

Dr. Suma Rao.

2011  
WEEK-26  
18/10/21

loss of  $e^- \rightarrow$  oxidation  
gain of  $e^- \rightarrow$  reduction

$$\Delta G = -nFE$$

FRIDAY  
DAY (175-190)

24

## Chemistry Ch-1 Electrochemistry [Notes]

WORK TO DO

**Electrochemistry** = Electrochemistry is a branch of chemistry which deals with the properties and behaviour of electrolytes in solution and inter conversion of chemical and electrical energies.

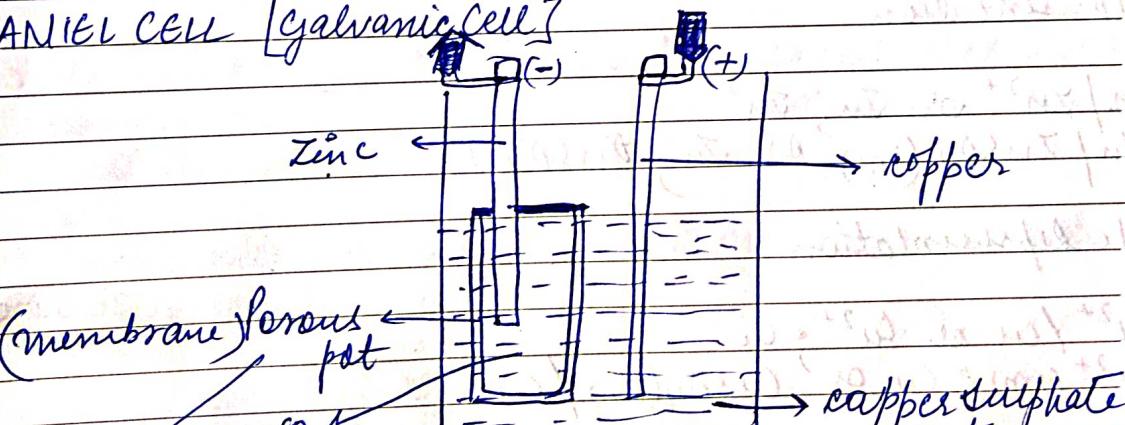
An electrochemical cell can be defined as a single arrangement of two electrodes in one or two electrolytes which converts chemical energy into electrical energy, or electrical energy into chemical energy.

APPOINTMENTS

It can be classified into two types

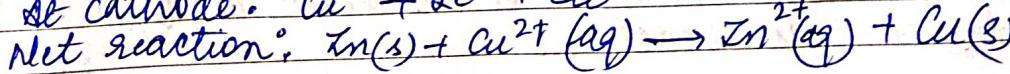
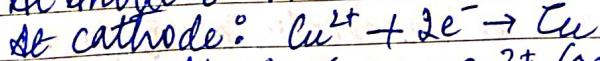
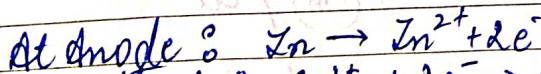
- Galvanic cells  $\rightarrow$  chem  $\rightarrow$  elec
- Electrolytic cells  $\rightarrow$  elec  $\rightarrow$  chem

DANIEL CELL [Galvanic Cell]



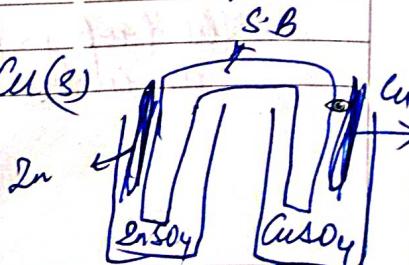
(membrane) porous pot  
2 electrolytes  
are in contact  
with porous pot

The liquid junction potential can be reduced from about 1 to 2 mV by using salt bridge.



JUNE		2011				JULY		2011			
W.	S.	1	2	3	4	5	6	1	2	3	4
23		24	25	26	27	28	29	30	31	1	2
5	6	7	8	9	10	11	12	13	14	15	16
12	13	14	15	16	17	18	19	20	21	22	23
19	20	21	22	23	24	25	26	27	28	29	30
26	27	28	29	30							

$$\text{Emf} = 1.1 \text{ V.}$$



25

SATURDAY  
DAY (176-189)

WORK TO DO

## Galvanic Cell

- (1) Negative anodic part  
Positive cathodic
- (2) Electrochemical reaction  
is spontaneous
- (3) Produces electrical energy

APPOINTMENTS  
 09      Used as portable source of  
 10      electric energy.

## Electrolytic cell

Positive anode  
Negative cathode

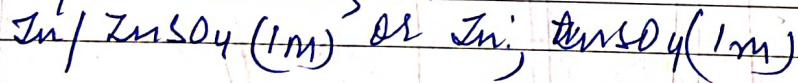
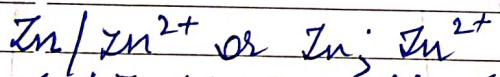
It is non spontaneous  
It is forced

Consumes electrical energy

Used for several applications  
such as electroplating

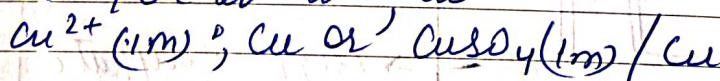
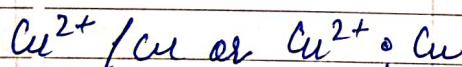
## Representation of Galvanic Cell:

\* Anode representation

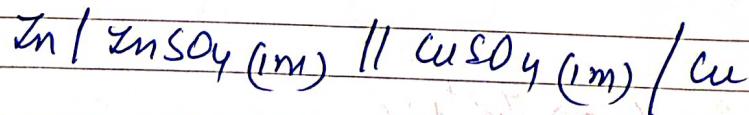


PHONES

\* Cathode representation:



\* Cell Representation:



The drop in potential energy is seen as electrical energy. This is an indirect redox reaction.

26 Sunday

APRIL 2011							MAY 2011							
Wk.	S	M	T	W	T	F	S	Wk.	S	M	T	W	T	F
14	3	4	5	6	7	8	9	19	1	2	3	4	5	6
15								20	8	9	10	11	12	13
16	10	11	12	13	14	15	16	21	15	16	17	18	19	20
17	17	18	19	20	21	22	23	22	22	23	24	25	26	27
18	24	25	26	27	28	29	30	23	29	30	31			

EMF of a Cell

WORK TO DO

- The difference of Potential, which causes a current to flow from the Electrode of higher potential to one of lower potential.

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}} \rightarrow [\pm \mathcal{E} - \mathcal{I}R]$$

- The  $\mathcal{E}_{\text{cell}}$  depends upon:

- \* The nature of the electrodes
- \* Temperature

- \* Concentration of the electrolyte solutions

APPOINTMENTS

- The standard emf of a cell ( $\mathcal{E}^{\circ}_{\text{cell}}$ ) is defined as the emf of a cell when the reactants & products of the cell reaction are at Unit Concentration or unit activity, at 298 K and at 1 atm.

- The EMF of cannot be measured accurately using a Voltmeter:

- \* As some current is drawn from the cell that alters the concentration of the electrolytes and thereby causes a change in the emf of the cell.

- \* As a part of the emf is used to overcome the internal resistance of the cell.

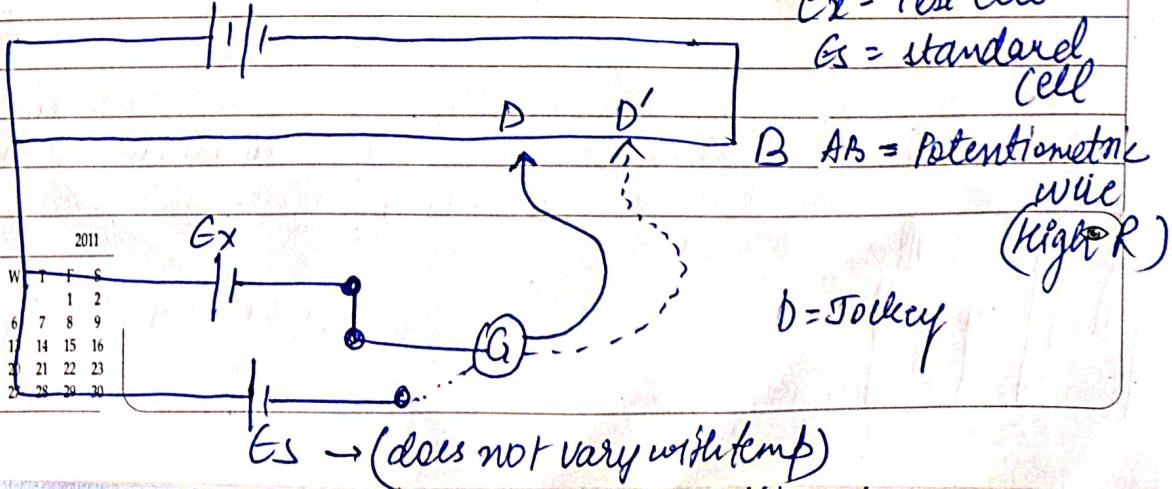
PHONES

Measurement of EMF

## POCIGRE NDORFF's COMPENSATION METHOD.

$A'$  = Balancing point A  
indicates 0 deflection

JUNE 2011						JULY 2011											
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	F	S			
23		1	2	3	4			27	31		1	2					
24	5	6	7	8	9	10	11	28	3	4	5	6	7	8	9		
25	12	13	14	15	16	17	18	29	10	11	12	13	14	15	16		
26	19	20	21	22	23	24	25	30	17	18	19	20	21	22	23		
27	26	27	28	29	30			31	24	25	26	27	28	29	30		



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# TUESDAY

**JESDAY** (179-186) Find the null point by sliding the jockey on the potentiometric wire. This length  $AB$  is called balancing length. It is same for standard cell. Its balancing length is  $AO'$ . June

## WORK TO DO

- The emf of the cell  $E_x$  is proportional to length  $AD$

$E_x \propto AD$

$$E_S \propto A D'$$

$$\frac{Ex}{Es} = \frac{AD}{AD'}$$

## APPOINTMENTS

$$Gx = \frac{AD}{AD'} x \in S$$

Principle: In this method, the emf to be measured is opposed by the emf of another cell or battery until the two emfs become equal and there is no net flow of current in the circuit.

# STANDARD CELL

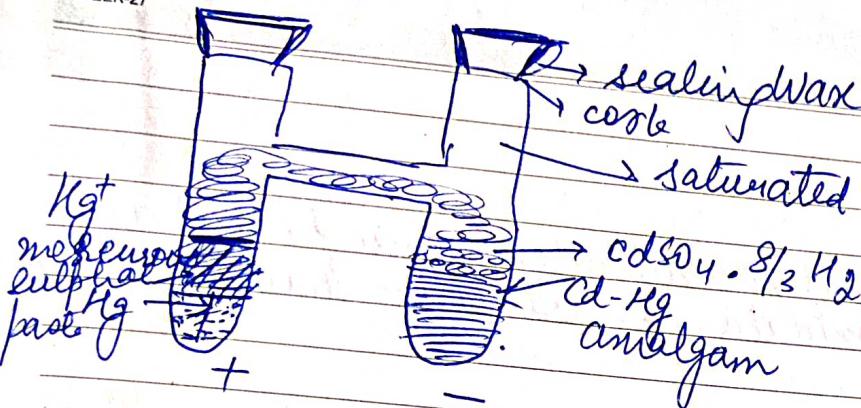
- It is one which is capable of giving constant and reproducible emf.
  - It has a negligible temperature coefficient of the emf

Eg : Weston Cadmium Cell. The emf of the cell is 1.0183 V at 293 K and 1.018 V at 298 K

$$\text{Temp. Coefficient of emf} = -4 \times 10^{-5} \text{ V/K}$$

2011

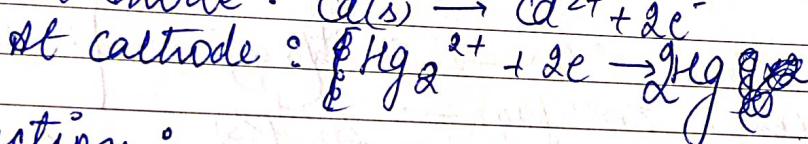
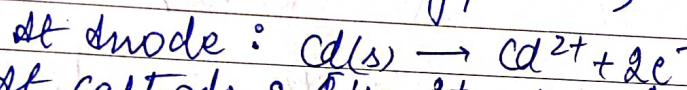
WEEK-27

WEDNESDAY  
DAY (180-185) 29

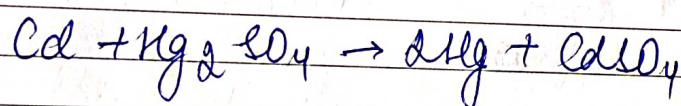
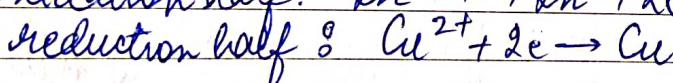
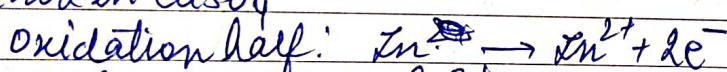
WORK TO DO

(By conversion anode left cathode right)

out of syllabus

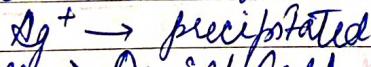
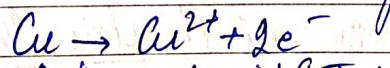
Cell representation:  $Cd - Hg / Cd^{2+} \text{; } Hg_2 SO_4 / Hg$ 

Cell reaction:

NOTEIn rod in  $CuSO_4$ 

$$\left. \begin{array}{l} 4H = -ve \\ \text{(Exothermic)} \end{array} \right\}$$

PHONES

 $Cu$  in  $ZnSO_4 \rightarrow$  No change due to reactivity series $Cu$  in  $SgNO_3 \rightarrow$   $Cu$  will dissolve and start giving blue colour to solutionElectrochemical cell  $\rightarrow$  Daniel CellChem  $\rightarrow$  Electrical  $\rightarrow$  Galvanic CellElect  $\rightarrow$  Chem  $\rightarrow$  Electrolytic Cell

JUNE 2011							JULY 2011								
W.	S	M	T	W	T	F	S	W.	S	M	T	W	T	F	S
23				1	2	3	4	27	31		1	2			
24	5	6	7	8	9	10	11	28	3	4	5	6	7		
25	12	13	14	15	16	17	18	29	10	11	12	13	14	15	16
26	19	20	21	22	23	24	25	30	17	18	19	20	21	22	23
27	26	27	28	29	30			31	24	25	26	27	28	29	30

$$\Delta G = -nFE$$

$$\text{EMF} = (-ve) \quad \Delta G = (+ve), \text{ Non-spontaneous}$$

$$\text{EMF} = (+ve) \quad \Delta G = (-ve) \quad \checkmark$$

Anode  $\rightarrow$  oxidationCathode  $\rightarrow$  reduction

$$E_{cell} = \text{Cathode} - \text{Anode}$$

$$0.34 - (-0.76)$$

Zn

30

THURSDAY  
DAY (181-184)Jun/Jul  
WEEK-27

WORK TO DO

## Single Electrode Potential.

A single electrode or half cell develops a definite electric potential due to the spontaneous oxidation or reduction half reaction occurring at it.

[Potential arises at interface of electrode and electrolyte]  
 → tendency to undergo oxid or Red.

+ Origin of single electrode potential.

APPOINTMENTS

09 • Consider  $\text{Zn}(s)/\text{ZnSO}_4$

(much faster)

[oxidation more predominant]

10

11 fast  $\leftarrow$  Anodic process :  $\text{Zn}^{2+}(s) \rightarrow \text{Zn}^{2+}(aq)$ 

12 initial

Cathodic process :  $\text{Zn}^{2+}(aq) \rightarrow \text{Zn}^{2+}(s)$ [2 e<sup>-</sup> are left on rod]

always.

causes acc of Zn on rod  
also Zn is being formed.

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14

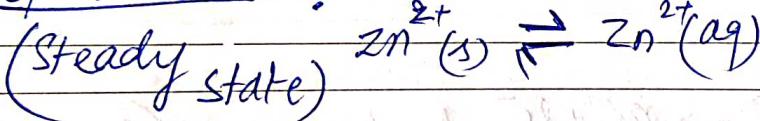
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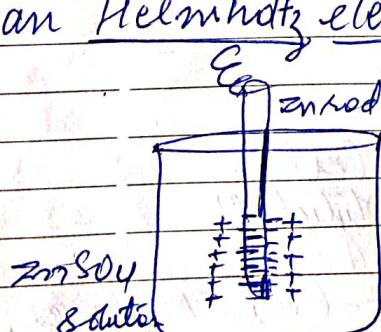
At Equilibrium :

Cathodic process is  
Creating deficiency  
of electrons

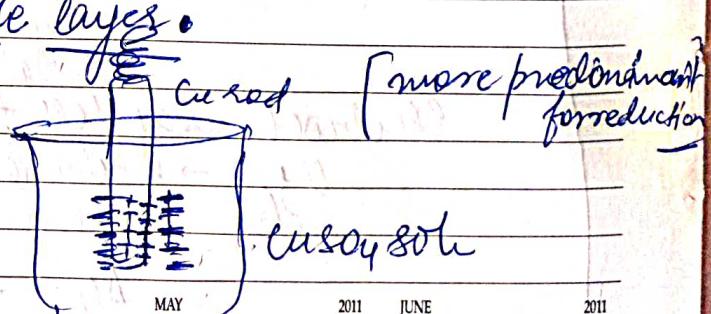
PHONES

Metal has net negative charge and solution has equal positive charge leading to formation of an Helmholtz electrical double layer.

will favour deposition process



The zinc moves into solution leaving behind e<sup>-</sup> making it electronrich



Copper ions get deposited as Cu on the cathode  
 Copper leaving behind free SO4<sup>2-</sup>  
 in negatively charged sulphate ions makes the electrode e<sup>-</sup> poor.

MAY JUNE 2011

Wk S M T W T F S Wk S M T W T F S

20 8 9 10 11 12 13 14 24 5 6 7 8 9 10 11

21 9 10 11 12 13 14 15 25 6 7 8 9 10 11

22 10 11 12 13 14 15 16 26 7 8 9 10 11 12

23 11 12 13 14 15 16 17 27 8 9 10 11 12 13

24 12 13 14 15 16 17 18 28 9 10 11 12 13 14

25 13 14 15 16 17 18 19 29 10 11 12 13 14 15

26 14 15 16 17 18 19 20 30 11 12 13 14 15 16

27 15 16 17 18 19 20 21 1 12 13 14 15 16 17

28 16 17 18 19 20 21 22 2 13 14 15 16 17 18

29 17 18 19 20 21 22 23 3 14 15 16 17 18 19

30 18 19 20 21 22 23 24 4 15 16 17 18 19 20

2011  
WEEK-27

By convention → Electrode Potential = Reduction E°  
FRIDAY  
DAY (182-183)

- \* layer on metal is thin layer → 0.9 nanometre approx ( $\times 10^{-9}$ ) WORK TO DO
- \* on solution side is thicker → 30 nanometer approx.

$$E_m \approx E_{\text{at}} \text{ at } 82^\circ \text{ L}$$

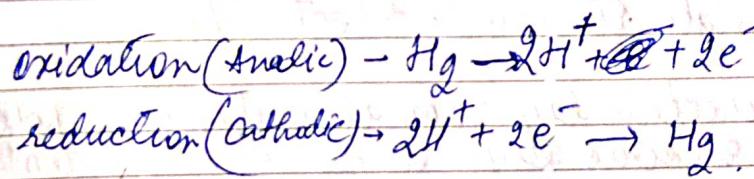
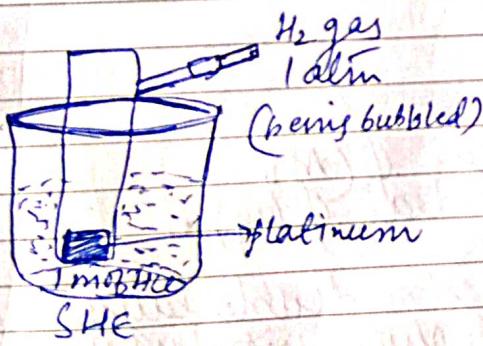
Electrode potential diff between electrical double layer on electrode-electrolyte interface is the single electrode potential

APPOINTMENTS

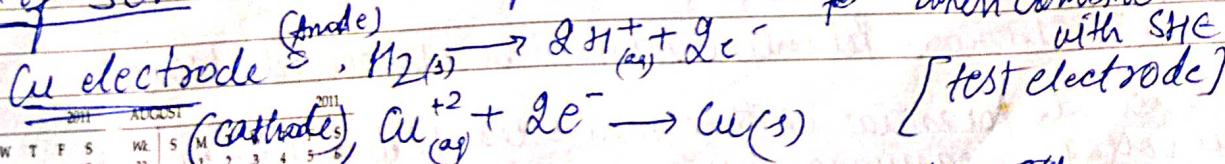
## Measurement of SEP :

- It is impossible to determine the absolute half cell potential.
- We can only measure the difference in potential between two electrode potentiometrically, by combining them to form a complete cell.

Reference electrode = SHE [standard hydrogen electrode] = 0 [SEP]



Sign of SEP : electrode potential is (+) → when there is reduction  
(Anode)  $\text{H}_2(s) \rightarrow 2\text{H}^+ + 2\text{e}^-$  when combined with SHE



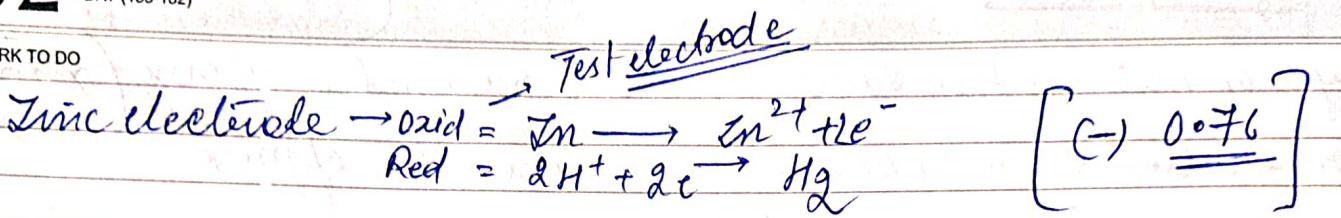
(+ 0.34)

JULY							AUGUST						
Wk.	S	M	T	W	T	F	S	Wk.	S	M	T	W	T
27	31			1	2			32	2	3	4	5	6
28	3	4	5	6	7	8	9	33	7	8	9	10	11
29	10	11	12	13	14	15	16	34	14	15	16	17	18
30	17	18	19	20	21	22	23	35	21	22	23	24	25
31	24	25	26	27	28	29	30	36	28	29	30	31	

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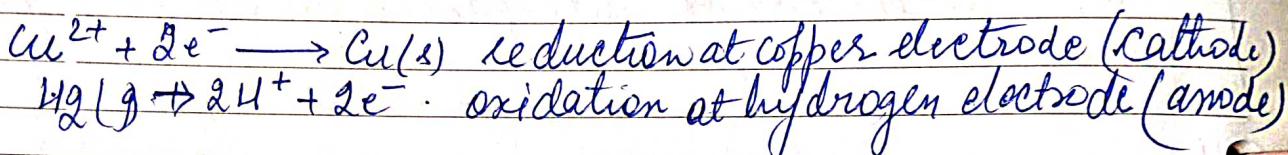
SATURDAY  
DAY (183-182)

WORK TO DO



- When an electrode is coupled with SHE, if reduction occurs then EP is given +ve sign.

e.g. → Copper electrode + SHE



APPOINTMENTS

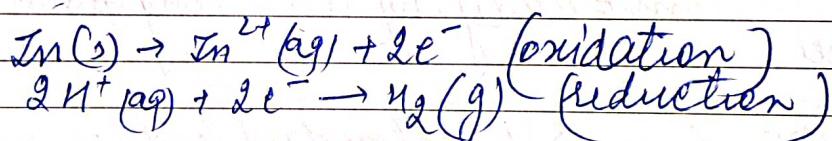
09  $E^\circ = + 0.34$  volt.

10

- 11 When an electrode is coupled with a SHE, if oxidation occurs then EP is given a -ve sign.

13 e.g. → Zinc electrode + SHE

14



17

18  $E^\circ = -0.76$  volt.

PHONES

## Single Electrode Electrode

03 Sunday

Electric layer on the metal has a potential  $\phi(\text{M})$ :

Electric layer on the solution has a potential  $\phi(\text{aq})$ .

- ✓ Electric Potential difference between the electric double layer existing across the electrode / electrolyte interface of a single electrode or half cell.

Absolute Electrode Potential cannot be measured. Why?

Electrode Potential can't be measured with one device all voltage measuring devices measure only the difference in potential.

MAY							JUNE								
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	T	F	S
1	8	9	10	11	12	13	14	23	1	2	3	4			
2	2	3	4	5	6	7			5	6	7	8	9	10	11
3	1	14	15	16	17	18			13	14	15	16	17	18	
4	15	16	17	18	19	20			26	27	28	29	30		
5	22	23	24	25	26	27	28	27	26	27	28	29	30		
6	29	30	31					27	26	27	28	29	30		

2011

WEEK-37

Voltmeter has 2 knobs to measure the potential of an electrode.

FRIDAY

09

One contact of an voltmeter is connected to the test electrode.

DAY 12 (113)

The other contact from the voltmeter must then be brought into electrical contact with the solution in the electrode compartment via another conductor.

WORK TO DO

So this second contact inevitably involves solid / solution interphase. This acts as a second half cell at which chemical change must occur if current is to flow and potential is to be measured.

So, a potential is associated with this second reactions.

## Liquid Junction Potential

Difference between the electric potentials developed in the two solutions across their interface.

APPOINTMENTS

09

$$\mathcal{E}_j = \phi_{\text{solution}(R)} - \phi_{\text{solution}(L)}$$

e.g.: contact between two different electrolytes ( $\text{In-SO}_4/\text{Cu-SO}_4$ )

$\text{Ce}^{2+}$  is more mobile, this lead to excess  $\text{Ce}^{2+}$  charge in zinc side.

$$\times \left[ E_{ljp} = (t_a - t_c) \frac{RT}{F} \log \left( \frac{a_2}{a_1} \right) \right]$$

transference number  
of anion ( $t_a$ )

17

18

PHONES

$$E_{ljp}(+) = t_a > t_c$$

$$E_{ljp}(-) = t_c > t_a$$

$$E_{ljp}(0) = t_c = t_a.$$

## Salt Bridge:

The liquid junction potential can be reduced to about 1-2 mV by joining the electrolyte compartments through a salt bridge.

SEPTEMBER		2011		OCTOBER		2011	
W	S	M	T	F	S	M	T
36	4	5	6	7	8	9	10
37	11	12	13	14	15	16	17
38	18	19	20	21	22	23	24
39	25	26	27	28	29	30	
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$\Rightarrow$  Why  $\text{KCl}$  is chosen - ?

because  $\text{K}^+$  and  $\text{Cl}^-$  have almost same mobility.

[Agar-Agar in hot solution of  $\text{KCl}$ ] [Saturated  $\text{KCl}$ ]

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SATURDAY  
DAY (253-112)September  
WEEK-37

WORK TO DO

- Function of salt Bridge  $\rightarrow$  (how can we eliminate  $J_p$ )
- It provides electrolytic contact between the two electrolyte solutions of a cell.
- It avoids or at least reduces junction potential in galvanic cells containing two electrolyte solutions in contact.

APPOINTMENTS

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10 Nernst Equation

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$$E = E^{\circ} - \frac{RT}{nF} \log \frac{1}{[m^{n+}]} \quad (7)$$

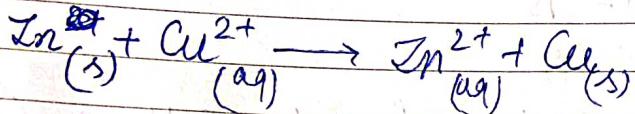
At 298 K.

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{1}{[m^{n+}]} \quad (8)$$

Single Electrode

For Daniell Cell

Half cell



$$K = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

[equation should be balanced]

APPOINTMENTS

## Energetics of Cell Reactions

Net electrical work performed by the cell reaction of a galvanic cell:

$\Delta G$  = change in free energy.

$\Delta H$  = enthalpy

$\Delta S$  = entropy

• ~~W~~  $W = QE \quad (1) \quad (E = \text{EMF})$   
 charge on 1 mole electrons  $\& F (96,500 \text{ C})$  coulombs

When  $n$  mole of  $e^-$  are involved in the cell reactions,  
 the charge on  $n$  mole of  $e^- = nF$

$$\vartheta = nF$$

Substituting for  $\vartheta$  in eq(1)

$$W = nFE \quad (2)$$

The cell does net work at the expense of  
 $(-\Delta G)$  accompanying

$$(-\Delta G) = nFE$$

OCTOBER 2011		(-) $\Delta G$	
EMBER	2011	Wk	S M T W T F S
S	1	40	30 31
M	2	41	1
T	3	42	2 3 4 5 6 7 8
W	4	43	9 10 11 12 13 14 15
T	5	44	16 17 18 19 20 21 22
F	6		23 24 25 26 27 28 29
S	7		30
8			
9			
10			
11			
12			
13			
14			
15			
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17			
18			
19			
20			
21			
22			
23			
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25			
26			
27			
28			
29			
30			

MONDAY  
DAY (255-110)

12

WORK TO DO

09

10

11

12

13

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15

16

17

18

PHONES

13

TUESDAY  
DAY (256-109)

September

WORK TO DO

$$\Delta G = -nFE$$

$$G = H - TS$$

Derivation  
Not in course

$$(U + PV) = TS$$

internal energy

differentiating L1  $dG = dU + PdV + VdP - TdS - SdT \quad \text{--- (1)}$

From second Law of Thermodynamics

$$\frac{dq}{T} = \frac{de}{T}$$

$$dq = Txds$$

APPOINTMENTS

09

10

11

12

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18

PHONES

$$dU + PdV = TdS \quad \text{--- (2)}$$

(2) in (1)

$$dG = dU + PdV + VdP - (dU + PdV) - SdT$$

$$dG = VdP - SdT \quad \text{--- (3)}$$

At constant Pressure  $dG = -SdT$

$$\frac{\Delta G_r}{\Delta T} = -S \quad \text{--- (4)}$$

For a finite change:

$$\int \Delta G_r / \Delta T \text{ at constant } \cancel{P} = -\Delta S$$

$$\Delta G_r = \Delta H - T\Delta S$$

$$\Delta H + T(-\Delta S)$$

eye  $\Delta G_r = \Delta H + T \left[ \frac{\delta(\Delta G_r)}{\delta T} \right]_P \quad \text{--- (5)}$

Gibbs Helmholtz equation

	JULY 2011						AUGUST 2011							
Wk.	S	M	T	W	T	F	S	Wk.	S	M	T	W	F	S
27	31					1	2	32	1	2	3	4	5	6
28	3	4	5	6	7	8	9	33	7	8	9	10	11	12
29	10	11	12	13	14	15	16	34	14	15	16	17	18	19
30	17	18	19	20	21	22	23	35	21	22	23	24	25	26
31	24	25	26	27	28	29	30	36	28	29	30	31		

2011

WEEK-50

**MONDAY**

05

Replace  $\Delta G$  with  $-\eta F E$

## WORK TO DO

$$-nFE = \Delta H + T \left[ 8 \cancel{\frac{(-nFE)}{(ST)_{\text{p}}}} \right] - 6$$

~~$$\Delta H = nF \left[ T \left( \frac{SE}{(S+T)p} \right) - E \right] - \star$$~~

$$\text{we know that } \left[ \frac{8(1G)}{8T} \right]_P = -1S$$

$$\Delta S = nF \left( \frac{\delta E}{\delta T} \right)_P \quad \star$$

## Decimals Numericals

## Redox & Potential

Q16 Calculate the Standard emf of a cell containing

$\text{Sn}^{2+}/\text{Sn}$  and  $\text{Br}_2/\text{Br}^-$  electrodes

$$\left[ \begin{array}{l} E^\circ(Sn^{2+}/Sn) = -0.14 V \\ E^\circ(Br_2/Br^-) = 1.08 V \end{array} \right]$$

Ans  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$   
Because reduction potential of  $E^\circ(\text{Br}_2/\text{Br}^-)$  is higher, it is cathodic

$$E_{cell}^\circ = 1.08 - (-0.14)$$

$$= \underline{1.22V}$$

DECEMBER						2011		JANUARY						2012	
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	T	F	S
49					1	2	3	01	1	2	3	4	5	6	7
50	4	5	6	7	8	9	10	02	8	9	10	11	12	13	14
51	11	12	13	14	15	16	17	03	15	16	17	18	19	20	21
52	18	19	20	21	22	23	24	04	22	23	24	25	26	27	28
53	25	26	27	28	29	30	31	05	29	30	31				

06

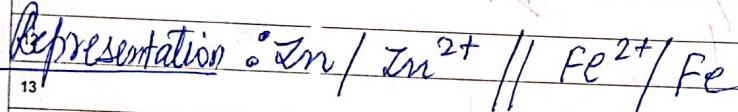
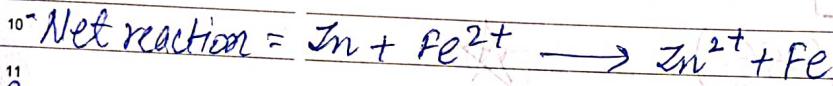
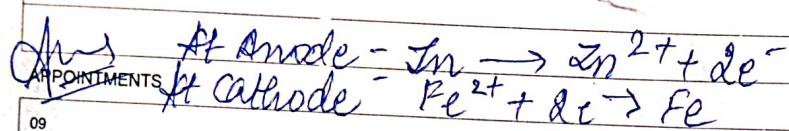
TUESDAY  
DAY (340-025)December  
WEEK-50

WORK TO DO

Q2 Write the electrode reaction, cell reaction and calculate Standard EMF at 298 K for the following Cell.

→ The Standard  $E^\circ$  values for In and Fe are  $-0.76\text{ V}$  and  $-0.44\text{ V}$  respectively.

Fe is at higher R.P. → cathode  
In is at lower → Anode.



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$\Rightarrow \cancel{-0.76} (-0.44) + 0.76.$$

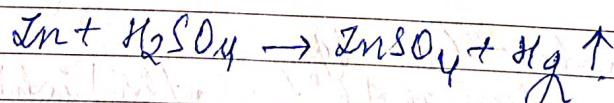
$$\Rightarrow \cancel{0.76} \cancel{(-0.44)} 0.32\text{ V}$$

$\boxed{-q \text{ } \text{NFE}}$   
spontaneous

$\boxed{\text{Zn has bbe } (-)}$   
 $\text{EMF} = (+).$

Q3 Using the Electrochemical series predict whether In and Ag would react with dil  $\text{H}_2\text{SO}_4$  or not.

Ans The reaction of In with dil  $\text{H}_2\text{SO}_4$  can be =



The galvanic Cell can be written as =  $\text{In}/\text{In}^{2+} \parallel \text{H}^+, \text{H}_2(\text{g})/\text{Pt}$

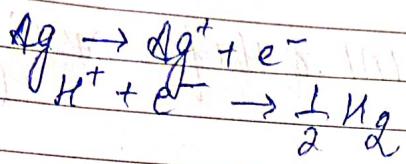
$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$= 0 - (-0.76) = 0.76\text{ V}$$

Since  $E_{\text{cell}}^\circ$  is (+ve), the reaction is feasible.

Wk.	OCTOBER 2011						NOVEMBER 2011					
	S	M	T	W	T	F	S	S	M	T	W	F
40	30	31					1					
41	2	3	4	5	6	7	8	45	1	2	3	4
42	9	10	11	12	13	14	15	46	6	7	8	9
43	16	17	18	19	20	21	22	47	13	14	15	16
44	23	24	25	26	27	28	29	48	20	21	22	23
								49	27	28	29	30

Now consider the reaction of Ag with dilute  $HgSO_4$



The cell will be  $Ag(Ag^+) \parallel H^+, H_2(g)/Pt$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= 0 - (0.80)$$

$$= \underline{\underline{-0.80\text{V}}}$$

$E_{cell}$  is negative, the reaction is not feasible.

### NERNST EQUATION

Q1) Using the electrochemical series, calculate the emf of the cell

$Fe(s) / Fe^{2+}(0.1\text{M}) \parallel Cd^{2+}(0.2\text{M}) / Cd$  at 298 K. Write the cell reactions

Ans: From the series we have,

$$E_{Cd^{2+}/Cd} = -0.40\text{V}$$

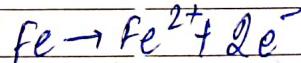
$$E_{Fe^{2+}/Fe} = -0.44\text{V}$$

$$\Rightarrow E_{cell} = E_{cathode} - E_{anode}$$

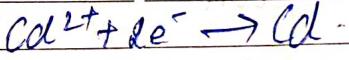
$$E_{cell} = -0.40 + 0.44$$

$$= \underline{\underline{0.04\text{V}}}$$

At Anode



At Cathode



Net:  $Fe + Cd^{2+} \rightarrow Fe^{2+} + Cd$ .

$$E_{cell} = E_{cell} - \frac{0.0592}{n} \log \left[ \frac{Cd^{2+}}{Fe^{2+}} \right]$$

DECEMBER 2011					JANUARY 2012					Wk.	S	M	T	W	F	S	
Wk.	S	M	T	W	F	S	Wk.	S	M	T	W	F	S	Wk.	S	M	
49	4	5	6	7	8	9	01	1	2	3	4	5	6	7	01	1	2
50	11	12	13	14	15	16	02	8	9	10	11	12	13	14	02	8	9
51	18	19	20	21	22	23	03	15	16	17	18	19	20	21	03	15	16
52	25	26	27	28	29	30	04	22	23	24	25	26	27	28	04	22	23
53							05	29	30	31					05	29	30

$$E_{cell} = 0.04 - \frac{0.0592}{2} \log \left[ \frac{0.1}{0.2} \right]$$

$$= 0.04 - \frac{0.0592}{2} \times 0.3010 \{ \log a - \log b \}$$

$$= 0.04 - \frac{0.0592}{2} \times 0.3010 \{ \log 1 - \log 2 \}$$

10

SATURDAY  
DAY (344-021)

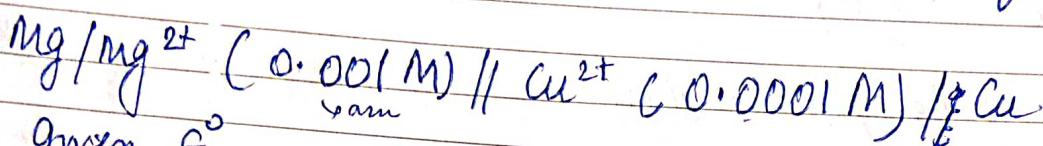
WORK TO DO

December

WEEK-50

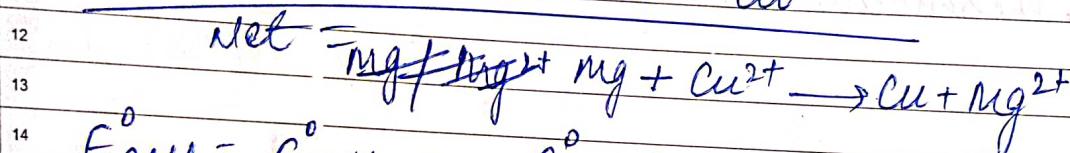
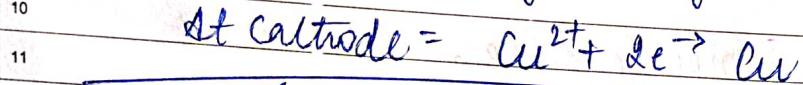
$$0.04 - [0.0296x - 0.3010] \\ 0.04 - [-0.00890] \\ = + 0.0488 \text{ V}$$

Q2 Write the cell reactions and calculate EMF of the following cell at 298 K.



Given  $E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ V}$  and  $E^\circ_{Mg^{2+}/Mg} = -2.37 \text{ V}$ .

APPOINTMENTS



$E^\circ_{\text{Cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$E^\circ_{\text{Cell}} = 0.34 - (-2.37)$

$E^\circ_{\text{Cell}} = 0.34 + 2.37$

= 2.71

PHONES

$E_{\text{Cell}} = 2.71 - \frac{0.0592}{2} \log \left[ \frac{0.0001}{0.001} \right] \left[ \frac{0.001}{0.0001} \right]$

11 Sunday

$E_{\text{Cell}} = 2.71 - 0.0296 \log \left[ \frac{0.0001}{0.001} \right] \left[ \frac{0.001}{0.0001} \right]$

$E_{\text{Cell}} = 2.71 - 0.0296 \log \left[ \frac{1}{10} \right] \left[ \frac{10}{1} \right]$

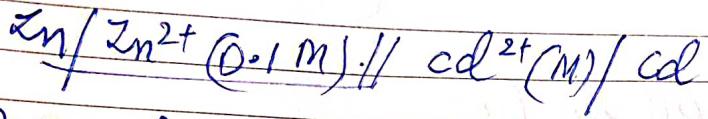
$E_{\text{Cell}} = 2.71 - 0.0296 \log \left[ \frac{1}{10} \right] 10$

$E_{\text{Cell}} = 2.71 - 0.0296 \log 1$

$E_{\text{Cell}} = 2.71 - 0.0296$   
~~0.0296~~  
 $= 2.6805 \text{ V}$

OCTOBER 2011							NOVEMBER 2011								
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	T	F	S
40	30	31					1	45	1	2	3	4	5		
41	2	3	4	5	6	7	8	46	6	7	8	9	10	11	12
42	9	10	11	12	13	14	15	47	13	14	15	16	17	18	19
43	16	17	18	19	20	21	22	48	20	21	22	23	24	25	26
44	23	24	25	26	27	28	29	49	27	28	29	30			

**B3.** Find the concentration of  $\text{Cd}^{2+}$  ions in the given electrochemical cell.

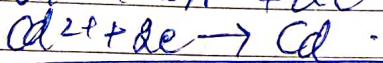
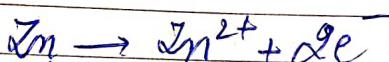


$$\text{Given } E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

$$E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$$

$$E_{\text{cell}} = 0.3305 \text{ V at } 298 \text{ K}$$

~~Ans~~



$$E_{\text{cell}} = -0.40 + 0.76 \\ = 0.36$$

$$E_{\text{cell}} = E_{\text{cell}} - \frac{0.0592}{2} \log \left[ \frac{\text{Zn}^{2+}}{\text{Cd}^{2+}} \right]$$

$$0.3305 = 0.36 - \frac{0.0592}{2} \log \left[ \frac{0.1}{x} \right]$$

$$0.3305 = 0.36 - 0.0296 \log \left[ \frac{0.1}{x} \right]$$

$$0.3305 - 0.36 = -0.0296 \log \left[ \frac{0.1}{x} \right]$$

$$-0.0295 = -0.0296 \log \left[ \frac{0.1}{x} \right]$$

$$1 \approx \frac{0.0295}{0.0296} = \log \left[ \frac{0.1}{x} \right]$$

$$\log \left[ \frac{0.1}{x} \right]$$

$$\log \frac{0.1}{x}$$

$$10 = \frac{0.1}{x}$$

$$x = \frac{0.1}{10} = 0.01 \text{ M}$$

SEPTEMBER							OCTOBER 2011								
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	T	F	S
36				1	2	3		40	30	31	1				
37	4	5	6	7	8	9	10	41	2	3	4	5	6	7	
38	11	12	13	14	15	16	17	42	9	10	11	12	13	14	15
39	18	19	20	21	22	23	24	43	16	17	18	19	20	21	22
40	25	26	27	28	29	30		44	23	24	25	26	27	28	29

APPOINTMENTS

09

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PHONES

27

TUESDAY  
DAY (270-095)September  
WEEK-40

WORK TO DO

Q4b Calculate EMF of the zinc - silver cell at  $25^\circ\text{C}$  when  $[\text{Zn}^{2+}] = 1.0\text{M}$  and  $[\text{Ag}^+] = 10\text{M}$

Write cell representation and cell reaction.

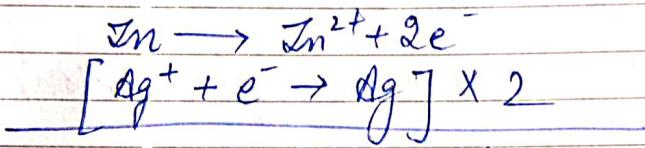
[Given  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{ V} \rightarrow (\text{low E.P.} \rightarrow \text{anode})$

$$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{ V} \text{ at } 25^\circ\text{C}$$

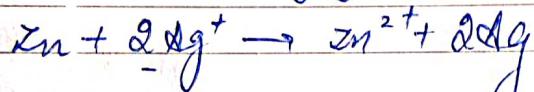
~~ANS~~

APPOINTMENTS

09

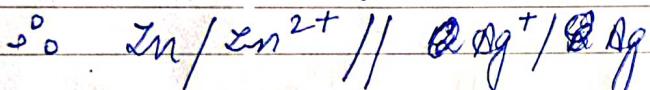


10



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14

$$E^\circ_{\text{cell}} = 0.80 - (-0.76)$$

15

$$= \underline{\underline{1.56\text{ V}}}$$

16

17

$$E^\circ_{\text{cell}} = 1.56 - 0.0592 \log \frac{1.0}{10^2}$$

18

PHONES

$$E^\circ_{\text{cell}} = 1.56 - 0.0296 \log \frac{1}{100}$$

$$\begin{aligned} E^\circ_{\text{cell}} &= 1.56 - 0.0296 \cancel{(-2)} \cancel{(-2)} \\ &= 1.56 - 0.026(-2) \\ &= 1.56 + 0.052 \\ &= \underline{\underline{1.6192\text{ V}}} \end{aligned}$$

JULY						AUGUST						2011		
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	F	S
27	31					1	2	32	1	2	3	4	5	6
28	3	4	5	6	7	8	9	33	7	8	9	10	11	12
29	10	11	12	13	14	15	16	34	14	15	16	17	18	19
30	17	18	19	20	21	22	23	35	21	22	23	24	25	26
31	24	25	26	27	28	29	30	36	28	29	30	31		

2011

WEEK-41

# Energetics of cell Reactions

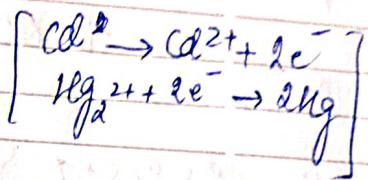
MONDAY 03  
DAY (276-069)

81) For a cell, EMF is 1.018 V at 298 K. Calculate  $\Delta G^\circ_f$  for the cell reaction at 293 K.

$$\underline{\text{Ans}} \quad \Delta G_r = -nFE$$

$$\Delta G = -\Delta F \times 1.018$$

$$= -1.964 \times 10^5 \text{ J}$$



Q2p Calculate the thermodynamic parameter ( $\Delta G$ ) for the reaction  
 $Zn + Fe_3O_4 \rightarrow ZnSO_4 + Fe$ .

Reduction Potentials of Zn and Fe = -0.76 and 0.44 V respectively.

$$\text{E}^\circ_{\text{cell}} = \frac{0.0592}{2} \log$$

$$\begin{aligned}
 \text{Ans} \\
 \cancel{\text{Emf}} &= \text{Cathode - Anode} \\
 &= -0.44 + 0.76 \\
 &\underline{\underline{0.32\text{V}}}
 \end{aligned}$$

$$\Delta U_2 = -nFE$$

$$= -2 \times 96500 \times 0.32$$

$$= 61,760 \text{ J}$$

EMF of Weston Cadmium cell is 1.0183 V at 293 K and 1.0181 V at 298 K. calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the cell reaction at 298 K

$$\Delta G_r = -nFE$$

$$\Delta G_2 = -2 \times 96500 \times 100181$$

$$= \underline{\underline{-196.493 \cdot 3}} \text{ J}$$

$$-196.5 \text{ kJ.}$$

$$\Delta H = mF[T \left( \frac{8E}{8T} \right)_p - E]$$

NOVEMBER 2011

OCTOBER					2011		NOVEMBER							
Wk.	S	M	T	W	T	F	S	Wk.	S	M	T	W	T	F
40	30	31					1	45	1	2	3	4		
41	2	3	4	5	6	7	8	46	6	7	8	9	10	11
42	9	10	11	12	13	14	15	47	13	14	15	16	17	18
43	16	17	18	19	20	21	22	48	20	21	22	23	24	25
44	23	24	25	26	27	28	29	49	27	28	29	30		

$\Delta G = \Delta H - T\Delta S$  October  
WEEK-41

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{1.0181 - 1.0183}{298 - 293} = \frac{-0.0002}{5}$$

$$T = 298 \text{ K} \quad = -0.00004 \text{ V/K}$$

$$\Delta H = 2 \times 96500 \left\{ [298 \times (-0.00004)] - 1.0181 \right\}$$

$$= -198.8 \text{ kJ}$$

APPOINTMENTS  $\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_p$

$$\Delta S = 2 \times 96500 \times \frac{-0.0002}{5}$$

$$= -7.72 \text{ J/K}$$

Q4 The EMF of the cell

is  $0.6753 \text{ V}$  and  $0.6915 \text{ V}$  at  $298 \text{ K}$  and  $273 \text{ K}$  respectively

Calculate  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of the cell reaction at  $298 \text{ K}$

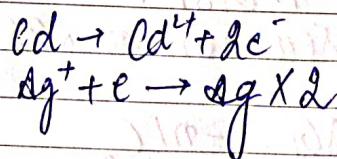
PHONES

Here  $n=2$ ,  $E = 0.6753 \text{ V}$  at  $298 \text{ K}$  and  $0.6915 \text{ V}$  at  $273 \text{ K}$

ans  $\Delta G = -nFE$

$$= -2 \times 96500 \times 0.6753$$

$$= -130275 \text{ J}$$



$$\Delta H = nF \left[ T \left( \frac{\partial E}{\partial T} \right)_p - E \right]$$

$$= 2 \times 96500 \left[ 298 \times \left( \frac{0.6753 - 0.6915}{298 - 273} \right) - 0.6753 \right]$$

$$= -167273 \text{ J}$$

$$\approx 193,000 \times \left[ 298 \left[ \frac{-0.0162}{25} \right] - 0.6753 \right]$$

$$193,000 \times (-298 \times 0.000648 - 0.6753)$$

AUGUST

2011

Wk	S	M	T	W	T	F	S
32		1	2	4	5	6	
33	7	8	9	10	11	12	13
34	14	15	16	17	18	19	20
35	21	22	23	24	25	26	27
36	28	29	30	31			

SEPTEMBER

2011

Wk	S	M	T	W	T	F	S
37	4	5	6	7			
38	11	12	13	14	15	16	17
39	18	19	20	21	22	23	24
40	25	26	27	28	29	30	

$$\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_p$$

$$= 193,000 \times -0.8667$$

$$= -125,451 \text{ J}$$

Classification of Electrodes 25  
 $193000 \left[ 2.98 \times 0.00086 \right] = 0.0573$   
 → gas electrodes (hydrogen electrode)  $= 193000 \left[ (-0.25628) - 0.0573 \right]$   
 → metal-metal insoluble salt (calomel electrode)  $= 193000 \left[ -0.19898 \right]$   
 → ion selective electrode (glass electrode)  $= -38403.14 \text{ J}$   
-160.37 kJ  
Gas Electrode.

- It consists of gas bubbling over an inert metal wire or foil immersed in a solution containing ions of the gas.
- Reference electrodes are these with reference to those, the electrode potential of any electrode can be measured.
- Standard electrode is the primary reference electrode, whose electrode potential at all temp is taken as zero arbitrarily.

SEPTEMBER 2011							OCTOBER 2011								
Wk	S	M	T	W	T	F	S	Wk	S	M	T	W	T	F	S
36				1	2	3		40	30	31		1			
37	4	5	6	7	8	9	10	41	2	3	4	5	6	7	8
38	11	12	13	14	15	16	17	42	9	10	11	12	13	14	15
39	18	19	20	21	22	23	24	43	16	17	18	19	20	21	22
40	25	26	27	28	29	30		44	23	24	25	26	27	28	29

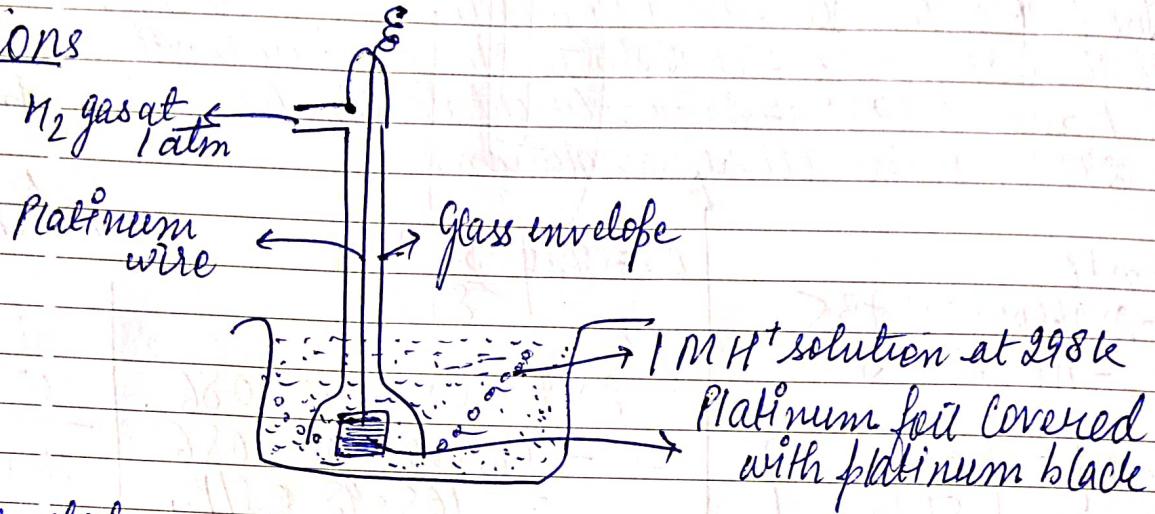
29

THURSDAY  
DAY (272-093)

September

WEEK-4

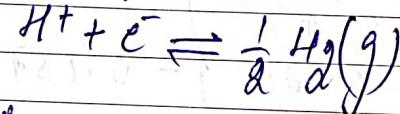
WORK TO DO

Constructions

APPOINTMENTS

Representation: Pt, H₂(g)/H<sup>+</sup>

09 • Electrode Reaction:

Forward - Reduction  
Reverse - Oxidation

- 10     12     13     14     15     16     17     18     19     20     21     22     23     24     25     26     27     28     29     30     31
- The electrode reaction is reversible as it can undergo either oxidation or reduction depending on the other half cell.
  - If the concentration of the H<sup>+</sup> ions is 1M, pressure of H<sub>2</sub> is 1 atm at 298 K, it is called as SHE

- 17     18     19     20     21     22     23     24     25     26     27     28     29     30     31
- The Pt electrode is made of a small square of foil (0.5 cm x 0.5 cm) which is platinumized (known as Pt black).

PHONES

- Hydrogen gas, at a pressure of 1 atm, is bubbled around the Pt electrode through a inlet provided in the outer glass tube.
- The platinum black serves as large surface area for the reaction to take place. It adsorbs the hydrogen gas and it also speeds up the equilibrium between the hydrogen gas and hydrogen ion.
- This redox reaction occurs at platinumized platinum electrode. Usage of such electrode is caused by several factors.
- Necessity to employ electrode with very large area. The greater the electrode area, the faster electrode kinetics.
- Necessity to use electrode material which can adsorb hydrogen at its interface. This factor also improves electrode kinetics.

Wk	JULY 2011					AUGUST 2011				
	S	M	T	W	F	S	S	M	T	F
27	31			1	2	32	1	2	3	4
28	3	4	5	6	7	8	9	10	11	12
29	10	11	12	13	14	15	16	17	18	19
30	17	18	19	20	21	22	23	24	25	26
31	24	25	26	27	28	29	30	31	28	29

Applications

- To determine electrode potential of other electrodes
- To determine pH of a solution.

The solution whose pH is to be determined is taken in a vessel, and pt electrode is dipped in it. A slow current of H<sub>2</sub> gas at 1 atm is bubbled through a solution. The electrode develops a definite potential depending on the H<sup>+</sup> ion conc. of the solution under test.

$$E = E^{\circ} - \frac{2 \cdot 303 RT}{nF} \log \frac{[H_2]/2}{[H^+]}$$

$$= 0 - 0.0592 \log \frac{1}{[H^+]} \quad [H_2] \text{ at } 1 \text{ atm} = 1 \\ = -0.0592 \text{ pH}$$

The above half-cell so formed is connected to S.H.E., the EMF of the cell is then determined potentiometrically. Since emf of the reference electrode is zero, the observed emf gives directly emf of half-cell containing the solution under test.

$$E_{\text{cell}} = E_C - E_A \\ = 0 - (-0.0592 \text{ pH})$$

$$E_{\text{cell}} = 0.0592 \text{ pH} \quad \text{OR} \quad \text{pH} = E_{\text{cell}} / 0.0592$$

Limitations

- Construction and working difficult
- Pt is susceptible for poisoning
- Cannot be used in the presence of oxidising agents.

METAL-METAL SALT ION ELECTRODE

These electrodes consist of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion.

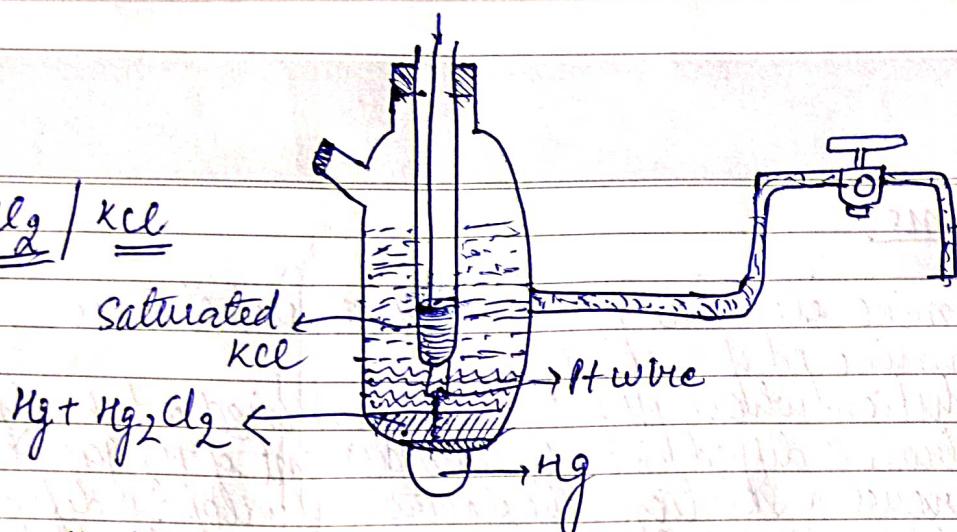
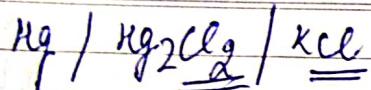
eg - Calomel electrode  
- Ag/AgCl electrode

SEPTEMBER						
Wk.	S	M	T	W	F	S
36	4	5	6	7	8	9
37				10	11	12
38	11	12	13	14	15	16
39	18	19	20	21	22	23
40	25	26	27	28	29	30

01

SATURDAY  
DAY (274-091)October  
WEEK-40

WORK TO DO



- Representation  $\text{Hg}; \text{Hg}_2\text{Cl}_2/\text{KCl}$

It can act as anode or cathode depending on the nature of the other electrode.

APPOINTMENTS

09

10

11

12

13

14

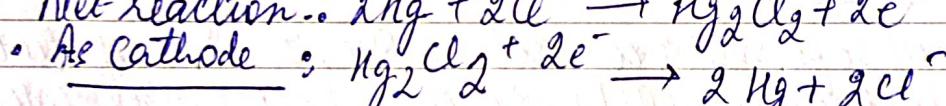
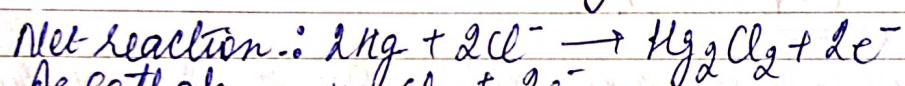
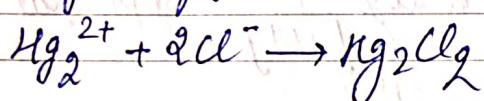
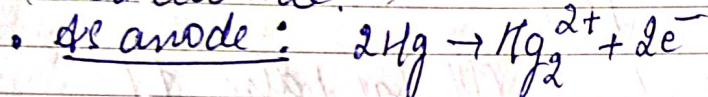
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16

17

18

PHONES



- Its electrode potential depends on the conc. of KCl.

conc of $\text{Cl}^-$	$E^\circ$
0.1 M	0.3335 V

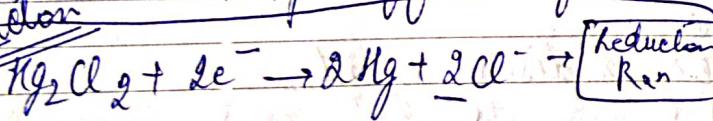
1.0 M	0.2810 V
Saturated	0.2422 V

$$E = E^\circ - \frac{2.303}{F} \log [\text{Cl}^-] \quad [E^\circ = 0.2677 \text{ V}]$$

With inc of temp. potential of Calomel electrode decreases.

Temp Coefficint of  $25^\circ\text{C}$  are 0.1 N KCl  $+ 0.06 \text{ mV}^\circ\text{C}$

1 N KCl  $+ 0.24 \text{ mV}^\circ\text{C}$   
Sat. KCl  $- 0.65 \text{ mV}^\circ\text{C}$

~~Reduction~~

$$E = E^\circ - \frac{2.303}{F} \log [\text{Cl}^-]^2$$

(2)  
2F

$\times \log \text{Cl}^-$

$\rightarrow Q$  Imp

Show dependence of Calomel electrode

$$\Rightarrow E = E^\circ - \frac{2.303}{F} \log [\text{Cl}^-]$$

AUGUST		SEPTEMBER				OCTOBER	
SUN	MON	TUE	WED	THU	FRI	SAT	SUN
32	1	3	4	5	6	7	8
33	7	8	9	10	11	12	13
34	14	15	16	17	18	19	20
35	21	22	23	24	25	26	27
36	28	29	30	31			
					37	4	5
					6	7	8
					9	10	11
					12	13	14
					15	16	17
					18	19	20
					21	22	23
					24	25	26
					27	28	29
					30		

## Applications

- (1) Since the electrode potential is a constant it can be used as a secondary reference electrode.
- (2) To determine electrode potential of other unknown electrodes.
- (3) To determine the pH of a solution