

## Chapter 29

# Electromotive Force

Cont.

- ✚ The “pull,” or driving force, inspiring the electron transfer.
- ✚ The electrical energy permitting the transfer of a given charge.

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## EMF/ $\Delta G$ (free energy) relationship

- ✚ When a cell produces a current (*electricity*), it can be used to do work— *e.g.*, to run a motor.
- ✚ Thermodynamic can predict the maximum work ( $W_{max} = \Delta G$ ) this current (electrical energy) may produce.
- ✚  $W_{max}$  is the product of charge flowing in the circuit and the potential difference (EMF),  $E$ , via which the charge is transferred.

$$W_{max} = \Delta G = -nFE$$

- ✚  $n$  = number of moles of  $e^-$ 's transferred (= the valence of the ion participating in the cell reaction)
- ✚  $F = 96,500$  C/mol  $e^-$ 's

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✚ According to Gibbs-Helmholtz equation

at constant  $P$ ,

$$-\Delta G = -\Delta H - T \left( \frac{\partial(\Delta G)}{\partial T} \right)_P$$

✚  $-\Delta G$ : the decrease in free energy of a system at constant pressure

✚  $-\Delta H$ : the decrease in heat content (or heat of reaction) of a system at constant pressure

Substitute with  $\Delta G = -nFE$

$$nFE = -\Delta H - T \left( \frac{\partial(-nFE)}{\partial T} \right)_P$$

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$$E = \frac{-\Delta H}{nF} + T \left( \frac{\partial E}{\partial T} \right)_P$$

✚ The coefficient  $\left( \frac{\partial E}{\partial T} \right)_P$  determines the dependence of the electrical energy ( $\Delta G = -nFE$ ) on the heat of reaction ( $\Delta H$ ).

$$\left( \frac{\partial E}{\partial T} \right)_P = 0 \quad \Rightarrow \quad -\Delta H = nFE$$

$$\left( \frac{\partial E}{\partial T} \right)_P > 0 \quad \Rightarrow \quad -\Delta H < -nFE$$

Additional energy (above the change in heat content) will come either from the surroundings or the temperature of the cell would fall.

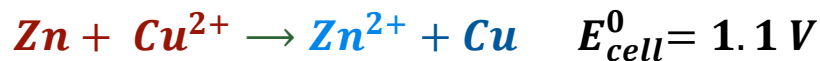
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$$\left(\frac{\partial E}{\partial T}\right)_P < 0 \quad \Rightarrow \quad -\Delta H > -nFE$$

Excess energy (above the change in heat content) will be given to the surroundings or the temperature of the cell would rise.

### Example

In the Daniel cell



$$\left(\frac{\partial E}{\partial T}\right)_P \approx 0, n = 2 \text{ and } \Delta H = -50,100 \text{ Cal}$$

$$-\Delta H = nFE$$

$$E = \frac{-\Delta H}{nF} = \frac{-(-50,100 \text{ Cal}) \times 4.185 \text{ J Cal}^{-1}}{2 \text{ mol e}'s \times 96500 \text{ C mol e}'s^{-1}} = 1.09 \text{ V}$$

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## Single electrode potential

- ✚ An electrochemical cell consists of two half-cells.
- ✚ At an **open-circuit** (no current flows), the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution.
- ✚ The potential of a single electrode in a half-cell is called the **Single electrode potential**.
- ✚ In a Daniel cell, if electrodes are **not connected** externally, the anode **Zn/Zn<sup>2+</sup>** develops a **negative charge** and cathode **Cu/Cu<sup>2+</sup>**, a **positive charge**.
- ✚ The **amount of the charge** produced on individual electrode determines its single electrode potential.
- ✚ The single electrode potential of a half-cell depends on :  
(a) **concentration** of ions in solution;(b) **tendency** to form ions; and (c) **temperature**

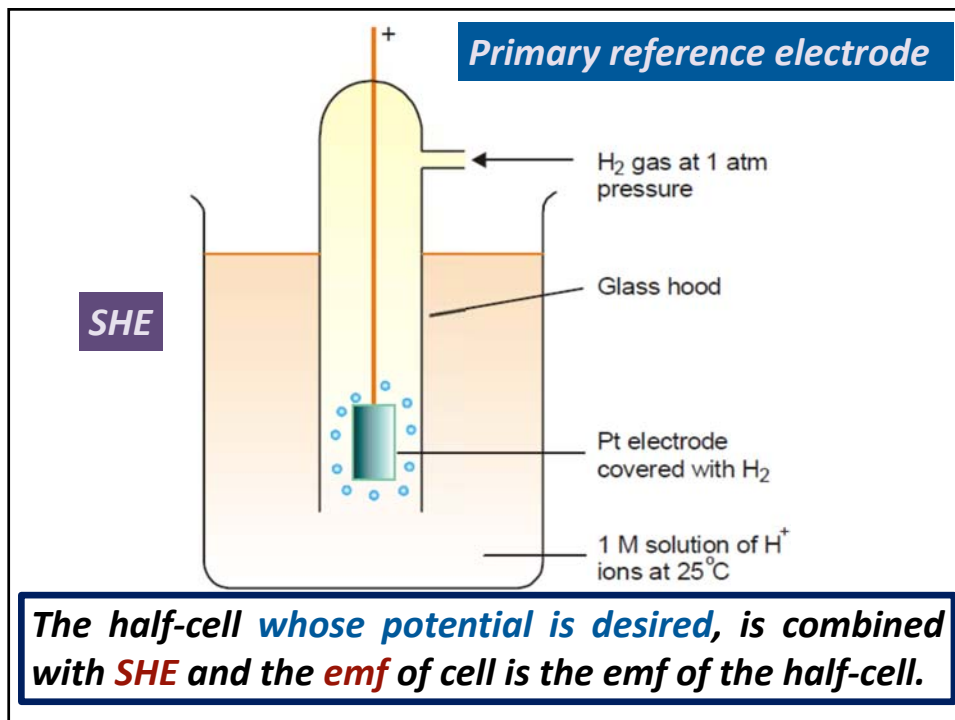
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## Determination of emf of a half-cell

- By a single electrode potential, we also mean the **emf** of an **isolated half-cell** or its half-reaction.
- There is no way of measuring the emf of a single half-cell directly.
- It has to be combined with another standard half-cell (**Reference electrode, RE**) as the **standard (saturated) Hydrogen Electrode (SHE)**.
- SHE** consists of a Pt electrode immersed in a 1 M solution of  $H^+$  ions and subjected to  $H_2$  gas (1 atm) at 25°C.

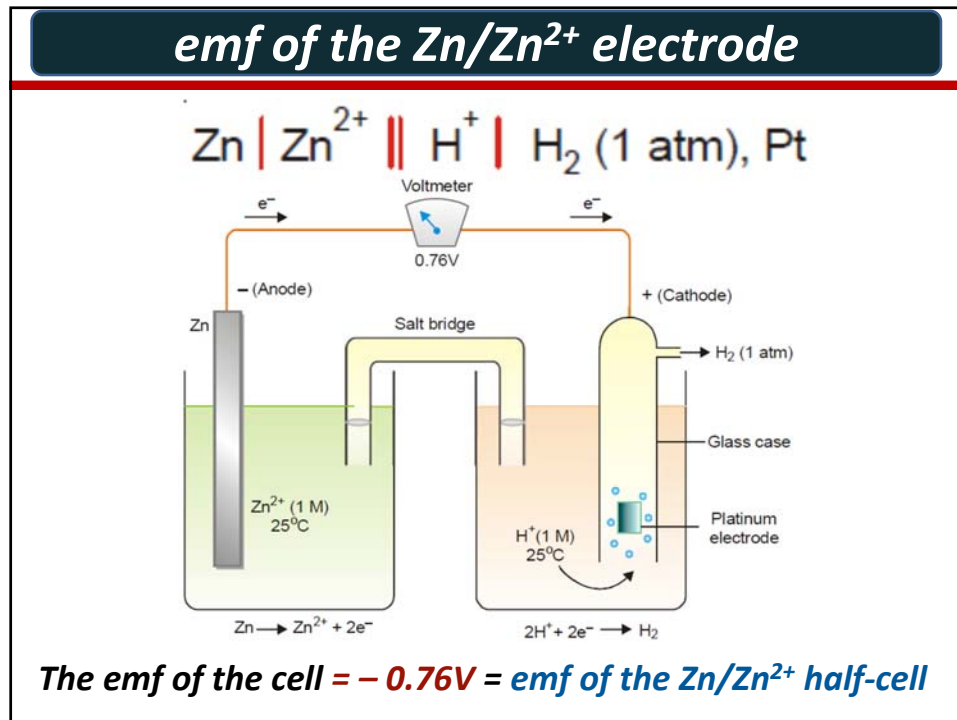


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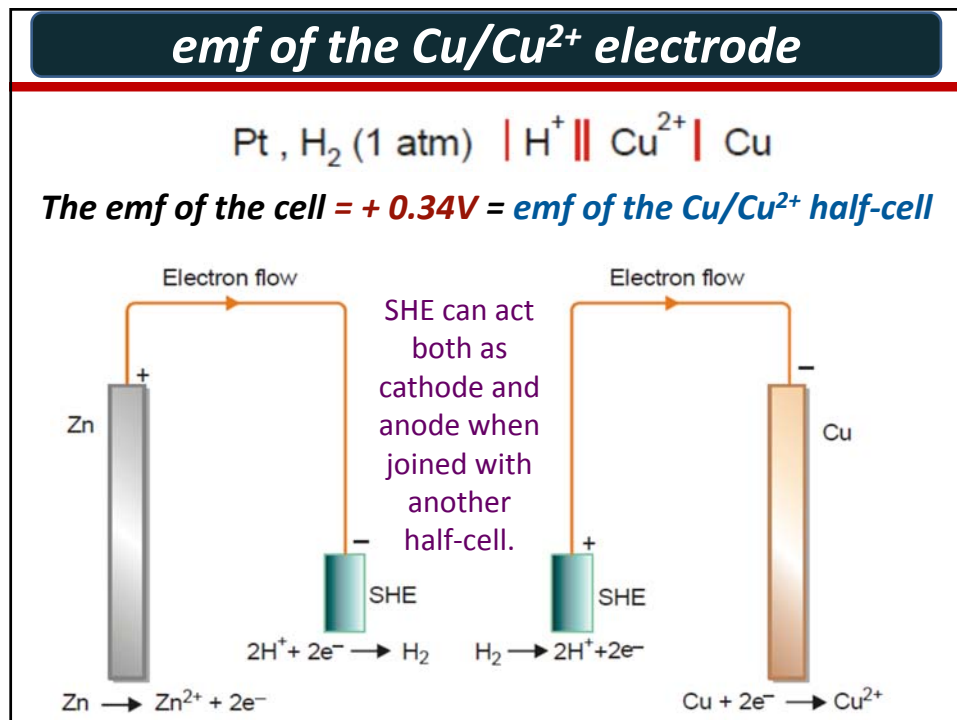


The half-cell whose potential is desired, is combined with **SHE** and the **emf** of cell is the emf of the half-cell.

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STANDARD REDUCTION POTENTIALS AT 25°C (298 K)		<b>Reduction Half-reaction</b>	<b><math>E^\circ</math> (V)</b>
↑ Stogner oxidizing agent  Weaker oxidizing agent		$F_2 + 2e^- \longrightarrow 2F^-$	2.87
		$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
		$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
		$Au^{3+} + 3e^- \longrightarrow Au$	1.50
		$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
		$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
		$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
		$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
		$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
		$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
		$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
		<b><math>2H^+ + 2e^- \longrightarrow H_2</math></b>	<b>0.00</b>
		$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.14
		$Cd^{2+} + 2e^- \longrightarrow Cd$	-0.40
		$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
		$H_2 + 2e^- \longrightarrow 2H^-$	-2.23
	$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37	
	$Na^+ + e^- \longrightarrow Na$	-2.71	
	$Li^+ + e^- \longrightarrow Li$	-3.05	
		<b>Oxidizing or Reducing Ability</b>	
		↓ Stronger reducing agent  Weaker reducing agent	

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### Predicting Feasibility of Reaction

**Problem** ⚡ Predict the feasibility of this redox reaction

$Zn(s) | Zn^{2+}(aq) || Ag^+(aq) | Ag$

Using  $E_{Zn^{2+}/Zn}^0 = -0.763 V$  and  $E_{Ag^+/Ag}^0 = 0.8 V$

**Solution**

*Reduction/Cathode*

$2Ag^+(aq.) + 2e^- \rightarrow 2Ag(s) \quad E^0 = 0.8 V$

$Zn^{2+}(aq.) + 2e^- \rightarrow Zn(s) \quad E^0 = -0.763 V$

*Oxidation/Anode*

$Zn(s) \rightarrow Zn^{2+}(aq.) + 2e^- \quad E^0 = 0.76 V$

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$2Ag^+ + Zn \rightarrow Zn^{2+} + 2Ag \quad E_{cell}^0 = 1.563 V$

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$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

**Employing red. pot.**

$$E_{cell}^0 = E_{Ag^+ \rightarrow Ag}^0 + E_{Zn \rightarrow Zn^{2+}}^0$$

$$E_{cell}^0 = 0.8 + 0.763 = 1.563 V$$

$E_{cell}^0 = +Ve$ , the reaction is feasible

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**Problem** Predict the feasibility of this redox reaction

$$2Al^{3+}(aq.) + 3Sn^{2+}(aq.) \rightarrow 2Al(s) + 2Sn^{4+}(aq.)$$

Using  $E_{Al^{3+}/Al}^0 = -1.66 V$  and  $E_{Sn^{4+}/Sn^{2+}}^0 = 0.15 V$

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**Solution**

*Reduction/Cathode*

$$2Al^{3+}(aq.) + 6e^- \rightarrow 2Al(s) \quad E_{Al^{3+}/Al}^0 = -1.66 V$$

$$3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^- \quad E_{Sn^{2+}/Sn^{4+}}^0 = -0.15 V$$

*Oxidation /Anode*

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$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

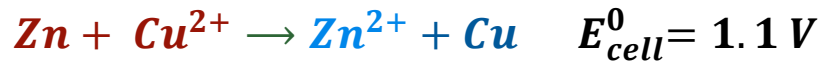
**Employing red. pot.**

$$E_{cell}^0 = -1.66 - 0.15 = -1.81 V$$

$E_{cell}^0 = -Ve$ , the reaction is not feasible

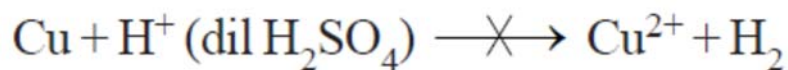
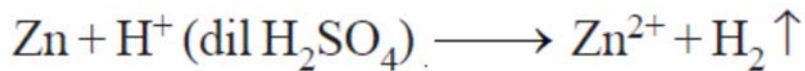
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## Metal displacement from solution



✚ If a Zn rod is placed in  $\text{CuSO}_4$  solution, Cu is expected to precipitate and  $\text{Zn}^{2+}$  is supposed to replace  $\text{Cu}^{2+}$  in the salt solution.

✚ Zn that is lying below hydrogen in the electrochemical series reacts with dil  $\text{H}_2\text{SO}_4$  to liberate  $\text{H}_2$ , while Cu that is lying above hydrogen does not.



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## Nernst Equation

✚ It represents the dependence of the cell potential ( $E$ ) on concentration.

✚ The potential of a single electrode or half-cell varies with the concentration of ions in the cell according to Nernst equation

For this half cell reaction  $M^{n+}(\text{aq}) + n e^- \rightarrow M(\text{s})$

$$E = E^0 - \frac{RT}{nF} \ln K \quad E = E^0 - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$$[M] = 1 \quad E = E^0 + \frac{2.303RT}{nF} \log [M^{n+}]$$

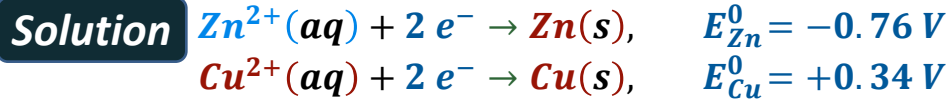
$$\text{At } 25^\circ\text{C} \quad E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

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**Example**

Calculate the electrode potential and the electromotive force of the following cell knowing that  $E_{Zn}^0 = -0.76 V$ , and  $E_{Cu}^0 = +0.34 V$

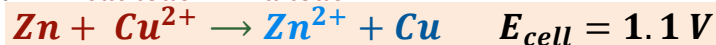
**Calculate E**

$$E = E^0 + \frac{0.059}{n} \log[M^{n+}]$$

$$E_{Zn} = E_{Zn}^0 + \frac{0.059}{2} \log[0.1] = -0.7895 \quad \text{Anode}$$

$$E_{Cu} = E_{Cu}^0 + \frac{0.059}{2} \log[0.1] = +0.3105 \quad \text{Cathode}$$

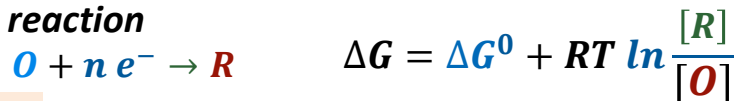
$$E_{cell} = E_{cathode} - E_{anode} = 0.3105 + 0.7895 = 1.1 V$$



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### Nernst Equation: derivation

For this reaction



However,

$$\Delta G = -nFE \quad \Delta G^0 = -nFE^0$$

$$-nFE = -nFE^0 + RT \ln \frac{[R]}{[O]}$$

$$E = E^0 - \frac{2.303 RT}{nF} \log \frac{[R]}{[O]}$$

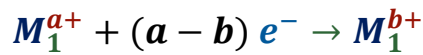
At 25 °C

$$E = E^0 - \frac{0.0591}{n} \log \frac{[R]}{[O]} \quad \left| \quad E = E^0 + \frac{0.0591}{n} \log \frac{[O]}{[R]} \right.$$

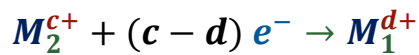
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## Nernst Equation

For this reaction



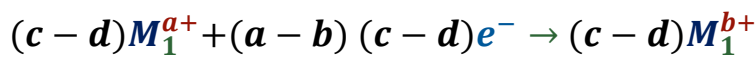
$$E_1 = E_1^0 + \frac{0.0591}{a - b} \log \frac{[M_1^{a+}]}{[M_1^{b+}]}$$



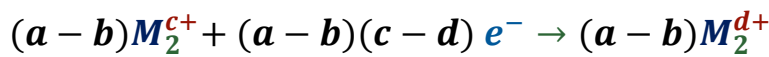
$$E_2 = E_2^0 + \frac{0.0591}{c - d} \log \frac{[M_2^{c+}]}{[M_2^{d+}]}$$

- ✓ **Equalize the No of e's**
- ✓ **Let us assume that on designing a cell, the first reaction will be the cathode and the other one will be the anode. Apply  $E_{cell} = E_{cathode} - E_{anode}$**

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$$E_1 = E_1^0 + \frac{0.0591}{(a - b)(c - d)} \log \frac{[M_1^{a+}]^{(c-d)}}{[M_1^{b+}]^{(c-d)}} \quad \text{Cathode}$$



$$E_2 = E_2^0 + \frac{0.0591}{(a - b)(c - d)} \log \frac{[M_2^{c+}]^{(a-b)}}{[M_2^{d+}]^{(a-b)}} \quad \begin{array}{l} \text{Anode} \\ \text{Still red.} \\ \text{pot} \end{array}$$

$$E_{cell} = E_{cathode} - E_{anode} = E_1 - E_2$$

$$E_{cell}^0 = E_1^0 - E_2^0$$

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For this reaction where  $a > b$  and  $c > d$

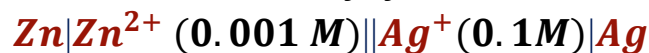


$$E_{cell} = E_{cell}^0 + \frac{0.0591}{(a-b)(c-d)} \log \frac{([M_1^{a+}]^{(c-d)})([M_2^{d+}]^{(a-b)})}{([M_1^{b+}]^{(c-d)})([M_2^{c+}]^{(a-b)})}$$

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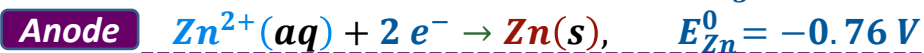
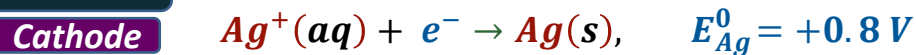
**Example**

Calculate at 25 °C the emf of the cell



Knowing that  $E_{\text{Zn}}^0 = -0.76 \text{ V}$ , and  $E_{\text{Ag}}^0 = +0.8 \text{ V}$

**Solution**



$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0 = 0.8 + 0.76 = 1.56 \text{ V}$$

$$E_{cell} = E_{cell}^0 + \frac{0.0591}{(a-b)(c-d)} \log \frac{([M_1^{a+}]^{(c-d)})([M_2^{d+}]^{(a-b)})}{([M_1^{b+}]^{(c-d)})([M_2^{c+}]^{(a-b)})}$$

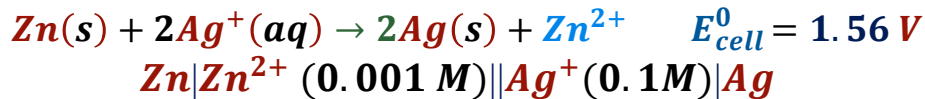
$$E_{cell} = E_{cell}^0 + \frac{0.0591}{(1-0)(2-0)} \log \frac{([\text{Ag}^+]^{(2-0)})([\text{Zn}]^{(1-0)})}{([\text{Ag}]^{(2-0)})([\text{Zn}^{2+}]^{(1-0)})}$$

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**Utilizing**

$$[Zn] = [Ag] = 1$$

$$E_{cell} = E_{cell}^0 + \frac{0.0591}{2} \log \frac{[Ag^+]^2}{[Zn^{2+}]}$$



$$E_{cell} = 1.56 + \frac{0.0591}{2} \log \frac{(0.1)^2}{0.001} = 1.58955 V$$

**Generally**

For this reaction



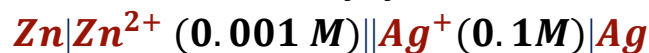
$$E_{cell} = E_{cell}^0 + \frac{0.0591}{2} \log \frac{1}{K} = E_{cell}^0 - \frac{0.0591}{2} \log K$$

$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log K$$

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**Example**

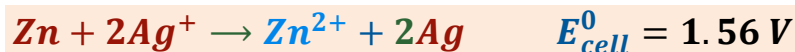
Calculate at 25 °C the emf of the cell



Knowing that  $E_{Zn}^0 = -0.76 V$ , and  $E_{Ag}^0 = +0.8 V$

**Solution**

$$E_{cell} = E_{cathode} - E_{anode} = 0.8 + 0.76 = 1.56 V$$



$$E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log K = E_{cell}^0 - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$E_{cell} = 1.56 - \frac{0.059}{2} \log \frac{0.001}{(0.1)^2} = 1.58955 V$$

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**Example** Calculate the electrode potential and the electromotive force of the following cell knowing that  $E_{Zn}^0 = -0.76 V$ , and  $E_{Cu}^0 = +0.34 V$

$$Zn|Zn^{2+} (0.1 M) // Cu^{2+} (0.1 M) | Cu$$

**Solution**

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s), \quad E_{Zn}^0 = -0.76 V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s), \quad E_{Cu}^0 = +0.34 V$$

**E for the cell**

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

**Nernst Equation**

$$E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log K$$

$$E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$[Zn^{2+}] = [Cu^{2+}]$

$$E_{cell} = E_{cell}^0 = 1.1 V$$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \quad E_{cell} = 1.1 V$$

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**Equilibrium constant**

At equilibrium, the cell reaction is balanced and the potential  $E_{cell} = 0$ .

$$E_{cell} = 0 = E_{cell}^0 - \frac{0.059}{n} \log K$$

$$E_{cell}^0 = \frac{0.059}{n} \log K$$

$$\log K = \frac{nE_{cell}^0}{0.059}$$

**Example**

Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc. Knowing that  $E_{Zn}^0 = -0.76 V$ , and  $E_{Ag}^0 = +0.8 V$

$$Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag \quad E_{cell}^0 = 1.56 V$$

$$\log K = \frac{nE_{cell}^0}{0.059} = \frac{2 \times 1.56}{0.059} = 52.88$$

$$K = 7.6 \times 10^{52}$$

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## Ideal non-polarizable electrode

- ✚ It is a hypothetical electrode in which a **faradic current** can freely pass (without polarization).
- ✚ Its potential is almost **fixed** regardless the reactions it participates in.
- ✚ The **reason** for this behavior is that the electrode reaction is infinitely fast, having an infinite exchange current density, and behaves as an electrical short.
- ✚ Eg., Reference electrodes (**SHE, SCE, Ag/AgCl, ..etc.**)

## Ideal polarizable electrode

- ✚ It is a hypothetical electrode characterized by an absence of **net DC current** between the two sides of the electrical double layer, i.e., **no faradic current** exists between the electrode surface and the electrolyte

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## Secondary Reference electrodes

- ✚ The SHE is not the most convenient **reference** to use in the laboratory. The gas has to be carefully controlled and hydrogen gas can form explosive mixtures with air.

**Ag/AgCl/Cl<sup>-</sup>**

**Ag, AgCl|Cl<sup>-</sup> (1M)**



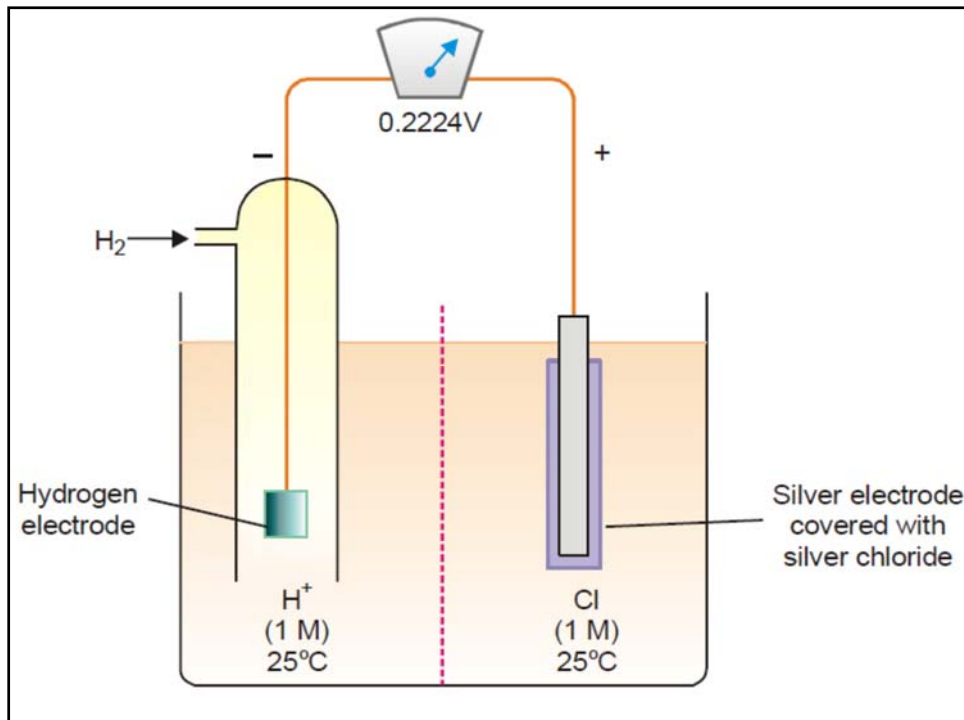
- ✚ **Ag wire (or strip)** is covered with **AgCl** (a highly insoluble substance) then dipped in **KCl (1 M)** solution.
- ✚ A setup of this electrode with SHE gives



At 25 °C



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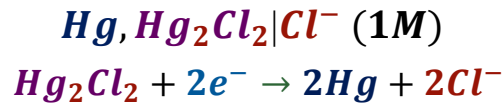
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### Calomel electrode



- ✚ It is the most commonly used secondary standard reference electrode.
- ✚ The **standard calomel electrode**, SCE, consists of a wide glass-tube with a narrow side-tube.
- ✚ A platinum wire is dipping into liquid mercury covered with solid mercurous chloride. ( $\text{Hg}_2\text{Cl}_2$ , calomel). The tube is filled with a 1 M solution of KCl (or saturated KCl solution).
- ✚ The side-tube containing KCl solution provides the **salt bridge** which connects the electrode to any other electrode.

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**Calomel electrode**

A setup of this electrode with SHE electrode gives



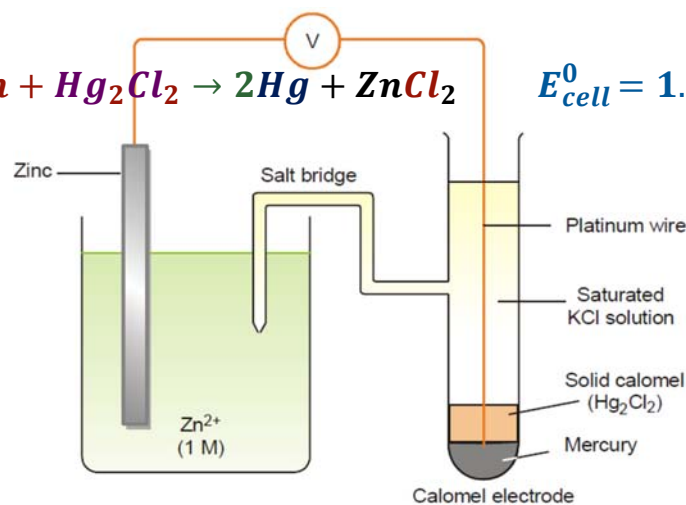
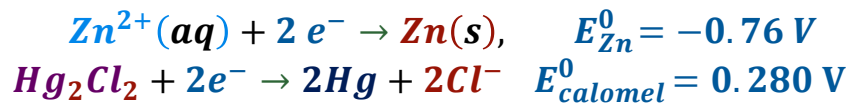
At 25 °C



$E_{\text{cell}}^0$  of calomel electrode depends on [KCl] solution.

For 0.1 M KCl solution  $E_{\text{cell}}^0 = 0.3338 \text{ V}$ ; for 1 M solution  $E_{\text{cell}}^0 = 0.2800 \text{ V}$ ; and for saturated KCl solution  $E_{\text{cell}}^0 = 0.2415 \text{ V}$ .

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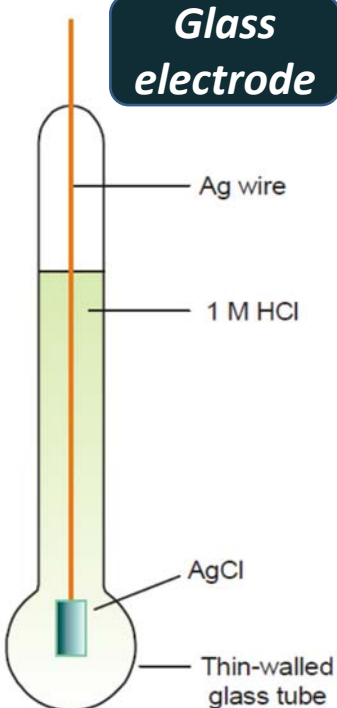
**Standard zinc half-cell using calomel electrode**

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- ✚ its emf is determined by coupling with a **SCE**.
- ✚ It provides the easiest method for measuring **pH** of a given solution.
- ✚ It consists of a glass tube having a **thin-walled bulb** (containing 1M HCl) at the lower end.
- ✚ Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into HCl, forming **Ag/AgCl** electrode.

### Glass electrode

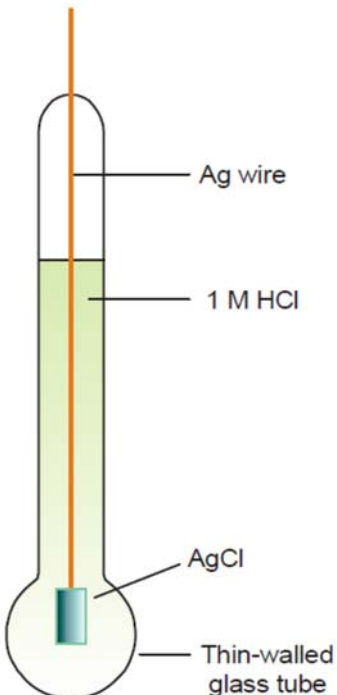


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### Glass electrode

**Ag, AgCl | 1 M HCl : H<sup>+</sup> (test soln.)**

- ✚ When placed in a solution, the potential of the glass electrode depends on **[H<sup>+</sup>]** of the solution.
- ✚ The potential develops across the glass membrane as a result of the difference in **[H<sup>+</sup>]** on the two sides of the membrane; **similarly to a concentration cell**.



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**Quinhydrone Electrode**

It involves the redox reaction between **quinone (Q)** and **hydroquinone (QH<sub>2</sub>)**,

$$\text{Quinone} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Hydroquinone}$$

**Quinone** +  $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$  **Hydroquinone**

**It consists of a Pt strip immersed in a sat. solution of quinhydrone at a definite [H<sup>+</sup>] (buffered solution).**

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**Quinhydrone Electrode**  $\text{Pt}|\text{QH}_2, \text{Q}, \text{H}^+$

Quinhydrone is a molecular compound which gives equimolar amounts of quinone and hydroquinone in solution.

**Quinhydrone**

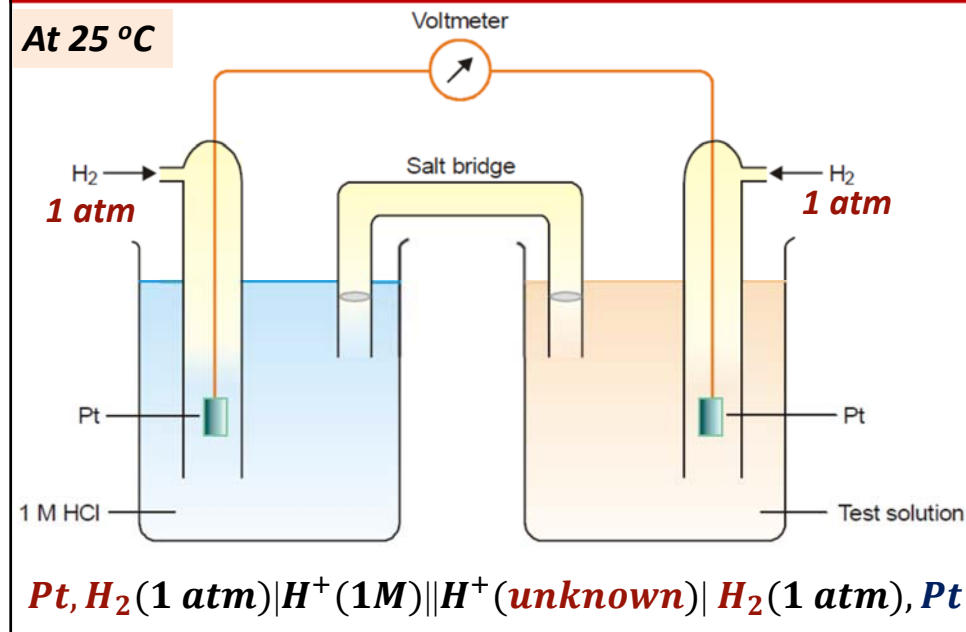
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## pH measurements

- A half-cell is set up with the **test solution** as electrolyte.
- The emf of the cell depends on  $[H^+]$  or pH of the solution.
- The emf of the half-cell is determined by coupling it with another standard half-cell and measuring the emf of the complete cell.
- The commonly used standard electrodes are the **hydrogen, quinhydrone & glass electrodes**.

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## pH / Hydrogen electrode



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## pH / Hydrogen electrode

$Pt, H_2(1 \text{ atm}) | H^+(1M) || H^+(\text{unknown}) | H_2(1 \text{ atm}), Pt$

At 25 °C, for the half cell containing the **unknown solution**



$$E = E^0 - \frac{0.059}{n} \log K = 0 + \frac{0.059}{1} \log \frac{[H^+]}{H_2^{1/2}}$$

$$H_2^{1/2} = 1 \quad \rightarrow \quad E = 0.059 \log [H^+]$$

$$E = -0.059 \text{ pH}$$

Hence,  $E$  of this half cell depends on  $pH$

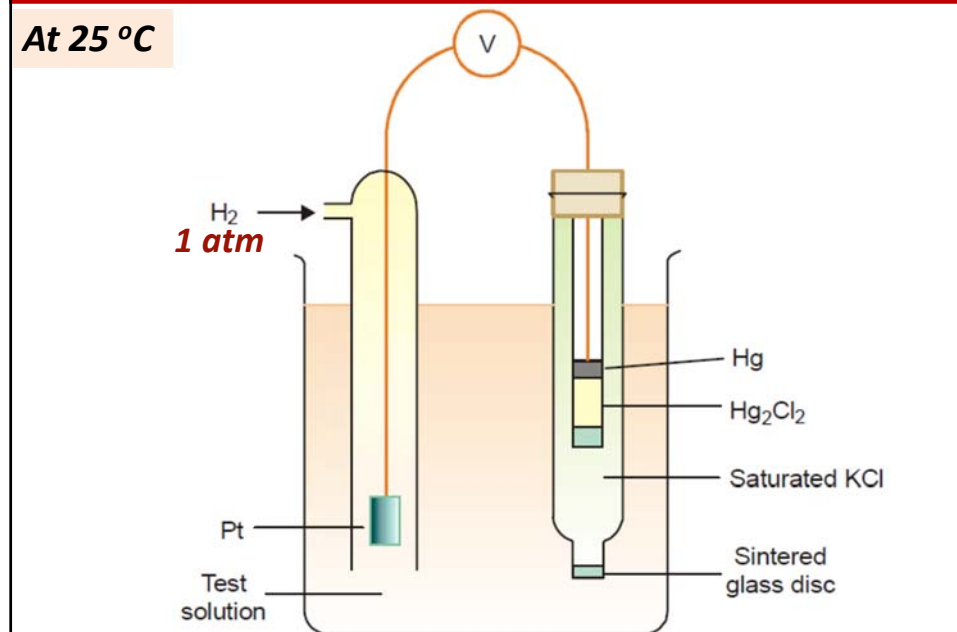
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.059 \text{ pH} - 0 = -0.059 \text{ pH}$$

$-0.059 \text{ pH}$  is supposed to be +Ve, otherwise the test electrode will be anode not a cathode

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## pH / Hydrogen electrode vs. SCE

At 25 °C



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$$E_{\text{unknown}} = -0.059 \text{ pH}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.2415 + 0.059 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.2415}{0.059}$$

### Hydrogen electrode: merits & demerits

- ✦ It gives absolute values of pH (other electrodes yield relative values).
- ✦ It is not convenient for routine measurement
  - ✦ It requires H<sub>2</sub> gas (difficult handling)
  - ✦ It requires considerable volume of test solution.
  - ✦ The test solution might 'poison' the surface of the platinum electrode.
  - ✦ The potential of the electrode changes with pressure.

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### Example

- ✦ Calculate the pH of the unknown solution if  $E_{\text{cell}}$  at 25°C is 0.445V.



### Solution

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \\ = 0.2415 + 0.059 \text{ pH} = 0.445$$

$$0.059 \text{ pH} = 0.2035$$

$$\text{pH} = 3.45$$

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## pH / Glass electrode

**At 25 °C**

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

$$= E_{SCE} - E_G$$

$$E_{cell} = 0.2415 - E_G$$

$$E_G = E_G^0 + 0.059 \text{ pH}$$

$E_G^0$  is determined using a solution of **known pH**

$E_{cell} = 0.2415 - E_G^0 - 0.059 \text{ pH}$

**$Ag, AgCl|HCl(1M) | Glass||H^+(unknown)||SCE$**

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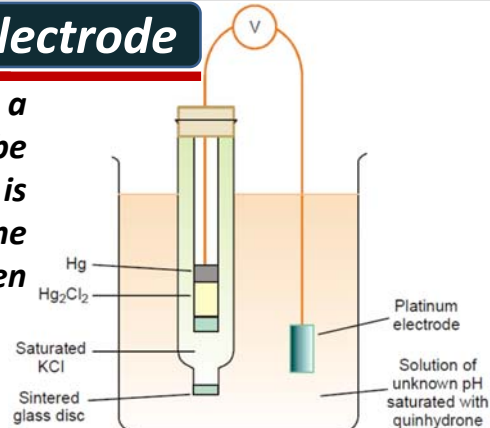
## Glass electrode: merits & demerits

- ✚ A glass electrode is **universally used** because:
  - ✚ It is simple to operate.
  - ✚ It is not easily **poisoned**.
  - ✚ Its activity is not affected by strong oxidizing and reducing agents.
  - ✚ Since  $E_G^0$  depends on a particular glass electrode used, it is not a universal constant and also changes with time. **Hence a glass electrode only compares pH values while the hydrogen electrode measures pH absolutely.**

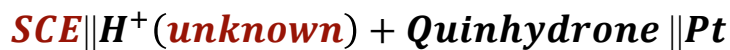
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## pH / Quinhydrone electrode

A Pt electrode is suspended in a solution whose pH is to be determined. The solution is saturated with quinhydrone compound. This half-cell is then combined with SCE.



$$E_Q = E_Q^0 - \frac{0.059}{2} \log \frac{[QH_2]}{[Q][H^+]^2} = E_Q^0 + 0.059 \log [H^+]$$



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At 25 °C

$$E_Q^0 = 0.6996 V$$

$$E_Q = E_Q^0 + 0.059 \log [H^+]$$

$$E_Q = E_Q^0 - 0.059 \text{ pH}$$

$$E_Q = 0.6996 - 0.059 \text{ pH}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} = E_Q - E_{SCE} \\ &= 0.6996 - 0.059 \text{ pH} - 0.2415 \end{aligned}$$

$$\text{pH} = \frac{0.4581 - E_{\text{cell}}}{0.059}$$

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### Quinhydrone electrode: merits & demerits

- ✚ *Quinhydrone electrode is easily set up by simply immersing a platinum strip in the test solution.*
- ✚ *The pH values are very accurate even in the presence of oxidizing ions which interfere with the working of a hydrogen electrode.*
- ✚ *It does not give satisfactory results for solutions whose pH is more than 8.5 due to the ionization or oxidation of hydroquinone.*

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### Example

- ✚ *Find the pH of a solution placed in a hydroquinone half-cell which was coupled with standard calomel electrode. The emf of the combined cell was determined to be 0.123 V at 25°C.*

### Solution

$$pH = \frac{0.4581 - E_{cell}}{0.059} = \frac{0.4581 - 0.123}{0.059}$$

$$pH = 5.67$$

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