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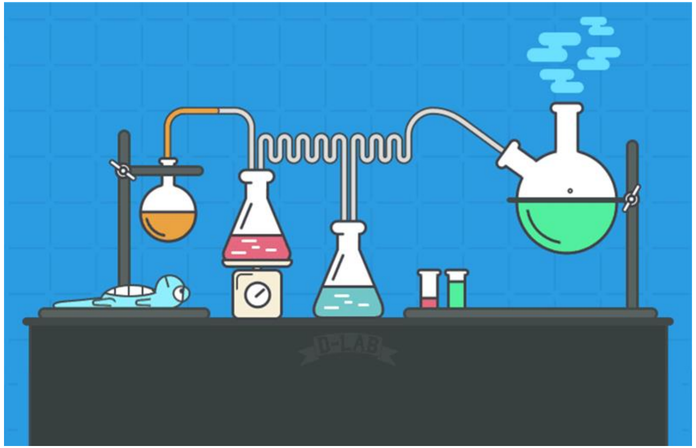
Paaras Thakur

- Mentored 1 lakh+ Students
- Content Partner in MHRD DIKSHA Project
- 10 Yrs Teaching experience

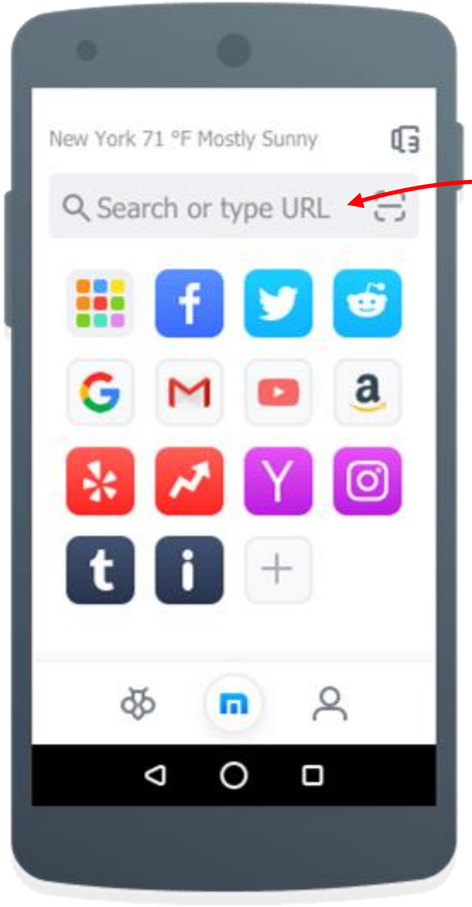
Electrochemistry

LECTURE 3



Topics we will learn today

- Measurement of electrode potential
- Standard Hydrogen electrode
- Electrochemical Series
- Using electrochemical Series



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Example

Which cell will measure standard electrode potential of copper electrode?

(i) ~~Pt (s) | H_2 (g,~~0.1 bar) | H^+ (aq., 1 M) || Cu^{2+}(aq., 1M) | Cu

~~(ii) Pt(s)~~ | H_2 (g, 1 bar) | H^+ (aq., 1 M) || Cu^{2+} (aq., 2 M) | Cu

(iii) Pt(s) | H_2 (g, 1 bar) | H^+ (aq., 1 M) || Cu^{2+} (aq., 1 M) | Cu

(iv) Pt(s) | H_2 (g, 1 bar) | H^+ (aq., 0.1 M) || Cu^{2+} (aq., 1 M) | Cu

Conc = 1 M

Pressure = 1 bar

Example

Which of the following statement is correct?

(i) E_{Cell} and $\Delta_r G$ of cell reaction both are extensive properties.

(ii) E_{Cell} and $\Delta_r G$ of cell reaction both are intensive properties.

(iii) E_{Cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.

(iv) E_{Cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

Example

A variable opposite external potential (E_{ext}) is applied to the cell $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$, of potential 1.1 V. When $E_{ext} < 1.1$ V and potential 1.2 V, respectively, electron flow from

(1) anode to cathode and cathode to anode.

(2) cathode to anode and anode to cathode.

(3) cathode to anode in both cases.

(4) anode to cathode in both cases.

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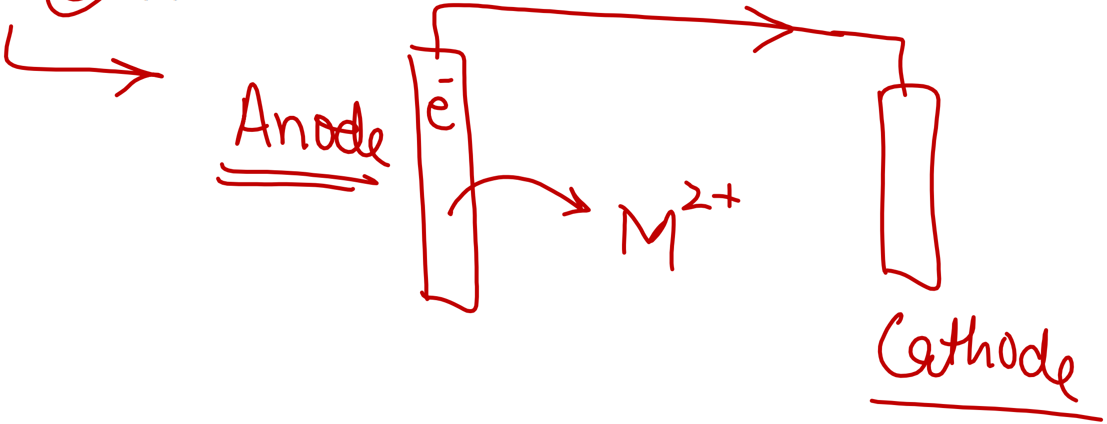
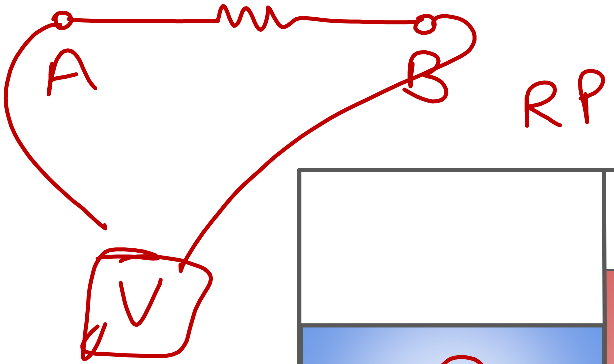
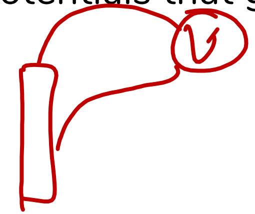


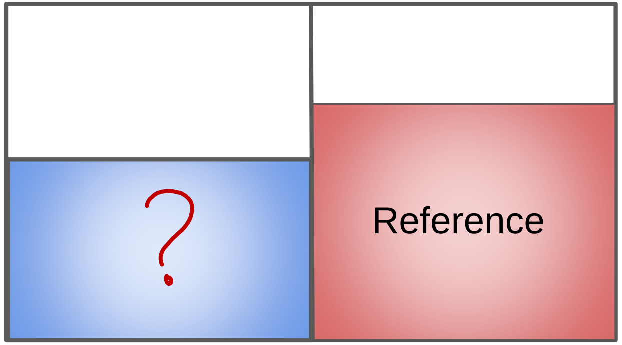
Measurement of electrode potential

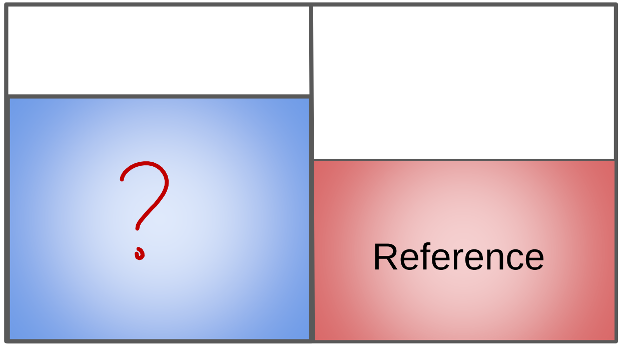
The potential of individual half-cell can't be measured. We can only measure the difference between two half-cell potentials that gives the E_{cell}.



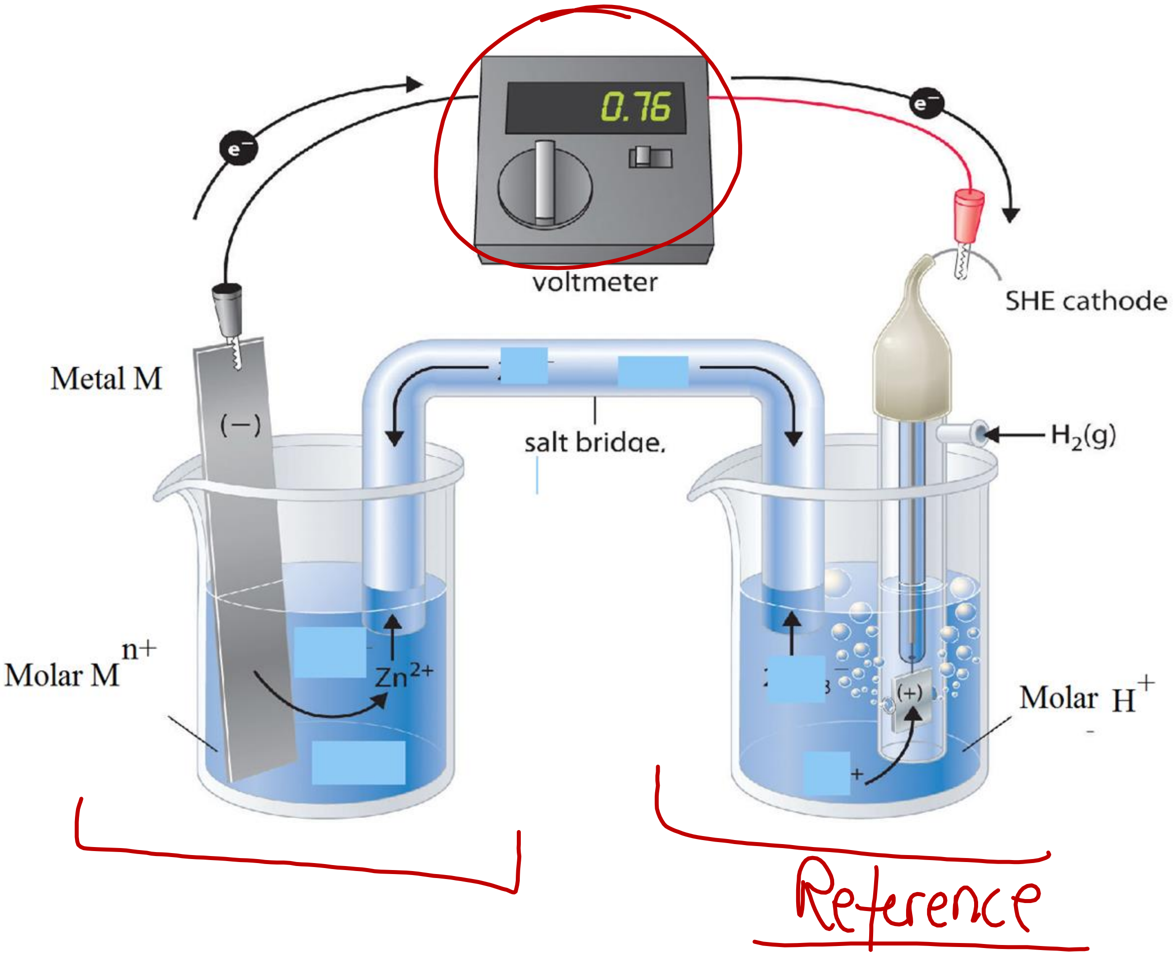


$$E = E_1 - \cancel{E_2}^{\,0}$$





$$E_{cell} = \cancel{E_{cathode}}^{\,0} - E_{anode}$$



Electron flow if metal M has a high negative potential

Electrone flow if metal M has positive potential

Standard hydrogen electrode SHE

It's a convenient reference electrode against which the potentials of all other half-cells can be measured.

$$E^{\circ}_{Zn^{2+}|Zn} = -0.76\,V$$

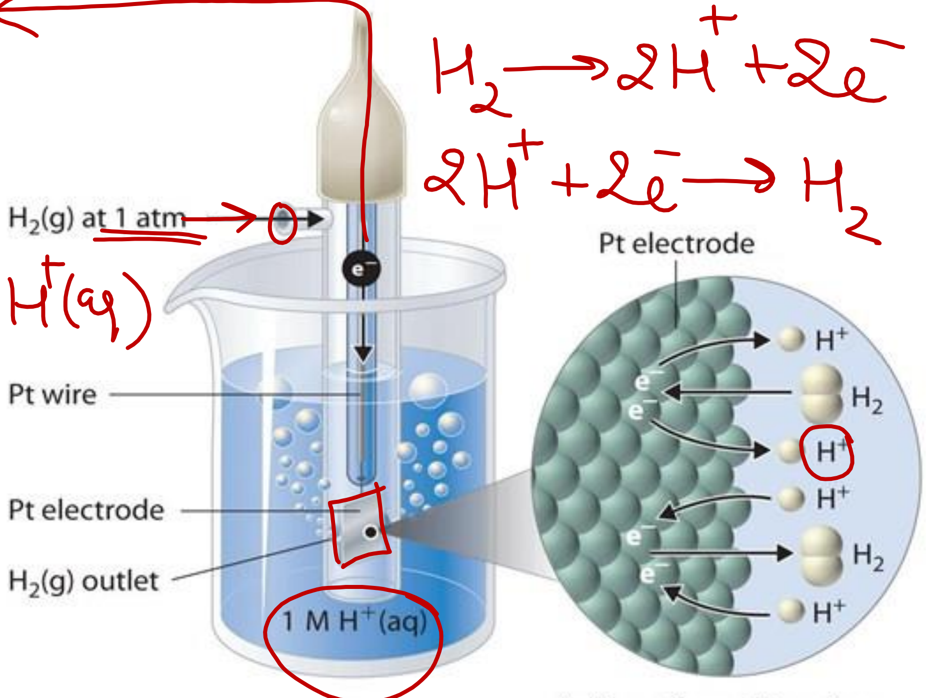
$H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \rightarrow H_2$

1M $H^+(aq)$

0 SHE

$-0.76 \rightarrow 0$



half-reaction at Pt surface:
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Standard hydrogen electrode

As Anode

$$H_2(g, 1\,bar) \longrightarrow 2H^+(aq) + 2e^-$$

$$Pt(s) \mid H_2(g, 1\,bar) \mid H^+(aq, 1M)$$

As Cathode

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

$$H^+(aq) \mid H_2(g) \mid Pt(s)$$

Can we use any other electrode as reference electrode?

Example

Consider the following E^{o} values:

$$E^{o}_{Fe^{3+}/Fe^{2+}} = +0.77\text{ V} \qquad E^{o}_{Sn^{2+}/Sn} = -0.14\text{ V}$$

Under standard conditions the potential for the reaction

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

(1) 1.68 V (2) 0.63 V

(3) 0.91 V (4) 1.40 V

$$E_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$= 0.77 - (-0.14)$$

Electrochemical series

Values of SRP of various half-cells arranged in decreasing order.

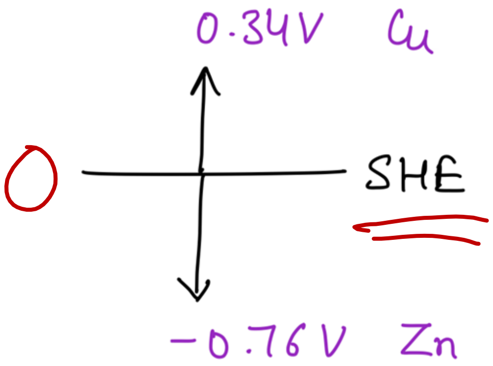
$\Rightarrow$ SHE || Unknown half-cell

$$E^\circ_{cell} = E^\circ_{RHS} - \cancelto{0}{E^\circ_{LHS}} = \text{SRP of 2nd half-cells}$$

Cathode Anode

e.g. $\underbrace{Pt(s) \mid H_2(g, 1\ bar) \mid H^+(aq, 1M)}_{SHE} \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$

$$E^\circ_{cell} = \underset{+0.34\ V}{E^\circ_{Cu^{2+}|Cu}} - \cancelto{0}{E^\circ_{H^+|H_2}}$$



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Stronger

OA

Stronger oxidizing agent		SRP
Half-Reaction	E° (V)	
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87	
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01	
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$	+1.69	
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$	+1.63	
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$	+1.51	
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$	+1.46	
$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$	+1.44	
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.42	
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36	
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+1.23	
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07	
$NO_3^-(aq) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+0.96	

Ox Power $\propto$ R.P.

	$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$	+0.80	
	$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$	+0.77	
	$I_2(s) + 2e^{-} \rightleftharpoons 2I^{-}(aq)$	+0.54	
	$NiO_2(s) + 2H_2O + 2e^{-} \rightleftharpoons Ni(OH)_2(s) + 2OH^{-}(aq)$	+0.49	
	$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$	+0.34	
	$SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-} \rightleftharpoons H_2SO_3(aq) + H_2O$	+0.17	
	$AgBr(s) + e^{-} \rightleftharpoons Ag(s) + Br^{-}(aq)$	+0.07	
	$2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2(g)$	0	

Stronger oxidizing agent

Half-Reaction	$E°$ (V)	
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14	
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.25	
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	–0.28	
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	–0.36	
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.40	
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44	
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74	
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76	
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83	
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.66	
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.37	
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71	

Using electrochemical series

- Predicting the oxidising or reducing ability.

$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^\circ = +0.34\,V$

$2H^+ + 2e^- \longrightarrow H_2 \quad E^\circ = 0.00\,V$

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

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

→ Cu^{2+} can oxidise ____________________

H^+ can oxidise ____________________

Ni^{2+} can oxidise ____________________

Using electrochemical series

$Cu^{2+} + 2e^- \rightarrow Cu \quad E^\circ = +0.34\,V$

$2H^+ + 2e^- \rightarrow H_2 \quad E^\circ = 0.00\,V$

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

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

→ H_2 can reduce ______________

Ni " " ______________

Zn " " ______________

Example

Standard reduction electrode potentials of three metals A, B and C are, respectively, +0.5 V, –3.0 V and –1.2 V. The reducing powers of these metals are

(1) B > C > A
(2) A > B > C
(3) C > B > A
(4) A > C > B

Example

Given

$$E^{o}_{Cr^{3+}/Cr} = -0.74\,V;\ E^{o}_{MnO_4^-/Mn^{2+}} = 1.51\,V,\ E^{o}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\,V;\ E^{o}_{Cl/Cl^-} = 1.36\,V$$

Based on the data given above, strongest oxidising agent will be

(1) Cr^{3+}
(2) Mn^{2+}
(3) MnO_4^-
(4) Cl^-