. (i) and (ii) gives : $x = 3.18\ y$.

Now, substituting $x = 3.18y$ in Eq. (i)

$$3.067 = pK_a + \log \frac{y}{2.18\ y} = pK_a + 0.338$$

$$\Rightarrow \quad pK_a = 3.4 \text{ and } K_a = 3.9 \times 10^{-4}.$$

111. For the cell $Zn^{2+} + 2Ag + 2Cl^- \rightleftharpoons 2AgCl + Zn$

$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{[Cl^-]^2[Zn^{2+}]}$$

$$= E^\circ - \frac{0.059}{2} \log \frac{1}{[Cl^-]^2} + \frac{0.059}{2} \log [Zn^{2+}]$$

$$= K + \frac{0.059}{2} \log [Zn^{2+}] \text{ where } K \text{ is constant.}$$

$$\Rightarrow \quad -1.116 = K + \frac{0.059}{2} \log 5 \times 10^{-6} = K - 0.156 \quad ...(i)$$

$$-1.509 = K + \frac{0.059}{2} \log [Zn^{2+}] \quad ...(ii)$$

Solving Eqs. (i) and (ii) gives $[Zn^{2+}] = 2.45 \times 10^{-19}$ M

113. (a) $E = E^\circ - \frac{0.059}{6} \log \frac{[Sc^{3+}]^2[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$

$$= 3.7 - \frac{0.059}{6} \log \frac{(0.35)^2(0.75)^2}{6.2 \times 10^{-5}(0.014)^{14}} = 3.14 \text{ V}$$

115. $\kappa = \frac{\Lambda C}{1000} = \frac{195 \times 0.05}{1000} = 9.75 \times 10^{-3}\ S\ cm^{-1}$

Also, $G = \frac{1}{R} = \kappa\left(\frac{A}{l}\right) = 9.75 \times 10^{-3}\ S\ cm^{-1} \times \frac{1.5\ cm^2}{0.50\ cm}$

$$= 29.25 \times 10^{-3}\ ohm^{-1}$$

Also, $V = IR \Rightarrow I = \frac{V}{R} = 5 \times 29.25 \times 10^{-3}$

$$= 0.146 \sim 0.15\ A$$

116. $\Lambda(KCl) = \frac{\kappa \times 1000}{C} = \frac{0.0116 \times 1000}{0.10} = 116\ S\ cm^2\ mol^{-1}$

Also, $G = \frac{1}{R} = \kappa\left(\frac{A}{l}\right)$

$$\Rightarrow \quad \frac{R_1}{R_2} = \frac{\kappa_2}{\kappa_1}$$

$$\Rightarrow \quad \kappa_2(CH_3COOH) = \kappa_1\left(\frac{R_1}{R_2}\right) = \frac{0.0116 \times 25}{1982}$$

$$= 1.46 \times 10^{-4}\ S\ cm^{-1}.$$

$$\Rightarrow \quad \Lambda(CH_3COOH) = \frac{\kappa \times 1000}{C} = \frac{1.46 \times 10^{-4} \times 1000}{0.01}$$

$$= 14.60\ S\ cm^2\ mol^{-1}.$$

117. Specific conductance of $KCl(aq) = \frac{\Lambda C}{1000} = \frac{138.3 \times 0.03}{1000}$

$$= 2.766 \times 10^{-3}\ S\ cm^{-1}.$$

Also, $G = \frac{1}{R} = \kappa\left(\frac{A}{l}\right)$

$$\Rightarrow \quad \left(\frac{l}{A}\right) = \text{Cell constant} = K.R. = 2.766 \times 10^{-3} \times 85$$

$$= 0.2351\ cm^{1}$$

$$\Rightarrow \kappa(H_2O) = \frac{\text{Cell constant}}{R(H_2O)} = \frac{0.2351}{9200} = 2.55 \times 10^{-5}\ S\ cm^{-1}$$

Now, $\kappa(\text{NaCl solution}) = \frac{0.2351}{7600} = 3.9 \times 10^{-5}\ S\ cm^{-1}$

Now, κ (NaCl alone) $= 3.09 \times 10^{-5} - 2.55 \times 10^{-5} = 5.4 \times 10^{-6}$

Also, $\Lambda(NaCl) = \frac{\kappa \times 1000}{C}$

$$\Rightarrow \quad C = \frac{5.4 \times 10^{-6} \times 1000}{126} = 4.28 \times 10^{-5}\ M$$

Moles of NaCl dissolved $= \frac{500}{58.5}$

$$\Rightarrow \text{Volume} = \frac{\text{Mole}}{\text{Molarity}} = \frac{500}{58.5 \times 4.28 \times 10^{-5}}$$

$$= 199.43 \times 10^3\ L$$

118. $\kappa(KCl) = \frac{\Lambda c}{1000} = \frac{129 \times 0.1}{1000} = 1.29 \times 10^{-2}\ S\ cm^{-1}$

Also, $G = \frac{1}{R} = \kappa\left(\frac{A}{l}\right)$

(a) $\Rightarrow$ Cell constant

$$\left(\frac{l}{A}\right) = \kappa R = 1.29 \times 10^{-2} \times 60 = 0.774\ cm^{-1}.$$

(b) $K(MgCl_2) = \frac{\text{Cell constant}}{R} = \frac{0.774}{142}$

$$= 5.45 \times 10^{-3}\ S\ cm^{-1}$$

(c) $\Lambda(MgCl_2) = \frac{\kappa \times 1000}{c} = \frac{5.45 \times 10^{-3} \times 1000}{0.03}$

$$= 181.67\ S\ cm^2\ mol^{-1}.$$

119. $\alpha = \frac{\Lambda}{\Lambda^\infty} = \frac{176}{405} = 0.43$

Also for HF : $\underset{c(1-\alpha)}{HF} \rightleftharpoons \underset{c\alpha}{H^+} + \underset{c\alpha}{F^-}$

$$K_a = \frac{c\alpha^2}{1-\alpha^2} = \frac{2 \times 10^{-3}(0.43)^2}{1-0.43} = 6.48 \times 10^{-4}.$$

120. Specific conductivity of KCl solution is

$$\kappa(KCl) = \frac{\Lambda c}{1000} = \frac{150 \times 0.01}{1000} = 1.5 \times 10^{-3}\ S\ cm^{-1}$$

Also, $\frac{R_1}{R_2} = \frac{\kappa_2}{\kappa_1}$ when cell constant are same.

$$\Rightarrow \quad \kappa(NH_4OH) = \kappa(KCl)\frac{R(KCl)}{R(NH_4OH)}$$

$$= 1.5 \times 10^{-3} \times \frac{525}{2030}$$

$$= 3.88 \times 10^{-4}\ S\ cm^{-1}.$$

$\Lambda(NH_4^+ + OH^-) = 73.4 + 198.6 = 272\ S\ cm^2\ mol^{-1}.$

Let c be the molarity of NH_4^+ or OH^- in solution:

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$$272 = \frac{3.88 \times 10^{-4} \times 1000}{c}$$

$\Rightarrow$ $c = 1.43 \times 10^{-3}$ M

$\Rightarrow$ $\underset{0.10(1-\alpha)}{NH_4OH} \rightleftharpoons \underset{0.01\,\alpha}{NH_4^+} + \underset{0.10\,\alpha}{OH^-}$

$0.10\alpha = 1.43 \times 10^{-3}$

$\Rightarrow$ $\alpha = 1.43 \times 10^{-2}$

$\Rightarrow$ 121. Specific conductance of CaF_2 alone $= 4.2 \times 10^{-5} - 2.8 \times 10^{-6}$

$= 3.92 \times 10^{-5}$ S cm^{-1}.

$\Lambda_m^\infty(CaF_2) = \Lambda_m^\infty(Ca^{2+}) + 2\Lambda^\infty(F^-)$

$= 2 \times 52 + 2 \times 48$

$= 200$ S cm^2 mol^{-1}.

Saturated solution of CaF_2 (a sparingly soluble salt) can be considered to be present at infinite dilution. Let c be the molar concentration of Ca^{2+}.

$$200 = \frac{3.92 \times 10^{-5} \times 1000}{c}$$

$\Rightarrow$ $c = 1.96 \times 10^{-4}$ M $= S$ (solubility of CaF_2)

$\Rightarrow$ Solubility in g/L $= 1.96 \times 10^{-4} \times 78$

$= 1.529 \times 10^{-2}$ g/L

Also solubility product $(K_{sp}) = 4S^3 = 4(1.96 \times 10^{-4})^3$

$= 3.01 \times 10^{-11}$ M^3.

122. Specific conductivity of $Ag_2C_2O_4$ alone

$= 3.8 \times 10^{-5} - 6.2 \times 10^{-8}$

$= 3.7938 \times 10^{-5}$ S cm^{-1}.

Also, $K_{sp} = 4S^3 = 1.2 \times 10^{-11}$

$S = (3 \times 10^{-12})^{1/3} = 1.44 \times 10^{-4}$ M

$$\Lambda_m^\infty = \frac{\kappa \cdot 1000}{S} = \frac{3.7938 \times 10^{-5} \times 1000}{1.44 \times 10^{-4}}$$

$= 263$ S cm^2 mol^{-1}.

Also, $\Lambda_m^\infty(Ag_2C_2O_4) = 2\Lambda_m^\infty(Ag^+) + \Lambda_m^\infty(C_2O_4^{2-})$

$\Rightarrow$ $263 = 2 \times 62 + \Lambda_m^\infty(C_2O_4^{2-})$

$\Rightarrow$ $\Lambda_m^\infty(C_2O_4^{2-}) = 263 - 124 = 139$ S cm^2 mol^{-1}.

123. $$\Lambda^\infty(AgCl) = \frac{\kappa \times 1000}{S}$$

$\Rightarrow$ $$S = \frac{1.8 \times 10^{-6} \times 1000}{138} = 1.3 \times 10^{-5}$$

$K_{sp} = S^2 = 1.7 \times 10^{-10}\ M^2$

124. $$\kappa(NaNO_3) = \frac{\Lambda c}{1000} = \frac{121 \times 0.001}{1000}$$

$= 0.121 \times 10^{-3}$ S cm^{-1}

(b) $$\frac{1}{R} = \kappa\left(\frac{A}{l}\right)$$

Cell constant $\left(\frac{l}{A}\right) = \kappa R = 0.121 \times 10^{-3} \times 1650$

$= 0.199$ cm^{-1}.

(c) $$\kappa(HCl) = \frac{\text{Cell constant}}{R} = \frac{0.199}{468}$$

$= 4.25 \times 10^{-4}$ S cm^{-1}

$$\kappa(NaCl) = \frac{0.199}{1580}$$

$= 1.26 \times 10^{-4}$ S cm^{-1}

$\Rightarrow$ $\kappa(HNO_3) = \kappa(HCl) + \kappa(NaNO_3) - \kappa(NaCl)$

$= 4.25 \times 10^{-4} + 1.21 \times 10^{-4} - 1.26 \times 10^{-4}$

$= 4.2 \times 10^{-4}$

$\Rightarrow$ $$R(HNO_3) = \frac{\text{Cell-constant}}{\kappa}$$

$$= \frac{0.199}{4.2 \times 10^{-4}} = 474\ \Omega$$

$$\Lambda_m(HNO_3) = \frac{\kappa \times 1000}{c} = \frac{4.2 \times 10^{-4} \times 1000}{0.001}$$

$= 420$ S cm^2 mol^{-1}.

125. $$G = \frac{1}{R} = \kappa\left(\frac{A}{l}\right)$$

$\Rightarrow$ Cell constant $\left(\frac{l}{A}\right) = \kappa \cdot R = 6.67 \times 10^{-3} \times 245 = 1.634$ cm^{-1}.

$$\Rightarrow \kappa(NaOH) = \frac{\text{Cell-constant}}{R} = \frac{1.634}{680} = 2.4 \times 10^{-3}\ S\ cm^{-1}.$$

$$\Lambda(NaOH) = \frac{\kappa \times 1000}{c} = \frac{2.4 \times 10^{-3} \times 1000}{0.01}$$

$= 240$ S cm^2 mol^{-1}.

126. (a) $2\Lambda^\infty(HCl) + \Lambda^\infty(Na_2SO_4) - 2\Lambda^\infty(NaCl) = \Lambda^\infty(H_2SO_4)$

$\Rightarrow$ $\Lambda^\infty(H_2SO_4) = 2 \times 426 + 260 - 126.5 = 859$ S cm^2 mol^{-1}

(b) $\Lambda^\infty(K_2SO_4) = 2\Lambda^\infty(KCl) + \Lambda^\infty(Na_2SO_4) - 2\Lambda^\infty(NaCl)$

$= 2 \times 150 + 260 - 2 \times 126.5 = 307$ S cm^2 mol^{-1}

(c) $\Lambda^\infty(CaSO_4) = \Lambda^\infty(CaCl_2) + \Lambda^\infty(Na_2SO_4) - 2\Lambda^\infty(NaCl)$

$= 272 + 260 - 2 \times 126.5 = 279$ S cm^2 mol^{-1}.

127. The molar conductivity of dissociated form of crotonic acid is :

$\Lambda^\infty(H^+ + C^-) = \Lambda(HCl) + \Lambda(NaC) - \Lambda(NaCl)$

$= 426 + 83 - 126 = 383$ S Cm^2 mol^{-1}.

Apparent molar conductivity,

$$\Lambda_m = \frac{k \times 1000}{c} = \frac{3.83 \times 10^{-5} \times 1000}{0.001}$$

$= 38.3$ S cm^2 mol^{-1}.

$\Rightarrow$ $$\alpha = \frac{\Lambda_m}{\Lambda_\infty} = \frac{38.3}{38.3} = 0.1$$

and $$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.1)^2}{1 - 0.1}$$

$= 1.11 \times 10^{-5}$.

128. Let α be the degree of dissociation :

$\Rightarrow$ $[H^+] = [OH^-] = C\alpha$ where $C = \frac{1000}{18} = 55.56$ M

Also, $k(H_2O) = k(H^+) + k(OH^-)$

$= [\lambda(H^+)[H^+] + \lambda(OH^-)[OH^-]\ \frac{1}{1000}$

$= \frac{C\alpha}{1000}(\Lambda[H^+ + OH^-])$

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$$= 548 \times \frac{55.56}{1000}\alpha$$

$$\Rightarrow \quad \alpha = \frac{0.554 \times 10^{-7} \times 1000}{548 \times 55.56} = 1.8 \times 10^{-9}$$

$$\Rightarrow \quad [H^+] = [OH^-] = C\alpha = \frac{1000}{18} \times 1.8 \times 10^{-9} = 10^{-7}$$

$$K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

129. (a) Specific conductivity due to Na_2SO_4 alone

$$= 2.6 \times 10^{-4} - 5 \times 10^{-7}$$

$$= 2.595 \times 10^{-4}\ S\ cm^{-1}$$

$$\Rightarrow \quad \Lambda_m(Na_2SO_4) = \frac{2.595 \times 10^{-4} \times 1000}{0.001}$$

$$= 259.5\ S\ cm^2\ mol^{-1}$$

$$\Rightarrow \quad \lambda(SO_4^{2-}) = \Lambda(Na_2SO_4) - 2\lambda(Na^+)$$

$$= 259.5 - 2 \times 50 = 159.5\ S\ cm^2\ mol^{-1}$$

$$\Rightarrow \quad \Lambda(CaSO_4) = \lambda(Ca^{2+}) + \lambda(SO_4^{2-}) = 120 + 159.5$$

$$= 279.5\ S\ cm^2\ mol^{-1}$$

(b) Specific conductivity due to $CaSO_4$ alone

$$= 7 \times 10^{-4} - 2.6 \times 10^{-4}$$

$$= 4.4 \times 10^{-4}\ S\ cm^{-1}$$

Specific conductivity of $CaSO_4$ solution $= k(CaSO_4) + k(H_2O)$

$$= 4.405 \times 10^{-4}\ S\ cm^{-1}.$$

$\Rightarrow$ Concentration of Ca^{2+} ion is solution

$$= \frac{k \times 1000}{\Lambda} = \frac{4.405 \times 10^{-4} \times 1000}{279.5}$$

$$= 1.57 \times 10^{-3}\ M$$

$\Rightarrow$ $[SO_4^{2-}]$ in solution $= 1.57 \times 10^{-3} + 10^{-3} = 2.57 \times 10^{-3}$

$$\Rightarrow \quad K_{sp} = [Ca^{2+}][SO_4^{2-}] = 1.57 \times 2.57 \times 10^{-6}$$

$$= 4.03 \times 10^{-6}.$$

Multiple Choice Questions (*Base Level*)

1. (d) Orange juice is electrolytic, acts as salt bridge.
2. (d) Mn is more electropositive than Fe, can give cathodic protection to iron.
3. (b) H_2O_2 in acidic medium has higher reduction potential than Au, can oxidise Au to Au^{3+}.
4. (a) Al has lower reduction potential than Br_2. Al will be oxidised and Br_2 will be reduced spontaneously.
5. (b) $E = E^\circ - \frac{RT}{nF} \ln \frac{[Cr^{+3}]^4}{[Cr^{+2}]^{6+}[H_3O^+]^4}$

   Increasing $[Cr^{+2}]$ will increase emf.
6. (b) H^+ is reduced to produce $H_2(g)$ in standard hydrogen electrode.
7. (d) All the mentioned metal ions will be reduced spontaneously on the surface of iron.
8. (a) Number of Faraday $= \frac{0.3 \times 15 \times 60}{96485} = 2.8 \times 10^{-3}$

   = Gram Eq of Au

   $$\Rightarrow \quad m(Au) = 2.8 \times 10^{-3} \times \frac{197}{3}\ g = 0.184\ g$$
9. (c) Electrons flow from Zn anode to Fe cathode via external circuit.
10. (c) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.40 - (-0.44) = 0.84\ V$
11. (d) $\Delta G = -nEF$.

    For spontaneous cell, $\Delta G < 0$ therefore $E > O$.

    From Faraday's Law, the amount of electrolytes discharged is proportional to quantity of electricity passed.
12. (d) $\Delta G^\circ = -nE^\circ F = -2 \times 2.041 \times 96500 = -3.93 \times 10^5\ J$
13. (d) In a concentration cell, same electrodes are used both as cathode and anode, hence $E^\circ = 0$.
14. (d) This is the purpose of using salt bridge in a Galvanic cell.
15. (d) $O_2 + 4H_3O^+ + 4e^- \longrightarrow 6H_2O \quad E^\circ = 1.23\ V$

    $2I^- + 2e^- \longrightarrow I_2 \quad E^\circ = -0.54\ V$

    $O_2 + 4H_3O^+ + 4I^- \longrightarrow 2I_2(aq) + 6H_2O \quad E^\circ = 0.69\ V$

    $\because E^\circ > 0$, above redox reaction is spontaneous. (for E° values, see the table-3 of appendix).
16. (d) Both Mn and Cr are more electropositive than iron.
17. (d) For a spontaneous redox reaction, $\Delta G < 0$. Also $\Delta G = -nEF$ hence $E > 0$.
18. (b) There must be electric contact between electrodes in order to move electrons.
19. (c) Water acts both as oxidising and reducing agent in electrolysis of water.
20. (b) Porous disk plays the role of salt bridge, allows ions to move through in order to maintain electroneutrality in the two half-cells.
21. (c) Zn is more electropositive than hydrogen, it will start oxidising resulting in decrease in mass of Zn electrode.
22. (b) Since the tubes are not connected, ions can't flow out of tube to maintain the electrical neutrality in two half-cells.
23. (a) Mg, being more electropositive, will be oxidised and Fe^{2+} will be reduced to Fe.
24. (d) For sacrificial anode, its E° must be less than $-0.41\ V$.
25. (a)

    $$E = 0.12 - \frac{0.0591}{2} \log [(1.7)^2 - (3.5)]^{-1}$$

    $$= 0.15\ V$$
26. (b) $\log K = \frac{nE^\circ}{0.059} = \frac{0.5}{0.059} \Rightarrow K = 2.98 \times 10^8$

    $$Q_c = \frac{6}{1.0\ (0.01)^5} = 6 \times 10^{12} > K, \text{ backward reaction occur.}$$
27. (a) Lower the value of E°, stronger the reducing agent.
28. (d) There is no Ag^+ ions available for reduction, hence no current will flow in wire. Iron would corrode as usual by moist air.
29. (a) The reaction will occur spontaneously releasing energy ($\Delta U < 0$), hence temperature of solution will increase.
30. (c)

    (i) $3Cu^{2+} + 6e^- \longrightarrow 3Cu \quad E^\circ = 0.34\ V$

    (ii) $2Al^{3+} + 6e^- \longrightarrow 2Al \quad E^\circ = -1.66\ V$

    (i)—(ii) $3Cu^{2+} + 2Al \longrightarrow 3Cu + 2Al^{3+} \quad E^\circ = 2.0\ V$
31. (a) Al is oxidised and Cu^{2+} is reduced spontaneously.
32. (d) Calculated in (30)

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33. (c) $\ln K = \frac{nE^\circ F}{RT} = \frac{6 \times 2 \times 96500}{8.314 \times 298} = 467$

$\Rightarrow K = e^{467}$

34. (d) The cell reaction will be spontaneous and apple will act both as electrolyte and salt bridge.

35. (c) (i) $3Sn^{2+} + 6e^- \longrightarrow 3Sn$ $E^\circ = -0.14$ V

(ii) $2Cr^{+3} + 6e^- \longrightarrow 2Cr$ $E^\circ = -0.74$ V

(i)-(ii) $3Sn^{2+} + 2Cr \longrightarrow 2Cr^{+3} + 3Sn$ $E^\circ = 0.60$ V

36. (a) Cr is oxidised and Sn^{2+} is reduced spontaneously. Hence Cr is anode and Sn is cathode.

37. (c) Calculated is 35.

38. (d) $\log K = \frac{6 \times 0.6}{0.059} = 61$

$\Rightarrow K = 10^{61}$

39. (d) $\Delta G^\circ = -nE^\circ F = -6 \times 0.6 \times 96500 = -347.4 \times 10^3$ J

40. (d) Br_2 is weaker oxidising agent than Cl_2. Hence, the reaction: $Br_2 + 2Cl^- \longrightarrow Cl_2 + Br_2$ does not occur spontaneously.

41. (c) Number of Faraday $= \frac{10 \times 20 \times 60}{96500} = 0.12$ = Number of gram equivalent of Zn.

$\Rightarrow$ Moles of Zn $= \frac{0.12}{2} = 0.06$

42. (a) For a galvanic cell: $\Delta G < 0$, $E > 0$.

43. (c) In hydrogen gas electrode, Pt wire acts as solid support on the surface of which electrolysis occur.

44. (a) Al is more electropositive than both Cu and Zn, will reduce both Cu^{2+} and Zn^{2+} to metals.

45. (b) Fe is more electropositive than hydrogen, displaces H^+ from acid solution oxidising itself to Fe^{2+}.

46. (b) Galvanic cell is not used in study of kinetics of a reaction.

47. (d) The reaction $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$ is spontaneous hence $\Delta G < 0$ and $E > 0$.

48. (b) $E = 1.56 - \frac{RT}{2F} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$

Increasing $[Zn^{2+}]$ will decrease emf.

49. (a) Number of Faraday's $= \frac{10^6 \times 2.2 \times 60 \times 60}{96500} = 8.2 \times 10^4$

Number of equivalents of Mg^{2+} reduced $= 8.2 \times 10^4$

$\Rightarrow$ Number of moles of Mg(s) produced $= \frac{8.2}{2} \times 10^4 = 4.1 \times 10^4$ moles.

50. (c) In a dead battery $\Delta G = 0$ and $E_{cell} = 0$.

51. (b) Zn is at lower reduction potential, acts as anode and Ni acts as cathode.

52. (d) As cell works, electrons flow from Zn to Ni electrode *via* external circuit. K^+ diffuses to cathode half-cell to compensate the deficiency of Ni^{2+} and Cl^- diffuses to anode half-cell to neutralise Zn^{2+} produced.

53. (c) Ni^{2+} from solution gets reduced at Ni electrode. It can also be reduced at Pt electrode. However Zn^{2+} comes from Zn-electrode, it is must required as anode.

54. (c) Higher the E°, stronger the oxidising agent.

55. (b) Smaller the E°, stronger the reducing agent.

56. (d) No half-cell has E° greater than 1.50 V, no one can oxidise Au to Au^{3+}.

57. (c) $E = E^\circ - \frac{0.059}{3} \log \frac{[Ag^+]^3\, p(NO)}{[NO_3^-][H^+]^4}$

$= 0.16 - \frac{0.059}{3} \log \frac{(0.01)^3 (0.2)}{2 \times (0.1)^4} = 0.219 \approx 0.22$ V

58. (a) $\log K = \frac{2 \times 0.14}{0.059} = 4.74$

$\Rightarrow K = 5.4 \times 10^4$

59. (b) In concentration cell: $E = -\frac{0.059}{n} \log \frac{[Fe^{2+}]_{Anode}}{[Fe^{2+}]_{Cathode}}$

For $E > 0$, $[Fe^{2+}]_{anode} < [Fe^{2+}]_{cathode}$

60. (d) $PbSO_4$ is formed at both cathode and anode.

61. (d) A metal with E° lower than that of Fe gives cathodic protection from rusting of iron.

62. (c) Alkali metals are themselves very strong reducing agents, have large negative E°, no convenient chemical reducing agents are available for reduction of alkali metal ions from their salt.

63. (b) Mass of Cr to be plated $= 0.25 \times 10^4$ cm$^2 \times 2 \times 10^{-3}$ cm $\times 7.19$ g/cm^3 = 35.95 g (one side)

Number of gram equivalent $= \frac{35.95 \times 2}{\left(\frac{52}{3}\right)} = 4.14$ = Number of Faraday's

$\Rightarrow 75t = 4.14 \times 96500$

$\Rightarrow t = 5337$ sec $= 1.5$ hr

64. (b) $E = E^\circ - \frac{0.059}{2} \log \frac{[Cu^{2+}]^2 [Cl^-]^2}{[Cu^+]^2}$

$0.06 = (0.27 - 0.15) - \frac{0.059}{2} \log \frac{(1.2)^2 (3.5)^2}{[Cu^+]^2}$

$\Rightarrow [Cu^{2+}] = 0.42$ M

65. (c) Ce^{+4} is a very strong oxidising agent as $E^\circ_{Ce^{4+}/Ce^{+3}} = 1.61$ V

66. (b) $\Delta G^\circ = -nE^\circ F = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow \Delta H^\circ = T\Delta S^\circ - nE^\circ F = 298 \times 110 - 2 \times 1.5 \times 96500$

$= -256.52 \times 10^3$ J ≈ -257 kJ

67. (a) $E = 0 - \frac{0.06}{2} \log \frac{(0.2)}{(0.7)} = 0.016$ V

It is concentration cell whose $E^\circ = 0$.

68. (b) Salt bridges are not connected, cell can't function.

69. (d) The cell reaction is :

$Ni + Cl_2 \longrightarrow Ni^{2+} + 2Cl^-$

Ni and Cl_2 decreases, Ni^{2+} and Cl^- increases, Pt remains unchanged.

70. (a) $E = 0.02 - \frac{0.06}{6} \log \frac{[0.2]^3}{[2.5]^2} = 0.05$ V

71. (d) $E^\circ = 0.80 - 0.34 = 0.46$

$\Delta G^\circ = -nE^\circ F = -2 \times 0.46 \times 96500$ J $= -88.78$ kJ

72. (a) $E^\circ = -0.13 + 2.37 = 2.24$ V

$\log K = \frac{nE^\circ}{0.059} = \frac{2 \times 2.24}{0.059} = 75.93$

$\Rightarrow K = 8.5 \times 10^{75}$

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73. (a) A concentration cell will set-up in which electrolyte at lower concentration will act as anode (left) and one at higher concentration (right) will act as cathode.

74. (b) For $MX_2(s) \longrightarrow M^{2+} + 2X^-$

$\ln K = -10 = \frac{2E^\circ}{0.059} \times 2.3$

$\Rightarrow E^\circ = -0.128$ V ...(i)

$M^{2+} + 2e^- \longrightarrow M(s) \quad E^\circ = 0.10$ V ...(ii)

Adding (i) and (ii) gives $MX_2(s) + 2e \rightarrow M(s) + 2X^-$

$E^\circ = -0.028$ V

75. (d) $E^\circ = 0.15 - (-1.18) = 1.33\text{V} > 0$

76. (c) Number of electron transfer depends on stoichiometry of reactions not on amount of reactions.

77. (c) Reduction occurs at cathode and cations migrates to cathode chamber to maintain electroneutrality.

78. (b) $\Delta G^\circ = -nE^\circ F$; independent of concentrations of reactants and products i.e. composition.

79. (b) $E = E^\circ - \frac{0.059}{2} \log \frac{[Pb^{2+}]}{[Cu^{2+}]}$

Increasing $[Cu^{2+}]$ will increase E.

80. (b) $E = E^\circ - 0.059 \log \frac{[H^+]}{[Ag^+]} = E^\circ + 0.059 \text{ pH} + 0.059 \log [Ag^+]$

$\Rightarrow \text{pH} = \frac{1}{0.059}[1.05 - 0.799 - 0.059 \log (0.1)] = 5.25$

81. (c) $\log (1.356 \times 10^9) = \frac{2E^\circ}{0.059} \Rightarrow E^\circ = 0.27$ V

$\Rightarrow$ E° for reverse reaction is -0.27 V.

82. (d) Ni is being oxidised and Fe^{3+} is being reduced.

83. (b) For $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \; E^\circ = -0.729$ V

$\Rightarrow \log K_{sp} = \frac{E^\circ}{0.059} = \frac{-0.729}{0.059} = -12.35$

$\Rightarrow K_{sp} = 4.4 \times 10^{-13}$

84. (d) 3 mol Cu = 6 equivalents of Cu = 6 F electricity.

$\Rightarrow 6 \times 96500 = 50t$

$\Rightarrow t = \frac{6 \times 9650}{5 \times 3600}$ hrs = 3.22 hrs

85. (c) ΔG° is an extensive property while E° is intensive.

86. (a) $E^\circ = -0.126 - 0.771 = -0.897$ V, non-spontaneous.

87. (c) Cell reaction is $2Fe^{3+} + Pb \rightleftharpoons Pb^{2+} + 2Fe^{2+}$

$E = 0.897 - \frac{0.059}{2} \log \frac{(0.04)(0.01)^2}{(0.20)^2} = 1.105$ V

88. (b) Mg is more electropositive than Fe.

89. (a) Number of Faraday's $= \frac{8 \times 40 \times 60}{96500} = 0.1989$

Mass of Cr $= 0.1989 \times \frac{52}{3} = 3.44$ g

90. (c) $E = E^\circ - \frac{0.06}{6} \log \frac{[Al^{+3}]^2}{[Fe^{2+}]^3} = 1.21 - 0.01 \log \frac{(0.1)^2}{(0.02)^3} = 1.18$ V

91. (d) $\log K = \frac{nE^\circ}{0.059} = \frac{3 \times 1.884}{0.059} = 95.7$

$K = 5 \times 10^{95}$

92. (c) $E^\circ \sim 2V$. Connect six cells in series to make battery of 12V.

93. (b) Fe is oxidised.

94. (b) $F = \frac{15 \times 80 \times 60}{96500} = 0.746$

Faraday = Number of equivalents of Ni.

$\Rightarrow$ Mass of Ni $= 0.746 \times \frac{58.5}{2} = 21.8$ g

95. (d) $E = E^\circ - \frac{0.059}{2} \log \frac{[Zn^{2+}][pH_2]}{[H^+]^2}$

Increasing $[H^+]$ to cathode chamber and decreasing partial pressure of H_2 will increase E.

96. (c) $E^\circ = 0.34 - (-0.13) = 0.47$ V

97. (a) $E = -\frac{0.059}{2} \log \frac{10^{-3}}{2} = 0.098$ V, concentration cell.

98. (c) If $E^\circ > 0$, $\Delta G^\circ < 0$ and cell reaction will be spontaneous.

99. (a) $\Delta G^\circ = -nE^\circ F = -2 \times 0.62 \times 96500 \text{ J} = -119.66 \times 10^3$ J

100. (b) At chemical equilibrium, rate of forward reaction becomes equal to rate of backward reaction.

101. (b) $\Delta G < 0$ can spontaneously transport A^{n+} from inside to outside of membrane.

102. (a) End point is obtained after 15 mL 0.2 M (3 m mol) H_2SO_4 is added. Therefore 6 m mol KOH were present.

$\Rightarrow [KOH] = \frac{6}{20} = 0.3$ M

103. (d) In a galvanic cell, electrons move from anode to cathode via external circuit, anion to anode chamber and cation to cathode chamber from the salt bridge.

104. (b) $E^\circ = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Sn^{4+}/Sn^{2+}} = 0.771 - 0.154 = 0.617$ V

105. (a) $\frac{2.19 \times 3}{52} \times 96500 = 35.2t$

$\Rightarrow t = 346.38$ s $= 5.77$ min.

106. (b) Cl_2 will be reduced to Cl^- and I_2 will be oxidised to IO_3^-.

107. (a) Adding 2nd and 4th half-cells and subtracting 1st and 3rd gives the desired reaction.

$E^\circ = (0.80 - 0.44) - (0.52 - 0.31) = 0.15$ V

$\Delta G^\circ = -nE^\circ F = -1 \times 0.15 \times 96500 = -14.475 \times 10^3$ J

108. (d) $\frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{2}{(0.5)(2)^2} = 1$

$\Rightarrow E = E^\circ$

109. (d) $E^\circ = 1.058 - 0.00017 (t - 25°C)$

$= 1.058 - 0.00017 (T - 298 \text{ K})$

$= 1.10866 - 0.0017 T = -\frac{\Delta H^\circ}{nF} + \frac{\Delta S^\circ}{nF} T$

$\Rightarrow \Delta H^\circ = -1.10866 \times 2 \times 96500$ (Equating intercepts)

$= -214 \times 10^3$ J

110. (c) $E = E^\circ - \frac{0.06}{2} \log \frac{[Zn^{2+}]}{[H^+]^2} = E^\circ - 0.06 \text{ pH}$

$\Rightarrow \text{pH} = \frac{E^\circ - E}{0.06} = \frac{0.771 - 0.653}{0.06} = 1.96 \sim 2$

111. (c) $V \times C = J \Rightarrow V = \frac{788 \text{ J}}{255 \text{ C}} = 3.09$ volt

112. (c) Number of Faraday's $= \frac{0.12 \times 65 \times 60}{96500}$

$= 4.8 \times 10^{-3}$ = Number of Equivalents.

$\Rightarrow$ mole of $O_2 = \frac{1}{4} \times 4.8 \times 10^{-3} = 1.21 \times 10^{-3}$ moles

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113. (b) $\Delta G = -nEF = -6 \times 0.56 \times 96500\,J = -3.24 \times 10^5\,J$ (for 3 mol Cl_2)

For 1.5 mol Cl_2 : $\Delta G = \frac{1}{2} \times (-3.24 \times 10^5) = -1.62 \times 10^5\,J$

114. (b) At equilibrium, $E = 0$.

115. (d) There is no salt bridge in electrolytic cell.

116. (b) $E = E° - \frac{0.06}{2} \log \frac{[Zn^{2+}]}{[Cl^-]^2}$

$\Rightarrow \quad 2.1 = 2.12 - 0.03 \log \frac{(0.20)}{x^2} \quad \Rightarrow \quad x = 0.2\,M$

117. (d) $E° = E°_{Ag^+/Ag} - E°_{Fe^{3+}/Fe}$

$\Rightarrow E°_{Fe^{3+}/Fe} = 0.80 - 0.84 = -0.04\,V$

118. (b) $\Delta G°_{RXN} = -228.6 \times 2 - 394.4 - (-50.80) = -800.8\,kJ$

$\Rightarrow \Delta G° = -800.8 \times 10^3\,J = -8 \times E° \times 96500$

$\Rightarrow \quad E° = 1.04\,V$

119. (d) Salt bridge allows ions to flow into anode chamber and cathode chamber to prevent build up of charge and maintain electroneutrality, otherwise cell will not function.

120. (a) Reversing a half reaction reverse the sign of $E°$. $E°$ is an intensive property, does not depends on amount of reaction.

121. (b) $\Delta G < 0$ in concentration cell.

122. (d) For $PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$; $E° = -0.239\,V$

$\log K_{sp} = \frac{-2 \times 0.239}{0.059} = -8.1 \Rightarrow K_{sp} = 8 \times 10^{-9}$

123. (d) $E°$ is intensive property.

124. (b) First we need to calculate $E°$ for $Fe^{2+} + 2e \longrightarrow Fe(s)$

$E°_{Fe^{2+}/Fe} = \frac{-3 \times 0.036 - 0.770}{2} = -0.439\,V$

Now $E°$ for $3Fe^{2+}(aq) \longrightarrow 2Fe^{3+}(aq) + Fe(s)$

$E° = -0.77 - 0.439 = -1.209\,V$

$\log K = \frac{nE°}{0.059} = \frac{-2 \times 1.209}{0.059} = -40.98$

$K = 1.2 \times 10^{-41}$

125. (c) $E° = 0.80 - 0.152 = 0.648\,V$

$\Delta G° = -nE°F = -0.648 \times 96500\,C = -62.5 \times 10^3\,J$

126. (c) The number of Faraday passed

$= \frac{1.5 \times 90 \times 60}{96500} = 8.39 \times 10^{-2}$

$\Rightarrow$ The number of equivalents of Cl_2 formed $= 8.39 \times 10^{-2}$

$\Rightarrow$ Volume of $Cl_2 = 8.39 \times 10^{-2} \times \frac{22.4}{2}$ (1 eq Cl_2 = 0.5 mol

= 11.6 L at STP) = 0.94 L

127. (b) Zn is anode and Cr is cathode. Electrons flow from Zn to Cr electrode.

128. (c) The number of moles of Cu^{2+} reduced will be equal to number of Cu^{2+} produced in oxidation reaction.

129. (d) $E° = E°_{cathode} - E°_{anode} = 0.80 - (-0.74) = +1.54\,V$

130. (c) Reactants (Ag^+ and Cr) will decrease, products (Ag, Cr^{+3}) will increase.

131. (c) Possible oxidations are

$2Br^- \longrightarrow Br_2 + 2e^-$; $E° = -1.08\,V$ ...(i)

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$; $E° = -0.82\,V$ ...(ii)

Higher the oxidation potential easier the oxidation.

132. (a) Reducing power Zn > Cr > Ni, Cd > Ni

$\Rightarrow$ overall reducing power Zn > Cr > Cd < Ni

133. (c) Mg is anode and Ag is cathode.

134. (b) Zn is anode and Ni is cathode.

135. (b) Al is produced at cathode.

136. (a) Electrolyte at lower concentration serves as anode chamber.

137. (d) Density of acid solution will decrease, $[H^+]$ will decrease. Hence, pH will increase.

138. (c) $E = E° - \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$

Change in $[Ag^+]$ by a factor has greater effect on E than change in $[Cu^{2+}]$ by same factor.

139. (c) Sn^{2+} will be reduced in preference to Ni^{2+}. Br^- will be oxidised in preference to Cl^-.

140. (b) $E = E° - \frac{0.059}{2} \log \frac{[H^+]^2}{[Ag^+]^2}$

$= E° + 0.059 \log [Ag^+] + 0.059\,pH$

$\Rightarrow \quad E = C + 0.059\,pH\,(C = E° + 0.059 \log [Ag^+])$

E vs pH is a straight line with positive slope. Remember the starting point is not origins.

141. (b) $E° = E°_{Fe^{2+}/Fe} - E°_{Zn^{2+}/Zn} = 0.31$

$\Rightarrow \quad E°_{Fe^{2+}/Fe} = 0.31 - 0.76 = -0.45\,V$

$Fe^{2+} + 2e \longrightarrow Fe \quad E° = -0.45$

$Fe^{3+} + e \longrightarrow Fe^{2+} \quad E° = 0.77 \quad E°(Fe^{3+}/Fe)$

$= \frac{-2 \times 0.45 \times 0.77}{3} = -0.325\,V$

142. (c) Higher the $E°$, easier the reduction. Mg^{2+} will not be reduced because it is more electropositive than hydrogen.

143. (c) Between Mn^{2+} and H^+, H^+ will be reduced. I^- will be oxidised in preference to water.

144. (b) $E = E° - \frac{0.059}{4} \log \frac{[Cr^{+3}]^4}{[Cr^{+2}]^4\,[H_3O^+]^4\,p(O_2)}$

As $[Cr^{+2}]$ is increased, E will increase.

145. (c) $E = (0.88 - 0.77)\,V - \frac{0.059}{1} \log \frac{[Fe^{3+}]^2\,[HO^-]^2}{[Fe^{2+}]^2\,[H_2O_2]}$

$\Rightarrow \quad \frac{0.059}{2} \log \frac{(0.5)^2\,(0.10)^2}{x^2(0.35)} = 0.11 - 0.16 = -0.05$

$\Rightarrow \quad x = 0.60\,M$

146. (a) $W_{max} = -\Delta G = nEF = 2 \times 2.5 \times 96500\,J = 4.82 \times 10^5\,J$

147. (b) At left hand electrode: $Mg + 2OH^- \longrightarrow Mg(OH)_2 + 2e^-$

$E° = 2.7\,V$

At right hand electrode : $Cu^{2+} + 2e^- \longrightarrow Cu \quad E° = 0.6\,V$

$\Rightarrow \quad Mg + 2OH^- + Cu^{2+} \longrightarrow Mg(OH)_2 + Cu \quad E° = 3\,V$

$E = E° - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]\,[OH^-]^2} = E° - 0.059\,pOH$

$\Rightarrow \quad pOH = \frac{E° - E}{0.059} = \frac{3 - 2.7}{0.059} = 5$

$\Rightarrow \quad pH = 9$

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148. (d) $BrO_3^- + 4e^- \longrightarrow BrO^-$ $E° = 1.5$

$BrO^- + e^- \longrightarrow \frac{1}{2}Br_2$ $E° = 1.6$

$5e^- + BrO_3^- \longrightarrow \frac{1}{2}Br_2$ $E° = \frac{1.5 \times 4 + 1.6}{5} = 1.52$ V

149. (c) $\Lambda_m = \frac{K \times 1000}{C}$. Increasing concentration decreases molar conductance. However, conductance increases on increasing concentration.

150. (d) For strong electrolyte, molar conductance increases linearly on dilution. In case of weak electrolyte, dilution first increases molar conductance slowly but very rapidly near to $C = 0$.

151. (b) At infinite dilute, all electrolytes are completely ionised.

152. (c) Cell constant $= \frac{l}{a}$ is a property of equipment.

153. (b) $\Lambda^\infty_{CH_3COOH} = \Lambda^\infty_{CH_3COOK} + \Sigma^\infty_{HCl} - \Lambda^\infty_{KCl}$

$= 114.42 + 426.2 - 271.5 = 269.12$

154. (a) $\alpha = \frac{\Lambda^c}{\Lambda^\infty} \Rightarrow \Omega^\infty = \frac{\Omega^c}{\alpha} = \frac{19}{0.01} = 1900$ s cm^{2}mol^{-1}.

155. (d) Dilution increases interionic distance hence decreases interionic attraction

Multiple Choice Questions *(Advanced Level)*

1. (d) Since Au is less electropositive than hydrogen and Pb is more electropositive than hydrogen, Pb will form anode and Au will form cathode of galvanic cell. During electrolysis, Pb^{2+} will come into solution and Au^{3+} will go out of solution, hence (d)

2. (c) $E = 0.65 = -\frac{0.059}{1}\log\frac{[Ag^+]_{Anode}}{0.1}$

$\Rightarrow [Ag^+]_{anode} = 10^{-12}$ M

$\Rightarrow K_{sp} = [Ag^+][Br^-] = 10^{-12} \times 10^{-1} = 10^{-13}$

3. (c) Change in concentration of Ag^+ by a factor has greater effect on EMF than change in $[Cu^{2+}]$ by same factor.

4. (b) No. of Faraday passed $= \frac{96.5 \times 10^3}{96500} = 1.0$

$\Rightarrow$ No. of gram equivalent of Ag deposited = 1.0

$\Rightarrow$ Mass of Ag deposited = 1.0 × 108 = 108 g

5. (a) $E°$ for the reaction: $AgI(s) \rightleftharpoons Ag^+ + I^-$ is $-0.164 - 0.80$ $= -0.964$ V.

$\Rightarrow \log K_{sp} = \frac{-0.964}{0.0591} = -16.3$ and $K_{sp} = 5 \times 10^{-17}$

6. (b) For (ii) $E° = 0.59 - 0.34 = 0.25$ V > 0, spontaneous.

For (i) $E° = 0.34 - 0.68 = -0.34$ and for (iii) $E° = 0.59 - 0.68 = -0.09$.

Hence, (i) and (iii) are non-spontaneous.

7. (c) $E = 0 - \frac{0.059}{2}\log\frac{0.05}{1.5} = 0.044$ V

8. (b) As in the previous problem,

Equivalent weight of mercury $= \frac{0.26 \times 96500}{210 \times 10^{-3} \times 1200} = 99.56$

$\Rightarrow$ Valency $= \frac{\text{Molar mass}}{\text{Equivalent weight}} = \frac{200}{99.56} = +2$

9. (b) $E° = 0.53 - (-0.41) = 0.94$ V

$\Delta G° = -nE°F = -2 \times 0.94 \times 96500$ J

$= -181.42 \times 10^3$ J

10. (a, b, c) In both galvanic cell, and electrolytic cell, redox reaction take place. In electrolytic cell, non-spontaneous redox reaction is carried out with the help of external current. Reduction always occur at cathode. There is no salt bridge in electrolytic cell.

11. (b, c) Since, both electrodes are Fe, $E°_{cell} = 0$: (a) is correct.

Since, the cathode and the anode chambers have different concentration of Fe^{2+}, $E_{cell} \neq 0 \Rightarrow \Delta G \neq 0$: (b) is false.

Because the concentration cell is a galvanic cell, $E > 0$: (c) False.

At equilibrium $E_{cell} = 0 \Rightarrow [Fe^{2+}]_{anode} = [Fe^{2+}]_{cathode}$: (d) is correct.

12. (b, d) Both temperature and concentration of electrolytes affect the emf of a Galvanic cell. Surface area of electrodes and volume of electrolytes have no direct influence.

13. (a, b, d) Reaction quotient Q is 1 in all these cases.

14. (b, c) $HOBr \longrightarrow BrO_4^- + Br_2$ $E° > 0$

$HOBr \longrightarrow BrO_3^- + Br_2$ $E° > 0$

Both of the above disproportion reactions are spontaneous.

15. (b, c) The balanced reaction for reduction of acrylonitrile is

$2CH_2{=}CH{-}CN + 2H^+ + 2e^- \longrightarrow NC{-}(CH_2)_4{-}CN$

No. of faraday passed $= \frac{3 \times 10^3 \times 10 \times 3600}{96500} = 1119.17$

$\because$ 2.0 F of electricity produces 1.0 mol adiponitrile

16. (a, b, c) $A^{a+} \longrightarrow A^{b+}$ $E_1°$

$A^{b+} \longrightarrow A^{c+}$ $E_2°$

$A^{a+} \longrightarrow A^{c+}$ $E° = \frac{(a-b)E_1° + (b-c)E_2°}{a-c} = \frac{E_1° + E_2°}{2}$

Choices (a, b, c) satisfy the above expression.

17. (a, c) Given information indicates that Z is stronger oxidising agent than X but weaker than Y.

18. (a, d) The discharging reaction in lead storage battery is

$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

19. (a, b, d) In "a" and "b" water will be oxidised at anode giving O_2. In "c" Cu will be oxidised to Cu^{2+} and Cu^{2+} from solution will be reduced at Cu cathode. In "d", OH^- will be oxidised at anode giving O_2.

20. (a, b) $\Lambda^\infty = 62.3 + 67.7 = 130$ S cm^2 mol^{-1}

$\Rightarrow \Lambda^\infty = \frac{K\ 1000}{S}$

$\Rightarrow S = \frac{3.4 \times 10^{-6} \times 1000}{130} = 2.6 \times 10^{-5}$ mol L^{-1}

In gL^{-1} unit : solubility $= 2.6 \times 10^{-5} \times 143.5 = 3.7 \times 10^{-3}$ gL^{-1}

21. (a, d) For a spontaneous redox reaction, $\Delta G < 0$, hence emf must be positive because $\Delta G = -nEF$.

22. (a, c) The spontaneous redox reaction is

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

23. (a, b) Cu^{2+} is reduced and Br^- is oxidised during electrolysis of aqueous $CuBr_2$.

24. (b) $E = -0.059 \log\left(\frac{x_1}{x_2}\right)\left(\frac{p_2}{p_1}\right)^{1/2}$

(a) $P_1 = P_2$ and $x_1 > x_2 \Rightarrow E < 0$; non-spontaneous

(b) $P_1 = P_2$ and $x_1 < x_2 \Rightarrow E > 0$; spontaneous

(c) $x_1 = x_2$ and $P_1 > P_2 \Rightarrow E > 0$; spontaneous

(d) $x_1 = x_2$ and $P_1 < P_2 \Rightarrow E < 0$; non-spontaneous.

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25. (a, b) Cu will be oxidised to Cu^{2+} and Cu^{2+} from solution will be reduced at Cu cathode.

mass of Cu oxidised/reduced $= \frac{2.68 \times 3600}{96500} \times 32 = 3.2$ g

26. (d) $-2E^{\circ}F = \Delta H^{\circ} - T\Delta S^{\circ}$

$\Rightarrow -2 \times 0.6915\, F = \Delta H^{\circ} - 273\Delta S^{\circ}$ ...(i)

and $-2 \times 0.6753\, F = \Delta H^{\circ} - 298\Delta S^{\circ}$ ...(ii)

$\Rightarrow 25\Delta S^{\circ} = 2F(0.6753 - 0.6915) = -3126.6$

$\Rightarrow \Delta S^{\circ} = -125.064\ JK^{-1}$

Substituting in (ii) gives

$\Delta H^{\circ} = 298 \times (-125.064) - 2 \times 0.6753\, F$

$= -167.6 \times 10^3$ J

27. (a, b, c) For the reduction process : $Fe^{3+} + e \longrightarrow Fe^{2+}$

Moles of electrons required = moles of Fe^{3+} present = 0.10

Number of F passed $= \frac{4 \times 60 \times 60}{96000} = 0.15$

$\Rightarrow$ 0.075 F is used for reducing Fe^{3+} to Fe(s) and the same 0.075 F is used for Fe^{3+} to Fe^{2+}

$\Rightarrow$ 8 eq of Fe^{3+} reduced to Fe(s) = 0.075

$\Rightarrow$ mol of Fe(s) produced $= \frac{0.075}{3} = 0.025$

Also, 8 eq of Fe^{3+} reduced to Fe^{2+} = 0.075

$\Rightarrow$ Mole of Fe^{2+} produced = 0.075

28. (a, d) When Galvanic cell starts working, E_{cell} decreases and finally becomes zero where $Q = K$.

29. (a, b) When E° for a reduction half-cell is negative, metal will be oxidised and H^{+} will be reduced spontaneously. Reverse will be true if E° is positive. M will act as negative electrode (anode) if $E^{\circ}(M^{n+}/M)$ is negative.

30. (a, b, c) $E = E^{\circ} - \frac{RT}{nF} \ln [A^{n+}]$

with increase in $[A^{n+}]$, $E(A/A^{n+})$ decrease with constant $[A^{n+}]$, $E(A/A^{n+})$ decreases on increasing temperature, hence $E(A^{n+}/A)$ will increase. Also increasing $[A^{n+}]$ will increase $E(A^{n+}/A)$ because $E(A/A^{n+})$ decreases.

31. (a, c) $\Delta G^{\circ} = -RT \ln K = -2.303\, RT \log K$, i.e. (a) is correct.

$\Delta G = \Delta G^{\circ} + RT \ln Q$. i.e. (b) is wrong

At equilibrium : $E = E^{\circ} - \frac{0.059}{n} \log K = 0$

$\Rightarrow E^{\circ} = \frac{0.059}{n} \log K$, i.e. (c) is correct.

$E = E^{\circ} - \frac{0.059}{n} \log Q$; hence (d) is wrong.

32. (b, c, d) In aqueous solution, Li^{+} has larger hydrated radius than Na^{+}, hence Na^{+} has greater conductivity. It is due to greater polarising power of Li^{+} ion than Na^{+} ion.

33. (a, c) Initial mass of $H_2SO_4 = 750 \times 1.29 \times 0.38 = 367.65$ g

Final mass of $H_2SO_4 = 750 \times 1.19 \times 0.26 = 235.05$ g

$\Rightarrow H_2SO_4$ consumed during uses of battery = 135.60 g

$\because$ 1.0 mol of electron are transferred per mol of H_2SO_4 consumed.

$\therefore$

$$Q = \frac{135.60}{98} \times 96500 = 133.52\ kC$$

Time required for recharging $= \frac{133.52 \times 10^3}{22.4} = 5961$ s

$= 1.65$ hrs

34. (b, c) $E = E^{\circ} - \frac{RT}{2F} \ln \frac{[Cd^{2+}]}{[Cu^{2+}]}$

Decreasing $[Cd^{2+}]$ or increasing $[Cu^{2+}]$ will increases emf.

35. (b, d) $\because \Lambda = \frac{K \times 1000}{c}$

Both molar and equivalent conductivity increase on dilution. Specific conductivity (k) is independent of concentration. Increasing temperature increases ionic speeds, increases conductance of solution.

36. (a, c) Cell with $Q < 1$ has $E > E^{\circ}$.

37. (b, c) Cations are of comparable sizes.

38. (c) Decreasing concentration increases interionic distance, decreases electrostatic attraction between oppositely charged ions, increases ionic mobility, hence conductance.

39. (a) Zn has lower E° than Fe, gives cathodic protection from rusting to Fe.

40. (a) It is the large potential difference between electrodes due to which electrons flow from anode to cathode *via* external circuit.

41. (d) E° for H^{+}/H_2 is zero at 25°C. It is used as standard reference.

42. (a) Oxidation or reduction can't occur alone, hence absolute value of half-cell reduction potential can't be determined.

43. (a) Both cathode and anode reactions involved solid reactants, their direct contact does not take place and electrons flow through external circuit.

44. (a) $E \approx E^{\circ}, Q = 1$.

45. (d) Salt bridge is used in galvanic cell to maintain electroneutrality in anode and cathode chambers. Ions of salt bridge should have same transport numbers so that they reaches to respective electrodes chamber simultaneously.

46. (d) With dilution, molar conductivity of strong electrolytes increases.

47. (c) Cryolite is added to lower the melting points and improve electrical conductivity of Al_2O_3.

48. (a) Mg is more electropositive (has lower E°) than Fe.

49. (a) $2H^{-} \longrightarrow H_2 + 2e^{-}$ at anode.

50. (a) In electrolysis of aqueous NaCl, H_2O is reduced at cathode producing HO^{-}.

51. (c) 1.0 F brings about discharge of 1.0 gram equivalent of any ion. However moles of electrons required for discharge of a metal ions is equal to valency of metal ions.

52. (d) H_2 gas is evolved at cathode.

53. (c) Cu^{2+} is reduced completely making solution colourless from initially blue coloured.

54. (c) In case of strong electrolytes increase in conductance on dilution is due to decrease in electrostatic attraction between oppositely charged ions.

55. (a) It is a concentration cell. Hence

$$E = 0 - \frac{0.059}{2} \log \frac{C_1}{C_2} > 0 \text{ if } C_1 < C_2$$

56. (a) K^{+} and Cl^{-} have comparable size hence comparable ionic mobility, a requirement of salt bridge.

57. (d) Emf will remain unchanged.

58. (d) Cell constant $= \frac{l}{a}$; a property of equipment.

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59. (a) Electron transfer occur through internal circuit (electrolyte) and no current flow.

Reading 1 Electrons flow from X to Y, therefore $E^\circ(X) < E^\circ(Y)$. Also electrons flow from X to SHE, $E^\circ(X) > 0 \Rightarrow E^\circ_2 = -0.25$ V, $E^\circ_1 = +0.34$ V.

60. (d) $E^\circ_1 = 0$, $E^\circ_2 > 0$

61. (c) The cell reaction will be $X + Y^{+3} \longrightarrow X^{2+} + Y$

$$E = E^\circ - \frac{0.059}{2}\log\frac{[X^{2+}]}{[Y^{3+}]} = 0.59 - \frac{0.059}{2}\log\frac{0.1}{1} = 0.62 \text{ V}$$

62. (b) $Y^{3+} + e^- \longrightarrow Y^{+2}$ $E^\circ = 0.15$V

$Y^{+2} + 2e^- \longrightarrow Y$ $E^\circ = 0.34$ V

$Y^{3+} + e^- \longrightarrow Y$ $E^\circ = \dfrac{0.34 \times 2 - 0.15}{1} = 0.53$ V

63. (c) $Y^{3+} + e \longrightarrow Y$ $E^\circ = 0.53$V

$YI + e \longrightarrow Y + I^-$ $E^\circ = -0.27$ V

$YI \rightleftharpoons Y^{+3} + I^-$ $E^\circ = -0.80$ V

$\log K_{sp} = -\dfrac{0.80}{0.059} = -13.6 \Rightarrow K_{sp} = 2.7 \times 10^{-14}$

Reading 2 Left hand electrode is at higher reduction potential, acts as cathode and right hand electrode acts as anode.

64. (b) Electrons flow from right to left electrode.

65. (c) $E^\circ = 0.77 - 0.34 = 0.43$

$E = 0.43 - 0.06 \log [H^+]^2$ (all other species are at 1 M)

$= 0.43 - 0.06 \log 10^{-4} = 0.67$ V

66. (b) $W_{max} = -\Delta G^\circ = nE^\circ.F = 0.43 \times 96500 = 41.495$ kJ

67. (c) Ni is at lower reduction potential, acts as anode, hence

$$Ni \longrightarrow Ni^{2+} + 2e^-$$

68. (c) As Ni^{2+} is formed in anode chamber, negative ions flow from salt bridge to anode chamber to maintain electrical neutrality.

69. (d) X is more electropositive than Cu but less electropositive than Zn. Hence E° : Zn < X < Cu.

70. (d) E° of Y is greater than Zn but less than Cu. No comparison can be drawn between E° of X and Y.

71. (b)

$$E^\circ_{Ga^{3+}/Ga} < E^\circ_{Cd^{2+}/Cd}$$

$$E^\circ_{Cd^{2+}/Cd} < E^\circ_{In^{3+}/In}$$

$\Rightarrow$ Reducing power is Ga > Cd > In

Overall order of reducing power is Ti > Al > Ga > Cd > In.

72. (a) 0.06 mol Ga = 0.18 Equivalent of Ga^{3+} = 0.18 Equivalent Cd^{2+} = 0.09 mol Cd^{2+}

73. (d) Half-cells with $E^\circ > 0$ can oxidise H^+ to H_2.

74. (d) Metal with higher E° will be reduced first. Metal with negative E°(Mg) will not be deposited.

75. (b) Half cells with $E^\circ > +0.54$ V will be able to oxidise I^- to I_2.

76. (c) $[X^{2+}]$ will increase and $[Ag^+]$ will decrease.

77. (d) Ag is cathode hence Ag^+ will be deposited at Ag electrode.

78. (b) X^{2+}/X will become cathode (higher E° than -0.76 V) and Zn^{2+}/Zn will be anode.

79. (c) $E = 1.05 - \dfrac{0.06}{2}\log\dfrac{[X^{2+}]}{[Ag^+]^2} = 1.05 - 0.03\log\dfrac{(0.1)}{0.01} = 1.02$ V

80. (b) $E^\circ = -0.45 + 1.18 = 0.73$ V

$$E = 0.73 - \frac{0.06}{2}\log\frac{[Mn^{2+}]}{[Fe^{2+}]} = 0.73 \text{ V}$$

81. (b) E° of Fe^{2+}/Fe is smaller, Fe will be oxidised.

82. (b) Eq of Cu $= \dfrac{0.95}{32}$ = Eq of Cr

$\Rightarrow$ Mass of Cr oxidised $= \dfrac{0.95}{32} \times \dfrac{52}{3} = 0.52$ g

83. (d) $E^\circ(Cr - Fe) = -0.45 + 0.74 = 0.29$ V (minimum)

84. (c) At anode : $Pb \longrightarrow Pb^{2+} + 2e^-$ $E^\circ = -0.13$ V

At cathode : $Au^{3+} + 3e^- \longrightarrow Au$ $E^\circ = +1.50$ V

overall : $3Pb + 2Au^{3+} \longrightarrow 3Pb^{2+} + 2Au$ $E^\circ = 1.37$ V

85. (c) Total number of positive ions in system will increase as $3Pb^{2+}$ are produced for every two Au^{3+} deposited.

86. (d) Electrons flow from Pb to Au *via* external circuit.

87. (a) Cu^{2+} will be deposited at cathode, hence mass of Cu electrode will increase.

87. (d) $E^\circ = 0.34 - (-0.76) = 1.10$ V

89. (b) Eq of Zn oxidised $= \dfrac{5.64 \times 2}{65}$ = Eq of Cu^{2+} reduced.

$\Rightarrow$ Mass of Cu deposited $= \dfrac{5.64 \times 2}{65} \times \dfrac{63.5}{2} = 5.5$ g

90. (c) $E = E^\circ = 0.34 - (-0.74) = 1.08$ V

91. (c) Cu can't reduce Cr^{+3}.

92. (d) Eq of Fe oxidised $= \dfrac{5.58 \times 2}{56}$ = Eq of Cu^{2+} reduced.

$\Rightarrow$ mass of Cu formed $= \dfrac{5.58 \times 2}{56} \times \dfrac{63.5}{2} = 6.33$ g

93. (b) When electrodes with most negative and most positive E° are connected, maximum voltage would be produced.

94. (a) $E = E^\circ = 0.80 - (-0.13) = 0.93$ V

95. (c) Eq. of Pb oxidised $= \dfrac{2.07 \times 2}{207}$ = Eq of Ag^+ reduced.

$\Rightarrow$ Mass of Ag formed $= \dfrac{2.07 \times 2}{207} \times 108 = 2.16$ g

96. (a) $E = E^\circ = -0.13 - (-0.25) = 0.12$ V

97. (b) Pb can't reduce Ni^{2+}.

98. (d) 0.10 Eq of Ni will be oxidised to Ni

$\Rightarrow$ Mass of Ni oxidised $= 0.1 \times \dfrac{60}{2} = 3$ g

99. (b) Pb can reduce Ag^+ and Ni can reduce Pb^{2+}.

100. (d) Water will be oxidised before Ag start oxidising.

Reading 14

D is more electropositive than A and C i.e. $E^\circ_{D^{2+}/D}$ is more negative than the same of A and C.

Also B is more electropositive than D and E.

$E^\circ_{C^{+2}/C}$ is most positive.

101. (a) $E^\circ_{A^{+2}/A} < E^\circ_{C^{2+}/C}$ therefore A will displace C^{2+}.

102. (b) $C > A > E > D > B$ explained above.

103. (c) A will displace C^{+2} from solution.

104. (c) 1.0 equivalents of A to E will constant of $\frac{1}{2}$ moles of each A to D but $\frac{1}{3}$ mol of E.

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105. $\alpha = \frac{\Lambda^c}{\Lambda^\infty} = \frac{10}{200} = \frac{1}{20}$

$\Rightarrow [H^+] = C\alpha = 0.2 \times \frac{1}{20} = \frac{1}{100}$

$\Rightarrow pH = -\log \frac{1}{100} = 2$

106. Equivalent weight of water $= \frac{18}{2} = 9$

Eq of H_2O needs to be electrolysed $= \frac{72}{9} = 8$

107. Number of Faraday's $= \frac{8 \times 10^{-3} \times 60}{96000} = 5 \times 10^{-6}$

$=$ Eq of HO^- formed

$\Rightarrow [HO^-] = 5 \times 10^{-6} \times \frac{1000}{500} = 10^{-5}$ M

pOH $= 5$, pH $= 9$

108. No of Eq. of Na $= \frac{115}{23} = 5 =$ No of Faraday's.

109. $E = 0.3175 = 0.76 - \frac{0.06}{2} \log \frac{[Zn^{2+}]}{[H^+]^2}$

$\Rightarrow \log \frac{(0.1)}{[H^+]^2} = \frac{0.76 - 0.3175}{0.03} = 14.75$

$\Rightarrow \log (0.1) + 2 \log \frac{1}{[H^+]} = 14.75$

$\Rightarrow pH = \frac{14.75 + 1}{2} = 7.88 \approx 8$

110. Number of Faraday's $= \frac{1.25 \times 212 \times 60}{96000} = 0.165$

$\Rightarrow$ 0.16 mol of HPO_4^- will be converted into $H_2PO_4^-$ because 0.16 mol H^+ will be produced at anode.

$\Rightarrow pH = pK_a + \log \frac{(1 - 0.16)}{(1 + 0.16)} = 7.1 - 0.1 = 7$

111. Eq of $I_r = \frac{0.072\, n}{192} = \frac{0.01 \times 3 \times 3600}{96000}$

$\Rightarrow n = 3$

112. Eq of Cl_2 formed $= \frac{5 \times 200 \times 60}{96000} = 0.625$

Vol of Cl_2 at STP $= 0.625 \times 11.2 = 7$ L

(1 eq of Cl_2 at STP $= 11.2$ L)

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